

OLI SYSTEMS, INC

OLI ESP User Guide

A guide to using OLI ESP 9.1

OLI Systems

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This manual was authored by OLI Systems, Inc. The underlying software is the product of over 40 years of effort by the staff of OLI and over \$30 MM dollars of financial support from our clients.

Disclaimer:

This manual was produced using the OLI/ESP version 9.1.2. As time progresses, new data and refinements to existing data sets can result in values that you obtain being slightly different than what is presented in this manual. This is a natural progress and cannot be avoided. When large systematic changes to the software occur, this manual will be updated.

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Chapter 1. Overview

OLI Systems, Inc., the world leader in aqueous systems modeling, has developed software to model aqueous, conventional and other complex chemical systems. OLI's software is built on the OLI Engine, which is a software package in its own right and also comprises the basis for OLI's specialty software. OLI's specialty software includes the OLI/Analyzer line, ESP, the Environmental Simulation Program, and CSP, the Corrosion Simulation Program. OLI's original software, ProChem, has been incorporated into these newer OLI products.

Users, who lease the ESP Program, but not the CSP Program, will want to utilize both the OLI Engine and ESP Users Manuals. Users who lease the CSP Program, but not the ESP Program, will want to utilize both the OLI Engine and CSP Users Manuals.

Users who are interested in the OLI/Analyzers should OLI for product information.

Chemical Phenomena

OLI can model complex chemical phenomena, including:

- **Interphase Equilibria** between aqueous, organic liquid, vapor and multiple solids phases;
- **Intraphase Equilibria** (particularly aqueous) including redox and speciation reactions;
- **Biochemical Reactions**;
- **Reaction Kinetics**;
- **Other Phenomena** including ion exchange, co-precipitation and both ionic and molecular adsorption.

OLI/Software

OLI Engine The OLI Engine is the basis for all other OLI Software. The Engine provides the OLI Databank, the OLI thermodynamic framework and OLI Solvers together with user access facilities in the form of the OLI Databook, OLI WaterAnalyzer and OLI Express. Taken as a whole, the Engine allows for single-stream point calculations as well as parametric studies for streams defined on either a molecular or ionic basis.

ESP The Environmental Simulation Program, ESP, is a comprehensive computer simulation tool which allows the simulation, design, and optimization of a wide variety of chemical processes including complete, process flowsheets. For example, ESP can simulate various environmental waste minimization, treatment, and ex-situ remediation processes as well as more conventional manufacturing processes involving separation and distillation.

CSP The Corrosion Simulation Program, CSP, is an OLI simulation tool which addresses problems particular to corrosion. CSP has the ability to produce different kinds of real solution, phase stability diagrams, as well as to calculate the redox potentials for systems which contain oxidation and reduction phenomena.¹

ProChem is the original tool which utilized the aqueous chemistry solver upon which the OLI Software is based. The facilities of ProChem, other than dynamic simulation, which is accessed via the DynaChem component of ProChem, are largely available now in other OLI products. ProChem can still be accessed directly through the OLI ToolKit.

OLI Studio

Stream Analyzer The Stream Analyzer is an MS-Windows based product and is the logical extension of the OLI/Engine. The Stream Analyzer has access to the OLI Databank, the OLI thermodynamic framework and the OLI Solvers. The Stream Analyzer allows for single-stream point calculations as well as parametric studies for streams. It can also separate a stream into phases for use in other calculations and can mix several streams together to create a new stream.

¹ The CSP program is largely replaced by the OLI Studio Corrosion Analyzer program.

Corrosion Analyzer The Corrosion Analyzer is an MS-Windows based product and is the logical extension of the Corrosion Simulation Program, CSP. The Corrosion Analyzer has the ability to produce different kinds of real solution, phase stability diagrams, as well as to calculate the oxidation/reduction potentials for systems which contain oxidation and reduction phenomena. In addition, the rate of uniform corrosion can be calculated and the underlying polarization curves can be examined. The inclusion of an Alloys databank (developed by Oak Ridge National Laboratory) allows for Pourbaix diagrams for many types of metals.

Lab Analyzer Many definitions of a stream start with a laboratory water sample. These samples are frequently not charge balanced and have different calculated properties than what were measured. The pH of a solution is such a property. The Lab Analyzer reconciles the imbalance in charges and corrects for pH errors. The ionic representation of the solution can then be converted into a molecular representation for use in other OLI programs.²

OLI Services OLI Services is the callable version of the OLI/Engine.

Features

OLI provides a refined user interface for solving problems. This interface allows access to many major features, including:

Process Unit Simulation in ESP Process, which supports a wide variety of commonly used environmental (e.g., bioreactor, neutralizer) and conventional (e.g., mixer, stripper) process units. Selection and specification of operating parameters is achieved via a series of easy-to-read displays.

Flowsheet Simulation, also in ESP Process, allows a user to simulate a single process unit or link together any process units simulating a complete plant operation including recycles. The facilities are

² With version 2.0 of the Analyzers, the Lab Analyzer was incorporated into the Stream Analyzer and is no longer a separate product.

available to model a process at steady state or, via ProChem's DynaChem component, under transient (i.e., dynamic) conditions.

Thermodynamic Framework, an advanced, state-of-the-art framework which is the basis for predicting complex aqueous-based chemistry in equilibrium with optional vapor, nonaqueous liquid, and solid phases. The aqueous model is predictive over the general range: -50-300 C, 0-1500 bar and 0-30 molal ionic strength.

OLI Databank, an extensive, high quality thermodynamic and physical property databank of over 8,000 inorganic and organic species. All data is verified and validated from source literature which is referenced in the databank. The databank, which supports the predictive thermodynamic framework of the OLI software, may additionally be used as a reference library.

OLI Express, a facility which allows the user to define, simulate, and display the results of stream studies; both single case as well as parametric case studies.

Flexible Feed Stream Definition, allows stream composition data to be supplied on either an ionic species basis, or the more conventional molecular species concentration basis. The option to input data on an ionic basis is advantageous since laboratory, water sample analysis data, often the basis of an aqueous simulation study, is normally expressed in terms of ionic species concentrations.

Stability Diagrams, a facility, applicable to REDOX systems, available in CSP Corrosion, which generates two-dimensional phase stability diagrams with coordinates of Eh-pH (normally referred to as Pourbaix Diagrams), Eh-species amount and user-defined specifications.

Open Architecture, problems are formulated from a series of easy-to-follow screens. An import facility allows interfacing to other databanks.

Calculation Techniques

OLI uses a highly advanced thermodynamic and mathematical framework for predicting the equilibrium properties of a chemical system. This predictive framework is based upon:

- the **Revised Helgeson Equation of State** for predicting the partial molal standard-state thermodynamic properties of all species, including organics, in water;
- the **Bromley-Zemaitis framework** for the prediction of excess thermodynamic properties of ions;
- the **Pitzer and Setschenow** formulation for the prediction of the excess thermodynamic properties calculation of molecular species in water; and
- the **Enhanced SRK Equation of State** for the prediction of vapor and non-aqueous, liquid phase thermodynamic properties. This enhanced equation of state applies to organics which are sparingly soluble in water, and which form a second liquid phase which is largely ideal.
- the **Mixed Solvent Electrolyte (MSE)** thermodynamic framework replaces the Bromley-Zemaitis activity model. Water is no longer required to be the solvent and the solutes can now have concentrations approaching mole fractions of 1.0.³

Calculation Ranges

The extensive OLI databanks support the predictive frameworks, and allow chemical systems to be simulated accurately over the following conditions:

Aqueous Systems

Temperature -50 to 300° C

Pressure 0 to 1500 bar

³ The MSE model became available with version 7.0 of the Engine/ESP and with 2.0 of the Analyzers.

Species Concentration 0 to 30 molal

Non-aqueous Systems (MSE)

Temperature 0 to 1200° C

Pressure 0 to 1500 bar

Species Concentration 0 to 1.0 mole fraction

Support Service

OLI Systems, Inc. also offers a wide range of support services for the software which include:

Hotline Support, which allows users to obtain guidance from OLI when trying to simulate difficult chemistry and new processes;

Update Service, which offers updates of the software or thermodynamic property databanks, as the need arises;

Data Service, which offers OLI's personnel who will create thermodynamic property databanks for user chemistry not covered by the in place OLI Databanks. Requests are considered on a priority basis; and,

Professional Service, which offers OLI personnel to model user chemistry and processes on an individually billed basis.

OLI Software - Engine Components

The OLI Software contains these software components:

OLI Databook, a component which enables a user to review and add to an extensive thermodynamic library containing over 10,000 chemical species;

OLI ToolKit, a component which provides access to several important facilities including **OLI Express** (convenient stream studies), the **WaterAnalyzer** (defining feed streams based upon a water analysis) and **ProChem** (OLI's older software, ElectroChem). Please note that the DynaChem component of ProChem, also available via the Toolkit, is considered part of the ESP software.

The OLI ToolKit (with the exception of DynaChem), the OLI Databook, the extensive OLI Databanks and the numerical solver code form the **OLI Engine**, which is the name given to those components of the system which are common to all OLI's software packages.

OLI Software Packages

The OLI Engine is available in each of these packages:

OLI Engine, a package in its own right, which allows for convenient single-stream simulation studies.

Environmental Simulation Program, or ESP, which features **ESP Process**, a component to simulate environmental and conventional processes;

Corrosion Simulation Program, or CSP, which features **CSP Corrosion**, a component to predict the corrosive properties of solutions via stability diagrams.

The organization of the OLI Engine is summarized in the schematic diagram at the end of this chapter.

OLI Databook and the OLI Databanks

OLI Databook allows the review of OLI's extensive databanks where the species physical and thermodynamic information are stored. The OLI databanks support the predictive thermodynamic framework of the simulation tools and may also be used as a reference library for information. Included are: most organic species in the DIPPR Project 801 data compilation (DIPPR is the Design Institute for Physical Properties which is administered by the American Institute of Chemical Engineers); many additional organic species on the United States EPA (Environmental Protection Agency) List of Lists and most of the inorganic chemistry of 78 elements from the Periodic Table.

Additionally, OLI Databook has a facility for creating private user databanks, to allow species not covered in the OLI supplied databanks to be used in simulations.

Supporting Data

The OLI databanks also contain supporting information on species properties. This information includes literature references, data quality (i.e., accuracy) and, where applicable, source and experimental data.

OLI Supplied Databanks

The data for chemical species are organized into several separate databanks which support a wide spectrum of chemistry. These databanks include:

PUBLIC	This databank contains thermodynamic and physical properties for nearly 10,000 different organic and inorganic chemicals and is used by the OLI Software to carry out simulations.
MSEPUB	This is the mixed-solvent electrolyte public database. It is a subset of the aqueous framework PUBLIC Database.

GEOCHEM	This databank contains approximately 90 solid chemical species which are typically found in geological formations and which generally equilibrate with water over long periods of time.
GEMSE	This is the mixed-solvent electrolyte version of the GEOCHEM database
LAB	This databank contains more than 100 primary anion and cation species and strictly supports OLI's WaterAnalyzer facility for accepting a feed stream composition based upon ionic concentrations.
LOWTEMP	This databank contains approximately 200 solids whose data has been extrapolated from the former minimum temperature of 0 C to -50 C. It should be used when applications involving solids operate below either 0 degrees C or below the minimum temperature, implied by the PUBLIC Databank for a particular solid (which could be above 0 C).
CORROSION	This databank contains the oxides and related thermodynamic data needed for the Corrosion Simulation Program. It is a default databank when using OLI Corrosion.
CRMSE	This is the mixed-solvent version of the CORROSION databank.
ALLOYS	This databank contains thermodynamic data for mixed metal alloys for use in predicting stability diagrams in the CSP program
CERAMICS	This databank contains thermodynamic data for minerals which may be formed from hydrothermal melts of ceramics.
CEMSE	This is the mixed-solvent version of the CERAMICS databank.

Private Databanks

In addition to the OLI supplied databanks, the facility is available for the user to create a private species databank to augment or override species data in the OLI databanks.

Reference Library

The databanks can also be used as a reference library for species property information. The OLI Databook software provides a high-level user interface and allows the user to access the values for physical and thermodynamic property data as well as supporting information such as literature references, experimental data, data quality (i.e., accuracy), etc.

Chemistry Models

The link between the OLI Databanks and the simulation components of the OLI Software is via the Chemistry Model Definition, a collection of files which describes a particular chemistry in a concise way.

A Chemistry Model Definition is created by the user in the Chemistry Models "mode" of the OLI software. The Chemistry Models mode can be accessed from most of the individual OLI components of the software, including OLI Express, ESP Process, OLI WaterAnalyzer, and CSP Corrosion.

In Chemistry Models, the user provides a simple description of the molecular species involved in the chemical system to be simulated. From this description, OLI automatically generates the detailed speciation (e.g., ionic species in the aqueous solution), the inter-phase and aqueous speciation equilibria reactions and the required physical and thermodynamic property information for the particular mix of chemicals involved.

OLI Toolkit

In conjunction with the OLI Databook and associated Databanks, the OLI ToolKit forms an important part of problem solving with the OLI software. The ToolKit allows the user to access a number of facilities including:

OLI Express, which provides the user with a facility for performing single stream studies including ScratchPad (single point calculations such as adiabatic, bubble point, etc.) and Survey (multipoint calculations such as a pH sweep) calculations. Convenient graphical facilities allow the user to display plots reflecting the results of Surveys.

WaterAnalyzer, which enables the user to store, manage, and reconcile individual ionic species lab analyses prior to using these analyses as the basis for molecular species feed streams in ESP Process and in CSP Corrosion.

ProChem, which provides the user with, among other things, access to DynaChem, for dynamic simulation of processes based upon OLI chemistry.

OLI Express

OLI Express provides a quick way for the OLI Software to run single or multiple point equilibrium calculations on a given stream. The stream is either one which has been defined in ESP Process, in the WaterAnalyzer, or in OLI Express.

OLI Express is also broken into modes:

- **Chemistry Model**
- **Express Calculate**
- **Summary**

In **Chemistry Model**, the user provides a description of the molecular species which are involved in the chemical system to be simulated. From this description, OLI automatically generates the detailed speciation (e.g. ionic species in the aqueous solution), the interphase and aqueous speciation equilibria reactions and the required physical and thermodynamic property information for the particular mix of chemicals involved.

In **Express Calculate**, the user has access to ScratchPad and Surveys, the single and multiple point equilibrium calculation facilities of the OLI Software. Isothermal, adiabatic, bubble and dew point, and composition and vapor fraction calculations are available through ScratchPad. Surveys available include temperature, pressure, composition, and pH.

In **Summary**, OLI Express generates disk or printer reports of the stream, including the results of the latest ScratchPad or Surveys calculation.

WaterAnalyzer

The WaterAnalyzer, like the rest of OLI's software components, is further divided into parts called Modes, which are:

- **Chemistry Model**
- **Sample Manager**
- **Stream Manager**
- **Summary**

In **Chemistry Model**, the user provides a simple description of the ionic and neutral species upon which the input description will be based. The titrants which will be used in pH reconciliation, or in a pH survey of the sample, are also defined as neutral species to the system. OLI generates a detailed speciation from the user input species for the particular mix of chemicals involved.

The **Sample Manager** of the WaterAnalyzer organizes and stores up to 100 samples per WaterAnalyzer Study. The data kept in the WaterAnalyzer includes name and date, concentration data, conditions including temperature, pressure, density, qualities (not directly used in the calculations), and pH. Reconciliation for both electroneutrality and pH is offered. Samples can be combined using a user specified weighted average into a composite sample.

Scratch Pad and Survey calculations can be performed on any given sample with the Sample Manager.

In the **Stream Manager**, a sample which has been reconciled for electroneutrality can be converted into a stream suitable for use in other parts of the OLI Software. This conversion involves mapping the ions in the samples into molecular flows. This conversion is done automatically so that OLI equilibrium calculations can be performed on the stream. The produced stream is then available for use by other components of the OLI software, such as ESP Process or OLI Express.

The **Summary** mode of the WaterAnalyzer generates disk or printer reports of the samples and streams in a given study.

ProChem

The ProChem software is OLI's earlier aqueous chemistry simulator package. ProChem contains a few facilities which allow certain simulations to be performed which, at present, cannot be done within other

parts of the OLI software. Dynamic simulation via DynaChem is the most important example of such a simulation.

It is envisaged that future releases of the OLI Engine, ESP and CSP will incorporate all simulation capabilities of the ProChem programs.

ProChem components include:

ElectroChem (part of the OLI Engine Package) allows for the simulation of the phase separation and intraphase speciation of single-stage, steady state processes. In addition to interphase and intraphase electrolyte equilibria, ElectroChem can optionally consider reaction kinetics and/or redox and ion exchange phenomena.

DynaChem (part of the ESP Package) allows for the dynamic simulation of flowsheets of one or more aqueous based process units and streams with or without process control loops.

OLI Specialty Software Packages

The OLI Engine, described in the preceding section, is required by all of OLI's specialty software packages. Currently, two such packages are available:

ESP, the Environmental Simulation Program, a flowsheet simulation tool which models both conventional and environmental processes, from mixers and splitters to steam strippers and biotreaters; and,

CSP, the Corrosion Simulation Program, a corrosion simulation tool which produces real solution phase stability diagrams with coordinates of Eh-pH, Eh-species amounts or user defined.

The Environmental Simulation Program, ESP

ESP, OLI's unique flowsheet simulation tool provides ESP's unique component, **ESP Process**. The organization of ESP is shown in the schematic diagram.

ESP Process is software which defines a process comprised of one or more units, and which actually builds and executes the process simulations including, where required, recycles.

ESP Process is divided into four working parts, called Modes, which are:

- **Chemistry Model**
- **Process Build**
- **Process Analysis**
- **Summary**

In **Chemistry Model**, the user provides a simple description of the molecular species involved in the chemical system to be simulated. From this description, OLI automatically generates the detailed speciation (e.g., ionic species in the aqueous solution), the interphase and aqueous speciation equilibria reactions and the required physical and thermodynamic property information for the particular mix of chemicals involved.

If the system involves reaction kinetics, sorption phenomena, REDOX, or bioreactions; or if the feed streams are to be described based upon a laboratory water (i.e., ionic species) analysis, the user can supply additional information beyond the statement of the molecular species involved.

Once a Chemistry Model is built, it can be used for all simulation studies that use this chemistry.

In **Process Build**, the user describes the process flowsheet to be simulated. This is achieved by selecting individual unit operations from a series of icons for those currently supported by ESP. By working with the screen menu interface, the user can provide the information required to specify the individual unit operations.

The currently available unit operations are:

Absorber, Bioreactor, Clarifier, Compressor, Controller, Crystallizer, Dehydrator, Extractor, Electrolysis, FeedForward, Heat Exchanger, Incinerator/Combustor, Manipulate, Membrane,

Mixer, Neutralizer, Precipitator, Reactor: (Aqueous, Nonaqueous, Bioreactor), Saturator, Sensitivity, Separator, Splitter: (Full Stream, Component), Stripper

In **Process Analysis**, the execution and analysis of a process flowsheet is accomplished using information defined in Chemistry Model and Process Build.

In **Process Summary**, the user can direct a report describing the simulation results to an appropriate output device (i.e., disk, printer).

OLI ScratchPad

In addition, the user has access to OLI ScratchPad with respect to process streams. This facility allows the user to select an individual stream in a process flowsheet and perform additional "scratch pad" calculations. Such point calculations include: isothermal, adiabatic, set pH, bubble point, dew point, etc.

OLI CSP

This section describes the OLI Corrosion Simulation Program (CSP). The same corrosion technology is also available in OLI's new software: **The OLI/Corrosion Analyzer**.

CSP, OLI's corrosion simulation tool provides a unique component, **CSP Corrosion**.

In CSP Corrosion, a stream, which is defined either in another OLI component or within CSP Corrosion, can be examined for corrosive properties relative to any metal, or alloy which the user may select.

CSP Corrosion, like ESP Process, is divided into working parts called Modes, which are:

- **Chemistry Model**
- **CSP Stability**
- **Summary**

In **Chemistry Model**, the user provides a simple description of the molecular species involved in the chemical system to be simulated. The system includes the solution, the metal, and the titrants which will be used to general pH studies on the solution.

Once a Chemistry Model is built, it can be used for all simulation studies that use this chemistry with this metal.

In **CSP Stability**, the user enters more detailed information about the solution, particularly the temperature, pressure, and composition. The amount of the metal to be studied in relation to the solution, unless the metal is specifically present in the solution, is not a concern. Once the solution chemistry is defined, the user can generate different types of phase stability diagrams which describe the behavior of the solution in contact with the metal of interest.

In **Summary**, the user will be able to receive printed output or export data to another software package.

OLI ScratchPad and Surveys

From within CSP Corrosion, the user has access to ScratchPad and Surveys with respect to the stream or solution of interest. These facilities allow the user to perform additional single or multiple point calculations. Such calculations include: isothermal, adiabatic, set pH, bubble point, dew point for ScratchPad, and temperature, pressure, composition and pH surveys for Surveys.

User Manual

The user documentation for OLI software is comprised of informal, easy to understand manuals, covering specific aspects or sections of the software. The OLI Manuals (OLI Engine, ESP and CSP) are written to allow clear understanding of the uses of the software.

Each section of each OLI Manual contains different levels of detail ranging from the "High Level" software concepts to "Low Level" detail such as computer operation and keyword functions. This gives the user a coherent understanding of the overall computer software operation. The manuals also provide the detail required for optimization or diagnostics of computer application cases after the user has had time to become familiar with detailed software operation.

The sections available in the OLI Manuals are (please note, the particular manual where the section appears is noted):

Introduction (ALL), descriptions of the software scope and concepts;

Getting Started (OLI Engine), an installation guide which also contains a guided tour of examples to give the user a feel for how to operate the software as well as knowledge of common and regularly used functions;

Databook (OLI Engine), descriptions of facilities for locating and reviewing database information and procedures for preparing private databanks;

Data Preparation (OLI Engine), descriptions of facilities and services for adding new chemistry to an OLI Private Databank.

Chemistry Models (OLI Engine), procedures for building a basic chemistry model and inclusion of other chemical phenomena;

Process Modeling (ESP), principles for using ESP Process, containing a description of individual process blocks;

Process Applications (ESP), collection of ESP Process examples for all process blocks featuring plant modeling on real engineering applications with engineering troubleshooting aids;

Corrosion (CSP), principles for using CSP Corrosion, with a detailed description of the creation and interpretation of real solution phase stability diagrams;

Corrosion Applications (CSP), collections of examples of the application of CSP Corrosion to corrosion studies;

ToolKit (OLI Engine), which contains instructions for using ToolKit Blocks, including WaterAnalyzer and OLI Express;

Dynamic Modeling (ESP), descriptions of the scope and principles of dynamic modeling (at present a ProChem DynaChem function);

Reference (ALL), index, keyword summary, detailed software structure, and descriptions of the various software Action Key facilities available.

Chapter 2. Getting Started

Hardware and Software Specifications

The OLI Software is available for Windows based PC computers. Hardware and support requirements that are required are detailed below.

PC Platform

The OLI Software can be installed on any Microsoft Windows computer. The recommended minimum memory requirements is 2 gigabytes of memory.

Disk storage for the OLI Software is estimated at 75 megabytes of disk storage for a full ESP/CSP system, but the user should have at least 100 megabytes of free disk storage prior to installation to allow for the system plus workspace.

The following operating systems are supported:, Vista, Windows 7, Windows 8.

Getting Started Suggestions

How to Install OLI Software

A separate installation guide is included with each copy of OLI software.

Where To Work

Select a working directory for your OLI problems. This directory can be any directory, other than the system directory (i.e., where the OLI software has been installed). Avoid working in the system directory so that updates of the OLI software can be applied easily.

For the PC, a start-up working directory has been made as part of the installation process. The working directory is `C:\My Documents\My OLI Cases\ESP 9.1`. Note that example problems have been included in the folder: `C:\My Documents\My OLI Cases\ESP 9.1\Samples`

Copying the Example Problems

On each computer, example problems have been included along with the OLI software. These problems can be copied to your working directory, and can be used to learn how to formulate problems.

Location of Examples

`\My Documents\My OLI Cases\ESP 9.1\Samples`

How To Begin

Change to the working directory which you have selected and type the command for your system (e.g. ESP or CSP). The initial OLI screen will display the choice of OLI components available to you. We recommend that you use the tutorials available in the next chapter to become more familiar with the software components.

Conventions to Remember

Throughout this manual, including immediately below, we will refer to specific keys and how to access an Action Bar including individual items on this bar. For Windows 95 and NT users, the mouse can be used as noted just below.

Throughout OLI software there are several Keys available to aid the user in working. The keystroke to access each Key varies with the platform on which the user is running the software. The keystrokes are listed on the bottom of the screen. The available Keys are:

Help Key Help is available through the Help Key. Position the cursor to the field in question and press the Help Key. Help pertinent to that field should be available. The position of the cursor bar always determines the first line of help. Pressing the Help Key again enters Extended Help. Under Microsoft™ Windows the user will probably prefer to simply double click the left mouse button on this Action Bar field.

Enter Key After entering field information press the Enter Key to continue. Alternatively the user can simply double click the left mouse button on the desired field. Please note that when the field is already highlighted, only one click is necessary.

Action Key Press the Action Key to access the facilities available on the Action Bar, located on the first line of each OLI screen. The double click the left mouse button on the desired field also works.

End Key When done entering a set of information press the End Key to move on to the next step. Under Microsoft™ Windows just single click on the right mouse button.

Quit Key Use the Quit Key to leave the current step. The Quit Key typically moves backward one screen. Under Microsoft™ Windows just double click the right mouse button.

Keystroke Shortcuts

Select either Menu and Action Bar choices by typing the first letter of your choice. (Normally, menu and Action Bar choices are selected by moving the cursor bar to the choice and pressing <Enter>.) If the first letter of your choice is ambiguous (e.g., S for SPECIES, SYNONYMS, or STRUCTURES) then use the first two letters. Upper or lower case letters are allowed, and there is no need to press <Enter>.

On the PC, <Alt> and <F10> are synonymous. Use either key to move to the Action Bar.

Setting Options

Setting the Sound: Use the Options Action on entry to either program to customize the sound on your PC. The option chosen will be stored in a profile dataset which will be kept between sessions.

Naming an Editor: Also on the Options Action, the Setup menu choice allows setting your favorite editor (and also browser) for editing and viewing disk files.

Using File Management: Use the Utility facility for disk file management.

Customizing Display Units: The Units facility allows changing the default display units for OLI Databook, ESP Process, and the OLI Express and Water Analyzer components of the OLI ToolKit.

Touring OLI

This chapter contains, among others, "A Tour of OLI Databook," "A Tour of ESP Process," "A Tour of ESP Biotreatment." These tutorials have been designed as introductions to the ESP software.

"A Tour of OLI Databook," illustrates how to search for chemicals in a databank using the periodic table. The tutorial also shows how to find the data for a species, and how to find the supporting reference and the experimental data for a particular data item. Several OLI Databook features including plot, the ability to draw structures, and the ability to calculate temperature-based properties are also highlighted.

In "A Tour of ESP Process," an example process involving pH neutralization is described.

An advanced application using a control/manipulate block scheme to control pH is described in "An Advanced Tour of ESP Process." In this tour we remove the neutralizer from a previous tour and add a control block, mix block and manipulate block.

The use of a recycle stream is illustrated in "Another Advanced Tour of ESP Process." This tour recycles a stream produced in an earlier tour.

In "A Tour of ESP Biotreatment" the user is introduced to steady-state modeling involving a bioreactor.

A Tour of the OLI Databook

The Tour Starts Here ...

- Start ESP by clicking on the OLI ESP icon or by using **Start > Programs > OLI Systems > ESP 9.0 > ESP 9.0**
- You will now see the initial window of ESP - "**Selecting Which Program**". You should see that **ESP Process** (if you licensed ESP) or **OLI/Toolkit** (if you only licensed the OLI/Engine) is highlighted with the cursor bar⁴. Use the down arrow key to select **OLI Databook**. Press <Enter> to select this program. (The up and down <Arrow Keys> should be used whenever you would like to move the cursor bar to another line). You may also double-click the item using your mouse.
- You will now see the initial window of the OLI Databook - "**Opening Which Databook**". The first database that is installed will be highlighted. This will vary depending on which options were licensed with the software. Use the arrow keys to highlight the **PUBLIC AQUEOUS** Databank and then press <Enter> to continue.
- You will now be given a choice of several different Chapters. Open OLI Databook to the **SPECIES** Chapter (which is currently highlighted) by pressing <Enter>.

Searching for a Species Via the Periodic Table ...

- You can now enter a particular Species Name. Let us suppose that we do not remember the name of the species we are seeking and all we remember is that the species we are looking for contains both calcium (Ca) and sulfur (S). The next step should be to press <F10>, the **Action Key**. The Action Key is used throughout the OLI/Software as the means of reaching the Action Bar. The first field on the Action Bar, **Search**, will now be highlighted. At this point press <Enter> to select Search.
- A pull down menu will now present a series of Search options. Use the down arrow to highlight the **Periodic Table** as the Search option. Once this is done, press <Enter> and the periodic table will be displayed.

⁴ You may also see CSP Corrosion if licensed and the OLI Databook which is included in all licensed versions.

- Using the Arrow Keys to move around, highlight **Ca** and then **press the <Space Bar>** to select Ca. Next highlight **S** and then **press the <Space Bar>** to select S. Once this is done, press **<Enter>** and the search will be done.
- At this point, you will see a display of all species containing both Ca and S. Use the down arrow to highlight CaO3S. **CaO3S**, is Calcium Sulfite. Press **<Enter>** to access information stored in OLI Databook for this species.

Looking at the Information Stored for Calcium Sulfite ...

- We now see that there is General Information as well as Solid Phase data available in the databank for this solid species. An arrow key (→) is used to show that information is present. Using the down arrow, you can highlight the **Solid Phase** and press **<Enter>** to select it.
- Several data items for the Solid Phase are displayed. Move the cursor bar with the down arrow to the line beginning with **SREF** (Reference State Entropy).
- At this point, we can take a small excursion in the tour looking at ESP's online help system. Press **<F1>**, the **Help Key**, and peruse the description of SREF. Now, press **<Esc>**, the Quit Key, to return us to where we were before we selected help. (This is the general convention in the OLI/Software for moving back to the just previous step).
- Continuing the tour of the data, press the **Action Key** to move to the Action Bar. The first field on the Action Bar, **View**, will now be highlighted. Press **<Enter>** for a pull down menu of View options.
- You can now view various information about this data entry. Since the **Reference** option is highlighted, press **<Enter>** to review the detailed reference. Note that since this reference is a multivolume compilation of data, the reference includes the specific volume and page number on which the data appears. To continue the tour, press **<Enter>** to return to the choices on the View menu.
- Now highlight the **Quality** option, and press **<Enter>** to look at the information on uncertainty. When you are ready to continue, press **<Enter>** again to go back to the View menu.

We have now completed our excursion into calcium sulfite data.

Viewing the Data on the Vapor Pressure of CO₂ ...

- To continue the tour, we now use <Esc> repetitively to work back to the page of OLI Databook, - "**Opening Chapter to Which Entry**", where we describe the species of interest.
- The cursor will now be on the field which allows us to Enter a species name. Please Enter **CO₂** (all caps) being sure that the entry is followed by all blank characters. At this point press <Enter> so that the data for CO₂ can be made available.
- The next step is to highlight the **Vapor Phase** information. Once this is done, pressing <Enter> will give us access to this information.
- To access more information about the vapor pressure, highlight the line that begins with "**VP**". This line contains the curve fit coefficients for vapor pressure. Using **Action Key** we can make an excursion to the Action Bar. The **View** facility will be highlighted; press <Enter> to display the alternatives offered on the corresponding pull down menu.
- Since the **Reference** option of the pull down menu is already highlighted, press <Enter> to look at the reference. Press <Enter>, then <Esc> to return to the Action Bar. Using the right arrow key, move to the **Evaluate** facility and press <Enter>. The Evaluate Action will prompt for a value for temperature at which to evaluate the vapor pressure equation. Fill in any value for temperature, press <Enter>, and the corresponding calculated value will be computed and displayed. If the temperature entered is outside the displayed temperature range for the fit of vapor pressure, a warning message will be displayed on the message line at the bottom of the screen.

Dynamically Changing the Units for OLI Databook Displays ...

- We can now press the **Quit Key** and return to the Action Bar. To continue the tour, you should use the left arrow key to highlight the **Units** facility on the Action Bar. Press <Enter> to pop up the window which allows changes to the display units.
- The cursor will be active on the field which allows entire default systems of units to be set. Using the right arrow, toggle to **ENGLISH** units and press <Enter> to activate these units. At this point, all scalar

values should be changed to the new system of units. If you press the Action Key to go back to the Action Bar and then, the right arrow to go back to **Evaluate** and then, <Enter> to reactivate the calculator mode, you will now see the displayed temperature range for the fit in the new units. You can now repeat the earlier type of calculation, but in the new system of units. When done, **press <Esc>** repetitively to back out to the Chapter Selection window of OLI Databook.

Viewing the Experimental Data for the CO₂ Vapor Pressure ...

- In addition to providing a Reference for the curve fit coefficients for the CO₂ vapor pressure (which we examined earlier), OLI Databook allows us to access the several data sets upon which the fit was based. To begin this excursion, please highlight the **Experimental Chapter** line on the current display and press <Enter>. At this point, OLI Databook is opened to the Experimental Chapter.
- You should now see a window which allows you to access the actual experimental data sets used for the coefficient fits for those particular properties which are a function of temperature. The highlight should be on **Vapor Pressure**, so just press <Enter>.
- The next window, which requests the Species Name, will already have **CO₂** filled in, so press <Enter> to continue.
- We now see five data set choices displayed. These are the five actual experimental data sets upon which the coefficients for VP are based. Let's **highlight the fourth** of these data sets. At this point, press the **Action Key** and the **View** facility on the Action Bar will be highlighted. Press <Enter> to pull down the View menu.
- The **Reference** option will be highlighted. Pressing <Enter> will allow us to look at the reference. Pressing <Enter> again will bring us back to the pull down menu for View.
- Continue by highlighting the **Data** option of the pull down menu. By pressing <Enter>, we will be able to peruse the experimental data.

You may notice that some of the sets of experimental data are beyond the range of the coefficients for the OLI model. This is because the data in the Experimental Chapter includes the DIPPR pure component data for that property.

Plotting the Experimental Data ...

- The next excursion on our tour through the Databook will be to look at a plot of the data. We do this by using the **Action Key** and moving to the Action Bar. By using the right arrow, we can move to the **Plot** facility on the Action Bar and then press <Enter> to obtain a plot of the stored data versus the plot based upon the curve fit.
- By pressing <Esc> repetitively, we can now go back to the Chapter Selection Menu.

Viewing the Structure of an Organic Species ...

- The final excursion on our tour through the Databook will be to look at the structural drawing for an organic species. Start by selecting the **Structure Chapter**. After highlighting this Chapter, press <Enter> to open this Chapter of the Databook.
- To find an interesting organic species to display, type in the wildcard species name: **CHOL***. The first screen of a list of all of the species containing CHOL at the start of their name will be displayed. **Highlight Cholesterol** and then press <Enter>. The structure, headed by the ESP internal name, CHOLESTEROL, is then displayed.

Exiting the Databook ...

- Press <Esc> repetitively until the prompt, "**Do you wish to exit the Databook?**" Press <Enter> to exit OLI Databook, and then with <Esc> once more, we can back our way out to the system prompt.

This completes our brief tour of some of the features of OLI Databook.

A Tour of ESP Process

As background to "The Tour of ESP Process," here is a short description of the sample application we will be using as we look at some of the features of ESP Process.

The Application ...

The tour of ESP Process is based on a sample application of ESP, a pH neutralization problem. Suppose we have two waste streams that must be mixed together. One of the streams is an acid stream (in that the pH is less than 7.0 at room temperature) and the other stream is a base stream. We know from general chemistry that when acid and base streams mix, generally heat is evolved resulting in gases being produced. In addition, if the pH changes significantly, solids may form.

We want to treat any resulting gases from this mixing separately (we may need to recover the gases for another process) and we also want to remove any solids which may form. Finally, we want to make sure that the pH of the resulting liquid has been made basic.

Formulating the Process ...

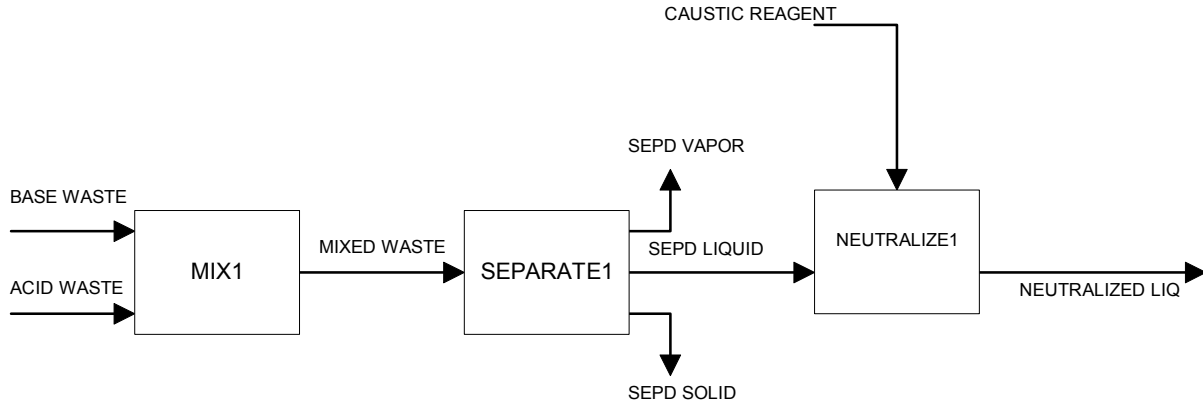
The figure 2-1 on the next page is a diagram which represents this process in ESP.

MIX1 is a mixer which adiabatically mixes the acid stream and the base stream. The resultant stream has a pH, temperature and composition different from those of the inlet streams.

The next block chosen is a separator called SEPARATE1. This unit allows us to physically separate the multiphase product stream from MIX1 into separate vapor, liquid and solids streams.

Figure 2-1

Process Diagram pH Neutralization Process



	Base Waste	Acid Waste	Caustic Reagent
Temperature (C)	40	25	30
Pressure (Atm)	1	1	1
Total Flow (mole/hr)	200	150	100
H2O	55.51	55.51	55.51
NH3	1.0	0	0
CO2	0.1	0	0
SO2	0.1	0	0
HCL	0	0.1	0
H2SO4	0	1	0
NaOH	0	0	1

The combination of the mixer and separator represents a surge tank. Generally, a surge tank would be used in a pH neutralization process to dampen flow and composition fluctuations as well as to vent vapor release and to settle solids.

The neutralizer block then adds a reagent to adjust the pH of the liquid from that of the separator effluent liquid to the desired value.

The following instructions are designed to take you on a tour through some of the interesting features of the ESP Process Analysis facilities.

The Tour Starts Here ...

- Start ESP by clicking on the **OLI ESP** icon or by using **Start > Programs > OLI Systems > ESP 9.1 > ESP 9.1**
- You will now see the initial window of ESP, - "**Selecting Which Program?**". The line for selecting the **ESP Process** program should be highlighted. Just press <Enter> to access the process simulation system.
- Our objective is to produce a computer simulation of a simple environmental process made up of three distinct processing blocks. This simple process is described shown in Figure 2-1
- Assuming you are in the ESP working directory, the first line "**New Process**" is highlighted. Simply press <Enter> and you will be prompted to enter a name for this process. Type the name **NEUTRAL1** and press <Enter>. (For consistency we will be using all caps throughout tour, names are case sensitive.) There may be other process names in this directory. Ignore them for now.
- You will now see a display which reflects the four distinct steps, called Modes, applicable to preparing a simulation: Chemistry Model, Process Build, Process Analysis, Summary. We can begin the process by highlighting **Chemistry Model** and pressing <Enter>.

Defining the Chemistry Model ...

- The cursor should be highlighting the first line, "**New Model**". There may be other models present in this directory, ignore them for now. Press <Enter>, and ESP will prompt for a name for the Chemistry Model. (Once we enter a given combination of chemicals and make a Chemistry Model, that Model may be used for many simulations in ESP.)

We can also call this Chemistry Model **NEUTRAL1**. (There is no requirement that this be the same as the name of the process itself.) Now press <Enter> and the single chemical H₂O will appear at the top of an otherwise empty list of inflows.

- We will now be asked to select the thermodynamic framework. For this example we can use the default **Aqueous Framework**. Press the <Enter> key.
- We will now be asked to select a databank. We will use the default public database. Press the <Enter> key.
- The next step is to enter the names of the other chemicals in your system. Enter the names **NH₃, CO₂, SO₂, HCL, H₂SO₄ and NAOH**. Enter each on a separate line. Simply press <Enter> or use the down arrow after entering each name.

If ESP does not recognize a name, a warning message will appear at the bottom of the screen. If the ESP name for a chemical is different than the name entered, ESP will display a message and change that name. When all names have been entered, simply press <Enter> on the next blank field to save your edit.

- You will now be prompted for the phases to consider in the simulation. Phases are selected by **highlighting the relevant phase** and then pressing the <Space Bar> as indicated on the screen. For this example, we ask that you select the default which is the **Vapor** and **Solid** Phases in addition to the aqueous. You make this choice by pressing <Enter>. You will be asked to confirm that a Model Definition should be created. Answer affirmatively by pressing <Enter> on the **Continue** field. (Once you have already created a Model Definition, you will find it quicker to bypass this step.)
- ESP will automatically create a Chemistry Model Definition file which will contain the full speciation in all phases implied by your chemicals as well as all equilibria between phases and within the aqueous phase. When it is completed you will be prompted to press any key to continue. Press any key to continue.
- After the Chemistry Model Definition has been created, you have an opportunity to review the Chemistry Model Definition File. Simply press the **Action Key** and highlight the **File** facility on the Action Bar and press <Enter>. To see this file you simply select **View** and press <Enter>. Now, by pressing the Page Down Key repetitively, you can browse this file. After reviewing this file you can press <Esc> and then <Enter> to continue.

- At this point you will be asked to create the rest of the files needed for the Model Solver. You should select **Continue** by pressing <Enter>. This step, which serves to create a customized equation file and a customized thermodynamic data file, specific to your chemistry, takes no more than a very few minutes to complete in most cases. When the Generate step is complete you will be prompted to "Press any key to continue". Press any key to continue.

You will receive a confirming prompt. Simply press <Enter> to continue. When the original screen which allowed you to begin Chemistry Model is refreshed, you have completed preparing the Chemistry Model and you are now free to run any number of process simulations utilizing this chemistry or any subset thereof.

We are now ready to proceed with the next step on the tour.

Preparing to Build the Process ...

- We are ready to define the individual unit operations which make up the process shown in Figure 2-1. First, highlight the **Process Build** line on the current screen and then press <Enter>. You will now see a series of unit operations (called blocks) groupings, each containing several ESP Process Blocks. The first block we are interested in is **Conventional Blocks**. This selection should already be highlighted so simply press <Enter> to continue. We will now see several icons for individual blocks that are available. The **Mix Block** should be highlighted, so just press <Enter> to access the facilities for describing the Mix Block.
- The Mix Block schematic will now appear on the screen with the cursor set at the Block Name field. Simply type the name **MIX1** and press <Enter>.
- The cursor is now at the name for the first feed stream. Simply type **BASE WASTE** and press <Enter>.
- You will now be prompted to fill out the description of the physical state of the first feed stream. You want to simply enter the values shown in Figure 2-1 for this stream. First, however, you need to change the default units to metric. This is done by pressing the **Action Key** and highlighting the **Units** facility on the Action Bar. Once this is done, press <Enter> and a units selection window will be activated. Use the right arrow to toggle the first field to **METRIC** and then press <Enter>. Metric will now be the default for the balance of this session. Now, enter the values shown for this stream in **Figure 2-1** (where dashes are shown the corresponding fields should be left blank). When all values have been entered, press the <End> key or <Esc> key to move along.

- You will now be prompted to enter the name of the second feed stream. Simply type **ACID WASTE** and press <Enter>.
- Once again, you will be prompted to fill out the description of the physical state of the second feed stream. Again, you should utilize the values shown on **Figure 2-1**, but this time there will be no need for an excursion to the Action Bar to change units. When this step is complete, return via <End> or <Esc>.
- You will now be prompted to enter the name of the product stream. Simply type **MIXED WASTE** and press <Enter>. A window which will ask you for the **Type of Equil Calc** will appear. Select **Adiabatic** and press <Enter> to continue. You will now enter a screen which prompts for a pressure or pressure drop. Just press <End> to default to the feed pressure. At this point the description of the Mix Block is complete. You can use the File facility to exit the block, or simply use <Esc>, where you will be asked if you are saving the data. **Save** should be highlighted, and then press <Enter>. You can explicitly request that the data be checked using the Check Action; however, a block is automatically checked for errors and inconsistencies when saving the data.
- You will now see a screen which reflects the Mix Block as well as **New Block**. Move to **New Block** and press <Enter>. The next block is also a **Conventional Block**, so simply press <Enter>. Then, use the Arrow Keys to move to the **Separate Block** and press <Enter>.

Describing the Separator Block ...

- You should now see the schematic for the Separate Block. As before, you initially need to type a name for the block. Type **SEPARATE1** and press <Enter>.
- You are now being prompted for the feed stream to the Separator. Enter the name **MIXED WASTE** and press <Enter>. Alternatively you could have just pressed <Enter> on the blank field to get a list of available streams. Note that you are not prompted for the feed stream state because ESP realizes that this stream was a product stream from another block (MIX1). (Note that ESP Process only matches identical stream names.)
- The vapor product stream should be named **SEPD VAPOR**, and the aqueous product stream will be named **SEPD LIQUID**.
- You are now being prompted for the organic product stream name. Use the down arrow to move to the solid product, since we did not include an organic liquid phase in the Chemistry Model for NEUTRAL1.

- The solid product stream name is **SEPD SOLID**.
- After you finish entering the solid stream name a list of unit parameters will appear. You will be given a choice of **Entrainment** or **Equil Calc types**. This example has no entrainment so we will skip that choice. The Separator Block has the same type of equilibrium calculations as does the Mix Block. Select **Equil Calc types** and then **Adiabatic**. Enter a pressure of 1.0 atmospheres. Now press <Esc>.
- Using <Esc> repetitively to leave the block, the prompt as to whether or not to save the description of the Separator appears. Be sure **SAVE** is highlighted and press <Enter> to check the data, save the data, and leave the block.
- You will now see three lines; one for the Mix Block (MIX1), one for the Separator Block (SEPARATE1) and one for **New Block**. Move to **New Block** and press <Enter>. Then from the **Environmental Blocks** select the **Neutralizer**.

Describing the Neutralizer Block ...

- You should see the schematic for the Neutralizer Block. As before, the first field to describe is the name for the process. Simply type **NEUTRALIZE1** and press <Enter>.
- The name of the first feed stream? By position you can see that this is the reagent stream. Enter the name **CAUSTIC REAGENT** and press <Enter>.
- The window for describing the state of the feed stream will now be activated. The values, already assumed to be in METRIC, should be entered based upon the detail provided in **Figure 2-1**. Once this is complete, simply press <Enter> and then <Esc> to move onto the next stream.
- You will now be prompted to enter the name of the second feed stream. Type the name **SEPD LIQUID** (a product stream from the Separator Block) and press <Enter>.
- The name of the product will be **NEUTRALIZED LIQ**. Enter that name then press <Enter>.
- You will now be prompted to select the type of neutralizer. Select **"Fix pH"** and press <Enter>. At the prompt for a value for pH, enter **9.0** and press <Enter>, then <Esc> back to the Neutralizer schematic.

- Press <Esc> once again to leave the block and press <Enter> to **Save** the information you provided.
- The Process Block Summary shows all three blocks in our process. Use the **Quit Key** to return to the **Working in Which Mode** screen; we are now ready to go to **Process Analysis**.

Simulating the Process ...

- We are now ready to execute the simulation. Select **Process Analysis** and press <Enter>. The "home screen" of Process Analysis displays what results are available to be viewed. On this screen **Calculate** should already be highlighted so just press <Enter> to run the simulation.
- Once the simulation is complete, we will be prompted to **Press any key to continue**. Press any key and we can then examine the results of simulation.

Examining the Results ...

- There are two ways to access information generated from the simulation. One is display the Stream and Block results from within the Process Analysis mode. The other is to move to the Summary mode, which will allow a report of the Stream and Process Block results to be sent to the disk or printer. In this case, let us stay where we are (the Process Analysis mode) and select the **Process Stream Results** and press <Enter>. Now, various streams of interest can be perused. We suggest that CAUSTIC REAGENT (the flow-adjusted neutralizer feed stream) and NEUTRALIZED LIQ (the eventual, pH=9.0, process product stream) be reviewed. The output is shown in Figure 2-2. *(please note, the results in this manual may not be the latest values. Please see the OLI support website, for the latest output.*

<http://support.olisystems.com/Documents/Manuals/OLI-ESP>

This concludes our tour of ESP Process. You may now exit the program.

Figure 2-2

Stream	CAUSTIC REAGENT	NEUTRALIZED LIQ
Phase	Aqueous	Aqueous
Temperature, C	3.0000E+01	3.9575E+01
Pressure, atm	1.0000E+00	1.0000E+00
pH	1.3667E+01	9.0000E+00
Total mol/hr	2.5761E+02	6.0689E+02
Flow Units	mol/hr	mol/hr
H2O	2.4865E+02	5.9556E+02
CO2		6.2907E-05
NH3		1.5754E+00
SO2		1.1521E-10
OHION	4.4796E+00	4.8729E-04
CO3ION		1.4225E-02
H3OION	1.0738E-13	1.8788E-08
HCO3ION		5.5992E-02
HSO3ION		1.7551E-03
NH2CO2ION		5.4431E-02
NH4ION		1.8970E+00
SO3ION		3.3547E-01
H2SO4		4.9849E-22
HCL		1.6769E-17
SO3		
HSO4ION		6.4181E-08

CLION		2.6498E-01
SO4ION		2.6498E+00
NAOH	1.1565E-10	2.5057E-14
NAION	4.4796E+00	4.4796E+00
Total g/hr	4.6588E+03	1.1192E+04
Volume, m3/hr	4.4867E-03	1.0935E-02
Enthalpy, cal/hr	-1.7469E+07	-4.1533E+07
Density, g/m3	1.0384E+06	1.0235E+06
Vapor fraction		
Solid fraction		
Organic fraction		
Osmotic Pres, atm	4.8753E+01	2.1601E+01
Redox Pot, volts		
Ionic Strength	1.7389E-02	1.5450E-02

Please see <http://support.olisystems.com/Documents/Manuals/OLI-ESP> for the latest values for this output.

An Advanced Tour of ESP Process

Now that we have completed the tour of the essential elements of ESP, we can now proceed on to some more advanced topics. One of these is the use of a unit operation called a control block. Controllers can be employed to set specifications for temperature, pressure, pH, composition or flow on any stream in the flowsheet and then to adjust appropriate flowsheet unit or stream parameters to meet these specifications.

The Application...

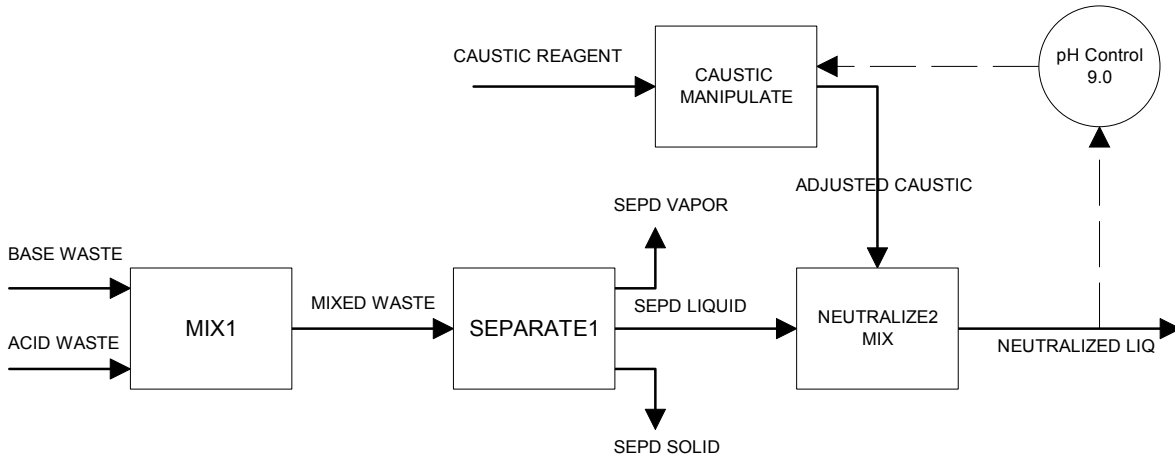
In this application we will rebuild the example process **NEUTRAL1** using a pH control loop rather than the neutralizer block. We frequently use a control loop for pH in cases where the set point of the controller is near the equivalence point of the solution (an area in which mathematical solutions are difficult to obtain).

We will be re-using portions of the **NEUTRAL1** process⁵ described in the ESP Process Tour. There are several aspects to keep in mind; first - a chemistry model already exists for this process (*NEUTRAL1*) so you do not need to re-generate the chemistry, second - do not enter any information for the neutralizer since we are replacing that unit. The revised process diagram can be seen in Figure 2-3.

⁵Or use the name you supplied.

Figure 2-3

Neutralization Process with Manipulate/Mix Block and pH Controller



Formulating the Process...

- Start the **OLI/Software**
- Select "**ESP Process**"
- Select "**New Process**" and use the name **NEUTRAL2**. Repeat the steps found under "**Preparing to Build the Process**" in the ESP Process Tour up to, but not including, the "**Describing the Neutralizer Block...**" using Figure 2-1..
- You may skip the "**Defining the Chemistry Model...**" section if you have previously developed and have saved the **NEUTRAL1** chemistry model. You thus simply select **Chemistry Model** and press <Enter>, then select **NEUTRAL1** and press <Enter> and then press <ESC>.
- Stop following the original tour when you get to the "**Describing the Neutralizer Block...**"

Describing the Manipulate Block...

- Now, select **New Block** and press <Enter>. Then from **ESP Control Blocks** select **Manipulate**
- You should now see a schematic for the Manipulate block. For the name of the block type in **CAUSTIC MANIPULATE**. When using control/manipulate blocks it is generally recommended that the type of the block (in this case "Manipulate") be included in the name. This makes identifying the block, from a list of blocks, easier.

Manipulate blocks are very simple in operation. Either the total flow of the inlet stream is multiplied by some factor or a specific component in the stream is multiplied by a factor. This factor can be controlled by a *Controller Block*.

Enter the name **CAUSTIC REAGENT** on the inlet stream. The conditions of this stream can be found in Figure 2-1.

- On the outlet stream enter the name **ADJUSTED CAUSTIC**. Again, it is a good idea to name the stream in a manner which indicates that a Manipulate block has acted on the stream.
- Press <Enter> after naming the outlet stream. A blue/white box should appear (referred to as the "Parameter List") indicating which parameters may be manipulated: *Total Flow* or *Stream Components*. Select **Total Flow** and enter 1.0 as a value.
- Press the <End> key twice to save this block.

Describing the Second Mix Block...

- Again, select **New Block** and press the <Enter> key. Now select **Conventional Blocks** from the menu. Finally, select **Mix** as the next block.
- This mix block is similar to the first mix block. Use the title **NEUTRALIZE2** as the name.
- On the first inlet stream enter the name **SEPD LIQUID** making sure you have spelled the stream correctly. Alternatively, you may press the <Enter> key on the blank field and a list of available streams should be displayed. Move the cursor to **SEPD LIQUID** and press <Enter>.
- On the second stream press <Enter> and select **ADJUSTED CAUSTIC** from the list. Please note that the name of the stream may be truncated.
- For the outlet stream enter the name **NEUTRALIZED LIQ** and press the <Enter> key. As with the first mixer you will be asked for the type of calculation. Select **Adiabatic** from this list and then press <Esc> repetitively and **Save** the block.
- Please note: Unlike the previous process, we are not defining the set point pH in this block. That will be done in the next block.

Describing the Control Block...

- Select **New Block** and then **ESP Control Blocks**. From this menu select **Controller**.
- For the name of this block we recommend **pH CONTROL** once again following the recommendation that the type of block be included in the name.
- For the **Specification Stream**, the stream which will be monitored by the controller, press <Enter> on the blank field and select **NEUTRALIZED LIQ** from the list.
- For the **Specification Type**: press <Enter> on the blank field and select **pH**.
- On the next field enter the desired pH of 9.0.
- In the section "**...to be Controlled by Process Block**" Press <Enter> on the blank field and select **CAUSTIC MANIPULATE** (please note, the name may be truncated).
- Finally press enter on **Block Parameter** and select **Factor, Flow** from the list. Press the <End> key to leave the block and then the <Esc> key to return to the **Working in Which Mode** screen.

Simulating the Process...

- To run the process, repeat the steps which are found in the ESP Process Tour.

Examining the Process...

- Select the **Process Stream Results** line and view the **NEUTRALIZED LIQ** stream. In the previous tour the pH was exactly 9.0. Now the pH may be slightly different from pH 9.0 (higher or lower depending on the current data in the database).

The controller has a built-in tolerance of 0.001 pH units. The pH on any iteration falls within ± 0.001 pH units the controller is said to be "Converged" and the calculation stops.

Figure 2-4 shows the stream report.

Figure 2-4

Stream	ADJUSTED CAUSTIC	NEUTRALIZED LIQ
Phase	Aqueous	Aqueous
Temperature, C	3.0000E+01	3.9575E+01
Pressure, atm	1.0000E+00	1.0000E+00
pH	1.3667E+01	9.0000E+00
Total mol/hr	2.5761E+02	6.0689E+02
Flow Units	mol/hr	mol/hr
H2O	2.4865E+02	5.9556E+02
CO2		6.2908E-05
NH3		1.5754E+00
SO2		1.1521E-10
OHION	4.4796E+00	4.8728E-04
CO3ION		1.4225E-02
H3OION	1.0738E-13	1.8788E-08
HCO3ION		5.5992E-02
HSO3ION		1.7551E-03
NH2CO2ION		5.4431E-02
NH4ION		1.8970E+00

SO3ION		3.3547E-01
H2SO4		4.9851E-22
HCL		1.6770E-17
SO3		
HSO4ION		6.4182E-08
CLION		2.6498E-01
SO4ION		2.6498E+00
NAOH	1.1565E-10	2.5056E-14
NAION	4.4796E+00	4.4796E+00
Total g/hr	4.6587E+03	1.1192E+04
Volume, m3/hr	4.4866E-03	1.0935E-02
Enthalpy, cal/hr	-1.7469E+07	-4.1533E+07
Density, g/m3	1.0384E+06	1.0235E+06
Vapor fraction		
Solid fraction		
Organic fraction		
Osmotic Pres, atm	4.8753E+01	2.1601E+01
Redox Pot, volts		
Ionic Strength	1.7389E-02	1.5450E-02

The most recent values for this example can be found on the OLI Support website

<http://support.olisystems.com/Documents/Manuals/OLI-ESP>

Another Advanced Tour of ESP Process

We have just seen that a control block, combined with mix blocks and manipulate blocks, can be used to control the pH of a stream. Frequently a process recycles part or all of certain streams back to up-stream units. There are many reasons for this including minimization of waste, increase of residence time and purification of product.

The Application...

This application extends the previous application by adding a new mix block, a split block and a recycle stream. We will be adding sodium chloride (salt) to the process to remove some solids from the solution. We will then recycle some of those solids back to an upstream unit to see the effect, if any, on the amount of caustic required to adjust the pH.

We will be reusing the previous process **NEUTRAL2**⁶.

+

Formulating the Process...

- When selecting the process, use the existing process **NEUTRAL2**. This process is displayed in Figure 2-5
- If the previous process does not exist, please review the ESP Process Tour and the Control Block Tour.

The chemistry model must be modified for this tour (in previous tours the chemistry model name was *NEUTRAL1*.) Please add the following inflows: **NACL, NAHCO3, NA2CO3, NA2SO4, NH42SO4**.

⁶Or the name you supplied. The example file found on the OLI Support website uses the name Neutral3.

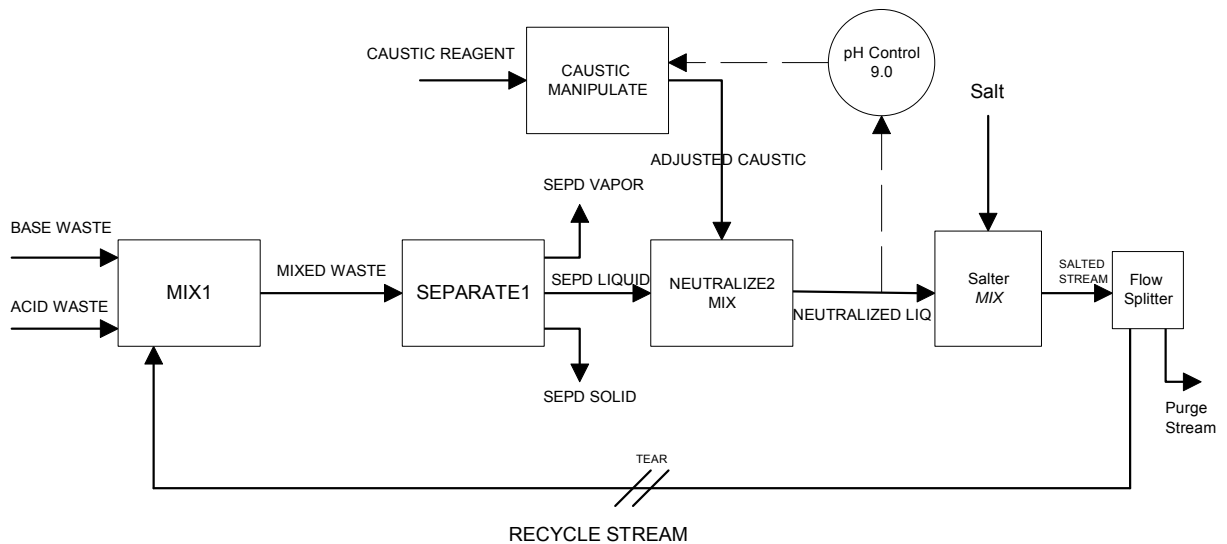
You will have to completely regenerate the chemistry model.

Describing the New Mix Block...

- Select **Process Build** from the "WORKING IN WHICH MODE?" menu. Then select **New Block** and then press <Enter>. Then, select **Conventional Blocks** and then select **Mix** from the list of blocks.

Figure 2-5

Neutralization Process with Manipulate/Mix Block, pH Controller, and Recycle Loop



- Name the new Mix block an appropriate name. Since we are adding a salt stream we suggest the name **SALTER** as an appropriate name.
- Press <Enter> on the first blank field to access a list of available stream names. Select **NEUTRALIZED LIQ** from the list and press <Enter>.
- On the second blank field, type in the name **SALT** and press <Enter>. The conditions of the stream are as follows:

Temperature	25.000° C
Pressure	1.0000 atm
Total Flow	75.000 mol/hr
NACL	75.000 moles

- There is no water associated with this stream. Under most conditions, we require water as a component. In those cases where we specifically do not want water in a stream, we must use the **Setphase** action.

Press the <Action> key and highlight **Setphase**. From the pull-down menu, position the cursor on **Solid Only** and press <Enter>. We have now informed the program not perform any aqueous equilibrium on this stream.

- Press the <End> key to save the stream composition.
- Position the cursor on the outlet stream (if not already there) and enter the name **SALTED STREAM** and press <Enter>.
- On the parameters list which appears after entering the name of the outlet stream, select **Isothermal** and press <Enter>. On the parameters screen, enter 40 °C for the temperature and press <End>. If the parameter list does not appear, press the <Action> key and select **Parameters** from the Action Line. Now select **Isothermal** and press <Enter>.
- Press the <End> key to save this block.

Describing the Flow Split Block...

- As with previous block, select **New Block** and then **Conventional Blocks**. Now select the **Split Block** and press <Enter>.
- There are two types of split block; a **Stream Split** block in which a stream is divided into 2 or more streams, and a **Component Split** block in which a specific component is divided into 2 or more streams.

Select **Stream Split** and press <Enter>.

- Type in a suitable name for the split block. We recommend **FLOW SPLITTER**. Position the cursor on the blank line and press <Enter>. From list of available streams, select **SALTED STREAM** and press <Enter>.
- For the **Outlet1 Stream** enter the name **PURGE STREAM**. This stream will exit the process.
- For the **Outlet2 Stream** enter the name **RECYCLE STREAM**. This stream will be recycled to an up stream unit.
- After pressing the <Enter> the parameter list should appear (if it does not, press the <Action> key and select **Parameters** from the action line). There are three columns in this list. The first column lists the names of the streams leaving the split block. The second column lists the fraction of the flow which will leave through the corresponding stream. The third column lists the flow of each stream.

If an actual flow rate is specified, the program will place that flow of material in the designated streams before adjusting the fractions of the flow. When all the specified flows have been accounted then the remaining flow is split according to the split fractions.

Enter 0.75 for the **PURGE STREAM** and 0.25 for the **RECYCLE STREAM** and press <End> when done. The program will then divide the overall stream flow allocating 75 percent to the stream **SALTED STREAM** and 25 percent to the stream **RECYCLE STREAM**.

- Press <End> twice to save this block.

Editing the First Mix Block...

- We now will modify the original mix block. Position the cursor on the **MIX1** block and press <Enter>.
- Currently there are no additional inlet streams available. Press the <Action> key and select **Config**. A pull-down menu will ask to add and additional stream or delete a stream. Select **Add Stream**.

The program will inform you that an *Inlet Stream* is being added to the block. Accept the information by selecting **Continue**.

- On the new blank stream line, press <Enter>. From the list of available streams select **RECYCLE STREAM** and press <Enter>. The outlet of the block **FLOW SPLITTER** has been recycled.

Simulating the Process...

Processes with recycle streams require some additional information to be provided prior to running the simulation. In processes without a recycle stream, the order of block calculation is easy to determine. Generally the first block defined is the first calculated.

In recycle processes, we must tell the program where to begin calculating. We do this by defining a process stream as a *Tear* stream. Tear streams are treated as normal process entry streams and require an initial composition. These compositions should be representative of the process and some care should be taken in specifying the stream.

- Use the <End> key or the <Esc> key to return the “**Working in which mode?**” Screen
- Select **Process Analysis**.
- Press the <Action> key and select **Recycle** from the action line.

- A list of *Recycle Options* will appear. Position the cursor on the **Select Tear(s)** and press <Enter>
- There are 5 possible tear streams. Reviewing Figure 2-5 will show this more clearly. Position the cursor on **RECYCLE STREAM** and press <Enter>.
- Position the cursor on **Tear Stream Guess** and press <Enter> (if the program returned you to the main Analysis menu, press the <Action> key, re-select **Recycle** and then select **Tear Stream Guess**).

- Enter the following *Tear Stream Guess*⁷:

Temperature	40.00	C
Pressure	1.000	atm
Total Flow	213.19	mol/hr
H2O	186.74	moles
NH3	0.33096	moles
CO2	0.00185	moles
HCL	0.00058	moles
NACL	25.0880	moles
NAHCO3	0.00521	moles
NA2CO3	0.02331	moles
NA2SO4	0.46092	moles
NH42SO4	0.42233	moles

Note: Any inflows not mentioned should be left blank.

⁷ The values for this guess were determined from a previously converged case. This guess will speed up the execution of the process.

Press <End> when done.

- Continue to press <End> till the cursor is on the "**WORKING WITH WHICH ANALYSIS AREA?**" menu. Position the cursor on **Calculate** and press enter.

Unlike the previous tours, this tour will recalculate many of blocks as the program attempts to converge the recycle, in other words, to make the values in the recycle loop consistent between successive iterations. This may take several iterations to complete.

Examining the Process...

- From the "**WORKING WITH WHICH ANALYSIS AREA?**" menu position the cursor on **Process Stream Results** and press enter.
- Determine if any solids have formed in the stream **SALTED STREAM**.
- What is the flowrate and pH of the **RECYCLE STREAM**?
- How much **ADJUSTED CAUSTIC** was required? Was this amount different from the non-recycle case?

The stream reports for this tour are shown in **Figure 2-6**

Figure 2-6

Stream	RECYCLE STREAM		ADJUSTED CAUSTIC	SALTED STREAM	
	Aqueous	Solid	Aqueous	Aqueous	Solid
Temperature, C	4.0000E+01	4.0000E+01	3.0000E+01	4.0000E+01	4.0000E+01
Pressure, atm	1.0000E+00	1.0000E+00	1.0000E+00	1.0000E+00	1.0000E+00
pH	8.9780E+00		1.3667E+01	8.9780E+00	
Total mol/hr	2.4413E+02	3.5318E+00	2.5429E+02	9.7652E+02	1.4127E+01
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr
H2O	1.9744E+02		2.4545E+02	7.8975E+02	
CO2	5.6636E-06			2.2654E-05	
NH3	5.2087E-01			2.0835E+00	
SO2	4.3720E-10			1.7488E-09	
OHION	7.7490E-05		4.4218E+00	3.0996E-04	
CO3ION	8.1010E-03			3.2404E-02	
H3OION	8.0177E-10		1.0599E-13	3.2071E-09	
HCO3ION	1.2942E-02			5.1769E-02	
HSO3ION	1.7157E-03			6.8629E-03	
NH2CO2ION	9.4282E-03			3.7713E-02	
NH4ION	6.4531E-01			2.5813E+00	
SO3ION	1.1205E-01			4.4820E-01	
H2SO4	9.2344E-24			3.6938E-23	
HCL	4.8388E-15			1.9355E-14	
SO3					
HSO4ION	3.7615E-09			1.5046E-08	
CLION	2.1557E+01			8.6228E+01	
SO4ION	8.8327E-01			3.5331E+00	
NAOH	8.9661E-15		1.1416E-10	3.5864E-14	
NAION	2.2943E+01		4.4218E+00	9.1771E+01	
NACL		3.5318E+00			1.4127E+01

Total g/hr	4.9649E+03	2.0641E+02	4.5987E+03	1.9860E+04	8.2562E+02
Volume, m3/hr	4.1405E-03	9.5393E-05	4.4288E-03	1.6562E-02	3.8157E-04
Enthalpy, cal/hr	-1.5866E+07	3.4693E+05	-1.7244E+07	6.3463E+07	-1.3877E+06
Density, g/m3	1.1991E+06	2.1638E+06	1.0384E+06	1.1991E+06	2.1638E+06
Vapor fraction					
Solid fraction		1.0000E+00			1.0000E+00
Organic fraction					
Osmotic Pres, atm	4.4036E+02		4.8753E+01	4.4036E+02	
Redox Pot, volts					
Ionic Strength	1.0073E-01		1.7389E-02	1.0073E-01	

For the most recent set of values please see the example file on the OLI Support website:

<http://support.olisystems.com/Documents/Manuals/OLI-ESP>

Chapter 3. Databook

Overview

General Description

The OLI Engine contains these user components: OLI Databook, a component to review and add to an extensive thermodynamic library containing over 10,000 chemical species; OLI ToolKit, a component which provides access to several important facilities including OLI Express (convenient stream studies), OLI WaterAnalyzer (feed stream definition based upon a water analysis), and ProChem (certain specialized single-stream calculations via OLI's older ElectroChem Software)

Reviewing OLI Data

The first chapters of this section describe how OLI Databook is used as a window into the reference library of physical and thermodynamic data for chemical components. The species information available through OLI Databook and the search procedures used to access this data are discussed in detail.

Building A Private Databank

This section also describes the procedures for the user to build additional databanks for particular species of interest that are not included in the OLI provided data libraries. In this way the Databook facility is a vital component of the OLI Engine, and in particular, in the building of a Chemistry Model. A model cannot be generated for an application if the Chemistry Model requires thermodynamic information for one of more species which are not contained within an OLI databank.

Content

OLI Databook provides an interface to an extensive thermodynamic and physical property library for nearly 10,000 different chemicals. The OLI libraries include: organic species that are listed in the DIPPR Project 801 data compilation (DIPPR is the Design Institute for Physical Properties which is administered by the American Institute of Chemical Engineers); the EPA (Environmental Protection Agency) List of Lists; the European Red, Gray and Black lists; and an extensive list of inorganic chemical species.

Here is a link to the content listing of all the OLI supplied databases:

<http://support.olisystems.com/Documents/Release%20Notes/Database%20Content.xls>

Data Organization

The chemicals are organized into eight separate system databanks, each of which can be accessed through OLI Databook. These databanks are called:

PUBLIC - This databank contains more than 10,000 different chemicals and contains all the physical and thermodynamic property data required to use the ESP Process simulation program.

MSE PUB – This is the mixed-solvent electrolyte (MSE) framework version of the aqueous database. It is a subset of the PUBLIC database and will eventually replace the PUBLIC database.

GEOCHEM - This databank contains approximately 90 chemical species used to describe typical geological formations. These minerals tend to equilibrate with water over long periods of time and hence should not normally be included in equilibrium based calculations.

GEMSE – this is MSE version of the GEOCHEM database

LAB - This databank contains approximately 150 primary anion and cation species and contains the required data to perform WaterAnalyzer calculations (Reference OLI ToolKit section for further details). It is

recommended that the user only accesses this databank to determine the ionic species recorded and available for use in WaterAnalyzer calculations (Reference on pg. and on pg.).

LOWTEMP - This databank contains approximately 200 solids, whose data has been extrapolated from the minimum temperature to -50 C.

CORROSION - This databank contains the oxides and hydroxides required to perform Corrosion calculations.

CRMSE – this is the MSE version of the CORROSION database

ALLOYS - This databank contains information on alloys required to perform corrosion calculations.

CERAMICS - This databank contains information on certain ceramic materials.

CEMSE – this is the MSE version of the CERAMICS database,

SURCMPX - This databank contains information to support the surface complexation adsorption model.

Data Protection

Note: All the data contained within the 8 databanks are write protected to maintain data integrity. This data can be reviewed, but cannot be edited/modified without the express permission of OLI Systems, Inc. For further information please contact:

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Suite 301

Cedar Knolls, New Jersey 07927

Tel: (973) 539-4996

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Oli.support@olisystems.com

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Chapter Descriptions

Databook Chapters

OLI Databook is divided into sections to aid the user in searching for, and accessing, the required species information. The sections available are called Databook Chapters and are: Species, Synonyms, Experimental, Interactions, Literature, Structure, Coprecipitation, Sorption, Redox and Electrical. Each Chapter is considered in more detail below. The content of OLI Databook is shown in Figure 2.1 at the end of this chapter.

Species Chapter

The Species Chapter of OLI Databook contains general information on chemical species such as chemical name, molecular weight and other identifying characteristics (e.g., CAS - Chemical Abstracts Registry - Number). In addition, thermodynamic and physical property data for each relevant phase (i.e., solid, aqueous, vapor) of the species is available. Each thermodynamic property is referenced and documented individually.

Once the data for a specific species has been accessed the user can select the type of information to be viewed: General Information, Aqueous Phase, Vapor Phase, Solid Phase. When data for a species exists for a given type of information, a "", or ">>" symbol is used next to that type. The user simply selects the information of interest using the Arrow Keys and Enter Key.

The data available in each section is listed below. Each entry is recognized with a software keyword.

General Information

<u>Keyword</u>	<u>Description</u>
DATE	Last modification date of the data
CREA	Initials of user who created/modified the data
LOLN	Environmental Protection Agency (EPA) List of Lists Name
IDNO	A species ID number
IUPA	IUPAC Name
FORM	Empirical chemical formula (Reference pg. for further details)
CHEM	Standard chemical formula
STRU	Structural chemical formula (organic formula listed by structural group e.g., C ₃ H ₆ listed as CH ₃ CHCH ₂)
CAS	Chemical Abstracts (CAS) Registry Number
MOLW	Molecular weight
MATC	OLI defined code for an element, group of elements, or a molecule

STOI Species chemical elements stoichiometry (listed in the same order as elemental material codes)

DUSE Data use (i.e., PUB, GEO, LAB) which defines which databank contains the species data

ORG Type of species (i.e., organic/inorganic)

Aqueous Phase Information

Keyword

Description

DATE Last modification date of the data

GRES Reference state (25° C, 1 bar) Gibbs free energy of formation

HREF Reference state enthalpy of formation

SREF Reference state entropy

VREF Reference state volume

CPRE Reference state heat capacity

ZRAC Rackett Z value (used in density calculations of organic liquids)

HKF Helgeson Equation of State constants

HTYP	Helgeson ion type (Ion T)
EQUA	Aqueous chemical equilibrium equation
CHAR	Species ion charge
IONC	OLI defined ion code
KFIT	Coefficients for predicting the equilibrium constant as a function of temperature and pressure (maximum of 7 coefficient entries)
IONT	Ion type (Helgeson)
STYP	<p>Solubility type. This is a single integer value which assists in estimating the molecular species distribution between the aqueous and nonaqueous liquid phases. The integer values used are:</p> <p>0 Species prefers the aqueous phase</p> <p>1 Species prefers the nonaqueous liquid phase</p>
BINT	Binter Parameter, which represents the self interaction contribution for an aqueous molecular species to its own activity coefficient
SPR	Shannon-Prewitt Radii (Angstroms)
SURF	Surface Complexation Model Constants

Vapor Phase Information

<u>Keyword</u>	<u>Description</u>
DATE	Last modification date of the data
ACEN	Acentric factor
TCRI	Critical temperature
PCRI	Critical pressure
VCRI	Critical volume
BOIL	Normal boiling point of the pure liquid
VP	Coefficients for determining the pure component vapor pressure as a function of temperature (maximum of 5 coefficient entries)
GRES	Reference state Gibbs free energy of formation
HREF	Reference state enthalpy of formation
SREF	Reference state entropy
CPRE	Reference state heat capacity

CP	Coefficients for determining heat capacity as a function of temperature (maximum of 5 coefficient entries)
SOLU	Coefficients for determining the binary solubility of the species in water as a function of temperature (maximum of 5 coefficient entries)
EQUA	Vapor-Aqueous equilibrium equation
KFIT	Coefficient for predicting VLE constant as a function of temperature (maximum of 5 coefficient entries)

Solid Phase Information

<u>Keyword</u>	<u>Description</u>
DATE	Last modification date of the data
RHO	Coefficients for determining pure solid density as a function of temperature (maximum of 5 coefficient entries)
GRES	Reference state Gibbs free energy of formation
HREF	Reference state enthalpy of formation
SREF	Reference state entropy
VREF	Reference state volume

CPRE	Reference state heat capacity
EQUA	Solid-Aqueous equilibrium equation
MELT	Pure solid species melting point
KFIT	Coefficients for determining the equilibrium constant as a function of temperature (maximum of 5 coefficient entries)
TRN	Number of solid phase transitions expressed as an integer (i.e., 0-7 transitions allowed)
TTR	Phase transition temperatures at which a species goes from one modification to another (maximum of 7 temperature entries)
HTR	Phase transition enthalpy of the solid for each corresponding transition temperature (maximum of 7 enthalpy entries)
CP1-CP7	<ul style="list-style-type: none"> i) For solids with no phase transitions (TRN=0) coefficients for determining species heat capacity as a function of temperature. ii) For solids with phase transitions (TRN>0) coefficients for determining species heat capacity for each crystal modification are entered in the corresponding phase transition temperature range: 298.15-TTR1, TTR1-TTR2; etc.

More Detail In Help

Further information on individual data entries can be obtained using the Help facility. This is achieved by highlighting the particular information of interest and using the Help <F1> key. This function automatically displays the Help information for the specific entry.

Synonyms Chapter

The Synonym Chapter of OLI Databook contains name listings of each species as well as recognized synonyms for each species. The user may specify a name or partial name and select from among several choices.

This chapter is mainly used to determine complete synonym names for a particular species, which can then be used when searching for information in the Species Chapter of OLI Databook.

The search procedures available are described in on page of this section.

Experimental Chapter

The Experimental Chapter of OLI Databook contains the source data used to develop a limited portion of the temperature dependent data-fit equations for the thermodynamic properties in the Species Chapter.

The experimental data contained in this chapter includes: vapor pressure, vapor heat capacity and aqueous solubility information for a pure component species as a function of temperature; as well as mean activity coefficient and density information for a single salt solution in water, as a function of salt concentration.

Literature Reference

The user can access the literature reference from which the data was taken, as well as display the experimental data in tabular or graphical format using the Action Key facilities (Reference pg.).

Interactions Chapter

The Interactions Chapter of OLI Databook contains the regressed binary interaction coefficients for calculating activity coefficients and excess density. These coefficients are developed from information stored in the Experimental Chapter of the databank and are used in the calculation of the aforementioned thermodynamic excess properties.

The regressed coefficients for interactions between two species currently stored in the databank include:

Bromley Coefficients - These describe ion-ion interaction parameters and are used to determine the activity coefficients in the aqueous phase.

Density Coefficients - These describe ion-ion interaction parameters and are used in aqueous density calculations.

Pitzer Coefficients - These describe certain ion-molecule and molecule-molecule interactions and are used in activity coefficient equations. If they are entered they are used in the calculations.

SRK Coefficients - These are interaction parameters used in the Kabadi-Danner extensions for the calculation of fugacity coefficients in the Soave-Redlich-Kwong (SRK) Equation of State.

