

Chapter 9

Gibbs Energy for Reactions Involving Components Not in Their Standard State

Chapter 6 described how enthalpy and entropy data may be used to calculate the Gibbs energy change for a reaction at any T when all the involved reactants and products are in their standard states:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \quad (9.1)$$

Once this capability is established, the question naturally arises as to how to account for Gibb's energy changes when some are all of the components are in a state other than their standard states. This question is really a question about the Gibbs energy changes that occur when components move from their standard states to their non-standard states. For a gas, this would involve being at some fugacity (pressure, if ideal gas) other than 1 atmosphere. For a liquid or solid it would be the Gibbs energy change associated with the component going into solution.

Gases

The treatment of Gibbs energy changes for solutions is patterned after the Gibbs energy changes for gases. In the cases of an ideal gas, the Gibbs energy change is the integrated fundamental equation for Gibbs energy at constant T

$$G_i - G_i^\circ = RT \ln(p_i / p_i^\circ) \quad (9.2)$$

where p_i° is the standard pressure of 1 atm. This is more often written using the chemical potential, which is simply the molar Gibbs energy

$$\mu_i = \mu_i^\circ + RT \ln(p_i / p_i^\circ) \quad (9.3)$$

If the gas does not behave ideally, then the fugacity is introduced as the *value needed* to determine the actual Gibbs energy change

$$\mu_i = \mu_i^\circ + RT \ln(f_i / f_i^\circ) \quad (9.4)$$

where f_i° is unity.

Experimental work is needed to compute fugacities, which are then used to compute adjustments in Gibbs energy for a gas as it moves away from its standard state. Consequently, Equation (9.4) is the formal thermodynamic definition of fugacity, implicit though it is.

Solutions

In the case of non-aqueous solutions, such as encountered in alloys, slags, magma, ceramics, the Gibbs energy of solution is written as

$$\mu_i = \mu_i^o + RT \ln(a_i/a_i^o) \quad (9.5)$$

where a_i is the activity of component i in the solution of interest and a_i^o is the activity of the standard state, which is always unity. The activity must be measured for each solution for which the change in Gibbs energy for a component in solution is needed. This a burdensome task, but over the 20th century considerable solution behavior has been determined for a wide range of metallic systems and to a lesser extent molten salts and ceramic systems. Additionally, by the turn of the century, considerable progress has been made in constructing useful theoretical solution models from which estimates of solution properties such as Gibbs energies of solution are obtained.

The simplest solution model is that of the ideal solution. Even though it is rarely, if ever, observed, a considerable number of systems are nearly ideal. The concept of ideal is also useful because it is a reference from which the behavior of real solutions may be compared. Also, in the absence of any solution data, it is the starting assumption for a solution's behavior.

In an ideal binary solution of components i and j , one would expect i and j to interact with each other just as they would interact with themselves. This is to say that the i - i , j - j , and the i - j bonds are the same. In such a solution, the equilibrium pressure of either component above the solution would be expected to be directly proportional to its mole fraction. For example, if the solution were 20 atomic percent j , the pressure of j would be $0.20 p_j^o$ and the pressure of i would be $0.80 p_i^o$ where the superscript denotes the vapor pressure of the pure component. Figure 9.1 shows this idealized behavior.

Equation (9-5) may be written more simply for ideal solutions, because the pressure of a component then varies directly with mole fraction. Consider the calculation path in Figure 9.2 along which the Gibbs energy of solution is computed. The gases have been assumed to exhibit ideal gas behavior. If the gaseous components do not behave ideally, the pressures would be written as fugacities.

Since each gas is in equilibrium with its corresponding liquid, ΔG_1 and ΔG_3 are zero and the change in Gibbs energy for a component going into solution is then ΔG_2 . Substituting the direct relationship of the solution vapor pressure with mole fraction gives

$$G_i - G_i^o = RT \ln \frac{x_i p_i^o}{p_i^o} \quad (9.6)$$

or

$$\mu_i = \mu_i^o + RT \ln x_i \quad (9.7)$$

This relationship is true for both liquid and solid solutions.

