Modern Chemistries

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Preface

This book is written for engineers, researchers, and others, and covers a wide range of chemistry topics in the form of Q and A. Additionally, the authors have intended this book to be used as a practical, common sense reference for university students.

This book consists of three chapters:
Chapter 1 covers Physical Chemistry, Inorganic Chemistry, Organic Chemistry and Analytical Chemistry.
Chapter 2 addresses the subjects of Radiation Chemistry, Bio-Chemistry, Environmental Chemistry, Fuel Chemistry, and Outlines for Writing Research Papers.
Chapter 3 details Chromatography, NMR Spectroscopy, Lasers and Infrared Spectroscopy, and Color Chromaticity Diagram.

Various chapters and sections of this book were written by:
Masatada Satake: Chapters 1-2, and Section 3.1
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Masahiro Ueda: Section 3.3
Yoichi Yamamoto: Section 3.4

We hope that this book will be useful to readers and invite suggestions for updates in subsequent printings.

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The Authors

Contents

Chapter 1: Basic Chemistry

Chapter 2: Applied Chemistry

Chapter 3: Separation Chemistry

Chapter 1: Basic Chemistry

In this chapter, several examples of Physical Chemistry, Inorganic Chemistry, Organic Chemistry and Analytical Chemistry are described.

Additionally, some problems are presented at the end of each section.

1.1 Physical Chemistry

In this section, basic principles such as the ideal gas law, half-life period, and the first law of thermodynamics are described in the form of Q and A.

Q. 1.1.1 Explain Boyle's Law

A.1.1.1 At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure, that is,

$$V \propto \frac{1}{p} \qquad (Temp.\ T:\text{ constant})$$

$$V = \frac{K}{p} \quad \text{or} \quad pV = K \qquad (1.1.1)$$

Where, K is a constant, the value of which depends upon the nature of the gas in question, the temperature of the gas, and the mass of the gas. For a given mass of a gas at constant temperature, **Boyle's Law** gives

$$p_1V_1 = p_2V_2 \qquad (1.1.2)$$

Where, V_1 and V_2 are volumes at pressure p_1 and p_2, respectively.

Equation (1.1.1) can be represented graphically by plotting pressures as ordinates and the corresponding volumes as abscissa (See Fig. 1.1.1).

The nature of the curve is a rectangular hyperbola. The general term isothermal or isotherm (meaning at constant temperature) is used to describe these plots.

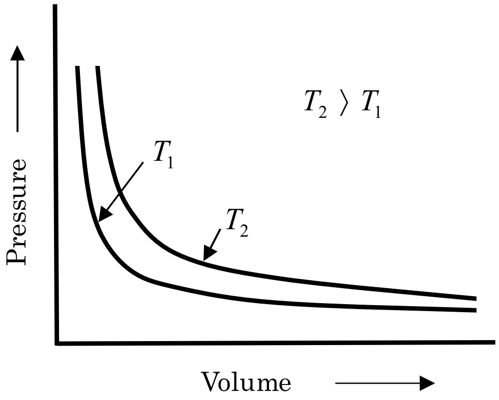


Fig. 1.1.1 Variation of pressure of a gas with volume

[Reference [1], p.2]

Q.1.1.2 Explain Boyle-Gay-Lussac's Law

A. 1.1.2 In n mole gas, relationships among ideal gas pressure p ,volume of gas V, and room temperature T are expressed as follows:

$$pV = nRT \qquad (1.1.3)$$

Where R is the gas constant (R = 8.3144621 J K^{-1} mol^{-1}). This is called **Boyle-Gay-Lussac's Law**.

【Comment1.1.1】

https//en.wikipedia.org/wiki/**Gas constant**

【Comment1.1.2】

(1) $1(n=1)$ mole of any gas occupies 22.4 dm^3 at room temperature (about 20 ℃) and 1 atmosphere pressure. (http://www.chemguide.co.uk/)

(2) In Van der Waals gas: $(p + n^2 \frac{a}{V^2})(V - nb) = nRT$, where, a and b are van der Waals constants. [Reference [12], p.55]

Q. 1.1.3 Explain the concept of an ideal gas

A. 1.1.3 So far, we have assumed that all gases obey the gas laws under all conditions of temperature and pressure; however, for real gases this is not true. Real gas obeys these laws only under limited conditions of low pressures and high temperatures. They exhibit deviations from the gas laws and these deviations are greater when the temperature and pressure are close to the conditions at which the gas can be condensed into a liquid. Thus Boyle's Law, Gay-Lussac's Law, and the equation of state derived from these two laws may be regarded as approximations for real gases and are expected to be applicable only at relatively low pressures and moderately high temperatures.

[Reference [1], p.2]

Q.1.1.4 Explain the half-life period

A.1.1.4 Half-life time of a reaction is the time required for the concentration of a reactant to decrease by half, i.e.,

$$\text{at } t = t_{1/2} \quad [A]_t = [A]_0 / 2. \qquad (1.1.4)$$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k_1} \qquad (1.1.5)$$

$t_{1/2}$ is independent of the initial concentration of reactant.

For second order reaction ($2A \rightarrow B$),

$$t_{1/2} = \frac{0.693}{k_2[A]_0} \qquad (1.1.6)$$

That is, $t_{1/2}$ is inversely proportional to the initial concentration of A.

[Reference [12], p.70]

Q.1.1.5 Derive the equations described in Q.1.1.4

A.1.1.5 (1) For the first order reaction (A → B) of reactor A , an equation of the first order reaction can be described in the following form:

$$\frac{d[A]}{dt} = -k_1[A] \qquad (1.1.7)$$

Where, k_1 is the constant of the first order reaction, and t is time.

From Eq.(1.1.7), $$\frac{d[A]}{[A]} = -k_1 dt \qquad (1.1.8)$$

By integrating Eq.(1.1.8), $$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_1 \int_0^t dt,$$

$$[A] = [A]_0 e^{-k_1 t} \qquad (1.1.9)$$

Where, $[A]_0$ is the initial concentration at t=0.

In Eq.(1.1.9), if $[A] = \frac{[A]_0}{2}$,then $\frac{1}{2} = e^{-k_1 t_{1/2}}$,

$$t_{1/2} = \frac{0.693}{k_1} \qquad (1.1.10)$$

(2) For the second order reaction (2A → B) of reactor A , an equation of the second order reaction can be described in the following form:

$$\frac{d[A]}{dt} = -k_2[A]^2 \qquad (1.1.11)$$

Where k_2 is the constant of the second order reaction, and t is time.

From Eq. (1.1.11),

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k_2 \int_0^t dt \qquad [A] = \frac{[A]_0}{1 + k_2[A]_0 t} \qquad (1.1.12)$$

Where, $[A]_0$ is initial concentration at t=0.

In Eq.(1.1.12), if $[A]=\frac{[A]_0}{2}$, then, $k_2[A]_0 t_{1/2}=1$,

$$t_{1/2}=\frac{1}{k_2[A]_0} \qquad (1.1.13)$$

【Comment1.1.5】 **(1)** $\int_{[A]_0}^{[A]}\frac{d[A]}{[A]}=-k_1\int_0^t dt \rightarrow \left[\ln[A]\right]_{[A]_0}^{[A]}=-k_1 t \rightarrow$

$$\frac{[A]}{[A]_0}=e^{-k_1 t} \rightarrow [A]=[A]_0 e^{-k_1 t}$$

(2) $\int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2}=-k_2\int_0^t dt \rightarrow -\frac{1}{[A]}+\frac{1}{[A]_0}=-k_2 t$, $\quad [A]=\frac{[A]_0}{1+k_2[A]_0 t}$

Q.1.1.6 Explain the First Law of Thermodynamics

A.1.1.6 We consider now the effect of delivering a certain amount of energy, such as heat, to a system. Since energy must be conserved, the heat q added to the system must appear as a change in the internal energy ΔE of the system, or as work w which is done by the system. The mathematical statement of this fact is

$$q = \Delta E + w.$$

This is at once an algebraic expression of the law of conservation of energy and of the first law of thermodynamics. It is more commonly written in the form

$$\Delta E = q - w \qquad (1.1.14)$$

Equation (1.1.14) abbreviates the words: any change in the internal energy of a system is the sum of the heat q which is added to the system and the amount of work $-w$ done by the system. Notice carefully that heat added to the system is assigned a positive symbol q; in contrast, it is work done by the system which is assigned a positive symbol w. Work done on a system is denoted by $-w$.

In order to prevent this inconsistency in sign convention, always remember that heat added to a system, or work done on a system, must tend to raise E and thus make ΔE positive. Then the sign to be associated with heat or work can be deduced from Eq. (1.1.14).

[Reference [3], pp.14-16]

Q.1.1.7 Explain ΔU in terms of heat exchange under constant volume

A.1.1.7 From the first law of thermodynamics, we have

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad (1.1.15)$$

Now $\quad \mathrm{d}w = -\,p_{\mathrm{ext}}\,\mathrm{d}V$

Hence $\quad \mathrm{d}U = \mathrm{d}q - p_{\mathrm{ext}}\,\mathrm{d}V$

For a process at constant volume, $-p_{\mathrm{ext}}\,\mathrm{d}V$ is equal to zero.

Hence

$$\mathrm{d}U = \mathrm{d}q_V \qquad (1.1.16)$$

or $\quad \Delta U = q_V$

that is, heat transferred under constant volume by a system changes its internal energy.

[Reference [12], p.86]

1.1.8 Problems

Discuss Each of the Following Descriptions:

1. Charles's Law
2. Boiling point

1.1.9 Examples of Answers

1. The volume of a given mass of a gas under constant pressure is directly proportional to its absolute temperature, that is

$$V \propto T$$

or $\quad V = KT, \quad K = V/T \quad$ (K : Constant value)

where K is a constant of proportionality. According to this law, we can write

$$V_1 / T_1 = V_2 / T_2 \qquad (p : \text{Constant})$$

Where, V_1 and V_2 are the volumes at temperatures T_1 and T_2, respectively.

2. The boiling points of a liquid depend on pressure. The normal boiling point is defined as the temperature at which the vapor pressure of a liquid is

equal to 1 atom or 760 mm (100℃ for water). The boiling point of water decreases under lower atmospheric pressures and at higher altitudes, being 97.7℃ at pressure of 700 mm. On the other hand, water boils at 120.1 ℃in a pressure cooker if the pressure is 2 atm. [Reference [11], p.147]

1.2 Inorganic Chemistry

In this section, several examples of poison of lead, activated charcoal, covalent bond, hydrogen bond, coordination compound, complex formation, activated complex, catalysts, and enzymes are described in the form of Q and A.

Q.1.2.1 Give an example of the poisonous effects of lead

A.1.2.1 The natural concentration of lead in soil is in the range of 2-200 mg/kg with mean values of about 16mg/kg; however, the variation from one location to another is considerable.

Grass samples may show high lead concentrations near roads with heavy traffic, with mean values ranging from about 250 mg/kg at the roadside to about 100 mg/kg at a distance of 25 m.

The mean concentration of lead in rainwater ranges from 8 μg/L in residential areas to about 30 μg/L in business areas.
[Reference [8], p.149]

【Comment1.2.1】

(1) The function for lead added to gasoline is to reduce engine knocking.
(2) Due to concerns over air pollution and health risks, this type of gas was banned in all on-road vehicles during the 1970s in the United States.
http://www.todayifoundout.com/index.php/,
(3) Lead: Chemical Element Symbol Pb, Atomic Number 82, Period 6, Group 14, Electronic Array $1s^2\ 2s^22p^6\ 3s^23p^6\ 3d^{10}4s^24p^6\ 4d^{10}\ 5s^25p^6\ 4f^{14}5d^{10}\ 6s^2\ 6p^2$

Q.1.2.2 Discuss activated charcoal

A.1.2.2 The materials obtained by charring wood or coconut shells are able to take up large volumes of certain gases and the amounts can be increased by subjecting the charcoal to a process of activation.

This generally involves heating in a vacuum or in inert gas or in steam, air, chlorine or carbon dioxide at temperatures varying from 350 ℃ to 1000 ℃. [Reference [12], p.2]

【Comment1.2.2】

(1) Activated charcoal is also called activated carbon, or activated coal, or an AC filter..

(2)These are used in medical fields, analytical chemistry applications, environmental applications, agriculture fields, etc.

(3) The photograph below is an example of activated charcoals.

Cited from http://en.wikipedia.org/wiki/Activated

Q. 1.2.3 Explain the covalent bond

A. 1.2.3 A bond formed by the mutual sharing of a pair of electrons between two atoms, each atom contributing one electron, is called the covalent bond. The shared pair of electrons will not belong to any one particular atom but will belong to both atoms simultaneously.

For example, a hydrogen molecule consists of two atoms of hydrogen, each having one electron in its valence cell ($1s^1$).

As shown in **Fig.1.2.1**, each hydrogen atom contributes one electron towards a pair shared by the two atoms.

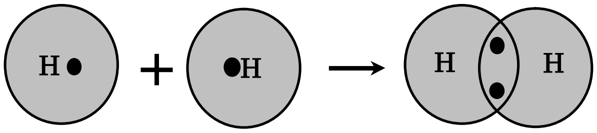


Fig. 1.2.1 Covalent bond

[Reference [8], pp.78-79]

Q.1.2.4 Explain the hydrogen bond

A.1.2.4. In a molecule, if hydrogen is covalently attached to a highly electro-negative atom such as fluorine, oxygen, or nitrogen, the bond is polarized and thus hydrogen acquires a small positive charge, whereas the electro- negative atom acquires a small negative charge.

The slightly positively charged hydrogen atom gets attached to an adjacent highly electronegative atom (containing a lone pair) through a weak directional bond, known as the hydrogen bond.

This can be represented by **Fig.1.2.2**,

$\delta^{-}\,\delta^{+}\qquad\delta^{-}\,\delta^{+}$
A—H …… A—H…(… : Hydrogen bond)

Fig.1.2.2 Hydrogen bond

[Reference [12], p.76]

【Comment1.2.3】(1) In **a** hydrogen bond, a weak directional bond between A—H, and A—H can be expressed by using the symbol “ … ” .

(2) lone pair = unshared electron pair

Q. 1.2.5 Explain the definition of a coordination compound

A. 1.2.5 The molecules or ions, which attach to the central metal ion are called ligands.

They are electron pair donors and thus act as Lewis bases. Ligands may be neutral molecules such as ammonia, water, ethylenediamine, etc.

They may also be ions such as Cl^-, CN^-, NO_2^-, SCN^-, etc.

Ligands may be unidentate, that is, they may possess only one coordinating atom. Examples of unidentate ligands are NH_3, H_2O, Cl^-, CN^-, etc.

Bidentate ligands may possess two coordinating atoms.

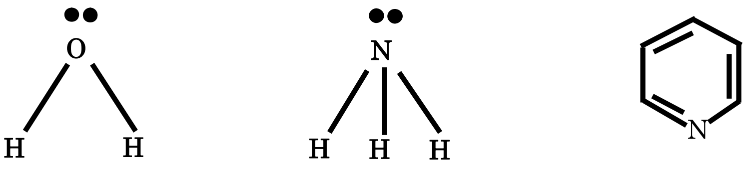
Ethylenediamine and oxalate are examples of bidentate ligands.

When a bidentate, tridentate or a polydentate ligand forms coordinate bonds with the same metal ion, the ring structure formed is called a chelate ring and the ligand is called a chelating agent.

Some of the most common ligands are shown in **Fig. 1.2.3** along with their structures. The name of the ligand is given below its structure.

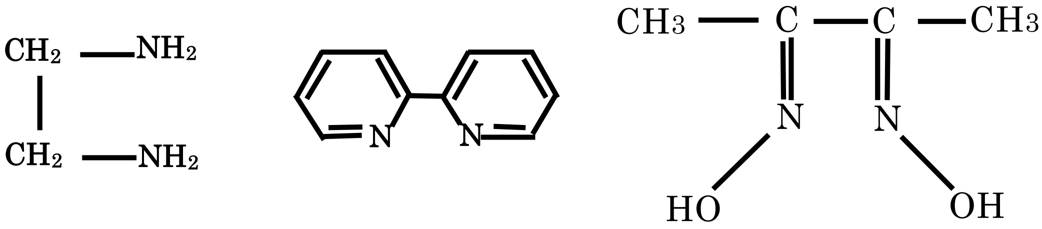
(1) Monodentate ligands :

Cl^- Br^- I^- CN^-



Water Ammonium Pyridine

(2) Bidentate ligands :



Ethylenediamine 2,2’-Dipyridyl Dimethylglyoxime

Fig. 1.2.3 Ligands and their structures

[Reference [9], p.160]

Q.1.2.6 Explain the complex formation

A.1.2.6 The atom or molecule that attaches itself to a central atom or ion is known as a ligand. For example, the deep blue of a solution of copper sulfate containing ammonium hydroxide is caused by $[Cu(NH_3)_4]^{2+}$ ions.

Hemoglobin, the red coloring matter in blood, is a complex ion of iron; chlorophyll, the green coloring matter in plants, is a complex ion of magnesium; and vitamin B_{12}, a constituent of the vitamin-B group, is a complex ion of cobalt.

Because water tends to hydrate ions readily, most ions in aqueous solution may be considered complex ions. Complex ions occur both in the solid state and in solution. [Reference [9], p.16]

Q.1.2.7 Explain the activated complex theory

A.1.2.7 The conversion of reactants to products is done through the formation of activated complex.

This compound is not an intermediate molecule, but is a molecule that is in the process of breaking or forming bonds.

Eyring and others have developed the quantitative treatment of the activated complex theory (or transition state theory or absolute rate theory) based on the assumption that there exists an equilibrium between the reactants(A and B) and the activated complex($X^‡$) and that the products are obtained by the decomposition of the activated complex, that is:

$$A + B \rightarrow X^{‡} \rightarrow \text{Products}$$

[Reference [12], p.2]

Q.1.2.8 Discuss catalysts

A.1.2.8 The addition of small amounts of certain substances to a reaction mixture increases the rate of reaction. These substances are called catalysts.

A catalyst is defined as a substance that changes the rate of a reaction and can be recovered essentially unaltered.

Substances decreasing reaction rate are called inhibitors.

The catalyst (or inhibitor) is not shown in a balanced chemical equation as a reactant or product since it is recovered unchanged after reaction.

Nevertheless, it is necessary to mention that a catalyst or inhibitor has been used in the reaction. This information is usually given by writing the catalyst or inhibitor above or below the arrow in the balanced equation.

[Reference [11], p.189]

Q.1.2.9 Explain the catalytic reaction

A. 1.2.9 Consider the general reaction represented by the reaction:

$$\mathrm{A + B} \xrightarrow{\text{catalyst}} \mathrm{Z + Y}$$

The catalyst combines with A to give an activated complex:

$$\mathrm{A} + \text{catalyst} \rightarrow [\text{catalyst}\text{–}\mathrm{A}]$$

This activated complex then interacts with the other reactant to give the products and regenerates the catalyst:

$$[\text{catalyst} - \mathrm{A}] + \mathrm{B} \rightarrow \mathrm{Z} + \mathrm{Y} + \text{catalyst}$$

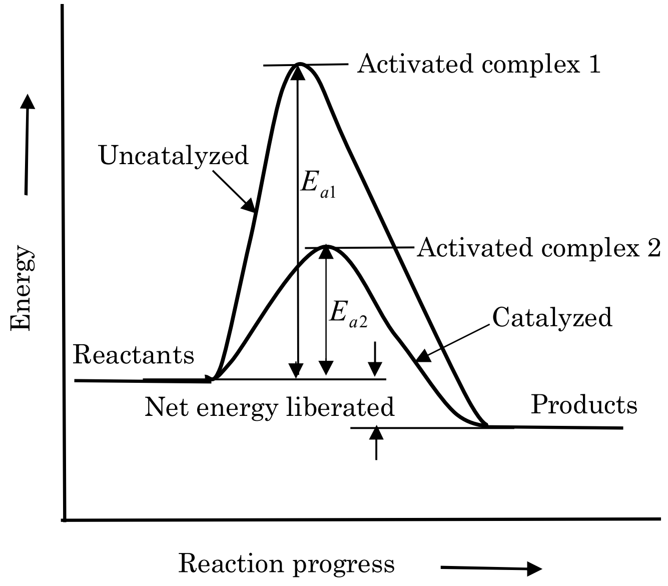


Fig. 1.2.4 Comparison of reaction energies for an uncatalyzed and catalyzed reaction

The activation energy for the formation of the activated complex between catalyst and reactant is lower than that for the activated complex formed between the reactants.

A reaction energy diagram for an uncatalyzed and catalyzed reaction is given in **Fig. 1.2.4**.

[Reference [11], p.186]

Q.1.2.10 **Discuss enzymes**

A.1.2.10 The catalyst and inhibitor are used in the manufacture of many materials. Biologically, catalysts and inhibitors are of great importance.

