

GIBBS FREE ENERGY

4.1 STABILITY CRITERIA

For a spontaneous process or reaction it is noted from Section 3.4 that ΔS_{Net} is positive. Expressing [3-19] in differential form for such a process

$$dS_{\text{Net}} = dS_{\text{Sys}} + dS_{\text{Surr}}^{\text{Rev}} > 0 \quad [4-1]$$

and substituting [3-20] into [4-1], Swalin (1964, p. 25–26) shows that

$$dS_{\text{Net}} = dS_{\text{Sys}} - dH_{\text{Sys}}/T > 0.$$

The designation Sys is dropped since the inequality refers to the *system*, hence $TdS - dH > 0$. Reversing the inequality sign,

$$dH - TdS < 0 \quad [4-2]$$

According to [4-2], $dH - TdS$ is less than zero for a *spontaneous* reaction. If the reaction is *nonspontaneous*,

$$dH - TdS > 0 \quad [4-3]$$

At equilibrium,

$$dH - TdS = 0 \quad [4-4]$$

The expression $dH - TdS$ is related to the *Gibbs free energy* function G as follows: Starting with the definition

$$G = H - TS \quad [4-5]$$

and taking its differential,

$$dG = dH - TdS - SdT \quad [4-6]$$

At constant temperature, [4-6] reduces to

$$dG = dH - TdS \quad [4-7]$$

Substituting [4-7] into [4-2], [4-3], and [4-4] and integrating, stability criteria are defined in terms of Gibbs free energy:

- (1) If $\Delta G = 0$, the reaction is at equilibrium;
- (2) If $\Delta G < 0$, the reaction is spontaneous in the direction specified;
- (3) If $\Delta G > 0$, the reaction is nonspontaneous in the direction specified.

The Gibbs free energy provides a chemical reaction stability criteria that is based only on the properties of the *system* at constant pressure and temperature.

Example Problem 4-1

Referring to the fusion of supercooled gold, Example Problem 3-5, determine whether or not fusion is spontaneous. Use the Gibbs free energy criteria. Is the result in agreement with entropy criteria?

Solution

Integrating [4-7] at constant temperature,

$$\Delta G_T = \Delta H_T - T\Delta S_T \quad [4-8]$$

From Example Problems 2-6 and 3-5, $\Delta H_{1106, \text{Au}}^f = 12,930 \text{ J/mol}$ and $\Delta S_{1106, \text{Au}}^f = 9.69 \text{ J/(mol}\cdot\text{K)}$, hence

$$\begin{aligned}\Delta G_{1106, \text{Au}}^f &= 12,930 - 1106(9.69) = 12,930 - 10,717 \\ &= \underline{2,213 \text{ J/mol.}}\end{aligned}$$

Since $\Delta G_{1106, \text{Au}}^f > 0$, fusion is *not* spontaneous at 1106 K. This agrees with the answer in Example Problem 3-5.

4.2 STANDARD STATES: GIBBS FREE ENERGY OF FORMATION AND REACTION

The standard state Gibbs free energy of compounds and elements, ΔG_T^0 , is chosen at a reference pressure of 1 atm (or 1 bar) and the state of aggregation (solid, liquid, or gas) defined at the temperature of interest. For pure compounds $\Delta G_T^0 = \Delta G_T^{0,f}$, the *Gibbs free energy of formation* of the compound. $\Delta G_T^{0,f}$ is calculated from the reaction involving formation of the compound from its constituent *elements*. This is consistent with the definition of enthalpy of formation in that Gibbs free energy of formation may be calculated at any temperature at which the compound and its component elements are in the *most stable* configuration. For pure *elements* in the *most stable* configuration, standard state Gibbs free energy is normally assigned the arbitrary value $\Delta G_T^0 = 0$. Table 4.1 summarizes the standard free energy states for elements and compounds.

Table 4.1: Standard State Gibbs Free Energy

<i>State of Aggregation</i>	<i>Pure Elements</i> $P^0 = 1 \text{ atm}^*$, Stable at T (K)	<i>Pure Compounds</i> $P^0 = 1 \text{ atm}^*$, Stable at T (K)
Solid	$\Delta G_T^0 = 0$	$\Delta G_T^0 = \Delta G_T^{0,f}$
Liquid	$\Delta G_T^0 = 0$	$\Delta G_T^0 = \Delta G_T^{0,f}$
Gas (ideal)	$\Delta G_T^0 = 0$	$\Delta G_T^0 = \Delta G_T^{0,f}$

* See footnote about standard pressure: Table 2.1.

As in the case of enthalpy, only changes in Gibbs free energy are computed. Hence for a chemical reaction occurring at 1 atm pressure and $T = T(\text{K})$,

$$\Delta G_T^0 = \sum n \Delta G_T^{0,f} (\text{Products}) - \sum n \Delta G_T^{0,f} (\text{Reactants}) \quad [4-9]$$

where ΔG_T^0 now represents the *standard Gibbs free energy of the reaction* and n is the number of moles of each reactant or product in a *balanced* chemical reaction. Note the analogy between [4-9] and [2-14].

Suppose element A oxidizes at 298 K and 1 atm to form a hypothetical oxide A_2O according to



From [4-9] and Table 4.1,

$$\Delta G_{298}^0 = (1)\Delta G_{298, A_2O(s)}^{0,f} - 2\Delta G_{298, A(s)}^0 - (1/2)\Delta G_{298, O_2(g)}^0$$

or

$$\Delta G_{298}^0 = \Delta G_{298, A_2O(s)}^{0,f}$$

Note, as mentioned in Chapter 2 (Section 2.6), that the superscript *f* applies to *compounds* but not to elements.

4.3 METHODS FOR DETERMINATION OF ΔG_T^0

Tables, Charts, and Computer Programs

The choice of source materials for thermodynamic data (tables, charts, or computer programs) is often determined by the accuracy required. For the purposes of this book, adequate data is given in the tables in Appendix A for solving either Example or Exercise Problems.

