Thermo-Calc Software

Educational Material:

Pourbaix Diagrams

1. Contents

2. Introduction to Pourbaix Diagrams

This document is for Thermo-Calc software users who know the basics of thermodynamics and want to know more about Pourbaix Diagrams.

You are introduced to the concept of a Pourbaix diagram and shown how to interpret such diagrams through a series of examples.

Materials corrosion occurs almost everywhere. It may lead to serious material damages, unexpected application failures, tremendous economic costs and environmental degradations. Consequently, scientists and engineers must often conduct expensive and time-consuming corrosion experiments as part of failure analyses, risk evaluations, quality improvements and application enhancements.

Under certain conditions, when a metal or alloy is exposed to an aqueous solution with a concentration of inorganic/organic mixture, corrosion phenomena occur at a corresponding degree. During corrosion, some metallic phases dissolve, the metal or alloy surface gets damaged and some secondary solid phases form at the solid-liquid interfaces (such as oxides, hydroxides, silicates, sulphides, sulphates, carbonates, nitrates, phosphates, borates, or halides). Such corrosive chemical or electrochemical reactions can be studied by means of the so-called Pourbaix diagrams if the reactions reach their equilibrium states (Pourbaix, 1973, 1974; Cramer and Covino, 2003; Verink, 2011; Thompson et al., 2011).

2.1 Pourbaix Diagrams

Marcel Pourbaix applied thermodynamics to predict materials corrosion resistance. He determined the phase stability relations in terms of varied pH and Eh values for an interaction system of metal and pure water or dilute aqueous solution. He presented the stability regions of metal and secondary phases (such as metal-oxides/hydroxides) on a pH-Eh diagram, which is now known as a Pourbaix diagram.

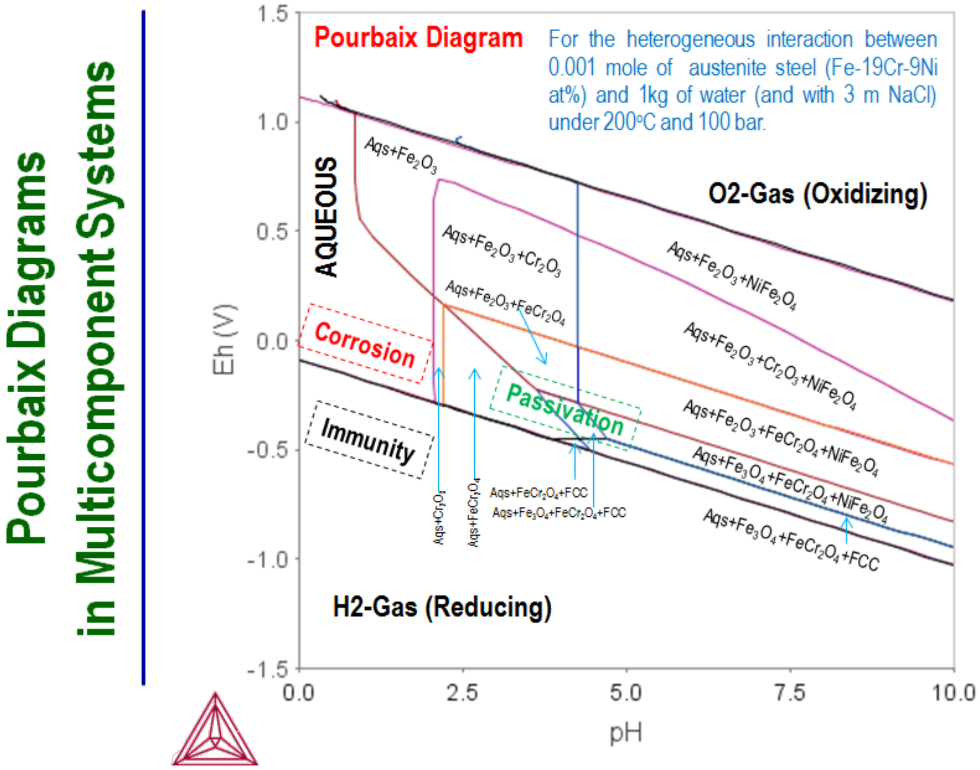
A Pourbaix diagram is a kind of phase diagram that shows the stability boundaries for a metal-aqueous interaction system. The phase boundaries are shown as a function of pH (acidity) and Eh (standard hydrogen electronic potential). An aqueous solution phase is always present in such a system. At a given pH and Eh, a metal may lose its stability to a soluble or corrosive aqueous solution, or be in equilibrium with either the aqueous solution (insoluble/immune) or with a secondary-phase file that has formed (consisting of oxides, hydroxides, sulphides or other solids). In the latter case, further dissolution of the passive or protective metal is prevented.

The speciation and partition in the aqueous solution and the interacting phases depend not only on pH and Eh, but also on other factors such as the bulk composition, temperature and pressure in the system. The interacting phases may be gas mixtures, stoichiometric solids or solid solutions.

A Pourbaix diagram is divided in regions of *immunity*, *corrosion* and *passivity*. These regions provides information about the stability of a particular metal or alloy in a specific aqueous electrochemical environment under certain pH, Eh, pressure and temperature conditions.

- The immunity region is the region in which there is no metal dissolution.
- The corrosion region is the region in which there is active metal dissolution.
- The passivation region is the region in which a protective metal-oxide film that prevents metal dissolution is formed.

The following figure shows these three regions in a Pourbaix diagram 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:



Depending on the system's bulk chemical composition, secondary phases may form during the transformation process. These can not only be oxides, but also be, for example, hydroxides, sulphides, sulphates, carbonates, nitrates, phosphates, borates, silicates, hydrous silicates and halides. Information about these secondary phases may help one understand the passivation behaviours in corrosion processes. For example, it may be important to understand whether any secondary phases are formed in different pH-Eh regions during hydrolysis, oxidation, reduction or other reaction processes.

In a Pourbaix diagram, the predominant ion boundaries are often 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). 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. A line is then simply determined by a reaction constant of its corresponding electrochemical reaction in the homogeneous aqueous solution phase. However, this is not the case in Thermo-Calc. You cannot get any information about predominant ion boundaries from a Pourbaix diagram in Thermo-Calc.