Nature employs catalysts in almost all biological reactions. These biological catalysts are specially designated as enzymes. Many drugs used in the medical treatment of disease are inhibitors.

Catalysts take part in the reaction in such a way as they are regenerated during reaction. Their role in a reaction is to lower the activation energy for a reaction by providing an alternate way for reaction to occur. In many cases, the lowering of the activation energy is accomplished by a combination of the catalyst with one of the reactants to form an intermediate or activated complex.

[Reference [11], p.108

1.2. 11. Problems

Discuss the following items:

1. Hydrogen bond
2. Water molecule
3. Ligand (or coordinating group)
4. Alumina

1.2. 12. Examples of Answers

1. When two molecules of water come near each other, slightly negatively charged oxygen attracts the positive charge of hydrogen atom of the second molecule and a weak bond is established. The attractive force is known as hydrogen bond and is represented by a dotted line in **Fig1.2.5.**

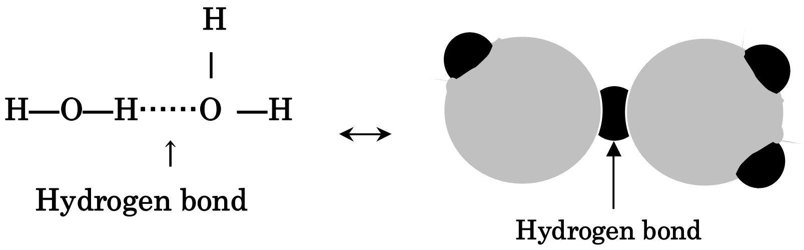


Fig. 1.2.5 Hydrogen bond

2. Oxygen has only six outer electrons. To attain the desired eight electrons, it must form two covalent bonds. Since hydrogen forms only one bond, two hydrogen atoms are necessary to satisfy an oxygen atom.

$$H\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\cdot + \cdot H \rightarrow H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H$$

[Reference [11], p.108]

3. A ligand is an atom, ion or molecule, which can donate a pair of electrons to the central metal atom in a complex bond. The particular atom in a ligand, which actually donates the pair of electrons are called the donor atom. If a ligand contains only one donor atom it is a uni or monodentate ligand. Examples of some monodentate ligands are:

F^-, Cl^-, CN^-, OH^-, H_2O, NH_3, pyridine, etc.

4. Hydrated alumina is the natural bauxite mineral, $Al_2O_3 \cdot nH_2O$ (n=1-3). Pure Al_2O_3 can be prepared in the laboratory by heating aluminum hydroxide or ammonium alum.

Freshly prepared alumina reacts with both acids and alkalis showing its amphoteric nature.

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$

$$Al_2O_3 + 2OH^- + 2H_2O \rightarrow 2[Al(OH)_4]^-$$

Alumina is refractory material used in the manufacture of heat resistant bricks and for the internal lining of furnaces. As a finely divided powder, it is often used as the adsorbing stationary phase in column chromatography. Alumina can be fused with oxides of chromium, iron and cobalt to form synthetic semi-precious stones. It is also used as a hydrating agent, e.g.

$$\underset{\text{Ethanol}}{CH_3\text{-}CH_2\,OH} \xrightarrow[575K]{Al_2O_3} \underset{\text{ethylene}}{H_2C{=}\,CH_2} + H_2O$$

1.3 Organic Chemistry :

In this section, several examples regarding solvents and other organic chemicals, organochlorine compounds, dry cleaning of clothes, Vitamin C (ascorbic acid), caffeine, tautomer, and the chemical qualities of uric acids are described in the form of Q and A.

Q.1.3.1 Discuss solvents and other organic chemicals

A.1.3.1 Organic solvents are today produced almost entirely from petroleum.

Table 1.3.1 lists the solvents which are in most common use, along with their principal properties and applications.

Table 1.3.1 properties of some important solvents

Compound	Boiling point (℃)	Odor perception (mg/m^3)	Applications
Acetic acid	118	0.1-1.5	Synthesis, pharmaceutical, Photographic, polymers
Acetone	56	5-50	Solvent for cellulosic resins and Vulcanisates, adhesives, paints
Benzene	80	3	Motor fuels, synthesis especially flavors, perfumes, paints
Chloroform	62	1000	refrigerants, pharmaceuticals
Toluene	111	1-100	Fuels, paints and coatings, isocyanate, Benzene substitute

A detailed study of solvents encompasses a large proportion of organic chemistry and the discussion here is limited to those which offer the greatest environmental risk.

[Reference [6], p.105]

Q.1.3.2 Discuss organochlorine compounds

A.1.3.2 Chloroform occurs in air at levels up to $5\mu g/m^3$ and has been detected in foodstuffs at 30 mg/kg. It is common in water samples being produced by the haloform reaction during the chlorination of water and sewage; in air, it may be formed by the photochemical degradation of trichloroethylene.

Chloroform causes cancer in rats and mice. Studies have shown that the chlorination of tap water does not lead to enhanced chloroform levels in human blood plasma; the WHO has set a guideline of 0.03 ppm for chloroform in drinking water. [Reference [6], p.109]

【Comment1.3.1】

The haloform reaction is a chemical reaction during which a haloform (CHX_3, where X is a halogen) can be produced by the exhaustive halogenations of a methy1 ketone [a molecule containing the R-CO-CH_3 group, See **Fig1.3.1**].

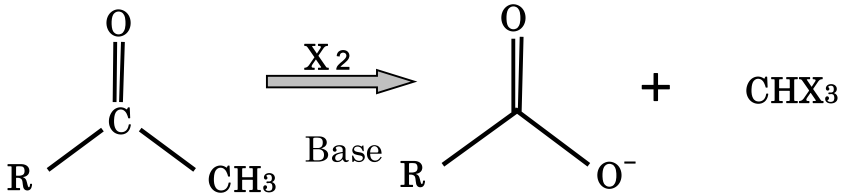


Fig.1.3.1 Haloform reaction

R = H, alkyl, aryl
X = Cl, Br, l

This reaction can be used to produce the following products :

Chlorohorm($CHCl_3$), (2)brohorm($CHBr_3$), (3) idoform(CHI_3). [Reference [6], p.109],

Q.1.3.3 Discuss the dry cleaning of clothes

A.1.3.3 Organic solvents are used because, unlike water, they do not distort fibers. The solvents available are listed in **Table 1.3.2**. According to the provisions of the Montreal Protocol for protection of the ozone layer, CFC-113 (ODP 0.8) and TCE (ODP 0.1) is not acceptable and was phased out during the 1970s. This presented practical problems since dry cleaning equipment has a lifetime of about 15 years and is only suitable for the solvent originally specified. Even HCFC-225 will be unacceptable by the year 2020.

Table 1.3.2 Some solvents used in dry cleaning

Solvent	Boiling point (°C)
CFC-113	48
Perchloroethylene	121
Petrol based	150-210
1,1,1-TCE	74
HCFC-225 ($CF_3CF_2CHCH_2$)	53

Carbon tetrachloride is still used for dry cleaning in Eastern Europe, the former USSR and in South East Asia. It is produced by the high temperature chlorination of methane, propylene or carbon disulfide for use as a feedstock in the synthesis of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2.). As these solvents are phased out they will only be used in a limited number of special syntheses, for example that of picloram.
[Reference [6], p.108]

Q.1.3.4 Discuss Vitamin C (Ascorbic acid)

A.1.3.4 Before 1912, it was not known that the severe disease scurvy was due to a lack of vitamin C, although already at the end of the 19th century the Russian physician V. Pashutin advanced the idea that scurvy appears owing to a lack in the organism of a very important substance.

In 1922, N. Bessonov isolated from cabbage a crystalline substance healing scurvy, while in 1928 the Hungarian scientist A. Szent-Gyorgyi separated from the adrenar cortex a substance of an acidic nature with sharply pronounced reducing properties and a molecular mass of 176. As this substance healed scurvy, it was called ascorbic acid (from the Latin scorbut scurvy).

When determining the structure of ascorbic acid, it was found that the acid can form a tetramethyl ether, which points to the presence of four hydroxyl groups (OH groups) in its molecule.

In the catalytic hydrogenation of ascorbic acid, one mole of hydrogen is absorbed, which confirms the presence of a double bond in its molecule. It was also established that the ascorbic acid molecule contains a lactone ring. These data led to the conclusion that ascorbic acid is a γ-lactone of

2,3-dihydro-L-gulconic acid.

The chemical structure of ascorbic acid (Vitamin C) is shown in **Fig.1.3.2**.

The synthesis of ascorbic acid in 1933 conformed its structure. The acid is synthesized commercially from D-glucose, which is produced in large amounts when starch is decomposed by sulfuric acid.

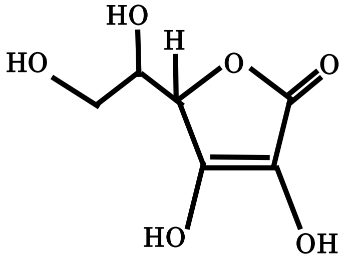


Fig. 1.3.2 Ascorbic acid (Vitamin C)

[Reference [2], p.31]

Q.1.3.5 Discuss caffeine

A.1.3.5 Caffeine is contained in coffee seeds. At present, cheaper and readily available synthetic methods are used for the production of caffeine.

Caffeine forms white silky acicular crystals with a slightly bitter taste. It weathers in the air. It dissolves well in hot water and chloroform, and sparingly in cold water, benzene, and alcohol. It dissolves very poorly in ether. Caffeine is a weak base. The chemical structure of caffeine is shown in **Fig.1.3.3**.

Caffeine is administered as a stimulator of the central nervous system and a cardiotonic. The stimulating action of the caffeine increases the mental and physical capacity for work, but its use in large doses results in exhaustion of the nerve cells.

[Reference [13], p.183]

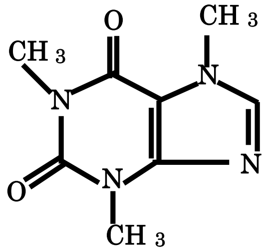


Fig. 1.3.3 Caffeine (1,3,7-trimethylxanthine)

Q. 1.3.6 Discuss tautomer

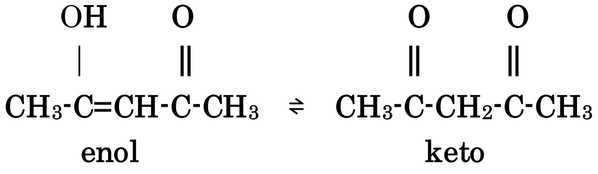
A.1.3.6 The reversible reaction:

Enol form ⇌ Keto form

is called tautomerism and the two forms are different tautomers of the same compound. In the present example, almost all of the substance exists as the keto tautomer (the equilibrium position is near to the right). However, the enol tautomer may be the more stable form in other compounds, e.g. acetylacetone. **Fig.1.3.4** shows the equilibrium of the eto-enol form of acetylacetone.

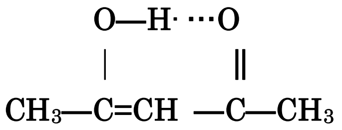
If acetylacetone existed as a simple chain molecule, it would take the keto form, as in acetone. However, in the enol form only, a more stable ring structure can be formed by intramolecular hydrogen bonding and, therefore, 80% of the molecules of acetylacetone exist in the enol form. **Fig.1.3.5** shows the form of the hydrogen bond of acetylacetone.

enol ⇌ keto tautomerism is very important in biochemistry.



$$\underset{\text{enol}}{CH_3\text{-}\overset{\overset{OH}{|}}{C}=CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3} \rightleftharpoons \underset{\text{keto}}{CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3}$$

Fig.1.3.4 Equilibrium of keto–enol form of acetylacetone



$$\begin{array}{ccccc} & \mathrm{O}\text{—}\mathrm{H}\cdots & & \mathrm{O} & \\ & | & & \| & \\ \mathrm{CH_3}\text{—} & \mathrm{C} & \text{=CH —} & \mathrm{C} & \text{—}\mathrm{CH_3} \end{array}$$

··· : hydrogen bond

Fig.1.3.5 Hydrogen bond of acetylacetone

Q.1.3.7 Discuss uric acid chemical qualities

A.1.3.7 Uric acid is a diprotonic acid with $pKa_1=5.4$ and $pKa_2=10.3$.

Thus at higher pH, it forms the dually charged full urate ion, but at biological pH or in the presence of carbonic acid or carbonate ion, it forms the singly charged hydrogen or acid urate ion, as its pKa_1 is lower than the pKa_1 of carbonic acid. **Fig.1.3.6** shows the structure of uric acid and its keto-enol type.

As its second ionization is so weak, the full urate salts tend to hydrolyze back to hydrogen urate salts and free base at pH values around neutral.

(1) Solubilities : In general, the water solubility of uric acid and its alkali metal and alkaline Earth salts is rather low. All these salts exhibit greater solubility in hot water than in cold water, allowing for easy recrystallization. This low solubility is significant for the etiology of gout.

The solubility of the acid and its salts in ethanol is very low or negligible. In ethanol water mixtures, the solubilities are somewhere between the end values for pure ethanol and pure water.

The chemical structural formula of uric acid is shown in **Fig.1.3.6.**

(2)Medicine :

In human blood plasma, the reference range of uric acid is typically 3.4-7.2 mg/dL for men, and 2.4-6.1 mg/dL for women. However, blood test results should always be interpreted using the range provided by the laboratory that performed the test.

Uric acid concentrations in blood plasma above and below the normal range are known, respectively, as hyperuricemia and hypouricemia.

Likewise, uric acid concentrations in urine above and below normal are known as hyperuricemia and hypouricemia.

Such abnormal concentrations of uric acid are not medical conditions, but are associated with a variety of medical conditions.

(3)Causes of high uric acid:

In many instances, people have elevated uric acid levels for hereditary reasons, as well as high intake of dietary purine and table sugar.

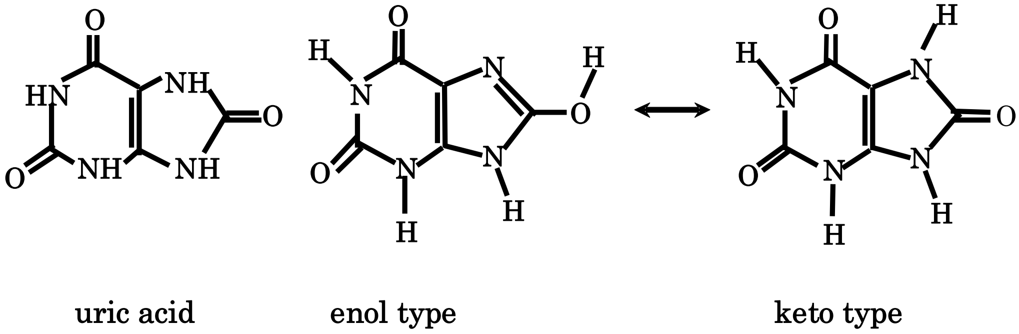


Fig.1.3.6 Chemical structure form of uric acid and its keto-enol type

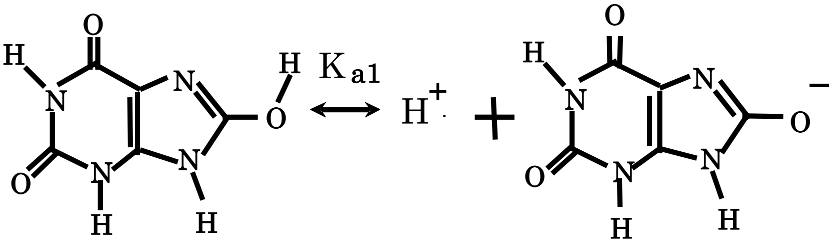


Fig.1.3.7 Dissociation equilibrium of uric acid

【Comment 1.3.2】Dissociation equilibrium of uric acid [12]

The equilibrium constant of a weak acid is defined as pKa=-logKa. Dissociation equilibrium due to pKa_1 of uric acid is shown in **Fig.1.3.7**.

The value of dissociation equilibrium due to pKa_1 is 5.4, where, pKa_1 is the first equilibrium constant of a weak acid. At subscriptor“a_1”, “a” and “1” express acid and chain initiation step, respectively. Furthermore, the value of dissociation equilibrium due to pKa_2 is 10.3. Ka_2 is the second equilibrium constant of a weak acid.

At subscriptor“a_2”, “a” and “2” express acid and chain propagation step, respectively.

【Comment1.3.3】Difference between uric acid and urea

(1)Uric acid[https//en.wikipedia.org/wiki/Uric acid]

Uric acid is a heterocyclic compound with the chemical formula $C_5H_4N_4O_3$.

The structure of the chemical formula $C_5H_4N_4O_3$ of uric acid is shown in **Fig.1.3.6**.

In many cases, people may have elevated uric acid levels by high Intake of dietary purine. Consequently,

(a) Saturation levels of uric acid in blood may generate uric acid crystals,
(b) Hyperuricemia is associated with components metabolic syndrome,
(c) High blood concentrations of uric acid may lead to gout.

(2)Urea [https//en.wikipedia.org/wiki/urea]

Urea is an organic compound with the chemical formula $CO(NH_2)_2$.

The structure of the chemical formula $CO(NH_2)_2$ of urea is shown to the right side in **Fig.1.3.8** and a procedure of the synthesis of urea is also shown in **Fig.1.3.8.**

Urea serves an important role in the metabolism of nitrogen-containing compounds for animals.

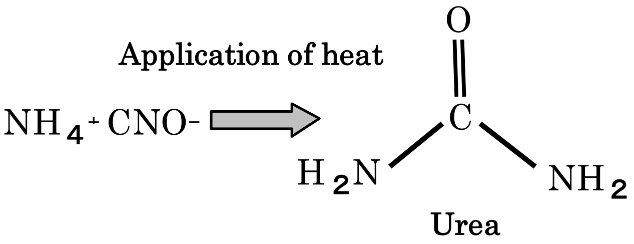


Fig.1.3.8 Chemical synthesis of urea

1.3.8 Problems

Discuss Each of the Following Descriptions:

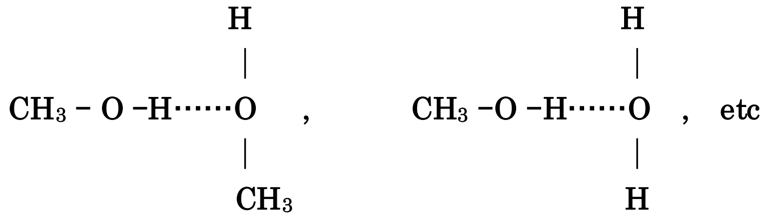
1. Chemical qualities of caffeine
2. Properties and reactions of alcohols

1.3.9 Examples of Answers

1. Chemical qualities of caffeine
   - (a) Caffeine forms a white precipitate with a tannin solution. This dissolves in an excess of the tannin solution.
   - (b) Spectrophotometry in the ultraviolet region can also be used for the quantitative determination of caffeine.
   - (c) To identify caffeine, the murexide test and reactions of precipitation with the group alkaloid reagents are employed. It should be noted that these reactions have a number of distinctions for caffeine.

[Reference [2], p.55]

2. Properties and reactions of alcohols
   - (a) The alcohols are aliphatic (not aromatic) compounds containing one or more hydroxyl groups attached to a hydrocarbon chain, which may be straight or branched, saturated or unsaturated.
   - (b) If we compare the melting and boiling points of alcohols with those of the corresponding alkanes, we find that the alcohols have much higher values, although the difference diminishes as the molecules become longer. One result of these higher values is that there are no gaseous alcohols.
   - (c) The relatively higher temperature for change of state and the very higher water stabilities of the lower alcohols (C1 to C5) are due to the formation of strong hydrogen bonds between the hydroxyl groups of alcohol molecules and also between the hydroxyl groups and water molecules, e.g.



$$CH_3-O-H\cdots\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{O}}\quad,\qquad CH_3-O-H\cdots\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{O}}\quad,\ \text{etc}$$

…… : hydrogen bond

[Reference [13], p. 190]

(d) Acid-base properties of alcohols

Alcohols are very weak acids. For the ionization

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$$

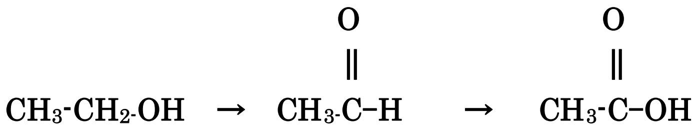
Ka ($10^{-18} < K\text{a} < 10^{-13}$) depends upon the length and nature of R. Under certain vigorous condition, salts of alcohols can be formed, e.g. the reaction of pure alcohols with alkali metals:

$$2ROH + Na \rightarrow 2Na^+ RO^- + H_2\uparrow$$

(e) Redox reactions of alcohols

These reactions are used in the laboratory to distinguish between primary, secondary and tertiary alcohols.

