

Introduction to Electrolytes

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Overview

A great many industrial processes cannot be designed and optimized effectively without comprehensively and accurately addressing electrolyte chemistry and phenomena. The same statement can be made with regard to many production and environmental problems as well. Electrolyte chemistry plays an important role in many chemical operations, including:

- Aqueous chemical and separations processes
- Chemical conversion
- Solution crystallization
- Pharmaceutical and specialty chemical manufacturing
- Reactive separations including acid gas treatment
- Waste water treatment
- Environmental behavior of wastes, discharges, and accidental releases
- Corrosion and scaling of equipment

Electrolyte chemistry is particularly complex and challenging to understand and predict, especially for real industrial systems containing many components and operating over broad ranges of temperature, pressure, and concentration. Simplified aqueous modeling and computational approaches using approximation are usually useless, or worse yet, dangerously misleading, when applied to real world applications. Aqueous systems often behave in complex and counter-intuitive ways, introducing great risk into plant design and operation if not properly understood and accounted for. On the other hand, reliable electrolyte models make possible tremendous insight, process alternatives, and efficiencies in plant design, trouble-shooting, and optimization.

OLI has developed a theoretical framework, database, data regression techniques, and applications software that comprehensively and accurately simulate and predict

electrolyte systems. The OLI electrolyte approach is based on and distinguished by the following unique elements:

- **Complete speciation.** The OLI model predicts and considers all of the true species in solution, and accounts for these in the computations.
- **Robust standard state framework.** Based on the Helgeson equation of state and parameter regression and proprietary estimation techniques, the OLI model provides accurate equilibrium constants and other standard state properties over the broadest possible aqueous range of conditions.
- **Activity coefficients for complex, high ionic strength systems.** Based on the combined work of Bromley, Zemaitis, Meissner, Pitzer, and OLI technologists, OLI models can predict behavior under real world conditions.
- **Comprehensive databank.** The OLI Databank covers 79 inorganic elements and their associated compounds and complexes, and over 3000 organic chemicals. OLI Data Service provides customized coverage of clients' chemistry and private databanks.
- **Thermo-physical properties.** OLI has developed unique chemical-physical based models to compute thermodynamic and transport properties for complex aqueous environments.

OLI clients have used this unique and powerful electrolyte capability to provide hundreds of millions of dollars benefit through a host of applications in the oil and gas, chemicals, government research, paper, metals and mining, pharmaceutical, petroleum, and energy industries. Example applications are listed in Table 1.

Table 1 – Examples of OLI Electrolyte Applications

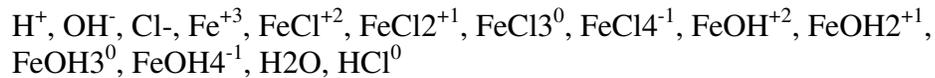
<ul style="list-style-type: none"> • Emergency Chlorine Scrubber • Caustic Wash Tower • Acid Stream Neutralization • Manufacture of KF • Dynamic pH Control • Removal of Fluoride Ions from Waste Water • Scrubbing Refinery Process Streams with DEA • Chlor-Alkali Brine Treatment • Ahlstron NSSC "Stora" Process • Tower Scale Control 	<ul style="list-style-type: none"> • Foul Feed Stripper • Multi-Effect Evaporator • Cooling Tower • Coke Oven Gas • Ammonia Still • Organic Acid Removal in Brines • BTEX Stripper • MSF Desalination Plant • Removal of Chlorobenzene with Biological Treatment • Dregs Washer and Clarifier • CO₂ Corrosion • Corrosion Rates in Acids 	<ul style="list-style-type: none"> • Inhibitor Squeeze in Oil/Gas Reservoirs • Corrosion in LiBr Refrigeration Brines • Thermodynamic Analysis of Corrosion Inhibitors • Electrostatic Precipitator Separation • H₂S/CO₂ Corrosion Products under Gas Pipeline Conditions • Hazardous Waste Deep well Disposal • Contaminated Groundwater Management
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Understanding Aqueous Electrolyte Systems

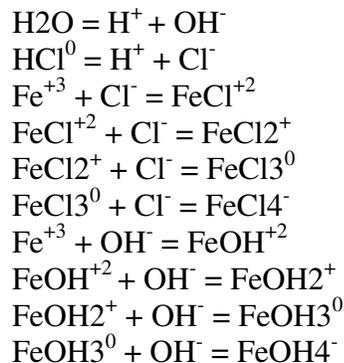
1. The challenge and opportunities of aqueous electrolytes

- Why are electrolytes in water challenging?

Many chemicals react with water to form one or more new species via chemical equilibrium reactions. The resulting process is often termed **speciation**. A particularly complex system occurs when a single chemical compound, like ferric chloride (FeCl_3) is dissolved in water. This actually results in 14 different species within the aqueous phase. The list is as follows:



And, the following independent equilibrium reactions are occurring in the aqueous phase:

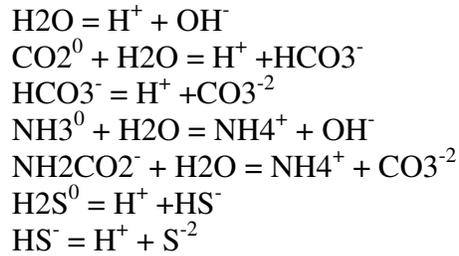


The specific roster of species is usually confirmed by experimental means.

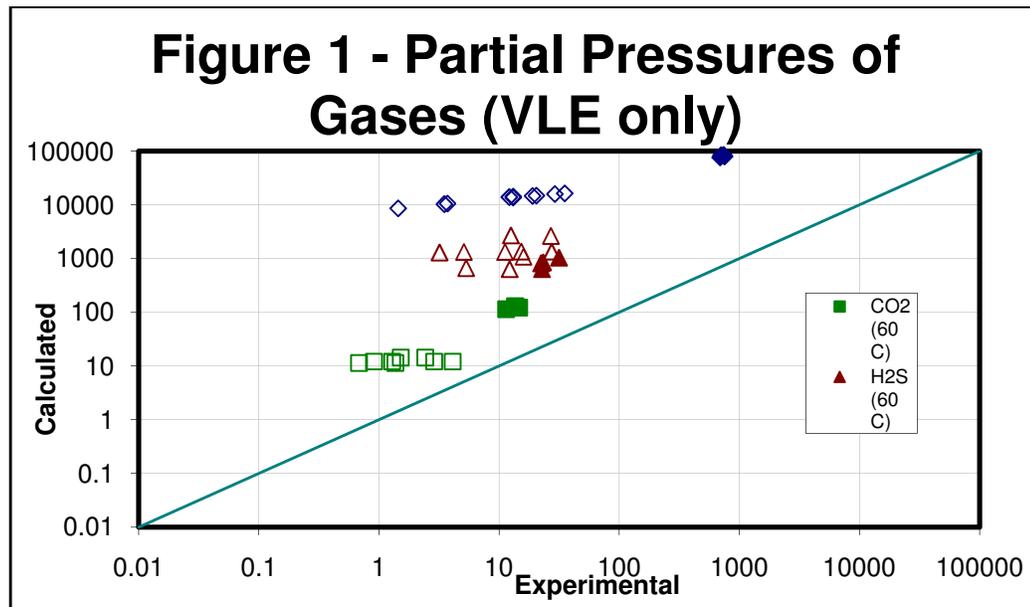
This process of aqueous speciation via reaction, together with the physical equilibria with other phases can produce results, which are quite counter-intuitive. For example, one mole of ferric chloride dissolved in water produces a solution with pH of about 2, making ferric chloride in water a fairly strong acid. This non-intuitive result occurs because of the reactions, shown above, wherein OH^- combines with Fe^{+3} via a series of stepwise reactions. This depletion of hydroxide ions then causes the water dissociation equilibrium reaction to move to the right liberating more hydrogen ions.