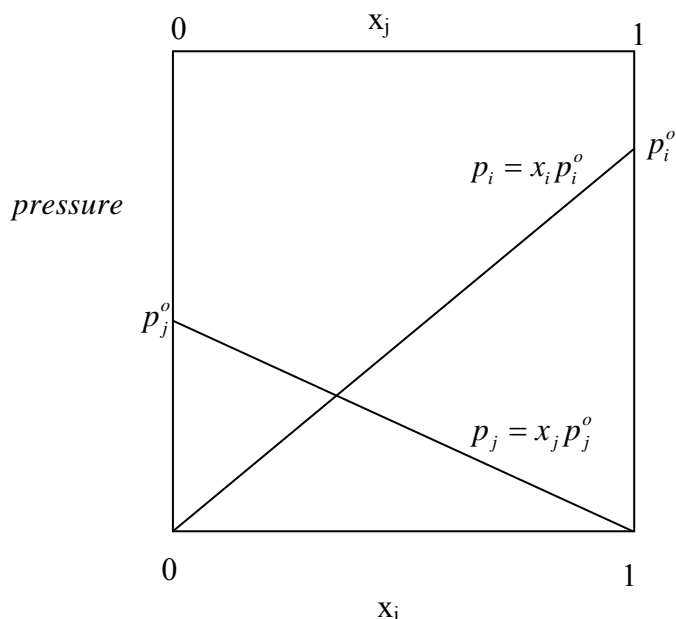


Figure 9.1 – Pressure variation for an ideal binary solution

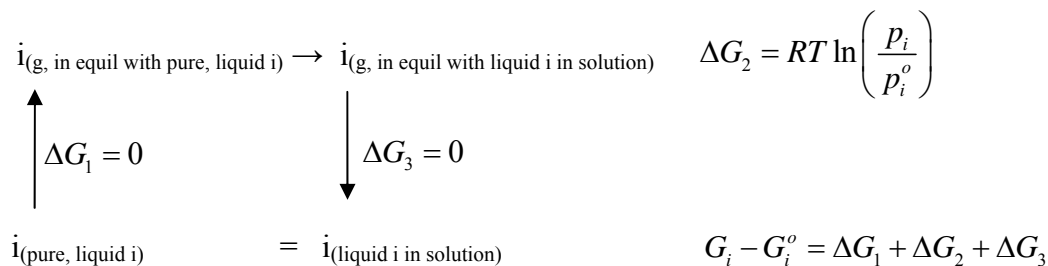


Figure 9.2 – Calculation schematic for determining the Gibbs energy change for an ideal solution

Aqueous Solutions

In an ideal aqueous solution, the standard state for a dissolved component in solution is chosen as the one molar solution, $[C_i^o] = 1 \frac{\text{gmole}}{\text{liter}}$. The use of brackets indicates molarity. Therefore,

$$\mu_i = \mu_i^o + RT \ln \frac{[C_i]}{[C_i^o]} \quad (9.8)$$

For real aqueous solutions

$$\mu_i = \mu_i^o + RT \ln \frac{[a_i]}{[a_i^o]} \quad (9.9)$$

As with the previous real behavior, $[a_i]$ must be measured although there are theoretical models for estimating the value. The standard state is a hypothetical 1 molar solution that behaves as the infinitely dilute solution. This seeming unusual convention is very useful because the solution becomes more ideal as it becomes more dilute, which is commonly the concentration of many solutions of interest.

The Big Six Equations

The six equations above describe the change in Gibb's energy as components move from their standard states and may be summarized as follows:

Gas	Ideal:	$\mu_i = \mu_i^o + RT \ln(p_i)$	(9.10)
	Real:	$\mu_i = \mu_i^o + RT \ln(f_i)$	(9.11)
Solution	Ideal:	$\mu_i = \mu_i^o + RT \ln x_i$	(9.12)
	Real	$\mu_i = \mu_i^o + RT \ln(a_i)$	(9.13)
Aqueous solution	Ideal:	$\mu_i = \mu_i^o + RT \ln[C_i]$	(9.14)
	Real:	$\mu_i = \mu_i^o + RT \ln[a_i]$	(9.15)

Again, experimental data are required to determine the values of the fugacity or activities in non-ideal systems. If the system is ideal, the pressure, mole fraction, or molarity may be used.