Primary alcohols are oxidized by strong oxidizing agents (e.g. potassium dichromate or potassium permanganate) to give, first, aldehydes and, subsequently, carboxylic acids, e.g.



$$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \rightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH$$

ethanol acetaldehyde acetic acid

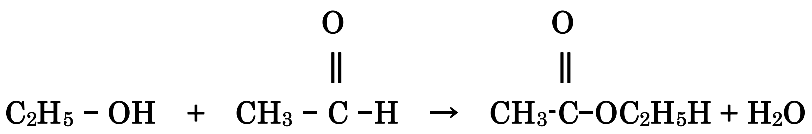
A practical example of this reaction is the production of sour wine or beer (containing acetic acid) when a fermentation mixture becomes contaminated with ethanol-oxidizing micro-organisms.

Secondary alcohols can be oxidized to ketones by these reagents.

Tertiary alcohols cannot be oxidized.

(f) Esterification of alcohol

Alcohols react with carboxylic acid to give esters. For example, the reaction of ethanol with acetic acid



$$C_2H_5 - OH + CH_3 - \overset{\overset{O}{\|}}{C} - H \rightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OC_2H_5H + H_2O$$

ethanol acetic acid methyl ethyl ester

yields the fruit-smelling ester, an ethyl acetate which is a versatile solvent for organic substances (e.g. in glues and varnishes, and in dry cleaning textiles). Esters play a part in many biochemical pathways, notably in energy and lipid metabolism, as well as acting, due to their strong pleasant smells, as a chemical attractant in nature (i.e. ripe fruit, and between insects). [Reference [13], pp.190-191]

1.4 Analytical Chemistry

In this section, several examples about dissolution of substances, dissociation of pure water, acids and bases, the Bronsted-Lowry concept, indicators, application of buffer action, and solubility product are described in the form of Q and A.

Q.1.4.1 Discuss dissolution of substances

A.1.4.1 Most chemical reactions occur in solutions. The study of such solutions constitutes one of the most important branches of physical chemistry. In general, if we analyze the solubility of the solutes in various solvents, we find that the polar solutes are more soluble in polar solvents whereas nonpolar solutes are more soluble in nonpolar solvents. This is the first rule of solubility, i.e., *like dissolves like*. For example, sodium chloride is soluble in water whereas it is insoluble in carbon tetrachloride.

Q.1.4.2 Discuss dissolution of pure water

A.1.4.2 Pure water is itself a very weak electrolyte and ionizes according to the equation

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

or simply written as

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1.4.1)$$

For which the ionization constant is given by

$$K_i = \frac{[H+][OH-]}{[H2O]} \qquad (1.4.2)$$

Since water is found to be poorly ionized (the degree of dissociation is 1.8×10^{-9} at 25 ^{O}C), the concentration of water remains practically the same{(1000g dm^{-3})/(18 g mol^{-1}) = 55.56 mol dm^{-3}}. Its concentration can be combined with the ionization constant K_i to give a new constant, known as the ionic product of water, K_w. From Eq.(1.4.2), we get

$$K_w = K_i[H_2O] = [H^+][OH^-] \qquad (1.4.3)$$

The concentration of OH^- in pure water will be the same as that of H^+, therefore

$$K_w = [H^+]^2 \qquad (1.4.4)$$

The value of $[H^+]$ in water at 25 °C is found to be 1.0×10^{-7} mol dm^{-3}.

The value of the ionic product at 25 °C is thus equal to

$$K_w = (1.0\times10^{-7}\ \text{mol dm}^{-3})(1.0\times10^{-7}\ \text{mol dm}^{-3})$$
$$= 1.0\times10^{-14}\ (\text{mol dm}^{-3})^2 \qquad (1.4.5)$$

Because of equal concentrations of hydrogen and hydroxyl ions in pure water, this water is neutral in its behavior.

The acidity or alkalinity of a solution depends upon the concentration of hydrogen ions relative to that of hydroxyl ions. In any aqueous solution, both hydrogen and hydroxyl ions coexist in accordance with Eq.(1.4.1). The product of hydrogen and hydroxyl ion concentrations is given by Eq.(1.4.3), the value of which depends only on the temperature and not on the individual ionic concentrations. If the concentration of hydrogen ions exceeds that of the hydroxyl ions, the solution is said to be acidic; whereas, if the concentration of hydroxyl ions exceeds that of the hydrogen ions, the solution is said to be alkaline. Taking into account Eq.(1.4.3), it amounts to

For neutral solution $[H^+] = [OH^-] = \sqrt{Kw}$

For acidic solution $[H^+] > [OH^-]$ or $[H^+] > \sqrt{Kw}$

For alkaline solution $[H^+] < [OH^-]$ or $[H^+] < \sqrt{Kw}$

At 25 °C, these reduce to

Neutral solution $[H^+] = 10^{-7}$ mol dm^{-3}

Acidic solution $[H^+] > 10^{-7}$ mol dm^{-3}

Alkaline solution $[H^+] < 10^{-7}$ mol dm^{-3}

[Comment 1.4.1]

Table 1.4.1 shows the values of several kinds of pH.

Table 1.4.1 Values of several kinds of pH

materials	pH	materials	pH
0.1M HCl	1	Intestinal juice	7.7
Gastric juice	1.5~2.0	0.1M $NaHCO_3$	8.3

Vinegar	2.5	Seawater	8.3
Lemon	2~3	0.1M $NaCO_3$	11.4
Soda water（1atm, CO_2）	~4	0.1M $NaCO_3$	11.4
Distilled water（In the air）	5.7	0.1M NaOH	13
Milk	6.5~ 6.6		
Pure water	7.0		
Blood	7.4		

[Reference [1], p.211]

Q.1.4.3 Discuss acids and bases

A.1.4.3 The solution of an acid in water raises the hydrogen ion concentration above10^{-7} mol dm^{-3}, and correspondingly lowers the pH. The solution of a base in water raises the hydroxyl ion concentration above 10^{-7} mol dm^{-3},andcorrespondingly decreases the hydrogen ion concentration (i.e. pH rises). This behavior suggests that acids and bases may be defined as compounds which dissociate in water to yield H^+ and OH^- ions respectively.

Acid： $HA \rightleftharpoons H^+ + A^-$

Base： $BOH \rightleftharpoons B^+ + OH^-$

[Reference [10], p.125]

[Example 1.4.1] Calculation of pH for strong and weak acids.

Calculate the pH of the following solution:

(a) A 0.1 mol dm^{-3} solution of hydrochloric acid which is 83% dissociated at 298 K

(b) A 0.1 mol dm^{-3} solution of acetic acid which is 1.35% dissociated at the same temperature.

[Solution 1.4.1]

(a) Since the HCl is 83% dissociated, the $[H^+]$ in its 0.1 mol dm^{-3} solution

$= 0.83 \times 0.1 = 8.3 \times 10^{-2}$ mol dm^{-3}.

Since $pH = -\log [H^+]$, its $pH = -\log (8.3 \times 10^{-2}) = 1.08$.

(b) Since the acetic acid is 1.35% dissociated, the $[H^+]$ in its 0.1% mol dm^{-3} solution

$[H^+] = 0.0135 \times 0.1 = 1.35 \times 10^{-3}$ mol dm^{-3}.

$pH = -\log [H^+]$, $pH = -\log (1.35 \times 10^{-3}) = 2.87$.

[Reference [10], p.131]

Q.1.4.4 Discuss the Bronsted-Lowry concept.

A.1.4.4 In 1923, a more general concept of acids and bases was introduced independently by J.N. Bronsted of Denmark and T.M. Lowry of England. According to Bronsted-Lowry definition, an acid is a substance that give a proton and a base is a substance that accepts a proton.

In a typical acid-base reaction,

$$HX + B \rightleftharpoons X^- + HB^+$$

HX being a proton donor is an acid and B being a proton acceptor is a base in the forward reactions. In the back reaction, HB^+ being a proton donor, is an acid and $X,^-$ being a proton acceptor, is a base. To make a distinction between the two acids and two bases, those on the right-hand side of the equation are referred to as the conjugate acid and the conjugate base. Thus

HB+ is a conjugate acid of the base B and X^- is a conjugate base of the acid HX, $HX\text{–}X^-$ and $HB^+\text{–}B$ constitute two conjugate acid-base pairs.

The acid and base in each conjugate differ by a proton. In order that an acid may exhibit its acidic properties, there must be a proton acceptor (base) present. Some examples are shown in **Fig.1.4.1**.

acid		base		conjugate acid		conjugate base
HCl	**+**	**H_2O**	$\rightleftharpoons$	**H_3O^+**	**+**	**Cl^-**
NH_4^+	**+**	**H_2O**	$\rightleftharpoons$	**H_3O^+**	**+**	**NH_3**

| |____conjugate ___| |

|____________________conjugate ____________________|

Fig. 1.4.1 Conjugate relationship of acid and base

[Reference [8], pp.2-3]

Q.1.4.5 Discuss indicators

A.1.4.5 Indicators, in general, are either organic weak acids or weak bases with a characteristic of having different colors in the ionized and unionized forms. For example, phenolphthalein(**See Fig.1.4.2 (a)**) is a weak acid (its ionized form is pink and its unionized form is colorless) and methyl orange (**See Fig.1.4.2 (b)**) is a weak base (its ionized form is red and its unionized form is yellow).

The equilibrium of these substances could be treated like that of any other weak electrolyte. Considering an acid indicator HIn, the equilibrium involving it and its conjugate base In^- can be represented as

$$HIn \rightleftharpoons H^+ + In^-$$

Its equilibrium constant K_{in} is given by

$$K_{In} = \frac{[H\cdot][In^-]}{[HIn]} \qquad (1.4.6)$$

This K_{In} is known as the indicator constant and like any other dissociation constant, its value depends only on the temperature and not on individual concentrations of H^+, In^- and HIn. These are usually tabulated as $pK_{In}\{= -\log(K_{In}/\text{mol dm}^{-3})\}$.

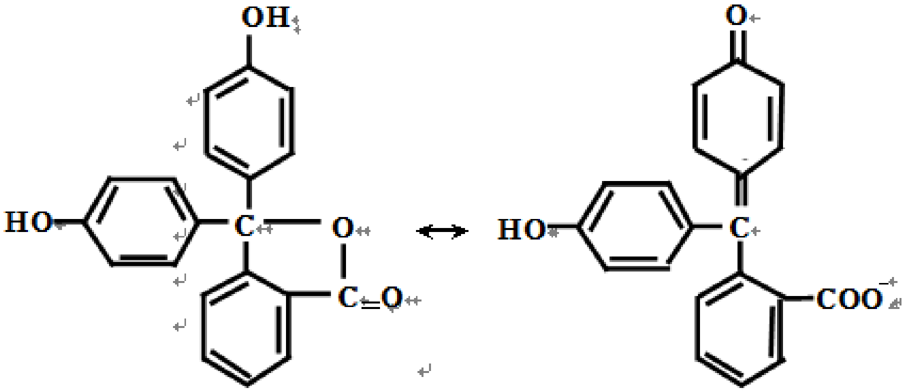
Rewriting the above expression, we get

$$[H^+] = K_{In} \times \frac{[HIn]}{[In^-]} \qquad (1.4.7)$$

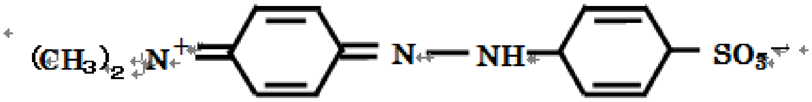
or

$$pH = pK_{In} + \log\frac{[In^-]}{[HIn]} \qquad (1.4.8)$$

In general, the intensity of a colored solution depends on the concentration of the color imparting species. If the solution contains two colored species, say In^- and HIn, the color of the solution depends on the relative amounts of the two species. On an average, the solution acquires a distinct color characteristic of In^- if the concentration of the latter is approximately 10 or more times greater than that of Hin, and vice versa. [Reference [1], p.274]



(a) Phenolphthalein



(b) Methyl orange

Fig. 1.4.2 Examples of indicators

[Comment 1.4.2] https//en.wikipedia.org/wiki/Phenolphthalein, and https//en.wikipedia.org/wiki/Methyl orange]

"Phenolphthalein" and "Methyl orange" are used as indicators in acid-base titrations. For these applications,

(1) Phenolphthalein turns colorless in acidic solutions and pink in basic solutions.

(2) Methyl orange has a clear and distinct color change. It changes color at the pH of a mid-strength acid. Therefore it is often used in titrations for acids.

Q. 1.4.6 Discuss application of buffer action

A.1.4.6 Buffers are an important part of many industrial processes, e.g., electroplating, leather processing, photographic material and dyeing.

In bacteriological research, it is essential to maintain the pH required for the growth of certain bacteria. Human blood is buffered to a pH of 7.3-7.4 by means of HCO_3^-, PO_4^{3-} and other nitrogenous bases.

Q.1.4.7 Discuss solubility product

A.1.4.7 If a slightly soluble salt is placed in water, after some time an equilibrium is established when the rate of dissolution of ions from the solid equals the rate of precipitation of ions from the saturated solution. Thus, a dynamic equilibrium exists between the undissociated solid species and the dissolved ionic species in the saturated solution. For example, in AgCl, we have the following equilibrium

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

With the equilibrium constant

$$K' = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since the concentration of a pure solid is almost a constant, [AgCl] may be multiplied with *K'* to give a new constant, called the *solubility product*:

$$K_{sp} = K[AgCl] = [Ag^+][Cl^-]$$

Thus, it is equal to the product of the ionic concentration present in a saturated solution. When the salt dissolves to give unequal numbers of positive and negative ions, each concentration term must be raised to a power equal to the coefficient of the ion in the equation. Some of solubility product expressions are shown in **Table 1.4.2**.

Table 1.4.2 Examples of solubility product expression

Salt	Reaction	Solubility product expression
CaF_2	$CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$	$K_{sp}(CaF_2) = [Ca^{2+}][F^-]^2$
PbI_2	$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$	$K_{sp}(PbI_2) = [Pb^{2+}][I^-]^2$
Hg_2Cl_2	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+} + 2Cl^-$	$K_{sp}(Hg_2Cl_2) = [Hg_2^{2+}][Cl^-]^2$
$Al(OH)_3$	$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^-$	$K_{sp}(Al(OH)_3) = [Al^{3+}][OH^-]^3$

Since the solubility of a salt varies with temperature, the numerical value of K_{sp} for a salt changes with temperature; values are usually recorded at 25 °C. The numerical values of the standard solubility products for some of the common sparingly soluble salts are listed in **Table 1.4.3**

Table1.4.3 Solubility product, 25 °C

salt	K^o_{sp}	salt	K^o_{sp}
CaF_2	3.9×10^{-11}	AgCl	1.7×10^{-10}
PbI_2	8.3×10^{-9}	AgBr	5×10^{-13}
Hg_2Cl_2	1.1×10^{-18}	AgI	8.5×10^{-7}
$Al(OH)_3$	5×10^{-33}	PbI_2	8.3×10^{-9}

[Reference [1], p.301]

1.4.8 Problems

Discuss or Calculate Each of the Following Descriptions:

1. The Arrhenius concept,
2. The Bronsted-Lowry concept,
3. The Lewis concept,
4. Acid base indicators,
5. The Arrhenius theory of dissociation,
6. The ionization of water,
7. Acids and bases,
8. Acid solutions.
9. At 25 °C, the degree of ionization of water was found to be 1.8×10^{-9}. Calculate the ionization constant and the ionic product of water at this temperature.

1.4.9 Examples of Answers

1. An acid is a substance which ionizes in water to produce the $H^+(aq)$ ion or the hydronium ion [$H_3O^+(aq)$]. [Reference [12], p.2]

2. A substance is said to be an acid if it can donate a proton to another substance. [Reference [12], p.2]

3. An acid is a substance that can form a covalent bond by accepting an electron pair from some other substance. [Reference [12], p.2]

4. Indicators, in general, are either organic weak acids or bases with a characteristic of having different colors in the ionized and unionized forms. For example, phenolphthalein is a weak acid (its ionized form is pink and its unionized form is colorless) and methyl orange is a weak base (its ionized form is red and its unionized form is yellow).

[Reference [12], p.2]

5. According to the Arrhenius theory, a weak electrolyte in a solution exists in equilibrium with its characteristic ions. For example,

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

[Reference [12], p.6]

6. All aqueous solutions contain positively charged hydrogen ions (or protons H^+), and negatively charged hydroxyl ions (OH^-). In pure water these ions are entirely derived from the ionization of water molecules,

$$H_2O \rightleftharpoons H^+ + OH^-$$

In fact, the H^+ ion is always hydrated in the aqueous medium, and is predominantly present as H_3O^+, the hydronium ion. Thus the protolysis of water might better be presented by the following equation,

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

[Reference [1], p.213]

7. The solution of an acid in water raises the hydrogen ion concentration above10^{-7} mol dm^{-3} and correspondingly lowers the pH. The solution of a base in water raises the hydroxyl ion concentration above 10^{-7} mol dm^{-3}, and correspondingly decreases the hydrogen ion concentration (i.e. pH raises). This behavior suggests that acids and bases may be defined as compounds which dissociate in water to yield H^+ and OH^- ions respectively:

Acid: $HCl \rightleftharpoons H^+ + A^-$

Base: $BOH \rightleftharpoons B^+ + OH^-$

8. Consider what happens when some HCl is added to a liter of water. HCl dissociates to furnish H_3O^+ and Cl^- ions:

$$HCl + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

The added substance (HCl) releases H_3O^+ ions into the water.

9. If α is the degree of dissociation of water, then we have

$H_2O \rightleftharpoons H^+ + OH^-$

$[H^+] = [OH^-] = c\alpha$

$C = 1000\ g\ dm^{-3}/18\ g\ mol^{-1} = 55.56\ mol\ dm^{-3}$

thus

$$K_i = \frac{[H+][OH-]}{[H2O]} = \frac{(c\alpha)2}{c(1-\alpha)} \approx c\alpha2 \qquad (\alpha \ll 1)$$

$$= (55.56\ mol\ dm^{-3})(1.8\times10^{-9})^2 = 1.8\times10^{-16}\ mol\ dm^{-3}$$

and $$K_w = [H^+][OH^-] = (c\alpha)^2 = \{(55.56\ mol\ dm^{-3})\ (1.8\times10^{-9})\}^2$$

$$= 1.0\times10^{-14}\ (mol\ dm^{-3})^2$$

[Reference [1], p.213]

Chapter 2 Applied Chemistry

In this chapter, several examples of Radiation Chemistry, Bio Chemistry, Environmental Chemistry, and Fuel Chemistry are described in the form of Q and A. Furthermore, outlines for Writing Research Papers and an example are described.

Additionally, some problems are presented at the end of each section.

2.1 Radiation Chemistry

In this section, basic phenomena such as a natural radioactivity, discovery of radioactive elements, the nature of radioactivity, disintegration of radioactive elements, half-life periods of radioactive elements, radionuclides, artificial radioactivity, and nuclear fusion reaction are described in the form of Q and A.

Q.2.1.1 Discuss natural radioactivity

A.2.1.1 Atoms of certain elements, mainly some of the heavier elements such as uranium, radium and polonium, break up spontaneously and in so doing emit rays and particles, and the atom disintegrates. This discovery was made in 1896 by the Frenchman Henri Becquerel. He found that photographic plates wrapped in black paper were darkened by uranium salts, and he suggested that the uranium salts emitted some form of rays

that affected the film.
[Reference [13], p.64]

Q.2.1.2 Discuss the discovery of radioactive elements

A.2.1.2 In 1898 Marie Curie found that uranium minerals such as pitchblende had more radioactivity than that expected from the amount of uranium present. She therefore looked for other radioactive elements in the pitchblende and discovered polonium (named after her homeland of Poland) and radium (named after the Latin word for a ray). Since then many other elements that are radioactive have been found.
[Reference [13], p.64]

Q.2.1.3 Discuss nature of radioactivity

A.2.1.3 The radioactivity in all cases originates from reactions occurring in the nuclei of the atoms of the elements concerned. This is different from all chemical reactions as discussed elsewhere in this book. These involve only the electrons which surround the nucleus.

The rays resulting from radioactivity are of three types:

(1) **α (alpha) particles**. These are positively charged helium atoms, He^{2+}, i.e. helium atoms without their two electrons. As they are charged they will be deflected in a magnetic field.

(2) **β (beta) particles**. These are fast moving electrons. As these have a much smaller mass than α-particles and as they are negatively charged, they are deflected more in a magnetic field and in the opposite direction to α-particles.

(3) **γ (gamma) rays.** These are a form of radiant energy. They are unaffected by a magnetic field (See **Fig.2.1.1**).

