

**Project Title: Prediction of Corrosion of Alloys in Mixed-Solvent Environments**

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**Project Objective:** Develop computational tools and software that will enable corrosion and chemical engineers to predict the corrosion behavior of engineering alloys in mixed-solvent environments. For this purpose, the software should include: (1) A model for the prediction of thermodynamic properties of mixed-solvent electrolyte systems; (2) A comprehensive tool for the thermodynamic analysis of corrosion of alloys, which will enable the users to predict the tendency of a given alloy to corrode in a given environment; (3) A tool to compute the corrosion rates of alloys that will allow users to make quantitative predictions of the effects of process variables on corrosion rates of candidate materials.

**Executive Summary:** Corrosion is much less predictable in organic or mixed-solvent environments than in aqueous process environments. As a result, US chemical companies face greater uncertainty when selecting process equipment materials to manufacture chemical products using organic or mixed solvents than when the process environments are only aqueous. Chemical companies handle this uncertainty by over designing the equipment (wasting money and energy), rather than by accepting increased risks of corrosion failure (personnel hazards and environmental releases). Therefore, it is important to develop simulation tools that would help the chemical process industries to understand and predict corrosion and to develop mitigation measures. To develop such tools, we have developed models that predict (1) the chemical composition, speciation, phase equilibria, component activities and transport properties of the bulk (aqueous, nonaqueous or mixed) phase that is in contact with the metal; (2) the phase equilibria and component activities of the alloy phase(s) that may be subject to corrosion and (3) the interfacial phenomena that are responsible for corrosion at the metal/solution or passive film/solution interface. During the course of this project, we have completed the following: (1) Development of thermodynamic modules for calculating the activities of alloy components (2) Development of software that generates stability diagrams for alloys in aqueous systems; these diagrams make it possible to predict the tendency of metals to corrode. (3)

Development and extensive verification of a model for calculating speciation, phase equilibria and thermodynamic properties of mixed solvent electrolyte systems (4) Integration of the software for generating stability diagrams with the mixed-solvent electrolyte model, which makes it possible to generate stability diagrams for nonaqueous or mixed-solvent systems. (5) Development of a model for predicting diffusion coefficients in mixed solvent electrolyte systems (6) Development of fundamentals of a detailed kinetic model of general corrosion, which includes a detailed treatment of local chemistry changes near the metal/solution interface coupled with transport through a liquid layer and solid phases at the interface. (7) Development of parameters for OLI's kinetic model of general corrosion of common engineering alloys in aqueous systems with a variety of solutes. With this model, the users will be able to predict the effect of various process conditions (such as environment composition, temperature, pressure) on the general corrosion of alloys. (8) Comprehensive review of the fundamentals of the models by an Academic Review Panel, which was performed in conjunction with three annual review meetings. (9) Development and commercial release of the Corrosion Analyzer, a Windows software product that encompasses the thermodynamic model, a facility for generating stability diagrams and the model for predicting the rates of general corrosion of selected alloys in aqueous systems.

**PROJECT ACTIVITIES, SCIENTIFIC APPROACHES AND RESULTS** The project activities, scientific approaches and results will be described here in detail for each task of the project. Task 1: Development of Stability Diagrams for Alloys and Their Components in Aqueous Environments Thermodynamic stability diagrams have been extensively used for predicting and rationalizing corrosion-related processes since Pourbaix (1964) developed a comprehensive collection of diagrams for most elements in water. The Pourbaix diagrams depict the areas of thermodynamic stability for various, solid or aqueous, species as functions of the potential (E) and pH. Thus, the diagrams indicate under which E and pH conditions the metal of interest is thermodynamically stable (or immune to corrosion) and which conditions may cause its dissolution in the form of ions or its transformation into metal oxides or other solids that may give rise to passivation. However, the stability diagrams that are described in the literature are subject to some inherent limitations. First, the classical stability diagrams have been constructed for arbitrarily assumed activities of dissolved species. This has been due to the difficulties in developing predictive activity coefficient models for multicomponent solutions. Without a comprehensive activity coefficient model, it is possible to use only numerical values of activity coefficients that correspond to a solution of well-known composition such as seawater. The absence of an activity coefficient model limits the accuracy of the diagrams to very dilute solutions, for which the assumed activities can be identified with concentrations. Second, stability diagrams were available only for pure metals because of a lack of suitable methodology to account for the activity of alloy components. Another limitation of the classical diagrams is the fact that pH is introduced as an independent variable without regard to the chemical identity of the sources of the H<sup>+</sup> and OH<sup>-</sup> ions, which determine pH. Additionally, the classical diagrams are restricted to E and pH as independent variables whereas it is frequently of interest to analyze the effects of species other than the H<sup>+</sup> or OH<sup>-</sup> ions. For example, it may be worthwhile to use the concentrations of complexing species as independent variables. Also, it is often more convenient to consider pH as a dependent rather than independent variable because it results from the presence of various acidic or basic components whose concentrations may be more natural as independent variables. In this project, we have developed a methodology to overcome these limitations with the help of comprehensive thermodynamic models. With the new approach, stability diagrams are constructed to achieve the following goals: (1) Incorporation of an

activity coefficient model for multicomponent aqueous systems; (2) Incorporation of a model for calculating the activities of metals within alloys. (3) Applicability for concentrated solutions (i.e., for ionic strengths up to 30 mol/kg) (4) Applicability over extended temperature and pressure ranges (i.e. for temperatures up to 300 °C and pressures up to 1 kbar); (5) Flexibility with respect to the choice of independent variables so that the effect of any solution components can be explicitly studied. Since the diagrams are based on a realistic model for the aqueous phase, they will be referred to as the real-solution stability diagrams. Subtask 1.1: Calculation of the activity of individual components in alloys. This subtask was performed at the Oak Ridge National Laboratory. The overall aim of the ORNL research task was to develop software modules to calculate activity of individual alloying elements as a function of concentration and temperature for a phase that is of interest. These calculated activity values are used in the OLI corrosion model for stability diagram calculations. The alloy systems that are of interest to current research project were copper alloys (Cu-Ni system), low-alloy steel (Fe-C-Mn), stainless steels (Fe-Cr-Ni-Mo-C), nickel alloys (Ni-Cr-Fe-Mo-C) and duplex stainless steels (Fe-Cr-Ni-Mo-C-N). The structure of the ORNL alloy module is depicted in Figure 1. Methodology: The activity ( $a_i$ ) of alloying element is related to its chemical potential ( $\mu_i$ ) as given by equation (1) [Lupis, 1983], Text Box: Fig. 1. Schematic illustration of ORNL research tasks (1). The chemical potential in-turn is related to the molar free energy ( $G_m$ ) and molar concentration ( $x_j$ ) through the following relation, (2). The molar free energy of the alloys as a function of alloying element concentration were described using sublattice model [Sundman et al, 1985 and Saunders & Miodownik, 1998] and is given by the following formulation, (3). In the above equation,  $G^0$  is the contribution due to pure components [Dinsdale, 1991],  $G^i$  is the ideal mixing contribution,  $G^m$  is the contribution due to non-ideal mixing,  $G^p$  is the contribution to magnetic Gibbs energy, and  $G^v$  is the contribution due to pressure term [Saunders and Miodownik, 1998]. Results: Published thermodynamic data for constituent binary systems (e.g. Fe-C, Gustafson, 1985), ternary systems (e.g. Fe-Cr-C by Andersson, 1988) and quaternary systems (e.g. Cr-Fe-N-Ni by Frisk, 1991) were used to develop the software module for stainless steels, nickel alloys and duplex steels. The software modules were designed to calculate the activity of constituent alloying elements in both austenite (face-centered cubic crystal structure) and ferrite (body-centered cubic crystal structure) as a function of concentration and temperature. The software modules were evaluated with ThermoCalc® calculations for accuracy [Sundman et al, 1985]. The calculations shown in Fig. 2 show good agreement with ThermoCalc® predictions. In addition, the plots show the activity of Mo in BCC phase will be many orders of magnitude higher than that in FCC phase. The above results are significant since the corrosion stability diagrams can be evaluated for different phases with the same compositions. Text Box: Fig. 2. Calculated variations of activity as a function of molybdenum concentration in a Fe-22Cr-5Ni-0.02C-0.16N (wt.%) alloy with ORNL model and ThermoCalc® software version N. Subtask 1.2: Review of the basis of the model by Academic Review Panel The team members met with the Academic Review Panel three times during the course of the project: (1) June 10, 2000 in St. Louis in conjunction with a regular meeting of the Materials Technology Institute (MTI). (2) June 5, 2001 in Memphis, also in conjunction with an MTI meeting and (3) May 16, 2002 in Philadelphia at a special meeting. At these meetings, a detailed technical review of the fundamentals of the models has been performed. The members of the Academic Review Panel were Professors Gerald S. Frankel (Ohio State University), Lloyd L. Lee (University of Oklahoma), Zi-Kui Liu (Pennsylvania State University) and Mark E. Orazem (University of Florida). The reviewers provided the team members with their comments, which were taken into account in the research and development process. Subtask 1.3: Incorporation of the alloy model into stability diagram software. The alloy thermodynamic modules

have been integrated with the software for generating stability diagrams. For this purpose, the stability diagram code has been revised to incorporate a Gibbs energy model not only for the aqueous phase, but also for the solid (alloy) phase. In this section, we describe the algorithm for generating stability diagrams for alloys. A stability diagram for a given physical system can be viewed as a superposition of elementary diagrams for the redox subsystems that make up the system of interest. For example, a system composed of a Fe-Ni alloy in an H<sub>2</sub>S solution can be treated as a superposition of five redox subsystems defined as: (1) All species containing Fe in any possible oxidation state (0, +2, +3 and +6) (2) All species with Ni in the 0, +2, +3 and +4 oxidation states; (3) All species with S in any possible oxidation state ranging from -2 to +8; (4) All species with H in the 0 and +1 oxidation state and (4) All species with O in the -2, 0 and, possibly, -1 oxidation states. Thus, each redox subsystem is associated with an element that can exist in two or more oxidation states. Each of the elementary redox subsystems is characterized by a set of equations that may occur between the species that belong to the subsystem. The subsystems are interdependent because the reactions in each subsystem involve species that belong to more than one subsystem. However, the relationships between the potential and activities or concentrations of species can be separately plotted for each subsystem. For example, the classical Pourbaix diagrams (1966) are shown as superpositions of three elementary diagrams, i.e., one for a redox subsystem containing a selected metal, one for the oxygen subsystem and one for the hydrogen subsystem. The latter two subsystems are usually represented by single lines that correspond to the H<sup>+</sup>/H<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub>O equilibria. To compute a stability diagram for each redox subsystem, it is necessary to enumerate all distinct chemical species that belong to this subsystem. Each of these species contains the particular element that is associated with the subsystem. Then, equilibrium equations are written between all species in the subsystem. If the number of species is n, then n(n-1)/2 reactions are defined. A reaction between the species X and Y is written as (4) where A<sub>i</sub> (i = 1, ..., k) are the basis species that are necessary to define equilibrium equations between all species in the redox subsystem and .i are the stoichiometric coefficients. For convenience, each reaction is normalized so that the stoichiometric coefficient for the right-hand side species (Y) is equal to 1. To establish a general algorithm for defining the basis species A<sub>i</sub>, we note that the species X and Y from equation (4) can be represented as (5) (6) where M is the element that is associated with the redox subsystem, H and O are the usual symbols for hydrogen and oxygen, respectively, and C, D, E, ... are the additional elements that exist in the species X and Y. For the purpose of defining the basis species, we separately treat elements in different oxidation states. For example, C and D can represent the same element in two different oxidation states. The basis species are then defined as the species that contain H, O, C, D, E, etc., but do not contain M. Although this definition allows considerable flexibility in choosing the basis species A<sub>i</sub>, additional rules are introduced to simplify the algorithm: (a) H<sup>+</sup> is always the basis species that contains H; (b) H<sub>2</sub>O is always the basis species that contains O; (c) The basis species containing C, D, E, etc. are selected so that they contain the minimum possible number of hydrogen and oxygen atoms in addition to C, D, E, ... . To illustrate the selection of basis species, let us consider two examples. In a system composed of Cu, H<sub>2</sub>O and NH<sub>3</sub>, the species in the copper-containing redox subsystem are copper hydroxides, oxides and complexes formed by Cu with the OH<sup>-</sup> and NH<sub>3</sub> groups. Therefore, the general formula for the species is Cu where N-3 denotes N in the -3 oxidation state. Thus, the basis species for constructing reactions (5) are H<sup>+</sup>, H<sub>2</sub>O and NH<sub>3</sub>(aq). In a system composed of iron, water and sulfur-bearing compounds, the species in the iron subsystem are iron hydroxides, oxides, hydroxycomplexes, sulfides, polysulfides and sulfates. The general

