

Some recent developments in process simulation for reactive chemical systems

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Abstract - Recent developments have extended the application of process simulation technology from conventional petrochemical processes to chemical processes involving reactive chemical systems. Of particular importance are electrolyte systems and aqueous systems in which chemical reactions, such as dissociation, association, or solvation occur and reach chemical equilibrium. This paper reviews 1) the effects of chemical reactions upon thermophysical properties and process simulation of these chemical systems, and 2) the computer-aided process simulation tools available for investigating and modeling reactive chemical systems. Examples are given to illustrate the application and significance of these developments.

INTRODUCTION

Computer-aided process simulation technology for simulating industrial scale petroleum and petrochemical processes have evolved over the past twenty years and most of the petroleum, chemical and engineering companies have access to process simulation tools (ref. 1). However, most of these simulation tools were developed for application to non-reactive systems. Until recently the simulation of reactive chemical systems has been treated by empirical correlations (refs. 2, 3). These empirical correlations are in general applicable to only one particular system, over a limited range of conditions, and are awkward to implement in process simulators.

Recently, because of increased emphasis on simulating aqueous industrial systems and significant progress in applied thermodynamics for electrolyte systems, process simulation technology has been gradually extended to handle such reactive chemical systems (refs. 4-12). Some aspects of these developments are briefly discussed in this paper.

REACTIVE CHEMICAL SYSTEMS

Reactive chemical systems often exist in chemical processes involving electrolyte systems or aqueous solutions. Examples include hydrometallurgical processes, aqueous geochemistry, sour water stripping, flue gas desulfurization, amine gas treating, soda ash manufacture, etc. In these reactive chemical systems, chemical reactions are the dominant interactions that characterize the observed, apparent solution nonideality. Sometimes such chemical interactions are represented by models that account for only physical interactions in solutions. However, if these chemical reactions are real and significant, a correct account of them is essential for the success of the representation of thermophysical properties and process simulation for these reactive chemical systems.

The chemical reactions, or the solution chemistry, may involve complete dissociation of molecular species to ionic species, association reactions between molecular species and/or ionic species to form other molecular species and/or ionic species, and precipitation of solid salts. These chemical reactions take place very rapidly in solution and chemical equilibrium conditions can be assumed for all practical purposes.

These chemical reactions have major effects on the treatment of such reactive chemical systems in process simulators. The solution chemistry affects physical properties, phase equilibrium, and other fundamental characteristics of these systems. For most conventional hydrocarbon systems, chemical reactions occur only in reactors. For reactive chemical systems, chemical equilibrium calculations are an integral part of the modeling of all types of unit operations.

CHEMICAL EQUILIBRIUM RELATIONSHIPS

The solution chemistry dictates the true species in solution and imposes equality constraints on the composition of the true species. The chemical equilibrium relationship for reaction j may be expressed as follows:

$$\ln K_j = \sum_i \nu_{ij} \ln a_i \quad (1)$$

where K_j is the chemical equilibrium constant, ν_{ij} is the reaction stoichiometric coefficient of component i , and a_i is the activity of component i .

Note that salt precipitation equilibrium constraints are active only when salt concentrations reach or exceed salt saturation limits. Below salt saturation limits, salt dissolves in the solution and the salt precipitation equilibrium constraint need not be active.

It is important that chemical reactions be properly identified for a system to be simulated. Physical interactions in solutions are sometimes described by postulating chemical reactions at equilibrium. The chemical theory of solutions should be used only for real chemical reactions. Inaccuracies in simulating reactive chemical systems are often due to incorrect assumptions about the solution chemistry.

Chemical equilibrium constants are often available in the literature (refs. 13, 14). If such chemical equilibrium constants are not available, they may be estimated from the reference state free energies of the reaction-participating components (ref. 15).

SIMULATION APPROACH: APPARENT COMPOSITION VS. TRUE COMPOSITION

In general, there are two simulation approaches in treating reactive chemical systems. The true composition approach represents the system composition in terms of concentrations of the true species that exist in chemical equilibrium. The apparent composition approach represents the system composition in terms of concentrations of the apparent components that exist prior to the reactions that occur in solution. These two approaches are equivalent since a set of apparent components with chemical equilibrium relationships uniquely defines the compositions of the true species in chemical equilibrium. The composition based on the true species is connected to that based on the apparent components with mass balance equations and chemical equilibrium expressions (refs. 7, 8, 16-18).

From a process simulation viewpoint, the true composition approach requires that process specifications be given in terms of the true species. The true species and their compositions are to be carried in each process stream and each unit operation. This approach requires development of an array of new unit operation computational algorithms to solve the chemical equilibrium relationships in addition to the unit operation describing equations (refs. 5, 9, 19).

The apparent composition approach requires that process specifications be made only in terms of apparent components. The solution chemistry and the true species are transparent to process flowsheets and unit operations. The apparent composition approach makes it possible to use existing unit operation computational algorithms, such as flash algorithms for vapor-liquid equilibrium, liquid phase splitting algorithms for liquid-liquid equilibrium, and distillation algorithms. Note that rigorous representation of the effective partial molar properties of apparent components requires solution of the chemical equilibrium and knowledge of the partial molar properties of the true species (refs. 18, 19).

The choice between the apparent composition approach and the true composition approach often is a matter of personal preference. Generally, the apparent composition approach is preferred for simple reactive chemical systems. It offers the advantage that only apparent components need to be taken into account. When the system becomes more complex and it is difficult to select the apparent components, true composition is the desired approach. Sometimes it may be most convenient to use the true composition approach for the modeling of some unit operations and the apparent composition approach for other unit operations.

THERMOPHYSICAL PROPERTY MODELS

In the computer-aided process simulation environment, it is essential that the following thermophysical properties be computed at given temperature, pressure and composition:

- fugacity
- molar enthalpy
- reference state free energy

These properties are necessary to perform phase equilibrium calculations, chemical equilibrium calculations, and mass and energy balance calculations.

Often, the most critical properties for process simulation are the fugacities, which determine the amounts, compositions and phases involved. Table 1 summarizes some of the models that are widely used in process simulation.

