

HETEROGENEOUS EQUILIBRIA: VARIABLE GAS PHASE COMPOSITION

5.1 IDEAL GAS MIXTURES, DALTON'S LAW, AND GIBBS FREE ENERGY OF A GAS

In most cases of interest in this book, gases are at low enough pressure to exhibit ideal behavior as expressed by the ideal gas law, [1-1]. Additionally, gases at these pressures are normally treated as *ideal mixtures* (Chapter 6, Section 6.3). *Dalton's law* states that the total pressure P_T of an *ideal gas mixture* is equal to the sum of the pressures exerted by each component. For example, the *partial pressure*, P_i , is the pressure that component i alone would exert if it occupied the same volume as the gas mixture at the same temperature. By Dalton's law,

$$P_T = \sum P_i \quad [5-1]$$

Since each pure gas component occupies a total mixture volume of V' at temperature T , P_i can be expressed by rewriting [1-1] as

$$P_i = \frac{n_i RT}{V'} \quad [5-2]$$

Substituting [5-2] into [5-1],

$$P_T = (\sum n_i) \frac{RT}{V'} \quad [5-3]$$

Dividing [5-2] by [5-3],

$$\frac{P_i}{P_T} = \frac{n_i}{\sum n_i} = Y_i$$

or

$$P_i = Y_i P_T \quad [5-4]$$

where Y_i is the mole fraction of component i in the ideal gas mixture. [5-4], a useful alternate form of Dalton's law, states that the partial pressure of component i in an ideal gas mixture can be obtained by multiplying the mole fraction of that component by the total gas pressure. Substituting the molar volume V of an ideal gas component i in a mixture from [1-1] into [4-14] at constant temperature and integrating,

$$\begin{aligned} G_i - G_i^0 &= \Delta G_i = \int_{P_i^0}^{P_i} \frac{RT}{P_i} dP_i \\ &= RT \ln(P_i / P_i^0) \end{aligned} \quad [5-5]$$

The *standard state pressure*, P_i^0 , of an ideal gas, insoluble in any condensed phase with which it is in contact, is chosen to be 1 atm (Chapter 6, Section 6.2) at any temperature. Inserting [5-4] into [5-5] at $P_i^0 = 1$ atm,

$$\Delta G_i = RT \ln(Y_i P_T) \quad [5-6]$$

From [5-4],
$$\Delta G_i = RT \ln(P_i) \quad [5-7]$$

5.2 TL ANALYSIS AND ELLINGHAM DIAGRAMS

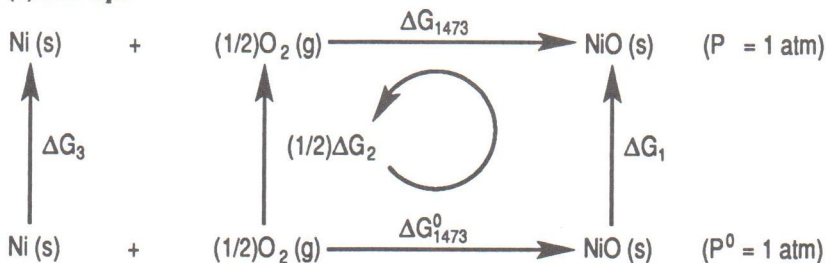
TL analysis of *heterogeneous equilibria** is demonstrated below with a variety of Example Problems. In this chapter, all condensed phases are pure, hence, $\Delta G_T = 0$. This result follows from [4-14] since at constant or relatively low pressures, $VdP \approx 0$ and at constant temperature, $dT = 0$.

Example Problem 5-1

Calculate the equilibrium P_{O_2} over Ni at 1200°C. Determine the corresponding vacuum below which NiO will begin to dissociate. Give answers in mm Hg.

Solution

(1) Set Up.



(2) Sum. Summing in the counterclockwise direction,

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{1473}^0 + \Delta G_1 - \Delta G_{1473} - (1/2)\Delta G_2 - \Delta G_3.$$

(3) Substitute. From Table A.4,

$$\Delta G_{1473}^0 = -244,580 + 98.54(1473) = -99,431 \text{ J/mol.}$$

$$\Delta G_{1473} = 0 \text{ at equilibrium.}$$

$$\Delta G_1 = \Delta G_3 = 0 \text{ for pure condensed phases.}$$

$$(1/2)\Delta G_2 = (1/2)RT \ln(P_{O_2}) = 8.3144(1473) \ln(P_{O_2}^{1/2}).$$

* Heterogeneous equilibria refers to component equilibrium in systems of two or more phases.

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

$$0 = -99,431 - 8.3144 \times 1473 \ln(P_{O_2}^{1/2}).$$

(4) Solve.

$$\ln(P_{O_2}^{1/2}) = -99,431/8.3144(1473), \text{ hence}$$

$$P_{O_2} = 8.9 \times 10^{-8} \text{ atm} \times (760 \text{ mm Hg/atm})$$

$$= 6.8 \times 10^{-5} \text{ mm Hg.}$$

The vacuum below which the reaction will shift from oxidation to deoxidation is found from Dalton's law. In air, $Y_{O_2} \approx 0.22$ ($Y_{N_2} \approx 0.78$). Substituting P_{O_2} and Y_{O_2} into [5-4],

$$P_T = 6.8 \times 10^{-5} \text{ mm Hg}/0.22 = 3.1 \times 10^{-4} \text{ mm Hg.}$$

