or

\[ p_{CO} + 3.346 p_{CO}^2 + 1.624 p_{CO} - 2.019 = 0 \]  \hspace{1cm} (vii)

Eq. (vii) has the solution \( p_{CO} = 0.541 \) atm, and thus the new equilibrium state is

\[ p_{CO} = 0.541 \text{ atm} \]
\[ p_{CO_2} = 0.185 \text{ atm} \]
\[ p_{H_2} = 0.412 \text{ atm} \]
\[ p_{H_2O} = 0.088 \text{ atm} \]
\[ P = 1.226 \text{ atm} \]

Now add excess CaO to the system. The partial pressure of CO\(_2\) in the gas (\( p_{CO_2} = 0.185 \) atm) is greater than the value of 0.053 atm required for equilibrium between CaO, CaCO\(_3\), and CO\(_2\) at 1000 K. Thus the CO\(_2\) reacts with the CaO to form CaCO\(_3\) until, thereby, the partial pressure of CO\(_2\) has been decreased to the equilibrium value of 0.053 atm, and the gas phase equilibrium shifts in order to maintain the C–CO–CO\(_2\) equilibrium. Thus, at the new equilibrium,

\[ p_{CO_2} = 0.053 \text{ atm and } p_{CO} = (1.579 \times 0.053)^{1/2} = 0.289 \text{ atm} \]

Also,

\[ K_{p, \text{eq}, 1000 K} = 0.618 = \frac{0.289 p_{H_2O}}{0.053 p_{H_2}} \]

which gives

\[ \frac{p_{H_2O}}{p_{H_2}} = 0.133 \]

which, with \( p_{H_2} + p_{H_2O} = 0.5 \) atm, gives \( p_{H_2} = 0.449 \) atm and \( p_{H_2O} = 0.051 \) atm.

Thus the new equilibrium gas is

\[ p_{H_2} = 0.449 \text{ atm} \]
\[ p_{H_2O} = 0.051 \text{ atm} \]
\[ p_{CO} = 0.289 \text{ atm} \]
\[ p_{CO_2} = 0.053 \text{ atm} \]
\[ P = 0.842 \text{ atm} \]

which, necessarily, is the same state as that produced by introducing the CaO before the graphite.

**PROBLEMS**

12.1 To what temperature must MgCO\(_3\) be heated in an atmosphere containing a partial pressure of CO\(_2\) of \( 10^{-2} \) atm to cause decomposition of the carbonate?
12.2 Using the standard Gibbs free energies of formation of NiO from solid Ni and liquid Ni, calculate the melting temperature, molar heat of melting, and the molar entropy of melting of nickel.

12.3 Calculate the temperature at which pure Ag₂O decomposes to Ag metal and O₂ gas when heated in (1) pure oxygen at 1 atm pressure, and (2) in air.

12.4 Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic?

12.5 A mixture of argon gas and hydrogen gas at 1 atm total pressure is passed through a reaction vessel containing a mixture of liquid Sn and liquid SnCl₂ at 900 K. The composition of the gas leaving the vessel is 50% H₂, 7% HCl, and 43% Ar. Has equilibrium been attained between the gas phase and the liquid phases in the vessel?

12.6 Fe and FeO are in equilibrium with a gas mixture of composition 71.8% CO–28.2% CO₂ at 1273 K. Which of the two solid phases disappears if the composition of the gas is held constant and the temperature of the system is decreased?

12.7 Calculate the vapor pressure of Mg exerted at 1400°C by the system in which the reaction equilibrium

\[ 4\text{Mg}_2\text{O}(s) + \text{Si}(s) \rightleftharpoons 2\text{Mg}(g) + \text{Mg}_2\text{SiO}_4(s) \]

is established.

12.8 One gram of CaCO₃ is placed in an evacuated rigid vessel of volume 1 liter at room temperature, and the system is heated. Calculate (1) the highest temperature at which the CaCO₃ phase is present, (2) the pressure in the vessel at 1000 K, and (3) the pressure in the vessel at 1500 K. The molecular weight of CaCO₃ is 100.

12.9 Calculate the total pressure \( p_{\text{SO}_3} + p_{\text{SO}_2} + p_{\text{O}_2} \) exerted by equilibrated CoO and CoSO₄ at 1223 K.