TABLE 1. A summary of fugacity models

<u>Nonelectrolytes:</u>	
<u>Activity coefficient models</u>	<u>Equation of state models</u>
Ideal solution	Redlich-Kwong
Van Laar	Redlich-Kwong-Soave
Margules	Peng-Robinson
Wilson	BWR-Starling
NRTL	
UNIQUAC	
UNIFAC	
<u>Electrolytes:</u>	
<u>Activity coefficient models</u>	
Debye-Hückel	
Davis	
Bromley	
Pitzer	
Electrolyte NRTL	

Although there are thermophysical property models that adopt the chemical theory of solutions, most thermophysical property models attempt to account for physical interactions between the true species. There are two categories of models commonly used for nonelectrolytes: liquid activity coefficient models and equation of state models (refs. 20, 21). The liquid activity coefficient models are more accurate for highly nonideal chemical mixtures, but at high pressures the equation of state models are generally more convenient. Among the models available for nonelectrolytes, the UNIFAC model is particularly interesting since its group contribution method provides a reasonable methodology to estimate physical interactions between the true species (ref. 12).

The liquid activity coefficient approach is preferred for electrolytes particularly because ionic activity coefficients are required for chemical equilibrium calculations, and because the development of equations of state for electrolytes is a relatively new endeavor (refs. 22, 23).

Until recently, the treatment of electrolytes in process simulation has been greatly limited by the lack of generally applicable models for activity coefficients of the molecular and ionic species present. In most cases empirical correlations have been used that are applicable only to one particular system, over a limited range of conditions. However, the empirical correlations do not provide a framework for treating new systems or for extending the range of existing data.

Recently there have been a number of significant developments in the modeling of electrolytes. Among the models available, the electrolyte NRTL model (refs. 24-26) may prove to be the most valuable engineering model. The model is applicable to the entire electrolyte concentration range, it requires only binary interaction parameters, and it provides a continuous thermodynamic framework for aqueous electrolytes, mixed-solvent electrolytes, and nonelectrolytes.

Given temperature, pressure, compositions of the true species, and physical interactions of the true species in solution, thermophysical property models compute thermophysical properties for the true species and the mixture of the true species. If the apparent composition approach is used in process simulation, thermophysical properties of apparent components must be computed from the properties of the true species and their compositions (refs. 7, 17). For example,

$$\gamma_i^a = (x_i / x_i^a) \gamma_i \quad (2)$$

where γ_i and x_i are, respectively, the activity coefficient and mole fraction of true species i in solution; and γ_i^a and x_i^a are, respectively, the effective activity coefficient and mole fraction of component i in the apparent composition approach.

DATA REGRESSION

Data regression is an essential step in representing thermophysical properties in process simulation. Most of the thermophysical property models used in process simulation require interaction parameters to be determined from experimental data through data regression. With the presence of the solution chemistry, chemical equilibrium and solubility product constants need to be determined in addition to the interaction parameters.

The most general mathematical formulation of data regression uses the maximum likelihood principle (or generalized least squares criterion) (refs. 27, 28). The maximum likelihood principle can be extended for reactive chemical systems (refs. 7, 17). One key consideration in the extension is that the chemical equilibrium constraints of the solution chemistry must be satisfied.

Often, experimental measurements of thermophysical properties of reactive chemical systems are available as thermophysical properties of apparent components. Typical measurements are listed below:

- solute properties, such as mean ionic activity coefficients
- solvent properties, such as osmotic coefficients
- fugacity coefficient data, such as vapor pressure depression,
vapor-liquid equilibrium data and liquid-liquid equilibrium data
- solution properties, such as heat capacity, enthalpy
- solubility or salt saturation limits

PROCESS SIMULATION WITH THE SOLUTION CHEMISTRY

Typically process simulation of reactive chemical systems may involve flowsheet simulation with several unit operation blocks that are to be simulated with unit operation models such as those listed in Table 2. The solution chemistry may be associated with any of the unit operation models. Different solution chemistries may be involved in different unit operation blocks. The chemical reactions may take place in vapor, aqueous, or organic liquid phases. The true species may be molecular solvents, molecular solutes, ionic solutes, or solid salts.

TABLE 2. A summary of unit operation models

<u>Single stage unit operation models:</u>	
mixer	flow splitter
component separator	pump
compressor/turbine	heater/cooler
flash	heat exchanger
stoichiometric reactor	specified yield reactor
chemical equilibrium reactor	continuous stirred tank reactor
plug flow reactor	stream duplicator
stream multiplier	
<u>Multiple stage unit operation models:</u>	
distillation	multiple column distillation
absorber/stripper	liquid-liquid extractor

Chemical equilibrium calculations are the core of process simulation with reactive chemical systems. With the apparent composition approach, the chemical equilibrium expressions are solved for the computation of apparent component thermophysical properties, which are required by unit operation models. With the true composition approach, the chemical equilibrium expressions are solved with the unit operation describing equations.

Numerous mathematical algorithms have been proposed for solving the chemical equilibrium expressions (refs. 29, 30). Some solve the sets of nonlinear algebraic equations from the numerical point of view. Others adopt minimization techniques. Some require knowledge of the stoichiometric coefficients for a linearly independent set of reactions from the problem specification point of view. Others require atomic matrix, ionic charge, and product component specifications.

In the process simulator environment, it is very important that the algorithm adopted for solving chemical equilibrium expressions be both efficient and robust. Solving chemical equilibrium expressions, a computing-intensive task, is an integral part of the process simulation and is performed repetitively. For example, in solving a typical flash model with the apparent composition approach, it is estimated that 90% of computing effort goes to apparent component thermophysical property calculation, of which 60% of computing effect is consumed by solving chemical equilibrium expressions. Without an efficient algorithm for solving chemical equilibrium expressions, prohibitively excessive computing time may be encountered for large flowsheets.

With proper selection of numerical algorithms, intelligent checking of the solution chemistry to avoid solving redundant reactions or infeasible reactions, and with the progress in computing power, it is feasible to have a reasonably efficient and robust algorithm to meet the needs of process simulation with reactive chemical systems.

