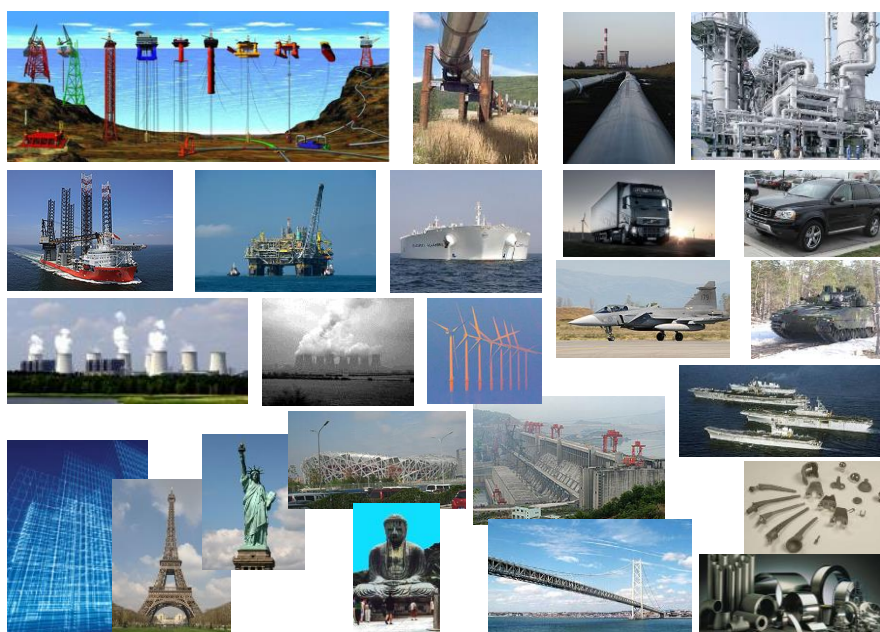
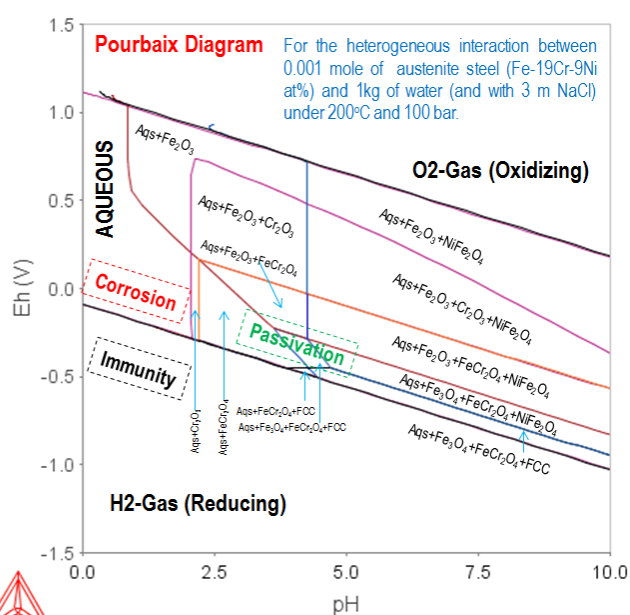




A close-up photograph of a metal joint, likely a hinge or a bolted connection. The metal surface is heavily corroded, with large areas of orange-brown rust peeling away from the grey metal. A circular metal fastener, possibly a bolt head or a rivet, is visible on the right side of the joint, showing some surface corrosion. The background is dark and out of focus.

- ☐ Aqueous corrosion
- ☐ Non-aqueous corrosion
- ☐ Molten salt corrosion
- ☐ High-T oxidation/sulfidation
- ☐ Low-T atmospheric corrosion

Pourbaix Diagrams in Multicomponent Systems



Materials Corrosion Applications with Thermo-Calc Software

- A. Introduction
- B. Thermo-Calc Software:
 - B1. Thermodynamic Models and Databases
 - B2. Calculations of Pourbaix Diagrams and Other Diagrams
- C. Applications in Aqueous Corrosion of Stainless Steels
- D. Applications in Aqueous Corrosion of Carbon Steels in Seawater
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A. INTRODUCTION

Materials corrosion *almost occurs everywhere*, which may appear as serious material damages, lead to unexpected application failures, cause tremendous economic costs, bring environmental degradations, provoke natural disasters, and so forth. Therefore, scientists and engineers often have to conduct many expansive and time-consuming corrosion experiments in the processes of failure analysis, risk evaluations, quality improvements and application enhancements.

Thermodynamic investigation of materials corrosion under various environments are extremely important for efficient design and production of high-quality materials, for advanced processing of corrosion-resistant coatings, for optimal performances of commercial materials in industrial, environmental, medical and military applications, and for environmental protections and safety assessments.

Traditionally, Pourbaix diagrams, Latimer diagrams, Frost diagrams, Ellingham diagrams, potential diagrams, predominance diagrams, and other types of phase diagrams and property diagrams were often used as some sort of basic thermodynamic guidance for studies of materials corrosion behaviours under some selected environments (Pourbaix, 1973, 1974; Cramer and Covino, 2003; Verink, 2011; Thompson *et al.*, 2011; Revie, 2011); however, the usage of such tools were rather limited, due to the facts that thermodynamic models were inadequate, used data were inconsistent and incomplete, calculation routines were somewhat amateurish, considered interactions were over-simplified, and system-reality relevancies might be inappropriate.

In order to provide powerful academic and engineering tools for studying thermodynamics of complex corrosion phenomena, within the Thermo-Calc software/database/programming-interface package which is well-known worldwide in the field of Computational Thermodynamics, some sophisticated models, critically-assessed and internally-consistent databases, comprehensive calculation techniques and advanced simulation modules have been successfully developed over the past 15 years (Sundman and Shi, 1997; Shi, 2013; Shi *et al.*, 2011a, 2011b). With such comprehensive contributions, better understandings of corrosion schemes and corrosion mechanisms of a wide range of materials, under various corrosive environments (such as aqueous solutions, non-aqueous solutions, molten salts, high-temperature gases, low-temperature atmospheres, *etc.*) during materials application/service processes, can be effectively achieved, even although corrosion kinetics is not considered in the current approach.

This extensive technical document gives some general descriptions about thermodynamic model, databases and modules which are currently available within the Thermo-Calc software, and illustrates some specific application examples of thermodynamic investigations on several types of materials corrosion phenomena in some industrial and environmental processes.

B. Thermo-Calc Software

The Thermo-Calc software (Sundman *et al.*, 1985; Sundman and Shi, 1997; Andersson *et al.*, 2002; Shi, 2013; Shi *et al.*, 2005, 2007, 2011a, 2011b; TCSAB, 2013) can precisely calculate various thermodynamic properties, complicated heterogeneous phase equilibria and multi-component phase/ property diagrams, which are ensured by many comprehensive thermodynamic models for complex solution/compound phases (in stable/metastable/amorphous forms, and in solid/liquid/gaseous states) over a wide T-P-X range and by an extensive spectrum of critically-assessed, internally-consistent and high-quality thermodynamic databases for many different types of materials (such as various steels/Fe-alloys, Ni-/NiFe-/Co-based superalloys, Ti-/Al-/Mg-/Zr-based alloys, slag, Au-/Ag-/Cu-/Sn-based solder alloys, metal powders, noble metals, semi-/superconductors, fuel-cell materials, ceramics, automotive and aerospace materials, heavy/precision instrument materials, medical materials, nuclear materials, molten salts, aqueous solution, minerals, organic materials, polymers, inorganic/organic gases, and so forth).

Thermo-Calc is also served as the thermodynamic calculation engine, not only within the DICTRA software which can effectively simulate diffusion-controlled phase transformations in multicomponent metallic systems, but also within the TC-PI application programming interfaces (*i.e.*, TQ, TCAPI, and TC-Toolbox in MATLAB) which are flexible and easy-to-use for secondary developments of programs and tools for calculating material properties and simulating material structures. All such software are most renowned worldwide for their powerful functionality, unique facilities, user-friendliness and wide applications.

Currently, Pourbaix diagrams (Eh-pH), Ellingham diagrams (ΔG_f° -T), potential diagrams (*e.g.* p_{O_2} - p_{SO_2}), Psychrometric charts (dew-point vs air temperature), and other types of phase diagrams and property diagrams for various types of materials corrosion (such as aqueous corrosion, molten salt corrosion, high-temperature oxidation/sulfidation, low-temperature atmospheric corrosion, *etc.*) can be thermodynamically calculated by the Thermo-Calc software, as illustrated in the following sections. Moreover, the DICTRA software can also be used for kinetic simulations of *e.g.* (diffusion-controlled) formations of oxides on alloy surfaces.

