Chapter 11 Reactions Involving Gases

§11-1 Introduction

When gases exhibiting marked chemical affinity for one another are mixed   Final composition ?

e.g. $A_{(g)} + B_{(g)} = 2C_{(g)}$

   $2H_{2(g)} + O_{2(g)} = 2 H_2 O_{(g)}$
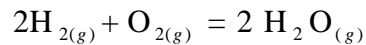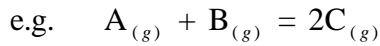
at T $\begin{cases} \text{initial state : } 1 \text{ mole } H_{2(g)} + 1 \text{ mole } O_{2(g)} \\ \\ \text{final state : } ? H_{2(g)} + ? O_{2(g)} + ? H_2 O_{(g)} \end{cases}$

1.   If the pressure is low enough
    $\Rightarrow$ $\begin{cases} \text{ideal gas can be assumed .} \\ \text{partial pressure of } i , \quad p_i = x_i P \end{cases}$
2. Change of Gibbs Free Energy : ΔG
    ΔG $\begin{cases} (1) \ \Delta G^R \ (\text{ chemical reaction }) \\ (2) \ \Delta G^M \ (\text{ mixing of remaining reactant gases and final product gases }) \end{cases}$

3. Final equilibrium state $\Leftrightarrow$ ΔG_{min}
4. Equilibrium constant for reaction : K

§11-2 Reaction Equilibrium in Gas Mixture and Equilibrium Constant

Consider $A_{(g)} + B_{(g)} = 2C_{(g)}$

At constant T , $P_{(total)} = 1$ atm

Initial : (1 mole A) + (1 mole B)
Final (any time) : (n_A mole A) + (n_B mole B) + (n_C mole C)
At any instant during reaction :

$G^{'} = n_A \overline{G_A} + n_B \overline{G_B} + n_C \overline{G_C}$

final $n_A, n_B, n_C \Rightarrow G' = G'_{min}$ reaction stops .

$n_A = n_B$ (Reaction consumes equal amount of A , B)

$n_C = 2 \quad n_A \qquad n_B = 2 (1 \quad n_A)$

$G' = n_A \overline{G_A} + n_B \overline{G_B} + n_C \overline{G_C}$

$G' = n_A (\overline{G_A} + \overline{G_B} \quad 2\overline{G_C}) + 2\overline{G_C}$

Ideal gas mixture : $d\overline{G_i} = RT \, d(\ln p_i)$

$$\overline{G_i} = G_i^o + RT \ln p_i$$

$$\overline{G_i} = G_i^o + RT \ln X_i + RT \ln P$$

$X_A = \dfrac{n_A}{2} \quad , \quad X_B = \dfrac{n_B}{2} \quad , \quad X_C = \dfrac{2(1 - n_A)}{2} = (1 - n_A)$

$G' = n_A (G_A^o + G_B^o \quad 2 G_C^o) + 2 G_C^o + 2 RT \ln P$

$\qquad + \; 2RT \left[n_A \ln\left(\dfrac{n_A}{2} \right) + (1 - n_A) \ln(1 - n_A) \right]$

$\Delta G^o = (2 G_C^o \quad G_A^o \quad G_B^o)$: Standard Gibbs Free Energy Change

$G' \quad 2 G_C^o = n_A (\quad \Delta G^o) + 2RT \ln P$

$\qquad +2RT \left[n_A \ln\left(\dfrac{n_A}{2} \right) + (1 - n_A) \ln(1 - n_A) \right]$

If total pressure P = 1 atm

$\qquad G' \quad 2 G_C^o = n_A (\quad \Delta G^o) + 2RT \left[n_A \ln\left(\dfrac{n_A}{2} \right) + (1 - n_A) \ln(1 - n_A) \right]$

$\begin{cases} \text{First term :} \quad \Delta G \text{ due to reaction} \\ \text{Second term :} \quad \Delta G \text{ due to mixing of gas} \end{cases}$

$\Delta G' = G' \quad (G_A^o + G_B^o)$

$\qquad = \left[2 G_C^o \quad (G_A^o + G_B^o) \right] + n_A (\quad \Delta G^o)$

$\qquad + 2RT \left[n_A \ln\left(\dfrac{n_A}{2} \right) + (1 - n_A) \ln(1 - n_A) \right]$

$$\Delta G' = (1 \quad n_A) \quad \Delta G^o + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1-n_A)\ln(1-n_A)\right]$$
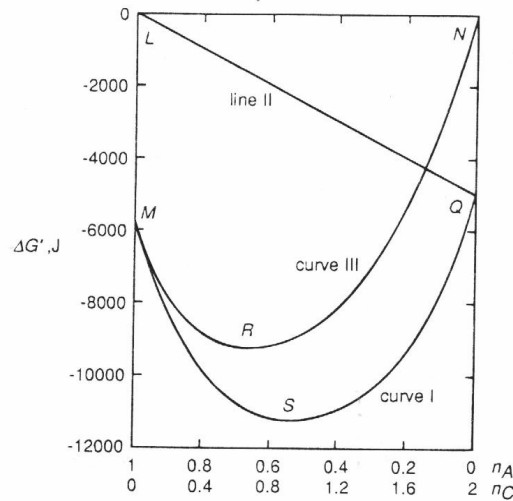