Literature Chapter

The Literature Chapter contains the references for the information stored in both the Species Chapter and Experimental Chapter of OLI Databook. It is divided into four sections: References, Equations, Material Codes, and Ion Codes.

References

In the Reference Section, the user can access all the literature references used in the OLI Software; these are indexed with a reference code. The user can determine the reference code for a particular reference when using the Experimental Chapter of the Databook. References are organized by year and by first and second author.

Equations

The Equations Section of the Literature Chapter contains the equations used in the various temperature and concentration relationships, also indexed by a code. It must be noted that these equations are for documentation only. Adding a new equation to this section does not expand the program's capabilities.

Material Codes And Ion Codes

Species material and ion codes are also available and can be located either by the respective code number or by the chemical species formula. The respective species material or ion code number can be viewed, as well as the species chemical symbol, ion charge, and molecular weight.

Access to species material codes is an important facility when defining species in private databanks. They are also used by the software when defining redox reactions.

Structures Chapter

The Structures Chapter of OLI Databook contains two dimensional drawings of organic molecules for each organic species contained within the databank. This drawing is for display purposes only. Searching for a species by structure or substructure is not yet available. However, searches for species can be performed using a variety of methods and are detailed in the following chapter of this section.

Coprecipitation Chapter

The Coprecipitation Chapter of OLI Databook contains coefficients which allow for the prediction of the free energy of ions coprecipitating into a regular crystal (solid) lattice. These coefficients are then used in proprietary OLI formulations, based upon a Linear Free Energy (LFE) correlation and Regular Solution Theory model in predicting the required free energies. This implementation is proprietary to OLI and the user has limited Databook access.

Sorption Chapter

The Sorption Chapter of OLI Databook contains data needed for ion exchange. The molecular weight of the medium, the K-Equation Coefficients, and the Margules Interaction Coefficients are all included here.

This data is usually entered by the user from the Chemistry Models facility, IonxEntry, rather than being directly entered from OLI Databook. (Reference , on page for further details.)

Redox Chapter

The Redox Chapter of the OLI Databook contains the information needed for the automatic generation of reduction/oxidation equations. Two kinds of information are collected in this chapter:

1. Logical association between different oxidation states of the same element. For example, the elementary species containing elemental Fe and Fe²⁺ and Fe³⁺ ions (i.e., FEELPPT, FEIIIION and FEIIIIION) are grouped together. This is accomplished by the EQUA ASSO record in the Redox Chapter.
2. Equations for inclusion in the Model Definition file if the Oxidation/Reduction option is requested by the user at the stage of chemistry model generation.

Electrical Chapter

The Electrical Chapter of the OLI Databook contains the information needed to support the calculation of the Electrical Conductivity in aqueous solutions.

Locating a Species

Various search procedures are available to the user for locating species information, and are detailed next. Some procedures are chapter specific and are noted accordingly.

Search By Databook Catalog

A facility is available for the user to obtain either a complete listing, or class of species listing, for compounds contained within a specific databank. From the listing, the specific species of interest can be chosen and the data displayed.

Method

Initially when using OLI Databook, the user must specify which databank is to be opened (i.e., PUBLIC, GEOCHEM, LAB, LOWTEMP, CORROSION) followed by the appropriate Databook Chapter to be used in the data search. A listing of the chemical species contained within the databank can be produced by using the Action Key and then choosing the Catalog facility.

On choosing this Catalog facility, species listings can be produced on either an inorganic, organic, or on an entire species basis. Alternatively, a species search can be carried out on a selected element basis. This option allows the user to select particular chemical elements of interest from the periodic table. From this selection a species index list is displayed showing all the databank compounds containing the specified elements, with the phases for which data exists.

From the index listings displayed, the user can determine if a particular species is included in the specified databank. This can be time consuming, especially when listing PUBLIC Databank species, and more efficient search methods are available to the user.

Catalog Views

The default setting for the catalog is a list organized by:

Formula (phases)

CAS Number

Instead of CAS Number, the user can produce catalogs using the IUPAC name or the ESP name as the secondary identifier. This is done by using the Action Key and selecting the View facility.

Catalog Output

The output from the catalog is automatically sent to the disk in the file called PUBLIC.CAT. The user can select screen, disk, or print the output, by using the Action Key and selecting the Output facility, when the Catalog listing is displayed.

Catalog Sort

The Catalog is initially produced in "Computer Sort Order". This listing is produced based on the first character and digit of the species formula. For example, an organic listing for species containing between 1 to 12 C atoms is displayed as C10, C11, C12, C2, C3....C9, C. Alternatively, a "chemical sort" listing can be produced which lists species based on the first element amount expressed in the chemical formula. The listing is ordered sequentially as follows; C, C2, C3, ..., C11, C12.

The sorted disk file is called PUBLIC.SRT.

Search By Species Formula

This facility is only available when using either the Species, Synonym, and Structures Chapters, or the Vapor Pressure, Heat Capacity and Solubility Sections of the Experimental Chapter of OLI Databook.

The chemical must be entered in the Empirical formula and in the correct letter case definition.

For inorganic compounds the Empirical formula expresses the elements of a chemical formula in alphabetical order (e.g., sodium hydroxide is expressed as HNaO, NH₃ as H3N, and CaCO₃ as CCaO3). Organic compound formulas must be defined as the number of carbon atoms, the number of hydrogen

atoms, followed by any other elemental definition expressed in alphabetical order (e.g., Sodium Ethanoate, CH₃COONa is expressed as C₂H₃NaO₂).

When searching for an ionic species the Empirical formula must be suffixed with the respective charge of the species (e.g., CO₃⁻²).

Method

Initially the databank to be searched (i.e., PUBLIC, GEOCHEM, LAB, LOWTEMP, CORROSION) must be specified followed by the required chapter (i.e., Species, Synonym, Experimental, Structures) on the following screen. The Action Key is then used and the Search facility chosen. (Note: When using the Experimental Chapter of the Databook the appropriate data section - Vapor Pressure, Heat Capacity, Solubility - must also be defined prior to using the Search facility).

From the list displayed, the search "By Formula" option is specified. The user can then enter the chemical formula of the species of interest, and the databank search is carried out.

Wildcards

Alternatively, if the user is unsure of the exact chemical formula of a particular compound, a databank search can be performed on an elemental basis. This type of search is known as a wildcard entry, and provides a listing of species within the databank containing the specified elemental wildcard.

Elemental Search

To perform a wildcard search the user simply has to enter the species elemental formula, prefixed and suffixed with "*" symbol (e.g., *Na*). A databank search is carried out and a list displayed in empirical chemical formula of all databank species containing the specified wildcard. An entire species formula listing from the databank can be produced by entering only the "*" symbol when prompted for the species formula. The user can highlight the chemical compound of interest, and access the required data by using the Arrow Keys and the Enter Key.

Guidelines

1. *To view the data in the Experimental Chapter, highlight the required data set, and then press the Action Key and choose the View facility.*
2. *The search procedure described does not apply directly to the Lab Databank. It is advised that the LAB Databank be searched only to determine the ionic species available for WaterAnalyzer calculations (Reference the OLI ToolKit section for further details).*
3. A full listing of databank cationic or anionic species can be obtained using the (+) or (-) sign respectively, prefixed and suffixed with a "*" symbol (i.e., *+*, *-*).

Search by Species Name

This facility is only available when using either the Species, Synonym, and Structures Chapters or the Vapor Pressure, Heat Capacity and Solubility Sections of the Experimental Chapter of OLI Databook.

Method

Initially, the databank to be searched must be specified (e.g., PUBLIC, GEOCHEM) followed by the required chapter (i.e., Species, Synonym, Experimental, Structures) on the following screen. The Action Key is then used and the Search facility chosen.(Note: When using the Experimental Chapter of the Databook the appropriate data section - Vapor Pressure, Heat Capacity, Solubility - must also be defined prior to using the Search facility).

From the subsequent list displayed, the search "By Species Name" option is specified. The user can then enter the chemical name or a synonym for the species of interest, and a databank search carried out. Note: If a synonym name is used it is advised that the user also accesses the Databook Synonym Chapter to confirm that the particular species has been located.

Wildcards

Alternatively, if the user is unsure of the exact chemical name of a compound, and only a particular elemental component is known, a databank search can be performed on an elemental name basis. This type of search is known as a wildcard entry and provides a listing of species, by name, within the databank containing the specified wildcard.

To perform a wildcard search the user simply has to enter the chemical component elemental name, prefixed and suffixed with "*" symbol (e.g., *sulfur*). Depending on the elemental name involved, the user must take care in providing either a full or partial elemental name.

For example, if a search is performed with the wildcard *sulfur* fewer species will be found in the databank than if the partial species name *sulf* is used. With the latter, a full listing of species containing different forms of sulfur (i.e., sulfides, sulfites, sulfates, etc.) is obtained.

Guidelines

1. A general guideline to be followed *is the shorter the elemental name specified, the more general the databank search performed*. Hence, if only the symbol "*" is entered, an entire species name listing for the databank is produced.
2. *The search "By Species Name" option can be used for a general search for ionic species included in the databank*. Either a specific search can be carried out by entering the element name followed by the recognized keyword "ION" (i.e., SODIUM ION) or alternatively, a full ionic species list can be produced by entering the keyword "ION" prefixed with a "*" symbol (i.e., *ION).
3. *The species name search facility should not be used in the LAB Databank*. It is advisable not to perform a name search in the LAB Databank. This is because the LAB Databank is a special library and exists for WaterAnalyzer calculations only. It should not be searched to determine species property data, and should only be accessed to provide an index of ionic species available for use in WaterAnalyzer calculations.

4. *The Search facility has a maximum of 1000 entries.* When a search is general (e.g., C*) and more than 1000 matches are found, the display is truncated at 1000.

Search by Periodic Table

This function allows the user to select elemental species of interest from a displayed periodic table of the elements and perform a databank search for compounds involving the chosen elements.

This facility is only available when using the Species, Synonym, and Structures Chapters and the Vapor Pressure, Heat Capacity and Solubility Sections of the Experimental Chapter of OLI Databook.

Method

Initially the databank to be searched must be specified (e.g., PUBLIC, GEOCHEM) followed by the chapter of interest (i.e., Species, Synonym, Experimental, Structures) on the following screen. The Action Key is then used and the Search facility chosen. (Note: When using the Experimental Chapter of the Databook the appropriate data section - Vapor Pressure, Heat Capacity, Solubility - must also be defined prior to using the Search facility).

From the list displayed the search "By Periodic Table" is specified. The user can select elements from the displayed periodic table using the Arrow Keys and selecting with the <Space Bar>. A search of the databank is performed and a compound listing is displayed showing all the species containing all of the selected elements within the databank.

From the list produced by the search, the user can choose the particular species of interest and display its relevant property information.

Different Search Methods

When selecting more than one element, the default search method is for species which contain *all of the elements selected* (i.e., the intersection of the elements). Pressing the Action Key and choosing the Select facility allows for changing the method of search to *any of the elements selected* (i.e., the union of the elements), or to *only the elements selected* (e.g., H and Cl would produce species HCl).

Specifying the Amount Of An Element

When an element is selected, species containing any stoichiometric amount of that element are considered. The user can make the search more specific by entering the number of occurrences of the element. For example, selecting "C" will produce a list of all species containing carbon in the databank. Entering a "6" when positioned on "C" (i.e., choosing "C6") will produce a listing of all species containing six carbons in the databank.

Multiple Compounds

When there are multiple species with the same formula, these formulas are marked with a "*". Selection of a starred formula results in a display of all compounds with that formula along with a second identifier to distinguish the compounds. The second identifier defaults to the first synonym. OLI name, CAS number, or the IUPAC name, can be used as the second identifier by pressing the Action Key and selecting the View facility.

Guidelines

1. *The search procedures for locating a single species are summarized in the schematic diagram () on page .*
2. *When using the LAB Databank it is advisable to specify singular elements only from the periodic table. Otherwise, a data search cannot be carried out.*

Search by Pairs of Species

This function allows the user to access interaction coefficients for selected pairs of species. This facility is only available when using the Interactions Chapter and the Activity and Density Coefficient Interaction Sections of the Experimental Chapter of the PUBLIC Databank.

Method

Initially the PUBLIC databank search must be specified followed by the desired chapter (i.e., Experimental, Interactions). If the Experimental Chapter is used the user must then select either the Activity or Density Coefficient Interactions Sections.

The user can then enter the species pair of interest. This entry must use software recognized identifiers for the species and can either be a one word synonym or the OLI Name. If the species is an ion, the species entry must also be suffixed with the keyword "ION". For example, the acetate ion is recognized with the identifier "ACETATEION" but is not recognized if the entry is made by the chemical formula $C_2H_3O_2ION$.

Wildcards

Alternatively, if the user is unsure of the exact chemical identifier for a species, a databank search can be carried out on an elemental basis. This type of search is known as a wildcard entry and provides a listing of ionic species within the databank containing the specified wildcard.

To perform a wildcard search the user simply has to enter the software recognized identifier (i.e., Na, ACETATE, etc.) for the species suffixed with "*" symbol (Note: The keyword "ION" is not needed in a wildcard entry). A list is displayed showing the species pair within the databank containing the wild card entry. The user can then choose the pair of interest, using the Arrow Keys, and display the interaction coefficient data. The species pair list for an entire databank can be obtained by entering the symbol "*", when prompted for the species ionic identifiers.

Accessing the Data

From the pair specified, an index of interaction coefficients available to be viewed is displayed. When using the Experimental Chapter a reference code for the coefficients is also displayed and is defined in the Literature Chapter of OLI Databook (Reference on pg. for further details).

In order to access the coefficient data the user highlights the type of coefficients to be viewed from the index using the Arrow Keys. The Action Key is then used and the View facility chosen. The subsequent menu allows the user to determine the literature reference from which the data is taken, display the coefficient values, their quality (accuracy), and the last modification date of the information.

Search By Code

This facility is available for searching the Literature Chapter of OLI Databook. The Literature Chapter contains the following types of data:

- **References**
- **Equations**
- **Material Codes**
- **Ion Codes**

Method

Initially, the databank to be searched (e.g., PUBLIC, GEOCHEM) must be specified followed by the Literature Chapter on the succeeding screen. (Note: When using the LAB Databank the Literature Chapter should not be accessed). The user must then specify the particular section to be accessed (i.e., References, Equations, Material Codes, Ion codes). Each section is now discussed in more detail.

References Section

This section contains listings of the references used in OLI data and are indexed using a short reference code.

Short Reference Code

The code consists of two digits (or three if the year is before 1900), representing the last digits of the literature's year of publication, followed by three characters (maximum), which are normally the first three letters of the principal author's last name. For literature produced by co-authors the first two surnames are summarized, separated by a "/" symbol (e.g., 11aaa/bbb). If an author has more than one reference for a given year, the references are numbered with a suffix counting from 1 (e.g., 90RAF1).

Types of Searches

When using the References Section, the user can perform a specific or general literature search. A general search can be carried out either by literature publication year or by author surname. A specific search is performed by entering the complete literature short reference code as described above. From this entry the full literature reference is displayed.

Wildcards

Alternatively, if a complete short code reference is not known a more general search, known as a wildcard entry, can be carried out. Complete short code listings can be produced either by literature publication year or by author surname.

Guidelines

1. From the listings produced, *access to the complete literature reference is obtained by selecting the appropriate short code reference* using the Arrow Keys and selecting with the Enter Key.
2. *A complete publication year listing can be produced by entering the relevant year in two digit format suffixed with the "*" symbol (i.e., "11*").*
3. *A complete author publication index can be obtained by entering the author surname in three character format prefixed and suffixed with the "*" symbol (i.e., *aaa*).*

Equations Section

This section contains the temperature/concentration equations to which coefficients have been fit in the Species and Experimental Chapters of OLI Databook (e.g., specific heat, vapor pressure, solubility, etc.). The equations are indexed by code which begins with the letter "E" followed by a reference number (3 digits).

A specific equation search can be performed by entering the appropriate complete code, from which the full equation is displayed.

Wildcards

Alternatively, a more general search, known as a wildcard entry, can be carried out. This is achieved by entering the letter "E" followed by a partial code number suffixed with a "*" symbol. This produces a complete code list for the equations with the partial wildcard number. For example, the wildcard entry "E00*" will find equations with codes in the range 000-009 inclusive.

Access to the relevant equation is obtained by highlighting the appropriate code using the Arrow Keys and selecting with the Enter Key.

Material Codes Section

Material codes are OLI defined integer numbers which describe the constituents of a species. They are used in OLI software to maintain proper material balances. Material Codes become important to the user when making a Chemistry Model which includes redox reactions, and in OLI Databook, when defining private databanks.

For electrolytes, two or more material codes are needed to define a species. Typically, the constituents of an electrolyte will already exist and can be found in the Material Codes section. For electrically neutral molecular species, a single material code is assigned which represents the entire species.

The Material Codes Section of any OLI databank contains the OLI defined material codes for the species defined in all OLI databanks. The data accessed along with the material code include the molecular weight, the charge, and the software recognized symbol associated with the material code. Access to the information in the Material Code Section is either by material code or symbol.

Method

When using this facility the user must initially specify the Material Codes Section of the Literature Chapter and then use the Action Key, followed by the Search facility. From the list displayed, the user can define the search to be performed either by material "Number" or "Symbol". Both options allow specific or more general (i.e., wildcard) searches to be carried out.

Searching By Number

When using the search "By Number" option, the user performs a specific data search by entering the required species material code value and the relevant data will then be displayed. Alternatively, a wildcard search can be carried out using a partial material code value, suffixed with "*" symbol (e.g., 8*). A material code index is then displayed showing all the codes within the databank, starting with the specified value. The appropriate code can be selected, and the data displayed, using the Arrow Keys and Enter Key.

Searching By Symbol

The search "By Symbol" option also allows a specific or wildcard search to be performed. The symbol entered must be recognized by the software and can be either a chemical formula or name.

Wildcards

Alternatively, a wildcard search is performed by entering either the species formula, or partial chemical name, prefixed and suffixed with "*" symbol (e.g, *Fe*). A list is then displayed showing all species containing the specified characters in succession, either in a chemical formula or name. The relevant data is accessed by selecting the appropriate species of interest using the Arrow Keys and Enter Key.

Guidelines

1. *Generally, for inorganic species, the chemical formula is used; for organics either a chemical formula or name is entered.* This entry depends on the software recognizable identifier of a particular species (i.e., methane is only recognized by formula, CH₄; methanol is only recognized by name, METHANOL).
2. *A specific inorganic species search can be performed by entering the species formula, succeeded by its oxidation state enclosed in brackets (i.e., Fe(+3)).* Similarly, for organics, either the respective formula, or software recognized species name is entered.

Ion Codes Section

This section contains all the symbols and numbers used to define ionic species ions. Access to the information can be achieved either by species ion code or symbol.

Method

When using this facility the user must initially specify the Ion Codes Section of the Literature Chapter and then use the Action Key, followed by the Search facility. From the list displayed the user can define the search to be performed either by the ion "Number" or "Symbol". Both options allow specific or more general (i.e., wildcard) searches to be carried out.

Searching By Number

When using the "By Number" option the user performs a specific data search by entering the required species material code value, the relevant data will then be displayed. Alternatively, a wildcard search can be carried out using a partial ionic code value suffixed with "*" symbol (e.g., 6*). An ion code index is then displayed showing all the codes within the databank, starting with the specified value. The appropriate code can be selected and the data displayed using the Arrow Keys and Enter Key.

Searching By Symbol

The search "By Symbol" option also allows a specific or wildcard search to be performed. The symbol entered must be recognized by the software, and can either be a chemical formula or name.

Alternatively, a wildcard search is performed by entering the species formula, or partial chemical name, prefixed and suffixed with "*" symbol (i.e., *NA*). A list is then displayed showing all species containing the specified characters in succession, either in a chemical formula or name. The relevant data is accessed by selecting the appropriate species of interest using the Arrow Keys and Enter Key.

Guidelines

1. Generally, for inorganic species the chemical formula is used; for organics either a chemical formula or name is entered, depending on the species involved. For example, the acetate ion is only recognized by the name ACETATE, and not by its formula.
2. A specific species search can be performed by entering the species symbol, either name or formula, succeeded by the ionic charge. A positive charge is represented by "+" symbol and a negative charge by "-" symbol. The number of symbols used represents the total ionic charge of the species (i.e., FE⁺⁺⁺, CO⁻⁻).

Reviewing Species Data

The species data accessed in the different chapters of OLI Databook can be reviewed in a variety of ways. The user can determine supporting literature references for the species information, the quality (accuracy) of the data stored, complete temperature/concentration function relationships used to predict specific variables and the range in which the relationships are accurate. The user can perform calculations using these relationships, to determine accurate results for specific values of interest (within the defined range). Graphical plots of experimental data can be produced and data can be displayed in a variety of units, subject to the user's requirements.

It must be noted that some of the above review facilities are specific to certain chapters of the Databook, and the procedures described below relate to review facilities available in each chapter.

Display Units

At any point in the use of OLI Databook the user has the facility to change the units in which values are displayed. Initially, the data is expressed in SI units, but the values can also be displayed in ENGLISH or METRIC equivalent values. Alternatively, the user can customize a set of USER display units to suit specific requirements.

To change the display units, the user simply uses the Action Key and chooses the Units facility. A summary of the units currently being displayed is shown and are changed using the Arrow Keys. Chosen display units are saved between sessions and are displayed until re-specified by the user.

Species Data

Two important review facilities are available in the Species Chapter:

View Allows the user to determine literature references and quality of the data stored.

Evaluate Calculates temperature/concentration dependent variables within the specified temperature ranges.

View

The View facility provides full literature references, the reference key, quality (accuracy) information for the data, the creator, date of the last data modification, and comments if any. For function dependent variables for which coefficient information is displayed, the complete function relationship can be viewed as well as the range over which the equation is accurate. The equations that can be viewed include heat capacity, vapor pressure, equilibrium constant and solubility function relationships.

Method To Use View

To use this facility the user must first select the type of data to be accessed (i.e., General Information, Aqueous Phase, Vapor Phase, Solid Phase) using the Arrow Keys and selecting with the Enter Key. The appropriate information is then displayed. In order to determine further information for a particular item, the user must highlight the specific data of interest using the Arrow Keys, and then use the Action Key, and select the View facility.

View Menu

On choosing this function a small menu appears, and the relevant information can be selected. Choices include:

<u>CHOICE</u>	<u>DISPLAYS</u>
REFERENCE	Full literature reference
QUALITY	Accuracy of the data
DATE	Last modification date of the data
CREATED BY	Initials of the user who created/modified the data
COMMENTS	Any comments associated with the data
KEYS	The short reference code

This menu is slightly different if coefficient data for function dependent variable relationships (i.e., CP, VP, SOLU, KFIT) is highlighted. An "EQUATION" choice is added. This facility displays the complete function dependent relationship, and the range over which the equation is accurate.

Evaluate

The Evaluate facility provides a utility for calculating specific values for function dependent variables. It can only be used for data in which coefficient data is displayed, that is specific heat (CP), vapor pressure (VP), solubility (SOLU) and equilibrium (KFIT) function dependent relationships.

Method

To access this facility, the coefficient data for the required variable must be highlighted using the Arrow Keys. The Action Key is then used and the Evaluate facility chosen. Upon this selection, the complete function dependent relationship is displayed as well as the function range over which the equation is accurate.

In order to determine the selected variable value for a specific function quantity (within the quoted range) the user simply enters the required quantity and presses the Enter Key. The corresponding variable value is then displayed.

Internal calculations are performed in SI units, but data can be entered and displayed in units preferable to the user, by using the "Units" option of the Action Key, prior to choosing the "Evaluate" function (Reference on pg.).

The Species Chapter data review procedures are summarized in the schematic diagram () on page .

Synonym Chapter Data Review

This chapter does not include any specific review facilities. For further information on general facilities refer to on page .

Experimental Chapter Data Review

Two important review facilities are available in the Experimental Chapter:

View Allows the user to determine full literature references, display the experimental data in tabulated format, the quality (accuracy) of the data, and the last modification date of the information.

Plot Display the experimental data in graphical format.

View

The View option provides full literature references, tabulated experimental data values, the quality of the data, and the last modification date of the information.

To use this facility, the user must first highlight the short code reference for the data set of interest and then press the Action Key and select the View facility.

On choosing this function a small menu appears and the relevant information can be selected using the Arrow Keys and Enter Key. Choices include:

<u>CHOICE</u>	<u>DISPLAYS</u>
REFERENCE	Full literature reference
DATA	Tabulated experimental data values predicted from function relationships contained in the Species Chapter of the Databook (Reference on pg.)
QUALITY	Accuracy of the data
DATE	Last modification date of the information

Plot

The Plot facility allows experimental data to be plotted in graphical format. To use this facility the experimental data must first be accessed using the Action Key, followed by the View facility and selecting the Data function on the succeeding screen. The experimental values are then displayed. A plot of this data is produced by re-using the Action Key and selecting the Plot facility. At present, a plot can only be displayed on the screen. In order for data to be viewed in user preferred units, the Units facility via the Action Key should be used prior to selecting the View facility (Reference pg.).

Interactions Chapter Data Review

The View facility is available to determine full literature references, display interaction coefficients, the quality (accuracy) of the coefficients and the last modification date of the information contained in the Interactions Chapter of the Databook.

To use this facility the user must first highlight the coefficient type of interest from the list using the Arrow Keys. The Action Key is then used and the View facility chosen.

On choosing this function a small menu is displayed and the relevant information can be selected using the Arrow Keys and Enter Key. Choices include:

<u>CHOICE</u>	<u>DISPLAYS</u>
REFERENCE	Full literature reference
DATA	Interaction coefficient values
QUALITY	Accuracy of the data
DATE	Last modification date of the information
COMMENTS	Any comments associated with the data
KEYS	The short reference code

Other Databook Chapters

There are no specific review facilities for the Literature, Structure, Coprecipitation, Sorption, Redox and Electrical Chapters.

For further information on general facilities, refer to on page . For an example of material code review, see the following page.

Data Reports

The facility is available to report specific information for either an individual species, or class of species. This facility is normally used to compare data for a class of species, using a wildcard entry. The function can be used for any databank and in any chapter of OLI Databook.

Method

Initially, the databank to be searched (e.g., PUBLIC, GEOCHEM, LAB) must be specified followed by the relevant chapter on the succeeding screen. The Action Key is then used and the Reports facility chosen. (Note: When using the Experimental or Literature Databook Chapters the required chapter section must be specified prior to using the Action Key).

From the report type list displayed the "Quick Lists" option is specified. An index of data items available for reporting from the particular working chapter is then shown. The user can select the specific information to be reported using the Arrows and <Space Bar> keys. (Note: A maximum of 10 items to be reported from a chapter can be selected).

On completing the Report Item definition and pressing the Enter Key, the user then specifies for which species the report will be made. The species to be reported can then be specified, normally using a wildcard entry. Optionally, the user can use the Action Key and choose the Search facility, to change the way the species in the report are located (e.g., "By Species Name" instead of "By Formula").

The Search options available depend upon which Databook Chapter is being used.

Output Choices

Reports are sent to the screen by default. Alternately, a report can be sent to a disk file or to the printer by using the Action Key and choosing the Output facility.

Report Options

The "Quick Lists" option automatically assigns headings to a report, determines whether the report will be presented in Row (>80 characters) or column (<80 characters) format, and uses the internal order of the data to determine the data order in a report. The Options facility, when implemented, will allow the user to override the Quick List defaults.

Additional Facilities

Facilities in addition to those already described in the previous chapters of this section, are available to the user to perform various operations within OLI Databook. The functions are available in all chapters of the Databook and are screen specific (i.e., only available on certain screens). Access to the required facility is obtained by pressing the Action Key and choosing the appropriate facility.

The available facilities are described by screen Option heading below.

Options

This function allows the user to change directories, switch audible sound signal on or off, and set up file options. Each facility is described below:

Change Directories - This facility is used if a private databank either has been created or is to be created in a directory other than the working directory (e.g., OLI\ESP\TEST). The user simply enters the directory name in the correct format.

Sound On/Off - On Databook is designed to give an audible on Error response to incorrect user input. This is known as the "Sound on Error" option. "Sound Off" is also available. The preferred option is selected using the Arrows and Enter Key.

Set Up Options - This option allows OLI software users to customize Editor and Browser facilities to meet their requirements. The default settings of the two facilities are identical. Both use the MS-DOS editor, recognized by the name "EDIT". If a different editor/browser is desired, enter the command name of the editor in place of the default name.

New Item

When this facility is implemented, it will provide the ability to display and update the OLI Databook Dictionary. The Databook Dictionary is where data items and their attributes are defined and stored.

Import/Export

This option allows data to be either imported to or exported from OLI Databanks. At present, usable import formats include "ESP Readable" and "ASCII Transfer", while export formats are limited to "ASCII Transfer".

This facility is mainly used for private user defined databanks but is also available to the OLI defined databanks (i.e., PUBLIC, GEOCHEM, LAB). However, the data within these databanks are password protected and the Import/Export facility cannot be used without obtaining permission (i.e., the password) from OLI Systems, Inc. For further information please contact:

OLI Systems, Inc. (Customer Services)

240 Cedar Knolls Road

Suite 301

Cedar Knolls, New Jersey 07927Tel: (973) 539-4996

Fax: (973) 539-5922

Oli.support@olisystems.com

www.olisystems.com

The two facilities will now be described in detail.

Import

Initially the file containing the data to be imported must be loaded onto the computer. The file name must comply with either ASCII Transfer or ESP Readable formats file extensions .Axx or .ESR respectively. Descriptions of the ESP Readable file are found on the following pages. A description of the ASCII Transfer file is not given, since this file is used for internal Import/Export only.

Note, the ASCII Transfer file extension is given a sequential identification number which corresponds to the particular Databook chapter the data is to be imported to, i.e.,

<u>Import to:</u>	<u>ASCII file extension</u>
Species Chapter	.A01 - .A03
Synonym Chapter	.A04
Experimental Chapter:	
Vapor Pressure	.A05
Specific Heat	.A06
Solubility	.A07
Activity Coefficients	.A08
Density Interactions	.A09
Interactions Chapter	.A10

Literature Chapter:	
References	.A11
Equations	.A12
Material Codes	.A13
Ion Codes	.A14
Structures Chapter	.A15
Coprecipitation Chapter	.A16
Sorption Chapter	.A17
REDOX Chapter	.A18
Transport	.A19

The ESP readable format, also called ESR format, was developed by OLI to allow an alternative to Databook screen entry when preparing species. The ESR format allows a text editor to be used to collect the data needed for a species. The Databook Import function then reads the ESR file, and adds the species to the current databank.

The outline of an ESR file has been included below. This format can be followed when making new species or new species' phases for an OLI private databank. A template file called OUTLINE.ESR contains this outline and is included with other system files in the ESP system directory.

Esr Template Guidelines

1. *Each line in an ESR file is organized into a keyword, and then values.* The keyword always starts in column 1, and the value, always in column 9. For data items which have more than one value, (e.g., MATC), values are separated by one or more blanks.
2. *The character ";" in column 1 of the record signals a comment.*
3. *The character "+" in column 1 of the record signals continuation.* The data which follows on that record is a continuation of the data on the previous record.
4. *The square brackets in the outline file, [], indicate the data which should be entered for that line.* When using the OUTLINE.ESR file, replace the brackets with the values for that keyword.
5. *The use of < > in the outline file indicates that a Support Record can be added for that value.* There are two forms of the Support Record syntax, depending on whether the value is a single value, or a set of coefficients. These forms are listed at the end of the file.
6. *The keyword is up to eight characters long, however, only the characters in columns 1-4 are used to identify the record.* The names allowed as keywords are the same names which are listed in the ASCII file PUBLIC.DIC, located in the ESP system directory. The PUBLIC.DIC file contains the descriptions and required units for each of the keywords and may prove helpful when creating an ESR file.
7. *An ESR file can be used to either add a species, a species phase, or to update a species.* The Import function of the Databook controls this choice.
8. *If there are no values for an item, its keyword can be omitted from the file.*

ESP Readable Format

; ESR FILE

;

NAME [Up to 16 characters]

;

SYN [Up to 80 characters]

+ [Unlimited synonyms, starting each synonym on a new "+" line]

;

ORG [Organic/inorganic indicator, I or O]

CHEM ["Common" Chemical formula, up to 28 characters]

LOLN [List of Lists Name, up to 75 characters]

IUPAC [IUPAC name, up to 74 characters]

FORM [Empirical formula, up to 20 characters]

CAS [CAS registry number, up to 12 characters]

MOLWT [Molecular weight, up to 13 characters]

MATC [Material codes, up to 5 integers, separated by blanks]

STOI [Stoich coeffs, up to 5 real numbers, separated by blanks]

;

;

PHASE VAPOR

;

ACENT [Acentric factor, up to 13 characters] <Form 1>

TCRIT [Critical temperature, up to 13 characters] <Form 1>

PCRIT [Critical pressure, up to 13 characters] <Form 1>

VCRIT	[Critical volume, up to 13 characters]	<Form 1>
BOIL	[Boiling point, up to 13 characters]	<Form 1>
GREF	[Free energy of formation (ref.), up to 13 characters]	<Form 1>
HREF	[Enthalpy of formation (ref.), up to 13 characters]	<Form 1>
SREF	[Entropy (ref.), up to 13 characters]	<Form 1>
CPREF	[Heat capacity (ref.), up to 13 characters]	<Form 1>
VP	[Vapor pressure coefs, 5 values up to 13 characters, separated by blanks]	
+	<Form 2>	
CP	[Heat capacity coefs, 5 values up to 13 characters, separated by blanks]	
+	<Form 2>	
SOLU	[Solubility coefs, 5 values up to 13 characters, separated by blanks]	
+	<Form 2>	
EQUA	[Equilibrium equation, up to 80 characters, enclosed in \$...=...\$]	

PHASE AQUEOUS

;

GREF	[Free energy of formation (ref.), up to 13 chars]	<Form 1>
HREF	[Enthalpy of formation (ref.), up to 13 characters]	<Form 1>
SREF	[Entropy (ref.), up to 13 characters]	<Form 1>
CPREF	[Heat capacity (ref.), up to 13 characters]	<Form 1>
VREF	[Volume (ref.), up to 13 characters]	<Form 1>
ZRAC	[Rackett Z value, up to 13 characters]	<Form 1>
CHARGE	[Ion charge, real number]	
IONTYPE	[Ion type, integer code]	
HTYPE	[Helgeson ion type, integer code]	

IONCODE [Ion code, integer (see literature chapter)]

STYPE [Solubility indicator: 0 or 1]

KFIT [Kfit coefs, 5 values up to 13 characters, separated by blanks]
+ <Form 2>

HKF [Helgeson coefs, 7 values up to 13 characters, separated by blanks]
+ <Form 2>

EQUA [Equilibrium equation, up to 80 characters, enclosed in \$...=...\$]

BINT [Binter Parameter, up to 13 characters] <Form 1>

SPR [Radii, 6 values up to 13 characters] <Form 1>

;

PHASE SOLID

;

GREF [Free energy of formation (ref.), up to 13 chars] <Form 1>

HREF [Enthalpy of formation (ref.), up to 13 characters] <Form 1>

SREF [Entropy (ref.), up to 13 characters] <Form 1>

CPREF [Heat capacity (ref.), up to 13 characters] <Form 1>

VREF [Volume (ref.), up to 13 characters] <Form 1>

TRN [Number of solid phase transitions, one character]

RHO [Density coefs, 5 values up to 13 characters, separated by blanks]
+ <Form 2>

KFIT [Kfit coefs, 5 values up to 13 characters, separated by blanks]
+ <Form 2>

TTR [Phase transition temperatures, 8 values up to 13 characters]
+ <Form 2>

HTR [Phase transition enthalpy, 8 values up to 13 characters]

```

+           <Form 2>
CP1  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for first phase]
+           <Form 2>
CP2  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for second phase]
+           <Form 2>
CP3  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for third phase]
+           <Form 2>
CP4  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for fourth phase]
+           <Form 2>
CP5  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for fifth phase]
+           <Form 2>
CP6  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for sixth phase]
+           <Form 2>
CP7  [Heat capacity coefs, 5 values up to 13 chars, sepd by blanks for seventh phase]
+           <Form 2>
EQUA      [Equilibrium equation, up to 80 char, enclosed in $...=...$]
END

```

```

; Form 1: \reference page#\date\creator\history uncert\

```

```

;   Form 1 Example: \90DIP D:1570\11/22/92\OLI\REC 10%\

```

```

;

```

```

; Form 2: \reference page#\date\creator\history uncert\t1 t2\eqno\

```

To import data, the user must initially select the appropriate databank to which the species data is to be added, followed by the relevant Databook chapter (i.e., Species, Synonym, etc.). The Action Key is then used and the "Import/Export" option chosen, followed by the "Import" title on the succeeding screen.

(Note: When importing data to either the Experimental or Literature Chapters the relevant chapter section (i.e., Vapor Pressure, References) must be specified prior to using the Action Key).

The Action Key is then re-used and the "Format" option selected. The type of file to be imported (i.e., ASCII or ESP Readable) can then be selected using the Arrow Keys and Enter Key.

The name of the file to be imported is then specified and the data transfer performed.

After importing several files into a databank, the databank should then be re-indexed to increase performance. Reference on page for the re-indexing procedure.

Export

This facility is used either to export data to a separate file or to copy data to another databank. At present, data exporting can only be achieved using the ASCII Transfer format, that is the export file is given the extension .Axx identifier. (Note: The identifier is given a sequential number value which corresponds to the chapter from which the data is exported - See Import description for full listing). When exporting data to an ASCII Transfer file the software automatically provides the appropriate file extension code.

Method For Export

To export data, the user must initially select the relevant databank and chapter from which the data is to be exported. The Action Key is then used and the "Import/Export" option chosen, followed by the "Export" title on the succeeding screen. (Note: When exporting data from either the Experimental or Literature Chapters the relevant chapter section (i.e., Vapor Pressure, References) must be specified prior to using the Action Key).

Control

This facility allows the user to perform specific actions on a private databank which include: re-indexing the databank, assigning password protection to the databank and copying or deleting species information. A schematic of the procedure, , is on the following page.

Method

To use the Control facility the user must initially select the relevant private databank to be accessed, followed by the specific Databook chapter. The Action Key is then used and the Control facility chosen. An index of facilities available are displayed and the appropriate function chosen using the Arrow Keys and Enter Key. The functions include:

- **Re-index Data**
- **Delete Data**
- **Copy Data**
- **Password Control**

Re-Index Databank

This option is available to enable the user to update the databank species index after performing various functions. The databank should be re-indexed after either importing to (Reference pg.) or deleting species data from the databank.

This procedure is performed by selecting the appropriate heading from the menu and pressing the Enter Key. The databank is automatically re-indexed.

Delete Data

The "Delete Data" option is available for the user to delete specific information from the relevant Databook chapter.

For example, when working in the Species Chapter, the user can delete all data for a particular species, or a particular type (phase) of data (i.e., General information, Aqueous/Vapor/Solid phase).

To delete data the user must specify the data to be deleted from the accessed Databook chapter, by identifying the species to be deleted either by name, formula, periodic table, etc. The Search facilities are described in on page .

Once the species to be deleted has been identified a message is displayed asking the user to confirm the deletion request. The user can either cancel or proceed with the data deletion by selecting the appropriate response and pressing the Enter Key.

Copy Data

This option is currently not available in OLI Databook. If the user wished to copy species data either to disk or another directory or databank the Import/Export facility must be used. After exporting the file, the file must be manually edited and the name of the new databank must be substituted for the exporting databank's name prior to performing an Import to the target databank.

Password Control

This option allows the user to password protect a private databank in order to insure the integrity of the data. Once assigned the user cannot modify (i.e., delete, import, export, etc.) the databank information, using the available options without entering the password code.

When assigning a password code, the user must first select the "Password Control" option of the "Control" facility. The user is prompted to enter the password code to be assigned, which must then be verified by re-entering the assigned password code.

The password protection does not come into effect until the user exits from the Databook. A new password can be assigned at any time.

Edit

This facility is used to either modify existing data or define new data in a private databank.

The Species Chapter can be edited by simply using the Action Key and selecting the Edit facility. Data can then be added, deleted or modified accordingly. For all other Databook chapters, data can only be edited by using the Edit Facility in conjunction with the Mode facility (Reference , , on page). This facility is discussed in greater detail in on page .

Mode

This facility is only available after the Edit facility has been selected. It must be used when editing data in all chapters other than the Species Chapter of a private databank.

The function is accessed by using the Action Key and selecting the Mode facility. The user can then specify if data is to be inserted or deleted from a chapter.

On selecting the "Insert" option the user can enter or modify data accordingly.

The "Delete" option allows the user to remove specific data entries. This is achieved by simply highlighting the item to be deleted and pressing the Enter Key.

File

This facility is used when the user completes editing data in a private databank. It allows the user to either save the new data, cancel the changes made, or exit the Edit Mode of operation.

The function is accessed using the Action Key and selecting the File facility. The appropriate option (i.e., Save, Cancel, Exit) is then chosen.

Records

This is an important facility and can only be accessed after selecting the Edit facility (Reference pg. for either the Species, Experimental or Interactions Chapter of the Databook). The Records facility is accessed by using the Action Key and selecting Records.

The facility allows the user to specify either Supporting data or Comment (e.g., user notes) on data previously specified in the private databank.

It is a critical facility when the user specifies either literature references or function dependent equations in the Literature Chapter of the Databook (Reference on pg. for further details). This is because reference codes, equations codes and equation calculation limits and units must be defined in this Records facility in order for Literature Chapter user definitions to be recognized by the software.

If these items are not recorded in the Records facility, the Literature Chapter defined items are ignored by the software.

Upon selecting the Records Facility, the user can choose to either define Support, Comment or Archive information for the species of interest.

Support Record

This option allows the user to specify important supporting information for a particular species. If a function dependent equation has previously been specified for a particular species property, its respective Equation Code identifier and calculation limits must be specified in this section. Similarly, a reference code must also be defined if a literature reference is to be included in the databank.

The supporting information which can be entered is identified with a displayed keyword. The user simply enters the relevant information adjacent to the respective keyword. The displayed keywords are as follows:

<u>KEYWORD</u>	<u>DATA DESCRIPTION</u>
DATE	File modification data
CREA	User initials
REF ¹	Literature Reference Code
PAGE	Literature Reference page number
EQNO ²	Function dependent relationship Equation Code
TRAN ²	Calculation limits for function dependent equation. Two entries required.
QUAL	<p>Specifies the data history and quality (accuracy).</p> <p>The data history can be identified with either:</p> <p>REC - user recommended</p> <p>EST - estimated</p> <p>EXP - experimental</p> <p>The data quality can be expressed as either a percentage, standard deviation or variable deviation.</p>
UNIT ³	<p>Specification of units for which experimental or function relationships are defined.</p> <p>Two entries are normally required. If no units are entered, SI units are assumed.</p>

Note 1 REF must be defined when a literature reference has been specified.

Note 2 EQNO and TRAN must be defined when a function dependent equation has been specified.

Note 3 UNIT must be defined when either experimental or function relationships are defined.

Comments Record

This option allows the user to comment on defined information for a particular species. The function is optional and is generally used to clarify previously specified data.

Archive Record

This is currently not available but it will contain the date, value and reason for updating a specific data entry in the Databank.

Making a Private Databank

The facility is available for the user to build a private species databank. It is used to specify data for species that are not included in the OLI supplied databanks (e.g., PUBLIC, GEOCHEM, etc.).

The user can define species data in all chapters of the Databook except Structures. However, important species property information is generally entered into the Species Chapter of the Databook, with supporting data entered into remaining chapters.

When specifying a private databank the user must select the "New Databank" option from the initial display. The databank is then identified with a name which can be between 1-8 characters in length. *The first three characters of the new databank name must be unique (i.e., different from the first three characters of any other databank in the directory the user is working in).* This completes the generation of a skeletal private databank into which species information can be defined.

The appropriate chapter of the Databook is chosen and species data entered, by using the Action Key and selecting the Edit facility.

The format for data entry into each chapter is described below.

Species Chapter

This chapter is the most commonly used by the user when specifying species data in a private databank. It is possible to specify all the required information which is used in equilibrium calculations in this one chapter of the Databook.

Method

In order to enter data in this chapter the user must first select the Species Chapter of the Databook and name the species to be included. A message is then displayed asking the user to confirm that new species data is to be entered into the databank.

Upon confirmation, the user can select the type of data to be specified (i.e., General Information, Aqueous Phase, Vapor Phase, Solid Phase) using the Arrow Keys and Enter Key.

The data is entered by editing the displayed species information. This is achieved by using the Action Key and selecting the Edit facility. The relevant information is then inserted adjacent to the appropriate software keyword identifier. Complete keyword descriptions for this chapter can be referenced in on page .

The entered data is saved by using the Action Key, selecting the File facility, and choosing the "Save" or "Exit" option on the succeeding menu.

For convenience, the entry of a new aqueous complex is made convenient and is described under below.

Minimum Data Required

When specifying species data which is to be used in OLI's thermodynamic calculations, a minimum amount of information must be specified by the user. Some items need to be defined regardless of which species phase is to be considered, while other items are phase specific. The data items for each chapter section include:

General Information

<u>Software Keyword</u>	<u>Data Description</u>
FORM	Empirical formula
MOLW	Molecular weight
MATC	Species elements material codes (defined in Literature Chapter)
STOI	Stoichiometry of species material code elements

Aqueous Phase Data

<u>Software Keyword</u>	<u>Data Description</u>
-------------------------	-------------------------

GRES¹ Gibbs free energy of formation

HRES¹ Enthalpy of formation

SRES¹ Reference state entropy

Software Keyword Data Description

CPRES Reference state heat capacity

HKF Helgeson coefficients (determined by ESP Estimate)

ZRAC Rackett Z value (required for organic species only)

EQUA Aqueous intraphase equilibrium equation

Note 1: Either KFIT or GRES, HRES, and SRES data need to be specified. If KFIT coefficients are defined for a relationship, then equilibrium can be predicted, by the software accordingly. However, if GRES, HRES and SRES are missing, then applications involving the enthalpy or volume of the aqueous phase species will be in error.

For convenience, aqueous, stepwise complexes can be entered in a convenient way as follows:

First, select the Aqueous Phase. Next, from the Action Bar select Complex. A convenient screen will now appear which allows for the following entries:

- Metal - This must be a primary (only containing a single element) cation already contained in a standard OLI Databank or the one invoked by the user.
- Ligand - This must be a primary anion already contained in a standard OLI Databank or the one invoked by the user.
- Background Electrolyte - The default is NaCl. Since most published stability constants are reported at ionic strength greater than 0.0, OLI must extrapolate the published constant to $I=0.0$. To do this, some background electrolyte must be identified for such cases.
- Maximum Order for Metal - The default is 1. The entry should be the highest stoichiometric order the cation will achieve.
- Temperature - This is the temperature (one or two can be entered) at which the stability constant was measured.

Once the appropriate entries are made, press the <ENTER> key and a screen will appear which will provide an equation for each stage of complexation plus a column for user entry of LogK (mandatory) and DeltaH (optional).

Vapor Phase Data

<u>Software Keyword</u>	<u>Data Description</u>
ACEN	Species acentric factor
TCRI	Critical temperature
PCRI	Critical pressure
VCRI	Critical volume

GRES	Gibbs free energy of formation
HREF	Enthalpy of formation
SREF	Reference state entropy
CPRE	Reference state heat capacity
EQUA	Vapor-Aqueous phase equilibrium equation

Solid Phase Data

<u>Software Keyword</u>	<u>Data Description</u>
GRES ¹	Gibbs free energy of formation
SREF ¹	Reference state entropy
HREF ¹	Enthalpy of formation
CPRE	Reference state heat capacity
EQUA	Solid-Aqueous phase equilibrium equation
KFIT ¹	Equilibrium constant polynomial relationship coefficient values.

Note 1: Either KFIT or GREF, HREF, and SREF data need to be specified. If KFIT coefficients are defined for a relationship, then equilibrium can be predicted, by the software accordingly. However, if GREF, HREF and SREF are missing, then applications involving the enthalpy or volume of the solid phase(s) will be in error.

Ionic Species

When defining data for an aqueous phase ionic species three additional items need to be specified, namely:

<u>Software Keyword</u>	<u>Data Description</u>
CHAR	Species ion charge (defined in Literature Chapter)
IONC	Species ion code
IONT	Helgeson ion type (A list of ion types is displayed via the <F1> Help Key). The above lists are the minimum data requirements to be specified for species to be used in equilibrium calculations. However, the user may define any other data which is relevant to this chapter. A complete listing of software keywords for this chapter can be referenced in , on page of this section.

Guidelines

When specifying data in this chapter the user should comply with the following guidelines to insure correct data specification:

1. **Ionic Species** - *The species name must be suffixed with the keyword ION and data can only be defined for aqueous phase species.*
2. **Equations** - *When specifying equilibrium equation must be defined in upper case characters (e.g., a species must be defined in an equation as NACLAY and not as NaClay for example).*

3. **Equation naming conventions** - *The species for which data is being defined must be entered as the first reactant species of its equilibrium equation. Also, the reactant and product species phases in the equation must be identified using a software keyword suffix. The keywords available are:*

<u>Software Keyword</u>	<u>Phase Description</u>
AQ	Aqueous phase
PPT	Solid phase
VAP	Vapor phase
ION	Ionic species in aqueous phase
SUS	Suspended solids phase (normally used for biotreatment models)
SOL	Solution phase not in equilibrium with bulk aqueous phase (normally used for ion exchange models)

4. **Species Elements** - *When a species is defined which contains elemental components which are already defined in the PUBLIC Databank the private databank definition for the element (i.e., OLI Name, Material Code Number, Ion Code Number) must be consistent with the PUBLIC Databank Specification.*
5. **Material Codes** - *For new species not already defined in the PUBLIC Databook, a material code must be assigned. An integer value must be used which does not exist in the PUBLIC Databank (i.e., no material codes listing two species can have the same material code). The user should use integers in the range 9001-9999 which are reserved for specific user requirements. Species material codes are defined in the Literature Chapter of the Databook (Reference , on page for further details).*
6. **Ion Codes** - *An ion code must be assigned for species not defined in OLI's PUBLIC Databank. An integer value must be used which does not exist in the PUBLIC Databank ion codes listing. The user should*

assign values in the range 9001-9999 which are reserved for specific user requirements. Species ion codes are defined in the Literature Chapter of the Databook (Reference , on page for further details).

7. **Equation Coefficients** - *When defining a function dependent relationship for either CP, VP, SOL, KFIT or RHO variables, the coefficients must be defined as real values in the Species Chapter of the Databook.* The actual function-dependent relationship should be found in the Literature Chapter (Reference , on page for further details). New function-dependent relationships can only be added by contacting OLI and requesting the addition.

Synonyms Chapter

This chapter is normally accessed to supply supporting information for a particular species. The user can define alternative names (synonyms) for which a species is recognized. Generally, synonyms are only specified for species which have been defined in the Species Chapter of the Databook. Once a synonym has been defined, data can be accessed in the Species Chapter for a species using any of the specified synonym name.

Method

In order to enter data in this chapter the user must first select the Synonym Chapter of the Databook and name the species to be included. For new species not previously defined in another chapter of the Databook, the user is asked to confirm the new data entry into the Synonym Chapter.

Data Entry

The data is entered by editing the displayed species. This is achieved by using the Action Key and selecting the Edit facility. The Action Key is then re-used and the Mode facility chosen. Upon the selection of Mode, the user can specify if data is to be inserted or deleted into this chapter.

The "Insert" option allows the user to enter species synonym names into the displayed file. Only one species name can be defined per row of the file. The user exits the Insert mode by moving the cursor to the row below the last data entry and pressing the Enter Key. The information is then saved by using the Action Key, selecting the File facility, and choosing the "Save" option from the displayed menu. "Exit" will also save the data.

The "Delete" option of the Mode facility allows the user to delete synonym name information. Data is simply deleted by choosing this option, highlighting the specific name to be deleted and pressing the Enter Key. The user is asked to confirm the data deletion request, prior to the item being removed.

Experimental Chapter

This chapter allows the user to enter source (e.g., experimental) data sets for species variables which are dependent on temperature or concentration properties. The user can tabulate data for specific heat, vapor pressure and solubility variables as a function of temperature. Activity coefficient and density coefficient interaction parameter data can also be entered as a function of concentration if required.

Method

In order to enter data, the appropriate section of the Experimental Chapter must initially be accessed. The user then specifies the species for which data is to be defined. When specifying either activity coefficient or density interaction coefficients the species must be defined as an pair of ionic compounds. On confirming the new data entry the user must define the species phase and quote a reference code for the data.

Phase/Reference

This is achieved by using the Action Key and selecting the Edit facility. The Action Key is then re-used and the Mode facility chosen. From the succeeding screen the "Insert" option is selected. The user can then enter the required species phase and reference code data. The phase must be defined as either Solid, Aqueous or Vapor. The reference code format is at the discretion of the user; however, the format described in , , on page is recommended. Both items must be entered by the user, otherwise species experimental values cannot subsequently be defined.

The entry is saved by using the Action Key, selecting the File facility and choosing the "Save" or "Exit" option.

Experimental Data

In order to include experimental data the following procedure needs to be performed.

Initially, the user should highlight the Phase/Reference Code which has previously been defined and then use the Action Key and select the View facility.

From the succeeding menu, the "Data" option is chosen. This then displays a new screen into which the information of interest is entered.

Data Entry

The data is edited by using the Action Key and selecting the Edit facility. The Action Key is then re-used and the Mode facility chosen. The user can then specify if data is to be inserted or deleted.

On selecting the "Insert" option, the data can then be entered into the file under the appropriate displayed headings.

If required, the user can select the type of data units (i.e., Metric, SI, English, etc.) to be displayed

The data is saved by using the Action Key, selecting the File facility, and specifying the "Save" or "Exit" options from the succeeding menu.

Guidelines

1. *When defining experimental data the user should insure that the phase of a species is correctly specified for a particular data entry.* For example, the solid phase for a species should not be specified when entering data in the Vapor Pressure section of the Experimental Chapter. Generally, data is specified in the Chapter sections for the following phases:

<u>Chapter Section</u>	<u>Species Phase</u>
Vapor Pressure	Vapor
Heat Capacity	Vapor, Aqueous, Solid
Density (pure solid)	Solid
Solubility	Vapor
Activity Interaction Coefficients	Aqueous
Density Interaction Coefficients	Aqueous

2. *The supporting literature reference and quality of the defined data are specified in the Literature Chapter (Reference, pg.) and in Records (Reference , , pg.) respectively.*

3. *The units in which experimental data has been specified must also be defined through the Records facility* (Reference , , pg.). If this is not carried out, the defined data will not be recognized by the software.

Interactions Chapter

This chapter allows the user to enter interaction parameters for species of interest which are used in thermodynamic calculations performed by the software.

The following five types of parameters may be defined:

<u>Interaction Type</u>	<u>Description</u>
BROMLEY	Ion-Ion interaction parameters used in ProChem and ESP's activity coefficient equations
DENSITY	Interaction parameters (ion-ion, and molecule-molecule) used in ProChem and ESP's aqueous density equations
PITZER	Ion-molecule and molecule-molecule interaction parameters used in ProChem and ESP's activity coefficient equations
SRK	Interaction parameters used in the Soave-Redlich-Kwong (SRK) Equation of State which is used in ProChem and ESP's nonaqueous thermodynamic framework

Method

In order to enter data, the Interactions Chapter must initially be accessed. The user then specifies the pair of species for which data is to be defined. On confirming the new species data entry, the user must define the type of interaction parameter to be entered.

Interaction Type

Selecting an alternative type is achieved by using Action Key and selecting the Edit facility. The Action Key is then re-used and the Mode facility chosen. From the succeeding screen the "Insert" option is selected. The user can then enter the type of interaction parameter to be specified. This is achieved by using one of the above quoted parameter type keywords. The entry is saved by using the Action Key, selecting the File facility and choosing the "Save" or "Exit" option. Exit automatically saves the data.

Coefficient Data Entry

In order to include interaction coefficient data the following procedure can be used. Initially, the user should highlight the Interaction Type which has previously been defined, and then use the Action Key and select the View facility. From the succeeding menu, the "Data" option is chosen. This then displays a new data file into which the interaction parameters are entered. Data entry is achieved by using the Action Key and selecting the Edit facility.

The information is saved by using the Action Key, selecting the File facility, and choosing the "Save" or "Exit" option from the succeeding menu.

Reference

If the interaction data is taken from literature which is to be referenced, the full literature reference and code needs to be defined in the Literature Chapter of the Databook (Reference , pg.). However, in order for the reference to be identified the reference code must be defined in the Records facility (Reference , , pg. for further details).

Literature Chapter

This chapter allows the user to specify full literature references, function dependent relationships for specific properties, and new material and ion codes for species.

References

A full literature reference can be defined for experimental data, interaction parameter data and function dependent equations for a species, if required.

This is achieved by initially selecting the References Section of the Literature Chapter and then entering a Reference Code by which the full literature reference is to be identified. The code format is at the discretion of the user; however, OLI recommends that the reference code conventions of year and author be followed. This allows organization within the private databanks as well as consistency with existing references (Reference , pg. for reference code syntax). On pressing the Enter Key a new reference screen is displayed which can then be edited.

Method

The reference is edited by using the Action Key and selecting the Edit facility. In order to insert data the Action Key must be re-used, the Mode facility selected and the "Insert" option chosen from the succeeding screen. The full literature reference can then be added to the databank. The user can save this information by using the File facility.

Initially, the cursor should be moved to the next line succeeding the literature reference and the Enter Key pressed. The Action Key is then used, the File facility chosen and the "Save" or "Exit" option selected.

Guidelines

1. When defining a complete literature reference the user must insure that *the respective reference code is defined in the Records facility of the appropriate Databook Chapter* (Reference , , on page for further details).
2. *The Records facility is available in the Species, Experimental and Interaction Chapters of the Databook.* Hence, if data is defined in either the Experimental or Interactions Chapters for a species, the literature reference code must be included in the appropriate Chapter Section Record, as well as in the Species Chapter.

For example, if experimental data for vapor pressure and specific heat are defined for the same species of interest, the respective literature reference codes for the two sets of data must be specified in the appropriate sections of the Experimental Chapter of the Databook.

An exception to this rule is if a function dependent relationship is defined in the Equations section of the Literature Chapter. The respective literature reference code is included in the Species Chapter Record of the Databook. This procedure is described in detail in the following chapter.

Equations

If desired, the user can define relationships to express variables as a function of temperature. The variables that can be defined include vapor pressure, specific heat, equilibrium constant, density and solubility variables.

At the present time, the relationships are defined in the Equations Section for documentation purposes only. For the program to use a new relationship, OLI Systems must be contacted.

Method

In order to add a function relationship (for documentation purposes only), the Equations section of the Literature Chapter is initially accessed. The user can then enter an Equation Code by which the function

relationship is to be identified. The format of the code is at the discretion of the user but it is advisable to use the PUBLIC Databook Equation Codes format (See below).

On pressing the Enter Key a new equation file is displayed which can then be edited.

Data Entry

The equations file is edited by using the Action Key and selecting the Edit facility. In order to insert data the Action Key must be re-used, the Mode facility selected, and the "Insert" option chosen from the succeeding screen.

The full function relationship can then be added to the file. The relationship data is saved by using the File Facility. Initially the cursor should be moved to the succeeding line below the equation definition and the Enter Key pressed. The Action Key is then used, the File facility chosen and the "Save" option selected.

The relationships that can be used are listed below. The PUBLIC Databook Equation Codes are also shown and may be used by the user, if entering new data.

Vapor Pressure

Code E004 $\text{LOG}_{10}(Y) = A - B/(C+T)$

Code E101 $Y = \text{EXP}(a+b/T+c*\text{LN}(T)+d*T**e)$

Specific Heat

Code E002 $Y = a + b*T + c/T**2 + d*T**2$

Code E003 $Y = a + b \cdot T + c/T^{**2} + d \cdot T^{**2} + e \cdot T^{**3}$

Equilibrium Constant

Code E001 $\text{LOG}_{10}(Y) = a + b/T + c \cdot T + d \cdot T^{**2}$

Solubility

Code E001 $\text{LOG}_{10}(Y) = a + b/T + c \cdot T + d \cdot T^{**2}$

Density

Code E003 $Y = a + b \cdot T + c/T^{**2} + d \cdot T^{**2} + e \cdot T^{**3}$.

Guidelines

1. *When defining a function relationship the user must specify the equation coefficients to be used, in the Species Chapter of the Databook. A maximum of five coefficients may be defined and are recognized by the following keywords:*

<u>Keyword</u>	<u>Coefficient Type</u>
VP	Vapor Pressure

CP	Specific Heat
KFIT	Equilibrium Constant
SOLU	Solubility
RHO	Density

For further details refer to , on page of this section.

2. *The user must also insure that the respective equation calculation limits and code units are defined through the Records facility of the Species Chapter of the Databook for the species of interest. If this is not performed, the defined equation will not be recognized by the software.*

The procedure for using the Records facility is described in on page of this section.

Material/Ion Codes

Material and ion codes need to be defined for new species which are not included in the PUBLIC Databank. The two types of code are a requirement of OLI's equilibrium calculations and are used to uniquely identify a particular species.

In order to insure new species are identified with unique variables, the integer values in the range 9001-9999 are reserved for use in private databanks.

When defining a new material or ion code, the user can either specify the new number to be specified or enter the species symbol for which the number is to be defined.

Accessing By Number

Initially, the user should access the appropriate section (i.e., Material Codes, Ion Codes) of the Literature Chapter of the Databook. The new code to be defined can then be specified on the succeeding screen. On pressing the Enter Key, a new screen is displayed which must be edited to include the required information.

Accessing By Symbol

If preferred, the user can define a new material or ion code using the species symbol rather than code number.

On selecting the appropriate Literature Chapter section to be accessed, the user should use the Action Key and select the Search facility. From the resulting menu displayed, the user should select the "By Symbol" option. The new species symbol can then be entered. This symbol can either be a chemical formula or a species name, and must be suffixed with either the species valence or ionic charge state respectively.

Valence

For material codes, the species valence state is represented with an integer value prefixed with either a positive +, or negative - symbol enclosed in brackets (i.e., A(+2)). The species symbol does not have to be suffixed with the valence state for species exhibiting zero valence.

Ionic Charge For Ion Codes

For ionic species the charge is represented by suffixing the species symbol with either positive "+", or negative "-", signs. The number of signs used represents the ionic charge (i.e., A⁺⁺).

On confirming the new species entry, a new file is displayed which must be edited to include the required information.

Data Entry

In order to edit the displayed screen the Action Key is used and the Edit facility chosen. The Action Key is then re-used, the Mode facility selected and the "Insert" option chosen from the succeeding display. The entry can then be edited.

When defining material codes the user must define four items, namely:

Material Code Example

<u>Keyword</u>	<u>Description</u>
NUMB	Material code number to be specified (9001-9999)
SYMB	Species symbol and valence state
CHAR	Species valence state
MOLW	Species molecular weight

Consider a species A with a valence of +2 and a molecular weight of 24.5 for which a new material code is to be defined.

The data entry will conform to the following format:

<u>Keyword</u>	<u>Value</u>
NUMB	9001
SYMB	A(+2)
CHAR	+2
MOLW	24.5

Ion Code Example

When defining ion codes, the user must define two items, namely:

<u>Keyword</u>	<u>Description</u>
NUMB	Ion code number to be specified

SYMB

Species symbol and ionic charge state

Consider a species A with an ionic charge of +2 for which a new ion code is to be defined.

The data entry will conform to the following format:

Keyword Value

NUMB 9001

SYMB A++

Guidelines

After several additions of material or ion codes, the databank should be re-indexed using the Control facility. The defined codes should also be included in the Species Chapter of the Databook for the species of interest in order to completely define the code specification.

Chapter 4. Chemistry Models

Overview

In most cases, the user defines a chemistry model by simply entering the names of the chemicals to be covered by the model and the software does the rest. However, this chapter describes all of the advanced facilities available to the user.

Every component of the OLI Software which provides for simulation (OLI Express, ESP, CSP, ProChem) utilizes chemistry model generation as the basis for actual simulations at specific conditions. The ultimate objective of chemistry model generation is the creation of simulation-support files to allow the actual simulation studies to be carried out.

Location of The Chemistry Model Function

Within various components of the software, there are several places where the Chemistry Model Facility can be accessed. They are:

In **OLI Express** (located in the ToolKit)

- Chemistry Model
- Express Calculate
- Summary

In **OLI WaterAnalyzer** (also found in the ToolKit)

- Chemistry Model
- Sample Manager
- ESP Stream Manager
- Summary

In **ESP Process**

- Chemistry Model
- Process Build
- Process Analysis
- Summary

In **CSP Corrosion**

- Chemistry Model
- CSP Stability
- Summary

This section will now consider the Chemistry Model of the OLI software in further detail.

To aid the reader, reference can be made at any time to the schematic diagram at the end of this Chemistry Model section, which is an outline screen-by-screen guide of the Chemistry Model Building Structure.

Chemistry Model Overview

This section describes in detail the requirements to build a Chemistry Model. The Chemistry Model is important as it describes the specific chemical species and chemical equilibria involved in the application being considered.

The OLI software uses a highly advanced thermodynamic and mathematical framework to predict the equilibrium properties of the chemical system. This predictive framework is based upon:

- the **Revised Helgeson Equation of State** for predicting the standard state thermodynamic properties of all species, including organics, in water;
- the **Bromley-Zemaitis** framework for predicting the contribution of excess thermodynamic properties of ionic species in water;
- the **Pitzer** formulation for the prediction of the excess thermodynamic properties calculation of molecular species in water; and
- the **Enhanced SRK Equation of State** for the prediction of vapor and organic liquid phase thermodynamic properties. This enhanced equation of state applies to organics which are sparingly soluble in water, and which form a second liquid phase which is largely ideal.

The extensive OLI Databanks support this predictive framework and are accessed for any required thermodynamic data during Chemistry Model definition.

The building of a basic Chemistry Model is a quick and simple operation. It is also an essential requirement for the modeling of an aqueous system. Generally, from a user statement of molecular chemical species, a Model Definition file is automatically created by the software. This file contains a list of the chemical species in each phase (i.e., vapor, aqueous molecules and ions, and anhydrous and hydrated solids) and the corresponding thermodynamic phase and aqueous speciation equilibrium relationships for the system.

For many OLI applications, this created Model Definition file is all that is needed to describe the chemistry of the system. However, if required, the Model Definition can be augmented by the user to include chemical reaction kinetics, coprecipitation, or bioreactions.

ESP Chemistry Model

The objective in building a Chemistry Model is for the software to create a file containing properties data based upon the Chemistry Model Definition file. This step is done automatically by the software.

The next chapter describes building Chemistry Models involving more than just thermodynamic equilibrium. The building of a basic thermodynamic equilibrium Chemistry Model can be divided into a number of easily performed steps which are described below.

Model Name

Initially, when building a new Chemistry Model, the model must be given a reference name between 1-8 characters in length. Once this has been achieved, the specific chemistry for the model can be entered.

Process Chemistry

After the Chemistry Model has been named, the process chemistry (referred to as inflow species) of interest is defined. This can be achieved by either entering the chemical formula or the chemical name (e.g., H₂SO₄ or sulfuric acid) for each species. After each entry, the software searches the extensive OLI PUBLIC Databank to determine if the thermodynamic data is available for the species stated. If the data is not present a warning message appears and if the user confirms that the species is, in fact, unavailable in the OLI PUBLIC Databank, the user will need to define a private databank for the species (Reference **Chapter 3: Databook** for procedure). A private databank is accessed through the Databank facility.

If a species is defined by chemical name and its thermodynamic properties are available in the PUBLIC Databank, the software converts the chemical name to its respective OLI name on the displayed inflow list (e.g., Acetic Acid is displayed as ACETACID).

Search

Alternatively, if the user is unsure of either the chemical name or formula of a particular species, a search can be carried out by using the Action Key to access the Search facility (Reference the Databook section for detailed search procedures). A search on the PUBLIC Databank is performed and the selected species is added to the model inflow list. If a private databank is to be searched, the Action Key is used again and the Databook facility is used to specify the required databank.

Alt Entry

An alternative method of defining the process chemistry is to use the Action Key to access Alt Entry. This facility provides access to either BioEntry, IonxEntry, Alloys, Petroleum Fractions, and Pseudo-components.

BioEntry

When using process chemistry which includes biotreatment, the ALT Entry can be used to access BioEntry. The BioEntry facility is the recommended way to define the substrate, biological microorganisms, and types of bioreactions which will be present in the model.

Ionxentry

When using process chemistry which includes ion exchange, the ALT Entry can be used to access IonxEntry. For further information, refer to [on page](#) in this section.

Alloys

To predict the stability diagrams in the CSP programs, the user can add an alloy that they define. There are several classes of alloys from which to select:

```
Select Alloy Class:
Cu-Ni
Fe-C-Mn
Fe-Cr-Ni-Mo-C (BCC)
Fe-Cr-Ni-Mo-C (FCC)
Fe-Cr-Ni-Mo-C-N (BCC)
Fe-Cr-Ni-Mo-C-N (FCC)
```

Figure 4-1 Alloy Selections

Each of these alloy classes can have each of its component mass fractions specified. The terminology BCC means body-centered-cubic (ferritic phase) and FCC means face-centered-cubic (austenitic phase). The class Cu-Ni is FCC and Fe-C-Mn is BCC.

The user may name the alloy and specify the components as in the next figure.

```
Alloy Name: ██████████

Alloy Composition
(Weight Fraction)

Fe ██████████
Cr ██████████
Ni ██████████
Mo ██████████
C ██████████
```

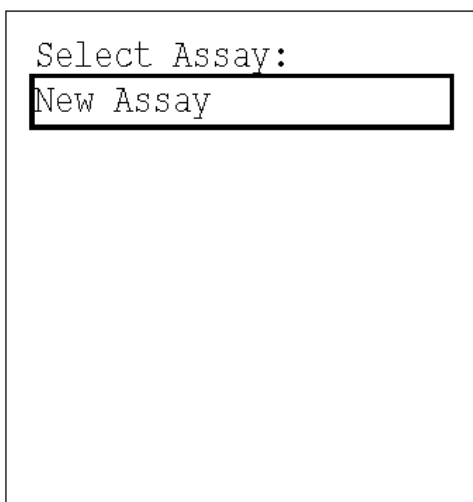
Figure 4-2 Specifying the composition of the alloy.

All the underlying bulk-phase species are automatically included in the model.

Petroleum Fractions

Frequently a hydrocarbon analysis is the only data available for entry into the software. This analysis is usually a distillation curve where the volume distilled as a function of temperature of a petroleum fraction has been analyzed. This information must be turned into a vapor, organic and aqueous component for use in the simulator.

The user may enter up to 20 assays. The first assay screen looks like this:



The image shows a rectangular window titled "Select Assay:". Inside the window, there is a text input field with a black border. The text "New Assay" is entered into this field. The rest of the window is empty.

Figure 4-3 Selecting a new assay.

After entering the name of the assay, the user can select from four correlation methods to create the petroleum fractions:

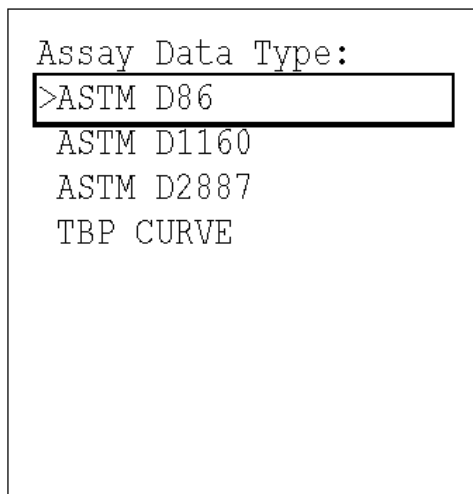


Figure 4-4 The assay data types.

Each of the data types corresponds to the conditions of the experiments used to measure the assay. These are summarized below:

ASTM D86

Used for light and medium petroleum products and is carried out at atmospheric pressure. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline.

ASTM D1160

Used for heavier petroleum products and is often carried out under vacuum. Sometimes as low as 1 mm Hg. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

ASTM D2887

Uses gas chromatography to produce the distillation curve and is applicable to a wide range of petroleum products. The results are always reported on a volume percent basis. The results are converted internally in the OLI model generator to a TBP (True Boiling Point Curve). This curve is then fit to a spline to smooth the curve. The cuts are taken from the spline

TBP

This is the true boiling point curve. These curves, in practice, are difficult to obtain. The other methods are usually used instead.

After selecting a method, the bulk density of the assay is entered:

Average Bulk Density:

Specific Gravity

API Gravity

Watson K

Only Enter one value

Figure 4-5 Entering the assay bulk density

The density units for the average bulk density are:

Specific Gravity Unitless

API Gravity Degrees API ($^{\circ}$ API). This is calculated via the following equation:

$$^{\circ}API(60F) = \left(\frac{141.5}{SG(60F)} \right) - 131.5$$

SG is the specific gravity at 60 $^{\circ}$ F.

Watson K The Watson K has no units but is calculated via:

$$K = \left(\frac{NBP^{1/3}}{SG} \right)$$

Where NBP is the normal Boiling point and SG is the specific gravity.

After the bulk density information has been entered, the actual distillation can be entered as a volume percent v. temperature:



Distillation Data	
Volume Percent Distilled	Temperature F
	

Figure 4-6 Enter percent volume distilled v. temperature

Once the data has been entered, the user will be prompted for the number of “Cuts”. These are the actual pseudo-components that will be created.

Distillation Curve Cuts:

Number of Cuts:

This is the number of Pseudo components that will be created from the distillation curve

Figure 4-7 Entering the number of pseudo-components

The user will then be asked to select a method from which to estimate the phase behavior of the pseudo-components:

Select Thermo method

CAVETT

LEE KESLER

Figure 4-8 Selecting the thermodynamic method

Each of the thermodynamic methods estimate the critical properties of the pseudo-component. Each method uses slightly different methods:

Thermodynamic Methods (pseudo-components and petroleum fractions)

API Uses the specific gravity to estimate the critical parameters. The specific gravity, if not entered, can be estimated from the API gravity or the Watson K. The boiling points are taken from the assay data.

Cavett This method uses the API gravity method to determine the critical properties. The API gravity, if not entered can be estimated from the actual specific gravity or the Watson K. The boiling points for the pseudo-components are taken from the assay.

Lee-Kesler This method uses the Watson K and the specific gravity (which can be estimated via the Watson K) to determine the critical parameters.

The conversion to the pseudo-components are made and a report is generated.

Assay Conversion Results							
Name	NBP,F	Sp Gr	Mol Wt	Mol %	TC,F	PC,psia	Acentric
TAS1_338K	148.28	0.954	67.1	14.95	537.26	924.4351	0.2015
TAS1_365K	197.78	0.979	78.1	30.81	602.6	834.7841	0.2207
TAS1_394K	250.16	1.004	91.1	31.73	670.1	758.3602	0.2443
TAS1_431K	315.86	1.034	109.2	22.50	751.64	680.4666	0.2767

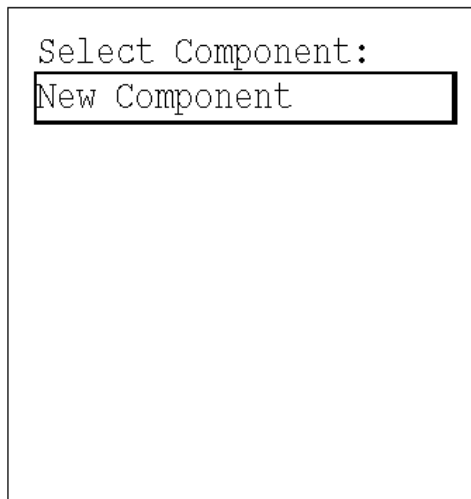
Figure 4-9 The conversion results

Each pseudo-component is now added the chemistry model. The pseudo-component name is based on the original assay name (TAS1 in the example above) and the temperate cut. Thus for the name TAS1_338K is the pseudo-component derived from assay TAS1 at a boiling point of 338K.

The chemistry model generation is completed in the normal manner from here. The assay appears as an inflow species. A new section will be added to the chemistry model termed **GROUPS** which contains the pseudo-component information.

Pseudo-Components

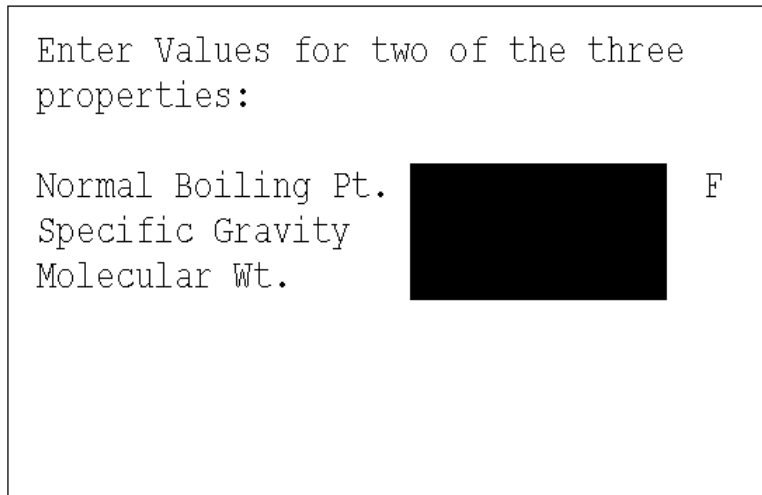
Sometimes the assay data will have only bulk data and no true boiling point or distillation data. In this instance, individual pseudo-components can be entered. As with the other techniques, a new component can be entered.



Select Component:
New Component

Figure 4-10 Entering a new pseudo-component

The name of the pseudo-component can be entered and then the thermodynamic properties of the pseudo-component can be entered.



Enter Values for two of the three properties:

Normal Boiling Pt. [Redacted] F
Specific Gravity [Redacted]
Molecular Wt. [Redacted]

Figure 4-11 Entering pseudo-component properties

The normal boiling point (the boiling point at atmospheric pressure), specific gravity or molecular weight can be entered. Only two (2) of the three (3) components should be entered.

Once the properties have been entered, the thermodynamic method is then selected.

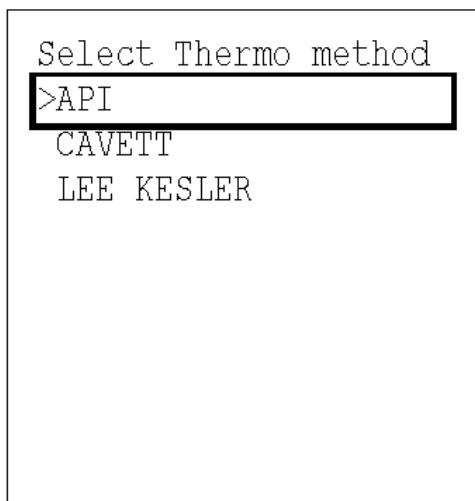


Figure 4-12 Selecting thermodynamic methods.

These methods have been described in a previous section. The model is then created normally. The pseudo-component appears as an inflow species. A new section will be added to the chemistry model termed **GROUPS** which contains the pseudo-component information.

Once the chemistry list is completed, the chemical phases to be considered can be defined.

Phase and Phenomena

After the model chemistry has been defined, it is possible to select which physical phases are to be considered. The software assumes the aqueous phase, vapor phase, and solid phase are to be included, but the user can also specify an organic liquid. Inclusion of the oxidation reduction phenomena can also be added. The user may also specify that a Non-Electrolyte Model is to be created in addition to the Electrolyte Model.

Electrolyte Model

An Electrolyte Model is an aqueous-based system in which the aqueous phase, as well as other possible phases, may exist in equilibrium with each other.

Non-Electrolyte Model

A Non-Electrolyte Model is used to describe a reactive system which does not contain an aqueous ionic phase. Rather, it involves physical equilibrium between a non-aqueous liquid and a vapor phase or two non-aqueous liquids. Either liquid and/or vapor equilibrium/kinetics reactions can be specified if required (Reference: beginning on for further details). This type of model should be used when a process contains non-aqueous, reactive unit operations.

At present, OLI always generates an Electrolyte Model for all process units. However, a Non-electrolyte model must be additionally created for the incinerator unit, and can be created for the reactor, stripper, absorber and solvent extractor blocks if required.

Once the user has defined the model type and phases to be considered, the Model Definition file can be created.

Chemistry Model Definition

From the user defined species inflows, phase, and model requirements, the software creates a Model Definition file for the chemistry. This file contains a listing of all species existing in the aqueous, and user-selected (i.e., solids, vapor, and organic liquid) phases as well as a listing of the corresponding equilibrium relationships for the system.

Once the Model Definition file has been created, the remaining files can be automatically generated in order to complete this Chemistry Model. Note that this stage is needed to prepare for process simulation, but does not require any special user intervention, nor does it affect the user-defined Chemistry Model.

However, before the remaining model files are produced, the user has the facility to view the Model Definition File, using the Action Key to access the View facility.

The automatically created Model Definition file is divided into three sections, namely: Input, Species, and Equilibrium Equations.

Input

The Input Section lists the Chemistry Model Inflow Species defined by the user. Each species is suffixed with the keyword IN, thereby identifying the species as an inflow.

