

Chapter 7

- [7.1] Using the Bi-Pb phase diagram in Appendix E, Figure E.8, calculate the activity of Bi in an equimolar liquid solution of Bi and Pb at 625 K. Assume regular solution behavior.

Solution

Since the activity of Bi is desired, the high Bi liquidus side of the eutectic must be analyzed (\bar{G}_{Bi}^m is defined relative to pure liquid Bi). The following data is obtained from the Bi-Pb phase diagram:

Point on Liquidus	Temperature		a/o Bi
	°C	K	
1.)	125	398	56
2.)	175	448	70
3.)	200	473	76

Using [7-5], regular solution, no solid solubility and data from Table A.2:

$$(1) 398 = \frac{\Omega^{\prime}(1-.56)^2 + 10,879}{-8.3144 \ln(.56) + 20.00}$$

$$(2) 448 = \frac{\Omega^{\prime}(1-.70)^2 + 10,879}{-8.3144 \ln(0.7) + 20.00}$$

$$(3) 473 = \frac{\Omega^{\prime}(1-.76)^2 + 10,879}{-8.3144 \ln(.76) + 20.00}$$

Solving for Ω^{\prime} and averaging:

$$\left. \begin{array}{l} (1) \Omega^{\prime} = -5167 \\ (2) \Omega^{\prime} = -6560 \\ (3) \Omega^{\prime} = -5898 \end{array} \right\} \Omega_{\text{ave}}^{\prime} = -5875 \text{ (J/mol)}$$

Substituting into [6-43],

$$\begin{aligned} \bar{G}_{\text{Bi}}^m &= -5875(1-.5)^2 + 8.3144(625)\ln(.5) \\ &= -5071 = 8.3144(625)\ln(a_{\text{Bi}}) \\ a_{\text{Bi}} &= \underline{0.38} \end{aligned}$$

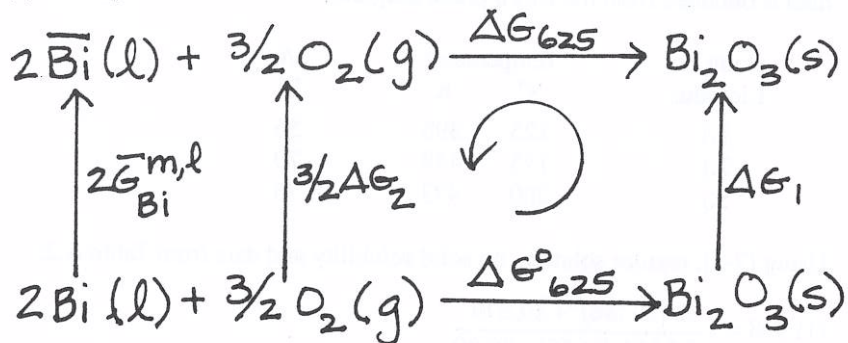
Note: From Kubaschewski and Alcock (1979, p. 411) $\bar{H}_{\text{Bi}}^{m,\ell} = -1109 \text{ J/mol}$ and $\bar{S}_{\text{Bi}}^{m,\ell} = 0.167 \text{ J/(mol}\cdot\text{K)}$.

Using this data, $a_{\text{Bi}} = 0.396$. Although the regular solution model assumes $\bar{S}_{\text{Bi}}^{\text{xs}} = 0$, the agreement is within experimental error.

[7.2] Using the results from Exercise Problem [7.1], calculate the equilibrium $P_{\text{O}_2(\text{g})}$ over an equimolar Bi-Pb liquid solution at 625 K. The Gibbs free energy of formation of dibismuth trioxide, Bi_2O_3 , is $\Delta G_{\text{Bi}_2\text{O}_3}^{0,f} = -407,250 \text{ J/mol}$ at 625 K (Wicks and Block, 1963, p. 21).