The above results can be confirmed from the Ellingham diagram, Figure E.2. A nomograph, superimposed on this diagram, is used to determine the equilibrium P_{O_2} directly. Figure 5.1, a simplified portion of Figure E.2, illustrates the graphical procedure. A straight line is drawn from the point labeled O (top of the vertical line on the left side of the diagram) so as to intersect the NiO reaction line at 1200°C . This line is extrapolated to the right hand scale corresponding to the P_{O_2} . Interpolating,

$$P_{O_2} \approx 5 \times 10^{-8} \text{ atm} \times (760 \text{ mm Hg/atm}) = 3.8 \times 10^{-5} \text{ mm Hg.}$$

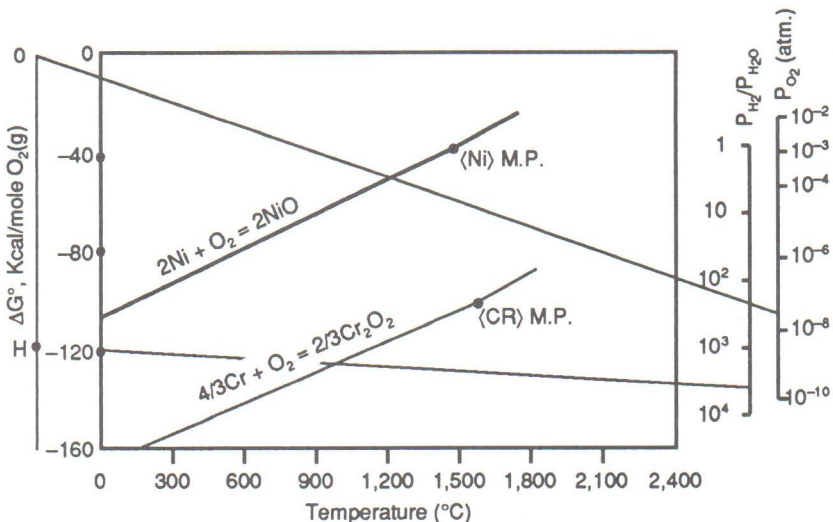


Figure 5.1 Nomographic determination of equilibrium gas partial pressures over metallic Ni at 1200°C and Cr at 1000°C . Points O and H on the vertical line at the left side of the Ellingham diagram are extended through the selected temperature/reaction point to the vertical scale at the right as illustrated.

Substituting into [5-4], $P_T = P_{O_2} / Y_{O_2} = 3.8 \times 10^{-5} \text{ mm Hg} / 0.22 = 1.7 \times 10^{-4} \text{ mm Hg}$. Extrapolation from the diagram is somewhat less precise than the technique utilizing TL analysis because of graphical and interpolation errors.

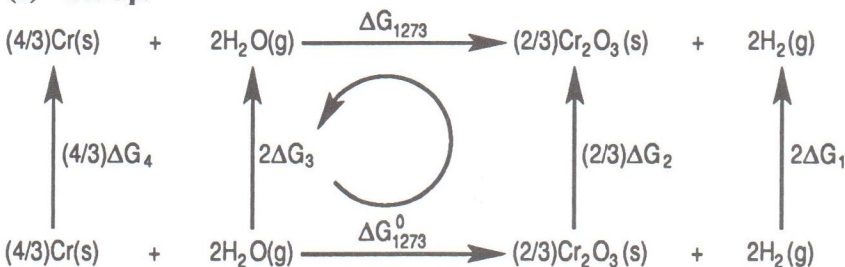
In a manner analogous to that just presented, Ellingham diagrams can also be used to graphically estimate the equilibrium ratios P_{H_2} / P_{H_2O} and P_{CO} / P_{CO_2} in oxide equilibria. The next example demonstrates the procedure after first presenting the solution using TL analysis.

Example Problem 5-2

Calculate the equilibrium ratio P_{H_2} / P_{H_2O} for the oxidation of chromium in water vapor at 1000°C .

Solution

(1) Set Up.



(2) Sum.

$$\Sigma \Delta G_{\text{TL}} = 0 = \Delta G_{1273}^0 + 2\Delta G_1 + (2/3)\Delta G_2 - \Delta G_{1273} - 2\Delta G_3 - (4/3)\Delta G_4.$$

(3) Substitute. From Table A.4,

$$\begin{aligned}
 \Delta G_{1273}^0 &= (2/3)[-1,120,370 + 259.85(1273)] + 2[-246,460 + 54.82(1273)] \\
 &= -173,039 \text{ J.}
 \end{aligned}$$

$$\Delta G_{1273} = 0 \text{ at equilibrium.}$$

$$2\Delta G_1 = 2R(1273) \ln(P_{H_2}) \text{ and } 2\Delta G_3 = 2R(1273) \ln(P_{H_2O}).$$

$$(2/3)\Delta G_2 = (4/3)\Delta G_4 = 0.$$

Substituting the above into $\Sigma \Delta G_{\text{TL}} = 0$,

$$0 = -173,039 + 2(8.3144)(1273) \ln(P_{H_2}) - 2(8.3144)(1273) \ln(P_{H_2O}).$$

(4) Solve.

$$P_{H_2} / P_{H_2O} = \underline{3.55 \times 10^3}.$$

Note that if $P_{H_2} / P_{H_2O} > 3.55 \times 10^3$, $\text{Cr}_2\text{O}_3(s)$ will tend to be reduced because excess P_{H_2} drives the reaction to the left. If $P_{H_2} / P_{H_2O} < 3.55 \times 10^3$, $\text{Cr}(s)$ will tend to oxidize because excess P_{H_2O} drives the reaction to the right. A qualitative statement of this behavior, known as *LeChatelier's principle*, states that "when a system, which is at equilibrium, is subjected to the effects

of an external influence, the system moves in that direction which tends to nullify the effects of the external influence" (Gaskell, 1981, p. 132).