Species

The Species Section lists all the possible species in each phase that could exist in the chemical system based upon the optional phases (e.g., solid) selected by the user. This list is developed automatically by the software, and each species is suffixed with an identifier to its respective phase. These keywords include:

<u>Keyword</u>	<u>Phase</u>
AQ	Aqueous molecular
ION	Aqueous ionic
VAP	Vapor
PPT	Anhydrous solid
.vH2O	Hydrated solid
SUS	Suspended solid (biotreatment)
SOL	Ion exchange media

Equilibrium Equations

The Equilibrium Equations section lists all the equilibrium relationships developed automatically by the software, and any user provided input to describe additional chemical phenomena for the defined chemical system.

Viewing The Model Definition

The Model Definition file can be viewed by using the File facility, after the file has been created.

Alternately, all the related model files can be viewed after the Model Solver files have been generated. This is achieved by using the Action Key to access the Utility facility. An index of related model files are displayed and can be viewed accordingly. These files are referenced by file extension identifiers, namely:

<u>File Extension</u>	<u>Description</u>
.MDL	Chemistry Model Inflow Species - lists inflow species defined for the Chemistry Model.
.MOD	Electrolyte Chemistry Model Definition - lists inflows, species in each phase, and equilibrium relationships. Also includes input for user defined chemical phenomena.
.MD2	Non-Electrolyte Chemistry Model Definition - lists species inflows and any user defined chemical phenomena.
.MOU	Model Definition Log - summarizes number of inflows, created species, and created equations produced in the Chemistry Model Definition file generation.

.WRN

Warning Log - displays error and warning messages for problems encountered during Model Definition/Solver file generations.

Model Definition Bypass

Creating the Model Definition should only be bypassed if the Model Definition File has previously been created and the user is satisfied with the model chemistry and the model phases previously specified.

Generally, this bypass facility is used to access the Model Definition file that has previously been created, in cases for which the user wishes to include additional, user defined, chemical phenomena.

Model Solver Bypass

This step should only be used for previously created Model Solver files that have not been modified in any way. If the defined chemical phenomena and/or solids deletion specifications are amended, then the Model Solver files must be re-created.

The Bypass facility allows the user to return to view an existing Chemistry Model and all the related files.

Solids Deletion

If the user specifies the solid phase to be considered in the model generation (Reference , pg.), the software predicts all possible solid species, including hydrates, for the system. This can result in the creation of a Chemistry Model too large for the software to prepare. The facility is therefore available for the user to selectively remove any solids which are not of interest from the model. Beyond the issue of feasibility,

deleting solids results in faster execution and convergence times. Solids deleted may include species which are known not to form at the system conditions (Temperature, Pressure, and Concentrations).

Solids deletion is achieved by using the Action Key and choosing the Solids facility. From the Solids list displayed, the user can selectively remove any solid species from the model. (Note: The software automatically deletes the corresponding equilibrium relationship).

Scaling Tendencies

The solid can be marked for scaling tendency only rather than for deletion. When a solid is included for scaling tendency only, it is not considered in the equilibrium calculations, just the scaling tendency index is calculated. Scaling tendency is a measure of the tendency of a solid species forming at the specified conditions. Solids with a scaling index greater than one will form if the solid formation is governed by equilibrium (as opposed to kinetics) and if there are no other solids with a common cation or anion portion which also has a scaling tendency greater than one. If more than one solid exists with a common ion and scaling tendency greater than one, then at least one will form. Scaling tendencies can be used by the user to learn more about which solids can safely be deleted from the model.

Scaling Tendencies for a solid are always calculated, unless a solid is deleted. The scaling tendencies can be viewed in the Stream Section of the output.

Electrolyte Model

Once the Model Definition file has been automatically created based upon physical and aqueous intraphase equilibria, the user can add various other chemical reaction phenomena by using the Action Key and choosing the Sections facility.

For an Electrolyte Model, these sections can be added to the model:

- **Equations**
- **Chemical Kinetics**
- **Reduction/Oxidation Reactions**

- **Co-precipitation**
- **Bioreactions**
- **Ion Exchange**

When defining either equations, chemical kinetics, co-precipitation or bioreactions, the Model Definition file must be expanded using the Sections facility. The procedures for performing this function are described in the following chapters of this section. In general, the user types the relevant statements into the Model Definition file. An exception to this procedure is the addition of bioreaction kinetics, which can be added through a series of easy-to-read menus.

The following sections describe in detail the procedures for defining chemical phenomena with the use of examples.

Equations

The Chemistry Model may be edited to include new user-defined equation specifications. The Equations section is available for the user to define new variables based upon software recognized keywords. This section is very flexible and, among other purposes, can be used to calculate specific species properties. For example, species partial pressure, total species content in a chemical system, total mass of vapor present, and the electrical potential of the solution can all be determined using this section.

Method

In order to include an equation specification, the Model Definition file must first be created and then edited using the Action Key and choosing the Sections facility. From the resultant list displayed, the Equations option is chosen, followed by Continue.

The Model Definition file is displayed and can be edited as required, by inserting the relevant data at the end of the equilibrium equations listing. (Note: The data insertion must be prior to the final END statement displayed in the Model Definition file).

Data Entry

Initially, the Equations section must be identified with a header record comprised of the single keyword EQUATIONS inserted into the Model Definition file. The user-variables can then be defined on succeeding rows of the file. Generally, an Equations section will be of the form:

EQUATIONS

DEFINE user-variable=expression

END

Syntax Of Define Statements

Each statement must begin with the keyword DEFINE, followed by an equation:

DEFINE user-variable=expression

The user-variable in the DEFINE statement must be a unique name of 1-15 characters in length. The expression which calculates the user variable must consist only of:

- Software recognized variables (e.g., T, PT; a complete description is in Appendix I)
- Previously defined user variables
- Numerical coefficients expressed as real numbers in double precision format (see below)
- Mathematical operators +, -, *, /, **
- Mathematical functions LOG, EXP, LOG10
- Calculation limiting function STEP

Double Precision Format

If any coefficients expressed in scientific notation are included in the DEFINE expression, they must be expressed in double precision format. That is, the letter "E", normally used to express standard form coefficients (i.e., 1.0E+03), must be replaced with the letter "D" (i.e., 1.0D+03).

This requirement is for software purposes only and does not effect the Chemistry Model Definition.

Calculation Limits On Define Expressions

If required, lower and upper calculation limits can be included on user variable definition expressions. This allows an expression to be determined only when a specified variable lies within a specified range. The DEFINE expression is determined to be zero when the specified variable value falls outside of the required limits.

This facility is used by entering the keyword STEP followed by the limiting variable and the lower and upper values to be considered. The syntax for the STEP function is of the form:

STEP (variable, lower limit, upper limit)

The STEP specification is entered as a multiplier (linked by an asterisk ("*") multiplier operand) to the required variable definition expression. Hence, STEP is equal to one if the required variable value is within the specified limits, or zero if either limiting value is exceeded.

Example

This description on how to specify user defined variables can be summarized with a simple example.

Consider a species A existing in a multi-component liquid-vapor system. The partial pressure of this species is to be determined within specified limits. The limits of interest are:

- 1) The total vapor content of the system is zero.
- 2) The total vapor content of the system exceeds 1,000 gmoles.

The input to the Model Definition file will be of the following form:

EQUATIONS

```
DEFINE PA = PT*YA*STEP(V,1D-08,1D+03)
```

END

where PA = user defined variable (i.e., partial pressure of A)
PT = software recognized variable for the total pressure of the system
YA = software recognized variable for the vapor mole fraction of species A
STEP = software recognized function for imposing calculation limits to an expression
V = software recognized variable for the total vapor content of the system

(Note: The lower limit concentration value is expressed as 1D-08 and not as zero. This practice is recommended when formulating user STEP functions. A complete description of software recognized variables appears in Appendix I).

Chemical Kinetics

Reaction Kinetics Overview

The OLI thermodynamic framework supports reaction kinetics. Reaction kinetics can be defined in standard Arrhenius terms or in terms defined by the user. There are only two unit operations that support reaction kinetics: REACTOR unit and Multistage COLUMNS such as STRIPPERS and ABSORBERS.

New Thermodynamic Framework

With the introduction of ESP version 7.0, we now have two thermodynamic models available for use. The first thermodynamic model is the standard aqueous model that has been in use since the early days of OLI Systems. The new model is the MSE model (Mixed Solvent Electrolyte). This model allows solution concentrations from dilute systems to fused salt conditions (no water).

With the introduction of the MSE thermodynamic framework there has been a change in the internal OLI concentration units. In previous versions to 7.0, the internal concentration unit was mole/Kg H₂O (molal). Now the internal concentration unit is mole fraction for both the aqueous model and for the MSE model.

If required, the Model Definition file can include an aqueous phase reaction section to describe non-equilibrium phenomena. The reaction kinetics facility allows user definitions in terms of species conversion limitations, standard rate expressions based upon Arrhenius-derived equilibrium constants, or user defined rate expressions.

Variable Names relating to Activities

In version 7.0, we have changed the definition of some of the internal variables. The primary variables are:

<i>IION</i>	The species "I" has units of mole fraction. Such a species could be the sodium ion, Na ⁺ which is represented as NAION.
<i>AAQ</i>	The species "A" has units of mole fraction. Such a species could be the neutral carbon dioxide molecule, CO ₂ ⁰ which is represented as CO2AQ.
<i>AION</i>	This variable is the natural log of the activity coefficient for the "I" species. The actual expression is:

$AION = Ln(\gamma_{IION})$ in the case of the sodium ion this expression is:

$$ANAION = Ln(\gamma_{NAION})$$

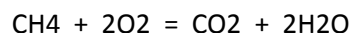
AAAQ This variable is the natural log of the activity coefficient for the “A” species. The actual expression is:

$AAAQ = Ln(\gamma_{AAQ})$ in the case of the carbon dioxide neutral molecule this expression is: $ACO2AQ = Ln(\gamma_{CO2AQ})$

At present, the reaction kinetics must be added by editing the Model Definition file (i.e., the user has to type in all the relevant information, including software keyword statements).

The Kinetics are divided into two classes of reactions. The first class is distinguished by a material balance code change across the reaction or another way of saying the same thing is that an element changes oxidation states across the reaction. All other kinetics reactions are of the second type.

Example type 1 kinetic reaction

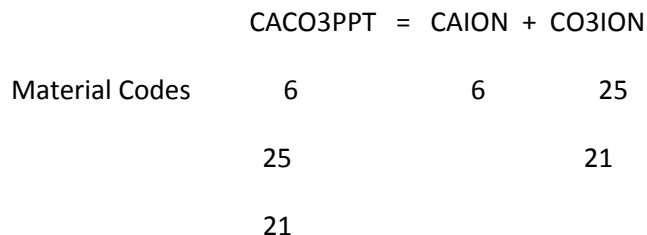


Material Codes 1001 57 = 25 1 21

Due to the material balance code changes across this reaction there will be no equilibrium reaction or any combination of equilibrium reaction to produce this reaction. This assumes that no oxidation / reduction reactions are present in the equilibrium reactions.

In fact, this is a requirement of our kinetic models that kinetics and oxidation/reduction reactions can not be mixed. You must use all kinetic or all oxidation/reduction, not a mixture of both.

Example type 2 kinetic reaction



The material codes on both sides of the equation are the same. Therefore the equilibrium model will contain this reaction either directly or as a combination of equilibrium reactions. In order to include this kinetic reaction, the equilibrium model must be changed to remove the equilibrium between these species. The software will re-write the equilibrium reactions by removing the CACO3PPT from the equilibrium reaction set. As a result, the only way to make or consume $\text{CaCO}_{3\text{ppt}}$ is by the kinetic reaction. If the user wants to feed $\text{CaCO}_{3\text{ppt}}$ to the reactor, an additional input has been provided in the interface routine to specify the amount of $\text{CaCO}_{3\text{ppt}}$ feed. An additional key word has been added to the kinetics section of the model file where the user can specify which species will be removed from the equilibrium calculation:

NOEQx CAION

With this specification, the CAION will be removed from the equilibrium set instead of the caco3ppt . By default the software will remove any solid species in the equation unless a NOEQx record has been supplied.

Chemistry Model File

In order to create a chemistry model with kinetics, the user needs to create the standard equilibrium model and then edit the .MOD file and add a kinetics section to the bottom of the file. The user does **not** need to modify the equilibrium reactions, the software will make the modifications. The following is an example of kinetics section to be added to the model file (see OLI documentation for details):

KINETICS

REAC1 CACO3PPT=CAION+CO3ION

RATE1 STD KF=1.0E+03 KR=1.0E+05

NOEQ1 CACO3PPT

← OPTIONAL

Method

In order to include chemical reaction kinetics, the Model Definition must first be created, and then edited using the Action Key, choosing the Sections facility. From the list displayed, the Kinetics heading is chosen, followed by Continue on the succeeding screen.

Data Entry

The Model Definition is then displayed and can be edited as required by inserting the relevant data at the end of the equilibrium relationships listing. (Note: the data insertion must be prior to the final END statement displayed on the file).

The first requirement is to input the keyword KINETICS as a header record at the end of the equilibrium relationship listing. The chemical kinetics to be considered can then be added.

Generally, the Kinetics section will be in the form:

KINETICS

REACn

RATEn

END

A maximum of fifty aqueous phase reactions may be specified if required. Each reaction is defined in two parts, namely:

Keyword

Definition

REAC	Chemical reaction equation
RATE	Chemical reaction kinetics

Each part will now be considered in more detail.

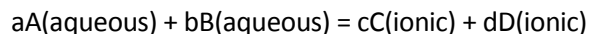
Chemical Reaction Equation

Initially, the chemical reaction must be recognized with the keyword REAC, followed by a sequential identification number (1-50). The aqueous based, chemical reaction equation to be considered is then entered. *The reactant species must appear in the Model Definition species list.* Reaction stoichiometry must also be included as well as the individual species reactant and product phases. The following species suffix identifiers are used to define species phases.

<u>Suffix Identifier</u>	<u>Species Phase</u>
AQ	Aqueous Molecular (Neutral)
ION	Aqueous Ionic (Charged)
PPT	Precipitate (Solid)
VAP	Vapor
.vH2O	Hydrate (Solid)

Example

The format required to define a chemical equation can be summarized with the following example. Consider the general reaction:



where a, b, c, d , are stoichiometric coefficients

A, B are aqueous reactant species

C, D are ionic product species

Hence, the input to the Model Definition file is of the form:

KINETICS

REAC1 aAAQ + bBAQ = cCION + dDION

Chemical Reaction Kinetics

The kinetics for a particular chemical reaction are defined once the chemical reaction equation has been defined. Initially, the rate-limiting kinetics to be considered are identified with a keyword, namely RATE, followed by the reaction equation identification number. (*Note: Only one RATE expression can be defined per REAC expression*). Once the reaction identification number is specified, the type of rate kinetics to be considered must be specified. Two options are available; namely:

Use of standard rate expressions - where the reaction rate is calculated from the forward and reverse reaction rates, and the respective equilibrium constants are determined by the Arrhenius equation.

User defined rate expressions - where the reaction rate and any associated variables are defined by the user.

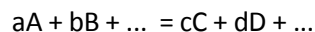
Each will now be considered in more detail.

Standard Rate Expressions

In this mode, the rate of reaction is calculated using a standard rate expression. This expression takes into account both the forward and reverse reaction rates, the individual species reaction orders, and the forward and reverse reaction constants (determined using the Arrhenius Equation).

Example

The standard rate expression is best illustrated by means of an example. Consider the general equation:



where: a, b ... c, d are stoichiometric coefficients.

and: A, B, ... are reactant species

C, D, ... are product species

The standard rate expression is of the form:

$$Rate = (k_f a_A^{r_1} a_B^{r_2} \dots - k_r a_C^{p_1} a_D^{p_2} \dots) * Vol$$

where:

$$Rate = \text{Reaction rate} \left(\frac{\text{mole}}{\text{m}^3 \text{hr}} \right) / \text{hr}$$

k_f	=	Forward reaction rate constant $\left(\frac{\text{mole}}{\text{m}^3 \text{hr}}\right) / \text{hr}$
k_r	=	Reverse reaction rate constant $\left(\frac{\text{mole}}{\text{m}^3 \text{hr}}\right) / \text{hr}$
a_A, a_B, \dots	=	Activities of reactant species (unitless)
r_1, r_2, \dots	=	Reaction order of individual reactant species (normally from experimental data. Default is stoichiometric coefficients; a, b, ...)
a_C, a_D, \dots	+	Activities of product species
p_1, p_2, \dots	=	Reaction order of individual product species (normally from experimental data. Default is stoichiometric coefficients; a, b, ...)
Vol	=	Liquid product volume (m^3)

The forward and reverse reaction rate constants are determined using the general Arrhenius Equation:

$$K = A * \exp(-E/RT)$$

where: k = Reaction rate constant $\left(\frac{\text{mole}}{\text{m}^3 \text{hr}}\right) / \text{hr}$

A = Arrhenius frequency factor for the forward or reverse reaction and is in $\left(\frac{\text{mole}}{\text{m}^3 \text{hr}}\right) / \text{hr}$

E = Forward or reverse activation energy (joule/gmole)

R = Universal gas constant (8.314 joule/(gmole*K))

T = Temperature (K)

When specifying a standard rate expression the user must define the Arrhenius frequency factor, reaction activation energies divided by the universal gas constant, or, alternatively, the reaction rate directly. In addition, the user can specify the individual species order coefficients for the forward and reverse reactions if these differ from the stoichiometric coefficients (which are the default).

Data Entry

Initially, the keyword STD is entered, succeeded by a list of the above coefficient values, each individually specified with one of the following keywords:

<u>Keyword</u>	<u>Description</u>
KF	Forward reaction rate constant $\left(\frac{\text{mole}}{\text{m}^3\text{hr}}\right)/\text{hr}$
KR	Reverse reaction rate constant $\left(\frac{\text{mole}}{\text{m}^3\text{hr}}\right)/\text{hr}$
AF	Forward reaction Arrhenius factor $\left(\frac{\text{mole}}{\text{m}^3\text{hr}}\right)/\text{hr}$
AR	Reverse reaction Arrhenius factor $\left(\frac{\text{mole}}{\text{m}^3\text{hr}}\right)/\text{hr}$
BF	Forward reaction activation energy divided by the universal gas constant (K)
BR	Reverse reaction activation energy divided by the universal gas constant (K)
ERi	Reaction order of reactant species i
EPI	Reaction order of product species i

It should be emphasized that when the keywords KF and KR, the forward and reverse reaction rate constants are used for a particular reaction, this would preclude using the other keywords for that reaction. However, these keywords are not normally specified by the user, as these variables are usually calculated by the software from user defined Arrhenius factors and activation energies.

When defining the reaction order for a species, the order in which the species appears in the reaction equation must be defined (i.e., subscript i) with a sequential number, for either the reactant or product species. Hence, the first reactant is identified with the number 1, the second, 2 and so on. Similarly, the product species are identified with the integers 1, 2, 3 ... etc.

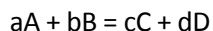
Default Values

If any of the keywords are not defined, the software assumes a default value for that particular variable. These default values are assumed to be zero for the reaction rate constants, Arrhenius factors, and activation energies (divided by the universal gas constant). For the species reaction order coefficients, the reaction stoichiometric values are assumed.

In order to complete the standard rate expression definition, the reaction temperature and initial reactant molalities are included in the process stream composition definition. This is performed in the Process Build facility of ESP Process (Reference the Process Modeling section for further details).

Example

This description on how to define a chemical reaction can be summarized with a simple example. Consider the general equation:



where a, b, c, d are stoichiometric coefficients.

The rate of reaction is expressed by:

$$\text{Rate} = K_f [A]^{0.5} [B]^{0.7} - K_r [C]^c [D]^{0.3}$$

where $K_f = 7.6 \times 10^9 \exp(-(8106)/RT)$

$$K_r = 5.2 \times 10^9 \exp(-(7300)/RT)$$

then the user defined RATE section will be of the form

```
RATE1      STD AF = 7.6D+09 BF = 975                (i.e., BF=8106/8.314)
+          ER1 = 0.5 ER2 = 0.7
+          AR = 5.2D+09 BR=878                    (i.e., BR=7300/8.314)
+          EP2 = 0.3
END
```

Note: *If user defined data is entered onto more than one line of the Model Definition file, the key symbol "+" must be inserted at the start of each additional line of data.* If this symbol is not included, the software does not recognize the additional entered lines and the Model Solver and related files cannot be generated.

User Defined Rate Expressions

This facility allows for a very flexible description of chemical reaction kinetics to suit the user's specific requirements. Generally, this function is used if the reaction kinetics to be considered do not conform to the conversion type or standard rate type kinetics described previously.

Data Entry

To use this function the keyword SPEC must first be entered in the RATE record of the Model Definition file: RATEn SPEC. The user can then specify the user-defined relationships of interest.

Define

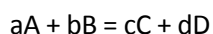
Each relationship must be preceded by the keyword DEFINE and can consist of coefficients, expressed as real values, and/or software recognized variables. The syntax and rules for the DEFINE statement are the same as those described in the Equations Section (Refer back to , pg. of this chapter).

Guidelines For Rate Defines

1. *The order in which user-defined variables are defined is important.* For example, if a user-defined variable is to be used in a succeeding user-defined relationship, the variable must be determined prior to the relationship definition.

Example

This description of how to define a chemical reaction can be summarized with a simple example. Consider the following reaction:



where a, b, \dots, c, d are stoichiometric coefficients.

and A, B, \dots are reactant species

C, D, \dots are product species

where the reaction kinetics are described by the user-defined relationship⁸:

$$\text{rate} = K[\text{Aaq}]^x \text{VOL}$$

where $K = 3.0 \text{ EXP}(700/T)$

$$x = 20 \text{ LOG}_{10}(\text{AION}/T)$$

$$\text{VOL} = \text{VOLLIQ}/1000^9$$

Therefore the RATE section of the Model Definition file will be of the form:

```
RATE1 SPEC  
  
DEFINE KK = 3.0*EXP(700.0/T)  
  
DEFINE XX = 20.0*LOG10(AION/T)  
  
DEFINE VOL=VOLLIQ/1000  
  
DEFINE RATE1 = KK*(AAQ**XX)*VOL  
  
END
```

Extent of Reaction

To determine the extent of reaction we need to the residence (hold-up time). For both STD and SPEC type kinetics, the rate variable has the units of mole/hr.

⁸ In principle, the rate can follow non-Arrhenius kinetics and be very complicated.

⁹ The variable VOLLIQ is the internal variable for liquid volume and has units of Liters. We must divide by 1000 to convert to m³.

Since the rate constant in STD kinetics has reciprocal m^3 units we will multiply the RATE1 variable by the liquid volume to get RATE in mole/hr.

In SPEC kinetics, the user defines the rate. It is recommended that a volume term be included such that the RATE calculated is in mole/hr.

The EXTENT of reaction is then calculated by multiplying the RATE by the TSTEP. TSTEP is the time step. TSTEP should not be confused with TINC in DynaChem which is the DynaChem time step. By default, DynaChem sets TSTEP = TINC.

Reduction/Oxidation Reactions

Reduction/oxidation, or redox are reactions in which the valence state of elements are changed. Some specific applications which can be modeled include NO_x chemical systems, and sulphite/chlorite/sulphate/chloride systems which can occur in corrosion processes.

Reduction

Reduction is a process in which the valence state of an element is reduced by the gaining of electrons.

Oxidation

Oxidation is a process in which the valence state of an element is increased by the losing of electrons.

If required, the Model Definition file can include reduction/oxidation reactions. Both equilibrium and kinetics reactions can be considered in the liquid and/or vapor phases.

Automatic Generation of Redox Equations

In ESP, the user has to request the automatic generation of redox equations because it is not a default feature. The automatic generation is activated before the Chemistry Model generation. The default screen for the model generation reads:

```
INCLUDE WHICH MODELS/PHASES?  
(The aqueous phase is assumed.)
```

```
> Electrolyte Model  
  > Vapor Phase  
  _ Organic Liquid Phase  
  > Solid Phase(s)  
    Oxidation/Reduction
```

```
Non-Electrolyte Model
```

To activate the automatic generation of redox reactions, move the cursor to highlight **Oxidation/Reduction** and press the space bar. The > sign will appear on the left-hand side of Oxidation/Reduction, i.e.,

```
> Oxidation/Reduction
```

In CSP, the Oxidation/Reduction option is a default feature because most corrosion-related processes involve oxidation and reduction. If this option is not desired in some specific case, it should be highlighted and the space bar should be used to remove the > sign.

If the Oxidation/Reduction option is selected, the software will analyze what redox subsystems are possible in the chemical system defined by the inflows. A redox subsystem is defined as a collection of species containing a given element in any oxidation state. For example, the iron subsystem will contain all species containing Fe in the 0, 2+ and 3+ oxidation states. After determining which redox subsystems are possible, the software displays a question:

INCLUDE WHICH REDOX SYSTEMS?

followed by the list of possible redox subsystems. To include a redox subsystem, highlight it and press the space bar to select it. As always, the space bar acts as a toggle that can be used either to include or eliminate a subsystem. As a default, the software selects the subsystems that contain metals of engineering importance. This default is motivated by corrosion applications, for which redox transformations of engineering metals are important.

With version 9.1 of ESP, we now allow you to select individual oxidation states. You are no longer limited to the entire subsystem.

Example

Let us assume that the inflows contained aluminum, titanium, chlorine and sodium in addition to hydrogen and oxygen, which are

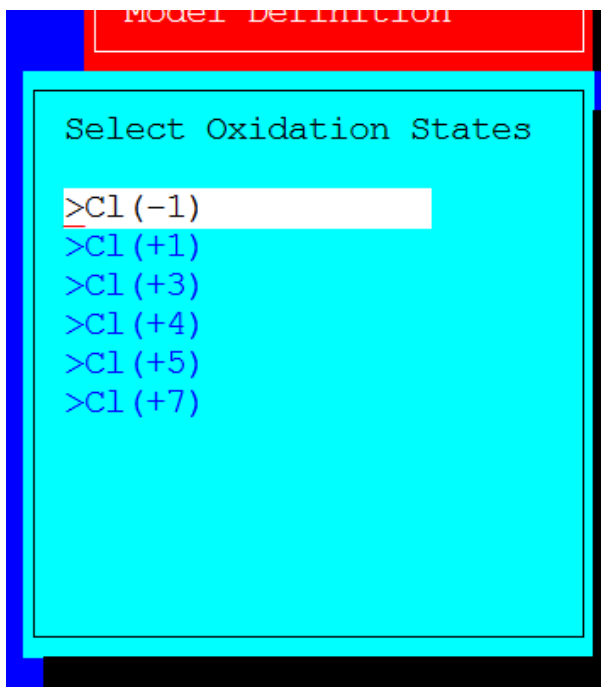
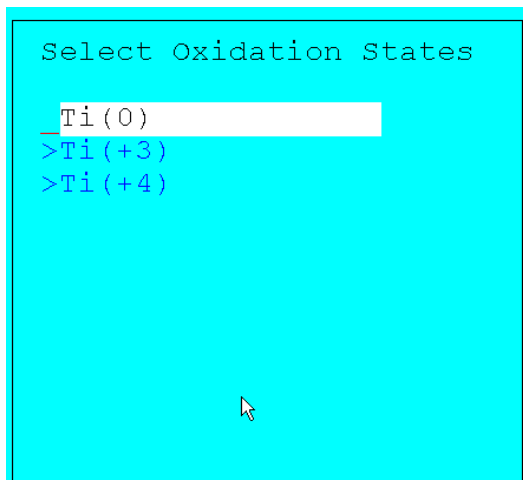
always present in an aqueous environment. In this case, the software will display the following list:

```
INCLUDE WHICH REDOX SYSTEMS?  
  
Al (0) Al (+3)  
> Ti (0) Ti (+3) Ti (+4)  
Na (0) Na (+1)  
> Cl (-1) Cl (+1) Cl (+3) Cl (+5) Cl (+7) Cl (+4)
```

The > sign denotes the subsystems that have been selected. Let us modify the chlorine subsystem. We will assume that the oxidation states of +3, +5, +7 and +4 are not needed for this model and we want titanium but not the metal Ti(0).

We select the overall subsystems using the spacebar.

Press Enter



Press Enter to bring up the next selected subsystem (in our example Cl)

Press Enter to continue.

Guidelines

1. *In principle, you can select all redox subsystems. However, this will most likely result in time-consuming calculations.* Therefore, a judicious selection of subsystems is recommended.
2. *If you are studying corrosion of any metal, you have to include the redox subsystem corresponding to that metal.* Most likely, the software will recommend including that metal as a default.
3. *There is a large number of elements that usually occur in only one oxidation state.* Metals of the first and second group of the periodic table (e.g., Na, K, Ca, etc.) are a good example. There is usually no need to include such metals in their elemental form.
4. *There are some nonmetals that may or may not be important in redox equations. A typical example is sulfur.* If you are studying, for example, corrosion of metals in H₂S-containing environments, it will be necessary to include the sulfur redox subsystem because H₂S may form sulfides, which commonly undergo redox transformations. However, if you are using H₂SO₄ only as an acid and do not anticipate any redox reactions, you do not have to select the sulfur redox subsystem.

After selecting the desired redox subsystems, press Enter and the software will continue generating the chemistry model. Then, the relevant redox reactions will be automatically retrieved from the Redox Chapter of the Public and Corrosion (if included) Data Banks and added to the Model Definition file.

Manual Inclusion of REDOX Equations

In order to manually add reduction/oxidation reactions, the Model Definition file must first be created and then edited using the Action Key facility and choosing the Sections facility. From the list displayed, the REDOX heading is chosen, followed by Continue on the succeeding screen.

Edit

The Model Definition is then displayed and can be edited, as required, by inserting the relevant data at the end of the equilibrium relationships listing. (Note: The data insertion must be within the EQUILIBRIUM section and prior to the final END statement displayed on the file).

The user then simply defines the REDOX reaction equations to be included at the end of the Chemistry Model Equilibrium relationships.

Example

This procedure can be summarized with a simple example. Consider a species B undergoing the following REDOX reaction in a chemical system containing the three elements B, O (oxygen) and H (hydrogen).



This reaction contains three valence states of species B, one of oxygen, and one of hydrogen, namely:

<u>Element</u>	<u>Valence</u>
B in BO	+2
B in BO ₂ (-1)	+3
B in BO ₃ (-1)	+5
B in BO ₂	+4

<u>Element</u>	<u>Valence</u>
O in H ₂ O	-2
O in O ₂	0
H in H ₂ O	+1

Data Entry

Hence, the data entry to define the redox reaction in the Chemistry Model Definition are the EQUILIBRIUM equations:



Guidelines

1. *Since the generated material balance and valence equations are not displayed in the Model Definition file, but are added during the Model Solver generation, errors can occur during the generation step. In order for the Model Solver to be generated the following relationship must be true for the model:*

Total number of equilibrium relationships in the model	+	Total number of species exhibiting different valence states in the Model Inflow list (e.g., IN)	+	Total number of Redox reactions included in the Model (by the user)	+
One overall generated conservation of valence equation	+	Number of species groups defined in the ASSOCIATE record	-	Total number of species (e.g., number of material codes) defined in the ASSOCIATE record	=

Total number of species created in the Chemistry Model species list (e.g., VAP, AQ, ION, PPT, .vH2O)

For some redox cases, this relationship may not be satisfied when the material balance and valence equations are added to the model. This is generally caused by the left side of the relationship being greater than the right side. If such a case occurs, the Model Solver cannot be generated. The user must edit the equilibrium relationships section of the Model Definition file. Usually, this entails deleting appropriate equilibrium relationships from the definition until the above requirement is satisfied.

Equation Deletion

The equilibrium relationships deleted are at the user's discretion. Generally relationships should be omitted for species specified in the redox reactions.

An initial guideline to determine which equilibrium relationship to delete is to compare the first species entries expressed in the equilibrium relationships with the first species entries defined in the redox equations. If the same species exists as the first entry in both types of equation, the equilibrium relationship must be deleted from the Model Definition file. The reason for this is that all reactions specified in a model must have a unique species identifier as its first entry in order for the software to recognize individual equations.

Reference Example

For the previous example, if the equilibrium relationship

BOAQ=BOVAP

is defined as part of the Chemistry Model it must be deleted from the definition as its first species entry is identical to that defined in the redox reaction.

Alternatively, if the species BOVAP is not listed as the first species entry in any other the above relationship could be rearranged by the user, so that it reads

BOVAP=BOAQ

This would allow the Model Solver to be generated without error.

Species Check

Upon deleting an equilibrium relationship, a check must be performed (by the user) to insure that all the species listed in the Model Definition file appear in the remaining equilibrium or redox relationship.

An initial approach that may help the user: *select an equation to delete, and then confirm that the species involved are defined in the added redox reactions.* However, this is not always true and the user will have to perform a complete species cross checking procedure. (Note: It is advisable to use a print of the Model Definition file to perform a complete species/equation check).

A specific example of this Chemistry Model can be referenced in the Applications sections.

Co-precipitation

Coprecipitation is a phenomena in which an ion in solution replaces an ionic element in a solid species. An example of this would be Mg^{+2} replacing Ca^{+2} in the $CaCO_3$ solid.

Presently, co-precipitation reactions can be included in Chemistry Models created through ESP and simulated by only ElectroChem, a ProChem component accessed through ESP Toolkit.

The Chemistry Model Definition may be edited to include Coprecipitation type reactions.

Edit

To include Coprecipitation, the Chemistry Model Definition file must be created and then edited using the Action Key and choosing the Sections facility. From the list displayed, the Coprecipitation option is chosen,

followed by Continue on the succeeding screen. The Chemistry Model is then displayed and can be edited by inserting the relevant information. This consists of adding one new species and one new section.

Data Entry

The co-precipitant species is added to the SPECIES section of the Model Definition. This species is added anywhere below the SPECIES keyword record, and before the next section. The section which will follow SPECIES is either SOLIDS, if any solid species have been set for scaling tendencies only, or EQUILIBRIUM.

The Coprecipitation section should be added just prior to the END record for the file. The section is identified with a header record COPRECIPITATION inserted into the file. The co-precipitation equation is then entered on the succeeding line. Generally, the section is in the form:

COPRECIPITATION

equilibrium equation

END

Multiple species and equations are supported.

Reaction Equation

The Coprecipitation reaction can be described in the following equation:

host solid + coprecipitating cation = coprecipitant solid + host cation

where:

host solid	=	the solid species which will receive the coprecipitating cation
coprecipitating cation	=	the cation which will replace the host cation
coprecipitant solid	=	the species that forms when coprecipitating cation replaces the host cation
host cation	=	the cation in the host solid which will be replaced by the coprecipitating cation

OLI Form Of The Equilibrium Equation

The Coprecipitation reaction is entered as an OLI equilibrium equation by simply writing the equation as described above, but switching the left and right sides. This will place the name of the coprecipitant solid as the first term of the equation (an OLI requirement). This appears as follows:

coprecipitant solid + host cation = host solid + coprecipitating cation

Coprecipitant Solid

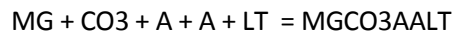
The name of the coprecipitating species is defined as:

coprecipitating		host		letter for		letter for		species suffix
cation	+	anion	+	lattice type	+	host cation	+	(LT)

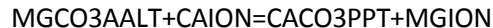
Example

This example will demonstrate how to write a COPRECIPITATION Section for Mg⁺² ion coprecipitating into a CaCO₃ (calcite type) solid:

First the name of the new coprecipitant species must be created. To create this name, simply combine the names as described above (Refer to the tables on the following pages for the lists of code letters). This will give:



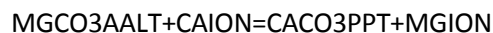
This new name must be inserted into the SPECIES Section. Next the COPRECIPITATION Section must be added just prior to the final END followed by the Equilibrium equation:



Note that the new species name is the MGCO3AALT, which represents the coprecipitant species into the established (regular) crystal lattice.

The new section will appear just prior to the final END as:

COPRECIPITATION



Guidelines

1. *The present implementation of Coprecipitation models is limited to substitution of species cations into specific types of solid (crystal) lattices. A complete list of the cations and solids is given in the following pages.*
2. *The reaction equation for the Coprecipitation must be written precisely in the order illustrated, starting with the coprecipitant form of the solid with the suffix LT.*

3. *The current implementation is limited to the prediction of small amounts of Coprecipitation into an established solid.* The mole fraction of an "LT" species in the solid solution phase is greater than 0.05, the simulation is invalid.
4. *The PUBLIC Databank does not currently contain all of the solids implied by the tables at the end of this subsection.* If the user wishes to use such a solid in a coprecipitation reaction, a Private Databank containing the necessary solid must be created. It will, however, not be necessary to have a COPRECIPITATION Chapter in that Databank.

solids Supported by the Coprecipitation Model

General	Lattice	Letter
Formula	Type	Code
MCO3	Calcite	A
MCO3	Aragonite	B
MO	Rocksalt	C
MO	Zincite	D
MF2	Fluorite	E
MF2	TiO2	F
MCl2	CdCl2	G
M(OH)2	CdCl2	H
MSO4	BaSO4	I
M2SiO4	Olivine	J
M2SiO4	Phenacite	K
M(UO)22(PO4)2.nH2O	Phosphate	L
M2O3	Corundum	M
MO2	Fluorite	N
MS	NaCl	O

MSO4*

BaSO4

P

* Please note, the MSO4 with the code letter "P" is reserved for a special Ra^{+2} into BaSO4 correlation. All others of the MSO4 type should use code "I".

Host Cations Supported by the Coprecipitation Model

Cation Name Letter Code

CAION A

BEION B

MGION C

MNION D

FEIIION E

COIIION F

NIION G

CUION H

ZNION I

CDION J

SRION K

SNION L

BAION M

EUIIIION N

HGION O

PBION P

RAION	Q
UO2ION	R

Bioreactions

At present, ESP Process allows for a Biotreatment Process Block which is a steady state bioreactor (Reference the Process Modeling sections for further details) and a dynamic bioreactor simulated using DynaChem (Reference the DynaChem Handbook for further details).

The OLI Biotreatment model is a synthesis of 3 modeling approaches: 1) Perry McCarty's basis for biological oxidation of organic and inorganic substrates and balanced chemical reactions, 2) the IAWPRC model for biochemical reactions as enhanced and refined by Professor C.P. Leslie Grady, Jr. of Clemson University, and 3) the OLI rigorous aqueous electrolyte thermodynamic model.

The simulation processes of denitrification (NO_3 to N_2) and nitrification (NH_3 to NO_3) are accurately modeled. Aerobic, anoxic and anaerobic bioreactions are all considered. The rigorous and accurate biotreatment simulation allows:

- study of pH control;
- estimation of optimum O_2 flow;
- study of stripping effects of the air;
- determination of optimum blending of inlets to prevent washout; and,
- determination of clarifier sizing.

Currently, OLI models "suspended growth" processes only (i.e., completely mixed, homogeneous, solution based reactions). The substrate, microorganisms, and other constituents are assumed to be suspended within the liquid, therefore the aqueous composition is used to determine the reaction rates and reaction extent. Future releases of ESP Process are expected to provide for modeling "attached growth" processes where the microorganisms are attached to an inert medium.

Model Inflows

After the Chemistry Model is named for the process which will include a biotreatment block, the inflow species can be defined by using the Action Key and selecting the **BioEntry** facility. The BioEntry facility is the recommended way to define a Chemistry Model with bioreactions. The facility prompts for the types of bioreactions which will be considered in the model, the substrates, and the biological microorganisms involved. The BioEntry facility then determines which other inflows are required for these reactions, and writes the necessary records to the Model Definition file.

Biochemical Reactions

Once in BioEntry, there are two types of synthesis biochemical reactions that can be selected: **heterotrophic** organism reactions, which operate on a substrate; and **autotrophic** organism reactions, which occur in the presence of ammonia and carbon dioxide.

Aerobic, anoxic, and anaerobic energy reactions are supported with heterotrophic biochemical reactions. Aerobic energy reactions are supported with autotrophic biochemical reactions. The energy reactions which will occur are selected by the solution concentration.

For modeling typical biotreatment processes, *it is recommended that both heterotrophic and autotrophic biochemical reactions be included in the Chemistry Model.* Either biochemical reaction can then be selectively activated or suppressed through the use of the **bioreaction constants**. (Reference pg.).

Substrate Definition

In BioEntry, the user specifies the substrate to be degraded for a heterotrophic reaction. The substrate can be specified by either naming a particular species (e.g., propanate) or by characterizing a "lumped" substrate. Up to 50 substrates can be defined as heterotrophic organism reactions in one Chemistry Model. Individual substrates are either particular species which already exist in an OLI supplied databank, or in a user supplied private databank. In addition, up to ten of the substrates can be defined as a *lumped substrate*, that is, as a substrate characterized by properties such as (representative) MW, ThOD, TON, or TOC.

The Search facility can be used within the BioEntry facility to locate a particular species in the databank, and private databanks can be used to define a particular species if it is not in the OLI databanks.

Alternatively, a lumped substrate can be characterized by entering the following data about the substance:

MW	Molecular Weight
ThOD	Theoretical Oxygen Demand, g ThOD/mol
TON	Total Organic Nitrogen, g N/mol
TOC	Total Organic Carbon, g C/mol

Estimated stoichiometry for

C, H, O, N, Cl, S, P (fractional coefficients are allowed).

Guidelines For Lumped Substrates

1. *OLI recommends a 0.95 COD/ThOD ratio as a rough approximation.*
Contact OLI for a list of the COD to ThOD ratios of some common organics.
2. *In general, when characterizing a lumped substrate, the user should enter as much data about the substrate as is known.*
3. *At a minimum, either the molecular weight (MW) or the theoretical oxygen demand (ThOD) is required.*
The stoichiometry for Cl, S, and P is required when these elements are present in the lumped substrate.
4. *If the stoichiometry for C, H, O, and N is known, these are preferred to the MW, ThOD, TON, and TOC values.*

Selection Of Energy Reactions

For each substrate defined, the possible energy reactions which can occur are also selected. The aerobic and anoxic reactions are assumed. The anaerobic reaction is not included, unless it is specifically selected.

When the anaerobic reaction is selected for one of the substrates, acetic acid is automatically added as another substrate in the model, if it has not already been defined as a substrate. This is because acetic acid is one of the byproducts of the anaerobic reaction.

Microorganism Definition

For each type of bioreaction, the microorganisms which are present in the process are represented as two species, an "active biomass" and an "inert biomass." A default characterization of these species has been made, and the species data are available in the Public Databank in the following species:

Heterotrophic

Active Biomass BUGHACTIV

Insert Biomass BUGHINERT

Autotrophic

Active Biomass BUGAACTIV

Insert Biomass BUGAINERT

In the BioEntry facility, these species are automatically assigned when the user requests the default microorganisms. This is done pressing the Enter Key on the blank field which prompts for the Biomass name.

Properties

The BioEntry facility allows the user to view the thermodynamic properties of the biological microorganisms selected, and override them as necessary. This is achieved by using the Action Key and selecting the Properties facility. The Properties facility displays the existing properties of interest for the species, and allows override values to be used (which are in effect for this model only). The Properties facility also allows the user to enter thermodynamic properties for a lumped substrate.

Creation Of The Model Definition

Once the BioEntry data have been entered for each of the bioreactions, the user returns to the usual method for building a Chemistry Model. This is achieved by selecting the Exit option from the bioreactions selection menu. The inflow list is automatically updated to include other chemicals which will be needed in the model to support biotreatment (e.g., O₂, N₂, NH₃). The phase selection for a biotreatment model will include the vapor and solids phases.

Bioreaction Constants

After the Model Definition is created, the Model Definition can be modified to include values for any of the bioreaction constants. This is achieved by using the Action Key and selecting the Sections facility, and then choosing the Bioreactions option. The bioreaction constants are organized by the type of biochemical reaction, and within type, by individual and composite substrates. Constants include:

Heterotrophic Bioreaction Rate Constants

RATE	maximum specific growth rate constant, 1/hr
YIELD	true growth yield, g cells/g subst ThOD removed
DECAY	decay rate constant, 1/hr
KSUB	substrate half-saturation constant, g subst/m ³
KOXY	O ₂ half-saturation constant, g O ₂ /m ³
KNO3	NO ₃ -N half-saturation constant, g NO ₃ -N/m ³
KCO3	carbonate half-saturation constant, g CO ₃ /m ³
ANOF	anoxic growth factor
ANAF	anaerobic growth factor
KINH	self-inhibition coefficient, g subst/m ³

Autotrophic Bioreaction Rate Constants

RATE	maximum specific growth rate constant, 1/hr
YIELD	true growth yield, g cells/g N removed
DECAY	decay rate constant, 1/hr
KNH4	NH3-N half-saturation constant, g NH3-N/m3
KOXY	O2 half-saturation constant, g O2/m3

All values for the Bioreaction constants initially are set to default values. *With multiple substrates, composite substrate Bioreaction constants can be set.* The range and defaults for the constants are:

Heterotrophic Constants: Ranges and Defaults

	Recommended Range	Default
RATE	0.1 to 0.8	0.3
YIELD	0.3 to 0.5	0.35
DECAY	0.002 to 0.08	0.02
KSUB	5 to 180	15
KOXY		0.15
KNO3		0.4
KCO3		0.1
ANOF	0.6 to 1.0	0.8
ANAF		0.05
KINF		Infinity

Individual substrate bioreaction constants can be set, either in the Model Definition Sections, or in the Bioreactor Block itself, overriding the composite substrate constants.

Autotrophic Constants: Ranges and Defaults

	Recommended Range	Default
RATE	0.006 to 0.035	0.027
YIELD		0.17
DECAY		0.005
KOXY		1.0
KNH4	0.6 to 3.6	1.0

The constants can also be set in the Bioreactor during Process Build. In this way, constants can be tuned to individual reactors.

Temperature Dependent Rate, Decay Functions

Rather than use the RATE or DECAY constant to describe a biochemical reaction, the temperature dependency of these values can be expressed in the Arrhenius form.

$$\text{Rate} = A \exp(-u/RT)$$

To use this form for the growth or decay rate, select the Sections facility, choose Bioreactions, and then select the Temperature Function of interest. To use the temperature dependency functions, at least the reference rate must be entered. Defaults are accepted for u (the Arrhenius Temperature Characteristic), and the reference and maximum temperatures.

VG INHIB

Generation of The Model Solver

Once any specific bioreaction constants for the model have been entered, the user returns to the usual method to finish building a Chemistry Model. This is achieved by selecting the Exit option from the bioreactions selection menu, and then continuing to build the Model Solver. Once the Model Solver is built, the user can view the biotreatment equations which have been generated. This is achieved by selecting the Bioreactions option in the Model Solver Report menu.

Ion Exchange

OLI can model ion exchange, a sorption phenomenon in which an ion in solution replaces an ion on a charged medium. An example of this would be Zn^{+} replacing Na^{+} on a polystyrene sulfonate resin. This facility can be used to simulate various treatment and purification processes including water softening and desalting.

IonxEntry

IonxEntry is an ESP facility which allows easy entry of ion exchange species, media, and sorption interaction parameters into OLI Databanks and OLI Chemistry Models. Specification of at least one medium and the ions of interest are required. IonxEntry builds the necessary species names and prompts for the necessary thermodynamic data and sorption interaction parameters.

Private Databanks

All ion exchange data, media data, species data, and interactions, must exist in either the OLI PUBLIC Databank or in a private databank. IonxEntry automatically will create the necessary databank, handle much of the bookkeeping associated with private databanks, and will prompt the user for the required data as it is needed.

ACCESSING Ionxentry

IonxEntry is accessed through the AltEntry facility, located in Chemistry Models.

IonxEntry is organized into four parts:

- Ionx Medium
- Ions
- SOL Species
- SORPTION Interactions

Ion Exchange Medium

Ionx Medium is facility used to enter data about the ion exchange medium.

An ion exchange medium is described in terms of its charge and its capacity in meq/g. Capacities for a medium can be estimated from reference data about a similar type of medium.

Estimations or measurements of the density and heat capacity of the medium are also needed, since these are used in estimating the thermodynamic properties of the ion exchange species.

Media data is stored in a databank. It is entered either through IonxEntry in Chemistry Model or through the Material Codes Section of the Literature Chapter of the OLI Databook (reference **Chapter 3: Databook, Literature Chapter**).

Data needed includes:

Ion Exchange Media Data

CODE	DESCRIPTION	COMMENTS
------	-------------	----------

MATC	Material Code number	A unique integer assigned to the material
SYMB	Material Code name	A name to identify the material (e.g., PS4-polystyrene sulfonate 4% cross-linked)
CHAR	Charge	Either +1 or -1
MOLW	Molecular weight	MW = 1000/Capacity

Data Entry

A medium name is given. Either the media already exists as an OLI Material Code in an existing databank, or it will be a new medium. The polystyrene sulfonate resins have already been defined in the PUBLIC databank. Other media must be added by the user.

If the medium already exists, the data about the medium is displayed. Otherwise the user must enter the data. The software prompts for a unique material code number with the number 9001. Any number which is not already assigned in your private databanks is valid. OLI also assumes that the ion exchange will be a cation exchange, that is, that the medium is negatively charged. Anion exchange is supported by overriding the default charge on a new medium.

Up to 10 media can be supported in a single Chemistry Model.

Ion Exchange Ions

Once a medium is specified, the ions associated with the exchange are entered. IonxEntry uses the Template facility, which allows the user to select the ions from a list of possible ions.

Up to 10 ions can be selected for a single medium.

Ion Exchange Species

Both general information for ion exchange species (called SOL species) and their solid solution thermodynamic properties are required. The thermodynamic properties for ion exchange species include:

SOL Species Data

CODE	DESCRIPTION	COMMENTS
NAME	Species name	ion + medium + stoich coeff +SOL Examples: NAPS4SOL, ZNPS42SOL
MATC	Material Codes	ion material code, medium material code
STOI	Stoich coefs	ion stoich = 1; medium stoich = ABS ion charge
MOLW	Molecular Weight	MW of Medium * ABS ion charge + MW of ion
VREF	Reference State Volume	Species MW / Medium density in gm/ml
HREF	Ref. State Heat of Formation	HREF of the ion in cal/gm-K
CPREF	Ref. State Heat Capacity	MW of the species * heat capacity of Medium

Species data are stored in a databank. Data are entered through IonxEntry in Chemistry Model or through the Species Chapter of the OLI Databook

Sol Species Data Entry

IonxEntry generates a name for each of the ion exchange species which must be specified, given the list of ions and medium. The name is formed automatically:

SOL Species Name = ion name+medium name+ABS|ion charge|if> 1+SOL

Example:

NAPS4SOL = NA + PS4 + + SOL

If the species exists in the PUBLIC databank, the data is displayed. Otherwise, IonxEntry prompts for the thermodynamic properties of the species. Data is stored in a user specified databank.

All SOL species must be defined and stored in a user specified databank called a Private databank, if they do not already exist in OLI's databanks. IonxEntry prompts for the name of the private databank and creates it if necessary.

Sorption Interaction Parameters

Given ions A and B, and medium XX, by definition the ion exchange equation is:

reactants products

$A_{XXSOL} + B_{ION} = B_{XXSOL} + A_{ION}$

The data needed to support this reaction includes the coefficients of the Log K equation, and the A_{IJ} , A_{JI} , and D values for the Three-Constant Margules model which is used for the solid solution activity coefficients.

The Log K equation is:

$$\text{Log K prod/reac} = C1 + C2/T + C3*T + C4*T**2$$

where T = Temperature, in Kelvin

A Three-Constant Margules model is being used for OLI's solid solution activity coefficient model. For the Three-Constant Margules model, supplying the number of constants determines the rigor of the model.

<u># of</u> <u>Margules</u> <u>Constants</u>	<u>Rigor</u>
0	Ideal Solution (no interactions)
1	Regular Solution (A _{IJ} =A _{JI})
2	2 - term Margules
3	3 - term Margules

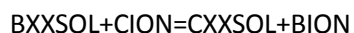
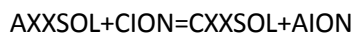
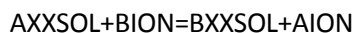
Regression is the most commonly used technique to determine the SORPTION interaction parameters. The data needed for regression is based on the nature of the experimental data available. OLI Customer Service can make recommendations on regression approaches, based on individual clients' data.

Sorption Data Entry

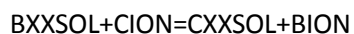
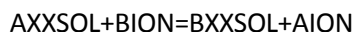
IonxEntry will determine all possible combinations of interactions between the SOL species in the model. Data can be entered for as many of these interactions as available. The minimum number of interactions for each medium which must be entered is one less than the number of ions (NION).

Reversing the Equation

OLI has a requirement that each equation in the SORPTION data section be written starting with a unique SOL species name. For example, given A, B, and C ions and XX medium, consider the following Equilibrium Equations:



The first and second equations both begin with the same species, AXXSOL. Reversing the second equation would produce this list:



The Reverse facility is used to reverse the equation. If the corresponding coefficients for the Log K equation are already entered, the Reverse facility will multiply each coefficient by -1. If the Margules constants are already entered, the AIJ and AJI terms will be switched.

Model Generation

Once IonxEntry is finished, inflows can be added to the SOL Species which were named for the model. The Chemistry model definition and the Model Solver can then be generated in the normal manner. (Reference beginning on page , for further detail).

A common error which is detected during the Chemistry Model definition step for ion exchange models involves the number of equilibrium equations which are found in the databank. It is the user's responsibility

first to include Sorption interactions for at least NION - 1 sets of interactions, and then to insure, via the Reverse facility if necessary, that each of these equations begins with a unique SOL species name.

The Exchange Section

During Chemistry Model definition, when SOL species are present, an EXCHANGE Section is included in the Model Definition to indicate ion exchange. The equations used in the EXCHANGE section are the same equations which are entered in the sorption data of IonxEntry.

These equations can be viewed by using the Sections facility, once a Model Definition is made.

Non-Electrolyte Model

As noted earlier, the user has the option of preparing a Non-Electrolyte model (Reference pg.). If required, the Non-Electrolyte Model Definition file can include a liquid phase and/or vapor phase reaction section. Equilibrium and/or kinetic type reactions can be specified for either, or both phases. This facility can be used to model nonaqueous liquid phase and vapor phase chemical systems. Specific examples of its application include rate-limited reactions for organic tower units and equilibrium reactions occurring in a waste gas incineration unit.

Non-Electrolyte Models containing kinetic type reactions are not supported for any of the PC Versions. Please contact OLI for details.

Chemical Kinetics

Chemical Reaction Kinetics and Equilibria can be included in the Non-Electrolyte Chemistry Model for either the vapor phase or the organic liquid phase, or for both phases.

Edit

In order to include chemical reaction kinetics, the Non-Electrolyte Model Definition file must first be created, and then edited using the Action Key and choosing the Sections facility, followed by Non-Electrolyte model title on the succeeding screen. From the list displayed, either the Liquid Phase Kinetics or the Vapor Phase Kinetics heading is chosen, followed by Continue on the succeeding screen.

The Non-Electrolyte Model Definition file (extension MD2), created only for a Non-Electrolyte model, is then displayed and can be edited, as required, by inserting the relevant data at the end of the file listing. (Note: The data insertion must be prior to the final END statement displayed on the file).

Data Entry

A maximum of fifty (kinetics and/or equilibrium) reactions may be specified for each phase. Each phase is considered as a separate system. The reaction section for a phase is structured into four easily defined parts, namely:

- **Reaction Keyword**
- **Reaction Stoichiometry**
- **Reaction Kinetics (multiple entries if required)**
- **Reaction End**

Each part will now be considered in more detail.

Reaction Keyword

Initially, the kinetics or equilibrium section of the Model Definition file must be identified with a header record. This requirement is achieved by entering either of the phase keyword expressions, LIQUID REACTION or VAPOR REACTION, just before the END record at the end of the file listing. The chemical reaction stoichiometry to be considered can then be added on the succeeding line.

Only one reaction keyword is used for each Chemical Kinetics or Equilibrium section.

Reaction Stoichiometry

In this part of the reaction section, the reaction to be considered is given a sequential number. This is for identification purposes and is based on the number of reaction sections to be defined. Hence, the first reaction is given the identification number 1, the second 2, etc.

Following the reaction identification number, the reaction species stoichiometric values are defined. Reaction products are identified with a positive value, and the reactants with a negative value. The stoichiometric values must be displayed in the same order as the compounds listed in the Model Definition files species inflow list. If a particular species does not take part in the reaction, it should be given a stoichiometric value of zero. (An example of this syntax is on page).

Reaction Kinetics

In this part of the reaction section the chemical reaction kinetics or equilibrium are defined. This is achieved by the user defining a rate expression which is then made equivalent to the keyword EXTNT for reaction kinetics or RESIDU for chemical equilibrium.

In order to comply with the required FORTRAN syntax, all data in this section must be entered starting with the seventh column of the Model Definition file.

Variables

The user defined kinetics or equilibrium reaction may include user-defined variables. These variables must be defined prior to the rate expression and must be identified with a name 2-6 characters long.

The variable can be defined using a combination of user defined variables and reserved software variables, a list of which is included in Appendix II for reference.

An additional requirement is that any numbers expressed in the definition equations must be expressed as real values.

Rate Expression

Once the user-defined variables have been specified, the rate expression can be defined. Normally, this is identified with the character "R" followed by a sequential identification number shown in brackets. However, the expression can be identified with other characters provided that they do not appear on the reserved variable list. More than one rate expression can be defined per reaction.

Finally, the defined rate expression is made equivalent to the keyword EXTNT for reaction kinetics or RESIDU for chemical equilibrium, and usually has the format:

EXTNT (reaction identification number) = user defined rate expression

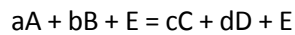
Reaction End

In order to complete the reaction the keyword END must be entered. This must be placed on the succeeding line to the keyword define (i.e., EXTNT) rate expression.

Example

This description on how to define a Non-Electrolyte chemical reaction can be summarized with a simple example.

Consider the following liquid phase kinetic reaction:



where a, b, c, d are stoichiometric coefficients

A, B are reactant species

C, D are product species

E is an inert species

The reaction rate expression is:

$$\text{rate} = x * (\text{Flow of species B})^{3/2} - y * (\text{Flow of species C})$$

where $x = 960.7 \exp(220/\text{Temperature } ^\circ\text{K})$

$$y = 350 \exp(110/\text{Temperature } ^\circ\text{K})$$

If the chemical species have been entered into the model file in the following order:

A, B, E, C, D

then the reaction section of the model file will be of the form:

LIQUID REACTION

1 -a -b 0 c d

$$x = 960.7 * (\text{EXP}^{**}(220/T))$$

$$y = 350 * (\text{EXP}^{**}(110/T))$$

$$R(1) = x * (\text{FCOMP}(2))^{**3/2}$$

$$R(2) = y * \text{FCOMP}(4)$$

$$\text{EXTNT}(1) = R(1) - R(2)$$

END

A specific example can be referenced in “**A Guide to Using ESP, Chapter 3: Process Applications**”.

Selected Species Chemical Equilibrium

Chemical Equilibria can be included in the Non-Electrolyte Chemistry Model for either the vapor phase or the organic liquid phase, or for both phases.

Edit

In order to include chemical equilibrium reactions, the Non-Electrolyte Model Definition file must first be created and then modified using Action Key and choosing the Sections facility, followed by the Non-Electrolyte Model option on the succeeding screen. From the resultant list displayed, either the Liquid Phase Equilibrium or the Vapor Phase Equilibrium heading is chosen, followed by Continue.

Data Entry

This provides a listing of the chemistry model species inflows and the user simply has to choose which species are to be considered in equilibrium with one another.

Once this is performed, the Model Solver and related files can be generated to complete the Chemistry Model.

Using Additional Databanks

In certain cases the user may need to build a Chemistry Model containing species that are not included in the OLI PUBLIC Databank and/or other databanks distributed with the OLI Software. In these situations the user will need to build an additional private databank for the species of interest (Reference the Databook section for further details). The OLI GEOCHEM Databank is also available to supplement the species in the OLI PUBLIC Databank.

Model Definition File

However, if an additional databank is used in a Chemistry Model, it must be named prior to the Model Definition file being created. Following the user specifying the species phases to be considered in the Chemistry Model (Reference , pg.), a message is displayed informing the user the Model Definition can now be created with an option to either Continue or Bypass this function.

Databook Specification

Prior to choosing the Continue option the user must use the Action Key and choose the Databook facility. The user is then prompted to name any additional databanks to be used in the Chemistry Model Definition.

On completion of naming the additional databanks to be used the user is returned to the Model Definition file prompt. The Continue option is then chosen and the Model Definition file created. (Note: During the program, a message appears stating that the program is reading from the additional as well as the PUBLIC Databank).

Guidelines

1. *When using a private databank, the user must insure the minimum data requirements are specified for the private databank species.* For further information on these requirements, reference the Databook section.
2. *When defining a new species, any pertinent equilibrium relationship must also be defined.* In order for the Chemistry Model to be successfully created the following relationship must be true for the Model Definition:

$$\begin{array}{l} \text{Total Number of} \\ \text{Equilibrium} \\ \text{relationships listed in} \\ \text{the Chemistry Model} \end{array} + \begin{array}{l} \text{Total number of material balance} \\ \text{groups exhibiting different} \\ \text{valence states in Model Inflow} \\ \text{list (e.g., IN)} \end{array} = \begin{array}{l} \text{Total Number of} \\ \text{species in Model} \\ \text{Species list (e.g., VAP,} \\ \text{AQ, ION, PPT, .vH2O)} \end{array}$$

3. *The user must also insure no two reaction relationships are defined with identically (i.e., same species and phase) first reactant species in the Model Definition.* This is due to the software recognizing individual reaction equations by its first reactant species stated. Therefore, every first reactant species listed in the Model Definition must be unique.

If such a problem occurs, it may simply be resolved by rearranging the order in which the reactant species are stated for one of the reactions.

Software Reserved Variables

Variable Name	Value	Units
T	temperature	Kelvins
PT	pressure	atmospheres
I	ionic strength	gmoles/kg H2O
PH	pH	--
-IN	inflows	gmoles
-AQ, -ION	aqueous soln molalities	gmoles/kg H2O
-PPT, -nH2O	precipitates and hydrates	gmoles
H2O	water in soln	gmoles
-SOL	solid soln molalities	gmoles/kg solid medium
Y-	vapor mole fractions	--
X-O	2nd liquid phase mole fractions	--
SOLMAS	solid medium mass (for cation exchange medium, based upon H-Solid molecular weight)	kg
LIQMAS	total aqueous liquid mass	grams
LIQMAS2	total organic phase mass	grams
LIQMOL	total aqueous liquid moles	gmoles
V	total vapor moles	gmoles
SOLMOL	total solid moles	gmoles
TOTO	total organic liquid moles	gmoles

ENTHALPY	total enthalpy	cal
ENTHAL	aqueous liquid phase enthalpy	cal
ENTHAL2	organic liquid phase enthalpy	cal
ENTHAV	vapor phase enthalpy	cal
ENTHAS	solid phases enthalpy	cal
ENTHAI	inert phases enthalpy	cal
DENLIQ	aqueous liquid molar density	gmoles in soln/liter
DENLIQ2	organic liquid molar density	gmoles in soln/liter
DENMAS	aqueous liquid density	grams/liter
DENMAS2	organic liquid density	grams/liter
ZCOMP	vapor compressibility	--
VOL	total volume	liters
VOLLIQ	aqueous liquid volume	liters
VOLLIQ2	organic liquid volume	liters
VOLVAP	vapor volume	liters
VOLSOL	solid volume	liters
RATE-	kinetics rate of reaction	gmoles/hr
EXT-	kinetics extent of reaction	gmoles
BRATES-	rate of reaction - biosynthesis	gmoles/liter-hr
BEXTS-	extent of reaction - biosynthesis	gmoles
BRATEE-	rate of reaction - bioenergy	gmoles/liter-hr
BEXTE-	extent of reaction - bioenergy	gmoles
BRATED-	rate of reaction - biodecay	gmoles/liter-hr
BEXTD-	extent of reaction - biodecay	gmoles
TSTEP	kinetics time step	hr
REACVOL	bioreactor volume	liters
A-AQ, A-ION	loge (aq phase activity coef)	--

Note: When the electrolyte model contains a nonaqueous phase then A-AQ is the activity, rather than activity coefficient

AH2O	loge (aq phase H2O activity)	--
A-AQO	loge (org phase activity)	--
AY-	loge (vapor phase fugacity coef)	--
K-	loge (equilibrium K-values)	--
L-AQ, L-ION	loge (aq phase molalities)	--

Software Reserved Variables - Non-Electrolyte

Variable Name	Value	Units
R(i)	Rate	lbmole
EXTNT(i)	Reaction	lbmole
RESIDU(i)	Chemical equilibrium keyword	-
TK	Temperature Kelvin	
FVOL	Liquid volumetric flow ft ³ /hr	
FCOMP(j)	Liquid flowrate of component j from column stage	lbmole/hr
DENS	Overall liquid density on column stage	lb/ft ³
HOLDT	liquid holdup time on the column stage	hrs

Notes:

- 1) Subscript i refers to the reaction identification number
- 2) Mathematical expressions (e.g., EXP, LOG10, etc.) may also be used as part of the rate definition

Chapter 5. ToolKit

Overview

The OLI Engine contains these software components:

OLI Databook, a component which enables a user to review and add to an extensive thermodynamic library containing over 10,000 chemical species;

OLI ToolKit, a component which provides access to several important facilities including the **WaterAnalyzer** (defining feed streams based upon a water analysis), **OLI Express** (convenient stream studies), and **ProChem** (which contains ElectroChem for carrying out certain single-stream studies not supported by OLI Express).

This OLI ToolKit, the OLI Databook, the extensive OLI Databanks and the numerical solver code form the **OLI Engine**, which is the name given to those components of the system which are common to all OLI's software packages.

OLI Software Packages

The OLI Engine is available in each of these packages:

Environmental Simulation Program, or ESP, which features **ESP Process**, a component to simulate environmental and conventional processes and also provides, via ProChem, DynaChem for dynamic process simulation.

Corrosion Simulation Program, or CSP, which features **CSP Corrosion**, a component to predict the corrosive properties of solutions via stability diagrams.

Scope Of OLI Toolkit

The OLI ToolKit facility allows the user to simulate single-stream systems as well as to prepare simulation feed-streams which need to be specified on an ionic, rather than a molecular basis. The ToolKit is organized into three main areas:

- **WaterAnalyzer**
- **OLI Express**
- **ProChem**

WaterAnalyzer¹⁰

The WaterAnalyzer is a facility which allows the user to specify aqueous streams for which only ionic species concentrations are known. Such a specification is usually the result of a laboratory analysis of a water sample. Such samples are taken from groundwater, wastewaters, etc.

With the WaterAnalyzer such an aqueous stream can be adjusted for inconsistencies and, eventually, converted to a molecular stream.

¹⁰ The WaterAnalyzer is largely replaced by the OL Studio Lab Analysis feature. It is recommended that the Lab Analysis feature be used instead of the WaterAnalyzer.

The molecular stream composition which is developed by the WaterAnalyzer can then be used in the Process Blocks facility of ESP Process Build.

This is an important facility because ESP Process flowsheet feed streams must be on a molecular basis.

In order to use the WaterAnalyzer, special considerations need to be given when defining both the Chemistry Model and the water samples.

OLI Express

OLI Express allows the user to study individual streams. These studies can involve single calculations such as a bubble point. This is done with a facility called **ScratchPad**. Alternatively, these studies can involve a series of parametric calculations. This is done with a facility called **Survey**.

ProChem/Electrochem

The ProChem program allows for greater flexibility in single-stream studies than OLI Express. Specifically, the user can fix and free multiple input and calculation variables, rather than the single independent variable supported by surveys in OLI Express.

The procedures for using the ProChem/ElectroChem program is documented in the ProChem User Manual, available separately through OLI.

WaterAnalyzer Chemistry Model

Prior to using the WaterAnalyzer of OLI ToolKit, the user must first generate a Lab Entry Chemistry Model for the system on an ionic species basis. Generally, when using OLI Software, a conventional Chemistry Model is generated from a molecular species inflow listing for the system.

The procedures detailed for the Lab Entry Chemistry Model are written assuming the user is familiar with conventional Chemistry Model generation. The procedures for building a conventional Chemistry Model can be referenced in the Chemistry Models section.

Model Inflows

After the Chemistry Model file is named, inflow species can be defined. This is achieved by using the Action Key and selecting the Lab Entry facility. The Lab Entry facility organizes species in the Chemistry Model into three groups: cations and anions, dissolved gases, and neutrals/organics.

Lab Databank

On selecting the Lab Entry facility, the software automatically accesses OLI's LAB Databank. The LAB Databank contains ionic species information for approximately 150 ions, any of which can be named in the WaterAnalyzer Chemistry Model.

CATIONS AND ANIONS

The user is first prompted to define the ionic species to be considered in the Chemistry Model. To insure that the ion is available and named correctly it is advised that the user makes a selection from a displayed list of all available ions. This is done by using the Action Key and selecting the Template facility (Note: H⁺ and OH⁻ ions are automatically included by the software, in the Chemistry Model).

On selecting the Template facility for cations and anions, a list is displayed showing all the ionic species contained in the LAB Databank. From this list, the user simply selects the species of interest using the Arrow Keys and the <Space Bar>.

Dissolved Gases

After selecting the ionic species to be considered and pressing the Enter Key, the user is prompted to define any dissolved gases for the system.

It is advised that the Template Facility again be used, and a selection made from the displayed listing of the common dissolved gases using the Arrow Keys and the <Space Bar>.

Neutrals And Organics

After selecting the dissolved gases to be considered and pressing the Enter Key, the user is prompted to define any neutral species to be considered, including any organics in the model.

At present only three neutral species are displayed using the Template facility. However the user can select any species to be included by using the Search facility. A search of any databank can only be performed by Empirical Formula (Reference **Chapter 3: Databook** for further details). If a species of interest does not appear in the OLI supplied databanks, it can be defined in a private databank and used in a Lab Entry Chemistry Model.

Inflows Listing

After selecting the neutral and organic species to be considered and pressing the Enter Key, the complete user defined species inflow listing is displayed.

The ions selected by the user are displayed in OLI recognized format and are suffixed with the letter Z. This species data entry is unique to Lab Entry Chemistry Models and cannot be used in any other type of model definition.

Also, if the user has specified the Sodium ion species to be considered, the software automatically includes the NaOH species in the inflow listing.

Model Generation

The Chemistry Model definition and Model Solver are generated in the normal manner

The user must insure an Electrolyte Model is generated but can select the respective phases to be considered (Note: Both the solid and vapor phases are initially shown for consideration but can be deleted). ***The Non-Electrolyte Model should not be selected for a Lab Entry Chemistry Model.***

During the model definition creation, neutral molecular inflows are included into the file for all the ionic species (i.e., Z species) defined by the user.

Solids Inclusion

From the ionic species inflow listing, the software selects all possible solid species that could exist during the Chemistry Model Definition File creation.

This list may have many species as both anhydrous and hydrated solid species are predicted. Because of this, the solid phases will not be predicted from within the WaterAnalyzer. Instead, all solids will be evaluated for scaling tendency only.

However, the user can selectively include solids species of interest. This is achieved by using the Action Key and selecting the Solids facility. From the list displayed the user can choose the solid to be included by highlighting the species of interest using the Arrow Keys and pressing the letter "S" character key.

Scaling Tendency

Scaling tendency is a measure of the probability for a solid to form. The higher the scaling value the more probable the solid species exists in the Chemistry Model being defined. Values greater than 1.0 are likely to form.

On completing the initial WaterAnalyzer evaluation the user should check the solid species scaling tendencies predicted.

Guidelines

It is advised that a WaterAnalyzer evaluation is initially performed using a "scaling tendency only" Chemistry Model. The software predicts the probability of each solid species forming during the evaluation. If any values are greater than one, it is strongly recommended that the user include these species in the Chemistry Model, and then re-evaluate the water samples that have been entered.

Water Sample Specification

On completing the Lab Entry Chemistry Model generation, the user should use the Sample Manager function to define water samples.

The WaterAnalyzer is a facility which stores, organizes, and performs calculations on water samples. The user can enter the concentrations for a sample, measured qualities, and the conditions of the sample (e.g., pH and density). The stream composition can then be reconciled to an electrically neutral state (i.e., total positive charge equals total negative charge) by the addition of a charged species. The pH reconciliation allows the user to specify the stream pH value and meet this value by the addition of an acid or base chemical.

Up to 100 samples can be stored in one WaterAnalyzer block. Samples can be combined into composite samples using weighted averaging.

Water Sample Identification

Sample Name

Initially, the sample to be analyzed must be identified with a name. This is achieved by highlighting New Sample on the display and pressing the Enter Key. The sample can then be identified with a name between 1-12 characters in length. Blanks are not allowed in sample names.

Sample Date

On pressing the Enter Key, the user is prompted to specify the sample date. This requirement is optional, but is helpful when identifying multiple samples to be analyzed. If no date is entered, the date the sample is entered into the WaterAnalyzer is used.

Water Sample Data

After specifying the sample date, the user can define the aqueous ionic species composition for the sample. A variety of information can be defined, including species compositions, specific

qualities of the sample (i.e., total dissolved solids, biological oxygen demand, etc.), sample conditions (i.e., temperature, pressure, etc.) and sample pH value.

Each will now be considered in detail.

Sample Concentration

In this section the user can specify concentrations for species previously defined in the Chemistry Model Definition inflow listing.

Cations/Anions

The ionic species concentrations for the Lab Entry Chemistry Model inflows are defined in this section. The concentrations can be expressed in mg/l, ppm, or molal.

The required units are selected using the Action Key and selecting the Units facility.

Dissolved Gases

The concentrations of dissolved gases for any dissolved gases included in the Chemistry Model inflow list are defined in this section. The concentrations can be expressed in mg/l, ppm or molal. The required units are selected by using the Action Key and selecting the Units facility.

Neutrals/Organics

The neutral and organic species concentrations for any compounds included in the Chemistry Model inflow listing are defined in this section. The concentrations can be expressed in mg/l, ppm or molalities.

The required units are selected using the Units Facility.

Guidelines

1. *It is advised that the user select the required concentration units prior to entering any values. Once selected these units should be used for the complete species concentration specification.*
2. *If the units are changed during a specification, the concentration data previously defined by the user will not be converted to the selected units.*

Sample Qualities

This section allows the user to define specific qualities about the water sample to be analyzed. These values are not currently used in the calculations, however they are stored with the other information about the sample and are available for reference. Some of the qualities which can be defined are Biochemical Oxygen Demand, Oil and Grease content and water hardness.

Method

On selecting the Qualities sample data type and pressing the Enter Key, the Action Key should be used and the Template facility chosen from the succeeding screen. A list of the sample qualities that can be defined is displayed from which a selection can be made. The qualities include:

<u>Quality Keyword</u>	<u>Quality Description</u>
BOD5	5 Day biochemical oxygen demand
BODU	Ultimate biochemical oxygen demand
COD	Chemical oxygen demand
TOC	Total organic carbon
TOX	Total organic halogen
TSS	Total suspended solids
TDS	Total dissolved solids
FEC	Fecal coliforms
OIL	Oil and Grease
MBAS	MBAS surfactants
HARD	Hardness (expressed as CaCO ₃ concentration)
ALK	Total alkalinity (expressed as CaCO ₃ concentration)
MET	Metals (digestion)
MINA	Free mineral acidity
COND	Electrical conductivity
....	New quality

Specific qualities are selected by highlighting the item of interest by using the Arrow Keys and pressing the <Space Bar>.

Data Entry

On selecting the sample qualities to be considered and pressing the Enter Key, the user can define the respective quality concentrations. These values currently must be expressed in items of mg/l of sample.

New Quality

This option allows the user to define sample qualities not contained in the WaterAnalyzer.

Sample Conditions

This section allows the user to define the temperature and pressure conditions for which the water sample is to be evaluated. The volumetric amount of the sample, as well as the sample density, may also be specified.

The units used to express these parameters can be changed using the Action Key and selecting the Units facility.

If the user does not access this section, the software assumes default settings for these parameters. The values assumed are:

Temperature	25°C
Pressure	1 atm
Sample amount	1m ³
Density	1000 g/l

Sample pH

This section allows the user to define the pH of the sample measured in the laboratory.

The software determines the pH of the sample based on the user defined species concentrations. Acid or base chemicals (e.g., NaOH or HCl) can then added in order to reconcile the sample pH with the user specified value.

The reconciliation facilities of the WaterAnalyzer are described in the next chapter of this section.

Guidelines

1. *It is advisable to perform an initial water analysis evaluation without specifying a pH value for the sample. This evaluation will determine the sample pH based on the ionic species concentrations defined for the sample.*
2. *If the pH value is different from the sample measured value, the user can re-access the pH section of the sample data and reconcile the sample pH by the addition of an acid or base chemical.*

WaterAnalyzer Functions

Once the water sample data is fully specified by the user, its composition can be reconciled for electroneutrality and to a specified pH value. The sample can also be used in simple, single point, equilibrium calculations via ScratchPad. Finally, an equivalent OLI Stream, suitable for inclusion in all ESP Process Blocks and in CSP Corrosion, can be created.

Electroneutrality Reconciliation

Electroneutrality is achieved when the total positive charge of the sample equals the total negative charge. A sample must be reconciled for electroneutrality before any other calculations can be

performed on it. This is achieved by the addition of appropriately charged ions to the sample until electroneutrality is obtained.

Method

To perform an electroneutrality reconciliation, the user should re-access the sample composition data previously specified (i.e., cations/anions, dissolved gases or organic neutrals), use the Action Key, and select the Reconcile facility.

A menu is displayed showing the reconciliation methods. The sample composition can be reconciled either by Dominant Ion, Proration, User Choice, or Na⁺/Cl⁻ methods. Once the sample is electrically neutral, an isothermal equilibrium calculation is done on the sample.

A description of the methods for reconciling electroneutrality follows.

Dominant Ion Method

This method first predicts the overall charge of the sample specified by converting the concentrations to milliequivalents/kg H₂O. The procedure then adds the respective dominant (i.e., highest concentration) cation or anion from the user supplied species data until an electrically neutral sample composition is obtained.

For example, if a sample is defined with an overall positive charge, the most dominant anion specified by the user will be added until the electrically neutral composition is obtained.

Proration Method

This method first predicts the overall charge of the sample specified by converting the concentrations to milliequivalents/kg H₂O. The procedure then increases either all the respective anion or cation concentrations until the electrically neutral composition is obtained.

The ionic concentrations of the individual species are increased by the same relative percentage in order to obtain sample neutrality.

User Choice Method

This option allows the user to select both a cation and anion on which the electroneutrality balance is to be performed.

As with the other methods, the User Choice method first determines the overall charge of the sample using milliequivalents. Then one of the respective user specified ions is added until an electrically neutral sample composition is obtained.

The ions selected must exist in the Chemistry Model inflow list, and be defined with an OLI recognized name suffixed with the keyword ION (i.e., MGION, ACETATEION)

Na⁺,CL⁻ METHOD

When using this option, the software automatically adds sodium or chloride ions to the sample analysis until an electrically neutral composition is obtained.

Make Up Ion Method

When this option is invoked, the user enters a single ion which is then adjusted, up or down, as needed, to produce an electrically neutral solution.

A negative concentration for the make up ion (< 0.0) is not permitted.

Sample Reports

On completing an electroneutrality balance evaluation on a water sample, the user can access five types of result summaries. The results available are:

- **Calc Summary**
- **Electroneutrality**
- **Ionic Composition**
- **Ionic Phases**
- **Scaling Tendency**

Method

The appropriate report is accessed simply by exercising the View Action following reconciliation and highlighting the report type of interest using the Arrow Keys and then pressing the Enter Key. The home screen will contain the Electroneutrality Report immediately following reconciliation.

Electroneutrality Report

This report summarizes the electroneutrality balancing results for the water sample.

The report details the electroneutrality balancing method used and the amount of ionic species added to the sample to achieve electroneutrality. The succeeding pages of the report summarize the species distribution based on the user defined composition data.

Calc Summary

This report summarizes the overall physical and chemical properties of the sample. The information available includes:

Sample temperature

Sample pressure

Vapor Fraction

Total Molar Flowrate

Total enthalpy

Total Weight Flowrate

Sample pH

Scaling Tendency Report

This report summarizes the scaling tendencies of solid species that could exist in the water sample analysis.

Scaling tendencies are a measure of how close to saturation a solid species is in the sample at the specified conditions. The higher the scaling tendency value the closer the solid species is to burning. Scaling tendencies greater than 1.0 indicate that the formation of solids is likely to occur for those species at the system conditions.

The report lists the scaling tendencies from the highest to the lowest value. Species equilibrium constants, and temperature range limitations (when available) are also detailed in the report.

Guidelines

1. *It is recommended that an initial WaterAnalyzer evaluation be performed using a "scaling tendency only" Chemistry Model (Reference pg. for further details).*
2. *After this initial evaluation is completed, the user should view the Scaling Tendency Report to determine the likelihood of any solid species existing in the sample. If any species scaling tendencies are greater than 1.0, it is recommended that the Lab Entry Chemistry Model be updated to include these solids in the Model Definition.*

Re-Evaluation

To perform a re-evaluation, the user should return to the Chemistry Model and include the solid species of interest

The Model Solver files should then be re-generated and a water analysis evaluation repeated.

Ionic Composition Report

This report summarizes the full speciation of the sample without distinguishing physical phases.