B1. Thermodynamic Models and Databases

For various solid solution phases, many different sophisticated thermodynamic models have been applied; for instance, the General CEF (Compound-Energy Formalism) can have ionic constraints, chemical-/magnetic-ordering contributions and other physical and mechanic contributions. For various liquid solution phases, one can choose to use *e.g.* the General CEF Model, Two-Sublattice Ionic Solution Model, Quasi-Chemical Models, or Associate Model. The gaseous mixture phase is normally handled by the Ideal EOS (Equation of State) and Ideal Mixing Model, while other models (such as SUPERFLUID Model) can also be applied. There is a wide spectrum of *general and/or specialized thermodynamic databases* available for various phases and systems which are treated by their most appropriate thermodynamic models. All kinds of details on models and databases can be found in (Shi, 2013; TCSAB, 2013).

Particularly for aqueous solutions, several models for describing thermodynamic and transport properties over a wide T-P-X range (including the critical region of water) have been developed and implemented within the Thermo-Calc software system; namely, they are the DHLL (Debye-Hückel Limiting Law) Term, SIT Model (the Specific Ion Interaction Theory), HKF Model (the Complete Revised Helgeson-Kirkham-Flowers Model) and PITZ Model (the Generalized Pitzer Formalism) (Shi, 2013).

Take the HKF Model (which bears the most appropriate and complete thermodynamic descriptions for complex aqueous solutions) as an example, the following three parts have been implemented into GES (Gibbs Energy System) of the Thermo-Calc software:

- ✓ For solvent (H₂O): PVT EOS, standard thermodynamic, electrostatic, and transport properties, over a very wide range of P-T conditions (including within its critical P-T region);

- ✓ For solute species (cations/anions, and inorganic/organic metal complexes): PVT EOS and standard thermodynamic properties, over a rather wide range of P-T conditions in aqueous solution;
- ✓ For aqueous solution: non-ideal mixing properties (DHLL terms, ionic solvation, binary/ternary/... interactions), over a wide P-T-X conditions.

Being connected with these models, two thermodynamic databases have been created through critical assessment and data evaluations (against available experimental results, empirical correlations and theoretical equations), namely the TCAQ2 and AQS2 databases (Shi, 2013).

Different thermodynamic models (and thus their corresponding aqueous solution databases) are capable for applications in different P-T-X ranges, as illustrated in *Figure 1* and *Table 1*.

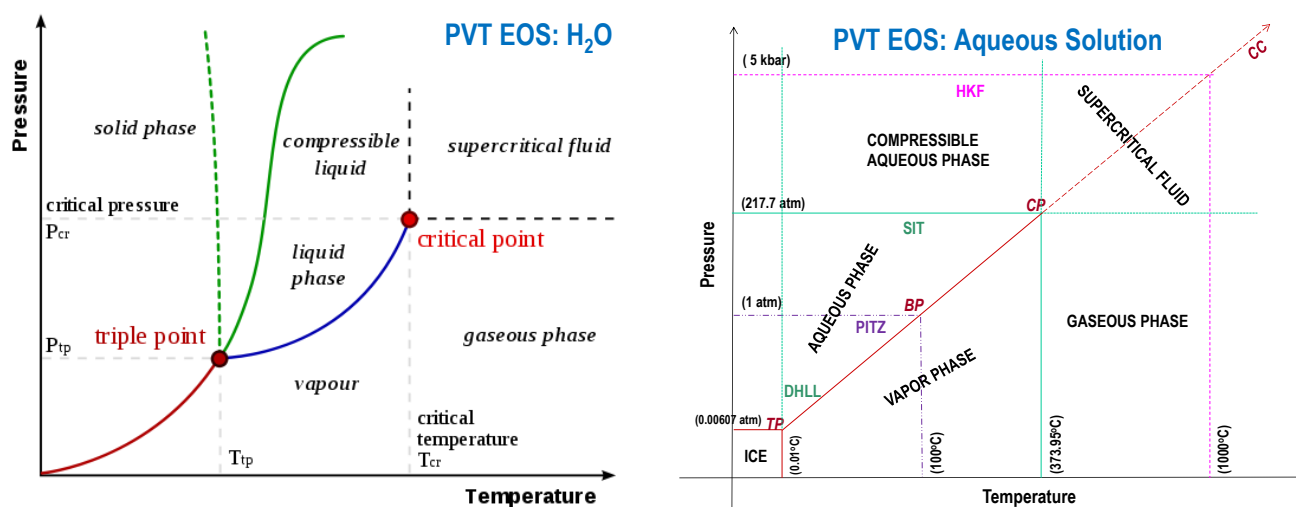


Figure 1. Schematic P-T relations for available thermodynamic models for H_2O and aqueous solution.

Table 1. Applicable P-T-X ranges of different available thermodynamic models for aqueous solution.

Thermodynamic Model	Pressure	Temperature	Concentration
DHLL (Debye-Hückel Limiting Law)	1 atm	0 -- $\sim 100^\circ\text{C}$	Dilute
PITZ (Generalized Pitzer Formalism)	1 atm	0 -- $\sim 100^\circ\text{C}$	up to saturation
SIT (Specific Ionic Interaction Theory)	1 -- ~ 200 atm	0 -- $\sim 350^\circ\text{C}$	~ 3 Eq. m NaCl
HKF (Complete Revised Helgeson-Kirkham-Flowers Model)	0 – 5 kbar	0 -- 1000°C	up to saturation

B2. Calculations of Pourbaix Diagrams and Other Diagrams

When a metal or alloy is exposed to an aqueous solution of a specific inorganic-/organic-mixture concentration under a given temperature-pressure condition for a defined time-period and over a certain spatial-configuration (in terms of e.g. surface shape/size, fracture structure/depth, welding-soldering position, flow path/direction, etc.), corrosion phenomena may occur at a corresponding degree, with some metallic phases being dissolved, the metal/alloy surface being damaged, and some secondary solid phases (such as oxides, hydroxides, silicates, sulfides, sulphates, carbonates, nitrates, phosphates, borates, halides, etc.) being formed at the solid-liquid interfaces. From the thermodynamic point of view, such corrosive chemical/electrochemical reactions (if reaching their equilibrium states) can be studied by means of the widely-applied Eh-pH, or the so-called Pourbaix diagrams (Pourbaix, 1973, 1974; Cramer and Covino, 2003; Verink, 2011; Thompson *et al.*, 2011).

Scientists and engineers in the materials corrosion field are rather familiar with the text book of “*Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd Ed” (Pourbaix, 1974) and other similar publications, where the plotted Pourbaix diagrams are often for pure metals in pure water (or extremely-simple dilute aqueous solutions) under room pressure and room temperature. Although there are many other limitations (as briefly listed here), Pourbaix diagrams can provide some basic and useful information about aqueous corrosion behaviours of various materials.

Limitations of Pourbaix Diagrams:

- Pourbaix diagrams are fully-equilibrium phase diagrams. No information on corrosion kinetics is provided by such thermodynamically-derived diagrams.
- Pourbaix diagrams are derived for some selected P and T conditions (normally, at 1 atm and 25°C).
- Pourbaix diagrams are derived for selected concentrations of ionic species (e.g., 10⁻⁶ M of metal in 1 kg of water).
- Most Pourbaix diagrams consider pure substances only (e.g., pure iron in pure water only). Additional computations must be made separately if other species are involved.
- In areas where a Pourbaix diagram shows some oxides to be thermodynamically stable, these oxides are not necessarily of a protective (passivating) nature.

With the Thermo-Calc software and associated databases, Pourbaix diagrams and other diagrams can be efficiently calculated and easily generated, for much more complex heterogeneous interactions between multicomponent primary alloy solution/compound phases, concentrated aqueous solutions (with dissolved inorganic and organic substances), complicated secondary solids (oxides, hydroxides, silicates, sulfides, sulphates, carbonates, nitrates, phosphates, borates, halides, ...) and oxidizing/reducing gaseous mixtures, over a wide range of P-T-X conditions. Beside a concentrated aqueous solution phase handled by the SIT, HKF or PITZ model, it is also possible to consider extraordinarily-complicated alloy solution/compound phases, as well as so-called secondary solid phases and gaseous mixtures that are treated by specific solution models.

Empowered by the Gibbs energy minimization technique, the Thermo-Calc software maps out possible stable (equilibrium) phases of an aqueous-bearing heterogeneous electrochemical interaction system over an electronic potential vs acidity space, therefore such a Pourbaix diagram shall be read much like a standard phase diagram with a different set of axes; actually, beyond the Eh (standard hydrogen electronic potential) vs pH (acidity) plots, other aqueous properties [such as Ah (electronic affinity), pe (electronic activity log₁₀ACRe), IS (ionic strength), TM (total aqueous concentration, in molality), OC (Osmotic coefficient), activity or activity coefficient of solvent H₂O, activities or activity coefficients or concentrations in *m* (molality) of charged or neutral solute species [e.g., Fe⁺², Fe⁺³, FeO, FeO⁺¹, FeO₂⁻¹, Fe(OH)⁺¹, Fe(OH)⁺², Fe₂(OH)₂⁺⁴, FeO(OH), FeO(OH)⁻¹, FeCl⁺¹, FeCl₂, FeCl₂⁺², FeCl₂⁺¹, FeCl₃, FeCl₄⁻¹, Fe(Formate)⁺¹, Fe(Formate)₂, Fe(Acetate)⁺¹, Fe(Acetate)₂, Fe(Propanoate)⁺¹, Fe(Propanoate)₂, Fe(Butanoate)⁺¹, Fe(Butanoate)₂, Fe(Pentanoate)⁺¹, Fe(Pentanoate)₂, Fe(Galycolate)⁺¹, Fe(Galycolate)₂, Fe(Galycinate)⁺¹, Fe(Galycinate)₂, Fe(Lactate)⁺¹, Fe(Lactate)₂, Fe(Alanate)⁺¹, Fe(Alanate)₂; ...], and so forth, can also be set as axis variables.

