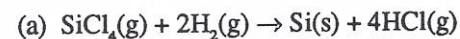## Chapter 8

[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

(a) $SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g)$
Substituting [5-4] and [6-2] into [8-2] where $Ja = K_{eq}$,

$$\underline{\underline{Keq}} = \frac{Y_{HCl}^4 P_T^4}{Y_{H_2}^2 P_T^2 \cdot Y_{SiCl_4} P_T}$$

$$= \frac{Y_{HCl}^4 P_T}{Y_{H_2}^2 \cdot Y_{SiCl_4}}$$

(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]: $\ln(K_{eq}) = \frac{-\Delta H_T^0}{RT} + C$, it is necessary to know whether the reaction is endothermic or exothermic.

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

$$\Delta H_T^0 \approx 4\Delta H_{298,HCl}^{0,f} - \Delta H_{298,SiCl_4}^{0,f}$$
$$= 4(-92.32) - (-662.81)$$
$$= +293.53 \text{ kJ/mol.}$$

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

[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 maximum $P_{CH_4}/P_{H_2}^2$ ratio that can exist without causing significant decarburization and subsequent hydrogen attack.

Solution

Decarburization in hydrogen involves dissociation of Fe_3C according to the reaction

$$Fe_3C(s) + 2H_2(g) \rightarrow 3Fe(s) + CH_4(g)$$
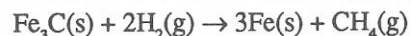
Using [8-3],

$$K_{eq} = P_{CH_4} / P_{H_2}^2 = \exp\left(\frac{-\Delta G_{773}^0}{8.3144 \times 773}\right).$$

From [4-9] and Table A.4,

$$\Delta G_{773}^0 = \Delta G_{773,CH_4}^{0,f} - \Delta G_{773,Fe_3C}^{0,f} = -69,126 + 51.26(773) \times$$

$$\log(773) - 65.36(773) - [26,700 - 24.77(773)]$$

$$= -12,761 \text{ J/mol.}$$

Hence, $K_{eq} = P_{CH_4} / P_{H_2}^2 = \exp\left(\frac{12,761}{8.3144 \times 773}\right)$

$$= \underline{7.283} \text{ (maximum)}$$

At $P_T = 1$ atm, simultaneous solution with $P_{H_2} + P_{CH_4} = 1$, yields

$$P_{CH_4} = 0.692 \text{ atm,}$$

$$P_{H_2} = 0.308 \text{ atm.}$$

[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.

Solution

According to the Fe-Fe$_3$C phase diagram, γ (austenite) transforms to α (ferrite) and Fe_3C (cementite) at the eutectoid temperature (1010 K) when cooling is slow. For quenching and isothermal hold (500°C) described in Exercise Problem [2.3], the problem becomes:

(1) Calculating ΔH_{773}^{Tr} for the $\gamma \rightarrow \alpha$ transformation.

(2) Calculating ΔH° for the reaction $3\overline{Fe} + \overline{C} \rightarrow Fe_3C$ at 773K. Assume that the weight fractions of α and Fe_3C are identical to that calculated by the lever rule at just above 1010 K on the Fe-Fe$_3$C phase diagram. Also assume that the activity of carbon in austenite at the austenitizing temperature will hold at the quenching temperature.

From Exercise Problem [2.3],

$$\Delta H_{773}^{Tr} = -6855 \text{ J/mol for the } \gamma \rightarrow \alpha \text{ transformation.}$$

ΔH_{Fe_3C} is calculated from TL analysis and application of the Gibbs-Helmholtz equation, [4-30]:

(1) Set Up
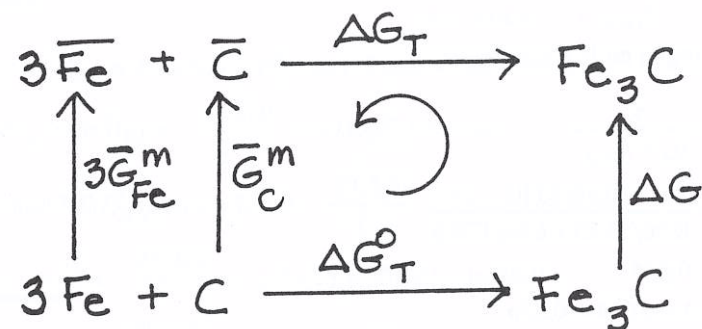
(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_T^0 + \Delta G_1 - \Delta G_T - \overline{G}_C^m - 3\overline{G}_{Fe}^m$$

(3) Substitute

At an austenitizing temperature of 800°C, the activity of carbon in 1050 steel (0.5 w/o C) is $a_c = 0.0273/0.054 = 0.51$, where, from Appendix A.6, $a_c(0.5$ w/o C) = 0.0273 and $a_c(0.876$ w/o C) = 0.054. (The solubility of carbon in austenite at 800°C is 0.876 w/o C.)

