

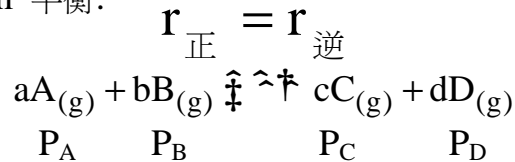
Ch 12 Gaseous chemical equilibrium

↳ 條件: 可逆反應



reversible reaction, reactants are not completely consumed.

Equilibrium 平衡:



$$P_i = n_i RT / V$$

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

12-1 N₂O₄-NO₂ equilibrium system

12-2 The equilibrium constant expression

12-3 Determination of K

12-4 Applications of the equilibrium constant

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

Le Châtelier principle

§ 12-1 The N₂O₄-NO₂ equilibrium system



$$r_{\text{正}} = k_1 [\text{N}_2\text{O}_4]$$

$$r_{\text{逆}} = k_2 [\text{NO}_2]^2$$

平衡:

$$r_{\text{正}} = r_{\text{逆}}$$

$$K = \frac{k_1}{k_2} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

P = C
T = C

平衡常數: K 僅隨 1.反應式

2.T → van't Hoff equation

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

Clausius-Clapeyron equation

§ 12-2 The equilibrium constant expression

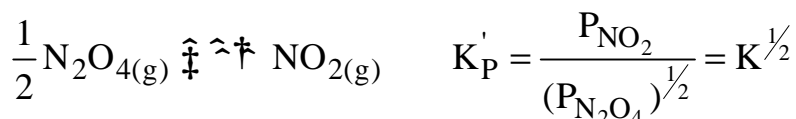
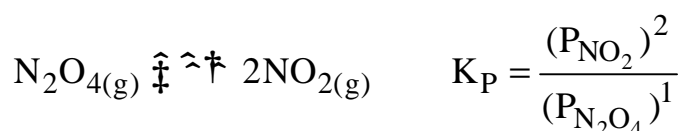


$$K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b}$$

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

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

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

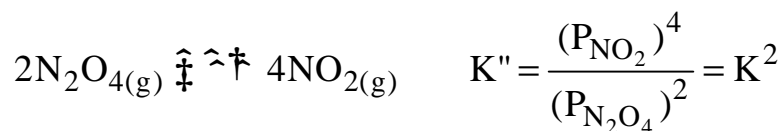


∴

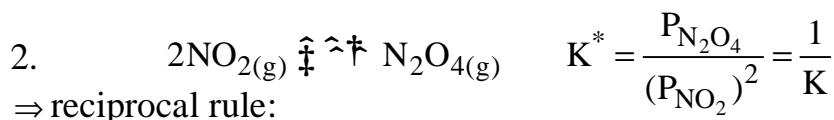
1. If the coefficients in a balanced equation are multiplied by a factor n, the equilibrium constant is raised to the nth power.

$$K' = K^n$$

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



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



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

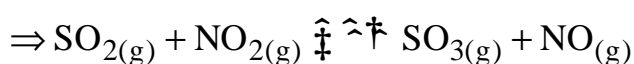
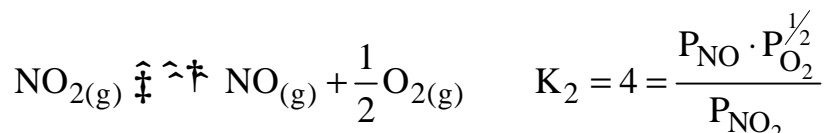
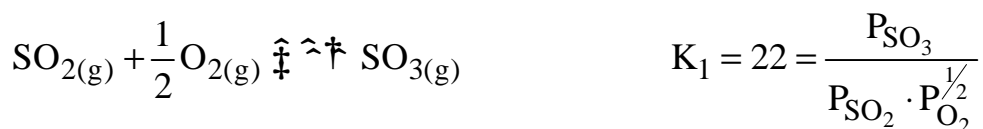
$$K_{\text{正}} = \frac{1}{K_{\text{逆}}}$$

$$K_{\text{正}} \cdot K_{\text{逆}} = 1$$

3. Adding chemical equations

rule of multiple equilibria

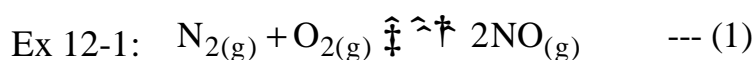
If a reaction can be expressed as the sum of two or more reactions, K for the overall reactions is the product of the equilibrium constants of the individual reactions.