STRUCTURE OF PROCESS SIMULATORS

General purpose steady-state process simulators have been developed to treat reactive chemical systems (refs. 10, 19). These simulators have been designed to simulate any process with reactive chemical systems, consisting of any number of unit operation blocks, reactions in the solution chemistry, and components.

Key elements of these process simulators can be summarized as follows:

1. user-friendly input language for simulator users
2. system databanks containing the information necessary to calculate thermophysical properties of pure components and mixtures
3. a library of state-of-the-art thermophysical property models
4. a facility for solving the chemical equilibrium expressions and computing apparent component thermophysical properties
5. data regression facility to allow users to develop user databanks from proprietary data
6. a facility to generate thermophysical property tables/plots
7. a library of unit operation models, including flash models and multistage column models
8. a facility for flowsheet simulations, such as flowsheet convergence, feed forward controller, feedback controller, etc.
9. a facility for case study and sensitivity analysis
10. a facility for costing, sizing and optimization
11. a facility for simulation report generation

INDUSTRIAL APPLICATIONS

There are numerous industrial applications for process simulation of reactive chemical systems. Examples include sour water stripping in the petroleum industry, caustic brine evaporation and chlorine recovery in the chlor-alkali industry, acid gas removal in the chemical, gas and power industry, nitric acid separation in the nuclear industry, trona mining in the soda ash industry, organic salt separation in the biochemical industry, black liquor evaporation in the pulp and paper industry, etc. Important process insights and significant economic benefits can be realized through process simulation.

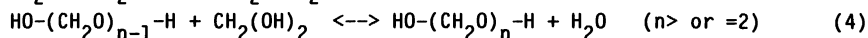
There are two key steps in building a simulation model for reactive chemical systems. The first step is to build a solution "chemistry" model which consists of the knowledge of the chemical reactions, the true species, and the physical interactions between the true species. The second step is to build a "process" model which consists of flowsheet topology, feed stream conditions, unit operation conditions, and optionally, feed forward controller and feedback controller. Once a simulation model is developed, engineering studies can be carried out easily to examine sensitivities of key process variables and to optimize the process.

Four small-scale simulation examples are given below to illustrate some typical industrial applications. Specifically, these examples illustrate how a simulator assists users in analyzing reactive chemical systems. More flowsheet-oriented examples are available elsewhere (refs. 8, 19). These examples were developed with the ASPEN/ASPEN PLUS simulator (see APPENDIX).

SATURATION PRESSURE OF WATER-FORMALDEHYDE SYSTEM

The thermophysical property table generation facility of the simulator is used to compute and plot the saturation pressure of a water-formaldehyde mixture as a function of water content at 373.15 K.

Maurer (ref. 12) has examined the solution chemistry of a water-formaldehyde system and reported the formation of methylene glycol and polyoxymethylene in the aqueous phase as follows:



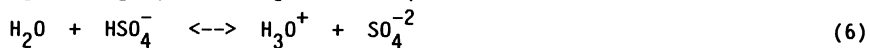
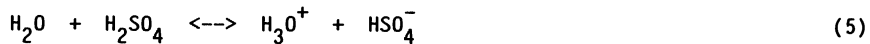
Maurer also reported chemical equilibrium constants for the reactions and the UNIFAC parameters for the physical interactions of the true species.

Figure 1 shows the simulation input file. Figure 2 gives a print-plot of the saturation pressure as predicted by the Maurer's model. The profound "L" shape curve of the saturation pressure is a result of the solution chemistry.

TRUE SPECIES COMPOSITIONS OF AQUEOUS SULFURIC ACID

The thermophysical property table generation facility of the simulator is used to compute and plot compositions of the true species of aqueous sulfuric acid as a function of sulfuric acid content at 298.15 K.

Goldfarb and Chen have recently reported a solution chemistry model for aqueous sulfuric acid (ref. 31). In the aqueous phase, the following two reactions are considered:



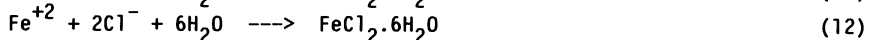
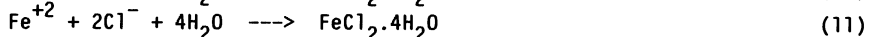
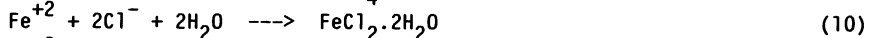
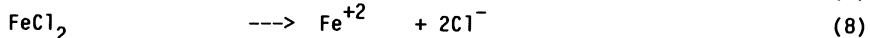
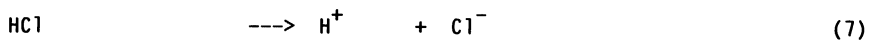
Water and sulfuric acid are the apparent components. The true species are the undissociated molecular species water and sulfuric acid, and the ionic species hydronium, bisulfate, and sulfate. The Electrolyte NRTL model parameters for molecular-electrolyte interactions have been reported by Goldfarb and Chen (ref. 31). This solution chemistry model is available in the simulator.

Figure 3 shows the simulation input file. Figure 4 shows the computed true species compositions of aqueous sulfuric acid. As predicted by the model of Goldfarb and Chen, bisulfate ion is the main sulfuric acid species up to 90 wt.% sulfuric acid. Above 90 wt.%, sulfuric acid exists primarily as undissociated sulfuric acid. Sulfate ion concentration is very low throughout the entire concentration range.

PRECIPITATION OF FERROUS CHLORIDE IN AQUEOUS HYDROCHLORIC ACID SOLUTION

The simulator is used to establish the saturation limit of ferrous chloride in aqueous hydrochloric acid solution at 298.15 K. A hydrogen chloride stream is gradually added to an aqueous ferrous chloride solution to precipitate ferrous chloride. A sensitivity study is performed to compute saturation limit of ferrous chloride in aqueous solution as a function of hydrogen chloride concentration.