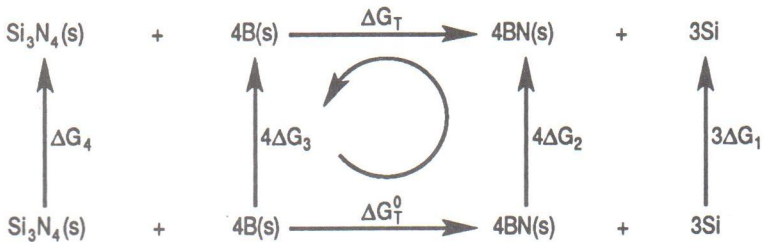
Using the nomograph on Figure 5.1, a straight line is drawn from the point labeled H so as to intersect the Cr_2O_3 reaction line at 1000°C . Extrapolation to the right hand scale gives $P_{\text{H}_2} / P_{\text{H}_2\text{O}} \approx 8 \times 10^3$. The procedure for graphically determining the $P_{\text{CO}} / P_{\text{CO}_2}$ ratio for the oxidation of an oxide in CO_2 gas is analogous to that used in the last two examples except that point C (Figure E.2, left hand vertical line) is used in conjunction with the $P_{\text{CO}} / P_{\text{CO}_2}$ scale.

Example Problem 5-3

Characterize the relative thermal stability of Si_3N_4 and BN in a mixture of Si_3N_4 and B at 1 atm pressure. Assume all components are pure. BN has been suggested as an abradable high temperature coating. Si_3N_4 is utilized in high temperature ceramic applications.

Solution

(1) Set Up.



(2) Sum.

$$\Sigma \Delta G_{T,L} = 0 = \Delta G_T^0 + 3\Delta G_1 + 4\Delta G_2 - \Delta G_T - 4\Delta G_3 - \Delta G_4$$

or

$$\Delta G_T = \Delta G_T^0 + 3\Delta G_1 + 4\Delta G_2 - 4\Delta G_3 - \Delta G_4.$$

(3) Substitute.

$\Delta G_T = 0$ at equilibrium.

$$3\Delta G_1 = 4\Delta G_2 = 4\Delta G_3 = \Delta G_4 = 0.$$

$$\Delta G_T^0 = 0.$$

The problem now becomes one of finding ΔG_T^0 as a function of temperature and setting that expression equal to zero. The value of ΔG_T^0 depends on whether Si is in the solid or liquid state, for which

$$\Delta G_T^0 = 4\Delta G_{T,\text{BN}(\text{s})}^0 - \Delta G_{T,\text{Si}_3\text{N}_4(\text{s})}^0$$

from [4-9]. Note that the f for Gibbs free energy of formation has been dropped. From Table A.4:

Assuming Si is solid,



Combining Gibbs free energies, substituting the result into [4-9], and setting the expression equal to zero:

$$0 = 4[(-217,590 + 81.18T)/2] - (-753,190 + 336.43T).$$

- (4) **Solve.** Solving the above expression, $T = 1827 \text{ K}$. Since $T = 1827 \text{ K}$ is outside the allowable temperature range for $\Delta G_{\text{Si}_3\text{N}_4(s)}^0$, the calculation is *invalid*.

Assuming Si is liquid,



Combining Gibbs free energies, substituting the result into [4-9], and setting the expression equal to zero:

$$0 = 4[(-217,590 + 81.18T)/2] - (-892,950 + 419.28T).$$

Solving, $T = 1782 \text{ K}$. Since $T = 1782 \text{ K}$ is within the allowable temperature range for $\text{Si}_3\text{N}_4(s)$, the calculation is *valid*. It can be concluded that $\text{BN}(s)$ is stable above 1782 K whereas $\text{Si}_3\text{N}_4(s)$ is stable below 1782 K. Depending upon reaction kinetics, $\text{BN}(s)$ as a coating on $\text{Si}_3\text{N}_4(s)$ would be satisfactory above $\approx 1782 \text{ K}$.

A graphical solution to the previous problem is obtained from a simplified portion of Figure E.4 shown in Figure 5.2. The intersection of the $\text{BN}(s)$ and $\text{Si}_3\text{N}_4(s)$ lines yields an equilibrium temperature of $\approx 1500^\circ\text{C}$ or 1773 K. Agreement with the computed result is excellent. Stability fields for these two compounds are identified. The field to the left of the intersection is stable $\text{BN}(s)$. The field to the right is stable $\text{Si}_3\text{N}_4(s)$.