The fugacity and activities in Equations(9.11), (9.13), and (9.15) may be written

$$\begin{aligned} \text{Real gas:} & \quad \mu_i = \mu_i^o + RT \ln(\gamma_i p_i) & (9.16) \\ \text{where} & \quad \gamma_i \equiv f_i/p_i \end{aligned}$$

$$\begin{aligned} \text{Real solution:} & \quad \mu_i = \mu_i^o + RT \ln(\gamma_i x_i) & (9.17) \\ \text{where} & \quad \gamma_i \equiv a_i/x_i \end{aligned}$$

$$\begin{aligned} \text{Real aqueous solution:} & \quad \mu_i = \mu_i^o + RT \ln(\gamma_i [C_i]) & (9.18) \\ \text{where} & \quad \gamma_i \equiv [a_i]/[C_i] \end{aligned}$$

Ideal solution behavior is a theoretical construct that assumes each constituent atom (or molecule) in solution interacts with every other atom in the same way it interacts with atoms of the same kind. The activity coefficient γ_i is a measure of departure from the ideal behavior. If a gas or solution is ideal, $\gamma_i=1$. A system with stronger-than-ideal bonding interactions among solution components exhibits a $\gamma_i < 1$ (negative departure from ideal behavior) while weaker-than-ideal interactions results in a $\gamma_i > 1$ (positive deviation from ideal behavior). The activity coefficient must always be greater than zero. In solutions where the pure component is the standard state, γ_i can never be so large that $\gamma_i x_i$ exceeds unity because the activity cannot exceed the activity of the pure component. This is not a constraint in the cases of $\gamma_i p_i$ and $\gamma_i [C_i]$ since gases and aqueous solutions often have fugacities and aqueous activities that exceed unity.

Chemical Reactions

For the general reaction



the Gibb's energy change for the reaction is the difference in the Gibb's energy of the products and the reactants

$$\Delta G = cG_C + eG_E - aG_A - bG_B \quad (9.20)$$

Each G term may be written in terms of the molar Gibbs energy at constant temperature given by Equations (9.16), (9.17), and (9.18) to give

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{a_C^c [a_E]^e}{f_A^a a_B^b} \right] \quad (9.21)$$

where the stoichiometric coefficients have been moved inside the logarithmic terms. Equation 9.18 is more conveniently written

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (9.22)$$

where Q is a measure of prevailing reaction conditions

$$Q = \left[\frac{a_C^c [a_E]^e}{f_A^a a_B^b} \right] \quad (9.23)$$

At reaction equilibrium, $\Delta G = 0$ and Equation (9.22) becomes

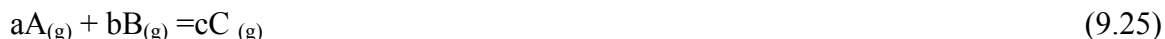
$$\Delta G^\circ = -RT \ln K \quad (9.24)$$

where Q is the particular measure of prevailing conditions called the *equilibrium constant* that brings the reaction into equilibrium. Whenever there are two or more terms comprising K , there are infinite combinations of those terms that equal K . This is to say that each independent reaction adds a constraint to the behavior of the reacting system. This concept is pursued in the chapter on the Gibbs Phase Rule.

A similar equation may be written for any reaction. If a gas involved in a reaction behaves ideally, which is often the case, $f_i = p_i$. Mole fractions may be used for a_i for non-aqueous ideal solutions and $[a_i] = [C_i]$ for ideal aqueous solutions. Such assumptions are questionable for non-aqueous solutions but are quite good for weak aqueous solutions.

Gaseous Reactions

For the general reaction



the Gibbs energy change may be computed from

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (9.26)$$

where

$$Q = \left[\frac{P_C^c}{P_A^a P_B^b} \right] \quad (9.27)$$

assuming ideal gas behavior. As the reaction proceeds in a closed system from left to right, the value of Q decreases. The reaction will continue until equilibrium is reached. The value of Q will then have decreased to equal the equilibrium constant K . This may be seen mathematically by substituting Equation (9.24) into equation (9.26) to give

$$\Delta G = RT \ln \frac{Q}{K} \quad (9.28)$$

which easily shows that when $Q < K$, the reaction proceeds to the right, when $Q > K$ the reaction proceeds to the left, and when $Q = K$ the reaction is at equilibrium.

The equilibrium constant for Reaction (9.25) is

$$K = \left[\frac{P_C^c}{P_A^a P_B^b} \right]_{Eq} \quad (9.29)$$

where the gases are sufficiently ideal to allow the use of pressure rather than fugacity. Furthermore, it is understood that each pressure is divided by the standard pressure of 1 atm, which is to say the pressures are in atmospheres. Consequently, the equilibrium constant is always unitless.

Reaction Extent Computations

A commonly encountered situation is determining the extent of reaction needed to achieve equilibrium from a given initial non-equilibrium state. For example, consider the final reaction in the Haber Process for ammonia production



where initially A, B, and C moles of nitrogen, hydrogen, and ammonia are in a reactor at T and a fixed pressure P_T . The following algorithm finds the equilibrium moles of each gas.

Algorithm

Step 1: Write the reaction and assign a reaction extent.

Let x = the moles of H_2 that react.

Step 2: Perform a mole balance including the equilibrium partial pressures

Species	Initial moles	Equilibrium moles	$p_i = x_i P_T$
N_2	A	A-x	$\frac{(A-x)}{(A+B+C-2x)} P_T$
H_2	B	B-3x	$\frac{(B-3x)}{(A+B+C-2x)} P_T$
NH_3	C	C+2x	$\frac{(C+2x)}{(A+B+C-2x)} P_T$
total		A+B+C-2x	

Step 3: Substitute the partial pressures into K

$$K = \frac{\left(\frac{(C+2x)}{(A+B+C-2x)} P_T \right)^c}{\left(\frac{(A-x)}{(A+B+C-2x)} P_T \right)^a \left(\frac{(B-3x)}{(A+B+C-2x)} P_T \right)^b} \quad (9.31)$$

Step 4: Solve for x

This typically requires a numerical method such as Goal Seek[®] in Microsoft Excel[®]. However, when $c = a + b$, Equation (9.31) simplifies considerably to

$$K = \frac{(C+2x)^c}{(A-x)^a (C-3x)^b} \quad (9.32)$$

A trial and error is facilitated by recognizing that the solution is bounded by those values of x that keep the final moles greater than zero. In this case $x < A$ or $x < B/3$, whichever is smaller and $x > -C/2$.

Ellingham Diagram

An Ellingham Diagram is a graph of the standard Gibbs energies as a function of temperature. Each reaction involves one mole of O_2 as a reactant. For example, one such reaction may be written



where M represents tetravalent elements such as Ti or Si. Such reactions differ with the stoichiometry of the oxidized compound as would be the case for trivalent Al reacting with one mole of O_2 .



where M might represent trivalent Al or Cr. Figure 9.3 is a typical Ellingham Diagram. The most stable oxides, which are formed from the most reactive metals, will appear at the bottom of the diagram while the least stable oxides, which are formed from more noble metals, will appear near the top. The diagram takes on additional meaning if M and its oxidized form are considered to be in their standard states. In this case

$$\Delta G^0 = -RT \ln \left(\frac{1}{p_{O_2}} \right) = RT \ln p_{O_2} \quad (9.35)$$

since the activities of both M and the oxidized form are unity. The vertical scale of the plot is both ΔG^0 and $RT \ln p_{O_2}$ where the p_{O_2} is the pressure of O_2 in equilibrium with M and its oxidized form. Comparison of Equation (9.35) with Equation (9.10) gives yet another name for the vertical scale of the Ellingham Diagram: the *relative chemical potential of oxygen* $\Delta\mu_{O_2}$

$$\Delta\mu_{O_2} \equiv \mu_{O_2} - \mu_{O_2}^0 = RT \ln p_{O_2} \quad (9.36)$$

The usefulness of the Ellingham is greatly enhanced by the addition of three nomographs: O_2 pressure, H_2/H_2O ratio, and the CO/CO_2 ratio.