Figure 11.1 The variations of the contributions to the decrease in the Gibbs free energy due to chemical reaction (line II), the contribution to the decrease in the Gibbs free energy due to gas mixing (curve III) with the extent of the reaction $A_{(g)} + B_{(g)} = 2C_{(g)}$ for which $\Delta G^o = -5000$ joules at 500 K

Figure 11-1

point L : initial state (1 mole A , 1 mole B)

point Q: 2 mole C (complete reaction) none of A , B

$$\overline{NQ} = \quad \Delta G^o$$

$$\overline{LM} = \quad 2RT \ln 2 \text{ (mixing 1 mole A , 1 mole B)}$$

$$= \Delta G_o^M$$

$$\overline{MRN} : (n_A : A) + (n_B : B) + (n_C : C)$$

$$\Delta G^M = RT \cdot \sum n_i \ln X_i = (2) \quad \text{(ideal gas mixing)}$$

S : Equilibrium state (minimum $\Delta G'$)

$$\left(\frac{\partial \Delta G'}{\partial n_A}\right)_{T,P} = \left(\frac{\partial G'}{\partial n_A}\right)_{T,P} = 0$$

$$G' = n_A \overline{G_A} + n_A \overline{G_B} + 2(1 \quad n_A)\overline{G_C}$$

$$\left(\frac{\partial G'}{\partial n_A}\right) = \overline{G_A} + \overline{G_B} \quad 2\overline{G_C} = 0$$

$$(G_A^o + RT \ln p_A) + (G_B^o + RT \ln p_B) = 2 G_C^o + 2RT \ln p_C$$

$$2\,G_C^o \quad G_A^o \quad G_B^o = \quad RT \ln \frac{p_C^2}{p_A \cdot p_B}$$

Define : Equilibrium constant for reaction $A + B = 2C$

$$K_P \qquad \frac{p_C^2}{p_A \cdot p_B}$$

$$\Delta G^o = \quad RT \ln K_P$$

i.e. If G_A^o, G_B^o, G_C^o known

$\Rightarrow \Delta G^o$ can be calculated at T , P

$\Rightarrow K_P$ can be obtained

$\Rightarrow p_A$, p_B , p_C and then n_A can be obtained

that is final equilibrium composition

e.g. $A_{(g)} + B_{(g)} = 2C_{(g)}$

$G_A^o = G_B^o = 0$, $G_C^o = 2500\,J$, $T = 500K$, $P = 1$ atm

$\Delta G^o = 2\,G_C^o \quad G_A^o \quad G_B^o = 5000\,J$

$$K_P = \exp(-\frac{\Delta G^o}{RT}) = 3.329$$

$$3.329 = \frac{p_C^2}{p_A \cdot p_B} = \frac{(X_C P)^2}{(X_B P)(X_A P)} = \frac{(X_C)^2}{(X_B)(X_A)} = \frac{(1 - n_A)^2}{\left(\dfrac{n_A}{2}\right)^2}$$

$n_A = 0.523$ ($n_A = 11.4$ nonphysical)

$n_B = 0.523$, $n_C = 2(1 \quad n_A) = 0.954$ mole

§ 11-3 Effect of Temperature on K_P

In Figure 11-1 , $\overline{LM} = \Delta G^M$ and $\overline{NQ} = \Delta G^{oR}$ and are dependent on T

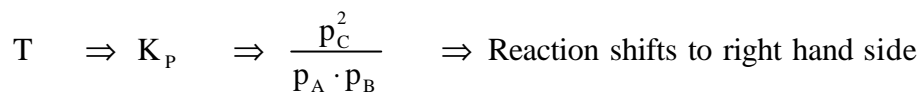Minimum point of curve $\overline{MSQ}$ is influenced by T

i.e. K_P is a function of T

$$\left[\frac{\partial(\Delta G^{\circ}/T)}{\partial T}\right]_P = \frac{\Delta H^{\circ}}{T^2} \quad \text{and} \quad \Delta G^{\circ} = RT \ln K_P$$

$$\boxed{\frac{\partial \ln K_P}{\partial T} = \frac{\Delta H^{\circ}}{RT^2}}$$

or $\boxed{\dfrac{\partial \ln K_P}{\partial(1/T)} = \dfrac{\Delta H^{\circ}}{R}}$ Van't Hoff Equation
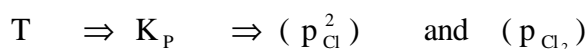
If $\Delta H^{\circ} > 0$, endothermic reaction

$T \Rightarrow K_P \Rightarrow \dfrac{p_C^2}{p_A \cdot p_B} \Rightarrow$ Reaction shifts to right hand side

i.e.   A + B $\rightleftharpoons$ C

e.g. $Cl_{2(g)} \rightleftharpoons 2\ Cl_{(g)}$

$\Delta H^{\circ} > 0$, $K_P = \dfrac{p_{Cl}^2}{p_{Cl_2}}$

$T \Rightarrow K_P \Rightarrow (p_{Cl}^2)$ and (p_{Cl_2})

Le Chatelier's Principle :

Equilibrium is shifted toward in the direction to eliminate the disturbance .

