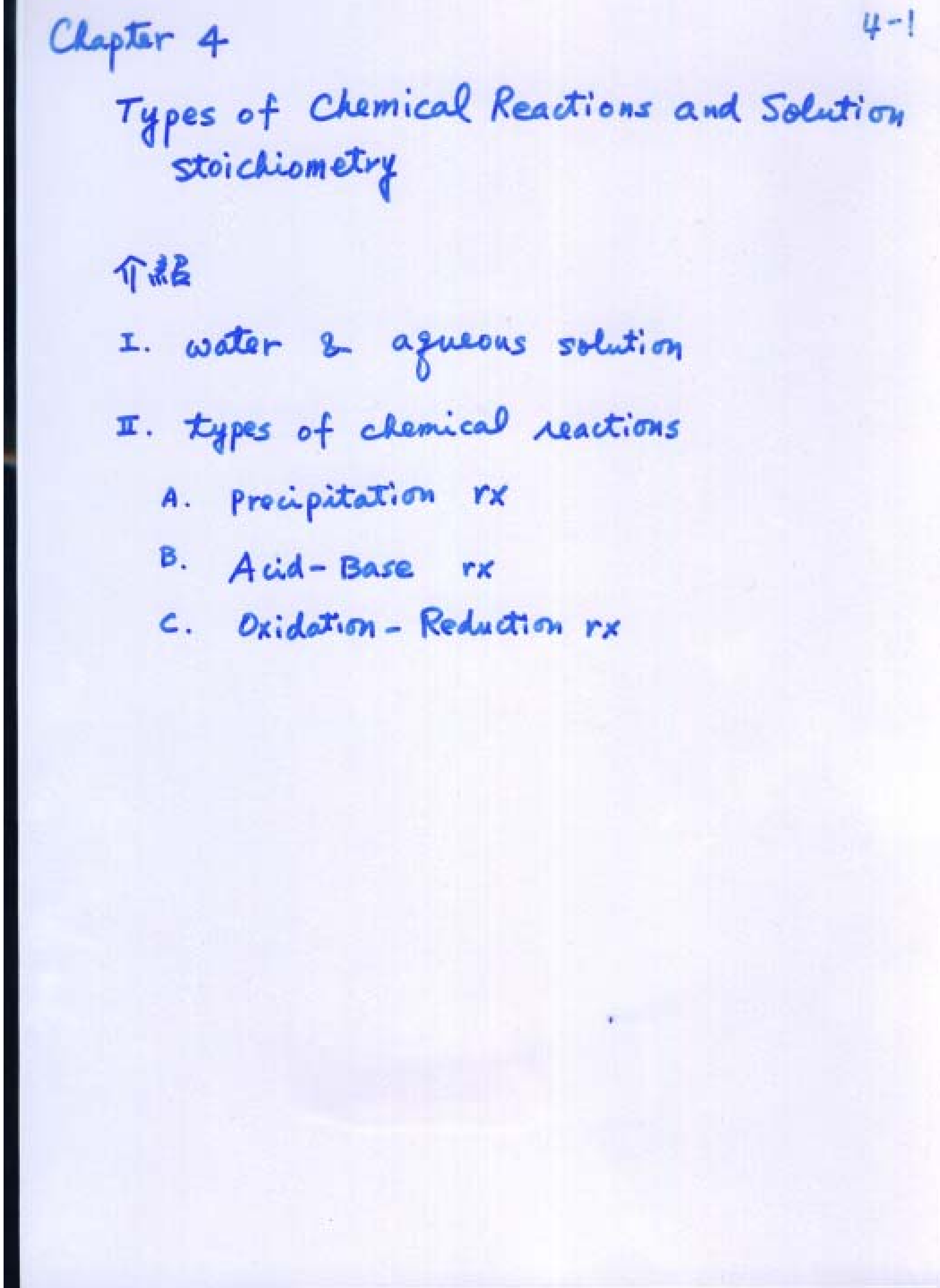
General Chemistry

Chapter 4



Chapter 4

Types of Chemical Reactions and Solution stoichiometry

介紹

I. water & aqueous solution

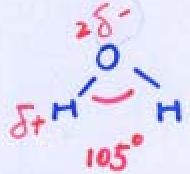
II. types of chemical reactions

  A. Precipitation rx

  B. Acid-Base rx

  C. Oxidation-Reduction rx

§4.1 Water



is a
polar molecule: Unequal charge distribution

Polarity of water gives water its great ability to dissolve compound.

Hydration (水合反應): 'positive ends' of the water molecules (H) are attached to the negatively charged anions; the 'negative ends' are attached to the positively charged cations.

Ex. See Fig 4.2 page 135

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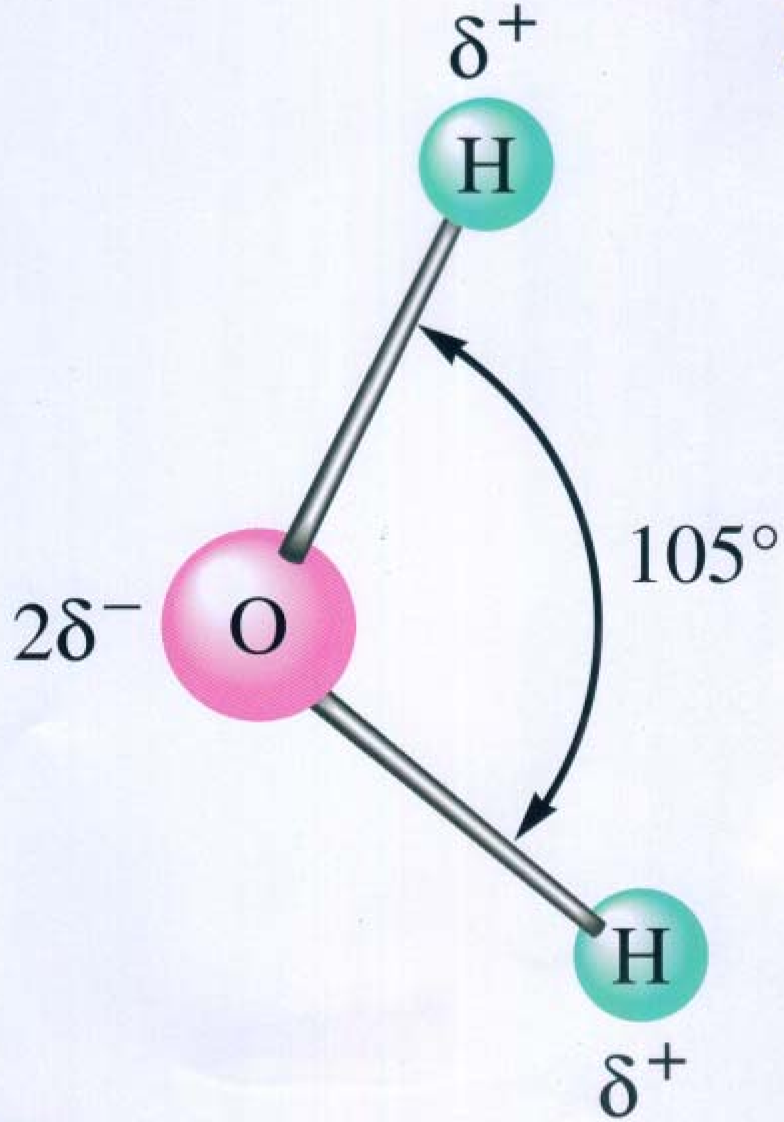

