§ Acid-base titration

Titration：Measuring the volume of a standard solution (a solution of known concentration) required to react with a measured amount of sample.

Fig 4.7 titration of vinegar (CH_3COOH) with sodium hydroxide

Step 1. 三角錐瓶加入已知量之 CH_3COOH ＋ 指示劑 (1-2 drop)

Step 2. 以滴定管滴入 $NaOH$ 酸管：全玻璃
鹼管：玻璃 ＋ 塑膠軟件

Step 3. 滴定至滴定終點

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O$$

$(HC_2H_3O_2)$

Equivalence point：當量點

The number of equivalent mole of base equal to the number of equivalent mole of acid .

$$N_AV_A = N_BV_B$$

CH_3COOH	1 M = 1 N
H_2SO_4	1M = 2N
$NaOH$	1 M = 1 N
$Ca(OH)_2$	1 M = 2 N

End point：滴定終點

The point of the indicator change color.

Neutralization point：中和點

The titration solution reaches pH = 7.0.

§ Ex 4-7：Three beakers labeled A, B, and C contain the weak acid H_2X. The weak acid is titrated with 0.125 M NaOH. Assume the reaction to be

$$H_2X\ (aq) + 2\,OH^-\ (aq) \rightarrow 2\,H_2O + X^{2-}\ (aq)$$

a) Beaker A contains 25.00 mL of 0.316 M H_2X . What volume of NaOH is required for complete neutralization?

b) Beaker B contains 25.0 mL of a solution of H_2X and requires 28.74mL of NaOH for complete neutralization. What is the molarity of the H_2X solution?

c) Beaker C contains 0.124 g of H_2X and 25.00 ML of water. To reach the equivalence point, 22.04 mL ofNaOH are required. What is the molar mass of H_2X?

Ans:

$a)\quad H_2X(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O + X^{2-}(aq)$

$$n_{H_2X} = \frac{25.00}{1000} \cdot 0.316 = 7.90\times10^{-3}\ \text{mol}$$

$$n_{H_2X} : n_{OH^-} = 1 : 2$$

$$7.90\times10^{-3} : n_{OH^-} = 1 : 2$$

$$n_{OH^-} = 0.0158\ \text{mol}$$

$$V_{OH^-} = \frac{n_{OH^-}}{M_{OH^-}} = \frac{0.0158}{0.125} = 0.126\ \text{L}$$

$b)\quad n_{OH^-} = 0.125 \times \dfrac{28.74}{1000} = 3.59\times10^{-3}\ \text{mol}$

$$n_{H_2X} : n_{OH^-} = 1 : 2$$

$$n_{H_2X} : 3.59\times10^{-3} = 1 : 2$$

$$n_{H_2X} = 1.80\times10^{-3}\ \text{mol}$$

$$M_{H_2X} = \frac{n_{H_2X}}{V_{H_2X}} = \frac{1.80\times10^{-3}}{0.02500} = 0.0720\ \text{M}$$

$c)\quad n_{OH^-} = 0.125 \times \dfrac{22.04}{1000} = 2.76\times10^{-3}\ \text{mol}$

$$n_{H_2X} : n_{OH^-} = 1 : 2$$

$$n_{H_2X} : 2.76\times10^{-3} = 1 : 2$$

$$n_{H_2X} = 1.38\times10^{-3}\ \text{mol}$$

$$MM_{H_2X} = \frac{m_{H_2X}}{n_{H_2X}} = \frac{0.124}{1.38\times10^{-3}} = 89.9\ \text{g/mol}$$

§ 4-4 **Oxidation-reduction Reactions** ⇒ Redox reactions

↳ involves a transfer of electrons between two species.