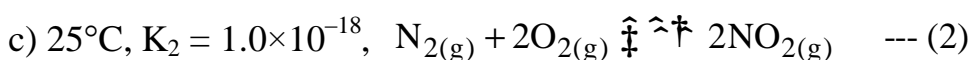
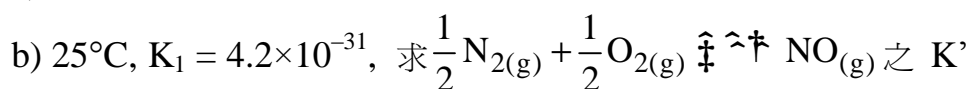
$$K = \frac{P_{\text{SO}_3} \cdot P_{\text{NO}}}{P_{\text{SO}_2} \cdot P_{\text{NO}_2}} = K_1 \cdot K_2 = 22 \cdot 4 = 88$$

∴ 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



a) K_1 for the reaction



求 $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ 之 K_3

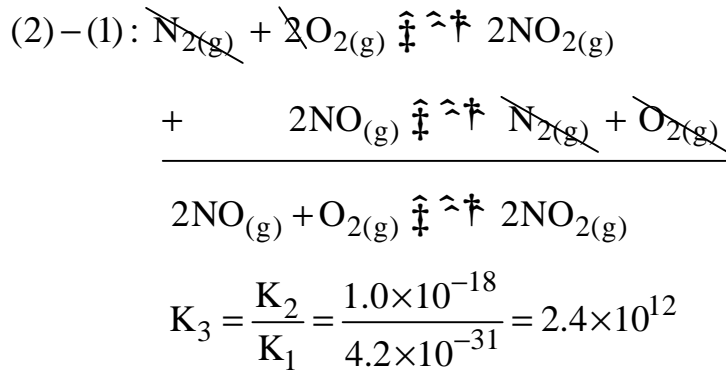
Sol:

$$K_1 = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} \cdot P_{\text{O}_2}} = 4.2 \times 10^{-31}$$

$$K' = \frac{P_{\text{NO}}}{P_{\text{N}_2}^{1/2} \cdot P_{\text{O}_2}^{1/2}} = K_1^{1/2} = (4.2 \times 10^{-31})^{1/2} = 6.5 \times 10^{-16}$$

$$K_2 = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2} \cdot P_{\text{O}_2}^2}$$

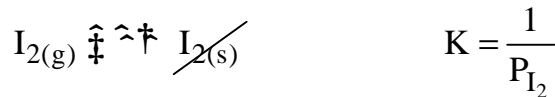
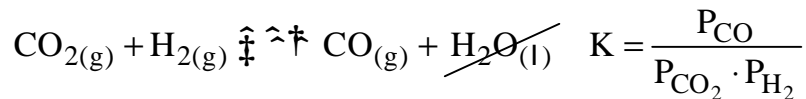
$$K_3 = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \cdot P_{\text{O}_2}} = \frac{K_2}{K_1}$$



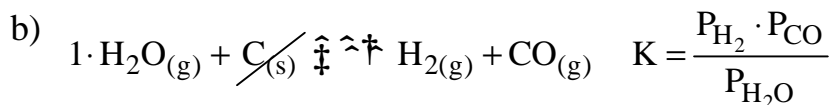
§ Heterogeneous Equilibria 非均匀平衡

*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.



Ex 12-2: 求 K

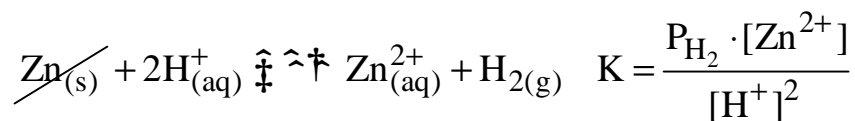


**平衡常數:

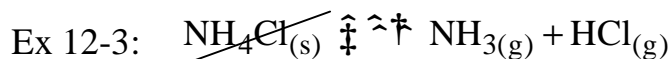
*(g): 以分壓(atm)計算

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

*(aq): 以 M 計算

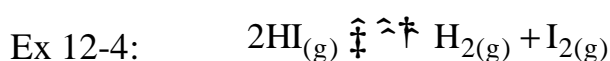


§ 12-3 Determination K



400°C, 22.6g NH_4Cl ; $P_{\text{NH}_3} = 2.5\text{atm}$, $P_{\text{HCl}} = 4.8\text{atm}$ 求 K at 400°C