Ionic Phases Report

This report summarizes the full speciation of the sample distinguishing physical phases.

It is advisable to perform an electroneutrality reconciliation on the sample prior to reconciling pH. This allows the user to set the calculated pH of the sample based on the user defined composition data, and analyze the composition of the sample further.

pH Reconciliation

To perform a pH reconciliation, the user should re-access the sample pH data (Reference on pg.), and specify the required value as a Measured pH.

The Action Key should then be used and the Reconcile pH facility chosen. This displays a menu showing the two reconcile methods available. The sample pH can be reconciled either by using a user specified inflow or by the addition of NaOH or HCl.

Select Titrant

On selecting the Choose Inflows option a message is displayed informing the user the specified pH is either greater or less than the Calculated pH determined during the electroneutrality balance. The message also informs the user that a suitable acid or base chemical needs to be added to the sample in order to meet the defined Measured pH value.

On selecting Continue and pressing the Enter Key, a list of molecular species contained within the sample is displayed. This molecular species list is determined from the electroneutrality balance using user supplied ionic species composition data.

Depending on whether the sample pH is to be raised or lowered, the user selects an appropriate acid or base species from the list using the Arrow Keys and the Enter Key.

Naoh, Hcl

This option simply allows either sodium hydroxide or hydrochloric acid to be added to the sample.

On selecting this option a message is displayed informing the user the specified Measured pH value is either greater or less than the Calculated pH value and that the appropriate acid (i.e., HCl) or base (i.e., NaOH) will be used.

On selecting Continue and pressing the Enter Key, the pH reconciliation is performed.

Guess

If the user Measured pH value differs greatly from the Calculated Value, it is advisable for the user to supply an initial estimate of the amount of acid or base chemical to be added. A guess should also be used if the calculations are not converging.

This is achieved prior to selecting Continue on the message display and pressing the Enter Key. The Action Key should be used and the Guess facility selected. An initial estimate of the reagent amount can then be specified in units of g/moles.

Report

The report options following a pH reconciliation are precisely the same as described in on page of this section. However, after the sample pH is reconciled, the amount of acid or base chemical used for the reconciliation is also displayed in the Calc Summary Report. Also, the home screen will contain this report following calculation.

WaterAnalyzer Scratchpad

The WaterAnalyzer ScratchPad facility allows the user to perform simple equilibrium calculations on a water sample. The sample reconciled composition should be used as a basis for these calculations.

Method

In order to use the ScratchPad facility, the first screen of the WaterAnalyzer should be displayed. This screen identifies the water samples specified within the WaterAnalyzer by name and date and also confirms if the sample compositions have been reconciled for electroneutrality and pH.

Initially, the sample of interest should be highlighted using the Arrow Keys. The Action Key should then be used and the ScratchPad facility chosen.

A menu is displayed showing the eight types of equilibrium calculations which can be performed.

Guidelines

It is advisable to perform a standard reconciliation of the water sample prior to performing an adiabatic calculation. This allows the user to determine the total enthalpy of the sample should allow the user to set a reasonable target enthalpy.

Bubble Point - This facility allows the user to determine either the bubble point temperature for a particular sample pressure or predict the sample pressure for a sample bubble point temperature of interest.

The user simply must define either the bubble point temperature or pressure and the sample vapor fraction to be considered. An initial vapor fraction value of 1×10^{-6} (to depict the onset of vapor) is displayed but can be changed by the user if required. (Note: At present, the sample pressure for a specified bubble point temperature cannot be determined).

Dew Point - This facility allows the user to determine either the dew point temperature for a particular sample pressure or, predict the sample pressure for a sample dew point temperature of interest. *The software can only determine a dew point if all species in the sample are volatile. This severely limits this facility with respect to the WaterAnalyzer.*

The user simply must define either the dew point temperature or pressure and the sample water fraction to be considered. An initial water fraction value of 0.001 (to depict the onset of liquid) is displayed but can be changed by the user if required.

Surveys

The WaterAnalyzer Survey facility allows the user to perform parametric equilibrium calculations on a water sample. The sample reconciled composition should be used as a basis for these calculations.

OLI Streams

This is an important facility as it allows the user to convert a WaterAnalyzer reconciled ionic stream into an OLI molecular species stream for use in other OLI software components (e.g., OLI Express, ESP Process).

Method

In order to perform this conversion, the first screen of the WaterAnalyzer should be displayed. This screen identifies the water samples within the WaterAnalyzer by name and date and also confirms if the sample compositions have been reconciled for electroneutrality and pH.

To use this function, the Action Key should be used and the OLI Streams facility chosen.

On selecting the new OLI Stream option from the succeeding screen, the user can specify the OLI stream name for the sample. On pressing the Enter Key, a list of samples within the WaterAnalyzer is displayed from which a selection can be made. The sample of interest is selected using the Arrow Keys and the Enter Key.

Stream Conversion

On selecting the sample of interest, the ionic species distribution is converted to molecular species inflows.

A message is displayed informing the user if the stream conversion has been successful, with the option to save the OLI stream composition.

Send

If the user saves the OLI Stream data, there is a facility available to export this stream to either an existing or new process defined within the Process Build Section of ESP.

However, in this release of ESP, we recommend retrieving a WaterAnalyzer stream from ESP Process Build, rather than using the Send facility. This is achieved by using the File facility located on the stream definition screen. Select the Open menu option, and then give the name of a WaterAnalyzer file. OLI will locate the stream and import it.

Guidelines

1. *A water sample ionic species composition should only be converted to an OLI Stream if it has previously been reconciled for electroneutrality.*

2. *Lab Entry Chemistry Models are specific to the WaterAnalyzer facility and cannot be used in conventional processes defined in the Process Blocks section of ESP Process Build.* Hence, if a water sample is converted to an OLI Stream and sent to an ESP process, the user must insure the Chemistry Model for this process include all the molecular species defined in the OLI Stream as Model Inflows.

The system will prompt the user for any missing inflows in the new process. The user then should re-make the Chemistry Model, so that the process can be simulated.

WaterAnalyzer Action Key Facilities

In addition to those facilities already described in the previous WaterAnalyzer chapters of this section, others are available to the user to perform various operations. Some functions are screen specific (i.e., only available on certain screens). Access to the required facility is obtained via the Action Key and selecting the appropriate facility.

The available facilities are described by screen option heading below. The options are presented alphabetically.

Calculate pH

This facility is available to allow the user to evaluate the water sample pH at specified isothermal conditions. On selecting this facility the user must define the sample temperature and pressure of interest for which the sample pH is to be evaluated.

File

This facility allows movement of information from screen to disk. Three options are available:

Save - This option transfers the user defined data to disk. The data is stored under the sample name and is given the file extension BIN.

Cancel - This option allows the user to cancel (i.e., delete) a water sample definition.

Exit - This option allows the user to exit from the respective sample data. When using this option, the data is automatically saved.

Output

When available, this facility will allow the user to send results to the screen, printer, or disk file.

Reconcile

This facility is previously described in on page and on page of this section respectively. However, if this facility is selected for an existing water sample reconciled for electroneutrality and/or pH, three options become available:

Reconcile Summary This option produces a report summarizing the reconcile method previously used and the amount of species added to obtain electroneutrality and/or desired pH.

Re-reconcile This option allows the user to re-reconcile the water sample data using a different method to that previously selected. On selecting this option, the various reconcile methods available for use are displayed. (Reference on page and on page of this chapter for further information)

Reports

This facility is currently not available but it will allow access to result reports for existing reconciled water samples.

Samples

The WaterAnalyzer Samples facility allows the user to delete, copy or re-name sample information. The user can also sort existing sample data and make composite samples from existing sample defined data.

Method

In order to use the Samples facility, the first screen of the WaterAnalyzer should be displayed. This screen identifies the water samples specified within the WaterAnalyzer by name and date and also confirms if the sample compositions have been reconciled for electroneutrality and pH.

To use this function, the Action Key should be used and the Samples facility chosen.

A menu is displayed showing the three types of options available to the user.

Sample Utility

This option allows the user to delete, rename, and copy sample data. The copy facility is important as it allows the user to reproduce composition information for multiple samples which may have many identical concentrations. Individual species concentrations can then be amended accordingly

When this facility is selected, a list is displayed showing the names of the defined sample data. The available actions are performed by entering the appropriate action character identifier adjacent to the respective sample name. The actions are identified with one of the following characters:

<u>Action</u>	<u>Character</u>
Delete	D
Rename	R
Copy	C
Keep	K

When using the Rename and Copy actions, the user is prompted to enter a new name for the sample.

Make Composite

This function allows the user to make composite sample compositions based on weighted averages of previously defined sample information. Composites can only be made from samples which are either not reconciled or completely reconciled for electroneutrality and/or pH (i.e., a composite cannot be made from two samples only one of which has been reconciled).

Method

Initially, the composite sample is named, then a selection is made from the succeeding list of the samples to be included in the composite using the Arrow Keys and the <Space Bar>.

The weighted fractions of the individual samples included in the composite are then defined by the user. A screen is then displayed prompting the user to specify if the composite sample composition is to be based upon Input or Reconciled values.

The Input option should be chosen for composites consisting of samples previously not reconciled. The Reconciled option is used for composites consisting of samples previously reconciled for electroneutrality and/or pH.

The composite sample composition is then determined and can be displayed by selecting the View Log option on the succeeding screen. If required, the user can save the composite sample information.

It must be noted that a composite sample is not reconciled for electroneutrality and/or pH even if it consists of previously reconciled samples. The reconciliation is achieved by following the procedures detailed in on page of this section.

Sample Sort

This function allows the user to sort samples either by name or by date.

If the samples are sorted by name, the list is sorted into alphabetical order. The sort by date option lists samples in chronological order with the most recent sample entry listed first.

Studies

This facility is currently not available. However, it will allow the user to perform various case studies on water samples (e.g., dilution study, pH curve, etc.)

Template

This facility allows the user to define additional inflow chemical species to those previously defined in the respective Chemistry Model for the sample. The species to be included are selected from a displayed listing using the Arrow Keys and the <Space Bar>.

If this facility is used, the chosen species are automatically included in the Chemistry Model Inflow list. However the user must return to the Chemistry Model section of ESP Process in order to re-create the Chemistry Model Definition and re-generate the Model Solver respectively.

Units

This facility allows the user to change the units in which lab analysis data is being defined. Initially, the data is expressed in mg/l, but the values can also be displayed in ppm or molality.

If the display units are changed during a lab analysis specification, any previously defined concentration *data is not converted to the newly selected display units*. The concentrations will be converted, if necessary, during any calculations.

OLI Express Overview

OLI Express offers the user a powerful option for carrying out various alternative studies with respect to single process streams. There are four distinct steps to OLI Express as follows:

- **Stream Definition**
- **Chemistry Model**
- **Express Calculate**
- **Summary**

Stream Definition

Stream Definition provides a means of identifying the specific stream to be studied. A stream can be either stand alone, or be from an existing process flowsheet.

Chemistry Model

Chemistry Model provides a means of linking the stream with a specific Chemistry Model.

Express Calculate

Express Calculate provides a means of carrying out the desired study.

Summary

Reports to disk or printer are located in this step.

OLI Express Stream Definition

OLI Express offers the user a powerful system for carrying out various alternative studies with respect to single process streams. The first step is to identify the stream to be studied. There are two distinct types of streams:

- **ESP Process Stream** - This is a stream which is contained within an existing ESP Process.
- **OLI Express Stream** - This is a stream which is standalone; defined within OLI Express specifically for the purpose of stream study. Such a stream can either already exist or can be a new stream.

Upon entering **OLI Express**, the user will find, in the following order lines offering access to **New Stream**, **OLI Defined Stream**, and if pre-existent, a list of previously defined OLI Express Streams.

OLI Defined Stream

Upon entering OLI Express, the user can select a line labeled **OLI Defined Stream**. Selecting this line then leads to a screen which lists all pre-existent ESP Process flowsheets. Selecting a specific process then leads to a menu of the individual streams of that process. Only those streams which are feeds or which have been previously calculated will appear for selection. Upon selecting a stream, the process of stream definition is complete.

Once an OLI Defined stream is defined in OLI Express, a copy is made and that copy becomes an OLI Express Stream.

OLI Express Stream

The OLI Express Stream is a standalone stream which is either pre-existent or must be defined.

Pre-Existing Stream

All such standalone streams will appear for selection upon entry to OLI Express. The user need only select the desired stream and the stream definition is complete.

New Stream

Upon selecting the New Stream option, the user must enter the stream name. This is the only action required at this stage of the process.

OLI Express Chemistry Model

Every calculation carried out in OLI must be associated with a Chemistry Model. If a stream is pre-existent either from an existing process or an existing standalone stream study, the Chemistry Model is automatically connected to the selected stream and the user can move on to Express Calculate. If a New Stream is selected, the user must then define a Chemistry Model.

The procedure for defining a Chemistry Model is precisely that which is described in **Chapter 4: Chemistry Models** in this manual.

OLI Express Calculate

All ESP Express calculations are done based upon the definition of a single stream. This definition consists of a specific temperature, pressure, total flowrate, and relative amounts of the remaining components.

If the stream was pre-existent, entry into **Express Calculate** will cause the full description, including the stream values (e.g., temperature to appear. If the stream is a **New Stream**, then the value fields will be blank and must be filled out prior to any calculations.

Alternative **Units** may be selected via the Action Key. The Action Key also provides access to **File**, **Normalize**, and **Inflows** which have been described earlier.

There are two principal **Express Calculate** options:

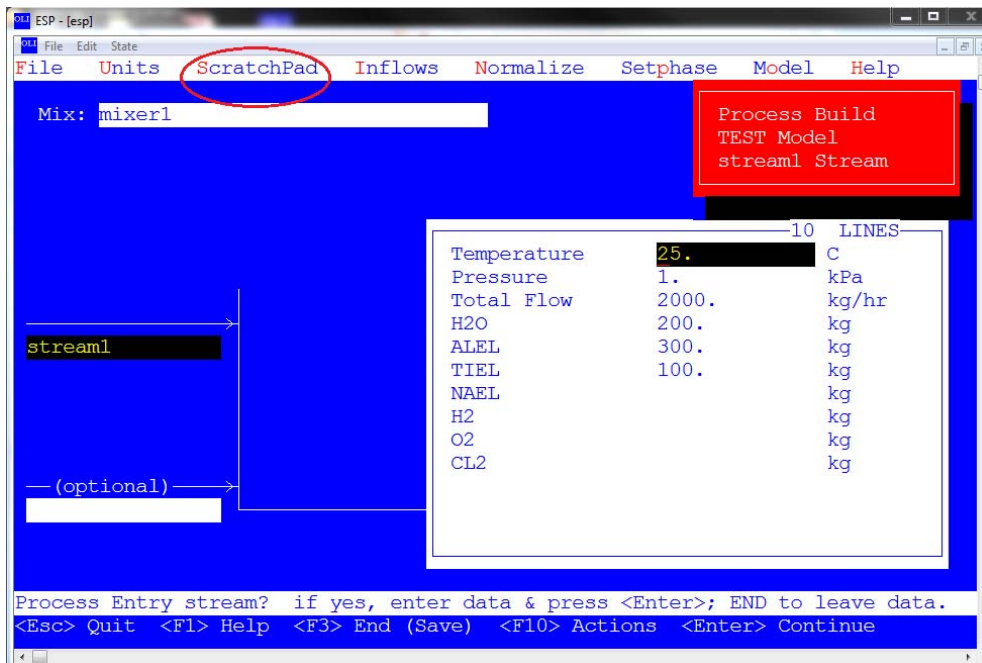
- **ScratchPad**
- **Surveys**

ScratchPad

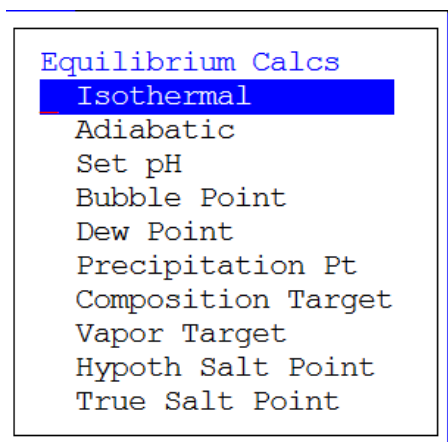
This option allows the user to perform individual point calculations on a single stream. At present, there are eight equilibrium calculations available.

Method

To use the ScratchPad facility, the user needs to define the temperature, pressure, flow rate and composition of the stream of interest. The user simply presses the Action Key to select the ScratchPad facility, and chooses the option of interest using the Arrow Keys and the Enter Key. The ScratchPad facility is also for streams that have been calculated during Process Analysis.



The options available are:



Isothermal - This option allows the user to perform an isothermal equilibrium calculation. The user simply has to supply the temperature and pressure of interest.

Adiabatic - This option allows the user to perform an adiabatic evaluation of the stream. The user simply has to supply the adiabatic pressure and enthalpy of interest.

Set pH - This option allows the user to set the pH of the stream by varying the composition of a particular component which the user selects from a list of the species defined in the Chemistry Model.

Bubble Point - This option allows the user to determine either the bubble point temperature for a particular stream pressure or predict the stream pressure for a sample bubble point temperature of interest.

The user defines the bubble point temperature or pressure. A vapor fraction value of 1×10^{-6} (to depict the onset of vapor) is used.

Dew Point - This option allows the user to determine either the dew point temperature for a particular stream pressure or, predict the stream pressure for a sample dew point temperature of interest. *The software can only determine a dewpoint if all species in the stream are volatile.*

The user simply must define either the dew point temperature or pressure to be considered. A water fraction value of 0.001 (to depict the onset of liquid) is used by the software.

Precipitation Point - This option allows the user to adjust the composition of one component until another specified component begins to precipitate. Both components are selected from a list of species in the Chemistry Model.

Composition Target - This option allows the user to specify the concentration of species (ionic or molecular) in the phase of interest by varying the amount of an inflow.

Vapor Target - This allows the amount of vapor to be defined in four ways:

T, Vapor Amount

P, Vapor Amount

T, Vapor Fraction

P, Vapor Fraction

The ScratchPad offers several Actions including:

Units	Customary selection of units
Guess	User guess for an Inflow to be varied to achieve the ScratchPad calculation option (e.g., vary CO2ION to achieve target pH value)
Last Result	To view the last scratch pad calculation.
Flows	To peruse the current flowrates of the components

Guidelines

1. *It is advisable to perform an Isothermal calculation of the stream prior to performing an adiabatic calculation.* This allows the user to determine the total enthalpy of the stream and should allow the user to set a reasonable target enthalpy.

Surveys

This option allows the user to perform a variety of alternative multiple case studies to explore the parametric sensitivity of streams to changes in specified variables.

Upon entering **Surveys**, the user is offered a default pH Survey with default Titrants (NaOH, HCl) without additional Reagents and over the range of pH=2.0-12.0 in increments of 1.0.

The user can either accept this Survey or involve an alternative as in the change section of the menus on the home screen.

Type Of Survey

To change the type of survey, the user simply chooses this option from the survey pull-down menu. This leads to several choices of parametric study including:

pH-	The Default
Temperature -	Self-explanatory
Pressure -	Self Explanatory
Composition-	Any single inflow may be selected from a list of all inflows.

Titration

This option can be chosen only for a pH survey. The default is NaOH and HCL. The user may select any other acid and base which is an inflow in the Chemistry Model. Otherwise, the Chemistry Model must be expanded.

Reagents

This option allows the user to add specific amounts of up to three reagents to the stream being studied. These increments to the base stream will not be made a permanent part of the stream but, rather, added for the specific study.

The user must select reagents based upon the Chemistry Model, otherwise the user should return to Chemistry Model, and augment the model for the desired reagents.

Range

Every survey must calculate the stream over a Range of conditions defined by the starting and ending values and increment for the Survey parameter. Up to three ranges can be entered. The values entered must all be numeric except for the symbol 'pH' which denotes the natural pH of the stream: This value can be used to define either the start or the end values.

Calculate

To calculate the Survey, the user chooses this option from the Survey pull-down menu.

Show Results

Once the Survey has been calculated, the user has two formats by which to display results, namely tubular and graphical. In both cases the user has full choice of the content (variables) of these tables and plots.

Following the computation, the selection of **Show Results** from the pull-down menu of Survey provides a screen containing a default table. For example, in a pH Survey, the table will contain pH and the two titrants.

The Action Bar provides access to the complete set of services as described below.

Units

The customary facility for varying units.

Plot

The facility to produce a graphical plot of the current tabulated values. The first column in the table is assumed to be the x-axis variable. All others are assumed to be y-axis variables.

Variables

This option is the heart of **Show Results**. The current **X** and **Y** variables are shown. The user may select any **X** variable and up to 5 **Y** variables by toggling to any of the six fields. If the field is blank (or made blank by the user), the use of the Enter key will lead to a menu offering a broad range of variables from which to select. The choices are:

CHOICE TYPE OF VARIABLE SELECTION

Dominant Species a facility to view and select species in order of their predominance.

Element a menu of all material balanced groups (e.g. S(-2), Cl(-1), etc.)

Inflow a menu of all Inflow variable names.

Species a menu of all true species, including aqueous complexes.

User Define a facility where the user can define new variables which are functions of existing variables.

Mass/Density a menu of various phase, mass, and density variables.

Miscellaneous a menu of several other variables including temperature and pressure.

Plot Options

This facility allows the user to modify various plot settings. This includes:

OPTION DESCRIPTION

Scaling log or conventional scale for each axis. The user can also override the automatic scaling for each axis.

Labels default labels, titles, legends, borders, and axis.

Device SCREEN, HP-GL, PostScript, etc.

Device Port COM1, LPT1, etc.

Color default colors for the curve.

Plot Type
scatter allows the user to override the "tag" curve and create either a line or a plot.

Plot Size a scaling factor applied to the entire plot (.5<fact<1.)

Chapter 6. Process Modeling

Overview

This section Process Modeling is a detailed guide to the use of unit operations, called Process Blocks, and for the use of the steady-state flowsheet simulation facilities provided via ESP Process. The document is divided into chapters which contains a brief overview and detailed specifications of the ESP Process Blocks. Limitations and guidelines for individuals units are included.

By selecting pertinent unit operations, a complete process can be modeled by combining individual process blocks into a process flowsheet to describe the process. The process is then simulated using the OLI's chemistry solver.

ESP Process Description

The Environmental Simulation Program (ESP), taken together with the OLI Engine, contains three main components: OLI Databook; a component to review and add to an extensive thermodynamic library for over 10,000 different chemical species, ESP Process; a component to simulate environmental processes, and OLI ToolKit, a component which provides access to several important facilities including OLI Express (convenient stream studies), OLI WaterAnalyzer (feed stream definition based upon a water analysis), and ProChem (dynamic simulation, data regression, etc.)

ESP Process has four stages (modes) for working with a process:

- **Chemistry Model**
- **Process Build**
- **Process Analysis**
- **Summary**

The **Chemistry Model** takes the user specification of the molecular species for a process along with any supplementary information which might be required and builds the necessary Model Definition and Model Solver support files needed for the specified chemistry (Reference the **Chemistry Models** section of the **OLI Engine Manual**).

In **Process Build**, individual process blocks are selected by the user and linked together, if required, to form a flowsheet. User data for the unit are specified, modified and displayed. Stream names are used to connect the individual units. This document considers this function in more detail.

Process Analysis allows for the execution, review, and analysis of a process simulation using the information defined in Chemistry Model and Process Build.

Summary combines the results of Process Analysis into one single file with a number of output and export options. At present, process analysis results can be exported to the disk or the printer. Data can be expressed on an ionic or molecular basis in a variety of units.

Process Build

ESP Process Build allows the user to access ESP Process Blocks. ESP Process Blocks allows the user to access various process unit operations which, in turn, leads to the definition of a flowsheet.

This section considers ESP Process Blocks.

Guidelines

It is recommended that a preliminary Chemistry Model be made for the Process before any process blocks are chosen. This document has been written on the basis that the reader understands how to generate a Chemistry Model

Scope of ESP Process Blocks

To aid the user in simulating processes involving complex chemistries, a variety of process blocks, or units are available. These process blocks can be used to model individual process unit operations (e.g., mixer, reactor) or can be linked together, by the naming of process streams, in order to define a complete plant operation.

Process Block Conventions

A process containing a number of individual process blocks is developed under one common Process Build case name, with reference to a particular Chemistry Model. The Chemistry Model defines all molecular species inflows and any special phenomena required by the case.

Process Build Menu

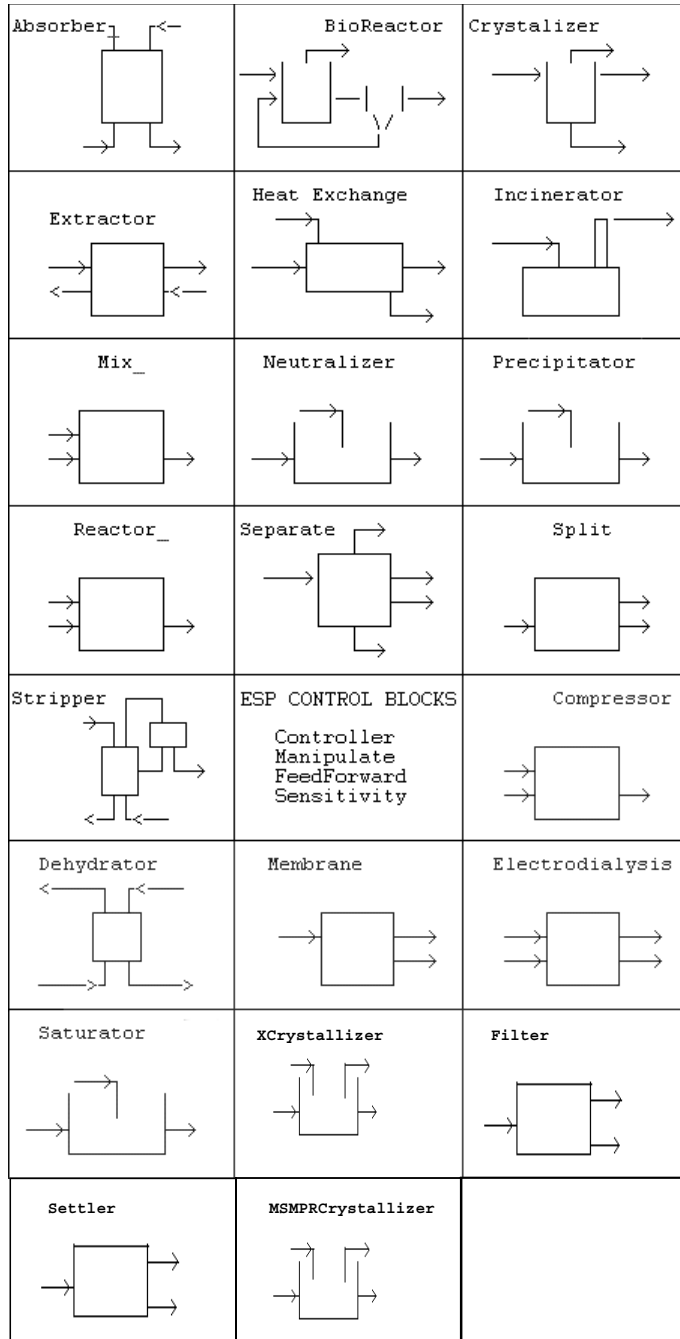
The choice of process blocks available to the user are displayed on an easy-to-read menu. The required process block is chosen by using the Arrow Keys and the Enter Key. Currently, there are 16 process units accessible

The choice of the required process block is made from this Process Build menu, and then stream information and operating parameters for that unit are entered via user friendly screens. Process units are linked together by continuity of stream names flowing from one block to another (i.e., the exit flow name from one unit can be given to the inlet flow to a succeeding process block).

For a specific example on how to link process blocks together refer to Getting Started section, the Tour of ESP Process.

Individual Process Block Data

Stream names and parameter data must be entered for each individual process block. In addition, when a feed to an individual process block is also a feed to the process, the stream inflow state must also be supplied.



Customizing Units

Before specifying any process block operating conditions, it is recommended that the user check the default units setting. Units can be customized to SI, METRIC, ENGLISH, or USER units (Reference: Controller pg. 310).

Process Stream Definition

Process Blocks are linked together through the use of streams. Streams are either process entry streams, process product streams, or intermediate streams.

All process entry streams must be defined by entering Temperature, Pressure, and Composition of the components in the stream.

Intermediate and process product streams are defined by simply naming them. The Model Solver will calculate the conditions and composition of these streams.

A special case stream is a tear stream used in cases with recycle. This stream is named as an intermediate stream during Process Build. During Process Analysis, the stream is named as a tear stream by using the Action Key and selecting the Recycle facility. Reference Process Analysis, Additional Facilities, Recycle on page 330 for details.

Stream Names

Stream names can be up to 16 characters in length. Additionally, names are case sensitive and spaces in the name are allowed. For intermediate streams and process product streams, the stream name is the only input required.

Process Entry Stream Definition

To define a process entry stream all that is required is the temperature, pressure, flowrate, and composition of the components. Additional facilities are available to aid the user in defining a stream, these are ScratchPad, Normalize, Inflows, and SetPhase.

Scratchpad

The ScratchPad facility allows the user to perform simple equilibrium calculations on a process stream. At present, there are eight equilibrium calculations available.

Method

To use the ScratchPad facility, the user needs to define the temperature, pressure, flow rate and composition of the stream of interest. The user simply presses the Action Key to select the ScratchPad facility, and chooses the option of interest using the Arrow Keys and the Enter Key. The ScratchPad facility is also for streams that have been calculated during Process Analysis.

The options available are:

Isothermal - This option allows the user to perform an isothermal equilibrium calculation. The user simply has to supply the temperature and pressure of interest.

Adiabatic - This option allows the user to perform an adiabatic evaluation of the stream. The user simply has to supply the adiabatic pressure and enthalpy of interest.

Set pH - This option allows the user to set the pH of the stream by varying the composition of a particular component which the user selects from a list of the species defined in the Chemistry Model.

Bubble Point - This option allows the user to determine either the bubble point temperature for a particular stream pressure or predict the stream pressure for a sample bubble point temperature of interest.

The user defines the bubble point temperature or pressure. A vapor fraction value of 1×10^{-6} (to depict the onset of vapor) is used.

Dew Point - This option allows the user to determine either the dew point temperature for a particular stream pressure or, predict the stream pressure for a sample dew point temperature of interest. *The software can only determine a dew point if all species in the stream are volatile.*

The user simply must define either the dew point temperature or pressure to be considered. A water fraction value of 0.001 (to depict the onset of liquid) is used by the software.

Precipitation Point - This option allows the user to adjust the composition of one component until another specified component begins to precipitate. Both components are selected from a list of species in the Chemistry Model.

Composition Target - This option allows the user to specify the concentration of species (ionic or molecular) in the phase of interest by varying the amount of an inflow.

Vapor Target - This allows the amount of vapor to be defined in four ways:

T, Vapor Amount

P, Vapor Amount

T, Vapor Fraction

P, Vapor Fraction

The ScratchPad offers several Actions including:

Units	Customary selection of units
Guess	User guess for an Inflow to be varied to achieve the ScratchPad calculation option (e.g., vary CO ₂ ION to achieve target pH value)
Last Result	To view the last scratch pad calculation.
Flows	To peruse the current flowrates of the components

Guidelines

1. *It is advisable to perform an Isothermal calculation of the stream prior to performing an adiabatic calculation.* This allows the user to determine the total enthalpy of the stream and should allow the user to set a reasonable target enthalpy.

Inflows

This facility allows the Chemistry Model to be extended, at stream, definition, to include additional or alternative chemical components.

Normalize

This facility allows stream composition and flow to be normalized in two ways, by:

Component - Keeping the ratio of the components constant, adjust the component fractions to sum to 1.0.

Total Flow - Given the compositions, sum them and arrive at the total flow of the stream.

Setphase

Eight special conditions can be named for a stream. They include:

No special condition

AQ Liq & Solid Only

Vapor Only

No Vapor

No Organic

Organic Liq Only

Organic & Vapor

Solid Only

Guidelines

Care should be taken when setting any special conditions on a stream, since the Model Solver will assume these conditions to be true, even if they are not.

Process Block Summary Descriptions

The current blocks available in ESP Process are:

Absorber, a Multi-stage or Environmental Process Block which allows species in a vapor feed to be absorbed by a countercurrent liquid stream. Conventional column capabilities are included, such as: multiple feeds, condenser, reboiler, side streams, pumparounds, specification/control and stage efficiencies.

Bioreactor, a Biotreatment Process Block which models all heterotrophic and autotrophic reactions, including nitrification and denitrification, for an activated sludge bioreactor (CSTR).

Clarifier, a Biotreatment Process Block which determines the flow separation among effluent, wastage, and recycle streams in a biotreatment process.

Compressor, a Conventional Process Block for carrying out an isentropic or polytropic pressure change on a product stream comprised of one or more feed streams.

Controller, an ESP Control Block which allows a specification on a stream to be met by varying a block parameter on an upstream unit.

Crystallizer, an Environmental Process Block which determines the block operating conditions necessary to achieve a specified solids concentration.

Dehydrator, an Environmental Process Block which predicts the removal of water from a vapor or nonaqueous liquid stream using a CaCl₂ packed bed.

Electrodialysis, an Environmental Process Block which predicts the distribution (separation) of salts from a single feed when an electrical current is applied with the result that both dilute and concentrated product streams are created.

Electrolyzer, is a chlorine – sodium chloride electrolyzer cell. Commonly referred to as a Chlor-Alkali cell. A current is applied to separate chlorine from a sodium chloride brine.

Extractor, a Multi-stage or Environmental Process Block which allows organic species in an aqueous feed to be extracted by a countercurrent solvent stream.

FeedForward, an ESP Control Block which sets a stream specification or a block parameter by transferring a block parameter from an upstream unit. The transferred value can be adjusted by addition, subtraction, multiplication or division.

Filter, is a crystallization process unit which models the separation of the liquid portion of the feed stream from the solid portion of the feed stream. The liquid and solid are divided between the filtrate and solids outlet streams based upon specified fractions or flows.

Heat Exchanger, a Conventional Process Block which allows energy to be transferred between a process and a utility stream, or allows energy to be added to, or removed from, a single stream. A utility stream may also be a stream from another process block.

Heat Transfer, is a control block that allows the heat duty (from an isothermal calculation) to be transferred to an adiabatic block.

Incinerator, an Environmental process block which allows non-electrolyte species to be incinerated either adiabatically or isothermally. A maximum of 7 inlet streams are allowed to the block.

Manipulate, an ESP Control Block which allows a multiplicative factor to be applied to the total flow of a stream, or to the components of a stream.

Membrane, an Environmental Process Block which predicts the distribution (separation) of salts from a single feed and, optional permeate feed, when a membrane is applied with the result that both a permeate (dilute) and concentrated product streams are created.

Mix, a Conventional Process Block which allows mixing of several (2-7) inlet streams adiabatically. The resulting phase separation and speciation within each phase is also evaluated.

MSMPRCrystallizer, a block that models a mixed-suspension, mixed-product-removal (MSMPR) crystallizer. The user specifies nucleation and growth rate constants, crystallizer volume, shape factors and crystal density. The block computes the saturation and supersaturation concentrations of the solid species of interest, the nucleation rate, the growth rate, the crystal size distribution and mass distribution, and the zeroth through fifth moments. Regression of experimental data is also available through the OLI ToolKit.

Neutralizer, an Environmental Process Block which allows a specified stream to be neutralized, either by adiabatically mixing the inlet streams, or by varying one of the inlet streams to meet a specified pH point.

Precipitator, an Environmental Process Block which determines the flow of precipitation reagent necessary to achieve a specified aqueous concentration. Currently, the concentration is specified based upon actual species in solution. Future versions will allow specification of concentration on an elemental or on a total dissolved solids (TDS) basis.

Reactor, an Environmental Process Block which determines the phase separation and intraphase speciation for a Chemistry Model including both equilibrium and user-defined rate-limited reactions (i.e., bioreactions, kinetics, redox reactions). Between 1-7 inlet streams are mixed and considered as a single feed. There are three types of reactors currently supported. They are:

Aqueous - This reactor is used to simulate electrolyte chemical reaction systems.

Nonaqueous - This reactor is used to simulate non-electrolyte chemical reaction systems.

Bioreactor - This reactor is used to simulate an electrolyte chemical system in which a bioreaction occurs.

Saturator, an Environmental or Conventional Process Block which determines how much a given feed stream is needed to saturate a product stream.

Sensitivity, an ESP Control Block which varies selected block parameters in a process, and reports on selected, monitored stream variables.

Separator, a Conventional Process Block which allows up to 7 inlets to be separated into distinct physical phases. Suspended solids, entrained liquid, dissolved vapor and dissolved liquid can be specified. An equilibrium will be performed adiabatically.

Settler, a crystallization process unit which models the separation of the liquid portion of the feed stream from the solid portion of the feed stream. The liquid and solid are divided between the filtrate and solids outlet streams based upon specified fractions or flows. The solid may be split as a total solid or, differentially, split by individual solid species.

Split, a Conventional Process Block which allows a stream to be split into required outlet flow fractions or specified flowrate for one of the streams. There are two types of splits currently supported. They are:

Flow Split - This split allows a single inlet stream to be divided into (2-7) outlet streams, all with the same temperature, pressure and relative species content.

Component Split - This type of split allows between 1-7 inlet stream to be divided into 2 outlet streams, one of which contains the required species component fractions.

Stripper, a Multi-stage Environmental or Conventional Process Block, allowing species in a liquid feed to be removed by a countercurrent vapor stream. Conventional column capabilities are included, such as: multiple feeds, condenser, reboiler, side streams, pumparounds, specification/control and stage efficiencies.

Xcrystallizer, a crystallization process unit which models the mass and energy balance of a simple crystallizer. The crystallizer may be a cooling type, evaporation and vacuum type, a dilution and reactive type, or a combined type. One feed stream is required and a feed addition stream is optional. The vapor outlet stream is also optional. The liquid outlet stream is a slurry, containing both liquid and solid.

Logical Block Divisions

The process blocks can be divided into five main groups, namely:

- **Conventional**
- **Multi-stage**
- **Environmental**
- **Biotreatment**
- **ESP Control**
- **Crystallization**

As implied in the brief descriptions above, certain blocks (e.g., membrane) can actually be utilized for both Environmental and Conventional applications. Each group of blocks is considered separately in this section.

Conventional Process Blocks

This section contains detailed specification requirements for conventional process blocks available in ESP. Conventional process blocks are those which simulate physical plant operations. Generally, these operations include effluent mixing and separation. The process blocks, also called units, that are detailed in this chapter are:

- **Mix**
- **Flow Split**
- **Component Split**
- **Separator**
- **Heat Exchanger**
- **Compressor**

The specific unit is chosen from a display of all available units by using the Arrow Keys and Enter Key.

Additional specification facilities are available using the Action Key and are detailed for each individual unit.

Mix Unit



This is a conventional process block which allows the mixing of up to 7 feed streams by one of several types of equilibrium calculations. The resulting phase separation and speciation within each phase is computed.

Data Requirement

The unit's stream inflows and exit flow must all be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one feed streams and the respective temperature, pressure, flow and composition must be defined by the user or as a product stream from another Process Block.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The type of equilibrium calculation which will be performed on the inflow stream(s) can then be selected. Choices include:

<u>Type of Calc</u>	<u>Specification Choices</u>
Adiabatic	P, with enthalpy at conditions
Isothermal	P, T
Bubble Point	P or T
Dew Point	P or T
Vapor Target	P or T, Vapor Amount or V/F

All specifications of pressure can be made by specifying either a pressure loss across the Mix unit or by specifying the exit stream pressure.

If the Parameter facility is not used, a zero pressure drop across the unit is assumed, and the streams will be mixed adiabatically.

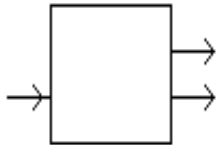
Unit Configuration

This facility allows the user to add or delete extra feed streams to the unit and is accessed via the Action Key and then by selecting the Config facility. An additional five inlet streams may be defined if required.

Guidelines

1. *When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.*

Flow Split Unit



This is a conventional process unit which allows a single inlet to be divided into a maximum of 7 outlet streams, all with the same temperature, pressure and relative species content.

Data Requirement

The unit's stream inflow and exit flows must all be given distinct names, so that they can be linked to other process units, if required.

One feed stream, and a minimum of two exit streams must be defined by the user. The inlet stream temperature, pressure, flow and composition data must be defined or be a product stream from another Process Block. Additionally, the split outlet stream fractions or flows must be defined.

Unit Parameters

The stream outlet fractions are defined using the Action Key and then by selecting the Parameters facility. The outlet fractions may be defined on one of a variety of bases, (e.g., mole fractions, flow, etc.) which are then automatically normalized by the software such that the sum of the outlet fractions is equal to 1.

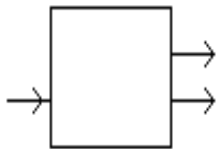
Unit Configuration

This facility allows the user to add or delete extra outlet streams from the unit and is accessed via the Action Key and then selecting the Config facility. An additional five exit streams may be defined if required.

Guidelines

When additional streams are to be added, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Component Split Unit



This is a conventional process unit which allows up to a maximum of 7 inlet streams to be divided into two exit streams, one of which contains user defined species component fractions.

Data Requirement

A minimum of one feed stream and two exit streams must be defined. The inlet stream temperature, pressure, flow and composition data must be defined by the user or as a product stream from another Process Block. The top exit stream from the unit is the stream for which the required species component fractions are specified.

Unit Parameters

The stream outlet fractions are defined using the Action Key and then by selecting the Parameters facility. The species fractions may be specified on either a mole fraction or flow basis, (e.g., mole fractions, flow, etc.) which are then automatically normalized such that the sum of the exit species mole fractions is equal to 1.

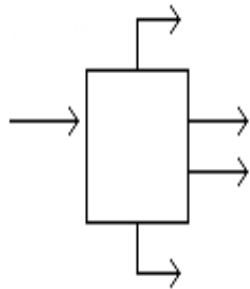
Unit Configuration

This facility allows the user to add or delete extra inlet streams to the unit and is accessed via the Action Key and then selecting the Config facility. An additional six feeds may be defined if required.

Guidelines

When additional streams are to be added, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Separate Unit



This is a process unit which allows up to 7 inlet streams to be separated into distinct physical phases. Outlet conditions including suspended solids, entrained liquid, dissolved vapor and dissolved liquid concentrations can be specified.

Data Requirements

A minimum of one feed and an aqueous exit stream must be defined. The feed stream must be defined by the user or be a product stream from another Process Block. Phases which would exist at outlet conditions but are unnamed, are added to the aqueous stream. Both streams must be named and the inlet temperature, pressure, flow and composition must be specified.

Units Parameters

Concentration limits can be defined for phase distribution among the outlet streams and is achieved via the Action Key and then by selecting the Parameters facility. These phase distributions include:

<u>Distribution</u>	<u>Stream</u>
Suspended solids	Liquid* outlet stream
Entrained liquid concentration	Vapor outlet stream
Dissolved liquid	Solid outlet stream
Dissolved vapor	Liquid* outlet stream
Dissolved aqueous phase	Organic outlet stream
Dissolved organic phase	Aqueous outlet stream

* The liquid outlet is the combined aqueous and organic outlet streams.

When the specified limits are exceeded for a particular phase distribution, the surplus quantity remains in its respective phase outlet stream.

Conversely, when one specified phase distribution requires all of the phase, the specification is satisfied, and that phase is eliminated. For example, if the amount specified for the dissolved vapor in the liquid is greater than the amount of vapor present, then all of the vapor is put in the liquid outlet, and the vapor outlet is set to zero.

If two specified phase distributions cannot be met, the error condition is raised.

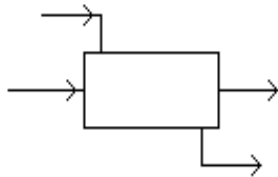
Unit Configuration

This facility allows the user to add or delete extra inlet streams to the unit and is accessed via the Action Key and then by selecting the Config facility. An additional six feeds may be defined if required.

Guidelines

When additional streams are to be added to the unit the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Heat Exchanger Unit



This is a conventional process unit which allows energy to be added to, or removed from, a single stream, or transferred between a process stream and a utility stream.

Data Requirement

A minimum of one inlet, and corresponding exit stream must be named for the unit. Optionally, when simulating heat transfer between two streams, the utility inlet and outlet flows must also be identified. The inlet stream(s) temperature, pressure, flows and composition data must also be defined by the user. Additionally, the unit operating conditions must be specified.

Unit Parameters

The unit operating conditions are specified via the Action Key and then by selecting the Parameters facility. Three options are available for defining the process exit stream requirements: the required exit flow temperature, the change in stream temperature, or the heating duty of the process unit may be specified.

For systems in which a utility stream is defined, the option is also available to specify the utility stream outlet temperature, change in temperature, or flowrate.

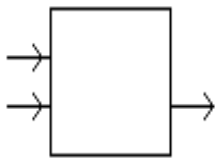
For definitions in which the utility stream exit temperature, or change in temperature, is specified, the utility stream flowrate is automatically modified. The initial user-defined value is changed in order to meet the required temperature operating requirements. Conversely, if the utility stream flowrate is defined its respective exit temperature is determined in order to comply with the process stream duty requirements.

Flow geometry can be either co-current or counter-current, and a minimum temperature approach can be specified.

Guidelines

1. *Additional inlet streams cannot be defined for this unit.*
2. *Process streams from other process units can be used as the utility stream if required. However, for this type of operation only the outlet temperature can be specified by the user.*

Compressor Unit



This is a conventional process block which allows the compression of 1-7 feed streams into a single product stream. The compression can be carried out on either an isentropic or polytropic basis. The resulting phase separation and speciation within each phase is computed.

Data Requirement

The unit’s stream inflows and exit flow must be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one feed stream, together with its conditions must be defined by the user or said stream must be a product stream from another process block.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The parameters available are as follows

Parameter	Value	Comment
Compressor/Turbine type	isentropic or polytropic	Must provide
Outlet Pressure	User	Must provide
Isentropic Efficiency	User (0.0 to 1.0)	Default = 0.72

Mechanical Efficiency	User (0.0 to 1.0)	Default = 1.0
Polytropic Efficiency	User (0.0 to 1.0)	Default = 0.72

Unit Configuration

This facility allows the user to add or delete extra feed streams to the unit and is accessed via the Action Key and then selecting the Config facility. An additional six inlet streams may be defined if required.

Guidelines

When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Multi-Stage Process Blocks

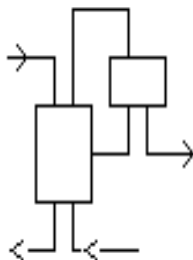
This section contains detailed specification requirements for multi-stage process blocks available in ESP. Generally, these process units are columns/towers. The process units available are:

- **Stripper**
- **Absorber**
- **Extractor**

The unit to be specified is selected from the display using the Arrow Keys and then the Enter Key.

Additional column specification facilities are available via the Action Key and then by selecting the Parameters and Config facilities. These facilities are detailed for each individual unit.

Distillation/Stripper Unit



This is a multi-stage conventional or environmental unit allowing species in a liquid to be separated either by distillation, or by the action of a countercurrent vapor stream (i.e., stripper). The unit can hold a maximum of 50 stages, 10 feed streams, and 10 exit streams.

When this block is selected the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, an aqueous phase must be present in every liquid stream. The liquid feed and/or liquid product can contain both an aqueous and nonaqueous liquid phase, or just an aqueous phase alone. In the case of a non-electrolyte column, only the non-electrolyte liquid phase exists (electrolyte chemistry is not considered).

Data Requirements

A minimum of one feed stream and two exit streams (i.e., distillate and bottoms) must be named when using the unit for distillation. An additional feed must be added when using the unit as a stripper. The feed stream temperature, pressure, flow and composition data must be specified by the user or be a product stream from another Process Block. The number of stages will default to 10 and appear that way on the initial screen. The user may override this value. If there is a condenser or reboiler, these will count as stages. Additionally, various column operating parameter information must be supplied by the user.

Column Parameters

The column operating parameters are accessed using the Action Key and then by selecting the Parameters facility. Five options are available:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop through the column is assumed. If no values are given, the entire column is assumed to operate at atmospheric pressure.

Column Estimates This option allows stage operating temperatures, vapor distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperature, as well as the vapor distillate rate and liquid reflux flowrates, must all be specified by the user. The Esc Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchanger duty) to meet specifications in the column operation. For example, vapor and/or liquid composition specifications, stage operating temperature, and vapor and/or liquid stream flowrate specifications can all be achieved.

Exchanger Duties This option allows column and pumparound heat exchanger duties to be specified. For columns using a condenser and/or reboiler, the user must define duties for the respective

units. Negative heat duties imply heat removal. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages and individual components. If no data is entered, the stage efficiency is assumed to be 1.0. The End Key returns the user to the process block display.

Tray Hold-Up Volumes This function is required for columns whose chemistry contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Column Configuration

Additional column parameters can be defined, via the Action Key, and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block includes the two units on the display.

Pumparounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

Mass and Heat Transfer Coefficients This option allows the user to specify vapor-liquid mass and heat transfer coefficients on each stage of the column. The coefficients are overall coefficients and apply to all components. The interfacial transfer area must also be specified. If the same coefficients are used throughout the column, the coefficient may be varied to meet a composition specification by means of the spec/control parameters. This option is only available if the Mass Transfer Column program has been licensed by the user.

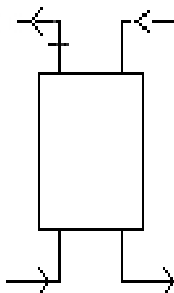
Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero. If this is not performed the data entry is not saved.*
2. *For columns with condenser and/or reboiler units the heat duty estimates defined by the user must be such that a vapor flow exists on the bottom stage and a liquid phase flow exists on the top stage of the column respectively.*
3. *The column can only operate if two (or optionally three) phases exist on every stage of the column.*
4. *For columns without a condenser and/or reboiler unit, a feed stream must be specified entering at the respective position of the omitted unit. The phase of this stream must be correctly defined. A liquid phase feed stream is required as an alternative to a column condenser, and a vapor phase*

stream in place of a reboiler unit (i.e., the column must have two phases flowing to and from every stage).

5. *When defining a stripper unit, an all liquid feed stream must be specified entering the top of the column and the stripping vapor must enter the bottom of the unit.*
6. *When defining stripper column parameters, a zero liquid reflux (i.e., distillate) flow must be made. This is because the distillate flow exiting the unit must only exist in the vapor phase.*
7. *All column stages are numbered from bottom to top.*
8. *If a feed stream contains both a vapor and a liquid phase, the liquid goes to the feed tray specified by the user and the vapor goes to the stage above.*

Absorber Unit



This is a multi-stage conventional or environmental process unit which allows species in a vapor feed to be absorbed by a countercurrent liquid stream. The unit can hold up to a maximum of 50 stages and up to a maximum of 10 feed and 10 product streams.

When this block is selected the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, an aqueous phase must be present in every liquid stream. The liquid feed and/or liquid product can contain both an aqueous and nonaqueous liquid phase or just an aqueous phase alone. In the case of a non-electrolyte column, there is only the non-electrolyte liquid phase (electrolyte chemistry is not considered).

Data Requirement

A minimum of one liquid stream entering the top of the column and one vapor stream entering the bottom of the unit must be specified. The respective feed stream temperature, pressure, flow and composition must be defined by the user or be a product stream from another Process Block.

When defining the feed stream, the temperature and pressures of each stream should be such that the species components reside in the correct phase for the respective stream.

The column exit vapor and liquid streams must be named, in addition to various column parameters.

Column Parameters

The column operating parameters are accessed using the Action Key and selecting the Parameters facility. Five options are available:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop is assumed through the column.

Column Estimates This option allows stage operating temperatures, vapor distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperature, as well as vapor distillate and liquid reflux flowrates must all be specified by the user. The Quit or End Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchange duty) to meet specifications in the column operation. For example, vapor and/or

liquid composition specifications, stage operating temperature and vapor and/or liquid stream component flowrate specifications can all be achieved.

Exchanger Duties This option allows column heat exchanger duties to be specified. For columns using a condenser and/or reboiler the user must define duties for the respective units. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages. If no data is entered the stage efficiency is assumed to be 1.0. The End Key returns the user to the process block display.

Tray Hold-Up Volumes This function is required for columns whose Chemistry Model contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Column Configuration

Additional column parameters can be defined, via the Action Key and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block does not include the two heat exchanger units.

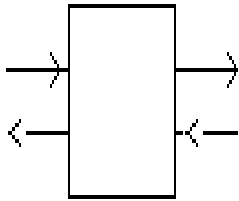
Pumparounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

Mass and Heat Transfer Coefficients This option allows the user to specify vapor-liquid mass and heat transfer coefficients on each stage of the column. The coefficients are overall coefficients and apply to all components. The interfacial transfer area must also be specified. If the same coefficients are used throughout the column, the coefficient may be varied to meet a composition specification by means of the spec/control parameters. This option is only available if the Mass Transfer Column program has been licensed by the user.

Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero.* If this is not performed the data entry is not saved.
2. *When defining column parameters a zero liquid reflux (i.e., distillate) rate should be defined.* This is because the distillate flow exiting the unit must only exist in the vapor phase.

Extractor Unit



The Extractor Unit is not supported in the MSE thermodynamic framework!

This is a multi-stage conventional or environmental process unit which allows countercurrent liquid-liquid extraction to be simulated. The unit can hold a maximum of 50 stages, 10 feed and 10 exit streams.

When this block is selected, the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, one of the two liquid streams is aqueous. In the case of a non-electrolyte column, both liquid streams are nonaqueous (electrolyte chemistry is not considered).

Data Requirement

A minimum of one aqueous feed stream must be defined entering the top of the column, and the solvent stream entering the bottom of the unit. The respective feed streams temperatures, pressures, flows and compositions must be specified, or be a product stream from another Process Block, and the unit outflows named. Additionally, various column operating parameter information must be specified by the user.

Column Parameters

The column operating parameters are accessed using the Action Key and selecting the Parameters facility. Five options are available:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop is assumed through the column.

Column Estimates This option allows stage operating temperatures, organic distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperatures, as well as organic distillate and liquid reflux flowrates must all be specified by the user. The End or Quit Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchanger duty) to meet specifications in the column operation. For example, vapor and/or liquid composition specifications, stage operating temperature, and component flowrate specifications can all be made.

Exchanger Duties This option allows column heat exchanger duties to be specified. For columns using a condenser and/or reboiler the user must define duties for the respective units. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages. If no data is entered, the stage efficiency is assumed to be 1.0. The End Key returns the user to the process block display.

Tray Hold-up Volumes This function is required for columns whose Chemistry Model contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Column Configuration

Additional column parameters can be defined, via the Action Key and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block does not include the two heat exchanger units on the display.

Pumparounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero. If this is not performed the data entry is not saved.*
2. *The feed stream conditions must be specified such that no vapor phase species exist in the streams or the column.*
3. *When specifying column flowrates exiting the top stage, the organic phase stream is defined as the vapor distillate flowrate.*

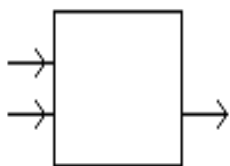
Environmental Process Blocks

This section contains detailed specification requirements for environmental process blocks available in ESP. Generally, these operations are treatment processes and the units available in ESP include:

- **Reactor**
- **Neutralizer**
- **Precipitator**
- **Incinerator**
- **Crystallizer**
- **Saturator**
- **Dehydrator**
- **Membrane**
- **Electrodialysis**
- **Electrolyzer**

The unit to be specified is selected from the display using the Arrow Keys and the Enter Key. Additional specification facilities are available using the Action Key and are detailed for each individual unit.

Reactor Unit



This is an environmental process unit which determines the phase separation and intra-phase speciation for a Chemistry Model which can include both equilibrium and rate-limited reactions. The various types of phenomena that can be modeled include ion exchange, bioreactions, kinetics, and redox reactions.

Three types of reactors are available:

Aqueous, Used to simulate electrolyte chemical reaction systems containing one or more rate-limited reactions, with vapor-liquid mass-transfer constraints;

Nonaqueous, Used to simulate non-electrolyte (e.g., organic) reaction systems containing one or more rate-limited reactions;

Bioreactor, Used to simulate an electrolyte chemical system in which a bioreaction occurs. (Reference:

Biotreatment Process Blocks on page 306 of this section for further details).

Data Requirement

A minimum of one feed stream entering the reactor must be named, along with the stream temperature, pressure, total flowrate, and composition data defined by the user or be a product stream from another Process Block. Also, the product stream exiting the unit must be named. Additionally, the reactor operating parameters must be specified.

Unit Parameters

The reactor operating conditions are specified using the Action Key and selecting the Parameters facility. CSTR or plug flow reactors can be modeled. Plug flow reactors are modeled by dividing the reactor into stages and then treating each stage as a CSTR. The reactor can be modeled adiabatically or isothermally. One of these options must be selected by the user. If an isothermal reaction is specified, the reactor operating temperature must also be defined.

When using an Aqueous Reactor, either the reaction duration needs to be specified (the associated rate information is given in the Chemistry Model), or conversion fractions of key reactants must be given. Reaction duration is achieved by specifying the time increment of reaction and the number of increments to be considered. Key Reactants are specified by naming the reactant, the fraction of the reactant which is converted, and the reaction equation.

The vapor-liquid equilibrium can be constrained by specifying a mass-transfer coefficient for the vapor and liquid phases along with an interfacial area. These coefficients are overall coefficients and apply to all components. If it is desired to have individual coefficients that depend on temperature and flow rates, a user added subroutine (USERM) can be added to calculate the coefficients and interfacial area (Contact OLI for specification for this user added subroutine). This subroutine overrides any specification supplied as block parameters.

For a Nonaqueous Reactor either the liquid or vapor hold-up volume in the unit must be defined.

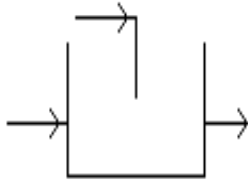
Unit Configurations

This facility is accessed using the Action Key and selecting the Config facility. It allows the user to add or delete extra inlet streams to the unit. An additional six aqueous feeds may be defined if required.

Guidelines

1. When using this process unit when specifying residence time, the user must insure that the chemical reaction kinetics are specified in the Chemistry Model for the system. (Reference the **Chemistry Models** chapter of the **OLI Engine Manual** for further details.)
2. When additional streams are to be added the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.
3. Either residence time and associated rate information or key reactions are given, not both.

Neutralizer Unit



This is an environmental process block which allows up to 6 feed streams to be neutralized by the addition of a suitable reagent. The neutralization can be modeled adiabatically by mixing the inlet streams, by varying the neutralizing reagent flow to meet a fixed pH set point.

Data Requirements

A minimum of one feed stream and one neutralizing reagent stream must be named. In addition, temperature, pressure, total flowrate and composition data of the feed stream(s) must be specified by the user or be a product stream from another process block. The user must supply the same information for the dosing stream. The dosing stream must be specified as the top entry stream to the process unit. The process block outlet stream must be named. Additionally, the process operating conditions must also be defined by the user.

Unit Parameters

The process mode of operation is defined by using the Action Key and selecting the Parameters facility. Two calculation options are currently available to allow the process to be modeled:

- **Adiabatic mixing of the feed streams**
- **Setting pH of the outlet stream**

If adiabatic mixing is chosen, the simulator determines the outlet stream properties, based upon the user specified inflows. However, if a fixed exit pH is required for the effluent, the simulator varies the reagent stream flowrate accordingly, until the effluent pH requirement is obtained.

Specifications of pressure can also be made by specifying either a pressure loss across the Mix unit or by specifying the exit stream pressure.

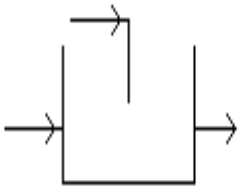
Unit Configuration

This facility is accessed using the Action Key and selecting the Config facility. It allows the user to add or delete extra inlet streams to the unit. An additional five feeds may be defined if required.

Guidelines

1. When additional streams are to be added, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.
2. The reagent stream must be a process entry stream. That is, the reagent stream cannot be a product from another process block, or be a recycle stream.
3. A guess for the flowrate of the reagent stream is required.
4. Systems with difficult chemistry (i.e., multiple phases, multiple solids) may have problems in converging this process block. If the block does not converge, a Crystallizer can be alternately simulated by using a Mix, Manipulate, and Controller block. (See **Chapter 3: Process Applications, ESP Control Block Applications, Manipulate/Controller** for an example of this configuration).

Precipitator Unit



This is an environmental process block which determines the flow of precipitating reagent necessary to achieve a specified aqueous ionic species concentration. Currently, the concentration is specified based on actual species in solution. Future versions will allow specification of concentration on an elemental or on a total dissolved solids (TDS) basis.

Data Requirement

A minimum of two feed streams must be named along with their respective temperature, pressure, total flowrate and composition data. The user must define the state of the reagent stream while the feed stream(s) can be defined by the user of be a product stream from another Process Block. The precipitating reagent must be specified as entering the top of the unit, and the exit stream must also be named. Additionally, the type of calculation and operating requirements need to be specified by the user.

Unit Parameters

The calculation type is defined by using the Action Key and selecting the Parameters facility. The calculation is specified by Aqueous Species or by Material Balance codes. At present only the Aqueous Species calculation option is available.

The reaction conditions must then be defined. The reaction can be modeled adiabatically or isothermally, one of which must be selected. For an isothermal reaction, the unit operating temperature must be supplied by the user.

Finally, the target *aqueous ionic species* concentration must be specified by the user. This target is the sum of all the aqueous species selected by the user.

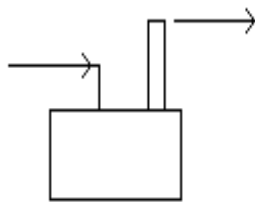
Unit Configuration

This facility is accessed using the Action Key and selecting the Config facility. It allows the user to add or delete extra feed streams to the unit. An additional five inlets can be defined if required.

Guidelines

1. When using this process unit, the user must insure the solid phase is included in the respective Chemistry Model Definition. (Reference the **Chemistry Models** chapter of the **OLI Manual** for further information).
2. When additional streams are to be added the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.
3. Systems with difficult chemistry (i.e., multiple phases, multiple solids) may have problems in converging this process block. If the block does not converge, a Precipitator can be alternately simulated by using a Mix, Manipulate, and Controller block. (See **Chapter 3: Process Applications, ESP Control Block Applications, Manipulate/Controller** for an example of this configuration).

Incinerator Unit



This is an environmental process unit which allows Non-electrolyte species to be incinerated either adiabatically or isothermally.

Data Requirement

A minimum of one feed stream to the unit must be named, and its temperature, pressure, total flowrate and composition data should be specified by the user or be the product stream from another Process Block. Note that the oxidation vapor stream composition (i.e., the air being used to burn the feed) must also be included as part of the feed stream(s) definition. The waste stream exiting the unit must also be identified.

Unit Parameters

The mode of unit operation (adiabatic or isothermal) and the unit hold up volume must be specified by the user. This is achieved using the Action Key and selecting the Parameters facility. The unit can operate adiabatically or isothermally, one of which must be selected. For isothermal operation, the incinerator operating temperature must be supplied by the user.

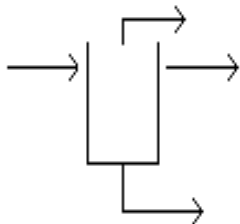
Unit Configuration

This facility allows the user to add or delete extra inlet streams to the unit, and is accessed via the Action Key and selecting the Config facility. An additional six feeds may be defined if required.

Guidelines

1. When using this unit the user must insure a Non-Electrolyte Chemistry Model Definition is created which includes equilibrium phase reactions or chemical reaction kinetics. (Reference the **Chemistry Models** chapter of the **OLI Manual** for further information).
2. For clarification purposes it is advised that the oxidation vapor stream is specified as a separate inlet flow to the unit, rather than as part of the feed stream composition. This is achieved using the Config facility.
3. When additional streams are to be added the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.
4. Species that may form through a reduction/oxidation process and be in the product stream must be named as a species in the Chemistry Model (e.g., NO_x compounds, SO₂, etc.)

Crystallizer



This is an environmental process block which calculates the operating conditions of the unit such that a specified amount of selected solids concentration will be present in the effluent.

Data Requirement

The unit's stream inflow(s) and exit effluent flow must be given names. Optionally, a vapor stream can also be named in order to model an open vessel. An optional solids stream can be named which will separate the solids from the effluent.

Unit Parameters

One or more solids can be selected whose concentrations will be combined to calculate the target solids specification value. This is achieved by using the Action Key and then selecting the Parameters facility. The solids of interest are selected from a list of all solids in the Chemistry Model by positioning the cursor bar on the solid and pressing the <Space Bar>. At least one solid should be selected. The value and units of the target concentration are then entered.

Other options in the Parameter facility include:

Pressure - The pressure loss across the unit, or the exit pressure of the effluent may be specified.

Temperature Bounds - The upper and lower limits of temperature can be set, along with the step size. The default temperature bounds are 0 and 400° C. The default step size for the first iteration is 1%. The default for subsequent iterations is 20° C minimum and (T_{max}-T_{min}/10).

Max Iterations - The number of iterations can be changed from the default of 50 iterations.

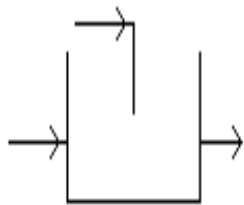
Unit Configurations

This facility is accessed using the Action Key and selecting the Config facility. It allows the user to add or delete extra inlet streams to the unit. An additional six aqueous feeds may be defined if required.

Guidelines

1. *Systems with difficult chemistry (i.e., multiple phases, multiple solids) may have problems in converging this process block.* If the block does not converge, a Crystallizer can be alternately simulated by using a Mix, Manipulate, and Controller block. (See the **Process Applications** chapter for an example of this configuration).

Saturator Unit



This is a conventional process block which allows for the creation of a single product stream which is saturated with respect to a user-specified solid. Up to six conventional feed streams can be specified together with a single product stream. In addition to the conventional feed streams, one additional feed stream must be specified. This additional feed stream will have its flow rate adjusted by the unit calculation to assure saturation of the product stream with regard to the user-specified solid. The resulting phase separation and speciation within each phase of the product stream is computed.

Data Requirement

The unit's stream inflows and exit flow must be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one conventional feed stream and one additional, adjustable feed stream, together with their conditions must be defined by the user. If the feed stream is not defined, it must be a product stream from another process block. The adjustable feed stream must be an inlet stream to the process. Also, the chemistry model used for this block must contain solids.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The parameters available are as follows

Parameter	Value	Comment
Type of Calculation	Adiabatic or Isothermal	
Temperature	User	Isothermal Only
Pressure or Press Drop	User	Both Cases

Selected Solid

Solid Name

Alternatives are Provided

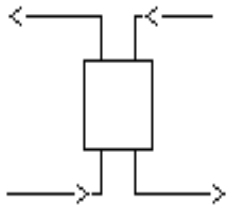
Unit Configuration

This facility allows the user to add or delete extra feed streams to the unit and is accessed via the Action Key and then selecting the Config facility. An additional five inlet streams may be defined if required.

Guidelines

When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Dehydrator Unit



This is an environmental or conventional process block which dehydrates a vapor or organic liquid stream using a packed bed of CaCl_2 . The dehydrator will convert all of the CaCl_2 to $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Data Requirement

The unit requires that the user provide distinct names for two feed streams as well as two product streams. One feed stream must be the process feed stream which is to be dehydrated. The second feed stream, which provides the CaCl_2 is adjusted by computation to satisfy equilibrium requirements for the process effluent. One product stream is simply the effluent from the unit. The second product stream is a saturated aqueous $\text{CaCl}_2 \cdot 5\text{H}_2\text{O}$ stream.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The parameters available are as follows

Parameter	Value	Comment
Computation Option	Adiabatic or Isothermal	
Temperature	User	Isothermal Only
Pressure or Press Drop	User	Isothermal and Adiabatic
Hydrates Selection	User	Default = All Four Hydrates

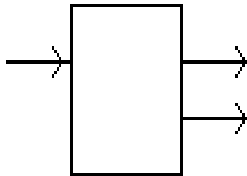
Unit Configuration

Unit has fixed configuration and therefore the Config option is inactive for this unit.

Guidelines

None

Membrane Unit



This is an environmental process block which allows for the separation of salts from a single process feed stream through the use of a semi-permeable membrane. As a result of this separation, two product streams result one called the “concentrate stream” and the other called the “permeate stream.” The specification of a permeate inlet stream is optional.

Data Requirement

The unit’s stream inflow(s) and exit flows must be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one conventional feed stream and one additional, optional permeate feed stream, together with their conditions must be defined by the user or said stream must be a product stream from another process block.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The parameters available are as follows

Parameter	Value	Comment
Total Membrane Area	User Specified	Mandatory
Pressure Differential	User Specified	Mandatory
Permeability of Water	User Specified	Mandatory
Number of Increments	User Specified	Default = 1
Cation/Anion Control	User Specified	Default = Cation
Permeabilities	User Specified	List Provided

Please note that permeabilities must be provided. The user will be given a list of all species (molecular and ionic) in the chemical system being simulated. Permeabilities are only entered for cations or anions depending upon the choice of Control (Anion or Cation) specified by the user.

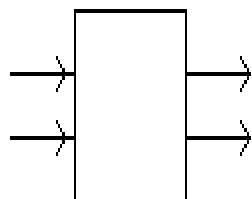
Unit Configuration

This facility allows the user to add a permeate inlet stream to the unit and is accessed via the Action Key and then selecting the Config facility. This is the only option provided for by the Config facility for this unit.

Guidelines

When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Electrodialysis Unit



This is an environmental process block which allows for the separation of salts from a single process feed stream through the use of electrodialysis. As a result of this separation, two product streams result, one called the “concentrate stream” and the other called the “dilute stream.” The feed must actually enter the unit as two separate streams (a dilute feed and a concentrate feed). This is accomplished either by the user specification of two feed streams or via a single feed stream and a user specified Parameter (see below) which specifies the split fraction to be applied to the feed.

Data Requirement

The unit’s stream inflow(s) and exit flows must be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one conventional feed stream and one additional, optional permeate feed stream, together with their conditions must be defined by the user or must be a product stream from another process block.

Unit Parameters

This facility is accessed using the Action Key and then selecting the Parameters facility. The parameters available are as follows

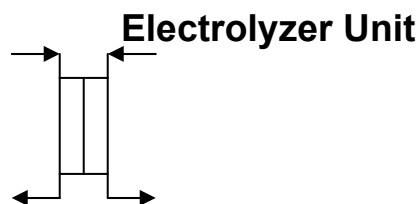
Parameter	Value	Comment
Computation Option	Calc # of Stages or Cation Out-Conc + Frac Demin	User Selection
General		
Flow Option	Fraction of Feed as Diluate	Only if using 1 feed
Capacity per Stack	User-Provided	
Geometry		
Transfer Area	User-Provided	
Spacer Thickness Ratio	User-Provided	Default Provided
Cell Pairs/Stack	User-Provided	
Stacks/Stage	User-Provided	
Number of Stages	User-Provided	Default Provided
Electrical		
Limiting Polarization	User-Provided	Default Provided
Exponent	User-Provided	Default Provided
Safety Factor	User-Provided	Default Provided
Current Efficiency	User-Provided	Default Provided
Resistance		
Coefficients for Each Stage	User-Provided	Defaults Provided
Species		
Selected Cations and Anions	User-Provided	List Provided

Unit Configuration

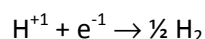
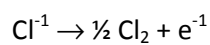
This facility allows the user to add an inlet stream to the unit and is accessed via the Action Key and then selecting the Config facility. This is the only option provided for by the Config facility for this unit.

Guidelines

When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.



The electrolyzer unit is a process unit that specifically converts a sodium chloride brine (NaCl) into chlorine (Cl₂) and sodium hydroxide (NaOH). This is done by applying a current to the solution and allowing chlorine to pass across a membrane. There are several chemical half-cell reactions that are taking place:



Data requirement

The unit's stream inflow(s) and exit flows must be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one conventional feed stream and one additional, optional permeate feed stream, together with their conditions must be defined by the user or must be a product stream from another process block.

Unit Parameters

This facility is accessed using <Action Key> and then selecting the Parameters Facility. There are three options in the Parameters Facility:

Diluate Exit Temperature

Retentate Exit Temperature

Computation Options

Each of these options is described below:

Parameter**Value**

Diluate Exit Temperature

Isothermal

Specify the diluate exit Pressure

Set Temperature

Specify diluate exit Temperature and Pressure or pressure drop

Temperature Change

Specify the change in temperature between the inlet and outlet on diluate side

Retentate Exit Temperature

Isothermal

Specify the retentate exit Pressure

Set Temperature

Specify retentate exit Temperature and Pressure or pressure drop

Temperature Change

Specify the change in temperature between the inlet and outlet on retentate side

Computation Options

Specify Current Density Specify the current density in amps/cm^2 and the effective transfer Area (in cm^2) and the current efficiency (in fractions)

Specify fraction of Total Na in diluate to be removed

Specify fraction of the total amount of sodium to be removed.

The current density is then calculated. The effective transfer

Area (in cm^2) and the current efficiency (in fractions) must also

Be entered.

Specify Total Na in diluate outlet

Specify the total amount of sodium to remain in the diluate Outlet (gmoles). The current density is then calculated. The effective transfer area (in cm^2) and the current efficiency (in fractions) must also be entered.

Unit Configuration

This facility allows the user to add an inlet stream to the unit and is accessed via the Action Key and then selecting the Config facility. This is the only option provided for by the Config facility for this unit.

Guidelines

When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.

Biotreatment Process Blocks

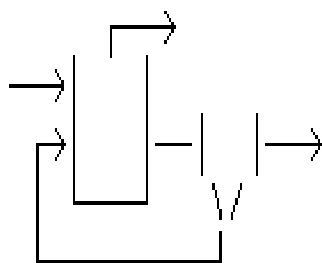
This section contains detailed specification requirements the biotreatment process block available in ESP. The units available are:

- **Bioreactor**
- **Clarifier**

In ESP there are two types of Bioreactors that are available. One Bioreactor has the clarifier built into the unit, the other does not.

The anaerobic reaction in ESP biotreatment has been upgraded to reflect the type of reaction typically found in municipal and industrial processes. From an aqueous solution perspective this is important, since the primary reaction product is acetic acid rather than methane. The biochemical reaction is simulated as a completely mixed, homogenous, solution based reaction, that is, the substrate and micro-organisms are suspended within the liquid. The composition of the solution at thermodynamic equilibrium is the composition used to determine the reaction rates and thus the reaction extent.

Bioreactor Unit



This is a biotreatment process block which models a steady state activated sludge bioreactor. The minimum space time (or solids retention time) required to prevent washout is calculated, along with the all heterotrophic and autotrophic reactions, including nitrification and denitrification, and the phase separation and intra-phase speciation of the effluent.

Optional layouts may be described. Open vessels may be modeled by including a vent stream, and a clarifier with recycle (with or without wastage) is supported.

Data Requirement

A minimum of one feed stream must be named, along with the stream temperature, pressure, total flowrate, and composition. The air required for the unit must also be specified, either in the feed or as a separate inlet. The product effluent must be named, and optional vapor and wastage streams can be

named if they will be included in the block. Additionally, the reactor operating parameters must be specified.

The Chemistry Model for this block must include the bioreaction data

Unit Parameters

The reactor operating conditions are specified using the Action Key and selecting the Parameters facility. The parameters include:

Computation Option - the bioreactor can be modeled isothermally or adiabatically. Isothermal simulations are recommended.

Reactor Volume - the volume of the reactor is required.

Oxygen Use - the O_2 mass transfer coefficient is required for the calculations. In addition, if the dissolved O_2 concentration is entered, the air flow required is calculated conversely, if the air flow is entered, the dissolved O_2 concentration is calculated.

Recycle - the recycle ratio, which is the recycle flow/volumetric liquid feed flow, the solids retention time, the wastage flow, and the clarifier area (including the flux curve data) are related data items which are optimized in the bioreactor. Two of these parameters must be entered. The other 2 will be calculated.

Bioreaction Constants - the ability to override the bioreaction constants in the Chemistry Model has been included. The new value of the constant is in effect for this process block only.

Flux Curve - Flux curve data, (Sludge concentration vs. flux) can now be entered, from 3 to 20 points are allowed.

Bioreactor Inhibition - the ability to override the bioreactor inhibition in the Chemistry Model has been included. The new values are in effect for this process block only.

Unit Configurations

This facility is accessed using the Action Key and selecting the Config facility. This facility allows the user to add or delete extra inlet streams to the unit (the air stream may be specified in this way). An additional six inlets may be defined if required.

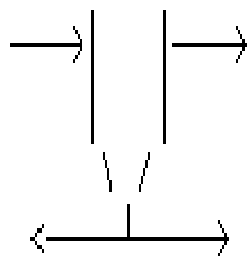
This facility also allows the clarifier with recycle to be added or removed from the layout of the bioreactor. This is achieved by selecting the Recycle option of Config. The wastage stream may also be added or removed from the layout in the same manner.

Guidelines

1. *When using this process block the user must insure that the bioreactions have been specified in the Chemistry Model for the system. (Reference **Chemistry Models** in the **OLI Manual** for further details.)*

2. When additional streams are to be added, the user must first insure the minimum stream configuration for the unit is specified prior to using the Config facility.
3. The recycle ratio controls whether the clarifier and recycle will be included in displays of the bioreactor layout. When a recycle ratio is not entered, the clarifier and recycle stream are removed from the display.
4. The O_2 mass transfer coefficient is now always used to specify oxygen use. When specifying dissolved O_2 , the air flow for the bioreactor will be calculated.
5. The bioreaction rate constants in the Chemistry Model and in the block can be varied in a parametric study in order to tune individual reactors. The key parameters which can be varied include the RATE, YIELD, KSUB (or KNH_4) and DECAY. Future releases of ESP will have facilities which will partially automate and simplify this tuning.
6. The minimum SRTs which are calculated and displayed in the Process Block Report can be used to determine if a bioreaction is occurring.
7. The aerobic, anaerobic, and anoxic fractions of the heterotrophic reaction are calculated. These results may be tuned to more closely match field results by manipulating ANAF and ANOF.

Clarifier Unit



This is a biotreatment process block which models a steady state clarifier in an activated sludge process. Recycle and wastage stream flows may be specified. This process block may also be used in conjunction with a series of activated sludge bioreactors in order to simulate a plug flow reactor.

The composition of the recycle stream and the wastage stream are the same. Optional layouts of the clarifier are allowed. When no wastage stream is specified, all outlet solids are placed in the effluent. A vapor stream may be named to simulate an open vessel.

Data Requirement

A minimum of one feed stream must be named. The product effluent must also be named, and the optional vapor, wastage, and recycle streams are named if they are to be included in the block. Additionally, operating parameters for the block must be specified.

Unit Parameters

The clarifier operating conditions are specified using the Action Key and selecting the Parameters facility. The parameters include:

Flows - The volumetric flowrates of the recycle stream and the wastage streams are required if the streams are named in the block.

Total Suspended Solids - Solids may be included in the effluent stream by specifying a TSS for the effluent.

Flux Curve - Flux curve data, (Sludge concentration vs. flux) can now be entered, from 3 to 20 points are allowed.

Unit Configuration

This facility allows the user to add or delete extra inlet streams to the unit and is accessed via the Action Key and then selecting the Config facility. An additional six feeds may be defined if required.

Guidelines

When additional streams are to be added, the user must first insure the minimum configuration of feed and product effluent are specified prior to using the Config facility.

ESP Control Blocks

Manipulate Unit

This is an ESP Control Block which allows the mixing of up to 7 feed streams adiabatically. Either the resulting flow or individual components can be multiplied by a factor. The resulting phase separation and speciation within each phase of the outlet stream is computed.

Data Requirement

The unit's stream inflow and exit flow must all be given distinct names. This enables streams and units to be recognized and linked together when building a complex process. A minimum of one feed stream and their respective temperature, pressure, flow and composition must be defined by the user.

Unit Parameters

This facility is accessed via the Action Key and then by selecting the Parameters facility. It allows the user to specify the factors by which either the Total Flow or Stream Component composition of the exit stream can be multiplied.

Unit Configuration

This facility allows the user to add or delete extra feed streams to the unit and is accessed via the Action Key and then by selecting the Config facility. An additional six inlet streams may be defined if required.

Guidelines

1. *When additional streams are to be added to the unit, the user must first insure the minimum data requirements for the unit are specified prior to using the Config facility.*
2. *This block is generally used in conjunction with the other ESP Control Blocks (e.g., Controller) to adjust the flow of a stream or a composition in the stream.*

Controller

This is an ESP Control Block which allows the user to specify a particular stream property by adjusting a block parameter of another process block.

Data Requirement

The Controller definition can be divided into two parts: defining the stream specification, and defining the block parameter of the process block to be varied to meet the stream specification.

Defining the Stream Specification

The specification stream is chosen from the streams already defined in other process block. This is achieved by pressing the <Enter> key on the blank "Specification Stream" field. Only streams which have been defined can be named in the Controller Block.

The stream's specification type is then selected from a list of possible specification types, which include the temperature, pressure, pH, flow, or composition of the stream. When flow is selected as a specification, the phase and the units can be named. When composition is selected as a specification, the phase and units of the composition can also be named. In addition, the target composition can be named in terms of either the species in the solution (e.g., CaCO_3), or in terms of the material balance groups in the solution (e.g., Ca^{+2} , C^{+4} , or O^{-2}).