Assuming $\Delta C_p \approx 0$ and substituting equations [2-19] and [3-17] into [4-8],

$$\Delta G_T^0 = \Delta H_{T_1}^0 - T\Delta S_{T_1}^0 \quad [4-10]$$

For $T_1 = 298$ K,

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 \quad [4-11]$$

Here, only the standard enthalpy and entropy of reaction at 298 K are needed to compute ΔG_T^0 , no C_p data is required. Often, the data at 298 K is the only information available, hence [4-11] is the only alternative.

For many materials, C_p is known as a function of temperature. It is common in such cases for $\Delta C_p = a$ (constant), hence substituting [2-20] and [3-18] into [4-8] gives

$$\Delta G_T^0 = \Delta H_{298}^0 + a(T - 298 \text{ K}) - T[\Delta S_{298}^0 + a \ln(T / 298 \text{ K})] \quad [4-12]$$

Collecting constants,

$$\Delta G_T^0 = A + BT \log(T) + CT \quad [4-13]$$

The constants *A*, *B*, and *C* are listed in Appendix A, Table A.4, for selected reactions. Note that log is \log_{10} in the table. In the remainder of this book, the letter *f* for formation will be dropped in order to simplify notation and avoid confusion with the letter *f* for fusion.

Ellingham Diagrams

Ellingham diagrams (Ellingham, 1944) are plots of standard Gibbs free energy, ΔG_T^0 , versus temperature *T*. Each plot is *approximated* by a straight line for which the linear equation is derived by:

- (1) Assuming $\Delta C_p \approx 0$ in the temperature interval for which no reaction components change phase;
- (2) Application of [4-10] where $-\Delta S_{T_1}^0$ is the slope (also see [4-27]) and $\Delta H_{T_1}^0$ is the ordinate intercept.

Consider, for example, the reaction $2\text{Mg} + \text{O}_2 = 2\text{MgO}$ shown in Figure 4.1 (taken from Figure E.2). Two breaks in slope appear on this diagram, one at 923 K corresponding to the melting point of Mg, and the other at 1378 K corresponding to the boiling point of Mg. Equation [4-11] is applicable to the linear segment between 298 K (arbitrary lower limit) and the melting point of Mg at 923 K. Between the melting and boiling points of Mg, ΔH^f and ΔS^f are incorporated into Hess's law as follows:

- (a) $2\text{Mg}(s) + \text{O}_2(g) = 2\text{MgO}(s) \quad \Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0$
 (b) $2\text{Mg}(s) = 2\text{Mg}(l) \quad 2\Delta G_{923}^f = 2\Delta H_{923}^f - 2T\Delta S_{923}^f$
 (c) Reaction (a) - Reaction (b):
 $2\text{Mg}(l) + \text{O}_2(g) = 2\text{MgO}(s)$

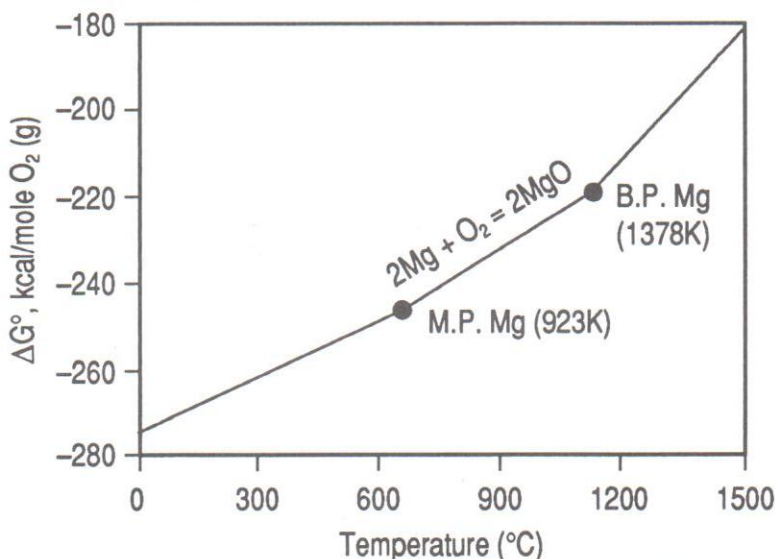


Figure 4.1 Ellingham diagram for the standard state oxidation of magnesium.

ΔG_T^0 for reaction (c) is given by

$$\Delta G_T^0 = \Delta H_{298}^0 - 2\Delta H_{923}^f - T(\Delta S_{298}^0 - 2\Delta S_{923}^f).$$

This expression is applicable to the nearly linear segment between 923 K and 1378 K in Figure 4.1. Since the enthalpy and entropy of fusion are positive, the entropy of reaction (c) is more negative than that of reaction (a). From [4-27], the slope of the reaction line for each segment is

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S,$$

hence the slope increases at the transformation point when Mg melts. Note that the change in slope is much greater for boiling than for melting because the entropy of vaporization is greater than the entropy of fusion. Ellingham diagrams for metallic oxides and sulfides are shown in Appendix E, Figures

E.2 and E.3 respectively. Particular attention should be given to the notation in the box inserts on each figure. Note that for computation, T ($^{\circ}\text{C}$) in these figures is converted to T (K).

Example Problem 4-2

Calculate $\Delta G_{298\text{ K}}^0$ for the reaction



- (a) Assume $\Delta C_p = 0$, (b) assume ΔC_p is constant, (c) use complete C_p expressions, and (d) use the Ellingham diagram for oxides.