Solution

(1) Set Up



(2) Sum

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{625}^0 + \Delta G_1 - \Delta G_{625} - \frac{3}{2} \Delta G_2 - 2\bar{G}_{\text{Bi}}^{m,l}$$

(3) Substitute

$$\Delta G_{625}^0 = -407,250 \text{ J/mol (given)}$$

$$\Delta G_1 = 0 \text{ (pure condensed phase)}$$

$$\Delta G_{625} = 0 \text{ (equilibrium)}$$

$$\frac{3}{2} \Delta G_2 = \frac{3}{2} RT \ln(P_{\text{O}_2})$$

$$2\bar{G}_{\text{Bi}}^{m,l} = 2RT \ln(a_{\text{Bi}})$$

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

$$0 = -407,250 - \frac{3}{2}(8.3144)(625) \ln(P_{\text{O}_2}) - 2(8.3144) \times (625) \ln(0.38)$$

(4) Solve

$$P_{\text{O}_2} \approx \underline{7.4 \times 10^{-23} \text{ atm}}$$

Note: The result indicates that Bi will oxidize from solution since it would be impossible to maintain such a low P_{O_2} .

[7.3] From Kubaschewski and Alcock (1979), solution data for a 70 a/o Bi-Pb solution (Exercise Problem [7.1]) are: $\bar{H}_{\text{Bi}}^{m,l} = -70 \times 4.184 = -292.9 \text{ J/mol}$ and $\bar{S}_{\text{Bi}}^{\text{xs}} = 0.03 \times 4.184 = 0.1255 \text{ J/(mol}\cdot\text{K)}$. Using this data, estimate the heat of fusion of Bi.

Solution

From Table A.2, $T^f = 544 \text{ K}$ and $\Delta H_{\text{Bi}}^f = 10,879 \text{ J/mol}$.

From [7-2],

$$448 = \frac{-292.9 + \Delta H_{\text{Bi}}^f}{0.1255 - 8.3144 \ln(0.7) + \Delta H_{\text{Bi}}^f/544}$$

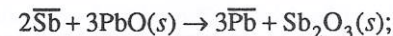
Solving, $\Delta H_{\text{Bi}}^f = 9507 \text{ J/mol}$ or 13% error.

The error is attributed to reading error from the phase diagram and assumption that $\Delta C_p \approx 0$.

[7.4] Repeat Exercise Problem [6.9] using the following solubility data estimated from the Pb-Sb phase diagram in Appendix E, Figure E.9: $X_{\text{Sb}} = 0.3$ at $T = 598 \text{ K}$ and $X_{\text{Sb}} = 0.2$ at $T = 533 \text{ K}$. Note that the solubility data is given at a much lower temperature than the refining temperature.

Assume:

- (1) Calculated solution parameters hold at the higher temperature,
- (2) The process involves the reaction



- (3) Sb behaves as a dilute solution component at these concentrations.

Solution

From Exercise Problem [6.9], approach 2 at 900°C , $a_{\text{Sb}} = 0.013$. If Sb acts as a dilute solution component at this temperature,

$$a_{\text{Sb}} = 0.013 = b_{\text{Sb}} X_{\text{Sb}} \text{ or } X_{\text{Sb}} = \frac{0.013}{b_{\text{Sb}}} \text{ where } b_{\text{Sb}} \text{ (dilute solution)} = \gamma_{\text{Sb}}$$

From [7-4], h_{Sb} and s_{Sb} are determined and then b_{Sb} is calculated:

$$(1) 533 = \frac{h_{\text{Sb}} + 19,876}{s_{\text{Sb}} + 13.382 + 22.01}$$

$$(2) 598 = \frac{h_{\text{sb}} + 19,876}{s_{\text{sb}} + 10.01 + 22.01}$$

Solving simultaneously, $h_{\text{sb}} = -3341$; $s_{\text{sb}} = -4.37$.

From [6-38],

$$b_{\text{sb}} = \exp\left[\frac{-3341 - 1173(-4.37)}{8.3144(1173)}\right] = 1.2.$$

Substituting,

$$X_{\text{sb}} = \frac{0.013}{1.2} \approx 0.011 \approx 6500 \text{ ppm Sb.}$$

Note: Assuming that Sb behaves ideally (Exercise Problem [6.9]-Method 2) yields a result 23% higher.

[7.5] For dilute solutions of carbon (graphite) in liquid sodium, solubility data was used to determine the partial molar free energy of solution as a function of temperature according to Johnson (1964, p. 23) as follows:

$$\bar{G}_C^l - G_C^{0,s} = 5272 + 68.62T + 8.3144T \ln(X_C).$$

(a) Determine \bar{H}_C^{XS} and \bar{S}_C^{XS} .