Defining The Block Parameter

The process block parameter which will be varied to meet the stream specification is named by first selecting the process block. The process block is selected from a list of process blocks already defined. This is achieved by pressing the <Enter> key on the blank "Block Name" field. Once the process block is selected, the parameters available for that block are listed. Parameters include:

<u>Process Block</u>	<u>Parameters</u>
Absorber	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
BioReactor	Volume, Temperature, Duty, Pressure, SRT, Dissolved O_2 , Recycle Ratio, Wastage Flow, Clarifier Area, BioReaction Constant
Clarifier	Wastage Flow, Recycle Flow, Total Suspended Solids
Controller	Target Spec Value
Crystallizer	Solids Specification Value
Csplit	Temperatures, Pressures, Component Fraction
Exchanger	Discharge T, Duty, Pressure, Utility Outlet T, Utility Pressure
Extractor	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
Incinerator	Liquid and Vapor Holdup Volume, Temperature, Pressure, Duty
Manipulate	Total Flow Factor, Species N Factor
Mix	Pressure, Spec 1, Spec 2
Neutralizer	pH, Pressure
Precipitator	Temperature, Composition Spec Value
Reactor	Temperature, Duty, Pressure (Holdup Volumes on Non-Aq Reactor)
Split	Split Fraction N

StripperExchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature

Unit Parameters

Controller parameters can be set which guide the convergence of the Controller Block. These optional parameters are accessed via the Action Key and then by selecting the Parameters facility. The parameters which can be set are:

StepSize Method - One of three calculation stepsize methods can be selected. The Slope Technique is the default.

Slope Technique - the slope between the last two guesses determines the next guess, unless the step size minimum or maximum is exceeded. This is the fastest technique, provided there are no large differences in slopes (as there are in titration curves, or precipitation curves).

Half Interval - a new minimum or maximum is computed each iteration, and the new guess is based on $(\min + \max)/2$. This is a conservative technique, but a solution is assured for unimodal functions.

Bracketed Slope - as with the Half Interval technique, a new minimum and maximum is computed each iteration. The slope is then used to calculate the next guess (rather than $(\min + \max)/2$).

Bounds - The upper and lower limits of the process block parameter and the stepsize can be set. The default stepsize for the first iteration is 1%. The default for subsequent iterations is:

50% for general process variables

20 deg C for temperature

25% for duty

Max Iterations - The number of iterations can be changed from the default of 20 iterations.

Not Converged Rule - The default rule in ESP for non-convergence is to stop execution. This rule can be changed to continue execution.

Return To Block - The block to calculate as the next block after the Controller can be named.

Tolerances - The tolerance for convergence for the stream specification can be changed from the default. Current defaults include:

Temperature	0.01 C
Pressure	0.001 Atm
pH	0.001
Flow	1.0E-05 (relative)
Composition	1.0E-05 (relative)

Guidelines

1. *Avoid trying to control a variable which is discontinuous.* For example, avoid trying to reach the saturation point of a solution with respect to a solid.
2. *When using a controller within a recycle stream loop, the tolerance of the controller may need to be adjusted.* A tolerance which is too loose may cause problems converging the recycle stream.
3. *When using a controller with the bioreactor, the bioreaction constants must be set in the bioreactor itself, in order to use the constant as a block parameter.*
4. *ESP Process now allows for controlling and tearing the same stream.*

Feedforward

This is an ESP Control Block which allows the measured value of a stream property or of a block parameter to be passed, or transferred, to a downstream block.

Data Requirement

The FeedForward definition can be divided into two parts: defining the measured stream property value or block parameter value that will be transferred, and defining the block parameter of the downstream process block which will receive the value.

Defining the Transfer Value

Either a stream property or a block output parameter can be chosen as the item to be transferred. Initially, ESP prompts for a stream name; this can be switched to a prompt for a block name via the <Action Key> by selecting Parameters, and switching the Block/Stream Toggle.

The stream or block is chosen from the those already defined for this ESP process. This is achieved by pressing the <Enter> key on the blank field. The block output parameter or the stream property is then selected from a list of possible names. For streams, this list includes temperature, pressure, pH, flow, or the composition of the stream. For blocks, this list includes any output parameter which is calculated by the block (e.g., exchanger or reactor duties). Finally, the value of the selected stream property or block output parameter can have an adjustment applied to it. Possible adjustments include:

Value + Constant

Value * Constant

Value / Constant

Constant / Value

An adjustment is selected by pressing <Enter> on the blank "Value Adjusted By" field.

Defining the Block Parameter

The process block parameter which will receive the transferred value is named by first selecting the process block. The process block is selected from a list of process blocks already defined. This is achieved by pressing the <Enter> key on the blank "Block Name" field. Once the process block is selected, the allowed parameters for that block are available. Parameters include:

<u>Process Block</u>	<u>Parameters</u>
Absorber	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
BioReactor	Volume, Temperature, Duty, Pressure, SRT, Dissolved O ₂ , Recycle Ratio, Wastage Flow, Clarifier Area, BioReaction Constant
Clarifier	Wastage Flow, Recycle Flow, Total Suspended Solids
Controller	Target Specification Value
Crystallizer	Solids Specification Value
Csplit	Temperatures, Pressures, Component Fraction
Exchanger	Discharge T, Duty, Pressure, Utility Outlet T, Utility Pressure
Extractor	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
Incinerator	Liquid and Vapor Holdup Volume, Temperature, Pressure, Duty
Manipulate	Total Flow Factor, Species N Factor
Mix	Pressure, Spec 1, Spec 2
Neutralizer	pH, Pressure
Precipitator	Temperature, Composition Spec Value
Reactor	Temperature, Duty, Pressure (Holdup Volumes on Non-Aq Reactor)

Split	Split Fraction N
Stripper	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature

Block Parameters

FeedForward parameters are available to control the following:

Block/Stream Toggle - This is the switch that selects whether a stream property value or a block output parameter value will be transferred.

Calc After Block - The default calculation order of the FeedForward block is immediately following the block which has the specification stream (or block) as output. (When the specification stream is an inlet stream, the FeedForward block is calculated first). This option allows the user to select another calculation order for the FeedForward block.

Sensitivity

This is an ESP Control Block which allows the user to vary selected block parameters in a process, and report on selected, monitored stream variables.

Data Requirement

The Sensitivity Block definition is comprised of two parts: defining one or more monitored stream variables, and defining one or more sensitivity block parameters which will be changed parametrically to form the study. These parts are defined independently of each other, by selecting either "New Monitored Stream Variable" or "New Sensitivity Parameter" from the Sensitivity Block menu.

The number of monitored stream variables does not have to equal the number of sensitivity parameters. A maximum of 20 monitored stream variables may be named, and 10 sensitivity block parameters.

There is a limit of 5 Sensitivity Blocks per process.

Defining the Monitored Stream Variable

A stream to be monitored is first chosen from the streams already defined in the process. This is achieved by pressing the <Enter> key on the blank "Stream Name" field. Only streams which have been defined can be named in the Sensitivity Block.

The type of variable to be monitored within the chosen stream is then selected from a list of possible types, which include the temperature, pressure, pH, flow, or composition of the stream. When flow is selected as a monitored stream variable, the units basis can be named. When composition is selected as a monitored stream variable, the phase and units of the composition can also be named. In addition, the target composition can be named in terms of either the species in the solution (e.g., CaCO₃), or in terms of the material balance groups in the solution (e.g., CA(+2), C(+4), or O(-2)).

Defining The Sensitivity Parameter

A sensitivity block parameter which will be changed parametrically is named, by first selecting the process block. The process block is selected from a list of process blocks already defined. This is achieved by pressing the <Enter> key on the blank "Block Name" field. Once the process block is selected, the parameters available for that block are listed. Parameters include:

<u>Process Block</u>	<u>Parameters</u>
Absorber	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
BioReactor	Volume, Temperature, Duty, Pressure, SRT, Dissolved O ₂ , Recycle Ratio, Wastage Flow, Clarifier Area, Bioreaction Constants
Clarifier	Wastage Flow, Recycle Flow, Total Suspended Solids
Controller	Target Specification Value
Crystallizer	Solids Specification Value
Csplit	Temperatures, Pressures, Component Fractions
Exchanger	Discharge T, Duty, Pressure, Utility Outlet T, Utility Pressure
Extractor	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature
Incinerator	Liquid and Vapor Holdup Volume, Temperature, Pressure, Duty
Manipulate	Total Flow Factor, Species N Factor
Mix	Pressure, Spec 1, Spec 2
Neutralizer	pH, Pressure
Precipitator	Temperature, Composition Spec Value
Reactor	Temperature, Duty, Pressure (Holdup Volumes on Non-Aq Reactor)
Split	Split Fraction N
Stripper	Exchanger N Duty, Side Draw Liquid and Vapor Flows, Pumparound N Flow and Temperature

The starting value of the sensitivity parameter, the ending value, and the size of the step are named for each sensitivity parameter. There are no defaults.

Unit Parameters

There are no unit parameters for this unit.

Guidelines

1. *Bioreactors: to use a bioreaction constant as a sensitivity parameter, the constant must first be defined as input for the bioreactor.* Only those constants defined for a particular bioreactor can be named in this block. Naming the constant in the Chemistry Model Mode of ESP is not sufficient. For example, to select KSUB as a sensitivity parameter for bioreactor ABC, first define KSUB, via the Unit Parameters, in bioreactor ABC.
2. *Columns: When specifying an exchanger, sidedraw, or pumparound, N refers to relative position within the process block, and not to the stage number.* For example, a pumparound can be defined for stage 5 in a column. If it is the first pumparound defined in the column, its number will be 1 for the purposes of this block.

Energy Transfer Block

This control block allows for a connection of just energy between a block that has a duty (an isothermal calculation) and a block that requires enthalpy (an adiabatic block).

Data Requirement

This block requires that at least one block in the flowsheet be adiabatic. Adiabatic blocks allow for an offset of enthalpy to be entered. This block uses that parameter for the transfer of energy.

Unit Parameters

There are no block parameters for this unit.

Unit configuration

A name of the block must be specified.

Source of Energy Block Name

This must be a block that has an enthalpy duty as an output parameter. These are frequently isothermal blocks.

Multiplication Factor

This allows the amount of energy to be transferred to be adjusted. For example, if a block has cooled, the duty is negative. Since it cooled, another block must have been heated and the duty required should be positive. The default multiplication factor allows for this relationship

Energy output name

This is the block that is to receive the energy. The block must be an adiabatic block.

Crystallization Process Blocks

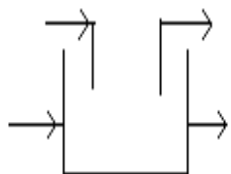
This section contains detailed specification requirements for crystallization process blocks available in ESP. Generally, these operations are crystallization and solids handling processes and the units available in ESP include:

- **XCrystallizer**
- **Filter**
- **Settler**
- **MSMPCrystal**

The specific unit is chosen from a display of all available units by using the Arrow Keys and Enter Key.

Additional specification facilities are available using the Action Key and are detailed for each individual unit.

XCrystallizer Unit



This is a crystallization process unit which models the mass and energy balance of a simple crystallizer. The crystallizer may be a cooling type, evaporation and vacuum type, a dilution and reactive type, or a combined type. One feed stream is required and a feed addition stream is optional. The vapor outlet stream is also optional. The liquid outlet stream is a slurry, containing both liquid and solid.

Three types of simple crystallizers are available:

Cooling Type, Used to model crystallizers that form solid as a result of indirect cooling of the feed stream (i.e., external removal of energy to cool the stream, resulting in precipitation). Generally, specification of a temperature or a duty will accomplish the cooling. Alternatively, specifying a solid rate and computing the temperature and duty will also accomplish the cooling.

Evaporative and Vacuum Type, Used to model crystallizers that form solid as a result of energy removal by evaporation or solvent removal by evaporation (i.e., cooling the stream to result in precipitation or increasing the salt concentration to result in precipitation) Specification of a reduced pressure or specification of a solid rate to produce a lowered pressure will accomplish the evaporation.

Dilution and Reactive Type, Used to model crystallizers that form solid as a result of component addition to change solubility or react. Addition of another reagent such as CaOH_2 is a common way to produce a solid.

Data Requirement

A minimum of one feed stream entering the XCrystallizer must be named, along with the stream temperature, pressure, total flowrate, and composition data defined by the user or be a product stream from another Process Block. Also, the product (slurry) stream exiting the unit must be named. Additionally, the XCrystallizer operating parameters must be specified. Naming a feed addition stream and vapor outlet stream is optional based upon the computation option specified.

Unit Parameters

The XCrystallizer operating conditions are specified using the Action Key and selecting the Parameters facility. One of six Calculation Options should be specified as follows:

Option	Specify	Compute
1	T, P, Feed Stream, (Feed Addition)	Solid Rate, Duty, (Evaporation Rate)
2	T, P, Solid Rate, Feed Concentration, (Feed Addition)	Feed Flow Rate, Duty, (Evaporation Rate)
3	P, Feed Stream, Solid Rate, (Feed Addition)	T, Duty, (Evaporation Rate)
4	T, Feed Stream, Solid Rate, (Feed Addition)	P, Duty, (Evaporation Rate)
5	P, Feed Stream, Duty, (Feed Addition)	T, Solid Rate, (Evaporation Rate)
6	T, P, Feed Stream, Solid Rate, Feed Addition Concentration	Feed Addition Flow Rate

The XCrystallizer Option and inclusion/exclusion of the feed addition stream and vapor outlet stream are used to determine the simple crystallizer type. Generally, the following simple crystallizer types require the specified streams:

Type	Specify
Cooling	No Feed Addition or Vapor Outlet
Evaporative and Vacuum	Vapor Outlet
Dilution and Reactive	Feed Addition
Combined	Feed Addition and Vapor Outlet

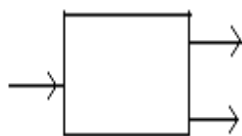
The XCrystallizer computes, based upon the Option and specification values, the amount of solid formed thermodynamically (precipitate). The solid and liquid is combined in the slurry outlet stream. The supersaturation condition and size distribution of crystals is not computed. For crystal distribution based upon nucleation and growth kinetics, use the MSMPCrystal block.

The specification of temperature and pressure may be by entering a value, a change value or allowing the temperature or pressure to default to the feed value. The solid rate may be specified in moles/hr, grams/hr or gram solid/gram liquid. The “solid” may be the total solid or the sum of a list of specified solid species. Since some computation options require iterative procedures for temperature, pressure or feed addition flow, convergence parameters may be entered. The minimum, maximum, step size and maximum number of iterations may be entered for temperature, pressure or feed addition flow convergence. If they are not entered, appropriate default values are used.

Guidelines

1. *The only inlet streams allowed are the feed stream and the optional feed addition stream.*
2. *The only outlet streams allowed are the slurry stream and the optional vapor outlet.*
3. *If Option 6 is specified, the feed addition stream must be a process entry stream. That is, the feed addition stream cannot be a product from another process block, or be a recycle stream.*
4. *For Options 2, 3, 4 and 6, the Solid Rate may be the total solid or a list of specified precipitates.*

Filter Unit



This is a crystallization process unit which models the separation of the liquid portion of the feed stream from the solid portion of the feed stream. The liquid and solid are divided between the filtrate and solids outlet streams based upon specified fractions or flows.

Data Requirement

One feed stream entering the Filter must be named, along with the stream temperature, pressure, total flowrate, and composition data defined by the user or be a product stream from another Process Block. (Often the feed stream is the slurry outlet from an XCrystallizer block). Also, the outlet (filtrate and solids) streams exiting the unit must be named. Additionally, the Filter operating parameters must be specified.

Unit Parameters

The Filter operating conditions are specified using the Action Key and selecting the Parameters facility. Two basic conditions must be specified:

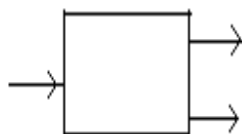
1. split of the total liquid to the filtrate and solids streams, and
2. split of the solid between the filtrate and solids streams.

The total liquid may be split by using fractions or flows. Once one fraction is specified (e.g., the fraction of the total liquid split to the filtrate stream), the other is known and cannot be specified (e.g., the fraction of liquid split to the solids stream). The total liquid may be split by specifying the flow of liquid in moles/hr, grams/hr or m³/hr to one of the outlet streams. Likewise, once one flow is specified, the other is known and cannot be specified. The same procedure is followed when specifying the split of the solid to each of the outlet streams.

Guidelines

1. *The only inlet stream allowed is the feed stream.*
2. *The entire liquid is split by fraction or flow to the two outlet streams, filtrate and solids.*
3. *The entire solid is split by fraction or flow. Individual solid species may not be selected. Thus, the makeup of the solid in the filtrate stream will be the same as the makeup of the solid in the solids stream.*
4. *Once the fraction or flow of liquid to the filtrate or solids stream is specified, the fraction and flow to the other stream is fixed and may not be specified. The same is true for the solid.*

Settler Unit



This is a crystallization process unit which models the separation of the liquid portion of the feed stream from the solid portion of the feed stream. The liquid and solid are divided between the filtrate and solids outlet streams based upon specified fractions or flows. The solid may be split as a total solid or, differentially, split by individual solid species.

Data Requirement

One feed stream entering the Settler must be named, along with the stream temperature, pressure, total flowrate, and composition data defined by the user or be a product stream from another Process Block. (Often the feed stream is the slurry outlet from an XCrystallizer block). Also, the outlet (filtrate and solids) streams exiting the unit must be named. Additionally, the Filter operating parameters must be specified.

Unit Parameters

The Filter operating conditions are specified using the Action Key and selecting the Parameters facility. Two basic conditions must be specified:

1. split of the total liquid to the filtrate and solids streams, and
2. split of the solid, or individual solid species, between the filtrate and solids streams.

The total liquid may be split by using fractions or flows. Once one fraction is specified (e.g., the fraction of the total liquid split to the filtrate stream), the other is known and cannot be specified (e.g., the fraction of liquid split to the solids stream). The total liquid may be split by specifying the flow of liquid

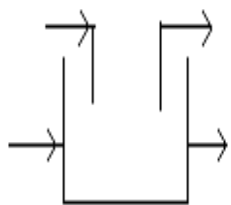
in moles/hr, grams/hr or m³/hr to one of the outlet streams. Likewise, once one flow is specified, the other is known and cannot be specified.

The total solid may be split by using fractions or flows or the solid may be split by specifying the fraction or flow of specific solid species to each of the outlet streams. A combination of the two may also be used. That is, you may split one or more individual solid species by fraction or flow and then split the remainder of the solid by an overall fraction or flow. Since the solid may be split by individual solid species, the resulting solid portion of each of the outlet streams are not necessarily of the same makeup.

Guidelines

1. *The only inlet stream allowed is the feed stream.*
2. *The entire liquid is split by fraction or flow to the two outlet streams, filtrate and solids.*
3. *When splitting the solid, individual solid species may be selected. Any solid species not selected will be split using the overall solid split fraction or flow. Thus, the makeup of the solid in the filtrate stream will be the same as the makeup of the solid in the solids stream.*
4. *Once the fraction or flow of liquid to the filtrate or solids stream is specified, the fraction and flow to the other stream is fixed and may not be specified. The same is true for the solid.*

MSMPCRCrystal Unit



This block models a mixed-suspension, mixed-product-removal (MSMPR) crystallizer. The user specifies nucleation and growth rate constants, crystallizer volume, shape factors and crystal density. The block computes the saturation and supersaturation concentrations of the solid species of interest, the nucleation rate, the growth rate, the crystal size distribution and mass

distribution, and the zeroth through fifth moments. Regression of experimental data is also available through the OLI Toolkit.

Data Requirement

A minimum of one feed stream entering the MSMPCRCrystal block must be named, along with the stream temperature, pressure, total flowrate, and composition data defined by the user or be a product stream from another Process Block. Also, the product (slurry) stream exiting the unit must be named.

Additionally, the MSMPCRCrystal kinetics and operating parameters must be specified. Naming a feed addition stream and vapor outlet stream is optional.

Unit Parameters

The MSMPCRCrystal requires kinetics parameters and operating parameters. The parameters are specified using the Action Key and selecting the Parameters facility. The parameters include:

Kinetics Parameters – Nucleation Rate - the nucleation rate constant, growth exponent and specific mass exponent are required. A set of nucleation rate default values is provided for low yield and high yield crystals. Temperature functionality in Arrhenius form may also be entered for the nucleation rate constant. Regression of experimental data to determine nucleation rate constants is available in OLI Toolkit.

Kinetics Parameters – Growth Rate – the growth rate form must be specified. Growth rate form 1 uses the traditional form where growth rate is directly proportional to the difference between the solute outflow concentration (supersaturation) and the saturation concentration. No activity coefficients are used. Growth rate form 2 uses the aqueous phase solution molalities and activity coefficients of the ionic species making up the solute. The solution molalities and activity coefficients are at supersaturation conditions. Form 2 is the recommended form since it takes into account nonideality due to the supersaturation concentrations. A set of growth rate default values is provided for low yield and high yield crystals. Temperature functionality in Arrhenius form may also be entered for the growth rate constant. Regression of experimental data to determine growth rate constants is available in OLI Toolkit.

Kinetics Parameters – Crystal Properties – the area shape factor, volume shape factor and crystal density are also required.

Kinetics Parameters – Distribution Properties – the distance between crystal sizes and the maximum crystal size are required for production of the crystal size and crystal mass distributions.

Operating Parameters – temperature, pressure and crystallizer volume are required.

Regression of Kinetics Parameters with OLI Toolkit – to regress kinetics parameters for use in the nucleation and growth model of the MSMPCRCrystal Block, the following steps are necessary:

1. Assemble the ESP process containing the MSMPCRCrystal block for which parameters are to be regressed.
2. Enter ESP Toolkit and select *MSMPR Regression*.
3. Name the regression and select the ESP process assembled in step 1
4. Select *Specify Regression Input* and enter the names of the parameters you wish to fit, the initial value, the minimum value and the maximum value. (press *Enter* for a list of available parameters to be fit, highlight the parameters and press the space bar to select.)
5. Enter the experimental data set of size and distribution.
6. Enter the outlet concentration of the solute (supersaturation concentration) and the specific mass of the outlet solution.
7. You may now run the regression and view the results. The regression minimizes the residual with respect to the distribution values, the outlet concentration of the solute and the specific mass of the outlet solution. The regressed values can vary depending upon the starting values of the parameters and different combinations of parameters will give different quality regressions.

Guidelines

1. *The only inlet streams allowed are the feed stream and the optional feed addition stream.*
2. *The only outlet streams allowed are the slurry stream and the optional vapor outlet.*
3. *Default values are provided for all of the kinetics parameters, but careful selection of appropriate values is recommended.*
4. *If experimental data are available, regression of those data to determine nucleation and growth rate constants with OLI ToolKit is recommended.*

Additional Facilities

In addition to those facilities already described in the previous chapters of this section, facilities are available for the user to perform various operations within ESP Process Build. The functions are available in all Process Blocks and are screen specific (i.e., they are only available on certain screens). Access to the required facility is obtained by pressing the Action Key and choosing the appropriate facility.

The available facilities are described by screen option heading below.

File

This facility allows the movement of defined information from the screen to the case definition file. The options available depend on the context. Possible options include:

- Cancel -** This option allows the user to ignore the new block or stream or model, or to ignore the changes made to an existing one. Exit is assumed.
- Delete Block -** This option is active from the Process Block Display Screen, and allows the deletion of any block.
- Exit -** This option allows the user to exit from the respective stream or block display. When using this option, data is automatically saved.
- Merge -** This option allows a stream or model to be brought into the current one. Inflows from a merging stream which are not in the current model can be automatically added to the model.
- New -** This option creates a new stream, block, process, etc.
- Open -** This option allows the user to open another stream, block, or process and bring it into the current one. This is now the recommended way for bringing WaterAnalyzer ESP Streams (stored in an SMP file) into ESP Process or ESP Express.
- Save -** This option transfers the user defined data for a stream, process, model, or water sample to the appropriate disk file. The data is stored with an extension, depending on the type. For examples, process data is stored with the extension .BIN.
- Save as -** This option transfers the current user defined model or process to another disk file, either new or existing. As with Save, the data is stored with an extension, depending on type.

Units

At any point in the use of ESP Process Build the user has the facility to change the units in which process data is being defined. Initially, the data is expressed in SI units, but the values can also be displayed in ENGLISH or METRIC equivalent units. Alternatively, the user can customize a set of USER displayed units to suit specific requirements.

When changing units, any previously specified data is automatically converted to the selected displayed units *with the exception of volumetric flow units*. The units on concentration are set in Process Build and are converted, when the user changes units, provided a valid Chemistry Model exists.

User selected display units are saved between ESP sessions and are utilized until re-specified by the user.

Process

This facility produces a summary listing for the defined process block. Two options are available:

List By Block - This option produces a listing of process block inflows and outflows, by stream name.

List By Stream - This option produces a listing summarizing the process block from which a process stream originates and its corresponding process block destination.

Check

This facility allows the user to perform an automatic check to insure that the minimum data requirements for defining an individual process block have been met. Warning messages are displayed informing the user of any data omissions from the block definition.

Scratchpad

This option allows the user to perform detailed equilibrium calculations on an individual stream or unit. Refer to Process Stream Definition on page 265 for a full description.

Normalize

The Normalize facility allows the user to normalize the relative amounts of each chemical present in a stream and is only available when defining feed streams to a process block. Two options are available:

Flow - Keeping the ratio of the components constant, adjust the component flows to sum to the total flow of the stream.

Total Flow - Given the compositions, sum them and arrive at the total flow of the stream.

Inflows

This facility allows the user to define additional inflow chemical species to those previously defined in the Chemistry Model being used for the process. If this facility is used, the species are automatically included in the Chemistry Model Inflow list. However, the user must return to the Chemistry Model

section of ESP Process in order to recreate the Chemistry Model Definition and regenerate the Model Solver respectively prior to performing any process simulations.

This facility is only available when specifying inlet stream compositions to process units.

Flowsheet

This facility allows the user to see a Process Flow Diagram (PFD) Display of a process. (Note: The computer monitor you are using must support graphical output e.g., a VGA monitor.)

Process Analysis

On completing and saving the process block definition, the user should use the Process Analysis mode of ESP Process to execute, review and analyze the defined process.

Analysis Areas

On accessing the Process Analysis mode, the Analysis Areas available to the user are displayed. These Analysis Areas include:

- **Display Stream Results**
- **Display Block Results**
- **Process Material Balances**
- **Display Material Balances**
- **Calculate**

Display Stream Results

After the simulation has been completed, this area is used to display the results for individual process streams. The streams are identified by the user defined names, along with their flow to and from Process Blocks. The results are accessed by selecting the stream of interest using the Arrow Keys and Enter Key.

The stream composition and phase distribution, as well as other properties such as stream density, flow, and enthalpy, are then displayed.

ScratchPad

At this point the ScratchPad facility is available to perform a variety of point calculations.

(Reference Process Stream Definition,

Process Entry Stream Definition pg. 265 for a full description of ScratchPad facilities.)

View

Initially, the stream results show the phase distribution of the stream species and the component flows on an ionic species basis.

The facility is available to the user to change these display parameters, and is achieved via the Action Key and selecting the View facility. First, the user would select the type of species flow distribution:

Molec Composition - This selection sums the respective species flows occurring in different phases and displays the results as a total component flow. Ionic species are also recombined to be displayed on a molecular basis.

Ionic Composition - This selection sums the respective species flows occurring in different phases and displays the results as a total component flow.

Molecular Phases - This selection displays the respective species phase distribution and shows the flow of a component occurring in each phase. Ionic species are also recombined to be displayed on a molecular basis.

Ionic Phases - This selection displays the respective species phase distribution and shows the flow of a component occurring in each phase.

Scaling Tendencies - This selection displays the scaling tendencies for the solids, in decreasing order. A scaling tendency of 1.0 or greater indicates that a solid is likely to form.

Units

The units in which results are displayed can be changed to suit user requirements and is achieved via the Action Key and selecting the Units facility. The results can be displayed in SI, METRIC or ENGLISH equivalent units or alternatively, the selection of USER allows the customization of a set of units in order to meet specific requirements.

Display Block Results

After the simulation has been completed, this area is used to display the results for a selected Process Block. This option is available for all Process Blocks for which such information is essential. Block reports display primary operating parameters such as: Conventional Blocks generally report the heating or cooling duty required to satisfy the user defined operating conditions; Multi-Stage Blocks report column profiles, liquid and vapor compositions, scaling indices, and exchanger duties; etc.

Display Material Balances

After the simulation has been completed, this area is used to display the overall process material balance.

Calculate

In order to perform the steady-state calculation for the process, the Calculate option is used. This is achieved by selecting this function from the Analysis Area using the Arrow Keys and Enter Key.

The calculation is performed in stages. Initially the Chemistry Model is compiled, linked and then executed for the process case. The equilibrium stream properties are then determined for all user defined process inflows, then the individual block conditions are evaluated for the process. Finally, the steady-state process outlet condition is determined.

Additional Facilities

Process Analysis provides additional facilities to those previously described for the user to perform various operations. Access to the required facility is obtained via the Action Key and selecting the appropriate facility. Facilities available are:

- **CalcAids**
- **Recycle**
- **Restart**
- **File**

The facilities available are described by screen Option heading below.

Calcaids

This facility gives the user additional control over the calculations. Four options are available:

- **Set Guess**
- **Set Trace**
- **Set State**
- **Set Order**
- **Set Conv**

Set Guess

This option allows the user to guess a concentration for any species in any stream. It is especially useful for streams that have difficulty in converging.

Set Trace

This option will create a file with the extension .OUE and will contain a detailed convergence history for all Process Blocks. This is useful in determining probable causes for the nonconvergence of Process Block calculations.

Set State

This feature is not functional in ESP.

Set Order

This option will allow the user to specify the order of the blocks to be calculated. It will also allow the choice of executing only part of the process.

Set Conv

This option allows the user to control the convergence algorithm to improve the time a process will take to converge.

Recycle

When this facility is selected, an analysis for process recycle streams is done automatically and, if recycle exists, the user is allowed to choose from several options to define the tear stream and recycle convergence. These options and their functions are:

- | | |
|---------------------------|---|
| Select Tear(s) | Allows the user to define the tear stream(s) for their recycle loops. Either one of a list of the minimum tear stream possibilities can be selected or the user can select tear stream possibilities. |
| Tear Stream Guess | Allows the user to supply estimates for the tear stream(s). |
| Max Iterations | Change the default number of iterations that will be performed before a non-convergent case will be terminated. |
| Not Converged Rule | The choice to continue or stop when a loop does not converge. |
| Set Tolerances | Change the default tolerances that determine when a case has converged. |
| Convergence Parm. | Allows adjustment of the Wegstein theta recycle parameter. |

Convergence Method

- | | |
|-----------------|--|
| <i>Wegstein</i> | The traditional method of converging a recycle loop. |
| <i>Newton</i> | This method perturbs each material balance group and Temperature, pressure and flow to obtain a matrix of derivatives. This allows for a slope-like technique to converge a recycle stream. This is very useful when the Wegstein method seems to be unstable. |

If the user selects the Calculate facility without having chosen the tear stream, the user is placed within the Recycle facility to select the tear stream.

Restart

This facility gives the user the option of initializing a recycle stream or a Multi-stage process block with the results from the previous case run.

Summary

A hard copy of the results produced from Process Analysis can be produced using the Summary mode of ESP Process. The results can be printed or stored in a disk file in a variety of units.

Planned facilities for the Summary Mode include the ability to export data and the ability to plot.

Method

On accessing the Summary mode, a report is displayed summarizing the process report output parameters. The report output destination, results units and stream option type are all displayed.

All of these settings can be changed using the Action Key and selecting the appropriate facility. The available facilities are described below.

Output

This facility allows the user to select the destination of the summary report. The results can be sent to printer or to a disk file. The required output destination is selected using the Arrows and Enter Key.

If the results are sent to disk, the file name is the same as that specified for the process during Process Build, and the file extensions is .LIS.

Units

This facility allows the user to specify the units in which results are produced in the summary report. The results can be produced in SI, METRIC, or ENGLISH equivalent units or, alternatively, the selection of USER allows the customization of a set of units to meet specific requirements. The required units are selected using the Arrow Keys and Enter Key.

Options

This facility allows the user to select the species type and distribution for stream results. Species concentrations can be expressed on an ionic or molecular component basis, and can be shown as a total flow or by their respective physical phase distributions. Four options are available:

Total species flows (molecular basis)

Total species flows (ionic basis)

Phase molecular flows (Aq, Vap, etc.)

Phase ionic flows (Aq, Vap, etc.)

A selection is made from this list using the Arrow Keys and Enter Key.

Guidelines

When selecting summary report requirements, the report parameters initially displayed are not updated until the user exits from the Action Bar facility.

Report Generation

The summary report is produced simply by positioning the cursor on the Generate Report option shown on the display and pressing the Enter Key.

Chapter 7. Process Applications

General Description

This Applications section contains specific examples of using ESP Process and should guide the user in generating Chemistry Models and simulating processes.

Overview

The Applications described in this section include simple Chemistry Model generation and the addition of chemical reaction phenomena, including the use of private databank information. The processes described include most individual, or combinations of, Process Blocks available through ESP Process inside Process Build. Dynamic simulation is also included and related to specific engineering problems.

Initially, the procedure for generating a simple Chemistry Model is described. This model is the one used for all the Conventional Process Block simulations. In addition, the procedure for generating a Chemistry Model is the same for the specific engineering examples described.

Process examples are then described. For applications involving specific chemistry, the rESPective Chemistry Models are included at the end of the section for reference.

Content

Some specific engineering applications described in this section include:

- **Two Stage Neutralization Process (Steady State and Dynamic)**
- **Solvent Extractor**
- **Stripper**

- **Absorber**

Each process will now be considered in more detail.

Chemistry Model Generation

This chapter describes the creation of a simple Chemistry Model and is used in various block examples described in the following chapters of this section.

Process Name

Using the ESP Process component of ESP, the user is first prompted to select the required process. The user should select the New Process option and then identify the process with a name (e.g., DEMO1).

Chemistry Model

On naming the New Process, the Chemistry Model Mode is selected and the New Model option should be chosen. The Chemistry Model can then be named (e.g., DEMO1). The name can be the same or different from the process name.

Thermodynamic Framework

Select the Aqueous Thermodynamic Framework by using the arrow keys to position the cursor and then press the <Spacebar> to select the framework. Press <Enter> to continue

Databooks

A list of available Databooks will be displayed. We will not use any additional Databooks. Press <Enter> to continue.

Process Chemistry

After naming the Chemistry Model, the user supplies a list of chemical inflow species to be considered. The species for this example are as follows:

H2O

C13H28

BENZENE

CACO3

NAOH

O2

The species phases are then defined.

Phase

The phases to be considered are selected using the Arrow Keys and the <Space Bar>. The default phases are Vapor and Solid phases. For this example an Electrolyte Model is to be created considering the Vapor, Organic Liquid and Solids phases.

Chemistry Model Definition

On specifying the phases to be considered the Chemistry Model Definition file is created.

Solids Deletion

Any hydrate species predicted through the automatic Chemistry Model creation do not need to be considered for this example. These are removed via the Action Key and selecting the SOLIDS facility. The species to be omitted are:

NA2CO3.10H2O

NA2CO3.1H2O

NA2CO3.7H2O

NAOH.1H2O

The species are selected using the Arrow Keys and the character "N" key.

The solver files can then be generated which completes the Chemistry Model generation.

The Chemistry Model Definition can be referred to below:

```
ESP FRAME EDAT TERM DISK
;
;      *** INPUT      ****
;
INPUT
H2OIN          INFL
C13H28IN       INFL
BENZENEIN      INFL
CACO3IN        INFL
NAOHIN         INFL
O2IN           INFL
CO2IN
NAHCO3IN
CAOH2IN
NA2CO3IN
TRONAIN
WEGSCHEIDERIN
CAHCO32IN
CAHCO32CO3IN
CAHCO3HCO3IN
CAHCO3OHIN
H2CO3IN
NA3HCO32IN
;
;          *** SPECIES ****
;
SPECIES
BENZENEVAP
C13H28VAP
CO2VAP
H2OVAP
O2VAP
H2O
BENZENEAQ
C13H28AQ
CACO3AQ
CO2AQ
NAHCO3AQ
O2AQ
CAHCO3ION
CAION
CAOHION
CO3ION
HCO3ION
HION
NACO3ION
NAION
OHION
CACO3PPT
CAOH2PPT
```



```

NA2CO3PPT
NAHCO3PPT
NAOHPPT
TRONAPPT
WEGSCHEIDERPPT
;
;          *** SOLID SCALING TENDENCY ****
;
SOLIDS
ALL
;
;          *** EQUILIBRIUM EQUATIONS ****
;
EQUILIBRIUM
BENZENEVAP=BENZENEAQ
C13H28VAP=C13H28AQ
CACO3AQ=CAION+CO3ION
CACO3PPT=CAION+CO3ION
CAHCO3ION=CAION+HCO3ION
CAOH2PPT=CAION+2OHION
CAOHION=CAION+OHION
CO2AQ+H2O=HION+HCO3ION
CO2VAP=CO2AQ
H2O=HION+OHION
H2OVAP=H2O
HCO3ION=HION+CO3ION
NA2CO3PPT=2NAION+CO3ION
NACO3ION=NAION+CO3ION
NAHCO3AQ=NAION+HCO3ION
NAHCO3PPT=NAION+HCO3ION
NAOHPPT=NAION+OHION
O2VAP=O2AQ
TRONAPPT=3NAION+CO3ION+HCO3ION+2H2O
WEGSCHEIDERPPT=5NAION+3HCO3ION+CO3ION
END

```

Conventional Process Block Applications

This chapter describes in detail specific applications for the Conventional Process Blocks available in ESP Process. The procedure for defining each block is described and the results produced by the Summary mode are included at the end of each section for reference.

The Conventional Process Blocks applications described in this chapter are:

Mix This process block is being used to combine two feed streams and bring the outlet temperature of the stream to the bubble point temperature.

Component Split This process block is being used to split a single multi-component effluent feed into two exit streams, one of which contains user-defined species component fractions.

Separate This process block is being used to separate a single feed stream into four distinct physical phases. Concentration limits for each of the four phases are specified.

Heat Exchange This process block is being used to simulate the heating of an effluent stream using a utility water flow. From the specified temperatures, the utility flow is determined for the required heat duty.

The following describes each process in more detail.

Mix Block

For this specific application, the Mix Block is used to combine two feeds into one stream, with the outlet conditions at the bubble point of the stream. The simple Chemistry Model previously described in is used for this particular example.

Process Summary

The Mix Block is used to combine two streams into a single stream at its bubble point condition. Generally, this block is used as part of a process involving several process blocks. However, for example purposes this block is simulated individually.

Process Build

On naming the process block (e.g., MIX) the first feed stream to the block is named (e.g., FEED1) and its parameters specified as:

Temperature	25° C
Pressure	1.0 atm
Total flow	800 mol/hr
H2O	798
CACO3	1.0
NAOH	0.6

The second stream feed stream to the block is named (e.g., FEED2) and its parameters specified as:

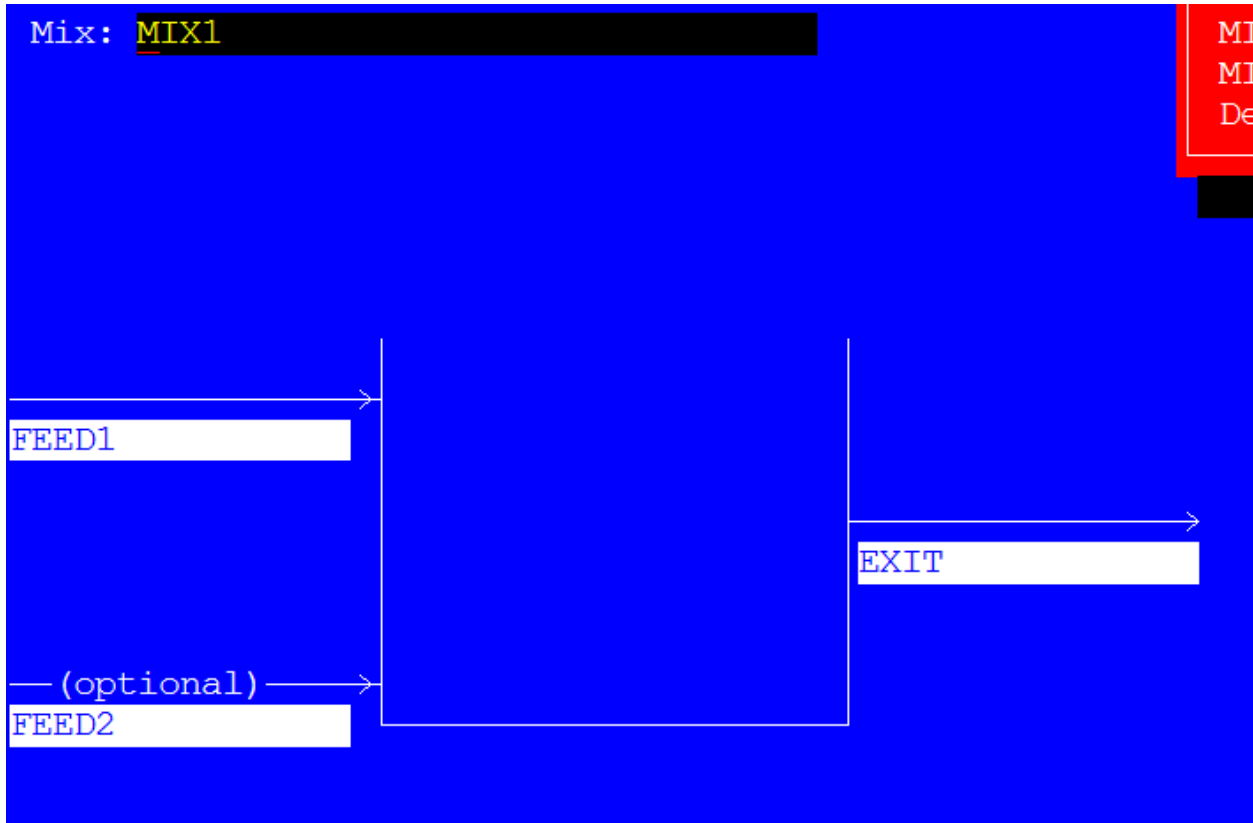
Temperature	30° C
Pressure	1.0 atm
Total flow	10 mol/hr
H2O	9.0
C13H28	0.1
BENZENE	0.9

The outlet stream from the block is then named (e.g., EXIT).

Parameters

The outlet conditions of the block outlet stream are defined using the Action Key and selecting the Parameters facility. The Bubble Point Temperature equilibrium calculation should be selected, varying the temperature of the stream with no change in the pressure.

The format of the process block display is:



Process Analysis

The process definition is now complete and should be saved. The case is executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis, a summary of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The inlet and outlet streams for the Mix Block are shown on an ionic basis as follows:

Stream	FEED1	FEED1	FEED2	FEED2	EXIT	EXIT	EXIT
Phase	Liquid-1	Solid	Liquid-1	Vapor	Liquid-1	Solid	Vapor
Temperature, C	25	25	30	30	25.52168	25.52168	25.52168
Pressure, atm	1	1	1	1	1	1	1
pH	12.537		6.917		12.516		
Total mol/hr	799.6032	0.99838	8.977	1.023	809.4481	0.998357	0.15513
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr
H2O	798.3992		8.957777	0.042223	807.3949		0.004291
CO2	3.05E-12				3.36E-12		9.28E-13
CACO3	0.000275	0.99838			0.000279	0.998357	
NAHCO3	2.40E-07				2.46E-07		
OHION	0.599844		1.95E-08		0.59984		
CAION	0.001384				0.001398		
CAOHION	0.000462				0.000466		
CO3ION	0.001767				0.001786		
HCO3ION	5.88E-06				6.19E-06		
HION	5.11E-12		1.95E-08		5.42E-12		
NACO3ION	7.25E-05				7.24E-05		
NAION	0.600227				0.600228		
CAHCO3ION	3.10E-09				3.17E-09		
C13H28			1.95E-06	0.099998	0.001251		0.098749
BENZENE			0.019221	0.880779	0.847911		0.052089
Total g/hr	14407.65	99.92511	162.8791	87.99863	14636.18	99.92284	22.35241
Volume, L/hr	14.42623	0.03687	0.163709	24.0645	14.66089	0.036869	3.061999
Enthalpy, cal/hr	-5.5E+07	-287559	-610890	7599.569	-5.5E+07	-287542	-6612.18
STD Liq Vol, L/hr	14.43901	0.045924	0.163571	0.104023	14.67772	0.045923	0.028878
Density, g/L	998.7122	2710.19	994.9298	3.656782	998.3146	2710.19	7.29994
Vapor fraction				1			1
Solid fraction		1				1	
Osmotic Pres, atm	1.945113				3.343055		
Ionic Str, Molal	0.042174		1.21E-07		0.041709		
Ionic Str, Mol Fra	0.000759		2.18E-09		0.000749		

Component Split Block

For this specific application, the Component Split Block is used to split a feed into two streams, one of which contains user defined species component fractions. The simple Chemistry Model previously described in this section is used for this particular example.

Process Summary

The Component Split Block is used to split a single multi-component feed stream into two exit streams, one of which contains user defined species component fractions. Generally, this block is used as part of a process involving several process blocks. However, for example purposes this block is simulated individually.

Process Build

On naming the process block (e.g., C-SPLIT) the feed stream to the block is named (e.g., FEED) and its parameters specified as:

Temperature	25° C
Pressure	1.0 atm
Total flow	100 mol/hr
H2O	55.51
C13H28	0.10
BENZENE	0.05
CACO3	0.10
NAOH	0.50
O2	0.25

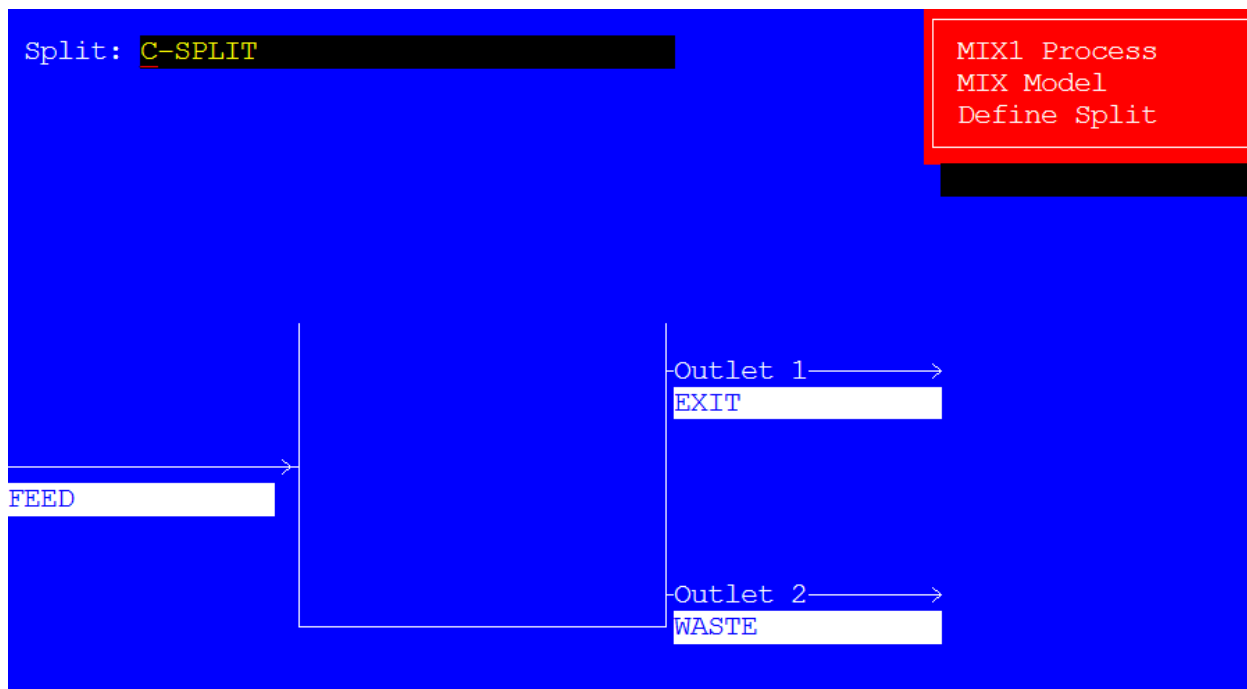
The outlet and residual streams are then named (e.g., EXIT, WASTE).

Parameters

The required individual species component fractions in the block outlet stream are defined using the Action Key and selecting the Parameters facility. The Split Flow/Frac parameter should be selected. The component fractions should be defined as:

<u>Component</u>	<u>Fraction</u>
H2O	0.5
C13H28	0.1
CO2	
BENZENE	0.02
CACO3	
NAOH	0.05
O2	0.25

The format of the process block display is:



Process Analysis

The process definition is now complete and should be saved. The case is executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis, a summary of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process results for this example.

Stream	FEED	EXIT	WASTE
Phase	Mixed	Mixed	Mixed
Temperature, C	25	25	25
Pressure, atm	1	1	1
Flow Units	mol/hr	mol/hr	mol/hr
H2O	98.23043	49.11438	49.11595
C13H28	0.1769602	0.01769602	0.1592635
CO2	8.15E-14		6.36E-14
BENZENE	0.0884799	0.001769599	0.0867104
O2	0.4423992	0.1105996	0.3318
NAHCO3	4.93E-08		7.96E-08
CACO3	0.1753857		0.1719763
OHION	0.88266	0.04424	0.830819
CAION	2.74E-04		5.20E-05
CAOHION	4.60E-04		1.23E-04
CO3ION	0.00156713		0.00498072
HCO3ION	1.75E-07		1.86E-07
HION	7.82E-14	2.68E-13	2.19E-14
NACO3ION	6.66E-06		2.83E-06
NAION	0.884792	0.04424	0.840556
CAHCO3ION	5.16E-11		1.42E-11
CAOH2	8.40E-04		0.00480859
Total mol/hr	100.8843	49.33292	51.54705

Total g/hr	1876.45	893.522	982.926
Volume, m3/hr	0.0185183	0.00409684	0.0145963
Enthalpy, cal/hr	-6.87E+06	-3.36E+06	-3.51E+06
Vapor fraction	0.006981099	0.002683137	0.01125981
Solid fraction	0.001746715		0.003429488
Organic fraction			

Separate Block

For this specific application the Separate Block is used to separate a single feed stream into four distinct physical phases. The Chemistry Model for this example is described in this section.

Process Summary

The process involves a single, multi-component feed stream being separated into vapor, aqueous, organic liquid and solid phases. Concentration limits are also specified for the four phases.

Process Build

On naming the process block (e.g., SEPARATOR) the feed stream to the block is named (e.g., FEED) and its composition specified. The feed properties are:

Temperature	50° C
Pressure	1.0 atm
Flow	100 mol/hr
H2O	55.58
C13H28	0.10
BENZENE	0.05
CACO3	0.05
NAOH	0.10
O2	0.01

On specifying the feed stream composition the four exit streams are named (e.g., GAS, EFFLUENT, ORGANIC, SOLIDS).

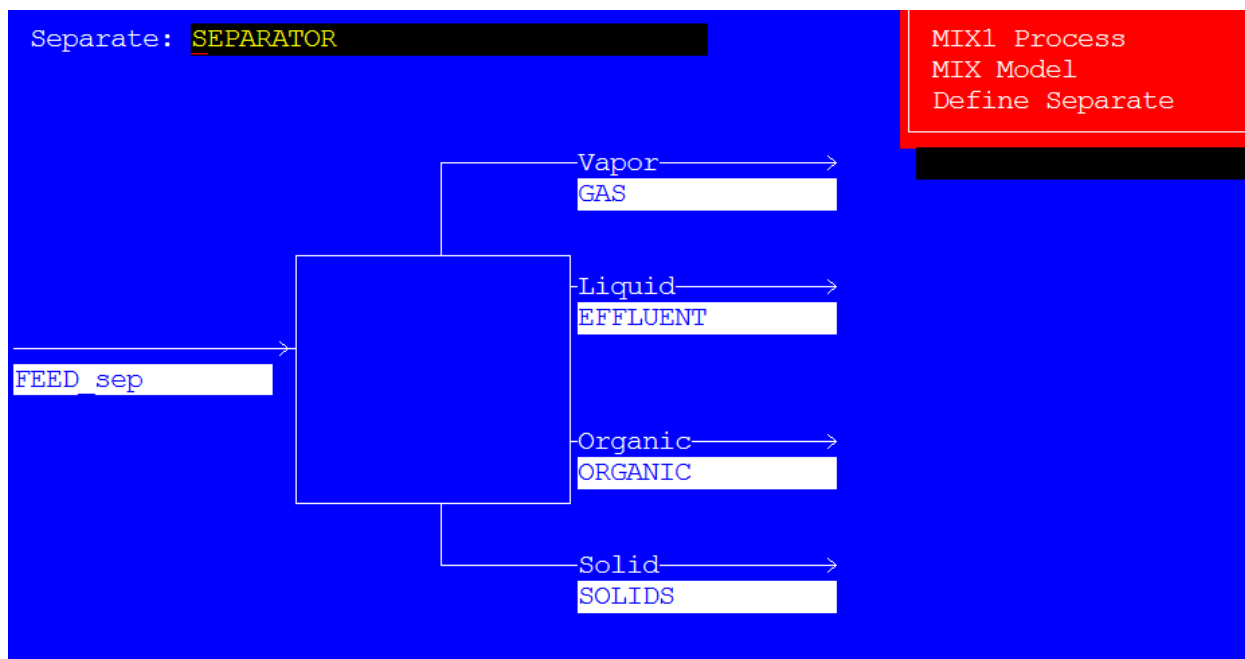
Parameters

The exit stream concentration limits are specified after naming the outlet streams. This is achieved via the Action Key and selecting the Parameters facility and the entrainment option.

For this example, the concentration limits are as follows:

<u>Parameter</u>	<u>Concentration gms/gms</u>
Suspended solids in liquid	0.002
Entrained liquid in vapor	0.002
Dissolved liquid in solid	0.03
Dissolved vapor in liquid	0.0002
Dissolved aqueous in organic	0.03
Dissolved organic in aqueous	0.001

The Block Parameters specification is now complete. The format of the process block display is:



Process Analysis

The process definition should be saved and the case executed using the Process Analysis mode of ESP Process.

Summary

On completing the Process Analysis, a copy of the results can be requested using the Summary mode.

The output on the next page summarizes the process for this example.

The streams for the Separate Block, shown on an ionic basis:

Stream	FEED	FEED	FEED	FEED
Phase	Aqueous	Solid	Vapor	Liquid
Temperature, C	50	50	50	50

Pressure, atm	1	1	1	1
pH	12.161			
Total mol/hr	99.81803	0.0891269	0.0215541	0.2504087
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr
H2O	99.4423		0.002642344	4.33E-04
C13H28	4.40E-08		7.03E-06	0.178916
CO2	1.21E-12		7.73E-13	1.48E-13
BENZENE	0.0161743		0.002783695	0.0705034
O2	0.00121521		0.01612103	5.56E-04
NAHCO3	4.89E-08			
CACO3	1.10E-05	0.0891269		
OHION	0.178772			
CAION	1.71E-04			
CAOHION	1.52E-04			
CO3ION	3.12E-04			
HCO3ION	1.29E-06			
HION	1.66E-12			
NACO3ION	1.02E-05			
NAION	0.178913			
CAHCO3ION	5.26E-10			
Total g/hr	1799.98	8.92047	0.782199	38.5192
Volume, m3/hr	0.00181427	3.29E-06	5.70E-04	5.34E-05
Enthalpy, cal/hr	-6.77E+06	-25625.2	-93.4137	-14794.6
Density, g/m3	992122	2.71E+06	1372.5	721308
Vapor fraction			1	

Solid fraction		1		
Organic fraction				1
Osmotic Pres, atm	5.16621			
Redox Pot, volts				
Ionic Strength	0.100415			

Heat Exchange

For this application, the Heat Exchange Block is used to simulate the heat transfer between two aqueous streams. The simple Chemistry Model previously described in this section is used for this example.

Process Summary

The process involves a waste effluent stream being heated to a specified temperature using a utility water stream. The utility stream inlet and outlet temperatures are known and the simulation is used to determine the utility flow required to provide the specified heat duty.

Generally, this block is used as part of a process involving several process blocks. However, the block is operated individually for this example.

Process Build

On naming the process block (e.g., WASTE HEATING) the process entry stream to the block is named (e.g., WASTE) and its parameters specified as:

Temperature	15° C
Pressure	1.0 atm
Flow	200 mol/hr
H2O	55.51
C13H28	0.25
BENZENE	8.0E-02
CACO3	0.12
NAOH	0.50

O2 0.30

The utility inlet stream to the block is then named (e.g., HOT WATER) and its parameters defined as:

Temperature	55° C
Pressure	1.0 atm
Flow	200 mol/hr
H2O	200

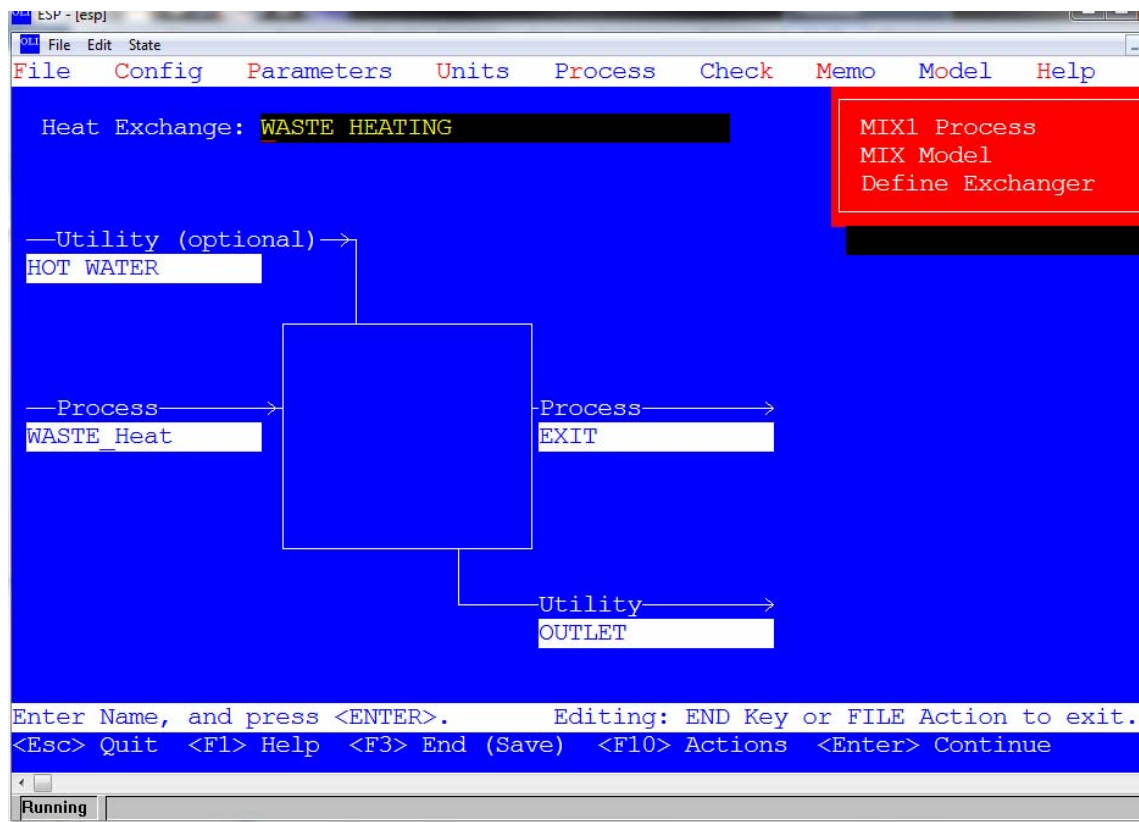
The process and utility exit streams from the block are named (e.g., EXIT, OUTLET)

Parameters

The block operating parameters are specified via the Action Key and selecting the Parameters facility. Initially, the process stream requirements are defined. The user should select the process Discharge Temperature and define the value as 40° C. For this example, the user should also confirm that a utility stream is to be used.

The utility stream Discharge Temperature option is then selected and specified as 35 Deg. C.

This completes the process definition and the format of the block display is:



Process Analysis

On saving the process block definition the case is executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis a copy of the results can be produced using the Summary mode.

The output on the next page summarizes the process results for this example.

The process and utility streams to the Heat Exchange Block, shown on an ionic basis:

Stream	Waste Heating	Hot Water	EXIT	OUTLET
Phase	Mixed	Aqueous	Mixed	Aqueous
Temperature, C	15	55	40	35
Pressure, atm	1	1	1	1
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr
H2O	195.5959	253.494	195.5958	253.494
C13H28	0.8809025		0.8809016	
CO2	5.08E-14		2.21E-12	
BENZENE	0.2818883		0.2818886	
O2	1.057082		1.057087	
NAHCO3	7.67E-08		1.38E-07	
CACO3	0.4197073		0.4196946	
OHION	1.75782	9.63E-07	1.75718	5.19E-07
CAION	6.36E-04		4.12E-04	
CAOHION	9.91E-04		8.25E-04	
CO3ION	0.00311509		0.00311505	
HCO3ION	1.87E-07		8.22E-07	
HION	6.86E-14	9.63E-07	4.64E-13	5.19E-07
NACO3ION	9.81E-06		2.21E-05	
NAION	1.76179		1.76178	
CAHCO3ION	6.70E-11		1.83E-10	

CAOH2	0.00149861		0.00190081	
Total mol/hr	201.7613	253.494	201.7606	253.494
Total g/hr	3854.76	4566.78	3854.76	4566.78
Volume, m3/hr	0.051433	0.00463297	0.061064	0.00459529
Enthalpy, cal/hr	-1.38E+07	-1.72E+07	-1.37E+07	-1.73E+07
Vapor fraction	0.01077982		0.0116613	
Solid fraction	0.002087556		0.002089486	
Organic fraction				

Multi-Stage Process Block Applications

This chapter describes in detail specific applications for the Multi-stage Process Blocks available in ESP Process. The procedure for defining each block is described and the Process Analysis results are included for reference.

The Multi-stage Process Blocks applications described in this chapter are:

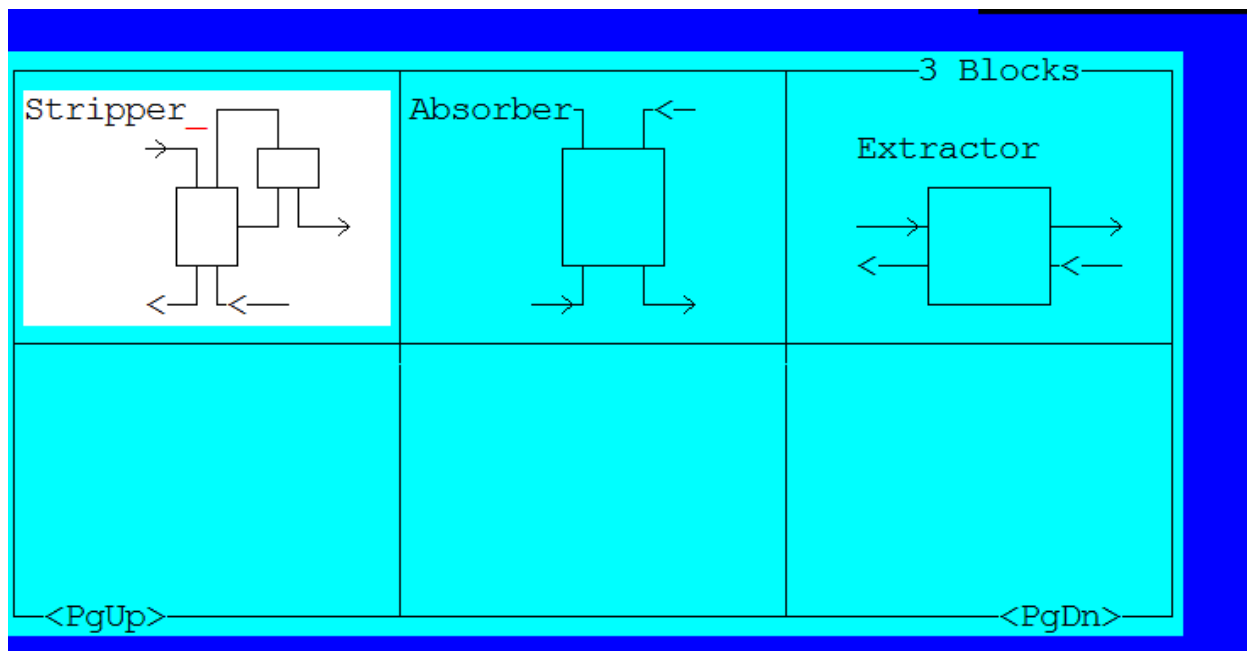
Stripper This process block is being used to determine the feasibility of steam stripping several organics from a wastewater effluent.

Stripper (Distillation) This process block is being used to simulate a chemically reactive organic distillation process. The vapor flow from the top of the column is controlled by modulating the condenser heat duty.

Absorber This process block is being used to determine the feasibility of removing sulfur contained in an off gas, using a sodium hydroxide absorbing stream. Preliminary column design parameters and caustic flow requirements are determined.

Solvent Extractor This process block is being used to simulate the extraction of phenol from a spent caustic stream, using light gas oil as the solvent. The solvent flow requirements are determined for a specific phenol removal.

The following sections describe each process in more detail.



Stripper Block

For this specific application the Electrolyte Stripper Block is used to determine the feasibility of steam stripping several organics from a wastewater stream and to determine preliminary design parameters to obtain a specified concentration of nitrobenzene. The Chemistry Model for this example can be created as in the preceding sections. The inflow chemistry is:

H₂O

NITBNZ

TOLUENE

BENZENE

NACL

MDCLBNZN

Process Summary

The process involves a wastewater stream passing to a 10 stage stripping column. Steam passes through the column counter-currently and strips the organics from the wastewater, which additionally contains dissolved inorganic salts.

Process Build

The condenser and reboiler will not be used in this example. Remove the reboiler by using the Action Key, selecting the Config facility and choosing the Reboiler option. The picture of the reboiler on stage 1 disappears. Remove the condenser using the Action Key, selecting the Config facility and choosing the Condenser option. The picture of the condenser on stage 10 disappears.

On naming the process block (e.g., STM-STRIPPER) the top entry stream to the column is named (e.g., WASTE WATER) and its parameters specified as:

Temperature	25° C
Pressure	1.0 atm
Flow	500 mol/hr
H2O	0.7156
NITBNZ	7.16E-02
TOLUENE	5.787E-02
BENZENE	5.166E-02
NACL	5.0E-02
MDCLBNZN	5.37E-02

The top and bottom exit streams from the block are then named (e.g., TOPS, BOTTOMS).

Configuration

The steam stripping stream is added to the block by using the Action Key, selecting the Config facility and choosing the Feed Streams option from the menu.

The stream entering the bottom of the column is then named (e.g., STEAM) and its parameters specified as:

Temperature	115° C
Pressure	1.5 atm
Flow	2000 mol/hr
H2O	2000

The stage location of this feed stream is then specified as -1.

Parameters

The block operating parameter estimations are made via the Action Key and then selecting the Parameters facility.

Pressure Profile The column operating pressure are specified as:

<u>Stage</u>	<u>Pressure, atm</u>
10	1.38
9	1.40
1	1.50

Column Estimates The top and bottom operating temperature are specified as:

<u>Stage</u>	<u>Temperature Deg. C.</u>
10	101
1	105

The vapor distillate rate is estimated as 1500 mol/hr and the liquid reflux rate as 540 mol/hr.

Spec/Controls This nitrobenzene flow in the liquid exiting the base of the column is to be controlled by varying the steam flowrate to the column. On selecting Add New Specification, the Specification Variable - Liquid Component rate from a stage is chosen using the Arrow Keys and Enter Key. The specification is the defined as:

Stage Number	1
Spec Value	0.1 mol/hr

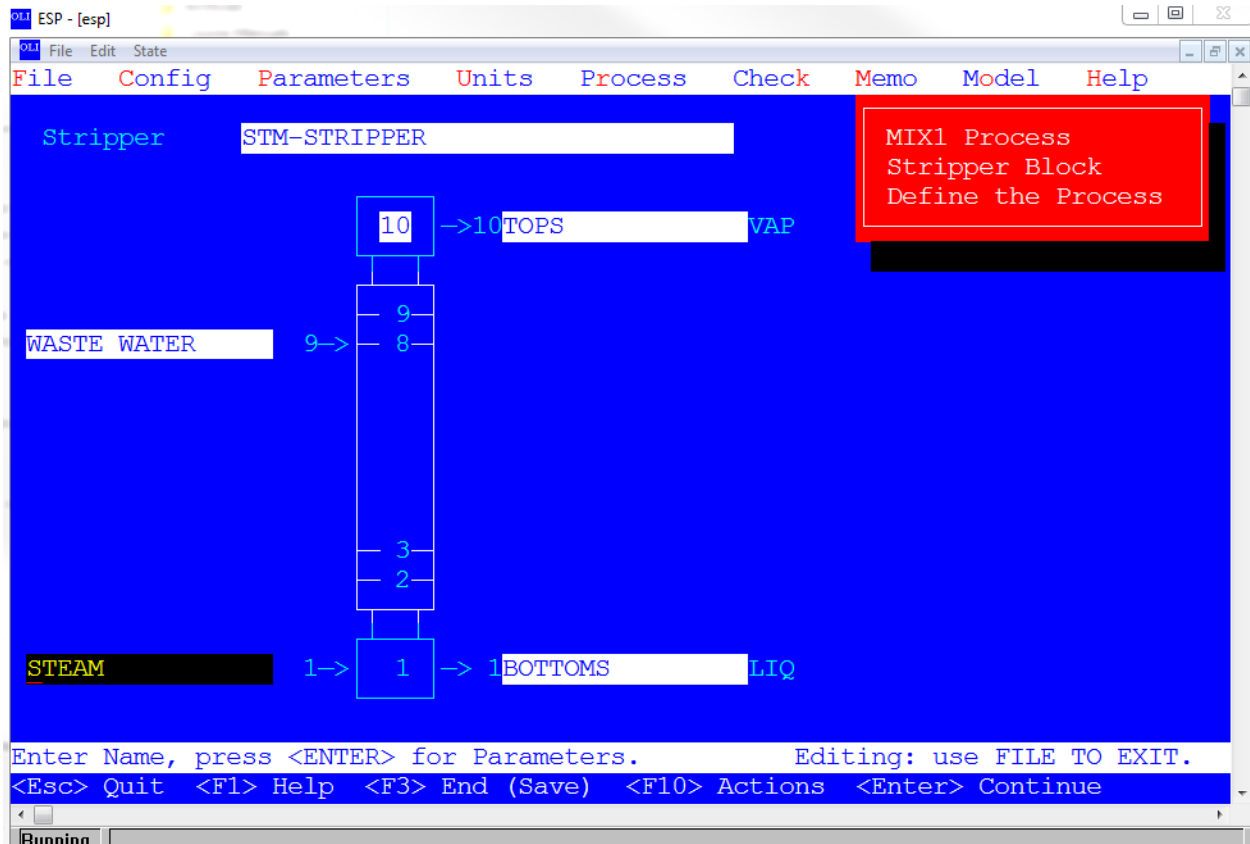
The Species for which its outlet concentration is to be controlled, Nitrobenzene, (i.e., NITBNZ), is then selected using the Space Bar and Enter Key. The variable to be controlled, which is Feed Stream Flow Rate, is chosen and the Stage Number for Control Variable is defined as stage 1.

The control requirement is now completely defined and the user should now Exit from this option.

Exchanger Duties This option is not used for this example because the condenser and reboiler are not used..

Tray Efficiencies This option is not used as the trays are assumed to have 100% efficiency.

The process definition is now complete and should be saved. The format of the process block display is:



Process Analysis

On saving the process definition, the case is executed using the Process Analysis mode of ESP. The results are displayed via the Process Streams Display and Process Block Display.

Summary

A results summary is shown at the end of this section and was produced using the Summary mode of ESP Process.

The process streams to this Stripper are shown on an ionic basis. Please note: a stream displayed on an ionic basis does not have the same number of moles as a stream displayed on a molecular basis. Thus the total flow for the stream "WASTE WATER" on this page (525.01 mol/hr) differs from the total flow that was entered (500 mol/hr).

Stream	WASTE WATER	STEAM	TOPS	BOTTOMS
Phase	Mixed	Vapor	Vapor	Aqueous
Temperature, C	25	115	48.3311	115.259
Pressure, atm	1	1.5	1.38	1.49999
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr
H2O	358.0042	99.4743	8.57399	448.904
BENZENE	25.59461		25.5946	4.74E-11
HCL	1.97E-11		3.69E-10	7.51E-10
MDCLBNZN	26.61513		26.6152	4.74E-11
NITBNZ	35.82043		35.7204	0.1
TOLUENE	28.95152		28.9515	4.74E-11
OHION	4.09E-07			9.74E-06
HION	4.09E-07			9.74E-06
NAION	25.0143			25.0143
CLION	25.0143			25.0143
Total mol/hr	525.0145	99.4743	125.4557	499.0326
Total g/hr	20900.9	1792.06	13131.6	9561.38
Volume, m3/hr	2.06322	2.08831	2.19155	0.00910225

Enthalpy, cal/hr	-2.55E+07	-5.68E+06	1.16E+06	-3.24E+07
Vapor fraction	0.1718909	1	1.000002	
Solid fraction				
Organic fraction				

===== BLOCK REPORT =====

BLOCK NAME: STM-STRIPPER

BLOCK TYPE: Absorber

=====

Overall Column Mass and Heat Balance

Duty, cal/hr 0.0

	In	Out	Rel. Diff.
Total Mass g/hr	22692.9	22692.9	4.84306E-13
Total Energy cal/hr	-3.12199E+07	-3.12200E+07	5.19916

Column Profile

Stage	Temperature	Liquid Rate	Vapor Rate	Pressure
	C	mol/hr	mol/hr	atm
10	48.33333	453.4518	125.4546	1.379967
9	68.31111	466.429	53.89585	1.399973
8	68.66667	466.5198	66.88673	1.412493

7	69.33333	466.5198	66.98199	1.425014
6	71.43889	466.6105	66.97745	1.437466
5	78.07778	468.7424	67.03188	1.449986
4	92.56111	478.54	69.17284	1.462507
3	107.5	491.6488	79.00218	1.475027
2	113.7556	497.5908	92.111	1.48748
1	115.2611	499.0423	98.01224	1.5

Absorber Block

For this particular example the Absorber Block simulates the removal of sulfur from an off gas stream using a sodium hydroxide absorbing stream. The Chemistry Model for this example is described in this section.

Process Summary

An organic phase off gas generated from a stripping unit contains water, methanol, hydrogen sulfide and methyl mercaptan. The sulfur contained in this stream is to be removed prior to transferring the off gas to a lime kiln. It is proposed to remove the sulfur by absorption using a sodium hydroxide solution.

The simulation uses an Absorber Block to determine preliminary unit design and operating conditions. Multiple cases are executed to determine optimum design parameters. The parameters which are varied include number of column stages, sodium hydroxide strength and flowrate, and the inclusion of column condenser and reboiler.

Process Build

On naming the process block (e.g., OFF GAS SCRUBBER) the number of column stages should be specified as 6 by changing the displayed value of 10. The inlet stream to the top of the column should then be named (e.g., WHITE LIQUOR) and its conditions specified as:

Temperature	100° C
Pressure	1 atm
Total Flow	112665 gmols/hr
H2O	106078
NAOH	4542.50

NA2S	1362.75
NA2CO3	681.375

On specifying the stream conditions its entry point into the column needs to be defined. The feed location is stage 6 and it is specified by changing the displayed value of 9. The vapor stream entering the bottom of the unit is then named (e.g., OFF GAS) with its phase enclosed in (), (i.e., (VAP)), and its parameters specified as:

Temperature	127° C
Pressure	2.36 atm
Flow	26697 mol/hr
H2O	13861
METHANOL	10626
H2S	1105

MEMERCAPTAN 1105

The top and bottom exit streams from the block are then identified (e.g., SCRUBBED GAS and WASTE LIQUOR)

Configuration

In order to improve methanol recovery from the top of the column, a reboiler is to be included on the Absorber Block. This is achieved via the Action Key, selecting the Config facility, and choosing the Reboiler option from the following menu.

The Absorber Block display is automatically updated to include the reboiler.

Parameters

On naming the column exit streams the column operating conditions are defined. This is achieved via the Action Key.

Pressure Profile The top and bottom column operating pressures are defined as 1 atm.

Column Estimates The column operating temperatures are as follows:

<u>Stage</u>	<u>Temperature</u>
6	90

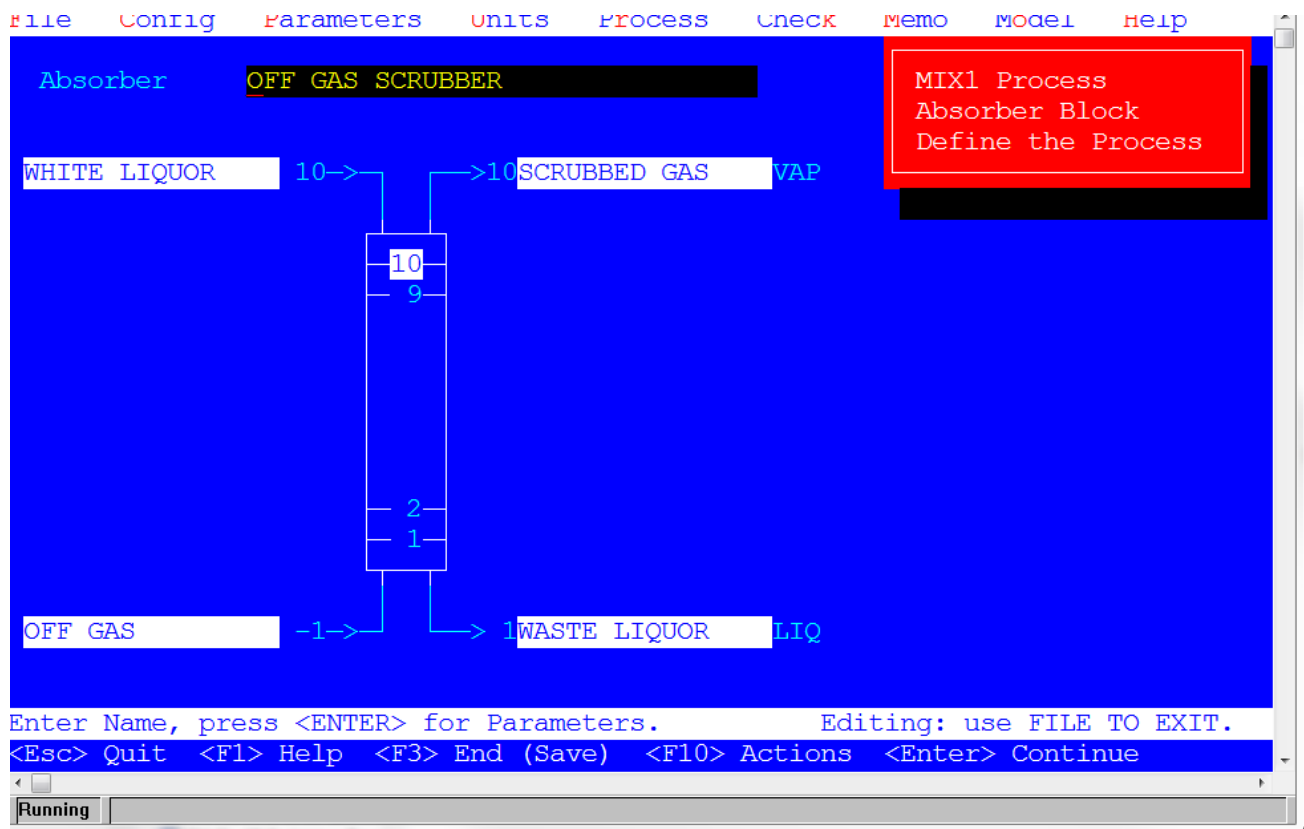
The vapor distillate flow exiting the top of the column is estimated as 37000 mol/hr. A zero liquid reflux flow estimation from the column is also specified.

Spec/Controls For this particular example no Spec/Control specifications are required.

Exchanger Duties This option is used to define the reboiler heat duty. A value of 85 MMcal/hr should be specified.

Tray Efficiencies This option is not used for this example as the trays are assumed to be 100% efficient.