Solution

- (a) **Method 1:** Assuming $\Delta C_p = 0$,* [4-11] is combined with data in Table A.1:

$$\begin{aligned}\Delta G_{298}^0 &= \Delta H_{298}^0 - (298)\Delta S_{298}^0 \Rightarrow \\ \Delta G_{298}^0 &= -240,600 - (298)[38.08 - 29.79 - 0.5(205.10)] \\ &= \underline{-212,510 \text{ J/mol}}.\end{aligned}$$

- (b) **Method 2:** Assuming $\Delta C_p = \text{constant}$, use Table A.4.

$$\begin{aligned}\Delta G_T^0 &= A + BT\log(T) + CT \\ \Delta G_{298}^0 &= -244,580 + 98.54(298) = \underline{-215,210 \text{ J/mol}}.\end{aligned}$$

- (c) **Method 3:** Using complete C_p expressions as in [2-18] and substituting [2-15] and [3-15] into [4-8], the result is identical to [4-11] at $T = 298\text{ K}$. Hence,

$$\Delta G_{298}^0 = \underline{-212,510 \text{ J/mol}}.$$

as in Method 1. However, when $T \neq 298\text{ K}$, ΔG_T^0 is calculated by using the above substitutions and integrating. For most engineering applications, calculation of ΔG_T^0 using the shorter techniques of either Method 1 or Method 2 above is adequate.

- (d) **Method 4:** Referring to Figure 4.2 (taken from Figure E.2),

$$\Delta G_{298}^0 = -(106,000/2)(4.184) = \underline{-221,750 \text{ J/mol}}.$$

* [4-11] is rigorous at $T = 298\text{ K}$, since ΔC_p does not enter into the calculation.

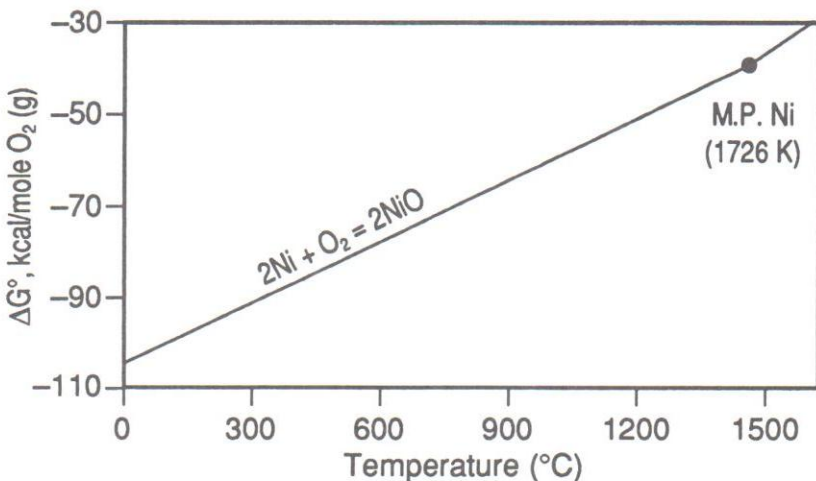


Figure 4.2 Ellingham diagram for the standard state oxidation of nickel.

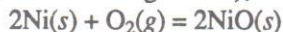
Referring to Figure E.2, many oxides are more stable than NiO because they appear below NiO and exhibit a more negative ΔG° . Since all of the reactions on the diagram are based on one mole of O_2 , the stabilities of the oxides are directly comparable. For example, carbon is a reducing agent for iron above about $750^\circ C$ since CO is more stable than FeO. On the other hand, TiO_2 is more stable than CO up to near the melting point of Ti.

Example Problem 4-3

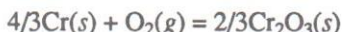
Which metal is more stable in water vapor (superheated steam) at $1000^\circ C$, Cr or Ni? Show calculations.

Solution

Referring to Figure 4.3 (taken from Figure E.2), the reaction lines for



and



are, respectively, above and below the reaction line for $2H_2(g) + O_2(g) = 2H_2O(g)$. Therefore, $Cr_2O_3(s)$ is more stable than $NiO(s)$ at $1000^\circ C$. In terms of the elements, Ni is more stable than Cr in superheated steam at $1000^\circ C$.

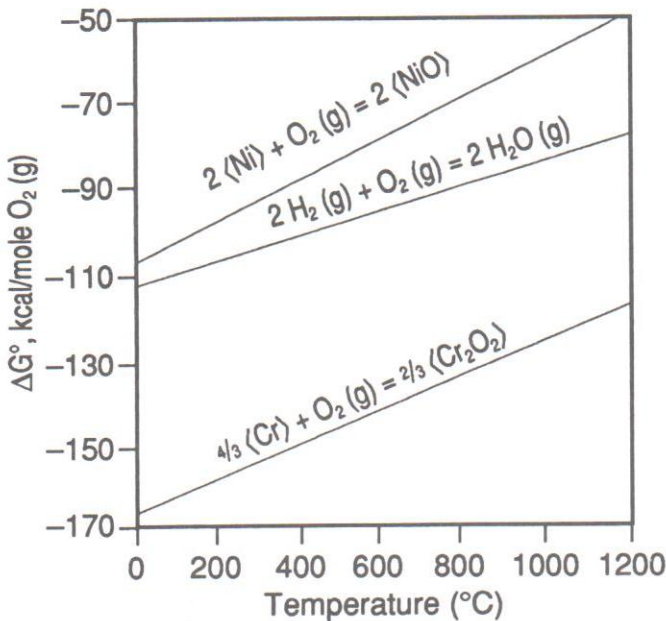


Figure 4.3 Ellingham diagram for the standard state oxidation of nickel, chromium, and hydrogen.

To illustrate numerically, data are read directly from the Ellingham diagram:

- (1) $2\text{Ni}(s) + \text{O}_2(g) = 2\text{NiO}(s)$ $\Delta G_{1273}^0 = -60 \text{ kcal/mol}$
 (2) $2\text{H}_2(g) + \text{O}_2(g) = 2\text{H}_2\text{O}(g)$ $\Delta G_{1273}^0 = -86 \text{ kcal/mol}$
 (3) $4/3\text{Cr}(s) + \text{O}_2(g) = 2/3\text{Cr}_2\text{O}_3(s)$ $\Delta G_{1273}^0 \approx -127 \text{ kcal/mol}$
 (4) Reaction (1) – Reaction (2):
 $2\text{Ni}(s) + 2\text{H}_2\text{O}(g) = 2\text{NiO}(s) + 2\text{H}_2(g)$ $\Delta G_{1273}^0 = \underline{26 \text{ kcal/mol}}$.