§ 11-4 Effect of Pressure on Equilibrium Constant

$$\Delta G^o = 2\ G_C^o - G_A^o - G_B^o$$

ΔG_i^o is defined as P = 1 atm , T

ΔG^o is independent of pressure

K_P is independent of pressure (But p_i can change)

e.g. $Cl_{2(g)} \rightleftharpoons 2\ Cl_{(g)}$

$$K_P = \frac{p_{Cl}^2}{p_{Cl_2}} = \frac{(X_{Cl}P)^2}{X_{Cl_2}P} = \frac{X_{Cl}^2}{X_{Cl_2}} \cdot P = K_x \cdot P$$

K_x is defined in terms of mole fraction

In general ,   aA + bB = cC + dD

$$\boxed{K_P = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = K_x \cdot P^{(c+d)-(a+b)}}$$

only if (a+b) = (c+d) , K_x is independent of P

if (a+b)   (c+d) , P $\Rightarrow K_x$

if (a+b)   (c+d) , P $\Rightarrow K_x$ (K_P is constant)

when K_x changes $\Rightarrow p_i$ changes

Reaction Equilibrium as a compromise between ΔH and ΔS

$$G = H \quad TS$$

Constant T , $\Delta G = \Delta H \quad T\Delta S$

$\Delta G_{min} \Rightarrow \Delta H_{min}$ and ΔS_{max}

e.g. $Cl_{2(g)} = 2\,Cl_{(g)}$

$\Delta H^o \quad 0$, $\Delta S^o \quad 0$

i.e. $\begin{cases} Cl_{(g)} \text{ has a higher H than } Cl_{2(g)} \\ \\ 2\,Cl_{(g)} \text{ has a higher S than } Cl_{2(g)} \end{cases}$

$Cl_{(g)} \quad \Rightarrow \begin{cases} \Delta H \quad \Rightarrow \Delta G \\ \\ \Delta S \quad \Rightarrow \Delta G \end{cases}$ compromise is required

For $A_{(g)} + B_{(g)} = 2C_{(g)}$

$$G \quad 2\,G_C^o = n_A(\quad \Delta G^o) + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A)\right]$$

$$= n_A(\quad \Delta H^o) + T\left[n_A \cdot \Delta S^o + 2R[n_A \ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A)]\right]$$

$$= \Delta H' \quad T\Delta S'$$

If $T = 500K$, $\Delta G^o = \quad 5000(J)$

$G_A^o \quad G_B^o = 0 \quad 2\,G^o = \quad 5000(J)$

Take $\Delta H^o = \quad 2500(J) \qquad \Delta S^o = 5\,(J/K)$

When T $\quad \Rightarrow \text{T}\,\Delta S^{'}$ is more important

$\Rightarrow \ (n_A)_{eg} \qquad , (n_C)_{eg}$

i.e. $G_{min}^{'}$ shifts to left

(Another viewpoint : $\Delta H^o \quad 0 \qquad T \quad \Rightarrow K_P \quad \Rightarrow$ equilibrium shifts to left)
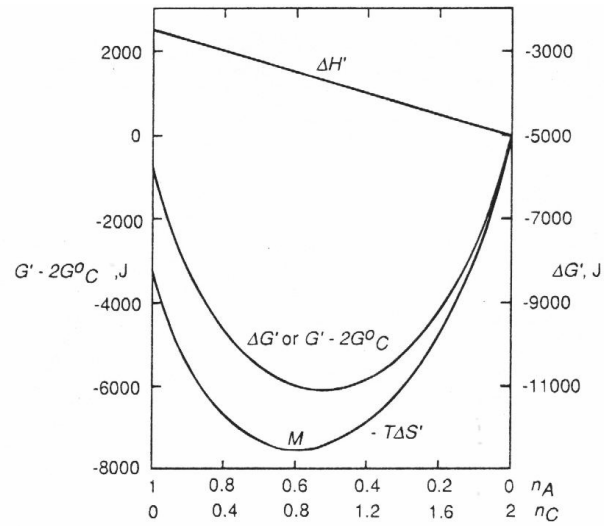

Figure 11.2 The variations at 500 K of $\Delta H'$, $-T\Delta S'$, and $\Delta G'$ with the extent of reaction $A(g) + B(g) = 2C(g)$ for which $\Delta G° = -2500 - 5T$

Figure 11-2

Note:

$\Delta G^o = \Delta H^o \quad T\,\Delta S^o = \quad RT \ln K_P$

$T \quad \Rightarrow \Delta G^o$
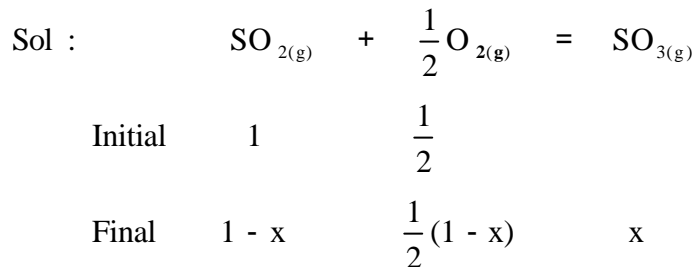
for $\Delta H^o \quad 0 \ , \quad \Delta G^o \quad 0$

$T \quad \Rightarrow K_P$

$(\dfrac{\partial \ln K_P}{\partial T} = \dfrac{\Delta H^o}{RT^2})$

§ 11-5 Reaction Equilibrium in $SO_{2(g)}$ - $SO_{3(g)}$ - $O_{2(g)}$ System

Given
$$\begin{cases} SO_{2(g)} \quad \frac{1}{2}O_{2(g)} \quad SO_{3(g)} \\ \Delta G^{o} = \ 94600 + 89.37\ T \end{cases}$$