The solubility of ferrous chloride in aqueous hydrochloric acid solution has been examined by Chen (ref. 32). The solution chemistry involves the following reactions:



Hydrogen chloride, water, and ferrous chloride are the apparent components. The true species include the ionic species hydrogen, chloride, ferrous, ferrous tetrachloride, the molecular species water, and the solid salts ferrous chloride dihydrate, ferrous chloride tetrahydrate, and ferrous chloride hexahydrate. The chemical equilibrium constants, the solubility product constants, and the Electrolyte NRTL model parameters for molecular-electrolyte interactions and electrolyte-electrolyte interactions have been published in the literature (ref. 32).

Figure 5 shows the simulation input file. Figure 6 shows the computed results of the ferrous chloride saturation limit. The ferrous chloride solubility drops significantly as the concentration of hydrogen chloride increases. Figure 7 shows the stream compositions including flow rates for various true species. Ferrous chloride dihydrate is the precipitated solid salt.

```

TGS
IN-UNITS SI
RUN-CONTROL MAX-TIME=100
; identify all species
COMPONENTS WATER H2O /
FA CH2O / MG1 C2H6O2 / MG2 C2H6O2 /
MG3 C2H6O2 / MG4 C2H6O2 / MG5 C2H6O2
; define the chemistry
CHEMISTRY MAURER
STOIC 1 WATER -1 / FA -1 / MG1 1
STOIC 2 MG1 -2 / MG2 1 / WATER 1
STOIC 3 MG2 -1 / MG1 -1 / MG3 1 / WATER 1
STOIC 4 MG3 -1 / MG1 -1 / MG4 1 / WATER 1
STOIC 5 MG4 -1 / MG1 -1 / MG5 1 / WATER 1
K-STOIC 1 -125.1608 11211.35 16.53361
K-STOIC 2 151.9185 -8666.626 -21.50844
K-STOIC 3 152.4102 -8523.298 -21.69641
K-STOIC 4 152.3718 -8502.615 -21.69478
K-STOIC 5 152.3669 -8491.151 -21.69644
; use UNIFAC model
PROPERTIES SYSOP7K CHEMISTRY=MAURER TRUE-COMPS=0 / SYSOP15
; Use ideal gas vapor phase PHIVMX00
PROP-OPTIONS SYSOP7K SYSOP7 PHILMX39/
PHIVMX PHIVMX00
; Ignore Poynting correction, use PHIL00
MP-ROUTE PHILMX39 PHILMX 5 PHILMX39
MODEL GMUFAC
MPROP PHIL PHIL00
SP-ROUTE XTRUE01 XTRUE 1 XTRUE01
MODEL GMUFAC
; define UNIFAC groups
UNIFAC groups: 1010 -> -CH2-
1200 -> -OH
1300 -> H2O
1610 -> -CH2O- (ETHER)
4000 -> CH2(OH)2
GROUPS GW 1300 / GE 1610 / GH 1200 / GC 1010 / GM 4000
; enter physical property data
PROP-DATA
; UNIFAC parameters
PROP-LIST UFGRP
PVAL WATER 1300 1
PVAL FA 1610 1
PVAL MG1 4000 1
PVAL MG2 1200 2 1010 1 1610 1
PVAL MG3 1200 2 1010 1 1610 2
PVAL MG4 1200 2 1010 1 1610 3
PVAL MG5 1200 2 1010 1 1610 4
PROP-LIST GMUFR / GMUFQ
PVAL GH 1.0 / 1.2
PVAL GE 0.9183 / 0.78
PVAL GC 0.6744 / 0.54
PVAL GW 0.9200 / 1.40
PVAL GM 2.6744 / 2.94
PROP-LIST GMUFB
BPVAL GH GE 28.06
BPVAL GH GC 156.40
BPVAL GH GW 353.5
BPVAL GH GM 353.5
BPVAL GE GH 237.7
BPVAL GE GC 83.36
BPVAL GE GW 240.0
BPVAL GE GM 240.0
BPVAL GC GH 986.5
BPVAL GC GE 251.5
BPVAL GC GW 1318.0
BPVAL GC GM 1318.0
BPVAL GM GH -229.1
BPVAL GM GE -149.0
BPVAL GM GC 300.0
BPVAL GM GM 0.0
BPVAL GM GH -229.1
BPVAL GM GE -149.0
BPVAL GM GC 300.0
BPVAL GM GW 0.0
PROP-LIST MG1 / MG2 / MG3 / MG4 / MG5
CVAL MW 48.04 / 78.07 / 108.09 / 138.12 / 168.14
PROP-LIST PLXANT
PVAL WATER 23.19636 -3816.44 -46.13 0 0 0 300 450
PVAL FA 21.37026 -2204.13 -30.15 0 0 0 300 450
PVAL MG1 17.98455 -1997.20 -142.72 0 0 0 300 450
PVAL MG2 -20 0 0 0 0 0 300 450
PVAL MG3 -20 0 0 0 0 0 300 450
PVAL MG4 -20 0 0 0 0 0 300 450
PVAL MG5 -20 0 0 0 0 0 300 450
; use physical property table generation facility to plot
; saturation pressure
PROP-TABLE F1 FLASHCURVE
MASS-FLOW WATER .796 / FA .204
STATE TEMP=373.15 VFRAC=0
VARY MOLE-FRAC COMP=WATER
RANGE LOWER=0 UPPER=1 INCR=.02
TABULATE PROPERTIES=P PRINT-PLOT=YES Y-SCALE=LOG GRID=NO
PROP-SET P PRES
    
```

Fig. 1. ASPEN PLUS input file for saturation pressure of water-formaldehyde system.