A Pourbaix diagram indicates regions of “immunity”, “corrosion” and “passivity” which thus give a guide to the stability of a particular metal/alloy in a specific aqueous electrochemical environment under a certain pH-Eh and P-T condition, as illustrated in Fig. 2 as an example: *immunity* means that the metal/alloy is not attacked, *corrosion* shows that general attack will occur and thus the damaged metal/alloy is dissolved into the aqueous solution, and *passivation* occurs when the metal/alloy forms a relatively-stable coating of an oxide or another protective solid on its surface.

Routines for Pourbaix Diagram Calculations: The advanced and easy-to-use POURBAIX Module in the Console Mode of the Thermo-Calc 3.0 software-version (and its previous Thermo-Calc Classic version e.g. TCCS) has been developed, for the calculations of Pourbaix diagram and other types of phase diagrams and property diagrams resulted from complex aqueous-bearing heterogeneous interactions in multicomponent systems involving metals/alloys, aqueous solutions, gaseous mixture and various secondary solid phases (Shi, 2013; Shi *et al.*, 2007, 2011b). The other way is to go through the ordinary TDB-GES-POLY-POST module-routine; in the same spirit, this also makes it possible to perform such calculations within the Graphical Mode of the Thermo-Calc 3.0 software-version.

As shown in Fig. 3, a calculation is always conducted for a multicomponent multi-phase system with 1 kg of water as the basis, and the other additional settings for equilibrium conditions should be appropriately made, on the initial amount and composition of the investigated alloy [or alloyed phase(s) of interest], on the initial concentration of aqueous solution (in terms of dissolved NaCl, for instance), and on the P-T conditions. Most frequently, a Pourbaix diagram is calculated for a specific alloyed phase with the initial alloying composition (e.g. the FCC solution phase in an austenite steel); however, one can also calculate a Pourbaix diagram for two coexisting phases (e.g. the FCC+BCC solution phases in a duplex steel) or even for more coexisting phases. In the decision on appropriately selecting the initial alloyed phase(s), one has to take into account of many details on how the applied alloy material has been originally produced and processed (in terms of e.g. its matrix phases and structures, casting/rolling parameters, aging temperature, joining/forging/welding/..., heat-treatment, surface treatment, and so forth). After a single mapping calculation over a defined “ $\ln \text{ACR}(\text{H}+1) - \text{MUR}(\text{ZE})$ ” space, a Pourbaix diagram and many other associated phase diagrams can be plotted for the same system.

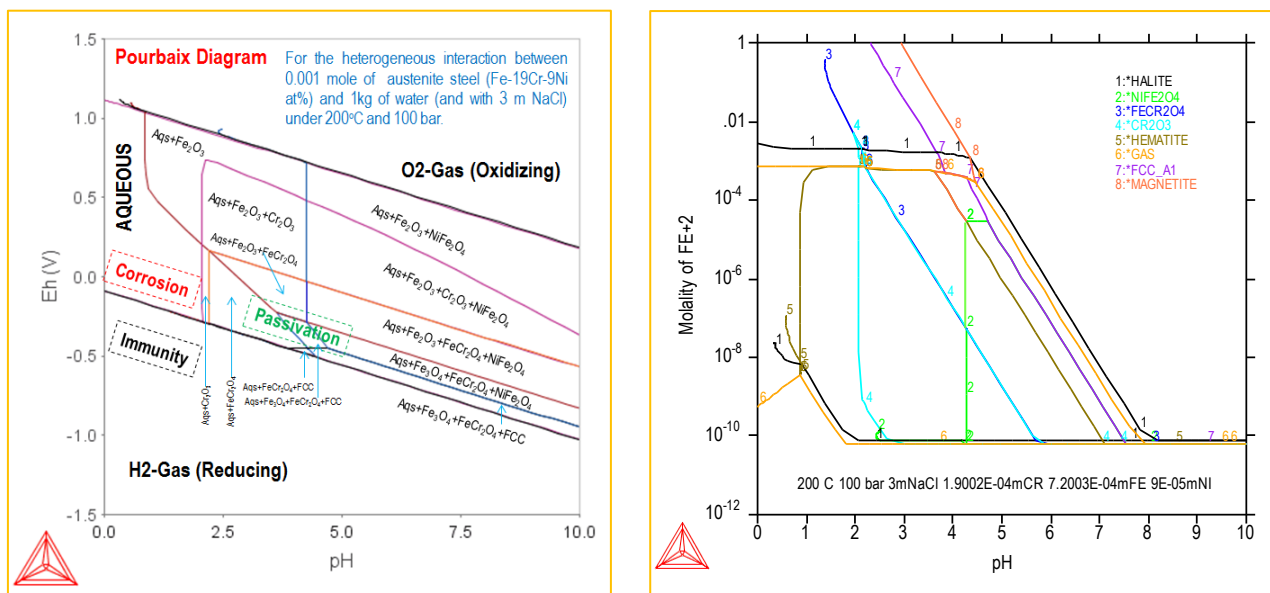


Figure 2. Pourbaix diagram (pH-Eh plot) and “Fe²⁺-molality vs pH” graph for the heterogeneous interaction between 0.001 mole of austenite steel [Fe-19Cr-9Ni (at%)] and 1 kg of water (with 3 m NaCl), at 200°C and 100 bar.

Aqueous-Bearing Calculation Modules

- ❖ **Defining Initial Multicomponent Heterogeneous Interaction Systems:**
 - Always with 1 kg of water (as the basis);
 - Plus initial concentrated solutes (e.g., composition in seawater);
 - Add initial amount of specific alloy or phases (e.g., 0.001 m SS or BCC);
 - Inclusion of various secondary phases that would form from interactions.
- ➔ **“Effective Interaction Ratio”** (an assumption having some dynamic meanings)
- **Advanced POURBAIX Module:**
 - ✓ Question-Answer-Driven user-interface;
 - ✓ Multiple options for various mapping/stepping calculations;
 - ✓ Multiple choices for different post-processing purposes;
 - ✓ Automatic and straightforward definitions/settings;
 - ✓ Standard Example: TCEX40 (extended TCEX40A/B/C/D/E)
- **Ordinary TDB-GES-POLY-POST Module-Routine:**
 - ✓ Command-Line-Driven user-interface;
 - ✓ Special requirements on proper definitions/settings;
 - ✓ Standard Example: TCEX53

Complex Heterogeneous Interaction Systems

The shape of a Pourbaix diagram of a complex multi-component alloy and the stability relations of various secondary phases (oxides, hydroxides, sulfides, sulfates, carbonates, nitrates, silicates, halides, or other forms) depend upon the following important factors:

- Initial amount and composition of the investigated alloy [the entire alloy or interested phase(s)];
- Initial amount and composition of the interacting aqueous solution phase;
- “Effective Interaction Ratio”;
- Temperature and pressure conditions;
- Model treatments on various primary phases and secondary phases: solution or compound

Figure 3. Various routines and important aspects for calculating aqueous-bearing heterogeneous systems.

One important concept used in defining an aqueous-bearing heterogeneous interaction system is the so-called “**Effective Interaction Ratio**” between the initial alloy (or alloyed phases) and initial aqueous solution; as the initial aqueous solution is always based on 1 kg of water, this is why a calculated Pourbaix diagram is usually presented for an initial amount of the interacting metal (or alloy) at a certain level, e.g., 10^{-6} , 10^{-3} , 0.1 or 1 mole of metal/alloy. The importance of this concept is double-fold:

- ✚ It has the implications of kinetic/dynamic effects (from e.g. chemical reaction mechanism and kinetics, fluid flow dynamics, surface area, interaction time, and other factors);
- ✚ When it is stated as at 10^{-6} mole of metal (or alloy), it is not a completely-arbitrary choice for a “common standard”, thanks to that it has been regarded (by the materials corrosion society) as the “detectable” solubility limit for cathodic corrosion protection by immunity.

For these obvious reasons, one may need to consider on making a series of calculations designed for some different levels of initial amount of the interacting metal/alloy (whilst the other settings for initial aqueous concentration, P-T and pH-Eh conditions are fixed).