3. Pourbaix Diagrams in Thermo-Calc

With the Thermo-Calc software package, Pourbaix diagrams can be calculated over a wide range of pressure, temperature and composition conditions for complex heterogeneous interactions between multicomponent primary alloy solution or compound phases, concentrated aqueous solutions (with dissolved inorganic and organic substances), complicated secondary solids and oxidizing/reducing gaseous mixtures. In the Console Mode, diagrams can be calculated and plotted either using the response-driven POURBAIX module or directly using the DATA, GIBBS, POLY and POST modules.

Note that it is possible in Thermo-Calc to set aqueous properties other than pH and Eh as axis variables. For example, the following properties can also be set as axis variables: `Ah` (electronic affinity), `pe` (electronic activity $\log_{10}$ACRe), `IS` (ionic strength), `TM` (total aqueous concentration, in molality), `OC` (Osmotic coefficient), activity or activity coefficient of solvent H_2O, and activities or activity coefficients or concentrations in m (molality) of charged or neutral solute species.

Beside a concentrated aqueous solution phase handled by a proper thermodynamic model named SIT, HKF or PITZ, it is also possible to consider complex alloy solution phases or compound phases, as well as secondary solid phases and gaseous mixtures, which are treated by specific solution models.

Most frequently, a Poubaix diagram is calculated for a specific alloyed phase with the initial alloying composition, such as the FCC solution phase in an austenite steel. However, it is possible to calculate a Pourbaix diagram for two co-existing phases, such as the FCC+BCC solution phases in a duplex steel for example, or even for more than two co-existing phases in a steel/alloy.

Note that each point on the lines in a pH-Eh diagram in Thermo-Calc represents a certain minimum state of Gibbs energy. When a line is crossed, a phase transformation should occur. This means that a Pourbaix diagram in Thermo-Calc does not provide any information about any predominant ion boundary.

The next sections discuss Basic Settings and Definitions and Key Concepts.

3.1 Basic Settings and Definitions

In a homogeneous aqueous solution or an aqueous-bearing heterogeneous interaction system, the most essential definition is for system-components there must be `H2O`, `H+1` and `ZE` (electron) plus those for elements dissolved in aqueous solution (such as `Na`, `Cl`, `S`) and associated in interacting metals/alloys (such as `Fe`, `Cr`, `Mn`, `Mg`, `Ni`, `Al`, `Si`, `Zn`). Three fundamental phases in a system are the `AQUEOUS` solution, the `GAS` mixture and the `REF_ELECTRODE`. The `REF_ELECTRODE` phase is used for setting the reference state for electrostatic potential in the system and for calculating the Eh condition (defined as `MUR(ZE)/RNF`). Other phases should be appropriately selected and retrieved from critically-assessed databases that cover not only the target phases (solution or stoichiometric) in interacting metals/alloys but also the secondary phases (solution or stoichiometric). The two public databases PAQ and PAQS are specially designed as single-database choices that cover all kinds of phases necessary for calculations. However, these databases are each limited to a framework of a very small number of elements. When it comes to simulations of complex multicomponent systems with a wide variety of elements and phases, the thermodynamic data must be selected and retrieved from several databases: `AQUEOUS` solution and `REF_ELCTRODE` phases must be retrieved from TCAQ or AQS; alloy phases (such as `FCC_A1`, `BCC_A2`, `HCP_A3`, `CEMENTITE`) from alloy solution databases (such as SSOL for general alloy phases, TCFE for steel/Fe-alloy phases, TCAL for Al-based alloy phases; TCMG for Mg-based alloy phases, and TCNI for Ni-based superalloy phases); gaseous mixture phase and secondary phases from specific substance or solution databases (such as SSUB for `GAS` phase and various solid compound phases or TCOX for oxide solution phases). Note that the `REF_ELECTRODE` phase should always be suspended in equilibrium calculations, while `GAS` phase could be set as `ENTERED`, `SUSPENDED` or `DORMANT`, depending on the purpose of the calculation.

When defining an interaction system, the initial condition for the `H2O` component is always set as 1 kg of water. The initial composition conditions for dissolving and interacting elements are normally defined in moles (such as `n(Fe)=0.009`, `n(Cr)=5E-4`, `n(Ni)=3E-4`, `n(Mn)=5E-5`, `n(S)=5E-5`, `n(Na)=3`, `n(Cl)=3`). This makes it straightforward and convenient to count various related aqueous solution properties based on molality. The initial conditions for the `H+1` and `ZE` components can be given as molar compositions (such as `n(H+1)=0`, `n(ZE)=0`) or their activities or potentials (such as `lnACR(H+1)=-9.21`, `MUR(ZE)=8400`).

The pH and Eh properties of the aqueous solution in the interacting system are always defined in the following way:

```
pH = -log10[ACR(H+1,AQUEOUS)*AH2O]]
Eh = MUR(ZE)/RNF
```

The symbol `AH2O` is the molecular weight of solvent H_2O (equals `55.508435`) and `RNF` is the Faraday constant (equals `96485.309`).

The activity of the solvent water (`ACRH2O`, `Aw`), the osmatic coefficient of aqueous solution (`OSMC`, `Os`), electronic affinity (`Ah`), electronic activity log10ACRe (`pe`), ionic strength (`IS`), total aqueous concentration, in molality (`TM`) and total alkaline concentrations under two definitions (`At1`/`AT2`) are calculated and listed for each equilibrium state.

POLY3 calculations for mass balances in Thermo-Calc are always based on site-fractions. Consequently, when functions for describing various properties of aqueous solutes are defined, such as molality (`MLi`), activity coefficient (`RCi`) and activity (`AIi`), they should be converted to molality-based quantities:

```
MLi = Y(AQUEOUS,i)*AH2O/YH2O
```

```
RCi = ACR(i,AQUEOUS)*YH2O/Y(AQUEOUS,i)
AIi = ACR(i,AQUEOUS)*AH2O
```

Here, `YH2O` is the site-fraction of solvent H_2O and `AH2O` equals `55.508435`.

Many more variables, functions and tables can be entered for various purposes. For instance, an equilibrium constant for a homogeneous reaction or a solubility product for a solid dissolution reaction can be entered.

3.2 Key Concepts

Below some key concepts are presented that are important for understanding how aqueous solutions behave and for understanding how an aqueous-bearing heterogeneous interaction system is properly defined and calculated in Thermo-Calc.