Since $\Delta G_{1273}^0 > 0$, Ni will tend to deoxidize in steam at 1000°C .

- (5) Reaction (3) – Reaction (2):
 $4/3\text{Cr}(s) + 2\text{H}_2\text{O}(g) = 2/3\text{Cr}_2\text{O}_3(s) + 2\text{H}_2(g)$ $\Delta G_{1273}^0 = \underline{-41 \text{ kcal/mol}}$.
 Since $\Delta G_{1273}^0 < 0$, Cr will tend to oxidize in steam at 1000°C . The computations in (4) and (5) confirm the conclusions drawn from the relative positions of the Ni(s) and Cr(s) oxidation lines shown in the diagram.

Example Problem 4-4

Determine the standard enthalpy and entropy change for the reaction
 $\text{Mg} + (1/2)\text{O}_2(g) \rightarrow \text{MgO}(s)$,

using Figure E.2 at temperatures up to the melting point of Mg. Compare the results with the data in Table A.1.

Solution

Arbitrarily selecting two points on the diagram,

$$(a) \quad \Delta G_{473}^0 = (1/2)(-268 \text{ kcal/mol})(4.184 \text{ J/cal}) = -561 \text{ kJ/mol};$$

$$(b) \quad \Delta G_{923}^0 = (1/2)(-245 \text{ kcal/mol})(4.184 \text{ J/cal}) = -513 \text{ kJ/mol}.$$

Substituting into [4-11],

$$(1) \quad -561 \text{ kJ/mol} = \Delta H_{298}^0 - (473) \Delta S_{298}^0;$$

$$(2) \quad -513 \text{ kJ/mol} = \Delta H_{298}^0 - (923) \Delta S_{298}^0$$

Solving (1) and (2) simultaneously,

$$\Delta H_{298}^0 = \underline{-612 \text{ kJ/mol}};$$

$$\Delta S_{298}^0 = \underline{-0.107 \text{ kJ/(mol} \cdot \text{K)}}.$$

From Table A.1,

$$\Delta H_{298}^0 = \underline{-601.3 \text{ kJ/mol}};$$

$$\begin{aligned} \Delta S_{298}^0 &= (27.41 - 32.51 - 205.02/2)/1000 \\ &= \underline{-0.108 \text{ kJ/(mol} \cdot \text{K)}}. \end{aligned}$$

The two data sets above compare favorably considering the assumptions inherent in [4-11].

Example Problem 4-5

Examine the reaction $2\text{Mg} + \text{O}_2 = 2\text{MgO}$ in Figure 4.1 (or E.2) and explain why the slope increases at 1105°C . Examine the reaction $2\text{Pb} + \text{O}_2 = 2\text{PbO}$ in Figure E.2 and explain why the slope decreases at 1480°C .

Solution

The standard entropy change for the reaction $2\text{Mg}(l) + \text{O}_2(g) = 2\text{MgO}(s)$ is

$$\Delta S_{\text{MgO}(s)}^0 = 2S_{\text{MgO}(s)}^0 - 2S_{\text{Mg}(l)}^0 - S_{\text{O}_2(g)}^0.$$

Because gas is a more random arrangement of atoms than liquid, $S_{\text{Mg}(g)}^0 > S_{\text{Mg}(l)}^0$. Hence, $\Delta S_{\text{MgO}(s)}^0$ decreases at the boiling point of $\text{Mg}(l)$. Since from [4-27]

$$\left(\frac{\partial \Delta G_{\text{MgO}(s)}^0}{\partial T}\right)_p = -\Delta S_{\text{MgO}(s)}^0,$$

the slope $-\Delta S_{\text{MgO}(s)}^0$ increases at 1105°C .

The reader should use similar arguments to explain the decrease in slope associated with the reaction involving the formation of PbO . Unlike the first reaction in which the reactant Mg changes phase, in the second reaction the product PbO changes phase.

Example Problem 4-6

Calculate the (a) entropy of fusion of Si at its normal melting point, and (b) Gibbs free energy of fusion of Si under unstable conditions at 1500°C. Assume $\Delta C_p = 0$.

Solution

- (a) At the normal melting point, $\Delta G_{1693}^f = 0$. Substituting heat of fusion data from Table A.2 into [4-8],

$$\begin{aligned}\Delta G_{1693,\text{Si}}^f &= 0 = \Delta H_{1693,\text{Si}}^f - (1693)\Delta S_{1693,\text{Si}}^f \\ &= 50,630 \text{ J/mol} - (1693)\Delta S_{1693,\text{Si}}^f\end{aligned}$$

or

$$\Delta S_{1693,\text{Si}}^f = \underline{29.91 \text{ J}/(\text{mol} \cdot \text{K})}.$$

- (b) Assuming $\Delta C_p = 0$, and substituting [2-19] and [3-17] into [4-8],

$$\begin{aligned}\Delta G_{1773,\text{Si}}^f &= \Delta H_{1693,\text{Si}}^f - (1773)\Delta S_{1693,\text{Si}}^f \\ &= 50,630 \text{ J/mol} - (1773)(29.91 \text{ J/mol}) \\ &= \underline{-2400 \text{ J/mol}}.\end{aligned}$$

Since $\Delta G_{1773,\text{Si}}^f < 0$, melting is spontaneous above the normal melting point at 1 atm pressure.

Example Problem 4-7

Calculate the (a) entropy of transformation of Ti(α) to Ti(β) at the normal transformation point of 882°C, and (b) Gibbs free energy of transformation of Ti(α) \rightarrow Ti(β) under unstable conditions at 930°C.

