ADVANCED THERMODYNAMICS

Handout V – Equilibrium Between Gases and Condensed Phases

(Gaskell Chapters 11 – 13, 15)

Background

It was seen in HIII that, in the absence of inter-atomic forces, such as in an ideal gas, the heat of mixing is zero. This is but one extreme of a range of possibilities, the other being a marked chemical affinity of two or more elements, leading to compound formation. The thermodynamics of these two extremes is treated on the one hand by considering the activities of a highly non-ideal mixture of H_2 and O_2, or, on the other hand by defining the activities and their changes after undergoing a chemical reaction. In the case of gases, if the pressure is low enough, a simpler approach is to examine the partial pressures of the final gas at equilibrium after reacting.

In this handout, we first study the reactions between gases alone, then we add in pure condensed phases, finally we include condensed phases that are real solutions. Examples are, respectively, oxidation of methane (CH_4) to produce a H_2-H_2O-CO-CO_2 mixture; the oxidation of C to produce a C-CO-CO_2 mixture; equilibrium between O_2 and metals (Ellingham Diagram); and finally, equilibrium between CO, CO_2 and an iron alloy. Electrochemistry, for which the ranking of Standard electrode potentials of elements is somewhat analogous to the Ellingham Diagram in its ranking of affinity of elements for oxygen, is also treated briefly.

Extension of the Gibbs Phase Rule to Chemical Reactions

In Handout IV, the Gibbs Phase Rule (GPR) was introduced as a useful tool for the interpretation of alloy phase equilibria. It was shown that calculation of the phase diagram itself is really an exercise in satisfying the GPR, as a solution is not guaranteed unless there are zero degrees of freedom for a particular equilibrium. However, as the number of components increases and the number of possible phases increases, the phase relationships are increasingly complex to depict correctly. Nonetheless, the GPR provides an increasingly invaluable guide, short of a full calculation.

An additional complication is the inclusion of chemical reactions, as well as inclusion of a gas phase. So, in consideration of a multi-component system, with condensed phases as well as a gas phase undergoing a chemical reaction, the GPR is essential in understanding the degrees of freedom available to the system, both in setting up experiments and in portraying the system.

From a multi-component perspective, consider a system of $\mathbb{C}$ chemical species $\boldsymbol{i, j, k \ldots}$ - none of which currently engage in a chemical reaction – which occur in $\wp$ number of phases $\boldsymbol{\phi = \alpha, \beta, \gamma, \delta,}$ ... The thermodynamic state is completely determined by specification of temperature, pressure and $(\mathbb{C} - \mathbf{1})$ composition variables $\boldsymbol{X^{\phi}_{i,j,k\ldots}}$. Then, the thermodynamic system is specified when $\wp \cdot (\mathbb{C} + \mathbf{1})$ *variables* are specified; viz.: $\wp \cdot [(\mathbb{C} - \mathbf{1}) + \mathbf{2}] = \wp \cdot (\mathbb{C} + \mathbf{1})$.

The equations that apply at equilibrium, are:

Equality of temperature:

$$\boldsymbol{T^{\alpha} = T^{\beta} = T^{\gamma} = T^{\phi} \Rightarrow (\wp - 1)\ \textbf{equations}}$$

Equality of pressure:

$$\boldsymbol{P^{\alpha} = P^{\beta} = P^{\gamma} = P^{\phi} \Rightarrow (\wp - 1)\ \textbf{equations}}$$

These two sets of equations number: $(\wp - \mathbf{1}) \cdot \mathbf{2}$.

Equality of chemical potential for each species i, j, k, …:

$$\boldsymbol{\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \mu_i^{\phi} \Rightarrow (\wp - 1)\ \textbf{equations}}$$

$$\boldsymbol{\mu_j^{\alpha} = \mu_j^{\beta} = \mu_j^{\gamma} = \mu_j^{\phi} \Rightarrow (\wp - 1)\ \textbf{equations}}$$

$$\boldsymbol{\mu_k^{\alpha} = \mu_k^{\beta} = \mu_k^{\gamma} = \mu_k^{\phi} \Rightarrow (\wp - 1)\ \textbf{equations}}$$

These $\mathbb{C}$ sets of equations number: $(\wp - \mathbf{1}) \cdot \mathbb{C}$.

Finally, the total number of *independent equations* is:

$$(\wp - \mathbf{1}) \cdot \mathbf{2} + (\wp - \mathbf{1}) \cdot \mathbb{C} = (\wp - \mathbf{1})(\mathbb{C} + \mathbf{2})$$

The *Degrees of Freedom* ***F*** is the maximum number of variables which can be independently altered in value without disturbing the equilibrium, here for the case of *no* chemical reactions:

$$\boldsymbol{F} = \#\ \textbf{independent variables} - \#\ \textbf{independent equations} \Rightarrow$$

$$\boxed{\boldsymbol{F} = \wp \cdot (\mathbb{C} + \mathbf{1}) - (\wp - \mathbf{1})(\mathbb{C} + \mathbf{2}) = \mathbb{C} - \wp + \mathbf{2}}$$

If a reaction occurs, the products of reaction are considered as additional species, along with the participating elemental chemical species before the reaction, $\mathbb{N}$. But, each chemical reaction establishes a stoichiometric relationship among the participating species. Let $\boldsymbol{\mathcal{R}}$ be the number of stoichiometric equations representing the reactions, so that, the number of independent equations is increased by $\boldsymbol{\mathcal{R}}$. Here, $\mathbb{N}$ refers to all species, including the products of reaction:

$$\boldsymbol{F} = \wp \cdot (\mathbb{N} + \mathbf{1}) - (\wp - \mathbf{1})(\mathbb{N} + \mathbf{2}) - \boldsymbol{\mathcal{R}} \Rightarrow$$

$$\boxed{\boldsymbol{F} = (\mathbb{N} - \boldsymbol{\mathcal{R}}) - \wp + \mathbf{2}}$$

In the above equation, which refers to including chemical reaction, $\mathbb{C} = (\mathbb{N} - \boldsymbol{\mathcal{R}})$. Of course, if there are no chemical reactions, then $\boldsymbol{\mathcal{R}} = \mathbf{0} \Rightarrow \boldsymbol{F} = \mathbb{C} - \wp + \mathbf{2}$. The number of components can be determined as either the minimum number of chemical species required to produce a system at equilibrium (typically, the participating elements), or as the total number of species (elements or compounds) minus the number of stoichiometric equations representing the reactions among them.

REACTIONS OF GAS MIXTURES

Consider the following reaction between two gases, producing a gas:

$$\boldsymbol{A(g) + B(g) = 2C(g)}$$

We may write the following *extensive* (noted by prime) Gibbs Free energy amount:

$$\boldsymbol{G' = n_A\overline{G}_A + n_B\overline{G}_B + n_C\overline{G}_C}$$

But, we have the following mass balance: $\boldsymbol{n_A = n_B}$ and $\boldsymbol{n_C = 2(1 - n_A)}$, where initially $\boldsymbol{n_A = 1 \; and \; n_C = 0}$. The extensive free energy $\boldsymbol{G'}$ is a minimum when:

$$\boldsymbol{\frac{\partial G'}{\partial n_{A}}_{|T,P} = 0}$$

Thus, we have:

$$\boldsymbol{\frac{\partial G'}{\partial n_{A}}_{|T,P} = \overline{G}_A + \overline{G}_B - 2\overline{G}_C = 0 \Rightarrow}$$

$$\boldsymbol{\overline{G}_A + \overline{G}_B = 2\overline{G}_C}$$

Or

$$\boldsymbol{\mu_A + \mu_B = 2\mu_C}$$

For each gas species:

$$\boldsymbol{\mu_i = \mu_i^o + RT \ln p_i}$$

In the above equation, it is remembered that $\boldsymbol{p_i = X_i P_{tot}}$ **and** $\boldsymbol{\sum X_i = 1}$. Thus, we have:

$$\boldsymbol{G_A^o + RT \ln p_A + G_B^o + RT \ln p_B = 2G_C^o + 2RT \ln p_C}$$

On re-arranging the above equation, we get, at equilibrium:

$$\boldsymbol{2G_C^o - G_A^o - G_B^o = -RT \ln \left[\frac{p_C^2}{p_A p_B}\right]}$$

We define $\boldsymbol{K_p}$ as the equilibrium constant:

$$\boldsymbol{K_p \equiv \left[\frac{p_C^2}{p_A p_B}\right]^{equil}}$$

And

$$\boldsymbol{\Delta G^o = -RT \ln K_p}$$

It is noted that $\boldsymbol{\Delta G^o = f(T)}$ alone.

Generally, for the reaction:

$$\boldsymbol{bX + cY + dZ + \cdots = mP + nQ + lR + \cdots}$$

$$\Delta \boldsymbol{G} = \left(\boldsymbol{m}\overline{\boldsymbol{G}}_{\boldsymbol{P}} + \boldsymbol{n}\overline{\boldsymbol{G}}_{\boldsymbol{Q}} + \boldsymbol{l}\overline{\boldsymbol{G}}_{\boldsymbol{R}} + \cdots\right) - \left(\boldsymbol{b}\overline{\boldsymbol{G}}_{\boldsymbol{X}} + \boldsymbol{c}\overline{\boldsymbol{G}}_{\boldsymbol{Y}} + \boldsymbol{d}\overline{\boldsymbol{G}}_{\boldsymbol{Z}} + \cdots\right)$$

Finally, we have for the general case:

$$\boxed{\Delta \boldsymbol{G^o} = -\boldsymbol{RT}\ln\left[\frac{\boldsymbol{a_P^m a_Q^m a_R^l} \ldots}{\boldsymbol{a_X^b a_Y^c a_Z^d} \ldots}\right] = -\boldsymbol{RT}\ln \boldsymbol{K_p}}$$

In the above equation $\Delta \boldsymbol{G^o}$ is the *Standard Free Energy Change of Reaction*, where all components of the reaction are in their standard states.

Generally, for all gases:

$$\boxed{\boldsymbol{a_i} = \frac{\boldsymbol{p_i}}{\boldsymbol{P_{Tot}}} = \boldsymbol{p_i} \text{ when } \boldsymbol{P_{Tot}} = \boldsymbol{1}}$$

This equation – for the Standard Free Energy of Reaction - is one of the most useful equations in thermodynamics.

It is noted that as $\boldsymbol{K_p} \gg \boldsymbol{1}, \Delta \boldsymbol{G^o} \ll \boldsymbol{0}$, and the reaction moves to the RHS.

Effect of Temperature on $\boldsymbol{K_p}$

We apply the Gibbs-Helmholtz Equation to determine the effect of temperature on $\boldsymbol{K_p}$:

$$\frac{\partial \Delta \boldsymbol{G}}{\partial \boldsymbol{T}} = -\frac{\Delta \boldsymbol{H}}{\boldsymbol{T}^2}$$

Thus, we have the following *Van't Hoff Equation*, at constant $\boldsymbol{P}$:

$$\boxed{\frac{\partial \Delta G^o}{\partial T} = -\frac{\Delta H^o}{T^2} = \frac{d \ln K_p}{dT}}$$

In the above equation, ΔH^o is expressed empirically as a function of temperature. Nonetheless, over small temperature intervals, we can assume that ΔH^o is essentially constant with temperature, giving:

$$\log \frac{K_1}{K_2} \cong \frac{\Delta H^o}{2.3R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For small changes in temperature, this becomes, on re-arranging:

$$\boxed{\Delta H^o \cong \frac{2.3RT_1T_2\left(\log K_{P,1} - \log K_{P,2}\right)}{T_1 - T_2}}$$

The relationship between K_p and ΔH^o is revealing – if ΔH^o is positive (where the reaction as written is *endothermic*), then K_p increases with increasing temperature.

Conversely, if ΔH^o is negative (where the reaction as written is *exothermic*), then K_p decreases with increasing temperature.

This direction of the variation in $K_p$with temperature can be anticipated from *Le Chatlier's Principle*:

If heat is added to a system at equilibrium, the equilibrium is displaced in the direction so as to absorb the heat.

So, if the reaction is endothermic – requiring heat - and if heat is made available to the system, the reaction will shift further to the right and make use of the extra heat, i.e., towards larger values of K_p .

Conversely, if the reaction as written is exothermic – giving off heat – and if heat is added to the system, it will shift the equilibrium to the left so as less heat is produced by the reaction, towards smaller values of $\boldsymbol{K_p}$.

Effect of Pressure on the Equilibrium Constant

This is deduced by replacing $\boldsymbol{p_i}$ with $\boldsymbol{X_i P_{Tot}}$. For our reaction, we have, where $\boldsymbol{K_X}$ refers to mole fraction:

$$\boxed{K_P = \frac{X_C^2 P_{Tot}^2}{X_A P_{Tot} X_B P_{Tot}} = \frac{X_C^2}{X_A X_B} \equiv K_X}$$

If the reaction is equimolar, where equivalent number of moles are produced as reacted, there is *no effect of pressure*! However, if the reaction is *not* equimolar, total pressure remains a variable. In general, we can state:

$$\boxed{K_P = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \left[\frac{X_C^c X_D^d}{X_A^a X_B^b}\right]\left[\frac{P_{Tot}^c P_{Tot}^d}{P_{Tot}^a P_{Tot}^b}\right] = K_X P_{Tot}^{(c+d-a-b)}}$$

Obviously, $\boldsymbol{K_X}$ and $\boldsymbol{K_P}$ are equivalent for equimolar reactions, as well as for $\boldsymbol{P_{Tot} = 1}$.

Le Chatelier's Principle could be also applied to the effect of pressure. If there is an increase in the number of moles of a gas on reaction, an increase in the total pressure will shift the reaction so as to minimize the number of moles produced, to the LHS. Conversely, if the number of moles of a gas are consumed by the reaction, then an increase in the total pressure will shift the reaction to the right. As an example, consider the reaction: $\boldsymbol{SO_2 + 1/2O_2 \rightarrow SO_3}$. As total pressure is increased, production of $\boldsymbol{SO_3}$ is favored. This is as if the reaction moves in the direction to accommodate the pressure requirement, where the reaction, in this case, wants to remove moles of gas so as to not add even more to the pressure.

Illustration of Gas Mixture Equilibria – Example of Important Industrial Gases

Working with gas equilibria involves solving simultaneously the reaction equilibria, given $\boldsymbol{K_P}$ and the mass balance that takes into account the stoichiometry of the reaction.

Example I – Production of SO_3

Consider the reaction:

$$SO_2(g) + 1/2O_2(g) \rightarrow SO_3\text{ (g) (I)}$$

To evaluate ΔG^o for this reaction, we first look up to Standard Free Energy of Formation of the key (non-elemental) reaction species in a table (such as the *Handbook of Thermochemistry* by O. Kubaschevski and C. B. Alcock (1979), ISBN 0-08-022107. From this, we obtain:

Rxn. 1: $1/2\, S_2(g) + O_2(g) = SO_2(g)\ \ \Delta G_1^o = 1/2(-173240 + 34.62T)$

And

Rxn. 2: $1/2\, S_2(g) + 3/2\, O_2(g) = SO_3(g)\ \ \Delta G_2^o = 1/2(-218440 + 77.34T)$

If we subtract (1) from (2), we get (I):

$$SO_2(g) + \ 1/2\, S_2(g) + 3/2O_2 = SO_3(g) + \ 1/2\, S_2(g) + O_2(g)$$

$$\Delta G_I^o = 22600 - 21.86T$$

Then, we need to choose a basis, say, 1 mole of SO_2. From this basis and the stoichiometry of the overall reaction, we see that x moles of SO_3 moles form from one moles of O_2 , leaving ***(1-x)*** moles of SO_2. The mole of oxygen remaining are: $(1/2 - 12x$. Thus, the total number of moles of gas is:

$$n_T = 1 - x - \frac{1}{2} - \frac{1}{2}x + x = \frac{1}{2}(3 - x)$$

Since:

$$p_i = \frac{n_i}{n_T} P_T$$

Then

$$p_{SO_2} = \frac{2(1-x)}{3-x} P_T$$

$$p_{SO_2} = \frac{(1-x)}{3-x} P_T$$

And

$$p_{SO_3} = \frac{2x}{3-x} P_T$$

Combining all partial pressures with the equilibrium constant, we get:

$$K_P = \frac{p_{SO_3}}{p_{SO_2} p_{O_2}{}^{1/2}} \Rightarrow K_P{}^2 = \frac{p_{SO_3}{}^2}{p_{SO_2}{}^2 p_{SO_2}} = \frac{(3-x)x^2}{(1-x)^3 P_T}$$

In the above equation, K_P is obtained from ΔG_I^o at the temperature of interest.

Example II – The Equilibrium of H_2/H_2O

Consider the reaction (all gases):

$$H_2 + \frac{1}{2} O_2 = H_2O \quad \text{(II)}$$

From the Standard Free Energy of Formation of $H_2O(g)$, we have:

$$\Delta G^o_{II} = -57250 + 4.48T \log T - 2.21T$$

(Note to be careful not to confuse water vapor with liquid or ice!)

In turn,

$$K_P = \frac{p_{H_2O}}{p_{H_2} {p_{O_2}}^{1/2}}$$

If we choose as our basis one mole of hydrogen, then, x moles of water are produced from x moles of hydrogen and ½ moles of O_2. This leaves $(1 - x)$ moles of H_2 and $\left(\frac{1}{2} - \frac{1}{2}x\right)$ moles of O_2.