formula for the species is then and the basis species are  $H^+$ ,  $H_2O$ ,  $S^{2-}$ ,  $S^0(s)$  and  $SO_4^{2-}$ . After selecting the basis species, the stoichiometric coefficients in equation (5) are determined by balancing the elements M, H, O, C, D, E, etc. Finally, the number of electrons (.e) is found by balancing the charges on the right- and left-hand sides of equation (5). The selection of basis species is slightly more complicated in cases when not only the element M (cf. eqs. 5 and 6) is subject to redox equilibria, but also some of the elements C, D, E, etc. can enter into their own redox equilibria. A typical example is the iron-water-sulfur system, in which both iron and sulfur can exist in several oxidation states. In the iron-containing subsystem, the transformations between the various Fe species can involve the oxidation and reduction of either iron or sulfur or both. In such cases, the basis species are modified in a two-step procedure: (1) First, it is determined which basis species are stable in which area of the stability diagram and (2) Only the stable species are retained in the basis and the remaining ones are deleted. The deleted species are not taken into account for constructing the equilibrium equations (4) but, otherwise, they are kept in the system. Since different basis species can be stable in various areas of a stability diagram, the steps (1) and (2) are usually repeated in as many areas of the diagram as necessary. This procedure ensures that only the stable basis species are included in the reactions. For example, elemental sulfur ( $S^0$ ) is stable only in a certain fraction of the E-pH plane. Therefore,  $S^0$  is used as a basis species to construct the reactions for the iron subsystem only when  $S^0$  stable, i.e., when solid sulfur can exist in a finite amount. The proposed procedure for constructing equilibrium equations is considerably more complicated than the techniques proposed in the literature in conjunction with the classical Pourbaix diagrams (1966). However, it makes it possible to include chemical transformations of any complexity and is not limited to those involving  $H^+$  and  $H_2O$ . Equilibrium lines. In the classical Pourbaix diagrams, each line represents the equilibrium between two chemical species for a given activity. Since the activity of dissolved species is assumed a priori, it is possible to derive analytical expressions for the equilibrium lines. Such expressions give pH values for the equilibrium between two species that do not undergo a redox reaction and express the potential as a linear function of pH for redox transformations. In the real-solution stability diagrams, the activities of all species vary because of the changing amounts of input species (such as an acid or a base used to adjust pH). Activity coefficients are nonlinear functions of composition and may cause nonlinearities in the equilibrium lines. Therefore, it is not possible to derive analytical expressions for the equilibrium lines. Instead, a certain number of points on the equilibrium lines have to be numerically computed. The points can be further interpolated to obtain an equilibrium line. Stability diagrams are constructed by performing a simulated titration with reactants that are appropriate for varying the independent variable of interest. If pH is the independent variable, two reactants - an acid and a base - are selected for the simulated titration. First, decreasing amounts of an acid are added to cover the acidic pH range in regular increments. Then, increasing amounts of a base are added to cover the basic pH range. If the influence of a complexing or other reactive species is studied, the input amount of this species or its equilibrium concentration can be chosen as possible independent variables. Then, a compound containing this species is added in regular increments. For each amount of the added reactant, equilibrium compositions of various species in the aqueous phase are computed. At the same time, the activity coefficients are obtained. The concentrations and activity coefficients are further used to calculate the points on the equilibrium lines as explained below. In typical diagrams, it is sufficient to calculate between 20 and 30 points on the equilibrium lines provided that they are evenly spaced to cover a full range of the selected independent variable. Chemical reactions. The chemical reactions

are defined as the ones for which the number of electrons  $.e$  (cf. eq. [4]) is zero. Since the chemical reactions are independent of the potential, they are represented on stability diagrams as vertical lines. In this case, an equation for the affinity  $A$  of reaction (4) is written as (7) where  $K$  is the equilibrium constant of reaction (5) and  $a_i$  denotes the activity of species  $i$ . The equilibrium constant is calculated from the standard-state Gibbs energies  $G$  as (8) The activities of dissolved species are related to the molalities  $m_i$  and activity coefficients  $.i$  by (9) At equilibrium, the affinity of the reaction is equal to zero. In the particular case when reaction (5) occurs between an aqueous and a solid species, the equilibrium corresponds to the precipitation of an infinitesimal amount of the solid phase. If reaction (5) is between two aqueous species, the point of zero affinity corresponds to equal activities of the species  $X$  and  $Y$ . If the affinity is positive, the species on the right-hand side of equation (5) predominates. Similarly, if the affinity is negative, the species on the left-hand side is predominant. The species that is not predominant may be either completely absent (which is usually the case for precipitation equilibria) or may be present in smaller quantities than the predominant species. The values of the affinity of the chemical reaction (equation [7]) are calculated for each step of the simulated titration. This allows us to construct a discrete function, i.e., (10) where  $varp$  is the independent variable (such as pH or concentration of a complexing agent) at the point  $p$  of the simulated titration,  $Ap$  is the corresponding value of the affinity of reaction (8) and  $N$  is the total number of steps in the simulated titration. The function (10) is then interpolated using cubic splines. The interpolating function is used to find the independent variable  $var0$  for which  $A=0.$ , i.e., (11) The independent variables found in this way are later used as the coordinates of the vertical lines on the stability diagram. After finding the root of equation (11), it is necessary to check which one of the two species is more stable at  $var>var0$  and at  $var<var0$ . This is easily accomplished by checking the sign of the function  $f(var)$ . For particular pairs of species, the root of equation (11) may not be found, which means that one of the species is more stable in the entire range of independent variables. The analysis of chemical equilibrium equations is repeated for each pair of species, for which the number of electrons  $.e$  is zero. Thus, a collection of vertical boundaries in the stability diagram is established. Electrochemical reactions. In the case of electrochemical reactions, the number of electrons  $.e$  in equation (5) is not equal to zero. In this case, equilibrium potentials that correspond to reaction (5) are computed for each pair of species  $X$  and  $Y$ , i.e., (12) where  $R$  is the gas constant,  $F$  is the Faraday constant and  $E0$  is related to the standard-state Gibbs energies by (13) In eq. (12), the activities  $a_i$  pertain to either solution or solid species. For solution species, they are calculated from the thermodynamic model of aqueous solutions (Rafal et al., 1995). For solid species that are components of alloys, the thermodynamic model of alloys (subtask 1.1) is used. For pure solid species, the activity is equal to one. The values of the potential are obtained from eqs. (12-13) for each step of the simulated titration and used to construct a discrete function of the independent variable, i.e., (14) where  $varp$  is the independent variable at the point  $p$  of the simulated titration and  $Ep$  is the value of the potential calculated from equation (12). The function (14) is then interpolated using cubic splines. Areas of predominance. After determining the equilibrium lines that correspond to chemical and electrochemical equilibria, areas of predominance are computed for each species in the redox subsystem of interest. For each species, four classes of boundaries are differentiated: (1) Upper boundaries, which correspond to equilibria with other species that are in higher oxidation states. If the number of electrons  $.e$  in equation (4) is positive, the line determined by equation (12) will be an upper boundary for the species  $X$ . Conversely, if  $.e<0$ , the line determined by equation (12) will be an upper

boundary for the species Y. (2) Lower boundaries, which correspond to equilibria with other species that are in lower oxidation states. The line determined by equation (12) will be a lower boundary for the species X if  $\Delta G < 0$  or a lower boundary for Y if  $\Delta G > 0$ . (3) Right-hand side boundaries, which mean that the species under consideration is predominant for independent variables that are lower than the root  $\varphi_0$  of equation (10). (4) Left-hand side boundaries, which mean that the species is predominant for independent variables that are greater than  $\varphi_0$ . The sign of the affinity (equation [10]) is used to determine whether a vertical boundary is a right- or left-hand side boundary. In general, there can be several boundaries of each kind. Therefore, an automatic procedure is set up to find intersection points between the boundaries and determine which ones are active (e.g., the lowest upper boundary and the highest lower boundary will be active for any given independent variable). In the case of systems in which the basis species are adjusted depending on the stability of the potential ligands, the stability areas of the ligands are determined prior to the calculation of the predominance areas for the redox subsystem of interest. Then, the predominance areas for the redox subsystem are separately determined within the stability area of each ligand. Despite the separate determination of the predominance areas in different parts of the diagram, there is always a smooth transition at the boundaries between the ligand stability areas because the reaction equilibria, concentrations and activity coefficients in each ligand stability area are interdependent and mutually consistent. Thus, stability diagrams can be now generated for common engineering alloys in aqueous environments. Also, the data bank of thermodynamic properties has been extended to include mixed metal oxides, which are responsible for passivity in stainless steels and nickel-based alloys. Subtask 1.4: Verification of the predictions of the real-solution alloy stability diagrams. The obtained stability diagrams for alloys have been extensively verified by comparing the predictions with experimentally obtained corrosion tendencies. This verification has been carried out by the development team at OLI Systems and by Steven L. Grise at DuPont. An example is shown in Figure 3 for carbon steel at high temperatures. As shown in the figure, the stability areas of passivating oxides correspond to low corrosion tendencies whereas the stability areas of aqueous ions correlate with high corrosion tendencies. The vertical bars in Figure 3 show the difference between the equilibrium potentials for predominant reduction and oxidation processes. The mixed potential establishes itself between the two equilibrium potentials. Thus, the stability diagrams can be used to predict whether the mixed potential corresponds to the presence of a potentially passivating oxide. Figure 3. Verification of the calculated stability diagram for carbon steel at 300 °C. The vertical bars show the difference between the equilibrium potentials for reduction and oxidation reactions and bracket the mixed potential. The numbers over the vertical bars denote the experimental corrosion tendencies (Partridge and Hall, 1959). Figure 4. Stability diagram for Fe species in pure iron Figure 5. Stability diagram for Fe species in type 316L stainless steel. Figure 6. Stability diagram for Monel at 25 °C. The alloy diagram shows a superposition of component diagrams for copper and nickel. The tendency for corrosion in aerated and deaerated H<sub>2</sub>SO<sub>4</sub> solutions is shown as vertical bars and compared with observed corrosion rates. Figure 7. Stability diagram for Monel as a function of the concentration of ammonia. The tendency for corrosion in aerated ammonia solutions is shown as a vertical bar and compared with observed corrosion rates. Further, corrosion tendencies have been analyzed for various Fe-Cr-Ni-Mo alloys and the stability fields of multicomponent oxides have been related to the observed corrosion tendencies. Figures 4 and 5 exemplify the substantial differences in the stability field that result from the presence of mixed oxides (Ni-Cr-Fe oxides). Such oxides are thermodynamically stable in the passive layers on stainless steels and nickel-base alloys. Figure 6 shows a stability diagram for