12.10 A gas mixture initially containing 90% CO, 0.4% COS, and 9.6% inert constituents (by volume) is passed over sponge iron at 1000 K to remove sulfur by the following reaction:

\[ \text{COS}(g) + \text{Fe}(s) = \text{CO}(g) + \text{FeS}(s) \]

(1) Assuming that the effluent gas is in equilibrium with Fe and FeS, calculate the percentage of sulfur removed from the gas by reaction with the sponge iron. (2) Calculate the partial pressure of S₂ in the effluent gas.

12.11 An Ar–H₂O gas mixture of \( p_{\text{Ar}} = 0.9 \text{ atm} \) \( (p_{\text{total}} = 1 \text{ atm}) \) is passed over solid CaF₂, as a result of which CaO forms according to

\[ \text{CaF}_2(s) + \text{H}_2\text{O}(g) = \text{CaO}(s) + 2\text{HF}(g) \]

The reaction proceeds to equilibrium and solid CaO and solid CaF₂ are mutually immiscible. When the gas flow rate (measured at 298 K and 1 atm pressure) over the sample is 1 liter per minute, the measured rates of weight loss of the sample are \( 2.69 \times 10^{-4} \) and \( 8.30 \times 10^{-3} \) grams per hour at 900 and
1100 K, respectively. Use these data to calculate the variation of $\Delta G^\circ$ for the
above reaction with temperature. The atomic weights are

\[ O = 16, \quad F = 19, \quad \text{and} \quad Ca = 40.08. \]

12.12 Magnetite ($Fe_3O_4$) is reduced to sponge iron (Fe) in a continuous reactor op-
erating at 800 K using methane gas ($CH_4$) as the reducing agent. The gaseous
reaction product leaving the reactor at a total pressure of 1 atm is a mixture of
CO, CO$_2$, H$_2$, and H$_2$O with a negligible methane content. The gas is at equi-
librium with the Fe–Fe$_2$O$_3$ mixture in the reactor. Calculate the consumption
of methane as moles of methane used per mole of Fe produced.

12.13 Three equations for the oxidation of Mg according to $Mg + \frac{1}{2}O_2(g) = MgO(s)$
are

\[ \Delta G^\circ = -604,000 - 5.36T \ln T + 142.0T \, J \] \hspace{1cm} (i)

\[ \Delta G^\circ = -759,800 - 13.4T \ln T + 3177T \, J \] \hspace{1cm} (ii)

and

\[ \Delta G^\circ = -608,100 - 0.44T \ln T + 112.8T \, J \] \hspace{1cm} (iii)

One of these expressions is for the oxidation of solid Mg, one is for the oxida-
tion of liquid Mg, and one is for the oxidation of gaseous Mg. Determine
which equation is for which oxidation and calculate the melting and normal
boiling temperature of Mg.

12.14 200 grams of liquid zinc are placed in a crucible at 1030 K. Two moles of air are
bubbled through the liquid zinc, and the gas comes to equilibrium with the liq-
uid before leaving the system. If the total pressure of the gas remains constant
at 0.8 atm throughout the process, how many grams of metallic zinc are left in
the crucible? The atomic weights of Zn and O are, respectively, 65.38 and 16.

12.15 Methane gas is burned with twice the amount of stoichiometric air (i.e., the
initial ratio of CH$_4$ and O$_2$ in the mixture is 0.25), and the combustion gas
produced, in which the concentration of methane is negligible, is used to calc-
cine CaCO$_3$ in an isothermal furnace. The gas and the solids are at 1080 K
and the pressure of the gas is maintained constant at 1 atm. How many moles
of CaCO$_3$ are decomposed per mole of CH$_4$ burned?

12.16 Mercuric oxide (HgO) is placed in a vessel which is then evacuated, filled
with nitrogen, and heated to 600 K, at which temperature it is observed that
the total pressure in the vessel is 2 atm. Calculate the mole fractions of O$_2$ and
Hg vapor in the gas phase.