O₂ Nomograph

Lines of constant P_{O_2} will pass through the origin and have a slope of $R \ln(P_{O_2})$. Placing such lines on the diagram would add to an already-crowded diagram. However, the P_{O_2} information is added as tick marks on a nomograph showing where lines of selected P_{O_2} 's would intersect the nomograph. Since lines of constant P_{O_2} all pass through the origin, a line for any particular P_{O_2} may easily be constructed with the origin and the nomograph tick mark of interest.

H₂/H₂O nomograph

The reaction for the H₂/H₂O line is



At equilibrium

$$\Delta G^0 = -RT \ln \left[\left(\frac{P_{H_2O}}{P_{H_2}} \right)^2 \left(\frac{1}{P_{O_2}} \right) \right] = RT \ln p_{O_2} + 2RT \ln \left(\frac{P_{H_2O}}{P_{H_2}} \right) \quad (9.38)$$

Since $\Delta G^0 = A + BT$, Equation (9.38) may be written

$$RT \ln p_{O_2} = A + \left(B - 2R \ln \left(\frac{P_{H_2}}{P_{H_2O}} \right) \right) T \quad (9.39)$$

This shows that lines of constant H₂/H₂O ratio radiate from the point (0 K, A). The H₂-H₂O line shown on the diagram assumes that the pressures of H₂ and H₂O are unity, or more generally, that the H₂ /H₂O ratio is unity. If the ratio were to exceed unity, the slope of the line would decrease compared to the drawn H₂-H₂O line. One may easily construct lines of selected H₂ /H₂O ratios varying the ratio by powers of 10 and writing Equation (9.39) in the Log form

$$RT \ln p_{O_2} = A + \left(B - 2 * 2.303R \log \left(\frac{P_{H_2}}{P_{H_2O}} \right) \right) T \quad (9.40)$$

Therefore, an H₂ /H₂O ratio of 10⁻¹⁰ would change the slope of the plotted H₂ -H₂O line downward by 95.1 cal/K.

$$slope = B - 2 * 2.303 * R \log (10^{10}) = B - 9.51 * 10 \frac{cal}{K * gmole} \quad (9.41)$$

This is more conveniently written as

$$slope = B - 95.1 \frac{Kcal}{1000 K * gmole} \quad (9.42)$$

If one moves out from 0 K to 1000 K (727 °C) and moves downward 95.1 Kcal from the plotted H₂ -H₂O line, a point on the line having an H₂ /H₂O ratio of 10¹⁰ is located. Extending a line from this point and the point through which all H₂ -H₂O lines radiate (0 K, A), gives a line along which H₂ /H₂O = 10¹⁰. Drawing these lines would add considerable confusion to the diagram so rather than drawing the actual lines, a nomograph along the right side of the Ellingham Diagram is constructed that shows the intersection of selected H₂ /H₂O ratios with the nomograph.

CO/CO₂ nomograph

The reaction for the CO/CO₂ line is



At equilibrium

$$\Delta G^0 = -RT \ln \left[\left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 \left(\frac{1}{P_{\text{O}_2}} \right) \right] = RT \ln p_{\text{O}_2} + 2RT \ln \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right) \quad (9.44)$$

This has the same form as Equation (9.38) and so the same result is obtained for the CO – CO₂ line as for the H₂ - H₂O line.

$$RT \ln p_{\text{O}_2} = A + \left(B - 2R \ln \left(\frac{P_{\text{CO}}}{P_{\text{CO}_2, \text{O}_2}} \right) \right) T \quad (9.45)$$

Of course, the values of A and B differ from the values for the H₂ - H₂O line.