The process definition is now complete and the format of the block display is as follows:



Process Analysis

The process definition can now be saved and the case executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis a results summary can be produced using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The process streams to this Absorber, shown on an ionic basis:

Stream	White Liquor	Off gas	Scrubbed gas	Waste Liquor
Phase	Aqueous	Vapor	Vapor	Aqueous
Temperature, C	100	127	97.9703	94.319
Pressure, atm	1	2.36	0.999997	0.999997
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr
H2O	106062	13863.4	31695	91504
CO2	7.74E-09		3.54E-05	6.41E-08
H2S	7.59E-06	1104.79	0.0073434	4.20E-05
NAHCO3	0.00345708			0.019413
OHION	4559.35			1286.16
CO3ION	161.681			557.506
HCO3ION	0.0581393			0.330027
HION	1.89E-09			2.07E-09
HSION	16.7552			48.7547
NACO3ION	519.637			123.525
NAION	8110.18			8506.27
SION	1345.51			2418.29
MEMERCAPTAN		1104.79	3.94651	4.94883

METHANOL		10624	7135.37	3488.66
CH3SION				1095.9
Total mol/hr	120775	26696.98	38834.32	109034
Total g/hr	2.27E+06	680976	799821	2.15E+06
Volume, m3/hr	2.04291	364.347	1171.69	1.92093
Enthalpy, cal/hr	-7.93E+09	1.30E+09	-2.15E+09	-7.00E+09
Vapor fraction		1.000001	0.9999994	
Solid fraction				
Organic fraction				

===== BLOCK REPORT =====

BLOCK NAME: Off Gas Scrubber

BLOCK TYPE: Stripper

=====

Overall Column Mass and Heat Balance

Duty, cal/hr 8.50000E+07

	In	Out	Rel. Diff.
Total Mass g/hr	2.95225E+06	2.95226E+06	2.51107E-06
Total Energy cal/hr	-9.23094E+09	-9.14599E+09	5.37388

Heat Exchanger Duties

Stage Duty, cal/hr

1 8.50557E+07

Column Profile

Stage	Temperature	Liquid Rate	Vapor Rate	Pressure
	C	mol/hr	mol/hr	atm
6	97.97222	121436.	38833.86	1.
5	96.31111	121363.	39459.82	1.
4	95.71667	121250.	39365.47	1.
3	95.43333	120978.	39237.56	1.
2	95.11111	120347.	38939.09	1.
1	94.32222	109035.	38249.63	1.

Solvent Extractor

For this application the Solvent Extractor is used to simulate the extraction of phenol from a spent caustic stream using light gas oil as the solvent. The Chemistry Model for this example is described in Electrolyte Chemistry Model For Solvent Extractor Example on page 485 of this section.

Process Summary

The process involves the removal of phenol from a spent caustic effluent using solvent extraction techniques. A light gas oil, cyclohexane, is to be used as the solvent.

Process Build

On naming the process block (e.g., PHENOL REMOVAL) the number of column stages will be specified as 10. The top column inlet stream should then be named (e.g, CAUSTIC WASTE) and its parameters specified as:

Temperature 25° C

Pressure 1.0 atm

Flow	22000.0 mol/hr	
H2O	21014.3	
H2S	25.0	
PCRESOLE	40.04	(Methylphenol - C6H4CH3OH)
C6H5OH	900.0	
NAOH	5.0	
H2SO4	15.0	

The solvent stream entering the bottom of the block is then named (e.g., HEXANE), use Setphase to set the stream to Organic Liquid Only parameters specified as:

Temperature	25° C
Pressure	1.0 atm
Flow	3400 mol/hr
C6H12	3400

The top and bottom exit streams are then named (e.g., WASTE SOLVENT and CLEAN CAUSTIC).

Parameters

On naming the column exit streams the column operating conditions are defined. This is achieved via the Action Key and selecting the Parameters facility.

Pressure Profile The top and bottom column operating pressure are defined as 1 atm.

Column Estimates The column operating temperatures are as follows

<u>Stage</u>	<u>Temperature °C</u>
10	25
9	25
1	25

The organic flow from the column, defined as the vapor distillate flow, is estimated as 4250 mol/hr. A zero liquid reflux flow from the column is also specified.

Spec/Controls No controls are required for this example.

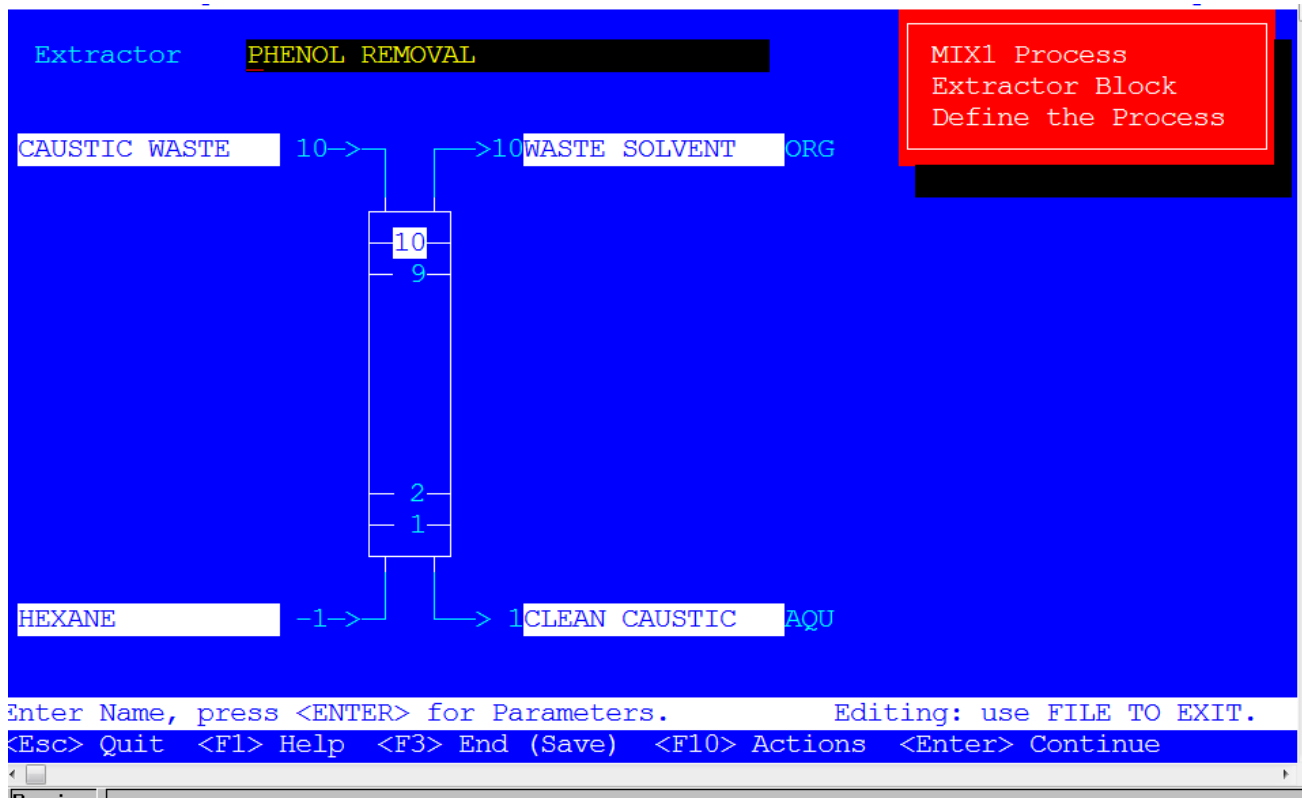
Exchanger Duties For this particular example no condenser and reboiler duty estimations are required.

Tray Efficiencies This option is not used for this particular example as the trays are assumed to be 100% efficient.

Configuration

The Config facility is not used for this particular example as no condenser, reboiler, pumparounds, or additional streams are required.

The process definition is now complete and the format of the block display is as follows:



Process Analysis

The process definition can now be saved and the case executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis a results summary can be produced using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The process streams to this Extractor, shown on an ionic basis:

Stream	Caustic Waste	Hexane	Waste Solvent	Clean Caustic
Phase	Mixed	Liquid	Liquid	Aqueous
Temperature, C	25	25	22.048	23.0489
Pressure, atm	1	1	0.999997	0.999997
Flow Units	mol/hr	mol/hr	mol/hr	mol/hr
H2O	21019.88		1.78914	21018.1
C6H5OH	900.027		193.913	706.115
H2SO4	2.86E-05		7.43E-08	2.28E-11
H2S	25.0008		25.0007	2.66E-05
PCRESOLE	40.0412		40.0412	7.38E-06
SO3	2.05E-15		5.31E-21	2.98E-15
OHION	1.26E-10			1.13E-10
HION	16.7087			17.7068
HSION	4.17E-05			8.98E-11
HSO4ION	8.29199			7.29393
NAION	4.91117			4.97161
NASO4ION	0.0889775			0.0285364
C6H5OION	1.22E-06			2.48E-06
SION	3.36E-16			6.38E-22

SO4ION	6.61946			7.67798
C6H14		2400	2399.96	0.0378954
Total mol/hr	22021.57	2400	2660.704	21761.93
Total g/hr	470149	206828	230289	446688
Volume, m3/hr	0.438051	0.314514	0.330782	0.397792
Enthalpy, cal/hr	-1.47E+09	1.14E+08	-1.23E+08	-1.46E+09
Vapor fraction				
Solid fraction				
Organic fraction	0.07527915	1	1	

===== BLOCK REPORT =====

BLOCK NAME: Phenol Removal

BLOCK TYPE: Extractor

=====

Overall Column Mass and Heat Balance

Duty, cal/hr 0.0

	In	Out	Rel. Diff.
Total Mass g/hr	676977.	676977.	8.86753E-08
Total Energy cal/hr	-1.58779E+09	-1.58780E+09	5.19654

Column Profile

Stage	Temperature C	Aqueous Rate mol/hr	2nd Liq Rate mol/hr	Pressure atm
10	22.04778	21957.05	2660.728	1.
9	21.99833	21942.98	2594.503	1.
8	21.98778	21939.81	2580.714	1.
7	21.98667	21938.9	2577.493	1.
6	21.99	21938.45	2576.677	1.
5	22.00167	21937.54	2576.223	1.
4	22.03389	21934.82	2575.225	1.
3	22.12444	21925.29	2572.322	1.
2	22.37389	21892.18	2562.752	1.
1	23.04889	21762.	2529.775	1.

Aqueous Composition (mole fractions)

Stage	H2O	C6H5OH	C6H14	H2SO4	H2S
10	0.957316	0.04030236	1.65472E-06	1.26066E-15	2.86485E-04
9	0.957916	0.04019409	1.68984E-06	1.25598E-15	7.42003E-05
8	0.958055	0.04016937	1.69771E-06	1.25494E-15	1.93229E-05
7	0.958091	0.04015994	1.69958E-06	1.25461E-15	5.03812E-06
6	0.958112	0.04014581	1.70009E-06	1.25423E-15	1.31386E-06
5	0.958154	0.04010531	1.70043E-06	1.25320E-15	3.42523E-07
4	0.958282	0.03997771	1.70120E-06	1.24986E-15	8.91468E-08

3	0.9587	0.0395604	1.70357E-06	1.23862E-15	2.30364E-08
2	0.960146	0.03811603	1.71153E-06	1.19878E-15	5.76931E-09
1	0.96582	0.0324472	1.74136E-06	1.04606E-15	1.22306E-09

Aqueous Composition (mole fractions)

Stage	PCRESOLE	SO3	NAOH	NA2S.0.5H2O	NA2S.5H2O
10	3.56289E-04	1.64822E-19	0.0	0.0	0.0
9	7.56885E-05	1.64010E-19	0.0	0.0	0.0
8	1.63445E-05	1.63829E-19	0.0	0.0	0.0
7	3.54243E-06	1.63778E-19	0.0	0.0	0.0
6	7.68524E-07	1.63731E-19	0.0	0.0	0.0

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5	1.66855E-07	1.63609E-19	0.0	0.0	0.0
4	3.62915E-08	1.63211E-19	0.0	0.0	0.0
3	7.93147E-09	1.61836E-19	0.0	0.0	0.0
2	1.74425E-09	1.56829E-19	0.0	0.0	0.0
1	3.39277E-10	1.37072E-19	0.0	0.0	0.0

Aqueous Composition (mole fractions)

Stage	NA2S.9H2O	NA2SO4.10H2O	NA2SO4M	NA2SO4	NA2S
-------	-----------	--------------	---------	--------	------

10	0.0	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0
7	0.0	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0

Aqueous Composition (mole fractions)

Stage	NA3HSO42	NAHSO4	NAOH.1H2O	NAHS	OH-1
10	0.0	0.0	0.0	0.0	4.61748E-15
9	0.0	0.0	0.0	0.0	4.60577E-15
8	0.0	0.0	0.0	0.0	4.60341E-15
7	0.0	0.0	0.0	0.0	4.60344E-15
6	0.0	0.0	0.0	0.0	4.60506E-15
5	0.0	0.0	0.0	0.0	4.61006E-15
4	0.0	0.0	0.0	0.0	4.62459E-15
3	0.0	0.0	0.0	0.0	4.66664E-15
2	0.0	0.0	0.0	0.0	4.78984E-15
1	0.0	0.0	0.0	0.0	5.17384E-15

Aqueous Composition (mole fractions)

Stage	H+1	HS-1	HSO4-1	NA+1	NASO4-1
10	8.27182E-04	9.18296E-10	3.11445E-04	2.27003E-04	7.21796E-07
9	8.27640E-04	2.37625E-10	3.11703E-04	2.27140E-04	7.28310E-07
8	8.27743E-04	6.18714E-11	3.11765E-04	2.27172E-04	7.29838E-07
7	8.27757E-04	1.61323E-11	3.11795E-04	2.27180E-04	7.30427E-07
6	8.27730E-04	4.20773E-12	3.11846E-04	2.27184E-04	7.31289E-07
5	8.27633E-04	1.09748E-12	3.11994E-04	2.27191E-04	7.33732E-07
4	8.27337E-04	2.86039E-13	3.12442E-04	2.27214E-04	7.41384E-07
3	8.26433E-04	7.42151E-14	3.13844E-04	2.27289E-04	7.66559E-07
2	8.23571E-04	1.88049E-14	3.18430E-04	2.27542E-04	8.58123E-07
1	8.13659E-04	4.12700E-15	3.35169E-04	2.28454E-04	1.31129E-06

Aqueous Composition (mole fractions)

Stage	C6H5O-1	S-2	SO4-2
10	1.34192E-10	6.01605E-21	3.71009E-04
9	1.33614E-10	1.55150E-21	3.71175E-04

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8	1.33486E-10	4.03680E-22	3.71210E-04
7	1.33452E-10	1.05248E-22	3.71206E-04
6	1.33425E-10	2.74587E-23	3.71168E-04
5	1.33357E-10	7.16805E-24	3.71048E-04
4	1.33127E-10	1.87282E-24	3.70684E-04
3	1.32290E-10	4.89312E-25	3.69555E-04
2	1.29004E-10	1.26424E-25	3.65912E-04
1	1.13799E-10	2.93014E-26	3.52816E-04

2nd Liquid Composition (mole fractions)

Stage	H2O	C6H5OH	C6H14	H2SO4	H2S
10	6.72412E-04	0.07287988	0.902002	2.79213E-11	0.009396278
9	6.09377E-04	0.06891563	0.925035	2.40016E-11	0.002424493
8	5.97406E-04	0.06814796	0.92998	2.32904E-11	6.30904E-04
7	5.94797E-04	0.06797209	0.93113	2.31347E-11	1.64471E-04
6	5.94201E-04	0.0679008	0.931432	2.30862E-11	4.28898E-05
5	5.94018E-04	0.06778553	0.931603	2.30315E-11	1.11810E-05
4	5.93751E-04	0.06745082	0.931951	2.28825E-11	2.90971E-06
3	5.92671E-04	0.06639378	0.933012	2.24149E-11	7.51576E-07
2	5.87907E-04	0.06292157	0.93649	2.09092E-11	1.87917E-07
1	5.66853E-04	0.05072559	0.948708	1.61178E-11	3.96434E-08

2nd Liquid Composition (mole fractions)

Stage	PCRESOLE	SO3	NAOH	NA2S.0.5H2O	NA2S.5H2O
10	0.01504909	1.99466E-24	3.17658E-20	1.40080E-19	1.69150E-19
9	0.003015241	1.81979E-24	2.76805E-20	1.30882E-19	2.45430E-19
8	6.43565E-04	1.74341E-24	1.97634E-19	1.35081E-21	7.88178E-21
7	1.39127E-04	1.69278E-24	6.21274E-19	2.65749E-20	3.28528E-22
6	3.01633E-05	1.65534E-24	1.61292E-20	5.55951E-19	1.76503E-20
5	6.54548E-06	1.62550E-24	3.71251E-19	6.52562E-23	4.59641E-20
4	1.42162E-06	1.59774E-24	3.92165E-19	8.07714E-20	1.05376E-19
3	3.09034E-07	1.56096E-24	5.14211E-21	3.96901E-19	3.00472E-20
2	6.66566E-08	1.48141E-24	5.22577E-20	4.30297E-19	1.53439E-19
1	1.24598E-08	1.24342E-24	1.77334E-19	7.90470E-20	0.0

2nd Liquid Composition (mole fractions)

Stage	NA2S.9H2O	NA2SO4.10H2O	NA2SO4M	NA2SO4	NA2S
10	1.47181E-19	3.11350E-20	0.0	0.0	0.0
9	0.0	9.97265E-19	0.0	0.0	0.0
8	3.21207E-20	3.55509E-22	0.0	0.0	0.0
7	8.72047E-22	3.91831E-20	0.0	0.0	0.0
6	8.57256E-20	3.39802E-19	0.0	0.0	0.0
5	1.39349E-21	3.72355E-19	0.0	0.0	0.0
4	1.09986E-20	1.38642E-19	0.0	0.0	0.0

3	9.19266E-20	5.23103E-20	0.0	0.0	0.0
2	9.29089E-24	1.01587E-19	0.0	0.0	0.0
1	2.95152E-22	4.64596E-19	0.0	0.0	0.0

2nd Liquid Composition (mole fractions)

Stage	NA3HSO42	NAHSO4	NAOH.1H2O	NAHS
10	0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0
8	0.0	0.0	0.0	0.0
7	0.0	0.0	0.0	0.0
6	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0

Scaling Index

Stage	NA2S.9H2O	NA2SO4.10H2O	NA2SO4	NA3HSO42	NAHSO4
-------	-----------	--------------	--------	----------	--------

10	<.0001	<.0001	<.0001	<.0001	<.0001
9	<.0001	<.0001	<.0001	<.0001	<.0001
8	<.0001	<.0001	<.0001	<.0001	<.0001
7	<.0001	<.0001	<.0001	<.0001	<.0001
6	<.0001	<.0001	<.0001	<.0001	<.0001
5	<.0001	<.0001	<.0001	<.0001	<.0001
4	<.0001	<.0001	<.0001	<.0001	<.0001
3	<.0001	<.0001	<.0001	<.0001	<.0001
2	<.0001	<.0001	<.0001	<.0001	<.0001
1	<.0001	<.0001	<.0001	<.0001	<.0001

Scaling Index

Stage NAOH.1H2O

10	<.0001
9	<.0001
8	<.0001
7	<.0001
6	<.0001
5	<.0001
4	<.0001
3	<.0001
2	<.0001
1	<.0001

Profile DATA

-----Aqueous----- -----Organic-----

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10

	Stage Density	Cp	Density	Cp	pH	Ionic
	Strength					
	g/m3	cal/mol/C	g/m3	cal/mol/C		
10	1.15519E+06	17.035	696275.	44.885	1.4278	0.082638
9	1.15262E+06	16.982	689082.	45.127	1.4279	0.0826303
8	1.15208E+06	16.971	687705.	45.186	1.4279	0.0826281
7	1.15195E+06	16.968	687400.	45.202	1.4279	0.082626
6	1.15187E+06	16.968	687320.	45.206	1.4279	0.0826207
5	1.15171E+06	16.969	687256.	45.209	1.4279	0.082605
4	1.15123E+06	16.973	687080.	45.215	1.4281	0.0825571
3	1.14968E+06	16.985	686567.	45.233	1.4287	0.0824077
2	1.14426E+06	17.025	684934.	45.286	1.4305	0.0819221
1	1.12304E+06	17.168	679391.	45.452	1.4371	0.080171

Murphree Efficiencies

Efficiencies are all 1.0

Environmental Process Block Applications

This chapter describes in detail specific applications for the environmental Process Blocks available in ESP Process. The procedure for defining each block is described and the results produced by the Summary mode are included for reference.

The Environmental Blocks applications described in this chapter are:

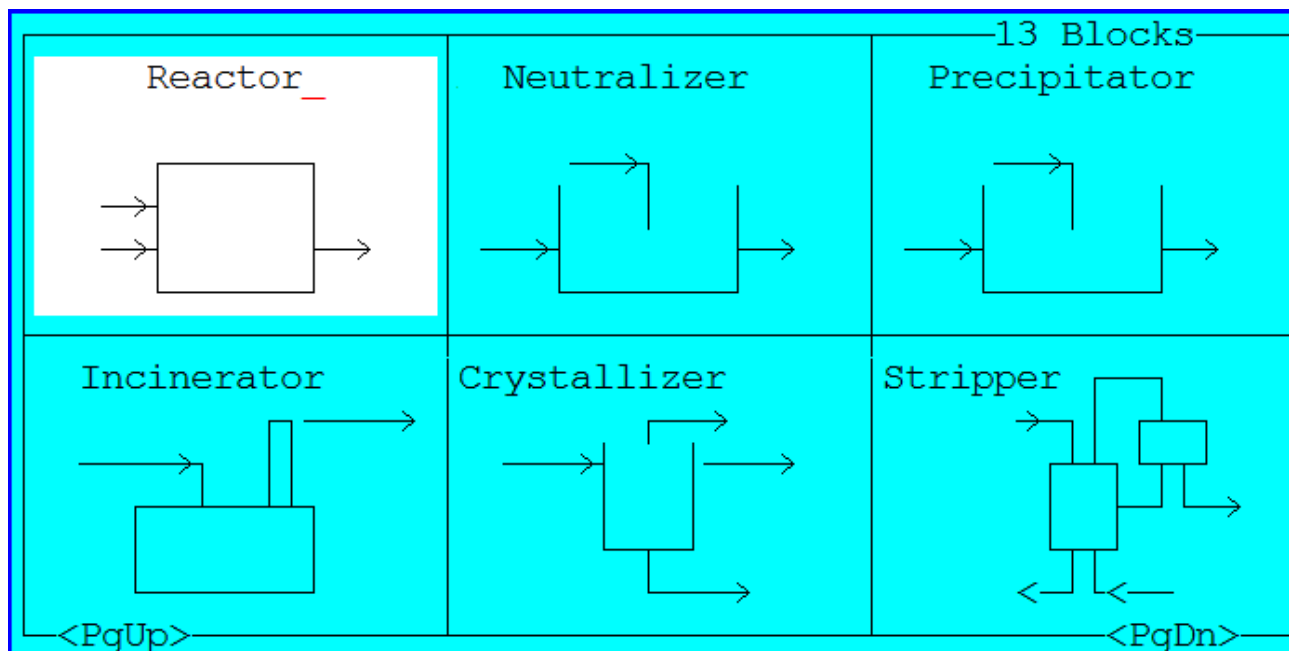
Reactor This process block is being used to simulate the isothermal hydrolysis of urea from aqueous ammonia and carbon dioxide. The chemical kinetics of the reaction are described by the Arrhenius Equation which is specified in the Chemistry Model.

Neutralizer This process block is being used to simulate the two stage neutralization of an effluent using sulfuric acid. The acid dosing requirements are determined and the process is further modeled dynamically to predict process control performance (Reference Dynamic Simulation Applications on page 454 for further details).

Precipitator This process block is being used with a Separate Block to simulate the precipitation and removal of selected metals from a waste effluent using sodium hydroxide. The caustic requirements are determined for final aqueous metal concentrations.

Incinerator This process block is being used to burn a waste organic vapor stream using an excess air stream. The Chemistry Model includes selected species chemical equilibria.

The following sections describe each process in more detail.



Reactor Block

For this application the aqueous Reactor Block is used to simulate the hydrolysis of urea in an aqueous stream. The Chemistry Model for this example is described in Electrolyte Chemistry Model With Reaction Kinetics on page 474 of this section.

Process Summary

The process involves aqueous ammonia and carbon dioxide reacting to form urea and water in an isothermal aqueous reactor. The chemical kinetics of the reaction are described by the Arrhenius Equation.

Process Build

Initially, an aqueous reactor type is selected and the block is named (e.g., UREA HYDROLYSIS). The inlet stream to the reactor is then identified (e.g., FEED) and its composition specified. The feed properties are:

Temperature 25° C

Pressure 1 atm

Total Flow	100 mol/hr
H2O	1.0
CO2	0.1
NH3	0.35
UREA	1.0×10^{-5}

The exit stream from the reactor is then named (e.g., PRODUCT).

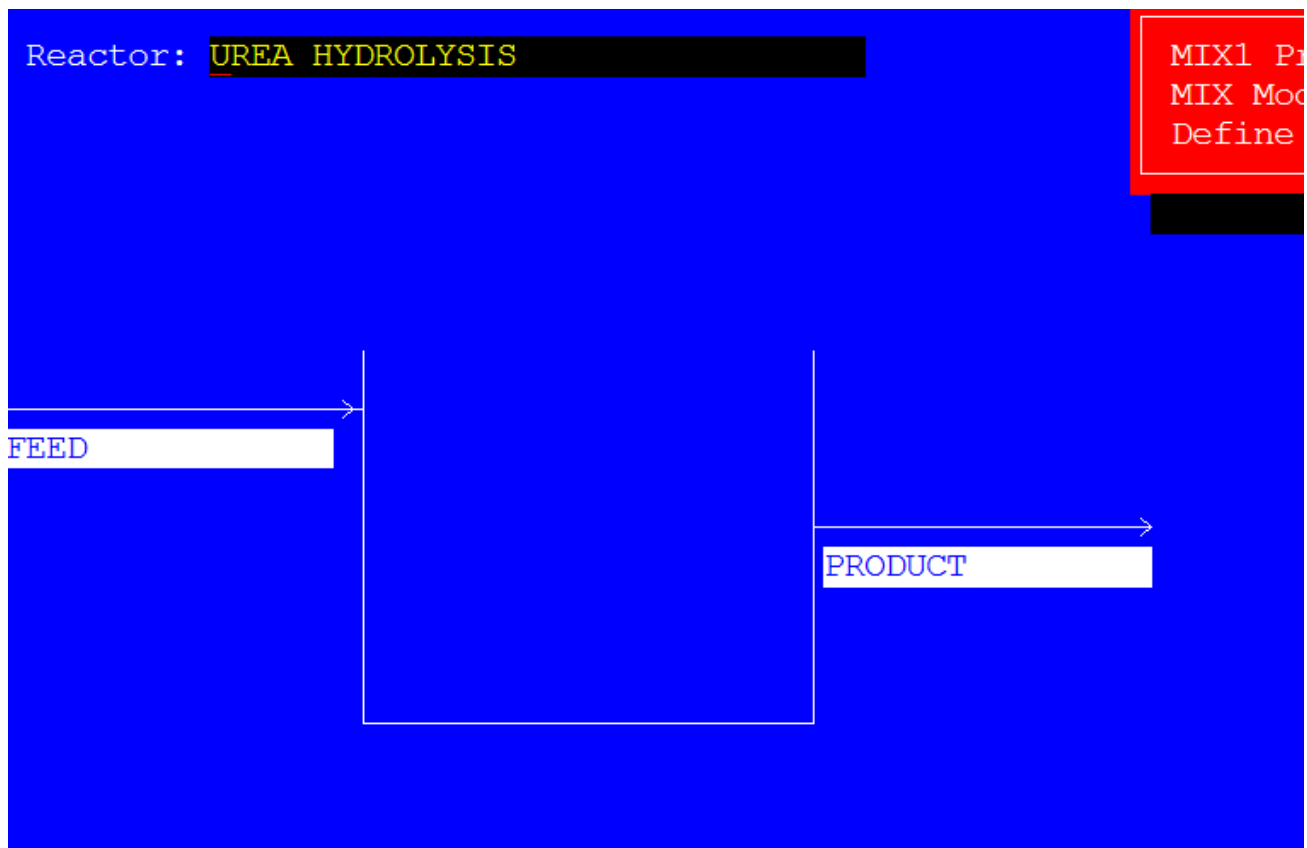
Parameters

The reactor operating conditions are specified using the Action Key and selecting the Parameters facility.

An isothermal reactor is selected and the operating conditions are defined as follows:

<u>Parameter</u>	<u>Data</u>
Reactor Type	Plug Flow
Reactor Residence Time	100 hrs
Number of stages	10
Temperature	25 Deg. C

This completes the Block Parameters definition. The format of the process block display:



Process Analysis

The process definition should be saved and the case executed using the Process Analysis mode of ESP.

Summary

On completing the Process Analysis a copy of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process for this example.

The streams for the Reactor Block, shown on an ionic basis:

STREAM: FEED		Total g/hr	1957.1
TO : UREA HYDROLYSIS		Volume, m3/hr	1.8192E-03
FROM :		Enthalpy, cal/hr	-5.9904E+06
		Vapor fraction	0.0
Temperature, C	25.000	SOLID fraction	0.0
Pressure, atm	1.0000	Organic fraction	0.0
pH	10.076	Osmotic Pres, atm	456.05
Total mol/hr	93.103	Redox Pot, volts	0.0
----- mol/hr-----		E-Con, 1/ohm-cm	.35130
-		E-Con, cm2/ohm-mol	20.592
H2O	68.054	Ionic Strength	6.7875
CO2	7.0311E-06		
NH3	10.543		
NH2CONH2	6.8965E-04		
OHION	1.1265E-04		
HCO3ION	.19878		
HION	1.0251E-10		
NH2CO2ION	5.9853		
NH4ION	7.6090		
CO3ION	.71243		
	=====		

STREAM: PRODUCT		NH2CO2ION	3.1750
TO :		NH4ION	4.3102
FROM : UREA HYDROLYSIS		CO3ION	.51684
			=====
Temperature, C	25.000	Total g/hr	1957.1
Pressure, atm	1.0000	Volume, m3/hr	1.7720E-03
pH	10.220	Enthalpy, cal/hr	-5.9652E+06
Total mol/hr	93.104	Vapor fraction	0.0
----- mol/hr-----		SOLId fraction	0.0
-		Organic fraction	0.0
H2O	71.450	Osmotic Pres, atm	374.58
CO2	4.3576E-06	Redox Pot, volts	0.0
NH3	10.446	E-Con, 1/ohm-cm	.21580
NH2CONH2	3.1041	E-Con, cm2/ohm-mol	15.189
OHION	2.2623E-04	Ionic Strength	3.7501
HCO3ION	.10133		
HION	1.0205E-10		

Neutralizer Block

For this specific application the Neutralizer Block is used to simulate a two stage neutralization process. The Chemistry Model for this example is described in Electrolyte Model For Neutralization Example on page 491 of this section.

Process Summary

The process involves a single multicomponent effluent having its pH lowered by the addition of 37% w/w sulfuric acid. A two stage process is required with the first neutralizer operating at pH 11.0 and the second block dosing acid to pH 9.0. Two Neutralizer Blocks are connected in series and the steady state simulation results are obtained.

These results are used to estimate the approximate acid dosing requirements in order to perform a dynamic simulation of the process. The dynamic simulation will be used to determine the proposed control scheme performance. The Chemistry Model for this example is described in Electrolyte Model For Neutralization Example on page 491 of this section.

Process Build - Stage 1

On naming the first process block (e.g., NEUTRALIZER), the acid dosing stream entering the top of the block is named (e.g., 37% H₂SO₄ -1) and its composition specified. The acid properties are:

Temperature	25° C
Pressure	1 atm
Total Flow	10000 mol/hr
H ₂ O	0.903
H ₂ SO ₄	0.097

The feed stream entering the side of the block is then named (e.g., EFFLUENT) and its properties defined. The effluent properties are:

Temperature	23° C
Pressure	1.0 atm
Total Flow	5.55 x 10 ⁶ mol/hr
H ₂ O	55.509
H ₂ SO ₄	2.04 x 10 ⁻⁴

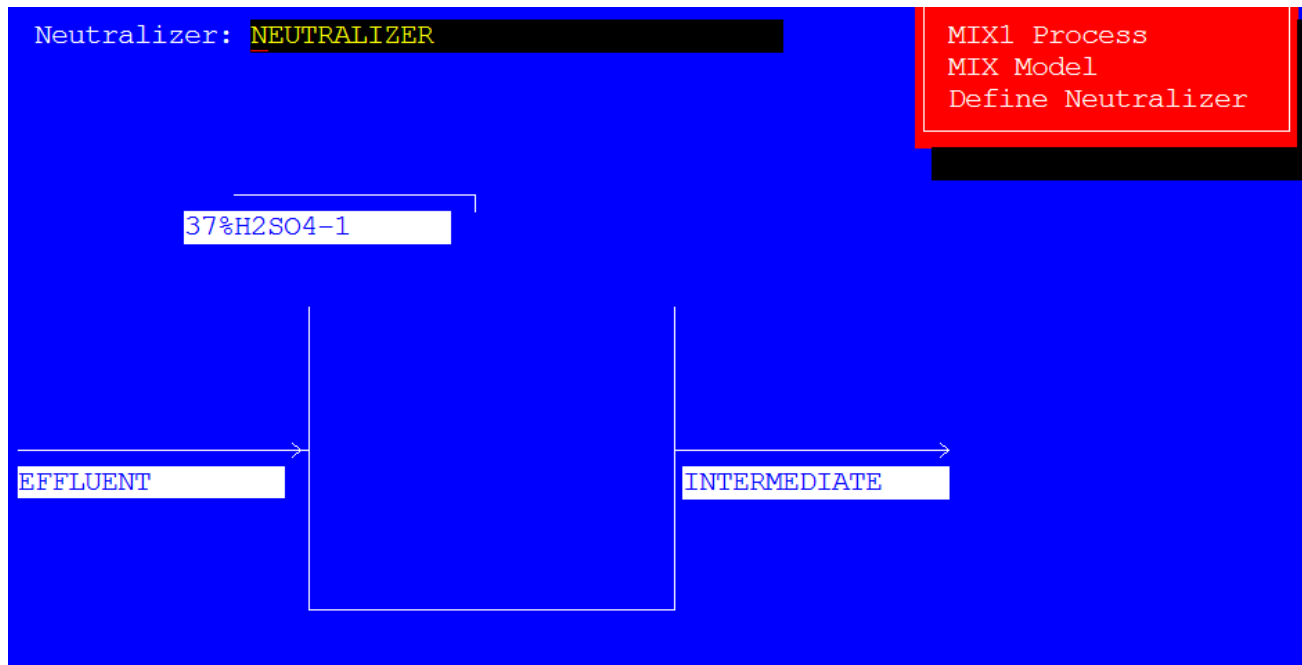
NA2CO3	7.5×10^{-2}
CAOH2	6.5×10^{-4}
CASO4	7.0×10^{-4}
MGCL2	1.5×10^{-3}
MGNO32	1.3×10^{-3}
NACL	0.200
NAOH	0.212

On specifying the feed stream composition the block exit stream is named (e.g., INTERMEDIATE).

Parameters - Block 1

The pH operating point of this first neutralizer is then specified using the Action Key and selecting the Parameters facility. The Fix pH option should be chosen and an operating value of 11.0 specified.

This completes the process definition of the first Neutralizer Block. The format of the process block display is:



The user should save this definition and then select the New Block option on the following screen. The Environmental Blocks should be selected and the Neutralizer Block selected from the displayed menu.

Process Build - Stage 2

Initially, the block should be named (e.g., NEUTRALIZER 2), and then the acid dosing stream entering the top of the block identified (e.g., 37% H₂SO₄ -2 which has the same composition as 37% H₂SO₄ -1) and its composition specified. The acid properties are identical to those specified for the first stage block, except the flowrate should be specified as 25000 mol/hr.

The effluent stream, entering the side of the block is then named. This stream is the exit stream from the first block and the same name should therefore be used (e.g., INTERMEDIATE).

The exit stream is then named (e.g., DISCHARGE).

Parameters - Block 2

The pH operating point of this block is then specified via the Parameters facility. The pH of this block is fixed at pH 9.0.

The Block Parameters specification is now complete.

Process Analysis

The process definition should be saved and the case executed using the Process Analysis mode of ESP Process.

Summary

On completing the Process Analysis, a copy of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The streams for the Reactor Block, shown on an ionic basis:

```
STREAM: 37% H2SO4 -1          FROM :  
TO      : NEUTRALIZER
```

Temperature, C	25.000	STREAM: EFFLUENT	
Pressure, atm	1.0000	TO : NEUTRALIZER	
pH	-1.025	FROM :	
Total mol/hr	1.2146E+05		
-----	mol/hr-----	Temperature, C	23.000
H2O	96202.	Pressure, atm	1.0000
H2SO4	3.6343E-05	pH	13.233
SO3	6.9965E-09	Total mol/hr	5.6041E+06
OHION	2.7623E-12	-----	mol/hr-----
HION	14927.	H2O	5.5013E+06
HSO4ION	5740.8	COCL2	0.0
SO4ION	4593.3	CO2	1.2226E-07
=====		H2SO4	0.0
Total g/hr	2.7467E+06	HCL	3.6176E-16
Volume, m3/hr	2.1326	HNO3	3.5615E-13
Enthalpy, cal/hr	-8.7952E+09	SO3	0.0
Vapor fraction	0.0	CASO4	4.6587E-04
SOLId fraction	0.0	MGSO4	1.1374E-07
Organic fraction	0.0	NAHCO3	.13835
Osmotic Pres, atm	553.26	NANO3	.94839
Redox Pot, volts	0.0	CACO3	133.42
E-Con, 1/ohm-cm	.79489	OHION	20546.
E-Con, cm2/ohm-mol	164.04	CAION	.21862
Ionic Strength	11.263	CANO3ION	2.7176E-04
		CAOHION	.15038
		CLION	20119.

CO3 ION	5630.3
HCO3 ION	1.6924
H ION	8.4852E-09
HSO4 ION	7.9123E-11
MGHCO3 ION	1.1803E-08
MG ION	1.0833E-04
MGOH ION	7.3615E-04
NACO3 ION	1667.4
NA ION	54023.
NASO4 ION	5.9342
NO3 ION	256.73
CAHCO3 ION	7.3585E-06
SO4 ION	83.658
MGOH2	277.50

=====

Total g/hr	1.0194E+08
Volume, m3/hr	99.741
Enthalpy, cal/hr	-3.8245E+11
Vapor fraction	0.0
SOLId fraction	7.3218E-05
Organic fraction	0.0
Osmotic Pres, atm	22.151
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	6.5486E-02
E-Con, cm2/ohm-mol	134.12
Ionic Strength	.60276

STREAM: INTERMEDIATE		CO3ION	5724.2
TO : NEUTRALIZER 2		HCO3ION	258.66
FROM : NEUTRALIZER		HION	1.5549E-06
		HSO4ION	1.6233E-06
Temperature, C	25.972	MGHCO3ION	3.3041E-02
Pressure, atm	1.0000	MGION	1.9684
pH	11.000	MGOHION	.10922
Total mol/hr	5.7104E+06	NACO3ION	1296.7
----- mol/hr-----		NAION	53786.
-		NASO4ION	594.52
H2O	5.6179E+06	NO3ION	256.84
COCL2	1.0126E-30	CAHCO3ION	1.2145E-03
CO2	3.0748E-03	SO4ION	9828.8
H2SO4	3.7018E-28	MGOH2	275.13
HCL	7.4951E-14		=====
HNO3	6.5581E-11	Total g/hr	1.0469E+08
SO3	1.0126E-30	Volume, m3/hr	102.27
CASO4	5.4938E-02	Enthalpy, cal/hr	-3.9124E+11
MGSO4	.25377	Vapor fraction	0.0
NAHCO3	19.851	SOLId fraction	7.1446E-05
NANO3	.83249	Organic fraction	0.0
CACO3	133.49	Osmotic Pres, atm	17.514
OHION	159.08	Redox Pot, volts	0.0
CAION	.24432	E-Con, 1/ohm-cm	4.2319E-02
CANO3ION	2.9290E-04	E-Con, cm2/ohm-mol	73.389
CAOHION	1.2904E-03	Ionic Strength	.68518
CLION	20119.		

STREAM: DISCHARGE		CLION	20119.
TO :		CO3ION	1184.3
FROM : NEUTRALIZER 2		HCO3ION	5360.2
		HION	1.5922E-04
Temperature, C	26.270	HSO4ION	2.1356E-04
Pressure, atm	1.0000	MGHCO3ION	68.490
pH	9.0000	MGION	176.90
Total mol/hr	5.7437E+06	MGOHION	.10603
----- mol/hr-----		NACO3ION	266.89
-		NAION	54241.
H2O	5.6479E+06	NASO4ION	774.78
COCL2	1.0180E-30	NO3ION	256.84
CO2	6.3999	CAHCO3ION	.11984
H2SO4	4.9019E-24	SO4ION	12759.
HCL	7.7092E-12		=====
HNO3	6.6530E-09	Total g/hr	1.0553E+08
SO3	6.5306E-28	Volume, m3/hr	103.06
CASO4	.34625	Enthalpy, cal/hr	-3.9392E+11
MGSO4	32.005	Vapor fraction	0.0
NAHCO3	414.36	SOLId fraction	2.2902E-05
NANO3	.83276	Organic fraction	0.0
CACO3	132.19	Osmotic Pres, atm	18.090
OHION	1.6299	Redox Pot, volts	0.0
CAION	1.1370	E-Con, 1/ohm-cm	4.2192E-02
CANO3ION	1.3957E-03	E-Con, cm2/ohm-mol	139.25
CAOHION	6.3093E-05	Ionic Strength	.67605

Precipitator Block

For this particular application the Precipitator Block is used with a Separate Block to precipitate and remove selected metals from a waste effluent stream. The Chemistry Model for this example is described in Electrolyte Chemistry Model For Precipitator Example on page 498 of this section.

Process Summary

The process involves ferric and nickel metal species being selectively removed from an acidic waste effluent stream containing several metals. The required metals are to be precipitated from solution using a 1.0 molal sodium hydroxide solution until their final aqueous phase concentrations are:

<u>Species</u>	<u>Final Concentration</u>
Ferric ion (Fe +3)	20 ppm
Nickel ion (Ni +2)	15 ppm

The process is used to determine the dosing requirements of caustic in order to precipitate the required metals from solution. Each metal is precipitated from solution individually and then removed from the effluent using a Separate Block.

Therefore a two stage process is simulated with each stage consisting of a Precipitator Block and a Separate Block in series.

Process Build - Stage 1

On naming the process block (e.g., PRECIPITATOR STAGE 1), the precipitating reagent dosing stream entering the top of the block is named (e.g., 1M CAUSTIC-1) and its composition specified as:

Temperature	25° C
Pressure	1 atm
Flow	200 mol/hr
H2O	55.51
NAOH	1.0

The inlet stream entering the side of the block is then named (e.g., WASTE STREAM) and its composition specified as:

Temperature	25° C
-------------	-------

Pressure	1 atm
Flow	250 mol/hr
H2O	55.51
NI ₂	0.18
CA ₂	0.061
MG ₂	0.076
FE ₃	0.026
HCL	1.0

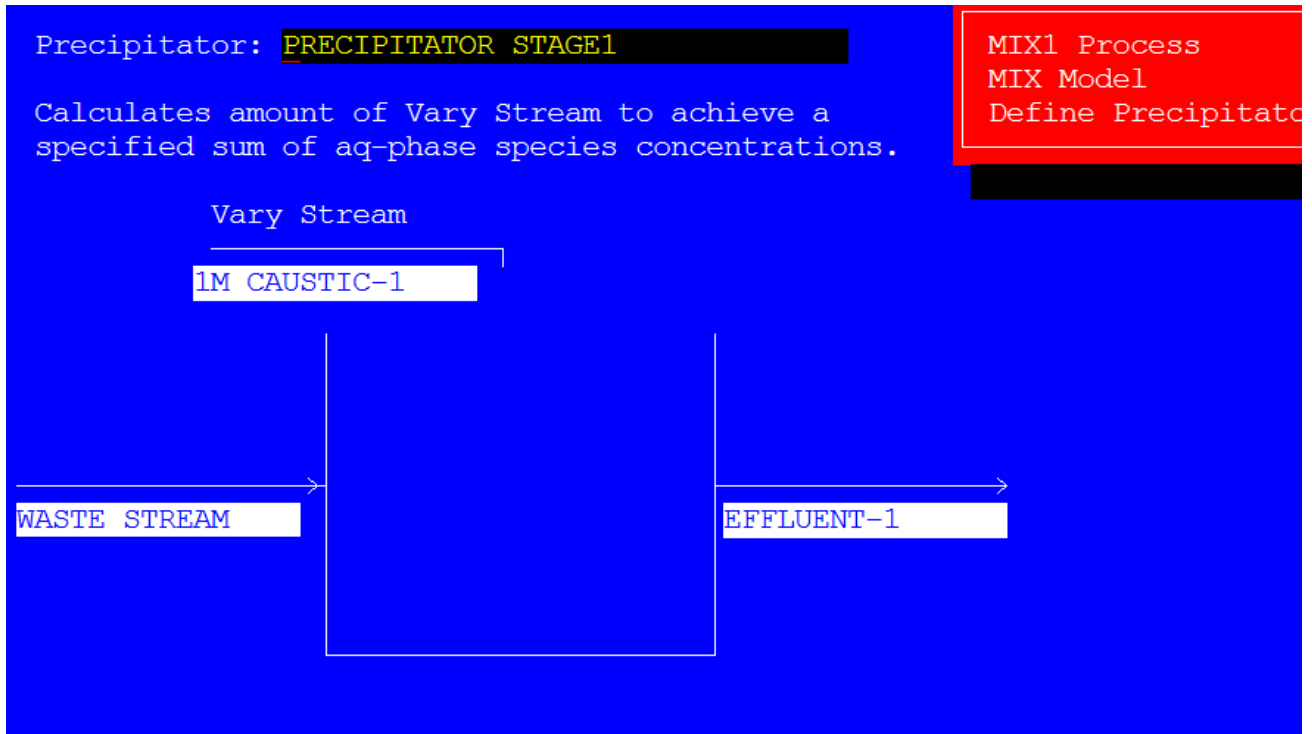
The exit stream from the block is then named (e.g., EFFLUENT-1).

Parameters

On naming the block exit stream, the precipitator operating requirements are defined. This is achieved via the Action Key and selecting the Parameters facility.

The type of calculation is to be performed by selecting Aqueous Species and the operating adiabatically. The aqueous species to be removed is then selected from the displayed list using the Arrow Keys and the <Space Bar>. For this first stage block, the user should select the ferric ion (FE₃ION) for removal. The final aqueous phase concentration for the selected ion is then specified. For this example, the aqueous ferric ion concentration is to be reduced to 20 ppm. (Note: Initially the units are expressed as molality, and are changed by the user simply by entering the required quantity adjacent to the displayed keyword Unit.

This completes the process definition for the first stage Precipitator Block. The format of the process block display is:



The user should save this definition and then select the New Block option the following screen. The user should then select the Conventional Process Blocks and the Separate Block selected from the displayed menu.

Separate Block Definition - Stage 1

This block is used simply to remove the ferric precipitate produced in the precipitator, prior to further treatment of the effluent.

Initially, the block is named (e.g., SEPARATOR STAGE1) and the inlet stream is then identified. This stream is the exit flow from the Precipitator Block and so should be given the same name to that previously used (e.g., EFFLUENT-1).

Two of the four exit streams from the block are then named. For this example, the liquid stream is identified (e.g., EFFLUENT-2) and the SOLID stream is also named (e.g., FERRIC WASTE).

The process definition for this block is now complete. (Note for this example no block parameters are specified).

The user should save this definition and then select the New Block option. The second stage of the process can then be specified.

Process Build - Stage 2

Initially, another Precipitator Block should be chosen and specified in a similar manner to that of the STAGE 1 Precipitator Block. The block is named (e.g., PRECIPITATOR STAGE2) and the dosing stream is identified (e.g., 1M CAUSTIC-2) the properties of which are the same as the STAGE 1 stream.

The block side entry stream is named using the stage 1 separator exit stream name (e.g., EFFLUENT-2). Finally, the block exit stream is identified (e.g., EFFLUENT-3).

Parameters

The block operating parameters are specified in the same manner as the STAGE 1 Precipitator block except nickel ion (NIION) is selected for removal and its final aqueous concentration is specified as 15 ppm.

Separate Block Definition - Stage 2

This block is used to remove the nickel precipitate produced in the precipitator. The block and appropriate streams are named and the format of the display is:

Process Analysis

The process definition is now complete and the case is executed using the Process Analysis mode of ESP.

The results can be displayed by selecting the Process Streams Results Display and Process Block Results Display.

Summary

A copy of the results can be obtained using the Summary mode of ESP.

The output at the end of this section summarizes the process results for this example.

The streams for the Precipitator Block, shown on an ionic basis:

STREAM: 1M CAUSTIC-1

TO : PRECIPITATOR STAGE1 Temperature, C 25.000

FROM : Pressure, atm 1.0000

pH	13.871	STREAM: WASTE STREAM	
Total mol/hr	271.19	TO : PRECIPITATOR STAGE1	
-----	mol/hr-----	FROM :	
-			
H2O	261.76	Temperature, C	25.000
OHION	4.7154	Pressure, atm	1.0000
HION	1.1430E-13	pH	4.1382E-02
NAION	4.7154	Total mol/hr	257.49
	=====	-----	mol/hr-----
Total g/hr	4904.2	-	
Volume, m3/hr	4.7364E-03	H2O	244.09
Enthalpy, cal/hr	-1.8409E+07	HCL	2.9292E-06
Vapor fraction	0.0	FEIIIIOH3	8.2839E-16
SOLId fraction	0.0	FECL3	2.0062E-04
Organic fraction	0.0	NIOH2	9.1929E-21
Osmotic Pres, atm	49.671	OHION	9.5206E-14
Redox Pot, volts	0.0	CAOHION	1.9470E-14
E-Con, 1/ohm-cm	.17347	CLION	7.4942
E-Con, cm2/ohm-mol	174.24	FEIII2OH2ION	7.9356E-13
Ionic Strength	1.0000	FEIIIICL2ION	4.4343E-03
		FEIIIICL4ION	7.3403E-06
		FEIIIICLION	7.5336E-04
		FEIIIION	.10891
		FEIIIIOH2ION	1.9419E-10
		FEIIIIOH4ION	4.2999E-25
		FEIIIIOHION	2.3161E-05
		HION	4.3973

MGION	.33420
MGOHION	3.0898E-13
NICLION	2.3778E-02
NIION	.76774
NIOH3ION	0.0
NIOHION	2.2745E-11
CAION	.26824
	=====
Total g/hr	4740.5
Volume, m3/hr	4.5194E-03
Enthalpy, cal/hr	-1.7056E+07
Vapor fraction	0.0
SOLId fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	78.846
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	.32072
E-Con, cm2/ohm-mol	245.43
Ionic Strength	2.0903

STREAM: EFFLUENT-1		MGION	.33420
TO : SEPARATE STAGE1		MGOHION	6.0699E-10
FROM : PRECIPITATOR STAGE1		NAION	4.7155
		NICLION	1.1710E-02
Temperature, C	32.130	NIION	.77981
Pressure, atm	1.0000	NIOH3ION	1.7134E-21
pH	3.1641	NIOHION	6.2637E-08
Total mol/hr	523.99	CAION	.26824
----- mol/hr-----			=====
-		Total g/hr	9644.7
H2O	510.24	Volume, m3/hr	9.3534E-03
HCL	2.8120E-09	Enthalpy, cal/hr	-3.5466E+07
FEIIIOH3	.10778	Vapor fraction	0.0
FECL3	6.2883E-07	SOLId fraction	2.0569E-04
NIOH2	4.7034E-14	Organic fraction	0.0
OHION	3.6181E-10	Osmotic Pres, atm	32.891
CAOHION	4.5022E-11	Redox Pot, volts	0.0
CLION	7.5164	E-Con, 1/ohm-cm	7.6899E-02
FEIII2OH2ION	6.5779E-09	E-Con, cm2/ohm-mol	67.697
FEIICL2ION	3.5560E-05	Ionic Strength	.96953
FEIICL4ION	7.3284E-09		
FEIICLION	2.3665E-05		
FEIIIION	3.4498E-03		
FEIIIOH2ION	4.4803E-05		
FEIIIOH4ION	5.3017E-13		
FEIIIOHION	2.9937E-03		
HION	8.2847E-03		

STREAM: EFFLUENT-2		MGION	.33420
TO : PRECIPITATOR STAGE2		MGOHION	6.0699E-10
FROM : SEPARATE STAGE1		NAION	4.7155
		NICLION	1.1710E-02
Temperature, C	32.130	NIION	.77981
Pressure, atm	1.0000	NIOH3ION	1.7134E-21
pH	3.1641	NIOHION	6.2637E-08
Total mol/hr	523.88	CAION	.26824
----- mol/hr-----			=====
-		Total g/hr	9633.2
H2O	510.24	Volume, m3/hr	9.3500E-03
HCL	2.8120E-09	Enthalpy, cal/hr	-3.5444E+07
FEIIIIOH3	3.6626E-07	Vapor fraction	0.0
FECL3	6.2883E-07	SOLId fraction	0.0
NIOH2	4.7034E-14	Organic fraction	0.0
OHION	3.6181E-10	Osmotic Pres, atm	32.891
CAOHION	4.5022E-11	Redox Pot, volts	0.0
CLION	7.5164	E-Con, 1/ohm-cm	7.6899E-02
FEIII2OH2ION	6.5779E-09	E-Con, cm2/ohm-mol	67.697
FEIICL2ION	3.5560E-05	Ionic Strength	.96953
FEIICL4ION	7.3284E-09		
FEIICLION	2.3665E-05		
FEIIIION	3.4498E-03		
FEIIIOH2ION	4.4803E-05		
FEIIIOH4ION	5.3017E-13		
FEIIIOHION	2.9937E-03		
HION	8.2847E-03		

STREAM: FERRIC WASTE

FROM :

TO :

FROM : SEPARATE STAGE1

Temperature, C 32.130
 Pressure, atm 1.0000
 pH 0.0
 Total mol/hr .10778
 ----- mol/hr-----
 -

FEIII(OH)3 .10778

=====

Total g/hr 11.519

Volume, m3/hr 3.3876E-06

Enthalpy, cal/hr -2.1669E+04

Vapor fraction 0.0

SOLID fraction 1.0000

Organic fraction 0.0

Osmotic Pres, atm 0.0

Redox Pot, volts 0.0

E-Con, 1/ohm-cm 0.0

E-Con, cm2/ohm-mol 0.0

Ionic Strength 0.0

Temperature, C 25.000

Pressure, atm 1.0000

pH 13.871

Total mol/hr 92.135

----- mol/hr-----

H2O 88.931

OHION 1.6021

HION 3.8833E-14

NAION 1.6021

=====

Total g/hr 1666.2

Volume, m3/hr 1.6092E-03

Enthalpy, cal/hr -6.2545E+06

Vapor fraction 0.0

SOLID fraction 0.0

Organic fraction 0.0

Osmotic Pres, atm 49.671

Redox Pot, volts 0.0

E-Con, 1/ohm-cm .17347

E-Con, cm2/ohm-mol 174.24

Ionic Strength 1.0000

STREAM: 1M CAUSTIC-2

TO : PRECIPITATOR STAGE2

STREAM: EFFLUENT-3		MGION	.33418
TO : SEPARATE STAGE2		MGOHION	1.0799E-05
FROM : PRECIPITATOR STAGE2		NAION	6.3175
		NICLION	4.0347E-05
Temperature, C	31.669	NIION	2.8700E-03
Pressure, atm	1.0000	NIOH3ION	3.8456E-11
pH	7.4078	NIOHION	4.3402E-06
Total mol/hr	614.42	CAION	.26823
----- mol/hr-----			=====
-		Total g/hr	11299.
H2O	599.18	Volume, m3/hr	1.0998E-02
HCL	1.6147E-13	Enthalpy, cal/hr	-4.1699E+07
FEIIIIOH3	6.5486E-03	Vapor fraction	0.0
FECL3	9.0417E-20	SOLId fraction	1.2941E-03
NIOH2	.78860	Organic fraction	0.0
OHION	6.5285E-06	Osmotic Pres, atm	30.421
CAOHION	8.1053E-07	Redox Pot, volts	0.0
CLION	7.5281	E-Con, 1/ohm-cm	6.8930E-02
FEIII2OH2ION	6.4862E-26	E-Con, cm2/ohm-mol	97.999
FEIICL2ION	5.5248E-18	Ionic Strength	.75349
FEIICL4ION	8.4558E-22		
FEIICLION	4.0790E-18		
FEIIIION	5.8148E-16		
FEIIIIOH2ION	2.9015E-09		
FEIIIIOH4ION	9.8485E-09		
FEIIIIOHION	1.0582E-11		
HION	5.5241E-07		

STREAM: OUTLET		MGION	.33418
TO :		MGOHION	1.0799E-05
FROM : SEPARATE STAGE2		NAION	6.3175
		NICLION	4.0347E-05
Temperature, C	31.669	NIION	2.8700E-03
Pressure, atm	1.0000	NIOH3ION	3.8456E-11
pH	7.4078	NIOHION	4.3402E-06
Total mol/hr	613.63	CAION	.26823
----- mol/hr-----			=====
-		Total g/hr	11226.
H2O	599.18	Volume, m3/hr	1.0980E-02
HCL	1.6147E-13	Enthalpy, cal/hr	-4.1595E+07
FEIIIIOH3	4.3324E-07	Vapor fraction	0.0
FECL3	9.0417E-20	SOLId fraction	0.0
NIOH2	5.9806E-08	Organic fraction	0.0
OHION	6.5285E-06	Osmotic Pres, atm	30.421
CAOHION	8.1053E-07	Redox Pot, volts	0.0
CLION	7.5281	E-Con, 1/ohm-cm	6.8930E-02
FEIII2OH2ION	6.4862E-26	E-Con, cm2/ohm-mol	97.999
FEIICL2ION	5.5248E-18	Ionic Strength	.75349
FEIICL4ION	8.4558E-22		
FEIICLION	4.0790E-18		
FEIIIION	5.8148E-16		
FEIIIIOH2ION	2.9015E-09		
FEIIIIOH4ION	9.8485E-09		
FEIIIIOHION	1.0582E-11		
HION	5.5241E-07		

STREAM: NICKEL WASTE		=====	
TO :		Total g/hr	73.791
FROM :	SEPARATE STAGE2	Volume, m3/hr	1.7823E-05
		Enthalpy, cal/hr	-1.0365E+05
Temperature, C	31.669	Vapor fraction	0.0
Pressure, atm	1.0000	SOLId fraction	1.0000
pH	0.0	Organic fraction	0.0
Total mol/hr	.79515	Osmotic Pres, atm	0.0
-----	mol/hr-----	Redox Pot, volts	0.0
-		E-Con, 1/ohm-cm	0.0
FEIIIIOH3	6.5481E-03	E-Con, cm2/ohm-mol	0.0
NIOH2	.78860	Ionic Strength	0.0

Incinerator Block

For this example the Incinerator Block is used to combust a waste vapor stream involving species equilibrium. The Chemistry Model for this example is described in **Non-Electrolyte Chemistry Model With Selected Species Equilibrium** on page 513 of this section.

Process Summary

The process involves a multi-component organic vapor stream being combusted in an isothermal incinerator using an excess oxidation vapor stream.

Process Build

On naming the process block (e.g., INCINERATOR) the feed stream to the block is named (e.g., WASTE GAS) and its composition specified:

The feed properties are:

Temperature	1700° F
Pressure	14.7 psia
Flow	100 lbmol/hr

H2O	33
CH4	16.5
C2H6	16.5
C3H8	16.5
C4H10	16.5
BENZENE	1

On specifying the feed stream composition the block exit stream is named (e.g., PRODUCT GAS).

Parameters

The block operating conditions are specified after naming the exit stream. This is achieved via the Action Key and selecting the Parameters facility.

For this example an isothermal incinerator is to be modeled operating at the following conditions:

<u>Parameter</u>	<u>Value</u>
Vapor Hold up Volume	3000 ft ³
Temperature	2300 Deg. F

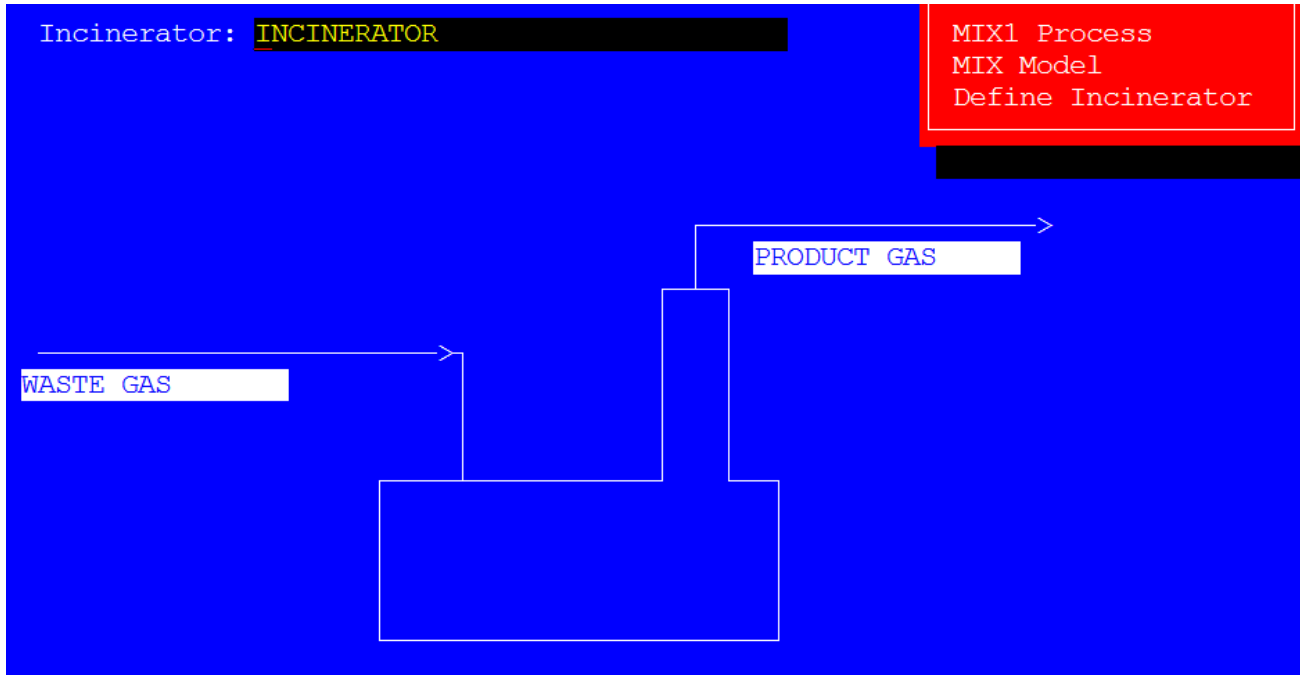
The Block Parameters specification is now complete.

Configuration

For clarification purposes, the oxidation vapor stream is included as an additional feed to the reactor. This is achieved via the Action Key and selecting the Config facility. The Add Stream option is then chosen and confirmed. The additional feed stream can then be named (e.g., AIR STREAM) and its composition specified. Use Set Phase to set the stream to Vapor Only. The oxygen rich air properties are:

Temperature	85° F
Pressure	14.7 psia
Flow	1200 lbmol/hr
CO2	.2762
O2	30.678

The format of the process block display is as follows:



Process Analysis

The process definition is now complete. The user should save this block and then execute the case using the Process Analysis mode of ESP Process.

Summary

On completing the Process Analysis a copy of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The streams for this Incinerator Block, shown on a molecular basis:

STREAM: WASTE GAS
 TO : INCINERATOR
 FROM :
 E-Con, cm2/ohm-mol 0.0
 Ionic Strength 0.0

Temperature, F 1700.0
 Pressure, psia 14.700
 pH 0.0
 Total l mol/hr 100.00
 ----- l mol/hr-----
 -
 H2O 33.000
 C2H6 16.500
 C3H8 16.500
 C4H10 16.500
 CH4 16.500
 BENZENE 1.0000
 =====
 Total lb/hr 3120.0
 Volume, ft3/hr 1.5768E+05
 Enthalpy, Btu/hr -2.4617E+06
 Vapor fraction 1.0000
 SOLId fraction 0.0
 Organic fraction 0.0
 Osmotic Pres, psia 0.0
 Redox Pot, volts 0.0
 E-Con, 1/ohm-cm 0.0

STREAM: AIR STREAM
 TO : INCINERATOR
 FROM :
 Temperature, F 84.999
 Pressure, psia 14.700
 pH 0.0
 Total l mol/hr 1200.0
 ----- l mol/hr-----
 -
 CO2 3.3144
 N2 828.55
 O2 368.13
 =====
 Total lb/hr 35137.
 Volume, ft3/hr 4.7707E+05
 Enthalpy, Btu/hr -4.9770E+05
 Vapor fraction 1.0000
 SOLId fraction 0.0
 Organic fraction 0.0
 Osmotic Pres, psia 0.0
 Redox Pot, volts 0.0

E-Con, 1/ohm-cm 0.0
 E-Con, cm2/ohm-mol 0.0
 Ionic Strength 0.0

STREAM: PRODUCT GAS
 TO :
 FROM : INCINERATOR

Temperature, F 2300.0
 Pressure, psia 14.700
 pH 0.0
 Total l mol/hr 1350.0
 ----- l mol/hr-----
 -
 H2O 267.00
 CO2 174.30
 CO 1.3430E-02
 H2 2.4577E-03
 N2 828.55
 O2 80.144
 =====
 Total lb/hr 38257.
 Volume, ft3/hr 2.7201E+06
 Enthalpy, Btu/hr -3.1221E+07
 Vapor fraction 1.0000
 SOLId fraction 0.0
 Organic fraction 0.0
 Osmotic Pres, psia 0.0
 Redox Pot, volts 0.0
 E-Con, 1/ohm-cm 0.0
 E-Con, cm2/ohm-mol 0.0

Biotreatment Process Block Applications

This chapter describes in detail specific applications for the Biotreatment Process Block available in ESP Process. The procedure for defining the block is described and the Process Analysis result is included for reference.

The Biotreatment Process Block application described in this chapter is:

Bioreactor, This process is used to simulate the biotreatment of a substrate in a waste effluent stream. The Chemistry Model includes the required bioreaction kinetics.

Clarifier, This process demonstrates the use of a clarifier.

The following sections describe the process in more detail.

Bioreactor / Clarifier

This example is used to demonstrate the use of the Clarifier for Biotreatment processes requiring several Bioreactors. The Chemistry Model for this example is described in Bioreactions on page 503.

Process Summary

This process will use the previous bioreaction (which possesses a bioreactor and clarifier as a single configuration) case as the basis for this one. This process will consist of one bioreactor and one clarifier.

Process Build - Bioreactor Block

On naming the process block (e.g., BIOREACTOR) the feed stream to the block is named (e.g., BIOWASTE) and its composition specified:

The feed properties are:

Temperature 20° C

Pressure 1 atm

Flow	2.3072E+06 mol/hr
H2O	2.3071E+06
WASTE	54.616
NH3	60.322

On specifying the feed stream composition the Vapor and Effluent streams are named (e.g., VAPOR, INTERMEDIATE).

Parameters - Bioreactor Block

The Bioreactor operating parameters are specified after naming the outlet streams. This is achieved via the Action Key and selecting the Parameters facility.

<u>Block Parameter</u>	<u>Parameter Type</u>	<u>Value</u>
Computation Option	Isothermal	20° C
Reactor Volume		300 m ³
Oxygen Use	Mass Transfer Coeff	100 hr ⁻¹
Bioreaction Constants	Heterotrophic	ANAF = 0.4

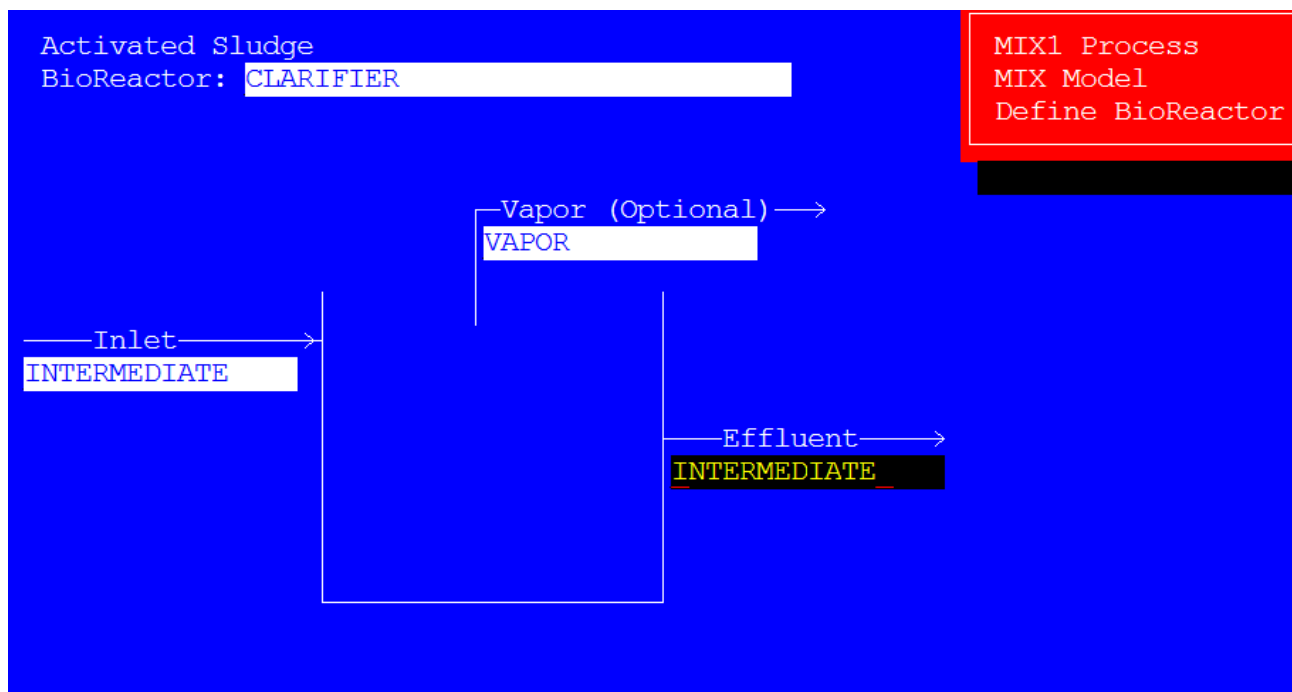
The Block Parameters specification is now complete.

Configuration - Bioreactor Block

For clarification purposes, the air stream is included as an additional feed to the reactor. This is achieved via the Action Key and selecting the Config facility. The Inlet option followed by the Add Stream option is chosen and confirmed. The additional feed stream can then be named (e.g., AIR) and its composition specified. Use Set Phase to set the stream to Vapor Only. The air properties are:

Temperature	20° C
Pressure	1 atm
Flow	1000 mol/hr
O2	210
N2	790

The format of the process block display is as follows:



Process Build - Clarifier Block

On naming the process block (e.g., CLARIFIER) the feed stream to the block is named as the outlet stream from the bioreactor (e.g., INTERMEDIATE).

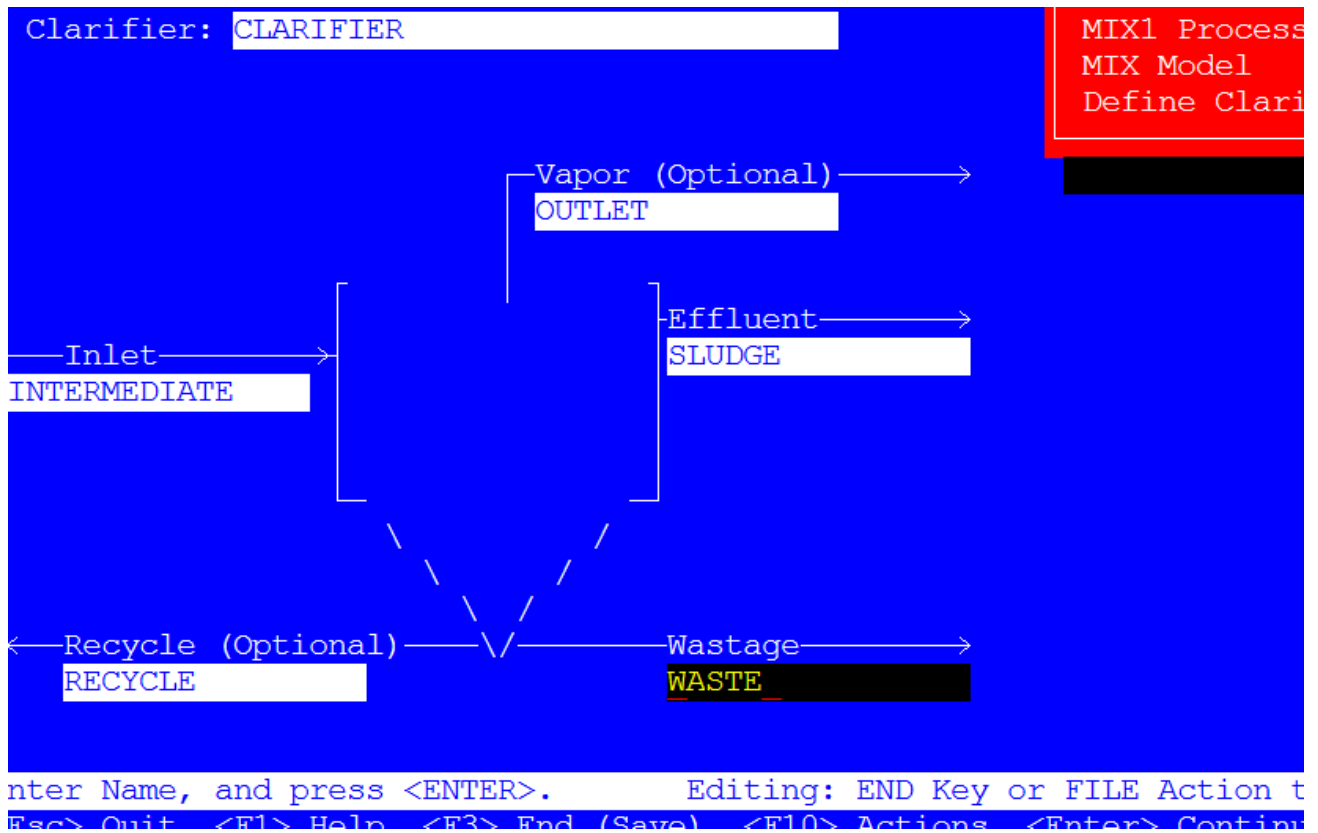
On specifying the feed stream the Effluent, Wastage and Recycle streams are named (e.g., OUTLET, SLUDGE, and RECYCLE).

Parameters - Clarifier Block

The Clarifier operating parameters are specified after naming the outlet streams. This is achieved via the Action Key and selecting the Parameters facility. For this case we will use the results from the previous problem.

<u>Block Parameter</u>	<u>Value</u>
Wastage Flow	0.28155 m ³ /hr
Recycle Flow	20.822 m ³ /hr
TSS	50 g/m ³

The format of the process block display is as follows:



Process Analysis

The process definition is now complete. The user should save this block and then execute the case using the Process Analysis mode of ESP Process.

Summary

On completing the Process Analysis a copy of the results can be requested using the Summary mode.

The output at the end of previous section summarizes the process results for this example.

The streams for this Bioreactor and Clarifier Block, shown on a molecular basis:

STREAM: BIOWASTE

TO : BIOREACTOR

FROM :

Temperature, C	20.000
Pressure, atm	1.0000
pH	10.335
Total mol/hr	2.3072E+06
----- mol/hr-----	
-	
H2O	2.3071E+06
NH3	60.322
WASTE	42.757
	=====
Total g/hr	4.1571E+07
Volume, m3/hr	41.644
Enthalpy, cal/hr	-1.5781E+11
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	6.3165E-02
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	3.7326E-05
E-Con, cm2/ohm-mol	15.080
Ionic Strength	1.5145E-04

STREAM: AIR

TO : BIOREACTOR

FROM :

Temperature, C	20.000
Pressure, atm	1.0000
pH	0.0
Total mol/hr	1000.0
----- mol/hr-----	
-	
N2	790.00
O2	210.00
	=====
Total g/hr	28850.
Volume, m3/hr	24.051
Enthalpy, cal/hr	-3.6556E+04
Vapor fraction	1.0000
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	0.0
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	0.0
E-Con, cm2/ohm-mol	0.0

Ionic Strength	0.0	Organic fraction	0.0
STREAM: VAPOR		Osmotic Pres, atm	0.0
TO :		Redox Pot, volts	0.0
FROM : BIOREACTOR		E-Con, 1/ohm-cm	0.0
		E-Con, cm2/ohm-mol	0.0
Temperature, C	20.000	Ionic Strength	0.0
Pressure, atm	1.0000		
pH	0.0		
Total mol/hr	921.26		
-----	mol/hr-----		
-			
H2O	21.510		
ACETACID	6.6772E-10		
CO2	.43707		
ACET2	2.5108E-20		
H2SO4	0.0		
H2S	7.1073E-04		
HCL	2.0960E-16		
N2	765.86		
NH3	9.4631E-04		
O2	133.46		
	=====		
Total g/hr	26132.		
Volume, m3/hr	22.155		
Enthalpy, cal/hr	-1.3184E+06		
Vapor fraction	1.0000		
Solid fraction	0.0		

STREAM: INTERMEDIATE

=====

TO : CLARIFIER

Total g/hr 4.1574E+07

FROM : BIOREACTOR

Volume, m3/hr 41.645

Enthalpy, cal/hr -1.5782E+11

Temperature, C 20.000

Vapor fraction 0.0

Pressure, atm 1.0000

Solid fraction 3.6444E-06

pH 8.0929

Organic fraction 0.0

Total mol/hr 2.3072E+06

Osmotic Pres, atm .10132

----- mol/hr-----

Redox Pot, volts 0.0

H2O 2.3071E+06

E-Con, 1/ohm-cm 1.7247E-04

ACETACID 1.1710E-04

E-Con, cm2/ohm-mol 6.5112

CO2 .76289

Ionic Strength 1.7739E-03

COCL2 1.5677

ACET2 .12719

H2SO4 7.7960

H2S 4.1689E-02

N2 24.144

NH3 8.6591

O2 8.2613

WASTE 27.080

NH4ACET 5.7129E-04

H3PO4 1.6191E-07

BUGHINERT .25134

BUGHACTIV 8.1568

NH44H2CO33 13.557

NH43PO4 1.5677

```

STREAM: OUTLET
=====
TO      :      Total g/hr      2.0507E+07
FROM    : CLARIFIER           Volume, m3/hr      20.542
                                           Enthalpy, cal/hr  -7.7841E+10
Temperature, C      20.000      Vapor fraction     0.0
Pressure, atm       1.0000      Solid fraction     7.3884E-06
pH                 8.0929      Organic fraction   0.0
Total mol/hr       1.1380E+06    Osmotic Pres, atm .10132
----- mol/hr-----
-
H2O                1.1380E+06      Redox Pot, volts  0.0
ACETACID           5.7763E-05    E-Con, 1/ohm-cm   1.7247E-04
CO2                .37630      E-Con, cm2/ohm-mol 6.5112
COCL2              .77326      Ionic Strength     1.7739E-03
ACET2              6.2738E-02
H2SO4              3.8454
H2S                2.0563E-02
N2                 11.909
NH3                4.2711
O2                 4.0749
WASTE              13.357
NH4ACET            2.8179E-04
H3PO4              7.9864E-08
BUGHINERT          .25134
BUGHACTIV          8.1569
NH44H2CO33        6.6869
NH43PO4            .77326

```

STREAM: SLUDGE		Volume, m3/hr	.28155
TO :		Enthalpy, cal/hr	-1.0670E+09
FROM : CLARIFIER		Vapor fraction	0.0
		Solid fraction	0.0
Temperature, C	20.000	Organic fraction	0.0
Pressure, atm	1.0000	Osmotic Pres, atm	.10132
pH	8.0929	Redox Pot, volts	0.0
Total mol/hr	15598.	E-Con, 1/ohm-cm	1.7247E-04
-----	mol/hr-----	E-Con, cm2/ohm-mol	6.5112
-		Ionic Strength	1.7739E-03
H2O	15597.		
ACETACID	7.9172E-07		
CO2	5.1577E-03		
COCL2	1.0599E-02		
ACET2	8.5992E-04		
H2SO4	5.2707E-02		
H2S	2.8185E-04		
N2	.16323		
NH3	5.8542E-02		
O2	5.5852E-02		
WASTE	.18308		
NH4ACET	3.8623E-06		
H3PO4	1.0947E-09		
NH44H2CO33	9.1653E-02		
NH43PO4	1.0599E-02		
	=====		
Total g/hr	2.8106E+05		

STREAM: RECYCLE		O2	4.1305
TO :		WASTE	13.540
FROM : CLARIFIER		NH4ACET	2.8564E-04
		H3PO4	8.0954E-08
Temperature, C	20.000	NH44H2CO33	6.7782
Pressure, atm	1.0000	NH43PO4	.78381
pH	8.0929		=====
Total mol/hr	1.1536E+06	Total g/hr	2.0786E+07
----- mol/hr-----		Volume, m3/hr	20.822
-		Enthalpy, cal/hr	-7.8909E+10
H2O	1.1535E+06	Vapor fraction	0.0
ACETACID	5.8551E-05	Solid fraction	0.0
CO2	.38143	Organic fraction	0.0
COCL2	.78381	Osmotic Pres, atm	.10132
ACET2	6.3594E-02	Redox Pot, volts	0.0
H2SO4	3.8979	E-Con, 1/ohm-cm	1.7247E-04
H2S	2.0844E-02	E-Con, cm2/ohm-mol	6.5112
N2	12.072	Ionic Strength	1.7739E-03
NH3	4.3294		

===== BLOCK REPORT

BLOCK NAME: BIOREACTOR

BLOCK TYPE: BioReactor

=====

Warnings

* Inadequate HRT/SRT for Autotrophic Growth

Characteristics

Reactor Volume, m3	300.00
HRT, hr	7.2037
O2 Mass Transfer Coef, 1/hr	100.00
Reactor Duty (Hout-Hin), cal/hr	-5.2101E+06

	Heterotrophic	Autotrophic
Minimum HRT, hr	6.6555	0.0

Flows

	m3/hr	gal/min
Feed	41.644	183.35
Air	24.051	105.89
Recycle	0.0	0.0
Wastage	0.0	0.0
Effluent	41.645	183.36
Suspended Solids, g/hr		951.10

Concentrations

	TOTAL FEED, mg/l	REACTOR, mg/l
Substrate	156.30	99.355
NH3 Nitrogen	20.289	22.733
Dissolved O2		6.2749
Dissolved NO3		0.0
MLVSS		22.838

	Heterotrophic	Autotrophic
Active Cells, mg/l	22.156	0.0
Inactive Cells, mg/l	.68269	0.0
Min. Subst Achievable, mg/l	5.0434	
Dissolved O2 - Saturated, mg/l	6.3477	

Nutrient & Molecular Utilization

	for Heterotrophic	Autotrophic
Required:	Cells	Cells
NH3 Nitrogen, g/hr	24.597	0.0
Phosphorus, g/hr	4.9194	0.0
Oxygen Utilization, g/hr	2184.9	0.0
Production:		
NO3 Nitrogen, g/hr	0.0	

Cell Production & Substrate Utilization

	Heterotrophic	Autotrophic
Observed Growth Yield, g Cell/g COD	.25995	
Substrate:		
in Total Feed, g COD/hr	9680.2	
from Reactor, g COD/hr	6147.3	
Utilization, g Subst COD/hr	3549.4	
Cell Production g Cell/hr	1064.8	0.0

BioReaction Rates

	Heterotrophic	Autotrophic
Cell Production, g Cell/m3-hr	3.5494	0.0
Cell Decay, g Cell/m3-hr	.47384	0.0
Subst Util. for Energy, g Subst/m3-hr	4.5796	
Aerobic Fraction	.99063	
Anoxic Fraction	0.0	
Anaerobic Fraction	9.3713E-03	

NH3 N Util. for Energy, g N/m3-hr 0.0

BioReaction Constants

Composite

	Heterotrophic	Autotrophic
Max Specific Growth Rate	0.0	2.0000E-02 1/hr
True Growth Yield	0.0	g Cell/g COD
		.10000 g Cell/g N
Decay Rate	0.0	5.0000E-03 1/hr
Subst Half-Sat Constant	0.0	mg/l
NO3 N Half-Sat Constant	0.0	mg/l
NH3 N Half-Sat Constant		1.0000 mg/l
O2 Half-Sat Constant	0.0	1.0000 mg/l
CO3 C Half-Sat Constant	0.0	mg/l
Anoxic Growth Factor	0.0	
Anaerobic Growth Factor	0.0	
Andrews Self-Inhibition Coef.	0.0	mg/l

WASTE

Max Specific Growth Rate	.20000	1/hr
True Growth Yield	.30000	g Cell/g COD
Decay Rate	2.2000E-02	1/hr
Subst Half-Sat Constant	22.000	mg/l
NO3 N Half-Sat Constant	.40000	mg/l
O2 Half-Sat Constant	.15000	mg/l

CO3 C Half-Sat Constant	.10000	mg/l
Anoxic Growth Factor	.80000	
Anaerobic Growth Factor	.40000	
Andrews Self-Inhibition Coef.	Infinite	mg/l

ACETACID

Max Specific Growth Rate	.36000	1/hr
True Growth Yield	.35000	g Cell/g COD
Decay Rate	2.0000E-02	1/hr
Subst Half-Sat Constant	40.000	mg/l
NO3 N Half-Sat Constant	.40000	mg/l
O2 Half-Sat Constant	.15000	mg/l
CO3 C Half-Sat Constant	.10000	mg/l
Anoxic Growth Factor	.80000	
Anaerobic Growth Factor	0.0	
Andrews Self-Inhibition Coef.	Infinite	mg/l

ESP Control Block Applications

This chapter describes in detail specific applications for the ESP Control Blocks.

