

## Chapter 5

[5.1] An ideal gas mixture at pressure  $P_{\text{Total}}$  contains a gas component  $i$  of atomic fraction  $Y_i$ . Show

$$G_i - G_i^0 = RT[\ln(P_{\text{Total}}) + \ln(Y_i)].$$

Solution

$$\begin{aligned} \text{From [5-6], } G_i - G_i^0 &= RT \ln(Y_i P_i) \\ &= RT[\ln Y_i + \ln P_{\text{Total}}]. \end{aligned}$$

[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

$$\Delta G_i = RT \ln(P_{2,\text{Total}}/P_{1,\text{Total}}).$$

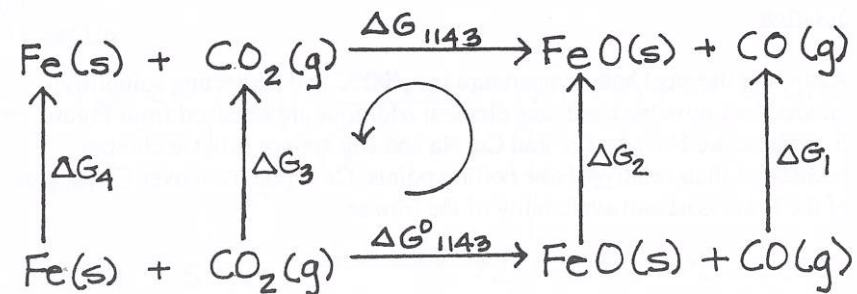
Solution

$$\begin{aligned} \Delta G_i &= RT \ln(Y_i P_2) - RT \ln(Y_i P_1) \\ &= RT \ln \left( \frac{Y_i P_2}{Y_i P_1} \right) \\ &= RT \ln \left( \frac{P_2}{P_1} \right). \end{aligned}$$

[5.3] During carburization processing of steel at 870°C in a mixture of CO and CO<sub>2</sub>, surface oxidation of iron may prevent penetration of carbon if  $P_{\text{CO}_2}$  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.

Solution

(1) Set Up



(2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_{1143}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{1143} - \Delta G_3 - \Delta G_4$$

$$\Delta G_3 - \Delta G_1 = \Delta G_{1143}^0 + \Delta G_2 - \Delta G_{1143} - \Delta G_4$$

(3) Substitute

$$\Delta G_{1143} = 0 \text{ at equilibrium}$$

$$\Delta G_2 = \Delta G_4 = 0 \text{ for pure condensed phases}$$

$$\Delta G_3 = RT \ln(P_{CO_2})$$

$$\Delta G_1 = RT \ln(P_{CO})$$

Substituting into the above,

$$\Delta G_{1143}^0 = RT \ln(P_{CO_2}/P_{CO})$$

$$\begin{aligned} \text{From Table A.4, } \Delta G_{1143}^0 &= \Delta G_{CO}^0 + \Delta G_{FeO}^0 - \Delta G_{CO_2}^0 \\ &= -111,723 - 87.66(1173) + [-259,600 + 62.55(1173)] - [-394,170 - 0.84(1173)] \\ &= -5622 \end{aligned}$$

$$\begin{aligned} \therefore \ln(P_{CO}/P_{CO_2}) &= 5622/[8.3144(1173)] \\ &= 0.576 \end{aligned}$$

(4) Solve

$$P_{CO}/P_{CO_2} = \underline{1.78} \text{ (compared to } \approx 2.0 \text{ from Figure E.2)}$$

If  $P_{CO}/P_{CO_2} \approx 10.0$  for example, then  $\Delta G_{1143} = 22,461 - 5622 = 16,839$  which is deoxidizing. The ratio should be held at or above 1.78.

[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.

Solution

Assuming the steel bath temperature is 1,400°C and neglecting solubility effects, four possible candidate element additions are obtained from Figure E.3. These are Na, Mg, Ca, and Ce. Na and Mg are not suitable choices because of their relatively low boiling points. Ca is preferred over Ce because of the lower cost and availability of the former.

[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  $\Delta G^0$  at 800 K.

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

Solution

$$\begin{aligned} \text{(a) } \Delta G_{800}^0 &= -47,000 + 12.4(800) \ln(800) - 11.36 \times 10^3 \\ &\quad \times (800)^2 + 0.54 \times 10^4 (800)^{-1} - 37.8(800) \\ &= -18,192 \text{ cal/mol } Li_3N \\ &\approx \underline{\underline{-76,120 \text{ J/mol}}} \end{aligned}$$

$$\begin{aligned} \text{(b) } \Delta G_{800}^0 &= -200,100 + 154.5(800) \\ &= \underline{\underline{-76,500 \text{ J/mol}}} \end{aligned}$$

The comparison is good considering the extrapolation of the expression in Example Problem 5-5.

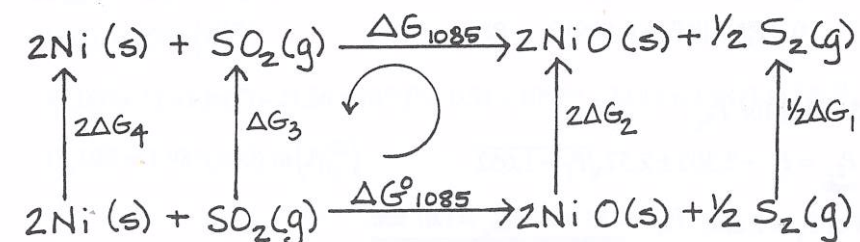
[5.6] It is proposed that a nickel-based alloy (assume pure Ni for this problem) be used in a structural application involving contact with  $SO_2$ .

- 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.
- 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  $P_T = 2$  atm.
- What is the significance of the increase in total pressure on oxidation?