例：金屬與酸之反應　Zn 與 HCl 反應

Oxidation： a specie loses electrons

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

↳ The ion or molecule donates electrons ⇒ Reducing agent

Reduction： a specie gains electrons

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

↳ The ion or molecule accepts electrons ⇒ Oxidizing agent

Redox reaction：

$$Zn(s) + 2H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

For a redox reaction：

1. Oxidation and reduction occur together.
2. There is no net change in the number of electrons in a redox reaction.

§ Oxidation number 氧化數

		Oxidation number	Ex.	
1. An element in an elementary substance		0	Cl_2	0
			P_4	0
			K	0
2. Monatomic ion		the charge of the ion	Cl^-	-1
			Al^{3+}	+3
			O^{2-}	-2
3. IA element in compound		+1	Na^+	+1
			K^+	+1
IIA		+2	Ca^{2+}	+2
			Mg^{2+}	+2
VIIA		-1	Cl^-	-1
			F^-	-1
Oxygen in ordinary compound		-2	H_2O	O：-2
	例外：		H_2O_2	O：-1
Hydrogen in ordinary compound		+1	HCl	H：+1
	例外：		NaH	H：-1
			CaH_2	H：-1

4. The sum of the oxidation numbers in a neutral species is O.

5. In a polyatomic ion, it is equal to the charge of that ion.

Ex 4-8 ：What is the oxidation number of phosphorus in

a) sodium phosphite, Na_3PO_3 ?

b) In the dihydrogen phosphate ion $H_2PO_4^-$?

Ans:

a) Na_3PO_3

$(+1)\times 3 + x + (-2)\times 3 = 0$

$x = +3$

b) $H_2PO_4^-$

$(+1)\times 2 + x + (-2)\times 4 = -1$

$x = +5$

§ Oxidation and Reduction

(陽極)

Oxidation：an increase in oxidation number 氧化數增加,失去電子,還原劑

Reduction：a decrease in oxidation number 氧化數減少,獲得電子,氧化劑

(陰極)

+1 -1; reduction 0

$$Zn(s) + 2H^+ \longrightarrow Zn^{2+}(aq) + H_2(g) \quad \Rightarrow \text{ Redox reaction.}$$

0 +2; oxidation +2

+2 -2; reduction 0

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s) \quad \Rightarrow \text{ Redox reaction.}$$

0 +3; oxidation +3

+1 0 +1

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O \quad \Rightarrow \text{ Not a redox reaction.}$$

+4 0 +4

§ Balancing half-equation (Oxidation or Reduction)

Oxidation $Fe^{+2}(aq) \longrightarrow Fe^{3+}(aq)$ 左、右元素一致

+2 +1 +3

$$\Rightarrow Fe^{+2}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

Reduction $Cl_2(aq) \longrightarrow 2Cl^-(aq)$ 左、右元素一致

0 -1×2 -1

$\Rightarrow Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq)$

若是:

$MnO_4^-(aq) \longrightarrow Mn^{+2}(aq)$ 　　左、右元素不一致

$Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$ 　　左、右元素不一致

平衡步驟：

a. Balance the atoms of the element being oxidized or reduced.
b. Balance the oxidation number by adding electrons.
平衡氧化數: 氧化數多的一邊加電子
c. Balance charge by adding H^+ ions in acidic solution, OH^- ions in basic solution.
平衡電荷數: 酸溶液加 H^+ (電荷數較少之一邊)，鹼溶液加 OH^- (電荷數較多之一邊)
d. Balance hydrogen by adding H_2O molecules. 平衡 H: **H 不夠一邊加 H_2O**
e. Balance Oxygen number. 平衡 O: O 左右相等即完成平衡

Ex 4-9： Balance the following half-equations

1) $MnO_4^-(aq) \longrightarrow Mn^{+2}(aq)$ (acidic solution)

2) $Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$ (basic solution)

Sol ：1) a) $x+(-2)\times 4=-1 \Rightarrow x=+7$

$MnO_4^-(aq) \longrightarrow Mn^{+2}(aq)$

+7 -5; reduction +2

b) 氧化數多的一邊加 e^-

∴ 左：+ $5e^-$

$MnO_4^-(aq) + 5e^- \longrightarrow Mn^{+2}(aq)$

c) **酸溶液加 H^+ (電荷數較少之一邊)**

電荷數: 左：-6 右：+2

∴ 左：+ $8H^+$

$\therefore MnO_4^-(aq) + 5e^- + 8H^+ \longrightarrow Mn^{+2}(aq)$

d) H：左 = 8 右 = 0

∴ 右：+ $4H_2O$

$$\therefore\ MnO_4^-(aq) + 5e^- + 8H^+ \longrightarrow Mn^{+2}(aq) + 4H_2O$$

e) O：左 = 4　　　右 = 4　　ok!!