1. $T = 1000\ K$, $n^{o}_{(SO_2)} = 1$ mole , $n^{o}_{(O_2)} = \frac{1}{2}$ mole

   $P = 1$ atm   final composition ? and $p_{i} = ?$

Sol :

	$SO_{2(g)}$	$\frac{1}{2}O_{2(g)}$	$SO_{3(g)}$
Initial	1	$\frac{1}{2}$	
Final	1 x	$\frac{1}{2}(1 \quad x)$	x

$T = 1000\ K$, $\Delta G^{o} = \ 5230\ J$

$$\ln K_{P} = \ \frac{\Delta G^{o}}{RT} = 0.629 \quad , \quad K_{P} = 1.876$$

$$K_{P} = \frac{p_{SO_3}}{p_{SO_2} \cdot p_2^{1/2}} \qquad K_{P}^{2} = \frac{p_{SO_3}^{2}}{p_{SO_2}^{2} \cdot p_{O_2}}$$

Total moles : $n_{T} = (1 \quad x) + \frac{1}{2}(1 \quad x) + x = \frac{1}{2}(3 \quad x)$

$$p_{i} = X_{i} P = \ \frac{n_{i}}{n_{T}} P$$

$$p_{SO_3} = \frac{2xP}{(3-x)} \quad , \quad p_{SO_2} = \frac{2(1-x)P}{(3-x)} \quad , \quad p_{O_2} = \frac{(1-x)P}{(3-x)}$$

$$K_{P}^{2} = \frac{(3-x)x^{2}}{(1-x)^{3}P}$$

$(1 \quad P K_{P}^{2}) \cdot x^{3} + (3 P K_{P}^{2} \quad 3) \cdot x^{2} \quad 3 P K_{P}^{2} x + P K_{P}^{2} = 0$ .....( )

$P = 1$ atm , $K_{P} = 1.876$ $x = 0.463$

 Final composition :

$$\begin{cases} n_{SO_2} = 0.537 \text{ mole} \\ n_{O_2} = 0.269 \text{ mole} \\ n_{SO_3} = 0.463 \text{ mole} \end{cases}$$

$$\begin{cases} p_{SO_2} = 0.423 \text{ atm} \\ p_{O_2} = 0.212 \text{ atm} \\ p_{SO_3} = 0.365 \text{ atm} \end{cases}$$

2. Effect of Temperature : T   (1000K   900K)

$\Delta G^o = 94600 + 89.37T$

$\Delta H^o = (94600) \quad 0$, $\Delta S^o = (89.37) \quad 0$

T $\Rightarrow$ equilibrium shifts to right $\Rightarrow$ p_{SO_3} , p_{SO_2} , p_{O_2}

From ( ) , T= 900K $K_P = 6.64$ P = 1 atm

x = 0.704

$$\begin{cases} n_{SO_2} = 0.296 \text{ mole} \\ n_{O_2} = 0.148 \text{ mole} \\ n_{SO_3} = 0.704 \text{ mole} \end{cases}$$

$$\begin{cases} p_{SO_2} = 0.258 \text{ atm} \\ p_{O_2} = 0.129 \text{ atm} \\ p_{SO_3} = 0.613 \text{ atm} \end{cases}$$

3. Effect of Pressure :   P   (1 atm   10 atm)

$T = 1000K$, $K_P = 1.876$ (independent of P) , $P = 10$ atm

$\Delta G^o = \quad 5230$ J

From( ) $x = 0.686$

$$\begin{cases} n_{SO_2} = 0.314 \text{ mole} \\\\ n_{O_2} = 0.157 \text{ mole} \\\\ n_{SO_3} = 0.686 \text{ mole} \end{cases}$$

$$\begin{cases} p_{SO_2} = 0.714 \text{ atm} \\\\ p_{O_2} = 1.357 \text{ atm} \\\\ p_{SO_3} = 5.929 \text{ atm} \end{cases}$$

i.e. K_P is independent of P , but compositions change

   Le Chatlier :

   P $\Rightarrow$ equilibrium shifts to decrease of total moles

       $\Rightarrow$ equilibrium shifts to right n_{SO_3} , n_{SO_2}

                n_{O_2}

   Effect of changes in both T , P

   From equation ( )   T $\Rightarrow$ K_P

      T , P changes $\Rightarrow$ P K_P changes

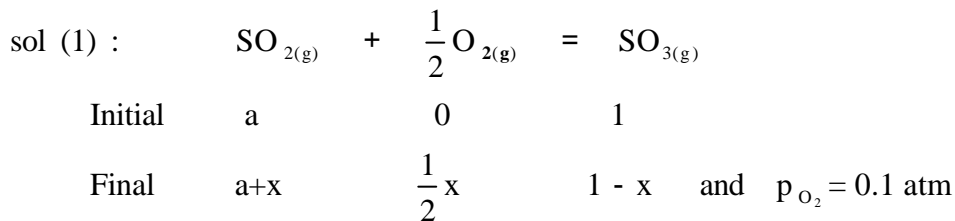 $\Rightarrow$ solution of x changes

§ 11-6 In a system to keep a constant p_{O_2} through gas mixture of SO_2/SO_3, CO/CO_2, H_2/H_2O

1. SO_2/SO_3 mixture with $\dfrac{n_{SO_2}}{n_{SO_3}} = a$

   at T=1000 K, P = 1 atm

(1) to keep $p_{O_2} = 0.1$ atm , a = ?