Solution

(a)

(1) Set Up



(2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_{1085}^0 + 1/2 \Delta G_1 + 2 \Delta G_2 - \Delta G_{1085} - \Delta G_3 - 2 \Delta G_4$$

(3) Substitute

$$\Delta G_{1085}^0 = 2 \Delta G_{NiO}^{o,f} - \Delta G_{SO_2}^{o,f}$$

$$= 2(-244,580) + 98.54(1085)(2) - \left[ -\frac{724,910}{2} + \frac{144.9}{2}(1085) \right]$$

$$= 8519 \text{ J/mol}$$

$$1/2 \Delta G_1 = R(1085) \ln(P_{S_2}^{1/2})$$

$$2 \Delta G_2 = 2 \Delta G_4 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{1085} = 0 \text{ (equilibrium)}$$

$$\Delta G_3 = R(1085) \ln(P_{SO_2})$$

$$\sum \Delta G_{TL} = 0 = 8519 + 9021 \ln(P_{S_2}^{1/2}) - 9021 \ln(P_{SO_2}) - 8519$$

$$= 9021 \ln(P_{S_2}^{1/2} / P_{SO_2})$$

(4) Solve

$$P_{S_2}^{1/2} / P_{SO_2} = 0.389$$

$$\text{Using } P_{S_2} + P_{SO_2} = 1,$$

$$P_{S_2} = 0.1513(1 - 2P_{S_2} + P_{S_2}^2)$$

$$0 = P_{S_2}^2 - 8.609P_{S_2} + 1$$

$$P_{S_2} = \frac{8.609 \pm \sqrt{74.115 - 4}}{2}$$

$$P_{S_2} = \underline{0.12 \text{ atm}};$$

$$P_{SO_2} = \underline{0.88 \text{ atm}}.$$

$$(b) P_{S_2} = 0.1513(P_T - P_{S_2})^2$$

$$0 = P_{S_2}^2 - (2P_T + 6.609)P_{S_2} + P_T^2$$

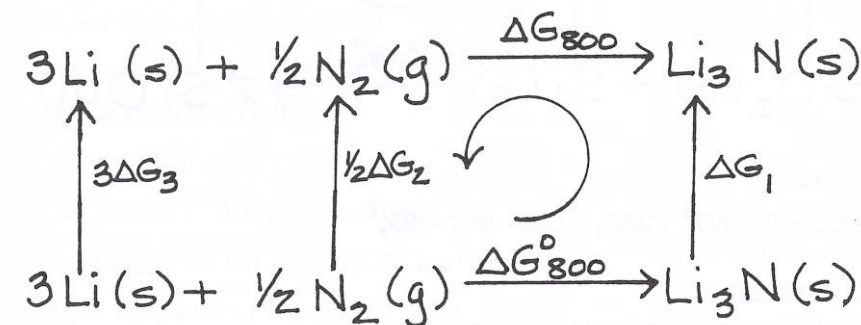
Solving for  $P_{S_2}$ ,

$$\underline{P_{S_2} = P_T + 3.305 \pm 2.57\sqrt{P_T + 1.652}}$$

$$\text{For } P_T = 2 \text{ atm: } P_{S_2} = \underline{0.39 \text{ atm}}; P_{SO_2} = \underline{1.61 \text{ atm}}.$$

(c) As  $P_{\text{Total}}$  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.

Solution(1) Set Up(2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_{800}^0 + \Delta G_1 - \Delta G_{800} - 1/2 \Delta G_2 - 3 \Delta G_3$$

(3) Substitute

$$\Delta G_1 = 3 \Delta G_3 = 0 \text{ (assume all condensed phases are pure)}$$

$$\Delta G_{800} = 0 \text{ (equilibrium)}$$

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

$$-47,000 + 12.4T \ln(T) - 11.36 \times 10^{-3} T^2 + 0.54 \times 10^4 T^{-1} - 37.8T = 1.987T \ln(P_{N_2}^{1/2})$$

$$-18,192 = 1.987(800) \ln(P_{N_2}^{1/2})$$

## (4) Solve

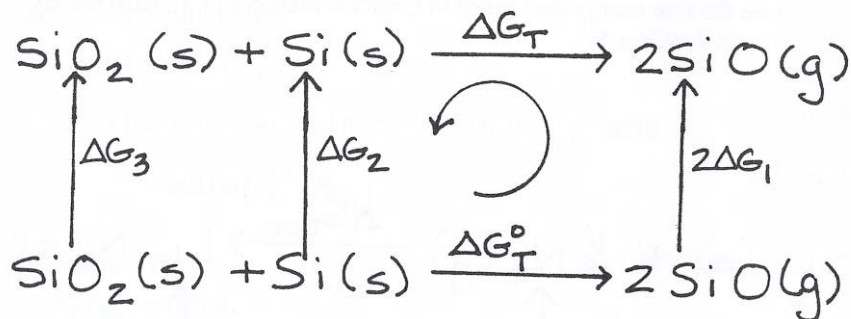
$$P_{N_2} = 1.15 \times 10^{-10} \text{ atm.}$$

Since 0.005 v/o (volume percent) is equivalent to  $5 \times 10^{-5}$  atm, tri-lithium nitride will form under experimental conditions.

[5.8] Estimate the temperature at which  $\text{SiO}_2$  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).

Solution

## (1) Set Up



## (2) Sum

$$\Sigma G_{TL} = 0 = \Delta G_T^0 + 2\Delta G_1 - \Delta G_T - \Delta G_2 - \Delta G_3$$

## (3) Substitute

$$\Delta G_T^0 = 697,540 + 53.98T \log(T) - 518.45T$$

$$2\Delta G_1 = 8.3144T \ln(P_{\text{SiO}}^2)$$

$$\Delta G_2 = \Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

$$0 = 697,540 + 53.98T \log(T) - 518.45T + 8.3144T \ln(0.001)^2$$

## (4) Solve

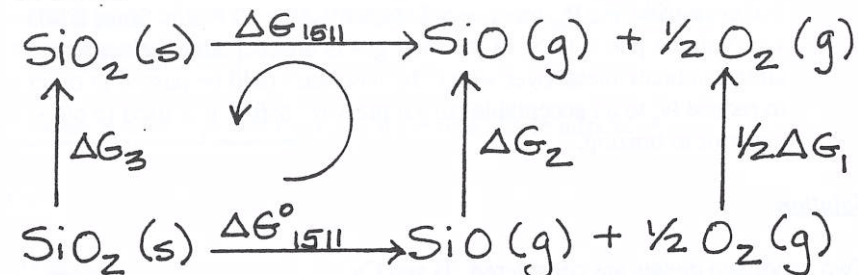
$$T \approx \underline{1511 \text{ K.}}$$

[5.9] In Exercise Problem [5.8], it is shown that the best vacuum obtainable is  $10^{-3}$  atm at 1511 K when impure  $\text{SiO}_2$  (containing excess Si) is used as containment for heat treatment, annealing, etc. Determine the best vacuum obtainable when stoichiometrically pure  $\text{SiO}_2$  is used for containment at the same temperature.