$$\therefore\ MnO_4^-(aq) + 5e^- + 8H^+ \longrightarrow Mn^{+2}(aq) + 4H_2O$$

B)

a) $x + (-2)\times 4 = -2 \Rightarrow x = +6$

$$Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$$

+3　+3; oxidation　+6

b) 氧化數多的一邊加 e^-

∴ 右：$+ 3e^-$

$$\Rightarrow Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 3e^-$$

c) **鹼溶液加 OH^- (電荷數較多之一邊)**

電荷數: 左：0　　右：-2 – 3 = -5

∴ 左：$+ 5OH^-$

$$\Rightarrow Cr(OH)_3(s) + 5OH^- \longrightarrow CrO_4^{2-}(aq) + 3e^-$$

d) check H：　左 = 3+5　　右 = 0

右：$+ 4H_2O$

$$\Rightarrow Cr(OH)_3(s) + 5OH^- \longrightarrow CrO_4^{2-}(aq) + 3e^- + 4H_2O$$

e) check O：　左 = 3 + 5 = 8　　右 4 + 4 = 8 ok!!

$$\Rightarrow Cr(OH)_3(s) + 5OH^- \longrightarrow CrO_4^{2-}(aq) + 3e^- + 4H_2O$$

§ Balancing Redox equation:

1. 分為 oxidation 及 reduction equation
2. 分別平衡 half-equation
3. 分別平衡另一 half-equation
4. (2 + 3) $\Rightarrow$ 消去電子

Ex 4-10：Balance the following redox equations.

a) $Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$　(acidic solution)

b) $Cl_2(g) + Cr(OH)_3(s) \longrightarrow Cl^-(aq) + CrO_4^{2-}(aq)$　(basic solution)

Ans:

a) +2 +1; oxidation +3

$$Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$$

+7 -5: reduction +2

Oxidation $(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-) \times 5$

Reduction $(MnO_4^-(aq) + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O) \times 1$ $\Rightarrow$ Ex 4.9 (1)

$\Rightarrow$

$$5Fe^{2+}(aq) \longrightarrow 5Fe^{3+}(aq) + 5e^-$$

$$+)\quad MnO_{4\,(aq)}^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+ \longrightarrow 5Fe^{3+}(aq) + Mn^{2+} + 4H_2O$$

b) +3 +3 +6

$$Cl_2(g) + Cr(OH)_3(s) \longrightarrow 2Cl^-(aq) + CrO_4^{2-}(aq)$$

0 -1 × 2 -1

Reduction：$(Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)) \times 3$

Oxidation：$(Cr(OH)_3(s) + 5OH^- \longrightarrow CrO_4^{2-}(aq) + 4H_2O + 3e^-) \times 2$ $\Rightarrow$ Ex 4.9(2)

$$3Cl_2(g) + 6e^- \longrightarrow 6Cl^-(aq)$$

$$+)\quad 2Cr(OH)_3(s) + 10OH^- \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O + 6e^-$$

$$3Cl_2(g) + 2Cr(OH)_3(s) + 10OH^- \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O$$

Ex 4-11: As you found in Example 4.10, the balanced equation for the reaction between $MnO_4^-(aq)$ and $Fe^{2+}(aq)$ in acidic solution is

$$MnO_4^-(aq) + 8H^+ + 5Fe^{2+}(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+} + 4H_2O$$

What volume of 0.684 M $KMnO_4$ solution is required to react completely with 27.5 mL 0.250 M $Fe(NO_3)_2$?

Ans:

$$n_{Fe^{2+}} = 0.250 \times \frac{27.5}{1000} = 6.88 \times 10^{-3} \text{ mol}$$

$$1 : 5 = n_{MnO_4^-} : 6.88 \times 10^{-3}$$

$$n_{MnO_4^-} = 1.38 \times 10^{-3} \text{ mol}$$

$$1.38 \times 10^{-3} = 0.684 \times \frac{x}{1000}$$

$$x = 2.02 \text{ mL}$$