3.2.1 Effective Interaction Ratio

A pH-Eh plot is always related to a certain amount of initial alloys or other condensed materials that has effectively reacted with an aqueous solution in the system. This is the amount of condensed material that is fully in equilibrium with the defined aqueous solution phase. The amount is specified relative to an aqueous solution that is normally comprised of 1 kg of water with certain specified solute concentrations at certain temperature and pressure conditions. (This is why a calculated Pourbaix diagram is typically presented for an initial amount of the interacting metal or alloy at a certain level, such as 10^{-6}, 1E-3, 0.1 or 1 mole of metal or alloy.) It is called the Effective Interaction Ratio (between the initial alloy or alloyed phases and the initial aqueous solution) and it is expressed in terms of molality (mol/kg).

The Effective Interaction Ratio is important for two reasons. First, the ratio has implications for kinetic or dynamic effects such as chemical reaction mechanism and kinetics, fluid flow dynamics, surface area and interaction time. Secondly, the ratio, being expressed as 10^{-6} mole of metal (or alloy), is the solubility limit that can be detected for cathodic corrosion protection by immunity.

One should always be careful when setting initial amounts and compositions in the original condensed materials, as well as when setting the initial concentrations of dissolved solutes in the original aqueous solution phase. It is often useful to make a series of calculations for different levels of initial amount of the interacting metal/alloy while the conditions are fixed for other settings (such as initial aqueous concentration, pressure, temperature, pH, and Eh).

3.2.2 Solubility

When a heterogeneous equilibrium has a dissolving solution or mixture phase and a stoichiometric or solution phase, then the concept of solubility becomes important. A solubility of a phase (the solute) is its property of dissolving in the solvent phase. This concept concerns the constitution of a phase and is applied where one or several of the constituents are dominant (which is highly concentrated and dissolving) while there are only small amounts of the other remaining species (which are less concentrated and dissolved). The dissolving solution or mixture phase can be liquid, gas, aqueous or solid, as long as it has dissolving capacity. The stoichiometric or solution phase has some constituents which tend to be dissolved into the dissolving solution or mixture phase.

Here are some specific points concerning solubility in various circumstances:

- Under certain temperature, pressure and composition conditions, a Fe- or Cr-dominant BCC phase can dissolve certain amounts of Ni and C from a carbide phase such as

M23C6, M7C3 or M3C. The Ni and C elements in the carbides have the solubility defined relative to the BCC phase.

- An aqueous solution phase is always dominant in the solvent water, that is, H2O. Under specific temperature, pressure and aqueous composition conditions, any other element (such as Fe and C) or substance (such as a pure SO2 gas, stoichiometric phase Cu2S and solution phase (Fe,Ni)1(O,Va)1) have a certain solubility limit in the defined aqueous solution.
- Under certain temperature and pressure conditions, and under given certain concentrations of other dissolved species in the mixture, an O2-dominant gaseous mixture phase can dissolve certain amounts of Fe+2 or Fe+3 species from magnetite (Fe3O4). The magnetite solid has solubility defined relative to the gaseous mixture under the given conditions.
- Under certain temperature and pressure condition, under specific concentrations of other dissolved species in the liquid phase, a Fe-dominant liquid mixture phase can dissolve certain amounts of, for example, Cr and O. The Cr and O components have the solubility defined in the liquid mixture.

4. Required Thermodynamic Data

To calculate a Pourbaix diagram, thermodynamic data for at least the following four types of phases must be available:

- The aqueous solution phase which applies a certain aqueous solution model. In Thermo-Calc, information about this phase could be retrieved from, for instance, the TCAQ or AQS database (these also include data for the `REF_ELECTRODE` phase that is used for setting the reference state of the standard hydrogen electrode).
- The alloy solution and/or compound phases for the primary matrix phases (and possibly also for the precipitated phases in the alloy. Examples of such phases include FCC_A1, BCC_A2, HCP_A3, SIGMA and CEMENTITE. In Thermo-Calc, information about such phases could be retrieved from, for example, the TCFE database for steels/Fe-alloys, the TCNI database for Ni-based superalloys, the TCAL database for Al-based alloys, the TCMG database for Mg-based alloys, the TCSLD for Sn-/Au-/Bi-/Zn-based solder alloys or the SSOL for general alloys.
- The secondary solid phases that would form as a result of the heterogeneous chemical or electrochemical reactions. These phases could be, for example, oxides, hydroxides, silicates, hydrous silicates, sulphides, sulphates, carbonates, nitrates, phosphates, borates or halides. In Thermo-Calc, information about such phases could be retrieved from, for example, the SSUB database for pure solid compounds or the TCOX database for complex oxide solids.
- The gaseous mixture phase. Information about this phase could be retrieved from, for example, the SSUB database. However, note that is also possible to perform Pourbaix diagram calculations that ignore the gaseous mixture phase.

All this thermodynamic data about the various phases must be critically assessed and internally consistent. Furthermore, when the data is retrieved from several databases, the data taken from each database must be consistent with the data taken from the other databases. When Pourbaix diagrams and other diagrams of steel corrosion processes are calculated, it is typically recommended that the TCAQ, TCFE, SSUB and TCOX databases or the AQS, TCFE, SSUB and TCOX are used in combination.

The public PAQ and PAQS databases each contains thermodynamic data for all four phase types and can be used for calculating Pourbaix diagrams. They have been designed specifically for the purpose of demonstrating the POURBAIX module functionality in Thermo-Calc. However, these databases only allow you to perform test calculations for simple cases with major phases in which only a few elements can be considered.

The next section is a discussion about Including or Excluding the Gas Phase.

4.1 Including or Excluding the Gas Phase

Under defined pressure and temperature conditions, the solvent water's thermodynamic stability limits are determined by the following two electrochemical reactions:

```
H2O(water) + 2e- = H2(gas) + 2OH-1

2H2O(water) = O2(gas) + 4H+1 + 4e-
```

The first reaction describes the formation of H_2-dominated gaseous mixture, under reducing conditions. The second reaction describes the formation of O_2-dominated gaseous mixture, under oxidising conditions.