Data Requirements for Pourbaix Diagram Calculations: For the purpose of calculating a Pourbaix diagram and/or other diagram for an aqueous-bearing heterogeneous interaction system, there should be sufficient thermodynamic data available for at least four different types of phases:

- 1) **AQUEOUS** solution phase which applies a certain aqueous solution model [retrieved from e.g. TCAQ2 or AQS2 database; either of them also includes data for the **REF_ELECTRODE** phase that is used for properly setting the reference state of the standard hydrogen electrode];
- 2) **ALLOY** solution and/or compound phases selected for the primary matrix (and maybe also precipitated) phases (such as **FCC_A1**, **BCC_A2**, **HCP_A3**, **SIGMA**, **CEMENTITE**, etc.) in the considered alloy [retrieved from e.g. TCFE7 database for steels/Fe-alloys, TCNI6 for Ni-based superalloys, TCAL2 for Al-based alloys, TCMG2 for Mg-based alloys, TCSLD1 for Au-/Ag-/Cu-/Sn-based solder alloys, SSOL5 for general alloys, etc.];
- 3) secondary **SOLID** phases (such as oxides, hydroxides, silicates, sulfides, sulphates, carbonates, nitrates, phosphates, borates, halides, and other solids) that would form as stable phases as a result of the heterogeneous chemical/electrochemical reactions [retrieved from e.g. SSUB5 database for pure solid compounds, and/or TCOX5 for complex oxide solids];
- 4) **GAS** (gaseous mixture) phase [retrieved from e.g. SSUB5 database].

It is important that all the thermodynamic data used for such an aqueous-bearing heterogeneous interaction system must be critically-assessed and internally-consistent, and that when data are retrieved from several databases they must also be externally consistent among other each, at a degree as high as possible. Practically, in order to calculate Pourbaix diagrams and other diagrams of steel corrosion processes, for instance, it is usually recommended using either the TCAQ2+TCFE7+SSUB5+TCOX5 or AQS2+TCFE7+SSUB5+TCOX5 database-combination. It is good to remember that the public PAQ2 or PAQS2 database (which contains thermodynamic data for all four types of phases and is thus capable of conducting Pourbaix diagram alone) is designed solely for demonstrating the functionality of the POURBAIX Module, and therefore any such testing calculations are only valid for some simple cases where some major phases within a small chemical framework of a few elements are considered.

Electrochemical Reactions of Water: From a full thermodynamics point of view, the **GAS** (gaseous mixture) phase must be considered in calculating a Pourbaix diagram, this is because of that, under a defined P-T condition, the solvent water has its thermodynamic stability limits that are governed by the electrochemical reactions $\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$ (forming H_2 -dominated gaseous mixture, under reducing conditions) and $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e^-$ (forming O_2 -dominated gaseous mixture, under oxidizing conditions). However, one may also choose to ignore the **GAS** phase in the calculation (as the aforementioned two major electrochemical reactions concerning H_2O (forming H_2 - or O_2 -dominated gases) have rather high kinetic barriers and are slower

than other electrochemical and chemical reactions in the interaction systems), and thus the generated Pourbaix diagram will not show the H₂O-stability limiting lines.

Regarding Predominance Diagrams: The predominant ion boundaries may also be represented by dashed and straight lines imposed on a traditional Pourbaix diagram for a simple interaction system (Pourbaix, 1973, 1974; Cramer and Covino, 2003; Verink, 2011; Thompson *et al.*, 2011). However, such a predominance boundary is normally an equal-molality (or equal-activity) line for a pair of two most-concentrated aqueous solute species (charged or neutral) involving a common metal [for instance, Fe⁺²/Fe⁺³ or Fe⁺²/Fe(OH)₂⁺¹ or Fe⁺³/Fe(OH)₃], which is determined simply by the reaction constant of its corresponding electrochemical reaction in the homogeneous aqueous solution phase [Fe⁺² = Fe⁺³ + e⁻, or Fe⁺² + 2H₂O = Fe(OH)₂⁺¹ + 2H⁺¹ + e⁻, or Fe⁺³ + 3H₂O = Fe(OH)₃ + 3H⁺¹]; as a result, its position on a plotted Eh-pH diagram really has nothing to do with any equilibrium state with a minimum total Gibbs energy in the defined interaction system. On the contrary, as a special type of phase diagram, each point on the lines/curves on an Eh-pH diagram represents a certain minimum state of Gibbs energy where a phase transformation should occur when crossing the line/curve from one side to the other. Therefore, in the Gibbs energy minimization approach implemented inside the Thermo-Calc software, a mapped and plotted Pourbaix diagram does not bear any predominant ion boundary. Restrictively speaking, the relative importance of different aqueous solute species (especially those major ones) can only be precisely calculated using the Gibbs energy minimization approach; after a proper mapping or stepping calculation, one can easily set the equilibrated concentrations (in molality or alike) or activities of a defined group of charged/neutral solute species as one axis variable in a plotted phase diagram or property diagram.

Other types of phase diagrams and property diagrams: For an aqueous-bearing heterogeneous interaction system, Pourbaix diagram [that is mapped over a “lnACR(H+1) – MUR(ZE)” space, and is presented on the “Eh–pH” plot] represents only one type of important graphs that provide useful thermodynamic information about an aqueous corrosion process, while there are many other types of phase diagrams and property diagrams that can be calculated and generated inside the Thermo-Calc software. One may choose other equilibrium conditions or condition-combinations as the (at least two) independent variables for another MAPPING calculation, and then generate other types of phase diagrams for the interaction system. However, a Pourbaix diagram or another type of phase diagram only shows the stability relationships (over a space constructed by two or more intensive state variables) among various stable phases, whilst it does not tell the equilibrium amounts (and other extensive properties) of stable phases, as well as some other thermodynamic properties of various phases and their phase constituents in the system. Compared with the Pourbaix diagram and other types of phase diagrams, property diagrams (resulted from a STEPPING calculation that uses one of the controlling condition as the independent variable) are often calculated and generated, for the purposes of reach a better and clearer understanding of how significant are various formed phases, how much the original alloy phases are damaged or transformed to other solid phases, what are the concentrations and activities of various dissolved aqueous solute species, and so forth, under different values of the defined controlling condition.

C. Applications in Aqueous Corrosion of Stainless Steels

Steels/Fe-alloys are used always everywhere nowadays. All steels/Fe-alloys (even stainless steels) are subject to aqueous corrosion under a wide range of application circumstances and service conditions. Using the available databases for steels/Fe-alloys, aqueous solution and various secondary solids and gaseous mixture, one can effectively conduct calculations of Pourbaix diagrams and many other types of phase diagrams or property diagrams that are relevant to various industrial, environmental, medical and military environments. Such calculated diagrams can gain some insights into that how the investigated steels/Fe-alloys would be preserved or corroded, depending upon the formations of various simple and complex oxides, sulfides (and/or other secondary solid phases) under different pH-Eh-T-P conditions.

Figure 10 consists of two panels. The left panel is an Eh-pH diagram showing the stability of various phases in the Fe-Cr-Mo-H₂O system. The x-axis represents the Eh (V) from -1.5 to 2.0, and the y-axis represents the stable phases in grams. The phases shown are Austenite, Gaseous Mixture (H₂-dominant), Magnetite, Pyrite, MoS₂, MoO_{2.75}, MoO_{2.889}, and MoO₂. The right panel shows the aqueous speciation of various species as a function of Eh (V) from -1.5 to 2.0. The y-axis represents the aqueous speciation in mole-fraction on a logarithmic scale from 10⁻⁸ to 10. The species shown include Fe²⁺, Fe³⁺, Cr³⁺, MoO₄²⁻, H₂O, OH⁻, and various Fe-Cr-Mo complexes.

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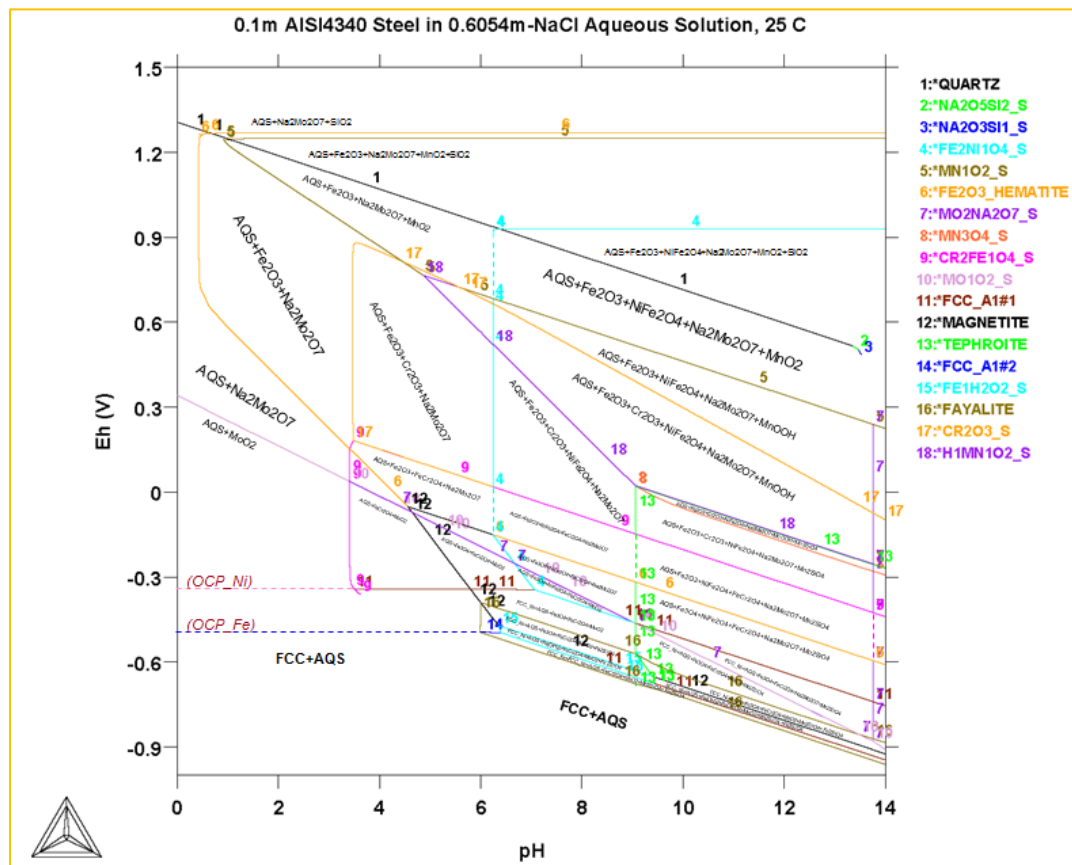
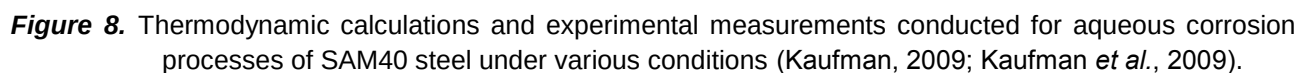


