Ch 12 Gaseous chemical equilibrium

└→ 條件: 可逆反應

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

reversible reaction, reactants are not completely consumed.

Equilibrium 平衡: $r_{正} = r_{逆}$

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

P_A P_B P_C P_D

$$P_i = n_i RT / V$$

$$K_P = \frac{P_C{}^c \cdot P_D{}^d}{P_A{}^a \cdot P_B{}^b}$$

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§ 12-1 The N_2O_4-NO_2 equilibrium system

$$N_2O_{4(g)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2NO_{2(g)}$$

無色 紅棕色

$$r_{正} = k_1[N_2O_4]$$

$$r_{逆} = k_2[NO_2]^2$$

平衡:

$$r_{正} = r_{逆}$$

$$K = \frac{k_1}{k_2} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{P_{NO_2}{}^2}{P_{N_2O_4}} \qquad \boxed{\begin{matrix} P = C \\ T = C \end{matrix}}$$

平衡常數: K 僅隨 1.反應式

2.T → van't Hoff equation

$$\ln\frac{k_2}{k_1} = \frac{\Delta H^2}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Clausis – Clapeyron equation

§ 12-2 The equilibrium constant expression

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

$$K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b}$$

$$K_C = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$$K_P = K_C \cdot (RT)^{\Delta n_g} \qquad \Delta n_g = (c+d)-(a+b)$$

§ Changing the chemical equation　K 值依反應式而定

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_P = \frac{(P_{NO_2})^2}{(P_{N_2O_4})^1}$$

$$\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)} \qquad K'_P = \frac{P_{NO_2}}{(P_{N_2O_4})^{1/2}} = K^{1/2}$$

$\therefore$

1. If the coefficients in a balanced equation are multiplied by a factor n, the equilibrium constant is raised to the nth power.

$$K' = K^n$$

上例: $n = \frac{1}{2} \Rightarrow \therefore k' = k^{1/2}$

$$2N_2O_{4(g)} \rightleftharpoons 4NO_{2(g)} \qquad K'' = \frac{(P_{NO_2})^4}{(P_{N_2O_4})^2} = K^2$$

$$n = 2 \quad \Rightarrow K'' = K^2$$

2. $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad K^* = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = \frac{1}{K}$

$\Rightarrow$ reciprocal rule:

The equilibrium constants for forward and reverse reactions are the reciprocal of each other

$$K_{正} = \frac{1}{K_{逆}}$$

$$K_{正} \cdot K_{逆} = 1$$

3. Adding chemical equations

rule of multiple equilibria

If a reaction can be expressed as the sum of two or more reactions, K for the overall reactions is the product of the equilibrium constants of the individual reactions.

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_1 = 22 = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{1/2}}$$

$$NO_{2(g)} \rightleftharpoons NO_{(g)} + \frac{1}{2}O_{2(g)} \qquad K_2 = 4 = \frac{P_{NO} \cdot P_{O_2}^{1/2}}{P_{NO_2}}$$

$$\Rightarrow SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$

$$K = \frac{P_{SO_3} \cdot P_{NO}}{P_{SO_2} \cdot P_{NO_2}} = K_1 \cdot K_2 = 22 \cdot 4 = 88$$

∴ 二反應式相加⇒ 平衡常數 $K = K_1 \cdot K_2$

二反應式相減⇒ 平衡常數相除

Ex 12-1: $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ --- (1)

a) K_1 for the reaction

b) 25°C, $K_1 = 4.2\times10^{-31}$, 求 $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{(g)}$ 之 K’

c) 25°C, $K_2 = 1.0\times10^{-18}$, $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ --- (2)