If the system reaches global equilibrium, then the water component is electrolyzed to H^+ and O^{-2} at all pH conditions. The degree of electrolysis depends on the pH value in the aqueous solution phase. If Eh gets high enough, then the O^{-2} anion is oxidized to $O_{2\,(aqs)}$. On the other hand, if Eh gets low enough, then the H^+ cation is reduced to $H_{2\,(aqs)}$. The major electrolysis and redox reactions are the following:

`H2O (water) = H+ + OH- → Electrolysis of water at all pH.`

$H_2O_{(water)}$ `= 2H`$^+$ `+ O`$^{-2}$ `→ Electrolysis of water at all pH.`

`O-2 - 2e- = 0.5O2 (aqs)→Oxidation or de-electronization of O-2 at high Eh.`

`2H+ + 2e- = H2 (aqs) → Reduction or electronization of H+ at low Eh.`

At a critically high Eh value under a given pH condition, an aqueous solution phase with a high enough O_2 activity becomes less stable than an O_2-dominated gaseous mixture phase. At this point, the gas phase replaces the aqueous solution phase in the system. The replacement process can be characterised by the following phase-transformation on the aqueous-gas phase boundary and oxidation of remaining water:

```
O2 (aqs)  = O2 (gas)
H2O (water) - 2e- = 2H+(gas) + 0.5O2 (gas)
```

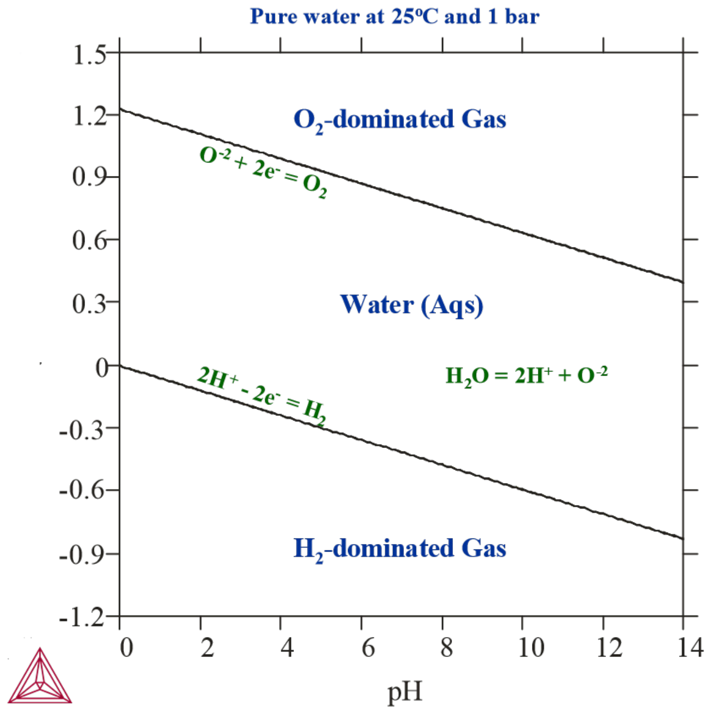
Similarly, at a critically low Eh value under a given pH condition, an aqueous solution phase with a high enough H_2 activity becomes less stable than a H_2-dominated gaseous mixture phase. At this point, the gas phase replaces the aqueous solution phase in the system, through the following phase-transformation on the aqueous-gas phase boundary and reduction of remaining water:

```
H2 (aqs)  = H2 (gas)
H2O (water) + 2e- = O-2 (gas) + H2 (gas)
```

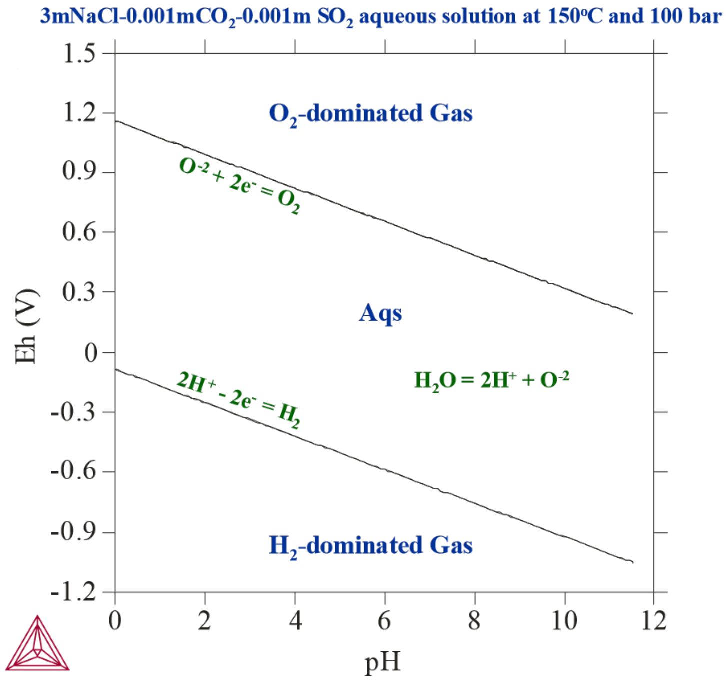
The phase transformation from an aqueous solution phase to an O_2- or H_2-dominated gaseous mixture phase also depends on the total molar Gibbs energies of the phases (which are complex functions of the phase constituents, the temperature and the pressure). The Gibbs energy minimization technique used in Thermo-Calc ensures that the phase transformation is accurately simulated.

The following Pourbaix diagrams show the result of a calculation where the gaseous mixture phase was included. In the upper region (high Eh) and lower region (low Eh), the aqueous solution phase has been oxidized and reduced, respectively, to an O_2- or H_2-dominated gaseous mixture phase.

The first diagram is a pH-Eh diagram for pure water at 25°C and 1 bar:



The second diagram is a pH-Eh diagram for 3mNaCl-0.001mCO$_2$-0.001mSO$_2$ aqueous solution at 150°C and 100 bar.



These two preceding diagrams show that the upper and lower boundaries between the aqueous phase (water) and the gas phase (dominated by either O_2 or H_2) can shift when solutes dissolve or when the temperature and pressure change.

Accordingly, if one does not take a gaseous mixture phase into account when performing a calculation of Pourbaix diagram (as above), then the aqueous solution phase may end up with an extremely high $O_{2\ (aqs)}$ concentration at high Eh condition, or an extremely high $H_{2\ (aqs)}$ concentration at low Eh condition. Under either of these two extreme circumstances, the concept of “aqueous solution phase” is no longer valid and consequently no proper aqueous solution model can actually be applied. Therefore, from a restrictive thermodynamic equilibrium point of view, one shall normally include a gaseous mixture phase in an aqueous-bearing heterogeneous interaction system. This is true for all types of equilibrium calculations for an aqueous-bearing heterogeneous interaction system, not only of Pourbaix diagram calculations.