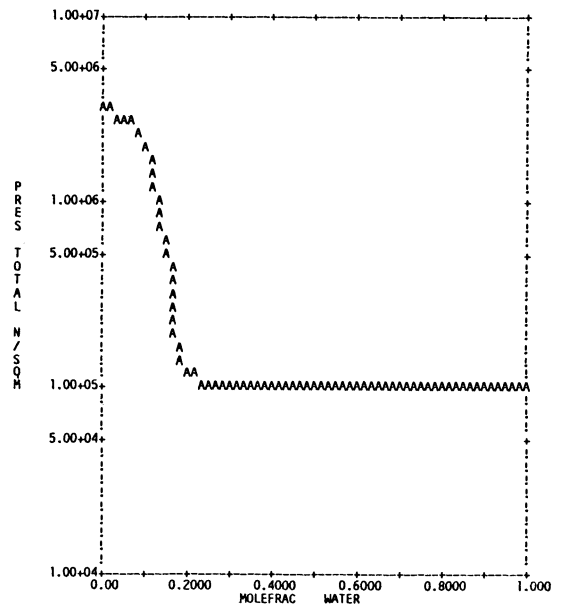


Fig. 2. A print-plot for saturation pressure of water-formaldehyde system at 373.15 K.

```

TGS
RUN-CONTROL MAX-TIME=100
IN-UNITS SI
; retrieve information on chemistry, true species, and
; physical property data for aqueous sulfuric acid
INSERT GLOBAL MH2SO4 H2O H2SO4
PROP-SET XTRUE XTRUE PHASE=L COMPS=H2SO4 HS04- S04-2 H2O
; use physical property table generation facility to plot
; true species compositions
PROP-TABLE FRAC PROPS
MASS-FLOW H2SO4 .5 / H2O .5
STATE TEMP=298.15 PRES=101325
VARY MASS-FRAC COMP=H2SO4
RANGE LOWER=0.01 UPPER=.99 NPOINT=50
TABULATE PROPERTIES=XTRUE PRINT-PLOT=YES GRID=NO
    
```

Fig. 3. ASPEN PLUS input file for true species compositions of aqueous sulfuric acid.

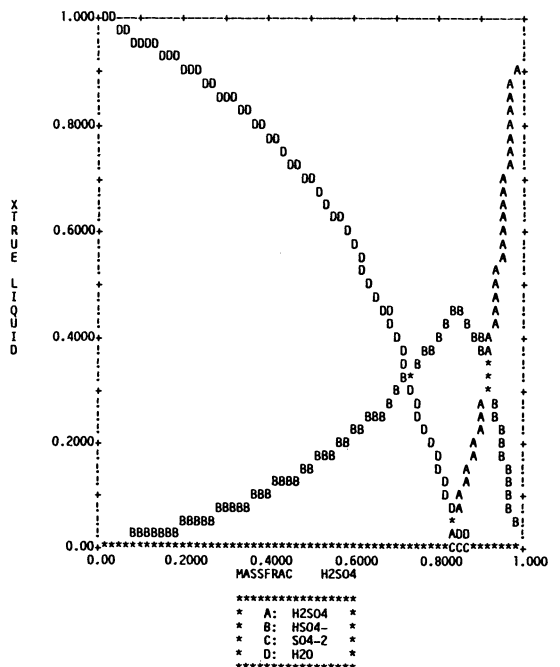


Fig. 4. A print-plot for true species compositions of aqueous sulfuric acid at 298.15 K.

```

IN-UNITS      SI
RUN-CONTROL  MAX-TIME=500
DATABANKS    AQUEOUS/SOLIDS
; specify all apparent components and true species
COMPONENTS   H2O H2O/HCL HCL/FECL2 FECL2/
              H+ H+/FE+2 FE+2/CL- CL-/FECL4-2 SO4-2/
              2H FECL2/4H FECL2/6H FECL2
; specify the solution chemistry
CHEMISTRY    FECL2
DISS FECL2  FE+2  1/ CL-  2
DISS HCL    H+    1/ CL-  1
STOIC 1     FE+2  -1/ CL-  -4/ FECL4-2  1
K-STOIC 1   1.998 -5683.9
SALT  2H    FE+2  1/ CL-  2/ H2O      2
SALT  4H    FE+2  1/ CL-  2/ H2O      4
SALT  6H    FE+2  1/ CL-  2/ H2O      6
K-SALT 2H   -8.7916 1135.2
K-SALT 4H  -389.66 19432.1 55.919
K-SALT 6H  -14.069 2178.5
PROPERTIES  SYSOP15 CHEMISTRY=FECL2
; enter physical property data
PROP-DATA
PROP-LIST    HENRY
BPVAL HCL H2O 60.812 -8891.4 0 0 273 500
PROP-LIST    MW
PVAL 2H      162.7838
PVAL 4H      198.8146
PVAL 6H      234.8454
PROP-LIST    GMELCC / GMELCD / GMELCE / GMELCN
PPVAL H2O (FE+2 CL-) 3.284 / 1716.7 / -10.764/ .2
PPVAL (FE+2 CL-) H2O -2.333 / -723.3 / 0 / .2
PPVAL HCL (FE+2 CL-) 0.001
PPVAL (FE+2 CL-) HCL -0.001
PPVAL H2O (H+ CL-) 39.747 / 5115.4 / -10.585/ .03
PPVAL (H+ CL-) H2O -20.961 / -2164.0 / 5.877/ .03
PPVAL HCL (H+ CL-) 0.001
PPVAL (H+ CL-) HCL -0.001
PROP-LIST    GMELCC / GMELCD
PPVAL (FE+2 CL-) (H+ CL-) 0.630 / -357.5
; specify process flowsheet
FLOWSHEET
BLOCK CRYST IN=FECL2 HCL OUT=OUTPUT
; specify feed stream conditions
STREAM FECL2 TEMP=298.15 PRES=100000 NPHASE=1 PHASE=L &
MASS-FLOW=1000
MASS-FRAC H2O .5 / FECL2 .5
STREAM HCL TEMP=298.15 PRES=100000 FLASH-OPTIONS=NOFLASH &
MASS-FLOW=100
MASS-FRAC HCL 100
; specify unit operation block conditions
BLOCK CRYST HEATER
PARAM TEMP=298.15 PRES=100000
; perform sensitivity study
SENSITIVITY SOLUBILITY
DEFINE FH MOLE-FLOW STREAM=OUTPUT COMPONENT=H+
DEFINE FFE MOLE-FLOW STREAM=OUTPUT COMPONENT=FE+2
DEFINE FFE1 MOLE-FLOW STREAM=OUTPUT COMPONENT=FECL4-2
DEFINE FH2O MOLE-FLOW STREAM=OUTPUT COMPONENT=H2O
F XFECL2 = (FFE+FFE1)/(FH+FFE+FFE1+FH2O)
F XHCL = FH/(FH+FFE+FFE1+FH2O)
VARY STREAM-VAR STREAM=HCL VARIABLE=MASS-FLOW
RANGE LIST=1 10 20 30 40 50 60 70 80 90 100
TABULATE 1 'XHCL' COL-LABEL='HCL' 'MOLE' 'FRAC'
TABULATE 2 'XFECL2' COL-LABEL='FECL2' 'MOLE' 'FRAC'
PLOT GRID=NO
    
```

Fig. 5. ASPEN PLUS input file for precipitation of ferrous chloride in aqueous hydrochloric acid solution.