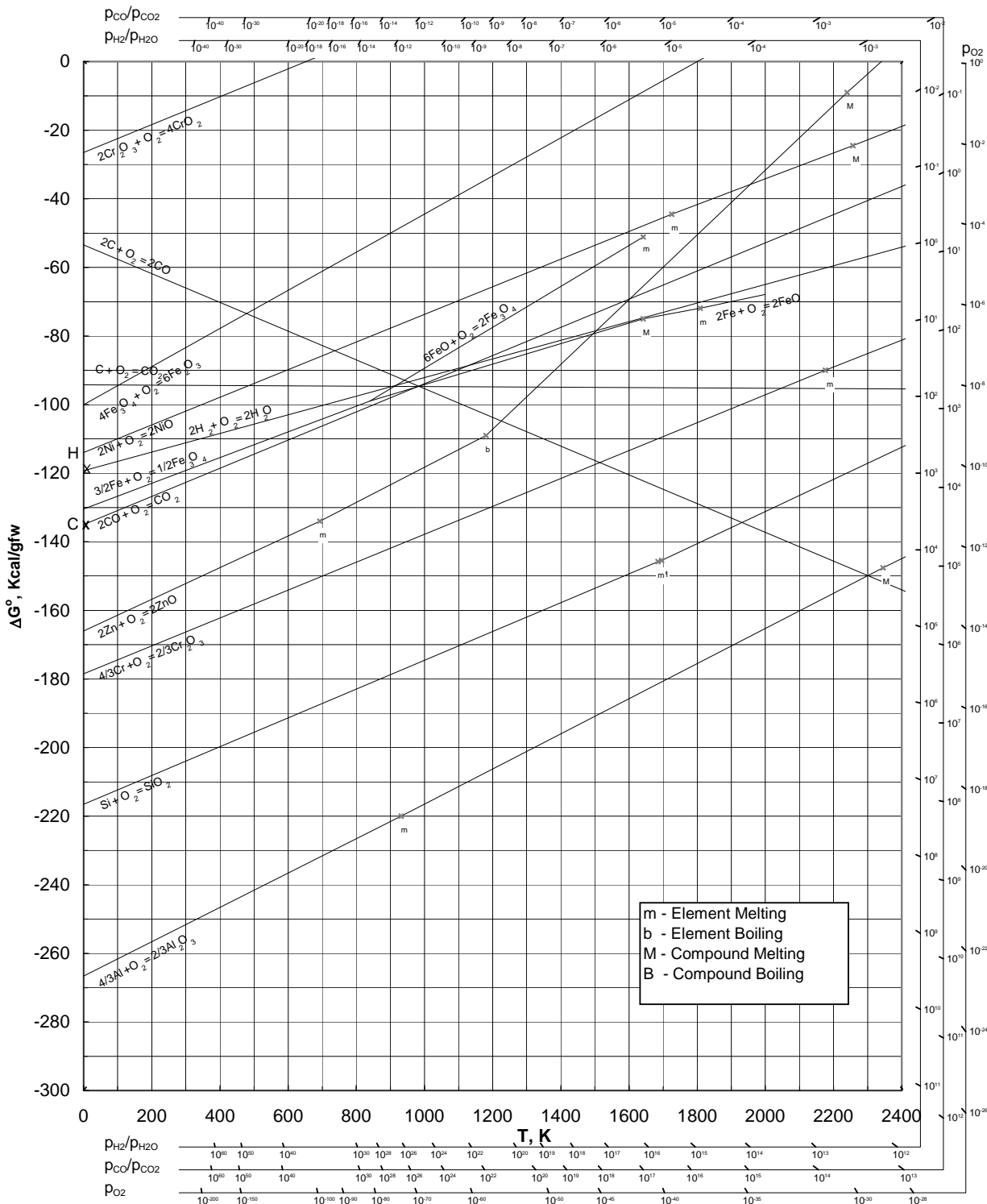


Figure 9.3 Ellingham Diagram for User-Selected Oxides

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Data from Thomas B. Reed, Free Energy of Formation of Binary Compounds, MIT Press, Cambridge, MA, 1971.

Figure 9.3 Ellingham Diagram