Hence, to perform a completely accurate Pourbaix diagram calculation, the gaseous mixture phase must be taken into account. However, since these electrochemical reactions normally have much higher kinetic barriers and are slower than other electrochemical and chemical reactions in the interaction system, one can sometimes ignore the gaseous mixture phase in the calculation. Note that if the gaseous mixture phase is ignored in this way, then the Pourbaix diagram does not show the H_2O-stability limiting lines.

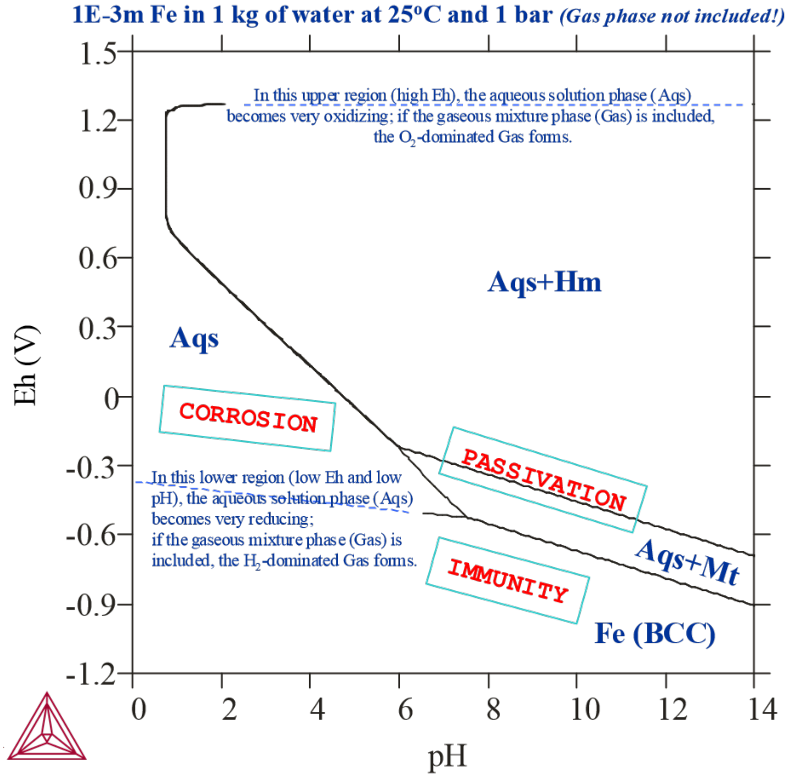
5. Examples of Pourbaix Diagrams for Fe

The following two sections are examples of Pourbaix diagrams for Fe. For the first example, Pourbaix Diagrams with Gas Phase Excluded, the calculations on which the diagrams are based have not taken the gas phase into account. The diagrams in the second example, Pourbaix Diagrams with Gas Phase Included, are based on calculations that have taken the gas phase into account.

5.1 Pourbaix Diagrams with Gas Phase Excluded

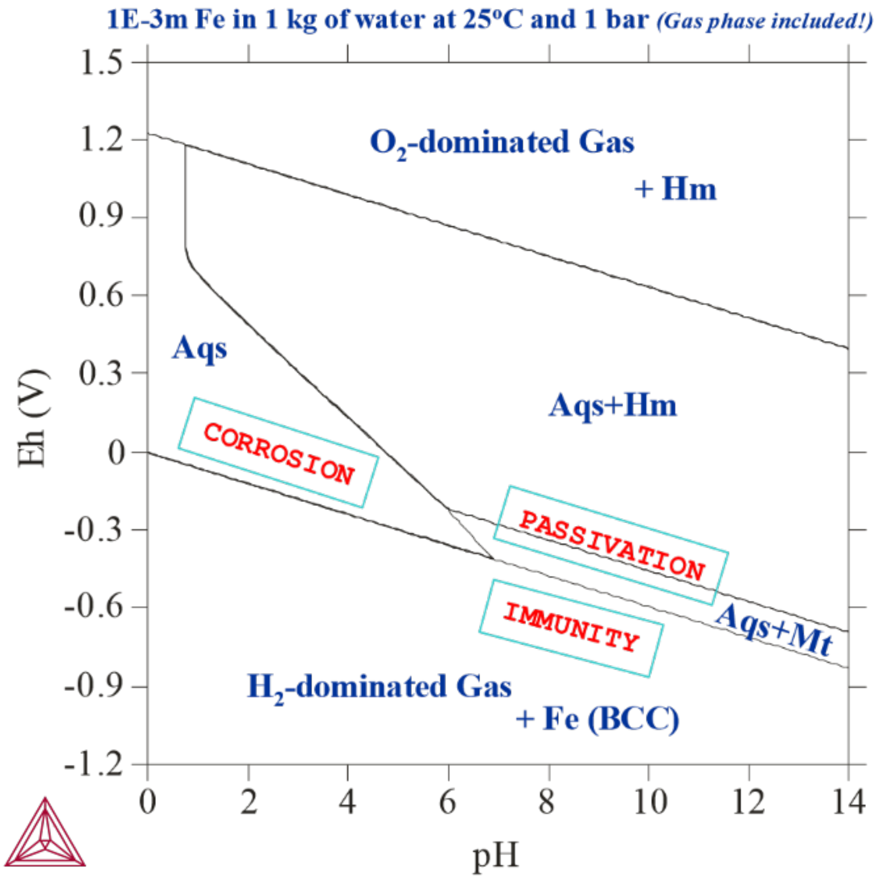
Below is an example of a Pourbaix diagram of Fe, in which the gas phase has not been considered in the calculation. The system has 0.001 mole of Fe in 1 kg of pure water at a temperature of 25°C and a pressure of 1 bar. Magnetite (Mt, Fe_3O_4) and hematite (Hm, Fe_2O_3) co-exist with the Fe-containing dilute aqueous solution. The formation of magnetite and hematite represent the passivation of iron in the upper right pH-Eh field.

If pH is low and Eh is relatively high, then Fe eventually completely dissolves into the aqueous solution phase. Under conditions of low Eh, Fe remains in its stable solid state, the BCC phase, and neither dissolves into water nor into alternates to Fe (the immunity of Fe).



5.2 Pourbaix Diagrams with Gas Phase Included

With all the possible redox reactions involving the aqueous solution phase and gaseous mixture phase being considered in the equilibrium system, that is, the gaseous mixture phase is included in the calculation, the Pourbaix diagram of Fe in a system with 0.001 mole of Fe in 1 kg of pure water at 25°C and 1 bar (illustrated in the following diagram).