求 $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ 之 K_3

Sol:

$$K_1 = \frac{P_{NO_2}^2}{P_{N_2} \cdot P_{O_2}} = 4.2\times10^{-31}$$

$$K' = \frac{P_{NO_2}}{P_{N_2}^{1/2} \cdot P_{O_2}^{1/2}} = K_1^{1/2} = (4.2\times10^{-31})^{1/2} = 6.5\times10^{-16}$$

$$K_2 = \frac{P_{NO_2}^2}{P_{N_2} \cdot P_{O_2}^2}$$

$$K_3 = \frac{P_{NO_2}^2}{P_{NO}^2 \cdot P_{O_2}} = \frac{K_2}{K_1}$$

$$(2)-(1):\ \cancel{N_{2(g)}} + \cancel{2}O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$+ \qquad 2NO_{(g)} \rightleftharpoons \cancel{N_{2(g)}} + \cancel{O_{2(g)}}$$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_3 = \frac{K_2}{K_1} = \frac{1.0\times10^{-18}}{4.2\times10^{-31}} = 2.4\times10^{12}$$

§ Heterogeneous Equilibria 非均勻平衡

*the position of the equilibria is independent of the amount of solid or liquid, as long as some is present.

*terms of pure liquids or solids need not appear in the expression of K.

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + \cancel{H_2O_{(l)}} \qquad K = \frac{P_{CO}}{P_{CO_2}\cdot P_{H_2}}$$

$$\cancel{I_{2(s)}} \rightleftharpoons I_{2(g)} \qquad K = P_{I_2}$$

$$I_{2(g)} \rightleftharpoons \cancel{I_{2(s)}} \qquad K = \frac{1}{P_{I_2}}$$

Ex 12-2: 求 K

a) $\cancel{CuO_{(s)}} + H_{2(g)} \rightleftharpoons \cancel{Cu_{(s)}} + H_2O_{(g)} \quad K = \dfrac{P_{H_2O}}{P_{H_2}}$

b) $1\cdot H_2O_{(g)} + \cancel{C_{(s)}} \rightleftharpoons H_{2(g)} + CO_{(g)} \quad K = \dfrac{P_{H_2}\cdot P_{CO}}{P_{H_2O}}$

**平衡常數:

*(g): 以分壓(atm)計算

*(s)及(l)不列入計算，solvent for a solution 也不列入計算

*(aq):以 M 計算

$$\cancel{Zn_{(s)}} + 2H^{+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + H_{2(g)} \qquad K = \frac{P_{H_2}\cdot[Zn^{2+}]}{[H^+]^2}$$

§ 12-3 Determination K

Ex 12-3: ~~$NH_4Cl_{(s)}$~~ $\rightleftharpoons NH_{3(g)} + HCl_{(g)}$

400°C, 22.6g NH_4Cl; $P_{NH_3} = 2.5atm, P_{HCl} = 4.8atm$ 求 K at 400°C

Sol:
$$K = P_{NH_3} \cdot P_{HCl}$$
$$= 2.5 \cdot 4.8$$
$$= 12$$

Ex 12-4: $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

originally P_{HI} = 1.00atm at 25°C, at equilibrium $P_{H_2} = 0.10atm$

Calculate a) P_{I_2}, b) P_{HI}, c) K

Sol:

	$2HI_{(g)}$	$\rightleftharpoons$	$H_{2(g)}$	+	$I_{2(g)}$
starting:	1.00atm		0atm		0atm
equilibrium:	1.00–2.00 = 0.80		0.10		0.10

$$K = \frac{P_{H_2} \cdot P_{I_2}}{(P_{HI})^2} \qquad P_{I_2} = 0.10atm$$
$$= \frac{0.10 \cdot 0.10}{(0.80)^2} \qquad P_{HI} = 0.80atm$$
$$= 1.6 \times 10^{-2}$$

§ 12-4 Applications of the equilibrium constant

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\quad K = \frac{(P_{NO})^2}{P_{N_2} \cdot P_{O_2}} = 1 \times 10^{-30}$ at 25 °C

$\Rightarrow$ K 值小 $\Rightarrow$ 反應物多

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\quad K = \frac{(P_{NH_3})^2}{P_{N_2} \cdot (P_{H_2})^3} = 6.5 \times 10^5$ at 25 °C

$\Rightarrow$ K 值大 $\Rightarrow$ 生成物多

§ Direction of Reaction: the reaction quotient (Q)

商數

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

$$K = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

Q: 任一狀態下之計算值

1) Q < K 反應 "→"
2) Q > K 反應 "←"
3) Q = K 平衡

Ex 12-5: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $K = 11$ at 100^oC

以 0.10mole N_2O_4 及 0.20mole NO_2, V = 2.0L 開始, predict the direction?

