CHAPTER 1

THERMODYNAMICS OF LIQUID IRON ALLOYS

Liquid steel is liquid solution of the atoms of iron (solvent) and the atoms of the alloying elements (solutes) like manganese, carbon, silicon, sculpture, phosphorous, oxygen, nitrogen, chromium, vanadium, titanium, tungsten, etc. In an ideal solution there are no interactions between different types of atoms and during the formation of solution the enthalpy and volume changes are zero (i.e. \( \Delta H = 0 \) and \( \Delta V' = 0 \)). The change in entropy is not zero because the addition of new type of atoms to a solvent increases the disorder. It can be shown from statistical thermodynamics that

\[
\Delta S = -R \sum X_i \ln X_i, \tag{1.1}
\]

Where \( X_i \) is the mole fraction of the component \( i \). From Equation

\[
\Delta G = \Delta H - T \Delta S
\]

And for an ideal solution \( \Delta H = 0 \); hence

\[
\Delta G = RT \sum X_i \ln X_i, \tag{1.2}
\]

Iron and manganese, upon alloying, form a nearly ideal solution. In non-ideal solutions, \( \Delta H \neq 0 \) and \( \Delta V' \neq 0 \) and the added solute atoms are attracted or repelled, to varying degrees, by the resident atoms in the solution. The intensity of such interactions will decide the departure from ideal behavior.

According to Raoult’s law, in the case of ideal solution if the activity of a component \( i \) (\( a_i \)) is plotted as a function of mole fraction (\( X_i \)), as shown in Figure 1.1(a), then a straight line will be obtained with a slope unity, i.e.

\[
a_i = X_i \tag{1.3}
\]

The dashed line in Figure 1.1(a) is called the Raoult’s law line. Most of the solutions are non-ideal and

\[
a_i = \gamma_i X_i \tag{1.4}
\]

where \( \gamma_i \) is called the Raoultian activity coefficient. It is obvious that only when \( \gamma_i = 1 \), Raoult’s law is obeyed. The deviation from through Raoult’s law can be positive or negative. For example, the plot in Figure 1.1(b), where \( a_i \) is greater than \( X_i \), is a typical example of positive deviation from ideal behavior (namely, in the Fe–Cu system). Similarly, Figure 1.1(c), where \( a_i \) is greater than \( X_i \), is a typical example of negative deviation from ideal behavior (namely, in the Fe–Si system).
Activity is related to free energy in the following way. The free energy change for a
system doing work against pressure p is
\[ dG = V dP - S dT \]
(1.5)
Where \( V \) is the molar volume, At constant temperature
\[ dG = V \, dp \]
(1.6)
For 1 mole of ideal gas, and since \( pV = RT \),
\[ dG = RT \, d(ln p) \]
(1.7)
If the gas is non-ideal pressure \( P \) is replaced by fugacity \( f \):
\[ dG = RT \, d(ln f) \]
(1.8)
now \( a = \frac{f}{f_0} \) and hence
\[ dG = RT \, d[(ln f_0 a)] \]
(1.9)
Since \( f_0 \) is constant at a given temperature and composition:
\[ dG = RT \, d(ln a) \]
(1.10)
In the standard state, the free energy of a substance is denoted by \( G_i^\circ \), whereas its partial
molar free energy in a solution is denoted by \( G_i^\ast \). Integrating equation (2.20):
\[
\left( \frac{\partial \tilde{G}_i}{\partial T} \right)_P = \left( \frac{\partial}{\partial T} (RT \ln a_i) \right)_p = -\Delta S_i^M dT
\]

Or
\[
\Delta S_i^M = -R \ln a_i - RT \left( \frac{\partial (\ln a_i)}{\partial T} \right)_p
\]  \hspace{1cm} (1.14)

Also, by definition,
\[
\Delta G_i^M = \Delta H_i^M + T \Delta S_i^M
\]

From Equations (2.22) and (2.24)
\[
\Delta H_i^M = -RT \left( \frac{\partial \ln a_i}{\partial T} \right)_p
\]  \hspace{1cm} (1.15)

By knowing the variation of the activity with temperature, one can calculate \( \Delta S_i^M \) and \( \Delta H_i^M \) at a given temperature.

The free energy change during a chemical reaction is also related to the activity and can be calculated as follows.