Figure 4.1
Polarity of the water molecule

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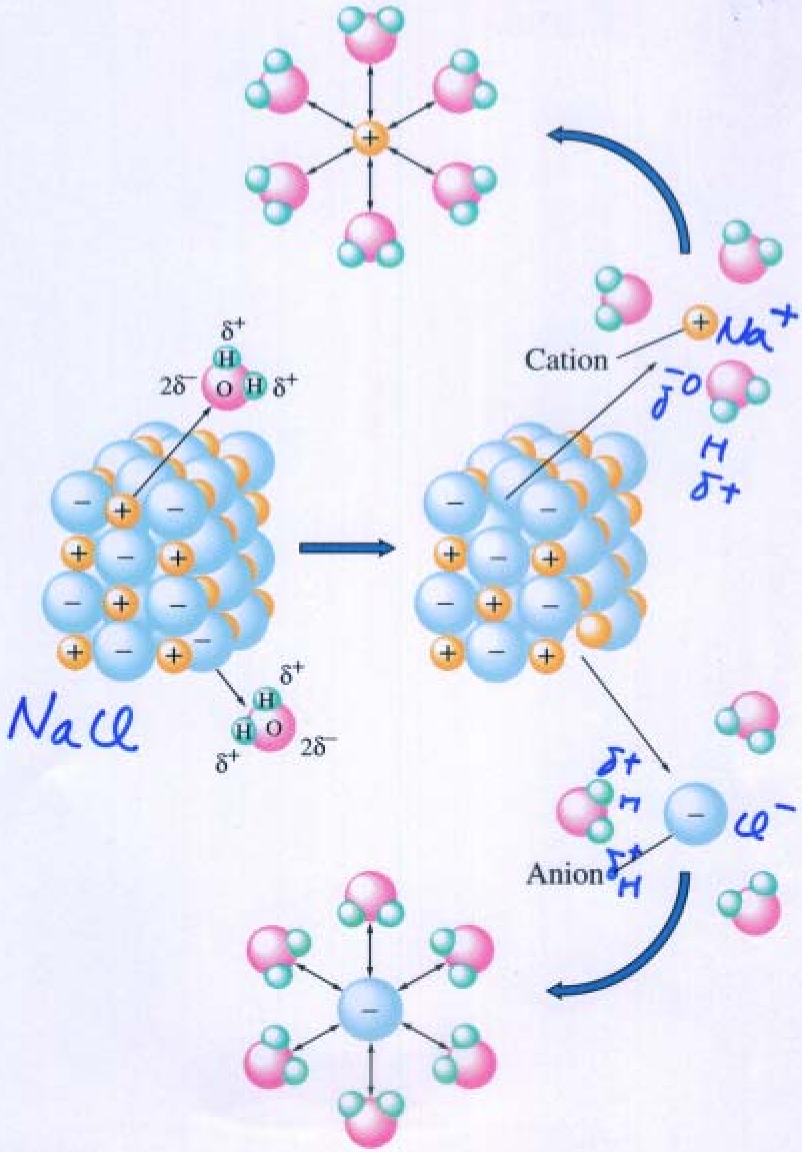

Figure 4.2
Ionic solid dissolving in water

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§ 4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

Solute 溶質

Solvent 溶劑

Solution 可用導电度 (electrical conductivity) 來分別

裝置如 Fig. 4.4.

strong electrolyte : 強电解質
ions move randomly (Ex. HCl)

weak electrolyte : 弱电解質
部分 compound 解離成 ions
(Ex. CH_3COOH)

non electrolyte : 非电解質
不解離成 ions . 不導电
(Ex. sucrose)

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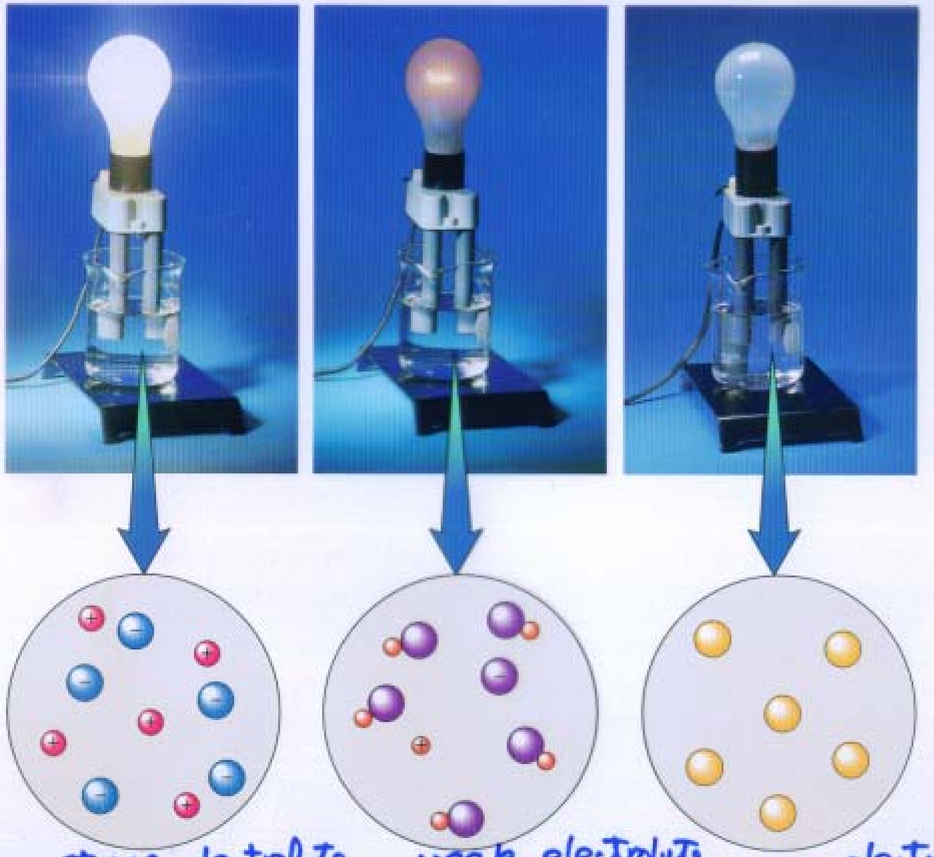
24 4.4 Electrical conductivity of aqueous solutions



(a) strong electrolyte (b) weak electrolyte (c) non-electrolyte

E.X HCl CH3COOH Sucrose

4-6

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I. Strong electrolyte : (1) soluble salts
(2) strong acids
(3) strong bases

Arrhenius found : Acids behaved as strong electrolytes.

$HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$

$HNO_3 \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$

$H_2SO_4 \xrightarrow{H_2O} H^+(aq) + HSO_4^-(aq)$

Acid : a substance that produces H^+ ions
(Arrhenius) (protons) when it dissolved in water.

strong acid : every molecule ionizes.

strong base : soluble ionic compounds containing the hydroxide (OH^-).

$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$

II. weak electrolytes : substances that exhibit a small degree of ionization in water

Ex. acetic acid 乙酸 or 醋酸

$CH_3COOH(aq) \underset{}{\overset{H_2O}{\rightleftarrows}} CH_3COO^-(aq) + H^+(aq)$

weak acid : dissociates (ionizes) only to a slight extent in aqueous solutions

III. Nonelectrolyte

Substances that dissolve in water but do not produce any ions.