Solution

Using direct dissociation of  $\text{SiO}_2$ :

## (1) Set Up



## (2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{1511}^0 + 1/2\Delta G_1 + \Delta G_2 - \Delta G_{1511} - \Delta G_3$$

## (3) Substitute

$$\Delta G_{1511} = 0 \text{ (equilibrium)}$$

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

$$1/2\Delta G_1 = 8.3144(1511) \ln(P_{\text{O}_2}^{1/2})$$

$$\Delta G_2 = 8.3144(1511) \ln(P_{\text{SiO}})$$

$$\Delta G_{1511}^0 = \Delta G_{1511, \text{SiO}(g)}^{0,f} - \Delta G_{1511, \text{SiO}_2(s)}^{0,f}$$

$$\text{From Table A.4, } \Delta G_{T, \text{SiO}(g)}^{0,f} = -91,848 + 20.72T \log(T) - 150T$$

$$\text{and } \Delta G_{T, \text{SiO}_2(s)}^{0,f} = -881,235 - 12.55T \log(T) + 218.51T$$

$$\Delta G_T^0 = 789,387 + 33.27T \log(T) - 368.51T$$

$$\Delta G_{1511}^0 = 789,387 + 159,825 - 556,819 = 392,393 \text{ J/mol}$$

## (4) Solve

$$0 = 392,393 + 1511(8.3144) \ln(P_{\text{O}_2}^{1/2} \cdot P_{\text{SiO}})$$

$$P_{\text{SiO}} P_{\text{O}_2}^{1/2} = 2.72 \times 10^{-14}$$

$$\text{Since } P_{\text{O}_2} = 1/2 P_{\text{SiO}},$$

$$P_{\text{SiO}} = 1.14 \times 10^{-9} \text{ atm}$$

$$P_{\text{O}_2} = 5.7 \times 10^{-10} \text{ atm}$$

$$P_T = P_{\text{SiO}(g)} + P_{\text{O}_2(g)} = \underline{1.71 \times 10^{-9} \text{ atm}}$$

Comment: Comparing the results from Exercise Problems [5.8] and [5.9], high purity  $\text{SiO}_2$  would allow for a six order of magnitude improvement in vacuum.

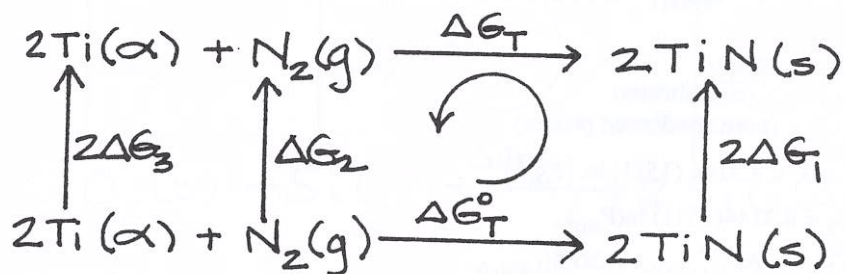
[5.10] Refer to Exercise Problem [5.7]. In order to limit the formation of tri-lithium nitride, the  $P_{\text{N}_2}$  must be held below  $1.15 \times 10^{-10}$  atm. Since 0.005 v/o (volume percent)  $\text{N}_2$  in the inert gas is unacceptable, select a possible candidate metal over which the inert gas could be passed in order to reduce  $\text{N}_2$  to an acceptable partial pressure before it is used to purge air prior to brazing.

### Solution

Two candidate metals are considered: Ti and Ca.

#### Ti ( $\alpha$ )

(1) Set Up



(2) Sum

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

(3) Substitute

$$2\Delta G_1 = 2\Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

$$\Delta G_2 = 8.3144T \ln(1.15 \times 10^{-10})$$

From Table A.4,

$$\Delta G_T^0 = -671,600 + 185.8T$$

$$0 = -671,600 + 185.8T - 8.3144T \ln(1.15 \times 10^{-10})$$

(4) Solve

$$T = \frac{671,600}{376.08} = 1786 \text{ K}$$

Note: the temperature  $T = 1786 \text{ K}$  is above the transformation  $\text{Ti}(\alpha) \rightarrow \text{Ti}(\beta)$ . Hence, from Table A.4:

#### Ti ( $\beta$ )

$$\Delta G_T^0 = -676,620 + 190.20T$$

$$0 = -676,620 + 190.20T - 8.3144T \ln(1.15 \times 10^{-10}) \Rightarrow T = 1778 \text{ K}$$

$T = 1778 \text{ K}$  is above  $1500 \text{ K}$  given in Table A.4 for applicability of the data.

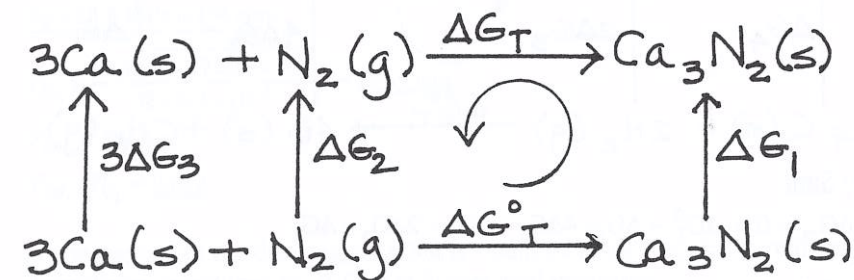
However, the  $\text{N}_2 - \text{Ti}$  phase diagram shows that the  $\beta$  phase is stable up to the melting point of  $1945 \text{ K}$  (according to Table A.2,  $T_{\text{Ti}(\beta)}^f = 1933 \text{ K}$ ). Hence,

Ti ( $\beta$ ) is one possibility

Calcium is another possibility, since it forms a stable nitride:

#### Ca

(1) Set up



(2) Sum

$$\sum \Delta G_{\text{TL}} = 0 = \Delta G_T^0 + \Delta G_1 - \Delta G_T - \Delta G_2 - 3\Delta G_3$$

(3) Substitute

$$\Delta G_1 = 3\Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

$$\Delta G_2 = RT \ln(1.15 \times 10^{-10})$$

From Table A.4,

$$\Delta G_T^0 = -439,360 + 209.2T$$

$$0 = -439,360 + 209.2T - 8.3144T \ln(1.15 \times 10^{-10})$$

(4) Solve

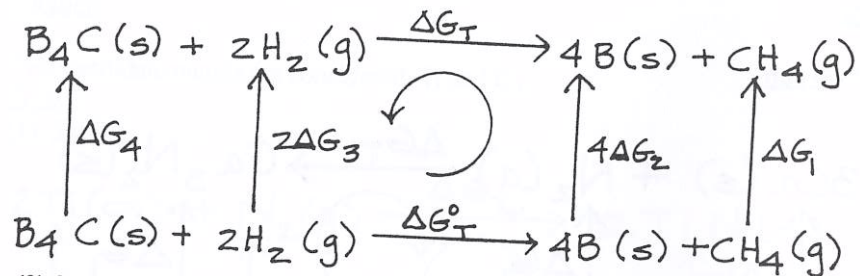
$$T = \frac{439,360}{399.48} = 1100 \text{ K}$$

Note: The required temperature of  $1100 \text{ K}$  is just below the melting point ( $1123 \text{ K}$ ) of calcium, hence Ti ( $\beta$ ) is the better choice.

[5.11] According to Kane and Chakachery (1992), possible coating materials for carbon/carbon composites include oxidation resistant SiC and Si<sub>3</sub>N<sub>4</sub> 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<sub>4</sub>C and H<sub>2</sub> 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.

### Solution

#### (1) Set Up



#### (2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_T^0 + \Delta G_1 + 4\Delta G_2 - \Delta G_T - 2\Delta G_3 - \Delta G_4$$

#### (3) Substitute

$$4\Delta G_2 = \Delta G_4 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

$$\Delta G_1 = 8.3144 (1088) \ln(P_{\text{CH}_4})$$

$$2\Delta G_3 = 8.3144 (1088) \ln(P_{\text{H}_2}^2)$$

$$\Delta G_T^0 = \Delta G_{T,\text{CH}_4}^{0,f} - \Delta G_{T,\text{B}_4\text{C}}^{0,f} \text{ From Table A.4,}$$

$$\Delta G_{T,\text{CH}_4}^{0,f} = -69,126 + 51.26T \log(T) - 65.36T.$$

$$\Delta G_{T,\text{B}_4\text{C}}^{0,f} = \Delta H_{298,\text{B}_4\text{C}}^{0,f} - T\Delta S_{298,\text{B}_4\text{C}}^{0,f} \text{, assuming } \Delta C_p \approx 0.$$

$$\begin{aligned}
 \Delta G_{T,\text{B}_4\text{C}}^{0,f} &= -57,700 - T(S_{298,\text{B}_4\text{C}}^0 - S_{298,\text{C}}^0 - 4S_{298,\text{B}}^0) = -57,700 - T[27.07 - \\
 &\quad 5.69 - 4(5.86)] \\
 &= -57,700 + 2.06T.
 \end{aligned}$$

$$\Delta G_T^0 = -69,126 + 51.26T \log(T) - 65.36T - (-57,700 + 2.06T).$$

$$\Delta G_{1088}^0 = 84,577 \text{ J/mol}$$

$$84,577 = -8.3144(1088) \ln(P_{\text{CH}_4}/P_{\text{H}_2}^2)$$

#### (4) Solve

$P_{\text{CH}_4}/P_{\text{H}_2}^2 = 8.7 \times 10^{-5}$ . Assuming  $P_{\text{H}_2} + P_{\text{CH}_4} = P_T$  and substituting from above:

$$P_{\text{H}_2} + 8.7 \times 10^{-5} P_{\text{H}_2}^2 - P_T = 0$$

$$P_T = 0.03 \text{ MPa} = 0.3 \text{ atm.}$$

$$P_{\text{H}_2} = \frac{-1 \pm \sqrt{1 + 10.44 \times 10^{-5}}}{2 \times 8.7 \times 10^{-5}} \approx \underline{0.2999 \text{ atm}}$$

$$P_{\text{CH}_4} \approx \underline{0.0001 \text{ atm}}$$

$$P_{\text{CH}_4}/P_{\text{H}_2} \approx \underline{0.0003}$$

$$P_T = 13.8 \text{ MPa} = 136 \text{ atm}$$

$$P_{\text{H}_2} = \frac{-1 \pm \sqrt{1 + 47.328 \times 10^{-3}}}{2 \times 8.7 \times 10^{-5}} \approx \underline{134.4 \text{ atm}}$$

$$P_{\text{CH}_4} \approx \underline{1.6 \text{ atm}}$$

$$P_{\text{CH}_4}/P_{\text{H}_2} \approx \underline{0.012}$$

A comparison of the data suggests that it would be more practical to maintain deoxidizing conditions for B<sub>4</sub>C(s) at higher total pressures.

[5.12] Calculate the *maximum* allowable  $P_{\text{CO}_2}$  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 any assumptions used in the calculation.

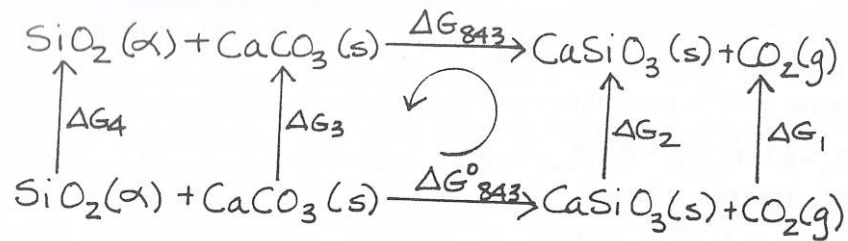
### Solution

From Example Problem [3.12], the reaction is  
 $\text{SiO}_2(\alpha) + \text{CaCO}_3(s) \rightarrow \text{CaSiO}_3(s) + \text{CO}_2(g)$

$$\Delta S_{298}^0 = 165.65 \text{ J/(mol}\cdot\text{K)}$$

$$\Delta H_{298}^0 = -393.51 - 1635.22 - (-910.70 - 1206.7) = 88,670 \text{ J/mol.}$$

$$\Delta G_T^0 = 88,670 - 165.65T, \text{ assuming } \Delta C_p \approx 0.$$

(1) Set Up

 (2) Sum

$$\Sigma \Delta G_{\text{TL}} = 0 = \Delta G_{843}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{843} - \Delta G_3 - \Delta G_4$$

 (3) Substitute

$$\Delta G_{843}^0 = 88,670 - 165.65(843) = -50,973 \text{ J/mol}$$

$$\Delta G_2 = \Delta G_3 = \Delta G_4 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{843} = 0 \text{ (equilibrium)}$$

$$\Delta G_1 = 8.3144(843) \ln(P_{\text{CO}_2})$$

$$0 = -50,973 + 8.3144(843) \ln(P_{\text{CO}_2})$$

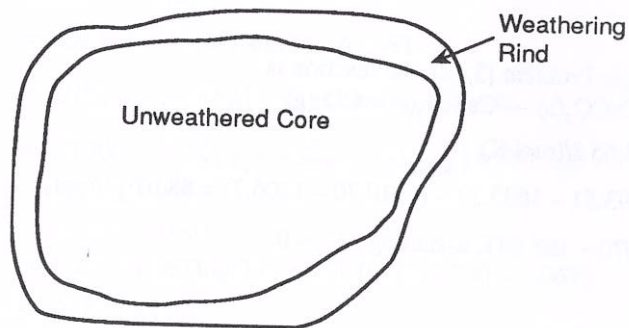
 (4) Solve

$$\ln(P_{\text{CO}_2}) = 50,973 / [8.3144(843)]$$

$$P_{\text{CO}_2} = \underline{1440 \text{ atm}}$$

Assumptions  $\Delta C_p = 0$ , 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.

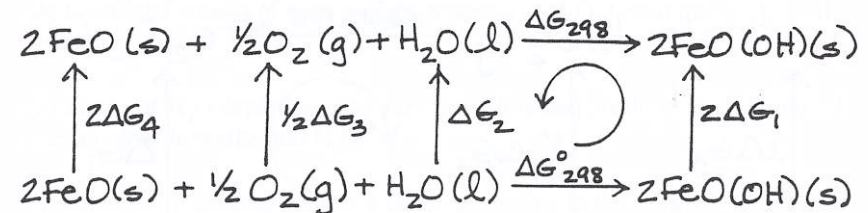


$\text{FeO}(s)$ , one of the initial chemical weathering products of Fe-rich minerals, frequently undergoes a combination of oxidation and hydration to produce the orthorhombic mineral goethite,  $\text{FeO}(\text{OH})$ . Goethite, a commercial source of iron, imparts a yellow-brown color to weathering 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.  
 (b) What assumption, if any, about the stability of goethite is inherent in the result from (a)?

Solution

(a)

 (1) Set Up

 (2) Sum

$$\Sigma \Delta G_{\text{TL}} = 0 = \Delta G_{298}^0 + 2\Delta G_1 - \Delta G_{298} - \Delta G_2 - 1/2\Delta G_3 - 2\Delta G_4$$

 (3) Substitute

$$2\Delta G_1 = \Delta G_2 = 2\Delta G_4 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{298} = 0 \text{ (equilibrium)}$$

$$1/2\Delta G_3 = 1/2RT \ln(P_{\text{O}_2}) = 1/2(8.3144)(298) \ln(P_{\text{O}_2})$$

$$\Delta G_{298}^0 = \Sigma n\Delta G_{298}^{0,f}(\text{Products}) - \Sigma n\Delta G_{298}^{0,f}(\text{Reactants})$$

From Tables A.1 and A.4,

$$\Delta G_{298}^0 = -239,706 \text{ J/mol.}$$

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

$$0 = -239,706 - 1/2(8.3144)(298) \ln(P_{\text{O}_2})$$

 (4) Solve

$$\ln(P_{\text{O}_2}) = \frac{239,706}{-0.5(8.3144)(298)}$$

$P_{\text{O}_2} = \underline{10^{-84} \text{ atm.}} \Rightarrow$  goethite is stable in air at the surface where  $P_{\text{O}_2} \approx 0.22 \text{ atm.}$

(b) 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.

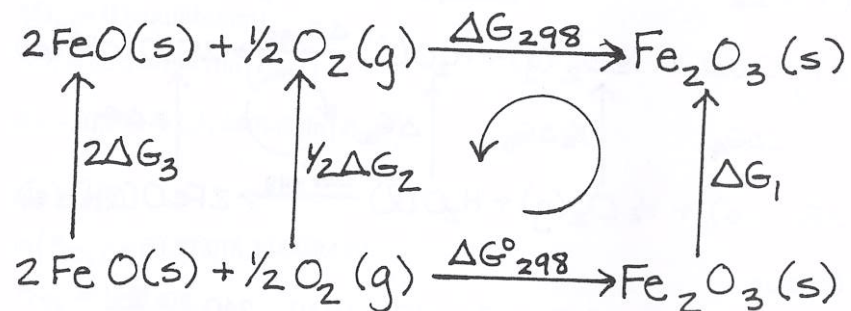
(a) Calculate the minimum  $P_{O_2(g)}$  required to form and stabilize hematite at 298 K.

(b) Discuss the significance of (a) with respect to the  $P_{O_2(g)}$  in air and the stability of hematite at the surface of the earth.

Solution

(a)

(1) Set Up



(2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_{298}^0 + \Delta G_1 - \Delta G_{298} - 1/2 \Delta G_2 - 2 \Delta G_3$$

(3) Substitute

$$\Delta G_1 = 2 \Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{298} = 0 \text{ (equilibrium)}$$

$$1/2 \Delta G_2 = 1/2 (8.3144)(298) \ln(P_{O_2})$$

From Tables A.1 and A.4,

$$\Delta G_{298}^0 = -260,395 \text{ J/mol}$$

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

$$0 = -260,395 - 1/2 (8.3144)(298) \ln(P_{O_2})$$

(4) Solve

$$\ln(P_{O_2}) = \frac{260,395}{-0.5(8.3144)(298)}$$

$$\underline{\underline{P_{O_2} = 5 \times 10^{-92} \text{ atm}}}$$

(b) 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.

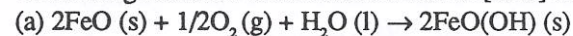
Solution

(1) Localized area(s) of rock remain depleted in  $H_2O$ , hence the mixture of minerals.

(2) Zones of  $H_2O$  depletion may vary over time and promote dissociation of goethite into hematite and  $H_2O$ .

(3) Changes in pH may also be a factor according to the Pourbaix diagram (see Exercise Problem [5.13]).

Combining reactions in Exercise Problems [5.13] and [5.14]:

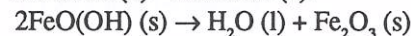


$$\Delta G_{298}^0 = -239,706 \text{ J/mol}$$



$$\Delta G_{298}^0 = -260,395 \text{ J/mol}$$

Reaction (b) - Reaction (a):



$$\Delta G_{298}^0 = -20,689 \text{ J/mol}$$

The above reaction is independent of  $P_{O_2}$  and favors the dissociation of  $FeO(OH)$  into  $Fe_2O_3$  with the release of  $H_2O$ . Regions that promote depletion of  $H_2O$  would favor this reaction since the removal of  $H_2O$  would shift the reaction from left to right.

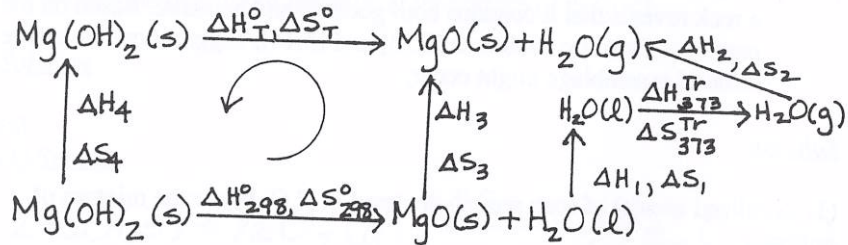


[5.16] Brucite,  $\text{Mg}(\text{OH})_2$ , is slowly heated in an atmosphere where the isobaric partial pressure of  $\text{H}_2\text{O}$  vapor is  $10^{1/2}$  atm. At what temperature will brucite begin to decompose?

Solution

Two TL's are employed in this problem. The first is used to find  $\Delta H_T^\circ$ ,  $\Delta S_T^\circ$ ; hence,  $\Delta G_T^\circ$ . The second is used to find  $P_{\text{H}_2\text{O}}$ .

(1) Set Up



(2) Sum

$$\sum \Delta H_{\text{TL}} = 0 = \Delta H_{298}^0 + \Delta H_1 + \Delta H^{\text{Tr}} + \Delta H_2 + \Delta H_3 - \Delta H_T^0 - \Delta H_4$$

$$\sum \Delta S_{\text{TL}} = 0 = \Delta S_{298}^0 + \Delta S_1 + \Delta S^{\text{Tr}} + \Delta S_2 + \Delta S_3 - \Delta S_T^0 - \Delta S_4$$

(3) Substitute

$$\Delta H_{298}^0 \text{ (J/mol)} = \sum n \Delta H_{298}^{\circ, f} \text{ (Products)} - \sum n \Delta H_{298}^{\circ, f} \text{ (Reactants)}$$

$$= \Delta H_{298}^{\circ, f}(\text{H}_2\text{O}) + \Delta H_{298}^{\circ, f}(\text{MgO}) - \Delta H_{298}^{\circ, f}(\text{Mg}(\text{OH})_2)$$

$$= -285,900 - 601,300 - (-925,500) \Rightarrow$$

$$\Delta H_{298}^0 = 38,300 \text{ J/mol}$$

$$\Delta S_{298}^0 = \sum n S_{298}^0 \text{ (Products)} - \sum n S_{298}^0 \text{ (Reactants)}$$

$$= S_{298}^0(\text{H}_2\text{O}) + S_{298}^0(\text{MgO}) - S_{298}^0(\text{Mg}(\text{OH})_2)$$

$$= 70.09 + 27.41 - 63.00 \Rightarrow$$

$$\Delta S_{298}^0 = 34.50 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta H_{373}^{\text{Tr}} = 41.09 \text{ kJ/mol}, \quad \Delta S_{373}^{\text{Tr}} = \frac{\Delta H^{\text{Tr}}}{T} = \frac{41.09 \text{ kJ/mol}}{373 \text{ K}} \Rightarrow$$

$$\Delta S_{373}^{\text{Tr}} = 110.16 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta H_1 = \int_{298}^{373} (75.44) dT = 5658 \text{ J/mol}$$

$$\Delta H_2 = \int_{373}^T (30.00 + 10.71 \times 10^{-3} T + 0.33 \times 10^5 T^{-2}) dT$$

$$= 30T + 5.36 \times 10^{-3} T^2 - 0.33 \times 10^5 T^{-1} - 11,847$$

$$\Delta H_3 = \int_{298}^T (42.59 + 7.28 \times 10^{-3} T - 6.19 \times 10^5 T^{-2}) dT$$

$$= 42.59T + 3.64 \times 10^{-3} T^2 + 6.19 \times 10^5 T^{-1} - 15,092$$

$$\Delta H_4 = \int_{298}^T (158.40 - 4.076 \times 10^{-3} T - 10.523 \times 10^5 T^{-2} - 1.1713 \times 10^3 T^{-0.5}) dT$$

$$= 158.4T - 2.038 \times 10^{-3} T^2 + 10.523 \times 10^5 T^{-1} - 2.3426 \times 10^3 T^{0.5} - 10,114$$

Using the same  $C_p$  and substituting into the general expression

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

$$\Delta S_1 = 16.94 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta S_2 = 30 \ln(T) + 10.71 \times 10^{-3} T - 16,500 T^{-2} - 182.52$$

$$\Delta S_3 = 42.59 \ln(T) + 7.28 \times 10^{-3} T + 3.1 \times 10^5 T^{-2} - 248.29$$

$$\Delta S_4 = 158.4 \ln(T) - 4.08 \times 10^{-3} T + 5.26 \times 10^5 T^{-2} + 2.34 \times 10^3 T^{-0.5} - 1042.83$$

(4) Solve

Using the summation equations  $\sum \Delta H_{\text{TL}} = 0$  and  $\sum \Delta S_{\text{TL}} = 0$ , the following expressions for  $\Delta H_T^0$  and  $\Delta S_T^0$  are obtained:

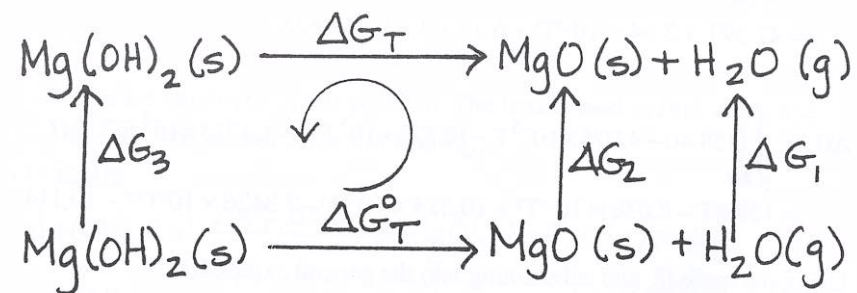
$$\Delta H_T^0 \text{ (J/mol)} = -85.81T + 10.86 \times 10^{-3} T^2 - 466,300 T^{-1} + 2342.6 T^{0.5} + 68,223$$

$$\Delta S_T^0 \text{ [(J/(mol} \cdot \text{K))]} = 22.07 \times 10^{-3} T - 232,500 T^{-2} - 2340 T^{-0.5} - 85.81 \ln(T) + 773.62$$

Substituting into [4-8],

$$\Delta G_T^0 \text{ (J/mol)} = -859.43T - 11.21 \times 10^{-3} T^2 - 233,800 T^{-1} + 4682.6 T^{0.5} + 85.81 T \ln(T) + 68,223$$

Applying the second TL:

(1) Set Up(2) Sum

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

(3) Substitute $\Delta G_T^0$ : Previously calculated

$$\Delta G_1 \text{ (J/mol)} = 8.3144 T \ln(10^{0.5}) = 9.57T$$

$$\Delta G_2 = \Delta G_3 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

Substituting into the summation equation,

$$0 = -859.43T - 11.21 \times 10^{-3}T^2 - 233,800T^{-1} + 4682.6T^{0.5} + 85.81T \ln(T) + 68,233 + 9.57T$$

(4) Solve

$$T = \underline{584 \text{ K}}$$

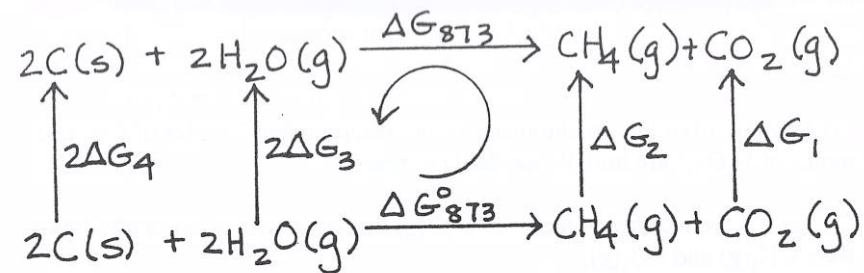
[5.17] Methane is produced when water saturated sedimentary rocks containing graphite are heated to elevated temperatures. Calculate the equilibrium  $P_{\text{CO}_2} \cdot P_{\text{CH}_4} / P_{\text{H}_2\text{O}}^2$  ratio for the reaction

$$2\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}_2(\text{g})$$

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

Solution

Elemental carbon in sedimentary rocks occurs only as grains of graphite or diamond, typically of organic origin. Sedimentary rocks heated to elevated temperatures ( $\approx 600^\circ\text{C}$ ) become textually and sometimes mineralogically transformed into metamorphic rocks.

(1) Set Up(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{873}^0 + \Delta G_1 + \Delta G_2 - \Delta G_{873} - 2\Delta G_3 - 2\Delta G_4$$

(3) Substitute

$$\Delta G_1 = 8.3144(873) \ln(P_{\text{CO}_2})$$

$$\Delta G_2 = 8.3144(873) \ln(P_{\text{CH}_4})$$

$$2\Delta G_3 = 2(8.3144)(873) \ln(P_{\text{H}_2\text{O}})$$

$$2\Delta G_4 = 0 \text{ (pure condensed phase)}$$

$$\Delta G_{873} = 0 \text{ (equilibrium)}$$

$$\Delta G_{873}^0 = \Delta G_{873,\text{CO}_2}^{0,f} + \Delta G_{873,\text{CH}_4}^{0,f} - 2\Delta G_{873,\text{H}_2\text{O}}^{0,f}; \text{ from Table A.4, } \Delta G_{873}^0 = 9511 \text{ J/mol (using } C_p \text{ data from Appendix A and TL analysis, } \Delta G_{873}^0 = 11,328 \text{ J/mol).}$$

Substituting into  $\Sigma \Delta G_{TL} = 0$  and using  $\Delta G_{873}^0 = 11,328$ ,

$$0 = 11,328 + 8.3144(873) \ln(P_{\text{CO}_2}) + 8.3144(873) \ln(P_{\text{CH}_4}) - 2(8.3144)(873) \ln(P_{\text{H}_2\text{O}})$$

(4) Solve

$$P_{\text{CO}_2} \cdot P_{\text{CH}_4} / P_{\text{H}_2\text{O}}^2 = \underline{0.21}$$

Since 2 moles of  $\text{H}_2\text{O}(\text{g})$  react to form 2 moles of gas, the reaction equilibrium is independent of pressure. This can also be shown by substituting the partial pressures into Dalton's law:

$$\frac{\left(\frac{n_{\text{CO}_2}}{n_T} \cdot P_T\right) \left(\frac{n_{\text{CH}_4}}{n_T} \cdot P_T\right)}{\left(\frac{n_{\text{H}_2\text{O}}}{n_T} \cdot P_T\right)^2} = 0.21$$

where  $P_T$  cancels.

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

Solution

(1) Assume, from the stoichiometry of the reaction, that 2 moles of C(s) and 2 moles of  $H_2O(g)$  are initially available to react.

(2) Let  $n$  = the number of moles of  $H_2O(g)$  that react with  $n$  moles of C(s) to form  $CH_4(g)$  and  $CO_2(g)$ .

(3) Gas	$H_2O(g)$	$CH_4(g)$	$CO_2(g)$
Initial Moles	2	0	0
Moles Reacting or Produced	$n$	$0.5n$	$0.5n$
Moles Remaining	$2-n$	$0.5n$	$0.5n$

The total number of moles of gas as a function of  $n$  are  $(2-n) + 0.5n + 0.5n = 2$  (check, initially  $n = 2$ ).