This and the following reaction $CO + \frac{1}{2}O_2 = CO_2$ are very important for controlling the oxygen partial pressure in experiments when it is needed to be much lower than possibly from dilution with argon – which has its own impurity level for oxygen. For example, if p_{O_2} needs to be 10^{-10} at 2000 °K, this can be achieved by controlling the ratio $\frac{p_{H_2O}}{p_{H_2}}$ to 3.4 10^{-2}, which is well within the precision of the flows of these gasses.

Example III – The CO/CO2 Equilibrium

Consider the reaction (all gases):

$$CO + \frac{1}{2}O_2 = CO_2 \quad (III)$$

We have the following Standard Free Energies of Formation:

$$\boldsymbol{C+\frac{1}{2}O_2=CO}\ \ (\mathbf{1})$$

$$\Delta\boldsymbol{G_1^o=-26700-70.95T})$$

$$\boldsymbol{C(s)+O_2=CO_2}\ \ (\mathbf{2})$$

$$\Delta\boldsymbol{G_2^o=-94200-0.2T})$$

If we subtract Rxn, (1) from Rxn. (2), we get:

$$\boldsymbol{C+O_2+CO=C+\frac{1}{2}O_2+CO_2\Rightarrow}$$

$$\boldsymbol{CO+\frac{1}{2}O_2=CO_2}$$

$$\Delta\boldsymbol{G_{III}^o=-67500+20.75T})$$

Similarly, as for the hydrogen/water equilibrium, this equilibrium can be used to precisely control oxygen partial pressures to even lower levels. For example, if it required to control $\boldsymbol{p_{O_2}}$ to 10^{-30} at 1000 °K (1 atm total pressure) ,the ratio $\frac{p_{CO_2}}{p_{CO}}$ needs to be a ratio of only 1.64.

Fugacity

Real gases in most applications encountered in materials science as well as process metallurgy are near 1 atm, and behave essentially ideally.

REACTION OF GASES WITH PURE CONDENSED PHASES

Up to this point in this handout, we considered only gases in equilibrium, but now, we want to include solids/liquids. First, we want to treat the case of these condensed phases being pure.

Consider the equilibrium between a pure solid M or its oxide MO and the respective vapor pressures, where the total pressure is 1 atm:

$$\bar{G}_M = G^o_{M(g)} + RT \ln p_M$$

$$\bar{G}_{MO} = G^o_{MO(g)} + RT \ln p_{MO}$$

The question is how do we change the standard state from a gas to a solid? This change is given by:

$$\bar{G}_M = G^o_{M(g)} + RT \ln p_M = G^o_{M(s),1\,atm} + \int_{P=1}^{p_M} V_{M(s)}\, dP$$

In the above equation, the integral is for evaluating the effect of the change in pressure from 1 atm to the partial pressure p_M. As it turns out, for solids, V is not a significant function of pressure up to several atmospheres, so that the value of this integral is negligible. Thus, we have:

$$\boxed{\begin{gathered}\bar{G}_M = G^o_{M(g)} + RT \ln p_M \approx G^o_{M(s),1\,atm} \\ \bar{G}_{MO} = G^o_{MO(g)} + RT \ln p_{MO} \approx G^o_{MO(s),1\,atm}\end{gathered}}$$

This means that the total pressure has little effect on the Gibbs Free Energy of condensed phases, so that in most applications near 1 atm, it is not necessary to specify 1 atm total pressure.

This deduction has a big implication on simplifying the treatment of such equilibria, in that the vapor pressure of the condensed phase is absent from the statement of the equilibrium.

For the gas equilibrium involving the vapor pressure of solids M and MO, we have:

$$M(g) + \frac{1}{2}O_2 = MO(g) \quad (1)$$

$$\Delta G_1^o = G_{MO(g)}^o - \frac{1}{2}G_{O_2}^o - G_M^o = RT\ln\frac{p_{MO}}{p_M p_{O_2}^{1/2}}$$

But, now, we already know $G_{M(g)}^o + RT\ln p_M \approx G_{M(s)}^o$, and $G_{MO(g)}^o + RT\ln p_{MO} \approx G_{MO(s)}^o$, so we can state:

$$M(s) = M(g) \;\; (2)$$

$$\Delta G_2^o = G_{M(s)}^o - G_{M(g)}^o - RT\ln p_{M(g)}$$

And

$$MO(s) = MO(g) \;\; (3)$$

$$\Delta G_3^o = G_{MO(s)}^o - G_{MO(g)}^o - RT\ln p_{MO(g)}$$

Summing the above reactions (1) – (3), we get:

$$\boxed{\begin{gathered} M(s) + \frac{1}{2}O_2 = MO(s) \\ \Delta G^o = RT\ln\frac{1}{p_{O_2}^{1/2}} \end{gathered}}$$

This is the Standard Free Energy change for this reaction. In turn, we have:

$$\boxed{\Delta G^o = -RT\ln K = RT\ln\frac{1}{p_{O_2}^{1/2}} \Rightarrow K = p_{O_2}^{1/2}}$$

This means that for the reaction equilibria involving pure condensed phases and a gas phase, the *equilibrium constant* $\boldsymbol{K}$ can be written *solely* in terms of the gas species participating in the reaction – here oxygen.

Since $\Delta\boldsymbol{G^o}$ is solely a function of temperature, a different equilibrium results for each unique value of the partial pressure of oxygen $\boldsymbol{p_{O_2} = f(T)}$.

Application of the Gibbs Phase Rule (GPR) to the Equilibrium Between Condensed Phases and a Gas Phase

In the preceding section, we considered the simple reaction:

$$\boldsymbol{M(s) + \frac{1}{2}O_2 = MO(s)}$$

We have two elemental components (M, O_2), and three phases (M(s), MO(s) and gas, consisting of $\boldsymbol{p_M, p_{MO}}$ **and** $\boldsymbol{p_{O_2}}$). Thus the degrees of freedom $\boldsymbol{F = \mathbb{C} - \wp + 2 = 2 - 3 + 2 = 1.}$ If temperature is fixed**,** $\boldsymbol{p_{O_2}}$ is fixed, and thus, so is total pressure, because $\boldsymbol{p_M, p_{MO}}$ **and** $\boldsymbol{p_{O_2}}$ are all functions of temperature.

In terms of chemical species, this works out to the same degrees of freedom, since there are three species M(s), MO(s)and O_2. Because there is one additional relationship – the equilibrium stoichiometric relationship, then, $\mathbb{C} = (\mathbb{N} - \boldsymbol{\mathcal{R}}) = \boldsymbol{3 - 1 = 2}$ as in the first approach.

The roles of temperature and oxygen partial pressure becomes readily apparent in an experiment involving a closed system containing initially M, MO and O_2. At a given temperature, the partial pressure of oxygen is set at equilibrium. If the initial, experimentally set $\boldsymbol{p_{O_2} > p_{O_2}^{equil}}$, then any M available will oxidize, consuming oxygen until $\boldsymbol{p_{O_2}^{equil}}$ is achieved. Only when this is achieved can the equilibrium be established, with no further oxidation of M. Similarly, if the initial, experimentally set $\boldsymbol{p_{O_2} < p_{O_2}^{equil}}$, the oxide would be reduced, providing oxygen to the gas until $\boldsymbol{p_{O_2}^{equil}}$ is achieved, whence no further reduction of the oxide occurs, so long as some MO remains.

Above, it was stated that the total pressure becomes fixed in this case, once temperature is set. This is because, all gases, including the partial pressures of M and MO, as well as $\boldsymbol{p_{O_2}^{equil}}$ are only functions of temperature. So, total pressure cannot be set independent of temperature in this situation. On the other hand, were we to add an inert gas, such as argon, this provides a way to control total pressure independently from temperature. This increases the degrees of freedom by one. It is noted that the inert gas added to control total pressure does not participate in the equilibrium reaction, thus does not count as a species!

The Ellingham Diagram

For oxidation and sulfidation of metals, Ellingham found over a large temperature range, $\Delta \boldsymbol{G^o}$ for these reactions were essentially linear in temperature:

$$\Delta \boldsymbol{G^o} \approx \boldsymbol{A} + \boldsymbol{BT}$$

In the above equation, it is easy to see that A is identified with $\Delta \boldsymbol{H^o}$, and B is identified with $-\Delta \boldsymbol{S^o}$. He plotted $\Delta \boldsymbol{G^o}$ with temperature, where the standard free energy is per mole of $\boldsymbol{O_2}$. He found that, the constant $\boldsymbol{A}$ varied considerably – hence the vertical position of the line for a particular reaction – all the lines were basically parallel, with similar slopes ($\boldsymbol{B}$). This is not surprising, since

$$\Delta \boldsymbol{S^o} = \boldsymbol{S^o_{oxide}} - \boldsymbol{S^o_{O_2}}$$

But, $\boldsymbol{S^o_{O_2}} \gg \boldsymbol{S^o_{oxide}}$ **or** $\boldsymbol{S^o_{metal}}$, so $\Delta \boldsymbol{S^o} \approx -\boldsymbol{S^o_{O_2}}$, corresponding to the entropy change (decrease) resulting from the disappearance of one mole of oxygen initially at 1 atm. As a result, per mole of diatomic oxygen, the entropy change is virtually the same – that is, the slope of each reaction is the same – for all metal/metal oxide reactions.

We may write:

$$\boldsymbol{RT} \ln \boldsymbol{K} = -\Delta \boldsymbol{G^o} = -\Delta \boldsymbol{H^o} + \boldsymbol{T}\Delta \boldsymbol{S^o} - \mathbf{RT} \ln \boldsymbol{p_{O_2}}(\boldsymbol{T^{eq}})$$

Thus, we have:

$$\ln \boldsymbol{K} = \frac{-\Delta \boldsymbol{G^o}}{\boldsymbol{RT}} = \frac{-\Delta \boldsymbol{H^o}}{\boldsymbol{RT}} + \frac{\Delta \boldsymbol{S^o}}{\boldsymbol{R}} = -\mathbf{RT} \ln \boldsymbol{p_{O_2}}(\boldsymbol{T^{eq}})$$

Thus, we have:

$$\boldsymbol{p_{O_2}(T^{eq}) = \exp\left(\frac{-\Delta H^o}{RT}\right)\exp\left(\frac{\Delta S^o}{R}\right) = \exp\frac{\Delta H^o}{RT}\cdot \mathbf{constant}}$$

We observe from the above equation that (since $\boldsymbol{\Delta H^o}$ is negative for oxidation):

- For a given $\boldsymbol{\Delta H^o}$, $\boldsymbol{p_{O_2}(T^{eq})}$ increases exponentially with temperature.
- For a given temperature, $\boldsymbol{p_{O_2}(T^{eq})}$ *decreases* with more negative values of $\boldsymbol{\Delta H^o}$.

We now want to explore the role of pressure as well as temperature on the change in the Gibbs Free Energy. We know for ideal gases:

$$\boldsymbol{G = G^o + RT\ln\frac{P}{1}}$$

In this simple equation – applied to, say, one mole of diatomic oxygen gas – gives the change in $\boldsymbol{G}$ for a given $\boldsymbol{T}$, as $\boldsymbol{P}$ is changed. Equivalently, for a given value of $\boldsymbol{G}$, it can give a temperature $\boldsymbol{T}$ for a given pressure $\boldsymbol{P}$.

In the latter case, one can plot a series of lines – each for a constant $\boldsymbol{P}$ – of $\boldsymbol{\Delta G^o}$ versus $\boldsymbol{T}$.

As see in Figure HV.1, we note that all lines pivot from 0 °K on the $\boldsymbol{\Delta G^o}$ axis, i.e.,

$$\boldsymbol{G - G^o = 0 \text{ for } T = 0 \text{ for any } P}$$

$$\boldsymbol{G - G^o = 0 \text{ for } P = 0 \text{ for any } T}$$

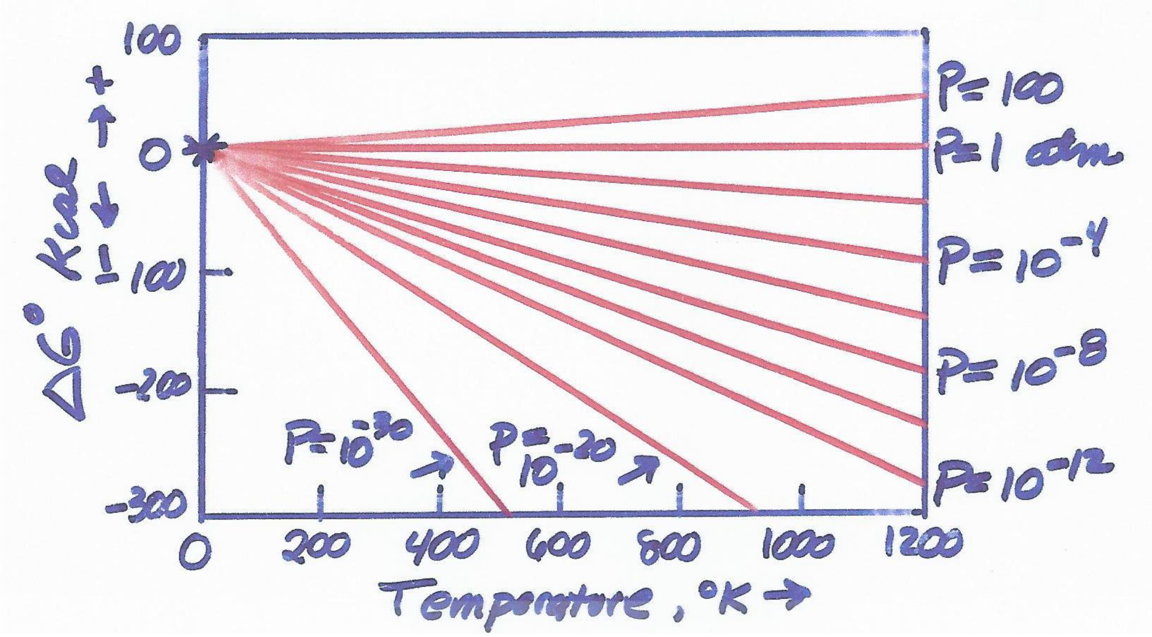
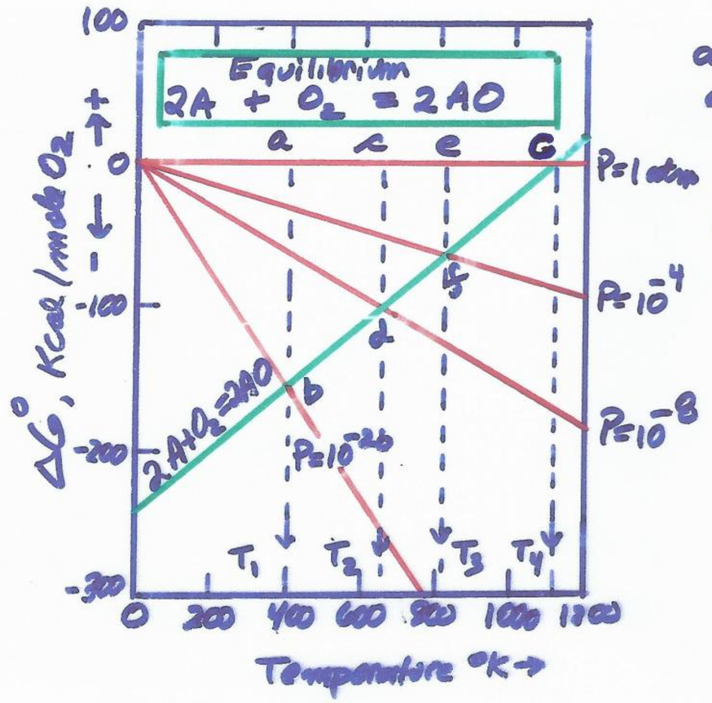


Figure HV.1 – Variation with temperature of the difference between the Gibbs Free Energy of 1 mole of ideal gas in the state ($\boldsymbol{P} = \boldsymbol{P}$ atm, $\boldsymbol{T}$) and the Gibbs Free Energy of one mole of gas in the state ($\boldsymbol{P} = 1$ atm, $\boldsymbol{T}$).

We now superimpose onto this plot $\Delta\boldsymbol{G^o}$ versus $\boldsymbol{T}$ for any oxidation reaction. Now, the isobaric lines become lines of constant $\boldsymbol{p_{O_2}}(\boldsymbol{T^{eq}})$ since diatomic oxygen is the only relevant gas. This is shown in Figure HV.2.



at T_1

ab = decrease in ΔG^0 at T_1 due to decrease of P_{O_2} from 1 atm down to 10^{-20} atm.

at T_2

cd = decrease in ΔG^0 at T_2 due to decrease of P_{O_2} from 1 atm to 10^{-8} atm.

at T_4 point G

$\Delta G^0 = 0$, thus $P_{O_2} = 1$

Figure HV.2 – The superposition of an Ellingham line on Figure HV.1.

Now consider two different oxidation reactions plotted in the same Ellingham Diagram, as shown if Figure HV.3.