Figure 7. Pourbaix diagrams for the heterogeneous interaction systems between 0.1 mole of AISI4340 stainless steel [Fe-0.80Cr-1.85Ni-0.70Mn-0.25Mo-0.25Si-0.40C wt%] and 1 kg of sea-water (with equivalent 0.6054 m NaCl), at 25°C and 1 bar; note that in this particular calculation the gaseous mixture is not considered, i.e. ignoring the two major electrochemical reactions concerning H_2O (forming H_2 - or O_2 -dominated gases). This application is particular useful for failure analysis of petroleum exploitation industry.

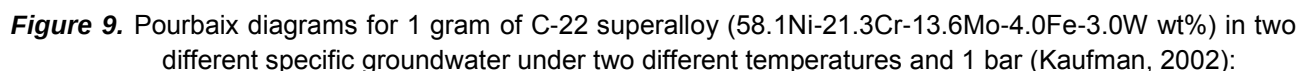
E. Applications in Aqueous Corrosion of HPCRM Alloys in Groundwater

Of particular importance to environmental safety assessments of the nuclear-waste repository in nature, the corrosion resistances of amorphous iron coatings offer substantial performance and cost saving as compared with other high-performance corrosion-resistant materials (e.g., C-22 superalloy, and amorphous steels SAM40, SAM7 & SAM2X5). In the course of experimental observations and calculations of corrosion behaviours of SAM40, SAM7, SAM2X5, C-22 and other HPCRM alloys, within the US-DOE Yucca Mountain Project for Nuclear Waste Repository, Kaufman and co-workers (Kaufman, 2002, 2009; Kaufman *et al.*, 2009) performed many series of thermodynamic calculations on Pourbaix diagrams and other phase diagrams and property diagrams for the complex heterogeneous interaction processes between such alloys and different types of natural groundwater and simulated waters, and made some comprehensive investigations by extensively comparing experimentally-measured corrosion data with the calculated results.

Demonstrated in Fig. 8 is the corrosion studies of the SAM40 steel [which is an amorphous Fe-19Cr-2.5Mo-1.7W-16B-4C (at%) alloy] that is exposed to a specific seawater at 90°C, and the calculation results fairly agree with experimental observations. Fig. 9 presents the corrosion case of the C-22 superalloy [58.1Ni-21.3Cr-13.6Mo-4.0Fe-3.0W wt%] in two different specific groundwater (BSW and BAW) under two different temperatures (30 and 90°C) and 1 bar.



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- ## F. Applications in High-Temperature Gaseous Corrosion

High-temperature gaseous corrosion processes normally involve many different types of redox reactions: oxidation (formation of oxides) and reductions (formations of sulphides, or sulfidations). Thermodynamic phase relations and equilibrium properties in such interaction systems often depend upon chemical potential of O_2 component (u_{O_2}) [in other words, oxygen activity a_{O_2} , oxygen fugacity f_{O_2} or oxygen partial-pressure p_{O_2}] and sometimes chemical potential or composition of another component (e.g., H_2 , CH_4 , CO , CO_2 , S_2 , H_2S , SO_2) or a certain ratio of properties for two components (e.g., CO_2/CO , H_2/CO_2 , H_2S/SO_2), beside the P-T conditions.

As an example, *Fig. 10* plots the calculated property diagrams of the heterogeneous interaction between 100 g of Incoloy 801 steel (wrought Fe-based superalloy with a composition of 44.5Fe-32Ni-20.5Cr-1.1Ti-0.8Mn-0.5Si-0.05C wt%) and a gaseous mixture (of 1 g H₂O, 0.001 mole HCl, 0.0001 mole HF and 0.001 mole H₂SO₄). The gaseous mixture will dissolve the steel components (especially with increasing temperatures); meanwhile LIQUID or SLAG+Ti₂O₃ phases may form during the interaction over certain temperature ranges.

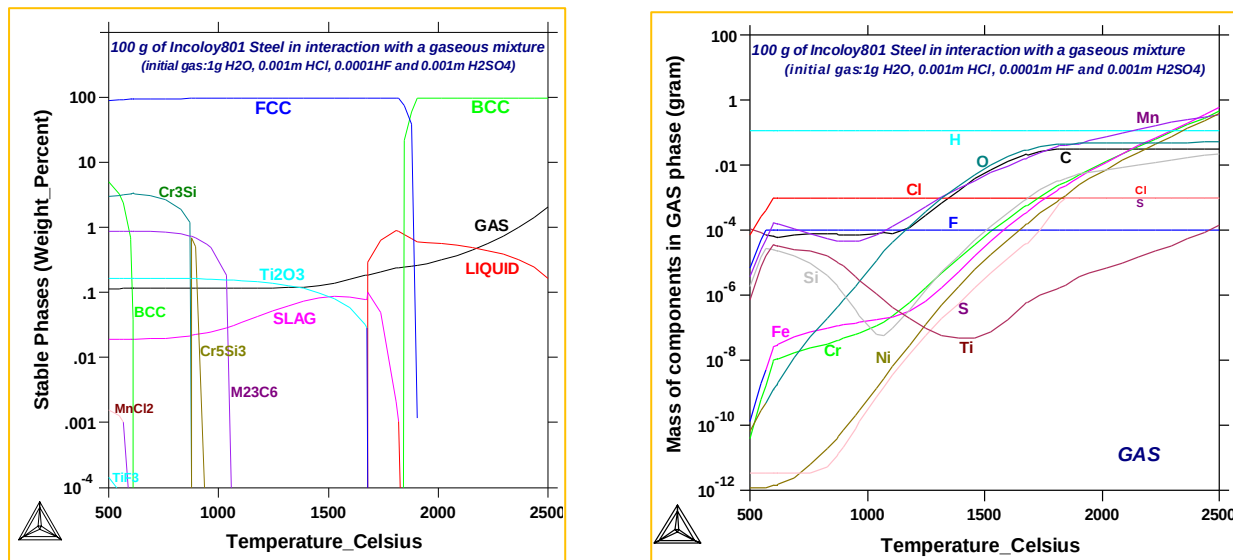


Figure 10. Property diagrams of the heterogeneous interaction between 100 g of Incoloy 801 steel and a gaseous mixture (of 1 g H₂O, 0.001 mole HCl, 0.0001 mole HF and 0.001 mole H₂SO₄).

