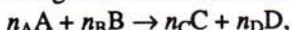# ACTIVITY QUOTIENT AND EQUILIBRIUM CONSTANT: APPLICATIONS

8.1 TL DERIVATION OF THE ACTIVITY QUOTIENT AND EQUILIBRIUM CONSTANT

The concept of the equilibrium constant, K_{eq}, leads to the introduction of a new thermodynamic variable. For most thermodynamic problems in simple systems, it is recommended that the thermodynamic loop approach be utilized. The use of the TL insures that the problem is correctly structured. The equilibrium constant concept, however, is most useful in complex multicomponent systems where numerous equilibria must be considered simultaneously. TL analysis is used in Example Problem 8-1 to derive the *activity quotient* and *equilibrium constant* of a chemical reaction. Several applications are presented throughout this chapter.

Example Problem 8-1

Using TL analysis and the general chemical reaction

$$n_A A + n_B B \rightarrow n_C C + n_D D,$$

derive:

(a) Activity quotient

$$J_a = \frac{a_C^{n_C} \cdot a_D^{n_D} \text{ (Products)}}{a_A^{n_A} \cdot a_B^{n_B} \text{ (Reactants)}};$$
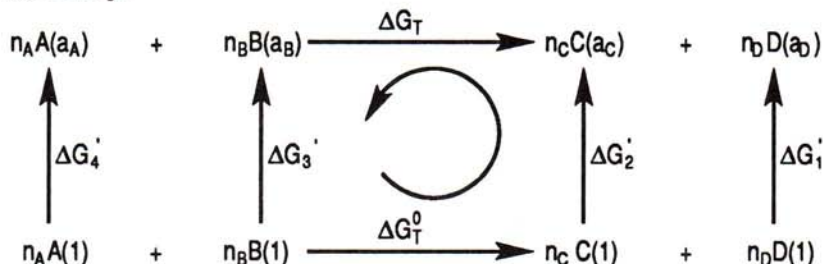
(b) Equilibrium constant

$$K_{eq} = \frac{a_C^{n_C} \cdot a_D^{n_D} \text{ (Products)}}{a_A^{n_A} \cdot a_B^{n_B} \text{ (Reactants)}};$$

What is the relationship between J_a and K_{eq}?

Solution

(a) The activity of each component is shown in parentheses.

(1) Set Up.

(2) Sum.

$$\Sigma\Delta G_{TL} = 0 = \Delta G_T^0 + \Delta G_1' + \Delta G_2' - \Delta G_T - \Delta G_3' - \Delta G_4'.$$

(3) Substitute. Applying [6-3],

$$\Delta G_1' = n_D RT \ln(a_D); \ \Delta G_2' = n_C RT \ln(a_C).$$
$$\Delta G_3' = n_B RT \ln(a_B); \ \Delta G_4' = n_A RT \ln(a_A).$$

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

$$0 = \Delta G_T^0 + n_D RT \ln(a_D) + n_C RT \ln(a_C) - \Delta G_T - n_B RT \ln(a_B) - n_A RT \ln(a_A).$$

(4) Solve. Collecting like terms and rearranging,

$$\Delta G_T = \Delta G_T^0 + RT \ln \left[\frac{a_C^{n_C} \cdot a_D^{n_D} \text{(Products)}}{a_A^{n_A} \cdot a_B^{n_B} \text{(Reactants)}} \right].$$

The activity quotient, J_a, is defined by

$$J_a = \frac{a_C^{n_C} \cdot a_D^{n_D} \text{(Products)}}{a_A^{n_A} \cdot a_B^{n_B} \text{(Reactants)}}.$$

Hence,

$$\Delta G_T = \Delta G_T^0 + RT \ln(J_a) \qquad [8\text{-}1]$$

For a reaction involving n_i moles of component i at activity a_i, the activity quotient becomes

$$J_a = \frac{\prod a_i^{n_i} \text{(Products)}}{\prod a_i^{n_i} \text{(Reactants)}} \qquad [8\text{-}2]$$

where $\prod$ is defined as the *product of activities*.