The ESP Control Blocks described in this chapter are:

- **Manipulate**
- **Controller**

The Manipulate and Controller will be used in conjunction with a Mix to model a neutralizer.

Manipulate/Controller

For this application, CONTROL, the process example described in Chapter 2: Getting Started, TOURING OLI, A Tour of ESP Process on page 30, will be used replacing the Neutralizer with Manipulate, Mix and Controller Blocks (See **Error! Reference source not found.**). The Chemistry Model for this example, CONTROL, is also described in the same chapter.

Process Summary

This process involved the combination of two effluent streams (one acid, one base). The resulting combination is then neutralized to the desired pH by adding a sufficient amount of reagent.

Process Build - Getting Started

As described in the Getting Started section of this manual, specify the Mix block, MIX1 along with the streams ACID WASTE and BASE WASTE.

Now specify the Separate Block SEPARATE1.

Manipulate Block Definition

The next block to be specified is the Manipulate Block. Initially, the block should be named (e.g., MANIPULATE CAUST) and then the stream entering the block identified (e.g., CAUSTIC REAGENT). The stream composition is the same as the reagent stream in the example in the Getting Started section of this manual.

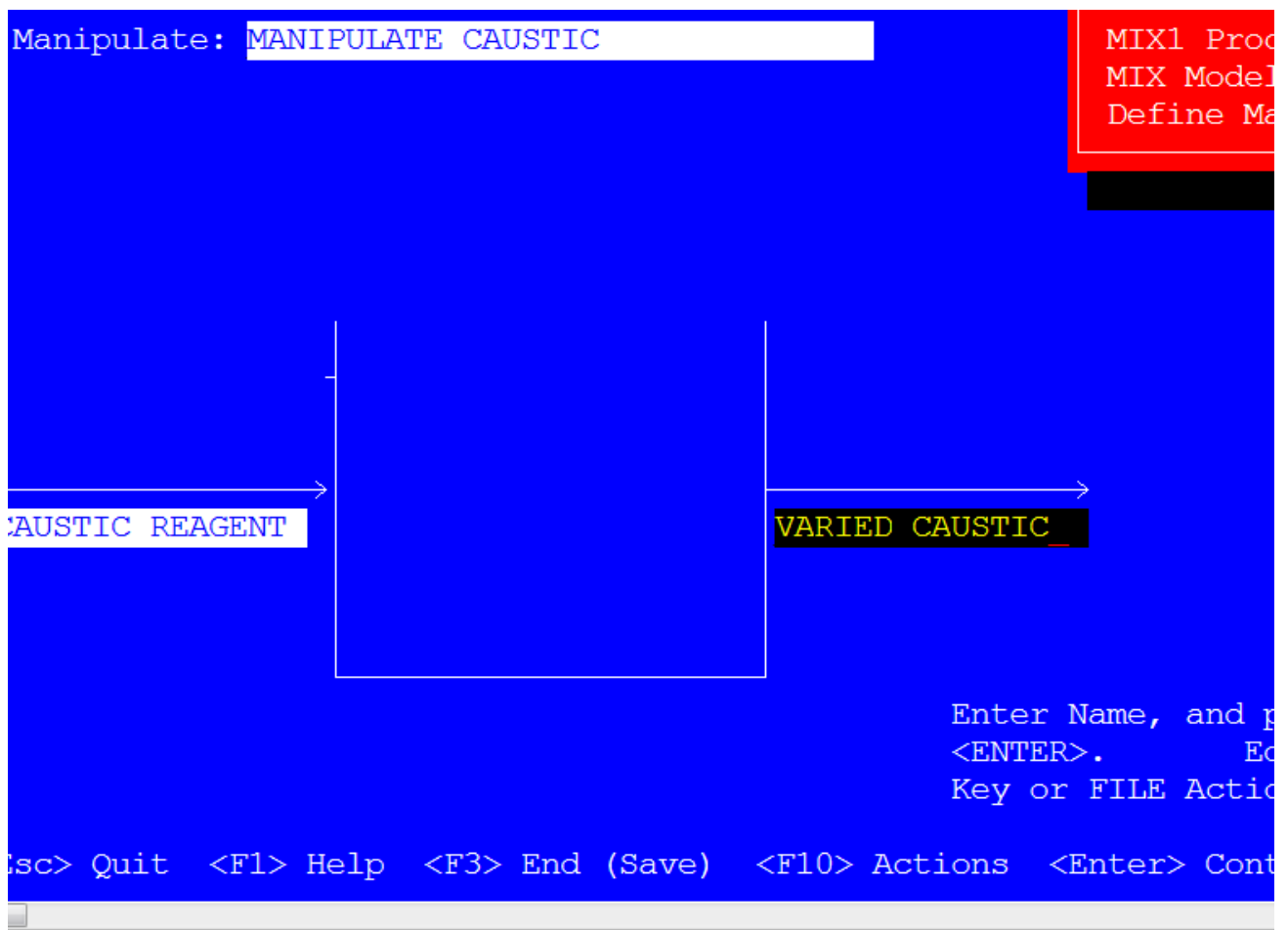
The exit stream is then named (e.g., VARIED CAUSTIC).

Parameters - Manipulate Block

On naming the block exit stream, the Manipulate operating requirements are defined. This is achieved via the Action Key and selecting the Parameters facility.

For this example the Total Flow of the stream will be varied. The initial multiplication factor will be 1.0.

The process definition of the block is now complete. The format of the block is:



Mix Block Specification

Initially the block should be named (e.g., MIX NEUTRALIZER) and the first stream to the block specified as the Liquid exit stream from the Separate Block (e.g., SEPD LIQUID). The next stream entering the block should be the outlet stream from the Manipulate Block (e.g., VARIED CAUSTIC). The exit stream should now be named (e.g., NEUTRALIZED LIQ).

Parameters - Mix Block

On naming the block exit stream, the Mix operating requirements are defined. This is achieved via the Action Key and selecting the Parameters facility.

The calculation is to be performed with the Mix Block operating adiabatically.

Controller Block Specification

Initially the block should be named (e.g., CONTROL pH). The Specification Stream is chosen by pressing the Enter Key on the blank field and selecting the outlet stream exiting the Mix block which will be acting as the neutralizer (e.g., NEUTRALIZED LIQ) from the displayed list of streams.

The Specification Type is selected in the same manner by pressing the Enter Key on the blank field and selecting pH from the displayed list of specifications.

The Spec Target Value for this example is 9.0. Enter the value in the blank field and press the Enter Key.

The Block Name which will be controlled is selected by pressing the Enter Key on the blank field and selecting the Manipulate Block (e.g., MANIPULATE CAUST) from the displayed list.

The Block Parameter which will be adjusted is selected in the same manner by pressing the Enter Key on the blank field and selecting Factor, Flow from the displayed list.

Process Analysis

The process definition is now complete. The user should save this block and then execute the case using the Process Analysis mode of ESP Process.

Summary

On completing the Process Analysis a copy of the results can be requested using the Summary mode.

The output at the end of this section summarizes the process results for this example.

The streams for this Controller Application, shown on a ionic basis:

STREAM: BASE WASTE

TO : MIX1

FROM :

Temperature, C	40.000
Pressure, atm	1.0000
pH	9.3407
Total mol/hr	199.29
-----	mol/hr-----
H2O	195.21
CO2	7.3508E-05
NH3	2.2570
SO2	1.5070E-11
OHION	3.3073E-04
CO3ION	6.8610E-02
HCO3ION	.14047
HION	2.2246E-09
HSO3ION	6.9497E-04
NH2CO2ION	.14352
NH4ION	1.1262
S2O5ION	5.3298E-12
SO3ION	.35198
	=====
Total g/hr	3625.0

Volume, m3/hr	3.6302E-03
Enthalpy, cal/hr	-1.3467E+07
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	26.435
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	4.2638E-02
E-Con, cm2/ohm-mol	36.574
Ionic Strength	.43984

STREAM: ACID WASTE

TO : MIX1

FROM :

Temperature, C	25.000
Pressure, atm	1.0000
pH	-9.8975E-03
Total mol/hr	153.32
-----	mol/hr-----
H2O	147.09
H2SO4	9.5722E-11
HCL	1.4339E-07
SO3	1.2930E-14
OHION	4.7684E-14
HION	3.3229
HSO4ION	2.2415
CLION	.26497
SO4ION	.40824
	=====
Total g/hr	2919.3
Volume, m3/hr	2.7572E-03
Enthalpy, cal/hr	-1.0622E+07
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	58.157
Redox Pot, volts	0.0

E-Con, 1/ohm-cm .42016

E-Con, cm²/ohm-mol 397.46

Ionic Strength 1.4081

STREAM: MIXED WASTE

TO : SEPARATE1

FROM : MIX1

Temperature, C	38.577
Pressure, atm	1.0000
pH	1.1080
Total mol/hr	350.10
-----	mol/hr-----
H2O	342.78
CO2	.35267
H2SO4	2.5519E-12
HCL	1.9077E-08
NH3	3.3612E-08
SO2	.27921
SO3	4.0601E-16
OHION	3.2613E-12
CO3ION	4.6785E-15
HCO3ION	1.4473E-06
HION	.72356
HSO3ION	7.3462E-02
HSO4ION	1.3876
NH2CO2ION	1.2667E-14
NH4ION	2.9786
NH4SO4ION	.54807
CLION	.26497
S2O5ION	4.1630E-08

SO3ION	2.6535E-07
SO4ION	.71406
	=====
Total g/hr	6544.4
Volume, m3/hr	1.2978E-02
Enthalpy, cal/hr	-2.4090E+07
Vapor fraction	7.4125E-04
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	24.180
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	.11337
E-Con, cm2/ohm-mol	112.18
Ionic Strength	.71519

STREAM: SEPD VAPOR

TO :

FROM : SEPARATE1

Temperature, C	38.577
Pressure, atm	1.0000
pH	0.0
Total mol/hr	.25951
-----	mol/hr-----
H2O	1.7466E-02
CO2	.22560
H2SO4	1.3605E-18
HCL	1.2765E-09
NH3	4.7629E-11
SO2	1.6444E-02
SO3	9.9978E-26
	=====
Total g/hr	11.297
Volume, m3/hr	6.6039E-03
Enthalpy, cal/hr	-2.3366E+04
Vapor fraction	1.0000
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	0.0
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	0.0
E-Con, cm2/ohm-mol	0.0

Ionic Strength 0.0

STREAM: SEPD LIQUID

TO : MIX NEUTRALIZER

FROM : SEPARATE1

Temperature, C	38.577
Pressure, atm	1.0000
pH	1.1080
Total mol/hr	349.84
-----	mol/hr-----
H2O	342.76
CO2	.12707
H2SO4	2.5519E-12
HCL	1.7800E-08
NH3	3.3564E-08
SO2	.26277
SO3	4.0602E-16
OHION	3.2613E-12
CO3ION	4.6785E-15
HCO3ION	1.4473E-06
HION	.72356
HSO3ION	7.3462E-02
HSO4ION	1.3876
NH2CO2ION	1.2668E-14
NH4ION	2.9786
NH4SO4ION	.54807
CLION	.26497
S2O5ION	4.1630E-08

SO3ION	2.6535E-07
SO4ION	.71406
	=====
Total g/hr	6533.1
Volume, m3/hr	6.3742E-03
Enthalpy, cal/hr	-2.4066E+07
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	24.180
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	.11337
E-Con, cm2/ohm-mol	112.18
Ionic Strength	.71519

STREAM: CAUSTIC REAGENT

TO : MANIPULATE CAUST

FROM :

Temperature, C	30.000
Pressure, atm	1.0000
pH	13.707
Total mol/hr	101.77
-----	mol/hr-----
H2O	98.230
OHION	1.7696
HION	6.2949E-14
NAION	1.7696
	=====
Total g/hr	1840.4
Volume, m3/hr	1.7804E-03
Enthalpy, cal/hr	-6.8999E+06
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	50.193
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	.18740
E-Con, cm2/ohm-mol	188.54
Ionic Strength	1.0000

STREAM: VARIED CAUSTIC
 TO : MIX NEUTRALIZER
 FROM : MANIPULATE CAUST

Temperature, C	30.000
Pressure, atm	1.0000
pH	13.707
Total mol/hr	245.33
-----	mol/hr-----
H2O	236.80
OHION	4.2660
HION	1.5175E-13
NAION	4.2660
	=====
Total g/hr	4436.7
Volume, m3/hr	4.2920E-03
Enthalpy, cal/hr	-1.6633E+07
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	50.193
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	.18740
E-Con, cm2/ohm-mol	188.54
Ionic Strength	1.0000

STREAM: NEUTRALIZED LIQ

TO :

FROM : MIX NEUTRALIZER

Temperature, C	39.734
Pressure, atm	1.0000
pH	9.0000
Total mol/hr	594.05
-----	mol/hr-----
H2O	583.46
CO2	8.0043E-05
H2SO4	9.9583E-28
HCL	2.2782E-16
NH3	1.3871
SO2	5.0475E-11
SO3	0.0
NAHCO3	5.3321E-03
OHION	4.5547E-04
CO3ION	2.3428E-02
HCO3ION	7.9238E-02
HION	1.7968E-08
HSO3ION	1.1840E-03
HSO4ION	4.8282E-08
NACO3ION	2.5170E-03
NAION	4.1651
NASO4ION	9.2952E-02
NH2CO2ION	1.6474E-02

NH4 ION	1.6616
NH4SO4 ION	.46149
CL ION	.26497
S2O5 ION	6.4403E-12
SO3 ION	.33504
SO4 ION	2.0953
	=====
Total g/hr	10970.
Volume, m3/hr	1.0747E-02
Enthalpy, cal/hr	-4.0700E+07
Vapor fraction	0.0
Solid fraction	0.0
Organic fraction	0.0
Osmotic Pres, atm	18.524
Redox Pot, volts	0.0
E-Con, 1/ohm-cm	5.8697E-02
E-Con, cm2/ohm-mol	56.472
Ionic Strength	.78779

Dynamic Simulation Applications

This chapter describes in detail a specific application for the dynamic simulation program, DynaChem, available in ESP ToolKit under ProChem. The procedures for defining the Process and executing the simulation are described, and graphical plots of the results are included for reference. The simulation described is:

pH Control Process A two stage effluent neutralization process is simulated. The process involves feedback PID controllers installed on both stages controlling acid dosing flows to the respective tanks. Effluent flow variations of $\pm 10\%$ to the process can occur, and the simulation is used to determine process controller settings in order to maintain the final effluent pH within the required range of $\text{pH } 9.0 \pm 0.5$.

The following sections describe in detail the required case input definition for the simulation. For further information it is advised the user refers to the Dynamic Modeling section and the DynaChem Handbook.

Two Stage Effluent pH Control

For the application, the dynamic simulation program DynaChem is used to simulate a two stage effluent pH control process. The simulation is used to determine controller settings for the pH controllers modulating the dosing reagent flows, for given process disturbances.

Process Summary

The neutralization process is previously described in Neutralizer Block on page 396 of this section. Generally a waste effluent is to be dosed with 37% w/w sulfuric acid using a two stage process. The first stage controls the effluent pH at 11.0 and the second stage further reduces the effluent pH to a value of 9.0.

The effluent flow to the process is normally $100\text{m}^3/\text{hr}$ but it can vary by $\pm 10\%$. A pH control scheme is therefore required to handle these disturbances and maintain the final effluent pH within the range of 9.0 ± 0.5 .

The steady state process described in Neutralizer Block on page 396 is used to determine the molecular species distributions of the various streams and the approximate acid dosing requirements to meet the required pH control points. The results from this steady state analysis are used to define the dynamic simulation starting conditions.

Process Control Scheme

Prior to using DynaChem it is advisable to produce a schematic diagram of the control scheme to be defined. For this example, it is proposed to use feedback P.I.D. on both neutralization stages. **Error! Reference source not found.** on page **Error! Bookmark not defined.** shows the schematic control scheme.

ESP Toolkit

In order to use DynaChem the user must generate a Chemistry Model in ESP Process. The Chemistry Model previously generated for the steady state application (Refer to Electrolyte Model For Neutralization Example on page 491 for further details) will be used. In order to do this, the user should generate a New Process by name (e.g., NEUTDYN) and then access the Chemistry Model mode. The required Chemistry Model (e.g., NEUTRAL) should then be selected. After the model is created the user should exit ESP Process.

The ESP ToolKit facility is now accessed and the user should select to use the ProChem set of programs, and in particular the DynaChem component.

DnaChem Case Input

The simulation is to be performed in two parts. First, the process is executed without any controller action and process disturbances, with the acid dosing values sectionally adjusted to meet the required pH control points. This case is executed over a short period of time, in this case 0.5hr, and allows the system to reach steady state conditions. The results of this simulation therefore provide accurate starting conditions and stream compositions for the second part of the simulation.

The simulation is then re-started with process disturbance and controller information, with process disturbances and controller action being introduced after 0.5 hrs.

The DynaChem Case Input Definition for the simulation needs to include all the process data, including the process disturbance and controller information, with the time specification being edited in order to perform the simulation in two parts.

This chapter describes how to define the case input file and perform the first part (i.e., steady state) of the simulation.

Dynamic Simulation on page 466 describes the modifications required to the case input in order to perform the second part (i.e., dynamic) of the simulation.

For detailed specification procedures the user should refer to the Dynamic Modeling section and the DynaChem Handbook

Chemistry Model

The Chemistry Model previously used for the steady state neutralization example is the basis for this DynaChem application also.

Case Definition

In order to define the case input, the user should select DynaChem on the display menu. The user can then create the DynaChem input file by specifying option 1 on the following screen.

The Chemistry Model must be named, followed by the process case name. For this example, the names should be specified as:

Model name: NEUTRAL1

Case name: NEUTRAL1

A selection of options are then displayed from which the user should choose to Display All Forms by entering option 1 on the display. The case input file can then be defined.

Case Title

Initially, the case is named (e.g., NEUTDYN) and the Time Increment of calculation and the simulation End Time are specified. For the first part of the simulation the following values are used:

Time Increment 0.01 hrs.

End Time 0.50 hrs

Restart Specifications

This option allows the user to specify how often the simulation results are to be saved to a restart file. In this simulation we are not interested in these options so the user should Continue to the next screen.

Unit Specifications

The process Units are then identified using a number, software keyword and description. The keywords which can be used are Entry, Tank and Pipe. Referring to **Error! Reference source not found.** the schematic diagram of the process, the following specification is required:

<u>Unit Number</u>	<u>Unit Type</u>	<u>Unit Description</u>
1	Entry	Waste Effluent
2	Entry	37% H2SO4 Stage 1

3	Entry	37% H2SO4 Stage 2
11	Tank	Stage 1 Neutralization Tank
12	Tank	Stage 2 Neutralization Tank

Entry Blocks

The downstream nodes for the defined Entry Units (Reference **Error! Reference source not found.**) are specified as:

<u>Unit</u>	<u>Downstream Node Number</u>
1	1
2	2
3	3

As all Entry Units are continuous and start at time = 0 the default settings are used.

Tank Blocks

The Tank Unit operating conditions and respective upstream and downstream nodes are then defined. **Error! Reference source not found.** shows the required node layout and the tanks are specified as follows:

<u>Unit</u>	<u>Cross Sectional Area m³</u>	<u>Maximum Level m</u>	<u>Upstream Node Numbers</u>		<u>Downstream Node Numbers</u>	<u>Exit Level m</u>
11	9.62	4	1	2	4	3.2
12	9.62	4	3	4	5	3.2

Note: The tank specifications are defined on individual screen displays.

Entry Block State Specifications

The Entry stream parameters and compositions are then defined. The steady state results, predicted using the Neutralizer Blocks available in ESP Process Blocks, are used to specify species mole fractions for the respective streams (refer to Neutralizer Block pg. 396 for further details)

The waste effluent (Entry Unit 1) is defined as having a total flow of 110m³/hr and not as 100m³/hr as in the steady state analysis. The extra 10m³/hr is to be used to test controller performance.

The respective acid flowrates to the two tanks are specified as 3m³/hr and 1m³/hr. These ratings are slightly greater than the steady state results (Reference Neutralizer Block pg. 396) and allow a margin for the control of effluent pH during process disturbance conditions.

The effluent vapor phase and species equilibria are not to be considered in this particular example. This is because they are fixed composition streams. By calculating the electrolyte equilibrium only at the start of the simulation as opposed to every time step, significant calculation time can be saved.

Therefore the three Entry Unit State Specifications are:

Unit 1 Waste Effluent

No vapor time 0 hrs No equil time 0 hrs

Temperature 23° C

Pressure 1.0 atm

Total flow 110 m³/hr

H2O 0.9912 mol frac

CO2 2.259E-14

NACL 3.625E-03

NAOH 3.702E-03

NA2CO3 1.315E-03

CASO4 1.219E-10

CACO3 2.400E-05

NAHCO3 3.955E-07

NANO3 4.643E-05

CACL2 1.021E-07

MGOH2	5.000E-05
NA2SO4	1.614E-05

Unit 2 37% H2SO4 Stage 1

No vapor time 0 hrs	No equil time 0 hrs
Temperature	25° C
Pressure	1.0 atm
Total Flow	3.0 m3/hr
H2O	0.903 mol frac
H2SO4	0.097

Unit 3 37% H2SO4 Stage 2

No vapor time 0 hrs	No equil time 0 hrs
Temperature	25° C
Pressure	1.0 atm
Total Flow	1.0 m3/hr
H2O	0.903 mol frac
H2SO4	0.097

Tank Block State Specifications

In order to make the simulation as realistic and as quick as possible the option is available to specify the composition of the initial tank contents. This does not have to be performed but it is advisable as it allows the simulation to reach realistic operating conditions as quickly as possible, thereby saving computer operating time.

For this particular example the tank effluent compositions are specified as these for the respective tank discharge streams predicted at steady state. (Refer to Neutralizer Block on pg. 396 of this section for further details).

The Tank State Specifications are defined as:

Unit 11 Stage 1 Neutralization Tank

Temperature	26.21° C
Pressure	1.0 atm
Initial	30 m ³
H2O	0.9932 mol frac
CO2	5.693E-10
NACL	3.556E-03
NAOH	2.778E-05
NA2CO3	1.232E-03
CASO4	1.485E-08
CACO3	2.357E-05
MGSO4	7.413E-07
NAHCO3	5.842E-05
NANO3	4.555E-05
CACL2	6.402E-08
MGOH2	4.831E-05
NA2SO4	1.847E-03

Unit 12 Stage 2 Neutralization Tank

Temperature	26.6° C
Pressure	1.0 atm
Initial volume	30 m ³
H2O	0.9927 mol frac
CO2	1.044E-06
HNO3	1.296E-15
NACL	3.506E-03
NA2CO3	2.195E-04

CASO4	1.069E-07
MGCL2	1.436E-05
CACO3	2.305E-05
MGSO4	3.426E-05
NAHCO3	1.063E-03
NANO3	4.528E-05

Valve Specification

The process values are then identified and their mode location, capacity, and type specified. For this particular example, all valves are of the linear type and their capacities are estimated from the steady state results. (Refer to Neutralizer Block pg. 396 for further details). **Error! Reference source not found.** shows the respective valve locations for the process.

The valve specifications should therefore be defined as:

<u>Valve Number</u>	<u>Downstream Node</u>	<u>Capacity</u>	<u>Valve</u>
	<u>Number</u>	<u>m³/hr</u>	<u>Type</u>
1	1	120	LINE
2	4	120	LINE
3	5	120	LINE
4	2	3	LINE
5	3	1	LINE

Each individual valve pressure function and override position if required, is then specified. For this particular example, all valves use the pressure default setting $f(p) = 1$ shown on the display.

The first part the simulation uses the same flows as those determined in the steady state analysis (Refer to Neutralizer Block on page 396):

Effluent flow	100 m ³ /hr
37% H2SO4 Stage 1	2.15 m ³ /hr
37% H2SO4 Stage 2	0.666 m ³ /hr

However, these valves are to be modulated either manually to produce process disturbances, or by controllers during the second part of the simulation. Therefore, valve override settings are required.

Valve 1, the effluent stream inlet valve is set to give a constant flow of 100m³/hr during the first part of the simulation, and is then used to produce random process disturbances during the second part.

The valve settings are defined as valve override positions. This is achieved as a vector input and the user should enter an "*" for the override specification. This accesses a display in which the valve positions are defined. The following data should be specified.

<u>Time hrs</u>	<u>Valve open position</u>
0	0.831
0.52	0.917
0.55	0.833
0.60	0.75
0.66	0.833
0.70	0.917
0.72	0.833
0.73	0.917
0.79	0.833

Note: The initial valve position produces an effluent flow of approximately 100m³/hr (i.e., 120m³/hr x 0.833- valve stem) for the first part of the simulation. The remaining positions are random \pm 10% changes in flow for use in the second part of the simulation.

Valves 2 and 3 are tank discharge valves from the two stages and are to remain open for the complete simulation. Their respective override positions should therefore be specified as 1.

Valves 4 and 5 are the sulfuric acid dosing control valves. During the first part of the simulation the valves are set to give flows of 2.15 and 0.666 m³/hr respectively. The valves are the modulated by the pH controllers during the second part of the simulation. The valve override positions should therefore be set to give the required flows. The settings are:

<u>Valve</u>	<u>Valve Override</u>
4	0.715 (i.e., 3 x 0.715)
5	0.666 (i.e., 1 x 0.666)

With the respective valve capacity the actual flow through the valve is obtained. The required flows through the valves are available from the steady state process results contained in Neutralizer Block on page 396 of this section. The Valve Override valves should be defined as:

<u>Valve N Deg.</u>	<u>Valve Override</u>
2	1.0
3	1.0
4	0.715
5	0.666

All valves use the pressure default settings $f(p) = 1$ shown on the display.

Pump Specification

The user is then prompted to define any process pump operating parameters. For this application, this specification is not required and the user should Continue to the next screen.

Control Loop Specification

The process control loops are then identified and the controller output destination and algorithm type defined. For this particular example velocity algorithms are to be applied, as distance of valve stem movement is to be controlled. The schematic diagram of the process shown on **Error! Reference source not found.** shows the controller positions and the output signal destinations, which in this case are valves.

Therefore the control loop specification is as follows:

<u>Control loop</u>	<u>Control loop output</u>	<u>Algorithm</u>
<u>Number</u>	<u>ID Number-Valve</u>	<u>Type</u>
1	4	VELO
2	5	VELO

The individual controller unit locations, process variables to be controlled, setpoint value, and process controller settings are then defined.

Due to the simulation requiring control action during the second part of the simulation only vector inputs are required for controller gain, integral and derivative times. The controllers also have dead time which must also be entered as a vector input.

This is achieved by entering a "*" symbol for the appropriate controller specification. A series of displays are then accessed which allow the user to specify the required controller settings for specific time periods of the simulation. Multiple settings are allowed in order to simulate self tuning controllers. However, for this example only one setting per parameter is required.

The control loop definitions are as follows:

Control Loop 1

Setpoint value: 11.0
 Setpoint value ID type: PH
 Setpoint unit ID number: 11
 Controller gain: *
 Integral time: *
 Derivative time: *
 Dead time: *

The controllers should then be specified to come on line after 0.51 hrs (i.e., the start to the second part of the simulation) The following settings should be specified

	<u>Time hrs</u>	<u>Value</u>	<u>Keyword</u>
Controller gain	0.51	0.24	KC
Integral time	0.51	4.15 minutes	TAUI
Derivative time	0.51	1.0375 minutes	TAUD
Deadtime	0.51	.03 hours	DEAD

Control Loop 2

Setpoint value: 9.0

Setpoint value ID type: PH

Setpoint unit ID number: 12

Controller gain: *

Integral time: *

Derivative time: *

Dead time: *

The following controller settings should be specified to become operational after 0.51 hrs:

	<u>Time hrs</u>	<u>Value</u>	<u>Keyword</u>
Controller gain	0.51	0.43	KC
Integral time	0.51	4.09 minutes	TAUI
Derivative time	0.51	1.0225 minutes	TAUD
Dead time	0.51	0.03 hours	DEAD

Node Order Calculation

The node order for calculations is then specified. For this example, the feeds to the Stage 1 neutralization tank are to be calculated, followed by the unit exit stream. The Stage 2 acid dosing node is then evaluated, followed by the tank exit stream. Referring to **Error! Reference source not found.**, the calculation node order is defined as:

1 2 4 3 5

Print Specifications

The frequency with which results are stored in the output and summary files are then specified as:

Output Print Frequency 50 Time Steps

Summary Print Frequency 25 Time Steps

The output is required to a terminal and an interactive simulation capability is also needed.

Log Nodes

This specifications is not required for this example and the user should continue to the next display.

This completes the Case Input definition and the user is returned to the case input option menu. The defined input file can be displayed by selecting option 11 and **Error! Reference source not found.** included at the end of this chapter shows the format of the case definition.

Steady State Simulation

The first stage of the simulation is now performed. This is the steady state simulation which runs for 0.5hrs. The user should Exit from the Case Input option menu, and then select the Run DynaChem option 2, from the following display. The simulation chemistry model and process input files are then named.

Due to the case input being defined with an interactive capability the user can select to display a variety of parameters in graphical or tabular format as the simulation proceeds. The required parameter is displayed by entering the appropriate character shown on the display.

The simulation is started by pressing the Enter Key.

Results

The results from the simulation can be displayed in graphical or tabular format. The results are stored in a file with the extension DOU.

Error! Reference source not found. shows the graphical plot of pH for units 11 and 12 exiting the two tanks with time. As expected, steady state conditions are achieved and the required pH control points are obtained.

These results are now used as the starting conditions for the second part of the dynamic simulation.

Dynamic Simulation

The second part of the simulation is performed to determine pH controller settings required to maintain the control points for given process disturbances.

Several cases were executed for this example until the previously stated optimum controller settings were achieved.

Restart File

In order to use the results produced from the first part of the simulation (Refer to Dynamic Simulation Applications on page 454) a restart file needs to be prepared.

Basically this file provides the initial starting conditions for the second part of the simulation by storing the final results predicted by the steady state case.

The restart file is simply prepared by copying the steady state results file (extension .ROU) to a restart file (extension .RIN). In order to do this the user should exit from the ESP Program.

After the restart file is prepared the user should re-enter DynaChem, through ESP, and edit the previously defined case input file.

Case Input Edit

In order to activate the previously defined process disturbances and controller settings, which do not become operational until the simulation time has exceeded 0.5 hrs, the Case Input Time Specification must be modified.

Time Specification

This is achieved by selecting option 2 from the case input option menu. The user should then change two parameters.

Firstly, the simulation End Time needs to be increased. This is because this second part of the simulation is to start after 0.5 hrs (i.e., at the end of the first part). For this example, the defined value of 0.5 hrs should be changed to 1.5 hrs.

Secondly, the user should confirm that the case is now to use results from a previous case. This case is the recently prepared restart file. The user should replace the character N with a character Y.

Dynamic Simulation

The editing of the Case Input is now complete and the second part of the simulation can now be performed. This is achieved following the same procedures as previously described for the first part.

Results

and at the end of this chapter show the outlet unit pH variations with time, and the corresponding control value responses to the effluent flow disturbances.

INPUT:

TITLE NEUTDYN

;

RESTART

;

; SPECIES INPUT ORDER

;

; 1 H2O

; 2 CO2

; 3 H2SO4

; 4 HCL

; 5 HNO3

; 6 SO3

; 7 MGNO32

; 8 NAACL

; 9 NAOH

; 10 NA2CO3

; 11 CAO2

; 12 CASO4

; 13 MGCL2

; 14 CACO3

; 15 MGSO4

; 16 NAHCO3

; 17 NANO3

; 18 CACL2

```

;      19  CANO32
;      20  MGCO3
;      21  MGOH2
;      22  NA2SO4
;      23  NA3HSO42
;      24  NA6SO42CO3
;      25  NAHSO4
;      26  CAHCO32CO3
;      27  CAHCO32
;

```

```

PRINT OUTPUT=50  SUMMARY=25  TERM  INTERA

```

```

;

```

```

TIME  TEND=1.5  TINC=1.000000E-02 (TIME=0)

```

```

;

```

```

UNIT1  ENTRY  DNODE=1  "WASTE EFFLUENT"

```

```

      COND=  TEMPERATURE          23.000
+          PRESSURE                1.0000
+          TOTAL                   110.00
+          H2O                      .99120
+          CO2                      .22590E-13
+          NAACL                    .36250E-02
+          NAOH                     .37020E-02
+          NA2CO3                   .13150E-02
+          CASO4                    .12190E-09
+          CACO3                    .24000E-04
+          NAHCO3                   .39550E-06
+          NANO3                    .46430E-04

```

```

+          CACL2          .10210E-06
+          MGOH2          .50000E-04
+          NA2SO4         .16140E-04

```

```
UNIT2  ENTRY  DNODE=2  "37% H2SO4 STAGE 1"
```

```

COND= TEMPERATURE      25.000
+          PRESSURE      1.0000
+          TOTAL         3.0000
+          H2O           .90300
+          H2SO4         .97000E-01

```

```
;
```

```
UNIT3  ENTRY  DNODE=3  "37% H2SO4 STAGE 2"
```

```

COND= TEMPERATURE      25.000
+          PRESSURE      1.0000
+          TOTAL         1.0000
+          H2O           .90300
+          H2SO4         .97000E-01

```

```
;
```

```
UNIT11 TANK  UNODE=1,2  DNODE=4  "STAGE 1 NEUTRALIZATION TANK"
```

```

CSA=9.62  MAXL=4  LEXI=3.2
COND= TEMPERATURE      26.210
+          PRESSURE      1.0000
+          TOTAL         30.000
+          H2O           .99320
+          CO2           .56930E-09
+          NACL          .35560E-02
+          NAOH          .27780E-04
+          NA2CO3        .12320E-02

```

```

+      CASO4      .14850E-07
+      CACO3      .23570E-04
+      MGSO4      .74130E-06
+      NAHCO3     .58420E-04
+      NANO3      .45550E-04
+      CACL2      .64020E-07
+      MGOH2      .48310E-04
+      NA2SO4     .18470E-02
;

```

```

UNIT12  TANK      UNODE=3,4  DNODE=5  "STAGE 2 NEUTRALIZATION TANK"

```

```

      CSA=9.62  MAXL=4  LEXI=3.2

```

```

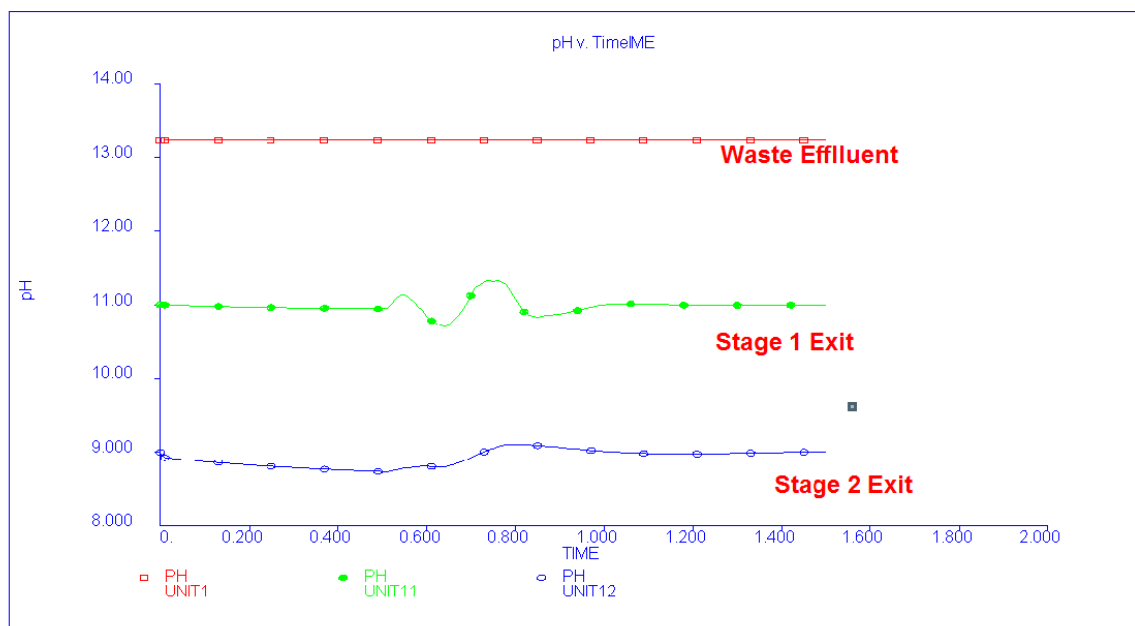
      COND= TEMPERATURE      26.600
+      PRESSURE      1.0000
+      TOTAL      30.000
+      H2O      .99270
+      CO2      .10440E-05
+      HNO3      .12960E-14
+      NAACL      .35060E-02
+      NA2CO3     .21950E-03
+      CASO4      .10690E-06
+      MGCL2      .14360E-04
+      CACO3      .23050E-04
+      MGSO4      .34260E-04
+      NAHCO3     .10630E-02
+      NANO3      .45280E-04
+      NA2SO4     .23680E-02
;

```

```

VALV1  DNODE=1  CV=120  VOPE=.831 (TIME=0.52)  VOPE=.917 (TIME=0.55)
        VOPE=.833 (TIME=0.6)  VOPE=.753 (TIME=0.66)  VOPE=.833
(TIME=0.7)
        VOPE=.917 (TIME=0.72)  VOPE=.833 (TIME=0.73)  VOPE=.917
(TIME=0.75)
        VOPE=.833 (TIME=0.79)
;
VALV2  DNODE=4  CV=120  VOPE=1 (TIME=0)
;
VALV3  DNODE=5  CV=120  VOPE=1 (TIME=0)
;
VALV4  DNODE=2  CV=3   VOPE=.715 (TIME=0)
;
VALV5  DNODE=3  CV=1   VOPE=.666 (TIME=0)
;
CLOO1  VID=4   SPUN=11  SPID=PH      SPVA=11 (TIME=0.51)  KC=.24
(TIME=0.51)
        TAU1=4.15 (TIME=0.51)  TAUD=1.0375 (TIME=0.51)
        DEADTIME=3.000000E-02 (TIME=0.51)
;
CLOO2  VID=5   SPUN=12  SPID=PH      SPVA=9 (TIME=0.51)  KC=.43
(TIME=0.51)
        TAU1=4.09 (TIME=0.51)  TAUD=1.0225 (TIME=0.51)
        DEADTIME=3.000000E-02 (TIME=0.51)
;
NODE  ORDER=1,2,3,4,5
;

```

Electrolyte Chemistry Models

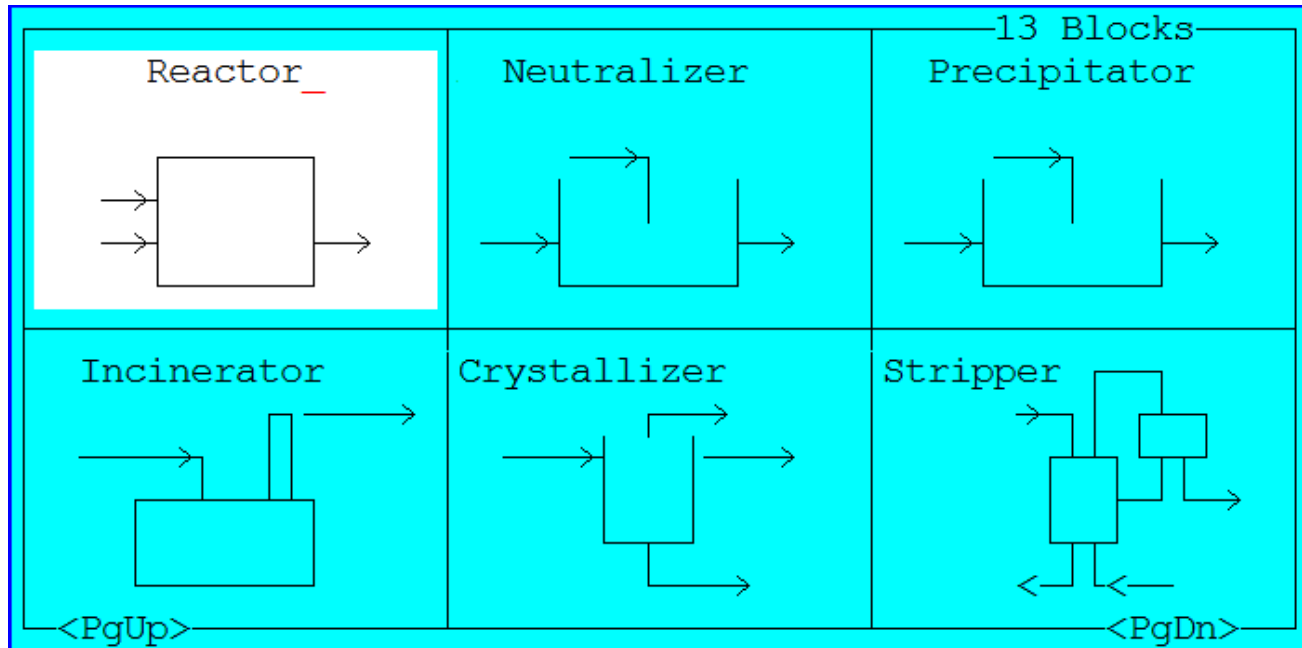
This chapter describes in detail the generation of electrolyte Chemistry Models for use in the previously described block applications. In particular Chemistry Models for use in the previously described block applications. In particular, Chemistry Models are described which include the following additional chemical phenomena:

- **Reaction Kinetics**
- **Bioreactions**

For some Chemistry Models it is necessary to build a private databank for species data. The procedures to do this are described as well as detailed instructions on creating Chemistry Models. This chapter also contains Chemistry Models which do not contain additional chemical phenomena sections. The models are included for reference purposes as they relate to specific block applications previously described in this section.

Electrolyte Chemistry Model With Reaction Kinetics

The following Chemistry Model describes an aqueous phase system involving chemical reaction kinetics. The model is generated to simulate a chemical Reactor Block which is described in



Reactor Block on page 391 of this section.

Chemistry Model

The following Chemistry Model describes an aqueous system involving chemical reaction kinetics for the hydrolysis of urea. The reaction kinetics equilibrium constants are defined using the Arrhenius Equation.

Process Chemistry

The Chemistry Model is created to simulate the hydrolysis of urea in a chemical reactor by Arrhenius based reaction kinetics. The following four species are identified as inflow species:

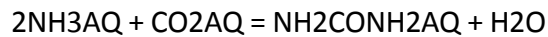
<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H2O	H2O
Carbon dioxide	CO2	CO2
Ammonia	NH3	NH3
Urea	NH2CONH2	UREA

Phase

The user must create an Electrolyte Chemistry Model which considers the vapor phase. The Chemistry Model Definition can then be created. The user must remember to name the private databank via the Action Key and selecting the Databank facility.

Sections - Kinetics

The chemical reaction to be considered is:



The rate of reaction is:

$$\text{Rate} = K_f[\text{NH}_3]^2 [\text{CO}_2] - K_r [\text{NH}_2\text{CONH}_2]$$

where:

K_f = forward reaction equilibrium constant = 20

$[a]$ = concentration of species a

K_r = reverse reaction equilibrium constant determined by Arrhenius Equation

$$= 1.2 \times 10^{-6} \exp [-28939.9/8.3142 \times T]$$

On creating the Chemistry Model (file extension .MOD) the reaction kinetics are included in the Definition. This is performed by editing the .MOD file and is achieved via the Action Key and selecting the Sections facility. The Kinetics option is then chosen and the kinetics data is entered by the user at the end of the equilibrium relationships listing and prior to the final END statement.

The reaction kinetics previously described are defined as follows:

KINETICS



RATE1 STD KF = 20 AR = 1.2E-06 BR = 3480.777 EP2=0

Model Solver Generation

On completing the chemical reaction kinetics definition the Model Solver files can be generated.

; *** INFLOWS ***

;

INPUT

H2OIN

CO2IN

NH3IN

NH2CONH2IN

H2CO3IN

HNH2CO2IN

NH42CO3IN

NH4OHIN

;

; *** SPECIES ***

;

SPECIES

;

; - VAPORS -

CO2VAP

H2OVAP

NH3VAP

;

; - AQUEOUS -

H2O

CO2AQ

NH2CONH2AQ

NH3AQ

;

```

;           - IONS -
CO3 ION
HCO3 ION
H ION
NH2CO2 ION
NH4 ION
OH ION
;
;           - PRECIPITATES -
;
;           - HYDRATES -
;
;           - SUSPEND SOLIDS -
;
;
;   ***EQUILIBRIUM EQUATIONS***
;
EQUILIBRIUM
CO2AQ+H2O=H ION+HCO3 ION
CO2VAP=CO2AQ
H2O=H ION+OH ION
H2OVAP=H2O
HCO3 ION=H ION+CO3 ION
NH2CO2 ION+H2O=NH3AQ+HCO3 ION
NH3AQ+H2O=NH4 ION+OH ION
NH3VAP=NH3AQ
KINETICS

```

```

REAC1 2NH3AQ + CO2AQ = NH2CONH2AQ + H2O

RATE1 STD KF=20 AR=1.2E-6 BR=3480.777 EP2=0

END

```

Electrolyte Model For Stripper Example

The following Chemistry Model describes a wastewater stream containing several organic species. The model is generated to simulate the possible removal of the organics from the wastewater using steam. The process is described in Stripper Block on page 365 of this section.

Process Chemistry

The Chemistry Model is created to simulate the chemical equilibrium behavior of a wastewater stream containing dissolved inorganic salts and several organic species. The following species are identified as inflows:

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H2O	H2O
Nitrobenzene	C6H5NO2	NITBNZ
Toluene	C6H5CH3	TOLUENE
Benzene	C6H6	BENZENE
Sodium Chloride	NaCl	NACL
1,2- Dichlorobenzene	C6H4CL2	MDCLBNZN

Phase

The user should create an Electrolyte Chemistry Model which considers the Vapor, Organic Liquid and Solid phases. The Chemistry Model Definition can then be created.

Model Solver Generation

On completing the Model Definition creation the Model Solver files can be generated.

The format of the Electrolyte Chemistry Model Definition is shown following this section.

```

;      *** INPUT      ****
;

```

INPUT
H2OIN
NITBNZIN
TOLUENEIN
BENZENEIN
NACLIN
MDCLBNZNIN
HCLIN
NAOH.1H2OIN
NAOHIN
;
;
; *** SPECIES ****
SPECIES
BENZENEVAP
H2OVAP
HCLVAP
MDCLBNZNVAP
NITBNZVAP
TOLUENEVAP
H2O
BENZENEAQ
HCLAQ
MDCLBNZNAQ
NITBNZAQ
TOLUENEAQ
CLION

```

HION
NAION
OHION
NACL PPT
NAOH PPT
NAOH.1H2O
;
;          *** SOLID SCALING TENDENCY ****
;
SOLIDS
ALL
;
;          *** EQUILIBRIUM EQUATIONS ****
;
EQUILIBRIUM
BENZENEVAP=BENZENEAQ
H2O=HION+OHION
H2OVAP=H2O
HCLAQ=HION+CLION
HCLVAP=HCLAQ
MDCLBNZNVAP=MDCLBNZNAQ
NACL PPT=NAION+CLION
NAOH.1H2O=NAION+OHION+H2O
NAOH PPT=NAION+OHION
NITBNZVAP=NITBNZAQ
TOLUENEVAP=TOLUENEAQ
END

```


Electrolyte Chemistry Model For Absorber Example

The following Chemistry Model describes an aqueous and vapor system. The model is generated to simulate the absorption of sulfur from an off gas stream using a sodium hydroxide stream containing trace amounts of sodium sulfide. The process is described in Absorber Block on page 371 of this section.

Process Chemistry

The Chemistry Model is created to simulate the absorption of sulfur from an organic vapor stream using a sodium hydroxide aqueous stream in an Absorber Block.

The following species are identified as inflow species.

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H2O	H2O
Methanol	CH3OH	METHANOL
Hydrogen mercaptan	H2S	H2S
Methyl mercaptan	CH3SH	MEMERCAPTAN
Sodium hydroxide	NaOH	NAOH
Sodium sulfide	Na2S	NA2S
Sodium carbonate	Na2CO3	NA2CO3

Phase

The user should create an Electrolyte Chemistry Model which considers the Vapor phase. The Chemistry Model Definition can then be created.

Model Solver Generation

The Model Solver files are then generated. The format of the Chemistry Model Definition is shown at the end of this section.

```

;          *** INFLOWS ***

;

INPUT

H2OIN

METHANOLIN

H2SIN

MEMERCAPTANIN

NAOHIN

NA2SIN

NA2CO3IN

CO2IN

```

H2CO3 IN

NAHS IN

NAHCO3 IN

;

;

*** SPECIES ***

;

SPECIES

;

;

- VAPORS -

CO2VAP

H2OVAP

H2SVAP

MEMERCAPTNVAP

METHANOLVAP

;

;

- AQUEOUS -

H2O

CO2AQ

H2SAQ

MEMERCAPTNAQ

METHANOLAQ

NAHCO3AQ

;

;

- IONS -

CH3SION

CO3ION

HCO3ION

HION
 HSION
 NACO3 ION
 NAION
 OHION
 SION

 ;
 ; - PRECIPITATES -
 ;
 ; - HYDRATES -
 ;
 ; - SUSPEND SOLIDS -
 ;
 ;
 ; ***EQUILIBRIUM EQUATIONS***
 ;
 EQUILIBRIUM
 CO2AQ+H2O=HION+HCO3 ION
 CO2VAP=CO2AQ
 H2O=HION+OHION
 H2OVAP=H2O
 H2SAQ=HION+HSION
 H2SVAP=H2SAQ
 HCO3 ION=HION+CO3 ION
 HSION=HION+SION
 MEMERCAPTNAQ=CH3SION+HION
 MEMERCAPTNVAP=MEMERCAPTNAQ

METHANOLVAP=METHANOLAQ

NA₂CO₃ ION=NA ION+CO₃ ION

NAHCO₃AQ=NA ION+HCO₃ ION

END

Electrolyte Chemistry Model For Solvent Extractor Example

The following Chemistry Model describes a chemical system involving the aqueous, organic and vapor phases. The model is generated to simulate the removal of organics from an aqueous stream using a solvent extraction process. The process is described in *Solvent Extractor* on page 376 of this section.

Process Chemistry

The Chemistry Model is created to simulate the extraction of phenol from an aqueous effluent using cyclohexane as the organic solvent.

The following species are identified as inflow species:

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H ₂ O	H ₂ O
Hydrogen sulfide	H ₂ S	H ₂ S
Methylphenol	C ₆ H ₄ CH ₃ OH	PCRESOLE
Phenol	C ₆ H ₅ OH	C ₆ H ₅ OH
Cyclohexane	C ₆ H ₁₂	C ₆ H ₁₂
Sodium hydroxide	NaOH	NAOH
Sulfuric acid	H ₂ SO ₄	H ₂ SO ₄

Phase

The user should create an Electrolyte Chemistry Model which considers the Vapor and Organic Liquid phases. The Chemistry Model Definition can then be created.

Model Solver Generation

The Model Solver files are then generated. The format of the Chemistry Model Definition is shown following this section.

ESP FRAME EDAT TERM DISK

;

; *** INPUT ****

;

INPUT

H2OIN

H2SO4IN

NA2CO3IN

CAOH2IN

CASO4IN

MGCL2IN

MGNO32IN

NACLIN

NAOHIN

CO2IN

COCL2IN

HCLIN

HNO3IN

SO3IN

CACO3IN

MGSO4IN

NAHCO3IN

NANO3IN

CACL2IN

CANO32IN

MGCO3IN

MGOH2IN

NA2SO4 IN

NA3HSO4 2 IN

NA6SO4 2 CO3 IN

NAHSO4 IN

CAHCO3 2 CO3 IN

;

;

*** SPECIES ****

;

SPECIES

CO2 VAP

COCL2 VAP

H2O VAP

H2SO4 VAP

HCL VAP

HNO3 VAP

SO3 VAP

H2O

CACO3 AQ

CASO4 AQ

CO2 AQ

COCL2 AQ

H2SO4 AQ

HCLAQ

HNO3 AQ

MGSO4 AQ

NAHCO3 AQ

NANO3 AQ

SO3AQ
CAHCO3 ION
CAION
CANO3 ION
CAOHION
CLION
CO3 ION
HCO3 ION
HION
HSO4 ION
MGHCO3 ION
MGION
MGOHION
NACO3 ION
NAION
NASO4 ION
NO3 ION
OHION
SO4 ION
CACL2PPT
CACO3PPT
CANO32PPT
CAOH2PPT
CASO4PPT
MGCL2PPT
MGCO3PPT
MGNO32PPT

MGOH2PPT

MGSO4PPT

NA2CO3PPT

NA2SO4PPT

NA3HSO42PPT

NA6SO42CO3PPT

NACLPPT

NAHCO3PPT

NAHSO4PPT

NANO3PPT

NAOHPPT

;

;

*** SOLID SCALING TENDENCY ****

;

SOLIDS

ALL

;

;

*** EQUILIBRIUM EQUATIONS ****

;

EQUILIBRIUM

CA₂CL₂PPT=CA₂ION+2CL₂ION

CA₂CO₃AQ=CA₂ION+CO₃ION

CA₂CO₃PPT=CA₂ION+CO₃ION

CA₂HCO₃ION=CA₂ION+HCO₃ION

CA₂NO₃2PPT=CA₂ION+2NO₃ION

CA₂NO₃ION=CA₂ION+NO₃ION

CA₂OH₂PPT=CA₂ION+2OH₂ION

CAOHION=CAION+OHION

CASO4AQ=CAION+SO4ION

CASO4PPT=CAION+SO4ION

CO2AQ+H2O=HION+HCO3ION

CO2VAP=CO2AQ

COCL2AQ+H2O=CO2AQ+2HCLAQ

COCL2VAP=COCL2AQ

H2O=HION+OHION

H2OVAP=H2O

H2SO4AQ=HION+HSO4ION

H2SO4VAP=H2SO4AQ

HCLAQ=HION+CLION

HCLVAP=HCLAQ

HCO3ION=HION+CO3ION

HNO3AQ=HION+NO3ION

HNO3VAP=HNO3AQ

HSO4ION=HION+SO4ION

MGCL2PPT=MGION+2CLION

MGCO3PPT=MGION+CO3ION

MGHCO3ION=MGION+HCO3ION

MGNO32PPT=MGION+2NO3ION

MGOH2PPT=MGION+2OHION

MGOHION=MGION+OHION

MGSO4AQ=MGION+SO4ION

MGSO4PPT=MGION+SO4ION

NA2CO3PPT=2NAION+CO3ION

NA2SO4PPT=2NAION+SO4ION

$3\text{NaHSO}_4\text{PPT} = 3\text{Na}^+\text{ION} + \text{HSO}_4^-\text{ION} + \text{SO}_4^{2-}\text{ION}$
 $6\text{Na}_2\text{SO}_4\text{CO}_3\text{PPT} = 6\text{Na}^+\text{ION} + 2\text{SO}_4^{2-}\text{ION} + \text{CO}_3^{2-}\text{ION}$
 $\text{NaClPPT} = \text{Na}^+\text{ION} + \text{Cl}^-\text{ION}$
 $\text{NaCO}_3\text{ION} = \text{Na}^+\text{ION} + \text{CO}_3^{2-}\text{ION}$
 $\text{NaHCO}_3\text{AQ} = \text{Na}^+\text{ION} + \text{HCO}_3^-\text{ION}$
 $\text{NaHCO}_3\text{PPT} = \text{Na}^+\text{ION} + \text{HCO}_3^-\text{ION}$
 $\text{NaHSO}_4\text{PPT} = \text{Na}^+\text{ION} + \text{HSO}_4^-\text{ION}$
 $\text{NaNO}_3\text{AQ} = \text{Na}^+\text{ION} + \text{NO}_3^-\text{ION}$
 $\text{NaNO}_3\text{PPT} = \text{Na}^+\text{ION} + \text{NO}_3^-\text{ION}$
 $\text{NaOHPPT} = \text{Na}^+\text{ION} + \text{OH}^-\text{ION}$
 $\text{NaSO}_4\text{ION} = \text{Na}^+\text{ION} + \text{SO}_4^{2-}\text{ION}$
 $\text{SO}_3\text{AQ} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4\text{AQ}$
 $\text{SO}_3\text{VAP} = \text{SO}_3\text{AQ}$
 END

Electrolyte Model For Neutralization Example

The following Chemistry Model describes a complex, multi-component aqueous system. The model is generated to simulate the neutralization of the aqueous stream which is described in Neutralizer Block on page 396 of this section.

Process Chemistry

The Chemistry Model is created to simulate the aqueous stream equilibrium. The following species are identified as inflow species:

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H ₂ O	H ₂ O
Sulfuric Acid	H ₂ SO ₄	H ₂ SO ₄
Sodium Carbonate	Na ₂ CO ₃	NA ₂ CO ₃
Calcium Hydroxide	Ca(OH) ₂	CAOH ₂

Calcium Sulphate	CaSO4	CASO4
Magnesium Chloride	MgCl2	MGCL2
Magnesium Nitrate	Mg(NO3)2	MGNO32
Sodium Chloride	NaCl	NACL
Sodium Hydroxide	NaOH	NAOH

Phase

For this example the user should create an Electrolyte Chemistry Model which considers the Vapor and Solids phases. The Chemistry Model Definition can then be created.

Solids

On creating the Chemistry Model Definition the user should selectively omit all predicted hydrates from the model. This is achieved via the Action key and selecting the Solids facility. The species are selected using the Arrow Keys and the character "N" key.

The species to be omitted are:

CACL2.1H2O

CACL2.2H2O

CACL2.4H2O

CACL2.6H2O

CANO32.3H2O

CASO4.2H2O

CANO32.4H2O

MGCL2.2H2O

MGCL2.4H2O

MGCL2.6H2O

MGCO3.3H2O

MGNO32.2H2O

MGNO32.6H2O

MGSO4.1H2O

MGSO4.6H2O

MGSO4.7H2O

NA2CO3.10H2O

NA2CO3.1H2O

NA2CO3.7H2O

NA2SO4.10H2O

NAOH.1H2O

This will leave 19 solids.

Model Solver Generation

On completing the solids deletion the Model Solver files can be generated.

The format of the Electrolyte Chemistry Model Definition is shown following this section.

```
;      *** INPUT      ****  
  
;  
  
INPUT  
  
H2OIN  
  
NACL2IN  
  
CACL2IN  
  
MGCL2IN  
  
FECL3IN  
  
HCLIN  
  
NAOHIN  
  
FEIII(OH)3IN  
  
NIOH2IN  
  
CACL2 . 1H2OIN  
  
CACL2 . 4H2OIN  
  
CACL2 . 6H2OIN  
  
CAOH2IN  
  
FECL3 . 2 . 5H2OIN
```

FECL3.2H2OIN

FECL3.6H2OIN

MGCL2.6H2OIN

MGOH2IN

NACLIN

NAOH.1H2OIN

NICL2.6H2OIN

CAOHCLIN

MGCLOHIN

;

;

*** SPECIES ****

;

SPECIES

H2OVAP

HCLVAP

H2O

FECL3AQ

FEIII OH3AQ

HCLAQ

NIOH2AQ

CAION

CAOHION

CLION

FEIII2OH2ION

FEIII CL2ION

FEIII CL4ION

FEIII CLION

FEIIIION

FEIII OH₂ION

FEIII OH₄ION

FEIII OHION

HION

MGION

MGOHION

NAION

NICLION

NIION

NIOH₃ION

NIOHION

OHION

CA₂CL₂PPT

CA₂OH₂PPT

FE₃CL₃PPT

FEIII OH₃PPT

MG₂CL₂PPT

MGO₂OH₂PPT

NA₂CL₂PPT

NA₂OH₂PPT

NIO₂OH₂PPT

CA₂CL₂ . 1H₂O

CA₂CL₂ . 4H₂O

CA₂CL₂ . 6H₂O

FE₃CL₃ . 2 . 5H₂O

FE₃CL₃ . 2H₂O

FECL3.6H2O

MGCL2.6H2O

NAOH.1H2O

NICL2.6H2O

;

; *** SOLID SCALING TENDENCY ****

;

SOLIDS

ALL

;

; *** EQUILIBRIUM EQUATIONS ****

;

EQUILIBRIUM

CACL2.1H2O=CAION+2CLION+1H2O

CACL2.4H2O=CAION+2CLION+4H2O

CACL2.6H2O=CAION+2CLION+6H2O

CACL2PPT=CAION+2CLION

CAOH2PPT=CAION+2OHION

CAOHION=CAION+OHION

FECL3.2.5H2O=FEIIIIION+3CLION+2.5H2O

FECL3.2H2O=FEIIIIION+3CLION+2H2O

FECL3.6H2O=FEIIIIION+3CLION+6H2O

FECL3AQ=FEIIICL2ION+CLION

FECL3PPT=FEIIIIION+3CLION

FEIII2OH2ION=2FEIIIIION+2OHION

FEIIICL2ION=FEIIICLION+CLION

FEIIICL4ION=FECL3AQ+CLION

$FEIIIION=FEIIIION+CLION$
 $FEIIIOH2ION=FEIIIOHION+OHION$
 $FEIIIOH3AQ=FEIIIOH2ION+OHION$
 $FEIIIOH3PPT=FEIIIION+3OHION$
 $FEIIIOH4ION=FEIIIOH3AQ+OHION$
 $FEIIIOHION=FEIIIION+OHION$
 $H2O=HION+OHION$
 $H2OVAP=H2O$
 $HCLAQ=HION+CLION$
 $HCLVAP=HCLAQ$
 $MGCL2.6H2O=MGION+2CLION+6H2O$
 $MGCL2PPT=MGION+2CLION$
 $MGOH2PPT=MGION+2OHION$
 $MGOHION=MGION+OHION$
 $NACLPPT=NAION+CLION$
 $NAOH.1H2O=NAION+OHION+H2O$
 $NAOHPPT=NAION+OHION$
 $NICL2.6H2O=NIION+2CLION+6H2O$
 $NICLION=NIION+CLION$
 $NIOH2AQ=NIOHION+OHION$
 $NIOH2PPT=NIION+2OHION$
 $GEN NIOH3ION=NIOH2AQ+OHION$
 $NIOHION=NIION+OHION$
 END

Electrolyte Chemistry Model For Precipitator Example

The following Chemistry Model describes an aqueous phase system containing several metal species. The model is generated to simulate the precipitation and subsequent removal of selected metals from the effluent by the addition of sodium hydroxide solution. The process is described in Precipitator Block on page 404 of this chapter.

Process Chemistry

The Chemistry Model is created to simulate chemical equilibrium behavior of a multi-component effluent. The stream consists of several metals contained in a hydrochloric acid solution. The detailed process description for this example can be referred to in Precipitator Block on page 404 of this chapter.

The following species are identified as inflows:

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H2O	H2O
Nickel chloride	NiCl2	NICL2
Calcium chloride	CaCl2	CACL2
Magnesium chloride	MgCl2	MGCL2
Ferric chloride	FeCl3	FECL3
Hydrochloric acid	HCl	HCL
Sodium hydroxide	NaOH	NAOH

Phase

The user should create an Electrolyte Chemistry Model which considers the Solids phase. The Chemistry Model Definition can then be created.

Solids

On creating the Chemistry Model Definition the user should selectively omit particular hydrates from the model. This is achieved via the Action Key and selecting the Solids facility. The species are chosen using the Arrow Keys and the character "N" key.

The species to be omitted are:

CACL2.2H2O

MGCL2.2H2O

MGCL2.4H2O

NICL2.2H2O

NICL2.4H2O

Model Solver Generation

On completing the solids deletion the Model Solver files can be generated.

The format of the Electrolyte Chemistry Model Definition is shown following this section.

```
;      *** INPUT      ****  
  
;  
  
INPUT  
  
H2OIN  
  
NICL2IN  
  
CACL2IN  
  
MGCL2IN  
  
FECL3IN  
  
HCLIN  
  
NAOHIN  
  
FEIII(OH)3IN  
  
NIOH2IN  
  
CACL2 . 1H2OIN  
  
CACL2 . 4H2OIN  
  
CACL2 . 6H2OIN  
  
CAOH2IN  
  
FECL3 . 2 . 5H2OIN  
  
FECL3 . 2H2OIN
```

FECL3.6H2OIN

MGCL2.6H2OIN

MGOH2IN

NACLIN

NAOH.1H2OIN

NICL2.6H2OIN

CAOHCLIN

MGCLOHIN

;

;

*** SPECIES ****

;

SPECIES

H2OVAP

HCLVAP

H2O

FECL3AQ

FEIIIOH3AQ

HCLAQ

NIOH2AQ

CAION

CAOHION

CLION

FEIII2OH2ION

FEIIICL2ION

FEIIICL4ION

FEIIICLION

FEIIIION

FEIII OH₂ ION

FEIII OH₄ ION

FEIII OH ION

H ION

MG ION

MGOH ION

NA ION

NI CL ION

NI ION

NI OH₃ ION

NI OH ION

OH ION

CA CL₂ PPT

CA OH₂ PPT

FE CL₃ PPT

FE III OH₃ PPT

MG CL₂ PPT

MGOH₂ PPT

NA CL PPT

NA OH PPT

NI OH₂ PPT

CA CL₂ . 1H₂O

CA CL₂ . 4H₂O

CA CL₂ . 6H₂O

FE CL₃ . 2 . 5H₂O

FE CL₃ . 2H₂O

FE CL₃ . 6H₂O

MGCL2.6H2O

NAOH.1H2O

NICL2.6H2O

;

; *** SOLID SCALING TENDENCY ****

;

SOLIDS

ALL

;

; *** EQUILIBRIUM EQUATIONS ****

;

EQUILIBRIUM

CACL2.1H2O=CAION+2CLION+1H2O

CACL2.4H2O=CAION+2CLION+4H2O

CACL2.6H2O=CAION+2CLION+6H2O

CACL2PPT=CAION+2CLION

CAOH2PPT=CAION+2OHION

CAOHION=CAION+OHION

FECL3.2.5H2O=FEIIIION+3CLION+2.5H2O

FECL3.2H2O=FEIIIION+3CLION+2H2O

FECL3.6H2O=FEIIIION+3CLION+6H2O

FECL3AQ=FEIIICL2ION+CLION

FECL3PPT=FEIIIION+3CLION

FEIII2OH2ION=2FEIIIION+2OHION

FEIIICL2ION=FEIIICLION+CLION

FEIIICL4ION=FECL3AQ+CLION

FEIIICLION=FEIIIION+CLION

$FEIII OH_2 ION = FEIII OH ION + OH ION$
 $FEIII OH_3 AQ = FEIII OH_2 ION + OH ION$
 $FEIII OH_3 PPT = FEIII ION + 3 OH ION$
 $FEIII OH_4 ION = FEIII OH_3 AQ + OH ION$
 $FEIII OH ION = FEIII ION + OH ION$
 $H_2O = H ION + OH ION$
 $H_2O VAP = H_2O$
 $HCL AQ = H ION + CL ION$
 $HCL VAP = HCL AQ$
 $MGCL_2 \cdot 6H_2O = MG ION + 2CL ION + 6H_2O$
 $MGCL_2 PPT = MG ION + 2CL ION$
 $MGOH_2 PPT = MG ION + 2OH ION$
 $MGOH ION = MG ION + OH ION$
 $NACL PPT = NA ION + CL ION$
 $NAOH \cdot 1H_2O = NA ION + OH ION + H_2O$
 $NAOH PPT = NA ION + OH ION$
 $NI CL_2 \cdot 6H_2O = NI ION + 2CL ION + 6H_2O$
 $NI CL ION = NI ION + CL ION$
 $NIOH_2 AQ = NIOH ION + OH ION$
 $NIOH_2 PPT = NI ION + 2OH ION$
 $GEN NIOH_3 ION = NIOH_2 AQ + OH ION$
 $NIOH ION = NI ION + OH ION$
 END

Bioreactions

The following Chemistry Model describes an aqueous phase system containing bioreactions. The model is generated to include the substrate, in this case a statistical molecule representing an organic waste product. The process to biodegrade the substrate is described in Bioreactor on page 420 of this section.

Bioentry

The Chemistry Model for this system will be created using the AltEntry facility, the BioEntry menu option, as an aid for the selection of species and creation of the Chemistry Model.

Species

Upon entering the BioEntry facility the user will see a screen displaying the type of information that has been specified for the Chemistry Model along with the type of reactions that have been included.

The first type of reaction to be defined is the heterotrophic reaction. At this point the user is prompted for the name of the substrate which will be included in the bioreactions. For this process we will not be using one of the organic species already in the ESP PUBLIC databank, but one of our own creation. For this Chemistry Model we will create our own substrate name (e.g., WASTE).

For this molecule the following information is to be specified:

ThOD	226.4
TON	14.0067
Cl	0.2
S	0.5
P	0.1

Specify Bioreactions

Consider the following bioreactions:

Aerobic/Anoxic/Anaerobic

Note: Inclusion of the Anaerobic bioreaction will cause Acetic Acid to be added as a Second Substrate.

Biomass

For this example we will use the default Active and Inert Biomass. Press the Enter Key on the blank field to select the defaults.

It is suggested that Autotrophic reactions be included in all bioreaction models. For this Chemistry Model we will use the default Active and Inert Biomass.

This completes the use of the BioEntry facility.

Inflow List

The user will now see an updated list of species which will be required to complete the Chemistry Model involving bioreactions. The user should accept this list and proceed to create the model.

Phase

The user should accept the default Vapor and Solid phases for the Electrolyte Chemistry Model. The Chemistry Model Definition can then be created.

Bioreactions

After the Chemistry Model Definition had been created it must be expanded to include Bioreactions. This is done by using the Action Key and selects the Bioreactions options of the Sections facility. The Reactions are to be modified by changing the default reaction constants as follows:

	<u>Constant</u>	<u>Value</u>
Heterotrophic (Waste)	RATE	0.20
	YIELD	0.30
	DECAY	0.022
	KSUB	22
Autotrophic	RATE	0.02
	YIELD	0.10

Model Solver Generation

The format of the Electrolyte Chemistry Model Definition is shown following this section.

ESP FRAME EDAT TERM DISK

;

; *** INPUT ****

;

INPUT

H2OIN

WASTEIN

ACETACIDIN

BUGHACTIVIN

BUGHINERTIN

BUGAACTIVIN

BUGAINERTIN

CO2IN

NH3IN

O2IN

HNO3IN

N2IN

H2SIN

H2SO4IN

HCLIN

H3PO4IN

ACET2IN

COCL2IN

SO3IN

H4P2O7IN

NH4ACETIN

NH4NO3IN

NH42HPO4 . 2H2OIN

NH42HPO4 IN

NH42SO4 IN

NH43PO4 . 3H2OIN

NH44H2CO33 IN

NH4CLIN

NH4H2PO4 IN

NH4HCO3 IN

NH4HSIN

P4O10 IN

H2CO3 IN

HNH2CO2 IN

NH42CO3 IN

NH42SIN

NH43PO4 IN

NH4OHIN

;

;

*** SPECIES ****

;

SPECIES

ACET2VAP

ACETACIDVAP

CO2VAP

COCL2VAP

H2OVAP

H2SO4VAP

H2SVAP

HCLVAP

HNO3VAP

N2VAP

NH3VAP

O2VAP

SO3VAP

H2O

WASTEAQ

ACET2AQ

ACETACIDAQ

CO2AQ

COCL2AQ

H2SAQ

H2SO4AQ

H3PO4AQ

H4P2O7AQ

HCLAQ

HNO3AQ

N2AQ

NH3AQ

NH4ACETAQ

NH4NO3AQ

O2AQ

SO3AQ

ACETATEION

CLION

CO3ION

H2P2O7ION

H2PO4ION

H3P2O7ION

HCO3ION

HION

HP2O7ION

HPO4ION

HSION

HSO4ION

NH2CO2ION

NH4ION

NH4SO4ION

NO3ION

OHION

P2O7ION

PO4ION

SION

SO4ION

NH42HPO4PPT

NH42SO4PPT

NH44H2CO33PPT

NH4CLPPT

NH4H2PO4PPT

NH4HCO3PPT

NH4HSPPT

NH4NO3PPT

P4O10PPT

NH42HPO4 . 2H2O

NH43PO4 . 3H2O

BUGAACTIVSUS

BUGAINERTSUS

BUGHACTIVSUS

BUGHINERTSUS

;

; *** SOLID SCALING TENDENCY ****

;

SOLIDS

ALL

;

; *** EQUILIBRIUM EQUATIONS ****

;

EQUILIBRIUM

ACET2AQ=2ACETACIDAQ

ACET2VAP=ACET2AQ

ACETACIDAQ=HION+ACETATEION

ACETACIDVAP=ACETACIDAQ

CO2AQ+H2O=HION+HCO3ION

CO2VAP=CO2AQ

COCL2AQ+H2O=CO2AQ+2HCLAQ

COCL2VAP=COCL2AQ

H2O=HION+OHION

H2OVAP=H2O

H2P2O7ION=HION+HP2O7ION

H2PO4ION=HION+HPO4ION

$H_2SAQ = HION + HSION$
 $H_2SO_4AQ = HION + HSO_4ION$
 $H_2SO_4VAP = H_2SO_4AQ$
 $H_2SVAP = H_2SAQ$
 $H_3P_2O_7ION = HION + H_2P_2O_7ION$
 $H_3PO_4AQ = HION + H_2PO_4ION$
 $H_4P_2O_7AQ = HION + H_3P_2O_7ION$
 $HCLAQ = HION + CLION$
 $HCLVAP = HCLAQ$
 $HCO_3ION = HION + CO_3ION$
 $HNO_3AQ = HION + NO_3ION$
 $HNO_3VAP = HNO_3AQ$
 $HP_2O_7ION = HION + P_2O_7ION$
 $HPO_4ION = HION + PO_4ION$
 $HSION = HION + SION$
 $HSO_4ION = HION + SO_4ION$
 $N_2VAP = N_2AQ$
 $NH_2CO_2ION + H_2O = NH_3AQ + HCO_3ION$
 $NH_3AQ + H_2O = NH_4ION + OHION$
 $NH_3VAP = NH_3AQ$
 $NH_4_2HPO_4 \cdot 2H_2O = 2NH_4ION + HPO_4ION + 2H_2O$
 $NH_4_2HPO_4PPT = 2NH_4ION + HPO_4ION$
 $NH_4_2SO_4PPT = 2NH_4ION + SO_4ION$
 $NH_4_3PO_4 \cdot 3H_2O = 3NH_4ION + PO_4ION + 3H_2O$
 $NH_4_4H_2CO_3_3PPT = 4NH_4ION + 2HCO_3ION + CO_3ION$
 $NH_4ACETAQ = NH_4ION + ACETATEION$
 $NH_4CLPPT = NH_4ION + CLION$

NH4H2PO4PPT=NH4 ION+H2PO4 ION
 NH4HCO3PPT=NH4 ION+HCO3 ION
 NH4HSPPT=NH4 ION+HSION
 NH4NO3AQ=NH4 ION+NO3 ION
 NH4NO3PPT=NH4 ION+NO3 ION
 NH4SO4 ION=NH4 ION+SO4 ION
 O2VAP=O2AQ
 GEN P2O7ION+H2O=2PO4 ION+2HION
 .1P4O10PPT+.6H2O=.4H2PO4 ION+.4HION
 SO3AQ+H2O=H2SO4AQ
 SO3VAP=SO3AQ

 ;
 ; *** BIOREACTION ****
 ;
 BIOREACTION
 REACALL
 BIOMASS BUGHACTIVSUS/BUGHINERTSUS
 REAC1 HETERO
 SUBSTRATE WASTE AQ (CL=.2,S=.5,P=.1,THOD=226.4,TON=14.0067)
 THERMO WASTE AQ MATC 2170 STOI 1
 RATE .2
 YIELD .3
 DECAY .022
 KSUB 22
 REAC2 HETERO
 SUBSTRATE ACETACIDAQ (C=2,H=4,O=2)
 RATE 0.36


```
KSUB 40.0
ANAF 0.0
REAC3 AUTO
BIOMASS BUGAACTIVSUS/BUGAINERTSUS
RATE .02
YIELD .1
END
```

Non-Electrolyte Chemistry Models

This chapter describes in detail the generation of Non-Electrolyte Chemistry Models for use in the previously described block applications. In particular Chemistry Models are described which include the following additional chemical phenomena:

- **Reaction Kinetics**
- **Selected Species Chemical Equilibria**

The procedures to generate these Chemistry Models are described in detail. The two models included relate to the Distillation and Incinerator Block applications previously described in this section.

Non-Electrolyte Chemistry Model With Selected Species Equilibrium

The following Chemistry Model describes a vapor phase system involving species equilibrium. The model is generated to simulate the incineration of an organic waste gas stream which is described in Incinerator Block on page 415 of this section.