(2) $(p_{O_2})_{max} = ?$

sol (1) :

	$SO_{2(g)}$	$\frac{1}{2}O_{2(g)}$	$SO_{3(g)}$
Initial	a	0	1
Final	a+x	$\frac{1}{2}$ x	1 x

and $p_{O_2} = 0.1$ atm

$$n_T = \frac{1}{2}(2a+2+x)$$

$$p_{O_2} = X_{O_2} P = \frac{n_{O_2}}{n_T} P = \frac{xP}{2a+2+x}$$

for P = 1 atm , $p_{O_2} = 0.1$ atm   a = 4.5x 1

$$K_p^2 = \frac{p_{SO_3}^2}{p_{SO_2}^2 \cdot p_{O_2}} = \frac{X_{SO_3}^2}{X_{SO_2}^2 \cdot X_{O_2}} \cdot \frac{1}{P} = \frac{(1-x)^2(2a+2+x)}{(a+x)^2 \cdot x \cdot P} \quad ....(\ )$$

T = 1000 K , $\Delta G^o = 5230$ J $K_p = 1.876$

   $96.45x^3$ $18.709x^2$ $6.481x = 0$

   $x \neq 0$

   x = 0.374

then a = 0.683

Final $p_{O_2} = 0.1$ atm

$$p_{SO_2} = \frac{(a + x)}{\frac{1}{2}(2a + 2 + x)} = 0.565 \text{ atm}$$

$$p_{SO_3} = \frac{(1 - x)}{\frac{1}{2}(2a + 2 + x)} = 0.335 \text{ atm}$$

$p_{O_2} / p_{SO_3} = 1.7$

c.p. $(p_{O_2} / p_{SO_3})_{initial} = a = 0.683$

(2) $O_{2(g)}$ is produced by decomposing $SO_{3(g)}$ into $SO_{2(g)} + O_{2(g)}$

maximum p_{O_2} can be obtained by setting $a = 0$

i.e. starting with 1 mole $SO_{3(g)}$ only , and from (   )

Final $\begin{cases} p_{O_2} = 0.212 \text{ atm} \\\\ p_{SO_2} = 0.423 \text{ atm} \\\\ p_{SO_3} = 0.365 \text{ atm} \quad\quad P = 1 \text{ atm} , \; T = 1000K \end{cases}$

2. To keep a very low p_{O_2} can be obtain by H_2O / H_2 or CO / CO_2

mixture

e.g. $P = 1$ atm , $T = 2000K$ $p_{O_2} = 10^{-10}$ atm

in a H_2O / H_2 gas mixture , $(p_{H_2O} / p_{H_2}) = ?$

$\begin{cases} H_2 + \dfrac{1}{2}O_2 = H_2O \\\\ \Delta G^o = \quad 247500 + 55.85 \; T \; (J) \end{cases}$

$T = 2000K$, $\Delta G^o = $ 135800 J

$\Delta G^o = $ RT ln K_P ln $K_P = 8.167$, $K_P = 3.521 \times 10^3$

$$K_P = \frac{p_{H_2O}}{p_H \cdot p_{O_2}^{\frac{1}{2}}}$$

$p_{O_2} = 10^{-10}$ atm $(p_{H_2O}/p_{H_2}) = 3.521 \times 10^{-2}$

Operation : If $p_{H_2} = 1$ atm , $p_{H_2O} = 0.03521$ atm

Equilibrium vapor pressure of $H_2O_{(l)}$

$$\log p_{H_2O}(\text{atm}) = \frac{2900}{T} \quad 4.65 \log T + 19.732$$

when $T = 27$, $p_{H_2O} = 0.0352$ atm

Bubbling $H_{2 (g)}$ at 1 atm through water , $T = 27$ then feeding gas mixture into

2000 K chamber

3. Keep $p_{O_2} = 10^{-20}$ atm , $T = 1000K$, $P = 1$ atm

using CO_2/CO mixture , $(p_{CO_2}/p_{CO}) = ?$

sol : $\begin{cases} CO + \dfrac{1}{2}O_2 = CO_2 \\ \\ \Delta G^o = 282400 + 86.81\, T \text{ (J)} \end{cases}$

$T = 1000$ K , $\Delta G^o = 195590$ J $=$ RT ln K_P

ln $K_P = 23.52$, $K_P = 1.646 \times 10^{10}$

$$K_P = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{p_{CO_2}}{p_{CO}} \cdot \frac{1}{(10^{-20})^{\frac{1}{2}}}$$

$$\frac{p_{CO_2}}{p_{CO}} = 1.646$$

$P = 1$ atm $\quad (p_{CO_2} + p_{CO} + p_{O_2}) \cong p_{CO_2} + p_{O_2} = 1$ atm

$$p_{CO_2} = 0.622 \text{ atm} \qquad V_{CO_2} = 62.2$$

$$p_{O_2} = 0.378 \text{ atm} \qquad V_{CO} = 37.8$$

$V_{CO_2} / V_{CO} = 1.646$

Note : Mixture of $A : a$ cm^3 , $B : b$ cm^3 , $P = 1$ atm

$$n_A = \frac{P \cdot a}{RT} = \frac{a}{RT} \quad , \quad n_B = \frac{b}{RT} \quad \text{Before mixing}$$