Monel as a function of pH. It illustrates how the predicted tendency for corrosion in acidic, aerated or deaerated solutions can be correlated with the observed corrosion rates. As expected, a greater corrosion tendency correlates with greater corrosion rates. Figure 7 shows a stability diagram for Monel in an ammonia solution. In contrast to the previous diagrams, the concentration of ammonia is used as an independent variable. Complexation with ammonia is a commonly known cause of corrosion in such systems. As shown in Figure 7, complexation leads to the dissolution of the oxide film, which accounts for the substantial corrosion rate. Similar diagrams can be generated with ease using the OLI software. Subtask 1.5: Commercialization of the real-solution alloy stability diagrams for aqueous systems. As a vehicle for the commercialization of the stability diagram code, we have developed the Corrosion Analyzer, a Windows software product that encapsulates the models developed in this project. The Corrosion Analyzer provides a convenient interface that allows the user to generate stability diagrams for alloys and pure metals in contact with aqueous systems containing virtually any combination of electrolyte components and organic solutes. The Corrosion Analyzer is commercially available from OLI Systems. Information about this software product can be obtained from the website [www.olisystems.com](http://www.olisystems.com). Task 2: Development of a Model for Thermodynamic and Transport Properties of Mixed-Solvent Electrolytes Prior to this project, a comprehensive thermodynamic model was available for aqueous systems, i.e., systems in which water is the dominant solvent with a mole fraction of at least 0.6 (Zemaitis et al., 1985, Rafal et al., 1995). While this model provides an excellent representation of the properties of aqueous solutions, it was not applicable to nonelectrolyte-based systems or very concentrated electrolyte solutions. Thus, the objective of this task was to develop a comprehensive model that would predict both speciation and phase equilibria in mixed-solvent electrolyte systems. Subtask 2.1: Identification of critical mixed-solvent systems. The objective of this subtask was to identify the most important systems that can be used as benchmarks for the development of the mixed-solvent electrolyte model. The key systems include: Acid-water systems: Sulfuric acid, principal carboxylic acids (formic, acetic, citric and other mono- and dicarboxylic acids), nitric, hydrochloric, hydrobromic, hydrofluoric and sulfamic acids; Other inorganic-water systems: Ammonia, calcium chloride Organic-water systems: Methanol, ethylene and propylene glycols, EDTA and monoethanolamine Mixed systems: CaCO<sub>3</sub> / formic or citric or sulfamic acid; Na<sub>2</sub>CO<sub>3</sub>\* / Na<sub>2</sub>SO<sub>4</sub>\* / Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> / catechol; H<sub>2</sub>SO<sub>4</sub> + FeSO<sub>4</sub> + H<sub>2</sub>O While these systems were used as benchmarks for model development, the model is applicable to a much wider variety of chemical systems. Subtask 2.2: Development of a thermodynamic model for mixed-solvent electrolytes. Numerous electrolyte solution models including those for mixed-solvent systems have been reported in the literature. In a recent paper [Anderko et al., 2002], electrolyte solution models have been reviewed with emphasis on mixed-solvent systems. In general, three classes of models can be distinguished, i.e., models that treat electrolytes on an undissociated basis, those that assume complete dissociation of electrolytes into constituent ions and speciation based models, which explicitly treat the solution chemistry. Although comparable results can be obtained for phase equilibrium calculations (especially vapor-liquid equilibria) with models that belong to various groups, speciation calculations become necessary whenever solution chemistry is sufficiently complex to manifest itself in thermodynamic properties. In mixed solvents, ion pairing can be significant in comparison with aqueous environments due to the change of solvent properties such as a decrease in the dielectric constant. It is known that the degree of ion association varies substantially with solvent composition and the dielectric constant [2,3]. The change in ion association with composition can also be significant in common acids, such as the H<sub>2</sub>O-HF and H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> mixtures. Speciation variations can also have a significant



effect on phase equilibria, such as the solubility of salts, especially in multisalt, mixed-solvent systems. In general, solution chemistry is an inherent part of the nonideality of electrolyte solutions and needs to be properly accounted for. Finally, speciation is of critical importance for corrosion analysis because it determines properties such as pH or complexation of metals. Thus, it is desirable to extend the definition of mixed-solvent electrolytes to include liquid salts and to develop thermodynamic models that are capable of reaching this limit. In this work, we present a new, general, speciation-based thermodynamic model for mixed-solvent electrolyte systems. Here, the term "mixed-solvent electrolyte" encompasses systems of the following types:

- Aqueous electrolyte solutions from infinite dilution to fused salt;
- Fully miscible inorganic systems (e.g. H<sub>2</sub>SO<sub>4</sub>-water and HF-water) in a full concentration range;
- Electrolytes in organic or mixed organic + water solvents;

The model is designed to represent phase and chemical equilibria as well as thermal and volumetric properties in mixed-solvent electrolyte systems. The model is validated using experimental data on vapor-liquid equilibria, solubility, activities and activity coefficients, acid dissociation constants, Gibbs energies of transfer, heats of dilution and mixing, heat capacities, and densities.

**Thermodynamic Framework.** The nonideality of an electrolyte solution arises from various forces including electrostatic (long-range) effects due to the electric charges of ionic species [Debye and Huckel, 1924, Robinson and Stokes, 1959], chemical forces that lead to association or complex formation, physical dispersion forces and structural differences (e.g. in shape and relative size) between species [Prausnitz et al., 1986]. While the long-range forces predominate in dilute electrolyte solutions, the chemical and physical forces become increasingly important at moderate and short separation distances between species. The physical chemistry of electrolyte solutions becomes rather complex when all of these interactions occur simultaneously. To take into account the various effects, an expression for the excess Gibbs energy can be constructed as a sum of three terms: (1) where represents the contribution of long-range electrostatic interactions;  $G$  is the short-range contribution resulting from molecule/molecule, molecule/ion, and ion/ion interactions; and an additional (middle-range) term  $G$  accounts for ionic interactions (e.g. ion/ion and ion/molecule) that are not included in the long-range term. Similarly, the activity coefficient is given by (2) To account for speciation, the chemical effects due to the formation of ion pairs and complexes or the dissociation of these species can be explicitly expressed using chemical equilibria. Thus, for a chemical reaction: (3) the equilibrium conditions can be determined from (4) with (5) where is the standard-state chemical potential of species  $i$ , the sum is over all species participating in the chemical reaction, and is the stoichiometric coefficient of species  $i$  in Eq. (3) with positive values for the species on the right-hand side of the equation and negative values for those on the left-hand side. The algorithm for the determination of the chemical speciation in a mixed-solvent electrolyte system is similar to that used for aqueous solutions as described by Rafal et al. (1995). Thus, additional constraints, such as charge balance and the material balance, are used in the computation. For VLE calculations, the nonideality of the vapor phase can be conveniently modeled using a cubic equation of state such as the Soave-Redlich-Kwong (SRK) EOS. Thus, the model presented in this work combines an expression for the excess Gibbs energy with chemical equilibrium relations that arise from ion association, complex formation, hydrolysis, etc. Reference state. An important issue in modeling electrolyte solutions is the selection of a reference state. For the long-range electrostatic interaction term, the commonly used expression is that originally developed by Debye and Hückel [1924]. The Debye-Hückel theory was originally developed in the McMillan-Mayer framework where the solvent appears only as a dielectric continuum, and the ionic reference state is always at infinite dilution in the dielectric medium. In

general, such an unsymmetrical reference state depends on the composition of the solvent mixture. On the other hand, the excess Gibbs energy models used to represent the short-range interactions, such as NRTL and UNIQUAC, use the pure liquid at the system temperature and pressure as the reference state. Thus, in modeling mixed-solvent electrolyte solutions, different reference states are generally used for ionic species and for solvents, i.e., the infinite-dilution state in pure water or in a mixed solvent has been used as the reference state for ions, and the pure liquid is commonly used as the reference state for solvents. In addition, concentration units used in some of these models are different for the electrolytes and for the solvents. Commonly, molality is used for the electrolyte or "solute", and mole fraction is used for the "solvent". The use of molality does not allow the model to be extended to very concentrated electrolytes that approach fused salts or pure acids. In some models, in which the long-range interaction contribution has been neglected, a symmetrical reference system is used for all components (i.e., for both the solutes and solvents). This is justified by the fact that the effect of long-range electrostatic interactions on phase equilibria is negligible for electrolyte concentrations sufficiently remote from infinite dilution. In addition, a reference state based on the infinite dilution in water limits the applicability of the model to water-dominated systems. On the other hand, models that neglect the long-range interaction contribution and use the symmetrical convention for all components do not show the correct limiting behavior according to the Debye-Hückel theory and are not suitable for chemical equilibrium calculations because the electrolyte is assumed to be undissociated. In view of the necessity to perform speciation calculations and in order to make the model applicable over wide ranges of compositions, the symmetrical reference state has been selected in the present work. Thus, for any of the three contributions to the excess Gibbs energy, the activity coefficient is normalized to the unit mole fraction, i.e. as for all of the species. Obviously, such a reference state is hypothetical for ions. The symmetrical reference state makes no distinction between the "solvent" and the "solute". This is especially convenient when modeling thermodynamic properties of liquid mixtures of any composition, e.g. electrolyte solutions from infinite dilution to fused salts or acids or non-electrolyte mixtures in full concentration ranges. The concentration unit in the model is mole fraction for all species. Standard state chemical potentials. As discussed above, speciation calculations require the use of standard-state chemical potentials,  $\mu_i^\circ$ , for all species that participate in a chemical reaction. For electrolyte solutions, the standard-state chemical potential can be generally based on the following conventions: (1) infinite dilution in water on the molality scale (unsymmetrically normalized,  $\mu_i^\circ$ , where "\*" in the superscript denotes infinite dilution with respect to water); (2) infinite dilution in water on the mole fraction scale (unsymmetrically-normalized,  $\mu_i^\circ$ ); (3) pure component on the mole fraction scale (symmetrically normalized,  $\mu_i^\circ$ ). Thermochemical data for aqueous species are available from extensive thermodynamic databases, and the temperature and pressure dependence of the standard-state properties can be calculated using a comprehensive model developed by Helgeson and coworkers (commonly referred to as the Helgeson-Kirkham-Flowers equation of state [Helgeson et al., 1974, 1976, 1981]). The parameters of this model are available for a large number of aqueous species including ions, associated ion pairs, and neutral species (inorganic and organic) [Shock and Helgeson, 1988, 1990, Shock et al., 1989, 1997, Sverjensky et al., 1997]. These standard-state property data, which provide a basis for speciation calculations, are based on the infinite-dilution-in-water reference state and on the molality concentration scale. When combined with symmetrically normalized activity coefficients for speciation calculations, these standard-state properties need to be appropriately converted. Conversion of the standard-state chemical