Process Chemistry

The Chemistry Model is created to simulate the organic waste gas stream and the oxidation vapor stream equilibria. The following species are identified as inflow species:

<u>Species</u>	<u>Formula</u>	<u>ESP Name</u>
Water	H2O	H2O
Methane	CH4	CH4

Ethane	C2H6	C2H6
Propane	C3H8	C3H8
Butane	C4H10	C4H10
Benzene	C6H6	BENZENE
Carbon dioxide	CO2	CO2
Oxygen	O2	O2
Carbon monoxide	CO	CO
Hydrogen	H2	H2
Nitrogen	N2	N2

Phase

For this example the user should create an Electrolyte and Non-Electrolyte Chemistry Model which considers the Vapor phase only. The Chemistry Model Definition can then be created.

Species Equilibrium

On creating the Non-Electrolyte Chemistry Model (file extension .MD2) the species equilibrium is included in the Definition. This is performed via the Action Key and selecting the Sections facility. The Non-Electrolyte Model option is chosen and the Vapor Phase Equilibrium heading selected.

From the list of inflows displayed, the required species are selected using the Arrow Keys and the <Space Bar>.

For this example, only the Nitrogen, N2, species should be omitted from the selection.

Model Solver Generation

On completing the species equilibrium selection the Model Solver files can be generated.

The format of the Non-Electrolyte Chemistry Model Definition is shown following this section.

```

;                *** INFLOWS ***
;
INPUT
H2O IN
CH4 IN

```

C2H6 IN

C3H8 IN

C4H10 IN

BENZENE IN

CO2 IN

O2 IN

CO IN

H2 IN

N2 IN

H2CO3 IN

;

;

*** SPECIES ***

;

SPECIES

;

;

- VAPORS -

BENZENE VAP

C2H6 VAP

C3H8 VAP

C4H10 VAP

CH4 VAP

CO2 VAP

CO VAP

H2O VAP

H2 VAP

N2 VAP

O2 VAP

;

;

- AQUEOUS -

H2O

BENZENEAQ

C2H6AQ

C3H8AQ

C4H10AQ

CH4AQ

CO2AQ

COAQ

H2AQ

N2AQ

O2AQ

;

;

- IONS -

CO3 ION

HCO3 ION

H ION

OH ION

;

;

- PRECIPITATES -

;

;

- HYDRATES -

;

;

- SUSPEND SOLIDS -

;

EQUILIBRIUM EQUATIONS

;

EQUILIBRIUM

BENZENEVAP=BENZENEAQ

C2H6VAP=C2H6AQ

C3H8VAP=C3H8AQ

C4H10VAP=C4H10AQ

CH4VAP=CH4AQ

CO2AQ+H2O=HION+HCO3ION

CO2VAP=CO2AQ

COVAP=COAQ

H2O=HION+OHION

H2OVAP=H2O

H2VAP=H2AQ

HCO3ION=HION+CO3ION

N2VAP=N2AQ

O2VAP=O2AQ

END

Chapter 8. Dynamic Modeling

DynaChem Overview

The dynamic modeling program, DynaChem, allows the user to simulate an unsteady-state system. Process control systems including engineering parameters such as system and control loop dead time, valve hysteresis and stick/slip can be included in the simulation if required.

This section outlines the theory and use of the DynaChem program. The user should refer to the DynaChem Handbook for detailed procedures.

Description Of DynaChem

The DynaChem program is one of the ProChem programs and allows a variety of transient processes to be simulated. The program can be used to evaluate process performance during process upset, start-up, and shutdown conditions, as well as other dynamic modeling conditions. Specific examples of DynaChem's use include the prediction of a single effluent's properties arising from the mixing of multiple feeds, the design and optimization of a treatment plant process control system, and the simulation of geological systems changing due to environmental conditions.

Philosophy

DynaChem is based on the principle of being able to simulate a chemical system as a series of discrete, modular, computational process units.

These discrete process units are assumed to be homogeneous and exist at both chemical and thermodynamic equilibrium. If required, the user can account for both imperfect mixing and non-equilibrium conditions for these units.

The dynamic nature of the series of discrete units is simulated using a two-tier calculation technique.

First-Tier Calculation

The first, or inner, calculation tier proceeds through the units in a user predefined order for a specified time increment.

The order typically begins with mass/energy flow into the process and ends with mass/energy flow out of the process. The calculation order is at the discretion of the user and may be altered to achieve special process conditions such as recycle and system dead time.

When passing from one unit to the next in sequence, small "packets" of mass/energy are introduced into the unit, mixed and the resulting equilibrium condition determined taking into account any user defined mixing dynamics and reaction kinetics.

The exiting packets of mass/energy leaving the unit are then determined by specified parameters such as tank level, valve opening and fluid pressure. These packets are then passed to the next unit in sequence and the calculation procedure repeated for that unit.

This first-tier of calculation can be summarized as the movement of mass/energy through a process during a small but finite increment of time.

Second-Tier Calculation

The second, or outer, calculation tier uses the final state of the process determined by the inner-tier calculation as the initial state of the next time increment evaluation.

This outer calculation proceeds through time increments, with each increment resulting from a complete pass through the inner calculation tier.

The discrete nature of this computation philosophy allows for a high level of flexibility when defining computation parameters for the simulation prior to execution and the altering of system parameters during the simulation.

Structure

In order to use DynaChem, the process to be simulated must be modeled as a series of Units connected in sequence. The connections between Units are known as Nodes and can generally be considered as pipelines through which streams flow from one unit to another. Either manual or automatic control valves can be included in these connections if required.

Units

The Unit of a process can be defined as any part of a process which can be isolated based upon homogeneity and equilibrium. These may include process equipment such as tanks and pipe sections but are also used to define schedules of mass/energy inflows to a process as a function of time.

During a simulation, packets of mass/energy are introduced to a Unit over a series of time increments defined by the user. These packets of mass/energy are combined with the mass/energy already present in the Unit and the equilibrium condition determined.

Based upon user defined Unit parameters (e.g., tank volumes, liquid levels, etc.) packets of mass/energy exiting the unit are determined and placed at collecting points called Nodes.

Nodes

Nodes can generally be considered as connecting pipelines through which stream flows from one Unit to another. Flow through these connections can be restricted or controlled with the addition of manual or automatic control valves.

Thus, the transmission of mass/energy from one Unit to another is achieved by accepting packets of mass/energy from Upstream Nodes and depositing packets of mass/energy at Downstream Nodes.

Node Order

The computation order of the inner tier is defined by the user and is known as the Node Order. The specification of a Node in the computation order results in the Unit computation for which that Node is a Downstream Node.

The Node Order specification is at the discretion of the user but can be manipulated to allow for process recycle and system dead time if required.

Interactive Capability

During a simulation, DynaChem offers an interactive capability which allows the user to monitor and modify a wide variety of process parameters under transient conditions. The parameters which can be monitored include stream flows, tank liquid levels, valve positions, component species concentration variations and control loop system responses.

This capability also allows the user to modify process parameters such as valve stem positions and controller settings during the simulation.

This facility is very flexible and allows, for example, the user to determine plant performance during upset conditions or optimize process controller settings.

Unit Specification

There are three types of Units available in DynaChem for defining operating conditions. Each Unit type is recognized with a software keyword:

- **ENTRY**, inflows to a process
- **TANK**, process tank (e.g., CSTR)
- **PIPE**, constant volume systems (e.g., Pipes, PFR)

When defining any of the above Units, the item must initially be identified with the keyword UNIT with an identification number, followed by the keyword ENTRY, TANK or PIPE (i.e., UNIT 3 TANK).

Entry Unit

This type of Unit provides a means for introducing mass/energy into the process by continuous flow, intermittent flow or scheduled flow. The mass/energy flow may be defined directly in the simulation case file or based upon values saved from a previous DynaChem execution.

Tank Unit

This type of Unit is used to define any vessel or collection of mass/energy which may change in quantity and/or volume as well as state.

Generally, this Unit is used to define a tank but may also be used to model the shell side of a process boiler, a tray of a distillation column or a continuous stirred tank reactor (CSTR).

The tank is physically defined by the user and the parameters which can be used include tank cross-sectional area, maximum liquid level, maximum liquid volume and exit stream level. The user must also include all upstream and downstream nodes, to and from the Unit, as part of the Unit definition.

During the simulation, the tank liquid level is determined and updated after every time increment.

Pipe Unit

This type of Unit is used to model any process Unit which maintains constant volume. Some examples of its use include modeling a section of pipe, the tube side of a heat exchanger, a heating or cooling coil or a plug flow reactor (PFR).

The Pipe is physically defined by the user and the parameters which can be used include cross-sectional area, length and maximum volume. Liquid level is not applicable for Pipe Units and no mass may exit this Unit until its volume is full. The user must also include all upstream and downstream nodes, to and from the Unit, as part of the Unit definition.

Valve Specification

If required, a valve can be installed in a connection Node to restrict the flow of mass/energy through the Node during a time increment.

A valve is identified with the keyword VALVE followed by an identification number, and its location is defined by its downstream node (DNODE) in which the valve is to be situated. (e.g., VALVE3, DNODE=1)

Valve Capacity

The maximum flow through the valve is specified as the valve capacity. It is defined by equating the flow rating to the keyword CV. (e.g., CV=20)

Valve Stem Position

The actual flow through the Valve is determined by the fraction of which the Valve is open. This fraction is known as the valve stem position and has a value between 0 and 1.

The stem position may be set by the user for manual valve operation and is achieved by equating the valve open fraction value to the keyword VOPEN. Alternatively, the user can manually alter the valve stem position while the dynamic simulation is in progress, or the valve stem position can be automatically controlled via the action of a controller.

Valve Hysteresis And Stick/Slip

In order to make valve performance as realistic as possible the user can include valve hysteresis and stick/slip characteristics into the simulation.

The characteristics are expressed as a value between 0 and 1 and are equated to the software recognized keywords HYSTERISIS and STICK respectively.

Valve Type

There are two types of valves available to the user. Either a linear opening or equal percentage opening valve can be defined and are identified with the keywords LINEAR and EQUAL respectively.

Pump Specification

If required, a pump can be installed in a connecting Node to increase the fluid pressure to a Unit.

A pump is identified with the keyword PUMP followed by an identification number, and its location is defined by the downstream node (DNODE) in which the pump is situated.

Pump Discharge Pressure

The discharge pressure of the pump is determined from the suction pressure and the head developed by the pump. The head is determined from a pump curve defined by the user as a function of flow and pump speed.

The above characteristics are all defined using software recognized keywords:

<u>KEYWORD</u>	<u>DESCRIPTION</u>
PSDROP	Pump suction pressure
PSPEED	Pump speed
PCURV	Pump curve data

The pump curve and speed information must be defined by the user, but the suction pressure is optional as it is assumed to be zero if no data is specified.

Pump Characteristics

The user can optionally specify additional pump characteristics such as pump elevation from tank zero liquid level (not including dished end) and pump speed override switch. Each characteristic is recognized with software keywords, PELEV and PSWITCH, respectively.

Control Loop Specification

When defining the dynamic simulation, the user has the option to control a process variable of interest with the introduction of a control loop.

During the simulation, the control loop measures the process variable of interest from a specified Unit or Node. The variables that can be measured include temperature, pressure, pH, level, flow and composition.

The measured process variable is then compared with a user defined setpoint, and an appropriate adjustment is made to the controlled parameter. This parameter could be a valve stem position, pump speed or another control loop setpoint.

Controller Types

The software allows for a wide variety of controllers to be specified. The controller algorithms which are available include Velocity, Positional, Switch, Multicascade, Ratio and Trim.

Each control loop must be identified with the software keyword CLOOP followed by an identification number. The controller location, the controlled parameter and the process variable and its setpoint value need to be defined by the user.

Controller Settings

When specifying a control loop, the controller settings need to be defined. These settings can be modified during the simulation in order to tune the controller and optimize system response.

The user can specify either a proportional, proportional-integral or proportional-integral-derivative controller with its respective gain, integral and derivative time values being equated to software keywords, namely KC, TAUI and TAUD.

If required, controller response dead time, output limits and output factors may be defined.

Time, Print And Save Specifications

In order to complete the dynamic simulation definition, the user must specify additional calculation parameters.

Time Specification

This specification defines the frequency of calculation and the total calculation time for the simulation.

The frequency of calculation, or time increment, relates to the frequency a packet of mass/energy is to be considered moving through the system. For each time increment, the packet of mass/energy properties and conditions are calculated.

The total calculation time relates to the total duration of the process simulation.

Both these specifications are achieved using keywords, TINC and TEND, respectively.

Print Specification

The Print Specification is used to define the frequency of storing results generated during a simulation. This is advantageous for long, time consuming simulations as it allows the user to view data for every 20 calculation steps, for example, rather than for every calculation time increment.

The Print specification is also used to set the simulation to an interactive working mode and produce hard copy graphical plots of the process parameter variations with time, if required.

Save Specification

At any point during a simulation, the process can be stopped, the results saved and the process restarted from the previous condition. In order to achieve this, the results must be saved in a restart file for the simulation.

The Save Specification is used to define the frequency of saving results in a restart file.

This section is a summary of the dynamic simulation capabilities of DynaChem. For detailed information on the software use and Unit specifications the user should refer to the DynaChem Handbook.

Chapter 9. Reference

Overview

This Reference section is a guide to the structure of the OLI Software and should be used in conjunction with the rest of the manual

Content

This section describes the function of commonly used keystrokes, the additional facilities available to the user via the Action Key, and also provides a reference index to the OLI Manual. Please note that the Reference Index has not been extended to cover the material contained within the two sections on Corrosion.

Commonly Used Keystrokes

The following list summarizes the special keystrokes which provide for efficient operation of the OLI software.

Keystroke Summary

PC

<u>Description</u>	<u>Keystroke</u>
Proceed to Next Screen	Enter
Exit to Previous Screen	Esc
Action Key	F10
Help Key	F1
Action Option	Alt + 1 st Character
Page Up	Page Up
Page Down	Page Down
Move to Fields	Arrow Keys

Action Key Facilities

The following documents the common Action Key facilities which are available throughout the OLI software.

File

Selection of File allows the user to select from the following options: New, Open, Edit, Merge, Print, Save, Save as, Cancel or Exit (which automatically saves the data in addition to leaving the screen).

Help

The Help facility is available in all components of ESP and is initially contextual, depending on the screen from which it is accessed. From this localized facility it is possible to access the extended Help facility by pressing the Help Key again (Note: It is possible to access the Help facility at any time). The extended Help offers a choice of:

How to use Help

Key Definitions

Help Index

System Limits

About OLI Systems

Options

This facility is available in all components of OLI software and allows the user to define general software operating environment. Three options are available:

Change Directories - Used to change the directory currently being accessed, to a different directory containing the required data for use.

Sound On/Off - A selection can be made from:

- 1) Sound On Error (when error is made).
- 2) All Sound Off.

Set-Up Options - Used for selection of Editor, Browser, and Printer. This must be used on initial installation of the system to select the user-preferred options. This allows for later file access (e.g., the View facility for the Model Definition in ESP Process). The PC default for the Editor and Browser is the system editor (e.g., the DOS 5.0 editor "EDIT"), and for the printer port, LPT1.

Output

This facility allows the user to select the destination of the ESP output. The results can be sent to the screen, the printer or a disk file.

Search

This facility is available in all components of OLI software and is used when the user is either not aware of the OLI name of the compound or where the constituent elements are known and a list of possible compounds is required. The possibilities available are to **Search By**:

Formula, where the user inputs the formula of the desired compound using the Empirical formula. For inorganics, this is a formula with the elements in alphabetical order. For organics the Empirical formula organizes the elements by the number of carbons, hydrogens and then the other elements in alphabetical order.

Structure, a Search technique not yet available.

Species Name, where the user enters the name, and a search is then made of the synonyms to find the species within the OLI databanks.

Periodic Table, where the user highlights those elements known to be present using the <Space Bar>, and then chooses the Select criterion via the Action Bar (Reference Chapter 3.1.6).

Select

This facility is only available when a Databank Search By Periodic Table is performed. The facility is used to limit the search of the Databank, and is accessed after the user selects the elements of interest from the periodic table. The Select facility offers four options:

All of Selected, which lists species containing the selected elements, together with any other elements which have not been specified. For example, if S and O were highlighted in the periodic table, the species listed would include H₂SO₄.

Any of Selected, which lists species which contain any of the selected elements. For the above example H₂S and HNO₃ species would be part of the listing.

Only Selected, which lists compounds which contain only the specified elements. In the case above this would include SO₂ and SO₃ but not the aforementioned.

Amount in Formula, which allows the user to select compounds with user defined stoichiometric amounts of an element. Elements are selected by highlighting the appropriate element on the periodic table and entering the stoichiometric number of interest adjacent to the selected elemental species. For example, selecting S with 1 and O with 4 produces a list of sulfates.

Sort

This facility is available after performing a Search by Periodic Table of OLI Databook. It is used to list species in a required order:

Chemistry Order - By convention, formula elements are alphabetic, and the formulas are arranged in ascending amount order, i.e., H, H₂, H₃...H₁₀.

Computer Order - By convention, formulas are alphabetic, but any numerics found come before characters, i.e., Na₂S before NaO₄S.

Units

This facility is available in all components of the OLI software and allows the user to select the units in which data is displayed. The options are Metric, SI, English and User. The User option can be any combination of units as defined by the user. Changing the units automatically converts data previously input, output, displayed or stored to insure consistency, with the exception of volumetric flow changes in ESP Process. (A change to volumetric flow basis is stored with the user data, but values entered are assumed to be in the new basis, no conversion is done).

The following contains the Action Key Facilities which are specific to OLI Databook.

Catalog

The Catalog facility is available in OLI Databook and produces ordered lists of the species in a databank and also lists the phases for which information is provided. The catalog can be used to determine whether a specific chemical is present in a databank.

Control

The Control facility is available in OLI Databook, and gives the user the ability to carry out specific actions on a private databank. Actions include deleting or copying a species, re-indexing a databook or assigning password protection.

Edit

The Edit facility is available in OLI Databook, and allows the user to add or amend existing data. When Edit is used a further facility, File, is displayed on the Action Bar (Reference Chapter 3.1.1)

Evaluate

The Evaluate facility is available in the Species Chapter of OLI Databook, and allows the user to evaluate a temperature dependent data property at a specific condition.

Format

The Format facility allows the choice of Import/Export file format. The two options presently available are ESP Readable format and ASCII Transfer formats.

Import/Export

The Import/Export facility allows the user to both Import data from a file into an OLI databank, and Export data from the databank into a file.

Mode

This facility is only available when data is being edited and allows specific data to be inserted or deleted from the databank.

New Item

New Item will provide the ability to display and update the OLI Data Dictionary. The Data Dictionary is where data items and their attributes are defined and stored. This facility is not yet available.

Plot

The Plot facility allows the user to plot experimental data sets for species within the databank.

Records

This facility is available in OLI Databook and provides supporting information on primary data within the databank. A databank item can have two types of records associated with it:

Support Record, which contains the Reference and Equation Codes, quality, and the correlation data range, where applicable.

Archive Record, which contains the date, value and reason for the update of any item which has been changed in the databank. Archive Records are not yet available.

Reports

The Reports facility is available in OLI Databook and allows the user to produce quick summary reports for specific species information. Three types of reports are available:

Quicklist - Quicklist is a report writer designed for display of one or more items for one or more species. Quicklist prompts first for items and then species. Species may be specified as a wildcard name, formula or as a list. Display options include screen, disk and printer.

SQL - Structured Query Language - Not yet available.

Formatted Reports - Not yet available.

View

In ESP Databook, whenever there is related data about the data being displayed, View has options which document the literature source, experimental data sets and quality of a data item. The facility provides eight options.

Reference - This option allows access to complete literature references for a data item. References are identified with a short reference code. The format of the code is to show the year of publication and the author(s) surname of reference.

Data - The actual data values, experimental or tabulated, for a specific data set can be accessed in the Experimental Chapter of OLI Databook. Data can be shown graphically using the Plot facility. The temperature range of the coefficients is noted on plot.

View Options

Data Quality - Two quality parameters are available for data items:

- **Data History** identifies the source of the data item and is normally identified with one of the following three character identifiers:

REC - recommended by literature source

EST - estimated

EXP - based on experimental data

- **Data Uncertainty** confirms the accuracy of a data item. It can be expressed as percentage error, standard deviation, or as a +/- value.

Date - This entry confirms the last modification date to a data item. Dates are automatically updated when other related data files are updated.

Created by - This option displays the initials of the user who previously entered the data for the species data item.

Comments - If an individual item has been updated, then a comment will be associated with the updated value. It is to be part of an archive system and is not yet available.

Keys - For cross reference purposes, the reference code and the equation code are stored in the support record. These are the codes which are used to identify and store the reference and equation form in the Literature Chapter of the Databook.

Equation - This option is available in the Species Chapter of the Databook and displays complete equation definitions for data in which coefficient values are specified.

OLI Databook Actions

To Select an Action, Either:

Press the Action Key, and position the cursor on the Action; or,

Press <Alt> and first character of Action (e.g., <Alt> H for Help)

The following contains the Action Key facilities which are specific to ESP Process.

Check

This facility is available in ESP Process, and allows the user to determine if an individual process unit definition is correct.

Config

The Config facility allows the user to add, delete, or reconfigure streams within a given process block of ESP Process.

Databank

This facility is available in ESP Process, and allows the user to specify additional private databanks for inclusion during Chemistry Model Definition creation.

Flowsheet

This facility allows the user to see a Process Flow Diagram (PFD) Display of a process.

Inflows

When specifying unit inflows in Process Build, additional species can be added to the list of inflows previously specified in the Chemistry Model Definition. If this is done, the Chemistry Model Definition must be recreated and the Model Solver regenerated.

.MOD, .EXE, and .FTN disk files will be deleted when the inflows lists is modified.

Normalize

The Normalize facility is available when defining process feed streams in ESP Process, and allows the user to normalize the relative amounts of each chemical in one of two ways:

Flow - Keeping the ratio of the components constant, adjust the component flows to sum to the total flow of the stream.

Total Flow - Given the compositions, sum them and arrive at the total flow of the stream.

Parameters

The Parameters facility is available in Process Build, and allows a user to enter values for the parameters that are associated with a particular process unit.

Process

This facility is available in ESP Process, and allows the user to request a summary statement of the defined process either by block or by stream.

Recycle

The software automatically performs an analysis for a recycle stream at the start of the Process Analysis stage. This same analysis can be explicitly requested with the Recycle Action Facility.

If a recycle exists in a process the user is prompted for which streams to designate as the recycle. The facility also allows the user to supply an initial estimate for the recycle stream flowrate.

Restart

This facility allows the user to specify that the next calculation be started from the results of a previous recycle stream or from the results of a column (multi-stage equilibrium calculation).

Scratchpad

This facility allows the user to perform equilibrium calculations on an individual stream. Calculations include adiabatic, isothermal, bubble and dew point, and pH precipitation point evaluations.

Sections

This facility is available in ESP Process and allows the user to define non-equilibrium chemical phenomena in the Chemistry Model Definition file. Phenomena may include; Ion Exchange, Bioreactions, Kinetics, Redox, Coprecipitation, and other user-defined Equations.

Simulator

This facility is used in conjunction with the Aspen+ or the Proll interface. It allows the user to generate the necessary OLI thermodynamic data blocks which can then be interfaced to these simulators.

Solids

This facility is available in ESP Process and allows the user to either remove solids from the Chemistry Model, or include them to calculate scaling tendencies only. This may be used if difficulties are encountered in converging a process case, or to save execution time.

Utility

This facility is available in ESP Process and allows on-line disk file management with options to view, print or delete.

View

This facility allows the user to view files including Chemistry Model definitions and Process Analysis results.

ESP Process Actions

To Select an Action, Either:

- Press the Action Key, and position the cursor on the Action; or,
- Press<Alt> and first character of Action (e.g., <Alt H> for Help)

The following contains Action Key facilities specific to the WaterAnalyzer.

The WaterAnalyzer organizes data from water samples. A water sample can be data returned from a laboratory analysis or it can be a composite of other samples. Once the data is entered, the sample can be reconciled for pH and electroneutrality, and simple ScratchPad calculations can be undertaken. Finally, the sample can be converted into a stream suitable for ESP Process calculations.

Facilities specific to the WaterAnalyzer are detailed in the following section.

Calculate pH

This facility allows the user to evaluate water sample pH values at specified isothermal conditions (e.g., temperature and pressure).

OLI Streams

The purpose of the OLI Streams facility is to convert an ionically-based, reconciled WaterAnalyzer stream into a molecular species based stream for use with Process Blocks in ESP Process.

Guess

This facility allows the user to specify an initial estimate for the amount of species to be added to a sample in order to reconcile pH. This facility is normally used when required sample pH values differ greatly from OLI calculated pH valued due to an incomplete water analysis being supplied.

Labentry

Approximately 100 primary anion and cation species are collected in a databank produces specifically for working with the WaterAnalyzer in ESP Process. At this time, the LabEntry facility can only be used when specifying WaterAnalyzer Chemistry Models.

Reconcile Electroneutrality

Typically most water analyses have either an excess positive or negative charge. Five options are available through the Reconcile facility to balance the excess charge:

Dominant Ion - The addition of the dominant anion/cation present in the sample.

User Choice - The addition of a user specified anion/cation.

Na⁺,Cl⁻ - The addition of Na⁺ or Cl⁻ ions.

Prorate - A percentage increase in all user defined anion/cation concentrations.

Make Up Ion - The addition or subtraction of a single anion or cation.

Reconcile pH

The reconciliation of pH from the calculated value, to the required user entered value, is achieved by one of two methods:

Select Titrant - This option allows the user to specify a suitable acid or base species from the inflow list which is used to reconcile the sample pH.

NaOH/HCl - This option reconciles the sample pH using either sodium hydroxide or hydrochloric acid as the reagent.

Samples

This facility allows access to reports for existing reconciled water samples.

Scratchpad

ScratchPad is a facility that allows simple equilibrium calculations on a water sample. Calculations that can be performed include: isothermal, adiabatic, bubble point, and dew point calculations.

Reconciled values of water sample concentrations are used if they are available.

Send

Send is the facility used to transfer a generated ESP stream to a named ESP process.

Surveys

The Surveys facility allows different case studies to be performed on a water sample. Concentration, dilution and precipitation studies are possible.

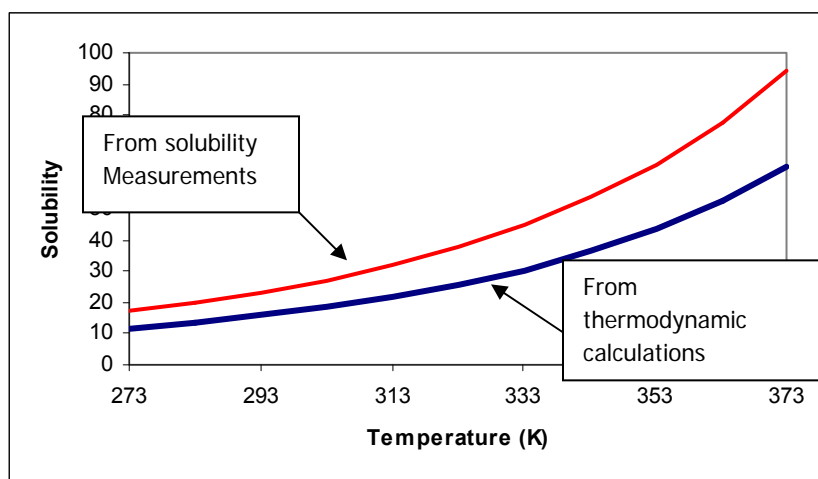
Template

This facility is available to aid the user when specifying inflow species for a WaterAnalyzer Chemistry Model. The facility lists species which are present in the Lab Databank and can be used in WaterAnalyzer calculations. Selections can be made from the list using the <Space Bar>.

Chapter 10. Temperature Ranges

What are temperature ranges (TRANGE)?

TRANGES are a short and name for Temperature ranges. The equilibrium constants for some solids in the OLI Databases have been fit to a polynomial in temperature rather than determined from pure thermodynamics. Lets consider a hypothetical solid "A". If we were to plot the solubility of "A" as a function of temperature based on both thermodynamically derived values and from solubility experiments, the plot may look like this:



The reason for the difference is that solubility measurements take time and may be kinetically limited. Thermodynamic calculations take values from a variety of sources and may be more stable. It is felt that the solubility measurements more closely represent industrial conditions and the database is adjusted to reflect that feeling.

The solubility data was fit to a polynomial. Polynomials are notorious for not extrapolating correctly. The polynomial used for this purpose is:

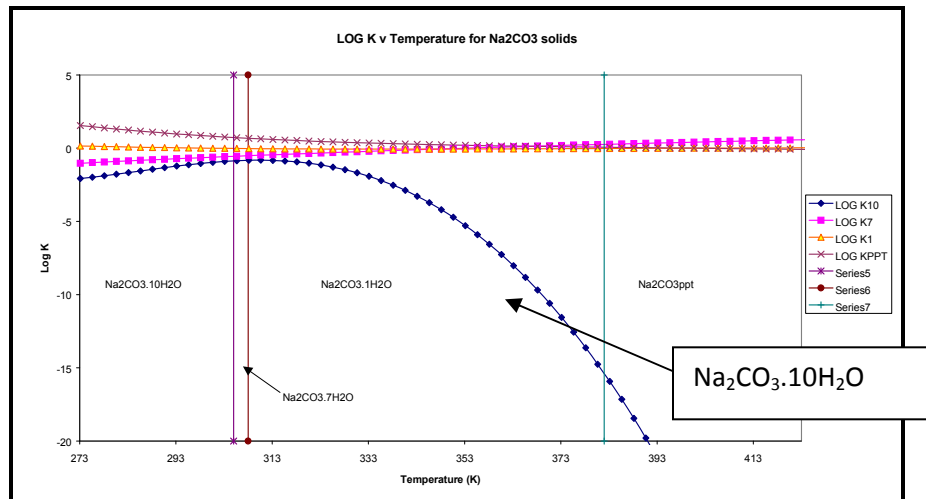
$$\text{Log K} = A + B/T + CT + DT^2$$

Incorrect predictions of Scaling Tendency may result outside the fitted temperature range. Therefore the applicable range is generally limited to data set.

For example, consider the solubility of sodium carbonate. There are four possible solids: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and Na_2CO_3 . The solubility temperature limits are:

Solid	Temperature Range (C)
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	0-35
$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	35-37
$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	37-109
Na_2CO_3	109-350

A plot of the log K for each solid is displayed below:



The temperature range in which each solid is stable is displayed with a vertical line on the plot. For a given solubility of Na_2CO_3 the lower on the plot, the smaller the K_{sp} (solubility product) and therefore the higher the scaling tendency. Solids with high scaling tendencies will predict to form. It can be seen that the deca-hydrate species does not extrapolate well to high temperatures. If we concern ourselves

with 350K, we can see that if the deca-hydrate was allowed to be in the model, the equilibrium based solver will attempt include it over the actual solid which is the mono-hydrate. Since the deca-hydrate species is outside its temperature range, it will be mathematically eliminated from the equations.

Such solids are frequently shown in ESP with the tag EXCL TR to indicate that the scaling tendency was calculated but not used actively in the software, the solid was **EXCL**uded due to **T**emperature **R**ange issues.

Chapter 11. Installing Private Databases

Overview

OLI Systems, Inc. performs a data service for chemical species that do not currently exist in the OLI databases or required improvement of the thermochemical data for species that do exist in the OLI databases. In either case, the updated thermochemical data is provided in a private database. This database is actually a set of files (38 to 39 depending on the OLI/Software version). These files are sent as a compressed file, usually a ZIP file.

There are two methods of installing the software. One is for local use on your computer. The database is installed into a folder and is only available in that folder. This is useful if you want to have different versions of the private database. For example, you may want to have a species that was specifically adjusted for high temperature calculations and high concentration, forgoing the accuracy at low temperature. You may also want the same species to be used at low temperature. This requires two private databases.

The other method is to install the database in the root of the OLI directory structure. This method allows you to access the database from any folder on your computer when running the OLI/Software. This saves disk space and increases your flexibility with the program.

Method 1 – Local Install

We are using the private database SILICA as an example for this method.

1. OLI normally provides the private database as a zip file. This file is frequently sent by E-mail. Detach the zip file and store it in a folder other than in the OLI tree. For example: c:\my projects\silica.zip
2. If sent via CD-ROM, copy the file to a folder other than in the OLI tree. For example: c:\my projects\silica.zip
3. Decompress the zip file into the local folder. If using WinZip, you can select all the files and drag and drop into the folder.
4. Verify that the database is intact by running the OLI/Software. Switch to the local folder using the <Options> action item. Select the private database and see if any thermochemical data has been entered. If there is data, then the database installed correctly.

Method 2 – Computer-wide installation.

We are using the private database SILICA as an example for this method.

1. OLI normally provides the private database as a zip file. This file is frequently sent by E-mail. Detach the zip file and store it the folder: **c:\OLI65\ESP** this assumes you have installed OLI version 6.5 in the default path. Change the path as necessary.
2. If sent via CD-ROM, copy the zip file to the folder: **c:\OLI65\ESP** this assumes you have installed OLI version 6.5 in the default path. Change the path as necessary.
3. Decompress the zip file into the local folder. If using WinZip, you can select all the files and drag and drop into the folder.
4. Verify that the database is intact by running the OLI/Software. Switch to the local folder using the <Options> action item. Select the private database and see if any thermochemical data has been entered. If there is data, then the database installed correctly.

Chapter 12. pH and MSE

Overview

The new mole fraction based concentration basis available in the OLI software (ESP version 7.0 or Analyzers 2.0 or later) report activity coefficients on a different basis than in the older software. Hand calculations of such values such as pH can be confusing. This document will take you through two examples of how pH is calculated.

Further confusion is that the reported activity coefficient is different depending on the basis selected. We will examine each basis in turn.

Definitions of Symbols and Superscripts

Definitions of symbols:

$\gamma_j^{m,\infty}$ activity coefficient of species j on the basis of molality and infinite dilution reference state (unsymmetrical) ($\gamma_j^{m,\infty} \rightarrow 1$ as $m_j \rightarrow 0$)

$\gamma_j^{x,\infty}$ activity coefficient of species j on the basis of mole fraction and infinite dilution reference state (unsymmetrical) ($\gamma_j^{x,\infty} \rightarrow 1$ as $x_j \rightarrow 0$)

γ_j^x activity coefficient of species j on the basis of mole fraction and fused salt reference state (symmetrical) ($\gamma_j^x \rightarrow 1$ as $x_j \rightarrow 1$)

- X_w The mole fraction of water
- X_{H^+} The mole fraction of the hydrogen ion

Superscripts

[∞] – infinite dilution in water reference state

^m – molality-based

^x – mole-fraction-based

The Standard Aqueous Model

In this simulation we have taken a sample at 25 °C, 1.0 Atmospheres, 55.508 moles of H₂O and 0.0001 moles of HCl. The standard Bromley-Zematis activity model was selected. The program reports the following information:

- pH = 4.005
- $\gamma_H^{x,\infty}$ = 0.98848 (activity coefficient for the hydrogen ion – Bromley Basis)
- X_H = 1.8×10^{-6} (mole fraction of hydrogen ion)
- X_{H_2O} = 0.999998 (mole fraction of water – true basis)
- m_H = 0.0001 mole/Kg H₂O

pH definition

The definition of pH in the OLI software is the following:

$$pH = -\text{Log}(a_{H^+})$$

Where a_{H^+} is the activity of the hydrogen ion and a_{H^+} is $a_{H^+} = m_{H^+} \gamma_{H^+}^{m,\infty}$

In the traditional molality based calculation, this expands to: $pH = -\log(m_{H^+} \gamma_{H^+}^{m,\infty})$

The molality concentration unit can be converted easily to the mole fraction basis via this equation:

$$m_{H^+} = 55.509 \frac{X_{H^+}}{X_w}$$

We can define the activity of the hydrogen ions on the molality basis as:

$$\gamma_{H^+}^{m,\infty} = X_w \gamma_{H^+}^{X,\infty} \text{ This combines to: } pH = -\log(55.509 X_{H^+}^{x,\infty} \gamma_{H^+}^{x,\infty})$$

Evaluating the above values we obtain:

$$pH = -\log(55.509 * 1.8 \times 10^{-6} * 0.98848) = -(-4.005) = 4.005$$

Converting to molality based activity coefficients

To calculate the pH on a molality basis we need to convert the activity coefficient. To do this we can use the following formula.

$$\gamma_{H^+}^{m,\infty} = X_w \gamma_{H^+}^{X,\infty}$$

Evaluating this equation using the simulation values we obtain:

$$\gamma_{H^+}^{m,\infty} = (0.999998)(0.98848) = 0.98848$$

The definition of pH on the molality basis is:

$$pH = -\text{Log}(a_{H^+}) = -\text{Log}(\gamma_{H^+}^m m_{H^+}) = -\log[(0.98848)(0.0001)] = -(-4.005) = 4.005$$

So you can see that the pH of the solution is the same regardless of the basis.

Calculating the pH on the MSE H+ Basis

The simulation is very similar to previous simulation. Here are the results:

$$pH = 4.005$$

$$\begin{aligned}\gamma_{\text{H}}^x &= 0.988501 \text{ (activity coefficient for the hydrogen ion – Bromley Basis)} \\ x_{\text{H}} &= 1.8 \times 10^{-6} \text{ (mole fraction of hydrogen ion)} \\ x_{\text{H}_2\text{O}} &= 0.999998 \text{ (mole fraction of water – true basis)}\end{aligned}$$

Since the definition of pH is the following: $pH = -\log(55.509 X_{\text{H}^+}^{x,\infty} \gamma_{\text{H}^+}^{x,\infty})$

We now enter this value in for pH and obtain:

$$pH = -\text{Log}[(55.509)(0.98848)(1.8 \times 10^{-6})] = -(-4.005) = 4.005$$

Calculating pH in the hydronium ion basis

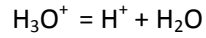
In the hydronium ion basis, there is no hydrogen ion. This makes a direct conversion difficult. Some additional conversions are required. We are using the same compositions as before.

The solution results are:

$$\begin{aligned}x_{\text{H}_3\text{O}^+} &= 1.8 \times 10^{-6} \\ x_{\text{H}_2\text{O}} &= 0.999996 \\ \gamma_{\text{H}_3\text{O}^+}^{x11} &= 0.988515 \\ \gamma_{\text{H}_2\text{O}}^x &= 1.0000 \\ \text{pH} &= 4.005\end{aligned}$$

Our major concern here is that we need to have an effective concentration of the hydrogen ion which does not exist in this framework. We know that the following definition is true:

¹¹ These activity coefficients are on the MSE basis.



Since the activities on both sides must be equal,

$$a_{\text{H}_3\text{O}^+} = a_{\text{H}^+} a_{\text{H}_2\text{O}}$$

Or

$$a_{\text{H}^+} = \frac{a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}}}$$

We also know that to convert the mole fraction basis to the molality basis we can use this conversion:

$$a_{\text{H}^+}^m = a_{\text{H}^+}^x \frac{1000}{M_{\text{H}_2\text{O}}}$$

Where $M_{\text{H}_2\text{O}}$ is the molecular weight of water (approximately equal to 18.1054 g/mole)

Thus the activity of the hydrogen ion on a molality basis is:

$$a_{\text{H}^+}^m = \frac{a_{\text{H}_3\text{O}^+}^x}{a_{\text{H}_2\text{O}}^x} \frac{1000}{M_{\text{H}_2\text{O}}}$$

So pH becomes

$$\text{pH} = -\log(a_{\text{H}^+}^m) = -\log\left(\frac{a_{\text{H}_3\text{O}^+}^x}{a_{\text{H}_2\text{O}}^x}\right) - \log\left(\frac{1000}{M_{\text{H}_2\text{O}}}\right)$$

Where

$$a_{H_3O^+}^x = \gamma_{H_3O^+}^x X_{H_3O^+} = (0.988515)(1.8 \times 10^{-6}) = 1.77933 \times 10^{-6}$$

And

$$a_{H_2O}^x = \gamma_{H_2O}^x X_{H_2O} = (1.000)(0.999996) = 0.999996$$

Thus pH becomes

$$pH = -\log(a_{H^+}^m) = -\log\left(\frac{1.77933 \times 10^{-6}}{0.999996}\right) - \log(55.509) = 4.005$$

Chapter 13. Converting Reported Equilibrium Constants

Overview

A change in the concentration basis has been introduced in ESP version 7.0 and OLI Analyzers 2.0. This change in basis from molal (moles/ Kg H₂O) to mole fraction was primarily done to support the Mixed-Solvent Electrolyte (MSE) thermodynamic package. The change in basis was also applied to the Aqueous Electrolyte (AQ) model.

Frequently a user needs to compare an equilibrium constant¹² reported by the OLI software with literature values. Frequently the literature reports equilibrium constants on the molal basis and not the mole fraction basis. Fortunately there is an easy conversion.

Conversion equation

The conversion equation is very simple. Let's define two equilibrium constants. $K(m)$ and $K(x)$. $K(m)$ is the molal based equilibrium constant and $K(x)$ is the mole fraction based equilibrium constant.

The conversion is:

¹² Also called K-values in the OLI parlance

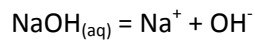
$$K(m) = K(x) \times 55.508^{\Delta n}$$

Where Δn is the change in moles across the equation excluding water (H₂O and solids):

$$\Delta n = \text{moles}_{\text{Product}} - \text{moles}_{\text{Reactant}}$$

Example 1: No water

Let's consider this equilibrium reaction:



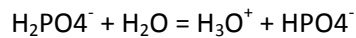
The software calculates an equilibrium constant, $K(x) = 7.90627\text{E}+08$ with

$\Delta n = (2 \text{ moles product} - 1 \text{ moles reactant}) = 1$. Thus the conversion is:

$$K(m) = K(x) * 55.5091^1 = 7.90627\text{E}+08 * 55.5091 = 4.38869\text{E}+10$$

Example 2: With water

Now let's consider a conversion where water is present.



The software calculates an equilibrium constant, $K(x) = 1.1224\text{E}-09$,

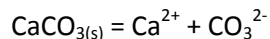
$\Delta n = (2 \text{ moles of product} - 1 \text{ mole of reactant}) = 1$. This our conversion equation is:

$$K(m) = K(x) \times 55.5091^1 = 1.1224\text{E-}09 * 55.5091 = 6.23033\text{E-}08$$

Why was there only 1 mole of reactant? In our conversion, we ignore the moles of H₂O (in the molality basis the activity of water is unity for the conversion)

Example 3: With a solid

Now let's consider a conversion where a solid is dissolving:



The software calculates an equilibrium constant, $K(x) = 9.66059\text{E-}13$,

$\Delta n =$ is 2 moles of product - 0 mole of reactant) = 2. This our conversion equation is:

$$K(m) = K(x) \times 55.5091^2 = 9.66059\text{E-}13 * 3081.26 = 2.97668\text{E-}09$$

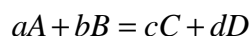
Why was there 2 moles of reactant? In our conversion, we ignore the moles of a solid (in the molality basis the activity of a solid is unity for the conversion)

Chapter 14. Using Constrained Reaction Kinetics

Overview

Frequently a user wants to describe a chemical reaction in terms of reaction kinetics rather than equilibrium. The user may also want to constrain the reaction kinetics such that the forward and reverse rates of reaction do not exceed the limits placed on it by chemical equilibrium.

To briefly explain the procedure we first need to look at a generic equilibrium reaction:



The standard equilibrium constant expression is¹³:

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

¹³ We are ignoring activity coefficients to simplify the example.

The forward rate v_F is:

$$v_F = k_F [A]^a [B]^b$$

And the reverse rate v_R is:

$$v_R = k_R [C]^c [D]^d$$

At equilibrium the forward rate and the reverse rate are equal.

$$v_F = v_R$$

This expands to:

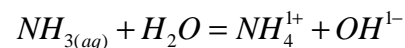
$$k_F [A]^a [B]^b = k_R [C]^c [D]^d$$

Upon re-arrangement, we get

$$\frac{k_F}{k_R} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = Keq$$

Example 1: Standard Reaction Kinetics

In this example we are using standard reaction kinetics to hydrolyze ammonia. The overall reaction is:



We know the forward rate constant (and hence the forward reaction rate) but we wish to constrain the forward and reverse reaction rates to the thermodynamic equilibrium constant stored in the OLI Databases.

To do this we create a standard model file and add the following section:

KINETICS

REAC1 NH3AQ+H2O=NH4ION+OHION

RATE1 STD AF=3.0 BF=0 **KR=KF/KEQ** ER1=1.0 ER2=1.0 EP1=1.0 EP2=1.0

This section is added to the end of the model file (MOD) but before the END statement. A special note: The standard equilibrium equation in the EQUILIBRIUM section must remain so we can obtain the equilibrium constant. In non-constrained reaction kinetics we would be forced to remove the default equilibrium equation.

The standard reaction rate syntax applies here with the addition of a new statement.

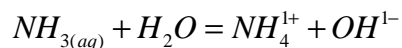
KR=KF/KEQ

This forces the reverse rate constant to be constrained by the equilibrium constant KEQ. In this example, the forward rate constant is being defined via the Arrhenius equation:

$$k_F = A_F e^{-B_F/RT}$$

Example 2: Non-Standard Reaction Kinetics¹⁴

In this example we are using non-standard reaction kinetics to hydrolyze ammonia. The overall reaction is:



We know the forward rate constant (and hence the forward reaction rate) but we wish to constrain the forward and reverse reaction rates to the thermodynamic equilibrium constant stored in the OLI Databases.

To do this we create a standard model file and add the following section:

```
KINETICS
REAC1 NH3AQ+H2O=NH4ION+OHION
RATE1 SPEC
DEFINE FXRATE=LNH3AQ+ANH3AQ+LH2O+AH2O
DEFINE RXRATE=LNH4ION+ANH4ION+LOHION+AOHION
DEFINE KF1=3
DEFINE KR1=KF1/KEQ1
DEFINE RATE1=(KF1*EXP(FXRATE)-KR1*EXP(RXRATE))*VOLLIQ/1000.
```

This section is added to the end of the model file (MOD) but before the END statement. A special note: The standard equilibrium equation in the EQUILIBRIUM section must remain so we can obtain the

¹⁴ It is beyond the scope of this document to explain how to use non-standard reaction kinetics.

equilibrium constant. In non-constrained reaction kinetics we would be forced to remove the default equilibrium equation.

The non-standard reaction rate syntax applies here with the addition of a new statement. In this case we may have several reaction rates and we need to create specific variables tied to the reaction rates. Here we have appended the number "1" to denote that these variables are linked to REAC1

$$KR1=KF1/KEQ1$$

This forces the reverse rate constant to be constrained by the equilibrium constant KEQ.

Chapter 15. Turn off the Run-Time Beep

Overview

The run-time beep, present in ESP since version 1.0, can be an annoying noise. Since it is driven by the PC Speaker and not via the sound card, there are very few options to modify the sound.

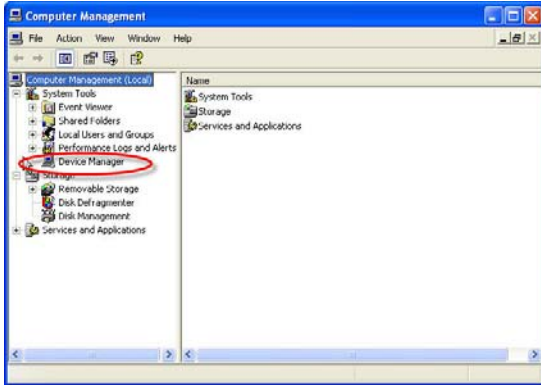
In fact, short of physically disabling the speaker, you can only turn the speaker on or off. This means that the POST (power-on-self-test) beep will also not be turned on. This is usually a minor issue.

Assumptions

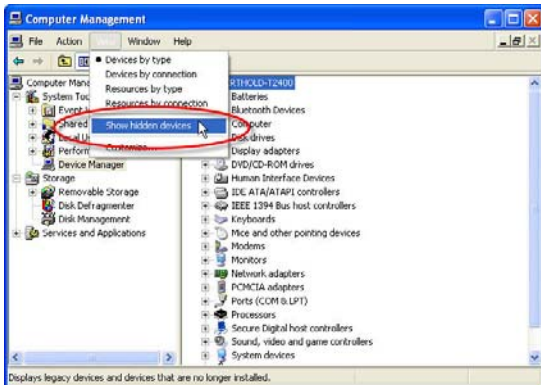
1. You must be using Microsoft Windows XP or later
2. You must have sufficient privilege to make changes to your system registry files.

Procedure

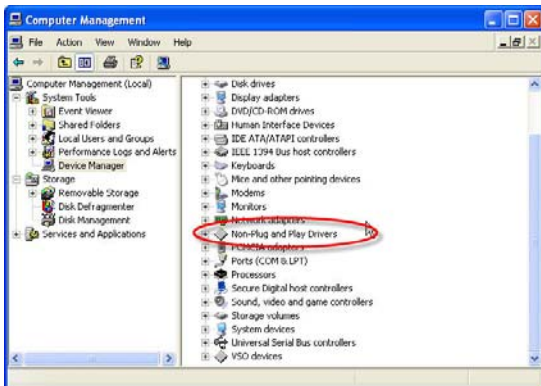
1. Locate the **My Computer** icon on your desktop
2. Right-click the **My Computer** icon.
3. Select the **Manage** option



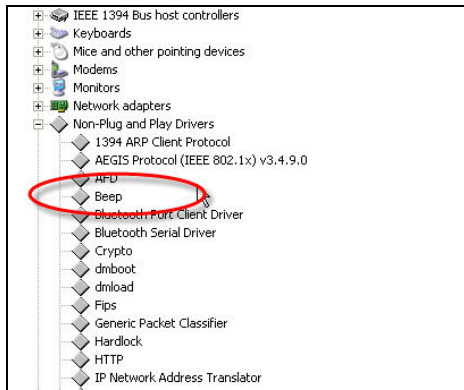
4. Select **View** from menu and select **Show Hidden Devices**



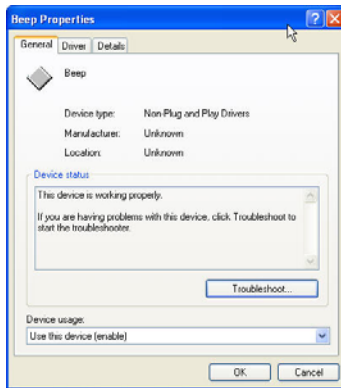
5. Scroll the right-hand window and expand **Non-Plug and Play Drivers**



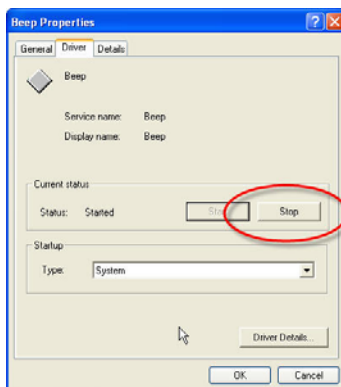
6. Double-Click the item **Beep**



7. Click on the **Driver** Tab



8. Click the **Stop** button.



9. Click the OK button.

The PC speaker has now been disabled. To re-enable the speaker, repeat these steps but start the driver instead of stopping it.

Chapter 16. Mass-Transfer Multi-Stage Process Blocks

Overview

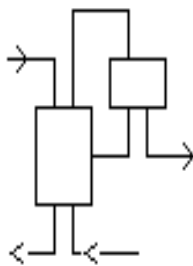
This section contains detailed specification requirements for multi-stage process blocks available in ESP. Generally, these process units are columns/towers. The process units available are:

- **Stripper**
- **Absorber**
- **Extractor**

The unit to be specified is selected from the display using the Arrow Keys and then the Enter Key.

Additional column specification facilities are available via the Action Key and then by selecting the Parameters and Config facilities. These facilities are detailed for each individual unit.

Distillation/Stripper Unit



This is a multi-stage conventional or environmental unit allowing species in a liquid to be separated either by distillation, or by the action of a countercurrent vapor stream (i.e., stripper). The unit can hold a maximum of 50 stages, 10 feed streams, and 10 exit streams.

When this block is selected the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, an aqueous phase must be present in every liquid stream. The liquid feed and/or liquid product can contain both an aqueous and nonaqueous liquid phase, and just an aqueous phase alone. In the case of a non-electrolyte column, only the non-electrolyte liquid phase exists (electrolyte chemistry is not considered).

When this block is selected the user is forced to choose either a standard column or a mass transfer limited column. The standard column applies for the rigorous equilibrium model which is based on the component material balance, energy balance and thermodynamic correlations and criteria of phase equilibria at each stage; however, the mass transfer limited column applies for the nonequilibrium model, which explicitly accounts for mass and heat transfer except material and energy balance and phase equilibria. Therefore, the mass transfer limited column may provide more realistic concentration and temperature profile through the column. In the mass transfer limited column, each stage is divided into five parts: vapor bulk, vapor film, vapor/liquid interface, liquid film and liquid bulk; the mass-transfer and heat-transfer resistances are assumed to lie in two thin film layers that are separated by the vapor/liquid interface; at the interface, the vapor and the liquid are in equilibrium.

The unit may be set to a single stage standard or mass transfer limited column without condenser and reboiler.

Data Requirements

A minimum of one feed stream and two exit streams (i.e., distillate and bottoms) must be named when using the unit for distillation. An additional feed must be added when using the unit as a stripper. The feed stream temperature, pressure, flow and composition data must be specified by the user or be a

product stream from another Process Block. The number of stages will default to 10 and appear that way on the initial screen. The user may override this value. If there is a condenser or reboiler, these will count as stages. Additionally, various column operating parameter information must be supplied by the user.

Column Parameters

The column operating parameters are accessed using the Action Key and then by selecting the Parameters facility. Nine options are available for the standard column:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop through the column is assumed. If no values are given, the entire column is assumed to operate at atmospheric pressure.

Column Estimates This option allows stage operating temperatures, vapor distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperature, as well as the vapor distillate rate and liquid reflux flowrates, must all be specified by the user. The Esc Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchanger duty) to meet specifications in the column operation. For example, vapor and/or liquid composition specifications, stage operating temperature, and vapor and/or liquid stream flowrate specifications can all be achieved.

Exchanger Duties This option allows column and pump-around heat exchanger duties to be specified. For columns using a condenser and/or reboiler, the user must define duties for the respective units. Negative heat duties imply heat removal. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages. If no data is entered, the stage efficiency is assumed to be 1.0. The End Key

returns the user to the process block display. This function is not available for mass transfer limited columns.

Component Efficiencies This function is optional and allows the user to specify Murphree efficiencies for individual components in each column stage. If no data is entered, the efficiency for individual component is assumed to be 1.0. The End Key returns the user to the process block display. This function is not available for mass transfer limited columns.

Convergence Parameters This function is optional and allows the user to specify the Maximum number of iteration and convergence tolerance and if initialize column each time in recycle loops. If no data is entered, the Maximum number of iteration is assumed to be 35, the convergence tolerance is assumed to 5.0E-7 and column has no initialization each time in recycle loops. The End Key returns the user to the process block display.

Tray Hold-Up Time This function is required for columns whose chemistry contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Condenser Type This function is optional and allows the user to specify the type of condenser. If no data is entered, the condenser is assumed to be partial condenser. The End Key returns the user to the process block display.

Except those options above, there are three more options available for the mass transfer limited column:

Mass Transfer Parm This option allows the user to specify vapor-liquid mass and heat transfer coefficients on each stage of the column. The coefficients are overall coefficients and apply to all components. The interfacial transfer area must also be specified. If the same coefficients are used throughout the column, the coefficient may be varied to meet a composition specification by means of the spec/control parameters. The End Key returns the user to the process block

display. If the mass and heat transfer coefficients are not specified by the user, then the software will calculate them based on column type the user chooses.

Column Type This option allows the user to specify column type and the specific parameters. There are four column types available: Packed column, Sieve Tray and Bubble Cup and Valve Tray. The End Key returns the user to the process block display. Since one of the transport properties, surface tension is not available in OLI Engine, they are set to be constant (0.07kg/s) in the column calculations. For packed column, the user is allowed to specify the height of stage, column diameter, column packing type, column packing material, and column packing size [1]; For sieve tray column [2], the user could set the column diameter, weir height, froth height and clear liquid height; for bubble cap column [3], column diameter is available to be specified by the user; for valve tray data [4], column diameter and weir height could be specified. The Chilton-Colburn analogy has been applied to correlate the heat transfer coefficient with mass transfer coefficient for species [5]. The method of Mathur et al (1967) has been adopted to calculate the overall heat transfer coefficients [6]. The users also could define their own column type by a user-defined subroutine.

Interface Film Type This function is optional and allows the user to specify the number of liquid interface film segments. The default value is 1. If a value more than 1 is set ($N=1-10$), the film discretization method is applied to calculate the concentration profile in the liquid film region. This approach is applied to take into account the possible influence of ionic interaction on the species mass transfer in the liquid film. In this approach, the liquid film is further divided into N films and the Nernst-Planck equation and Poisson equation are used to describe the electrolyte fluid in the liquid film. The user can choose to use the film discretization method by specifying the number of films (regular mass transfer limited column if the number of film is set to 1). [7-8].

Column Configuration

Additional column parameters can be defined, via the Action Key, and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block includes the two units on the display.

Pump-arounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

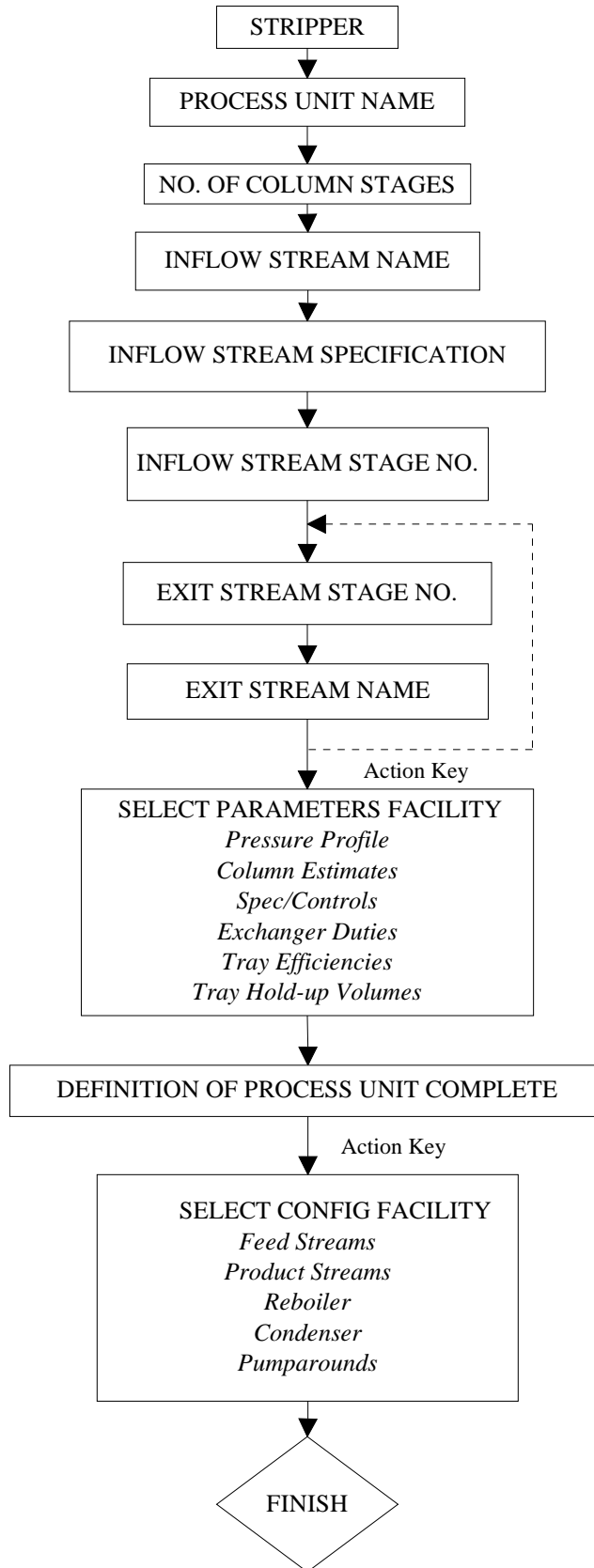
Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero. If this is not performed the data entry is not saved.*
2. *For columns with condenser and/or reboiler units the heat duty estimates defined by the user must be such that a vapor flow exists on the bottom stage and a liquid phase flow exists on the top stage of the column respectively.*
3. *The column can only operate if two (or optionally three) phases exist on every stage of the column.*
4. *For columns without a condenser and/or reboiler unit, a feed stream must be specified entering at the respective position of the omitted unit. The phase of this stream must be correctly defined. A liquid phase feed stream is required as an alternative to a column condenser, and a vapor phase stream in place of a reboiler unit (i.e., the column must have two phases flowing to and from every stage).*
5. *When defining a stripper unit, an all liquid feed stream must be specified entering the top of the column and the stripping vapor must enter the bottom of the unit.*
6. *When defining stripper column parameters, a zero liquid reflux (i.e., distillate) flow must be made. This is because the distillate flow exiting the unit must only exist in the vapor phase.*

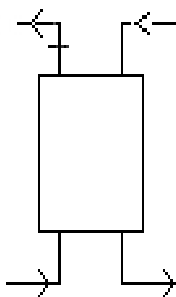
7. *All column stages are numbered from bottom to top.*

8. *If a feed stream contains both a vapor and a liquid phase, the liquid goes to the feed tray specified by the user and the vapor goes to the stage above.*

Stripper Schematic



Absorber Unit



This is a multi-stage conventional or environmental process unit which allows species in a vapor feed to be absorbed by a countercurrent liquid stream. The unit can hold up to a maximum of 50 stages and up to a maximum of 10 feed and 10 product streams.

When this block is selected the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, an aqueous phase must be present in every liquid stream. The liquid feed and/or liquid product can contain both an aqueous and nonaqueous liquid phase or just an aqueous phase alone. In the case of a non-electrolyte column, there is only the non-electrolyte liquid phase (electrolyte chemistry is not considered).

When this block is selected the user is forced to choose either a standard column or a mass transfer limited column. The standard column applies for the rigorous equilibrium model which is based on the component material balance, energy balance and thermodynamic correlations and criteria of phase equilibria at each stage; however, the mass transfer limited column applies for the nonequilibrium model, which explicitly accounts for mass and heat transfer except material and energy balance and phase equilibria. Therefore, the mass transfer limited column may provide more realistic concentration and temperature profile through the column. In the mass transfer limited column, each stage is divided into five parts: vapor bulk, vapor film, vapor/liquid interface, liquid film and liquid bulk; the mass-transfer and heat-transfer resistances are assumed to lie in two thin film layers that are separated by the vapor/liquid interface; at the interface, the vapor and the liquid are in equilibrium.

The unit may be set to a single stage standard or mass transfer limited column without condenser and reboiler.

Data Requirement

A minimum of one liquid stream entering the top of the column and one vapor stream entering the bottom of the unit must be specified. The respective feed stream temperature, pressure, flow and composition must be defined by the user or be a product stream from another Process Block.

When defining the feed stream, the temperature and pressures of each stream should be such that the species components reside in the correct phase for the respective stream.

The column exit vapor and liquid streams must be named, in addition to various column parameters.

Column Parameters

The column operating parameters are accessed using the Action Key and selecting the Parameters facility. The column operating parameters are accessed using the Action Key and then by selecting the Parameters facility. Nine options are available for the standard column:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop through the column is assumed. If no values are given, the entire column is assumed to operate at atmospheric pressure.

Column Estimates This option allows stage operating temperatures, vapor distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperature, as well as the vapor distillate rate and liquid reflux flowrates, must all be specified by the user. The Esc Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchanger duty) to meet specifications in the column operation. For example, vapor and/or liquid composition specifications, stage operating temperature, and vapor and/or liquid stream flowrate specifications can all be achieved.

Exchanger Duties This option allows column and pumparound heat exchanger duties to be specified. For columns using a condenser and/or reboiler, the user must define duties for the respective units. Negative heat duties imply heat removal. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages. If no data is entered, the stage efficiency is assumed to be 1.0. The End Key returns the user to the process block display. This function is not available for mass transfer limited columns.

Component Efficiencies This function is optional and allows the user to specify Murphree efficiencies for individual components in each column stage. If no data is entered, the efficiency for individual component is assumed to be 1.0. The End Key returns the user to the process block display. This function is not available for mass transfer limited columns.

Convergence Parameters This function is optional and allows the user to specify the Maximum number of iteration and convergence tolerance and if initialize column each time in recycle loops. If no data is entered, the Maximum number of iteration is assumed to be 35, the convergence tolerance is assumed to 5.0E-7 and column has no initialization each time in recycle loops. The End Key returns the user to the process block display.

Tray Hold-Up Time This function is required for columns whose chemistry contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Condenser Type This function is optional and allows the user to specify the type of condenser. If no data is entered, the condenser is assumed to be partial condenser. The End Key returns the user to the process block display.

Except those options above, there are three more options available for the mass transfer limited column:

Mass Transfer Parm This option allows the user to specify vapor-liquid mass and heat transfer coefficients on each stage of the column. The coefficients are overall coefficients and apply to all components. The interfacial transfer area must also be specified. If the same coefficients are used throughout the column, the coefficient may be varied to meet a composition specification

by means of the spec/control parameters. The End Key returns the user to the process block display. If the mass and heat transfer coefficients are not specified by the user, then the software will calculate them based on column type the user chooses.

Column Type This option allows the user to specify column type and the specific parameters. There are four column types available: Packed column, Sieve Tray and Bubble Cup and Valve Tray. The End Key returns the user to the process block display. Since one of the transport properties, surface tension is not available in OLI Engine, they are set to be constant (0.07kg/s) in the column calculations. For packed column, the user is allowed to specify the height of stage, column diameter, column packing type, column packing material, and column packing size [1]; For sieve tray column [2], the user could set the column diameter, weir height, froth height and clear liquid height; for bubble cap column [3], column diameter is available to be specified by the user; for valve tray data [4], column diameter and weir height could be specified. The Chilton-Colburn analogy has been applied to correlate the heat transfer coefficient with mass transfer coefficient for species [5]. The method of Mathur et al (1967) has been adopted to calculate the overall heat transfer coefficients [6]. The users also could define their own column type by a user-defined subroutine.

Interface Film Type This function is optional and allows the user to specify the number of liquid interface film segments. The default value is 1. If a value more than 1 is set ($N=1-10$), the film discretization method is applied to calculate the concentration profile in the liquid film region. This approach is applied to take into account the possible influence of ionic interaction on the species mass transfer in the liquid film. In this approach, the liquid film is further divided into N films and the Nernst-Planck equation and Poisson equation are used to describe the electrolyte fluid in the liquid film. The user can choose to use the film discretization method by specifying the number of films (regular mass transfer limited column if the number of film is set to 1). [7-8].

Column Configuration

Additional column parameters can be defined, via the Action Key and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

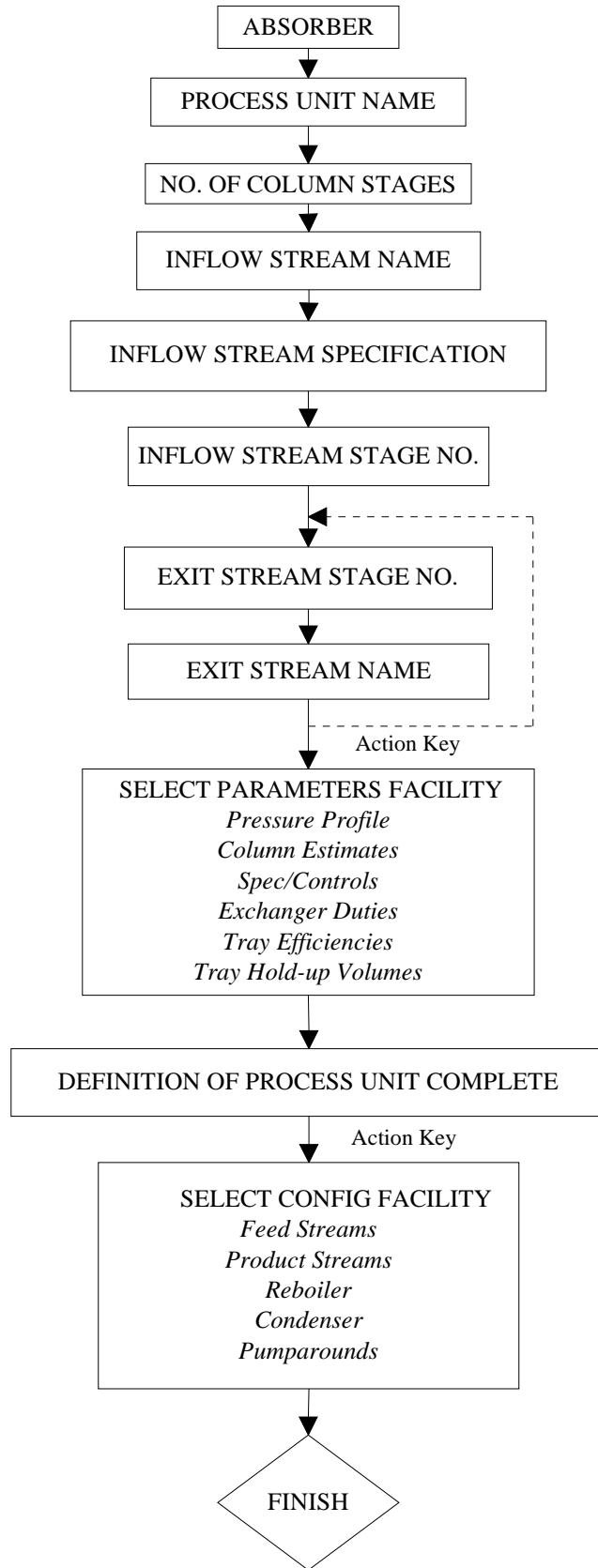
Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block does not include the two heat exchanger units.

Pumparounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

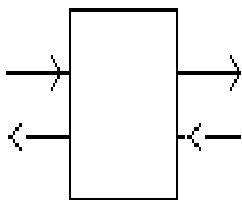
Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero.* If this is not performed the data entry is not saved.
2. *When defining column parameters a zero liquid reflux (i.e., distillate) rate should be defined.* This is because the distillate flow exiting the unit must only exist in the vapor phase.

Absorber Schematic



Extractor Unit



This is a multi-stage conventional or environmental process unit which allows countercurrent liquid-liquid extraction to be simulated. The unit can hold a maximum of 50 stages, 10 feed and 10 exit streams.

When this block is selected, the user can choose either an electrolyte column or a non-electrolyte column (if a non-electrolyte model was created). In the case of an electrolyte column, one of the two liquid streams is aqueous. In the case of a non-electrolyte column, both liquid streams are nonaqueous (electrolyte chemistry is not considered).

This unit does not support the mass transfer limited model and single stage functionality.

Data Requirement

A minimum of one aqueous feed stream must be defined entering the top of the column, and the solvent stream entering the bottom of the unit. The respective feed streams temperatures, pressures, flows and compositions must be specified, or be a product stream from another Process Block, and the unit outflows named. Additionally, various column operating parameter information must be specified by the user.

Column Parameters

The column operating parameters are accessed using the Action Key and selecting the Parameters facility. The column operating parameters are accessed using the Action Key and selecting the Parameters facility. The column operating parameters are accessed using the Action Key and then by selecting the Parameters facility. Nine options are available for the standard column:

Pressure Profile This option allows an accurate pressure profile to be specified. This is done by specifying top and bottom stage pressures, taking the reboiler and condenser into account. If only one stage pressure is given, a zero pressure drop through the column is assumed. If no values are given, the entire column is assumed to operate at atmospheric pressure.

Column Estimates This option allows stage operating temperatures, vapor distillate and liquid reflux flow estimates to be specified. The estimates for top and bottom stage temperature, as well as the vapor distillate rate and liquid reflux flowrates, must all be specified by the user. The Esc Key is used to change displays.

Spec/Controls This function is optional and allows the user to manipulate parameters (e.g., heat exchanger duty) to meet specifications in the column operation. For example, vapor and/or liquid composition specifications, stage operating temperature, and vapor and/or liquid stream flowrate specifications can all be achieved.

Exchanger Duties This option allows column and pumparound heat exchanger duties to be specified. For columns using a condenser and/or reboiler, the user must define duties for the respective units. Negative heat duties imply heat removal. The End Key returns the user to the process block display.

Tray Efficiencies This function is optional and allows the user to specify Murphree efficiencies for the column stages. If no data is entered, the stage efficiency is assumed to be 1.0. The End Key returns the user to the process block display. This function is not available for mass transfer limited columns.

Component Efficiencies This function is optional and allows the user to specify Murphree efficiencies for individual components in each column stage. If no data is entered, the efficiency for individual component is assumed to be 1.0. The End Key returns the user to the process block display. This function is not available for mass transfer limited columns.

Convergence Parameters This function is optional and allows the user to specify the Maximum number of iteration and convergence tolerance and if initialize column each time in recycle loops. If no data is entered, the Maximum number of iteration is assumed to be 35, the convergence

tolerance is assumed to 5.0E-7 and column has no initialization each time in recycle loops. The End Key returns the user to the process block display.

Tray Hold-Up Time This function is required for columns whose chemistry contains rate-limited reactions. This facility allows the user to specify both liquid and vapor hold-up volumes for specific column stages. The End Key changes the display and returns the user to the process block display.

Condenser Type This function is optional and allows the user to specify the type of condenser. If no data is entered, the condenser is assumed to be partial condenser. The End Key returns the user to the process block display.

Column Configuration

Additional column parameters can be defined, via the Action Key and selecting the Config facility. Five options are available:

Feed Streams This function is optional and allows the user to specify up to 8 additional feed streams to the column.

Product Stream This function is optional and allows the user to specify up to 8 additional product streams from the column.

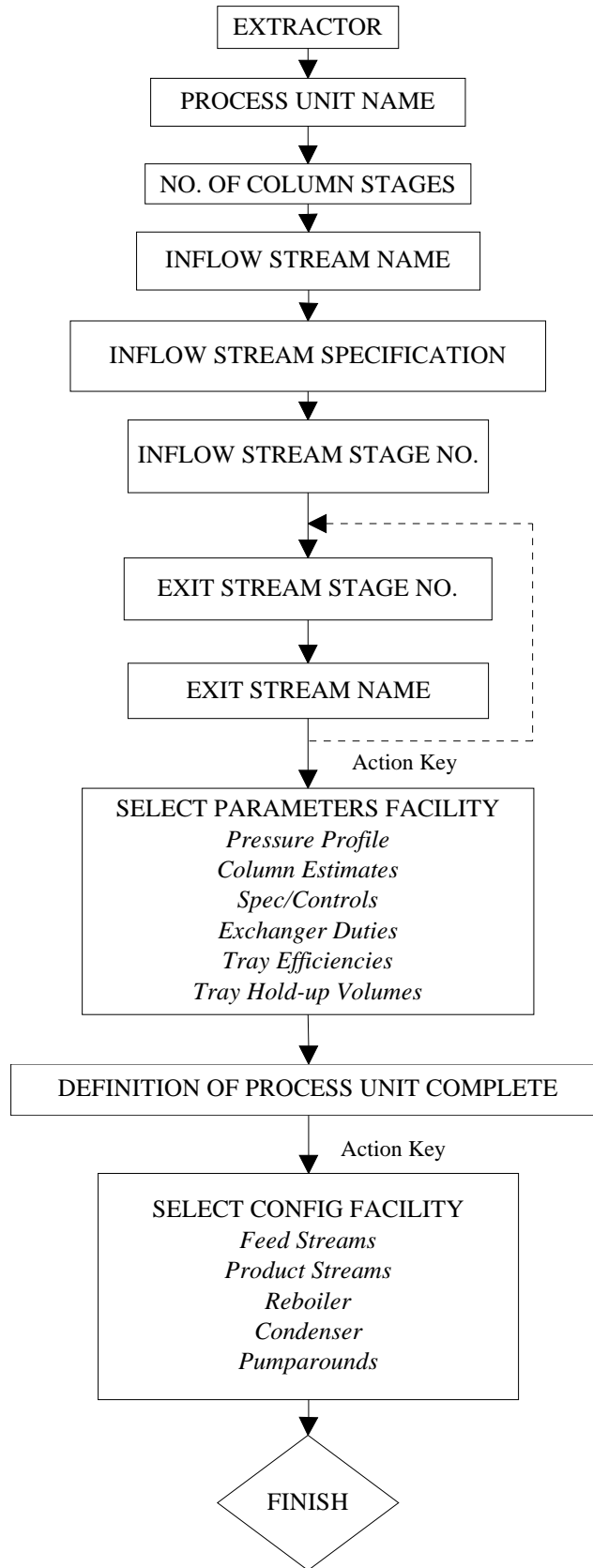
Condenser/Reboiler This option allows the user to delete, or insert, these respective units from/to the column. Initially, the process block does not include the two heat exchanger units on the display.

Pumparounds This function is optional and allows the user to specify side stream pumparounds if required. Pumparounds must be from a lower to a higher stage of the column and the flowrate must be defined.

Guidelines

1. *When defining feed stream compositions and column operating parameters the Enter Key must be pressed after every data entry, even if it is zero. If this is not performed the data entry is not saved.*
2. *The feed stream conditions must be specified such that no vapor phase species exist in the streams or the column.*
3. *When specifying column flowrates exiting the top stage, the organic phase stream is defined as the vapor distillate flowrate.*

Extractor Schematic



Reference:

[1] Billet, R., Schulte's, M. Trans. IchemE. , 77, 498-504 1999.

[2] Moniuk W.; Hungarian; Journal of Industrial Chemistry. Vol. 17; 93-105 1989

[3] Akita K and Yoshida F.; Ind. Eng. Chem. Process Des. Develop. Vol. 12 No. 1 1973

[4] Scheffe and Weiland Ind., Eng. Chem. Res. 1987, 26, 228-236

[5] Chilton T. H. and Colburn A.P., Ind. Engng Chem. 1934 26, 1183

[6] Mathur S. Tondon P.K. and Saxena S.C.; Molecular Physics 1967 12 569

[7] Taylor R., Krishna R., Multicomponent mass transfer, 1993, Wiley, New York

[8] Mafe R., Pellicer J. and Aguilera V. M. Journal of Computational Physics 75, 1-14, 1988

Chapter 17. Multistage Condenser Types

Overview

There are 8 condenser types from which the user may select when defining a condenser for an ESP multistage column. These types are:

1. Partial Condenser (default)
2. Total Condenser at the bubble point with fixed distillate rate
3. Total Condenser at the bubble point with fixed reflux rate
4. Total Condenser at the bubble point with fixed reflux ratio
5. Sub-Cooled Total Condenser with Fixed Distillate rate and Temperature
6. Sub-Cooled Total Condenser with Fixed Reflux rate and Temperature
7. Sub-Cooled Total Condenser with Fixed Reflux Ratio and Temperature
8. Decanter – Organic Phase removed, aqueous phase refluxed to column.

Condenser types

Partial Condenser (Default)

This is the default condenser type. A condenser of this type has the distillate as all vapor and the reflux as all liquid. In a two-liquid case, the vapor leaves as the distillate and both liquid phases are refluxed to the column. The user must specify an initial enthalpy via the heat exchanger parameter for this condenser to be properly specified.

Total Condenser at the bubble point with fixed distillate rate

The temperature is adjusted such that the vapor/liquid ratio is at the bubble point temperature. The distillate is all liquid at the specified rate. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

Total Condenser at the bubble point with fixed Reflux rate

The temperature is adjusted such that the vapor/liquid ratio is at the bubble point temperature. The distillate is all liquid but the refluxed liquid is at a specified rate. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

Total Condenser at the bubble point with fixed Reflux ratio

The temperature is adjusted such that the vapor/liquid ratio is at the bubble point temperature. The distillate is all liquid but the ratio of liquid distillate and liquid reflux is at a specified ratio. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

The definition of reflux ratio is

$$\text{Reflux Ratio} = \frac{\text{Distillate Rate (moles)}}{\text{Reflux Rate (moles)}}$$

Sub-cooled Total Condenser with a fixed distillate rate and temperature

The temperature of this condenser is set below the bubble point temperature. The distillate is all liquid and the enthalpy is adjusted to match the specified distillate rate. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

Sub-cooled Total Condenser with a fixed reflux rate and temperature

The temperature of this condenser is set below the bubble point temperature. The distillate is all liquid and the enthalpy is adjusted to match the specified reflux rate. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

Sub-cooled Total Condenser with a fixed reflux ratio and temperature

The temperature of this condenser is set below the bubble point temperature. The distillate is all liquid and the enthalpy is adjusted to match the specified reflux ratio. In the case of two-liquids, both liquids are considered the distillate. The user is required to make an initial estimate of the enthalpy using the heat exchanger parameter for the top stage.

Decanter –Organic phase removed, Aqueous phase is refluxed to column

There is no temperature specification for this type of condenser. If the fluid reaching the condenser is two phase (organic and aqueous) then the organic phase is removed and the aqueous phase is refluxed to the column. In the case of two-liquids, the water-rich phase is considered the aqueous phase. The user is required to set enthalpy using the heat exchanger parameter for the top stage.

This condenser type is not valid if there is no water in the simulation.

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