(b) At equilibrium, $\Delta G_T = 0$ and $J_a = K_{eq}$. Applying [8-1],

$$\Delta G_T^0 = -RT \ln(K_{eq}) \qquad [8\text{-}3]$$

The reader should note the similarity between [8-3] and [6-3]. For example, applying [6-14] to the reaction

$$A^0(s) \rightarrow \overline{A}(s),$$

$$\overline{G}_A^{m,s} = RT \ln(a_A) \qquad [8\text{-}4]$$

However, applying [8-3] for the same reaction at *equilibrium*,

$$\Delta G_T^0 = -RT \ln(a_A) \qquad [8\text{-}5]$$

8.2 EFFECT OF TEMPERATURE AND PRESSURE AT EQUILIBRIUM

Two cases define the relationship between the equilibrium constant, temperature, and pressure.

Case I. K_{eq} and Temperature:

Substituting [8-3] into [4-30],

$$\frac{\partial}{\partial T}\left[\frac{-RT\ln\left(K_{eq}\right)}{T}\right]_P = -\frac{\Delta H_T^0}{T^2}$$

or

$$\frac{d\ln(K_{eq})}{dT}\bigg|_P = \frac{\Delta H_T^0}{RT^2} \qquad [8\text{-}6]$$

[8-6] is known as the *Van't Hoff equation*. Assuming ΔH_T^0 is constant ($\Delta C_p = 0$) and integrating,

$$\ln(K_{eq}) = -\frac{\Delta H_T^0}{RT} + C \qquad [8\text{-}7]$$

where C is an integration constant. From inspection of [8-7], if $\Delta H_T^0 > 0$ (endothermic reaction), K_{eq} increases as temperature increases and the reaction tends to shift in the direction of the products until a new K_{eq} is established. Conversely, if $\Delta H_T^0 < 0$ (exothermic reaction), K_{eq} decreases as temperature increases and the reaction tends to shift toward the reactants until a new K_{eq} is established. Note from [8-7] that the standard enthalpy of a reaction can be obtained directly from experimental measurement of K_{eq} as a function of temperature.

Case II. K_{eq} and Pressure:

Based on [8-3], K_{eq} is a function of temperature only since ΔG_T^0 is defined at constant pressure ($P_T = 1$ atm). According to LeChatelier's principle, if a reaction at equilibrium is subjected to a change in pressure, the reaction will shift in a direction so as to relieve the pressure change. A simple example is the shift in mole fraction of a gas that occurs as a result of a pressure change for the reaction

$$A(s) + 2B(g) \rightarrow AB_2(g).$$
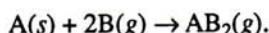
Substituting $a_i = Y_i P_T$ into [8-2] and assuming that the pressure effect on volume of solid A is negligible in comparison to the gas species,

$$K_{eq} = \frac{a_{AB_2(g)}}{a_{B(g)}^2} = \frac{Y_{AB_2(g)} \cdot P_T}{(Y_{B(g)} \cdot P_T)^2} = \frac{Y_{AB_2(g)}}{Y_{B(g)}^2 P_T}.$$

If P_T increases, the above equality shows that the ratio $Y_{AB_2(g)} / Y_{B(g)}^2$ increases in order to *maintain K_{eq} constant*. This result is consistent with LeChatelier's principle since the reaction shifts from left to right and $Y_{AB_2(g)}$ increases.

8.3 TL ANALYSIS AND K_{eq}: EXAMPLE PROBLEMS

In this section, example problems utilizing the equilibrium constant and TL analysis are presented. Some K_{eq} examples are solved using K_{eq} directly without applying the TL.

Example Problem 8-2

Using the same data presented in Example Problem 5-2, calculate P_{H_2} / P_{H_2O} from [8-3].

Solution
Inserting the data from Example Problem 5-2 into [8-3],

$$\Delta G_{1273}^0 = -173,039 = -8.3144(1273)\ln(K_{eq})$$

$$= -8.3144(1273) \times \ln(P_{H_2}^2 / P_{H_2O}^2)$$

where

$$a_{Cr_2O_3(s)} = a_{Cr(s)} = 1.$$

Hence,

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

Example Problem 8-3

The carburized steel in Example Problem 7-6 is exposed to an atmosphere of CO_2 and CO. It is suggested that decarburization may occur at 500°C. Under what circumstance is this a valid concern? Assume $P_T = 1$ atm.