§ 4.3 The composition of solutions

molarity (M) : moles of solute per volume of solution in liters

$$\frac{\text{moles of solute}}{\text{liters of solution}}$$

Ex. 4.1 11.5 g of solid NaOH → 1.50 ℓ solution

sol: $\frac{11.5\text{ g NaOH}}{40.00\text{ g/mole}} = 0.288$ mole NaOH

$\frac{0.288\text{ mole}}{1.50\ell} = 0.192$ M

Ex. 4.3 (b) 1 M $Fe(ClO_4)_3$

Iron (III) perchlorate

$$Fe(ClO_4)_{3(s)} \xrightarrow{H_2O} Fe^{3+}_{(aq)} + 3\,ClO_4^-{}_{(aq)}$$

1 M 1 M 3 M

Ex. 4.5

Typical blood serum is about 0.14^M NaCl. what volume of blood contains 1.0mg NaCl?

sol.

$$0.14^M \text{ NaCl} = \frac{\left(\frac{1.0\times10^{-3}\text{ g NaCl}}{58.45\ \text{g/mole}}\right)}{X\ \text{liter}}$$

$$\therefore X = 1.2\times10^{-4}\ \ell \text{ solution}$$

∴ 0.12 mℓ blood serum contains 1.0 mg NaCl

Standard solution: a solution whose concentration is accurately known.

Ex. 4.6 配標準溶液

Prepare 1.00ℓ of 0.200^M $K_2Cr_2O_7$ (potassium dichromate) → ? g solid $K_2Cr_2O_7$

See Fig 4.10

sol: $$1.00\ \ell \text{ solution} \times 0.200\ \frac{\text{moles}}{\text{liter}} = 0.200 \text{ mole } K_2Cr_2O_7$$

$$0.200 \text{ mole} \times 294.20\ \frac{\text{g}}{\text{mole}} = 58.8 \text{ g } K_2Cr_2O_7$$

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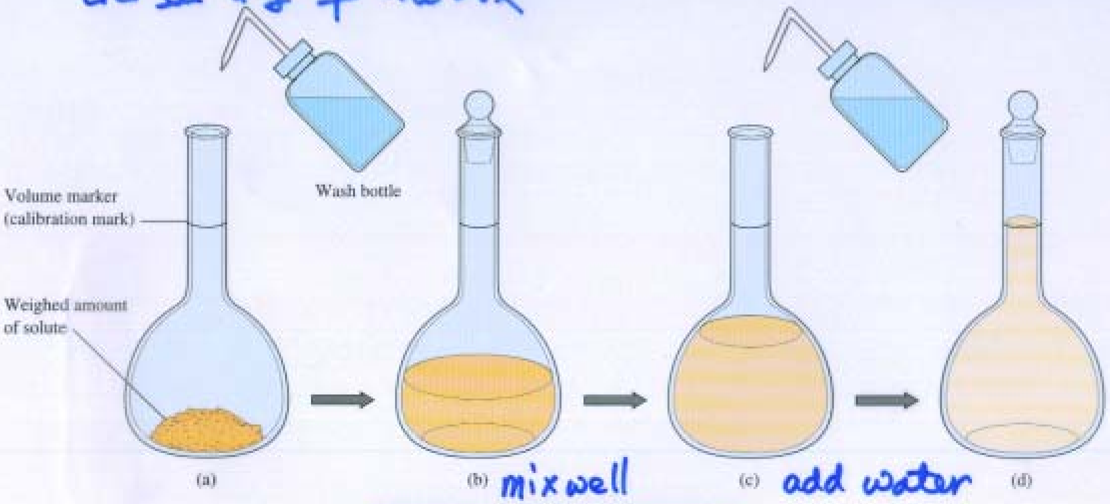
29 4.10 Preparation of a standard solution

配置標準溶液



4-10

Dilution 稀釋

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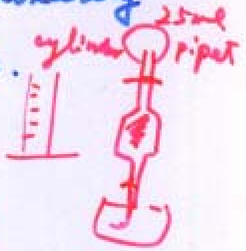
4-11

Two types of measuring pipets → Fig 4.11 (page 145)

To save time in laboratory, solutions which are routinely used are often prepared in concentrated form (stock solution)

water is added to achieve the molarity desired for a particular solution.



Remember:

moles of solute after dilution
= moles of solute before dilution
$(M_1 V_1 = M_2 V_2)$

Ex. 4.7

stock solution 16 M H_2SO_4

want to prepare 1.5 L of a 0.10 M H_2SO_4

Need to take ? volume of stock solution?

Sol: $M_1 V_1 =$
$1.5 \text{ L} \times 0.10 \text{ M} \left(\frac{\text{mole}}{\text{liter}}\right) = 0.15 \text{ mole}$
$M_2 V_2 = M_1 V_1$
$16^{\text{M}} \cdot V = 0.15 \text{ mole}$
$V = 9.4 \times 10^{-3} \text{ L} = 9.4 \text{ ml}$ stock solution

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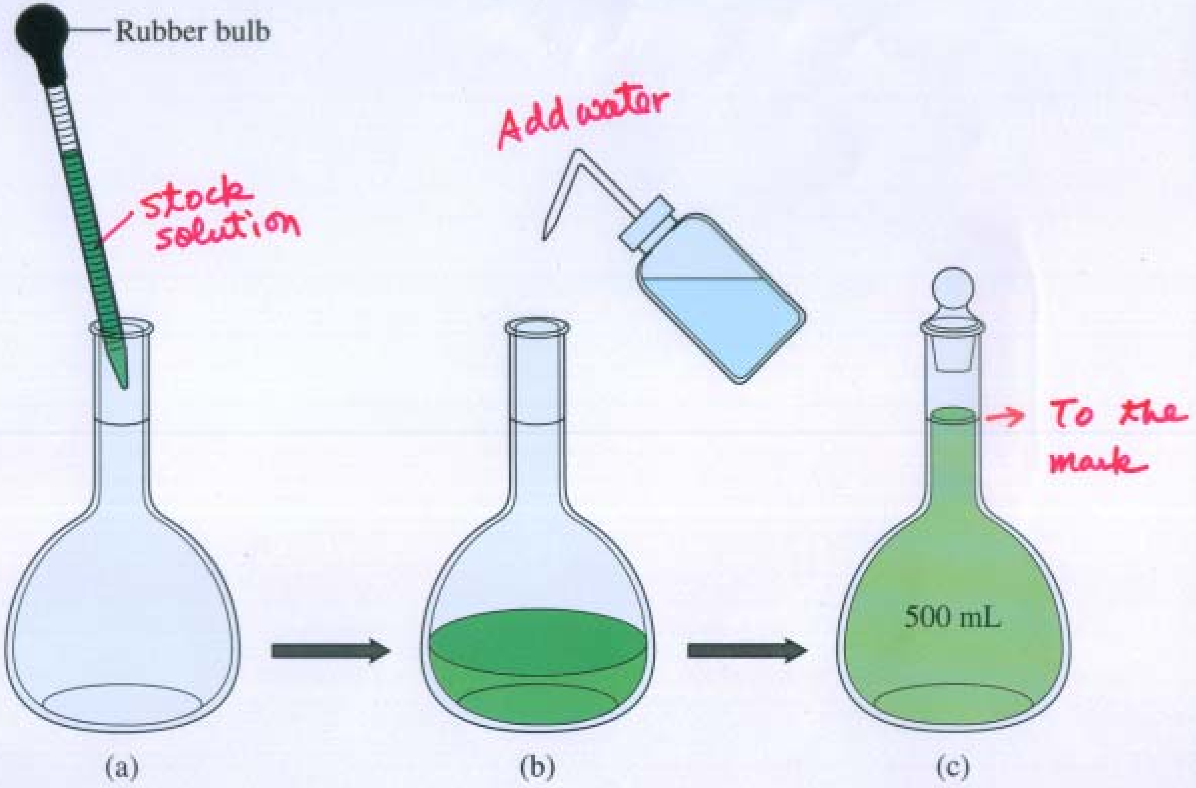