After mixing

$$\begin{cases} p_A = \dfrac{n_A RT}{V} = \dfrac{a}{a+b} \\[2mm] p_B = \dfrac{n_B RT}{V} = \dfrac{b}{a+b} \end{cases}$$

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{a}{b} = \frac{(a/a+b)}{(b/a+b)} = V_a \ / V_b$$

Ex 1 : $\quad P_{4(g)} = 2 P_{2(g)}$ (Endothermic Reaction)

$\Delta G^o = 225400 + 7.9\, T \ln T \quad 209.4\, T$

$$\begin{cases} (1) \ \ P = 1 \text{ atm} \qquad X_{P_4} = X_{P_2} = 0.5 \quad T = ? \\[3mm] (2) \ \ T = 2000 \text{ K} \quad X_{P_4} = X_{P_2} = 0.5 \quad P = ? \end{cases}$$

sol : (1) $\qquad K_P = \dfrac{p_{P_2}^{\ 2}}{p_{P_4}} = \dfrac{X_{P_2}^{\ 2} \cdot P}{X_{P_4}}$

when $P = 1$ atm $\quad X_{P_4} = X_{P_2} = 0.5 \implies K_P = 0.5\, P = 0.5$

$$\Delta G^o = \quad RT \ln K_P$$

$$\ln K_P = \ln(0.5) = \quad \frac{\Delta G^o}{RT} = \frac{-27109}{T} \quad 0.95 \ln T + 25.18$$

$T = 1429$ K

(2) when $X_{P_4} = X_{P_2} = 0.5 \quad K_P = 0.5\, P$

$T = 2000$ K $\quad \Delta G^o = \quad$ RT ln K_P

ln $K_P = \dfrac{\Delta G^o}{RT} = 4.405$

$K_P = 81.83 = 0.5$ P

P = 163.6 atm

Ex 2 : $\begin{cases} 2\ NH_{3(g)} \ = \ N_{2(g)} \ + \ 3\ H_{2(g)} \\ \\ \Delta G^o = 87030 \quad 25.8\ T\ \ln T \quad 31.7\ T\ (J) \end{cases}$

(1) T = 400 $\quad$, $\quad$ P = 1 atm $\quad$ Final composition : p_i = ?
(2) T = 400 $\quad$, $\quad$ V = constant $\quad$ p_i = ?

sol : $\quad$ (1) $\qquad 2\ NH_{3(g)} \ = \ N_{2(g)} \ + \ 3\ H_{2(g)}$

$\qquad\qquad$ initial $\qquad$ 1 $\qquad\quad$ 0 $\qquad\quad$ 0

$\qquad\qquad$ final $\qquad$ 1-2x $\qquad$ x $\qquad\quad$ 3x
$\qquad\quad n_T = (1+2x)$ moles

$\begin{cases} p_{H_2} \ = \ \dfrac{3x}{1+2x}P \\ \\ p_{N_2} \ = \ \dfrac{x}{1+2x}P \\ \\ p_{NH_3} \ = \ \dfrac{1-2x}{1+2x}P \end{cases}$ $\qquad$ $\begin{cases} T \ = \ 400 \quad = 673\ K \\ \\ \Delta G^o = \quad 47370\ J \\ \\ K_P = \exp(\quad\dfrac{\Delta G^o}{RT}) = 4748 \end{cases}$

$$K_P = \dfrac{p_{N_2} \cdot p_{H_2}^{\ 3}}{p_{NH_3}^{\ 2}} = \dfrac{27x^4 P^2}{(1+2x)^2(1-2x)^2} = \dfrac{27x^4 P^2}{[(1-4x)^2]^2}$$

$$K_P^{\frac{1}{2}} \ = \ \dfrac{5.196x^2 P}{(1-4x)^2}$$

Substitute $K_P = 4748$, $\quad$ P = 1 atm $\quad$ x = 0.4954

$$p_{H_2} = \frac{3x}{1+2x}P = 0.7465 \text{ atm}$$

$$p_{N_2} = \frac{x}{1+2x}P = 0.2488 \text{ atm}$$

$$p_{NH_3} = \frac{1-2x}{1+2x}P = 0.0047 \text{ atm}$$

(2) Initial 1 mole , Final (1+2x) moles

n_T , P = 1 atm = constant pressure

constant volume $\Rightarrow P = \dfrac{1}{(1+2x)}P^{'}$

Assume final pressure $= P^{'}$ at constant volume

$$p_{H_2} = \frac{3x}{1+2x}P^{'}$$

$$p_{N_2} = \frac{x}{1+2x}P^{'}$$

$$p_{NH_3} = \frac{1-2x}{1+2x}P^{'}$$

$$V = \frac{RT}{P} = \frac{(1+2x)RT}{P^{'}}$$

$P^{'} = (\,1+2x\,)P = (\,1+2x\,) \text{ atm}$

$$K_P^{\frac{1}{2}} = \frac{5.196x^2P^{'}}{(1-4x)^2}$$
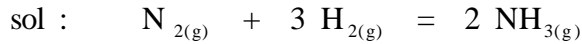
Substitute $K_P = 4748$, $P^{'} = (\,1+2x\,)$

$$K_P^{\frac{1}{2}} = \frac{5.196x^2(1+2x)}{(1-2x)(1+2x)} = \frac{5.196x^2}{(1-2x)} = 68.91$$

x = 0.4909 $P^{'} = 1.9818 \text{ atm}$

$p_{H_2} = 1.4727 \text{ atm}$

$p_{N_2} = 0.4909 \text{ atm}$

$p_{NH_3} = 0.0182 \text{ atm}$

Ex 2-1　What is the equilibrium ratio of $(n_{H_2} / n_{N_2}) = ?$　to maximize the yield of