Solution
At 500°C, decarburization involves dissociation of Fe_3C according to the reaction

$$Fe_3C(s) + CO_2(g) \rightarrow 3Fe(s) + 2CO(g).$$
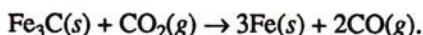
The amount of carbon dissolved in ferrite is assumed to be insignificant compared to the carbon in carbide form. ΔG_T^0 (J/mol) is obtained from the data in Table A.4:

(1) $Fe_3C(s) \rightarrow 3Fe(s) + C(s)$ $\Delta G_T^0 = -26,700 + 24.77T$

(2) $CO_2(g) \rightarrow C(s) + O_2(g)$ $\qquad\qquad \Delta G_T^0 = 394,170 + 0.84T$

(3) $2C(s) + O_2(g) \rightarrow 2CO(g)$ $\qquad\qquad \Delta G_T^0 = -223,440 - 175.32T$

Combining (1), (2), and (3) results in the decarburization reaction for which

$$\Delta G_T^0 \ (\text{J/mol}) = 144,030 - 149.71T.$$

At 773 K, $\Delta G_{773}^0 = 28,304$ J/mol. Inserting this data into [8-3],

$$28,304 = -8.3144(773)\ln(K_{eq}) = -8.3144(773)\ln(P_{CO}^2 / P_{CO_2})$$

where $a_{Fe} = a_{Fe_3C} = 1$. Hence,

$$P_{CO}^2 / P_{CO_2} = 1.22 \times 10^{-2}.$$

If $P_{CO} + P_{CO_2} = 1$, simultaneous solution gives $P_{CO} = 0.10$ atm, and $P_{CO_2} = 0.90$ atm. Decarburization at 500°C is a valid concern if $P_{CO}^2 / P_{CO_2} < 0.0122$.

Example Problem 8-4

Referring to Example Problem 7-4, estimate the carbon concentration that remains dissolved as graphite at 660°C just prior to forming the carbide Al_4C_3.

Solution

TL analysis is recommended for this problem because partial molar Gibbs free energy is obtained directly from the reference problem. It is unnecessary to convert to activity. For practical purposes, Al is a pure component.

(1) Set Up.
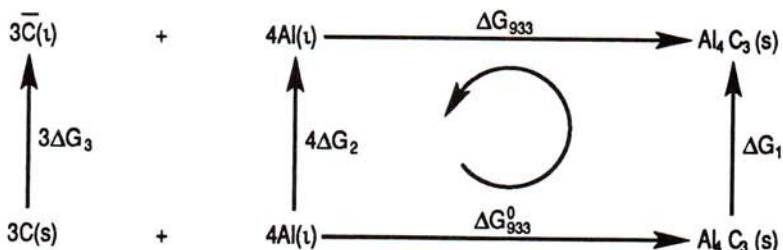
The maximum carbon concentration is established when $\Delta G_{933} = 0$.

(2) Sum.

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{933}^0 + \Delta G_1 - \Delta G_{933} - 4\Delta G_2 - 3\Delta G_3.$$

(3) Substitute.

$\Delta G_{933}^0 = -266,521 + 96.23(933) = -176,738$ J/mol from Table A.4.

$\Delta G_1 = 0$; $4\Delta G_2 \approx 0$ ($\overline{Al}(l)$ is almost pure).

$\Delta G_{933} = 0$ (equilibrium).

$3\Delta G_3 = 3(\overline{G}_C^l - G_C^{0,s}) = 3\{h - T[s - R \ln(X_C^l)]\}$

$= 3\{239,490 - 933[101 - 8.3144 \ln(X_C^l)]\}$.

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

$0 = -176,738 - 3\{239,490 - 933[101 - 8.3144 \ln(X_C^l)]\}$.