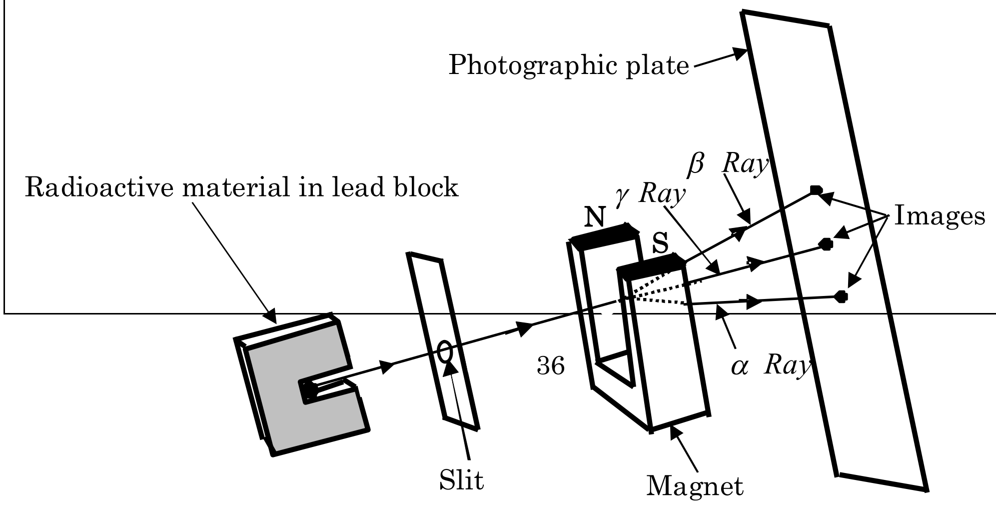


Fig.2.1.1 Effect of a magnetic field on α, β and γ rays.

The apparatus is assembled in a vacuum to prevent deflection of rays by gas molecules.

The rays that are not emitted forwards are absorbed by the lead block.

Three dark spots are produced on the plate showing that γ-rays are not deflected and that α-and β-rays are deflected to different extents in different directions.

[Reference [13], pp.64-65]

Q.2.1.4 Discuss disintegration of radioactive elements

A.2.1.4 When the atoms of elements disintegrate to form α, β and γ rays, atoms of new elements are left behind. These may also be radioactive and themselves disintegrate to atoms of other elements. The rate at which atoms disintegrate depends on how much radioactive material is present. As less and less is left, the rate of disintegration becomes slower and slower. A sample of radium, for example, will disintegrate to half its size in 1600 years. What is left will, in turn, disintegrate to half its size in a further 1600 years, and so on. Thus only after many such periods of 1600 years will the sample of radium have completely disappeared.

[Reference [13], p.65]

Q.2.1.5 Discuss half-life period of radioactive elements

A.2.1.5 As the total life of a radioactive element is infinite, it is usual to describe its rate of decay by means of its half-life, i.e. the time taken for half of the element to decompose. Half-lives vary considerably, e.g. radium-226 has a half-life of 1600 years, Radon-222 of 3.8 days, uranium-238 of 4.5×10^{9} years, polonium-212 of 3×10^{-7}seconds.

[Reference [13], p.65]

Q.2.1.6 Discuss radio- nuclides

A.2.1.6 Radio-nuclides are elements which spontaneously disintegrate into smaller particles and emit ionizing radiation. Certain types of this radiation, e.g., alpha particles and neutrons, have a high energy transfer per unit path length.[Reference [6], p.69]

Q.2.1.7 Discuss artificial radioactivity

A.2.1.7 When bombarded by particles travelling at suitably high speed, many stable nuclei become unstable and start decaying, giving new nuclear species. The radioactivity caused by such bombardment in stable nuclei is known as artificial radioactivity. For example, when nitrogen is bombarded by α -particles, hydrogen and oxygen are produced, the change being represented as

$$^{14}{}_{7}N + {}^{4}{}_{2}He \rightarrow {}^{17}{}_{8}O + {}^{1}{}_{1}H$$

Similar reactions are observed for many other elements and by many other bombarding particles.

[Reference [8], p.31]

Q.2.1.8 Discuss nuclear fusion reaction

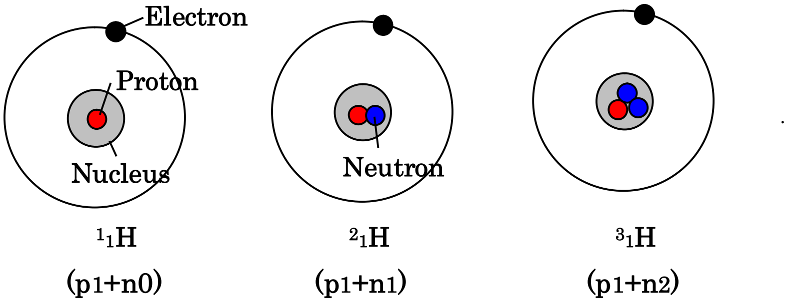
A.2.1.8 Nuclear fusion is the joining together of atomic nuclei, especially hydrogen or other light nuclei, to form a heavier nucleus, especially a helium nucleus. Fusion occurs when plasmas are heated to extremely high temperature, forcing the nuclei to collide at great speed. The resulting unstable nucleus emits one or more neutrons at very high speeds, releasing more energy than was required to fuse the nuclei, thereby making chain-reactions possible, since the reaction is exothermic. Fusion reactions are the source of the energy in the sun and in other stars, as well as in hydrogen bombs.

[Comment 2.1.1] https//en.wikipedia.org/wiki/**Nuclear fusion**

(1)Nuclear fusion

Nuclear fusion is a nuclear reaction in which two or more atomic nuclei come very close and then collide at a very high speed, finally joining to form a new nucleus. Fusion occurs only for lighter elements, and can lead to short periods of fusion with heavier nuclei.

The models of hydrogen（$^{1}_{1}H$）, deuterium（$^{2}_{1}H$）, and tritium （$^{3}_{1}H$）are shown in **Fig.2.1.2**.



(p: proton,　n: neutron, 0,1,2: the number written behind p and n)

Fig. 2.1.2 Models of hydrogen, deuterium and tritium

As an example, the nuclear fusion of two deuterium（$^{2}_{1}H$）nuclei generates the following reactions (D-D Reactions):

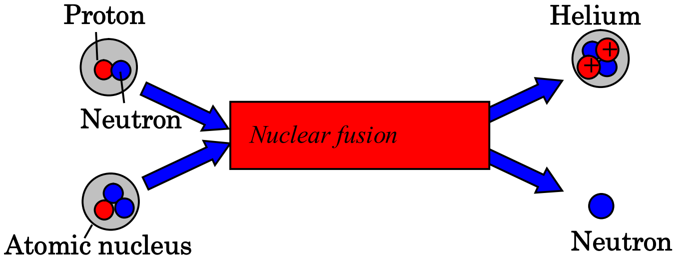
$^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He + ^{1}_{0}n$ (+3.3 MeV)

$^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{1}H + ^{1}_{1}H$ (+4.0 MeV)

$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$ (+17.6 MeV)

(2) An example of nuclear fusion reaction between Deuterium and Tritium, (D-T Nuclear Fusion Reaction):

Fig 2.1.3 shows a nuclear fusion reaction between Deuterium ($^{2}_{1}H$) and Tritium ($^{3}_{1}H$).



$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$$
$$(D + T \rightarrow {}^{4}_{2}He + {}^{1}_{0}n)$$

Fig. 2.1.3 Example of Nuclear fusion reaction

(3) The Sun : The sun generates its energy by the nuclear fusion of hydrogen nuclei into helium. Inside the sun, the following reactions are generated:

(1) ${}^{1}_{1}H + {}^{12}_{6}C \rightarrow {}^{13}_{7}N \rightarrow {}^{13}_{6}C + e^{+}$
(2) ${}^{1}_{1}H + {}^{13}_{6}C \rightarrow {}^{14}_{7}N$
(3) ${}^{1}_{1}H + {}^{14}_{7}N \rightarrow {}^{15}_{6}O \rightarrow {}^{15}_{7}N + e^{+}$
(4) ${}^{1}_{1}H + {}^{15}_{7}N \rightarrow {}^{12}_{6}C + {}^{4}_{2}He$

As a result shown above, the following reaction can be obtained:

$$4{}^{1}_{1}H \rightarrow {}^{4}_{2}He + 2e^{+}$$

That is, the two positive electrons and the helium (${}^{4}_{2}He$) can be generated from the four hydrogen elements ($4{}^{1}_{1}H$).

[Comment 2.1.2] https//en.wikipedia.org/wiki/**Nuclear fission**,

Nuclear fission reaction:

Nuclear fission is either a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into lighter nuclei.

The fission process produces free neutrons and generates gamma rays, while at the same time releasing a very large amount of energy due to the radioactive decay.

Nuclear fission produces energy for nuclear power.

However, the products of nuclear fission are far more radioactive than the heavy elements which are used as fuel, and remain radioactive for long periods of time.

The radioactive for long periods of time (At least, more than 30 years) is a nuclear waste problem.

2.1.9 Problems

Discuss Each of the Following Descriptions:

1. Applications of radioactive elements,
2. Use in medicine of radioactive elements,
3. Nuclear fission of heavier U-235,
4. Nuclear fusion due to deuterium nuclei ${}^{2}_{1}H$.

2.1.10 Examples of Answers

1. Radioactive elements are produced, as we have seen, by fission. Some occur naturally, such as radium, and many others can be produced by neutron bombardment of materials put inside a nuclear reactor.

Such radioactive elements have found numerous uses in industry, medicine, and scientific work. [Reference [13], p.65]

2. The best known use of radioactive elements is in the treatment of cancer. Some cancerous growths can be eliminated by exposure to gamma rays. Originally radium was used for this purpose, but now cobalt-60 and caesium-137 are used. Other radioactive isotopes can be implanted in cancerous growths to destroy them. [Reference [13], p. 66]

3. It is the nuclear reaction which involves the splitting of a heavier and bigger nucleus into smaller and lighter nuclei by bombardment of slow-moving neutrons. One of the possible reactions which takes place during nuclear fission of heavier U-235 is given below.

$$^{235}{}_{92}\mathrm{U} + {}^{1}{}_{0}\mathrm{n} \rightarrow {}^{139}{}_{56}\mathrm{Ba} + {}^{94}{}_{37}\mathrm{Kr} + 3{}^{1}{}_{0}\mathrm{n}$$

[Reference [8], p.182]

4. Fusion reaction is quite the opposite of nuclear fission. In such a reaction light nuclei combine to form heavier nuclei accompanied by the release of enormous energy.

For example, two light deuterium nuclei ($^{2}{}_{1}\mathrm{H}$) fuse together to a helium nucleus ($^{4}{}_{2}\mathrm{He}$) releasing 93.10×10^{8} kJ energy per mole of helium nucleus formed.

$$^{2}{}_{1}\mathrm{H} + {}^{2}{}_{1}\mathrm{He} \rightarrow {}^{4}{}_{2}\mathrm{He} + 93.\ 10 \times 10^{8}\ \mathrm{kJ\ mol^{-1}}$$

2.2 Bio Chemistry :

In this section, body fluid buffer systems (which play the most important role for our life), chlorophyll and hemoglobin, cobalamins $B_{12,}$ synthesis of Vitamin $B_{12,}$ oxy-hemoglobin, body temperature, combustion of cellulose, photosynthesis, exothermic and endothermic reactions of matters, and human blood are described in the form of Q and A.

Q.2.2.1 Discuss body fluid buffers : H_2CO_3/HCO_3^- buffer system

A.2.2.1 Body fluids contain three major buffer systems: the bicarbonate buffer（H_2CO_3/HCO_3^-）; the $H_2PO_4^-/HPO_4^{2-}$ buffer, and the protein buffer. The body uses each of these to carry out necessary buffering action.

Dissolved carbon dioxide gas from the body's metabolism combines with water in blood plasma to form unstable carbonic acid (H_2CO_3).

$$CO_2(g) + H_2O\ (l) \rightleftharpoons H_2CO_3(aq)$$

Where g is gas, l is liquid, aq is aqua (solution).

This equation indicates the amount of H_2CO_3 present is related to the amount of CO_2 present.

Carbonic acid is a weak acid that dissociates:

$$\underset{\substack{\text{carbonic acid}\\ \text{(acid)}}}{H_2CO_3} \rightleftharpoons H^+(aq) + \underset{\substack{\text{bicarbonate ion}\\ \text{(conjugate base)}}}{HCO_3^-\ (aq)}$$

Since the amount of CO_2 present governs the amount of H_2CO_3, it also affects the concentration of hydrogen and bicarbonate ions.
[Reference [11], p.214]

Q.2.2.2 Discuss body fluid buffers : ($H_2PO_4^-$)/(HPO_4^{2-}) buffer system

A.2.2.2 The dihydrogen phosphate ($H_2PO_4^-$)/monohydrogen phosphate (HPO_4^{2-}) buffer pair is unusual in that an anion functions as an acid:

$$\underset{\substack{\text{dihydrogen}\\ \text{phosphate ion}\\ \text{(acid)}}}{H_2PO_4^-} \rightleftharpoons H^+ + \underset{\substack{\text{monohydrogen}\\ \text{phosphate ion}\\ \text{(conjugate base)}}}{HPO_4^{2-}} \qquad Ka = 6.2 \times 10^{-8}$$

Functioning as a weak acid, $H_2PO_4^-$ releases a hydrogen ion to neutralize base added from an external source. The conjugate base HPO_4^{2-} accepts H^+ added from external sources. The plasma concentration of monohydrogen phosphate is normally four times greater than that of dihydrogen phosphate.
[Reference [11], p.215]

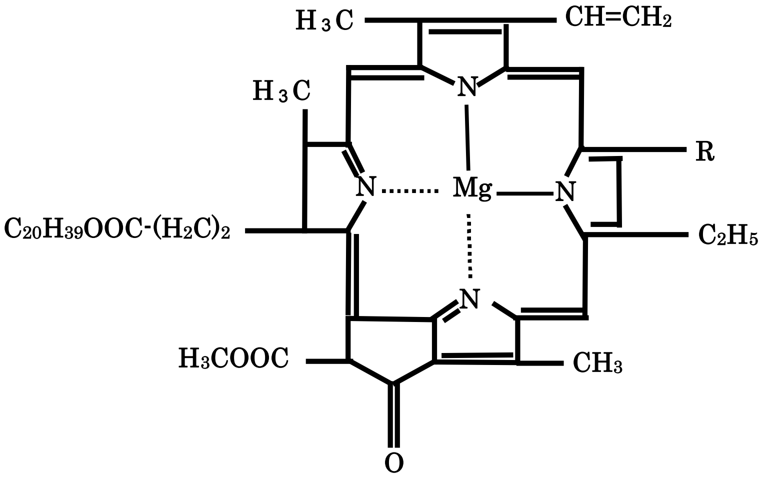
[Comment 2.2.1] In the human body, there is phosphate in the form of $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$.The normal pH of arterial blood is **7.4**. Whenever the pH falls within the range of **7.0-7.4**, a person is said to have **acidosis** caused by an increase in hydrogen concentration. Alkalosis occurs within the range **7.4-7.8** due to a decrease in hydrogen concentration.

Q.2.2.3 Discuss chlorophyll and hemoglobin

A.2.2.3 In living creatures, two important coordination compounds are chlorophyll in green plants and Hemoglobin in the blood of vertebrate animals. Chlorophyll, which is vital to photosynthesis in plants, is a magnesium complex, while hemoglobin, which carries oxygen to animal cells, is an iron complex. Structures of the two complexes are shown in **Figs.2.2.1 and 2.2.2**. [Reference [9], p.159]

[Comment 2.2.2] https//en.wikipedia.org/wiki/Hemoglobin,

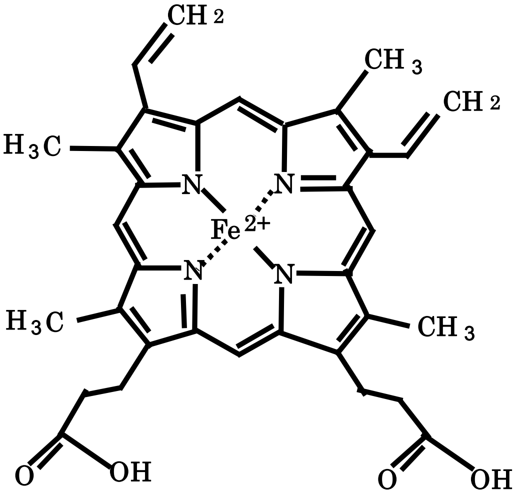
Hemoglobin in red blood cells, often abbreviated（HHb or Hb）, carries oxygen from the respiratory organs (lungs) to the tissues of the human body.



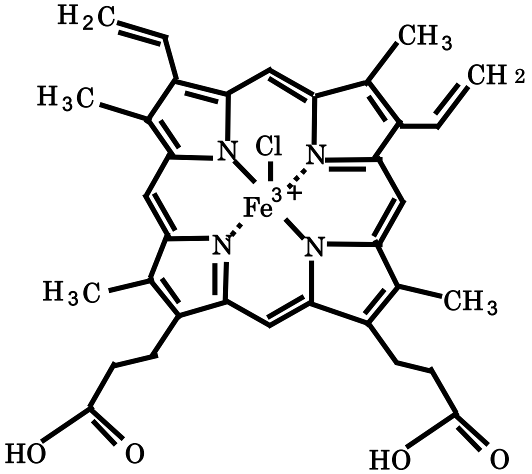
R : – CH_3 in chlorophyll$^{\alpha}$

R : – CHO in chlorophyll$^{\beta}$

Fig. 2.2.1 Structures of chlorophyll α and β



(a) Heme



(b) Hemin

Fig. 2.2.2 Structures of heme and hemin

Q.2.2.4 Discuss cobalamins B_{12} (Group B_{12} vitamins)

A.2.2.4 Vitamin B_{12} was discovered in 1948, when a dark red crystalline substance having a high activity against malignant (pernicious) anemia was isolated from liver extract. The substance was named vitamin B_{12}. Its empirical formula shows that it contains cobalt, which determined its name cobalamin.

Vitamin B_{12} is found widely in products of an animal origin, especially in the internal organs of fish, whale liver and the meat of mollusk. It is also present in poultry manure, the putrefied sludge of sewage refuse and in the stomach contents of ruminant animals.

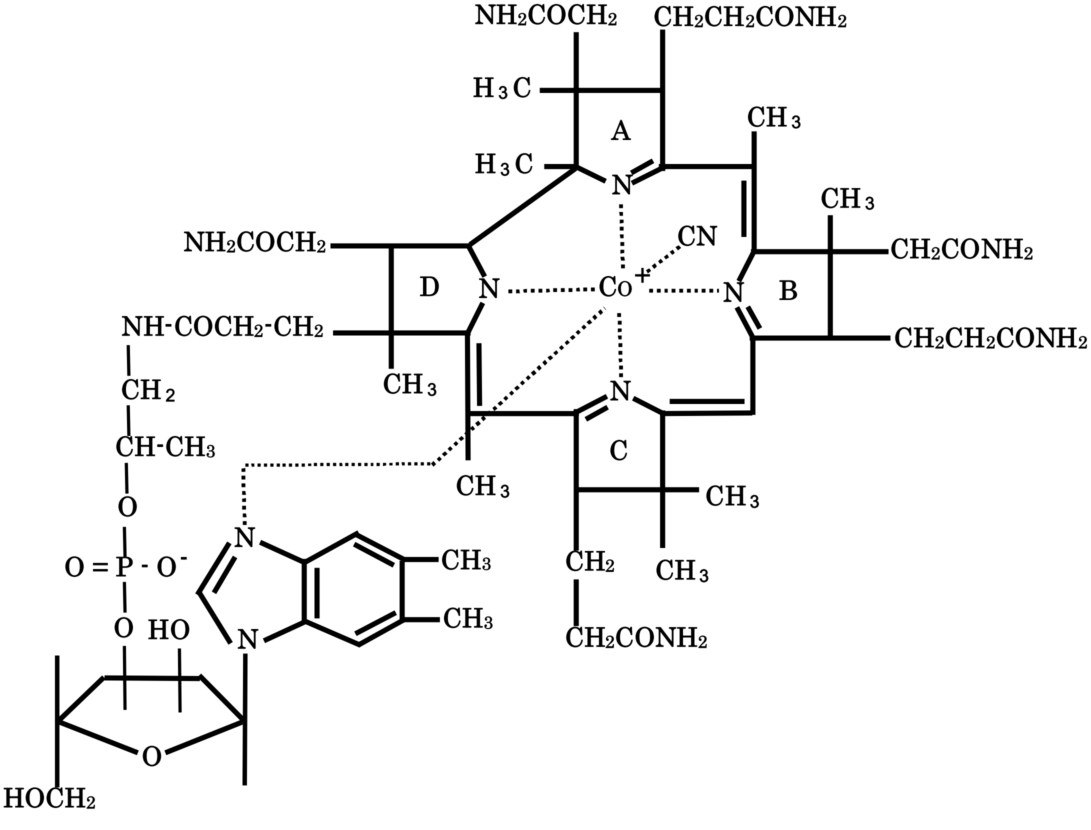


Fig. 2.2.3 Structure of vitamin B_{12}

[Comment 2.2.3] https//en.wikipedia.org/wiki/Cyanocobalamin,
Vitamin B_{12} is a very complicated chemical compound which has Co^{2+} at its center as shown in **Fig.2.2.3**. This is called the **Cyanocobalamin.** It usually does not occur in living organisms.