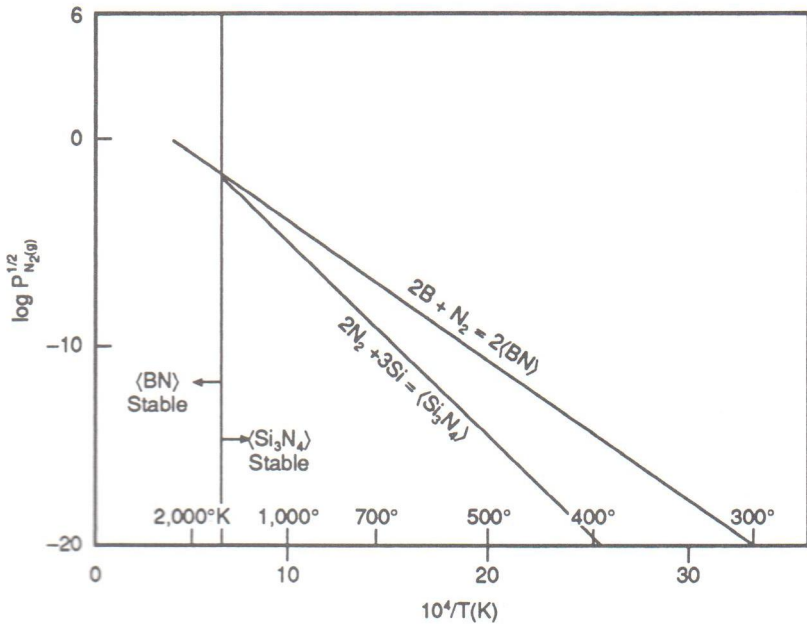


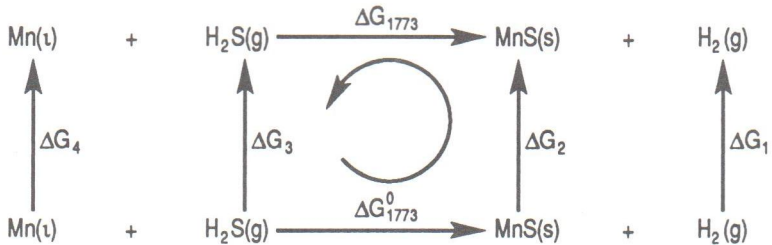
Figure 5.2 $\log (P_{N_2}^{1/2})$ vs. $10^4/T$ for $BN(s)$ and $Si_3N_4(s)$ equilibria.

Example Problem 5-4

Calculate the equilibrium ratio P_{H_2S} / P_{H_2} for the formation of MnS at 1500°C . The presence of MnS inclusions in steel can be critical to fracture toughness in hydrogen environments.

Solution

(1) Set Up.



(2) Sum.

$$\sum \Delta G_{TL} = 0 = \Delta G_{1773}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{1773} - \Delta G_3 - \Delta G_4.$$

(3) **Substitute.**

$$\Delta G_2 = \Delta G_4 = \Delta G_{1773} = 0.$$

$$\Delta G_1 = R(1773)\ln(P_{H_2}) \text{ and } \Delta G_3 = R(1773)\ln(P_{H_2S}).$$

$$\Delta G_{1773}^0 = \Delta G_{1773, MnS(s)}^0 - \Delta G_{1773, H_2S(g)}^0.$$

Using the data in Table A.4 to determine ΔG_{1773}^0 ,

$$\Delta G_T^0 = -198,470 + 29.53T \text{ J/mol.}$$

$$\Delta G_{1773}^0 = -198,470 + 29.53(1773) = -146,113 \text{ J/mol.}$$

Substituting above into $\Sigma \Delta G_{TL} = 0$,

$$0 = -146,113 + R(1773)[\ln(P_{H_2}) - \ln(P_{H_2S})].$$

 (4) **Solve.**

$$\ln\left(\frac{P_{H_2}}{P_{H_2S}}\right) = \frac{146,113 \text{ J/mol}}{[8.3144 \text{ J/(mol} \cdot \text{K)}](1773\text{K})} \Rightarrow \frac{P_{H_2}}{P_{H_2S}} = 20,165$$

or

$$P_{H_2S} / P_{H_2} \approx 5 \times 10^{-5}.$$

Figure 5.3, a simplified version of Figure E.3, offers an alternate solution. Using the nomograph, $P_{H_2S} / P_{H_2} \approx 8 \times 10^{-5}$.

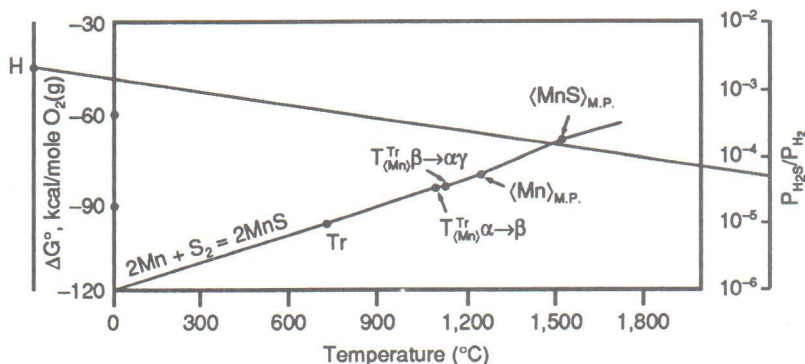


Figure 5.3 Nomographic determination of P_{H_2S} / P_{H_2} over Mn at 1500°C.

Example Problem 5-5

Li_3N formation has been thought to interrupt bonding between silver base-lithium alloys and titanium during brazing. Determine the temperature at which tri-lithium nitride begins to dissociate. Use Figure 5.4 (a portion of Figure E.4) to develop an expression for $\Delta G_{T, Li_3N(s)}^0$ (also see Exercise Problems [5.5] and [5.10]).