Comparing this Pourbaix diagram with that from section 3.1, we can see that both diagrams are for the same interaction system under the same temperature-pressure condition, but the present diagram shows the results of calculations where the gaseous mixture phase has been included. It presents the complete Pourbaix diagram for the defined interaction system, in a full thermodynamic equilibrium. In the upper region (high Eh) and lower region (low Eh), the aqueous solution phase is oxidised and reduced to the O_2- or H_2-dominated gas phase. Hematite coexists with the O_2-dominated gas, while Fe-BCC is stable with the H_2-dominated gas. The stability field of magnetite may extend slightly into the H_2-dominated gas region, where it coexists with the gaseous mixture instead of the aqueous solution. Its boundary with Fe (BCC) cannot be drawn due to the absence of aqueous solution phase.

It is not possible to calculate the pH value in both the O_2- and H_2-dominated gaseous mixture phase stability regions where the aqueous solution phase is absent. Hence, in a normal Pourbaix diagram, no line is drawn that indicates a phase boundary between the gas phase and the metallic phases or secondary phases (that is, metal-oxides).

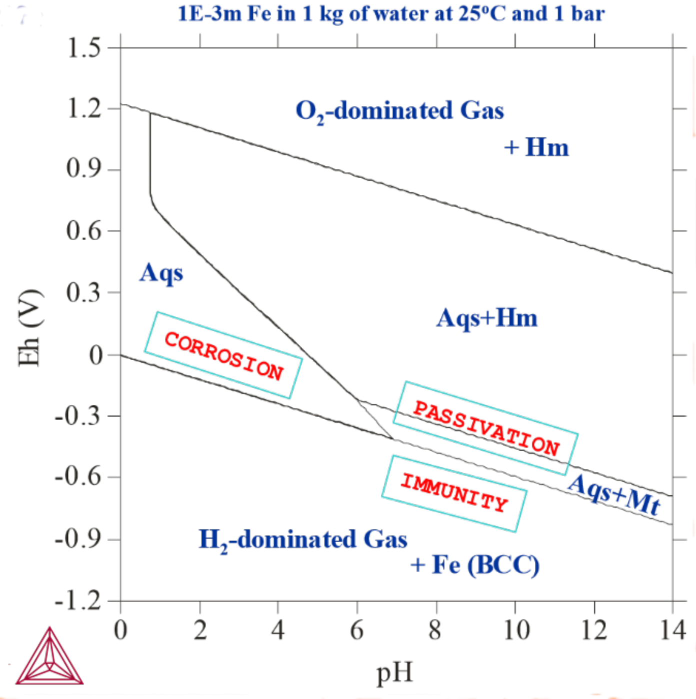
6. Variations of Pourbaix Diagrams

The shape of a Pourbaix diagram of an alloy or condensed material and the stability relations of various secondary phases depend upon the following system factors:

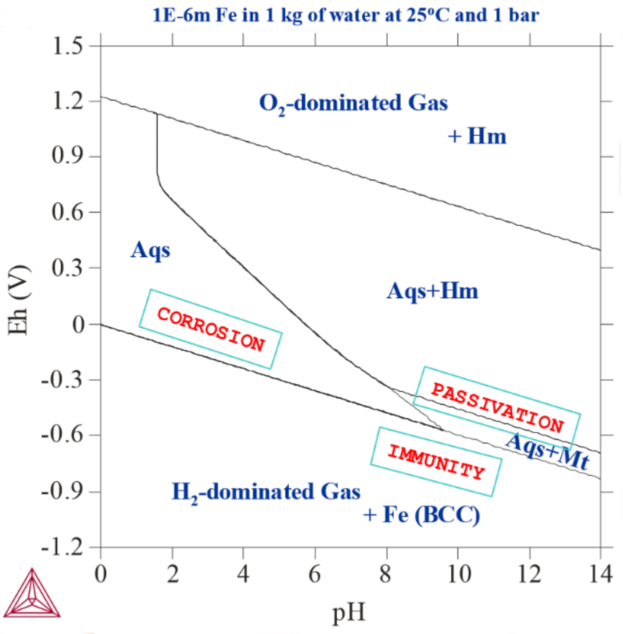
- Initial amount of the alloy or other condensed materials
- Initial composition of the alloy or other condensed materials
- Initial amount of the interacting aqueous solution phase
- Initial composition of the interacting aqueous solution phase
- Temperature and pressure conditions

In the interaction system that the diagrams in sections 5.1 and 5.2 are based on, the initial amount of pure Fe that was taken to have effectively reacted with 1 kg of pure water at 25˚C and 1 bar was 0.001 m. The following diagrams are Pourbaix diagrams of Fe where other initial amounts of pure Fe have been used, or where the interacting aqueous solution compositions have been alternated, or the temperature and/or pressure have been changed. Gaseous mixture phases have been included in all the calculations that these diagrams are based on.

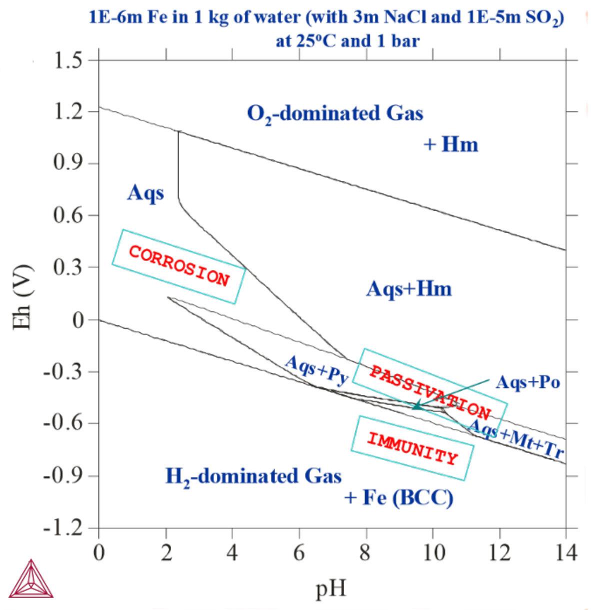
In the first diagram below, 1E-3 m Fe actively reacted with 1 kg of pure water at 25°C and 1 bar (as in the calculation in section 5.2):



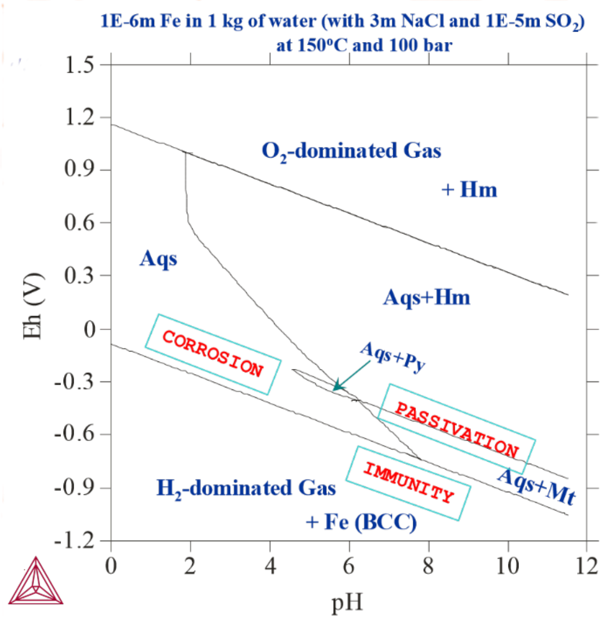
In the second diagram, 1E-6 m Fe actively reacted with 1 kg of pure water at 25°C and 1 bar. Note that the active metal corrosion region gets enlarged as the initial Fe amount decreases from 1E-3m to 1E-6m:



In the third diagram, 1E-6 m Fe actively reacted with 1 kg of water, 3m NaCl and 1E-5 m SO_2 at 25°C and 1 bar. Introducing SO_2 into the system leads to the formation of various metal-sulphides (Py-pyrite, Popyrrhotite, Tr-troilite). In addition, the passivation region becomes larger.



Finally, in the fourth diagram, 1E-6 m Fe actively reacted with 1 kg of water, 3m NaCl and 1E-5 m SO_2 at 150°C and 100 bar. Here, changing the temperature and pressure affects the stability fields of various Fe-oxides/sulphides.

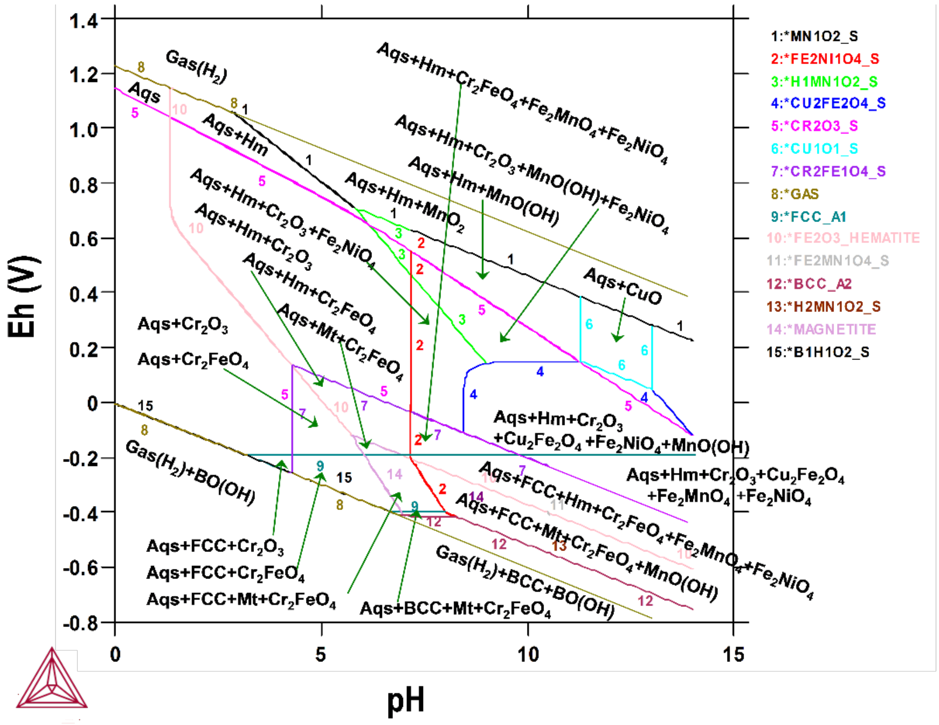


As you can see from the preceding four diagrams, the aqueous-gas phase boundaries shift as the initial bulk compositions, pressure and temperature conditions in the interaction system change.

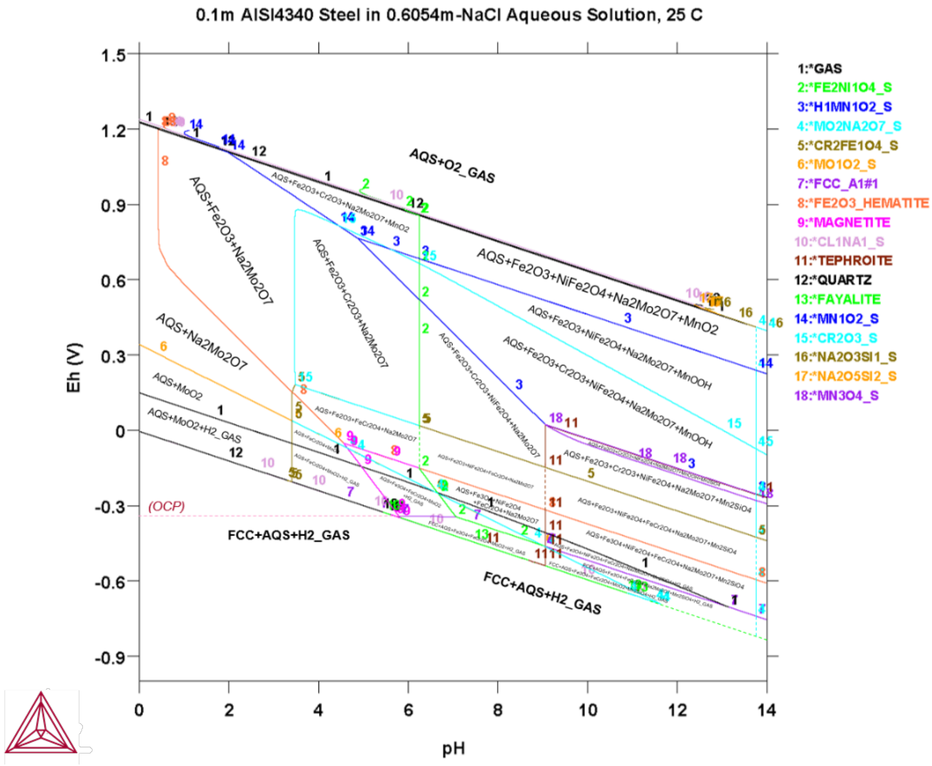
7. Pourbaix Diagrams for Complex Alloys

Thermo-Calc can not only be used to simulate how pure metals interact with pure water or simple aqueous solutions under normal pressure and temperature conditions. It can also be used to calculate how complex alloys and concentrated aqueous solutions interact over a very wide pressure, temperature and composition ranges. This is illustrated with the two examples that follow below.