12.17 In Fig. 12.14 the line AB, which represents the equilibrium

\[ FeO(s) + CO(g) = Fe(s) + CO_2(g), \]

interacts the carbon deposition line at the point A ($T = 972$ K, $P_{CO} = 0.595$
atm, $P_{CO_2} = 0.045$ atm, $P = 1.000$ atm). At what total pressure does the point
of intersection of the lines occur at 1000 K, and what are the values of the par-
tial pressures of CO and CO$_2$ in this state?
\[ \text{MgCO}_3(s) = \text{MgO}(s) + \text{CO}_2(g) \]

\[ \Delta G^\circ = -117,600 - 176 \, \text{T} \]

\[ K_p = \exp \left( \frac{-117,600 + 176 \, \text{T}}{8.31 \, \text{T}} \right) = P_{\text{O}_2} = 10^{-2} \, \text{atm} \]

\[ \frac{-117,600 + 176 \, \text{T}}{8.31 \, \text{T}} = -4.605 \]

\[ \frac{-117,600 + 176 \, \text{T}}{8.31 \, \text{T}} = -38.27 \, \text{T} \]

\[ 208.3 \, \text{T} = 117,600 \]

\[ T = 565 \, \text{K} \]
\[ 2 \text{Ni}(s) + O_2(g) = 2 \text{NiO}(s), \quad \Delta G^\circ = -471,200 + 172T \quad (1) \]

\[ 2 \text{Ni}(l) + O_2(g) = 2 \text{NiO}(s), \quad \Delta G^\circ = -506,180 + 192.2T \quad (2) \]

(1) - (2) ; \quad 2 \text{Ni}(s) - 2 \text{Ni}(l) = 0; \quad \Delta G^\circ = 3,4980 - 20.2T

\[ 2 \text{Ni}(s) = 2 \text{Ni}(l) \]

\[ \Delta H^\circ = 3,4980 \text{ J/mol of } \text{Ni} \rightarrow \Delta H^\circ = 17490 \text{ J/mol } \quad \text{Ans} \]

\[ \Delta S^\circ = -20.2 \text{ J/mol } \text{K of Ni} \rightarrow \Delta S^\circ = -10.1 \text{ J/mol K } \quad \text{Ans} \]

At equilibrium \( \Delta G = 0 \); \quad \Delta T = 3,4980 - 20.2 \quad \text{Ans.}
\[ \text{Ag}_2\text{O}(s) = 2\text{Ag}(s) + \frac{1}{2} \text{O}_2(g) \quad \Rightarrow \quad \Delta G^\circ = 30540 - 66.11 \: \text{T} \]

1. in \( \text{O}_2 \) 1 atm.

\[ \Delta G = \Delta G^\circ = 30540 - 66.11 \: \text{T} = 0 \]

\[ T = \frac{30540}{66.11} = 462 \: \text{K} \]

2. in \( \text{Air} \) \( p_{\text{O}_2} = 0.21 \) atm.

\[ \Delta G = \Delta G^\circ + \frac{1}{2}RT \ln p_{\text{O}_2} \]

\[ O = 30540 - 66.11 \: T + \frac{1}{2}(8.31 \: \text{K} \cdot \text{T}) \ln 0.21 \]

\[ O = 30540 - 72.6 \: T \]

\[ T = 420 - 1 \: \text{K} \]

\[ \text{Ans} \]
\[ 2Cr(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s) \quad \Delta G^\circ = -1110,100 + 247.3T \quad - (1) \]

\[ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta G^\circ = -241,800 + 55.85T \quad - (2) \]

\[(2) \times -3 \quad 3H_2O(g) \rightarrow 3H_2(g) + \frac{3}{2}O_2(g) \quad \Delta G^\circ = -742,500 + 167.55T \quad - (3)\]

\[(1) + (3) \quad 2Cr(s) + 3H_2O(g) \rightarrow Cr_2O_3(s) + 3H_2(g) \quad \Delta G^\circ = -367,600 + 99.75T \quad - (4)\]

\[ K_p = \exp\left(\frac{367,600 - 79.75(1500)}{8.31 \times 1500}\right) = \frac{p_{Cr}^3 \cdot p_{H_2}^2}{p_{H_2O}^3} \]

\[ p_{H_2O} = 1.32 \times 10^{-3} \text{ atm} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ = -367,600 + 79.75T \]

\[ \therefore \Delta H^\circ = -367,600 \text{ J/mol} \quad - \text{Exothermic. Positive} \]
\[
\begin{align*}
Sn(\ell) + Cl_2(\ell) &= SnCl_2(\ell), \quad \Delta G^\circ = -333,000 + 118.4T \quad -(1) \\
H_2(\ell) + Cl_2(\ell) &= 2HCl(\ell), \quad \Delta G^\circ = -128,700 - 12.80T \quad -(2)
\end{align*}
\]

\[(2)-(1) \quad H_2(\ell) + SnCl_2(\ell) = Sn(\ell) + 2HCl(\ell); \quad \Delta G^\circ = 144,800 - 131.2T \quad -(3)
\]

\[
K_p = \exp\left(\frac{-144,800 + (131.2)(900)}{(8.31)(900)}\right) = \frac{P_{HCl}^2}{P_{H_2}^2}
\]

\[
\frac{P_{HCl}}{P_{H_2}} = 0.0281 \text{ at equilibrium.}
\]

\[
\tilde{P}_{H_2} = 0.5 \quad \Rightarrow \quad P_{HCl} = \sqrt{0.0281 \times 0.5} = 0.119
\]

Im, Im \_ H_2 = 50 \% \text{ at } HCl = 7 \%, \text{ ถือว่าเป็นที่ Equilibrium.}
\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{CO}_2 (g) & \rightarrow \text{Fe}_3\text{O}_4 + \text{CO}_2 (g) \quad \text{(1)} \\
\text{Fe}_3\text{O}_4 (s) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{Fe}_3\text{O}_4 (s) \quad \Delta G^\circ = -263,700 + 64.35 T \quad \text{(2)} \\
\text{CO}_2 (g) + \frac{1}{2}\text{O}_2 (g) & \rightarrow \text{CO}_2 (g) \quad \Delta G^\circ = -282,400 + 86.41 T \quad \text{(3)}
\end{align*}
\]

\((1) = (3) - (2) ; \quad \Delta G_{(1)} = -18700 + 22.06 T \)

As T decreases, \(\Delta G_{(1)}\) becomes negative.

The reaction will go forward, \(\text{Fe}_3\text{O}_4\) will increase, while \(\text{Fe}_2\text{O}_3\) disappears.
\[ 4 \text{MgO (s)} + \text{Si (s)} = 2 \text{Mg (g)} + \text{Mg}_2 \text{SiO}_4 (s) \quad (1) \]

\[ 2 \text{MgO (s)} + \text{SiO}_2 (s) = \text{Mg}_2 \text{SiO}_4 (s) \quad \Delta G = -67,200 + 4.31T \quad (2) \]

\[ \text{Si (s)} + \frac{1}{2} \text{O}_2 (g) = \text{SiO}_2 (s) \quad \Delta G = -907,100 + 175T \quad (3) \]

\[ \text{Mg (g)} + \frac{1}{2} \text{O}_2 (g) = \text{MgO (s)} \quad \Delta G = -729,600 + 204T \quad (4) \]

\( (1) = (2) + (3) - (2 \times (4)) \); \quad \Delta G = \left[ (-67,200) + (-907,100) - (2 \times (-729,600)) \right] +

\[ + \frac{1}{4} \left[ 4.31 + 175 - (2 \times 204) \right] T \]

\[ K_T = \exp \left( \frac{-484900 + 228.7(1673)}{4.31(1673)} \right) = \frac{P_{\text{Mg}}}{P_{\text{Mg}}^2} \]

\[ P_{\text{Mg}} = 0.0253 \text{ atm.} \]
$\log$ of $CaCO_3 = \frac{1}{100} = 0.01 \text{ mol}$.

$V = 1 \text{ lit} \Rightarrow P_{CO_2} = \frac{n_{CO_2}RT}{1} = (0.08206)n_{CO_2}T$

$CaCO_3(s) = CaO(s) + CO_2(g)$ \quad $\Delta G = -168,400 - 144T$

$k_p = \exp \left( \frac{-168,400 + 144T}{8.31T} \right) = P_{CO_2}$

$P_{CO_2,\text{max}} = (0.08206)(0.01)(T) = \exp \left( \frac{-168,400 + 144T}{8.31T} \right)$