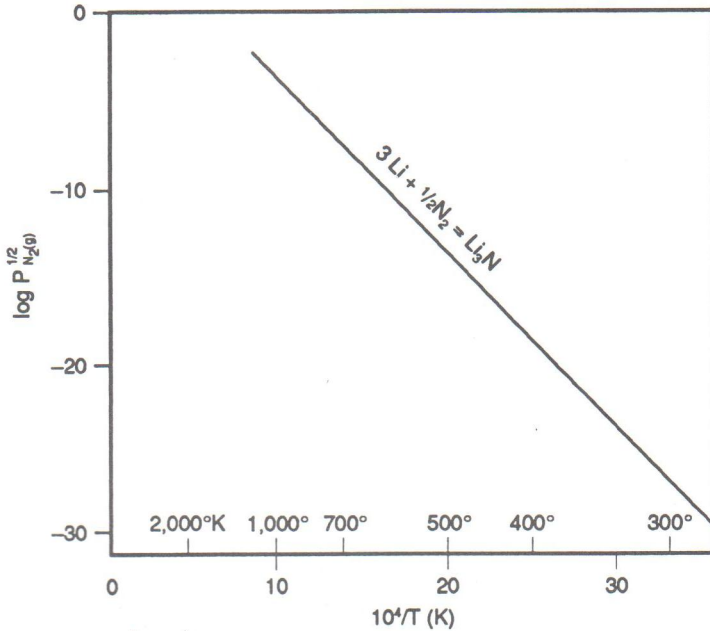
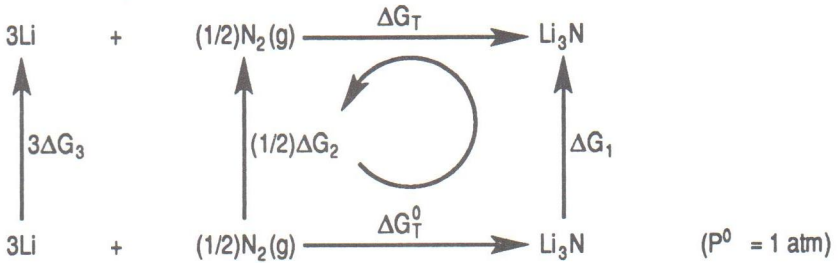


Figure 5.4 $\log(P_{N_2}^{1/2})$ vs. $10^4/T$ for lithium-nitrogen equilibria.

Solution

(1) Set Up.



(2) Sum.

$$\Sigma \Delta G_{TL} = 0 = \Delta G_T^0 + \Delta G_1 - \Delta G_T - (1/2)\Delta G_2 - 3\Delta G_3.$$

(3) Substitute.

$$\Delta G_1 = 3\Delta G_3 = 0.$$

$$(1/2)\Delta G_2 = (1/2)RT \ln(P_{N_2}) = RT \ln(P_{N_2}^{1/2}).$$

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

$$0 = \Delta G_T^0 - \Delta G_T - RT \ln(P_{N_2}^{1/2}).$$

(4) Solve.

$$\Delta G_T^0 = \Delta G_T + RT \ln(P_{N_2}^{1/2}) = \Delta G_T + RT(2.303) \log(P_{N_2}^{1/2}).$$

ΔG_T is unknown except at equilibrium for which $\Delta G_T = 0$. Assuming $\Delta C_p \approx 0$, [4-10] may be used with equilibrium partial pressure data from Figure 5.4 to write two equations. Simultaneous solution will give ΔG_T^0 . Selecting $\log(P_{N_2}^{1/2})$ values at two temperatures and substituting into the above expression:

$$\Delta G_{453\text{ K}}^0 = (8.3144)(453)(2.303)(-15) = \Delta H_T^0 - (453) \Delta S_T^0;$$

$$\Delta G_{298\text{ K}}^0 = (8.3144)(298)(2.303)(-27) = \Delta H_T^0 - (298) \Delta S_T^0$$

where $\log(P_{N_2}^{1/2}) \approx -15$ at 453 K and $\log(P_{N_2}^{1/2}) \approx -27$ at 298 K. Solving the two Gibbs free energy equations simultaneously,

$$\Delta H_T^0 = -200,100;$$

$$\Delta S_T^0 = -154.5.$$

The desired expression is

$$\Delta G_T^0 = -200,100 + 154.5T \text{ J/mol.}$$

Setting $\Delta G_T^0 = 0$, $T \approx 1295 \text{ K or } 1022^\circ\text{C}$ (Note: this result is approximate since the expression for ΔG_T^0 is strictly valid for $250 \text{ K} < T < 453 \text{ K}$).

Example Problem 5-6

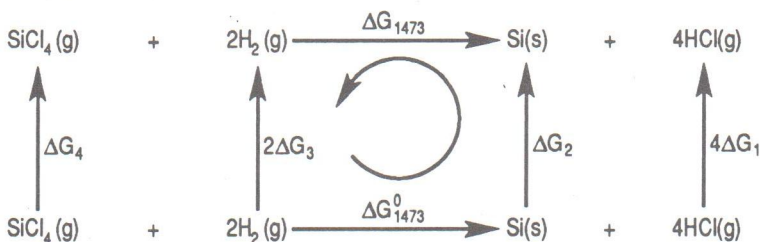
Characterize the thermodynamics of the epitaxial formation of pure solid Si on a metallic substrate according to the chemical reaction:



Note that both reactants and HCl are gases, while Si remains solid at 1200°C . The Si(s) product is a high purity, thin single crystal layer. $P_T = 1 \text{ atm}$. An understanding of thermodynamics is an important step in understanding coating processes.

Solution

(1) Set Up.