[Comment 2.2.4] https://en.wikipedia.org/wiki/Vitamin,
Vitamins are required to maintain the health of the organism, and these are classified by their biological and chemical activities. As shown in **Table 2.2.1**, thirteen vitamins are recognized at present.

Table 2.2.1 List of vitamins

Vitamin name	Solubility	Food sources
A (Retinol, Retinal, Four carotenoids including beta carotene)	Fat-soluble	Liver, Orange, Ripe yellow fruits, Leafy vegetables, Carrots, Squash, Pumpkin, Spinach, Fish, Milk, etc.
B_1 (Thiamine)	Water-soluble	Pork, Oatmeal, Brown rice, Vegetables, Potatoes, Liver, Eggs
B_2 (Riboflavin)	Water-soluble	Dairy products, Popcorn, Bananas, Green beans, Asparagus
B_3(Niacin, Niacinamide)	Water-soluble	Meat, Fish, Eggs, Vegetables, Mushrooms, Tree nuts
B_5 (Pantothenic acid)	Water-soluble	Meat, Broccoli, Avocados
B_6 (Pyridoxine, Pyridoxamine, Pyridoxal)	Water-soluble	Meat, Vegetables, Tree nuts, Bananas
B_7 (Biotin)	Water-soluble	Raw egg yolk, Liver, Peanuts, Leafy green vegetables
B_9 (Folic acid, Folinic acid)	Water-soluble	Leafy vegetables, Pasta, Bread, Cereal, Liver
B_{12} (Cyanocobalamin, Hydoxocobalamin, Methylcobalamin)	Water-soluble	Meat and other animal products
C (Ascorbic acid)	Water-soluble	Fruits, Vegetables, Liver
D (Cholecalcifelol:D_3),	Fat-	

(Ergocalciferol:D_2)	soluble	Fish, Eggs, Liver, Mushrooms
E (Tocopherols, Tocotrienols)	Fat-soluble	Fruits, Vegetables, Nuts, Seeds
K (Phylloquinone, Menaquinones)	Fat-soluble	Leafy green vegetables such as spinach, Egg yolks, Liver

Q.2.2.5 Discuss synthesis of vitamin B_{12}

A.2.2.5 Further investigations revealed that vitamin B_{12}, unlike all the other vitamins, is synthesized by microorganisms, including bacteria, molds, and actinomycetes. In human and animal organisms, vitamin B_{12} is synthesized by the microflora of the intestines, whereupon it is supplied and accumulated in the liver, kidneys and intestine walls.

Prior to the discovery of vitamin B_{12}, no cases were known of the syntheses of vitamins by microorganisms. When it was established that vitamin B_{12} is synthesized in the human organism by microflora in the intestines, nutrient media were developed for the artificial biosynthesis of vitamin B_{12} by microorganisms. The addition of cobalt salts to the microorganisms stimulates the biosynthesis of the entire vitamin.

Q.2.2.6 Discuss oxyhemoglobin

A.2.2.6 In the lungs, oxygen combines with hemoglobin (HHb) to form oxyhemoglobin:

$$HHb + O_2 \rightleftharpoons HHb \cdot O_2$$

In the lungs, the relatively high concentration of oxygen causes the forward reaction to be favored. The oxyhemoglobin is transported by the blood to the cells. Within cells that require oxygen, the oxygen concentration is low. As oxyhemoglobin is carried in a capillary adjacent to the cell, the low oxygen concentration creates a stress on the equilibrium above and oxygen is liberated. It diffuses across the cell membrane into the cells.

[Reference [11], p.175]

Q. 2.2.7 Discuss body temperature

A.2.2.7 Consider that our body temperature serves as a useful guide to our physiological condition. The normal 37.0°C value and its relative constancy results from the net metabolic changes in our body, even though our physical activities are not constant. We work, sit, eat, sleep—all different activities—and somehow our body accommodates these diverse functions without a drastic change in body temperature even in summer's heat and winter's cold.
[Reference [11], p.174]

Q.2.2.8 Discuss combustion of cellulose

A.2.2.8 During a chemical change, reactant molecules are transformed into product molecules. Bonds in the reactant molecules are broken and new bonds are made in forming product molecules during a reaction.

Wood and paper are primarily cellulose, which can be represented by the formula $(C_6H_{10}O_5)_n$, where n is a very large number. The reaction for the combustion of cellulose can be written

$$(C_6H_{10}O_5)_n) + 6nO_2 \rightarrow 6nCO_2 + 5nH_2O$$

From examination of this equation it is obvious that an oxygen-oxygen bond in the oxygen molecule must be broken so that the oxygen atoms can form new bonds with either carbon or hydrogen to produce the products.

Additionally, carbon-hydrogen bonds, carbon-carbon bonds, and perhaps carbon-oxygen or oxygen-hydrogen bonds in cellulose must be broken in order for new bonds to be formed to produce CO_2 and H_2O.
[Reference [11], p.181]

Q.2.2.9 Discuss photosynthesis

A.2.2.9 Photosynthesis consumes 686 kcal of radiant energy for each mole of glucose produced.

$$6CO_2 + 6H_2O + \underset{(+686\ \text{kcal})}{\text{radiant energy}} \xrightarrow{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2}$$

Therefore, energy absorbed during photosynthesis is stored in the bonded atoms in glucose molecules.

When animals eat green plants, the glucose stored in the plants is broken down to carbon dioxide and water with the liberation of 686 kcal/mol of glucose (See **Fig.2.2.4**).

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$ + 686 kcal/mol glucose

This exothermic conversion supplies the body with energy to be coupled with many endothermic processes such as muscle and nerve actions, cellular growth and repair, and maintenance of a relatively constant body temperature. [Reference [11], p.220]

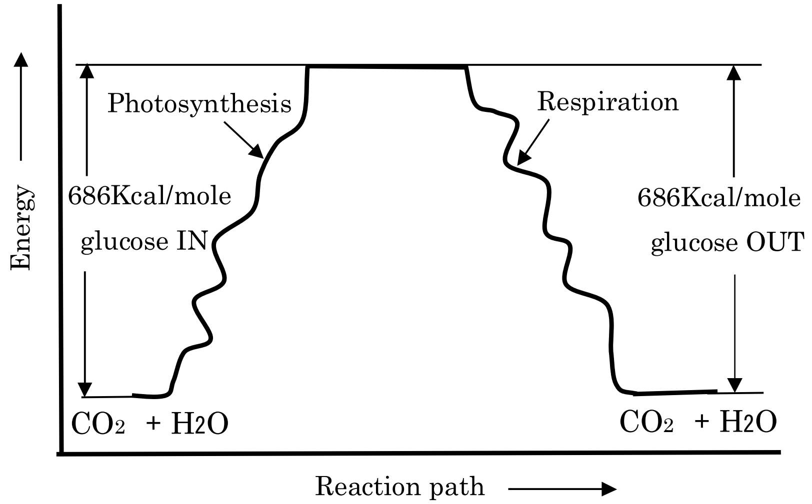


Fig. 2.2.4 Relationship of photosynthesis to respiration

[Comment 2.2.5] https://en.wikipedia.org/wiki/Photosynthesis,
Fig.2.2.5 shows process of photosynthesis in plants.

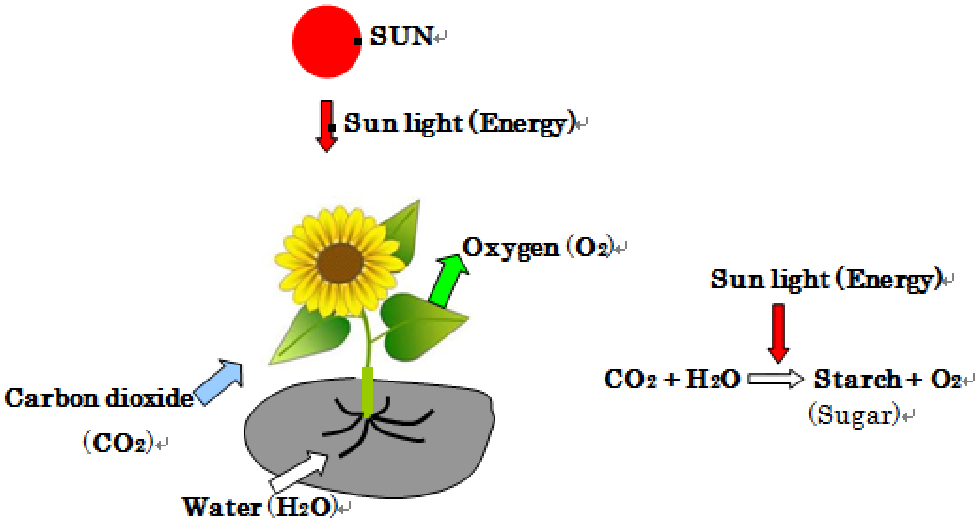


Fig.2.2.5 Process of photosynthesis in plants

https://www.google.co.jp/search?q=%E3%81%B2%E3%81%BE%E3%82%8F%E3%82%8A%E3%81%AE%E7%B5%B5&biw=1131&bih=381&tbm=isch&imgil=9PA_ZcgSzqXMIM%253A%253B1PQe_PynaLdfGM%253Bhttp%25253A%25252F%25252Fwww.h7.dion.ne.jp%25252F~fufu%25252Fbuhinn%25252Fhimawari.html&source=iu&pf=m&fir=9PA_ZcgSzqXMIM%253A%252C1PQe_PynaLdfGM%252C_&usg=__0tKpC2agHl00C43WuDBc_bsN244%3D&ved=0CDsQyjdqFQoTCJmh4bKczsgCFUG9lAod1twIEg&ei=2bckVtnQNcH60gTWuaOQAQ#imgrc=9PA_ZcgSzqXMIM%3A&usg=__0tKpC2agHl00C43WuDBc_bsN244%3D

Q.2.2.10 Discuss exothermic and endothermic reactions of matter

A.2.2.10 Exothermic reactions are energy yielding reactions and are termed exothermic. Endothermic reactions absorb energy, and since the energy source is heat, they are called endothermic reactions.

Since nature tends to move toward lower energy, we would expect the energetics of a reaction to determine the tendency of a reaction to occur. Chemists have found that most exothermic reactions have a tendency to occur, while endothermic reaction have little tendency to occur. These tendencies are not necessarily related to how rapidly a reaction takes place,

however. For example, wood, paper, and gasoline, among other things, will all react with oxygen to evolve heat in a process we call *burning*. The combustion of these materials is an exothermic reaction and has a great tendency to occur.
[Reference [11], p.180]

Q. 2.2.11 Discuss human blood

A.2.2.11 A human adult's body contains approximately 6 Liters of whole blood, which is a mixture consisting of plasma (55-60 percent by volume) and formed elements — red blood cells (erythrocytes), white blood cells (leukocytes), and platelets. Plasma can be separated from the formed elements by centrifuging whole blood (See **Fig.2.2.6**).

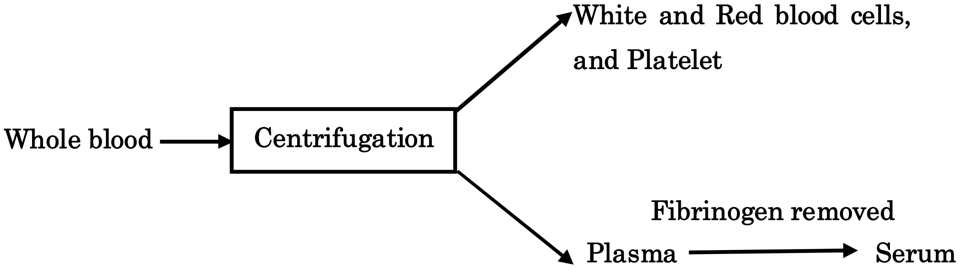


Fig. 2.2.6 Separation of whole blood

Plasma, the liquid portion of circulating or uncoagulated blood, is an aqueous solution containing plasma proteins and various cations and anions.

Other solutes such as glucose, uric acid, urea, and polysaccharides are also present. Trace amounts of metal ions (Mn^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+}, etc.) are also present.

The main plasma proteins are albumin, other globular proteins, and fibrinogen.

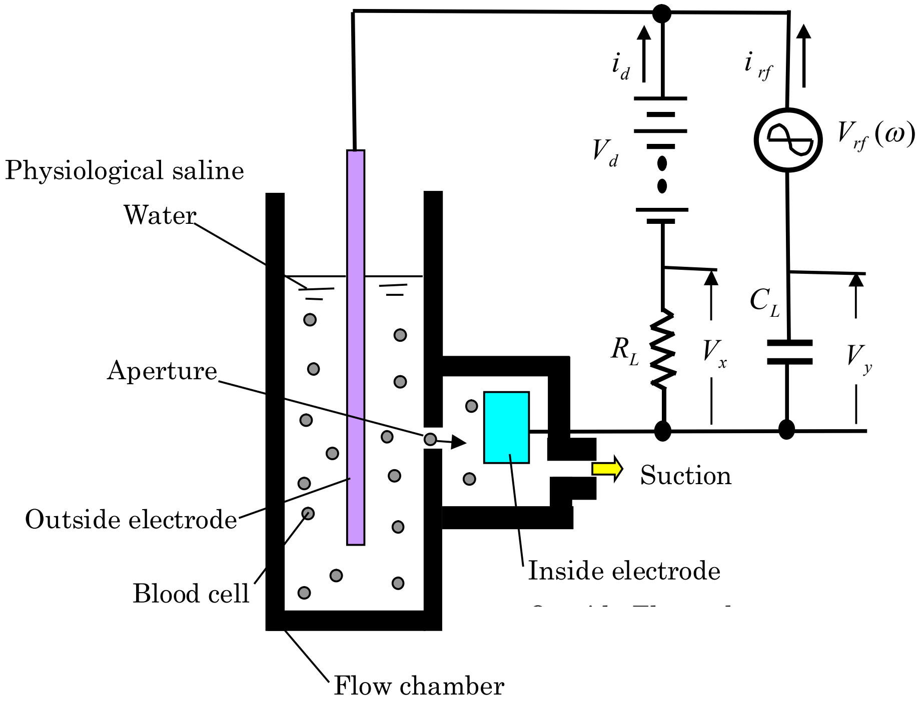
The main ions present are sodium, potassium, calcium, magnesium, chloride, bicarbonate, monohydrogen and dihydrogen phosphates, and sulfate. If fibrinogen is removed from plasma, the resulting liquid is called serum.

[Comment 2.2.6] Method for sensing blood cells, Reference (3)

(1) The sensing method for human blood cells passing through an aperture in the flow- chamber is shown in **Fig.2.2.7 (a)** The operation of this sensor is as follows:

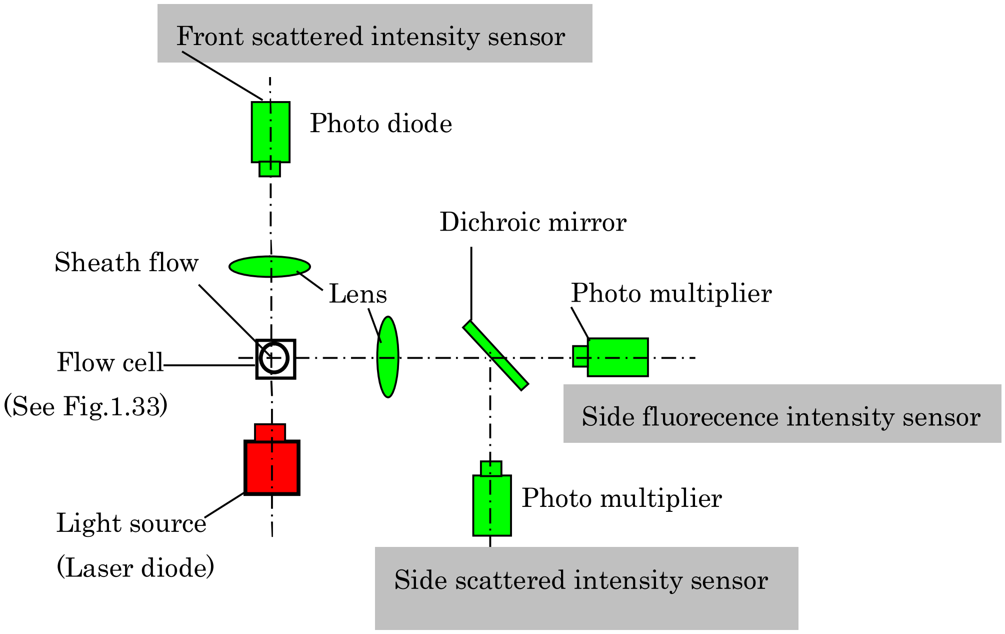
The blood cells suspended in physiological saline water passing through the aperture in the flow-chamber by the suction of the sheath-flowing system.

The cross-sectional area of the aperture where the DC and the RF currents flow is decreased by a blood cell, and then the resistance and the impedance between the inside and outside electrodes are varied.



(a) Sensing method for human blood cells passing through an aperture

(2) Fig.2.2.7 (b) shows the configuration of a sensor for an automated hematology analyzer using a photo-diode and two photo-multipliers.



(b) **Sensing method for automated hematology**

Fig. 2.2 .7 Sensing method for human blood cells

2.2.12 Problems

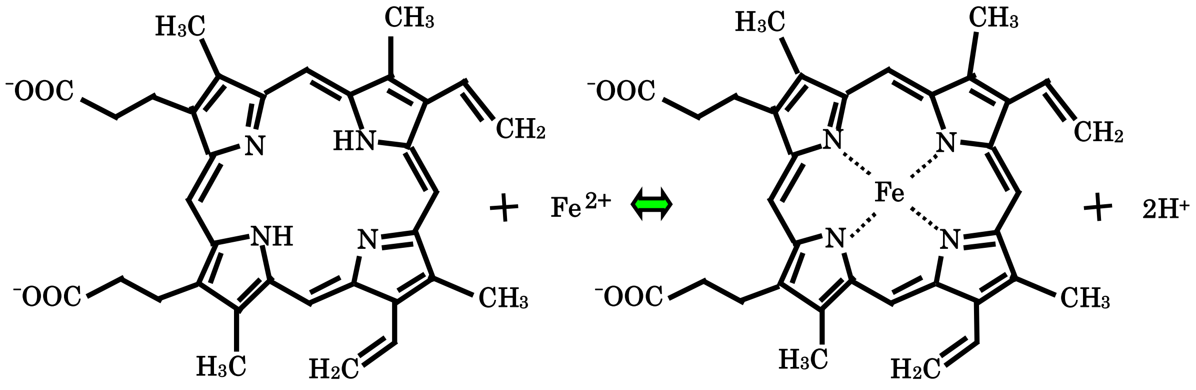
Discuss Each of the Following Descriptions:

1. Transport of oxygen from the lungs to the cells of animals,
2. Four subunits included in a hemoglobin molecule,
3. Bond of Fe^{2+} and O_2 in hemoglobin,
4. Bond of Fe^{2+} and CO in hemoglobin.

2.2.13 Examples of Answers

1. Let us see how we can use the idea of a coordinate covalent bond to explain an important biological process: the transport of oxygen from the lungs to the cells of animals, including humans. Hemoglobin in the red blood cells is responsible for the movement of oxygen molecules in these organisms. We are in a position to investigate in more detail how this occurs.

2. Each hemoglobin molecule contains four subunits called heme. The heme unit itself is rather complex with the Fe^{2+} ion at its center. It is this iron ion that actually does the work of carrying the oxygen molecule. By the use of some sophisticated techniques, chemists have found heme to have the following structure. The iron ion is bonded to four nitrogen atoms contained in a molecule known as protoporphyrin IX (**See Fig. 2.2.8**).

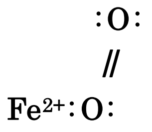


(a) Protoporphyrin IX **(b) Heme**

Fig. 2.2.8 Reaction of Fe^{2+} with protoporphyrin IX

3. The iron ion is capable of accepting a pair of electrons from an oxygen molecule to form a coordinate covalent bond. The exact arrangement of the oxygen molecule around the iron is yet unknown. One arrangement that has been suggested is as follows (See **Fig. 2.2.9**).