(b) The purification of liquid sodium with respect to carbon can be accomplished by *gettering* carbon with calcium at 920°C. Predict the carbon content of the liquid after addition of excess calcium. The solubility of Ca in Na is low, hence, it has no effect on the performance of sodium as a heat transfer medium.

Solution

(a) Comparing [6-37] with the given expression above, term by term, and noting $G_C^{0,s}$ as the standard state:

$$G_C^l - G_C^{0,s} = h_c - T[s_c - R \ln(X_C)] \\ = 5272 - T[-68.62 - 8.3144 \ln(X_C)]$$

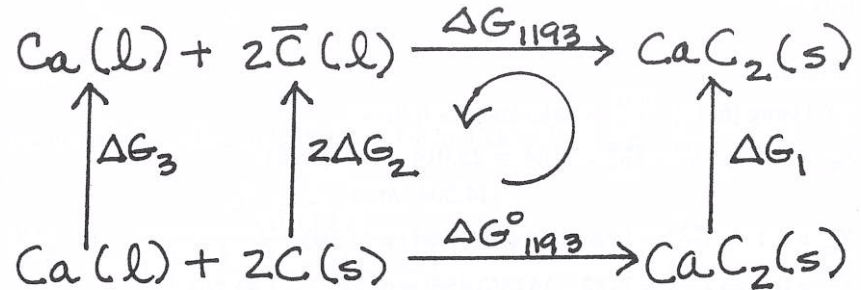
$$h_c = 5272 \text{ J/mol}$$

$$s_c = -68.62 \text{ J/(mol}\cdot\text{K)}$$

$$\bar{H}_C^{\text{XS}} = h_c = \underline{5272 \text{ J/mol}}; \bar{S}_C^{\text{XS}} = s_c = \underline{-68.62 \text{ J/(mol}\cdot\text{K)}}$$

(b)

(1) Set Up



(2) Sum

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_{1193}^\circ + \Delta G_1 - \Delta G_{1193} - 2\Delta G_2 - \Delta G_3$$

(3) Substitute

$$\Delta G_{1193}^\circ = -57,326 - 28.45T \text{ (Table A.4)}$$

$$\Delta G_1 = \Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{1193} = 0 \text{ (equilibrium)}$$

$$2\Delta G_2 = 2\{5272 - T[-68.62 - 8.3144 \ln(X_C)]\}$$

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

$$0 = -57,326 - 28.45(1193) - 2\{5272 - 1193[-68.62 - 8.3144 \ln(X_C)]\}$$

(4) Solve

$$\ln(X_C) = -13.39$$

$$X_C = \underline{1.5 \times 10^{-6}} \text{ or } \approx 0.8 \text{ ppm.}$$

[7.6] Using the following data from Kubaschewski and Alcock (1979, p. 386-389) for Cu in a Ag-Cu liquid alloy at 1423 K:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\bar{H}_{\text{Cu}}^{m,l}$ (J/mol)	23,014	15,692	7482	3766	1435	159
$\bar{S}_{\text{Cu}}^{\text{XS}}$ [J/(mol·K)]	5.980	3.084	0.456	0.100	0.084	0.004

(a) Calculate $\bar{G}_{\text{Cu}}^{\text{XS}}$.

(b) Calculate $\bar{G}_{\text{Cu}}^{\text{XS}}$ from the results in Example Problem 7-5 and compare with part (a).

Solution

(a) Using [6-47], $\bar{G}_{\text{Cu}}^{\text{XS}}$ is calculated as follows:

$$X_{\text{Cu}} = 0.0 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = \bar{H}_{\text{Cu}}^{\text{XS}} - T\bar{S}_{\text{Cu}}^{\text{XS}} = 23,014 - 1423(5.98) = 14,504 \text{ J/mol}$$

$$X_{\text{Cu}} = 0.1 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 15,692 - 1423(3.084) = 11,303$$

$$X_{\text{Cu}} = 0.3 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 7482 - 1423(0.456) = 6833$$

$$X_{\text{Cu}} = 0.5 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 3766 - 1423(0.1) = 3624$$

$$X_{\text{Cu}} = 0.7 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 1435 - 1423(.084) = 1315$$

$$X_{\text{Cu}} = 0.9 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 159 - 1423(.004) = 153.3$$