Let there be a reaction of the following form:
\[
a A + b B + \ldots = c C + d D + \ldots
\]  \hspace{1cm} (1.16)

Where \( a \) moles of \( A \), \( b \) moles of \( B \), \ldots combine to give \( c \) moles of \( C \) and \( d \) moles of \( D \), \ldots In a general case, where the components are considered to be present in solution, the free energy change of the reaction is given by

\[
\Delta G = \left[ c \tilde{G}_C + d \tilde{G}_D + \ldots \right] - \left[ a \tilde{G}_A + b \tilde{G}_B + \ldots \right]
\]  \hspace{1cm} (1.17)

Hence from Equation (2.22)
\[
\Delta G = \left[ c(G_c^o + RT \ln a_C) - d(G_d^o + RT \ln a_D) + \ldots \right]
- \left[ a(G_A^o + RT \ln a_A) + b(G_B^o + RT \ln a_B) + \ldots \right]
\]

\[
= \left[ c(\tilde{G}_C + d \tilde{G}_D + \ldots) - (a \tilde{G}_A + b \tilde{G}_B + \ldots) \right] + RT \ln \left( \frac{a_c a_d}{a_A a_B} \right)
\]

\[
= \Delta G^o + RT \ln Q
\]  \hspace{1cm} (1.18)

Where
\[ Q = \frac{a^c a^d \cdots}{a^i a^b \cdots} \] (1.19)

\( \Delta G^o \) is the free energy change of the reaction when all the reactants and products are in their standard states. At equilibrium \( \Delta G = 0 \); hence

\[ \Delta G^\circ = -RT \ln (Q)_{equilibrium} \] (1.20)

Since \( \Delta G^\circ \) is a constant at a given temperature and pressure, \( (Q)_{equilibrium} \) must also be a constant. This is known as the equilibrium constant \( K \), hence

\[ \Delta G = -RT \ln K \] (1.21)

The equilibrium concentration of different elements taking part in a chemical reaction in a closed system at constant temperature and pressure can change depending upon their initial concentrations, but only in such a way that \( K \) remains constant. This is basic principal of refining of liquid steel.

The chemical reactions taking place in closed system also obey the phase rule, according to which

\[ F = C - P + 2 \] (1.22)

Where \( F \) is the degree of freedom or minimum number of additional state variables required to be fixed for a specified system, \( C \) is the number of components in the system, and \( P \) is the number of phases. If the temperature and pressure are fixed (special restriction imposed on the system) then the degree of freedom would be zero and the composition of each phase would be fixed.

For a reacting system with \( i \) chemical species, \( r \) independent chemical reactions, \( P \) phases, \( x \) stoichiometric relations and \( n \), special constraints (restrictions already imposed on the system)

\[ F = C - P + 2 \]

Where

\[ C = i - r - x - n \]

Consider the oxidation of carbon by oxygen gas in a molten Fe-C-O alloy at constant temperature and pressure. Three possible chemical reactions are:

- \([C] + [O] = (CO)_{g}\]
- \([C] + [O] = (CO_2)_{g}\]
- \([Fe] + [O] = (FeO)\]

- There are three independent chemical reactions: \( r = 3 \).
- The species are CO, CO_2, C, O, Fe and FeO: \( i = 6 \).
- The reacting phases are slag, metal, gas: \( P = 3 \).
• Special constraints are constant temperature and pressure: \( n_r = 2 \).
• There is no stoichiometric constraint: \( x = 0 \).

Thus \( F = 6 - 3 - 0 - 2 - 3 + 2 = 0 \) i.e. the system has zero degrees of freedom.

**Dilute solutions in liquid steel**

Elements like oxygen, carbon, hydrogen, nitrogen, silicon, manganese, sulphur and phosphorus are generally present in small concentrations in liquid steel, i.e. in the form of a dilute solution. The thermodynamic treatment of dilute liquid steel solutions is greatly simplified by Henry’s law, according to which the Henrian activity of any component at infinite dilution is equal to its concentration. During day-to-day operations, the operator in steel prefers to express the concentration in wt % rather than in mole % (or mole fractions) according to Henry’s law for the dilute solutions, the Henrian activity \( h_i \) of a solute \( i \) as equal to the concentration expressed in wt %:

\[
h_i = (\text{wt}%) \quad (1.23)
\]

The term ‘dilute’ may be used as long as the above relationship is valid and thus the range of application of equation (1.23) may vary from one element to another. From thermodynamics, however, it can be shown that Equation (1.23) is valid only at infinite dilutions. If the concentration is expressed in mole fractions \( X_i \), then, according to Henry’s law for a solution at infinite dilution,

\[
h_i = X_i \quad (1.24)
\]

Both \( h_i \) and \( h_i \) are related to Raoult’s law. In order to derive the relationships between the Raoultian and the Henrian activities, it is necessary to understand the concept of standard states.

The solid line in Figure 1.2 depicts a marked negative deviation from ideal behavior and the dashed line AB represents the Rout’s law line. Up to point C (say 0.3 mole fractions), the Routine activity \( a_i \) may be assumed to fall on the straight line ACD. The line ACD also represents Henry’s law line corresponding to equation (1.23) and (1.24). The ratio The Ratio FD/AF gives the slope of the line ACD and if this is denoted by \( \gamma_i^0 \), then in the region AC the Routine activity \( a_i \) will be given by

\[
a_i = \gamma_i^0 X_i \quad (1.25)
\]

The numerical relationship between \( h_i, h_i^0 \) and \( a_i \), on the basis of Equations (1.23)-(1.25), may now be written as

\[
\frac{h_i}{(\text{wt}\%)} = \frac{h_i}{X_i} = \frac{a_i}{\gamma_i^0 X_i} = 1
\]

**Thermodynamics of liquid iron alloys**
It follows that
\[ a_i = \gamma_i \frac{h_i}{(\text{wt}\%)} \quad (1.27) \]

and
\[ a_i = h_i \gamma_i^{\alpha} \quad (1.28) \]

From Equation (2.22), the relative partial molar free energy of a substance in solution is related to the Raoultian activity, \( a_i \), by
\[ \Delta G_i = RT \ln a_i \]

Three cases of \( a_i \) may now be considered:

**Case I** \( a_i = 1 \) (pure substance)

Hence
\[ \Delta G_i = RT \ln 1 = 0 \quad (1.29) \]

**Case II** \( a_i = \gamma_i \frac{h_i}{(\text{wt}\%)} \) (from Equation (2.37))

When \( h_i = 1, (\text{wt}\%), = 1 \) (from Equation (2.33)). It can also be shown, as a first approximation, that at infinite dilution in iron the mole fraction of the solute \( i \) is related to the wt % of \( i \) by
\[ X_i = \frac{55.85}{100M} \quad (\text{wt}\%) \]

Where 55 85 is the atomic weight of iron and \( M \) is the atomic weight of the element \( i \).

The relative partial free energy of solution is therefore
\[ \Delta G_i = RT \ln a_i = RT \ln \left[ \gamma_i^{\alpha} \left( \frac{0.5585}{M_i} \right) (\text{wt}\%) \right] \quad (1.30) \]

The free energy change \( \Delta G_i \) associated with the change of standard state from pure substance to 1 wt%, i.e.,
\[ i_{\text{pure}} \to [i]_{1\text{wt\%}} \]

\( i \) is thus given by
\[ \Delta G_i = RT \ln \left[ \gamma_i^{\alpha} \left( \frac{0.5585}{M_i} \right) \right] \quad (1.31) \]

**Case III** \( a_i = h_i \gamma_i^{\alpha} \) (from Equation (2.38))

When \( h_i = 1 \),
\[ \Delta G_i = RT \ln a_i = RT \ln \gamma_i^{\alpha} \quad (1.32) \]
\[ \Delta G^M_2 \] is the free energy change of the standard state from pure substance to infinite dilution.

Beyond point C in Figure 1.2, Henry’s law is not obeyed and Equation (2.36) becomes

\[
\frac{h_i}{(\text{wt}\%)} = \frac{h_i}{X_i} = \frac{a_i}{\gamma_i"X_i} = f_i \quad (1.33)
\]

where the term \( f_i \) known as Henrian activity coefficient, accounts for the deviation from Henry’s law.

The Equations (2.41) and (2.42) now become

\[
\Delta G^M_i = RT \ln \left( f_i \gamma_i"X_i \right) \quad (1.34)
\]

\[
\Delta G_i^M = RT \ln \left( f_i \gamma_i" \right) \quad (1.35)
\]

For the most of the solute dissolved in liquid iron in the form of a dilute solution, the term \( \ln f_i \) varies linearly with mole fraction of the solute or \( \lg f_i \) varies linearly wt\% of the solute. From a Taylor’s series expansion one can write the first term as

\[
\ln f_i = \frac{\partial \ln f_i}{\partial X_i} X_i \quad (1.36)
\]

and

\[
\lg f_i = \frac{\partial (\lg f_i)}{\partial (\text{wt}\%)} \quad (1.37)
\]