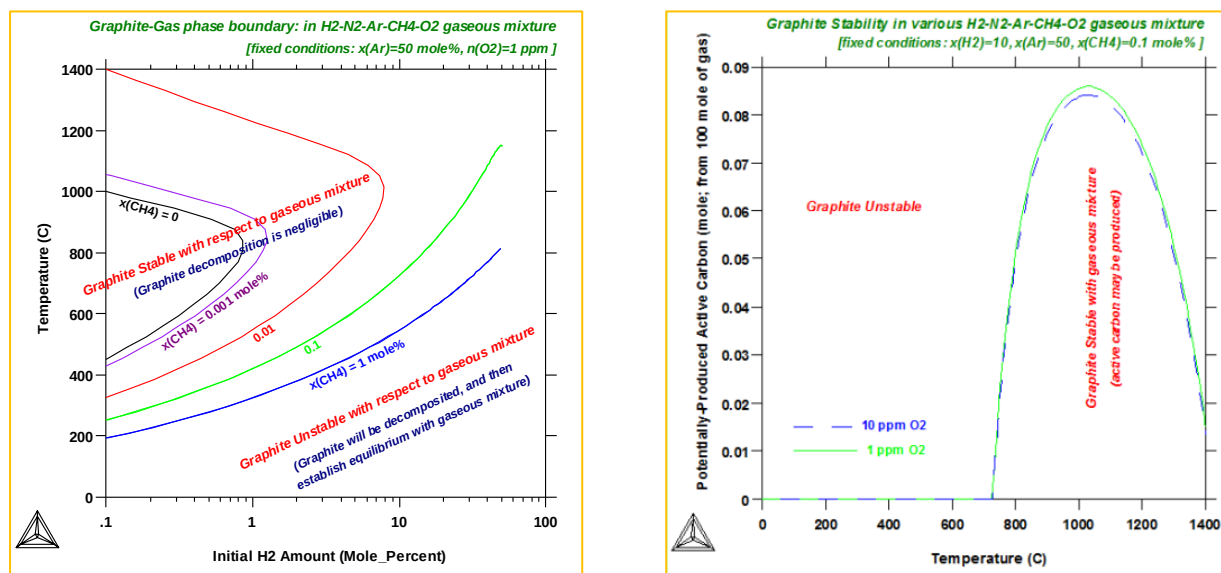


Figure 11. Graphite stability in certain H₂-N₂-Ar-CH₄-O₂ gaseous mixtures. The initial compositional rates of hydrogen, methane and oxygen in the gaseous mixtures determine the graphite-gas boundary.

Graphite-bearing furnace and refractory are widely used in heat treatments, steel-making and metallurgical processes, and many other industrial and engineering systems; the stability of graphite in various atmospheres and temperature-pressure settings is an extremely important subject in many scientific and technological fields. One example is given in *Fig. 11* as the calculated graphite-gas phase boundary in a specific gaseous mixture of H₂-N₂-Ar-CH₄-O₂. Such graphs (and many other related property diagrams from the same calculations) can tell

that in some T-P-X conditions graphite in furnace/refractory may be corroded by atmospheres and that in other conditions active-carbon may be formed in reaction chambers. Based on this type of calculation, one can find the optimal gaseous mixture settings and operation conditions.

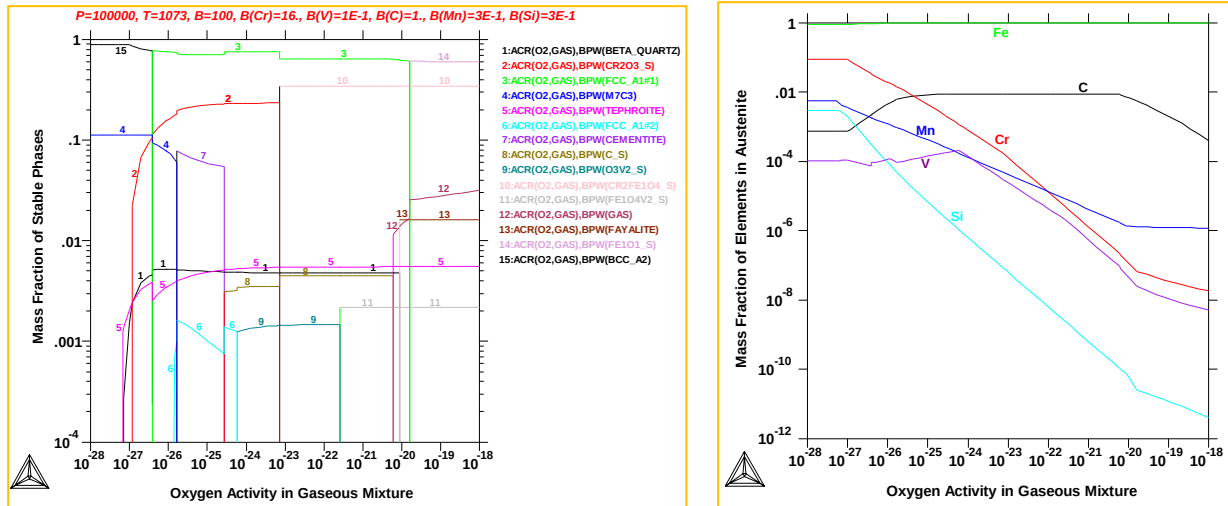


Figure 12. Stable phases and element distribution of remaining austenite during the surface oxidation of the Fe-16Cr-0.3Mn-0.3Si-0.01V-1C (wt%) steel at 800°C, as a function of oxygen activity in the atmosphere.

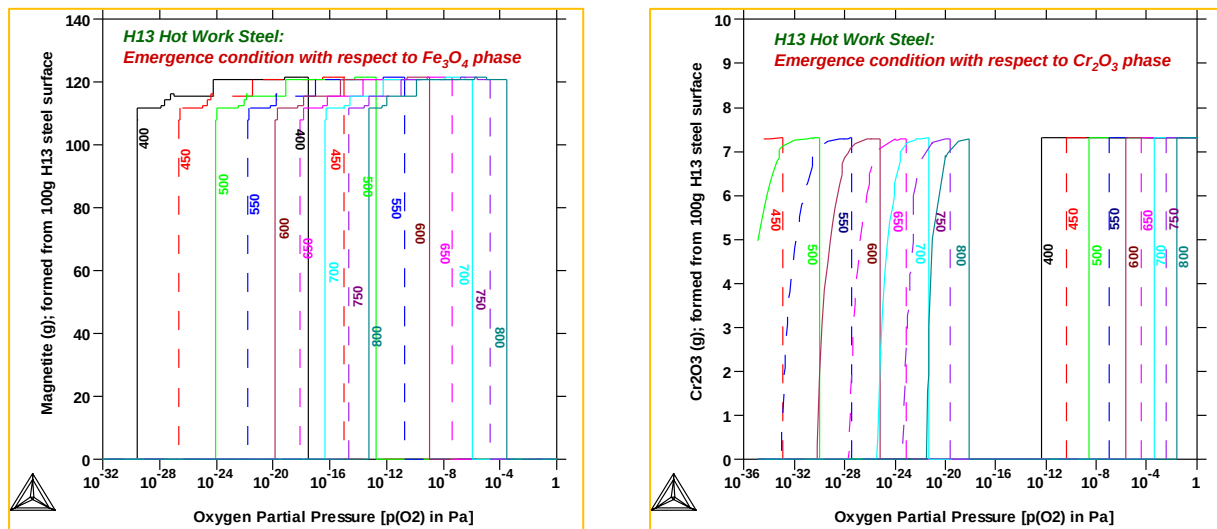


Figure 13. Emergence conditions with respect to the Fe₃O₄ and Cr₂O₃ oxides during oxidation of the H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.02Si-0.40C-0.93V-1.46Mo-0.001S-0.009P (wt%)], at different temperatures (between 400 and 800°C) and 1 bar.

Investigations of redox reactions and oxidation sequences are essential not only for empowering fundamental guidance on effective formations of protective oxide layers on steels and alloys, but also for providing useful information about potential corrosion scenarios in materials applications and engineering. During the surface treatment of a steel or alloy under specific oxygen fugacity conditions, various oxides (simple or multiple) may form or disappear. Fig. 12 illustrates the calculated results of complex oxidation sequences for an Fe-16Cr-0.3Mn-0.3Si-0.01V-1C (wt%) steel, under 800°C and varied oxygen activity, as well as the element distributions in the remaining austenite phase.

When a steel or alloy is used in a certain environment, its alloying elements may be extracted from material surface by some corrosive chemical agents (such as O_2 , H_2 , H_2S , SO_2 , H_2SO_4 , CO_2 , HCl , $NaCl$, among others) in the surroundings. It is good to know what the so-called Emergence Conditions are for formations of some specific oxides/silicates/carbonates/ sulphates/phosphates/borates/..., which are critical for judging the safe performance or damage occurrence. A calculated Emergence Condition diagram (normally plotted as stable oxide phase amount vs O_2 partial pressure, under several different service temperature conditions and a fixed total pressure) provides corrosion-tendency information similar as an Ellingham diagram, but gives more details on the redox states. As an example, *Fig. 13* shows the emergence conditions with respect to the Fe_3O_4 and Cr_2O_3 phases, during the oxidation processes of H13 Hot Work Steel [Fe-5.14Cr-0.41Mn-1.46Mo-1.02Si-0.93V-0.40C-0.001S-0.009P (wt%)] under several different temperatures (between 400 and 800°C) and 1 bar (Min *et al.*, 2006). Note that many more similar plots can also be generated (from the same) as the emergence conditions for formations of other concerned oxides/silicates/carbonates/..., e.g., FeO , Fe_2O_3 , $FeCr_2O_4$, V_2O_3 , VO_2 , FeV_2O_4 , FeV_2O_6 , SiO_2 , $FeSiO_4$, $MnSiO_4$, $FeCO_3$ and $MnCO_3$ in this defined system.