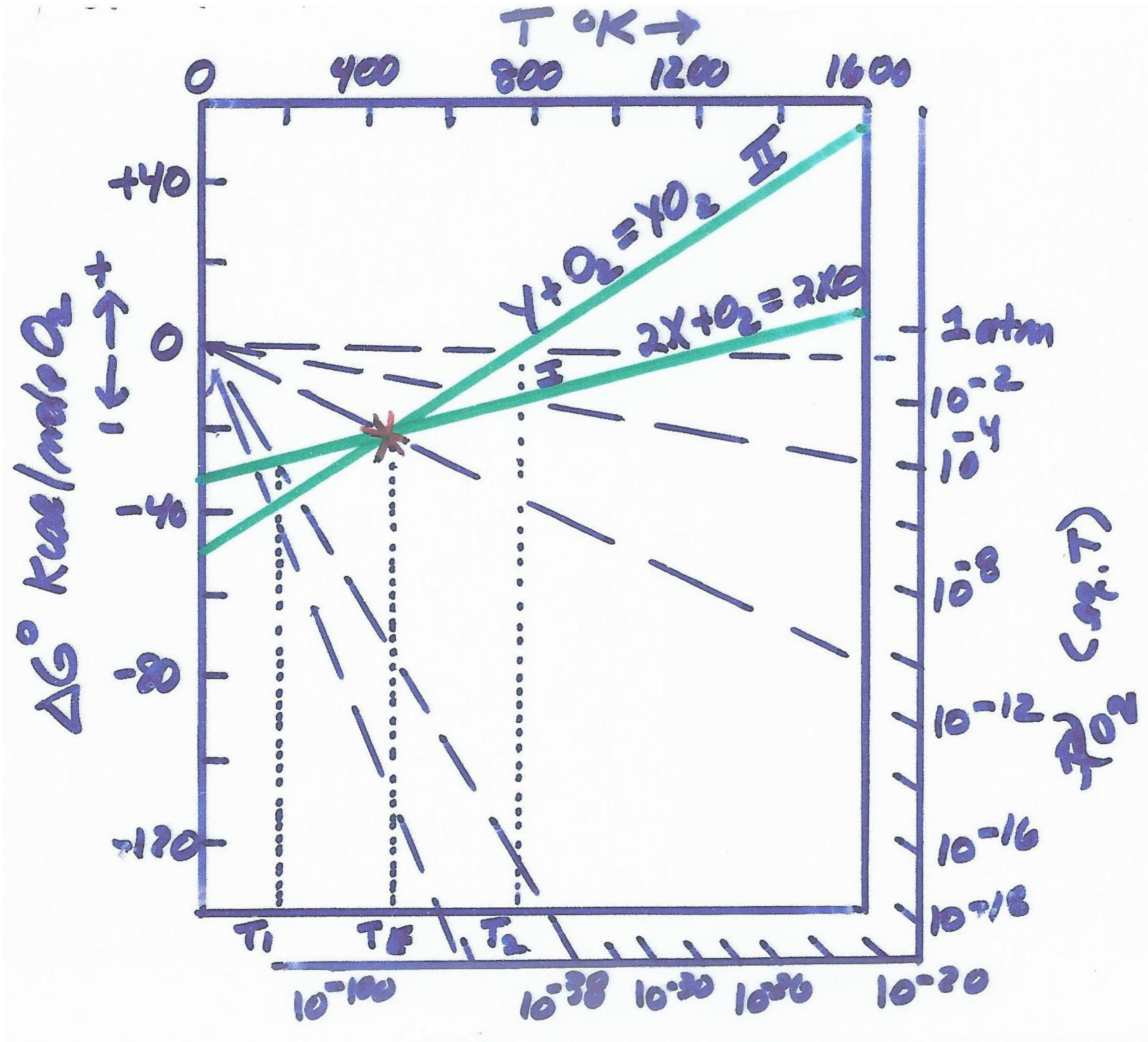


Figure HV.3 – Ellingham Diagram with two different oxidation reactions.

If metals X and Y were placed in a *closed* system, initially at 1 atm oxygen pressure and at $\boldsymbol{T_1}$, both metals would oxidize, consuming oxygen, and $\boldsymbol{p_{O_2}}$ would decrease. On reaching $\boldsymbol{p_{O_2} = 10^{-38}}$, metal X would cease further oxidation. But, metal Y continues to oxidize, since for Y, $\boldsymbol{p^{II}_{O_2(T_1)} < p^{I}_{O_2(T_1)}}$.

Thus $\boldsymbol{p_{O_2}}$ continues to drop. Simultaneously oxide XO becomes unstable, giving up its oxygen to metal Y. When complete equilibrium is finally achieved at this temperature, the closed system contains: $\boldsymbol{X + YO_2 + O_2}$. There is no XO remaining!

Generally, if the prevailing $\boldsymbol{p_{O_2}}$ at a given temperature is *below* the equilibrium line for an oxidation equilibrium, the oxide is *not* stable. (An easy way to remember this is to consider the $\boldsymbol{p_{O_2}}$ levels below the line at a given temperature as *lacking* sufficient oxygen to keep the metal oxidized.)

The reverse analysis is true for $\boldsymbol{T > T_E}$. At $\boldsymbol{T_2}$, starting with $\boldsymbol{X + Y + O_2}$ in a closed system, we would end up at equilibrium with no $\boldsymbol{YO_2}$, but only $\boldsymbol{X + XO + O_2}$. The oxide $\boldsymbol{YO_2}$is not stable at the equilibrium $\boldsymbol{p^I_{O_2(T_2)}}$,i.e., the prevailing $\boldsymbol{p_{O_2}}$ is below that for the *Y/YO2* equilibrium at $\boldsymbol{T_2}$, so $\boldsymbol{YO_2}$ is not stable.

However, at $\boldsymbol{T_E}$. and at $\boldsymbol{p_{O_2} = 10^{-11}}$, both oxides and metals would be present at equilibrium.

It is obvious that this diagram on which is plotted a series of reactions for different metals (and metalloids) and their oxides is immensely useful. A single diagram provides a ranking of the reducing power of one metal versus another at a given temperature

The proper Ellingham Diagram, such as is shown in Figure HV.4 shows at a glance the different tendencies of metals to oxidize.

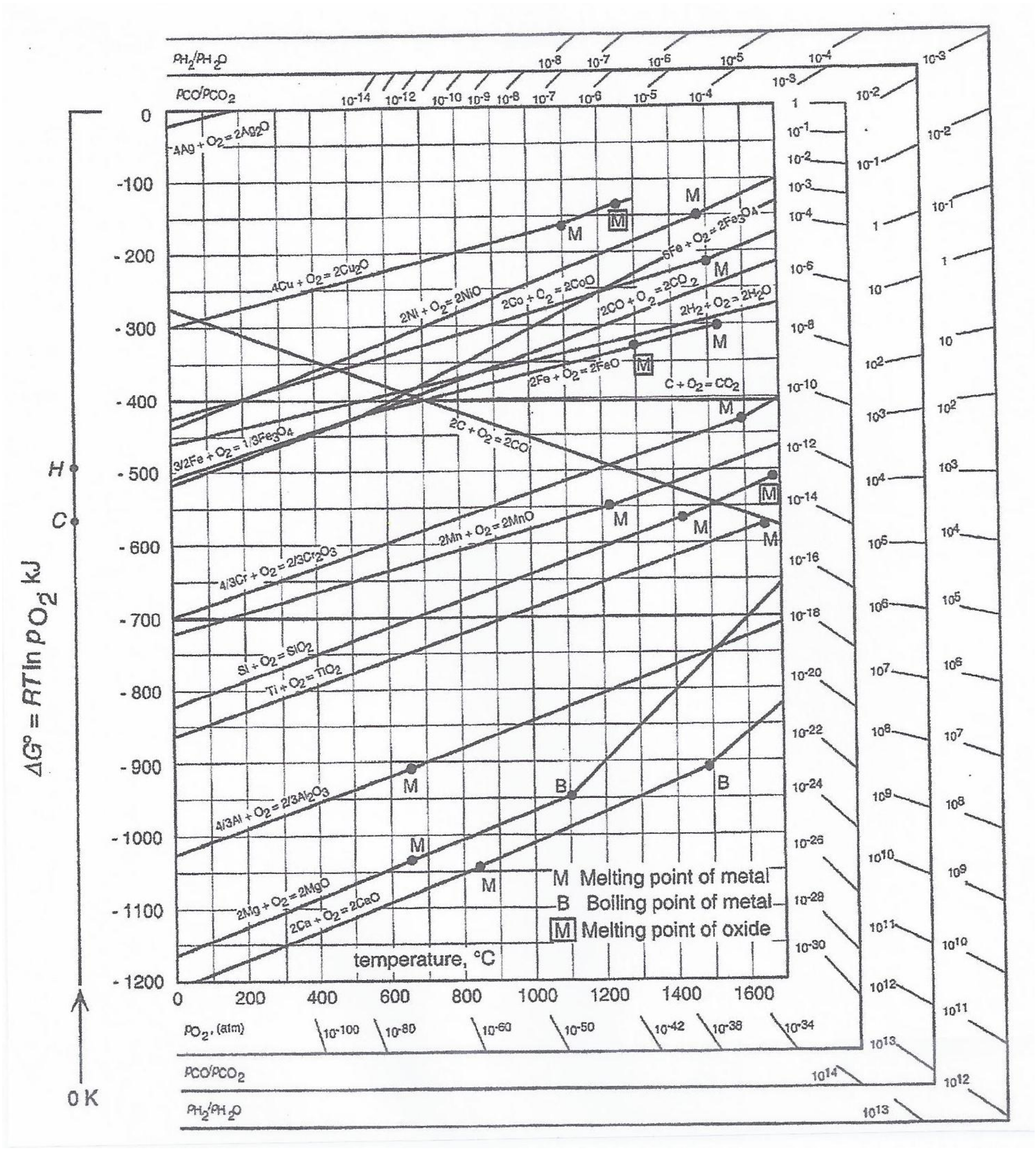


Figure HV.4 – The Ellingham Diagram for a variety of metals and metalloids.

There is no question that this is a powerful diagram in that it is very practical; nevertheless, it is very important to understand the assumptions behind the diagram, and whether they match the application at issue. Often in industry, the diagram is sought to be applied beyond its limits of applicability. This is because it is much easier to consult the diagram than to crank through the calculations involving the actual activities.

A key assumption is that all metals and their oxides are pure (i.e., in their standard states of pure species). (Otherwise, you would have a family of lines for each constituent of an equilibrium, depending on their activity, and the diagram would no longer be simple; in fact there would be essentially an infinite number of diagrams.) In practical applications – such as in steelmaking and extractive metallurgy in general – most of the elements at issue are *not* pure, but in *dilute concentrations* in some solvent metal (e.g., liquid iron), and the oxides are *not* pure, but *in solution* in a slag. So, not only are the constituents typically in far lower concentrations (than 100% pure) they are also in a solution, which is often non- ideal.

On the other hand there is a way to make the appropriate adjustments in the diagram for changes in standard state and activities less than unity. Since the lines representing the metal/oxide equilibria all radiate from a point at 0 °K, this becomes a pivot, where the lines will rotate with these adjustments. One still has to calculate the appropriate changes in terms of the Standard Free Energy for each constituent, but the advantage is that these changes can be viewed in the diagram, and are no less rigorous. This is illustrated in Figure HV.5.

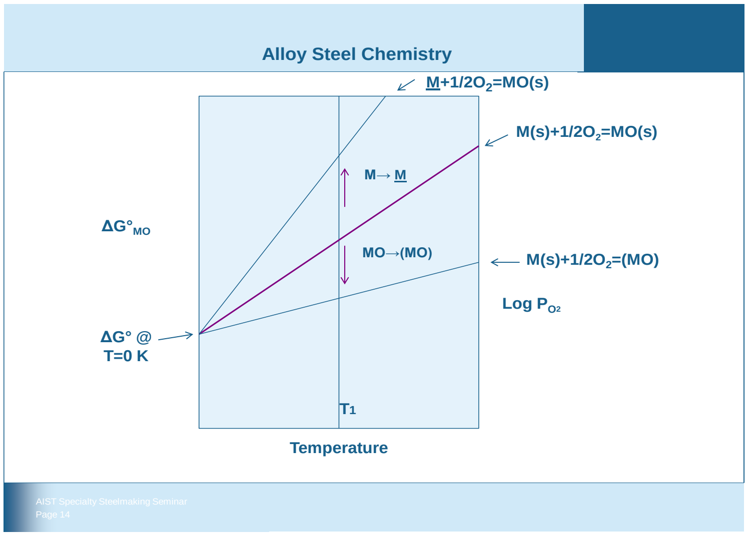


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Figure HV.5 – Rotation of the metal/oxide equilibrium line in response to changes in standard state and changes to the activities of each constituents. It is noted that the line will move *counter-clockwise* as the activity of the metal is lowered; whereas, it will move *clockwise* as the activity of the metal oxide is lowered.

In Figure HV.5, the line representing the metal/oxide equilibrium is seen pivoting about the point 0 °K. The following are the two key changes to make to the free energy for the equilibrium to accommodate activities less than unity.

For the metal/metalloid:

$$(\mathbf{1})\ \boldsymbol{M \rightarrow \underline{M}} \quad \Delta \boldsymbol{G_1^o}$$

For the metal oxide:

$$(\mathbf{2})\ \boldsymbol{MO \rightarrow (MO)} \quad \Delta \boldsymbol{G_2^o}$$

The first change is to convert the standard state to *infinite dilution*, where the activity is the concentration of the solute, multiplied by the Henrian activity coefficient (if oxidation of a solute from a solvent). Otherwise, it is simply for adjusting the activity to whatever it is in the solution at issue. The second change is to adjust for a less-than-unity activity, generally keeping the same standard state. (These conversions and adjustments are treated later in this handout.)

Effect of Phase Transformations in the Ellingham Diagram

Phase transformations at specific temperatures include changes in crystal structure, melting and boiling in either the metal/metalloid, oxide or both. These are revealed in the diagram by changes in slope for a particular equilibrium.

Generally, for the disappearance of one mole of O_2, the entropy change is negative. In the diagram for most metal/oxide equilibria, this is seen as a positive slope, where the slope is $-\Delta \boldsymbol{S^o}$. When a temperature is reached where the metal melts, the entropy change is decreased further, causing the slope in the diagram to increase further. As an example, consider melting of a metal X (note that for melting $\Delta \boldsymbol{H^{melting}}$ is negative; and that both $\Delta \boldsymbol{H^o}$ and $\Delta \boldsymbol{S^o}$ are negative numbers for oxidation):

$$\boldsymbol{X(s) \rightarrow X(l)} \quad \Delta \boldsymbol{H_X^{melting}}$$

In the above equilibrium, $\Delta \boldsymbol{H_X^{melting}}$ is a positive quantity, and that $\Delta \boldsymbol{S_X^{melting}} \approx \Delta \boldsymbol{H_X^{melting}} / \boldsymbol{T_X^{melting\ point}}$ is also a positive quantity. Thus, for the following reaction, we can say:

$\boldsymbol{X(s) + O_2(g) = XO_2(s)}$	$\boldsymbol{\Delta H_X^o}$	$\boldsymbol{\Delta S_X^o}$
$\boldsymbol{X(l) \rightarrow X(s)}$	$\boldsymbol{-\Delta H_X^{melting}}$	$\boldsymbol{-\Delta H_X^{melting}/T_X^{melting\ point}}$
$\boldsymbol{X(l) + O_2(g) = XO_2(s)}$	$\boldsymbol{\Delta H_X^o - \Delta H_X^{melting}}$	$\boldsymbol{\Delta S_X^o - \Delta H_X^{melting}/T_X^{melting\ point}}$

The net change of enthalpy is $\boldsymbol{-\Delta H_X^{melting}/T_X^{melting\ point}}$ and is a more negative number. The net change of entropy $\boldsymbol{\Delta S_X^o - \Delta H_X^{melting}/T_X^{melting\ point}}$ is a larger negative number, so that the slope of the equilibrium line in the Ellingham Diagram becomes more negative.

Therefore, above the melting point of a metal in the diagram, the slope (which is the negative of the entropy change) becomes more positive

The reverse is true for melting of the oxide – because it is on the RHS of the equilibrium, rather than on the LHS, where the metal appears. In this case, the slope of the line *decreases* above the melting point of the oxide, only to increase, once the melting point of the metal is reached for the case where the melting point of the oxide is below that of the metal. This is illustrated in Figure HV.6 for two different oxide equilibria, depending on the melting points of the metal relative to the oxide.