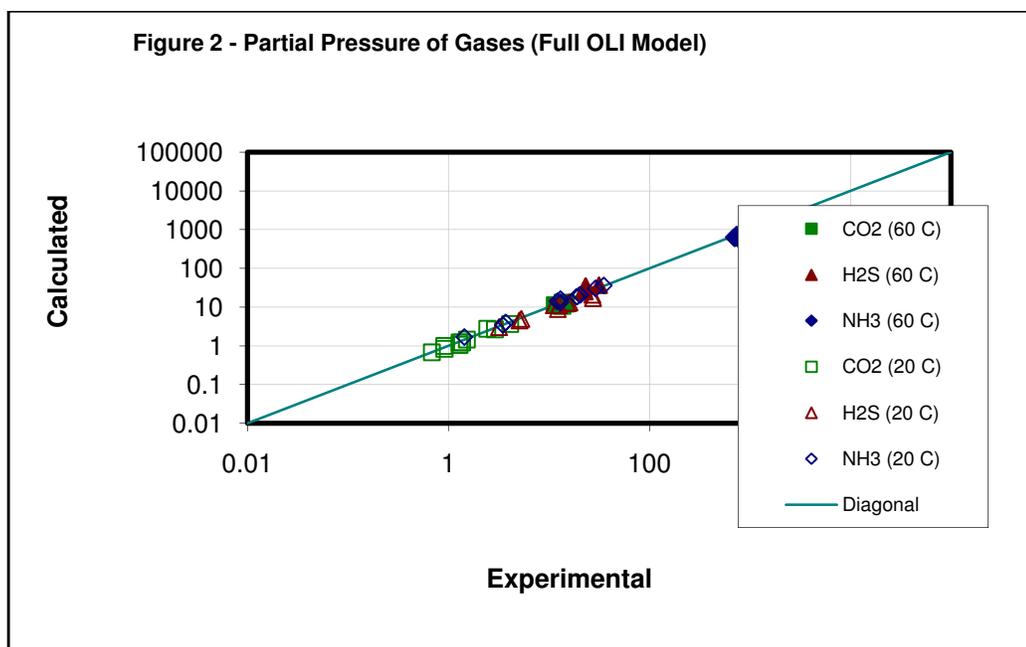
Now, imagine the complexity of not just a single chemical compound in water but, rather, several or even many. The opportunity for equilibrium reactions abounds in such systems. One of literally uncountable examples of multi-component systems is the four-component system water-ammonia-carbon dioxide-hydrogen sulfide (See Appendix 1 for a more detailed discussion and comparison of OLI predicted and experimental results for this system). In this case, the list of species and reactions in the aqueous phase is as follows:





If one were to take the standard thermodynamic properties for the VLE between H₂O, CO₂, NH₃, and H₂S in the aqueous and gas phases and ignore the seven aqueous speciation equilibrium reactions shown above, the errors in predicting VLE would be as high as several orders of magnitude. This is shown rather dramatically in Figure 1 below, where for some points, errors exceed three orders of magnitude. Figure 2 illustrates the accuracy of the OLI prediction based on complete speciation in the aqueous phase, and a robust thermodynamic framework and supporting databank.





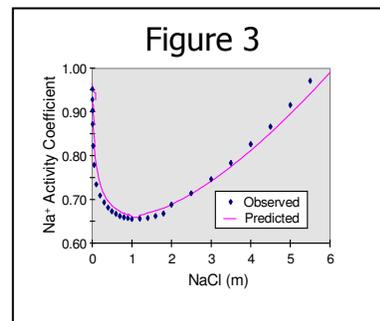
And, it is not just inorganic salts (e.g., FeCl_3) and gases (e.g., ammonia), which dissolve in water to form electrolytes. Many organic acids (e.g., formic acid) as well as other organic compounds dissociate in water forming ions. In addition, the resulting ions may form new species (called **complexes, ion pairs, or organo-metallic complexes**) by combining with metal ions. Many other organic compounds dissolve in water without dissociating.

For almost all chemical compounds, which dissolve in water, there are limits to their solubility. And, this solubility varies when other chemical compounds are present as well. Any attempt to dissolve more than this solubility limit, results in partitioning of the chemical compound to another physical phase. At room temperature, for example, this may be a solid phase in the case of dissolving sodium chloride, a gas phase in the case of carbon dioxide, or a second liquid phase in the case of benzene.

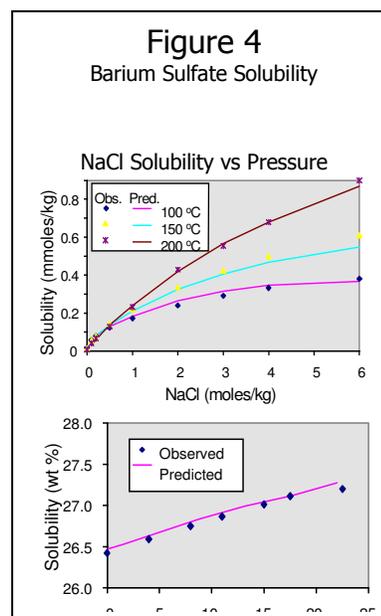
So, to get a complete picture of the thermophysical properties, speciation, and partitioning to other phases for a mixture of chemicals in water is a formidable challenge. The keys to solving this problem in the form of a predictive model are getting the speciation correct and then utilizing state-of-the-art models to represent the relevant thermodynamic properties of all species in the aqueous and related phases as well.

- Why are high ionic strength systems particularly problematic for less rigorous thermodynamic approaches?

The previous section discussed the complexities of speciation for aqueous electrolyte systems. It is important to understand that these complexities are much more significant for systems with many components at high concentrations. Simplified approaches are sometimes used for very dilute systems, but these methods are not valid for higher concentration, multi-component systems typical of real industrial processes. For example, Figure 3 shows that the assumption of a unity activity coefficient ($\gamma=1$) can lead to large errors.



At high concentration, interactions of ions and molecular species with each other and the solvent can become very significant and cannot be ignored. In addition, at high concentrations, the formation of complexes, as well as multi-component chemical interactions make accurate prediction difficult. The OLI framework is the only one in existence that incorporates a robust, predictive activity coefficient model that can accommodate these severe non-idealities. And, the OLI in-place Databank includes coefficients resulting from thousands of data regressions based on the best available thermodynamic data for binary and many ternary systems. Figure 4 illustrates the effect of temperature, pressure, and concentration, and the accuracy of OLI predictions.

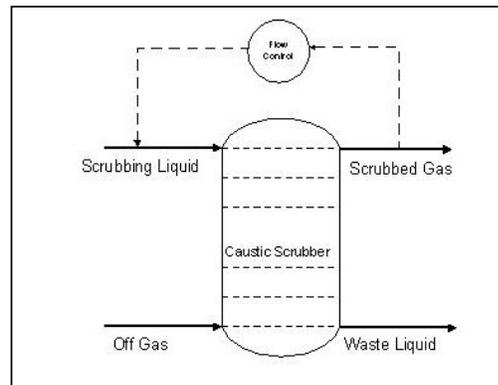


- Why is aqueous electrolyte thermodynamics not well understood and broadly taught at the university level?

Until the culmination of more than 20 years of applied R&D at OLI, no one had put together a complete, speciation-based model for prediction of the thermophysical properties of aqueous-based systems over a broad range of conditions (e.g., -50C to 300C, 0 to 1500 bar, 0 to 30 molal). Key elements of the OLI model were developed over the past 100 years by Debye and Huckel, Helgeson, Pitzer, Meissner, and others. However, no one has put all of this together with key extensions and synthesized a model such as the OLI model. Thus, the OLI model is not generally known and understood at the university level.

- What benefits, features, capabilities, calculations, and functionality are enabled only by a thorough understanding of aqueous electrolytes and what limitations and problems does a process/chemical engineer and a CPI company suffer by not understanding or considering aqueous electrolytes?

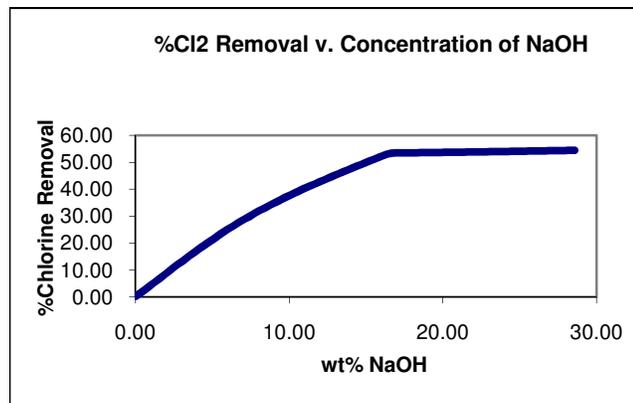
Consider a process application in which chlorine, a component of an off-gas product, is to be scrubbed with 10 % by weight sodium hydroxide solution. Several operating issues have evolved. Given the current design configuration, there is insufficient scrubbing efficiency.



The plant operators increased the sodium hydroxide concentration from 10% by weight to 20% by weight. In addition, the Waste Liquid from the scrubber was desired to be at pH > 8.3 for alkalinity control. The result of the change in concentration was frequent fouling of the scrubber and an inability to control the pH.

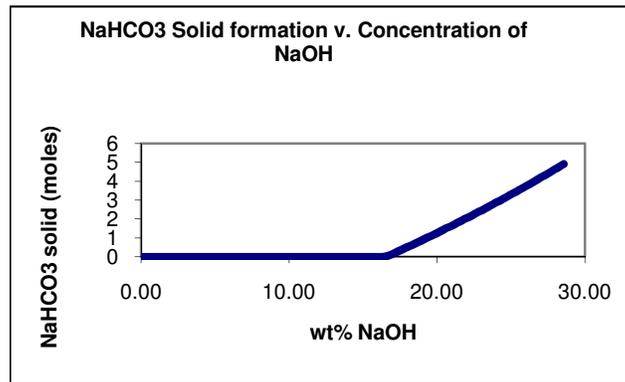
Using the OLI Electrolytes package, the plant operators found that increasing the concentration of sodium hydroxide to 20 % by weight did little to increase the scrubbing efficiency.

The amount of chlorine removal seems to be limited to approximately 50% at sodium hydroxide concentrations greater than 15% by weight. The plant operators also noticed that the column fouled frequently at the high concentrations of sodium hydroxide.



The off-gas contained carbon dioxide as well as chlorine. Using the OLI Electrolytes package, the plant operators found that sodium bicarbonate was created at the increased sodium hydroxide concentrations.

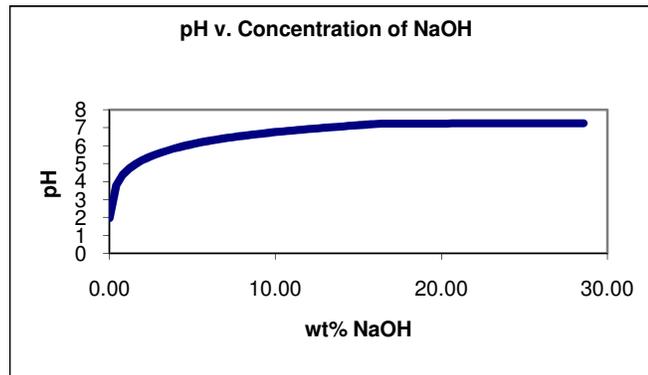
At the 20% by weight concentration of sodium hydroxide, sodium bicarbonate (a solid) begins to form. The plant operators confirmed the presence of this solid in their scrubber.



Another problem was that the pH could not be maintained at values greater than

8.3. The OLI Electrolytes package determined the pH response of the chemistry underlying the process.

The pH levels off at approximately 7.0 as the concentration of NaOH increases. This leveling effect, common in aqueous chemistry, is due the presence of solid NaHCO₃ forming inside the scrubber. As long as this solid continues to form, the pH cannot increase.



A lack of understanding aqueous electrolyte systems amongst engineers within the CPI area forces them to operate without the ability to predict the properties (e.g., pH) and phase separations associated with aqueous-based chemical systems. In a limited number of situations (e.g., sour water systems) there are some correlations available for predicting VLE or SLE for aqueous-based systems. Much more often designs and/or plant operations are based upon very conservative approaches (e.g., over-design) to avoid problems that could be predicted and avoided with the use of the OLI models.

A typical example is scaling in tower units. The formation of salts can result in scale formation within a tower, which will reduce a tower's effectiveness and, eventually, require shutdown of the unit and, perhaps, even the plant. With the OLI model such salt formation is readily predicted leading to avoidance by altering operating conditions, the level of use of a reagent, or the addition of a scale inhibitor all of which can be predicted with the OLI model.

2. Aqueous Electrolytes Primer

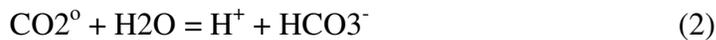
A somewhat more detailed Aqueous Electrolyte Primer is given in Appendix 2.

There are five principal partial molal properties in each phase about which we will be concerned. These are Gibbs Free Energy, Enthalpy, Entropy, Heat Capacity, and Volume. In particular, we will focus on the aqueous phase for which the thermodynamic approach is not well understood. The key to thermodynamic equilibrium, both aqueous intraphase speciation equilibria as well as the physical equilibria between phases is the Gibbs Free Energy (also called the Chemical Potential). For every thermodynamic equilibrium reaction the total Gibbs Free Energy for the species on the left-hand side of the reaction must be equal to the total Gibbs free energy on the right-hand side of the reaction. Thus:

$$G\text{-Left} = G\text{-Right} \quad (1)$$

Where G is defined as the Total Gibbs Free Energy

An example of such a reaction is:



In this case:

$$G_{\text{CO}_2^{\circ}} + G_{\text{H}_2\text{O}} = G_{\text{H}^+} + G_{\text{HCO}_3^-} \quad (3)$$

The total Gibbs Free Energy can be further defined in terms of a Standard State Gibbs Free Energy (G°) and an activity (a) as follows:

$$G_i = G_i^{\circ} + RT \ln(a_i) \quad (4)$$

Where R=Gas Constant and T is absolute temperature. Note that this classical definition is in terms of an activity rather than a concentration. To be able to write this in terms of concentration, we will have to introduce the notion of an activity coefficient, which captures the departure from ideality or, in other words, the relationship between the activity of a species and the concentration of that species. Thus,

$$a_i = \gamma_i * m_i \quad (5)$$

Please note that the Greek symbol γ is used to denote the activity coefficient and the concentration unit molality (m) is usually used as the concentration unit for aqueous systems thermodynamics. Molality is defined as the number of moles of a species in a kilogram (approximately 55.508 moles) of water. Defining concentration in this way makes the concentration definition independent of density and, therefore, temperature.

The standard state used for aqueous-based systems is the one most commonly in use in the literature. For any species other than water, the standard state is the concentration of a hypothetical one-molal solution of the species extrapolated to infinite dilution. This standard state is termed asymmetrical and is a function of temperature and pressure only. Another way of writing equation (4) is:

$$G_i = G_i^o + G_i^E \quad (6)$$

Where the superscript E denotes the Excess Gibbs Free Energy and is therefore by equation (4) defined as $RT\ln(a)$.

The formidable challenge faced by researchers over the past century is how to write closed form equations as a function of temperature, pressure and concentration, which would predict the standard state and excess Gibbs Free Energy. This challenge reduces essentially to one of how to predict the standard state Gibbs Free Energy and activity coefficient for every (and, therefore any) possible species in water.

Before proceeding to the specific framework used by OLI, it is useful to point out that there are similar expressions to (6) for all five principal partial molal properties. Specifically, for the other four (Enthalpy, Entropy, Heat Capacity, and Volume), these expressions are:

$$H = H^o + H^E \quad (7)$$

$$S = S^o + S^E \quad (8)$$

$$C_p = C_p^o + C_p^E \quad (9)$$

$$V = V^o + V^E \quad (10)$$

We saw earlier that the excess term for the Gibbs Free Energy was directly related to the activity coefficient. For the other four properties, denoted above, the excess terms all relate to various partial derivatives of the activity coefficient. For example, the excess enthalpy directly relates to the first partial derivative of the activity coefficient with respect to temperature.

3. The OLI Thermodynamic Framework

OLI has developed a thermodynamic formulation for equations (6) - (10) above by utilizing the framework of Helgeson and co-workers for the standard state terms (the ones with the superscripts of "0") and the frameworks of Bromley, Zemaitis, Pitzer, Debye-Huckel, and others for the excess terms (the ones with the superscripts of "E").

The key to the predictive nature of the OLI model is based upon the work of Harold Helgeson and co-workers. Helgeson, a Professor of Geochemistry at UC Berkeley, has worked for 40 years to develop a predictive equation of state for the

prediction of the partial molal standard state properties of any species within the aqueous phase. Co-workers such as Dimitri Sverjensky, now at Johns Hopkins University in the Department of Earth and Planetary Sciences, have contributed greatly to provide methods for estimating the coefficients of the equation of state for species where it is not practical to regress for the required coefficients. It is beyond the scope of this document to provide the specific formulas for the five principal standard state terms, however a general description is as follows:

$$\begin{aligned}G^{\circ} &= G(T, P, \omega, c1, c2, a1, a2, a3, a4) \\H^{\circ} &= H(T, P, \omega, c1, c2, a1, a2, a3, a4) \\S^{\circ} &= S(T, P, \omega, c1, c2, a1, a2, a3, a4) \\Cp^{\circ} &= Cp(T, P, \omega, c1, c2, a1, a2, a3, a4) \\V^{\circ} &= V(T, P, \omega, c1, c2, a1, a2, a3, a4)\end{aligned}$$

The seven parameters shown in each equation are equation of state coefficients that are unique to each species. In many cases of interest to chemical engineers, a1 through a4 can be ignored since these coefficients relate only to the effects of pressure on the properties of interest and until pressures get above 100 atmospheres the effects of pressure are negligible. OLI has incorporated a Helgeson framework and estimation methods that allows data banking for the ω , c1, and c2 for virtually any species in water and, in most cases, a1 through a4 as well. Remember that equilibrium constants depend solely on the individual G° values for the constituent species in each reaction. Since OLI, via its Helgeson framework, can predict these individual G° values for any species in water, we can, therefore, predict any equilibrium constant. This fully predictive framework for standard state properties relieves entirely the burden of speciation from the activity coefficients where, historically, this burden has been placed. Thus, the remaining compositional effects (called non-ideality) are placed, where they belong, on the activity coefficients without the added burden of speciation equilibrium.

For the excess properties, as noted earlier, everything relates to the activity coefficients. OLI's model for activity coefficients of ions has the following form:

$$\gamma = DH(I) + BZ(I, T, m)$$

where the first term DH is the so-called Debye-Huckel term, which is a function of I=ionic strength (this is the term that completely describes the activity coefficient for very dilute systems). The second term is the Bromley-Zemaitis term and is a function of ionic strength, temperature, and the individual species concentrations represented by m the vector of species molalities. The ionic strength is directly related to the various ionic concentrations.