Solution

- (a) At the normal transformation temperature, $\Delta G_{1155}^{\text{Tr}} = 0$. Substituting transformation enthalpy data from Table A.2 into [4-8],

$$\begin{aligned}\Delta G_{1155,\text{Ti}(s)}^{\text{Tr}} &= 0 = \Delta H_{1155,\text{Ti}(s)}^{\text{Tr}} - (1155)\Delta S_{1155,\text{Ti}(s)}^{\text{Tr}} \\ &= 3473 - (1155)\Delta S_{1155,\text{Ti}(s)}^{\text{Tr}}\end{aligned}$$

or $\Delta S_{1155,\text{Ti}(s)}^{\text{Tr}} = \underline{3.0 \text{ J}/(\text{mol} \cdot \text{K})}.$

- (b) Substituting [2-16] and [3-16] into [4-8] and using heat capacity data from Table A.3A,

$$\begin{aligned}\Delta G_{1203,\text{Ti}(s)}^{\text{Tr}} &= \Delta H_{1203,\text{Ti}(s)}^{\text{Tr}} - (1203)\Delta S_{1203,\text{Ti}(s)}^{\text{Tr}} \\ &= \Delta H_{1155,\text{Ti}(s)}^{\text{Tr}} + \int_{1155}^{1203} \Delta C_p dT - (1203) \left[\Delta S_{1155,\text{Ti}(s)}^{\text{Tr}} + \int_{1155}^{1203} \frac{\Delta C_p dT}{T} \right].\end{aligned}$$

Computation of the final answer is left to the reader. The result is

$$\Delta G_{1203, \text{Ti}(s)}^{\text{Tr}} = \underline{-131.14 \text{ J/mol.}}$$

Since $\Delta G_{1203, \text{Ti}(s)}^{\text{Tr}} < 0$, the $\text{Ti}(\alpha) \rightarrow \text{Ti}(\beta)$ transformation is spontaneous above the normal transformation temperature at 1 atm. Assuming $\Delta C_p = 0$, $\Delta G_{1203, \text{Ti}(s)}^{\text{Tr}} = -136 \text{ J/mol}$. The error is less than 4%.

4.4 TL ANALYSIS INCORPORATING PRESSURE DEPENDENCE

Solving for dH in [4-6] and substituting into [3-7]

$$dG + TdS + SdT = TdS + VdP$$

or

$$dG = VdP - SdT \quad [4-14]$$

At constant temperature [4-14] reduces to

$$dG = VdP \quad [4-15]$$

Integrating [4-15] assuming V is independent of P over the pressure interval,

$$\int_{G_1}^{G_2} dG = V \int_{P_1}^{P_2} dP$$

or

$$\Delta G = V \int_{P_1}^{P_2} dP \quad [4-16]$$

where

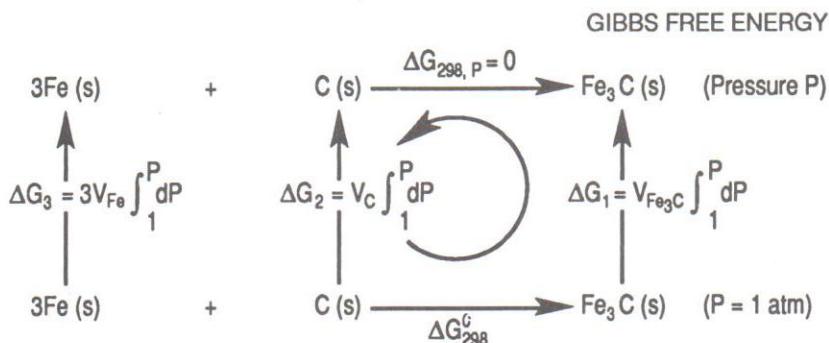
$$V = \frac{M}{\rho} = \frac{\text{molecular mass}}{\text{density}} = \left(\frac{\text{gm}}{\text{mol}} \cdot \frac{\text{cm}^3}{\text{gm}} \right) \\ = \text{molar volume} [\text{cm}^3/\text{mol}].$$

Example Problem 4-8

Calculate the minimum hydrostatic pressure required to stabilize Fe_3C at room temperature. Although Fe_3C is unstable at ordinary pressures, it exists as a separate phase in steel microstructures and is identified as a stable phase in the Fe-C phase diagram.

Solution

- (1) **Set Up.** An isothermal TL is structured to include the formation of $\text{Fe}_3\text{C}(s)$ directly from its constituent elements at a constant temperature of 298 K and variable pressure. It is assumed that densities, hence volumes, remain constant over the pressure interval.



(2) **Sum.** Summing in the counterclockwise direction,

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{298}^0 + \Delta G_1 - 0 - \Delta G_2 - \Delta G_3.$$

(3) **Substitute.** From Tables A.4 and B.1,

$$\begin{aligned} \Delta G_{298}^0 &= 25,941 - 23.14(298) = 19,045 \text{ J/mol} \\ &= (19,045 \text{ J/mol}) \times (82.057 \text{ cm}^3 \cdot \text{atm} / 8.3144 \text{ J}) \\ &= 187,960 \text{ cm}^3 \cdot \text{atm/mol}. \end{aligned}$$

$$\begin{aligned} \Delta G_1 &= V_{\text{Fe}_3\text{C}} \int_1^P dP = (179.53 \text{ cm}^3 / 7.40 \text{ mol})(P - 1 \text{ atm}) \\ &= 24.24(P - 1) \text{ cm}^3 \cdot \text{atm/mol}. \end{aligned}$$

$$\begin{aligned} \Delta G_2 &= V_{\text{C}} \int_1^P dP = (12.01 \text{ cm}^3 / 2.25 \text{ mol})(P - 1 \text{ atm}) \\ &= 5.34(P - 1) \text{ cm}^3 \cdot \text{atm/mol}. \end{aligned}$$

$$\begin{aligned} \Delta G_3 &= 3V_{\text{Fe}} \int_1^P dP = 3(55.85 \text{ cm}^3 / 7.87 \text{ mol})(P - 1 \text{ atm}) \\ &= 21.29(P - 1) \text{ cm}^3 \cdot \text{atm/mol}. \end{aligned}$$

Substituting into $\sum \Delta G_{\text{TL}} = 0$,

$$0 = 187,960 + 24.24(P - 1) - 0 - 5.34(P - 1) - 21.29(P - 1).$$

(4) **Solve.**

$$P \approx \underline{78,000 \text{ atm.}}$$

4.5 USEFUL THERMODYNAMIC RELATIONS

The concept of exactness as it pertains to thermodynamic properties has already been introduced in [1-4] and [1-5]. These equations and others are incorporated into relationships that are often found useful in solving a wide

variety of thermodynamic problems in materials applications. A collection of these useful relationships is provided below.