The term \( \frac{\partial \ln f_i}{\partial X_i} \) is called the interaction coefficient \( \varepsilon_i' \) and the term \( \frac{\partial (\lg f_i)}{\partial (\text{wt}\%)} \) the interaction coefficient \( \varepsilon_i'' \). At high dilution the relationship between \( \varepsilon_i' \) and \( \varepsilon_i'' \) can be written from equation (1.36) and (1.37) as

\[
2.303 \varepsilon_i'(\text{wt}\%) = \varepsilon_i' X_i \quad (1.38)
\]

As shown in Equation (1.30), for liquid iron at high dilution

\[ X_i = \frac{0.5585}{M_i} (\text{wt}\%) \]

Hence

\[
2.303 \varepsilon_i'(\text{wt}\%) = \varepsilon_i' \frac{0.5585}{M_i} (\text{wt}\%)
\]

Or
\[ e_i' = \frac{0.2445}{M_i} \epsilon_i' \]  \hspace{1cm} (1.39)

If the solutes \( i, j, k \ldots \) are present in dilution solution, i.e. in multicomponent systems, Equations (2.46) and (2.47) can be written in the form of Taylor’s series expansion,

\[ \ln f_i = \frac{\partial (\ln f_i)}{\partial X_i} X_i + \frac{\partial (\ln f_i)}{\partial X_j} X_j + \frac{\partial (\ln f_i)}{\partial X_k} X_k + \ldots \]

\[ = \epsilon_i'X_i + \epsilon_j'X_j + \epsilon_k'X_k + \ldots \]  \hspace{1cm} (1.40)

and

\[ \ln g_i = \frac{\partial (\ln g_i)}{\partial (w\%)} (w\%) + \frac{\partial (\ln g_i)}{\partial (w\%)} (w\%) + \frac{\partial (\ln g_i)}{\partial (w\%)} (w\%) + \ldots \]

Or

\[ \ln g_i = \epsilon_i'(w\%) + \epsilon_j'(w\%) + \epsilon_k'(w\%) + \ldots \]  \hspace{1cm} (1.41)

In general, \( \epsilon_i' \) and \( \epsilon_i' \) represent the effect of element \( k \) on the Henrian activity coefficient of element \( i \), when both \( i \) and \( k \) are present in dilute solution. The equilibrium constants for the reactions involving the elements dissolved in liquid steel are summarized in Table 1.1. The interaction parameter values \( (\epsilon_i' \) \) are summarized in Table 1.2. In some cases, when the variation of \( \ln f_i \) or \( (\ln f_i) \) against concentration is not linear, the second-order interaction coefficients. In the treatment of dilute solutions in liquid iron, it generally suffices to use first-order interaction coefficients only.

From Equation (1.33), the Raoultsian activity \( a_i \) is given by

\[ a_i = f_i \gamma_i X_i \]  \hspace{1cm} (1.43)

Since by definition

\[ f_i \gamma_i = \gamma_i \]  \hspace{1cm} (1.44)

then

\[ a_i = \gamma_i X_i \]  \hspace{1cm} (1.45)

where \( \gamma_i \) is the same as the Routine activity coefficient appearing in Equation (2.14).

The Henrian activity \( h_i \) is obtained from Equation (1.33) as

\[ h_i = (w\%)_i f_i \]  \hspace{1cm} (1.46)
Or

\[ \lg h = \lg (\text{wt} \%) + \lg f \]  

(1.47)

In a multicomponent system \( \lg f \) is obtained from Equation (1.42).

### 2.3.2 Thermodynamics of oxygen dissolution in liquid iron

The dissolution of oxygen in liquid steel may be represented by the equation

\[ \frac{1}{2} (O_2)_g = [O] \]  

(1.48)

Where \([O]\) denotes the oxygen dissolved in the metal as atomic oxygen with a reference state of 1 wt%. The equilibrium constant \( K_o \) for equation (1.48) can be written as

\[ K_o = \frac{h_o}{(P_{O_2})^\frac{1}{2}} \]  

(1.49)

The standard free energy is given by

\[ \Delta G_o^\circ = -RT \ln K_o \]

\[ = -117.3 - 2.889 \times 10^{-3}T \text{ kJ/mol} \]  

(1.50)

Where \( T \) is the temperature in Kelvin, \( R \) is the universal gas constant (equal to 8.314 J/mol K), \( P_{O_2} \) denotes the partial pressure of oxygen in the gas phase in atmospheres, and \( h_o \) activity of dissolved oxygen in steel in the 1 wt% standard state. Combining Equations (1.49) and (1.50) Yields

\[ \lg h_o - \frac{1}{2} \lg P_{O_2} = (6126/T) + 0.15 \]  