In the lungs, molecular oxygen bonds to the iron ions of the heme units in hemoglobin to produce oxyhemoglobin. The oxyhemoglobin is carried to other regions of the body where it releases the oxygen molecule for use by the cells.



$$\begin{array}{r} :O: \\ // \\ Fe^{2+}:O: \end{array}$$

Fig. 2.2.9 Bond of Fe^{2+} and O_2 in hemoglobin

4. The iron in hemoglobin will also form a coordinate covalent bond with certain other smaller molecules if they are present in the lungs.

Carbon monoxide is one such molecule, and moreover the bond formed between hemoglobin and carbon monoxide is more stable than the bond between hemoglobin and oxygen. If hemoglobin is bonded to CO, it cannot bond to O_2. This means that hemoglobin will preferentially bond with carbon monoxide rather than oxygen if both are present in the lungs. So great is this preference, that when only one out of every thousand gas molecules in the lungs is carbon monoxide, a sufficient amount of hemoglobin is bonded to carbon monoxide to cause paralysis or death because of a lack of oxygen movement to the cells.

2.3 Environmental Chemistry

In this section, Water pollution, Organic solvents and other organic chemicals, Carbon monoxide, Photochemical oxidants, Oxides of nitrogen, Air pollution, the Greenhouse effect, Acid rain, Environmental hormones, Global warming, Heat islands, and the Ozone layer are described in the form of Q and A.

Q.2.3.1 Discuss water pollution

A.2.3.1 Life is impossible without water. Good quality water is needed for drinking and innumerable other purposes. Industries discharge effluents into water bodies leading to a general contamination of water with toxic compounds. Water pollutants, originating from residential areas, are mainly organic matter, excess phosphate, nitrogen compounds and suspended solids.

The industrial effluents consist of heavy metals, oils, phenols, acids, etc.

Most industries allow their waste to mix with water bodies without any treatment. As a result, these pollutants progressively collect in natural water systems, first in the surface water and then in the ground water.

Thus, water obtained for drinking or irrigation from these sources becomes polluted and causes health hazards.

[Reference [8], p.265]

Q.2.3.2 Discuss organic solvents and other organic chemicals

A.2.3.2 Organic solvents are today produced almost entirely from petroleum. **Table 2.3.1** lists the solvents which are in most common use, along with their principal properties and applications. [Reference [6], p.105]

Table 2.3.1 Properties of some important solvents

Compound	Boiling Point(°C)	odor perception	application
Acetic acid	118	0.1-1.5 mg/m^3	synthesis, pharmaceutical
Benzene	80	3 mg/m^3	motor fuels, flavors, perfumes, paints,
Cyclohexane	81	4-10 mg/m^3	nylon, synthesis
Chloroform	62	1000 mg/m^3	refrigerants, pharmaceuticals
Ethanol	78	5-5- mg/m^3	synthesis, brewing, soaps, cosmetics

Q. 2.3.3 Discuss carbon monoxide

A.2.3.3 Carbon monoxide is a colorless, odorless gas produced by the incomplete combustion of carbon-containing fuels, as well as various biological and industrial processes. Every year human activities may put some 1500 teragrams (1 Tg = 10^{12} g) of carbon monoxide into the Earth's atmosphere, compared with the 1200 Tg/year from natural sources.

The major source of carbon monoxide emissions at breathing level outdoors is the exhaust of petrol-powered motor vehicles and the diesel engine (compression ignition). Locally, high concentrations of carbon monoxide may occur near industrial plants such as power stations, petroleum refineries, iron foundries and steel mills, as well as in the vicinity of refuse burning. Carbon monoxide concentrations in urban areas are closely related both to motor-traffic density and weather conditions.

Carbon monoxide is absorbed through the lungs and reacts with hemoproteins, especially with the hemoglobin of the blood. This in turn results in a reduction of the oxygen carrying-capacity of the blood, and also interferes with the release of the oxygen which is carried to the tissues.

Carbon monoxide has an affinity for hemoglobin(Hb) that is 200-400 times greater than that of oxygen, and carboxyhemoglobin (CoHb) is therefore a more stable compound than oxyhemoglobin. Carbon monoxide is not a cumulative poison, but is excreted or absorbed, depending upon the level of carbon monoxide in the ambient air, the amount of carboxyhemoglobin in the blood, barometric pressure, the duration of the exposure, and the rate of ventilation of the lungs. [Reference [7], p.35]

Q. 2.3.4 Discuss photochemical oxidants

A.2.3.4 Photochemical oxidants are secondary pollutants produced by the action of sunlight on an atmosphere containing reactive hydrocarbons and oxides of nitrogen. A complex series of photochemical reactions produces various oxidants, with the most important being ozone and peroxyacetyl nitrate (PAN). [Reference [7], p.41]

Q. 2.3.5 Discuss the oxides of nitrogen

A.2.3.5 Oxides of nitrogen (NOx) are produced by natural processes, including bacterial action in the soil, lightening and volcanic eruptions as well as by human activity during combustion processes at temperatures higher than about 1000 °C. Nitric oxide (NO) and nitrogen dioxide (NO_2) are the most important oxides of nitrogen for pollution studies because other oxides of nitrogen, such as nitrous oxide (N_2O), nitric acid (HNO_3) vapor, which may exist in ambient air, are not known to have any biological significance. The principal sources of the emission of oxides of nitrogen from human activities are the combustion of fossil fuels in stationary sources (heating, power generation) and in motor vehicles (internal combustion engines). The relative contribution of each source varies from country to country in relation to differences in fuel use. [Reference [7], pp.38-39]

Q. 2.3.6 Discuss air pollution

A.2.3.6 The atmospheric air is being increasingly polluted as a result of the disturbance of natural equilibrium caused by humans and our technology. By the term *air pollution* we understand the presence in the atmosphere of one or more contaminants or combinations thereof, in such amounts and of such durations that they are, or may tend to be, harmful to living organisms or other materials. These atmospheric contaminants (pollutants) find their origin in factories, power plants and motor vehicles. [Reference [8], p.8]

Q. 2.3.7 Discuss the greenhouse effect

A.2.3.7 The gaseous envelope surrounding the Earth is the atmosphere, comprised of a mixture of gases. Nitrogen makes up almost four-fifths of the atmosphere, while oxygen comprises a little more than one-fifth. Small quantities of other gases like argon, helium, neon, krypton, xenon, carbon, dioxide, hydrogen and ozone are also present.

The atmosphere also contains a considerable quantity of water vapor which is due to evaporation from rivers, lakes, oceans, etc. This atmosphere is retained on the Earth by gravitational attraction and, to a large measure, rotates with it.

The Earth's atmosphere acts like the glass walls and roof of a greenhouse in trapping heat from the sun. This is what is known as the "*Greenhouse Effect*". The atmosphere moderates the extremes of heat and cold upon the Earth. It is due to the greenhouse effect of the atmosphere that the change in temperature between day and night and similarly between summer and winter is reduced. The heat rays from the sun penetrate the air and warm the Earth's surface during the day. [Reference [8], p.109]

Q. 2.3.8 Discuss acid rain

A.2.3.8 Humankind's impact on atmospheric chemistry is steadily increasing with progressive industrialization and urbanization. In the last few decades precipitation in several areas of the world has become increasingly acidic.

The term *'acid rain'* is used to describe all precipitation of rain, snow, sleet, etc. that has a pH less than 5.6, the pH expected in pure rain.

Acid rain is produced due to an increase in sulfuric acid and nitric acid aerosols by fossil fuel combustion, metal smelting and industrial processes.

Sulphur dioxide and nitrogen oxides are the two main culprits responsible for the acidic precipitation problem. [Reference [8], p.1]

【**Comment 2.3.1**】https//en.wikipedia.org/wiki/acid rain, Acid rain

(1) Acid rain is rain with elevated levels of hydrogen ions (low pH；acidic). It can have harmful effects on plants, aquatic animals and infrastructure.
(2) Acid rain is caused by emissions of sulfer dioxide (SO_2) and nitrogen dioxide (NO_2), which react with the water molecules in the atmosphere to produce acids:（H_2SO_4）or（HNO_3）. These make acid rain, which falls on the ground and eventually flows to seawater through the rivers. Consequently, the water becomes more acidic, which causes water pollution. Natural water is always slightly alkaline. The PH of natural water is approximately 7.5-7.7, thereby weakly alkaline. When the pH is lowered, sea creatures, including fish, shellfish, etc. will not survive.
(3) (NO_2) can also be produced naturally by lightning strikes and (SO_2) is also produced by volcanic eruptions.
(4) As a result, paint peels, steel structures such as bridges become corroded, and stone statues are eroded due to the chemicals in acid rain.

【**Comment 2.3.2**】https//en.wikipedia.org/wiki/eutrophication,
Eutrophication: Chemical fertilizers, including nitrogen, phosphorus, potassium, etc. are essential for the growth of crops. When these fertilizers flow into rivers, they create eutrophication (a condition of excess nutrition) and cause red tide and blue-green algae. This state is caused by excessive nutrition.

Q. 2.3.9 Discuss environmental hormones（Endocrine disruptors）

A. 2.3.9 Endocrine disruptors are chemicals that may interfere with the body's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. A wide range of substances, both natural and man-made, are thought to cause endocrine disruption; These include pharmaceuticals, dioxins and dioxin-like compounds, polychlorinated biphenyls, DDT and other pesticides, and plasticizers such as bisphenol A. Endorine disruptors may be found in many everyday products, including plastic bottles, metal food cans, detergents, flame retardants, food, toys, cosmetics, and pesticides. The National Institute of Environmental Health Science (NIEHS) supports studies to determine whether exposure to endocrine disruptors may result in human health effects, including lowered fertility and an increased incidence of endometriosis and some cancers. Research shows that endocrine disruptors may pose the greatest risk during prenatal and early postnatal development when organ and neural systems are forming.

Q. 2.3.10 Discuss global warming

A.2.3.10 Global warming is the unequivocal and continuing rise in the average temperature of Earth's climate system. Since 1971, 90% of the increased energy has been stored in the oceans, mostly in the 0 to 700m region. Despite the oceans' dominant role in energy storage, the term "*global warming*" is also used to refer to increases in the average temperature of the air and sea at the Earth's surface. Since the early 20th century, the global air and sea surface temperature has increased about 0.8 °C (1.4 °F), with about two-thirds of the increase occurring since 1980. Each of the last three decades has been successively warmer at the Earth's surface than during any preceding decade since 1850. Scientific understanding of the cause of global warming has been increasing. In its fourth assessment (AR4 2007) of the relevant scientific literature, the Intergovernmental Panel on Climate Change (IPCC) reported that most global warming was being caused by increasing concentrations of greenhouse gases produced by human activities. In 2010, the findings were recognized by the national science academies of all major industrialized nations. Affirming these findings in 2013, the IPCC stated that the largest driver of global warming is carbon dioxide (CO_2) emissions from fossil fuel combustion, cement production, and land use changes such as deforestation.

【Comment 2.3.3】 https//en.wikipedia.org/wiki/global warming,

Global warming: Global warming is caused by increasing concentrations of greenhouse gases. As a result, the near-surface atmospheric temperature is increased.When fossil fuel (petroleum, coal, liquefied natural gas, etc.) is burned, the following chemical reaction will be caused:

$C + O_2 \rightarrow CO, CO_2$

$N + O_2 \rightarrow NO, N_2O, NO_2,$

$S + O_2 \rightarrow SO_2$.

That is, the fossil fuel including C and S will be oxidized by the chemical reaction due to high temperature.

As other elements of global warming, there are CCl_3F, CCl_2F_2, CH_4,etc.

Q. 2.3.11 Discuss heat islands

A. 2.3.11 The term "heat island" describes built up areas that are hotter than nearby rural areas. The annual mean air temperature of a city with 1 million people or more can be 1–3°C warmer than its surroundings. In the evening, the difference can be as high as 12°C. Heat islands can affect communities by increasing summertime peak energy demand, air conditioning costs, air pollution and greenhouse gas emissions, heat-related illness and mortality. Communities can take a number of common-sense measures to reduce the effects of summertime heat islands. [U.S. EPA Environmental Promotion Agency]

Q. 2.3.12 Discuss the ozone layer

A. 2.3.12 The ozone layer refers to a region of the Earth's stratosphere that absorbs most of the sun's ultraviolet (UV) radiation. The ozone layer contains high concentrations of ozone (O_3) relative to other parts of the atmosphere, although ozone is still very small relative to other gases in the stratosphere. The ozone layer contains less than ten parts per million of ozone, while the average ozone concentration in Earth's atmosphere as a whole is only about 0.3 parts per million. The ozone layer is mainly found in the lower portion of the stratosphere, approximately 20 to 30 kilometers above the Earth, though the thickness varies seasonally and geographically.

●ten parts per million：10 ppm (1 ppm=1 part per million=1/10^6).

https//en.wikipedia.org/wiki/ozone layer,

【Comment 2.3.4】About Sun's Ultra Violet (UV) Radiation

(1) Wavelength of the ultraviolet rays

Some kinds of ultraviolet rays are as follows:

UV-A [320-380nm, 1(**n**ano **m**eter, nm) =10^{-9}(m)]: Long wavelength, back ray phenomena, not absorbed by the ozone layer,

UV-B (280-320nm): Medium wavelength, mostly absorbed by the ozone layer,

UV-C (190-280nm):Short wavelength, germicidal effects, completely absorbed by the ozone layer and atmosphere.

(2) Relationship between ultraviolet rays and electromagnetic waves [4]

Fig.2.3.1 shows the relationship between ultraviolet rays and electromagnetic waves. [Reference [23], p.2]

2.4 Fuel Chemistry

In this section, shale gas, methane hydrate, and bio fuels are described in the form of Q and A.

Q.2.4.1 Discuss shale gas

A.2.4.1 Shale gas is a natural gas that is found trapped within shale formations. Shale gas has become an increasingly important source of natural gas in the United States since the start of this century, and interest has spread to potential gas shales in the rest of the world. In 2000 shale gas provided only 1% of U.S. natural gas production; by 2010 it was over 20% and the U.S. government's Energy Information Administration predicts that by 2035, 46% of the United States' natural gas supply will come from shale gas.

Some analysts expect that shale gas will greatly expand the worldwide energy supply. The U.S. government believes that increased shale gas development will help reduce greenhouse gas emissions.

[From Wikipedia]

Q. 2.4.2 Discuss methane hydrate

A.2.4.2 Methane hydrate is a crystalline solid-like ice that stores gas molecules, usually methane. Each flammable gas molecule is surrounded by a cage of water molecules. Methane hydrate can be found in the sediments of deep-sea regions where the temperature is low and the pressure is great.

Methane gas is used as fuel for vehicles and fuel cells, and is a cleaner fuel than oil or coal.

Deposits of methane hydrates have been reported to be in marine sediments in the Nankai Trough off the Pacific coast of central Japan, where the water depth is more than 500 meters. Some estimates indicate that the reserves of methane hydrate correspond to a 100-year supply of natural gas for Japan, making it an important potential source of energy.

[From Wikipedia; Nankai Methane Hydrate Site]

Q. 2.4.3 Discuss bio fuels
A.2.4.3 Biofuel is a product produced from biomass. This fuel is considered much cleaner than fuels such as petrol and diesel. Biofuel is considered carbon neutral, as the biomass absorbs roughly the same amount of carbon dioxide during growth as it does when burned. In many cases, large areas of forest are cut down to make space for the plantation of biofuel suitable crops. This deforestation not only harms the carbon cycle, but also harms surrounding civilizations which live off the forest. Some biofuels currently in use are biobutanol, biodiesel, bioethanol, biogas, vegetable oil, etc. We have used this type of fuel since the discovery of fire. Firewood can be classified as a biofuel, as wood is a biomass product which can be burned to release energy in the form of heat. As mentioned above, any deforestation resulting from biomass plantation can have negative effects on both the carbon cycle and the forest ecosystem. [From Wikipedia]

[Comment2.4.1] *https://ja.wikipedia.org/wiki/* **Stirling engine**

The Stirling engine was invented by Robert Stirling in 1816. This engine has the potential to be much more efficient than an internal combustion engine such as a gasoline or diesel engine. The Stirling engine is classified as an external combustion engine. The Stirling engine has the following features:

(1) The gasses used inside the Stirling engine always remain within the engine.

(2) There is no combustion inside the cylinders of the engine.

(3) Therefore, the engine has no exhaust valves and no high pressure gasses are vented, as opposed to the internal combustion engine which must have exhaust outlets.

(4) The efficiency η of this engine can be expressed as follows:

$$\eta = 1 - \frac{T_h}{T_c} \qquad (2.4.1)$$

Where, T_h is the temperature of heating part, T_c is the temperature of cooling part.

Fig. 2.4.1 shows a model of Stirling engine.

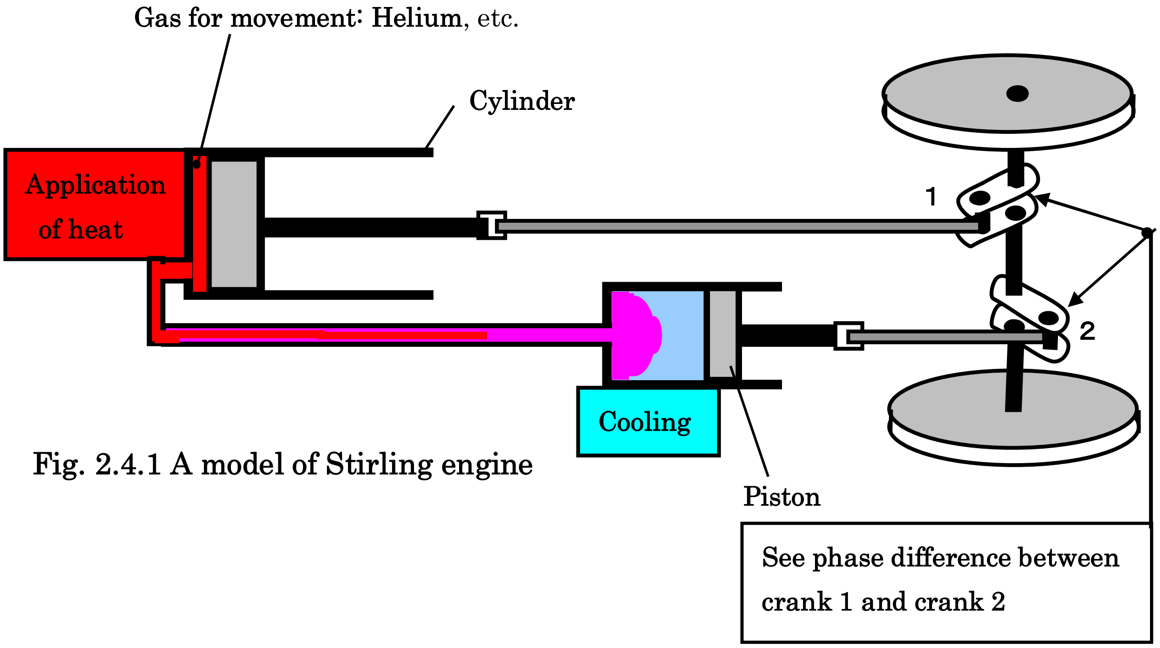


Fig. 2.4.1 A model of Stirling engine

2.4.4 Problem

Discuss green algae bio fuel（Botryococcus braunii）

2.4.5 Example of Answer

Biomass energy has recently attracted considerable attention as a renewable energy source to address global warming, air pollution and the depletion of fossil fuels. Biofuel production from microalgae is an example of biomass utilization that has a high rate of productivity per unit area.

Botryococcus, a colony-forming green microalga, produces hydrocarbons at a high rate per unit of dry cell weight.

Botryococcus is originally a freshwater green alga. Its tolerance to salinity varies among strains. When an industrial-scale culture is considered for nurturing alga for hydrocarbon production, the use of seawater as a culture medium would be more desirable compared to freshwater because of the global abundance of seawater. The use of seawater may also reduce the risk of contamination by other freshwater organisms living in the culture pond. [From Wikipedia, the free encyclopedia]

Chapter 3 Separation Chemistry

In this chapter, several examples of Chromatography, NMR Spectroscopy, Lasers and Infrared Spectroscopy, and Color Chromaticity Diagram are described. Additionally, several problems are presented at the end of section 3.1.

3.1 Chromatography

In this section, Chromatography – general principle, Chromatographic methods, Thin layer chromatography, Ion-exchange chromatography, Distilled water, and Solvent extraction are described in the form of Q and A.

Q.3.1.1 Discuss general principle of chromatography

A. 3.1.1 The term chromatography refers to any separation techniques in which the components of a test sample are caused to pass through a column at different rates of speed.

In every chromatographic separation, there is a stationary phase, which consists of the packing within the column, and a mobile phase, during which the test sample is introduced at one end of the column and caused to travel through the column.

As the mobile phase passes through the column, each component of the test sample is continuously partitioned between phases.