NH$_3$ when mixing H$_2$ and N$_2$?

sol :　　$N_{2(g)} + 3 H_{2(g)} = 2 NH_{3(g)}$

Assume that at equilibrium , $(p_{H_2} / p_{N_2}) = a$

$$P = p_{H_2} + p_{N_2} + p_{NH_3}$$

$$p_{NH_3} = P \quad (a+1)\, p_{N_2}$$

$$p_{N_2} = \frac{P - p_{NH_3}}{a+1} \quad , \quad p_{H_2} = \frac{a(P - p_{NH_3})}{a+1}$$

$$K_P = \frac{p_{NH_3}^{\,2}}{p_{H_2}^{\,3} \cdot p_{N_2}} = \frac{p_{NH_3}^{\,2}(a+1)^4}{a^3 (P - p_{NH_3})^4}$$

When NH$_3$ is maximized , $\Rightarrow p_{NH_3}$ is maximum

$$\frac{d\,(p_{NH_3})}{d\,a} = 0$$

$\ln K_P + 3 \ln a + 4 \ln (P \quad p) = 2 \ln p + 4 \ln (a+1)$

$$\frac{3}{a} \cdot da + \frac{-4}{P-p} \cdot dp = \frac{2}{p} \cdot dp + \frac{4}{a+1} \cdot da$$

$$(\frac{3}{a} \quad \frac{4}{a+1})da = (\frac{2}{p} + \frac{4}{P-p})dp$$

$$\frac{dp}{da} = 0 \qquad (\frac{3}{a} \quad \frac{4}{a+1}) = 0 \qquad a = 3$$
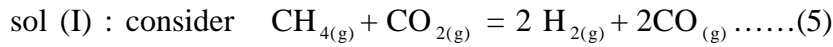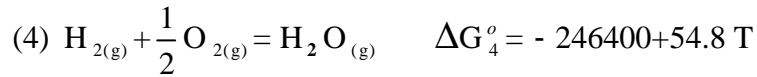
Ex 3 :　(1 mole CH$_4$ + 1 mole CO$_2$)

T = 1000 K , P = 1 atm

Final equilibrium composition ?　$p_i = ?$

Given (1) $CH_{4(g)} = C_{(s)} + 2H_{2(g)}$　　　$\Delta G_1^o = 69120 \quad 22.25T \ln T +65.35$

(2) $2 C_{(s)} = O_{2(g)} + 2CO_{(g)}$　　　$\Delta G_2^o = \quad 223400 \quad 175.3\ T$

(3) $C_{(s)} + O_{2(g)} = CO_{2(g)}$　　　$\Delta G_3^o = \quad 394100 \quad 0.8\ T$

(4) $H_{2(g)} + \frac{1}{2} O_{2(g)} = H_2 O_{(g)}$ $\Delta G_4^o = $ 246400+54.8 T

sol (I) : consider $CH_{4(g)} + CO_{2(g)} = 2\,H_{2(g)} + 2CO_{(g)}$ ......(5)

(5) = (1)+ (2)   (3)

   $\Delta G_5^o = 239820$ 22.25T ln T   109.15 T

   T = 1000 K $\Delta G_5^o = $ 23027 $K_{P_5} = \exp(\dfrac{-\Delta G_5^o}{RT}) = 15.95$

$$CH_{4(g)} + CO_{2(g)} = 2\,H_{2(g)} + 2CO_{(g)}$$
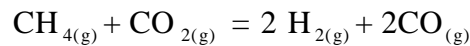
   initial   1   1   0   0
   final   1   x   1   x   2x   2x $n_T = 2(1+x)$

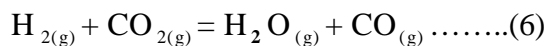$$\begin{cases} p_{CH_4} = p_{CO_2} = \dfrac{(1-x)P}{2(1+x)} \\[4mm] p_{H_2} = p_{CO} = \dfrac{xP}{(1+x)} \end{cases}$$

   $K_{P_5} = 15.95 = \dfrac{p_{CO}^{\;2} \cdot p_{H_2}^{\;2}}{p_{CH_4} \cdot p_{CO_2}} = \dfrac{(2x)^4 P^2}{[2(1+x)]^2 (1-x)^2}$

$K_{P_5}^{\frac{1}{2}} = 3.99 = \dfrac{(2x)^2 P}{2(1+x)(1-x)} = \dfrac{2x^2 P}{(1-x^2)}$

P = 1 atm   x = 0.8163

$$\begin{cases} p_{CH_4} = p_{CO_2} = 0.4494 \text{ atm} \\[4mm] p_{H_2} = p_{CO} = 0.0506 \text{ atm} \end{cases}$$

(II)   Then consider furthermore :

   $H_{2(g)} + CO_{2(g)} = H_2 O_{(g)} + CO_{(g)}$ ....(6)