Figure 4.12
Dilution procedure

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§ 4.5 Precipitation Reactions:

when two solutions are mixed, an insoluble substance sometimes forms. such a rx is called Precipitation rx, and the solid that forms is called precipitate.

$$K_2CrO_{4(aq)} + Ba(NO_3)_{2(aq)} \rightarrow \overset{\text{yellow}}{\text{ppt}}\downarrow$$

$$2K^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} + 2NO_3^{-}{}_{(aq)}$$

possible combinations:

reactant ← K_2CrO_4 , $\boxed{KNO_3}$ soluble

$\boxed{BaCrO_4}$, $Ba(NO_3)_2$

↑ reactant.

↓ ppt

Rules for solubility of Salts in water

Table 4.1 (page 152)

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Ex. 4.8

a $KNO_{3(aq)} + BaCl_{2(aq)}$

b $Na_2SO_{4(aq)} + Pb(NO_3)_{2(aq)}$ $\qquad PbSO_{4(s)}\downarrow$ ppt

c $KOH_{(aq)} + Fe(NO_3)_{3(aq)}$ $\qquad Fe(OH)_{3(ppt)}\downarrow$

Sol:

a. $\overbrace{K^+ + \underbrace{NO_3^- + Ba^{2+}}_{\times} + 2Cl^-}^{\times}$

No reaction

b. $\underbrace{2Na^+ + \overbrace{SO_4^{2-} + Pb^{2+}}^{ppt} + 2NO_3^-}$

↓

$PbSO_{4(s)} + NaNO_{3(aq)}$

c. $\overbrace{K^+ + \underbrace{OH^- + Fe^{3+}}_{\checkmark} + 3NO_3^-}^{\times}$

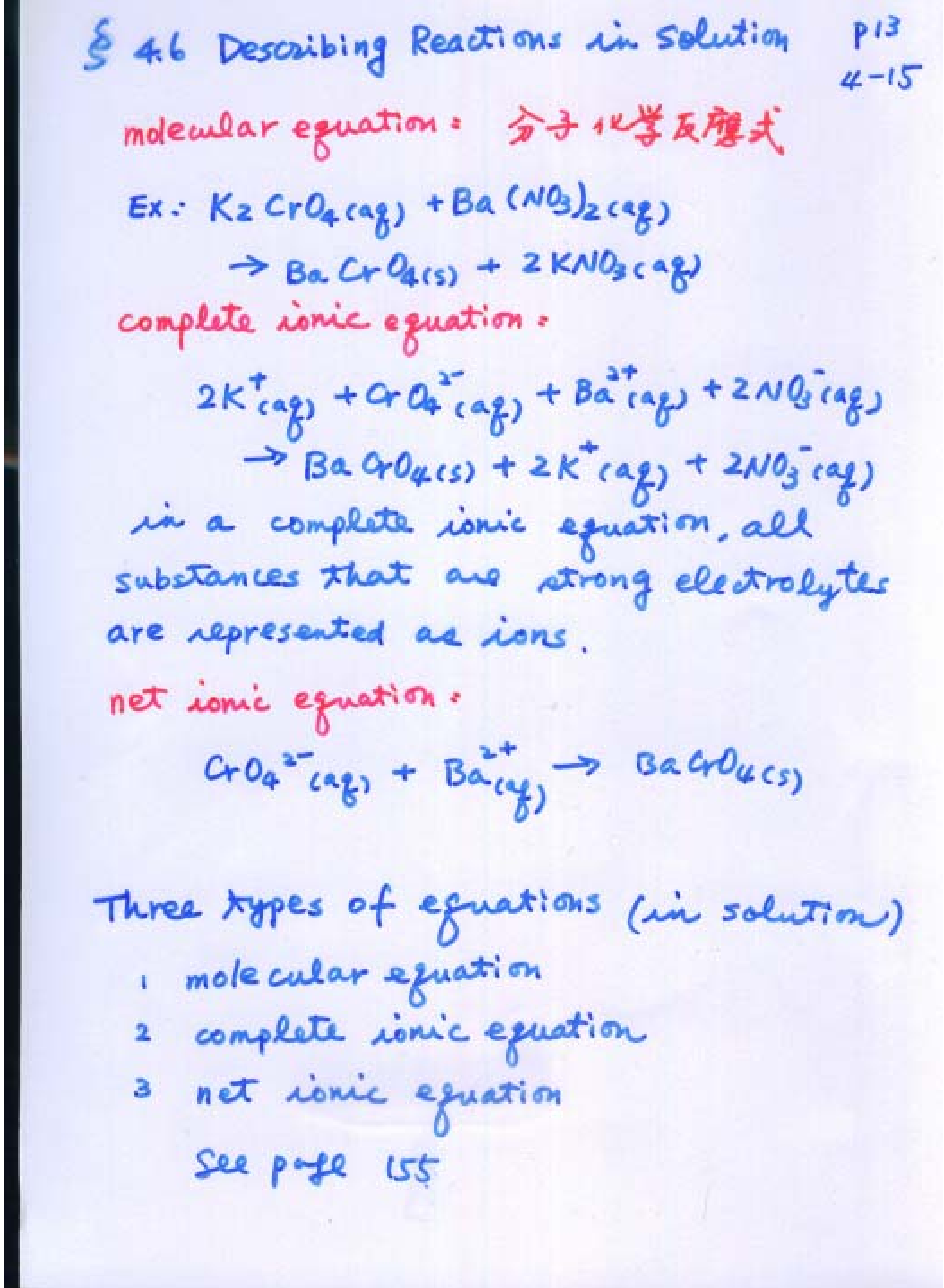
↓

$Fe(OH)_{3(s)} + KNO_3$

↓

balance

$$3KOH_{(aq)} + Fe(NO_3)_3 \rightarrow Fe(OH)_{3(s)} + 3KNO_{3(aq)}$$



§ 4.6 Describing Reactions in Solution p13 4-15

molecular equation: 分子化学反應式

Ex.: $K_2CrO_{4(aq)} + Ba(NO_3)_{2(aq)}$

$\rightarrow BaCrO_{4(s)} + 2KNO_{3(aq)}$

complete ionic equation:

$2K^+_{(aq)} + CrO_4^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$

$\rightarrow BaCrO_{4(s)} + 2K^+_{(aq)} + 2NO_3^-{}_{(aq)}$

in a complete ionic equation, all substances that are strong electrolytes are represented as ions.

net ionic equation:

$CrO_4^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} \rightarrow BaCrO_{4(s)}$

Three types of equations (in solution)

1 molecular equation
2 complete ionic equation
3 net ionic equation

See page 155

✓ $KCl + AgNO_3$

(1) molecular equation

$$\underbrace{K^+ + \underbrace{Cl^- + Ag^+}_{AgCl(s)} + NO_3^-}_{\times} \Longrightarrow$$

$$KCl_{(aq)} + AgNO_{3(aq)}$$

$$\rightarrow AgCl_{(s)} + KNO_{3(aq)}$$

(2) complete ionic equation

$$K^+_{(aq)} + Cl^-_{(aq)} + Ag^+_{(aq)} + NO_3^-{}_{(aq)}$$

$$\rightarrow AgCl_{(s)} + K^+_{(aq)} + NO_3^-{}_{(aq)}$$

(3) net ionic equation

$$Cl^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgCl_{(s)}$$

§ 4.7 Stoichiometry of precipitation Reactions

P14

4-17

Ex 4.10 & Ex 4.11

Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100M $AgNO_3$ solution to precipitate all the Ag^+ ions.

sol:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

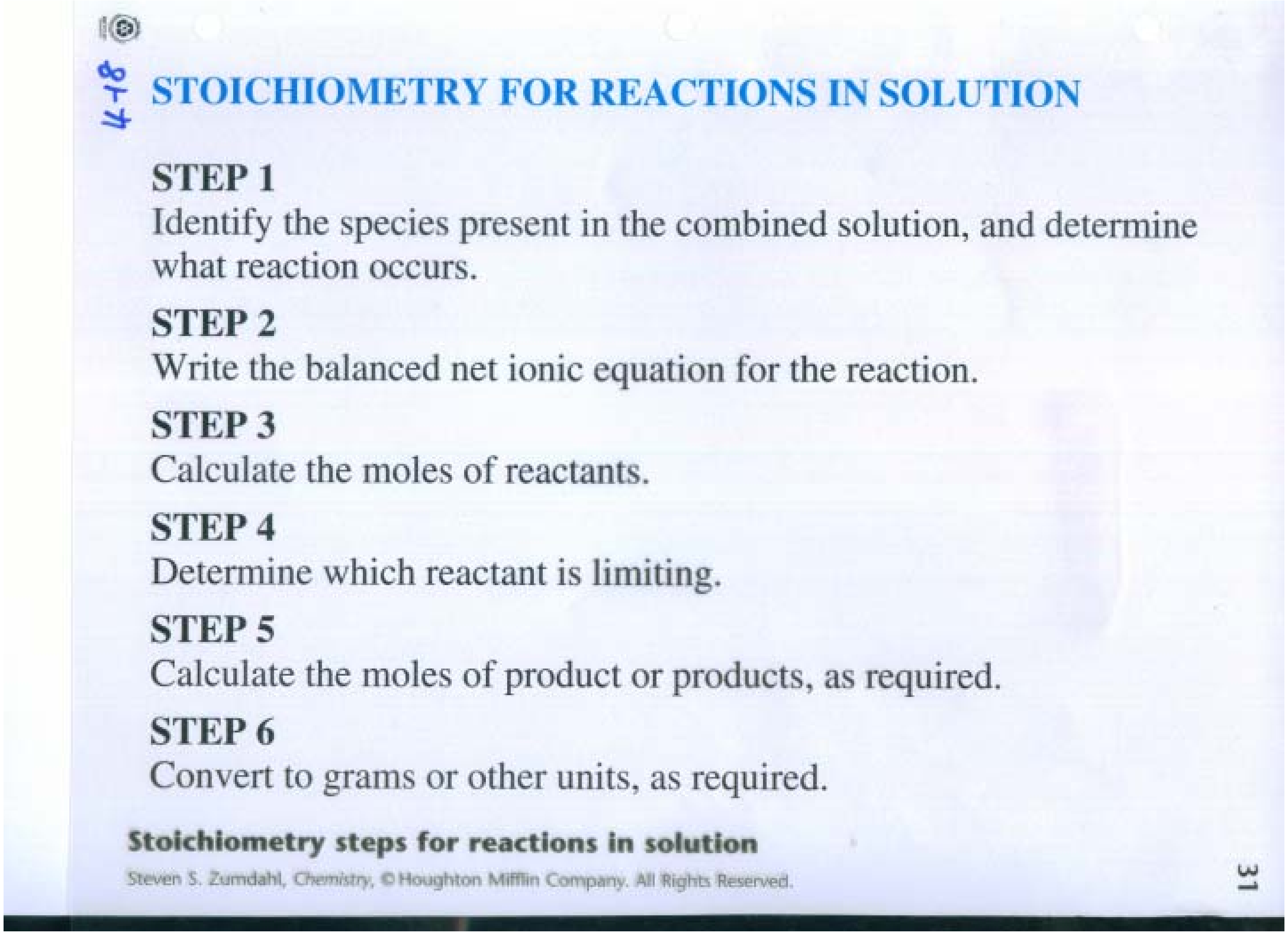
$$1.50L \times \frac{0.100\ \text{mole}\ Ag^+}{1\ L} = 0.15\ \text{mole}\ Ag^+$$

$$\therefore\ 0.15\ \text{mole}\ AgCl_{(s)}\ \text{forms} = 0.15\ \text{mole of}\ Cl^-$$

$$0.15\ \text{mole} \times 58.45\ \text{g/mole} = 8.77\ \text{g}\ NaCl$$

(NaCl molar mass)

Ex. 4.11. & Rules on Page 157



4-7-8

STOICHIOMETRY FOR REACTIONS IN SOLUTION

STEP 1
Identify the species present in the combined solution, and determine what reaction occurs.

STEP 2
Write the balanced net ionic equation for the reaction.

STEP 3
Calculate the moles of reactants.

STEP 4
Determine which reactant is limiting.

STEP 5
Calculate the moles of product or products, as required.

STEP 6
Convert to grams or other units, as required.

Stoichiometry steps for reactions in solution

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§ 4.8 Acid-Base Reactions

I Bronsted & Lowry 's Definition

Acid : a proton donor

Base : a proton acceptor

(∵ 有些鹼並沒有 OH^-)

Ex.

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

proton donor

(∵会解離 H^+)

Acid

proton acceptor

(∵会接受 H^+)

Base

II Acid -Base Rx

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)}$$

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftarrows H_2O_{(l)} + CH_3COO^-_{(aq)}$$

Ex 4.12 P2

Performing Calculations for Acid-Base Reactions 4-20

Step 1

List the Species present in the solution before any rx occurs.

$$\underbrace{H^+_{(aq)} + Cl^-_{(aq)}}_{\text{from HCl}} \quad + \underbrace{Na^+_{(aq)} + OH^-_{(aq)}}_{\text{from NaOH}}$$

Step 2

Write the balanced net ionic equation for the rx

$$\overbrace{H^+ + \underbrace{Cl^- \quad + Na^+}_{?} + OH^-}^{?}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$Na^+_{(aq)} + Cl^-_{(aq)} \not\rightarrow NaCl_{(s)}$$

Step 3 Calculate the moles of reactants.

OH^- 量 : $25.0^{ml} \times \frac{1\ l}{1000\ ml} \times 0.350\ \frac{moles}{l} = 8.75 \times 10^{-3}$ moles

p3
4-21

step 4 & step 5

Determine the limiting reactant

calculate the moles of the required reactant or product

需要 H^+ 的量：

$$0.100 \frac{mole}{l} \times V = 8.75 \times 10^{-3} \text{ mole}$$

H^+ mole 數 = OH^- mole 數

$$\therefore V = 8.75 \times 10^{-2} \, l = 87.5 \, ml$$

Acid-Base rx 又稱 Neutralization rx.

Ex. 4.13 28.0 ml 0.250 M HNO_3

53.0 ml 0.320 M KOH

calculate H_2O formed

H^+ or OH^- in excess

Step 1 & 2

$$\overbrace{H^+ + \underbrace{NO_3^- + K^+}_{} + OH^-}^{?}$$

$$H^+_{(aq)} + OH^-_{(aq)} \xrightarrow{?} H_2O_{(l)}$$

$$K^+ + NO_3^- \not\rightarrow KNO_{3(s)}$$

step 3-4

P4
4-22

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Amount of H^+ $= 28.0\ ml \times \frac{1\ l}{1000\ ml} \times 0.250 \frac{mole}{l}$

$= 7.00 \times 10^{-3}$ mole

amount of OH^- $= 53.0\ ml \times \frac{1\ l}{1000\ ml} \times 0.320 \frac{mole}{l}$

$= 1.70 \times 10^{-2}$ mole

$\therefore$ OH^- in excess

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

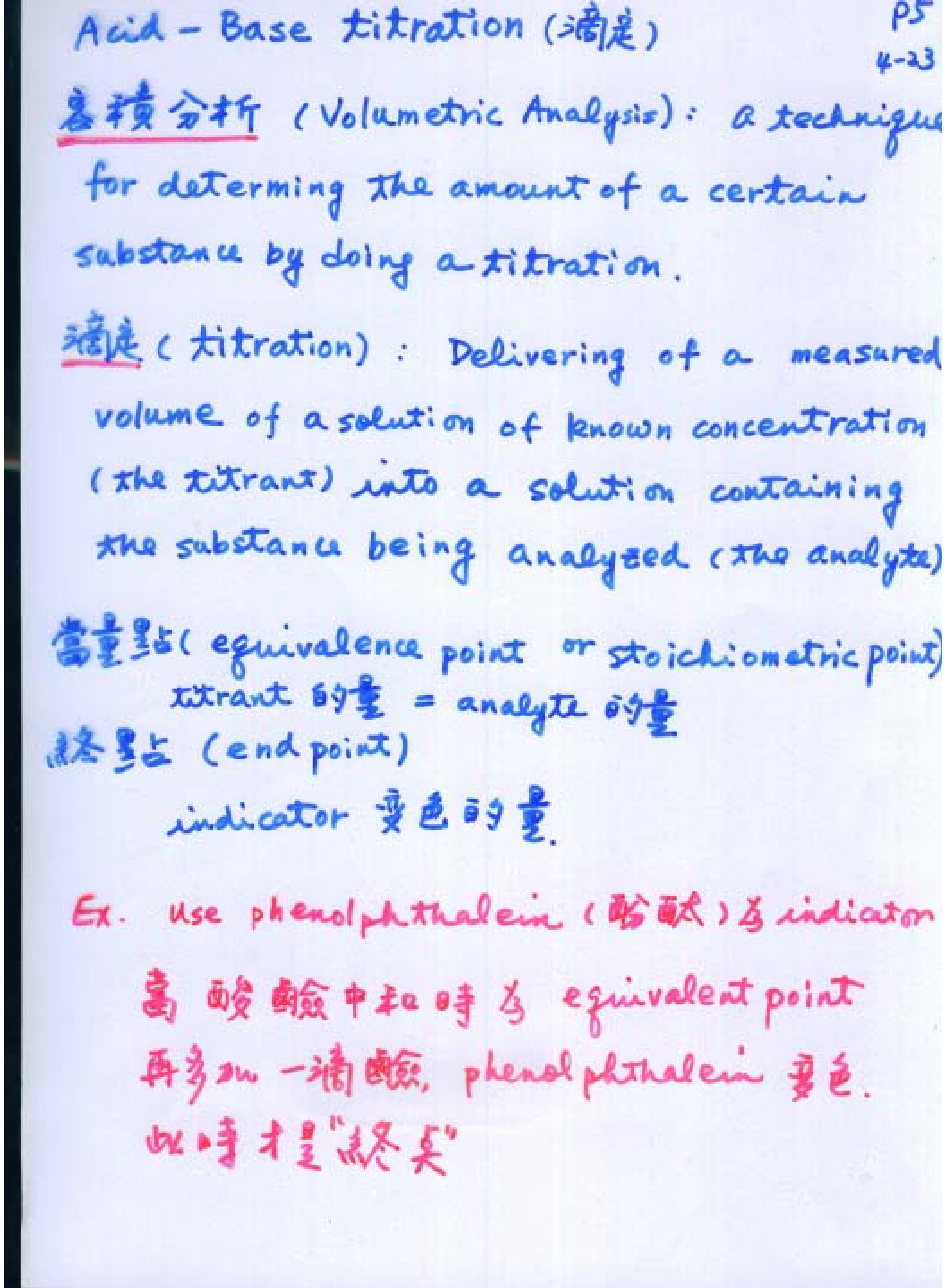
7.00×10^{-3} mol $\quad 1.70 \times 10^{-2}$ mol

$\sim 0 \quad 1.0 \times 10^{-2}$ mol $\quad 7.00 \times 10^{-3}$ mole

$\therefore$ 7.00×10^{-3} mol H_2O formed

$$[OH^-] = \frac{mole}{l} = \frac{1.00 \times 10^{-2}\ mol}{(28.0 + 53.0)\ ml}$$

$= 0.123$ M #



Acid - Base titration (滴定)

P5
4-23

容積分析 (Volumetric Analysis): a techniqu
for determing the amount of a certain
substance by doing a titration.

滴定 (titration): Delivering of a measured
volume of a solution of known concentration
(the titrant) into a solution containing
the substance being analyzed (the analyte)

當量點 (equivalence point or stoichiometric point)
titrant 的量 = analyte 的量

終點 (end point)
indicator 變色的量.

Ex. use phenolphthalein (酚酞) 為 indicator
當酸鹼中和時為 equivalent point
再多加一滴鹼, phenolphthalein 變色.
此時才是"終點"

Ex 4.14 標定 (standization) P6 4-24

KHP (potassium hydrogen phthalate)

$KHC_8H_4O_4$ molar mass 204.22 g/mol

Take 1.3009 g KHP

$$\frac{1.3009\text{ g}}{204.22\text{ g/mol}} = 6.3701 \times 10^{-3}\text{ mol KHP}$$

(amount of Acid)

Amount of Acid = amount of base

$$6.3701 \times 10^{-3}\text{ mole} = M \cdot 41.20\text{ml} \times \frac{1\text{ l}}{1000\text{ml}}$$

$$M = 0.1546\text{ M}$$

∴ [NaOH] = 0.1546M #

Ex. 4.15 an acid, donate 1 H$^+$/molecul

↑

2 酸廢棄物 : Benzoic Acid + CCl_4

total = 0.3518 g

use NaOH to titrate. 需 10.59ml of 0.1546 M NaOH

Amount of base (NaOH)

$$= 10.59\text{ ml} \times \frac{1\text{ l}}{1000\text{ml}} \times 0.1546\,\frac{\text{mol}}{\text{l}}$$

$$= 1.637 \times 10^{-3}\text{ mol } OH^-$$

Amount of Acid = amount of base

$= 1.637 \times 10^{-3}$ mol

1.637×10^{-3} mol $\times$ $122.12 \frac{g}{mol}$

$\uparrow$ molar mass of $HC_7H_5O_2$

$= 0.1999$ g $HC_7H_5O_2$

$\therefore$ Mass percent

$$= \frac{0.1999}{0.3518} \times 100\% = 56.82\% \ \#$$

---

§ 4.9 Oxidation – Reduction Reactions

Redox rx

Reactions in which one or more electrons are transferred, are called oxidation-reduction rx or redox rx.