The process is similar in principle to a multistage extraction process with a large number of stages.
[Reference [5], p.151]

Q. 3.1.2 Discuss chromatographic methods

A. 3.1.2 The chromatographic method of analysis was first proposed in 1903 by the Russian scientist M. Tswett.

It is a modern technique employed for concentrating and purifying a compound which occurs naturally in great dilution and has proved to be an extremely valuable method for the separation, isolation, purification and comparative identification of the constituents of a mixture.

This technique depends on the distribution of the mixture between two phases, one fixed and the other moving.

Different constituents migrate, therefore, at different rates through the fixed phase.

The mixture is dissolved in the moving phase and passed over the fixed phase which may be an absorbent column or a paper strip.

The moving phase may be a liquid or a gas. Based on the nature of the fixed and the moving phase, different types of chromatography are considered. [Reference [2], p.73]

Q. 3.1.3 Discuss thin layer chromatography

A.3.1.3 Chromatography in a thin sorbent layer (TLC) was used in pharmaceutical analysis for separating extracts and tinctures of medicinal plants by the Soviet scientists N. Izmailov and M. Shraider (1938).

TLC is employed to separate mixtures of medicinal agents, identify them, establish their purity, and determine the components quantitatively.

A merit of TLC is that it can separate drug mixtures into separate components similar in their chemical structure and properties, for example, mixtures of amino acids, alkaloids, barbiturates, and sulphanylamides.

This method is especially convenient for the analysis of small amounts of poisonous and highly potent substances in a compound drug when it is difficult to determine them by chemical methods. It is also employed for detecting impurities in a substance, which is especially important in industrial control of the quality of the synthesis intermediates.

Another merit of TLC is that it does not require intricate equipment and is, therefore, accessible for various investigations under any conditions.

TLC is carried out in two ways, i.e., between with a stationary and a mobile sorbent layer.

Over twenty different sorbents are employed, among which
the most popular are aluminum oxide, various grades of silica gel, cellulose, polyamide powder and synthetic resins. [Reference[2], p.73]

Q. 3.1.4 Discuss ion-exchange chromatography

A. 3.1.4 Ion-exchange chromatography is based on the exchange of ions between an analyte in a solution and a sorbent.

The sorbents contain inorganic functional groups and can dissociate and exchange ions with the analyte solution.

Such sorbents are known as ion exchangers. They are high-molecular compounds containing a large number of ionic functional groups and are divided into two types according to the nature of ion exchange, namely,

(1) cation exchangers with mobile cations that can be exchanged for the cations from the analyte solution (imparting acidic properties to the ion exchangers) and (2) anion exchangers with mobile anions that can be exchanged for the anions from the analyte solution (imparting basic properties to the ion exchangers).

The molecules of cation exchangers of various grades contain mobile $-SO_3H$, $-COOH$, and other groups. The molecules of anion exchangers contain mobile amino groups, quaternary ammonium bases, etc.

Cation exchangers are available in the hydrogen (H) form and the salt form. The former contains exchange hydrogen ions, and the latter, metal cations. An anion exchanger in the OH form contains exchange hydroxyl ions, and in the salt form, acid anions.

When salts react with cation exchangers in the H form, the process of cation exchange proceeds as follows:

$$Na^+Cl^- + R\text{-}SO_3^-H^+ \text{(cation exchanger)} \rightleftharpoons R\text{-}SO_3^-\,Na^+ + H^+Cl^-$$

A similar reaction occurs when salts react with anion exchanges in the OH form :

$$Na^+Cl^- + R\text{-}NH_4^+OH^- \text{(anion exchanger)} \rightleftharpoons R\text{-}NH_4^+Cl^- + Na^+OH^-$$

As a result, an equivalent amount of an acid or alkali evolves that can be titrated with the relevant titrant, and then the amount of the analyte salt (NaCl) can be calculated. [Reference [2], p.76]

Q. 3.1.5 Discuss distilled water

A.3.1.5 Ordinary potable water contains many organic and inorganic impurities. The latter may include sulphates, nitrates, chlorides, calcium and magnesium oxides, and small amounts of ammonia.

Natural water is thus a solution containing a multitude of various salts.

Such water cannot be used in pharmacy practice for preparing medicinal agents. This is because the salts contained in it may harm many pharmaceutical preparations, while organic impurities create favorable conditions for the development of pathogenic microorganisms. This is why water purified from organic and inorganic impurities by distillation is used in pharmacology. Such water is called distilled.

Distilled water must be colorless, transparent, without an odor and taste. Its pH must be within 5.0-6.8, its specific gravity at 4 ^{o}C must equal 1.000, and its boiling point at a pressure of 760 mm Hg must be 100 ^{o}C.

These properties determine the authenticity and at the same time the proper quality of distilled water. [Reference [2], p.100]

Q. 3.1.6 Discuss solvent extraction

A. 3.1.6 The technique of extraction of a solute in a solvent by another solvent is called solvent extraction. When a solution containing the solute is shaken with another immiscible solvent, the solute is distributed between the two solutions according to the Nernst distribution law. For efficient use of solvent, it is advantageous to carry out this process in a series of successive stages. [Reference [12], p.141]

3.1.7 Problems

Discuss Each of the Following Descriptions:

1. Distilled water

2. Ion-exchange chromatography

3. Chromatographic separation with ion-exchange sorbents
4. Pharmaceutical analysis with ion-exchange chromatography
5. Quantitative determination of salts of mineral and organic acids,
6. Quantitative determination of alkaloid salts and nitrogenous bases

3.1.8 Examples of Answers

1. Various kinds of test methods are recommended for controlling the quality of distilled water. These determine the absence of or tolerated limit of various impurities. First of all, the reaction of water is tested. To do this, several drops of methyl red are added to a small amount of freshly distilled water. Pure water is neutral, and therefore its color should become yellow when the indicator is added. The further addition of a drop of a 0.01N hydrochloric acid solution should cause a pink color to appear.

To test for salt admixtures containing water, a small amount of the water is evaporated. Pure water should leave no dry residue after its evaporation. A dry residue not exceeding 1 mg is tolerated by the pharmacopoeia after the evaporation of 100 mL of distilled water. [Reference [2], p.p.76-77]

2. Ion-exchange chromatography is not an independent method of quantitative analysis. It is employed as an auxiliary method for separating and extracting substances. The extracted components are then determined by conventional chemical, physical or physiochemical methods.
[Reference [2], p. 77]

3. Chromatographic separation with ion-exchange sorbents is widely used in quantitative analysis, especially when the quantitative determination of substances without their preliminary separation is impossible. It is employed to determine the concentration of salts in electrolyte solutions, to separate ions by extracting one of them (or a group of ions) from a mixture, and to remove ions interfering with an analysis from a solution.
[Reference [2], p. 77]

4. In pharmaceutical analysis, ion-exchange chromatography is widely used for the quantitative determination of salts of organic and mineral acids, salts of alkaloids and nitrogeneous bases, and other groups of drugs.
[Reference [2], p. 77]

5. Accurately weigh a specimen of an analyte (0.3-0.5 g), place it in a 50 ml volumetric flask, and add water up to the mark. Pass 5 ml of the obtained solution through a column with a cation exchanger at a rate of 20 drops per minute. Then rinse the cation exchanger with water (when analyzing salts of organic acids, for example sodium benzoate or salicylate) up to a neutral reaction of the effluent, and titrate the evolved equivalent amount effluent with a 0.1 N solution of sodium hydroxide in the presence of the relevant indicator.

Cation exchange follows the reactions:

$$2[\text{cat } SO_3]^- H^+ + Na_2SO_4 \rightarrow 2[\text{cat } SO_3]^- Na^+ + H_2SO_4$$

$$[\text{cat } SO_3]^- H^+ + [\text{Benz}]\text{-COONa} \rightarrow [\text{cat } SO_3]^- Na^+ + [\text{Benz}]\text{-COOH}$$

Where cat is a cation exchanger.

6. Accurately weigh a specimen (0.03-0.05 g) of the alkaloid salt being investigated, dissolve it in 5 ml of distilled water or alcohol, acidify with a drop of dilute hydrochloric acid, and slowly pass the solution through a column containing an anion exchanger. A base of the alkaloid being investigated will separate:

$$(an)^+OH^- + [RNH]^+Cl^- \rightarrow (an)^+Cl^- + [RNH^+]\ OH^-$$

Where $[RNH]^+$ is an alkaloid group and $(an)^+$ is an anion exchanger.

3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

In this section, the History of NMR, Basic NMR Techniques, the Larmour Frequency, and the Chemical Shift are described in the form of Q and A.

Q.3.2.1 Discuss the history of NMR

A.3.2.1 The basic concept of nuclear magnetic resonance has been used as a tool in the field of chemistry since its discovery by Bloch in 1946.

Its usefulness expanded tremendously in the 1980s due to the development of means to represent nuclear magnetic resonance signals in the form of tomographic images.

Q.3.2.2 Discuss basic NMR techniques

A.3.2.2 Nuclear magnetic resonance spectroscopy, well known as NMR spectroscopy, is a research technique that exploits magnetic properties of certain atomic nuclei. It can determine the physical and chemical properties of atoms.

When a human body is placed in a strong magnetic field, the atomic nuclei of hydrogen in the body tend to align with the magnetic field.

However, they do not remain oriented, but process because of torques resulting from the non-uniform magnetic dipole moment distribution.

Q.3.1.3 Discuss the Larmour frequency

A.3.1.3 As shown in **Fig. 3.2.4 (a)**, a hydrogen nucleus: ^1H , can process around the field direction at the Larmour frequency in the presence of an external magnetic field.

The Larmour frequency : f_0, can be expressed as follows:

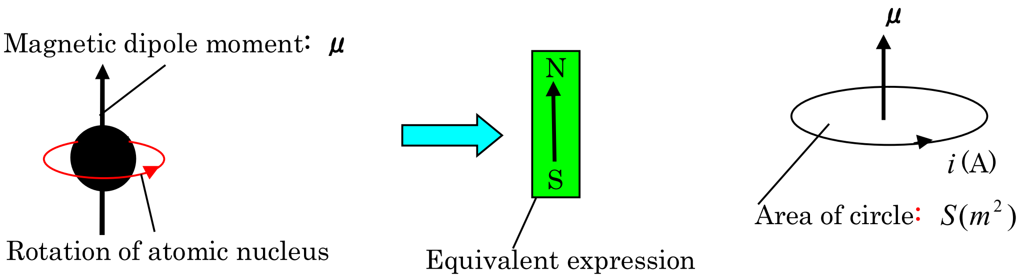
$$f_0 = \gamma H \,. \qquad (3.2.1)$$

where, γ is the gyromagnetic ratio (42.5 MHz/tesla), and H is the magnitude of the external magnetic field.

As mentioned previously, the resonant frequency is proportional to the strength of the magnetic field. For example, the resonant frequency of a proton in the magnetic field of a 12 tesla is as follows: $f_0 = \gamma H = 42.5 \times 12 = 510 MHz$

where, $\gamma = 42.5$ MHz / tesla.

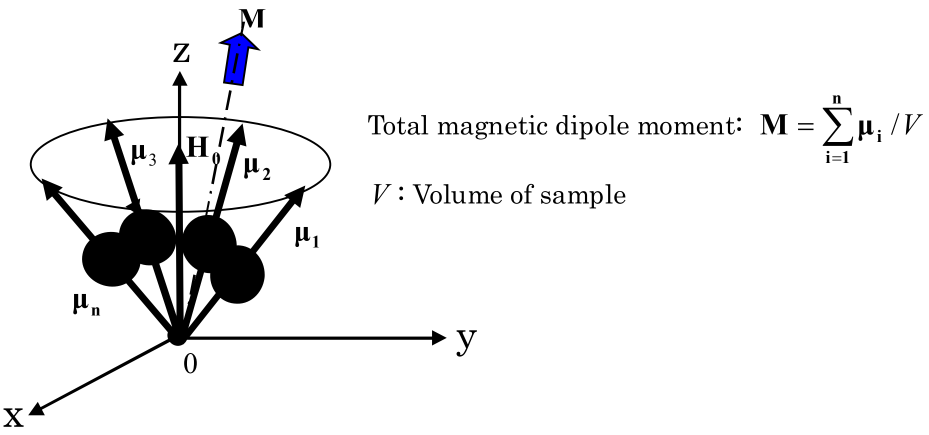
【Comment 3.2.1】Magnetic Dipole Moment[13], [14],[15],[17]



(a) Generation of magnetic dipole moment (b) Definition of magnetic dipole moment

(d) Magnetic field $H_0 \neq 0$

(c) Magnetic field $H_0 = 0$



Total magnetic dipole moment: $\mathbf{M} = \sum_{\mathbf{i=1}}^{\mathbf{n}} \boldsymbol{\mu}_{\mathbf{i}} / V$

V : Volume of sample

(e) Distribution of magnetic dipole moment μ inside of a sample

Fig. 3.2.1 Relationship between μ and M

【Comment 3.2.2】 Comments for Fig 3.2.1 and Fig. 3.2.2

(1) **Fig. 3.2.1(a)** shows a magnetic dipole moment generated by an atomic nucleus rotation, where $\mu = \gamma h I / 2\pi$, h : Plank's constant, γ : Gyromagnetic ratio, $I = 1/2$ for ^1H

(2) **Fig. 3.2.1(b)** shows the definition of magnetic dipole moment $\mu = iS(Am^2)$

(3) **Fig. 3.2.1(c)** shows the inside of a sample of magnetic field $H_0 = 0$, the magnetic dipole moment $\mu_i (i = 1, 2, \cdots)$ has random directions. Consequently, the magnetic dipole moment due to summation of $\mu_i (i = 1, 2, \cdots)$ is zero. This energy level is the constant. This situation is called degeneracy.

(4) **Fig. 3.2.1(d)** shows the inside of the sample of magnetic field $H_0 \neq 0$, the magnetic

dipole moment $\mu_i (i = 1,2,\cdots)$ has two directions; that is, same direction for H_0, and an inverse direction for H_0. These situations are called the Zeeman effect. In this case, the same direction is greater than the inverse direction.

(5) Fig. 3.2.1(e) shows the distribution of magnetic dipole moment μ_i $(i = 1,2\cdots,n)$ inside of the sample. For the non-uniform of phase distributions of μ_i, the total magnetic dipole moment **M** (Values due to the summations of μ_i) has a phase angle.

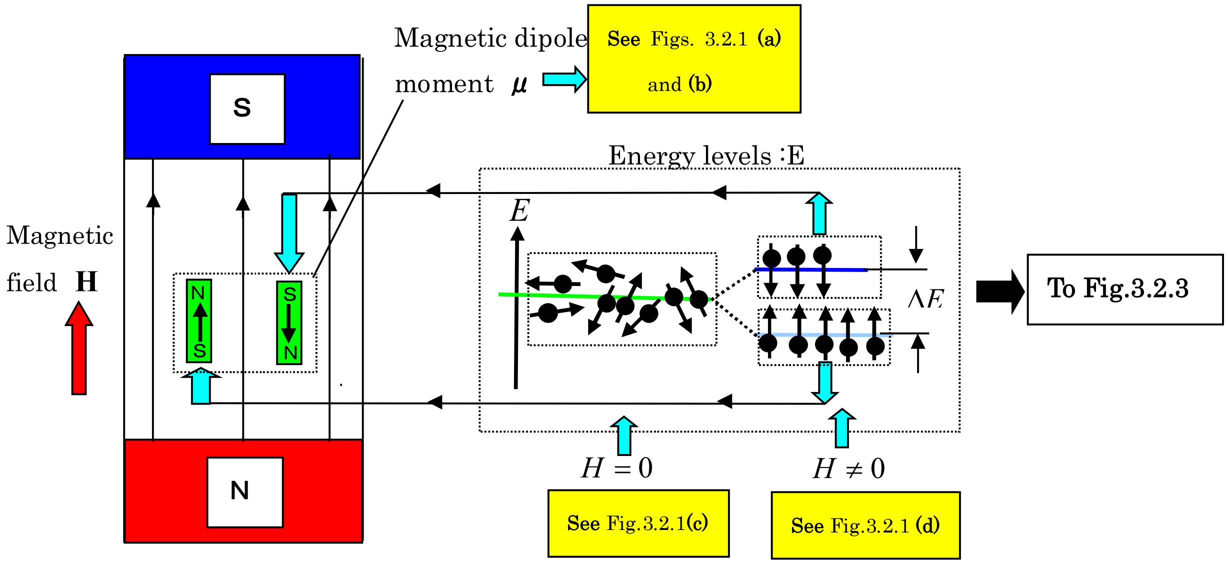
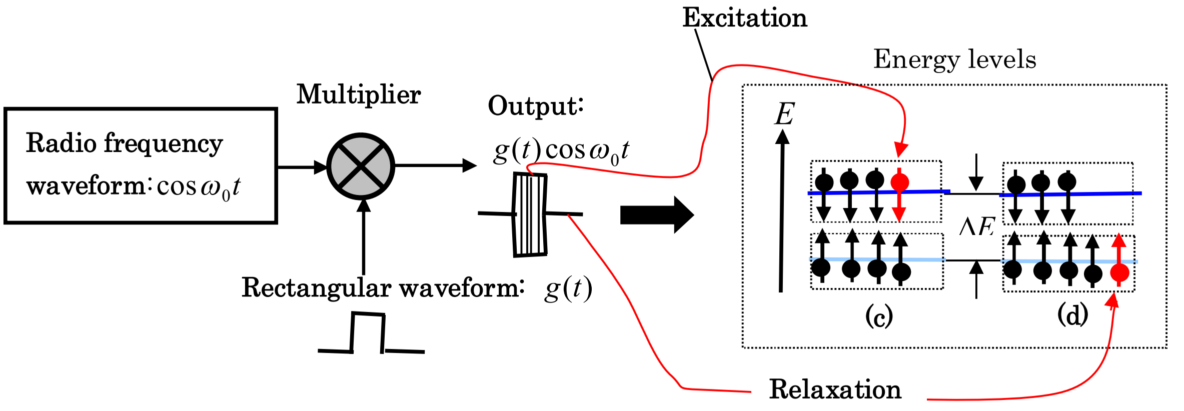


Fig.3.2.2 Magnetic dipole moment μ and their energy levels



(a) Generation of pulsed radio frequency wave (b) Energy levels of magnetic dipole moment

Fig.3.2.3 Generation of pulsed radio wave and energy levels of magnetic dipole moment

【Comment 3.2.3】 Comment for Fig 3.2.3

(1) **Fig.3.2.3 (a)** shows the generation of pulsed radio frequency wave

(2) In **Fig. 3.2.3 (a)**, Output: $g(t)\cos\omega_0 t$ can be obtained by multiplying the radio frequency wave: $\cos\omega_0 t$ times the rectangular wave: $g(t)$

(3) Output: $g(t)\cos\omega_0 t$ can be given for the magnetic dipole moments shown in **Fig.3.2.1 (d)**

(4) **Fig.3.2.3 (c)** shows energy levels of magnetic dipole moments in the case of **"Excitation"**

(5) **Fig.3.2.3 (d)** shows energy levels of magnetic dipole moments in the case of **"Relaxation"**

(6) **Fig.3.2.4 (a)** shows the process for a magnetic dipole moment $\boldsymbol{\mu}$ (See **Fig. 3.2.1(a)**)

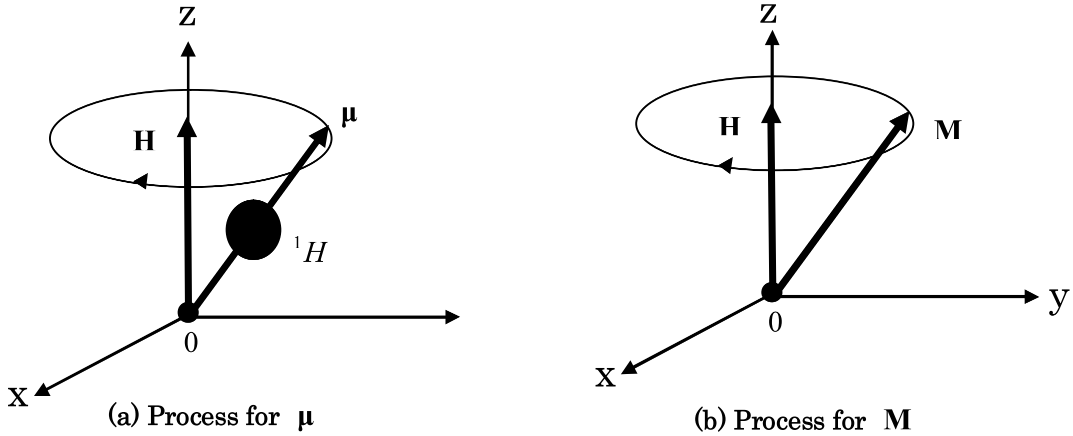
(7) **Fig.3.2.4 (b)** shows the process for the total magnetic dipole moment $\mathbf{M}$ (See **Fig. 3.2.1(e)**)

【Comment 3.2.4】 Bloch Equation[16]: Let us express the nuclear magnetization by $\mathbf{M} = [M_x, M_y, M_z]$ .Consequently, the Bloch equations are expressed as follows:

$$\frac{dM_x}{dt} = \gamma[\mathbf{M}\times\mathbf{H}]_x - \frac{M_x}{T_2}], \quad \frac{dM_y}{dt} = \gamma[\mathbf{M}\times\mathbf{H}]_y - \frac{M_y}{T_2}],$$

$$\frac{dM_z}{dt} = \gamma[\mathbf{M}\times\mathbf{H}]_z - \frac{M_z - M_b}{T_1}]$$

Where γ is the gyro-magnetic ratio, $\mathbf{H}$ is a given magnetic field, T_1 is a time constant for $M_z(t)$, T_2 is the time constant for $M_x(t)$ and $M_y(t)$, M_b is the saturation magnetization.