Often, potential diagrams (e.g., p_{O_2} - p_{SO_2}) and other types of diagrams with one or two axis variables set as controlling redox conditions (e.g., p_{O_2} , f_{O_2} , a_{S_2} , u_{CO_2} , p_{CO_2}/p_{CO} , p_{H_2}/p_{CO_2}) are calculated and plotted for investigating heat-treatment and gaseous corrosion processes. *Fig. 14* shows the calculation results on various oxide scale formations (halite, spinel and corundum) in an austenitic Fe-Mn-Cr stainless steel [Fe-17.8Mn-9.5Cr-1.0Ni-0.27C in wt%], which is widely applied in fusion reactors, under various oxygen partial-pressures during a heat treatment at constant 900°C: a Fe-Mn rich spinel phase is formed below the outer scale (that is stabilized as corundum phase), and a layer with halite phase and a Cr-Mn rich spinel phase are formed next to the substrate; these results are verified with available experimental information of Douglas *et al.* (1986).

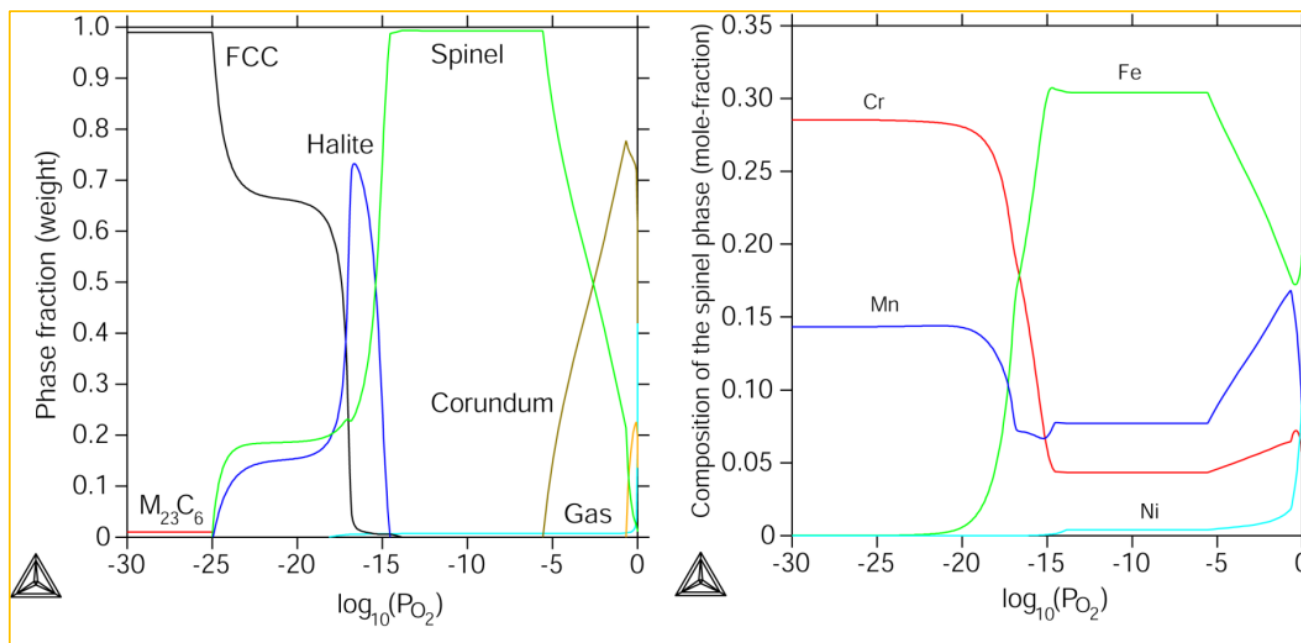
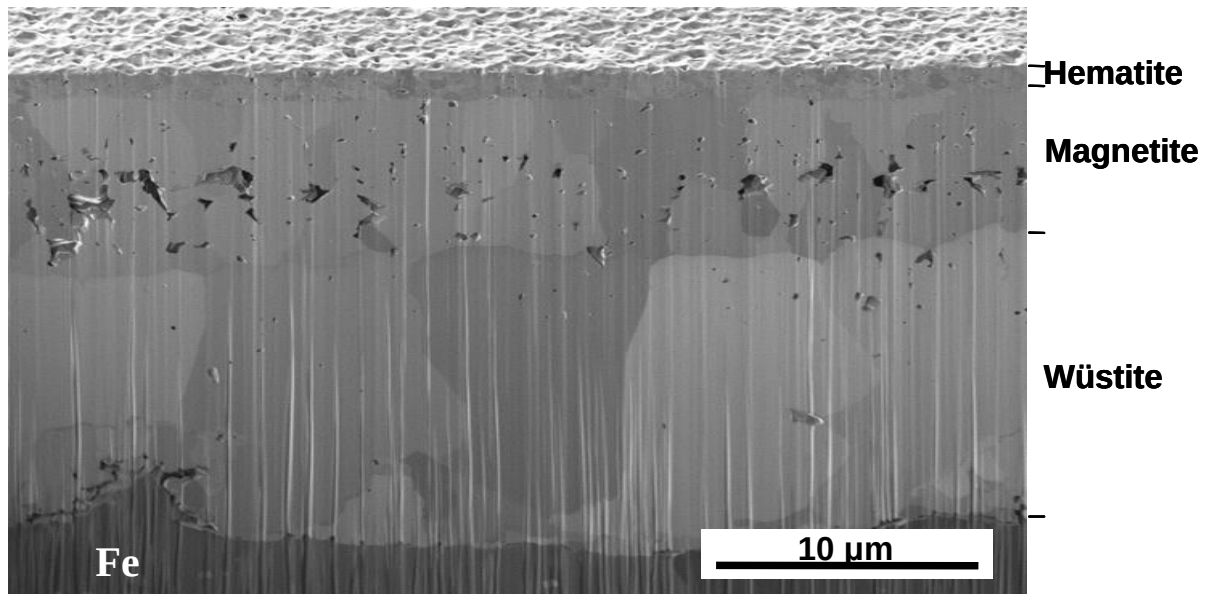


Figure 14. Thermo-Calc calculation of oxide scale formations in a Fe-17.8Mn-9.5Cr-1.0Ni-0.27C (wt%) steel under various oxygen partial pressures and a constant 900°C, verified with available experimental data of Douglas *et al.* (1986).



**Pure Fe, 600°C, dry O₂, 24h; Total oxide thickness is 34 μm.
(the hematite, magnetite and wüstite layers as 2, 11 and 21 μm, respectively)**

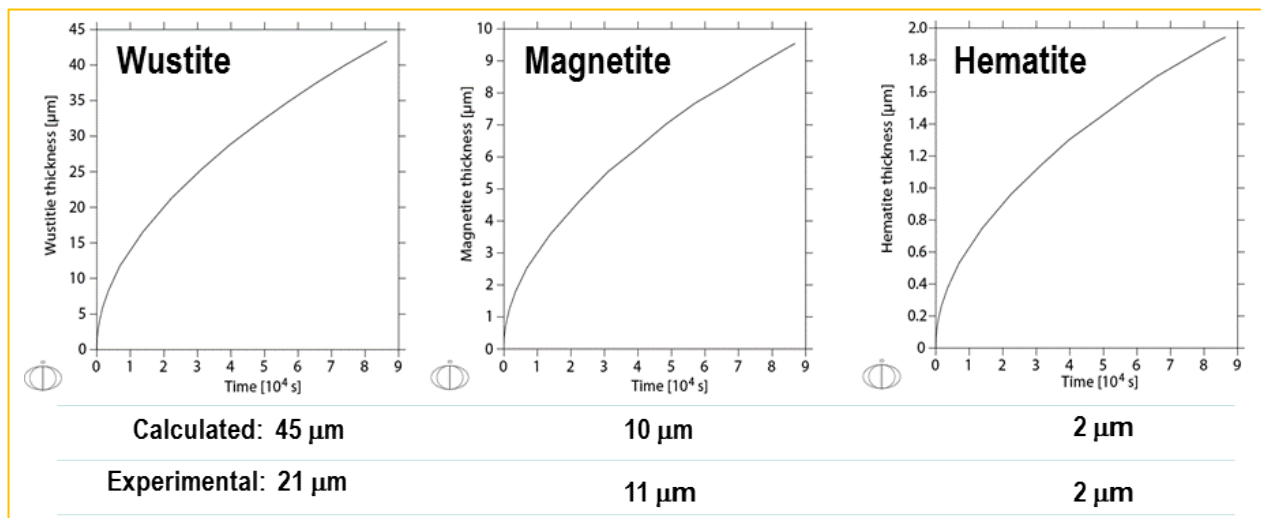


Figure 15. DICTRA kinetic simulation of oxide layer formations (wüstite, magnetite and hematite) on pure iron surface at 600°C, compared with available experimental data (Hallström *et al.*, 2011).

The DICTRA software and kinetic/mobility databases, coupled with the Thermo-Calc software and thermodynamic databases, can also be applied to perform kinetic simulations of certain types of material corrosion processes. *Fig. 15* illustrates the simulation results on formations of various oxide layers (wüstite, magnetite and hematite) on steel surface (as a simplified calculation, pure Fe was considered in this case) after 24 hours of surface-oxidation treatments under the conditions of 600°C and dry oxygen atmosphere, that compare fairly well with available experimental data of Hallström *et al.* (2011).