Ans:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\bar{G}_{\text{Cu}}^{\text{XS}}$ (J/mol)	14,504	11,303	6833	3624	1315	153.3

(b) Using [6-47], $\bar{G}_{\text{Cu}}^{\text{XS}}$ is calculated as follows:

$$X_{\text{Cu}} = 0.0 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = \bar{H}_{\text{Cu}}^{\text{m},l} = \Omega^l(1 - X_{\text{Cu}})^2 = 12,889(1-0)^2 = 12,889 \text{ J/mol}$$

$$X_{\text{Cu}} = 0.1 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 12,889(1-.1)^2 = 10,440$$

$$X_{\text{Cu}} = 0.3 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 12,889(1-.3)^2 = 6316$$

$$X_{\text{Cu}} = 0.5 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 12,889(1-.5)^2 = 3222$$

$$X_{\text{Cu}} = 0.7 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 12,889(1-.7)^2 = 1160$$

$$X_{\text{Cu}} = 0.9 \Rightarrow \bar{G}_{\text{Cu}}^{\text{XS}} = 12,889(1-.9)^2 = 129.$$

Ans:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\bar{G}_{\text{Cu}}^{\text{XS}}$ (J/mol)	12,889	10,440	6316	3222	1160	129

These results differ from those of part (a) by 11-16%. See Example Problem 7-5 for further discussion.

[7.7] Using the data from Example Problem 7-8 and Appendix B, Table B.1, predict the eutectic temperature shift resulting from a pressure increase from 1 to 1000 atm.

Solution

Using data from Example Problem 7-8 and Table B.1:

$$X_{\text{Cu}}^{\alpha} = 1 - \frac{7.9\left(\frac{1}{107.88}\right)}{7.9\left(\frac{1}{107.88}\right) + 92.1\left(\frac{1}{63.54}\right)} \Rightarrow X_{\text{Cu}}^{\alpha} = 0.952$$

$$X_{\text{Cu}}^{\beta} = 1 - \frac{91.2\left(\frac{1}{107.88}\right)}{91.2\left(\frac{1}{107.88}\right) + 8.8\left(\frac{1}{63.54}\right)} \Rightarrow X_{\text{Cu}}^{\beta} = 0.141$$

$$\Omega_{\text{Cu}}^{\alpha} = 21,111 \text{ J/mol and } \Omega_{\text{Cu}}^{\beta} = 22,720 \text{ J/mol}$$

Assuming $\bar{V}_{\text{Cu}}^{\alpha} \approx V_{\text{Cu}}^{\circ}$, $\bar{V}_{\text{Cu}}^{\beta} \approx \frac{63.54}{8.96} = 7.092 \text{ cm}^3/\text{mol}$. $\bar{V}_{\text{Cu}}^{\beta}$ is more difficult to

predict. Assuming $V_{\text{Cu}}^{\alpha} < \bar{V}_{\text{Cu}}^{\beta} < V_{\text{Ag}}^{\circ}$, the maximum possible value of

$$\bar{V}_{\text{Cu}}^{\beta} \text{ is } V_{\text{Ag}}^{\circ} = \frac{107.88}{10.49} = 10.284 \text{ cm}^3/\text{mol}$$

Substituting into [7-25b],

$$T_e =$$

$$\frac{21,111(1-.952)^2 + (7.092 - 10.284)(999)(.1013) - 22,720(1-.141)^2}{8.3144 \ln\left(\frac{0.141}{0.952}\right)}$$

$$= \frac{48.6 - 323 - 16,765}{-15.88} = 1073\text{K}$$

From Figure E.7, $T_e = 1053\text{K}$. The eutectic temperature shift is a maximum of +20K. In reality, the shift is less—depending upon the actual value of $\bar{V}_{\text{Cu}}^{\beta}$.

[7.8] Refer to the eutectic phase diagram shown in Appendix E, Figure E.10.

- Identify the components that constitute this system.
- Is the system isobaric or isothermal?
- Give the phase rule expression that is applicable to this diagram.
- Label the diagram at phase assemblages that are: *invariant* ($F = 0$), *univariant* ($F = 1$), and *divariant* ($F = 2$).

- (e) What is the equation (temperature) of the horizontal line through the eutectic point?
- (f) What is the equation (temperature) of the phase boundary between tridymite and cristobalite?