(a) Process for **μ**

(b) Process for **M**

Fig.3.2.4 Processes for **μ** and **M**

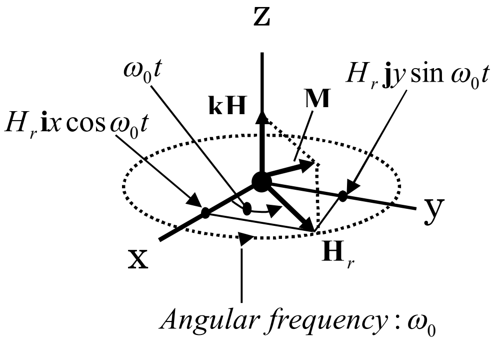


Fig.3.2.5 Vector diagram for Eq.(3.2.2)

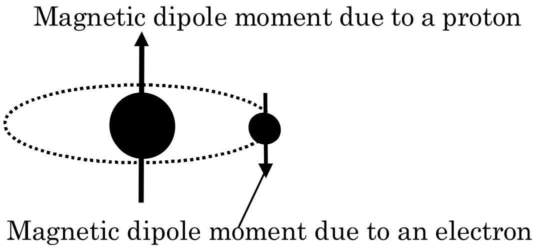


Fig.3.2.6 Magnetic dipole moments due to a proton and an electron

Q.3.2.4 Discuss the nuclear magnetic resonance effect

A.3.2.4 The nuclear magnetic resonance effect occurs when the atomic nucleus in the static magnetic field $\mathbf{H}$ is exited by a total magnetic dipole moment $\mathbf{M}$, which is described by the following equation:

$$\mathbf{M} = \mathbf{kH} + \mathbf{H}_r(\mathbf{i}\, x \cos\omega_0 t + \mathbf{j}\, y \sin\omega_0 t) \qquad (3.2.2)$$

where $\mathbf{H}_r$ is a rotating magnetic field in the x, y plane, $\omega_0 = 2\pi f_0'$, $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors of x, y, and z axes (See **Fig.3.2.5**).

On cessation of excitation, the total magnetic dipole moment $\mathbf{M}$ decays back to its original alignment (z axis) with the static magnetic field $\mathbf{H}$ radiating electromagnetic wave at the Larmour frequency f_0'.

Q.3.2.5 The chemical shift:

A.3.2.5 Electrons around an atomic nucleus produce an induced magnetic field $\mathbf{H}_i$, which opposes the static magnetic field $\mathbf{H}$ (See **Fig.3.2.6**).

As a result, the effective magnetic field $\mathbf{H}_e$ can be then expressed as follows: $\mathbf{H}_e = \mathbf{H} - \mathbf{H}_i$. (3.2.3)

In this case, the precession frequency f_0' is shifted to slightly a smaller value than f_0 which is given in Eq.(3.2.1) , and it can be expressed as follows: $f_0' = \gamma \mathbf{H}(1-\sigma)$ (3.2.4)

where σ is the shielding constant for the atomic nucleus.

3.3 Lasers and Infrared Spectroscopy [18],[19],[20],[21]

In this section, lasers and infrared spectroscopy are described in the form of Q and A.

Q.3.3.1 Discuss lasers and their merits

A.3.3.1 Many lasers, such as the Ruby laser and the YAG laser (solid-state lasers), the GaAs laser (a semi-conductor laser), the He-Ne laser, the Ar laser, the CO_2 laser and the excimer laser (gas lasers) have been developed and put to practical use for various purposes. Every laser light has, usually, only one wavelength, such as 694 nm for the Ruby laser, 1.06 µm for the YAG laser, 1.0 µm for the GaAs laser, 633 nm for the He-Ne laser, 514 and 488 nm for the Ar laser, 10.6 µm for the CO_2 laser, and 190~320 nm for the excimer laser (see Q.3.3.2). The laser has merits in various applications. For example, lasers have a coherency for an interferometric application in measurement, a directivity for the measurement of long distances, a high focus capability for metal cutting in manufacturing and for point measurement, as well as a high photon energy for chemical processes.

Q. 3.3.2 Discuss wavelengths and photon energy of the lasers

A. 3.3.2 Laser lights with wavelengths between 200 nm and 400 nm are mainly used for the application of chemical reactions. The lasers corresponding to these light wavelengths are excimer lasers as described in Q.3.3.1. Laser lights are generated by means of rare gases such as Ar, Kr, and Ze and halogen gases such as F and Cl. The representative lasers are the ArF excimer laser with a wavelength of 193 nm, the KrF excimer laser of 248 nm, the XeCl excimer laser of 308 nm, and the XeF excimer laser with a wavelength of 351 nm. The light absorbed in a material participates in photo-chemical reaction. Light with a wavelength of λ and the frequency v

has a photon energy of $E = h\nu = hc/\lambda$, that is, E kJ/mol$=1.2\times10^5/\lambda$ (λ is measured in nm unit), where h is Plank's constant, $h=6.63\times10^{-34}$ Js, and c is the velocity of light in a vacuum, $c=2.998\times10^8$m/s. An ArF laser with a wavelength of 193 nm has, then, a photon energy of 622 kJ/mol, a KrF laser 0f 248nm has 484 kJ/mol, a XeCl laser of 308 nm has 390 kJ/mol, and a XeF laser of 351 nm has 342 kJ/mol. The other units for laser energy are a kcal/mol and an eV. The relations among these units are 1 kJ/mol=0.2390 kcal/mol = 1.036×10^{-2} eV, or 1 kcal/mol = 4.184 kJ/mol = 4.336×10^{-2} eV.

Q. 3.3.3 Discuss bond energy, or Binding energy

A. 3.3.3 Bond energy in the chemical binding of a covalent bond and an ionic bond is between 300 and 1000 kJ/mol. Other chemical bindings include the metal bond, the molecular bond, and the hydrogen bond. For example, the bond energy between carbon and carbon is 366 kJ/mol as shown below.

$$CH_3\text{-}CH_3 \rightarrow 2CH_3\cdot \quad 366\ \text{kJ/mol}$$

Three of the excimer lasers, the ArF, KrF, and XeCl lasers, can cut the above carbon-carbon bond because these lasers have larger photon energy than 366 kJ/mol. Thus, we should avoid excess irradiation of ultraviolet light since our bodies are composed of these elements.

Q. 3.3.4 Discuss chemical processes by the irradiation of the excimer laser

A.3.3.4 The excimer laser has been effectively used in many fields of chemistry. Its wide applicability may be mainly attributed to the high photon energy of the laser light. The energy is usually great enough to dissociate each bond of the chemical compounds and thus a photochemical process energized by the laser light is capable of replacing costly chemical and thermochemical processes. This enables us to not only reduce the production cost but also to improve the quality of the chemical products. Furthermore, it should be mentioned that the effect of the process can be extensively and easily controlled by the irradiation condition.

Q. 3.3.5 Discuss infrared spectroscopy

A.3.3.5 Infrared spectroscopy is performed by using an electromagnetic wave at infrared wavelengths [700(nm) - 1(mm)]. In the typical instrument configuration, a Fourier Transform Infrared Spectrometer (FTIR) is combined with an optical microscope and an infrared detector. As the infrared detector, there is a linear array or a two-dimensional focal plane array. Such a technique is called infrared spectroscopy.

3.4 Color Chromaticity Diagram

In this section, the RGB Color System, Chromaticity Coordinates, the CIE(1931)XYZ color system, (*x, y, z*) chromaticity coordinates, and color chromaticity expressions of color fixed indicator are described in the form of Q and A.

Q.3.4.1 Discuss the RGB Color System

A.3.4.1 In three-dimensional (3D) linear space, a color equation C can be expressed as follows:

$$\mathbf{C} = R\mathbf{R_0} + G\mathbf{G_0} + B\mathbf{B_0} \qquad (3.4.1)$$

where R, G, and B are tri-stimulus values, and $\mathbf{R_0}, \mathbf{G_0}$, and $\mathbf{B_0}$ are unit vectors.

Q.3.4.2 Discuss Chromaticity Coordinates

A.3.4.2 Eq.(3.4.1) can be modified as follows:

$$\mathbf{C} = R\mathbf{R_0} + G\mathbf{G_0} + B\mathbf{B_0} = (R+G+B)[\frac{R}{(R+G+B)}\mathbf{R_0} + \frac{G}{(R+G+B)}\mathbf{G_0} + \frac{B}{(R+G+B)}\mathbf{B_0}] = (R+G+B)(r\mathbf{R_0} + g\mathbf{G_0} + b\mathbf{B_0})$$

If $R+G+B=1$, then（r, g, b）can be expressed as follows:

$$r = \frac{R}{R+G+B},\ g = \frac{G}{R+G+B},\ b = \frac{B}{R+G+B} \qquad (3.4.2)$$

where $r+g+b=1$.

Above equations are defined as（r, g, b）chromaticity coordinates.

Q.3.4.3 Discuss the CIE(1931)XYZ color system, and (*x, y, z*) chromaticity coordinates

A.3.4.3 The tri-stimulus values of the CIE (1931) XYZ color system can be calculated by the following equations:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 2.7689 & 1.7517 & 1.1302 \\ 1.0000 & 4.5907 & 0.0601 \\ 0.0000 & 0.0565 & 5.6943 \end{bmatrix} \begin{bmatrix} R \\ G \\ B \end{bmatrix} \qquad (3.4.3)$$

where R, G, and B are tri-stimulus values of the RGB Color System.

From the above equations, (*x, y, z*) chromaticity coordinates are defined as follows:

$$\begin{aligned} x &= \frac{X}{X+Y+Z} \\ y &= \frac{Y}{X+Y+Z} \qquad (3.4.4) \\ z &= \frac{Z}{X+Y+Z} \end{aligned}$$

where $x+y+z=1$. Consequently, we can make a two-dimensional diagram. **Fig.3.4.1** shows (x, y) chromaticity diagram.

For example, $x = 1/3$, and $y = 1/3$ then $z = 1 - x - y = 1/3$

In **Fig.3.4.1**, ⑧ expresses the white point.

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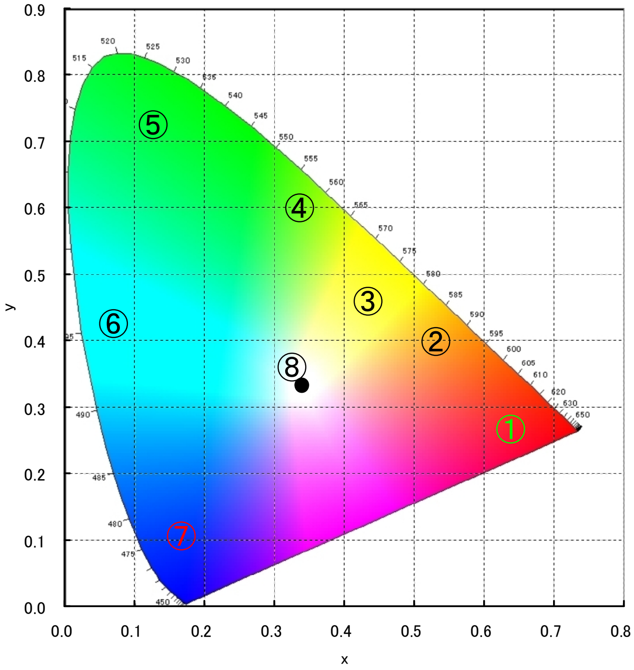


①Red、②Orange、③Yellow、④Yellow-Green、
⑤Green、⑥Cyan、⑦Blue、⑧White

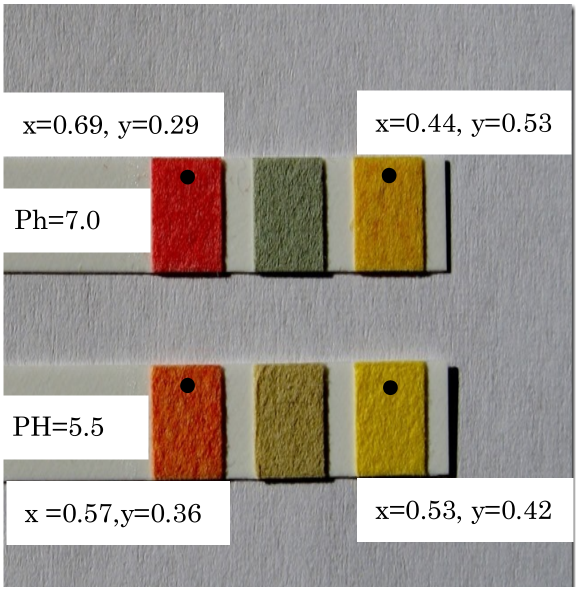
Fig.3.4.1 (x, y) chromaticity diagram

Q.3.4.4 Discuss the color chromaticity expression of the color fixed indicator

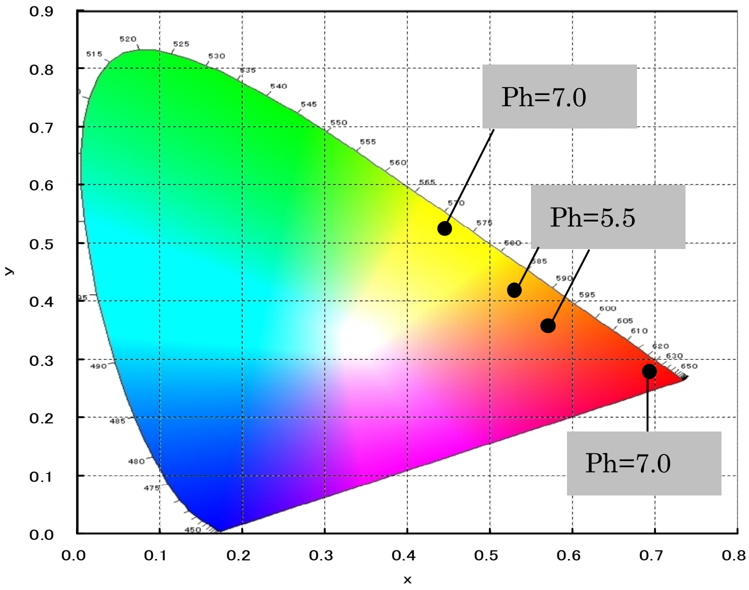
A.3.4.4. Fig.3.4.2 shows samples of color fixed indicators.

Fig.3.4.2 (a) shows an original sample (ph=7.0) and **Fig.3.4.2 (b)** also shows a sample for a urine inspection (ph=5.5).

The chromaticity expressions of these samples are shown in **Fig.3.4.3.**



(a) Color chromaticity values of color fixed indicators



(b) Color chromaticity diagram of color fixed indicators

Fig.3.4.2 Color chromaticity values of color fixed indicators

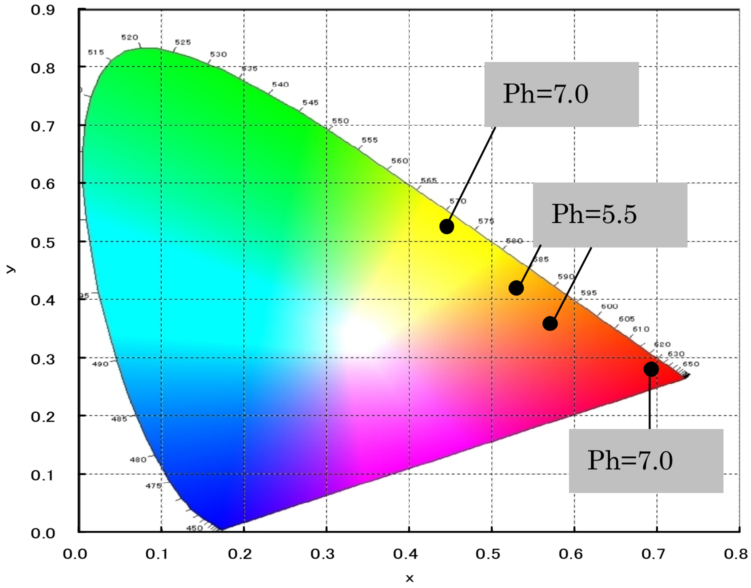


Fig.3.4.3 Color chromaticity diagram of color fixed indicators

References:

[1] K.L. Kapoor: A Textbook of Physical Chemistry, Volume 1, Second Edition: Macmillan India Limited (India), ISBN 0-8053-6801-9, (1963) ISBN 33390-337-4 (1986)

[2] **M.Satake**: Modern Dictionary-Pharmaceutical Chemistry, Discovery Publishing House (India), ISBN 81-7141-067-7 (1989)

[3] Bruce H. Mahan: Elementary Chemical Thermodynamics, The Benjamin/Cummings Publishing Company (California), ISBN 0-8053-6801-9 (1963)

[4] Y.Mido, **M.Satake**, Consulting Editors: M.S.Sethi, S.A.Iqbal: An Introduction to Nuclear Chemistry, Discovery Publishing House (India), ISBN 81-7141-277-7 (1995)

[5] S.A.Iqbal, **M.Satake**, Y.Mido, M.S.Sethi: An Introduction to Analytical Chemistry, Discovery Publishing House (India), ISBN 81-7141-244-0 (1994)

[6] Y.Mido, **M.Satake,** Consulting Editors: M.S.Sethi, S.A.Iqbal: Chemicals in the Environment: Discovery Publishing House

(India), ISBN 81-7141-267-X (1995)

[7] **M.Satake**, Y.Mido, M.S.Sethi, S.A.Iqbal, Y.Hayashi, G.Wang: Environmental Toxicology, Discovery Publishing House (India), ISBN 81-7141-350-1 (1997)

[8] G.Kano: Modern Chemistry - Inorganic Chemistry, Discovery Publishing House (India), ISBN 81-7141-053-7 (1994)

[9] M.**Satake**, Y.Mido, Consulting Editors: M.S.Sethi, S.A.Iqbal: Chemistry of Transition Elements, Discovery Publishing House (India),ISBN 81-7141-243-2 (1994)

[10] **M.Satake**, Y.Hayashi, M.S.Sethi, S.A.Iqbal: Bio Physical Chemistry, Discovery Publishing House (India), ISBN 81-7141-329-3 (1997)

[11] **M.Satake**, Y.Mido, Consulting Editors: M.S.Sethi, S.A.Iqbal: Chemistry for Health Science, Discovery Publishing House (India), ISBN 81-7141-284-2 (1995)

[12] **M.Satake**, T. Nagahiro: Modern Dictionary-Physical Chemistry, Discovery Publishing House (India), ISBN 81-7141-114-2 (1990)

[13] D. Christiansen: Electronics Engineers' Handbook, 4th Edition, pp. 21- 30, 22, IEEE Press (1997)

[14] R. C. Dorf : Electrical Engineering Hand Book, pp. 2378-2379, CRC Press (1993)

[15] http://en.wikipedia.org/wiki/Nuclear magnetic resonance spectroscopy

[16] http://en.wikipedia.org/wiki/Nuclear magnetic resonance spectroscopy— Bloch Equation

[17] **K.Taniguchi,** M. Ueda, N.Zeng, K. Ishikawa: Fundamentals and Practices of Sensing Technologies, pp.28-29, The BWW Society, and Kyoritsu-Publishing Co. (2009)

[18] **M. Ueda**, F. Sakan, H. Tanaka, H. Fujii, and K. Sakai: An Application of Excimer Laser for the Cross-linking of Polyethylene, Rev. Laser Engr. 21-9 (1992) p. 974-980

[19] Eds. K. Taniguchi, **M. Ueda**, and K. Atkinson: How to Write Technical Reports in English – 100 Basic and Effective Practical Sentences, Kyoritsu Publishing Company, 2011

[20] K. Taniguchi, **M. Ueda**, and K. Ishikawa: Practical Sensing Technology, Kyoritsu Publishing Company, 2008

[21] http://ja.wikipedia.org/wiki/infrared spectroscopy

[22] **K.Taniguchi** and Zhang Xiaomang: Digital Color Engineering, Kyoritsu Publishing Co. ISBN 978-4-320-12329-8, (2012)