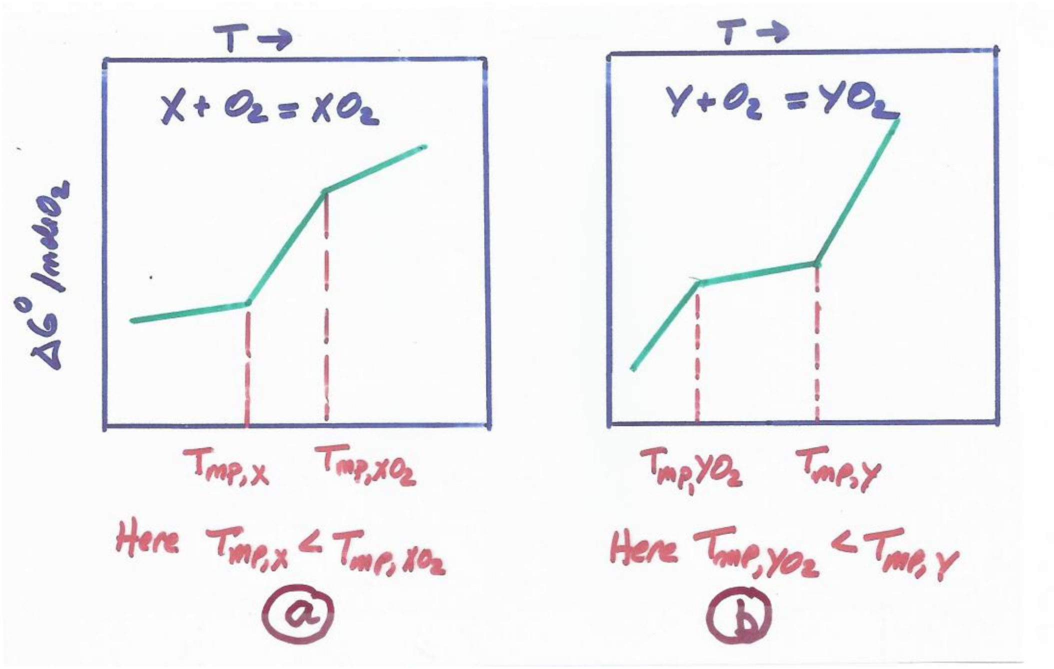

Figure HV.6 – Illustration of the effects of phase changes of the reactants and products of a reaction on the Ellingham line for the reaction. (a) Melting point of X less than the melting point of XO_2. (b) Melting point of Y greater than the melting point of YO_2.

EQUILIBRIUM BETWEEN A GAS AND A CONDENSED PHASE WITH MULTIPLE COMPONENTS IN SOLUTION

As an example of the equilibrium between a gas phase and a *pure* condensed phase is the oxidation of pure metals. This is represented in the Ellingham Diagram, which shows, at each temperature, each metal/oxide equilibrium has a unique oxygen partial pressure (constant total pressure at 1 atm.).

- If it were required to reduce the oxide back into a pure metal for a given temperature, the partial pressure of oxygen only has to be decreased.
- Alternatively, if the partial pressure of oxygen were, instead, fixed, then any increase in temperature has the effect of reducing the oxide.
- In general for the Ellingham Diagram, all metals and oxides are assumed to be pure, thus at unit activity, although changes can be made to express less than unit activity for a species in the diagram, by rotation of the equilibrium line about the origin at 0 °K.

In many experimental, or industrial situations, neither the metal, nor its oxide can be assumed to be pure, and possibly in solution, with a result that their activities would be lower.

In general, the key difference is that the equilibrium oxygen partial pressure simply changes in response to departures of the activities of the condensed phases involved in an equilibrium. The changes in the activities are from measurement, or calculated from a solution model that represents the interactions among the atomic species.

Consider the general equilibrium (constant $\boldsymbol{T}$,$\boldsymbol{P}$):

$$\boldsymbol{aA + bB = cC + dD}$$

In the above equilibrium, *a* and *b* are the moles of Species A and B, respectively, per mole of the species (A, B, C, or D), and *c* and *d* are the number of moles of Species C and D, respectively.

When all reactants and products are in their standard states, we say:

$$\boldsymbol{\Delta G^o = cG_C^o + dG_D^o - aG_A^o - bG_B^o}$$

When the reactants and products are *not* in their standard states, they still have a chemical potential:

$$\Delta G = c\overline{G}_C + d\overline{G}_D - a\overline{G}_A - b\overline{G}_B$$

Subtraction of the above two equations give:

$$\Delta G^o - \Delta G^o = c(\overline{G}_C - G_C^o) + d(\overline{G}_D - G_D^o) - a(\overline{G}_A - G_A^o) - b(\overline{G}_B - G_B^o)$$

Individually, the chemical potentials for each species not in its standard state is expressed in terms of the activity:

$$\overline{G}_i = G_i^o + RT\ln a_i = \mu_i - \mu_i^o + RT\ln a_i$$

Substitution of the above expression leads to the following:

$$\Delta G - \Delta G^o = c(RT\ln a_c) + d(RT\ln a_D) - a(RT\ln a_A) - b(RT\ln a_B) =$$

$$RT\ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right] \equiv RT\ln Q$$

Where

$Q \equiv \frac{a_C^c a_D^d}{a_A^a a_B^b}$= the *activity quotient*

The reaction is at equilibrium when $\Delta G = 0$, in which case:

$$\boxed{\begin{gathered}\Delta G^o = -RT\ln Q = -RT\ln K \Rightarrow \\ K = Q \text{ at equilibrium}\end{gathered}}$$

When the reaction is at equilibrium, $Q(= Q^{equil})$ is numerically equal to K.

It is important to not confuse ΔG **with** ΔG^o. The Standard Free Energy change ΔG^o is only equal to zero in the rare case where the equilibrium values of all activities happen to be unity; generally $\Delta G^o \neq 0$.

The key to understanding the thermodynamic treatment of multi-component, multi-phase reaction equilibria is to understand that, with K *set by temperature (and thus* Q *is set), if one or more activities are modified by being in a solution, other activities have to compensate so as to maintain the same value of* K *(and* Q*) for the temperature at issue. This is none other than Le Chatlier's Principle at work.*

Consider the simple oxidation reaction:

$$M(s) + O_2(g) = MO_2(s) at\ T, P$$

Generally, we have:

$$Q = \frac{a_{MO_2}}{a_M a_{O_2}}$$

Now, if *M* and *MO*$_2$ are pure (occurring in their standard states) then $a_M = a_{MO_2} = 1$ and $a_{O_2} = p_{O_2}/1\ \text{atm}$. Then, on reaching equilibrium, with both *M* and *MO*$_2$ *remaining pure*, we have:

$$Q \rightarrow Q^{equil} = \frac{1}{p_{O_2(equil\ @\ T)}} = K(T)$$

Note that, only in a rare case does $\boldsymbol{p_{O_2(equil\,@\,T)}}$ happen to be unity, with $\Delta \boldsymbol{G^o} = \boldsymbol{0}$.

Now at issue is what happens when *M* and/or *MO₂* become impure, due to, for example, being in solution? Then, the activities simply depart from their standard states.

For the simpler case where the oxide remains pure, but *M* does not, we have at equilibrium:

$$\boldsymbol{Q^{equil}} = \frac{\boldsymbol{1}}{\boldsymbol{a_M p_{O_2(equil\,@\,T)}}} = \boldsymbol{K(T)}$$

We can state the following:

For $\boldsymbol{a_M} < 1$:

$$\boldsymbol{p^{a_M<1}_{O_2(equil\;at\;T)}} > \boldsymbol{p^{a_M=1}_{O_2(equil\;at\;T)}}$$

For $\boldsymbol{a_M} > 1$:

$$\boldsymbol{p^{a_M>1}_{O_2(equil\;at\;T)}} < \boldsymbol{p^{a_M=1}_{O_2(equil\;at\;T)}}$$

Similarly, for unit activity for *M*, but activity of the oxide departed from unit activity, we have:

$$\boldsymbol{Q^{equil}} = \frac{\boldsymbol{a_{MO_2}}}{\boldsymbol{p_{O_2(equil\,@\,T)}}} = \boldsymbol{K(T)}$$

We can state the following:

For $\boldsymbol{a_{MO_2}} < 1$:

$$\boldsymbol{p}_{\boldsymbol{O_2}(\boldsymbol{equil\ at\ T})}^{\boldsymbol{a_{MO_2}}<1} < \boldsymbol{p}_{\boldsymbol{O_2}(\boldsymbol{equil\ at\ T})}^{\boldsymbol{a_{MO_2}}=\mathbf{1}}$$

For $\boldsymbol{a_{MO_2}} > 1$:

$$\boldsymbol{p}_{\boldsymbol{O_2}(\boldsymbol{equil\ at\ T})}^{\boldsymbol{a_{MO_2}}>1} > \boldsymbol{p}_{\boldsymbol{O_2}(\boldsymbol{equil\ at\ T})}^{\boldsymbol{a_{MO_2}}=\mathbf{1}}$$

In all cases, $\boldsymbol{K}$ is fixed by temperature, but it varies so as to maintain this value of $\boldsymbol{K}$ as activities depart from their standard states. In general, we have at equilibrium:

$$\boxed{\boldsymbol{Q}^{\boldsymbol{equil}} = \frac{\boldsymbol{a_{MO_2}}}{\boldsymbol{a_M p_{O_2(equil\ @\ T)}}} = \boldsymbol{K(T)}}$$

As an example, consider the equilibrium of liquid alloy Fe-Mn and a liquid slag, both in equilibrium with an oxygen-containing atmosphere at 1800 °C.

From thermodynamic tables, we have:

$$\mathbf{(1)}\ \boldsymbol{Mn(l)} + \frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{O_2(g)} = \boldsymbol{MnO(l)} \qquad \Delta\boldsymbol{G_1^o} = \mathbf{-82,400 + 13.36}\boldsymbol{T}\ (\textbf{cal per mole})$$

$$\mathbf{(2)}\ \boldsymbol{Fe(l)} + \frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{O_2(g)} = \boldsymbol{FeO(l)} \qquad \Delta\boldsymbol{G_2^o} = \mathbf{-55,620 + 10.83}\boldsymbol{T}\ (\textbf{cal per mole})$$

If we combine both of the above reactions, the equilibrium becomes one in which oxygen shifts between Fe and Mn, depending on the temperature and the prevailing oxygen partial pressure. At 1800 °C (=2073 °K):

$$(3)\ \boldsymbol{FeO(l) + Mn(l) = Fe(l) + MnO(l)} \qquad \Delta G_3^o = -21,530\ (\textbf{cal per mole})$$

Thus, we have:

$$\boldsymbol{k = \frac{a_{MnO}a_{Fe}}{a_{FeO}a_{Mn}} = 186}$$

Now, depending on the solutions of the mixture of Fe and Mn, and of MnO anf FeO, the activities may – or may not – exhibit ideality.

For simplicity, in this example, we are going to assume Raoultian behavior for all species in their respective solutions, in which case, we have:

$\boldsymbol{a_{MnO} = X_{MnO}}$	Standard State is pure liquid MnO
$\boldsymbol{a_{FeO} = X_{FeO}}$	Standard State is pure liquid FeO (in contact with solid Fe)
$\boldsymbol{a_{Mn} = X_{Mn}}$	Standard State is pure liquid Mn
$\boldsymbol{a_{Fe} = X_{Fe}}$	Standard State is pure liquid Fe

Thus, we have – with the notation of parentheses ( ) representing mole fraction in the slag phase, and brackets[ ] representing mole fraction in the metal phase:

$$\boldsymbol{\frac{(MnO)[Fe]}{(FeO)[Mn]} = 186}$$

This becomes:

$$\boldsymbol{186\frac{(FeO)}{[Fe]} = \frac{(MnO)}{[Mn]}} \quad \textbf{(I)}$$

So far, we merely showed that the metal ratio is fixed at a given temperature to the oxide ratio. But, what is the role of the partial pressure of oxygen? To answer this, we go back to the first two reactions at this temperature, from the free energy data:

$$\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]} = \mathbf{5.86\ 10^5} \boldsymbol{p_{O_2}^{1/2}} \qquad \text{(II)}$$

And

$$\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]} = \mathbf{3.2\ 10^3} \boldsymbol{p_{O_2}^{1/2}} \qquad \text{(III)}$$

If $\boldsymbol{p_{O_2}}$ is fixed (say, experimentally) then, both ratios $\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}$ and $\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]}$ become fixed at equilibrium.

Because the original equilibrium (I) is the result of combination of these two equations, it is automatically satisfied.

It is thus seen that the fixed values of $\boldsymbol{p_{O_2}}$ controls the ratios $\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}$ and $\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]}$ differently, despite (here) assuming Raoultian behavior for each!

If, at the same temperature, one of the ratios were to be fixed in lieu of $\boldsymbol{p_{O_2}}$, then the latter would be dictated at equilibrium by this ratio, and the other ratio would shift to the new value for $\boldsymbol{p_{O_2}}$ via the equations (II) of (III), or via the set ratio via (I).

For example, should one choose to determine $\boldsymbol{p_{O_2}}$ at which $\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}$ is an arbitrarily fixed ratio $\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}\boldsymbol{'}$, then, from (II):

$$\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}\boldsymbol{'} = \boldsymbol{p_{O_2}^{\frac{1}{2}}}\boldsymbol{'}\ \frac{\mathbf{1}}{\frac{\mathbf{1}}{\mathbf{5.86\ 10^5}}}$$

In the above equation, the number $\frac{\mathbf{1}}{\mathbf{5.86\ 10^5}}$ is actually $\boldsymbol{p_{O_2}^{1/2}}$ for the ratio $\frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]} = \mathbf{1}$.

Then, the ratio $\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]}$ is calculated from (III):

$$\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]}{'} = \boldsymbol{p}_{\boldsymbol{O_2}}^{\frac{1}{2}}{'}\ \frac{\mathbf{1}}{\frac{\mathbf{1}}{\mathbf{3.2\ 10^3}}}$$

Likewise in the above equation, the number $\frac{\mathbf{1}}{\mathbf{3.2\ 10^3}}$ is actually $\boldsymbol{p}_{\boldsymbol{O_2}}^{\mathbf{1/2}}$ for the ratio $\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]} = \mathbf{1}$.

Then, it is seen that the following equation is automatically satisfied:

$$\mathbf{186}\,\frac{(\boldsymbol{FeO})}{[\boldsymbol{Fe}]}{'} = \frac{(\boldsymbol{MnO})}{[\boldsymbol{Mn}]}{'}$$

Application of the Gibbs Phase Rule (GPR) to Metal-Oxide-Gas Equilibria – Example I

It is constructive to review the GPR in terms of the example of the FeO/Fe/MnO/Mn equilibrium just explored. Clearly, this is a three-component system (Fe-Mn-O) that consists of three phases (metal/oxide/gas). Note that the oxides FeO and MnO are part of the same solution phase (slag), and they are *not* separate phases in this example. Thus, by the GPR, we have:

$$\boldsymbol{F} = \mathbf{3 - 3 + 2 = 2}$$

Thus, any two of the following four variables can be selected to be independent: $\boldsymbol{T}, \boldsymbol{p_{O_2}}, \boldsymbol{X_{Fe}}$ **or** $\boldsymbol{X_{Mn}}, \boldsymbol{X_{FeO}}$ **or** $\boldsymbol{X_{MnO}}$ (noting that $\boldsymbol{X_{Fe} + X_{Mn} = 1}$ **and** $\boldsymbol{X_{FeO} + X_{MnO} = 1}$).

Alternatively, the GPR including reactions can be applied in this situation. Consider $\mathbb{N} = \mathbf{5}$ species of the group $\boldsymbol{O_2, Fe, Mn, FeO, MnO}$. But we have two equations:

$$Fe = \frac{1}{2}O_2 = FeO \ \ (i) \qquad K_i(T) = \frac{(X_{FeO})}{[X_{Fe}]p_{O_2}^{1/2}}$$

$$Mn = \frac{1}{2}O_2 = MnO \ \ (ii) \qquad K_{ii}(T) = \frac{(X_{MnO})}{[X_{Mn}]p_{O_2}^{1/2}}$$

If we choose T and p_{O_2} as the independent variables, then we have:

$$\frac{(X_{FeO})}{[X_{Fe}]} = K_i(T)p_{O_2}^{1/2} = \mathbf{fixed}$$

Then:

$$\frac{(X_{MnO})}{[X_{Mn}]} = \frac{(1 - X_{FeO})}{[1 - X_{Fe}]} = K_{ii}(T)p_{O_2}^{1/2} = \mathbf{fixed}$$

Thus, we have two remaining variables X_{FeO}andX_{Fe}, and two equations, so the system has zero degrees of freedom.

Application of the Gibbs Phase Rule to Metal-Oxide-Gas Equilibria – Example II

Four important oxide equilibria are the following:

$$M(s) + \frac{1}{2}O_2 = MO(s) \qquad K_i$$

$$M(s) + CO_2 = MO(s) + CO \qquad K_{ii}$$

$$M(s) + MC + CO_2 = MO(s) + MC + CO \qquad K_{iii}$$

And

$$M(s) + MC + C + CO_2 = MO(s) + MC + C + CO \quad K_{iv}$$

Application of the GPR to each of these four equilibria is explored below.

Equilibrium (i) - $M(s) + \frac{1}{2}O_2 = MO(s) \quad K_i$

The number of components is two: M and O. The number of phases is three: M, MO and gas. If temperature is fixed, so must the partial pressures be fixed: $p_M(T), p_{MO}(T), p_{O_2}(T)$.

So if p_{O_2} is fixed, so is total pressure, as: $P_{Tot} = p_{O_2} + p_M + p_{MO}$.

(Now, if an inert gas – such as argon – is included, this is a way to control total pressure independently from controlling oxygen partial pressure. This adds another component, increasing the Degrees of Freedom, so that, in addition to temperature, the partial pressure of oxygen as well as the total pressure both need to be specified.)

Consider the case sans Ar, prior to fixing any variable, we have: $F = \mathbb{C} + 2 - \wp = 2 + 2 - 3 = 1.$ If we choose to fix temperature, then p_{O_2} via K_i is fixed, and so is the total pressure, since$P_{Tot} = p_{O_2}(T) + p_M(T) + p_{MO}(T)$. Thus the system has no degrees of freedom, and it is completely specified.