**(4) Solve.**

From [6-5b], $X_C^l = 3.7 \times 10^{-12} \approx \underline{0.002 \text{ ppb}}$.

From a practical point of view, the formation of $Al_4C_3(s)$ is certain.

Example Problem 8-5

In this example problem, thermodynamic analysis of a three-component closed system is presented to illustrate the utility of the equilibrium constant. For example, in Na-C-O equilibria, seven chemical reactions are analyzed to characterize seven condensed phases and three gases. Selecting the following reaction for illustration:

$$Na_2CO_3(s) + CO(g) = 2Na(g) + 2CO_2(g),$$
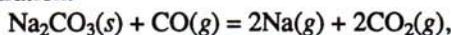
(a) Calculate P_{CO} as a function of P_{Na}.

Solution

At equilibrium,

$$K_{eq} = P_{CO_2}^2 \cdot P_{Na}^2 / P_{CO}.$$

Assuming $P_T = P_{CO} + P_{CO_2} + P_{Na}$, and substituting P_{CO_2} into the above expression for K_{eq},

$$P_{CO} = \frac{K_{eq} + 2P_T P_{Na}^2 - 2P_{Na}^3 \pm \sqrt{K_{eq}(K_{eq} - 4P_{Na}^3 + 4P_T P_{Na}^2)}}{2P_{Na}^2}.$$

P_{CO} is calculated from selected values of P_T and P_{Na}. K_{eq} is obtained from [8-3] at constant temperature.

(b) Plot the result from part (a) at $P_T = 1$ atm and $T = 1000$ K.

Solution

At $P_T = 1$ atm and $T = 1000$ K, $\Delta G_T^0 = 258,847$ J/mol.

Hence,

$$K_{eq} = \exp(-\Delta G_T^0 / RT) = \exp(-258,847/8.3144 \times 1000)$$
$$= 3.0157 \times 10^{-14}.$$

Substituting K_{eq} and $P_T = 1$ atm into the equation for P_{CO} and plotting P_{CO} versus P_{Na} results in the Na_2CO_3 *stability diagram* shown in Figure 8.1. Dissociation of Na_2CO_3 occurs to the left of the Na_2CO_3 equilibrium line.

Correlation of several equilibria derived in a similar fashion allows development of ternary isotherms. A detailed discussion of this system is given by Weaver et al. (1977) and by Gokhale and Johnson (1982).
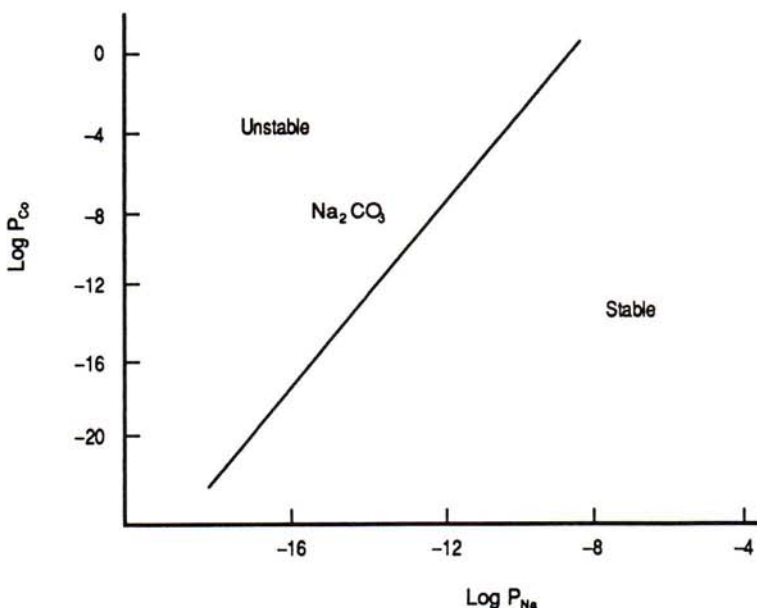

Figure 8.1 Calculated stability diagram for Na_2CO_3 according to the reaction $Na_2CO_3(s) + CO(g) = 2Na(g) + 2CO_2(g)$. $P_T = 1000$ atm; $T = 1000$ K.