(2) Sum.

$$\Sigma \Delta G_{\text{TL}} = 0 = \Delta G_{1473}^0 + 4\Delta G_1 + \Delta G_2 - \Delta G_{1473} - 2\Delta G_3 - \Delta G_4.$$

(3) **Substitute.** From Figure E.5,

$$\Delta G_{1473}^0 = 4\Delta G_{\text{HCl}(g)}^0 - \Delta G_{\text{SiCl}_4(g)}^0 = -99,000 - (-98,000) \text{ cal/mol} \\ = -4183 \text{ J/mol Si.}$$

$$4\Delta G_1 = RT \ln(P_{\text{HCl}}^4).$$

$$\Delta G_2 = \Delta G_{1473} = 0.$$

$$2\Delta G_3 = RT \ln(P_{\text{H}_2}^2).$$

$$\Delta G_4 = RT \ln(P_{\text{SiCl}_4}).$$

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

$$0 = -4183 + RT \ln(P_{\text{HCl}}^4) - RT \ln(P_{\text{H}_2}^2) - RT \ln(P_{\text{SiCl}_4}).$$

(4) **Solve.**

$$\ln\left(\frac{P_{\text{HCl}}^4}{P_{\text{H}_2}^2 \cdot P_{\text{SiCl}_4}}\right) = \frac{4183 \text{ J/mol}}{[8.3144 \text{ J/(mol} \cdot \text{K)}](1473 \text{ K})} = 0.342$$

or

$$\frac{P_{\text{HCl}}^4}{P_{\text{H}_2}^2 \cdot P_{\text{SiCl}_4}} \approx 1.4.$$

Since there are three gas components, three independent expressions incorporating 3 gases are required to determine the partial pressure of each gas. Note that Si remains solid and does not enter into the calculations.

- (1) Assume, from the stoichiometry of the reaction, that 1 mole of $\text{SiCl}_4(g)$ and 2 moles of $\text{H}_2(g)$ are *initially* available to react.
- (2) Let n = the number of moles of $\text{SiCl}_4(g)$ that reacts with $2n$ moles of $\text{H}_2(g)$ to form $\text{Si}(s)$ and $\text{HCl}(g)$.

(3) Gas	$\text{SiCl}_4(g)$	$\text{H}_2(g)$	$\text{HCl}(g)$
Initial Moles	1	2	0
Moles Reacting or Produced	n	$2n$	$4n$
Moles Remaining	$1 - n$	$2 - 2n$	$4n$

The total number of moles as a function of n are $(1 - n) + (2 - 2n) + 4n = 3 + n$.

(4) Applying [5-4],

$$P_{\text{SiCl}_4(g)} = \frac{1-n}{3+n} \quad P_{\text{H}_2(g)} = \frac{2-2n}{3+n} \quad P_{\text{HCl}(g)} = \frac{4n}{3+n}$$

where partial pressure is in atmospheres and $P_{\text{T}} = 1 \text{ atm}$.

Substituting into the partial pressure expression at 1200°C ,

$$\frac{\left(\frac{4n}{3+n}\right)^4}{[(2-2n)/(3+n)]^2(1-n)/(3+n)} = 1.4.$$

Expanding and solving for n ,

$$65.4n^4 - 8.4n^2 + 11.2n - 4.2 = 0 \Rightarrow$$

$$n \approx 0.368.$$

Substituting into each gas partial pressure expression:

$$P_{\text{SiCl}_4(g)} = (1 - 0.368)/3.368 = \underline{0.188 \text{ atm}},$$

$$P_{\text{H}_2(g)} = [2 - 2(0.368)]/3.368 = \underline{0.375 \text{ atm}},$$

$$P_{\text{HCl}(g)} = 4(0.368)/3.368 = \underline{0.437 \text{ atm}};$$

$$P_{\text{Total}} = 1 \text{ atm (check)}.$$

5.3 DISCUSSION QUESTIONS

- (5.1) An ideal gas mixture contains gas component i . In accordance with Dalton's law:
- Is the total volume of i the same as the total volume of the gas mixture? Why?
 - Is the molar volume of i the same as the molar volume of the gas mixture? Why?
- (5.2) Assume the reaction $A \rightarrow B$ is at equilibrium. Is $\Delta G_7^0 = 0$?
- (5.3) Are $\text{H}_2\text{O}(g)$ and $\text{H}_2\text{O}(l)$ polymorphs?
- (5.4) How does the partial pressure of a gas component in an ideal gas mixture vary with respect to the mole fraction of that component?
- (5.5) Does the Gibbs free energy of a gas in an isothermal ideal gas mixture increase or decrease when the partial pressure of the gas increases? Explain.

5.4 EXERCISE PROBLEMS

- [5.1] An ideal gas mixture at pressure P_{Total} contains a gas component i of atomic fraction Y_i . Show
- $$G_i - G_i^0 = RT[\ln(P_{\text{Total}}) + \ln(Y_i)].$$
- [5.2] An isothermal ideal gas mixture changes pressure from $P_{1,\text{Total}}$ to $P_{2,\text{Total}}$. The mole fraction of gas i in the mixture is Y_i . Prove
- $$\Delta G_i = RT \ln(P_{2,\text{Total}}/P_{1,\text{Total}}).$$
- [5.3] During carburization processing of steel at 870°C in a mixture of CO and CO_2 , surface oxidation of iron may prevent penetration of carbon if P_{CO_2} is too high. Calculate the equilibrium $P_{\text{CO}}/P_{\text{CO}_2}$ ratio. What effect does a higher than equilibrium ratio have on oxidation? Use Appendix A, Table A.4 data. Compare the results obtained with Figure E.2 in Appendix E.

Ans: $P_{\text{CO}}/P_{\text{CO}_2} = 1.78$ (compared to ≈ 2.0 from Figure E.2). A higher than equilibrium ratio is deoxidizing.

- [5.4] It is difficult to prevent the formation of MnS during the steel making process. One possible technique in reducing MnS content is to *getter* or selectively remove S by adding an element to the liquid steel bath that forms a more stable sulfide than manganese. Use Figure E.3 in Appendix E to select a possible addition. Identify the parameters used in making the selection and state assumptions.