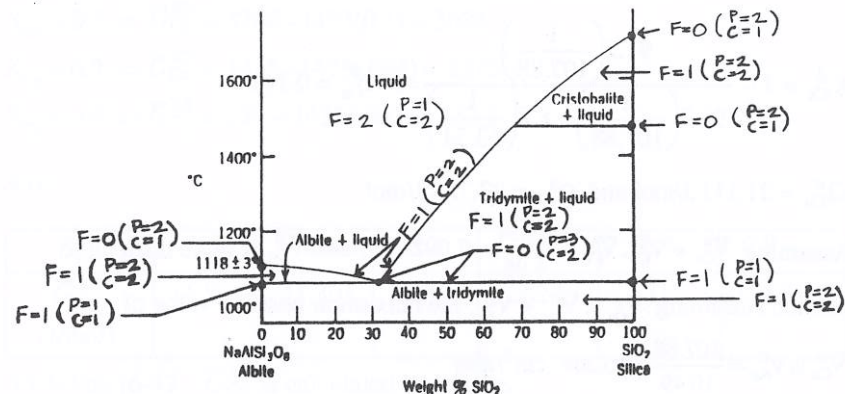
Solution

(a) Albite: $\text{NaAlSi}_3\text{O}_8$ and Silica: SiO_2

(b) Isobaric

(c) $F = \Gamma(\text{Components}) - \Phi(\text{Phases}) + 1$, since pressure is constant.

(d) The degrees of freedom and corresponding numbers of phases and components are labeled on the phase diagram illustrated below.



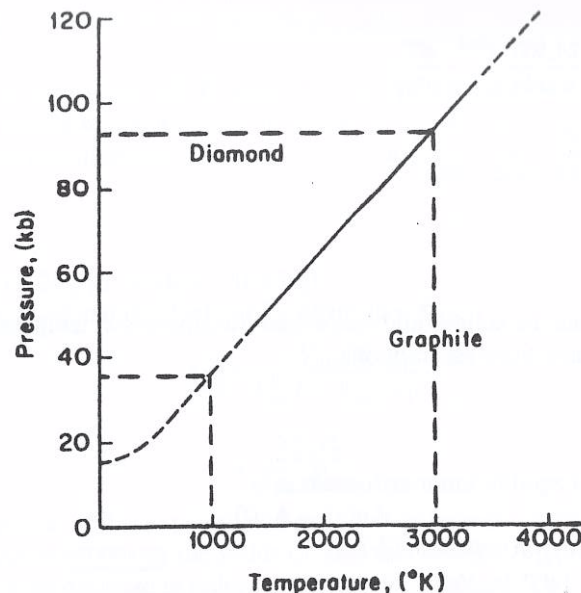
$\text{NaAlSi}_3\text{O}_8$ - SiO_2 eutectic phase diagram. (From C. Klein and C.S. Hurlbut, Jr., 1985, Manual of Mineralogy, Fig. 12.5. Reprinted by permission of John Wiley and Sons, Inc., Copyright © 1985.)

- (e) $T \approx 1060\text{C}^{\circ}$
- (f) $T \approx 1470^{\circ}\text{C}$.

[7.9] Using Figure E.11 in Appendix E, develop a temperature-dependent expression for the diamond-graphite phase boundary between 45–105 kbar. Is this boundary invariant, univariant, or divariant? See Exercise Problem [7.8].

Solution

As illustrated below, the plot is a straight line from 1000 to 3000 K. Hence, its equation is $P = mT + b$ where m is the slope and b is the P - intercept.



Diamond-graphite univariant phase diagram. (From E.G. Ehlers, 1972, The Interpretation of Geological Phase Diagrams, Fig. 93. Reprinted by permission of W.H. Freeman and Company.)

at 1000 K, $P \approx 36$ kbar
 at 3000 K, $P \approx 94$ kbar

$$\left. \begin{aligned} 94 &= 3000m + b \\ 36 &= 1000m + b \end{aligned} \right\} \text{solve simultaneously}$$

$$m = 0.029 \text{ kbar/K}$$

$$b = 7 \text{ kbar}$$

The equation is $P(\text{kbar}) = 0.029 \times T(\text{K}) + 7$

$$F = \Gamma - \Phi + 2 = 1 - 2 + 2 = 1 \Rightarrow \text{univariant boundary.}$$

[7.10] Estimate the equilibrium vapor pressure of $\text{SO}_2(\text{g})$ over $\text{SO}_2(\text{l})$ at 265 K. State assumptions.