(1) Condition of Exactness

If $z = f(x,y)$,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad [1-4]$$

and

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad [1-5]$$

where

$$M = M(x,y) = \left(\frac{\partial z}{\partial x}\right)_y \text{ and } N = N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x.$$

(2) Introduction of a New Thermodynamic Variable, w

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_z \left(\frac{\partial w}{\partial y}\right)_z \quad [4-17]$$

(3) Transformation Formula

Applying the definition of the total differential to $z = f(x,y)$, dividing by dy , and holding z constant:

$$\left(\frac{\partial z}{\partial y}\right)_z = 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial y}\right)_z \quad \uparrow$$

or

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z / \partial y)_x}{(\partial z / \partial x)_y} \quad [4-18]$$

Equation [4-18] is known as the *transformation formula*.

(4) Maxwell Equations

From Chapters 3 and 4,

$$dU = TdS - PdV \quad [3-6]$$

$$dH = TdS + VdP \quad [3-7]$$

$$dG = VdP - SdT \quad [4-14]$$

Helmholtz free energy, A, is defined as

$$A = U - TS \quad [4-19]$$

Taking the total derivative of [4-19],

$$dA = dU - TdS - SdT$$

and substituting for dU from [3-6],

$$dA = TdS - PdV - TdS - SdT$$

or

$$dA = -PdV - SdT \quad [4-20]$$

For easy reference, the four *Maxwell equations* are:

$$dU = TdS - PdV \quad [3-6]$$

$$dH = TdS + VdP \quad [3-7]$$

$$dG = VdP - SdT \quad [4-14]$$

$$dA = -PdV - SdT \quad [4-20]$$

Applying [1-5], the Maxwell equations can be restated in the following alternate form:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad [4-21]$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad [4-22]$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad [4-23]$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad [4-24]$$

Additionally, expressing [4-14] in partial derivative form, other useful relationships are:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad [4-25]$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad [4-26]$$

[4-25] and [4-26] may also be written in the form:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \quad [4-27]$$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \quad [4-28]$$

(5) Gibbs-Helmholtz Equation

Substituting [4-27] into [4-8],

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P \quad [4-29]$$

Dividing [4-29] by T^2 and rearranging,

$$\frac{1}{T} \left(\frac{\partial \Delta G}{\partial T} \right)_P - \frac{\Delta G}{T^2} = - \frac{\Delta H}{T^2}.$$

Applying the *differentiation theorem for a quotient of two functions*, ΔG and T (Protter and Morrey, 1970, p. 136),

$$\left[\frac{\partial(\Delta G/T)}{\partial T} \right]_P = \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T} \right)_P - \frac{\Delta G}{T^2}.$$

Combining the last two equalities,

$$\left[\frac{\partial(\Delta G/T)}{\partial T} \right]_P = - \frac{\Delta H}{T^2} \quad [4-30]$$

[4-30], known as the *Gibbs-Helmholtz equation*, is applicable to a *closed system* at constant pressure.

(6) Total Enthalpy

Applying the definition of the total differential to $H = f(T,P)$,

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad [4-31]$$

Dividing [3-7] by dP , holding temperature fixed, and assuming that molar volume is constant,

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V \left(\frac{\partial P}{\partial P} \right)_T$$

Substituting [4-23] and [1-2] into the above,

$$\begin{aligned} \left(\frac{\partial H}{\partial P} \right)_T &= -T \left(\frac{\partial V}{\partial T} \right)_P + V \\ &= -\alpha VT + V \end{aligned} \quad [4-32]$$

Substituting [4-32] and [2-12] into [4-31],

$$dH = C_p dT + V(1 - \alpha T) dP \quad [4-33]$$

(7) Total Entropy

Applying the definition of the total differential to $S = f(T,P)$,

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad [4-34]$$

Substituting [4-23] and the differential form of [3-10] into [4-34],

$$dS = \frac{C_p dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP \quad [4-35]$$

Substituting [1-2] into [4-35],

$$dS = \frac{C_p dT}{T} - \alpha V dP \quad [4-36]$$

4.6 DISCUSSION QUESTIONS

- (4.1) Refer to Figure E.2. Give examples, where possible, of four different types of phase transformations for both elements and oxides.
- (4.2) Consider element A in which the most stable standard state configuration at T_1 is α and at T_2 is β . From the definition of standard state Gibbs free energy of an element, answer the following and explain your reasoning:

(a) Is $\Delta G_{T_2, \alpha}^0 = 0$?

(b) Is $\Delta G_{T_1, \beta}^0 = 0$?

(c) Is $\Delta G_{T_1, \alpha}^0 = 0$?

(d) Is $\Delta G_{T_2, \beta}^0 = 0$?

- (4.3) A phase transformation occurs reversibly at temperature T and pressure P . The phases involved are A and A', and the transformations and corresponding Gibbs free energy changes are:



What is the relationship between ΔG_1^{Tr} and ΔG_2^{Tr} ?

- (4.4) For which mineral reaction below is $\Delta G_T^0 = \Delta G_{T, \text{Enstatite}}^{0,f}$? Explain.



- (4.5) Answer the following questions about Ellingham diagrams:

(a) How are ΔH^0 and ΔS^0 obtained from the diagram?

(b) How are the relative stabilities of oxides or sulfides compared directly from the diagram?

(c) Why does the slope of the line representing the oxidation of uranium decrease at $\approx 1300^\circ\text{C}$?

- (4.6) What effect does maintenance of a dynamic vacuum have on calculation of the standard Gibbs free energy change for a heterogenous reaction involving solids and gases?