Sol:

$$P_{N_2O_4} = \frac{nRT}{V}$$

$$= \frac{0.10 \cdot 0.0821 \cdot 373}{2.0} = 1.5atm$$

$$P_{NO_2} = \frac{n'RT}{2}$$

$$= \frac{0.20 \times 0.0821 \cdot 373}{2.0} = 3.1atm$$

$$Q = \frac{(P_{NO})^2}{P_{N_2O_4}} = \frac{(3.1)^2}{1.5} = 6.4 < 11$$

∴反應向右 "→"

§ Extent reaction; equilibrium partial pressures

利用 K 求平衡式中，其一項之分壓

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad K = \frac{(P_{NO})^2}{P_{N_2} \cdot P_{O_2}} = 1.0 \times 10^{-30} \text{ at } 25^oC$$

$P_{N_2} = 0.78atm, P_{O_2} = 0.21atm$ 求 P_{NO}

$$K = \frac{(P_{NO})^2}{P_{N_2} \cdot P_{O_2}} = \frac{(P_{NO})^2}{0.78 \cdot 0.21} = 1.0 \times 10^{-30}$$

$$P_{NO}^2 = 1.61 \times 10^{-31} \Rightarrow P_{NO} = 4.0 \times 10^{-16} atm$$

Ex 12-6:

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)} \quad K = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}} = 0.64 \text{ at } 900^{o}C$$

Calculate the equilibrium partial pressure of all species, starting with

a) $P_{CO_2} = P_{H_2} = 1.00atm; P_{CO} = P_{H_2O} = 0$

b) $P_{CO_2} = 2.00atm, P_{H_2} = 1.00atm; P_{CO} = P_{H_2O} = 0$

Sol: a)

	$CO_{2(g)}$	+ $H_{2(g)}$	$\rightleftharpoons$ $CO_{(g)}$	+ $H_2O_{(g)}$
starting:	1.00	1.00	0	0
equilibrium:	1.00–x	1.00–x	x	x

$$K = \frac{x \cdot x}{(1.00 - x)(1.00 - x)} = 0.64$$

$$\frac{x}{1.00 - x} = 0.8$$

$$x = 0.80 - 0.8x$$

$$1.8x = 0.80$$

$$x = 0.44atm$$

$$\therefore P_{CO} = P_{H_2O} = 0.44atm$$

$$P_{CO_2} = P_{H_2} = 0.56atm$$

b)

	$CO_{2(g)}$	+ $H_{2(g)}$	$\rightleftharpoons$ $CO_{(g)}$	+ $H_2O_{(g)}$
starting:	2.00	1.00	0	0
equilibrium:	2.00–x	1.00–x	x	x

$$K = \frac{x \cdot x}{(2.00 - x)(1.00 - x)} = 0.64$$

$$\frac{x^2}{2.00 - 3.00x + x^2} = 0.64$$

$$0.64x^2 - 1.92x + 1.28 = x^2$$

$$0.36x^2 - 1.92x + 1.28 = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.92 \pm \sqrt{(1.92)^2 - 4 \cdot 0.36 \cdot (-1.28)}}{2 \cdot 0.36} = \frac{-1.92 \pm \sqrt{3.69 + 1.84}}{0.72}$$

$$= \frac{-.192 \pm 2.35}{0.72}$$

$x = 0.60$ or ~~-5.93~~ (不合)

$$\therefore P_{CO} = P_{H_2O} = 0.60atm$$

$$P_{CO_2} = 1.40atm, P_{H_2} = 0.40atm$$

§ 12-5 Effect of changes in conditions on an equilibrium system

Henri Le Châtelier(法) principle 勒沙特列原理:

If a system at equilibrium is distributed by a change in concentration, pressure or temperature, the system will, if possible, partially counteract the change. 反作用，抵消

⇓

- ●Concentration
- ●Pressure
- ●Temperature

Equilibria that are stressed shift in the direction that minimized the stress.