Solution

The univariant equilibrium transformation is
 $\text{SO}_2(\text{l}) \rightarrow \text{SO}_2(\text{g})$

Using Table A.2 data, assuming $\Delta H^{\text{tr}} \approx \text{constant}$ ($\Delta C_p \approx 0$), and integrating the Clausius-Clapeyron equation, [7-20]:

$$\int_1^P d \ln(P) = \frac{24,937}{8.3144} \int_{263}^{265} \frac{dT}{(T^{\text{Tr}})^2}$$

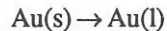
$$\ln(P) = \frac{-24,937}{8.3144} \left(\frac{1}{265} - \frac{1}{263} \right) \text{ or}$$

$$P = \underline{1.09 \text{ atm.}}$$

[7.11] Estimate the solid-liquid isothermal transformation temperature of Au at 75 atm. State assumptions.

Solution

The univariant equilibrium transformation is



From the Clapeyron equation, [7-21]:

$$\frac{dP}{dT} = \frac{\Delta H^{\text{Tr}}}{T \Delta V} \Rightarrow \frac{dT}{T} = \frac{\Delta V dP}{\Delta H^{\text{Tr}}}$$

From Table B.1,

$$\Delta V = V_{\text{Au(l)}} - V_{\text{Au(s)}} = \frac{197}{17.0} - \frac{197}{19.3} = 1.38 \text{ cm}^3/\text{mol}$$

From Table A.2, $\Delta H^{\text{Tr}} = 12,760 \text{ J/mol}$

Integrating [7-21] while assuming ΔV and ΔH^{Tr} constant:

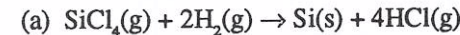
$$\int_{1336}^T \frac{dT}{T} = \frac{1.38}{12,760} \int_1^{75} dP$$

$$\ln\left(\frac{T}{1336}\right) = \frac{1.38(74)}{12,760} \left(\frac{8.3144}{82.057}\right) \text{ or } T_{75 \text{ atm}} = \underline{1337 \text{ K}} \text{ or } \Delta T = 1 \text{ K.}$$

Chapter 8

[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.

Solution



Substituting [5-4] and [6-2] into [8-2] where $J_a = K_{\text{eq}}$,

$$\begin{aligned} K_{\text{eq}} &= \frac{Y_{\text{HCl}}^4 P_T^4}{Y_{\text{H}_2}^2 P_T^2 \cdot Y_{\text{SiCl}_4} P_T} \\ &= \frac{Y_{\text{HCl}}^4 P_T}{Y_{\text{H}_2}^2 \cdot Y_{\text{SiCl}_4}} \end{aligned}$$

(b) Examination of this expression reveals that an increase in total pressure has the effect of decreasing the yields of Si(s) and HCl(g). Y_{HCl} in the expression must decrease in order to maintain K_{eq} constant.

(c) Referring to the Van't Hoff equation, [8-7]: $\ln(K_{\text{eq}}) = \frac{-\Delta H_T^0}{RT} + C$, it is necessary to know whether the reaction is endothermic or exothermic.

From Table A.1 and assuming $\Delta C_p = 0$,

$$\begin{aligned} \Delta H_T^0 &\approx 4\Delta H_{298, \text{HCl}}^{0,f} - \Delta H_{298, \text{SiCl}_4}^{0,f} \\ &= 4(-92.32) - (-662.81) \\ &= +293.53 \text{ kJ/mol.} \end{aligned}$$

Since $\Delta H_T^0 > 0$, K_{eq} increases as the temperature increases.

[8.2] The decomposition of $\text{Fe}_3\text{C}(s)$ (*decarburization*) in a steel exposed to a hydrogen environment can result in the internal formation of $\text{CH}_4(g)$. 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 $\text{H}_2(g)$ and $\text{CH}_4(g)$ at 500°C and determine the maximum $P_{\text{CH}_4} / P_{\text{H}_2}^2$ ratio that can exist without causing significant decarburization and subsequent hydrogen attack.