Equilibrium (ii) - $M(s) + CO_2 = MO(s) + CO \quad K_{ii}$

We now introduce a third component, but no additional phases. This means $\mathbb{C} = 3$, so that, prior to fixing any variable, we now have two Degrees of Freedom. Thus me may select two to be fixed from the group T, P_{Tot}, p_{CO} **and** p_{CO_2}, where we note that $P_{Tot} = p_{CO} + p_{CO_2} + p_M(T) + p_{MO}(T)$. If we choose temperature and total pressure, the system becomes fixed. (Note that, as $\frac{p_{CO}}{p_{CO_2}} = K_{ii}(T)$, this ratio is fixed when temperature is fixed – here for unit activities for M and MnO 0 , so that the total pressure is now fixed.)

Equilibrium (iii) - $M(s) + MC + CO_2 = MO(s) + MC + CO \quad K_{iii}$

Now we have the situation where there is evidence of solid MC in with the other constituents. This means that there is another phase – that of solid MC – so that $\wp = 4$, but we still have only three components. Thus, we have lost a degree of freedom, and : $F = 1.$ This means we can fix any one of the following variables: $T, P_{Tot}, p_{CO}, p_{CO_2}$.

Another way to understand this is in terms of the reaction equilibria:

$$\boldsymbol{M(s) + CO_2 = MO(s) + CO \quad K_{MO}(T) = \frac{p_{CO}}{p_{CO_2}}}$$

$$\boldsymbol{M(s) + 2CO = MC(s) + MC + CO_2 \quad K_{MC}(T) = \frac{p_{CO_2}}{p_{CO}{}^2}}$$

Here, we have $\mathbb{N} = \mathbf{5}$ species participating in the reaction $\mathbf{M, CO, CO_2, MO, MC}$. Note that oxygen is not included here as a species since it does not overtly participate in either of the above reactions. But, $\mathbb{C} = \mathbf{3}$, so, we have $\mathbb{R} = \mathbb{N} - \mathbb{C} = \mathbf{5 - 3 = 2}$ independent equilibria ($\boldsymbol{K_{MO}(T)}$ and $\boldsymbol{K_{MC}(T)}$), so $\boldsymbol{F} = (\mathbb{N} - \mathbb{R}) + \mathbf{2 = 2 + 2 - 4 = 0}$. If we fix temperature, than the ratios are fixed: $\frac{p_{CO}}{p_{CO_2}}$ and $\frac{p_{CO_2}}{p_{CO}{}^2}$. This means that, with $\boldsymbol{T}$ fixed, then, $\boldsymbol{p_{CO}}$ and $\boldsymbol{p_{CO_2}}$ are fixed, hence, total pressure ix fixed: $\boldsymbol{P_{Tot} = p_{CO} + p_{CO_2}}$.
Equilibrium (iv) - $\boldsymbol{M(s) + MC + C + CO_2 = MO(s) + MC + C + CO \quad K_{iv}}$

If solid carbon is present, along with solid MC, we have five distinct phases now: $\mathbf{M, MO, MC, C, gas}$. But $\mathbb{R}$ is also increased by one, since we have an equilibrium among C, CO and CO_2:

$$\boldsymbol{C + CO_2 = 2CO \quad K_C(T)}$$

Thus, since $\mathbb{R} = \mathbf{3}$, but $\wp = \mathbf{5}$, we are back to zero degrees of freedom.

It is noted that various other combinations can be written based on the three equilibria equations involving $\boldsymbol{K_{MO}, K_{MC}, K_C}$, but only three are independent, from which the other combinations can be obtained. Thus, the following equations are *not* unique, but are obtained from these three equilibria:

$$\boldsymbol{MC + 2MO + 3M + CO_2}$$

$$\boldsymbol{MC + MO = CO + 2M}$$

Alternative Standard States

We have already discussed two very different standard states for the binary system AB:

The Raoultian Standard State (also called the *pure* standard state):

$$\frac{\boldsymbol{a_B}}{\boldsymbol{X_B}} \rightarrow \mathbf{1\ as\ } \boldsymbol{X_B} \rightarrow \mathbf{1}$$

The Henrian Standard State (also called the *infinite dilution* standard state):

$$\frac{\boldsymbol{a_B}}{\boldsymbol{X_B}} \rightarrow \boldsymbol{\gamma_B^o} \mathbf{\ as\ } \boldsymbol{X_B} \rightarrow \mathbf{0}$$

The relationship between these two standard states is depicted in the following figure (HV.7). Here, we are assuming a negative departure from ideality of B in A):

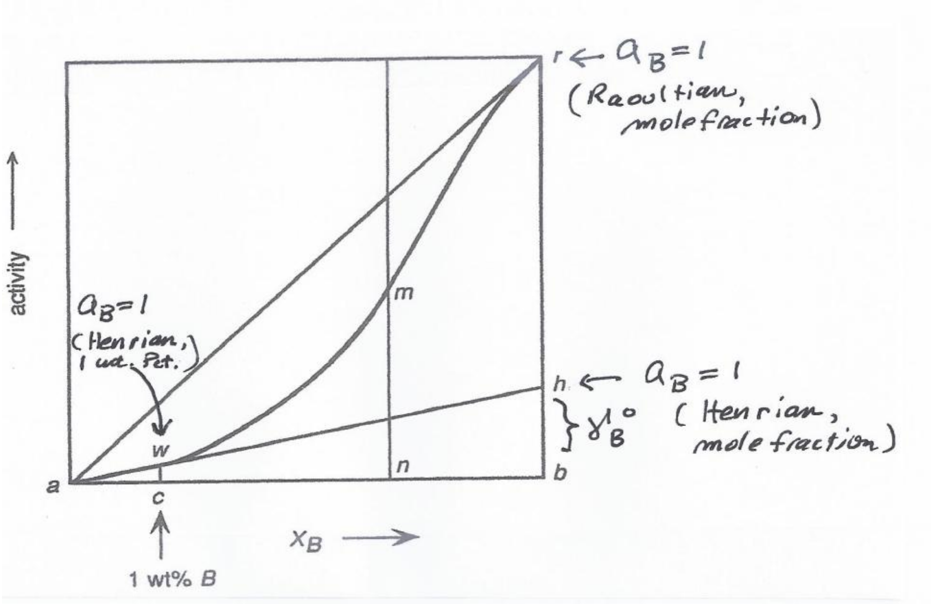

Figure HV.7 – Graphical illustration of the change of standard state from Raoultian to Henrian for the case where there is a negative departure from ideality of B in A.

In terms of the Gibbs Free Energy, the transformation from one standard state to another is relatively easy:

$$\boldsymbol{B(Raoultian) \rightarrow B(Henrian)}$$

$$\boldsymbol{\Delta G^{o} = G_B^{o}(H) - G_B^{o}(R) = -RT\ln K = +RT\ln\left[\frac{a_{B(Raoultian)}}{a_{B(Henrian)}}\right] = RT\ln\gamma_B^{o}}$$

In terms of the chemical potential, we have for this change in standard state:

$$\boxed{\boldsymbol{\mu_B^{o}(Henrian) = \mu_B^{o}(Raoultian) + RT\ln\gamma_B^{o}}}$$

At issue is the *deviation* of the activity in the dilute region from the Henrian ideal (where the slope of the activity approaches a constant as the concentration of solute approaches zero).

We express this deviation in terms of the Henrian activity coefficient $\boldsymbol{f_i}$ - which is distinguished from the activity coefficient $\boldsymbol{\gamma_B^{o}}$ for the pure standard state. At the Henrian standard state:

$$\boxed{\boldsymbol{f_i \equiv \frac{a_i}{X_i}\ as\ X_i \rightarrow 0}}$$

(It is to be noted that the activity itself, relative to this infinitely dilute standard state is sometimes designated as $\boldsymbol{h_i}$ in lieu of $\boldsymbol{a_i}$.)

So far in our discussion, we have *not* changed the concentration scale to any other than mole fraction. But, we can have any concentration scale we want.

For convenience, we may want to use the *weight percent scale*, rather than the mole fraction – this is simply because chemical analyses are generally reported as wt. pct.

The relationship between mole fraction and weight percent in system AB is (where $\boldsymbol{MW_i}$ is the molecular weight of $\boldsymbol{i}$):

$$\boxed{X_B = \frac{wt.pct.B/_{MW_B}}{wt.pct.B/_{MW_B} + 100 - wt.pct.B/_{MW_A}} \cong \frac{wt.pct.B \cdot MW_A}{100MW_B}}$$

We are interested in the standard state defined not just by conversion to the Henrian solution of B in A, but also as wt. pct. B instead of mole fraction B. So, we need to convert concentration scales in the definition of the activity, but we can choose where this activity is unity. We choose this to be true at 1wt. pct. B:

$$\boxed{\frac{a_{B(Henrian,\ one\ wt.pct.)}}{wt.pct.B} \to 1 \text{ as } wt.pct.B \to 0}$$

In the above equation, the activity is so defined, that it is unity in its standard state at 1 wt. pct. B. This is located on the Henrian Law line which corresponds to a concentration of 1 wt, pct. B (point w in Figure HV.7).

Deviation from unit activity on this scale is expressed by:

$$\boxed{f_{B,wt.pct.} = \frac{a_{B(Henrian,wt.pct.)}}{wt.pct.B}}$$

In this expression $\boldsymbol{f_{B,wt.pct.}}$ is the wt. pct. activity coefficient in the Henrian (dilute) composition range of B in A. When Henry's Law is obeyed, $\boldsymbol{f_{B,wt.pct.} \to 1}$. Then, we have:

$$\boxed{a_{B(Henrian,wt.pct.)} = wt.pc.B}$$

This standard state is called the *one weight percent standard state* because, numerically, the activity is unity at 1 wt. pct. B, if Henrian. In real, non-Henrian solutions, at 1 wt. pct., the activity will not be equal to unity.

Transformation from the Raoultian, mole fraction standard state to the Henrian, weight percent standard state is straightforward if done in three steps:

1. Change from Raoultian, mole fraction to Henrian mole fraction.
2. Change from Henrian, mole fraction to Henrian, weight percent
3. Combination of the first two steps:

Step 1: - Conversion from Raoultian, mole fraction to Henrian, mole fraction:

$$\frac{1}{\gamma_B^o} = \frac{(a_B)_{Raoultian, mole\ frtaction}}{(a_B)_{Henrian, mole\ frtaction}} = \frac{rb}{hb}$$

In Figure HV.7, this amounts to removal of the Henrian activity coefficient ($hb = \gamma Bo$) from the slope for the Raoultian activity coefficient (rb).

In terms of the Standard Gibbs Free Energy change, we have:

$$\Delta G_B^{o, Raoultian, mole\ fraction \rightarrow Henrian, mole\ fraction} = G^o_{B(Henrian, mole\ fract.)} - G^o_{B(Raoultian, mole\ fract.)} = -RT\ln[K] = RT\ln[\gamma_B^o]$$

Step 2: - Conversion from Henrian, mole fraction to Henrian, 1 weight percent standard state:

$$\frac{(a_B)_{Henrian, wt.pct.}}{(a_B)_{Henrian, mole\ fraction,}} = \frac{wc}{hb} = \frac{ac}{ab} = \frac{wt.pct.B}{X_B} \cong \frac{100MW_B}{MW_A}$$

In Figure HV.7 this conversion – from mole fraction to weight percent - is seen as a numerical adjustment on the mole fraction scale.

In terms of the Standard Gibbs Free Energy change, we have:

$$\Delta G_B^{o,Henrian,mole\ fraction \rightarrow Henrian,wt.pct.} = G^o_{B(Henrian,wt.pct.)} - G^o_{B(Henrian,mole\ fraction)}$$
$$= -RT\ln[K] \quad = +RT\ln\left[\frac{MW_A}{100MW_B}\right]$$

Combination of Steps (1) and (2) give:

$$\boxed{(a_B)_{Henrian,wt.pct.} = (a_B)_{Rooultian,mole\ fraction\cdot}\left[\gamma_B^o\,\frac{MW_A}{100MW_B}\right]^{-1}}$$

$$\boxed{\begin{aligned}&\Delta G_B^{o,Rooultian,mole\ fraction \rightarrow Henrian,wt.pct.}\\&\qquad = G^o_{B(Henrian,wt.pct.)} - G^o_{B(Rooultian,mole\ fraction)} = -RT\ln[K]\\&\qquad = +RT\ln\left[\gamma_B^o\,\frac{MW_A}{100MW_B}\right]\end{aligned}}$$

This relationship is usually tabulated for various Solutes B in Solvent A (e.g., Solvent A can be a base metal, such as Fe, Cu and Al, and Solutes B can be dilute alloying elements in Fe, such as C, Si, Mn, etc., or in Al, such as Si, etc.). It is seen in the above equation that the change of standard states can be expressed in terms of the Standard Free Energy.

Multi-component Solutions – the Epsilon Formalism

The thermodynamic behavior of a particular solute in a solution can be affected by the pressure of other solutes, depending on their concentrations and strengths of interactions with the solvent and other solutes.

In dilute solutions, where the Henrian coefficient ($\boldsymbol{\gamma_B^o}$) has already be taken out of the activity in changing the standard state from pure to dilute, there remains two types of interactions:

1. The interaction of the solute at issue with other solutes; and
2. The additional effect of the solute on itself at higher concentrations.

Real solutions are really multi-component solutions, no matter the *purity*, since no material cam be absolutely pure. The effects of the impurities may, or may not need to be taken into account. A good example in the freezing-point-lowering due to impurities in a so-called purest available metal, where the cumulative effect of all the measureable impurities can be a noticeable, experimentally verified reduced melting point (on the order of 1 to 2 degrees!).

This activity coefficient for Solute B $\boldsymbol{f_B}$ in a multi-component solution A (solvent)-B-C,… is both a function of $\boldsymbol{X_B}$ (its own concentration) but also the concentrations of the other solutes $\boldsymbol{X_C, X_D}$, ...

The interdependency of Solutes B, C, D, … on B is expressed as:

$$\boldsymbol{f_B = f_B^B f_B^C f_B^D \cdots}$$

Or

$$\boldsymbol{\ln f_B = \ln f_B^B + \ln f_B^C + \ln f_B^D + \cdots}$$

The activity coefficient for B $\boldsymbol{f_B}$ is at a given concentration of B in solution $\boldsymbol{X_B}$. The *self-interaction* activity coefficient $\boldsymbol{f_B^B}$ is for the same concentration of B, but in the absence of C, D, …, as the effects of these other solutes are handled independently. The interaction coefficients $\boldsymbol{f_B^C f_B^D}$ ... are a measure of the effects of Solutes C, D, …, respectively, on the activity coefficient of B.

Experimentally, $\boldsymbol{f_B^C f_B^D}$ ... have been found to be a logarithmic function of $\boldsymbol{X_C, X_D}$, ... , but independent of the concentrations $\boldsymbol{X_B}$. This first-order concentration dependency is expressed by the constant:

$$\frac{\partial \ln f_B^C}{\partial X_C} \equiv e^C_{B|wt.pct\,scale}$$

Or

$$\frac{\partial \log f_B^C}{\partial X_C} \equiv \varepsilon^C_{B|mole\,fraction\,scale}$$

Theoretically, this logarithmic dependency may be non-linear. In this case, we introduce second-order and cross-effects. The importance of these, of course, depends on the concentrations and strengths of interactions.

For the Mole Fraction Scale	For the Weight Percent Scale
$\frac{\partial^2 \ln f_B^C}{\partial X_C^2} \equiv \rho_B^C$	$\frac{\partial^2 \log f_B^C}{\partial wt.pct.C^2} \equiv r_B^C$
$\frac{\partial^2 \ln f_B^{B,C}}{\partial X_B \partial X_C} \equiv \rho_B^{B,C}$	$\frac{\partial^2 \log f_B^{B,C}}{\partial wt.pct.B \partial wt.pct.C} \equiv r_B^{B,C}$
$\frac{\partial^2 \ln f_B^{C,D}}{\partial X_C \partial X_D} \equiv \rho_B^{C,D}$	$\frac{\partial^2 \log f_B^{C,D}}{\partial wt.pct.C \partial wt.pct.D} \equiv r_B^{C,D}$
$\vdots$	$\vdots$

Note that all coefficients (first-order, second-order, cross-terms, etc.) are independent of concentration; they are, in effect, parameters of a Taylor expansion of the logarithm of $f_B$as a function of all solute components in the Henrian standard state (either for the mole fraction, or the weight percent concentration scales. This empirical representation of the activity coefficient at infinite dilution is called the *Epsilon Formalism*. Here is the Taylor series for the mole fraction scale, where all derivatives are taken at zero concentrations:

$$\begin{aligned}\ln f_B = {} & \left[\frac{\partial \ln f_B}{\partial X_B}\right]_{X_B=0} X_B + \left[\frac{\partial \ln f_B}{\partial X_C}\right]_{X_C=0} X_C + \left[\frac{\partial \ln f_B}{\partial X_D}\right]_{X_D=0} X_D \ldots \\ & + \frac{1}{2}\left[\frac{\partial^2 \ln f_B}{\partial X_B^2}\right]_{X_B=0} X_B^2 + \left[\frac{\partial^2 \ln f_B}{\partial X_B X_C}\right]_{X_B=X_C=0} X_B X_C \\ & + \left[\frac{\partial^2 \ln f_B}{\partial X_B X_D}\right]_{X_B=X_D=0} X_B X_D + \left[\frac{\partial^2 \ln f_B}{\partial X_C X_D}\right]_{X_C=X_D=0} X_C X_D + \cdots\end{aligned}$$

Thus, we have, in terms of the interaction coefficients for the Henrian solution based on *mole fraction*:

$$\boxed{\ln f_B = X_B\epsilon_B^B + X_C\epsilon_B^C + X_D\epsilon_B^D \ldots + X_B^2\rho_B^B + X_BX_C\rho_B^{B,C} + X_BX_D\rho_B^{B,D} + X_CX_D\rho_B^{C,D} + \cdots}$$

Likewise, for the *weight percent* scale, we have:

$$\boxed{\begin{aligned}\log f_B = {} & wt.pct.B \cdot e_B^B + wt.pct.C \cdot e_B^C + wt.pct.D \cdot e_B^D \ldots + wt.pct.B^2 \cdot r_B^B \\ & + wt.pct.B \cdot wt.pct.C \cdot r_B^{B,C} + wt.pct.B \cdot wt.pct.D \cdot r_B^{B,D} \\ & + wt.pct.C \cdot wt.pct.D \cdot r_B^{C,D} + \cdots\end{aligned}}$$

In practical applications, the higher-order coefficients are usually neglected, depending on strength and on concentration levels, as few have been evaluated from experiments. Obviously, the absence of these terms restricts application in concentrated solutions. In this case, it is very helpful to find a thermodynamic model (such as the regular solution model)to represent the interactions. Such a model might, in the absence of any data other than the first-order coefficients, might be based on them.