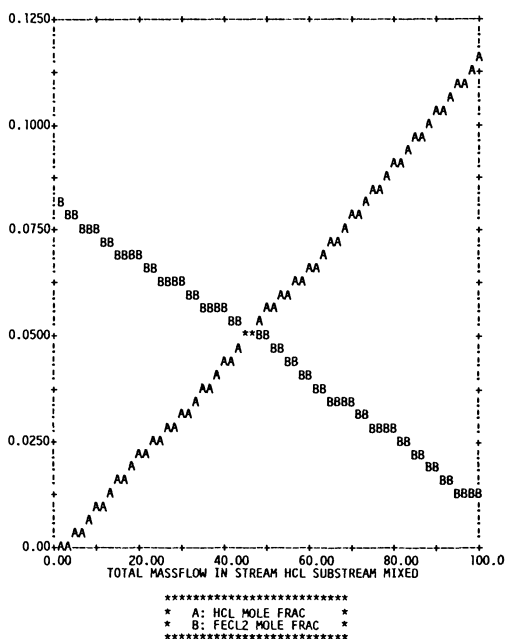


Fig. 6. A print-plot for ferrous chloride saturation limit vs. hydrochloric acid concentration at 298.15 K.

FECL2 HCL OUTPUT

STREAM ID	FECL2	HCL	OUTPUT
FROM :	-----	-----	CRYST
TO :	CRYST	CRYST	----
SUBSTREAM: MIXED			
PHASE:	LIQUID	MIXED	MIXED
COMPONENTS: KMOL/SEC			
H2O	27.7546	0.0	20.4749
HCL	0.0	2.7427	0.0
FECL2	0.0	0.0	0.0
H+	0.0	0.0	2.7427
FE+2	3.9447	0.0	0.3016
CL-	7.8894	0.0	3.3396
FECL4-2	1.9334-06	0.0	3.1875-03
2H	0.0	0.0	3.6399
4H	0.0	0.0	0.0
6H	0.0	0.0	0.0
TOTAL FLOW:			
KMOL/SEC	39.5887	2.7427	30.5018
KG/SEC	1000.0000	100.0000	1099.9998
CUM/SEC	0.5591	MISSING	0.5812
STATE VARIABLES:			
TEMP K	298.1500	298.1500	298.1500
PRES N/SQM	1.0000+05	1.0000+05	1.0000+05
VFRAC	0.0	MISSING	0.0
LFRAC	1.0000	MISSING	0.8807
SFRAC	0.0	MISSING	0.1193
ENTHALPY:			
J/KMOL	-2.3942+08	MISSING	-2.5097+08
J/KG	-9.4782+06	MISSING	-6.9593+06
WATT	-9.4782+09	MISSING	-7.6552+09
ENTROPY:			
J/KMOL-K	-2.3925+05	MISSING	-1.8188+05
J/KG-K	-9471.5046	MISSING	-5043.2560
DENSITY:			
KMOL/CUM	70.8102	MISSING	52.4796
KG/CUM	1788.6488	MISSING	1892.5921
AVG MW	25.2597	36.4610	36.0634

Fig. 7. True species flow rates with precipitation of ferrous chloride in aqueous hydrochloric acid solution.

SOUR WATER STRIPPER

The simulator is used to examine two configurations for a sour water stripper. The configuration of the sour water stripper is shown in Fig. 8. The feed compositions of the two feed streams to the stripper are summarized in Table 3. It is desired to determine the effect of changing the caustic feed location on the concentrations of hydrogen sulfide, carbon dioxide, and ammonia in the bottoms product. The simulator will be used to compute the change in column composition profiles, pH profile, and bottoms composition due to changing the caustic feed location from stage 4 (Case 1) to stage 9 (Case 2).

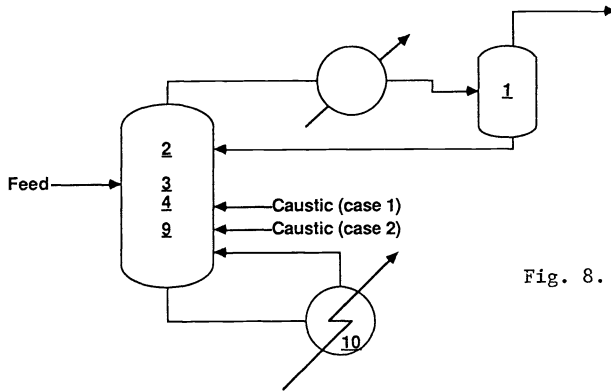


Fig. 8. Sour water stripper configuration.

TABLE 3. Composition and flow rates of feed streams to the sour water stripper

Stream	Feed	Caustic
Total	1.00 kgmole/sec	0.002 kgmole/sec
H ₂ S	0.02 kgmole/sec	
NH ₃	0.02 kgmole/sec	
CO ₂	0.002 kgmole/sec	
H ₂ O	0.958 kgmole/sec	0.0016 kgmole/sec
NaOH		0.0004 kgmole/sec

The sour water stripper system has been examined by many investigators (refs. 2, 24). The solution chemistry involves seven aqueous phase reactions:



Water, ammonia, carbon dioxide, hydrogen sulfide, and sodium hydroxide are the apparent components. The true species include the ionic species hydrogen, hydroxide, bisulfide, sulfide, bicarbonate, carbonate, and the undissociated molecular species water, ammonia, carbon dioxide, hydrogen sulfide. The chemical equilibrium constants and the physical interaction parameters have been well established in the literature for the sour water stripper system (ref. 24). This solution chemistry model is available in the simulator.