4. Other Physical Phases in Equilibrium With the Aqueous Phase

The OLI model takes into account the possible occurrence of other phases and also provides databank support so that all required thermodynamic calculations are carried out automatically. Almost any possible solid that might form from an aqueous mixture is accounted for since the OLI code can consider, simultaneously, up to 250 possible solids that might precipitate from a mixture. In reality it is rare that more than 5 solids actually will precipitate at one time, but the model will correctly predict the precipitating solids. In addition the model accounts for the possible formation of a gas phase and a second (non-aqueous) liquid phase.

The condition for physical equilibrium between phases is that the total Gibbs Free Energy (also known as chemical potential) is equal for the phases in equilibrium. Since we have already established the manner in which OLI calculates Gibbs Free Energy for the aqueous phase, we need only describe how OLI does this same calculation for solids, gases, and the second liquid phase.

Each solid in equilibrium with the aqueous phase is an independent phase. Thus, we need only be able to calculate the Gibbs Free Energy for individual solids. This is done via classical thermodynamics by the equation:

$$G_S = G_S^{Tr} + S_S^{Tr} (T - Tr) + \int C_p dT + \int V dP$$

Where, Tr is the Reference State temperature of 298.15K, and the two integrals are integrated from Tr to T .

For the gas and second liquid phase, OLI relies on an enhanced SRK formulation for the thermodynamic properties. For the free energy, the formulation is the classical formulation, which is:

$$G_i = G_i^{\circ} + RT \ln(f_i c_i P)$$

Where, f_i is the fugacity coefficient of species i in the gas or non-aqueous liquid phase and c_i is the mole fraction of species i in the gas or non-aqueous liquid phase.

5. What OLI Provides

OLI provides all facilities, which enable a user to avoid all of the complexities associated with aqueous electrolyte systems. This means that the user **never** has to:

- Write an equilibrium reaction
- Define true species in the aqueous phase (the user only provides the customary molecular chemical components)
- Deal with any complexities associated with solving for the occurrence of other physical phases in addition to the aqueous phase

- Carry out any data regressions to develop model coefficients (these are all provided by the in-place OLI databank)

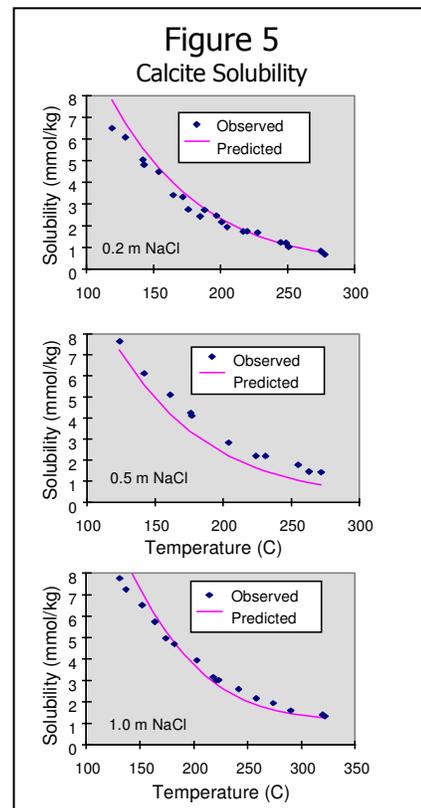
Essentially, from a user point of view, the description of process streams and process units is no different than with conventional simulation. For example, using the highly complex system of H₂O/FeCl₃, described earlier, the user deals only with the two component system while the OLI software, behind the scenes deals with the 14 true species in solution, the 10 equilibrium reactions in the aqueous phase, and the physical equilibrium between the aqueous phase and any solid, vapor, and second liquid phase that may occur.

6. Range of Applicability of the OLI Model

There are a number of limitations of the OLI Model as follows:

- The temperature resulting from the equilibrium calculation must fall in the range -50 and 300 centigrade.
- The pressure resulting from the equilibrium calculation must fall in the range 0 and 1500 atmospheres.
- The mole fraction of water **within the liquid phase** resulting from the equilibrium calculation must fall in the range between 0.65 and 1.0.
- The OLI model used for the gas phase and second liquid phase is based upon an enhanced SRK equation of state. This means that certain non-ideal second liquid phases may not be represented well due to limits of the SRK.
- OLI has done data regression for an enormous number of chemical systems. Generally, all single components plus water have been regressed. Figure 5 illustrates the accuracy of typical binary system predictions at different temperatures.

In addition, many ternary systems (water plus two other components) have been regressed together with the constituent binary systems. Figures 6 and 7 illustrate ternary system predictions compared to experimental data. (Also see Appendix 1 for other examples of data fits). Note particularly in Figure 7 the unusual behavior of gypsum at 25 °C and high NaCl concentrations (there is a maximum gypsum solubility at an intermediate NaCl concentration). This behavior, accurately predicted by OLI, could not be predicted



with less rigorous models. For regressed systems, the error between predicted and experimental values is generally less than 10%.

Eventually, for all multi-component systems with more than three components plus water, OLI must rely on some estimation/prediction. The key to these systems is whether or not the subsystems defined by water together with components present in excess of 1 molal concentration have been subjected to data regression by OLI. If not, the predictions will usually be good qualitatively but fairly substantial errors (25+%) may occur in the actual predictions. For most common ternary systems (e.g., H₂O/NH₃/CO₂, H₂O/CO₂/NaCl) it is safe to assume that OLI has done the required ternary system regressions. Well over 100 such systems have been regressed.

7. The OLI Databank

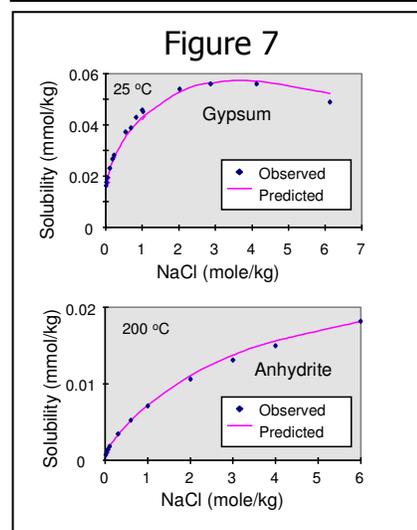
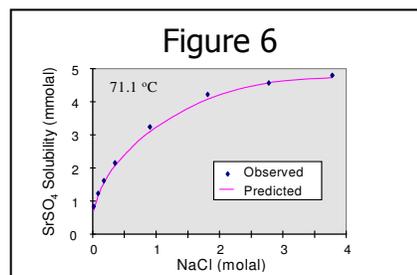
OLI Electrolytes includes the Full Databank and the GeoChem Databank.