The first example is a Pourbaix diagram calculated for the heterogeneous interaction between 0.001 mole of steel (Fe-7.676Cr-5.0Ni-2.1887Mn-1.0Cu [at%]) and 1 kg of water (and with 1.2 m H_3BO_3, 0.022 m Li and 0.001 m NH_3), at 25˚C and 1 bar. This application is particularly useful for safety assessments of nuclear reactors and nuclear waste repositories.



The next example is a Pourbaix diagram calculated 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 seawater (with the equivalent of 0.6054 m NaCl), at 25°C and 1 bar. This application is particularly useful for failure analysis of petroleum exploitation industry.


0.1m AISI4340 Steel in 0.6054m-NaCl Aqueous Solution, 25 C
Eh (V)
pH
1.5
1.2
0.9
0.6
0.3
0
-0.3
-0.6
-0.9
0
2
4
6
8
10
12
14
1:*GAS
2:*FE2NI1O4_S
3:*H1MN1O2_S
4:*MO2NA2O7_S
5:*CR2FE1O4_S
6:*MO1O2_S
7:*FCC_A1#1
8:*FE2O3_HEMATITE
9:*MAGNETITE
10:*CL1NA1_S
11:*TEPHROITE
12:*QUARTZ
13:*FAYALITE
14:*MN1O2_S
15:*CR2O3_S
16:*NA2O3SI1_S
17:*NA2O5SI2_S
18:*MN3O4_S
AQS+O2_GAS
AQS+Fe2O3+Cr2O3+Na2Mo2O7+MnO2
AQS+Fe2O3+Na2Mo2O7
AQS+Fe2O3+Cr2O3+Na2Mo2O7
AQS+Fe2O3+NiFe2O4+Na2Mo2O7+MnO2
AQS+Fe2O3+NiFe2O4+Na2Mo2O7+MnOOH
AQS+Fe2O3+Cr2O3+NiFe2O4+Na2Mo2O7+MnOOH
AQS+Fe2O3+Cr2O3+NiFe2O4+Na2Mo2O7
AQS+Na2Mo2O7
AQS+MoO2
AQS+MoO2+H2_GAS
AQS+Fe2O3+FeCr2O4+Na2Mo2O7
AQS+Fe2O3+NiFe2O4+FeCr2O4+Na2Mo2O7
AQS+Fe2O3+Cr2O3+NiFe2O4+Na2Mo2O7+Mn2SiO4
AQS+Fe3O4+NiFe2O4
+FeCr2O4+Na2Mo2O7
AQS+Fe2O3+NiFe2O4+FeCr2O4+Na2Mo2O7+Mn2SiO4
AQS+Fe3O4+NiFe2O4+FeCr2O4+Na2Mo2O7+Mn2SiO4
(OCP)
FCC+AQS+H2_GAS
FCC+AQS+H2_GAS

8. References

Andersson J-O, Helander T, Höglund L, Shi Pingfang, and Sundman B (2002): Thermo-Calc and DICTRA, Computational tools for materials science. *Calphad*, 26: 273-312.

Ciavatta L (1990): The specific interaction theory in equilibrium analysis. Some empirical rules for estimating interaction coefficients of metal ion complexes. *Ann Chim. (Rome)*, 80, 255-263.

Cramer SD and Covino BS Jr. (2003): *Corrosion: Fundamentals, Testing, and Protection*. ASM Handbook, Volume 13A.

Helgeson HC, Kirkham DH, and Flowers GC (1981): Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. *Am. J. Sci.*, 281, 1249- 1516.

Johnson JM and Norton D (1991): Critical phenomena in hydrothermal system: State, thermodynamic, electrostatic, and transport properties of H_2O in the critical region. *Am. J. Sci.*, 291, 541-648.

Kaufman L (2002) Calculation of Pourbaix diagrams for C22 in various well water chemistries. In: *Proceedings for the 5th Nickel Development Institute Workshop on Fabrication of Welding of Nickel Alloys* (R. Moeller, ed.), Nickel Development Institute, Las Vegas, Nevada, 16-17 Oct., 2002.

Kaufman L, Perepezko JH, Hildal K, Farmer J, Day D, Yang N, and Branagan D (2009): Transformation, stability and Pourbaix diagrams of high performance corrosion resistant (HPCRM) alloys. *Calphad,* 33: 89-99.

Pourbaix M (1973): *Lectures on Electrochemical Corrosion*. Plenum Press, New York.

Pourbaix M (1974): *Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd Ed*, Houston, Tex., National Association of Corrosion Engineers.

Shi Pingfang (2013a): *Thermo-Calc 3.0 (Console Mode) Manual* (including *TC3-CM User's Guide*, and *Thermo-Calc Software System*), Thermo-Calc Software, Stockholm, Sweden.

Shi Pingfang (2013b): *Materials Corrosion Applications with Thermo-Calc Software.* Thermo-Calc Software, Stockholm, Sweden.

Shi Pingfang, Engström A, and Sundman B (2011a): Thermodynamic investigations on materials corrosion in some industrial and environmental processes. *Journal of Environmental Sciences*, 23 (Supplement): S1-S7.

Shi Pingfang, Engström A, Sundman B, and Ågren J (2011b): Thermodynamic calculations and kinetic simulations of some advanced materials. *Materials Science Forum*, 675-677: 961-974.

Thompson WT, Kaye MH, Bale CW, and Pelton AD (2011): Pourbaix diagrams for multielement systems. In: *Uhlig's Corrosion Handbook, 3rd Edition (Revie RW, Ed.)*, The Electrochemical Society and Jon Wiley & Sons, New Jersey.

Verink ED (2011): Simplified procedure for constructing Pourbaix diagrams. In: *Uhlig's Corrosion Handbook, 3rd Edition (Revie RW, Ed.)*, The Electrochemical Society and Jon Wiley & Sons, New Jersey.