Example Problem 8-6

Referring to Example Problem 6-9: (a) Repeat the problem using the definition of the equilibrium constant; (b) Express the concentration of hydrogen in solution, C_H, as a function of the heat of solution.

Solution

(a) The dissociation reaction is
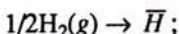
$$1/2H_2(g) \rightarrow \overline{H};$$
$$K_{eq} = a_H / P_{H_2}^{1/2} = (C_H / C_H^0) / P_{H_2}^{1/2} \Rightarrow C_H = C_H^0 K_{eq} P_{H_2}^{1/2}.$$

Hence,

$$C_H = k P_{H_2}^{1/2} \qquad [6\text{-}72b]$$

where $k = C_H^0 K_{eq}$.

(b) From [8-7],

$$\ln(K_{eq}) = -\frac{\Delta H_s^0}{RT} + C \qquad [8\text{-}8]$$

where $\Delta H_s^0 = \overline{H}_H - (1/2)H_{H_2}^{0,g}$, the *molar heat of solution* relative to gaseous hydrogen. Solving [8-8] for K_{eq},

$$K_{eq} = (C_H/C_H^0)/P_{H_2}^{1/2} = e^{[(-\Delta H_s^0/RT)+C]} = e^C \cdot e^{-\Delta H_s^0/RT}.$$

Hence,

$$C_H = C_H^0 e^{-\Delta H_s^0/RT} \qquad [8\text{-}9]$$

where $C_0 = C_H^0 e^C P_{H_2}^{1/2}$.

8.4 THE NERNST EQUATION

A definition of Electromotive Force E (EMF) for oxidation or charge transfer is given by $\Delta G = nFE$ where ΔG is the Gibbs free energy change, n is valence, and F is *Faraday's constant* (96,500 coulomb/eq). The *Nernst equation* is obtained by substituting this expression into [8-1] and dividing through by nF. The result is

$$E_{Cell} = E_{Cell}^0 + 2.303(RT/nF)\log_{10}(J_a) \qquad [8\text{-}10]$$

For corrosion reactions which normally occur at room temperature (298 K), [8-10] is simplified as follows:

$$2.303(RT/nF) = \frac{2.303 \times [8.3144 \text{ J/(mol} \cdot \text{K)}] \times 298\,\text{K}}{(n \text{ eq/mol}) \times 96,500 \text{ coulomb/eq}} = \frac{0.0592}{n} \text{ J/coulomb;}$$

substituting into [8-10],

$$E_{Cell} = E_{Cell}^0 + (0.0592/n)\log_{10}(J_a) \qquad [8\text{-}11]$$

The standard state is chosen such that for dilute concentrations, in corrosion, $a_i = C_i = 1$ mole/liter (1 *molar solution*).
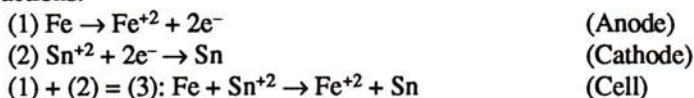
Example Problem 8-7

An *electrochemical cell* consists of Sn and Fe electrodes in an electrolytic solution at standard concentrations of Sn and Fe ions.
  (a) Which electrode will act as the anode and hence be the corroding one? Start by assuming that Fe is anodic to Sn at $T = 25°C$.

Solution

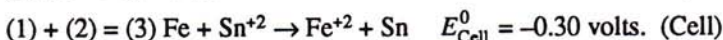The cell reaction is the sum of anodic (oxidation) and cathodic (reduction) reactions:
  (1) $Fe \rightarrow Fe^{+2} + 2e^-$ (Anode)
  (2) $Sn^{+2} + 2e^- \rightarrow Sn$ (Cathode)
  (1) + (2) = (3): $Fe + Sn^{+2} \rightarrow Fe^{+2} + Sn$ (Cell)

From [8-2],

$$J_a = \frac{C_{Fe^{+2}} \cdot C_{Sn}}{C_{Fe} \cdot C_{Sn^{+2}}} = \frac{1 \cdot 1}{1 \cdot 1} = 1$$