- Full databank

The full databank, listed in Appendix 3, covers thousands of species in water. In terms of inorganic chemistry this includes the much of the aqueous chemistry (including speciation reactions) for 79 elements from the Periodic Table in water. In addition, thousands of organic chemical compounds (electrolyte and non-electrolyte) are covered. **OLI's mission is to cover any species that might of possible interest to our customers.** The Full Databank delivers the results of much of this mission. However, where a customer finds that a species is missing or does not cover the range of conditions of interest, then the OLI Data Service (see below) takes over.

- Special databanks

In addition to the above-noted databank, OLI has a few other databanks that are generally distributed with the product. The Geochem databank (see list in Appendix 4) is separated from the public since it contains many solids, which only form via thermodynamic equilibrium after long periods of time (often thousands of years). These solids form in nature and are often different from the form of a solid, made up of the same elements, that may form in a much



shorter amount of time (usually instantly) within a process. Thus, the Geochem solids tend to form through aging of the aqueous environment in contact with a source of the elements comprising the solids.

- Private (custom) databanks - OLI Data Service

The OLI Engine Software allows users to provide their own supplementary databanks (Private Databanks) in addition to the Public (Limited, Full and Special) databanks. These databanks can be prepared by users with special training but are normally prepared by the OLI Data Service. The procedure is that OLI is informed that certain chemistry either not covered or inadequately covered by the Full Databank, is required. OLI will then estimate the amount of time that it will take to do such a job, which leads to a quotation for performing the work. The fee quoted will vary based upon whether or not OLI can do the work based upon public domain information and whether or not OLI is free to release the results with subsequent releases of its Public Databanks. OLI's Data Service starts all projects with a thorough literature search. Then all relevant literature is critically reviewed and the experimental data, which is deemed fit is placed into computer files from which nonlinear regression is carried out. As a result of these regressions, databank coefficients are developed.

8. The OLI Engine

The OLI Engine is the essential heart of all OLI Software. The OLI Engine is defined as the databanks and solvers that enable the prediction and numerical solution of the underlying chemical and physical equilibria and, therefore, the thermophysical properties and phase separations for almost any mixture of chemicals in water at almost any conditions ($T = -50$ to 300 C, $P = 0$ to 1500 bar, Ionic Strength = 0 to 30 Molal) of practical interest to industry. The thermophysical properties available in OLI Electrolytes are summarized in Table 2. In addition to the Thermodynamic Properties in Table 2, OLI has developed certain transport properties to support the rates of corrosion model. These properties include: viscosity, electrical conductivity and self-diffusivity.

Table 2 – Thermophysical Properties Available in OLI Electrolytes

Thermodynamic Properties	
Gibb's Free Energy	pH
Enthalpy	Osmotic Pressure
Entropy	Ionic Strength
Heat Capacity	Density
Volume	Scaling Index

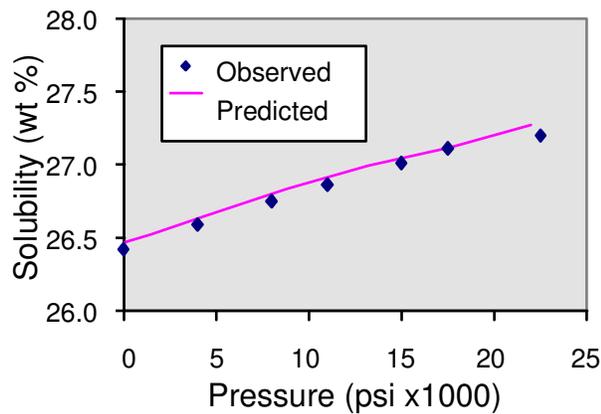
Appendix 1

Examples of OLI Prediction Accuracy

Solubility Prediction

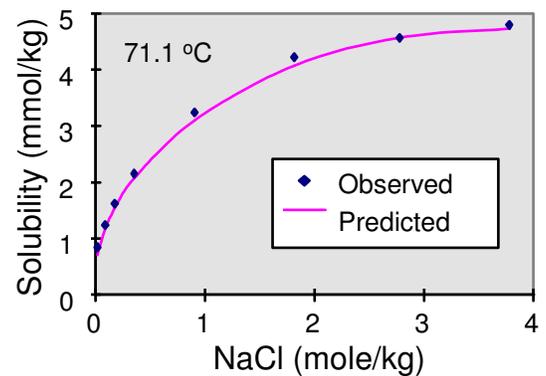
Sodium Chloride Data

OLI's extensive database allows for prediction of virtually all industrially important solids. Below is a plot of the observed versus predicted solubility of NaCl over a broad range of pressures.



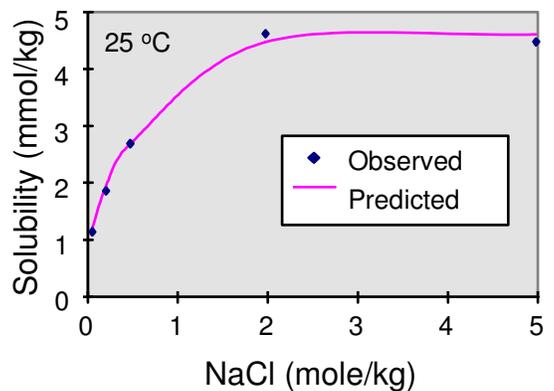
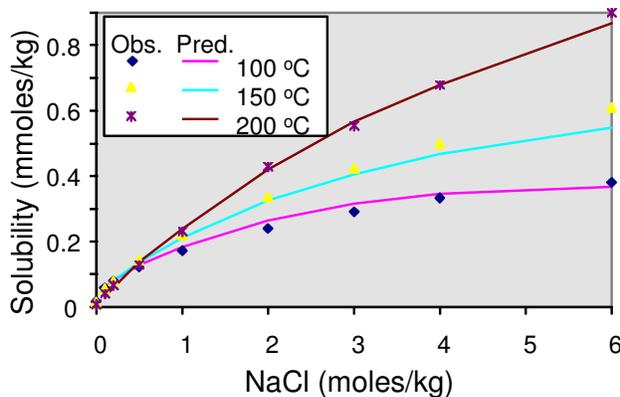
Celestite Data

Based upon quality fits, OLI Electrolytes software produces accurate predictions of strontium sulfate (celestite) solubility under a variety of conditions. In the two graphs shown below, celestite solubility is predicted at two separate temperatures, 25 and 71.1 °C. over the solubility range of NaCl (0 to 6 molal).



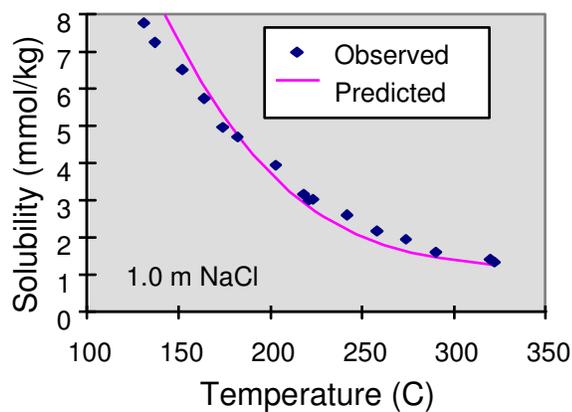
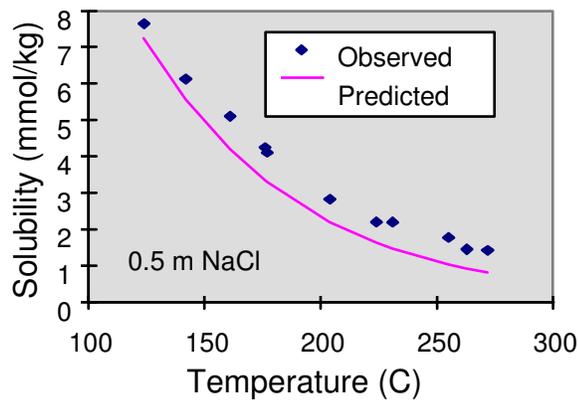
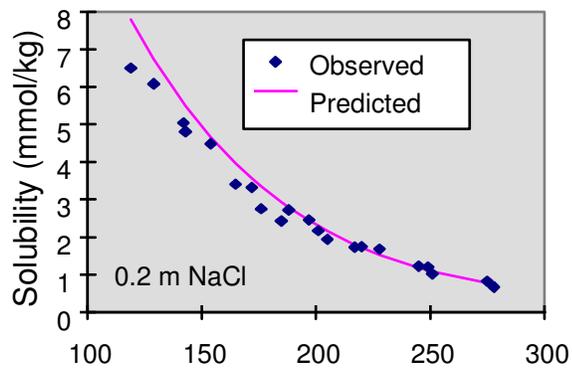
Barite Data

OLI Electrolytes accurately predicts the barite solubility over broad ranges of temperatures, pressures, and salinities.



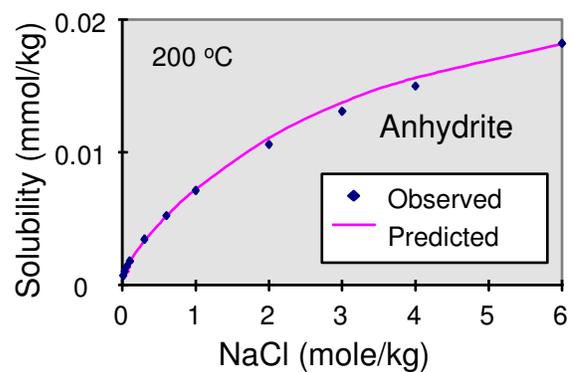
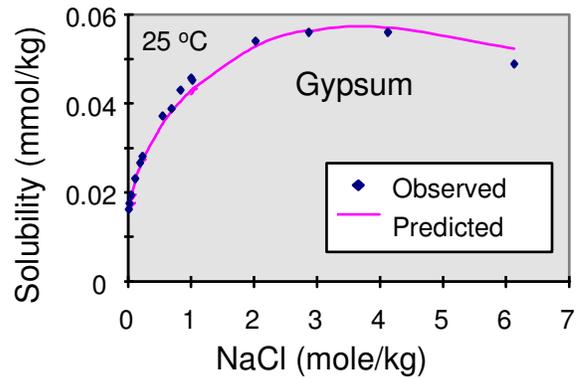
Calcite Solubility versus Temperature

The following graphs illustrate, the experimental and predicted solubility of calcite at high temperatures, pressures, and NaCl concentrations. As shown, the software accurately predicts calcite solubility over all conditions. This is due to the rigorous approach to computing the thermodynamic solubility of CaCO_3 and the activity coefficients for the complete speciation of the ions in solution.



Gypsum and Anhydrite Data

OLI software produces accurate predictions of calcium sulfate solubility under a variety of conditions for the two major crystalline phases. In the two graphs shown below, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) solubility is predicted over the NaCl range of 0 to 6 molal.



Speciation in Sour Water

For the sour water system (NH₃/H₂S/CO₂/H₂O) with Sour Water Species as follows:

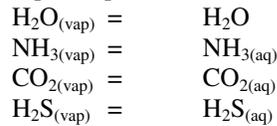
Vapor Species: H₂O, CO₂, H₂S and NH₃

Aqueous Neutral Species: H₂O, CO₂, H₂S and NH₃

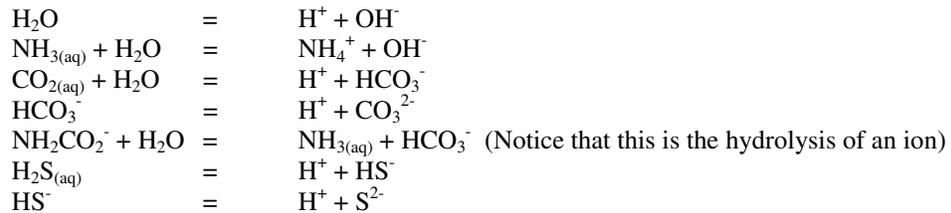
Aqueous Ionic Species: H⁺, OH⁻, NH₄⁺, HS⁻, S²⁻, HCO₃⁻, CO₃²⁻, and NH₂CO₂⁻

The chemistry can be summarized as:

Vapor - Liquid Equilibrium Reactions (Molecular Equilibrium)



Aqueous Chemical Reactions (Electrolyte Equilibrium) – Note additional electrolyte reactions are needed.



This example illustrates both the importance of considering the aqueous reactions and speciation, as well as the agreement of OLI predictions with experimental data. The data contained in Table 1 compares the experimental partial pressures of carbon dioxide, ammonia and hydrogen sulfide against a VLE only model and the full OLI speciated model.