Ans: Figure E.3 reveals that Ca may be a good selection since S reacts preferentially with Ca. The process is defined as *gettinger*.

- [5.5] The Gibbs free energy change for the reaction given in Example Problem 5-5 is provided by Wicks and Block (1963, p. 68):

$$\Delta G_T^0 \text{ (cal/mol)} = -47,000 + 12.4T \ln(T) - 11.36 \times 10^{-3}T^2 + 0.54 \times 10^4 T^{-1} - 37.8T \text{ where } 453 \text{ K} \leq T \leq 800 \text{ K. Using this information,}$$

- (a) Calculate ΔG^0 at 800 K.

Ans: $\Delta G_{800}^0 = -76,120 \text{ J/mol.}$

- (b) Compare the answer from (a) with the answer calculated from Figure 5.4. Discuss the difference. Also see Exercise Problem [5.10].

Ans: $\Delta G_{800}^0 = -76,500 \text{ J/mol.}$ The comparison is good considering the extrapolation of the expression in Example Problem 5-5.

- [5.6] It is proposed that a nickel-based alloy (assume pure Ni for this problem) be used in a structural application involving contact with SO_2 .

- (a) Find the partial pressure of S_2 and SO_2 in the contact gas when an equilibrium mixture is brought together at 812°C and a total pressure of 1 atm.

Ans: $P_{\text{S}_2} = 0.12 \text{ atm; } P_{\text{SO}_2} = 0.88 \text{ atm.}$

- (b) Derive an expression relating the partial pressure of S_2 (P_{S_2}) as a function of total pressure (P_T). Calculate P_{S_2} and P_{SO_2} when $P_T = 2 \text{ atm.}$

Ans: $P_{\text{S}_2} = P_T + 3.305 \pm 2.57\sqrt{P_T + 1.652}$, $P_{\text{S}_2} = 0.39 \text{ atm;}$
 $P_{\text{SO}_2} = 1.61 \text{ atm.}$

- (c) What is the significance of the increase in total pressure on oxidation?

Ans: As P_{Total} increases, so does the tolerable P_{SO_2} before appreciable Ni oxidation occurs.

- [5.7] Binary Li-Ag brazing alloys have been used to bond a commercially pure titanium honeycomb sandwich structure to a 6Al4V titanium base alloy sheet. Initial tests showed an irregular bonding pattern. It was suspected that the Li (alloyed with Ag as a fluxing agent) was reacting with N_2 trapped in the honeycomb to form tri-lithium nitride, Li_3N , thereby preventing the available lithium from reducing surface oxides

and fluxing away surface impurities. Gas analysis revealed that the inert gas used to purge air from the honeycomb contained 0.005 v/o (volume percent) N_2 . If brazing is conducted at 800 K, use thermodynamics to prove or disprove the validity of Li_3N formation. State assumptions. Use the free energy data given in Exercise Problem [5.5]. Also see Example Problem 5-5.

Ans: $P_{N_2} = 1.15 \times 10^{-10}$ atm; since 0.005 v/o is equivalent to 5×10^{-5} atm, Li_3N will form under experimental conditions. All condensed phases are assumed to be pure.

- [5.8] Estimate the temperature at which SiO_2 and Si metal will react to boil off SiO in a vacuum furnace pumped to 10^{-3} atm (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana).

Ans: $T \approx 1511$ K.

- [5.9] In Exercise Problem [5.8], it is shown that the best vacuum obtainable is 10^{-3} atm at 1511 K when impure SiO_2 (containing excess Si) is used as containment for heat treatment, annealing, etc. Determine the best vacuum obtainable when stoichiometrically pure SiO_2 is used for containment at the same temperature.

Ans: $P_T = 1.71 \times 10^{-9}$ atm.

- [5.10] Refer to Exercise Problem [5.7]. In order to limit the formation of trilithium nitride, the P_{N_2} must be held below 1.15×10^{-10} atm. Since 0.005 v/o (volume percent) N_2 in the inert gas is unacceptable, select a possible candidate metal over which the inert gas could be passed in order to reduce N_2 to an acceptable partial pressure before it is used to purge air prior to brazing.

Ans: $Ti(\beta)$ and Ca are two possibilities. $Ti(\beta)$ is preferable.

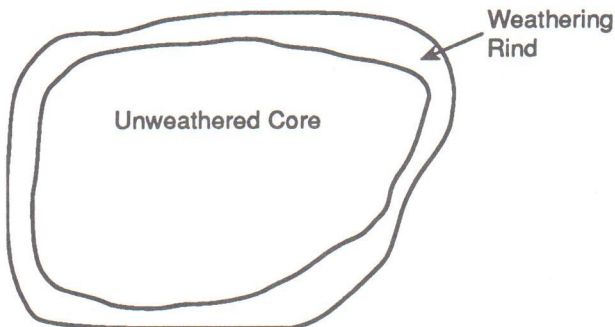
- [5.11] According to Kane and Chakachery (1992), possible coating materials for carbon/carbon composites include oxidation resistant SiC and Si_3N_4 coatings as well as glass forming inhibitors such as boron carbide. The stability of these coatings in hydrogen environments is unknown although data for B_4C and H_2 can be computed from information in the literature. Calculate equilibria for the B, C, H system at 0.03 MPa and 13.8 MPa and at a temperature of 815°C. Discuss.