§ Adding or removing a gaseous species

加入反應物 "→"

加入生成物 "←"

Ex 12-7: from Ex 12-4, $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ at $520^{o}C, K = 0.016$

0.80atm 0.10atm 0.10atm

若 HI 之 pressure 增至 1.00atm, 再達平衡求 P_{HI}, P_{H_2}, P_{I_2}

Sol: $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

starting: 1.00 0.10 0.10

$$Q = \frac{(0.10)\cdot(0.10)}{1.00} = 0.010 < 0.016 \therefore " \rightarrow "$$

equilibrium: 1.00 – 2x 0.10 + x 0.10 + x

$$\frac{(0.10+x)\cdot(0.10+x)}{(1.00-2x)^2} = 0.016$$

$$\frac{0.10+x}{1.00-2x} = 0.13$$

$$0.13 - 0.26x = 0.10 + x$$

$$1.26x = 0.030$$

$$x = 0.024$$

$$P_{HI} = 1.00 - 2\cdot 0.024 = 0.95atm$$

$$P_{H_2} = 0.10 + 0.024 = 0.12atm$$

$$\text{check}: \frac{(0.12)^2}{(0.95)^2} = 1.6\times 10^{-2} \quad \text{--- (OK)}$$

§ Compression or Expression:

僅對氣態反應有影響，P↑平衡向氣態平衡係數總和較小的一方

P↓平衡向氣態平衡係數總和較大的一方

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

compression (即 P↑) 1 : 2 ∴ “←”

expansion (即 P↓) 1 : 2 ∴ “→”

表 12-5

§ Temperature:

吸熱反應($\Delta H > 0$) T↑ “→”

放熱反應($\Delta H < 0$) T↑ “←”

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H^o = +57.2KJ \Rightarrow T\uparrow \because \Delta H > 0 \therefore "\rightarrow"$$

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H^o = -92.2KJ \Rightarrow T\uparrow \because \Delta H < 0 \therefore "\leftarrow"$$

T 對 K 之影響:

van’t Hoff equation:

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}[\frac{1}{T_1} - \frac{1}{T_2}]$$

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H^o = -92.2KJ$$

25°C $K_1 = 6\times10^5$

求 100°C K =?

$$\ln\frac{K_2}{6\times10^5} = \frac{-92.2\times10^3}{8.31}[\frac{1}{298} - \frac{1}{373}] = -7.5$$

$$\frac{K_2}{6\times10^5} = 5.5\times10^{-4}$$

$$K_2 = 3.3\times10^2$$

Ex 12-8:

a) $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta H = -566KJ$

b) $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ $\Delta H = -2.7KJ$

c) $H_{2(s)} + I_{2(s)} \rightarrow 2HI_{(g)}$ $\Delta H = +53.0KJ$

d) $I_{2(g)} \rightarrow 2I_{(g)}$ $\Delta H = +36.2KJ$

compressed (P ↑) 及 T ↑ 對平衡之影響

Sol:

a) P ↑ 3 : 2 "→" T ↑ $\Delta H < 0$ "←"

b) P ↑ 2 : 2 "×" T ↑ $\Delta H < 0$ "←"

c) P ↑ 1 : 2 "←" T ↑ $\Delta H > 0$ "→"

d) P ↑ 1 : 2 "←" T ↑ $\Delta H > 0$ "→"