(1.51)

Using Equation (2.56)

\[ h_o = f_o (\text{wt} \%) \]  

(1.52)

Where \( f_o \) designates the activity coefficient of dissolved oxygen in steel. In pure liquid iron containing dissolved oxygen, the only interaction parameter to be considered is \( e_o^2 = -0.20 \). Thus from Equation (1.42):

\[ \lg f_o = -0.20 [\text{wt} \% O] \]  

(1.53)

The above relation can be used to estimate the equilibrium value of oxygen \([\text{wt} \% O]\) in liquid iron at a given temperature and for a given value of \( P_{O_2} \). When liquid iron becomes saturated with oxygen, iron oxide forms, i.e. liquid iron and iron oxide are in equilibrium (see the top left-hand region in the Fe-O phase equilibrium diagram in Figure 1.3). The iron oxide, in equilibrium with pure iron, is denoted as \( \text{Fe}_x \text{O} \), where \( x \) is approximately 0.985 at 1873K. For the sake of simplicity, \( x \) can be assumed to be unity.
The general equation for calculating the solubility of oxygen in liquid iron, in equilibrium with FeO, is

\[(FeO) = \{Fe\} + [O] \quad (1.54)\]

The equilibrium constant for the above reaction can be written as

\[K_{Fe} = \frac{[h_{O}]_{\text{sat}}}{a_{FeO}} \quad (1.55)\]

and

\[\lg K_{Fe} = -(6372/T) + 2.73 \quad (1.56)\]

Where \(a_{Fe}\), the activity of iron in the form metal phase in the Raoultian scale, is approximately equal to 1, and \(a_{FeO}\) denotes the activity of FeO. For \(a_{FeO} = 1\) (i.e. if FeO is pure substance), the maximum solubility of oxygen, from equation (1.55).

\[K_{Fe} = [h_{O}]_{\text{sat}} \quad (1.57)\]

If FeO is impure for instance when it is present in slag phase along with other components, then \(a_{FeO} < 1\), and \(h_{O}\), i.e. the activity of dissolved oxygen in metal in equilibrium with the slag, will be lower. Using Equations (1.57) and (1.55)

\[K_{Fe} = [h_{O}]_{\text{sat}} = h_{O}/a_{FeO} \quad (1.58)\]

The Henry's activity of oxygen in liquid steel at a given temperature is thus directly depending upon the activity of iron oxide in the slag, or in the other words, the oxidizing power of the slag.

**Example 1 Calculate the maximum solubility of oxygen in pure iron at 1873K**

The Henry's activity of oxygen is related to its concentration in wt% by

\[\lg [h_{O}]_{\text{sat}} = \lg f_{O} + \lg [\text{wt}\%O]\]

On substituting the value of \(\lg f_{O}\) from equation (2.63)

\[\lg [h_{O}]_{\text{sat}} = -0.20[\text{wt}\%O] + \lg [\text{wt}\%O]\]

Again, at 1873K, from Equations (2.66) and (2.67)

\[\lg K_{Fe} = -0.672 = \lg [h_{O}]_{\text{sat}}\]

Writing \([h_{O}]_{\text{sat}}\) in terms of [wt\%O]
\[-0.20[\text{wt\%O}] + \lg[\text{wt\%O}] = -0.672\]

The above non linear equation can be solved by a suitable numerical procedure (e.g. the Newton-Raphson method) to yield

\[\text{[wt\%O]} = 0.235\text{wt\%}\]

Note: [wt\%O] at 1723K and 1923K are 0.185 and 0.29, respectively.

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**Thermodynamics of nitrogen and hydrogen dissolution in liquid iron**

The dissolution of nitrogen in iron represented by

\[\frac{1}{2}(N_2)_g = [N] \quad (1.59)\]

According to Sievert’s law

\[\%N = K_N \sqrt{P_{N_2}} \quad (1.60)\]

The equilibrium constant for the above reaction is

\[\lg K_N = -(255.6/T) - 1.26 \quad (1.61)\]

Thus, at equilibrium the percentage of nitrogen dissolved in liquid steel is directly proportional to the square of its partial pressure in the gas phase. Elements such as aluminum, vanadium, titanium and niobium form stable nitrides. If the nitrides are unable to float out during the solidification of steel then the total nitrogen content (i.e. dissolved nitrogen plus nitrogen present as nitrides of aluminum, titanium, etc.) of steel increases. The physical properties of steel are greatly affected by the precipitation of nitrides, for example, aluminum nitride (AlN) causes grain refinement.

The equation for the solubility of hydrogen in liquid iron is

\[\frac{1}{2}(H_2)_g = [H] \quad (1.62)\]

\[[H] = K_H \sqrt{P_{H_2}} \quad (1.63)\]

The equilibrium constant (when [H] is in ppm) is

\[\lg K_H = -(1670/T) - 1.68 \quad (1.64)\]

Titanium and tantalum increase the solubility of hydrogen in liquid iron. Unlike nitrogen, the hydrogen in liquid steel is absorbed primarily from the water vapor in the ambient atmosphere.
\[(H_2O)_{g} = 2[H] + [O]\] (1.65)

\[\Delta G^0 = 207653 - 0.292 \text{ T J/mol } H_2O\] (1.66)

**Example 2: Precipitation of aluminum nitride**

Suppose liquid iron at 1873K contains 0.2% aluminum and 300ppm nitrogen. Calculate the temperature at which aluminum nitride will begin to precipitate.

Assume all interaction parameters are zero.

From thermodynamic data:

\[\{\text{Al}\} + \frac{1}{2}\{N_2\}_{g} = <\text{AIN}> \Delta G^0 = -327063 + 115.520 \text{ T J/mol}\]

\[[\text{N}] = \frac{1}{2}\{N_2\}_{g} \Delta G^0 = -3598 - 23.891 \text{ T J/mol}\]

\[[\text{Al}] = [\text{Al}] \Delta G^0 = 63178 + 27.90 \text{ T J/mol}\]

\[[\text{Al}] + [\text{N}] = <\text{AIN}> \Delta G^0 = -267483 + 119.529 \text{ T J/mol}\]

Since the interaction parameters are zero the equilibrium constant for the above reaction can be written as

\[K_T = \frac{a_{\text{AIN}}}{[\text{wrt}\%\text{Al}][\text{wrt}\%\text{N}]}\]

Assuming that AIN is pure solid, \(a_{\text{AIN}} = 1\) and

\[K_T = \frac{1}{(0.2)(0.0300)}\]

From free-energy data:

\[-RT \ln K_T = -267483 + 119.529 \text{ T J/mol}\]

Substituting the value of \(K_T\), the temperature at which aluminum nitride will precipitate is \(T=1650\text{K}\).  

Thermodynamics of liquid iron alloys
Thermodynamics of carbon dissolution in liquid iron

Carbon is one of the most widely studied elements in steel making. The equation for the solubility of carbon (graphite saturation) in a binary Fe-C alloy is given [2] by

\[
\left[ \% C \right]_{\text{Saturated}} = 0.56 + 2.57 \times 10^{-3} T
\]

(1.67)

The ratio of Raoultian activity coefficient \((\gamma_c)\) to the activity coefficient at infinite dilution \(\gamma_c^\infty\), is given by [3]:

\[
\lg \left( \frac{\gamma_c}{\gamma_c^\infty} \right) = -2.38 \left( X_{Fe}^2 - 1 \right)
\]

(1.68)

where

\[
\gamma_c^\infty = (1180/T) - 0.8
\]

(1.69)

The solubility of carbon in iron is affected by the presence of other alloying elements like silicon, phosphorus, sulphur and manganese.
Three types of solutions

(a) Ideal solution, \( a_r = x_i \)
(b) Positive deviation, \( a_i > a_r \)
(c) Negative deviation, \( a_i < a_r \)

Figure 1. Schematic description of (a) ideal solution; (b) non-ideal solution with positive deviation; and (c) non-ideal solution with negative deviation.

Figure 2. Relationship between Raoult's law and Henry's law.

Figure 3. Fe-O phase equilibrium diagram. (Source: Darken, L. S. and Gurry, R. W., J. Am. Chem. Soc., 67 (1945) 1398-412; 68 (1946) 788-816.)

Thermodynamics of liquid iron alloys
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\lg K$</th>
<th>$K$ at 1600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{(FeO)} = {\text{Fe}} + [\text{O}]$</td>
<td>$-(6372/T) + 2.73$</td>
<td>0.212</td>
</tr>
</tbody>
</table>

**Oxides:**

$\text{FeAl}_2\text{O}_4 = \{\text{Fe}\} + 2[\text{Al}] + 4[\text{O}]$  
$-(70320/T) + 23.38$  
$6.9 \times 10^{-13}$

$\text{MnAl}_2\text{O}_4 = \{\text{Mn}\} + 2[\text{Al}] + 4[\text{O}]$  
$-(58473/T) + 17.74$  
$3.3 \times 10^{-14}$

$\text{Al}_2\text{O}_3 = 2[\text{Al}] + 3[\text{O}]$ (up to 0.4 wt % Al)  
$-(58473/T) + 17.74$  
$1.5 \times 10^{-8}$

$\text{B}_2\text{O}_3 = 2[\text{B}] + 3[\text{O}]$  
$-(68500/T) + 19.60$  
$0.1 \times 10^{-17}$

$\text{CaO} = \{\text{Ca}\} + [\text{O}]$  
$-(45531/T) + 20.25$  
$1.1 \times 10^{-4}$

$\text{Ce}_2\text{O}_3 = 2[\text{Ce}] + 3[\text{O}]$  
$-(2050/T) + 14.10$  
$9.3 \times 10^{-20}$

$\text{Cr}_2\text{O}_3 = 2[\text{Cr}] + 3[\text{O}]$ (wt % Cr < 80)  
$-(45796/T) + 18.83$  
$2.4 \times 10^{-6}$

$\text{HIO}_3 = \{\text{H}\} + 2[\text{O}]$  
$-(31040/T) + 12.00$  
$2.7 \times 10^{-2}$

$\text{La}_2\text{O}_3 = 2[\text{La}] + 3[\text{O}]$  
$-(32870/T) + 13.92$  
$2.6 \times 10^{-4}$

$\text{MgO} = \{\text{Mg}\} + [\text{O}]$  
$-(37950/T) + 12.52$  
$1.8 \times 10^{-2}$

$\text{Fe}\text{O}_3\text{MnO}_4 = \{\text{Fe}\} + [\text{Mn}] + 2[\text{O}]$  
$-(31040/T) + 12.00$  
$2.7 \times 10^{-2}$

$\text{Fe}\text{O}_3\text{MnO}_5 = \{\text{Fe}\} + [\text{Mn}] + 2[\text{O}]$  
$-(2556/T) - 1.26$  
$4.0 \times 10^{-2}$

$\text{FeNb}_2\text{O}_6 = \{\text{Fe}\} + 2[\text{Nb}] + 6[\text{O}]$  
$-(15050/T) + 6.73$  
$5.0 \times 10^{-2}$

$\text{Nb}_2\text{O}_5 = \{\text{Nb}\} + 2[\text{O}]$  
$-(31040/T) + 12.00$  
$2.7 \times 10^{-2}$

$\text{SiO}_3\text{SiO}_4 = [\text{Si}] + 2[\text{O}]$ (3 wt % Si)  
$-(13430/T) + 6.10$  
$8.5 \times 10^{-2}$

$\text{C}_{3}\text{SiO}_4 = 2[\text{Ca}] + [\text{Si}] + 4[\text{O}]$  
$-(37950/T) + 12.52$  
$1.8 \times 10^{-2}$

$\text{FeTa}_2\text{O}_6 = \{\text{Fe}\} + \{\text{Ta}\} + 6[\text{O}]$ (≤0.25 wt % Ta)  
$-(45531/T) + 20.25$  
$1.1 \times 10^{-4}$

$\text{Ti}_2\text{O}_3 = 2[Ti] + 3[O]$  
$-(63100/T) + 21.90$  
$1.6 \times 10^{-12}$

$\text{Ti}_2\text{O}_3 = 2[Ti] + 3[O]$  
$-(91304/T) + 29.34$  
$3.9 \times 10^{-20}$

$\text{Ti}_2\text{O}_3 = 2[Ti] + 3[O]$  
$-(46452/T) + 17.42$  
$4.2 \times 10^{-8}$

$\text{V}_2\text{O}_5 = 2[V] + 3[O]$  
$-(31040/T) + 12.00$  
$2.7 \times 10^{-2}$

$\text{VO} = [V] + [O]$  
$-(41528/T) + 11.86$  
$6.8 \times 10^{-11}$

$\text{ZrO}_2 = [\text{Zr}] + 2[\text{O}]$  
$-(41528/T) + 11.86$  
$6.8 \times 10^{-11}$

**Sulphides:**

$\text{CaS} = \{\text{Ca}\} + [\text{S}]$  
$-(20600/T) + 6.39$  
$2.5 \times 10^{-3}$

$\text{CeS} = \{\text{Ce}\} + [\text{S}]$  
$-(26000/T) + 8.98$  
$1.3 \times 10^{-3}$

$\text{LaS} = \{\text{La}\} + [\text{S}]$  
$-(8000/T) + 4.02$  
$0.56$

$\text{MgS} = \{\text{Mg}\} + [\text{S}]$  
$-(3000/T) + 3.0$  
$1.0 \times 10^{-2}$

$\text{MnS} = \{\text{Mn}\} + [\text{S}]$  
$-(2556/T) - 1.26$  
$4.0 \times 10^{-2}$

$\text{TiS} = \{\text{Ti}\} + [\text{S}]$  
$-(70320/T) + 23.38$  
$6.9 \times 10^{-13}$

$\text{ZrS} = \{\text{Zr}\} + [\text{S}]$  
$-(10610/T) - 0.99$  
$2.2 \times 10^{-7}$

**Equilibria involving gases ($p = 1$ bar):**

$\text{H}_2 = [\text{H}]$  
$-(1670/T) - 1.68$  
$2.68 \times 10^{-3}$

$\text{N}_2 = [\text{N}]$  
$-(2556/T) - 1.26$  
$4.01 \times 10^{-2}$

$\text{O}_2 = [\text{O}]$  
$-(6126/T) + 0.15$  
$2.64 \times 10^{3}$

$\text{CO} = [\text{C}] + [\text{O}]$  
$-(24232/T) - 1.367$  
$2.18 \times 10^{-3}$

$\text{CO}_2 = (\text{CO}) + [\text{O}]$  
$-(10415.23/T) + 5.623$  
$1.154$

$\text{H}_2\text{O} = 2[\text{H}] + [\text{O}]$  
$-(10610/T) - 0.99$  
$2.21 \times 10^{-7}$

Note: For the reactions marked *, reliable values are available at 1600 °C only.

Sources:
(a) Most of the values are adapted from: Olette, M. and Gatellic, C., Information Symposium on Casting and Solidification of Steel, Luxembourg, 29 November-1 December 1977, IPC Science and Technology: Guildford, paper 1, pp. 8-61.
(b) Fe-Cr-O, Fe-Al-O, Fe-Zr-O, Fe-V-O and Fe-Ti-O are taken from Ghosh and Murthy [50].
(c) CO-C-O and CO₂-C-O values taken from Deco [49].
### Table 1.2 Interaction coefficients of elements dissolved in liquid iron at 1873 K.

<table>
<thead>
<tr>
<th>J = Element j from Al to N</th>
<th>i Al</th>
<th>B</th>
<th>C</th>
<th>Ce_reversed</th>
<th>Ce</th>
<th>Cr</th>
<th>H</th>
<th>La</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
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<td>0.074</td>
<td>0.11</td>
<td>0.13</td>
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<td>0.074</td>
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<td>0.13</td>
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<td>-0.0022</td>
<td>0.0</td>
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<td>-0.139</td>
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<td>0.0</td>
<td>0.0</td>
<td>-0.027</td>
<td>-0.0014</td>
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<td>H</td>
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<td>0.05</td>
<td>-0.139</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.027</td>
<td>-0.0014</td>
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<td>0.0</td>
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<td>-0.0014</td>
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<td>0.18</td>
<td>-0.047</td>
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<td>-0.011</td>
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<td>-0.047</td>
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<td>0.18</td>
<td>0.117</td>
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<td>0.18</td>
<td>0.117</td>
<td>0.003</td>
<td>0.21</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
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<td>-0.229</td>
<td>0.055</td>
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<td>0.47</td>
<td>1.3</td>
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<td>-0.229</td>
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<td>1.1</td>
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<td>0.47</td>
<td>1.3</td>
<td>0.093</td>
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<td>1.3</td>
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<td>1.3</td>
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<tr>
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### Table 2: Element j from Nb to Zr (Table continued...)

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<th>Ni</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ta</th>
<th>Ti</th>
<th>U</th>
<th>V</th>
<th>Zr</th>
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<tr>
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<td>0.002</td>
<td>0.001</td>
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<td></td>
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</tr>
<tr>
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<td>-0.26</td>
<td>0.051</td>
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<td>0.008</td>
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**Sources:**
(b) $\alpha_j$ and $\delta_j$ values are taken from Dac [41].
(c) $\beta_j$, $\gamma_j$, $\beta_j$, $\gamma_j$, and $\delta_j$ values are taken from Ghosh and Murphy [50].

Thermodynamics of liquid iron alloys