Ans: At $P_T = 0.03$ MPa = 0.3 atm, $P_{H_2} \approx 0.2999$ atm, $P_{CH_4} \approx 0.0001$ atm; $P_{CH_4}/P_{H_2} \approx 0.0003$. At $P_T = 13.8$ MPa = 136 atm, $P_{H_2} \approx 134.4$ atm, $P_{CH_4} \approx 1.6$ atm; $P_{CH_4}/P_{H_2} \approx 0.012$.

- [5.12] Calculate the *maximum* allowable P_{CO_2} needed to stabilize wollastonite at 570°C. Use the data for the contact metamorphic reaction given in Exercise Problem [3.12] and Appendix A, Table A.1. Solid reaction components are in the standard state. State rationale for assumptions used in the calculation.

Ans: $P_{CO_2} = 1440$ atm. Assumptions: $\Delta C_p = 0$ and no correction for nonideal gas behavior.

- [5.13] Illustrated below is a *weathering rind*: a rim of chemically weathered and discolored rock enclosing an unweathered rock core.



$\text{FeO}(s)$, one of the initial chemical weathering products of Fe-rich minerals, frequently undergoes a combination of oxidation and hydration to produce the orthorhombic mineral goethite, $\text{FeO}(\text{OH})$. Goethite, a commercial source of iron, imparts a yellow-brown color to weathering rinds. $\text{FeO}(\text{OH})$ is also reported as a corrosion product on iron (Pourbaix diagram, *Metals Handbook*, v. 13, p. 38).

- (a) Calculate $P_{\text{O}_2(g)}$ required to form and stabilize goethite at 298 K. Condensed reaction components are in the standard state.

Ans: $P_{\text{O}_2(g)} = 10^{-84}$ atm \Rightarrow goethite is stable in air at the surface of the earth where $P_{\text{O}_2} \approx 0.22$ atm.

- (b) What assumption, if any, about the stability of goethite is inherent in the result from (a)?

Ans: See problem statement.

- [5.14] In the absence of sufficient H_2O , chemical weathering of a rock containing iron-rich minerals will produce hematite, Fe_2O_3 , instead of goethite (refer to Exercise Problem [5.13]). Hematite imparts a red to reddish-brown color to rocks.

- (a) Calculate the minimum $P_{\text{O}_2(g)}$ required to form and stabilize hematite at 298 K.

Ans: $P_{\text{O}_2(g)} = 5 \times 10^{-92}$ atm.

- (b) Discuss the significance of (a) with respect to the $P_{\text{O}_2(g)}$ in air and the stability of hematite at the surface of the earth.

Ans: See problem statement.

- [5.15] Chemical analysis of the reddish and yellow-brown weathering rind on a rock reveals that it contains both goethite and hematite. Based on the results of Exercise Problems [5.13] and [5.14], suggest how the above mineral assemblage might occur.

Ans: (1) Localized area(s) of rock depleted in H₂O, hence the mixture of minerals, (2) Zones of H₂O depletion vary over time and promote dissociation of goethite into hematite and H₂O; (3) Changes in pH may also be a factor according to the Pourbaix Diagram (see Exercise Problem [5.13]).

- [5.16] Brucite, Mg(OH)₂, is slowly heated in an atmosphere where the isobaric partial pressure of H₂O vapor is 10^{1/2} atm. At what temperature will Brucite begin to decompose?

Ans: $T = 584 \text{ K}$.

- [5.17] Methane is produced when water saturated sedimentary rocks containing graphite are heated to elevated temperatures. Calculate the equilibrium $P_{\text{CO}_2} \cdot P_{\text{CH}_4} / P_{\text{H}_2\text{O}}^2$ ratio for the reaction



at $T = 600^\circ\text{C}$ and $P_T = 2 \text{ atm}$. What is the effect of an increase in P_T ? Explain.

Ans: $P_{\text{CO}_2} \cdot P_{\text{CH}_4} / P_{\text{H}_2\text{O}}^2 = 0.21$. P_T has no effect on the reaction.

- [5.18] Using the ratio computed in Exercise Problem [5.17], calculate the partial pressures of each gas at 600°C and $P_T = 2 \text{ atm}$.

Ans: $P_{\text{H}_2\text{O}} = 1.044 \text{ atm}$, $P_{\text{CH}_4} = 0.478 \text{ atm}$; $P_{\text{CO}_2} = 0.478 \text{ atm}$.

- [5.19] The mineral siderite, FeCO₃, is found in low-temperature hydrothermal veins and low oxygenated continental waters where it is associated with clay and carbonaceous materials. Calculate the P_{CO_2} and P_{CO} required to equilibrate siderite and magnetite, Fe₃O₄, at 300 K in a CO₂-CO atmosphere containing 66 2/3 mole percent CO₂.

Ans: $P_{\text{CO}_2} = 12.48 \times 10^{-13} \text{ atm}$; $P_{\text{CO}} = 6.24 \times 10^{-13} \text{ atm}$. Actual partial pressures may be modified by: (1) hydrothermal volatiles associated with igneous processes or (2) decomposing organic matter.

- [5.20] Thorium metal is used as an alloying addition in magnesium technology and is also used as a deoxidant for molybdenum, iron, and other metals. However, thorium may corrode in water vapor to form thorium oxide and hydrogen and lose weight by spallation. Discuss the feasibility of controlling the gas phase composition as a method for minimizing corrosion. The following data is provided (Wilkinson and Murphy, 1958, p. 213-215):



$$\Delta G_{298}^0 = -171 \text{ kcal.}$$

Ans: $P_{\text{H}_2\text{O}} / P_{\text{H}_2} \approx 2 \times 10^{-63}$. It would be impossible to hold $P_{\text{H}_2\text{O}}$ low enough to shift the equilibrium from right to left.