potentials among the three reference states can be performed on the basis of an activity coefficient model [Anderko and Malanowski, 1992]. In addition, due to the change of the solvent from water to a solvent mixture, the Gibbs energy of transfer of the electrolyte must be correctly accounted for to ensure the correctness of the chemical potentials in the mixed solvent for speciation calculations. Long-range interaction contribution. Various Debye-Hückel-type excess Gibbs energy expressions have been proposed in the literature to represent the long-range electrostatic interactions between ions at low electrolyte concentrations. The extended form proposed by Pitzer et al. has been most satisfactory in empirical tests [Pitzer, 1973, 1980]. Thus, because of its empirical effectiveness, the Pitzer-Debye-Hückel expression is used for the long-range electrostatic contribution in this study. When normalized to mole fractions of unity for any pure species, the Pitzer-Debye-Hückel expression for the excess Gibbs energy is written as (6) where the sum is over all of the species (ionic and neutral) and  $I_{x,i}$  is the mole fraction-based ionic strength defined by (7)  $I_{x,i}$  represents the ionic strength when the system composition reduces to a pure component  $i$ , i.e.,  $I_{x,i} = \frac{1}{2} \sum z_i^2$ .  $\beta$  is related to a hard-core collision diameter and is treated as an empirical constant [34,40]. A value of  $\beta = 14.0$  is used in this study. The  $A_x$  parameter is given by (8) where  $N_A$  is the Avogadro number ( $6.022137 \times 10^{23} \text{ mol}^{-1}$ );  $d_s$  is the molar density of the solution ( $\text{mol} \cdot \text{m}^{-3}$ );  $e$  is the electron charge ( $1.602177 \times 10^{-19} \text{ C}$ );  $p = 3.14159$ ;  $\epsilon_0$  is the permittivity of vacuum ( $8.8541878 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$ );  $\epsilon_s$  is the dielectric constant;  $k_B$  is the Boltzmann constant ( $1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ ) and  $T$  is temperature in K. It has been long recognized from experimental evidence that there is a strong concentration dependence of the dielectric constant of ionic solutions [Akhadov, 1980]. For a comprehensive representation of the properties of mixed-solvent electrolyte systems, the effect of composition on the dielectric constant should be taken into account. A general model for the composition dependence of the dielectric constant has been developed in a previous paper [Wang and Anderko, 2001] and has been used in this study to calculate  $\epsilon_s$  in the Pitzer-Debye-Hückel long-range contribution term. By including this dielectric constant model, the long-range contribution reflects the electrostatic effects in the actual solution environment. Differentiation of Eq. (6) with respect to the number of moles at a constant temperature and pressure yields the following expression for the activity coefficient for any species  $k$  (ions and molecules): (9) It should be noted that the composition dependence of both density and the dielectric constant has been taken into account in the long-range interaction term. The sums in this expression cover all species. Short-range interaction contribution. The short-range interaction contribution includes the interactions between all species. Local composition models originally developed for nonelectrolyte mixtures, such as the NRTL, Wilson, and UNIQUAC models, are appropriate for representing the short-range interactions in mixed solvent electrolyte systems. In this work, the UNIQUAC model [Abrams and Prausnitz, 1975] is selected for this purpose. The advantages of using UNIQUAC in representing short-range interactions are that (1) its parameters often have a smaller temperature dependence compared to other models, which facilitates the use of fewer parameters when fitting data covering a wide temperature range; (2) it is applicable to solutions containing small or large molecules including polymers, because the primary concentration variable is the surface fraction, rather than the mole fraction; (3) it can be extended to a group contribution framework, such as UNIFAC, to enhance the model's predictive capability. The excess Gibbs energy in the UNIQUAC model is calculated as a sum of a combinatorial and a residual term [44]. (10) with (11) (12) (13) (14) (15) where  $q_i$  and  $r_i$  are the surface and size parameters, respectively, for the species  $i$ ;  $Z$  is a constant with a value of 10;  $a_{ij}$  is the binary interaction parameter between species  $i$  and  $j$  ( $a_{ij} = a_{ji}$ ). When applied to mixed-solvent electrolyte solutions, the subscripts  $i$  and  $j$  in

these equations include all molecules (solvent molecules and undissociated electrolyte or neutral complexes) and ions. The activity coefficient equations that correspond to eqs. (10-15) are given by Abrams and Prausnitz [1975]. Middle-range interaction contribution. The middle-range term arises from interactions involving charged species (i.e. ion/ion and ion/molecule) that are not included in the long-range term. A symmetrical second virial coefficient-type expression is used to represent this contribution: (16) The quantity is a binary interaction parameter between the species i and j (ion or molecule) and is similar to the second virial coefficient representing the hard-core effects of charge interactions, which are found to be ionic strength-dependent [Pitzer, 1973]. The parameter has been assumed to be symmetric, i.e. , and . The activity coefficient is expressed as: (17) Thermodynamic Consistency in Speciation Calculations. As discussed at the beginning of this section, the computation of chemical equilibria requires the simultaneous use of activity coefficients and standard-state thermodynamic properties of all species participating in chemical reactions. Since the standard-state properties from the available thermodynamic databases and the Helgeson-Kirkham-Flowers equation of state [Helgeson et al., 1974, 1976, 1981] are defined for infinite dilution in water on the molality basis, an appropriate conversion must be performed to make speciation calculations consistent when these properties are combined with the mole fraction based, symmetrically-normalized activity coefficients. For this purpose, the mole fraction-based activity coefficient of species k in the symmetrical reference state, , is first converted to that based on the unsymmetrical reference state, i.e. at infinite dilution in water, , via (18) where is the value of the symmetrically-normalized activity coefficient at infinite dilution in water, which can be calculated by substituting and into the activity coefficient equations. At the same time, the unsymmetrical, molality-based standard-state chemical potential, , can be converted to a mole fraction-based quantity, , by (19) where MW is the molar weight of water. The unsymmetrical activity coefficient based on Eq. (18) can then be used with the standard-state chemical potential calculated using Eq. (19) for chemical equilibrium calculations. It should be noted that this procedure remains valid even when the system of interest does not contain any water. Standard Gibbs energy of transfer. As discussed above, the available extensive databases of thermochemical properties for aqueous species provide a foundation for modeling speciation in aqueous systems. When applied to speciation calculations in mixed solvent electrolyte systems, the aqueous standard-state properties must be combined with accurately predicted Gibbs energies of transfer to ensure an accurate representation of chemical potentials. Thus, it is important for the activity coefficient model to reproduce the Gibbs energies of transfer. In the present model, an accurate representation of the Gibbs energy of transfer is achieved by imposing constraints on the parameters of the activity coefficient model. For this purpose, we derive an expression to relate the Gibbs energy of transfer to the activity coefficients in aqueous and nonaqueous (or mixed-solvent) environments. The Gibbs energy of transfer of ion i from solvent R to solvent S on a molal concentration (m) scale is defined as (20) where and are the standard state (infinite-dilution) chemical potentials of ion i in solvent S and R, respectively. Through appropriate thermodynamic manipulation, the standard state chemical potential of ion i in solvent S can be related to that in water ( ) and to the unsymmetrical (referenced to infinite dilution in water) activity coefficient, i.e., (21) where and are the molality and mole fraction, respectively, of ion i in solvent S, and is the mole fraction-based unsymmetrical activity coefficient of ion i in solvent S, which can be calculated using the excess Gibbs energy model described in previous sections. By substituting Eq. (21) into Eq. (20), a general expression is obtained: (22) where and are the molecular weights of solvent S and R, respectively.. At infinite dilution, the Gibbs energy of transfer for an electrolyte from solvent

R to S can be obtained by adding those of its constituent cation and anion. It should be noted that most published standard Gibbs energies of transfer are on the molar scale. Conversion of the standard Gibbs energy of transfer between the molar (M) and molal (m) scales is necessary for consistent calculations. This is made using the following expression [Marcus, 1997]: (23) where  $\rho$  is the density of the designated solvent, and  $\nu_+$  and  $\nu_-$  are the stoichiometric coefficients of the cation and anion in the electrolyte. Evaluation of model parameters. The validation of the model and the evaluation of model parameters require a large amount of experimental data of various types. The types of experimental data used in the determination of model parameters include the following: • Vapor-liquid equilibrium data; • Activity coefficients in completely dissociated aqueous systems (such as NaCl); • Osmotic coefficients (or activity of water) in aqueous solutions; • Solubility of salts in water, organic solvents and mixed solvents; • Acid dissociation constants as a function of solvent composition; • Gibbs energy of transfer of electrolytes; • Densities; • Heats of mixing and dilution; • Heat capacities. These experimental data cover the concentration ranges of (where  $x_+$  is the solubility of the salt) or  $x_+$ , whichever applies, and temperatures up to 300°C. The adjustable parameters in the model are the binary interaction parameters in the UNIQUAC and the middle range terms. These parameters are determined by simultaneous inclusion of all available experimental results of the above types in a single data regression run, and minimization of the differences between the experimental and calculated property values. The structural parameters (surface area and size) in the UNIQUAC term for all non-electrolyte components are based on Bondi's [1968] normalized values of van der Waals group volumes and surface areas. The values for ionic species are fixed to be 1.0. For inorganic neutral species, the surface and size parameters are assigned to be equal to those of water ( $r=0.92$ ;  $q=1.4$ ). For the UNIQUAC binary interaction parameters, and  $\beta$ , quadratic temperature dependence has been found, in most cases, satisfactory for fitting experimental data:  $\beta = \beta_0 + \beta_1 T + \beta_2 T^2$ . For mixed solvents, they are the weighted molar weights, i.e.  $\beta = \sum_k w_k \beta_k$ , where the sum is over all solvent components,  $w_k$  is the mole fraction of component  $k$ , and  $M_k$  is the molecular weight of  $k$ . (34) For the middle-range term, the second virial coefficient-type parameters,  $\beta_{ij}$ , for charge interactions (ion/ion, ion/molecule) are represented by an empirical expression: (35) where  $\beta_{ij}$ ,  $c$ ,  $\beta_{ij}^0$ ,  $\beta_{ij}^1$ , and  $\beta_{ij}^2$  are adjustable parameters and  $a$  is set equal to 0.01. The presence of the constant prevents the occurrence of an infinite value of  $\beta_{ij}$  at when Eq. (16) is differentiated to yield Eq. (17). The decrease of the second virial coefficient with ionic strength, which is embodied by Eq. (35), has been noted before [Pitzer, 1973]. In a statistical thermodynamic treatment of electrolyte solutions, Pitzer [1973] derived a function of ionic strength that qualitatively describes the behavior of the second virial coefficient that arises from charge interactions as "short-range" effects (relative to the Debye-Hückel long-range effect). This function has provided a basis for the expressions for the second virial coefficient-type parameters. The expression given in Eq. (35) varies with the ionic concentration in a way that is consistent with the trend described by Pitzer [1973] and is adopted based on its effectiveness in fitting experimental data. To model densities of mixed solvent electrolyte solutions, additional adjustable parameters are introduced to include the pressure dependence in binary parameters. For this purpose, the following function is used in the UNIQUAC term for representing densities at saturation pressures, (36) The function for the pressure dependence of the middle-range parameter is (37) Here, the parameters,  $a$ ,  $\beta_{ij}$  and  $\beta_{ij}^0$ ,  $\beta_{ij}^1$ ,  $\beta_{ij}^2$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ ,  $g$ ,  $h$ ,  $i$ ,  $j$ ,  $k$ ,  $l$ ,  $m$ ,  $n$ ,  $o$ ,  $p$ ,  $q$ ,  $r$ ,  $s$ ,  $t$ ,  $u$ ,  $v$ ,  $w$ ,  $x$ ,  $y$ ,  $z$ , are determined separately from parameters that are used for phase equilibrium and enthalpy calculations (cf Eqs. (34) and (35)). It should be noted that the complete model reduces to UNIQUAC for nonelectrolyte mixtures. Subtask 2.3: Review of the basis of the model by Academic Review Panel The Academic Review Panel (as described for Subtask 1.2) has reviewed the mixed-solvent electrolyte