Temp (C)	Liquid Concentration (molality)			Partial Pressure (mmHg)								
	NH3	CO2	H2S	NH3			CO2			H2S		
				Exper.	OLI	VLE	Exper.	OLI	VLE	Exper.	OLI	VLE
60	2.076	1.516	0.064	14.74 4	12.388	121.6	751.48 8	592.19 2	79594.8	31.616	36.936	1033.6
	2.098	1.601	0.052	13.60 4	10.792	129.2	738.11 2	744.57 2	84762.8	23.256	35.112	843.6
	1.954	1.471	0.04	11.47 6	11.172	114	691.90 4	638.4	76820.8	22.8	25.004	638.4
	2.16	1.581	0.05	13.68	12.92	129.2	705.28	590.52	83524	22.42	28.12	813.2
	1.231	0.424	0.196	4.104	3.648	12.16	1.444	1.672	8580.4	3.192	3.04	1292
20	1.236	0.507	0.201	2.888	2.66	12.16	3.496	3.42	10290.4	5.092	4.484	1325.44
	1.45	0.517	0.407	2.432	2.736	14.44	3.724	4.028	10526	12.54	10.944	2690.4
	1.439	0.665	0.396	1.52	1.444	14.44	13.072	13.148	13611.6	26.98	20.672	2634.16
	1.132	0.681	0.1	1.368	1.216	11.4	12.16	13.984	13892.8	5.32	4.94	663.48
	1.234	0.694	0.199	1.292	1.216	12.16	13.072	16.036	14181.6	11.172	11.096	1322.4
	1.238	0.712	0.203	1.292	1.064	12.16	19	18.62	14561.6	15.276	12.464	1345.2

1.234	0.725	0.199	0.912	0.988	12.16	20.444	20.672	14835.2	15.96	13.072	1079.2
1.235	0.771	0.2	0.912	0.836	12.16	29.184	30.324	15808	27.36	17.024	1333.04
1.126	0.794	0.095	0.684	0.684	11.4	35.188	36.252	16271.6	12.236	8.892	633.08

Table 1 - Comparing Experimental Partial Pressures to Calculated values.

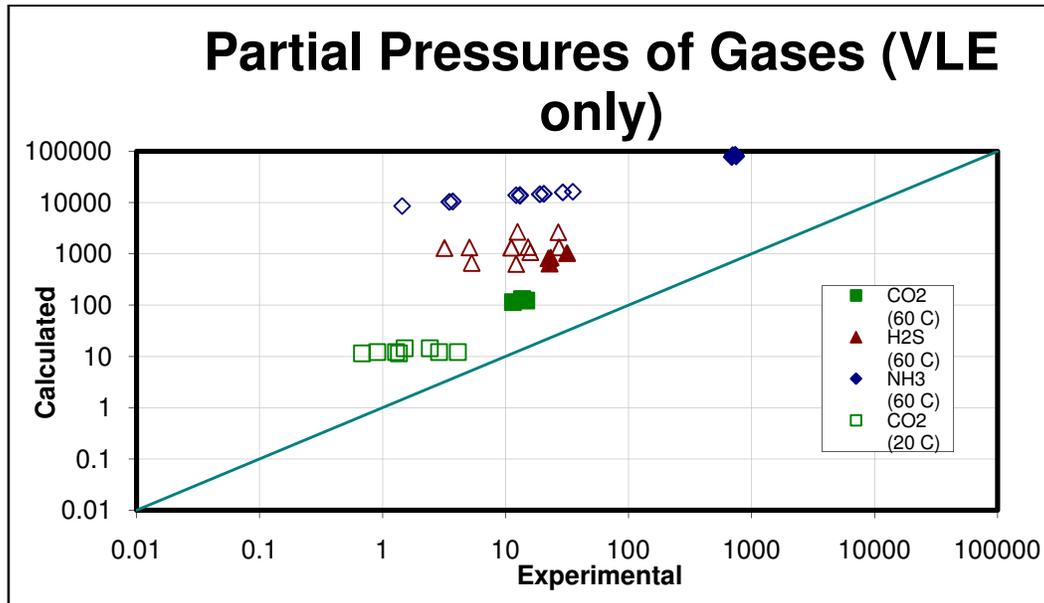


Figure 1 - Parity plot of the partial pressures of gases without aqueous reactions

In Figure 1, the calculated partial pressures of the gases are over predicted. In the case of ammonia (filled and open diamonds), the over prediction may be as much a five orders of magnitude. If the OLI full speciation approach is not followed, this data can be improved with statistical corrections or by applying a strong activity model. These corrections, however, may work for this set of conditions. But if conditions other than the conditions in these series of calculations are desired, then these “corrections” will not be valid. The OLI approach using full speciation is predictive over the entire range of OLI model conditions.

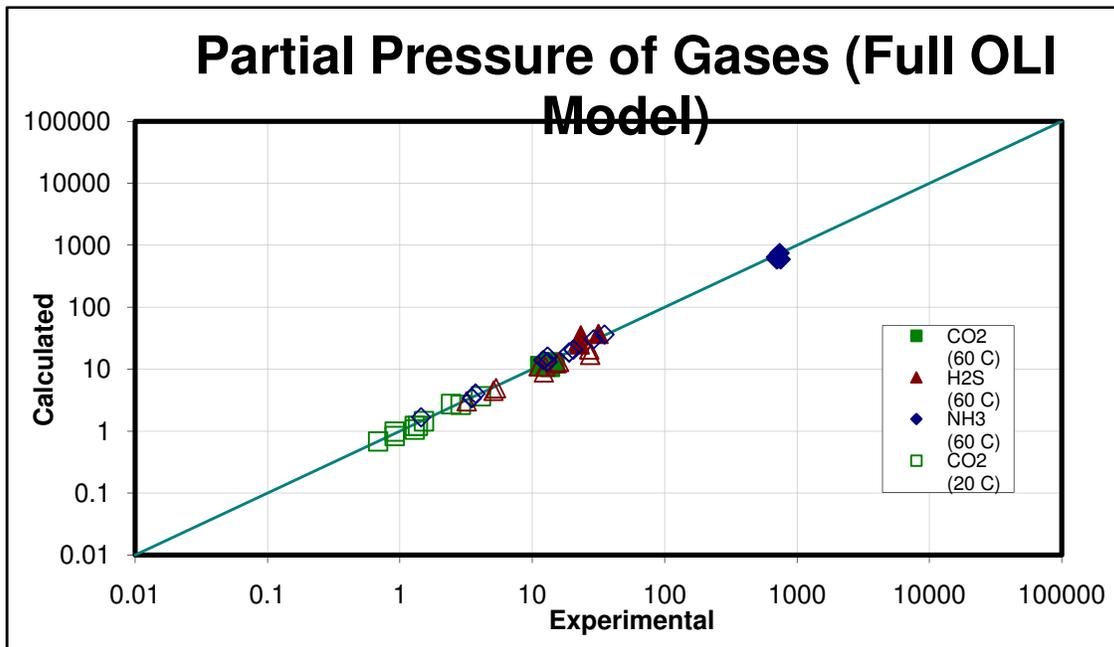


Figure 2 - Parity plot of the partial pressures of gases with aqueous reactions

When all the equilibria are included in the calculations, the calculated partial pressure of the gases agrees with the experimental values (Figure 2). This was done without specialized data regression to the general range of this data. This provides confidence that the predictions will hold at other conditions.