- (4.7) Is $\Delta H_{298, H(g)}^0 = 0$? Explain.

4.7 EXERCISE PROBLEMS

- [4.1] An ideal gas undergoes an isothermal process from an initial State 1: (P_1, V_1, T) to a final State 2: (P_2, V_2, T) . Prove

$$\Delta G_T = RT \ln(P_2/P_1).$$
- [4.2] The initial state of one mole of a monatomic ideal gas is $P_1 = 5$ atm and $T_1 = 300$ K. Calculate the entropy change of the gas for:
 (a) an isothermal decrease in pressure to 1 atm.
Ans: $\Delta S = 13.38$ J/(mol·K).
 (b) a constant volume decrease in the pressure to 1 atm.
Ans: $\Delta S = -20.07$ J/(mol·K).
- [4.3] Prove by two methods that at constant temperature,

$$\Delta H_{\text{Isothermal}} = 0$$
 for an ideal gas, regardless of the pressure path.
- [4.4] Prove that at constant temperature,

$$\Delta S'_{\text{Isothermal}} = -nR \ln(P_2/P_1)$$
 for n moles of an ideal gas.
- [4.5] Calcium boils at 1440°C . The standard free energy of vaporization of liquid calcium is given by

$$\Delta G_T^0 \text{ (cal/mol)} = 41,030 + 5.83T \log(T) - 42.23T,$$
 where $\log = \log_{10}$ (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana).
 (a) Find the linear Gibbs free energy equation of the form

$$\Delta G_T^0 = a + bT$$
 which approximates the above equation as closely as possible near 1500 K.
Ans: $\Delta G_T^0 \text{ (cal/mol)} = 37,235 - 21.2T.$
 (b) Calculate the boiling point from the linear equation and compare with the actual value.
Ans: $T = 1756$ K ($\approx 2.5\%$ error).
- [4.6] Phosphorous-bearing vanadium deposits of the western U.S. are a source of vanadium used in the steel industry as an alloy component. X-ray examination of a representative sample of raw material from these deposits reveals that the major impurity present in the ore is iron in the form of Fe_2P . A suggested method for removing the iron is to convert Fe_2P to Fe_3P and pure iron (ferrite) by vacuum distillation of the phosphorous and to remove the iron magnetically. Assuming the best vacuum obtainable in a large scale operation is 10^{-2} mm Hg, estimate the operating temperature of a vacuum furnace required to accomplish this distillation.
Ans: $T \approx 1411^\circ\text{C}.$

- [4.7] Estimate the pressure which must be applied to increase the melting point of pure Au by 20°C.

Ans: $P \approx 3370 \text{ atm.}$

- [4.8] Assuming that ΔH^0 and ΔS^0 are independent of temperature, calculate the temperature at which solid HgO will dissociate into liquid Hg and $O_2(g)$ at 1 atm.

Ans: $T \approx 567^\circ\text{C.}$

- [4.9] Thermodynamic analysis of the equilibrium state for carbon, chromium, and niobium carbide reveals that niobium is an effective alloying agent for limiting grain boundary precipitation of chromium carbide by preferentially removing carbon as niobium carbide.

(a) Write a single equation describing C-Nb-Cr equilibria neglecting solubility effects.

Ans: $6\text{Nb} + \text{Cr}_{23}\text{C}_6 \rightarrow 6\text{NbC} + 23\text{Cr.}$

(b) Confirm thermodynamically the alloying effect of Nb at 1200 K.

Ans: $\Delta G_{1200}^0 = -311,200 \text{ J/mol} < 0 \Rightarrow \text{NbC formation is favored.}$

- [4.10] Three equations for the oxidation of a metal M are given below. One of these equations is for the oxidation of solid M, one is for the oxidation of liquid M, and one is for the oxidation of gaseous M. Using the ΔG^0 data given, identify the reaction and the state of the reactant metal.



Ans: Reaction (a) solid M, (b) gaseous M; (c) liquid M.

- [4.11] For the reaction $\text{SiC}(s) \rightarrow \text{Si}(s) + \text{C}(s)$, $\Delta G_T^0 = 12,770 - 1.66T \text{ cal/mol}$ from 298–1680 K. Using this data, determine:

(a) ΔS^0 at 1000 K.

Ans: $\Delta S_{1000}^0 = 1.66 \text{ cal/(mol}\cdot\text{K).}$

(b) ΔH^0 at 1500 K.

Ans: $\Delta H_{1500}^0 = 12,770 \text{ cal/mol.}$

- [4.12] Using the general expression for $C_p - C_v$, given in Exercise Problem [1.3]:

(a) Show that $C_p - C_v = \alpha^2 VT/\beta$ for any substance.

(b) Use this expression to estimate $C_p - C_v$ for pure copper at 298 K.

Ans: $C_p - C_v \approx 0.01 \text{ J/(mol}\cdot\text{K).}$

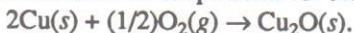
- [4.13] Use the data in Exercise Problem [3.8] and the Gibbs free energy criteria to confirm that solidification is spontaneous after supercooling.

Ans: $\Delta G = -2877 \text{ J/mol} < 0 \Rightarrow \text{spontaneous.}$

- [4.14] (a) Starting with [4-13], use [4-27] and [4-30] to compute ΔS^0 and ΔH^0 , respectively, as a function of temperature.

$$\text{Ans: } \Delta H_T^0 = A - \frac{BT}{2,303}, \quad \Delta S_T^0 = \frac{B}{2,303} [\ln(1/T) - 1] - C.$$

- (b) Use the results from (a) and Appendix A, Table A.4 to obtain ΔH^0 and ΔS^0 as a function of temperature for the reaction



Compare the results at $T = 298$ K with the data in Appendix A, Table A.1.