model and provided feedback to the developers. Subtask 2.4: Integration of the mixed-solvent electrolyte model with OLI software. The mixed-solvent electrolyte model has been integrated with the OLI Engine, which computes chemical and phase equilibria for multicomponent, multiphase systems. For this purpose, the OLI Engine was revised to work over the whole concentration range for mixtures containing both ionic and nonionic components. Also, a regression program has been developed to compute model parameters by simultaneously utilizing phase equilibrium and caloric data. An additional effort was made to accelerate the computation of standard-state properties from the equation of state of Helgeson et al. (1974, 1976, and 1981). Also, the code for computing activity coefficients has been streamlined to accelerate the computations. With these improvements, the computation time is now comparable to that observed for the OLI aqueous-only model. Subtask 2.5: Extension of transport property models to mixed-solvent systems. The diffusivities of electrochemically active species are necessary for modeling the kinetics of reactions that are responsible for corrosion at the metal-solution interface. Therefore, a comprehensive model has been developed for predicting the diffusion coefficients in mixed solvent electrolyte solutions. The model is designed to be applicable to mixed-solvent electrolyte solutions over wide ranges of solvent composition and electrolyte concentration (i.e. from infinitely dilute to concentrated salt solutions). Further, the model is designed to predict the self-diffusivity of all species in multisolvent, multi-solute solutions using information obtained from data for single-solute, single solvent systems. Also, the model accounts for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model consists of two parts: (1) computation of limiting diffusion coefficients of ionic or molecular species in pure and mixed solvents as a function of temperature and solvent composition and (2) computation of the dependence of the self-diffusion coefficients on electrolyte concentration. Limiting Self-diffusion Coefficients. Limiting diffusivities of ions have been reported in various pure solvents and in mixed-solvent systems as a function of the solvent composition. In general, diffusivity data in organic solvents are relatively few compared to those in aqueous solutions, and the majority of the available data are reported at 25°C or over a narrow temperature range. Marcus (1987) collected the transport properties of ions including the conductivity or self-diffusivity at infinite dilution in water and in a number of pure organic solvents at 25°C. Also, Krungalz (1983) compiled limiting diffusivity data at varying temperatures for 14 ions in several organic solvents. In the case of ions, the limiting self diffusion coefficient in a solvent  $s$ ,  $D_{i,s}^{\infty}$ , is related to the limiting equivalent conductance,  $\Lambda_{i,s}^{\infty}$ , by the Nernst-Einstein Equation: (38) where  $R$ ,  $F$ , and  $z$  are the ideal gas constant, Faraday constant, and ionic charge, respectively. In the case of aqueous solutions, Anderko and Lencka (1998) used the equation of Smolyakov and Veselova (1975) to reproduce the limiting self-diffusion coefficients of ions and neutral molecules. This method is also used in this study for aqueous solutions. However, for organic solvents, the transition state theory used by Oelkers and Helgeson (1988) has been found to be more effective for representing the temperature dependence of the limiting conductivity or self diffusivity of ions and neutral molecules. Thus, the ionic limiting conductivity in a pure solvent  $s$  can be reproduced by an Arrhenius-type equation of the form: (39a) or simply by (39b) For neutral molecules, an analogous equation can be obtained by combining Eqs. (38) and (39b): (40) where  $A_i$ ,  $B_i$ , and  $C_i$  are adjustable parameters specific to the ion or molecule ( $i$ ) and the solvent ( $s$ ). Equations (39) and (40) have been found to reproduce the temperature dependence of limiting ion conductivities and self-diffusion coefficients of neutral molecules in organic solvents within experimental uncertainty. For complex species, the limiting self-diffusivity can be estimated using the equation previously developed by Anderko and Lencka (1998),

i.e. (41) where the  $D_{i,0,s}$  values are the limiting diffusivities of the simple ions that make up the complex. Limiting diffusivity in mixed solvents. The limiting ion conductivity or diffusivity data in mixed solvents are relatively few compared to those in pure solvents. Thus, it is desirable to develop a model for representing the limiting diffusivity in mixed solvents using data obtained for the constituent pure solvents. In this study, a new, general model is developed for the limiting ion conductivity or self-diffusivity in solvent mixtures that may contain any combinations of components. For this purpose, a mixing rule is proposed to relate the limiting conductivity or diffusivity in the mixed solvent to those in the constituent pure solvents. Thus, the limiting conductance of an ion  $i$  in a mixed solvent is represented by (42) where  $j$  and  $k$  are solvents, and  $\bar{D}_{ijk}$  is a modified arithmetic average of limiting ion conductivities as defined by: (43)  $Y_j$  is a modified volume fraction of the solvent  $j$ : (44)  $v_{ij}$  is an adjusted molar volume of the solvent  $j$  in the presence of ion  $i$  and other solvents denoted by  $k$ : (45) Here,  $\lambda_{i0}$  is the limiting conductivity of ion  $i$  in the mixed solvent, and  $\lambda_{i0j}$  and  $\lambda_{i0k}$  are the limiting conductivities of ion  $i$  in pure solvents  $j$  and  $k$ , respectively;  $x_j$  is the mole fraction of the constituent solvent  $j$ ,  $v_j$  is the liquid molar volume of the pure solvent  $j$ , and  $\alpha_j$  are adjustable parameters determined from experimental limiting conductivity data. The parameter  $\alpha_j$  accounts for the effect of solvent molar volumes on the variation of the limiting ion conductivity with composition. It has been found that the limiting ion conductivity versus composition curve strongly depends on the redefined molar volumes ( $v_j$ ) of the components. The quantity may be interpreted as an effective molar volume of the solvent  $j$ , which is affected by the presence of other solvents and the ion  $i$  in the mixture. This effect can be represented by Eq. (45) where the pure liquid molar volume ( $v_j$ ) is corrected for the presence of other solvent components,  $k$  ( $k \neq j$ ) and the ion  $i$ . It should be noted that, when  $\alpha_j = 0$  for all solvents  $j$  and  $k$ , reduces to  $v_j$  and, when all  $\alpha_j = 0$ , Eq. (45) becomes a simple volume fraction-averaged ideal mixing equation. For neutral species (including solvent molecules), a similar equation can be derived for the limiting diffusivity based on Eq. (38): (46) In Eq. (45),  $\bar{D}_{ijk}$  is a modified arithmetic average of limiting diffusivities as defined by: (47) The modified volume fraction of the solvent component  $Y_j$  is given by expressions similar to Eqs. (43) and (44): (48) and (49) Similarly, the parameters  $\alpha_j$  and  $k$  are adjustable constants determined from experimental limiting diffusivity data. The model uses only pure liquid molar volumes and limiting ion conductivities or diffusivities in pure solvents. It can be applied to solvent mixtures of any composition. In this study, the term "limiting self-diffusion coefficient" pertains to solutions in which the concentration of any solute species is zero or at infinite dilution. Thus, the model described by Eqs. 46-49 is also applicable to self-diffusion coefficients of solvent components in a solvent mixture of any composition. Self-diffusion Coefficients in Concentrated Single Electrolyte Solutions. The method developed by Anderko and Lencka (1998) for modeling the concentration dependence of self diffusivity in aqueous solutions is extended in the present work to mixed-solvent electrolyte systems. In electrolyte solutions, the concentration dependence of the self-diffusion coefficient of a tracer species  $i$  can be accounted for by the combination of two effects. In relatively dilute electrolyte solutions, the relaxation effect plays a dominant role. As the electrolyte concentration increases, short-range forces due to inter-particle interactions become increasingly significant. The effect of short-range interactions can be represented by the hard-sphere theory, which was originally developed for nonelectrolyte solutions. Thus, the self-diffusion coefficient of a tracer  $i$  in a single-solvent, single-electrolyte solution can be expressed as (Anderko and Lencka, 1998): (50) where  $D_{i0}$  is the limiting self-diffusion coefficient of the tracer  $i$  in a given solvent;  $\Delta D_{i0}$  is a contribution resulting from the relaxation effect; and  $\Delta D_{i0}$  represents the effects of short-range forces, which are calculated