(4) Applying Dalton's law:

$$\left. \begin{aligned} P_{H_2O} &= Y_{H_2O} P_T \\ P_{CH_4} &= Y_{CH_4} P_T \\ P_{CO_2} &= Y_{CO_2} P_T \end{aligned} \right\} \frac{P_{CO_2} P_{CH_4}}{P_{H_2O}^2} = \frac{(n/2)^2}{(2-n)^2} = 0.21$$

Expanding and solving:

$$n^2 + 21n - 21 = 0$$

$$n = \frac{-21 \pm \sqrt{(21)^2 - 4(-21)}}{2} = 0.956$$

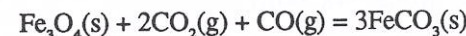
$$\left. \begin{aligned} P_{H_2O} &= \frac{(2-0.956)}{2} \times 2 = \underline{1.044 \text{ atm}}, \\ P_{CH_4} &= \frac{1/2(0.956)}{2} \times 2 = \underline{0.478 \text{ atm}}, \\ P_{CO_2} &= \frac{1/2(0.956)}{2} \times 2 = \underline{0.478 \text{ atm}}. \end{aligned} \right\} P_T = 2 \text{ atm (check)}$$

Note: Since the reaction is pressure independent, the partial pressures increase in direct proportion to total pressure.

[5.19] The mineral siderite,  $FeCO_3$ , 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,  $Fe_3O_4$ , at 300 K in a  $CO_2$ -CO atmosphere containing  $66\frac{2}{3}$  mole percent  $CO_2$ .

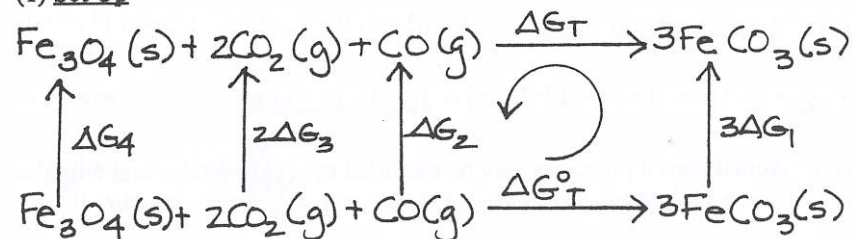
Solution

At equilibrium,



From the stoichiometry of the reaction,  $P_{CO_2} = 2P_{CO}$ .

(1) Set Up



(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_T^0 + 3\Delta G_1 - \Delta G_T - \Delta G_2 - 2\Delta G_3 - \Delta G_4$$

(3) Substitute

From Table A.4,

$$\begin{aligned} \Delta G_T^0 &= -220,915 + 46.94T \text{ from 298-700 K} \\ &= -220,915 + 46.94(300) = -206,833 \text{ J/mol} \end{aligned}$$

$$3\Delta G_1 = \Delta G_4 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_T = 0 \text{ (equilibrium)}$$

$$\Delta G_2 = RT \ln(P_{CO})$$

$$2\Delta G_3 = RT \ln(P_{CO_2}^2)$$

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

$$0 = -206,833 - RT \ln(P_{CO}) - RT \ln(P_{CO_2}^2)$$

(4) Solve

$$\ln(P_{\text{CO}} \cdot P_{\text{CO}_2}^2) = \frac{-206,833}{(8.3144)(300)}$$

$$\text{Since } P_{\text{CO}_2} = 2P_{\text{CO}},$$

$$\ln[P_{\text{CO}} \cdot (2P_{\text{CO}})^2] = \frac{-206,833}{(8.3144)(300)} \text{ or}$$

$$4P_{\text{CO}}^3 = \exp\{-206,833/[(8.3144)(300)]\}$$

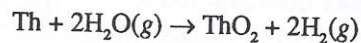
$$\text{Hence, } P_{\text{CO}} = \sqrt[3]{\frac{\exp\{-206,833/[(8.3144)(300)]\}}{4}} \Rightarrow$$

$$P_{\text{CO}} = \underline{6.24 \times 10^{-13} \text{ atm}}$$

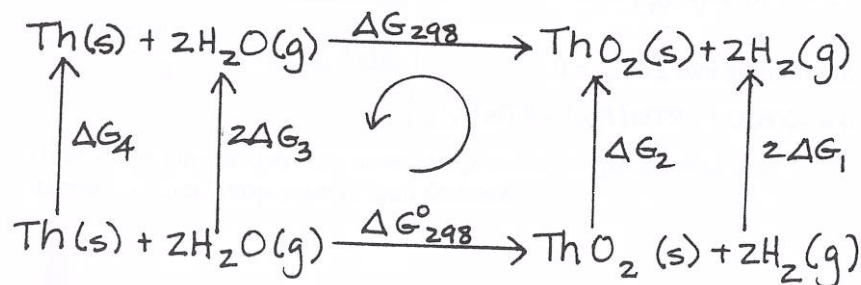
$$P_{\text{CO}_2} = 2P_{\text{CO}} = 2(6.24 \times 10^{-13} \text{ atm}) = \underline{12.48 \times 10^{-13} \text{ atm}}$$

Note: 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):



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

Solution(1) Set Up(2) Sum

$$\Sigma \Delta G_{\text{TL}} = 0 = \Delta G_{298}^0 + 2\Delta G_1 + \Delta G_2 - \Delta G_{298} - 2\Delta G_3 - \Delta G_4$$

(3) Substitute

$$\Delta G_{298}^0 = -171 \text{ kcal/mol (given)}$$

$$2\Delta G_1 = RT \ln(P_{\text{H}_2}^2)$$

$$\Delta G_2 = \Delta G_4 = 0 \text{ (pure condensed phases)}$$

$$\Delta G_{298} = 0 \text{ (equilibrium)}$$

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

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

$$0 = -171,000 + RT \ln(P_{\text{H}_2}^2) - RT \ln(P_{\text{H}_2\text{O}}^2)$$

(4) Solve

$$\ln\left(\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}\right) = \frac{171,000}{2(1.987)(298)}$$

$$\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = 5.1 \times 10^{62} \text{ or } \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \approx 2 \times 10^{-63}$$

It would be impossible from a practical point of view to hold  $P_{\text{H}_2\text{O}}$  sufficiently low to shift the equilibrium from right to left.