The simulation input files for Cases 1 and 2 are given in Figs. 9 and 10, respectively. Based on the computed column profiles, substantial effects can be seen when the caustic feed inlet location is changed. The effects are illustrated with the changes in vapor-liquid equilibrium K-values and compositions of ammonia and hydrogen sulfide and computed pH profiles in the column. Such changes are shown via print-plots, given in Figs. 11-16. The hydrogen sulfide concentration at the bottom of the column drops from 100 ppm by mole to less than 1 ppm by mole when the caustic feed location is changed from stage 4 to stage 9.

```

RUN-CONTROL MAX-TIME=1000
IN-UNITS SI
; retrieve the sour water chemistry model
INSERT GLOBAL SOURH H2O NH3 H2S CO2 NAOH SYSOP15 0
; specify the flowsheet
FLOWSHEET
  BLOCK COLUMN IN = FEED CAUSTIC   OUT = TOP BOT
; specify feed stream conditions
STREAM FEED TEMP=313 PRES=300000
  MOLE-FLOW H2S .02/ NH3 .02/ CO2 0.002/ H2O .958
STREAM CAUSTIC TEMP=313 PRES=300000 NPHASE=1 PHASE=L
  MOLE-FLOW NAOH .0004/ H2O .0016
; specify the distillation column conditions
BLOCK COLUMN RADFRAC
  PARAM NSTAGE=10 MAXOL=30
; case 1, casutic enters stage 4
FEEDS FEED 3 / CAUSTIC 4
PRODUCTS TOP 1 / BOT 10 0
P-SPEC 1 250000 / 10 310000
COL-SPECS RDV=1 D=.07 RR=2
T-EST 1 363 / 10 383
TRAY-REPORT TRAY-OPTION=ALL-TRAYS PROPERTIES=PHVALUE &
  PRINT-PLOT=YES GRID=NO
PLOT 1 KVL=H2S NH3 Y-SCALE=LOG GRID=NO
PLOT 2 Y=H2S NH3 Y-SCALE=LOG GRID=NO
PROP-SET PHVALUE PH25 PHASE=L
STREAM-REPORT NOZEROFLOW
    
```

Fig. 9. ASPEN PLUS input file for sour water stripper, Case 1.

```

RUN-CONTROL MAX-TIME=1000
IN-UNITS SI
; retrieve the sour water chemistry model
INSERT GLOBAL SOURH H2O NH3 H2S CO2 NAOH SYSOP15 0
; specify the flowsheet
FLOWSHEET
  BLOCK COLUMN IN = FEED CAUSTIC   OUT = TOP BOT
; specify feed stream conditions
STREAM FEED TEMP=313 PRES=300000
  MOLE-FLOW H2S .02/ NH3 .02/ CO2 0.002/ H2O .958
STREAM CAUSTIC TEMP=313 PRES=300000 NPHASE=1 PHASE=L
  MOLE-FLOW NAOH .0004/ H2O .0016
; specify the distillation column conditions
BLOCK COLUMN RADFRAC
  PARAM NSTAGE=10 MAXOL=30
; case 2, casutic enters stage 9
FEEDS FEED 3 / CAUSTIC 9
PRODUCTS TOP 1 / BOT 10 0
P-SPEC 1 250000 / 10 310000
COL-SPECS RDV=1 D=.07 RR=2
T-EST 1 363 / 10 383
TRAY-REPORT TRAY-OPTION=ALL-TRAYS PROPERTIES=PHVALUE &
  PRINT-PLOT=YES GRID=NO
PLOT 1 KVL=H2S NH3 Y-SCALE=LOG GRID=NO
PLOT 2 Y=H2S NH3 Y-SCALE=LOG GRID=NO
PROP-SET PHVALUE PH25 PHASE=L
STREAM-REPORT NOZEROFLOW
    
```

Fig. 10. ASPEN PLUS input file for sour water stripper, Case 2.

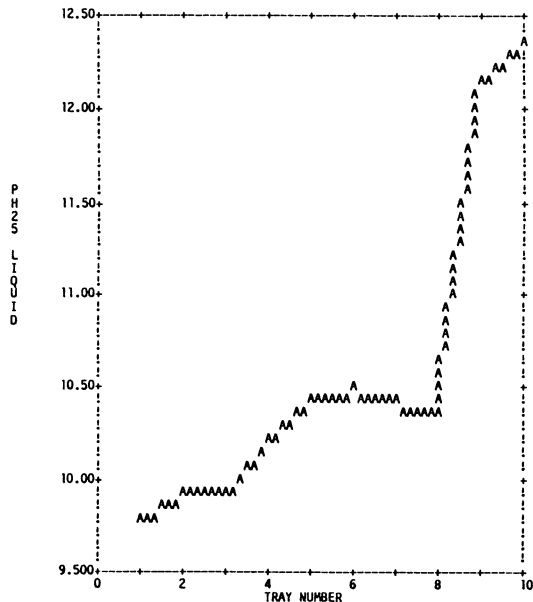


Fig. 12. A print-plot for pH profile in sour water stripper, Case 2.

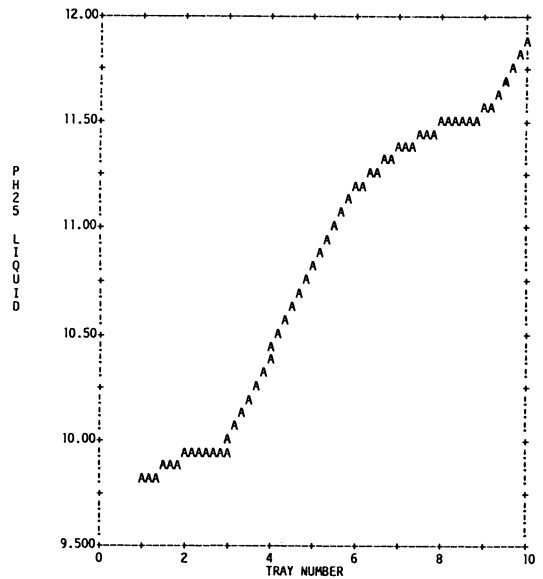


Fig. 11. A print-plot for pH profile in sour water stripper, Case 1.