from the hard sphere model. It should be noted that Eq. (50) and the equations that define the and terms pertain to a single-solvent electrolyte solution containing one cation and one anion. The relaxation factor is calculated from an expression developed by Bernard et al. (1992) and Chih et al. (1994) for systems containing ions of different sizes in a dielectric continuum. This expression was derived by combining the Onsager continuity equations with equilibrium correlation functions calculated from the Mean Spherical Approximation (MSA) theory. For a tracer  $i$ , the relaxation term is given by: (51) where  $z_i$  is the ionic charge,  $e$  is the charge of the electron,  $\epsilon_0$  is the permittivity of vacuum,  $k_B$  is the Boltzmann constant, and  $\epsilon$  is the dielectric constant of the solvent. In Eq. (51),  $r_i$  is the average ion diameter defined by (52) where  $\rho_i$  is the number density and  $d_i$  is the diameter of the  $i$ -th ion. The parameters  $\rho_i$  and  $d_i$  are given by (53) (54) and  $\kappa$  is the MSA screening parameter, calculated in the mean spherical approximation as (55) In Eqs. (52) ~ (55), the sums are over the two distinct ions (i.e., the cation and the anion). The hard-sphere contribution to the concentration dependence of the diffusion coefficient of a tracer ion in a solution containing a cation  $c$ , an anion  $a$ , and a solvent  $j$  can be expressed as: (56) where  $g_{ij}(0)$  is the radial distribution function at contact for rigid spheres of diameters  $d_i$  and  $d_j$ , and  $D_{ij}^0$  is the dilute gas diffusion coefficient for a mixture of molecules  $i$  and  $j$ . The superscript 0 denotes the pure solvent  $j$  at the same conditions as the solution. The coefficient is given by (57) where  $M_i$  is the molecular weight of species  $i$ ,  $N$  is the total number density, and  $d_{ij}$  is the average diameter defined as (58) The radial distribution function in Eq. (56), is calculated from (59) where (60) In order to apply the expressions for the relaxation and hard-sphere terms, it is necessary to calculate the relevant solvent properties, i.e., the dielectric constant (in the relaxation term), molecular weight (in the hard-sphere term) and density (in both terms). To extend the applicability of the relaxation and hard-sphere terms to mixed-solvent systems, the solvent properties need to be redefined as averaged values. Thus, the molecular weight of the solvent is calculated as a weighted average:  $M = \sum_j x_j M_j$  (61) where  $x_j$  and  $M_j$  are the salt-free mole fraction and the molecular weight, respectively, of solvent  $j$  and  $N$  is the number of solvent components in the solvent mixture. The density of the solvent mixture is calculated by assuming ideal mixing, i.e. (62) The dielectric constant of the mixed solvent,  $\epsilon$ , is calculated using a general model described in a previous paper (Wang and Anderko, 2001). The only species-dependent parameters in the model (Eqs. 50, 51 and 56) are the diameters,  $d_i$ . As a first approximation, crystallographic diameters can be used to estimate  $d_i$ . This approximation is reasonable for relatively dilute solutions. However, it becomes less accurate as the ionic concentration increases because of changes in the ionic environment. For example, a change in viscosity at higher concentrations entails a changing ionic mobility, which results from altered solvation structure and short-range interactions between ions. Therefore, to reproduce experimental diffusivities over wide composition ranges, Anderko and Lencka (1998) introduced an effective diameter. The effective diameter  $d_i^e$  reflects the effect of other species on the diameter of species  $i$  and is defined as (63) where  $c_l$  is the molar concentration of species  $l$  (i.e., ions or neutral species or solvent molecules). The parameter has the meaning of a species diameter and is treated as an adjustable parameter to reflect the interactions between species  $i$  and  $l$ . In mixed-solvent electrolyte solutions, the parameters that represent the interactions of species with the mixed solvent, and are defined as averages, i.e.,  $d_i^e$  and  $d_s^e$  (64) where  $i$  denotes a cation, an anion, or a neutral species including solvent molecules and  $s$  denotes the mixed solvent. Crystallographic diameters have been assumed for all of the parameters. It should be noted that, when applying Eq. 13 to mixed-solvent electrolyte systems, the value is the limiting self-diffusion coefficient of tracer  $i$  in the mixed solvent, as calculated from Eqs. 38 and 42



or Eq. 46. Self-diffusion coefficients in systems with multiple solutes and solvents. The equations for the relaxation and hard-sphere terms (Eqs. 50, 51 and 56) are limited to systems containing only a single electrolyte. For the treatment of multicomponent aqueous electrolyte solutions, Anderko and Lencka (1998) formulated a mixing rule on the basis of the Stefan-Maxwell formalism for multicomponent diffusion. Derivation of this mixing rule was described in a previous paper (Anderko and Lencka, 1998) and will not be repeated here. This formalism gives an accurate representation of the concentration dependence of self-diffusion coefficients in complex aqueous electrolyte solutions. By treating a mixed solvent as a single solvent with averaged properties, this mixing rule is readily extended to represent self-diffusion coefficients in systems with multiple solutes.

Subtask 2.6: Verification of the predictions of the mixed-solvent electrolyte model. The model has been validated using different types of experimental data for various classes of mixtures under wide ranges of conditions. The model can simultaneously reproduce VLE, activity coefficients, solubility, speciation in water and mixed solvents, Gibbs energy of transfer of electrolytes, heats of dilution and mixing, heat capacities, and densities in electrolyte solutions ranging from infinite dilution in water to fused salts or pure acids. Modeling results have been comprehensively described by Wang et al. (2002) and Wang and Anderko (2003). Here, we describe sample validation results for systems that are particularly important for modeling corrosion. The behavior of acids and bases in mixed solvents is of particular interest in the study of solution properties that are dependent on pH. For example, due to changes in ionization, the corrosivity of an acid or a base may change significantly with the composition of the solution in which the metal is immersed. In this work, systems containing acids in water and organic solvents were analyzed. The results of modeling VLE for the HCl-water and HCl-water-isopropanol systems are shown in Figs. 8 and 9. Figure 8 shows VLE results for HCl-water at 0 and 70°C. The results for the HCl-water-isopropanol system are shown in Fig. 9 at two compositions. In the systems shown in these figures, the electrolytes have been assumed to completely dissociate and the weak dissociation of the alcohols has been taken into account using acid dissociation constants from the literature. The results presented here show that the model can accurately reproduce experimental VLE and solubility data in salt-water-organic mixtures. Speciation is of particular interest in the study of solution properties that are dependent on pH, and in identifying the species that are responsible for certain phenomena such as corrosion or other electrochemical processes. Monoprotic acids such as formic and acetic acids in water-alcohol mixtures as well as the HF-H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O mixtures are among the systems that are characterized by moderate to strong ion association or polymerization. Extensive experimental VLE and thermal property data have been reported for these systems, and ionization constants for the monoprotic acids in water-alcohol mixtures are also available. These data are convenient for testing the speciation model. Acetic and formic acids are known to associate in aqueous solutions with the ionization constants of 10<sup>-4.76</sup> for the acetic acid and 10<sup>-3.75</sup> for the formic acid at 25°C. In mixed solvents, these ionization constants change with the solvent composition. The acids become more associated with an increase in the alcohol concentration and a decrease in the solvent dielectric constant. It is also well known that these acids are highly associated in the vapor phase to form dimers or higher polymers. Realistic modeling of these systems must take into account the speciation reactions (i.e., ionization and dimerization) in both the liquid and the vapor phases. The ionization constants for formic acid and acetic acid in water-alcohol mixtures such as water-methanol and water-ethanol have been reported in the literature [Panichajakul and Woolley, 1976, Sen et al., 1979]. Dimerization constants in the vapor phase for these acids are also available. With these constants, the model can reproduce both VLE and chemical speciation in both liquid and vapor

phases. The predicted apparent dissociation constants of the acids in alcohol-water mixtures are shown in Fig. 10 for the ionization constants of formic acid and acetic acid in ethanol-water mixtures, and in Fig. 11 for the same acids in methanol-water mixtures. Another system that exhibits significant speciation effects is HF-water. This system is of considerable interest from the perspective of industrial applications such as glass etching, stainless steel pickling, aluminum refining, alkylation catalysis, and manufacture of fluorine-containing plastics. This is a particularly difficult system because of a very strong change in dissociation as a function of composition, coupled with multimerization of HF. Hydrogen fluoride is known to have a fairly low ionic dissociation in water ( $pK_a=3.45$ ). Electrical conductivity measurements in extremely anhydrous hydrogen fluoride also indicate a very low concentration of dissociated HF, i.e.  $\sim 3 \times 10^{-8}$  at  $0^\circ\text{C}$ . At the same time, strong multimerization of pure HF in both the liquid and gas states has been recognized by many authors. The formation of dimers, hexamers and other products of self-association of HF in the vapor phase is well known and has been extensively investigated in the literature. Infrared spectroscopic data seem to indicate the existence of monomers, dimers, trimers, and higher polymers. Other studies have shown that PVT properties of the saturated HF vapor can be represented either by assuming only two molecular species, HF and  $\text{H}_6\text{F}_6$  and a single equilibrium,  $6\text{HF}(\text{vap})=\text{H}_6\text{F}_6(\text{vap})$  or by assuming multiple association models. The study of association of HF in the liquid phase is much less extensive. In the liquid phase, the HF dissociation is constrained by the acid dissociation constant of HF in water, as determined using available experimental data, and by the low ionic concentrations in anhydrous HF derived from conductivity measurements. Using vapor pressure data for the HF-water binary mixtures, and applying the constraints for the dissociation of HF, both phase equilibria and chemical speciation have been accurately reproduced over a wide temperature range and in the entire composition span as shown in Fig. 12. The speciation in the liquid phase and in the vapor phase in this system can be predicted as illustrated in Figs. 13 and 14 for  $40^\circ\text{C}$ . To validate the speciation results, the predicted and experimental vapor phase compressibility factors have been compared. This comparison is shown in Fig. 15. The compressibility factor is a measure of the association of HF, i.e., where  $Z$  is the total number of moles of all species in an associated mixture, and  $Z_0$  is the number of moles of all species that would exist in the absence of association. As shown in the figures, the present model can accurately represent the experimental results for vapor phase speciation. The thermodynamic treatment of sulfuric acid has been unusually difficult because of the change of the aqueous speciation ( $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ ) with concentration, and the dissociation of the acid in the vapor phase to form sulfur trioxide ( $\text{H}_2\text{SO}_4(\text{g}) = \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$ ). An accurate model of the system is highly desirable due to the great practical importance of this system. The interpretation of the Raman spectroscopic data indicates that a large fraction of the sulfuric acid is in the form of the associated  $\text{H}_2\text{SO}_4$  neutral species at high sulfuric acid concentrations (e.g.  $\sim 75\%$  of sulfuric acid is associated to  $\text{H}_2\text{SO}_4$  at  $\sim 0.4$ , and  $\sim 99\%$  is associated in pure sulfuric acid at  $25^\circ\text{C}$ ). The results of VLE calculations show a very good agreement between the experimental and predicted total vapor pressure over the entire concentration range at various temperatures, as shown in Fig. 16. The calculated partial pressure behavior in the  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  system is shown in Fig. 17 at  $100^\circ\text{C}$  in the vicinity of the sulfuric acid azeotrope. Of particular interest are the solubility relationships for corrosion products (e.g.,  $\text{FeSO}_4$ ) in  $\text{H}_2\text{SO}_4$  solutions. In particular, it can be shown that the corrosion rate of sulfuric acid is controlled by the solubility of  $\text{FeSO}_4$  in concentrated solutions. Figures 18 and 19 provide an example of the obtained results for solid-liquid equilibria and heat capacities, respectively, for the system  $\text{FeSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ . Figure 8. Calculated and experimental vapor liquid equilibrium results for the HCl-water

system at 0 and 70°C Figure 9. VLE results for the HCl-water-isopropanol mixture as a function of temperature at fixed liquid compositions. Figure 10. Apparent ionization constants of acetic acid and formic acid in ethanol-water mixtures as a function of the ethanol mole fraction Figure 11. Apparent ionization constants of acetic acid and formic acid in methanol-water mixtures as a function of the methanol mole fraction Figure 12. Calculated and experimental vapor-liquid equilibria for HF-water at 1.0 atm. Figure 13. Predicted liquid phase speciation in the HF-water system Figure 14. Predicted vapor phase speciation in the HF-water system. Figure 15. The reciprocal of the vapor phase compressibility factor,  $1/Z$ , of pure HF at various temperatures. Figure 16. VLE results for the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system at various temperatures Figure 17. The calculated partial pressures in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system at 100°C in the vicinity of the sulfuric acid azeotrope. Figure 18. Solubility results at 40°C for FeSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O mixtures as a function of the weight percent of sulfuric acid. Figure 19. Heat capacity of FeSO<sub>4</sub> solutions for various H<sub>2</sub>SO<sub>4</sub> concentrations at 20 and 25°C.