Ex. $2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

Combustion

P8
4-26

Oxidation state (oxidation numbers).

A way to keep track of electrons in oxidation-reduction reactions, particularly redox rxs involving covalent substances.

Ex. H_2 oxidation state = 0

H_2O H : oxidation state = +1

O : oxidation state = −2

Table 4.2 Rules for Assigning Oxidation states

oxidation state

1. an atom in an element 0

2. monatomic ion is the same as its charge.

Na^+ +1

Cl^- −1

3. Oxygen is assigned to −2 in its covalent compounds −2

Ex. CO, CO_2, SO_2

例外 : peroxides. (过氧化物) −1

Ex. H_2O_2

P9
4-27

4. Hydrogen is assigned to +1 in its 'nonmetal' covalent compound EX. HCl, NH_3, H_2O +1

5. fluorine is assigned to −1 in its compound −1

6 The sum of the oxidation states must be zero for neutral compound For an ion, the sum of the oxidation states must equal to the charge of the ion

Ex. 4.16

a. $\underset{+4}{C}\underset{-2}{O_2}$ b $\underset{+6}{S}\underset{-1}{F_6}$ c. $\underset{+5}{N}\underset{-2}{O_3^-}$

$\underset{\frac{8}{3}}{Fe_3}\underset{-2}{O_4}$ (磁鐵)

? oxidation state can be non-integer 非整

The characteristics of Oxidation - Reduction Reactions

P10
4-28

$$\underset{\underset{-4}{\uparrow}}{C}\underset{\underset{+1}{\uparrow}}{H}_4(g) + 2\underset{\underset{0}{\uparrow}}{O_2}(g) \longrightarrow \underset{\underset{+4}{\uparrow}}{C}\underset{\underset{-2}{\uparrow}}{O}_2(g) + 2\underset{\underset{+1}{\uparrow}}{H}_2\underset{\underset{-2}{\uparrow}}{O}(g)$$

$$\underset{\underset{-4}{\uparrow}}{C}H_4 \longrightarrow \underset{\underset{+4}{\uparrow}}{C}O_2 + \boxed{8e^-}$$

Oxidation !

$$2\underset{0}{O_2} + 8e^- \longrightarrow C\underset{\underset{\underset{\times 2}{-2}}{\uparrow}}{O}_2 + 2H_2\underset{\underset{\underset{\times 2}{-2}}{\uparrow}}{O}$$

Reduction !

Oxidation Rx : oxidation state ↑
or donate electron

reduction Rx : oxidation state ↓
or accept electron

~~Oxidation~~ oxidizing agent : electron acceptor

reducing agent : electron donor

Ex. 4.17

p11
4-29

$$2Al_{(s)} + 3I_{2(s)} \rightarrow 2AlI_{3(s)}$$

oxidation state ?

which is oxidizing agent ?

reducing agent ?

Sol: $$2\underset{\overset{\uparrow}{0}}{Al}_{(s)} + 3\underset{\overset{\uparrow}{0}}{I_2}_{(s)} \rightarrow 2\underset{\overset{|}{+3}}{Al}\underset{\overset{\uparrow}{-1}}{I_3}_{(s)}$$

$0 \rightarrow +3$: oxidation state ↑ oxidizing rx

$0 \rightarrow -1$: oxidation state ↓ reducing rx

∴ I_2 : oxidizing agent

Al : reducing agent

Ex. 4.18

冶鋁

§ 4.10 Balancing Oxidation – Reduction Equations

half - rx method : separate the oxidation-reduction rx into two half-reactions : one involving oxidation and the other involving reduction.

Ex. $Ce^{4+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow Ce^{3+}_{(aq)} + Sn^{4+}_{(aq)}$

separate into : reduction half - rx

$$\begin{cases} Ce^{4+}_{(aq)} \rightarrow Ce^{3+}_{(aq)} \\ Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} \end{cases}$$

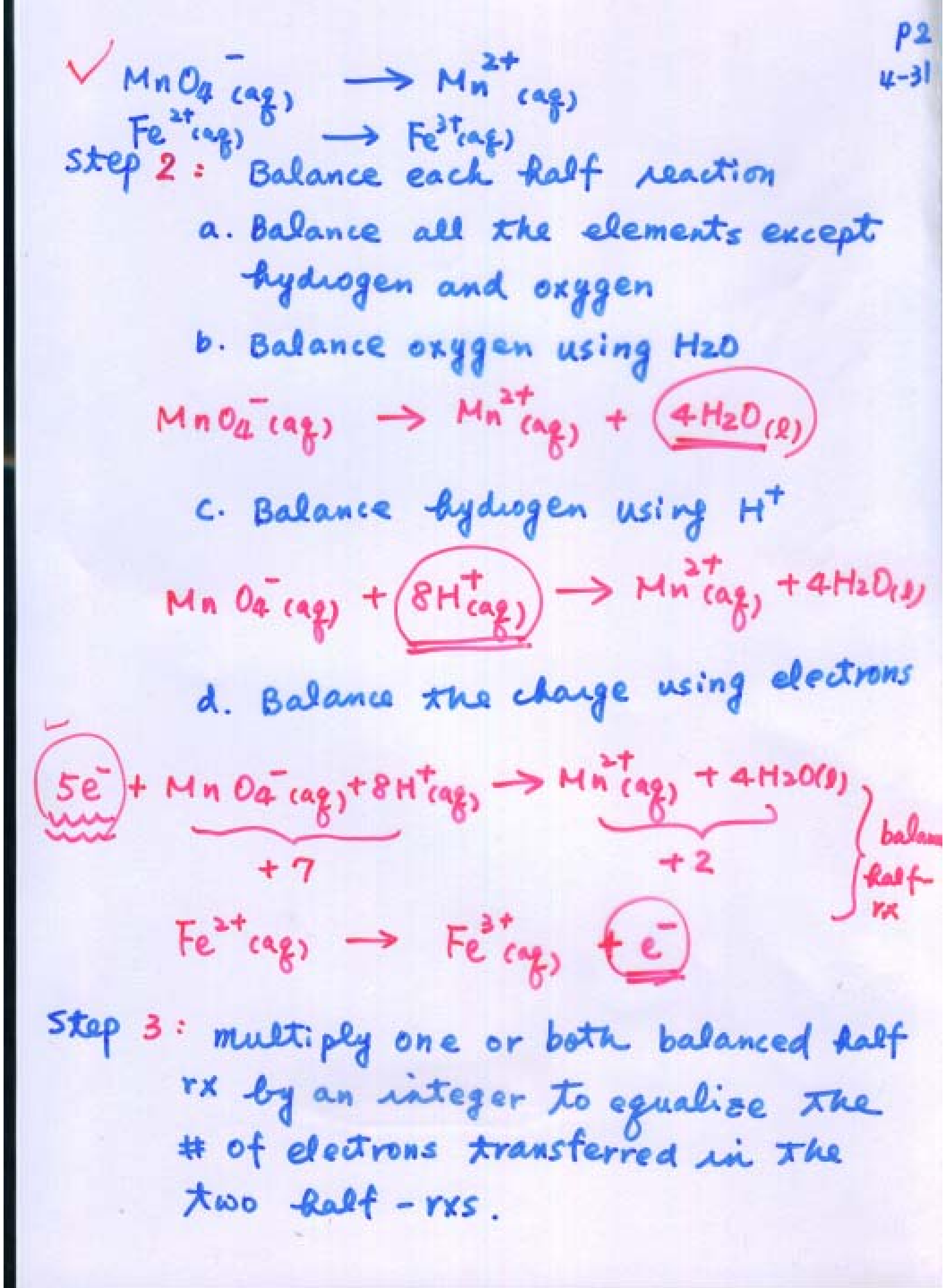
oxidizing half -rx

The Half-reaction method for balancing Oxidation-reduction rxs in aqueous solutions

I In Acidic solution (酸性溶液下)

Ex. $MnO_4^-{}_{(aq)} + Fe^{2+}_{(aq)} \xrightarrow{Acid} Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

Step 1. Write separate equations for oxidation and reduction half reactions



p2
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✓ $MnO_4^-{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)}$

$Fe^{2+}{}_{(aq)} \longrightarrow Fe^{3+}{}_{(aq)}$

step 2 : Balance each half reaction

a. Balance all the elements except hydrogen and oxygen

b. Balance oxygen using H_2O

$$MnO_4^-{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + \boxed{\underline{4H_2O}_{(l)}}$$

c. Balance hydrogen using H^+

$$MnO_4^-{}_{(aq)} + \boxed{\underline{8H^+_{(aq)}}} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

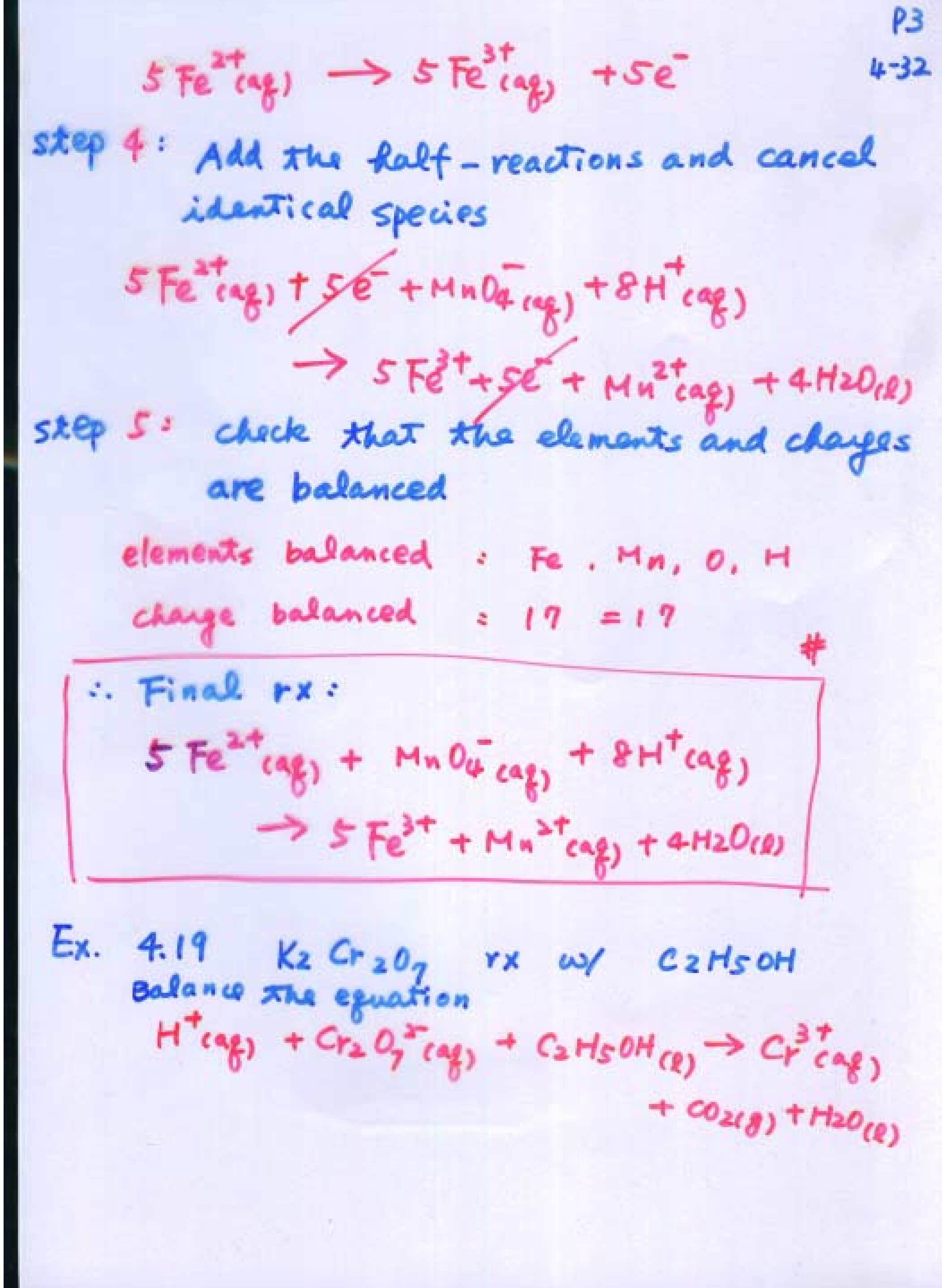
d. Balance the charge using electrons

$$\boxed{5e^-} + \underbrace{MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)}}_{+7} \rightarrow \underbrace{Mn^{2+}{}_{(aq)}}_{+2} + 4H_2O(l)$$

$$Fe^{2+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} \boxed{+e^-}$$

balan
half-
rx

Step 3 : multiply one or both balanced half rx by an integer to equalize the # of electrons transferred in the two half-rxs.



P3
4-32

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

step 4: Add the half-reactions and cancel identical species

$$5Fe^{2+}_{(aq)} + \cancel{5e^-} + MnO_4^-{}_{(aq)} + 8H^+_{(aq)}$$
$$\rightarrow 5Fe^{3+} + \cancel{5e^-} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

step 5: check that the elements and charges are balanced

elements balanced : Fe . Mn, O, H

charge balanced : 17 = 17

#

∴ Final rx:

$$\boxed{\begin{aligned} &5Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+_{(aq)} \\ &\quad \rightarrow 5Fe^{3+} + Mn^{2+}_{(aq)} + 4H_2O_{(l)} \end{aligned}}$$

Ex. 4.19 $K_2Cr_2O_7$ rx w/ C_2H_5OH

Balance the equation

$$H^+_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + C_2H_5OH_{(l)} \rightarrow Cr^{3+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$