G. Applications in Molten-Salt Corrosion

Molten salt corrosions of alloys often cause destructions of coating layers (by decomposing or transforming corrosion-protection and thermal-barrier layers) and even alloy matrixes.

A coated Cr_2O_3 layer is the typical protective layer on the surfaces of stainless steels, Ni-based superalloys or other alloys, under normal circumstances. However, such a layer, if exposed to molten salts at elevated temperature conditions under some specific salty environments (such as marine, salt lake, and salty rock bed environments), may be damaged by aggressive molten salty agents, resulting in that the alloy materials may be exposed to further corrosion attacks by other oxidizing or reducing substances in their application life-cycles. Thermodynamic calculations can effectively help predicting dissolution of a Cr_2O_3 layer caused by molten salt corrosion. The amount of stable phases (Fig. 16a) and Cr partitions in various stable phases (Fig. 16b) as a function of temperature are shown. The calculation was done for the heterogeneous equilibrium state in a multicomponent Cr-C-H-O-S-N-Na-Cl system which originally consists of 0.05 mole of Cr_2O_3 solid, a salt mixture (0.01 mole of NaCl, 0.46247 mole of Na_2SO_4 and 0.03253 mole of Na_2CO_3) and 431.16 g of C-H-O-N gaseous mixture (note that all such settings are actual data on chemical compositions of the interacting $\text{NaCl-Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3$ salt mixture and C-H-O-N gas mixture inside a specific gas turbine severing in an chemical engineering process). The calculation results show that at an operation temperature of 750°C , the Cr_2O_3 layer dissolves (with a remaining amount of 0.031756 mole), forming a crystalline $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ solid solution (Hexagonal) and a liquid mixture (Ionic_Liquid) that are stable with an equilibrated gaseous mixture. As temperature increases, the molten salt corrosion becomes more serious; and when 1200°C is reached, the entire Cr_2O_3 layer on the alloy surface may be completely destroyed if exposed for a long period under such a corrosive environment.

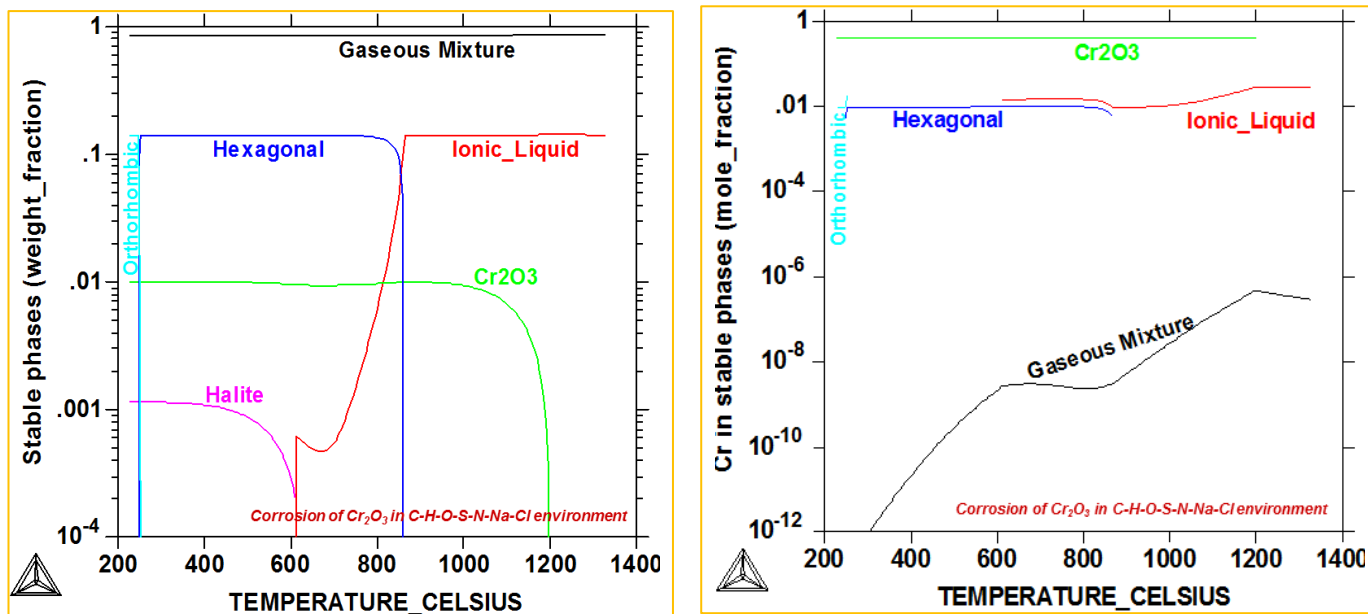
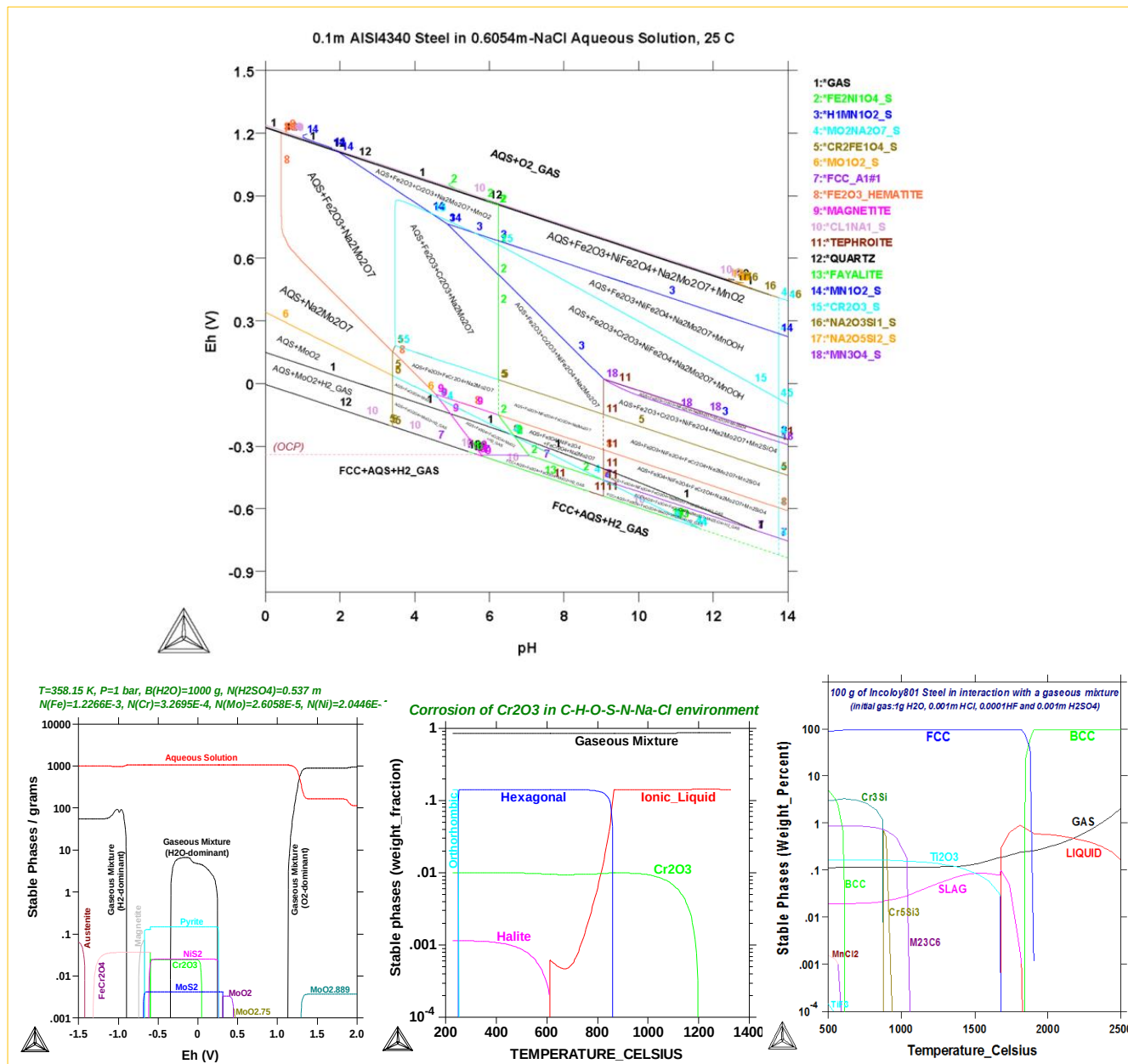


Figure 16. Stable phases remaining/formed (16a) and Cr-partition in various phases (16b) as a function of operation temperature condition, during the molten salt corrosion of the Cr_2O_3 layer (on surfaces of stainless steels, superalloys or other alloys) when it is attacked by a $\text{NaCl-Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3$ salt mixture and a C-H-O-N gaseous mixture, simultaneously.

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Thermo-Calc Software is capable for effectively performing many different types of advanced thermodynamic calculations on materials corrosion.



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