(6) = (4)   (3) $\dfrac{(1)}{2}$ $\Delta G_6^o = 36000$ 32.05 T

T = 1000 K   , $\Delta G_6^o = 3950$, $K_{P_6} = \exp(\dfrac{-\Delta G_6^o}{RT}) = 0.62$

$$K_{P_6} = 0.62 = \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}}$$

$$H_{2(g)} + CO_{2(g)} = H_2O_{(g)} + CO_{(g)}$$
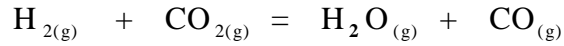
Initial   2x   2x   0   2x

Final   2x y (1 x) y   y   2x+y

Final composition :

$$n_{CH_4} = (1 \quad x)$$

$$n_{CO_2} = (1 \quad x \quad y)$$

$$n_{H_2} = (2x \quad y)$$

$$n_{CO} = (2x \quad y)$$

$$n_{H_2O} = y \qquad\qquad n_T = 2(1+x)$$

$$p_{CH_4} = \frac{(1-x)}{2(1+x)} P \quad , \quad p_{CO_2} = \frac{(1-x-y)}{2(1+x)} P$$

$$p_{H_2} = \frac{(2x-y)}{2(1+x)} P \quad , \quad p_{CO} = \frac{(2x+y)}{2(1+x)} P$$

$$p_{H_2O} = \frac{y}{2(1+x)} P$$

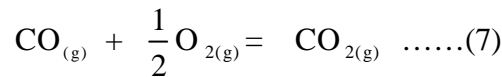$$K_{P_5} = 15.95 = \frac{(2x-y)^2 (2x+y)^2 P^2}{(1-x)(1-x-y)(2+2x)^2}$$

$$K_{P_6} = 0.62 = \frac{(2x+y)\ y}{(2x-y)(1-x-y)}$$

Computer solution with P = 1 atm

$$\begin{cases} x = 0.785 \\ y = 0.0775 \end{cases}$$

$$p_{CH_4} = 0.0602 \text{ atm}$$

$$p_{CO_2} = 0.0385 \text{ atm}$$

$$p_{H_2} = 0.4181 \text{ atm}$$

$$p_{CO} = 0.4615 \text{ atm}$$

$$p_{H_2O} = 0.0217 \text{ atm} \qquad P_{total} = 1 \text{ atm}$$

(III) CO/CO_2 and H_2/H_2O mixture will have their equilibrium p_{O_2}

$$CO_{(g)} + \frac{1}{2}O_{2(g)} = CO_{2(g)} \quad \ldots\ldots(7)$$

$(7) = (3) \quad \dfrac{(2)}{2} \quad , \quad \Delta G_7^o = \quad 282400 + 86.85 \text{ T}$

$T = 1000 \text{ K}, \quad \Delta G_7^o = \quad 195550, \quad K_{P_7} = \exp(\dfrac{-\Delta G_7^o}{RT}) = 1.64 \times 10^{10}$

$$K_{P_7} = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{0.0385}{0.4615 \cdot p_{O_2}^{\frac{1}{2}}} = 1.64 \times 10^{10}$$

$$p_{O_2} = 2.6 \times 10^{-23} \text{ atm}$$

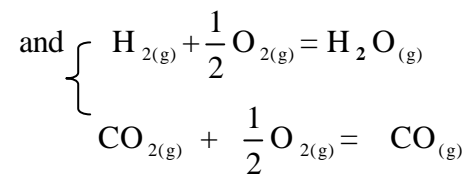Or , $\quad H_{2(g)} + \dfrac{1}{2}O_{2(g)} = H_2O_{(g)} \quad \ldots\ldots\ldots.(4)$
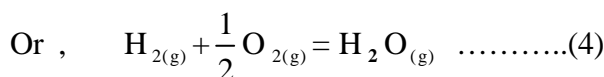
$T = 1000 \text{ K}, \quad \Delta G_4^o = \quad 191600 \quad , \quad K_{P_4} = 1.02 \times 10^{10}$

$$K_{P_4} = \frac{p_{HO_2}}{p_H \cdot p_{O_2}^{\frac{1}{2}}} = \frac{0.0217}{0.4181 \cdot p_{O_2}^{\frac{1}{2}}}$$

$$p_{O_2} = 2.6 \times 10^{-23} \text{ atm}$$

Note : 1. part (III) is part(I): $CH_{4(g)} + CO_{2(g)} = 2 H_{2(g)} + 2CO_{(g)}$

and $\left\{ \begin{array}{l} H_{2(g)} + \dfrac{1}{2} O_{2(g)} = H_2 O_{(g)} \end{array} \right.$

$$CO_{2(g)} + \frac{1}{2} O_{2(g)} = CO_{(g)}$$

i.e. further oxidation of $H_{2(g)}$ and $CO_{2(g)}$

2. Final equilibrium composition

$\left\{ \begin{array}{l} p_{CH_4} = 0.0602 \text{ atm} \\\\ p_{CO_2} = 0.0385 \text{ atm} \\\\ p_{H_2} = 0.4181 \text{ atm} \\\\ p_{CO} = 0.4615 \text{ atm} \\\\ p_{H_2O} = 0.0217 \text{ atm} \\\\ p_{O_2} = 2.6 \times 10^{-23} \text{ atm} \end{array} \right.$