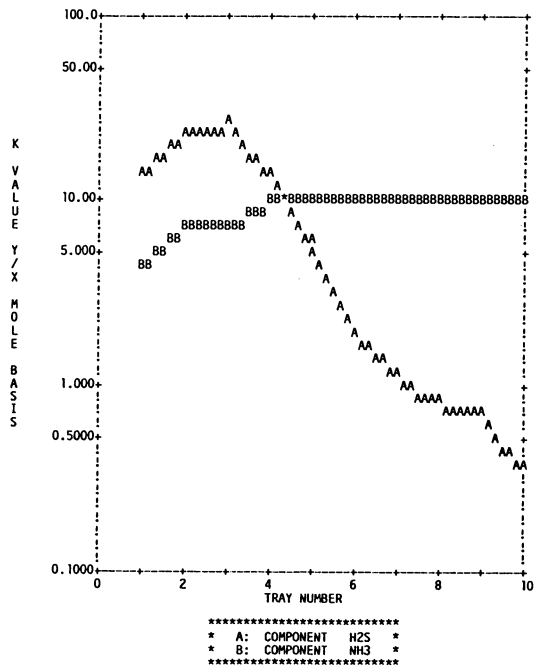


Fig. 13. A print-plot for vapor-liquid equilibrium K-value profile in sour water stripper, Case 1.

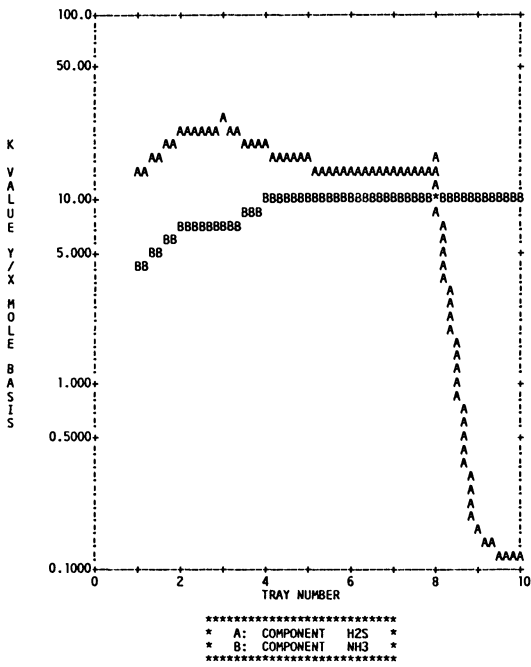


Fig. 14. A print-plot for vapor-liquid equilibrium K-value profile in sour water stripper, Case 2.

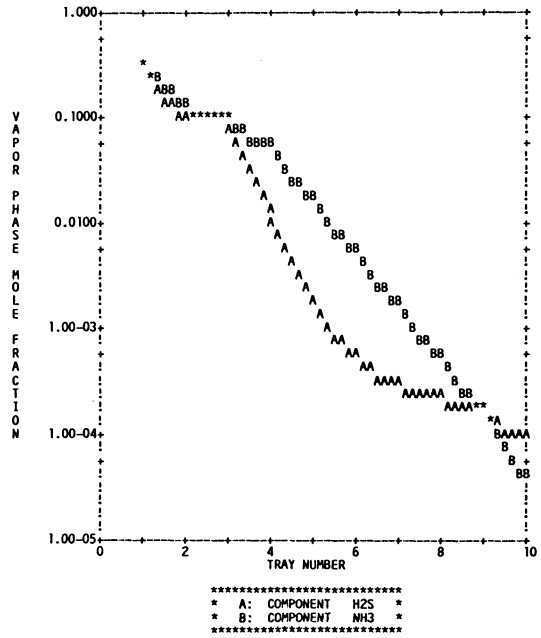


Fig. 15. A print-plot for vapor composition profile in sour water stripper, Case 1.

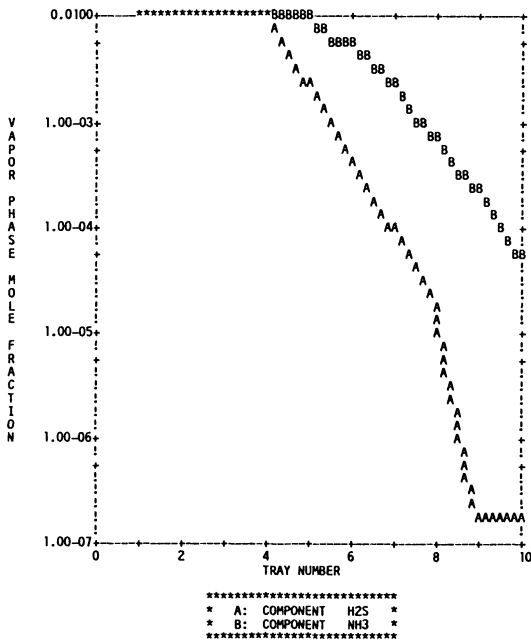


Fig. 16. A print-plot for vapor composition profile in sour water stripper, Case 2.

CONCLUDING REMARKS

The recent developments in computer-aided process simulation technology represent significant advancements in the modeling of reactive chemical systems. Such technology advancements and simulation tools enable scientists and engineers to analyze complex reactive chemical systems as routinely and conveniently as hydrocarbon systems.

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APPENDIX: ASPEN/ASPEN PLUS

ASPEN (Advanced System for Process Engineering) is a process simulator and economic evaluation system developed at the Massachusetts Institute of Technology. The concept of ASPEN was to extend the process simulation technology to cover a much broader range of chemical systems, such as fossil fuel conversion processes. The simulator has been designed to be very flexible so that it can be extended to meet future simulation requirements. General discussions of ASPEN may be found in the literature (refs. 33, 34)

ASPEN PLUS, which builds on the research and development efforts of ASPEN, has incorporated and developed state-of-the-art thermodynamic models, unit operation models, and flowsheeting capabilities for modeling a wide variety of process systems, including processes with reactive chemical systems such as electrolytes (ref. 35). ASPEN PLUS is now being used by many chemical and engineering companies and academic institutions worldwide.