Obviously, if the system is nearly ideal, the interaction coefficients will be very close to zero, so that, when multiplied by concentrations, the net effect on the activity coefficient would be effectively zero.

It can be shown that the interaction coefficients for the two concentration scales considered are related. Here, for the A-B-i solution:

$$\boxed{e_B^i \cong \epsilon_B^i \frac{MW_A}{230MW_i}}$$

Also, the interaction coefficients in each concentration scale are interrelated:

$$\boldsymbol{\varepsilon_C^B = \epsilon_B^C}$$

And

$$\boldsymbol{e_C^B = \frac{MW_C}{MW_D} e_B^C}$$

Solubility of Gases in Solutions

An example of direct application of the dilute treatment of solutes is the solubility of gases in condensed phases of various metals, as this occurs in dilute concentrations. The various impurities, or alloys in low concentration will affect the degree of solubility.

Gases tend to dissolve atomistically, but can also dissolve as a molecule. Diatomic gases, such as O_2, S_2, N_2 and H_2 dissolve in both liquid as well as solid metals as a single atom:

$$\boldsymbol{\frac{1}{2} X_2(g) = [X]}$$

The above equilibrium has an equilibrium constant that depends on temperature (dissolution in weight percent):

$$\boldsymbol{K(T) = \frac{[\%X]}{p_{X_2}^{1/2}}}$$

Gaseous compounds, such as CO, H_2O and SO_2 also tend to dissolve in their elemental form on solution. These equilibria are very important in control of the properties of many commercially important alloys. For example, in iron (the value of the equilibrium constant for a given temperature depends on which condensed phase), we have:

Gas Dissolution Equilibrium	**Equilibrium Equation**
$\boldsymbol{CO(g)=[C]+[O]}$	$\boldsymbol{K(T)=\frac{[\%C][\%O]}{p_{CO}}}$
$\boldsymbol{H_2}$O(g)=2$\boldsymbol{[H]+[O]}$	$\boldsymbol{K(T)=\frac{[\%H]^2[\%O]}{p_{H_2O}}}$
$\boldsymbol{SO_2(g)=[S]+2[O]}$	$\boldsymbol{K(T)=\frac{[\%S][\%O]^2}{p_{SO_2}}}$

In these equations, the gases are all sufficiently dilute so as to obey Henry's Law, so the standard state is the dilute mole fraction, or weight percent (more typically the latter). Also, as written is the implicit assumption that the coefficients $\boldsymbol{f_{gas}^{Y}}$ in the Epsilon Formalism for the self-interaction and remaining interactions are all unity, *Y* being other solutes in a solvent, such as Fe, Al or Cu. This is not necessarily the case, depending on concentration levels. Specifically of interest is evaluation of the effect of various important solute elements on the activity coefficient of the soluble gas, and therefore, on its equilibrium concentration in solution.

Note that an alternative practice is to underline the dissolved solute, rather than use brackets.

The foregoing treatment of dilute solutions gives us the apparatus for this evaluation.

Example I – Solubility of Oxygen and Silicon in Liquid Iron

Consider the equilibrium:

$$\boldsymbol{(I)\ \underline{Si}(wt.\%\ in\ Fe)+O_2(g)=SiO_2(s)\quad \Delta G_I^o = -199,200+54.79T\ (\text{cal per mole})}$$

$$\boldsymbol{(II)\ \ \frac{1}{2}O_2\ =\underline{O}(wt.\%\ in\ Fe)\quad \Delta G_{II}^o=-28,000-0.69T\ (\text{cal per mole})}$$

Combination of these two equilibria gives:

$$\boldsymbol{(III)\ \underline{Si}(wt.\%\ in\ Fe)+2\underline{O}(wt.\%\ in\ Fe)=SiO_2(s)}$$

$$\Delta G^{o}_{III} = -143,200 + 56.17T \; (\textbf{cal per mole})$$

(For simplicity, we are now dropping the notation *wt. % in Fe*.)

At 1600 °C (=1873 °K), we may write from the second equilibrium (II):

$$\frac{a_O}{p_{O_2}^{1/2}} = 2.63\ 10^3$$

Where

$$a_O = f_O \cdot wt.\%O$$

Also, we have from the third equilibrium (III):

$$\frac{a_{SiO_2}}{a_O^2 a_{Si}} = 2.73\ 10^4$$

Where

$$a_{Si} = f_{Si} \cdot wt.\%Si$$

Or

$$\frac{a_{SiO_2}}{(f_O \cdot wt.\%O)^2 (f_{Si} \cdot wt.\%Si)} = 2.73\ 10^4$$

If, experimentally, $p_{O_2}^{1/2}$ is set to, say, **4.4 10**$^{-4}$, and if it can be assumed that SiO_2 is pure (i.e., $a_{SiO_2} = 1$), then we can calculate $\underline{O}$ and $\underline{Si}$. If $f_O \textbf{and} f_{Si} = 1$, this is straight-forward:

$$\underline{O} = 2.63\ 10^3 p_{O_2}^{1/2} = 0.05\ wt.\%\ O$$

Given this result, we have:

$$\boldsymbol{\underline{Si} = \frac{1}{(\underline{O})^2(2.73\ 10^4)} = 0.012\ wt.\%\ Si}$$

But, we want to verify are assumption of unity for the activity coefficients at infinite dilution; With a first-iteration value for *<u>Si</u>* and for *<u>O</u>*, we can evaluate $\boldsymbol{f_O}$**and**$\boldsymbol{f_{Si}}$. For this, we employ the following:

$$\boldsymbol{\log f_O = \underline{O}e_O^O + \underline{Si}e_O^{Si}}$$

$$\boldsymbol{\log f_{Si} = \underline{Si}e_{Si}^{Si} + \underline{Si}e_{Si}^{O}}$$

Where

$\boldsymbol{e_O^O = 0}$; $\boldsymbol{e_{Si}^{Si} = 0.32}$; $\boldsymbol{e_O^{Si} = -0.16}$; and $\boldsymbol{e_{Si}^{O} = -0.262}$

Thus, for $\boldsymbol{f_O}$**and**$\boldsymbol{f_{Si}}$, we have:

$$\boldsymbol{\log f_O = 0.055 \cdot 0 + 0.012 \cdot -0.16 = -0.000106 \Rightarrow f_O = 0.9956 \Rightarrow \underline{O} = 0.0549\ \%\ O}$$

$$\boldsymbol{\log f_{Si} = 0.012 \cdot 0.326 + 0.055 \cdot -0.262 = -.0105 \Rightarrow f_{Si} = 0.976}$$

Insertion of $\boldsymbol{f_{Si}}$ back into the equilibrium (III) yields:

$$\boldsymbol{\frac{1}{(0.0549)^2(0.976\underline{Si})} = 2.73\ 10^4 \Rightarrow \underline{Si} = 0.01345\ \%\ Si}$$

In this example, it is now clear that the initial assumption that $\boldsymbol{f_O \text{and} f_{Si} = 1}$ didn't contribute significant error. This is not the case at significantly lower partial pressures of oxygen. Take $\boldsymbol{p_{O_2}^{1/2}}$ now set to $\mathbf{10^{-8}}$. As before, we first start assuming $\boldsymbol{f_O = 1}$. Then, we have $\boldsymbol{\underline{O} = 0.263\ \%\ O}$. Now assuming both $\boldsymbol{f_O \text{and} f_{Si} = 1}$, then
We get $\boldsymbol{\underline{Si} = 0.0005\ \%\ Si}$. We now evaluate $\boldsymbol{f_O \text{and} f_{Si}}$ (for the first iteration):
$\boldsymbol{\log f_O = 0.263 \cdot 0 + 0.0005 \cdot -0.16 = -0.00008 \Rightarrow f_O = 0.9998 \Rightarrow \underline{O} = 0.263\ \%\ O}$. But:

$$\boldsymbol{\log f_{Si} = 0.0005 \cdot 0.326 + 0.263 \cdot -0.0687 = -.0105 \Rightarrow f_{Si} = 0.8546 \Rightarrow}$$

$$\boldsymbol{\underline{Si} = \frac{1}{(\underline{O})^2 (0.85462.73\ 10^4)} = 0.00062\ wt.\%\ Si}$$

This last calculation shows that the calculated silicon level is actually much lower than when it was assumed that $\boldsymbol{f_{Si} = 1}$. The error from this assumption is considerable!

Example II - The Fe-C-O Equilibrium

Here, we wish to calculate $\underline{O}$ in equilibrium in liquid iron containing 1 wt. % C in solution (1 atm. pressure, 1600 °C).

The following data are available from thermodynamic compilations (where *gr* refers to graphite):

(i)	**Equilibrium**	**Standard Gibbs Free Energy Change ΔG_i^o (cal/mole)**
(I)	$\boldsymbol{C(gr) + \frac{1}{2} O_2(g) = CO(g)}$	-26,700-20.95*T*
(II)	$\boldsymbol{C(gr) = \underline{C}}$	5,400-10.1*T*
(III)	$\boldsymbol{\frac{1}{2} O_2(g) = \underline{O}}$(g)	-28,000-0.69*T*

Combination of these three equilibria gives (IV):

$$\underline{\boldsymbol{C}} + \underline{\boldsymbol{O}} = \boldsymbol{CO(g)} \quad \Delta \boldsymbol{G^{o}_{IV}} = \boldsymbol{-4,100 - 10.6T} \Rightarrow$$

$$\frac{\boldsymbol{p_{CO}}}{\boldsymbol{a_C a_O}} = \boldsymbol{-RT \ln \Delta G^{o}_{IV}}$$

Also, we have from the Epsilon Formalism:

$$\boldsymbol{a_C = f_C \cdot \underline{C}}$$

And

$$\boldsymbol{a_O = f_O \cdot \underline{O}}$$

At 1600 °C = 1873 °K, we can evaluate K_{IV}:

$$\frac{\boldsymbol{p_{CO}}}{(\boldsymbol{f_C \cdot \underline{C}})(\boldsymbol{f_O \cdot \underline{O}})} = \boldsymbol{476} = \frac{\boldsymbol{1}}{(\boldsymbol{f_C \cdot \underline{C}})(\boldsymbol{f_O \cdot \underline{O}})}$$

Also, we have from thermodynamic tables:

$$\boldsymbol{e^{C}_{C} = 0.22};\ \boldsymbol{e^{O}_{O} = -0.2};\ \boldsymbol{e^{O}_{C} = -0.097};\ \text{and}\ \boldsymbol{e^{C}_{O} = -0.13}$$

Taking the logarithm of both sides of the combined equilibrium gives:

$$\boldsymbol{-2.69 = \log f_C + \log \underline{C} + \log f_O + \log \underline{O}}$$

In the above, we see:

$$\log f_C = 0.22 \cdot 1 - 0.097 \cdot \underline{O}$$

$$\log f_O = -0.2\underline{O} = 0.13 \cdot 1 \Rightarrow$$

$$-2.77 = -0.297\underline{O} + \log \underline{O} \Rightarrow$$

$$\underline{O} = 0.0017\ \%\ O$$

Had f_C and $f_O$been assumed to be unity, then $-2.68 = \log \underline{O} \Rightarrow \underline{O} = 0.0021\ \%\ O$, which is an error of 24%!

STABILITY PHASE DIAGRAMS

We saw in the previous handout that, in a binary system, at constant T,P, fixing the activity of one component fixes the activities of the other – since for each component, the chemical potentials of the two phases are equal at equilibrium. Similarly, for the ternary system, fixing the activities of two of the three components fixes the activity of the third, in compliance with the GDE.

If, say, we have a ternary system A-B-C, where one of the components is a gas, such as oxygen, then if p_{O_2} is specified, along with an activity of the two remaining components, the equilibrium is completely specified. In turn, we may represent the phase relationships one of two ways:

1. At constant T, in a plot of a_A **and** a_B versus p_{O_2}; or
2. At constant a_A (or a_B) or p_{O_2} with *T* and either a_A, or a_B, or p_{O_2}as the variables.

Application of the GPR to the three-component system shows that up to five phases can co-exist, but all five phases in mutual equilibrium has no degrees of freedom: $\mathrm{F} = \mathbb{C} + 2 - \wp = 3 + 2 - 5 = 0$. In this case, since the five-fold equilibrium is unique – occurring at only one *T* and *P*, the later does not need to be fixed.

Now, if we consider one of the three components to be a gas phase, we have the following:

1. A maximum of four condensed phases can be in mutual equilibrium with one another and a gas phase – all being invariant, not requiring either T or P to be fixed.

2. Three condensed phases can be in equilibrium with each other and a gas phase at an arbitrarily chosen temperature. (Total pressure is not fixed independently.)

3. Two condensed phases can be in equilibrium with one another and a gas phase at an arbitrarily chosen temperature and value of $\boldsymbol{a_C}$, or $\boldsymbol{p_{O_2}}$. (Total pressure is not fixed independently.)

4. One condensed phase can be in equilibrium with the gas phase at an arbitrarily chosen temperature, $\boldsymbol{a_C}$ and $\boldsymbol{p_{O_2}}$. (Total pressure is not fixed independently.)

Now, we want to consider all the number of different ways we can represent this equilibria. For Case (1), as it is invariant, we have only one way to show this equilibrium. For Case (2), we have multiple combinations showing three of the four condensed phases in equilibrium with a gas phase, and so on.

Example of a Stability Diagram – The Si-C-O System at Constant *T*)

Let's examine this system at constant temperature, using $\boldsymbol{\log a_C \ \ and \ \log p_{O_2}}$ as the two independent variables. The six possible ways involving two condensed phases and a gas phase are:

1. $\boldsymbol{Si - SiO_2 - gas}$
2. $\boldsymbol{Si - SiC - gas}$
3. $\boldsymbol{SiC - SiO_2 - gas}$
4. $\boldsymbol{SiC - C - gas}$
5. $\boldsymbol{SiO_2 - C - gas}$
6. $\boldsymbol{Si - gas}$

Similarly, we have four possible equilibria involving three condensed phases and a gas phase:

1. $\boldsymbol{Si + SiC - SiO_2 - gas}$
2. $\boldsymbol{Si + SiC - C - gas}$
3. $\boldsymbol{C + SiC - SiO_2 - gas}$
4. $\boldsymbol{Si + C - SiO_2 - gas}$

The six ways involving two condensed phases and a gas phase at 1273 °K are now discussed.

1. *The equilibrium* $\boldsymbol{Si - SiO_2 - gas}$:

We have the equilibrium:

$$\boldsymbol{Si(s) + O_2 = SiO_2(s)} \quad (\boldsymbol{i}) \quad \Delta\boldsymbol{G_i^o = f(K)}$$

This gives (at 1273 °K): $\boldsymbol{\log p_{O_2} = -28.04}$, so in the plot of $\boldsymbol{\log a_C}$ **versus** $\boldsymbol{\log p_{O_2}}$, we have a vertical line AB, which is independent of $\boldsymbol{a_C}$ for the $\boldsymbol{Si - SiO_2}$ stability field. To the LHS of Line AB, $\boldsymbol{SiO_2}$is unstable, whereas, to the RHS of Line AB, Si is unstable. This is shown in Figure HV.8.

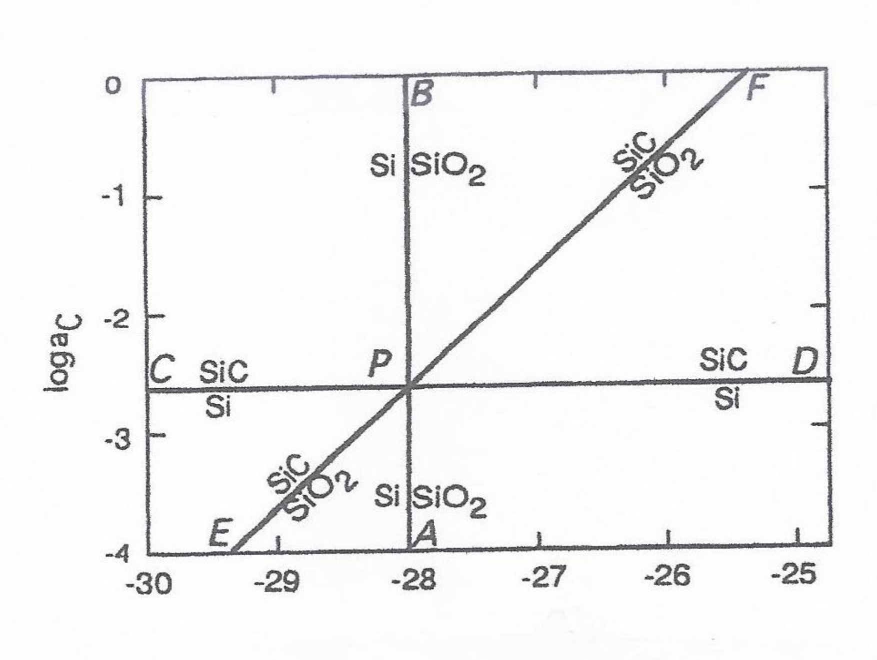

Figure HV.8 – Construction of the phase stability diagram for the system Si-C-O at 1000 °C.

2. *The equilibrium* $\boldsymbol{Si - SiC - gas}$:

The equilibrium is:

$$\boldsymbol{Si(s) + C(s) = SiC(s)} \quad (\boldsymbol{ii}) \quad \Delta\boldsymbol{G_{ii}^o = f(K)}$$

This gives: $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{-2.6}$, which is represented in Figure HV.8 as Line CD. This means that at 1000 °C, to have *Si* in equilibrium with *SiC*, the system must also be on this line - $\boldsymbol{a_C}$ has to be fixed at -2.6. Where line BA crosses Line CD, this is the invariant point P. Here, *only* at $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{-2.6}$ and $\mathbf{log}\,\boldsymbol{p_{O_2}} = \mathbf{-28.04}$ can we have all three solid phases co-existing: $\boldsymbol{SiC}, \boldsymbol{SiO_2}, \textbf{and } \boldsymbol{Si}$:

$$\boldsymbol{SiC(s) + O_2 = SiO_2(s)} \;\; (\boldsymbol{iii}) \quad \Delta \boldsymbol{G^o_{iii} = f(K)}$$

3. *The equilibrium* $\boldsymbol{SiC - SiO_2 - gas}$:

   From (iii), we have: $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{log}\,\boldsymbol{p_{O_2}} + \mathbf{25.44}$. This gives rise to Line EF in Figure HV.8, where, above this line, $\boldsymbol{SiC}$ is stable relative to $\boldsymbol{SiO_2}$, and below, the reverse - $\boldsymbol{SiO_2}$ is stable relative to $\boldsymbol{SiC}$.

4. *The equilibrium* $\boldsymbol{SiC - C - gas}$:

   This equilibrium between pure solid $\boldsymbol{SiC}$ and pure solid $\boldsymbol{C}$ can only occur where $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{0}$ (where $\boldsymbol{a_C} = \mathbf{1}$). Thus, in this figure, this equilibrium exists only along the line of $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{0}$, at values of $\mathbf{log}\,\boldsymbol{p_{O_2}} < \boldsymbol{-25.44}$, which would be the point of intersection of Line EF with the $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{0}$ line, Point F.

5. *The equilibrium* $\boldsymbol{SiO_2 - C - gas}$:

   For this equilibrium, $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{0}$. Thus, this equilibrium can only occur in the diagram along this line at values greater than -25.44.

6. *The equilibrium* $\boldsymbol{Si - C - gas}$:

   Here, the equilibrium is:

$$\boldsymbol{Si(s) + C(s) = SiC(s)} \;\; (\boldsymbol{ii}) \quad \Delta \boldsymbol{G^o_{ii} = f(K)}$$

Since, at this temperature, $\Delta \boldsymbol{G^o_{ii}}$ is negative (=-63,300 J/mole), then with $\boldsymbol{Si}$ and $\boldsymbol{C}$ both present, they would spontaneously react with each other to produce $\boldsymbol{C}$,

leaving either $\boldsymbol{C}$, or $\boldsymbol{Si}$, but not both (as one or the other becomes consumed). This implies that these two can't be in equilibrium with each other.
The solid carbon phase exists only along the $\mathbf{log}\,\boldsymbol{a_C} = \mathbf{0}$ line, thus, this figure contains fields of stability of the single phases $\boldsymbol{Si}, \boldsymbol{SiO_2}\,\mathbf{and}\,\boldsymbol{SiC}$. consequently, of the six lines in the diagram radiating from Point *P*, three represent stable equilibria involving two condensed phases and a gas phase, and three represent *metastable* equilibria involving two condensed phases and a gas phase. So, the problem is how to distinguish between the stable and the metastable. It is a property of these type of diagrams that the lines of metastable and stable equilibria radiate *alternatively* from a point, such as *P*. Thus, on set of lines is *PA-PC-PF*, and the other is *PE-PB-PD*. In Figure HV.8, $\boldsymbol{Si}$ is stable relative to $\boldsymbol{SiO_2}$in states to the left of *PA* and is stable relative to $\boldsymbol{SiC}$ in states below *PC*. As a consequence, the stable equilibrium lines are *PA-PC-PF* and defines the fields of stability as shown in Figure HV.9. These fields of stability of a single condensed phase and a gas phase, at constant temperature have two degrees of freedom. The boundary between these fields of stability is a line representing the equilibrium occurring among two condensed phases and a gas phase, indicating only one degree of freedom. Obviously, the intersection of the three boundary lines at Point *P* occurs when three condensed phases are in equilibrium with a gas phase, indicating zero degrees of freedom.

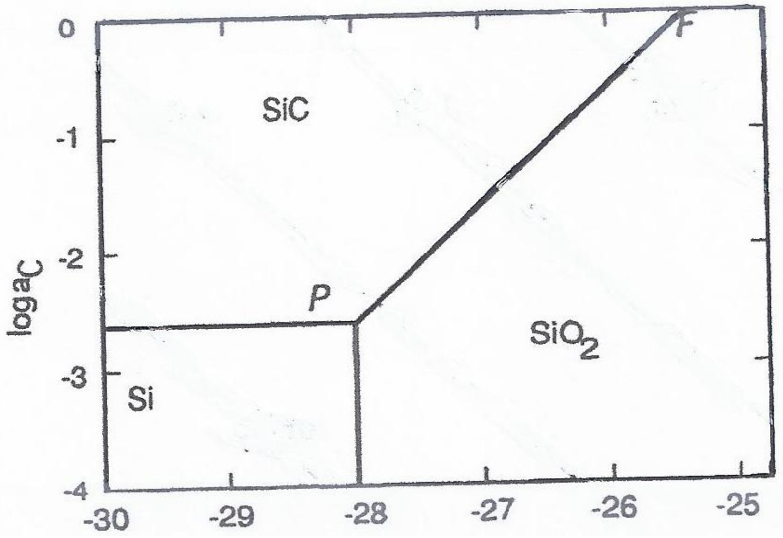

Figure HV.9 – The Si-C-O phase stability diagram, showing the fields of stability of the stable condensed phases.

OXIDE PHASES OF VARIABLE COMPOSITION

Phase diagrams of metals and metalloids with oxygen are an interesting class by themselves. Because of the relatively strong tendency to form oxides, there is typically only a very small range of stability of oxygen in solution in the metal, but the bulk of the M-O phase diagram consists of equilibria among the various stable oxides. In turn, these oxides tend to fall into one of the following stoichiometry: $\boldsymbol{MO, M_3O_4}$ **and** $\boldsymbol{M_2O_2}$. (Note that $\boldsymbol{M_3O_4}$ and $\boldsymbol{M_2O_3}$ are equivalent to $\boldsymbol{MO_{1.33}\ and\ MO_{1.5}}$, respectively.) In turn, particularly at higher temperatures, the oxides tend to depart somewhat from a strict stoichiometry. While this is, nevertheless, a solution phase, the fact that it is somewhat stoichiometric lends to its characterization in terms of a stoichiometric coefficient and a Gibbs Free Energy of formation, akin to the oxides in the Ellingham Diagram.

Figure HV.10 shows a schematic of the integral Gibbs Free Energy of a typical metal-oxygen system. This shows some solubility of oxygen in the metal, where the activity of M varies along f-g in the diagram.

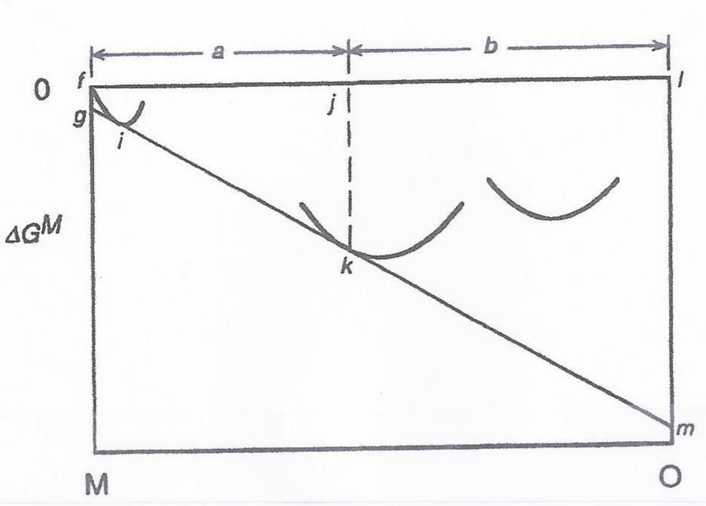

Figure HV.10 – The integral free energy of the system M-O which forms two oxide phases of variable composition showing a significant solubility of oxygen in the metal.

As the oxygen concentration increases from the M-rich corner, the first oxide phase to appear is “MO”, then “M_3O_4” (parentheses added to indicate that these compounds are quasi-stoichiometric). The common tangent *i-k* identifies the equilibrium between M at oxygen solubility ***i*** and oxide “MO”. In many systems, the extent of solubility of oxygen O is relatively very small, on the order of PPM. For the phase diagram, whose scale is 0 – 100%, this solubility is virtually zero, so that *f-g* in the figure effectively shrinks to a point. This is represented schematically in the following figure (HV.11).

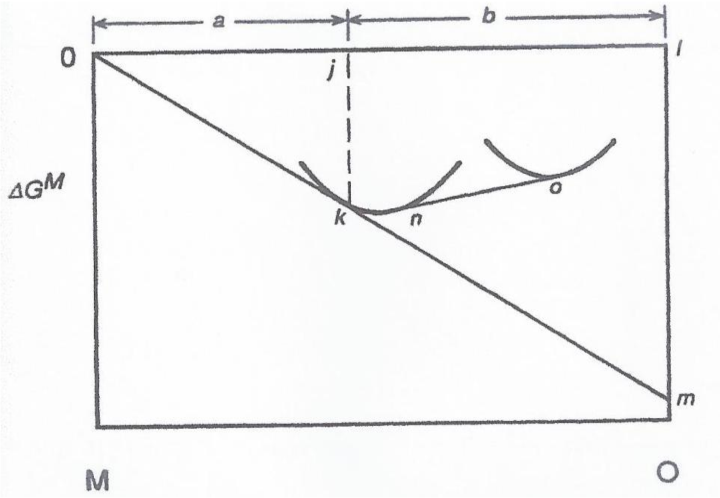

Figure HV.11 – The integral free energy of the system M-O which forms oxide phases of variable composition, and which shows a negligible solubility of oxygen in M.

The equilibrium between M and "MO" can be represented in terms of the Standard Free Energy of formation. In Figure HV.11, the distance *f-g* is $\boldsymbol{RT \ln a_M}$, but if the distance effectively shrinks to zero, we can say that the equilibrium is between "pure" M of activity of unity and "MO". Since the distance lm at 100 % oxygen is $\boldsymbol{RT \ln p_{O_2(M,\mathrm{MO})}}$, so we have:

$$\boldsymbol{yM + \frac{1}{2}O_2 = M_yO}$$

$$\boldsymbol{\Delta G^o = RT \ln p_{O_2(M,\mathrm{MO})}}$$

Now, if the oxygen partial pressure is increased, the metal phase disappears i.e., (the M-"MO" equilibrium becomes metastable) and the oxygen content of the phase "MO" increases.. Thus, the integral free energy of the system moves along line *k-n*, where a new equilibrium is established, between "MO" and the next higher oxide "M_3O_4", shown as the tangent *n-o*.

A classic demonstration of the foregoing discussion is the Fe-O system, shown in Figure HV.12 and 13.

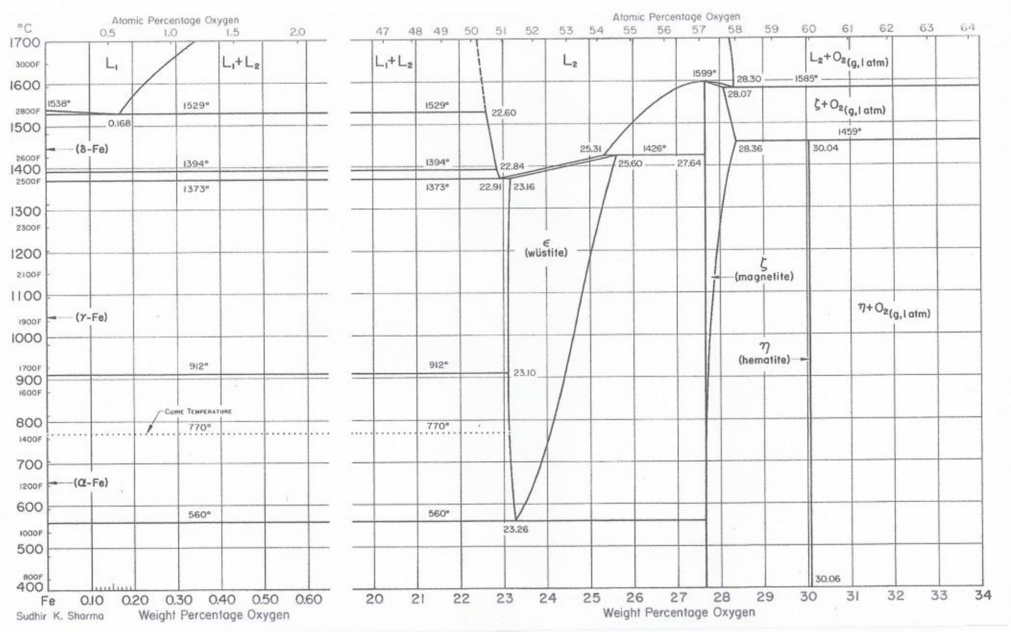

Figure HV.12 – The Fe_O system, showing the very low solubility of oxygen in iron in the iron-rich side. The oxygen-rich side (up to 34%) is also shown here and in the following figure between compounds FeO and Fe_2O3.

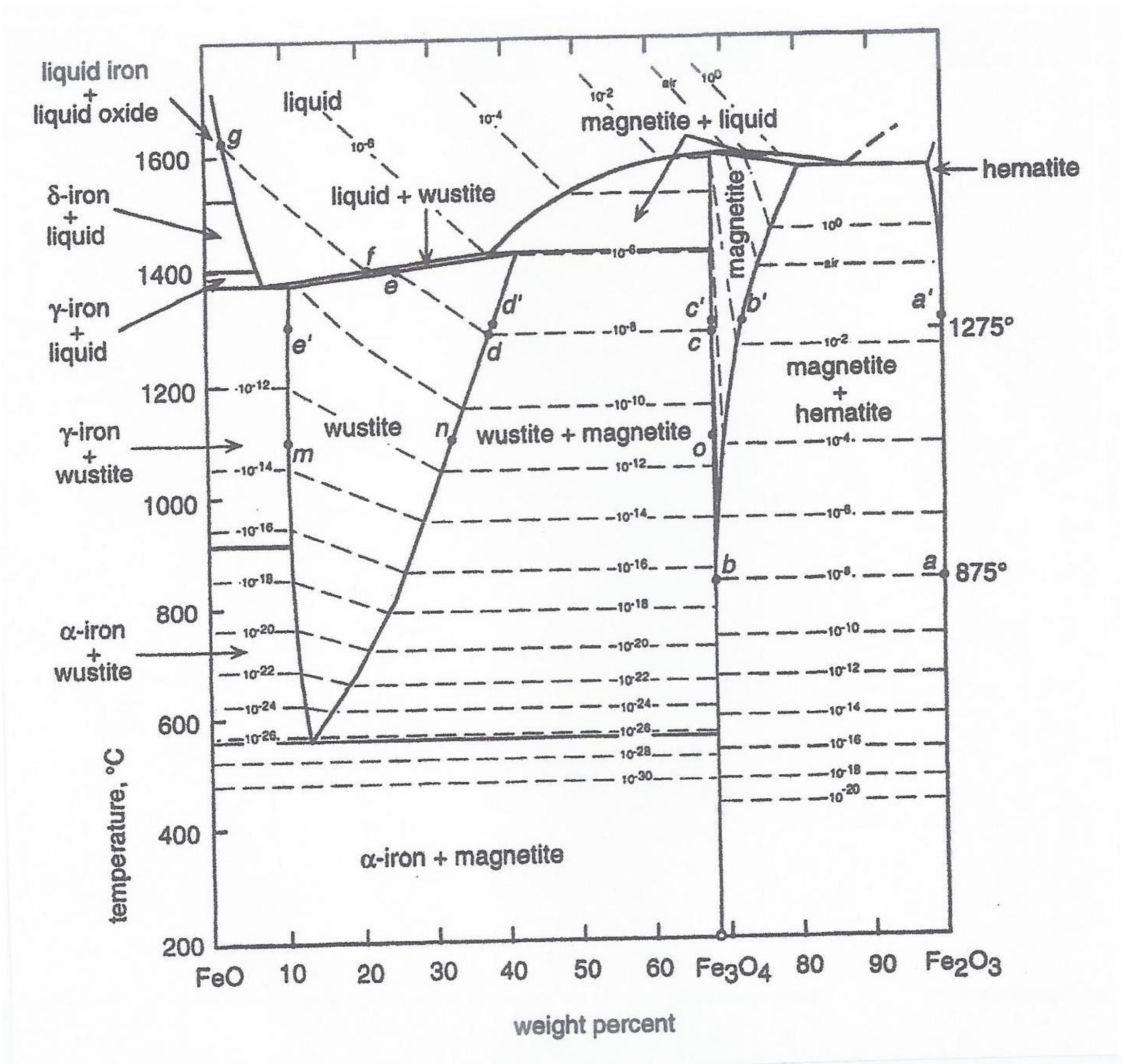

Figure HV.13 - A portion of the phase diagram for the system Fe-O between compounds FeO and Fe_3O_4 (where the concentration scale has been reset to be the relative proportions from 0 % FeO to 100 % Fe_3O_4). The dotted lines in the diagram are oxygen (atm) isobars (constant total pressure of 1 atm).