Task 3. Development of Software for Generating Stability Diagrams for Metals in Mixed-Solvent Systems Subtask 3.1: Integration of the mixed-solvent electrolyte model and the alloy stability diagrams. The software for generating stability diagrams for alloys has been integrated with the mixed solvent electrolyte model. For this purpose, the algorithm for generating real-solution stability diagrams (Task 1) has been extended so that the activities of solution species are calculated using the newly developed mixed-solvent electrolyte model (Task 2). With this extension, the liquid phase does not have to be aqueous and stability diagrams can be generated for any combination of components. Subtask 3.2: Verification of predictions of stability diagrams for mixed-solvent systems The stability diagrams for mixed-solvent systems have been verified for Fe-Cr-Ni-Mo alloys in systems containing protic solvents such as alcohols and glycols. In such systems, the formation of passive films depends on the presence of water in the system. Thus, water acts as a corrosion inhibitor when it is present in small concentrations. The stability diagrams are capable of representing this behavior by predicting the range of independent variables for which passive films are present. This is illustrated in Figures 20 and 21 for chromium. Similarly, Figures 22 and 23 show the difference in the stability fields for iron species in type 316L stainless steel in aqueous and methanolic solutions. As shown in these figures, the passivity range is much reduced in acidic and nearly-neutral methanolic solutions in comparison with aqueous solutions. This finding is in agreement with experimental results. Figure 20. E-pH stability diagram for Cr in aqueous solutions. PH was varied by changing concentrations of HCl and NaOH. Figure 21. E-pH stability diagram for Cr in methanolic solutions. PH was varied by changing concentrations of HCl and NaOH. Figure 22. E-pH stability diagram for Fe containing species in type 316 stainless steel in aqueous solutions. Figure 23. E-pH stability diagram for Fe-containing species in type 316 stainless steel in methanolic solutions. Figure 24. E-pH stability diagram for Zr in a mixture of methanol, a metal chloride and another solvent at 120 C. Severe general corrosion was observed. Figure 25. E-pH stability diagram for the system shown in Figure 25 with the addition of 1.5 wt% H<sub>2</sub>O. In this case, corrosion is inhibited. Figures 24 and 25 show the simulation of an actual experiment using stability diagrams for zirconium. Figure 24 was generated for Zr in a solution containing a mixture of methanol, a metal chloride and additional solvents at 120 °C. Such as solution is weakly acidic because of the hydrolysis of metal ions. As shown in Figure 24, the ZrO<sub>2</sub> passivating oxide is not stable under such conditions. This agrees with the observed severe general corrosion in this system (Saldanha, 1996). Figure 25 shows a stability diagram for the same system with the addition of 1.5 wt% H<sub>2</sub>O. In this case, the stability field of ZrO<sub>2</sub> is predicted to cover a wider range of pH, including the natural pH of the system. This prediction agrees

with the empirical observation that corrosion is inhibited by small concentrations of water in this system. Subtask 3.3: Commercialization of the software for generating stability diagrams for mixed-solvent systems The code for generating stability diagrams in mixed-solvent systems has been implemented in OLI's Corrosion Simulation Program (CSP). CSP provides the full functionality for corrosion analysis using a simple user interface. In the near future, this code will be integrated with the Corrosion Analyzer. Task 4. Development of a Kinetic Model of Metal Corrosion in Mixed Solvents Rates of general corrosion in aqueous environments depend on a multitude of factors such as the chemistry of the aqueous solution, concentrations of components, temperature, presence of nonaqueous phases, hydrodynamic conditions and metallurgical factors. Therefore, it is desirable to rationalize and predict the effects of these factors using computational models. For selected systems, models for calculating rates of corrosion have been developed by various investigators in the form of semi-empirical correlations, electrochemical models or expert systems. In this project, we have developed a model that is capable of taking into account the chemistry of the investigated systems in a comprehensive way. The model is designed to provide a realistic representation of chemical equilibria and thermophysical properties in the bulk solution and, at the same time, to account for the phenomena at the metal-solution interface. To achieve this, the model has been designed to satisfy the following requirements: (1) Utilize a comprehensive thermodynamic model to compute the speciation and activities of species in the aqueous solution; (2) Utilize models for calculating transport properties, which are necessary to predict mass transfer effects; (3) Represent the partial cathodic and anodic processes on the metal surface; (4) Reproduce the active-passive transition and the effect of active ions on passivity; (5) Reproduce experimental corrosion rates using parameters calibrated on the basis of a limited amount of data and (6) Be implemented in an easy-to-use program. The model has been described in detail in recently published papers (Anderko and Young, 2000, Anderko et al., 2001, Sridhar and Anderko, 2001). Here, we outline the fundamentals of the model and show sample validation results. Subtask 4.1: Extension of the kinetic model of corrosion to systems critical to the US chemical industry. Structure of the model. The starting point for corrosion analysis is the computation of speciation in the investigated system. For this purpose, the thermodynamic model outlined above is used. This model is used to predict the concentrations and activities of both ionic and neutral species in multicomponent systems that may contain an aqueous phase, any number of solid phases and, if necessary, a vapor and a nonaqueous liquid phase. The activities of individual species are further used in the electrochemical model. After completing speciation calculations, diffusion coefficients of individual species and viscosity of the solution are also computed. The electrochemical model takes into account reactions on the surface of the metal and transport processes for the species that participate in the reactions. The model includes passivation phenomena, which may be influenced by pH and the presence of aggressive or inhibitive species in the solution. Further, the model combines the partial processes to compute corrosion rates in the framework of the mixed potential theory. The model includes expressions for partial anodic and cathodic processes, which may occur under activation or mass transport control. The expressions are in agreement with the generally accepted views on the mechanisms of partial processes. In the active state, the current density of metal dissolution is given by (65) where the exchange current density  $i$  incorporates the effect of adsorption of species and is related to the activities of solution species as described in previous papers (Anderko and Young, 2000, Anderko et al., 2001). The active-passive transition is introduced into the electrochemical model by considering a current that leads to the formation of a passive layer in addition to the current that leads to active dissolution. At any instant, a certain fraction of

the surface  $\theta$  is assumed to be covered by a passive layer. The change of the passive layer coverage fraction with time can be expressed as (66) where  $i_{MeO}$  is the current density that contributes to the formation of a passive layer. The second term on the right-hand side of eq. (66) represents the rate of dissolution of the passive layer, which is proportional to the coverage fraction. Solution of this equation in the steady-state limit yields an expression for the anodic dissolution current: (67) where  $i_{Me}$  is the dissolution current density in the active state and the ratio  $i_p = c/K$  constitutes the passive current density. This formulation can represent the observable characteristics of the active-passive transition as demonstrated in a previous paper (Anderko et al., 2001). In the absence of specific active ions, the passive current density depends primarily on the pH of the solution. For acidic solutions, we consider a dissolution reaction between the passive oxide/hydroxide surface layers and protons from the solution, i.e.  $=MeO_a(OH)_b + sH^+ = Me(OH)_t +$  (68) where the symbol "=" denotes surface species. The corresponding kinetic equation is (69) where  $s$  denotes the surface concentration of hydrogen ions and  $\nu$  is a reaction order. In neutral solutions, the predominant dissolution reaction is:  $=MeO_a(OH)_b + \nu H_2O = Me(OH)_n + \nu OH^-$  (70) and the kinetic equation is: (71) Similarly, the predominant reaction in alkaline solutions is  $=MeO_a(OH)_b + \nu OH^- = Me(OH)_n + \nu H_2O$  (72) with a corresponding kinetic equation given by (73) The total passive current density as a function of pH is given by (74) The kinetic equations can be rewritten in terms of bulk concentrations of ions by considering the mass transfer equation: (75) where  $k_m$  is a mass transfer coefficient and  $a_i$  is the bulk activity of the reacting species. The mass transfer coefficient can be computed for various flow regimes as described by Anderko et al. (2001). Then, the surface concentration  $a_i^*$  can be obtained from eq. (75) and substituted into eq. (69), (71) or (73). For example, in the case when  $\nu=1$ , eq. (73) can be expressed in a closed form as: (76) The relative importance of the two terms on the right-hand side of eq. (16) depends on the particular system. In addition to pH effects, some active ions may influence the magnitude of the passive current density. The effect of active species on the dissolution in the passive state can be modeled by considering surface reactions between the metal oxide film and solution species, i.e.,  $=MeO_a(OH)_b + c_i X_i = =MeO_d(OH)_f X_{ci} + e_i OH^-$  (77) In eq. (77), the stoichiometry is usually difficult to define because of the dynamic nature of the system and may be, in general, fractional. It is reasonable to assume that eq. (77) is in quasiequilibrium and characterize it by an equilibrium constant. The surface species that forms as a result of reaction (17) may undergo irreversible dissolution reactions such as  $=MeO_d(OH)_f X_{ci} + \nu H_2O \rightarrow Me(OH)_3 + c_i X_i$  (78) Mathematical analysis of reactions (77-78) yields a relationship between the passive current density and activities of reactive species, i.e., (79) where  $i_p$  is given by eq. (74). Typical partial cathodic processes include the reduction of dissolved oxygen, water molecules, hydrogen ions and other electrochemically active species. In aerated systems, the reduction of dissolved  $O_2$  is usually the most important cathodic reaction, i.e.,  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$  (80) The oxygen reduction process is subject to mass-transfer limitations, due to the diffusion of dissolved oxygen molecules. Thus, the expression for the current density for oxygen reduction can be expressed as (81) where (82) (83) The reaction orders  $q$  and  $r$  in eq. (82) are, in general, specific to the metal surface although they are expected to be similar within families of alloys. On the other hand, the diffusion-limited current density (eq. 83) is practically independent of the surface because the mass-transfer coefficient depends only on flow conditions, diffusivity of oxygen and density and viscosity of the solution Another cathodic reaction is the reduction of water molecules, which predominates in deaerated neutral or alkaline systems:  $H_2O + e^- \rightarrow 0.5H_2 + OH^-$  (84) Unlike the reduction of oxygen, the water reduction does not exhibit a limiting current density because there

are no diffusion limitations for the transport of H<sub>2</sub>O molecules to the surface. Thus, the current density can be expressed as: (85) where (86) Other important examples of partial electrode processes include:

- Reduction of protons
- Reduction of carbonic acid, which is formed from dissolved carbon dioxide in a kinetically controlled reaction
- Reduction of oxidizing species such as chromates, nitrites, hypochlorites, etc.
- Reduction of metal cations such as ferric or cupric ions

A more detailed discussion of these processes can be found in previous papers (Anderko and Young, 1999, 2000, Anderko et al., 2000). The parameters of the electrochemical model are determined by utilizing a large number of experimental polarization and corrosion rate data. The partial electrochemical processes described above are combined into a total predicted polarization curve. Then, the corrosion potential is calculated by applying the mixed-potential theory, i.e., (87) where  $i_{c,i}$  and  $i_{a,j}$  denote the  $i$ -th cathodic and  $j$ -th anodic process. Detailed model of general corrosion. The model described above provides a very good representation of the effects of environmental variables on the rates of general corrosion. In addition, accurate predictions can be obtained very fast (after a computation time of the order of a minute). However, this model does not provide a detailed treatment of the changes in local chemistry and transport phenomena at the metal/solution interface. Therefore, its range of applicability is limited to aqueous systems, for which passivity phenomena can be successfully modeled using the simplified treatment described above. For systems in which water is a minor component or is absent altogether, a more detailed treatment of passivity is necessary. The fundamentals of this treatment are described in Appendix A.