From Table A.4,

$$\Delta G_T^0 = 26,700 - 24.77T$$

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

$$\overline{G}_C^m = 8.3144T \ln(0.51) = -5.6T$$

$3\overline{G}_{Fe}^m \approx 0$, $[RT\ln(a_{Fe}) \approx 0$ as $X_{Fe} \rightarrow 1]$

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

$$0 = 26,700 - 24.77T - \Delta G_T + 5.6T$$

(4) Solve

$$\Delta G_T = 26,700 - 19.17T$$

Substituting into [4-30],

$$\frac{\partial(26,700 - 19.17T)/T}{\partial T} = \frac{-\Delta H_T}{T^2}$$

$$\frac{-26,700}{T^2} = \frac{-\Delta H_T}{T^2}$$

$$\Delta H_T = 26,700 \text{ J/mol.}$$

(The same result can be obtained directly from the ΔG expression). Using the lever rule, the mass fractions of α and Fe_3C are:

$$f_\alpha = \frac{0.77 - 0.5}{0.77 - 0.02} = 0.36$$

$$f_{Fe_3C} = 1 - 0.36 = 0.64$$

Converting to mole fraction,

$$X_\alpha = \frac{n_\alpha}{\eta_\alpha + n_{Fe_3C}}$$

$$= \frac{0.36/55.85}{0.36/55.85 + 0.64/179.6}$$

$$= 0.644$$

$$X_{Fe_3C} = 1 - 0.644 = 0.356$$

Summing the respective enthalpy contributions:
$$\Delta H_{TOTAL} = 0.644(-6855) + 0.356(26,700)$$
$$= \underline{5091 \text{ J/mol}}.$$
The data suggests that heat absorption due to carbide formation is dominant.

[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?
   (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.

Solution

(a) From Example Problem 5-4,
$$P_{H_2S}/P_{H_2} = \underline{5 \times 10^{-5}}$$
(b) 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
$$\ln(P_{Cu}^l)(\text{atm}) = -40,349/T - 1.21\ln(T) + 23.79.$$

Solution

Using $\ln(P_{Cu}^l) = 2.303\log_{10}(P_{Cu}^l)$ and 1 atm = 760 mm Hg:

$$\log(P_{Cu}^l)(\text{mm Hg}) = \frac{-17,520}{T} - 1.21\log(T) + 13.21$$

$$2.303\log[760\, P_{Cu}^l (\text{atm})] = 2.303\left[\frac{-17,520}{T} - 1.21\log(T) + 13.21\right]$$

$$\underline{\ln\left[P_{Cu}^l(atm)\right] = \frac{-40,349}{T} - 1.21\ln(T) + 30.423 - \ln(760)}$$

$$= \frac{-40,349}{T} - 1.21\ln(T) + 23.79.$$

[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 means square treatment to derive the expression:
$$\Delta G_{Mo_2C}^{0,f} \text{ (J/mol)} = -68,270 + 8.23T$$
   where 1173 K $\leq T \leq$ 1573 K.
   (c) What assumption is implied but not directly mentioned in the article?

Solution

(a) Column 3
$$\Delta G° = -RT\ln(K) = RT\ln(P_{CH_4}/P_{H_2}^2)$$
$$= 8.3144(1173)\ln(47.4 \times 10^{-6})$$
$$= \underline{-97,107 \text{ J/mol}} \text{ (check)}$$

Column 4
From Table A.4,
$$\Delta G_{CH_4}^{0,f} = -69,126 + 51.26T\log(T) - 65.36T$$
$$= -69,126 + 51.26(1173)\log(1173) - 65.36(1173)$$
$$= \underline{38,757 \text{ J/mol}} \text{ (check)}$$

Column 5

1) $2Mo + C \rightarrow MO_2C$

2) $2H_2 + C \rightarrow CH_4$

$(1) - (2) = (3)$

(3) $2Mo + CH_4 \rightarrow Mo_2C + 2H_2$

or $(1) = (3) + (2) = $ col. 4 + col. 3

$= 38{,}790 + (-97{,}000)$

$= -58{,}210$ J/mol (check)

(b) Assume LMS linear correlation (see Fig. 2):

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

where $1173 \leq T \leq 1573$K

(c) $\Delta C_p \approx 0$.

[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 $\Delta C_p = 0$?

Solution

(a) $M(s) \rightarrow M(g)$

$$\frac{dP}{P} = \frac{\Delta H^v dT}{RT^2}$$

Substituting [2-20] into [7-20] and integrating,

$$\int \frac{dP}{P} = \frac{1}{R} \int \left[\frac{\Delta H^0_{T_1} + a(T - T_1)}{T^2} \right] dT$$

$$\ln(P) = \frac{-\Delta H^0_{T_1}}{RT} + \frac{aT_1}{RT} + \frac{a\ln(T)}{R} + I$$

where I is an integration constant. Hence, $\log_{10}(P) = AT^{-1} + B\log_{10}(T) + D$,

where $C = 0$.

(b) Substituting [2-19] into [7-20] and integrating,

$$\int \frac{dP}{P} = \frac{1}{R} \int \frac{\Delta H^0_{T_1}}{T^2} dT$$

$$\ln(P) = \frac{-\Delta H^0_{T_1}}{RT} + I$$

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

[8.8] Confirm that hydrogen dissolved in Ti(α) 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

Solution

From Sievert's Law, [6-72b], calculate k for each composition. Reasonable agreement of k values would confirm Seivert behavior.
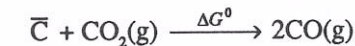
$$k_1 = \frac{235}{\left(5.263 \times 10^{-5}\right)^{1/2}} = 3.239 \times 10^4 \text{ ppm} \cdot \text{atm}^{-1/2}$$

$$k_2 = \frac{750}{\left(5.263 \times 10^{-4}\right)^{1/2}} = 3.269 \times 10^4$$

$$k_3 = \frac{1705}{\left(2.632 \times 10^{-3}\right)^{1/2}} = 3.323 \times 10^4$$

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.

Solution

$$\bar{C} + CO_2(g) \xrightarrow{\Delta G^0} 2CO(g)$$

$$\Delta G^0_{1173} \text{ (J/mol)} = 2\Delta G^{0,f}_{CO} - \Delta G^{0,f}_{CO_2} = -8.3144(1173)\ln(K_{eq})$$

From Table A.4,

$$\Delta G^0_{1173} = 2[-111{,}720 - 87.66(1173)] - [-394{,}170 - 0.84(1173)]$$

$$= -33{,}935 = -8.3144(1173)\ln\left(\frac{P^2_{CO}}{a_C P_{CO_2}}\right)$$

From Table A.6,

0.8 w/o C $\Rightarrow$ $a_c = 0.048/0.0803 = 0.60$

Substituting into the expression for $\Delta G^0_{1;73}$ and solving for the gas ratio,

$$P^2_{CO}/P_{CO_2} = 19,466$$

Assuming $P_{CO} + P_{CO_2} = 1$ atm,

$$P^2_{CO} = 19.466(1 - P_{CO})$$

$$P^2_{CO} + 19.466\,P_{CO} - 19.466 = 0$$

$$\left. \begin{array}{l} P_{CO} = 0.953 \text{ atm} \\ P_{CO_2} = 0.047 \text{ atm} \end{array} \right\} P^2_{CO}/P_{CO_2} \approx 19.466 \text{ (check)}$$

Note: Excess CO_2 ($P_{CO_2} > 0.047$ atm) drives the reaction from left to right, hence CO_2 is decarburizing.

[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 $s^0 = 1$ cm³/100 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^0_s.

Solution

From [6-72a] in Example Problem 6-9,

$$\log\left(C_H/C^0_H\right) - 1/2\,\log(P_{H_2}) = -\frac{\Delta H^0_S}{2.303RT} + \frac{\Delta S^0_S}{2.303R}$$

Comparing expressions,

Pure Al: $\dfrac{-\Delta H^0_S}{2.303(8.3144)T} = -2700/T$

$$\Delta H^0_S = 2700 \times 2.303(8.3144)$$
$$= 51,700 \text{ J/½ mole } H_2$$
$$= 103,400 \text{ J/mol } H_2$$

Al-1 pct Li: $\Delta H^0_S = 2113 \times 2.303(8.3144)(2)$
$$= 80,920 \text{ J/mol } H_2$$

Al-2 pct Li: $\Delta H^0_S = 2797 \times 2.303(8.3144)(2)$
$$= 107,114 \text{ J/mol } H_2$$

Al-3 pct Li: $\Delta H^0_S = 2889 \times 2.303(8.3144)(2)$
$$= 110,638 \text{ J/mol } H_2.$$

Pct Li	ΔH^0_s (J/mol H_2)
0	103,400
1	80,920
2	107,114
3	110,638

[8.11] Referring to Exercise Problem [8.10], the dissociation of molecular hydrogen in liquid aluminum alloys is a two step process involving: (1) Dissociation of diatomic hydrogen into monatomic hydrogen and (2) Solution of atomic hydrogen in the metal. Using enthalpy data for the Al-1 pct Li alloy, calculate ΔH for step 2 if for step 1, $\Delta H_{Ave.} = 419,500$ J/mol H_2. ΔH_{Ave}, defined as the enthalpy of dissociation of diatomic hydrogen, is effectively constant over the temperature range of interest. ΔH is the solute binding enthalpy for solution of monatomic hydrogen in the metal.

Solution

(1) Set Up
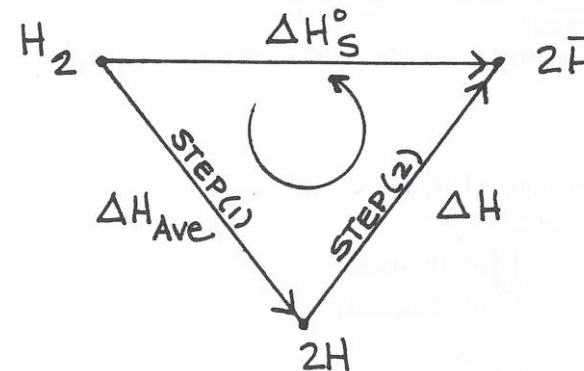
(2) <u>Sum</u>

$$\sum \Delta H_{TL} = 0 = \Delta H_{Ave} + \Delta H - \Delta H_S^0$$

(3) <u>Substitute</u>

$\Delta H_{Ave} = 419{,}500$ J/mol H_2

$\Delta H_S^0 = 80{,}920$ J/mol H_2

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

$0 = 419{,}500 + \Delta H - 80{,}920$

(4) <u>Solve</u>

$\Delta H = -338{,}580$ J/mol H_2

$\quad = -169{,}290$ J/gm atom H.

[8.12] Determine K_{eq} as a function of temperature for the reaction in Exercise Problem [4.22].

<u>Solution</u>

From [8-3], $\Delta G_T^0 = -RT\ln(K_{eq})$ at equilibrium.

Hence, $K_{eq} = \exp\left(\dfrac{-\Delta G_T^0}{RT}\right)$

Substituting the ideal gas constant R = 8.3144 J/(mol·K) and ΔG_T^0 from Exercise Problem [4.22],

$K_{eq} = \exp(-455.96 \times 10^{-9}T^2 + 8.46 \times 10^{-3}T - 2102.14 \times T^{-0.5} - 6399.74T^{-1}$

$\quad - 295.92 \times 10^3 T^{-2} - 28.65\ln(T) + 240.59)$ where $T = T(K)$.

[8.13] Referring to Exercise Problem [5.17]:
   (a) What is the equilibrium constant for the reaction?
   (b) In which direction will the reaction shift if *Ja* increases? If *Ja* decreases?
   (c) What would cause the equilibrium constant to change?

<u>Solution</u>
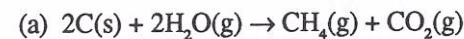
(a) $2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g)$
   From [8-2] with $Ja = K_{eq}$,

$$K_{eq} = \frac{\prod a_i^{n_i} \ (\text{Products})}{\prod a_i^{n_i} \ (\text{Reactants})} \quad \text{Hence,}$$

$$K_{eq} = \frac{P_{CO_2} \cdot P_{CH_4}}{a_C^2 \cdot P_{H_2O}^2} = 0.21$$

(b) According to LeChatelier's Principle,

If <u>Ja increases</u>, the reaction shifts to the <u>left</u> until equilibrium is reestablished $(Ja = K_{eq})$.

If <u>Ja decreases</u>, the reaction shifts to the <u>right</u> until equilibrium is reestablished $(Ja = K_{eq})$.

(c) The equilibrium constant would change in response to a <u>change in temperature</u>.