$T = 1167 \text{ K} \quad \text{Ans}$

At $T = 1000 \text{ K}$ \quad $k_p = \exp \left( \frac{-168,400 + 144(1000)}{8.31(1000)} \right) = 0.053 \text{ atm} \quad \text{Ans}$

At $T = 1500 \text{ K}$ \quad $P_{CO_2} = \frac{n_{CO_2}RT}{V} = \frac{(0.01)(0.08206)(1500)}{1}$

$= 1.23 \text{ atm} \quad \text{Ans}$
\[
\begin{align*}
\text{CoO(s)} + \text{SO}_3(\text{g}) & \rightarrow \text{CoSO}_4(\text{s}) \quad \Delta G = -227860 + 165.3 \text{ kJ} \quad \text{(1)} \\
\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) & \rightarrow \text{SO}_3(\text{g}) \quad \Delta G = -94,600 + 89.37 \text{ kJ} \quad \text{(2)}
\end{align*}
\]

\[
KP(1) = \exp\left(\frac{227860 - 165.3(1223)}{(8.31)(1223)}\right) = P_{\text{SO}_3}^{-1}
\]

\[
P_{\text{SO}_2} = 0.0798 \text{ atm}
\]

\[
KP(2) = \exp\left(\frac{-94600 - 89.37(1223)}{(8.31)(1223)}\right) = \frac{P_{\text{SO}_2}}{P_{\text{O}_2}^{1/2} P_{\text{SO}_2}} = \frac{0.0798}{P_{\text{O}_2}^{1/2} P_{\text{SO}_2}}
\]

\[
P_{\text{O}_2}^{1/2} P_{\text{SO}_2} = 0.339
\]

\[
P_{\text{SO}_2} = \frac{0.339}{P_{\text{O}_2}^{1/2}}
\]

\[
P_{\text{SO}_3} + P_{\text{SO}_2} + P_{\text{O}_2} = 1 \text{ atm}
\]

\[
\frac{0.0798 + 0.339}{P_{\text{O}_2}^{1/2}} + P_{\text{O}_2} = 1
\]

\[
P_{\text{O}_2} = 0.283 \text{ atm}
\]

\[
P_{\text{SO}_2} = \frac{0.339}{(0.283)^{1/2}} = 0.639 \text{ atm}
\]
\[ \cos(g) + Fe(s) = C_{0}(g) + FeS(s) \quad (1) \]

\[ C(s) + \frac{1}{2} O_2(g) + \frac{1}{2} S_2(g) = \cos(g) ; \: \Delta G^\circ = -202,800 - 996 \text{ J} \quad (2) \]

\[ C_{0}(g) + \frac{1}{2} O_2(g) = \cos(g) ; \: \Delta G^\circ = -1,117,000 - 87,65 \text{ J} \quad (3) \]

\[ FeS(s) + \frac{1}{2} C_{0}(g) = FeS_2(s) ; \: \Delta G^\circ = -1,502,800 + 52,35 \text{ J} \quad (4) \]

\[ (1) = (4) - (3) - (2); \: \Delta G^\circ(1) = -59,100 - 25,14 \text{ J} \]

\[ k_p(1) = \exp \left( \frac{-59,100 + 25,14 \times 1,000}{(8,13)(100)} \right) = 2.5265 \]

\[ k_p(1) = \frac{p_{CO}}{p_{CO}} = 2.5265 \]

\[ \cos(g) + Fe(g) = C_{0}(g) + FeS(g) \]

\[ 0.4 \quad \text{and} \quad 90 \]

\[ -x \quad \text{and} \quad +x \]

\[ 0.4 - x \quad \text{and} \quad 90 + x \quad \eta_T = 100 \]

\[ k_p(1) = \frac{(90 + x)}{100} = 2.5265 \]

\[ \frac{(0.4 - x)}{100} \]

\[ 90 + x = 10106 - 25265x \]

\[ x = \frac{10016}{25265} = 0.3964 \]

\[ \text{Percent removed} = \frac{0.3964}{0.4} \times 100 = 99.1 \% \quad \eta_T = 100 \]
\[ k(p) = \exp \left( \frac{150200 - 52.55 (1000)}{8.317 (1000)} \right) = P_{S_2}^{-1/2} \]

\[ P_{S_2} = 6.2 \times 10^{-11} \text{ atm} \quad \text{Ans} \]