Metallic Sn and Fe are present as pure solids, hence $C_{Sn} = C_{Fe} = 1$ and $C_{Sn^{+2}} = C_{Fe^{+2}} = 1$ mol/liter. Equation [8-11] becomes $E_{Cell} = E^0_{Cell}$ since $\log_{10}(J_a) = 0$. The standard EMF for each *half cell* (anode and cathode) is obtained from Appendix C, Table C.1, as follows:

(1) Fe → Fe^{+2} + 2e$^-$	$E^0 = -0.44$ volts	(Half Cell)
(2) Sn^{+2} + 2e$^-$ → Sn	$E^0 = +0.14$ volts	(Half Cell)

(1) + (2) = (3) Fe + Sn^{+2} → Fe^{+2} + Sn $E^0_{Cell} = -0.30$ volts. (Cell)

Since the cell voltage is negative, $\Delta G_{Cell} = nFE_{Cell} < 0 \Rightarrow$ the cell reaction will occur as written, i.e., Fe is anodic to Sn.

(b) If the ratio $C_{Fe^{+2}} / C_{Sn^{+2}} = 10^{15}$, is Fe anodic to Sn?

Solution
Applying [8-11] where $E^0_{Cell} = -0.30$ volts from part (a),

$$E_{Cell} = -0.30 + (0.0592/2)\log[(C_{Fe^{+2}} \cdot C_{Sn})/(C_{Sn^{+2}} \cdot C_{Fe})]$$
$$= -0.30 + (0.0592/2)\log(10^{15}) = 0.144 \text{ volts.}$$

Since E_{Cell} is now positive, the polarity is reversed ($\Delta G_{Cell} = nFE_{Cell} > 0$), and Sn is anodic to Fe. This illustrates the fact that a change in composition of the electrolyte can localize corrosion in unexpected areas. An evaluation based only on the EMF series often leads to error.

8.5 DISCUSSION QUESTIONS

(8.1) Explain the difference between activity quotient and equilibrium constant. Under what condition are they equal?

(8.2) Applying $\Delta G_T = \Delta G^0_T + RT \ln(J_a)$, are the reactants and products in equilibrium? Is this equation applicable to pure phases only? Why?

(8.3) What isobaric relationship relates the equilibrium constant of a reaction to the enthalpy change and temperature of the reaction?

(8.4) Explain how the equilibrium constant can be used to determine whether a reaction will tend to shift toward products or reactants.

(8.5) Explain how the EMF of a cell can be determined from half cell reactions. What law is this an example of?

(8.6) Two electrodes, A and B, are immersed in an electrolyte. If it is assumed that A is anodic to B and it is then determined that $E_{Cell} > 0$, will A corrode?

(8.7) Why is TL analysis applicable to problems utilizing the equilibrium constant?

(8.8) Develop [8-9] directly from [6-72a]. What does a comparison of [8-9]

and [6-72a] suggest concerning the integration constant in [8-8]?

8.6 EXERCISE PROBLEMS

[8.1] Referring to Example Problem 5-6: (a) Find the equilibrium constant for the reaction and discuss the effect of increasing (b) total pressure and (c) temperature.

Ans: (a) $K_{eq} = Y_{HCl}^4 P_T / (Y_{H_2}^2 Y_{SiCl_4})$, (b) The yield of Si(s) and HCl(g) decreases because $Y_{HCl(g)}$ must decrease in order to maintain K_{eq} constant; (c) K_{eq} increases because the reaction is endothermic.

[8.2] The decomposition of $Fe_3C(s)$ (*decarburization*) in a steel exposed to a hydrogen environment can result in the internal formation of $CH_4(g)$. Internal pressure created by accumulation of the CH_4 can lead to so called hydrogen attack because CH_4 cannot diffuse from the lattice structure. Repeat Example Problem 8-3 for exposure to a mixture of $H_2(g)$ and $CH_4(g)$ at 500°C and determine the minimum $P_{CH_4} / P_{H_2}^2$ ratio that can exist without causing significant decarburization and subsequent hydrogen attack.