In this system, the phase “MO” is called wustite, where the departure from the stoichiometry increases with temperature. With increasing oxygen, the next phase to appear is magnetite “Fe_3O_4”, and then hemetite “Fe_2O_3”. These latter two oxide phases also show a departure from stoichiometry at higher temperatures, but to a lesser extent than wustite.

What is unique of this system is the dependency of composition on independent variable $\mathbf{\ln p_{O_2}}$. The oxygen isobars in this figure trace the loci of variation of the equilibrium compositions with temperature for a fixed total pressure (1 atm). For example, consider a small quantity of hematite at room temperature held in a gas reservoir of $\mathbf{\ln p_{O_2} = 10^{-8}}$, the volume of which is sufficiently large that any oxygen gas produced by the reaction of the oxide has an insignificant effect on the pressure of oxygen in the gas reservoir. Let the oxide be heated slowly enough that equilibrium with the gas phase is maintained. From Figure HV.13 it is seen that the oxide remains as homogeneous hematite until 875 °C is reached, at which temperature 10^{-8} atm is the invariant partial pressure of oxygen required for the equilibrium:

$$\mathbf{2Fe_3O_4 + \frac{1}{2}O_2 = 3Fe_2O_3}$$

At 875 °C, magnetite of composition *b* is in equilibrium with hematite of composition *a*, and any increase in temperature upsets the equilibrium toward the magnetite side, with the consequent disappearance of the hematite phase. Further increase in temperature moves the oxide along the 10^{-8} atm isobar in the magnetite phase field until 1275°C is reached, at which temperature is the invariant partial pressure of oxygen required for the equilibrium:

$$\mathbf{3FeO'' + \frac{1}{2}O_2 = Fe_3O_4}$$

At 1275°C, wustite of composition *d* is in equilibrium with magnetite of composition *c*. Further increase in temperature causes the disappearance of the magnetite phase, and the composition of the solid homogeneous wustite moves along the 10^{-8} atm oxygen isobar until the solidus temperature of 1400°C is reached, in which state solid wustite of composition *e* melts to form a liquid oxide of composition *f* at $\mathbf{p_{O_2} = 10^{-8}}$ atm. Continued increase in temperature moves the composition of the liquid oxide along the 10^{-8} atm oxygen isobar to saturation with iron at the temperature 1635°C , where the liquid oxide has the composition *g*, and the oxygen-saturated liquid appears. In this state, the equilibrium:

$$\boldsymbol{Fe(l) + \frac{1}{2}O_2 = FeO(l)}$$

is established. An increase in temperature beyond 1635°C causes the disappearance of the liquid oxide phase and a decrease in the dissolved oxygen content of the liquid iron.

Similarly, isothermal reduction of hematite is achieved by decreasing the partial pressure of oxygen in the system. For example, from Figure HV.13, at 1300°C, hematite is the stable phase until the partial pressure has been decreased to 1.34 10^{-2} atm, in which state magnetite of composition b' is in equilibrium with hematite of composition *a'*. Magnetite is then stable until the partial pressure of oxygen has decreased to 2.15 10^{-8} atm, where wustite of composition *d'* is in equilibrium with magnetite of composition *c'*. Wustite is then stable until the partial pressure of oxygen has been decreased to 1.95 10^{-11} atm where solid iron appears in equilibrium with wustite of composition *e'*. Further decrease in the pressure of oxygen causes the disappearance of the oxide phase.

It is important to verify this diagram in terms of the GPR. The partial pressure of oxygen is obviously a thermodynamic variable in deciding the degrees of freedom. The GPR is easily modified to include the partial pressure of oxygen as another variable, in addition to total pressure (by adding argon) and temperature:

$$\boldsymbol{F = \mathbb{C} - \wp + 3}$$

But now, we have another phase, in addition to the condensed phases – the gas phase from equilibrium of the system with oxygen gas. If total pressure is held constant (at one atm), then, with two components and these three phases, $\boldsymbol{F = 2 - 3 + 2 = 1.}$ This means the system is completely fixed by fixing one of the two remaining variables, either temperature of partial pressure of oxygen. As a consequence, the oxygen isobars must run horizontally across the two-condensed phase region (it is actually a three-phase region since gas is included as a phase), as is shown in Figure HV.13. That is, if *T* is fixed, then $\boldsymbol{p_{O_2}}$is fixed, and vice-versa. Similarly, for the single-condensed phase region in the diagram, there are two degrees of freedom, so that if $\boldsymbol{T}$ and $\boldsymbol{p_{O_2}}$are both fixed, the system is completely specified.

Instead of the fields of stability being shown in a temperature versus composition plot, they can be shown in a temperature versus $\boldsymbol{\log p_{O_2}}$, as shown in Figure HV.14.

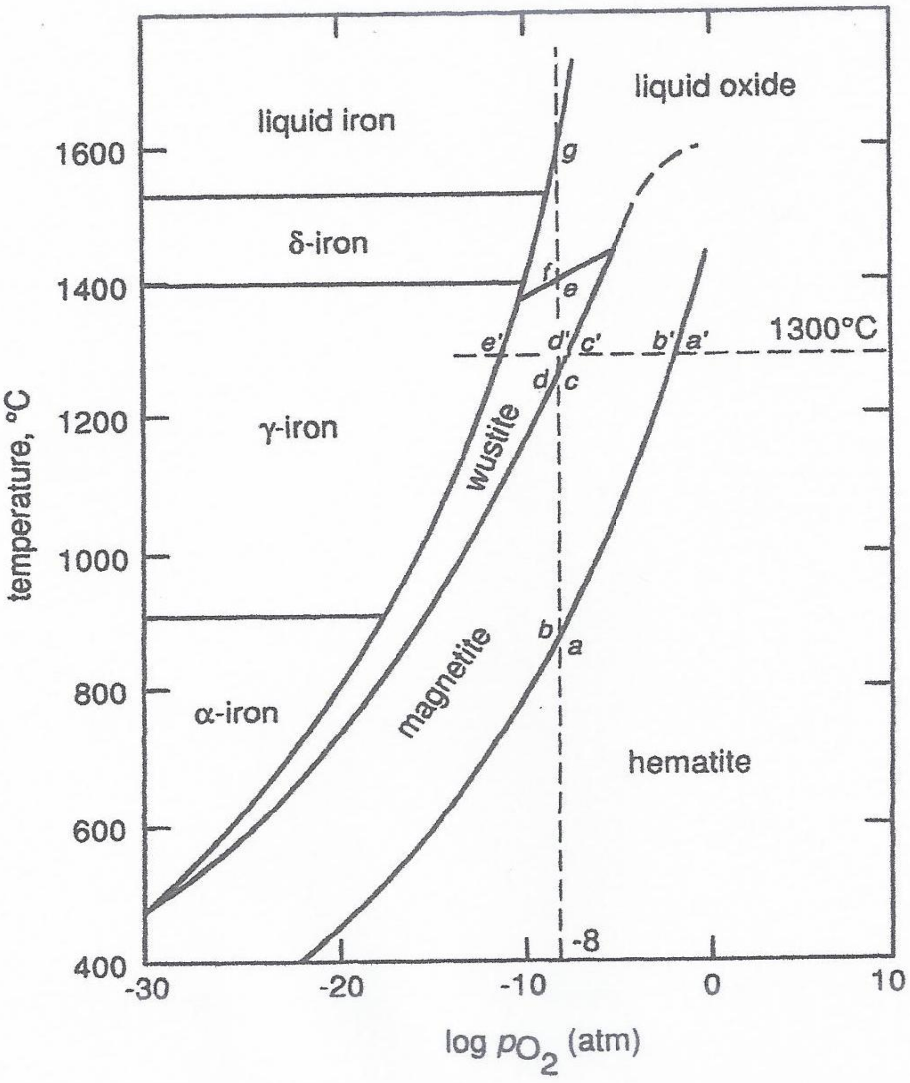

Figure HV.14 – Phase stability in the Fe-Fe_2O_3 system as a function of temperature and $\log p_{O_2}$.

Here, paths *a*-*g* and *a'*-*e'* compare to those in Figure HV.10 discussed above. Clearly, a disadvantage of this plot (Figure HV.13) is not having information of the compositions of the co-existing phases.

Yet another version of the latter plot is $\log p_{O_2}$ **versus** $1/T$, as shown in Figure HV.15 – which closely resembles the Ellingham Diagram. In this form, the slope of any of the invariant three-phase equilibrium lines at any temperature is the change in enthalpy per mole of oxygen during changes of oxidation states (i.e., $\boldsymbol{d}\log \boldsymbol{p_{O_2}}/\boldsymbol{d}(\mathbf{1}/\boldsymbol{T}) = \Delta \boldsymbol{H}/(\mathbf{8.314} \cdot \mathbf{2.303})$), where $\Delta\boldsymbol{H}$ is the enthalpy change per mole of oxygen consumed during the change of oxide phase. A linear variation of $\log \boldsymbol{p_{O_2}}$ **versus** $\mathbf{1}/\boldsymbol{T}$ occurs in ranges of temperature over which the composition of the oxide phases are constant.

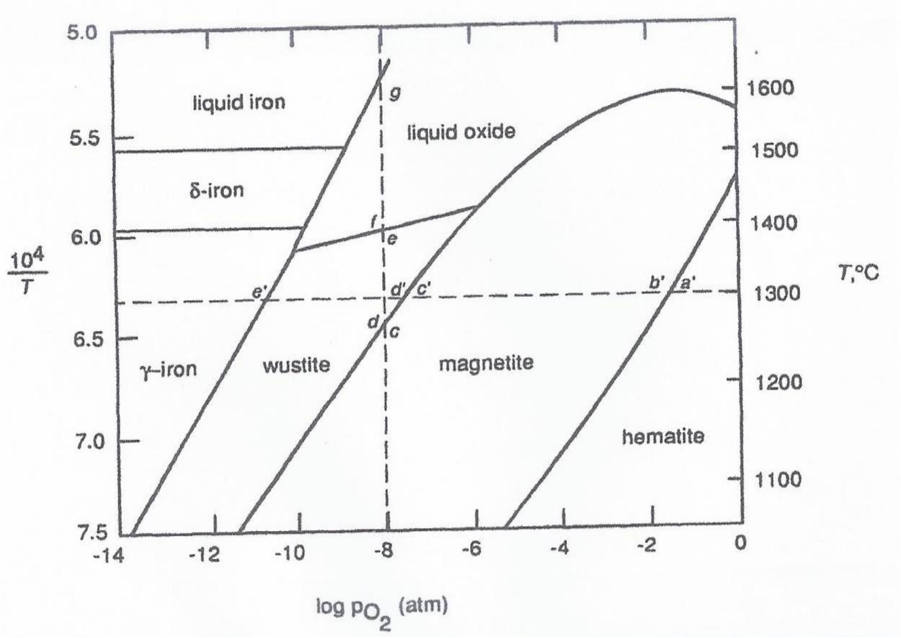

Figure HV.15 – Phase stability in the Fe-Fe_2O_3 system as a function of *1/T* and $\log \boldsymbol{p_{O_2}}$.

If the abscissa in Figure HV.15 is multiplied by $\mathbf{2.3}\boldsymbol{RT}$ and plotted versus $\boldsymbol{T}$ produces the Ellingham Diagram shown in the following figure (HV.16).

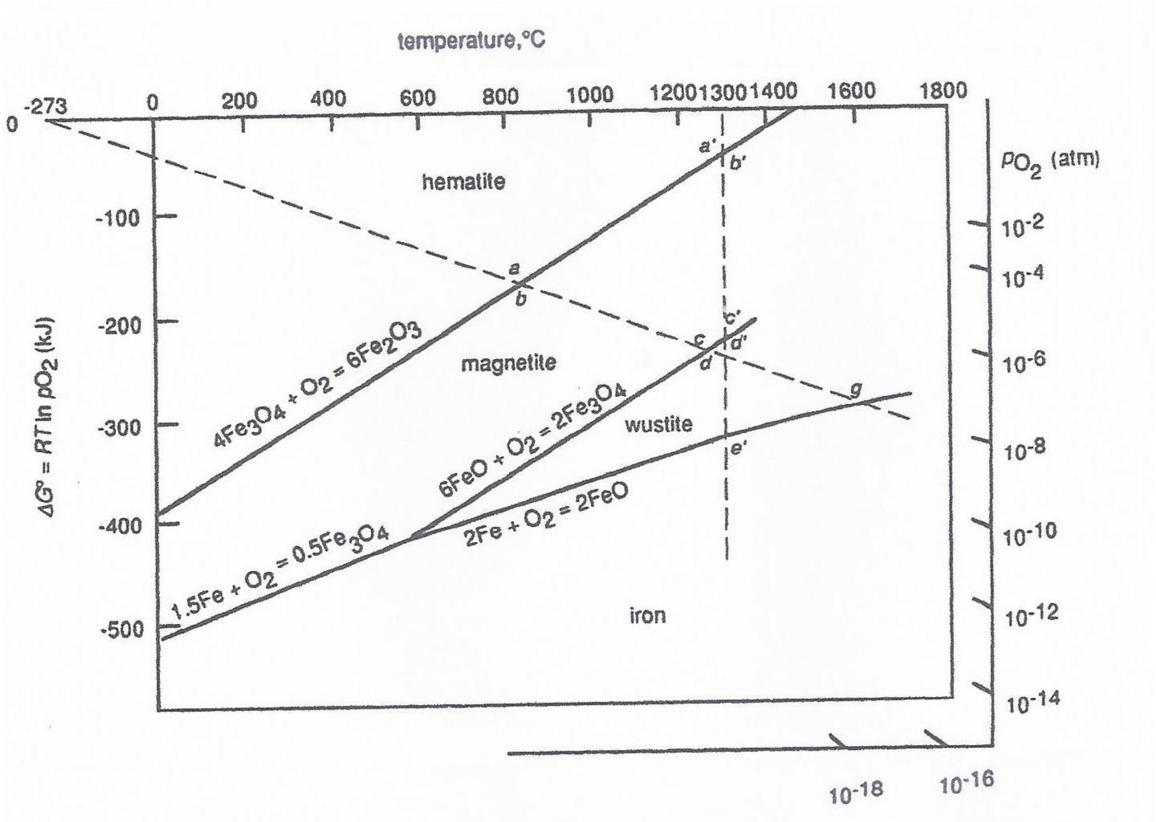

Figure HV.16 – Phase stability in the system Fe-Fe_2O_3 as a function of $\Delta\boldsymbol{G^o}$ and temperature.

Here, again, Paths *a*-*g* and *a'*-*g'* correspond to those in Figure HV.13. It is noted that, except for the Fe_3O_4-Fe_2O_3 line in Figure HV.15, the lines are all drawn for oxide reactions involving consumption of one mole of oxygen of the type:

$$\boldsymbol{Fe_xO_y + O_2 = Fe_xO_{(2+y)}}$$

in which the lower oxide of composition $\boldsymbol{Fe_xO_y}$ is in equilibrium with thehigher oxide of composition $\boldsymbol{Fe_xO_{(2+y)}}$. The Fe_3O_4-Fe_2O_3 line is hypothetical, referring to the completely stiochiometric compounds. In the Ellingham Diagram, lines radiating from the origin (for $\Delta\boldsymbol{G^o} = \boldsymbol{0}$ at 0 °K) are oxygen isobars. Clearly, in view of the diagram shown in Figure HV.12, 13, 14 or 15, a distinct advantage of the Ellingham Diagram is to view, at a glance, the relative stabilities of a large number of metal-oxide systems.

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