$$\text{Ans: } \Delta H_{298}^0 \text{ (derived equation)} = -167,350 \text{ J/mol,}$$

$$\Delta H_{298}^0 \text{ (Table A.1)} = -167,380 \text{ J/mol,}$$

$$\Delta S_{298}^0 \text{ (derived equation)} = -75.74 \text{ J/(mol}\cdot\text{K);}$$

$$\Delta S_{298}^0 \text{ (Table A.1)} = -75.27 \text{ J/(mol}\cdot\text{K).}$$

- [4.15] The thermodynamics of SiO is important in many materials applications because of its high vapor pressure. Develop an expression for the Gibbs free energy of formation of SiO(l), $\Delta G_{\text{SiO}(l)}^{0,f}$, as a function of temperature between 298–1700 K using the data in Appendix A, Table A.4.

$$\text{Ans: } \Delta G_{\text{SiO}(l)}^{0,f} \text{ (J/mol)} = -91,848 + 20.72T \log(T) - 150T.$$

- [4.16] One mole of a metal, m , at 1 atm pressure is heated at constant volume from 300 to 500 K. Calculate the hydrostatic pressure that results from such a process. What is the work done? Assume C_p is constant over the temperature interval. $\alpha_m = 5 \times 10^{-5} \text{ K}^{-1}$, and $\beta_m = 8 \times 10^{-6} \text{ atm}^{-1}$.

$$\text{Ans: } P \approx 1251 \text{ atm; } W = 0 \text{ since } V \text{ is constant.}$$

- [4.17] Referring to Exercise Problem [4.16], calculate the entropy change for the same process. Let $C_p^m = 20.9 \text{ J/(mol}\cdot\text{K)}$, $V_m = 6 \text{ cm}^3/\text{(gm mol)}$.

$$\text{Ans: } \Delta S_m = 10.64 \text{ J/(mol}\cdot\text{K).}$$

- [4.18] Use the Gibbs free energy criteria to confirm that liquid potassium and its vapor are in equilibrium at 950 K and 0.447 bar.

$$\text{Ans: } \Delta g^{v,l} \text{ (kJ/kg)} = 1979 - 1978 \approx 0 \Rightarrow \text{equilibrium.}$$

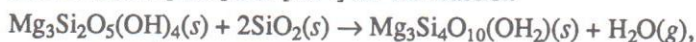
- [4.19] Use [3-6] to confirm the value of $u_g - u_l$ in Appendix D, Table D.2, at 900 K and 0.251 bar.

$$\text{Ans: } \Delta u = u_g - u_l = 1827 \text{ kJ/kg.}$$

- [4.20] Referring to Exercise Problems [4.16] and [4.17], estimate the enthalpy change for the same process if $V_m = 10 \text{ cm}^3/\text{mol}$. State assumptions in making the calculations.

$$\text{Ans: } \Delta H \approx 5440 \text{ J/mol, } V_m \text{ and } \alpha_m \text{ are assumed constant.}$$

- [4.21] Using the standard enthalpy and entropy changes computed in Exercise Problems [2.10] and [3.14] for the reaction



calculate ΔG_T^0 at temperature T where $373 \text{ K} < T < 800 \text{ K}$. No phase changes occur.

$$\text{Ans: } \Delta G_T^0 \text{ (J/mol)} = -82,315 - 4672.2T \ln(T) + 5.44 \times 10^3 T + 2.58T^2 + 3.47 \times 10^{-7} T^3 - 3.66 \times 10^7 T^{-1} - 2.63 \times 10^5 T^{0.5}.$$

- [4.22] Using the standard enthalpy and entropy changes computed in Exercise Problems [2.12] and [3.15] for the reaction



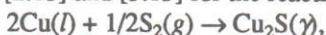
calculate ΔG_T^0 at temperature T where $298 \text{ K} < T < 844 \text{ K}$. No phase changes occur.

$$\text{Ans: } \Delta G_T^0 \text{ (J/mol)} = 53.21 \times 10^3 - 2000.4T + 238.21T \ln(T) - 70.349 \times 10^{-3} T^2 + 3.791 \times 10^{-6} T^3 + 17.478 \times 10^3 T^{0.5} + 2460.4 \times 10^3 T^{-1}.$$

- [4.23] The sorosilicate lawsonite, $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}(s)$, is a common constituent of metamorphic rocks formed at low temperature and high pressure. Assuming the molar volume of this mineral is independent of pressure, calculate the molar isothermal Gibbs free energy change for lawsonite subjected to a reversibly applied pressure increase from 1 to 5 bar at 298 K.

$$\text{Ans: } \Delta G = 40.5 \text{ J/mol.}$$

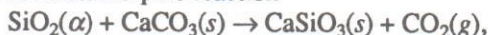
- [4.24] Using the standard enthalpy and entropy of formation computed in Exercise Problems [2.13] and [3.13] for the reaction



determine whether or not this reaction is spontaneous at 1356 K as written.

$$\text{Ans: } \Delta G_{1356}^0 = -274,260 \text{ J/mol} < 0 \Rightarrow \text{spontaneous.}$$

- [4.25] For the contact metamorphic reaction



- (a) Calculate the standard Gibbs free energy change at temperature $298 \text{ K} \leq T < 844 \text{ K}$. Assume $\Delta C_p = 0$ and use the value of ΔS_{298}^0 computed in Example Problem [3.12].

$$\text{Ans: } \Delta G_T^0 \text{ (J/mol)} = 88,670 - 165.65T.$$

- (b) Plot ΔG_T^0 as a function of T . Label line segments and points corresponding to a reversible reaction, a spontaneous reaction, and a nonspontaneous reaction as written.

$$\text{Ans: } T^{\text{Rev}} = 535 \text{ K}, T^{\text{Tr}} > 535 \text{ K}; T^{\text{Nonspon.}} < 535 \text{ K.}$$

- [4.26] Show that the Gibbs free energy change for an isobaric chemical reaction occurring at a temperature T is

$$\Delta G_T = \Delta H_{T_1} - T \Delta S_{T_1}$$

when $\Delta C_p = 0$ in the temperature range between T_1 to T .

- [4.27] Derive [4-13] showing all steps.

- [4.28] Derive [4-14] and show that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$