Ans: $P_{CH_4} / P_{H_2}^2 = 7.283$.

[8.3] Estimate the total enthalpy change associated with modified austempering of one gram mole of 1050 steel. Identify all assumptions made and source materials used.

Ans: $\Delta H_{Total} = 5091$ J/mol.

[8.4] Manganese sulfide inclusions in steel are interfacial traps (sinks) for hydrogen and hence tend to increase the total or "effective" hydrogen solubility. Depending upon the distribution and size of the inclusions, they may increase the susceptibility of the steel to *hydrogen embrittlement* or *hydrogen environment cracking* (HEC).

(a) If $H_2S(g)$ and $H_2(g)$ are present in the contacting atmosphere, what is the critical ratio P_{H_2S} / P_{H_2} above which MnS(s) and $H_2(g)$ form at 1500°C and 1 atm?

Ans: $P_{H_2S} / P_{H_2} = 5 \times 10^{-5}$.

(b) The calculated critical ratio in (a) for minimizing HEC in steel may not be confirmed experimentally. Name two factors that are not considered in these calculations.

Ans: Solid state kinetics are normally slow and are not involved in thermodynamic calculations. The calculated ratio does not take into account solubility effects.

[8.5] Referring to the data in Appendix A, Table A.5, show that

$$\ln(P_{Cu}^l)(atm) = -40,349/T - 1.21\ln(T) + 23.79.$$

[8.6] Referring to the paper by Iwai, Takahashi, and Handa (1986):
(a) Confirm the data in the last three columns of Table II.
(b) Equilibrium data are found in Tables II and III. Use the least mean

squares treatment to derive the expression:

$$\Delta G^{0,f}_{Mo_2C} \text{ (J/mol)} = -68{,}270 + 8.23T$$

where $1173 \text{ K} \le T \le 1573 \text{ K}$.

(c) What assumption is implied but not directly mentioned in the article?

Ans: $\Delta C_p \approx 0$.

[8.7] The vapor pressure data in Appendix A, Table A.5, can be expressed in the form

$$\log_{10}(P) = AT^{-1} + B\log_{10}(T) + D$$

where $C = 0$.

(a) Starting with [7-20], develop the above expression for the pressure of a vapor over its coexisting condensed phase at equilibrium.

(b) What is the form of the equation if $\Delta C_p = 0$?

Ans: $\log_{10}(P) = AT^{-1} + D$.

[8.8] Confirm that hydrogen dissolved in $Ti(\alpha)$ follows Sievert's law. Use the following data given at 610°C by McQuillan (1950):

$P_{H_2(g)}$ (atm)	Hydrogen Solubility in Ti(α) (ppm)
5.263×10^{-5}	235
5.263×10^{-4}	750
2.632×10^{-3}	1705

Ans: k values are constant within experimental error, thereby confirming the law.

[8.9] Repeating Example Problem 7-6 for carburization of a low carbon steel in a mixture of CO and CO_2 at 900°C, calculate the carburizing potential required to develop 0.8 w/o C at the surface.

Ans: $P_{CO}^2 / P_{CO_2} = 19.466$.

[8.10] The solubility of hydrogen in liquid binary Al-Li alloys is given by Anyalebechi, Talbot, and Granger (1988):

Pure Al: $\log(s/s^0) - (1/2)\log(P/P^0) = -2700/T + 2.720$

Al-1 Pct Li: $\log(s/s^0) - (1/2)\log(P/P^0) = -2113/T + 2.568$

Al-2 Pct Li: $\log(s/s^0) - (1/2)\log(P/P^0) = -2797/T + 3.329$

Al-3 Pct Li: $\log(s/s^0) - (1/2)\log(P/P^0) = -2889/T + 3.508$

where $s^0 = 1 \text{ cm}^3/100 \text{ gm}$ metal at STP and $P^0 = 1.01325 \times 10^5$ Pa. The equations are valid from 913 to 1073 K and from 5.3×10^4 to 10.7×10^4 Pa. Determine the enthalpy of solution at each concentration. The last term in each expression includes an activity correction; hence, it cannot be used to calculate ΔS_s^0 directly.