Subtask 4.2: Review of the basis of the model by Academic Review Panel The Academic Review Panel (as described for Subtask 1.2) has reviewed the kinetic model of general corrosion at its three review meetings and provided feedback to developers.

Subtask 4.3: Verification of the predictions of the kinetic model The kinetic model of general corrosion has been applied to a large number of systems containing the following solutes:

Neutral species: H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub> and all inert gases, Cl<sub>2</sub>, SO<sub>2</sub>, SO and NH<sub>3</sub>. Anions: OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HS<sup>-</sup>, S<sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, CN<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sup>-</sup>, acetate, formate, Cr(VI) anions, As(III) anions, P(V) anions, W(VI) anions, B(III) anions and Si(IV) anions. Cations: H<sup>+</sup>, alkali metals, alkaline earth metals, Fe(II) cations, Fe(III) cations, Al(III) cations, Cd(II) cations, Sn(II) cations, Zn(II) cations, Cu(II) cations, Pb(II) cations and NH<sub>4</sub><sup>+</sup>. Here, we demonstrate the capabilities of the model for selected systems that involve both active dissolution and passive behavior. Figure 26 shows the calculated corrosion rates of carbon steel in sulfuric, phosphoric and hydrochloric acids. In this case, the corrosion is entirely in the active state. Thus, the observed corrosion rates result from the interplay between two predominant electrode processes, i.e., the anodic dissolution of iron and the cathodic reduction of protons. The observed differences in the corrosion rates in the three acids can be easily rationalized in terms of the model. The difference between sulfuric and phosphoric acid is simply due to differences in speciation, i.e., the lower activity of protons in phosphoric acid makes it less corrosive than sulfuric acid. In the case of hydrochloric acid, the corrosion rates are lower than those for H<sub>2</sub>SO<sub>4</sub> for low and moderate concentrations of the acids. This is due to the adsorption of Cl<sup>-</sup> ions on iron. At high HCl concentrations, the rate becomes higher because of halide-accelerated dissolution. Both effects are taken into account by the model. It should be noted that the data shown in Figure 26 were used to regress the electrochemical parameters (i.e., the exchange current densities). The results shown in this figure can be regarded as a correlation of experimental data rather than a prediction. Therefore, it is worthwhile to verify the model by comparing predicted corrosion rates with experimental data that were not used to regress the model parameters. Such a comparison is shown in Figure 27 for carbon steel in acetic acid. In this case, the corrosion rate

is determined by the speciation (which determines the activity of protons) and the kinetic processes of iron oxidation and proton reduction. Both kinetic processes are influenced by water activity as discussed by Anderko and Young (2000 and references cited therein). The water activity effects manifest themselves in the decrease in the corrosion rate at high acetic acid concentrations, at which the water activity is reduced. The reaction orders with respect to water, which quantify the water activity effects were obtained from data on general corrosion in concentrated brines (Anderko and Young, 2000). Thus, the corrosion rates shown in Figure 27 could be predicted without using the acetic acid data to fit corrosion rates. In the case of stainless steels, active-passive transitions play a more significant role. Figure 28 shows the calculated corrosion rates of type 316 stainless steel in sulfuric and hydrochloric acids. Here, the trend is different from that observed for carbon steel (cf. Fig. 26) because HCl is more corrosive than H<sub>2</sub>SO<sub>4</sub> at the same low and moderate molalities. This is due to the effect of chloride ions on the dissolution of oxide films. It is particularly interesting to examine the predictions of the model for the corrosion rates in mixed acid systems. An example of such calculations is shown in Figure 29 for the mixture of sulfuric and hydrochloric acids at 40 °C. When small concentrations of HCl are added to a 20% H<sub>2</sub>SO<sub>4</sub> solution, the corrosion rate increases. This cannot be attributed to small changes in acidity. Rather, it is due to the effect of chloride ions on the active-passive transition. This effect is reproduced by the model and a reasonable agreement with experimental data is obtained. Since the model is based on a combined electrochemical and thermodynamic view of general corrosion, it can predict the corrosion potential in addition to the corrosion rate. This is illustrated in Figure 30 for type 304 stainless steel in aerated acidic solutions. Here, a distinct jump in the corrosion potential is observed as the pH is increased beyond a certain level. This jump is due to a transition from corrosion in the active state at strongly acidic conditions to corrosion in the passive state. Figure 31 shows the corrosion rate of type 304 stainless steel in nitric acid as a function of concentration and temperature. These rates are much smaller than those observed in sulfuric or hydrochloric acid of similar concentration and reflect the dissolution in the passive state. It is of particular interest to examine the transition between active and passive dissolution as HNO<sub>3</sub> is added to a H<sub>2</sub>SO<sub>4</sub> solution. This is illustrated in Figure 32. The model quantitatively reproduces this transition. It is noteworthy that the model predicts a certain concentration range in which the corrosion rate can oscillate between active and passive dissolution. Numerous additional results of validating the kinetic model of general corrosion have been reported in recently published papers (Anderko et al., 2001, Anderko and Young, 2001a, b, Sridhar and Anderko, 2001, Sridhar et al., 2003). Text Box: Figure 26. Calculated and experimental corrosion rates of carbon steel in sulfuric, hydrochloric and phosphoric acids at 33 °C. Text Box: Figure 27. Calculated and experimental corrosion rates of carbon steel in aqueous acetic acid. Text Box: Figure 28. Calculated and experimental corrosion rates type 316 stainless steel in sulfuric and hydrochloric acids. Text Box: Figure 29. Effect of HCl concentration on the corrosion rate of type 316 stainless steel. The lower line shows the corrosion rate in pure HCl solution and the upper line shows the rate in a 20% H<sub>2</sub>SO<sub>4</sub> solution with varying concentrations of HCl added to the system. Text Box: Figure 30. Calculated and experimental corrosion potential of type 304 stainless steel as a function of pH in aerated sulfuric acid solutions. Text Box: Figure 31. Calculated and experimental corrosion rates for type 304L stainless steel as a function of concentration and temperature. The experimental data have been taken from the Dechema Corrosion Handbook, vol. 10. Subtask 4.4: Commercialization of software products The Corrosion Analyzer software product (cf. the description under Subtask 1.5) encapsulates the kinetic model of general corrosion described above. The Corrosion Analyzer enables the user to:

(a) Calculate the rates of general corrosion for a given environment; (b) Perform surveys as a function of selected independent variables (c) View the predicted polarization behavior to understand the electrochemical processes that lead to corrosion. Corrosion Analyzer is currently available as a commercial product. Current information about this product can be obtained from the OLI web site ([www.olisystems.com](http://www.olisystems.com)). Further, OLI has entered into an agreement with InterCorr International, a leading provider of corrosion technology solutions, for the commercialization of the Corrosion Analyzer.

Subtask 4.5: Communication of the results to the US chemical industry For the communication of the results of this project to the U.S. chemical industry, OLI has taken the following steps: (a) Marketing materials, technical papers and software manuals have been prepared. They are available from OLI Systems. (b) In collaboration with the Materials Technology Institute (MTI) and InterCorr, OLI Systems has organized three free regional seminars to disseminate information about the newly developed technology. Two of these seminars have taken place in Baltimore (April 29, 2003) and Indianapolis (June 2, 2003, in conjunction with and MTI meeting). The last seminar is scheduled in Houston (June 17, 2003). Details about these seminars are given in the announcement below. Text Box: Figure 32. Calculated and experimentally obtained effect of nitric acid concentration on the corrosion rates of type 304 stainless steel in 10% H<sub>2</sub>SO<sub>4</sub> at 60 °C. The experimental data have been taken from the Dechema Corrosion Handbook, vol. 10. Figure 33. Announcement of the seminars to communicate the results of this project to the U.S. industry. Publications The results of the work performed during the course of this project have been published in the following papers: 1. A. Anderko, P. McKenzie and R.D. Young, "Computation of rates of general corrosion using electrochemical and thermodynamic models", *Corrosion*, 57 (2001) 202-213. 2. P. Wang and A. Anderko, "Computation of Dielectric Constants of Solvent Mixtures and Electrolyte Solutions", *Fluid Phase Equilibria*, 186 (2001) 103-122 3. A. Anderko, P. Wang and M. Rafal, "Electrolyte Solutions: From Thermodynamic and Transport Property Models to the Simulation of Industrial Processes", *Fluid Phase Equilibria*, 194-197 (2002) 123-142 4. P. Wang, A. Anderko and R.D. Young, "A Speciation-Based Model for Mixed-Solvent Electrolyte Systems", *Fluid Phase Equilibria*, 203 (2002) 141-176. 5. P. Wang and A. Anderko, "Modeling Self-Diffusion in Mixed-Solvent Electrolyte Solutions", *Ind. Eng. Chem. Res.*, in press. Also, the following papers were given at conferences: 1. N. Sridhar and A. Anderko, "Corrosion Simulation for the Process Industry", paper no. 1348, CORROSION/2001, Houston, Texas, and March 11-16, 2001. 2. A. Anderko, P. Wang and M. Rafal, "Electrolyte Solutions: From Thermodynamic and Transport Property Models to the Simulation of Industrial Processes" (invited lecture), 9th International Conference on Properties and Phase Equilibria for Product and Process Design", Kurashiki, Japan, May 20-25, 2001. 3. A. Anderko, P. Wang, R.D. Young, D.P. Riemer, S.S. Babu, P. Angelini and W.B.A. Sharp, "Prediction of Corrosion of Alloys in Mixed-Solvent Environments", paper 134e, 2002 AIChE Spring National Meeting, New Orleans, LA, March 10-14, 2002. 4. A. Anderko, "Simulation of Aqueous Corrosion Using Thermodynamic and Electrochemical Models" (invited lecture), 2002 Gordon Research Conference on Aqueous Corrosion, New London, New Hampshire, July 14-19, 2002. 5. P. Wang, A. Anderko and R.D. Young, "A Speciation-Based Model for Mixed-Solvent Electrolyte Solutions", 5th International Conference on Solvo-Thermal Reactions, East Brunswick, New Jersey, July 22-26, 2002. Software The results of the work reported here have been encapsulated in the Corrosion Analyzer, a software product that is available from OLI Systems Inc. Web site Up-to-date information about the Corrosion Analyzer software and new technology developments at OLI Systems can be found on the website [www.olisystems.com](http://www.olisystems.com). Acknowledgement The work reported herein was supported by the Department of Energy under the Cooperative Research Agreement DE-FC07-00CH11019. Disclaimer Any opinions, findings, and conclusions



or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the Department of Energy. References

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