Sol:
$$\begin{aligned} K &= P_{\text{NH}_3} \cdot P_{\text{HCl}} \\ &= 2.5 \cdot 4.8 \\ &= 12 \end{aligned}$$



originally $P_{\text{HI}} = 1.00\text{atm}$ at 25°C, at equilibrium $P_{\text{H}_2} = 0.10\text{atm}$

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

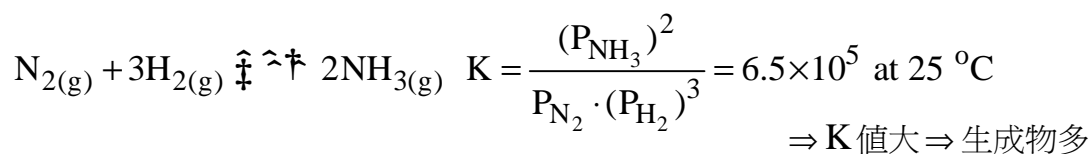
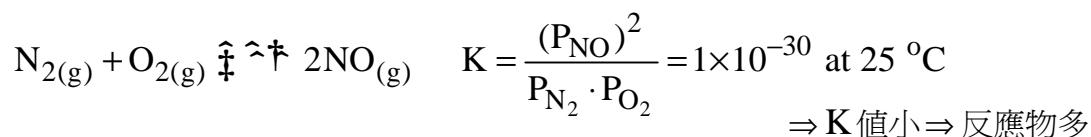


Sol:

starting:	1.00atm	0atm	0atm
equilibrium:	$1.00 - 2.00 = 0.80$	0.10	0.10

$$\begin{aligned} K &= \frac{P_{\text{H}_2} \cdot P_{\text{I}_2}}{(P_{\text{HI}})^2} & P_{\text{I}_2} &= 0.10\text{atm} \\ &= \frac{0.10 \cdot 0.10}{(0.80)^2} & P_{\text{HI}} &= 0.80\text{atm} \\ &= 1.6 \times 10^{-2} \end{aligned}$$

§ 12-4 Applications of the equilibrium constant



§ Direction of Reaction: the reaction quotient (Q)

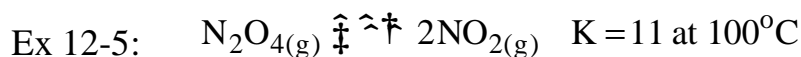
商數



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

Q: 任一狀態下之計算值

- 1) $Q < K$ 反應 “ \rightarrow ”
- 2) $Q > K$ 反應 “ \leftarrow ”
- 3) $Q = K$ 平衡



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

Sol:

$$P_{N_2O_4} = \frac{nRT}{V} \\ = \frac{0.10 \cdot 0.0821 \cdot 373}{2.0} = 1.5 \text{ atm}$$

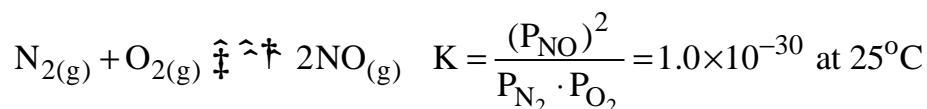
$$P_{NO_2} = \frac{n'RT}{2} \\ = \frac{0.20 \times 0.0821 \cdot 373}{2.0} = 3.1 \text{ atm}$$

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

\therefore 反應向右 “ \rightarrow ”

§ Extent reaction; equilibrium partial pressures

利用 K 求平衡式中，其一項之分壓

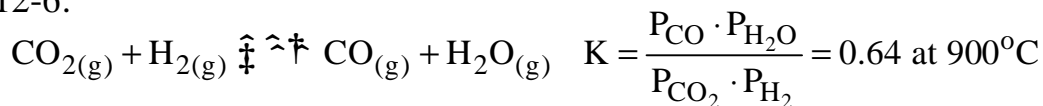


$P_{N_2} = 0.78 \text{ atm}, P_{O_2} = 0.21 \text{ atm}$ 求 P_{NO}

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

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

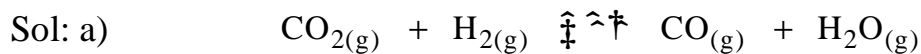
Ex 12-6:



Calculate the equilibrium partial pressure of all species, starting with

a) $P_{\text{CO}_2} = P_{\text{H}_2} = 1.00\text{atm}; P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0$

b) $P_{\text{CO}_2} = 2.00\text{atm}, P_{\text{H}_2} = 1.00\text{atm}; P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0$



starting:	1.00	1.00	0	0
equilibrium:	$1.00-x$	$1.00-x$	x	x

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

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

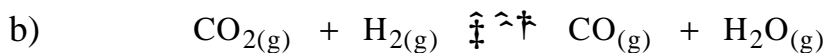
$$x = 0.80 - 0.8x$$

$$1.8x = 0.80$$

$$x = 0.44\text{atm}$$

$$\therefore P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0.44\text{atm}$$

$$P_{\text{CO}_2} = P_{\text{H}_2} = 0.56\text{atm}$$



starting:	2.00	1.00	0	0
equilibrium:	$2.00-x$	$1.00-x$	x	x

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

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

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

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

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

$$= \frac{-1.92 \pm 2.35}{0.72}$$

$$x = 0.60 \text{ or } -5.93 \text{ (不合)}$$

$$\therefore P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0.60\text{atm}$$

$$P_{\text{CO}_2} = 1.40\text{atm}, P_{\text{H}_2} = 0.40\text{atm}$$

§ 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 Equilibria that are stressed shift in the direction that
- Pressure minimized the stress.
- Temperature

§ Adding or removing a gaseous species

加入反應物 “→”

加入生成物 “←”

Ex 12-7: from Ex 12-4, $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$ at 520°C , $K = 0.016$
 0.80atm 0.10atm 0.10atm

若 HI 之 pressure 增至 1.00atm , 再達平衡求 $P_{\text{HI}}, P_{\text{H}_2}, P_{\text{I}_2}$

Sol: $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$
 starting: 1.00 0.10 0.10
 $Q = \frac{(0.10) \cdot (0.10)}{1.00} = 0.010 < 0.016 \therefore \text{ " } \rightarrow \text{ "}$

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

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

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

$$1.26x = 0.030$$

$$x = 0.024$$

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

$$P_{\text{H}_2} = 0.10 + 0.024 = 0.12\text{atm}$$

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

§ Compression or Expansion:

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



compression (即 P ↑) 1 : 2 ∴ “←”

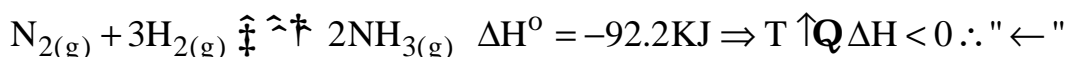
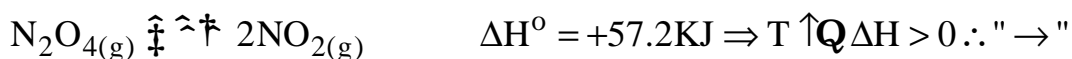
expansion (即 P ↓) 1 : 2 ∴ “→”

表 12-5

§ Temperature:

吸熱反應($\Delta H > 0$) T ↑ “→”

放熱反應($\Delta H < 0$) T ↑ “←”



T 對 K 之影響:

van't Hoff equation:

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



$$25^\circ\text{C} \quad K_1 = 6 \times 10^5$$

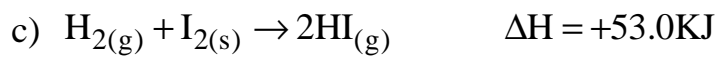
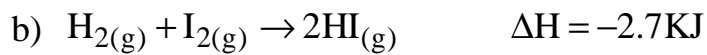
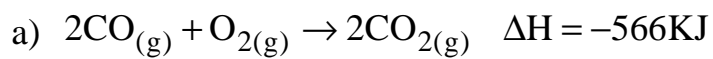
求 $100^\circ\text{C} \quad K = ?$

$$\ln \frac{K_2}{6 \times 10^5} = \frac{-92.2 \times 10^3}{8.31} \left[\frac{1}{298} - \frac{1}{373} \right] = -7.5$$

$$\frac{K_2}{6 \times 10^5} = 5.5 \times 10^{-4}$$

$$K_2 = 3.3 \times 10^2$$

Ex 12-8:



compressed (P ↑) 及 T ↑ 對平衡之影響

Sol:

