

CHM 101:

Kinetic theory of matter

[module 1]

Dr T.A. Afolabi

Gas properties

-all gases have similar physical properties, and the chemical identity of the substance does not influence those properties.

For example:

all gases **expand** when they are heated in a non-rigid container and **contract** when they are cooled or subjected to increased pressure.

They readily **diffuse** through other gases.

Any quantity of gas will occupy the entire volume of its container, regardless of the size of the container.

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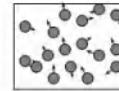
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The State of Matter

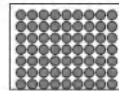
There are three main kinds of matter: solid, liquids, and gases.



(a) Gas



Liquid



Solid

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Units of Pressure

- ✓ The SI unit of pressure is the **Pascal (Pa)**,
1 Pa = 1 N/m²
- ✓ A much larger unit is the **standard atmosphere (atm)**, the average atmospheric pressure measured at sea level and 0°C.
1 atm = 1.01325 x 10⁵ Pa = 101.325 kPa
- ✓ Another unit is bar
1 atm = 1.01325 bar.
- ✓ Another unit is the **millimeter of mercury (mmHg)**, which is based on measurement with a barometer or manometer. In honor of Torricelli, this unit has been named the torr:
1 atm = 760 mmHg = 760 torr
- ✓ Another unit is pounds per square inch **psi** (commonly used in Engineering).
1 atm = 14.7 lb/in² = 14.7psi

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Exercise 1

Given that the pressure of an unknown gas is 183.45 mmHg. Convert the pressure to atmospheres, bar, psi, pascal, and torr.

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Exercise 2

a) Convert the following pressure to Pa, torr, mmHg, and atm:

25 psi
42 psi
75 psi

b) Convert the following pressure to psi and atm

250 KPa, 22.7 Pa
230 mmHg, 385 torr

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The relationship between Volume and Pressure: Boyle's Law

At constant temperature, the volume of a given sample of a gas is inversely proportional to its pressure.

$$V \propto \frac{1}{P} \quad (\text{at constant } T, n)$$

This relationship can also be expressed as:

$$PV = \text{constant} \quad \text{or} \quad V = \frac{\text{constant}}{P} \quad (T \text{ & } n \text{ fixed})$$

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The relationship between Volume and temperature: Charles's Law

At constant pressure, the volume of a given sample of gas is directly proportional to its absolute temperature.

$$V \propto T \quad [P, n \text{ fixed}]$$

This relationship can also be expressed as:

$$\frac{V}{T} = \text{constant} \quad \text{or} \quad V = \text{constant} \times T \quad [P, n \text{ fixed}]$$

NOTE: Absolute temperature signifies that the temperature calculations MUST be done in Kelvin scale
[273.15 kelvin = 0°C]

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Other relationships based on Boyle's and Charles's Laws.

1. The combined gas Law:

A simple combination of Boyle's and Charles's laws gives the combined gas law: which applies to situations when two of the three variables (V, P, T) change, hence the effect on the third can be calculated.

$$V \propto \frac{T}{P} \quad \text{or} \quad V = \text{constant} \times \frac{T}{P}$$

$$\frac{PV}{T} = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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2. Pressure – temperature relationships:

At constant volume, the pressure exerted by a fixed amount of gas is directly proportional to the absolute temperature.

$$P \propto T \quad [V \text{ and } n \text{ fixed}]$$

$$\frac{P}{T} = \text{constant}$$

$$P = \text{constant} \times T$$

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The relationship between Volume and Amount: Avogadro's Law

Avogadro's Law states that the volume occupied by a gas is directly proportional to the amount (mol) of gas (at constant temperature and pressure).

$$V \propto n \quad [P \text{ and } T \text{ fixed}]$$

$$\frac{V}{n} = \text{constant} \quad \text{or} \quad V = \text{constant} \times n$$

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AVOGADRO'S HYPOTHESIS

Avogadro's hypothesis states that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

Avogadro's hypothesis enables us to determine the relative masses of the molecules (molecular masses) of gases.

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The Ideal Gas Law

Each of the gas laws focuses on the effect that changes in one variable have on gas volume:

- ✓ Boyle's Law focuses on pressure ($V \propto 1/P$).
 - ✓ Charles's Law focuses on temperature ($V \propto T$).
 - ✓ Avogadro's Law focuses on amount (mol) of gas ($V \propto n$).
- A combination of these individual effects into one relationship gives Ideal Gas Law (Ideal Gas equation):

$$V \propto \frac{nT}{P} \quad \text{or} \quad PV \propto nT \quad \text{or} \quad \frac{PV}{nT} = R$$

$$\boxed{PV = nRT}$$

R is a proportionality constant known as the Universal gas constant

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Value of R

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

$$= \frac{1\text{atm} \times 22.4141\text{ L}}{1\text{ mol} \times 273.15\text{ K}} = 0.082058 \text{ atm.L mol.K}$$

$$\boxed{R = 0.0821 \text{ atm L mol}^{-1}\text{K}^{-1}}$$

$$R = \frac{1.01325 \times 10^5 \text{ Pa} \times 22.4141\text{ L}}{1 \text{ mol} \times 273.15 \text{ K}}$$

$$\boxed{R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}}$$

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The ideal gas law becomes one of the individual gas laws when two of the four variables are kept constant. When initial conditions (subscript ₁) change to final conditions (subscript ₂), we have:

$$P_1V_1 = n_1RT_1 \quad \text{and} \quad P_2V_2 = n_2RT_2$$

Thus,

$$\frac{P_1V_1}{n_1T_1} = R \quad \text{and} \quad \frac{P_2V_2}{n_2T_2} = R \quad \text{so} \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

E.g. when n & T are constant, then:

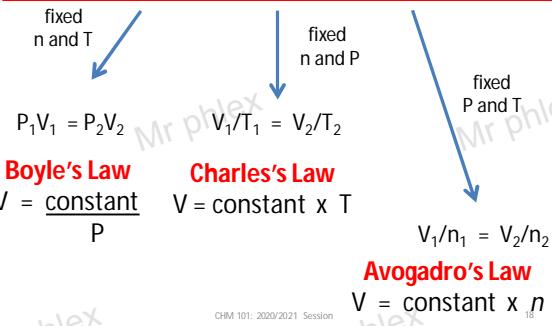
$$P_1V_1 = P_2V_2 \quad (\text{Boyle's Law})$$

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IDEAL GAS LAW

$$\boxed{PV = nRT \text{ or } (P_1V_1)/(n_1T_1) = (P_2V_2)/(n_2T_2)}$$



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Solving Gas Law Problems

Gas law problems are phrased in many ways but they can usually be grouped into 2 main types:

1. A change in one of the four variables causes a change in another, while the two remaining variables remain constant

[Reduce the Ideal gas law to the specific law needed for the problem solution]

2. One variable is unknown, but the other 3 are known and no change occurs.

[Apply the ideal gas law ($PV = nRT$) directly]

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Exercise 3

Bisola finds that the air trapped in a tube occupies 24.8cm^3 at 1.14atm . By adding mercury to the tube, she increases the pressure of the trapped air to 2.68 atm . Assuming constant temperature, what is the new volume of air (in L)?

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Exercise 4

At what temperature would 3.2 g of helium occupy a volume of 25 L at a pressure of 700 mmHg ?

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Exercise 5

A gas exerts a pressure of 2.0 atm, at 30°C, in a 10 L container. In what size container would the same amount of gas exert a pressure of 4.0 atm at 20°C?

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Exercise 6

A 0.10 mol sample of oxygen occupies 2.0 L. What volume would be occupied by 0.25 mol of oxygen? Both samples are at the same temperature and pressure.

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Exercise 7

Calculate the amount of oxygen gas (O_2) in a cylinder of 30L, if the pressure is 20 atm at 30°C.

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(module B)

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The Density of a Gas

One mole of any gas occupies nearly the same volume at a given temperature and pressure, so difference in gas density ($d = m/V$) depend on differences in molar mass.

E.g. 1 mol of O_2 occupies the same volume as 1 mol of N_2 , but since each O_2 molecule has a greater mass than each N_2 molecule, O_2 is denser.

All gasses are miscible when thoroughly mixed, but in the absence of mixing, a less dense gas will lie above a more dense one.

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The ideal gas law can be used to calculate the density of a gas from its molar mass.

$$n = m/M$$

(n = No. of moles; m = mass; M = molar mass).

$$\text{Recall } PV = nRT$$

Therefore,

$$PV = \frac{mRT}{M}$$

$$\text{Rearrange } \frac{MP}{RT} = \frac{m}{V} = \text{density}$$

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This shows that:

1. *The density of a gas is directly proportional to its molar mass* because a given amount of a heavier gas occupies the same volume as that amount of a lighter gas (Avogadro's law)
2. *The density of a gas is inversely proportional to the temperature.* As the volume of a gas increases with temperature (Charles's law), the same mass occupies more space; thus, the density is lower.

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Molar mass

To determine the molar mass of an unknown gas:

$$n = \frac{m}{M} = \frac{PV}{RT}$$

$$M = \frac{mRT}{PV}$$

or

$$M = \frac{dRT}{P}$$

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The partial Pressure of a gas

The ideal gas law holds for virtually any gas, whether pure or a mixture, at ordinary conditions for two reasons:

1. Gases mix homogeneously (form a solution) in any proportions.
2. Each gas in a mixture behaves as if it were the only gas present (assuming no chemical interactions).

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Dalton's law of Partial Pressures: states that "in a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases".

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

E.g. suppose a tank of fixed volume contains gas **a** and **b**. Each gas behaves independently,

$$P_a = \frac{n_a RT}{V} \quad \text{and} \quad P_b = \frac{n_b RT}{V}$$

Each gas occupies the same total volume and is at the same temperature, the pressure of a gas depends on its amount, n.

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Thus, the total pressure is:

$$\begin{aligned} P_{\text{total}} &= P_a + P_b = \frac{n_a RT}{V} + \frac{n_b RT}{V} \\ &= \frac{(n_a + n_b) RT}{V} \\ &= \frac{n_{\text{total}} RT}{V} \end{aligned}$$

$$n_{\text{total}} = n_a + n_b$$

Each component in a mixture contributes a fraction of the total number of moles in the mixture, which is the mole fraction (X) of that component.

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For n_a , the mole fraction is

$$X_a = \frac{n_a}{n_{\text{total}}} = \frac{n_a}{n_a + n_b}$$

Since the total pressure is due to the total number of moles, the partial pressure of gas **a** is the total pressure multiplied by the mole fraction of **a**,

$$P_a = X_a \cdot P_{\text{total}}$$

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Exercise 8

If 4.58 g of a gas occupies 3.33 L at 27°C and 808 torr, what is the molar mass of the gas?

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Exercise 9

Calculate the amount of oxygen gas (O_2) in a cylinder of 30 L, if the pressure is 20 atm at 30°C.

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Exercise 10

Calculate the absolute temperature of 0.118 mol of a gas that occupies 10.0 L at 0.933 atm.

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Exercise 11

What is the pressure of H₂ if 0.250 mol of H₂ and 0.120 mol of He are placed in a 10.0-L vessel at 27°C.

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Consider two gases with molar masses M₁ and M₂. The ratio of their rates of diffusion (or effusion) is given by:

$$\frac{r_1}{r_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$$

That is, the heavier a molecule of the gas, the more slowly it diffuses (or effuses).

The rate of effusion or diffusion of a gas is directly proportional to the "average" velocity of its molecules.

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**Graham's Law**

Graham's law states that "The rate of effusion or diffusion of a gas is inversely proportional to the square root of its mass".

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{m}}$$

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{m}}$$

Diffusion is the passage of a gas through another gas. **Effusion** is the process by which a gas escapes from its container through a tiny hole into an evacuated space.

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**Kinetic Molecular Theory**

The theory is based on 3 postulates (assumptions):

1. **Particle volume:** A gas consists of a large collection of individual particles. The volume of an individual particle is extremely small compared with volume of the container. In essence the model pictures gas particles having mass but no volume.

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2. **Particle motion:** Gas particles are in constant, random, straight-line motion except when they collide with the container walls or with each other.

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3. **Particle collisions:** Collisions are elastic, hence their total kinetic energy is constant. Between collisions, the molecules do not influence each other at all.

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KINETIC MOLECULAR THEORY (the model)

- ✓ Gases are composed of small particles (atoms or molecules).
- ✓ These particles move rapidly in a random, straight line motion.
- Particles will collide with each other and with the walls of the container.

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- ✓ The bonding forces between particles are extremely weak. It is assumed that particles move around independently.
- ✓ Collisions between particles are elastic, i.e. energy is conserved.

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- ✓ Kinetic energy (energy of movement) can be transferred from one particle to another, but the total kinetic energy will remain constant.
- ✓ The average kinetic energy of the particles increases as the temperature of the gas is increased.

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Exercise 12

A sample of calcium carbonate, mass 1.0 g, is heated until it has decomposed completely. Calculate:

- the mass of carbon dioxide produced
- the volume of carbon dioxide, measured at STP

SOLN:

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Exercise 13

Copper dispersed in absorbent beds is used to react with oxygen impurities in the ethylene used for producing polyethylene. The beds are regenerated when hot H₂ reduces the metal oxide, forming the pure metal and H₂O. On a laboratory scale, what volume of H₂ at 765 torr and 225°C is needed to reduce 35.5g of copper (ii) oxide?

SOLN:

- To find V_{H₂}, n_{H₂} must first be determined
- Write the equation for d reaction
- Solve for n (stoichiometry), then solve for V (gas law)

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Exercise 14: What is the density of methane, CH_4 , at 20°C and 2.00 atm.

Exercise 15: What is the molar mass of a gas whose density at 40°C and 785 torr is 1.286 kg/m³

Exercise 16: A collapsed balloon and its load weighs 216 kg. To what volume should it be inflated with H₂ gas in order to launch it from a mountain top at -12°C and 628 torr? The density of air under these conditions is 1.11 g/L.

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Exercise 17: An organic compound containing 55.8% C, 7.03% H, and 37.2% O; was found to have a gas density of 2.83 g/L at 100°C and 740 torr. What is the molecular formula of the compound?

[[Ans: Empirical formula is $\text{C}_2\text{H}_3\text{O}$; molar mass = 89g/mol. Divide 89g/mol by 43g/mol ($\text{C}_2\text{H}_3\text{O}$ molar mass) = 2. Therefore molecular formula is $\text{C}_4\text{H}_6\text{O}_2$]]

Exercise 18: Chlorine gas is evolved at the anode of a commercial electrolysis cell at the rate of 3.65 L/min, at a temperature of 647°C. On its way to the intake pump it is cooled to 63°C. Calculate the rate of intake to the pump assuming the pressure has remained constant.

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Exercise 19: A spark was passed through a 50cm³ sample of a H₂/O₂ mixture in a gas burette at 18°C and 1.00 atm; the formation of water went to completion. The resulting dry gas had a volume of 10 cm³ at 18°C, 1.00 atm. What was the initial mole fraction of H₂ in the mixture if:

- (a) the residual gas after sparking was H₂
- (b) the residual gas was O₂ ?

Exercise 20: A rigid plastic container holds 35.0g of ethylene gas (C₂H₄) at a pressure of 793 torr. What is the pressure if 5.0g of ethylene is removed at constant temperature?

Exercise 21: A scale model of a blimp rises when it is filled with helium to a volume of 55.0dm³. When 1.10mol of He is added to the blimp, the volume is 26.2 dm³. How many more grams of He must be added to make it rise? Assume constant T and P.

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CHM 101 GENERAL CHEMISTRY

FALL QUARTER 2008

Section 2

Lecture Notes – 10/6/2008

(last revised: 10/6/08)

2.5 The Modern View of Atomic Structure

- The components of an atom are protons, neutrons, and electrons.
 - Electrons
 - The particles discovered by Thompson (Cathode-ray Emissions).
 - Negatively charged.
 - Protons
 - Same charge as electrons, only the opposite sign
 - Approximately 1,800 times the mass of an electron
 - Neutrons
 - Zero charge (electrically neutral).
 - Same mass as the proton.

TABLE 2.1 The Mass and Charge of the Electron, Proton, and Neutron

| Particle | Mass | Charge* |
|----------|---------------------------|---------|
| Electron | 9.11×10^{-31} kg | 1– |
| Proton | 1.67×10^{-27} kg | 1+ |
| Neutron | 1.67×10^{-27} kg | None |

*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

- Structure of the Atom:

- A tiny nucleus (diameter $\sim 10^{-13}$ cm), made of protons and neutrons and containing nearly all the mass of the atom
- Surrounded by a sphere (diameter $\sim 10^{-8}$ cm) containing the electrons.

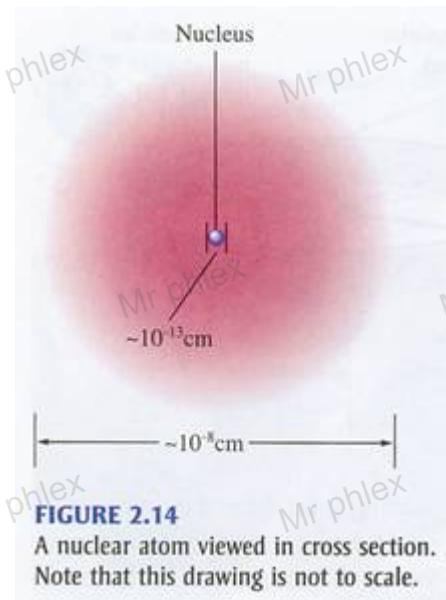


FIGURE 2.14
A nuclear atom viewed in cross section.
Note that this drawing is not to scale.

- How Elements Differ

- The atoms of a given element (Example: gold) each contain the same, characteristic number of protons (Example: An atom of gold always contains 79 protons). This number is called the **Atomic Number** of the element. (The symbol for atomic number is **Z**.)
- Since atoms are electrically neutral, an atom has the same number of electrons surrounding its nucleus as it has protons in its nucleus.
- The **number** and the **arrangement** of the **electrons** in the atoms of an element **determine the chemistry of that element**. This is because when atoms come together, it is the electrons that "touch" or interact with each other. To restate this point, the chemistry of a given element depends **critically** on the number of electrons in each of its atoms.

- Isotopes

- For any element, the particular number of protons in the nucleus of each of its atoms is a characteristic of the element. However, the number of neutrons can vary without changing the chemistry.
- An example is chlorine. Each chlorine atom contains 17 protons, but some chlorine atoms contain 18 neutrons while others contain 20. If we define the **Mass Number** of a particular atom as its number of protons plus its number of neutrons, then we can compute the mass numbers of these two kinds of chlorine as 35 and 37, respectively. (The symbol for mass number is **A**.)
- When the atoms of a given element occur in forms that have different numbers of neutrons, we call these forms **isotopes** of that element.
- The isotope of chlorine (atomic symbol: Cl) with mass number 35 (called chlorine 35) can be symbolized:



- Likewise, chlorine 37 can be symbolized:



- In general, an atom with the chemical symbol, Xx , the atomic number, Z , and the mass number, A , is written:



- Now we can work Sample Exercise 2.2 (page 52 in the text). The problem asks us to write the symbol for an atom with an atomic number of 9 and a mass number of 19. It also asks us to determine the numbers of electrons and neutrons in the atom.
 - Step 1: The data we need to look up are on the two facing pages of the inside front cover of the text. Looking in the periodic table, we see that the atomic number (9) is that of the element with the symbol, F. (If we look up F on the opposite page, we can find that it belongs to the element, fluorine.). Thus we can write the complete symbol for this atom (including the atomic number, Z , and the mass number, A , as:



- Step 2: The number of electrons is the same as the number of protons. This answer is given by the atomic number, 9.
- Step 3: The number of neutrons can be calculated by subtracting the atomic number from the mass number:

$$A - Z = 19 - 9 = 10$$

2.6 Molecules and Ions

- Now that we have studied the nuclear model of the atom and learned that electrons are responsible for chemistry, we turn to the study of the ways that atoms interact to form chemical compounds. At this stage we will look only at some simple ideas of chemical bonding. We will study chemical bonding in more depth during CHM 102.
- **Chemical bonds** are what we call the forces that bind atoms together in compounds. At this point we will consider covalent bonds and ionic bonds.
- **Covalent Bonds:** When two or more atoms form a molecule by sharing electrons, we say that these atoms are covalently bonded. We can represent these molecules symbolically in several ways:
 - The simplest representation is the **chemical formula**. The atoms are represented by their chemical symbols. (You will find these in the Table of Atomic Masses in the inside front cover of your text.) For molecules containing 2 or more of the same kind of atom, the number is written as a subscript after the chemical symbol. Thus a water molecule, containing 2 hydrogen (H) atoms and one oxygen (O) atom has the chemical formula



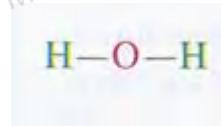
Another example of a chemical formula is that of ammonia, a molecule containing 3 hydrogen atoms and 1 nitrogen (N) atom:



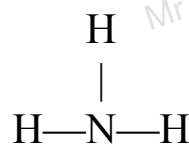
Still another example is methane, a molecule containing 4 hydrogen atoms and 1 carbon (C) atom:



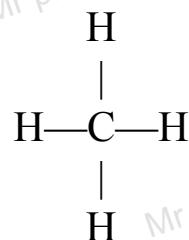
- A **topological formula** is a two dimensional representation of a chemical structure. It shows which atoms are bonded to which. The topological formula for water is:



The topological formula for ammonia is:



And the topological formula for methane is:



- A **structural formula** not only shows which atoms are bonded to which, but it also suggests the true shape of the molecule and the actual angles between the bonds. Here are structural formulas for water, ammonia, and methane:



In these diagrams, the letters represent the atoms, the light, solid lines represent bonds that lie in the plane of the screen (or paper, if this is a printout), the dotted lines represent bonds that project behind the screen, and the dark wedges represent bonds that poke out of the screen.

Note: The text does not give a separate definition of topological formula but includes it as a kind of structural formula without geometric information. (You will not be held responsible for knowing the difference.)

- A **molecular model** gives the truest representation of the structure and composition of a given molecule. Two commonly used types of models are the **space-filling** model (Figure 2.17) and the **ball-and-stick** model (Figure 2.18).

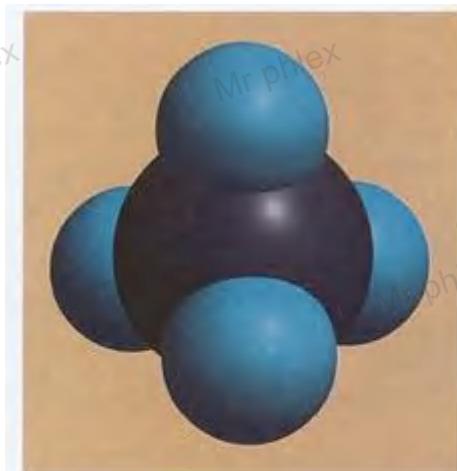


FIGURE 2.17
Space-filling model of methane. This type of model shows both the relative sizes of the atoms in the molecule and their spatial relationships.

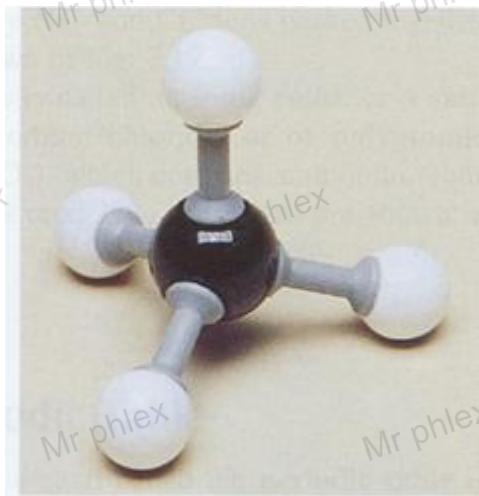
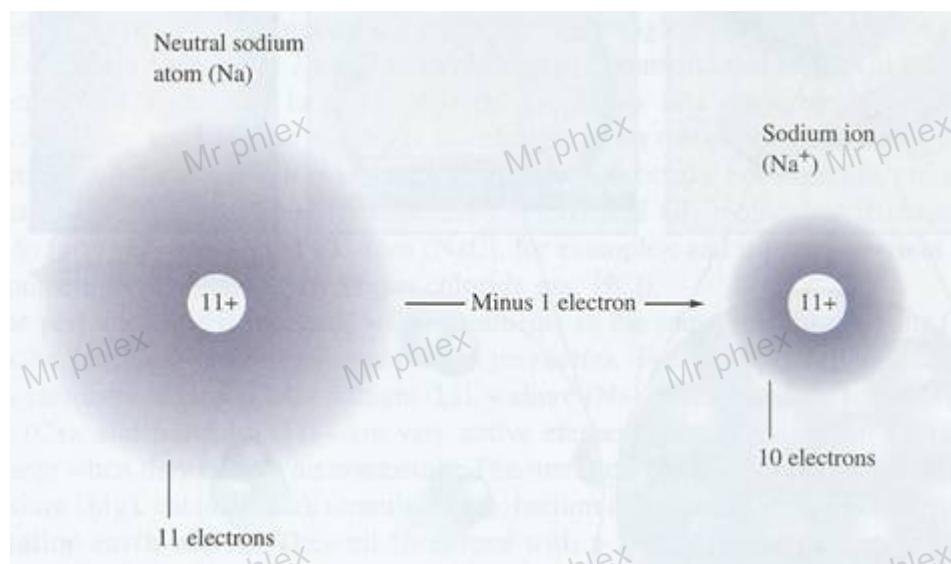


FIGURE 2.18
Ball-and-stick model of methane.

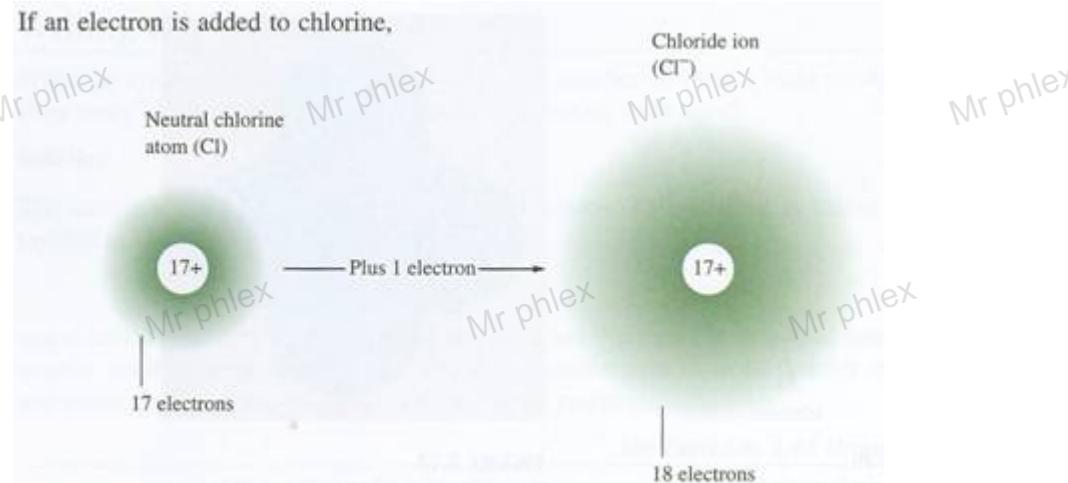
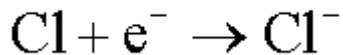
- **Ionic Bonds:** Not all chemical compounds are covalently bonded. A familiar example of a chemical compound entirely lacking in covalent bonds is sodium chloride (NaCl), also known as common table salt. The bonding in NaCl is ionic, not covalent. Let's see what leads to ionic bonding in NaCl.

- **Ionization of Sodium:** A sodium atom, with an atomic number of 11, has 11 electrons. One of the 11 electrons can be dislodged fairly easily, leaving an entity with 10 electrons that are very tightly held by a nucleus with a +11 charge. The charge on this entity is +1, and the entity can be called a sodium positive ion, a sodium cation, or (most commonly) a sodium ion. This ionization process can be written as a chemical equation:



- **Ionization of Chlorine:** A chlorine atom, with an atomic number of 17, has 17 electrons. These electrons are all tightly held, and there is a driving force to add one more and produce an entity with 18 electrons in a stable structure about a nucleus with a charge of +17. Thus the charge on the entity is -1, and the entity

can be called a chlorine negative ion, a chlorine anion, or (most commonly) a chlorine ion. This ionization process can be written as a chemical equation:



- **Ionic Bonds:** Since oppositely charged ions exert attractive forces on each other, they form bonds without sharing electrons. These are called ionic bonds. Figure 2.19 illustrates the reaction of the element, sodium, a soft metal, with chlorine, a pale green gas, to form the ionically bonded salt, sodium chloride, a colorless, crystalline solid.

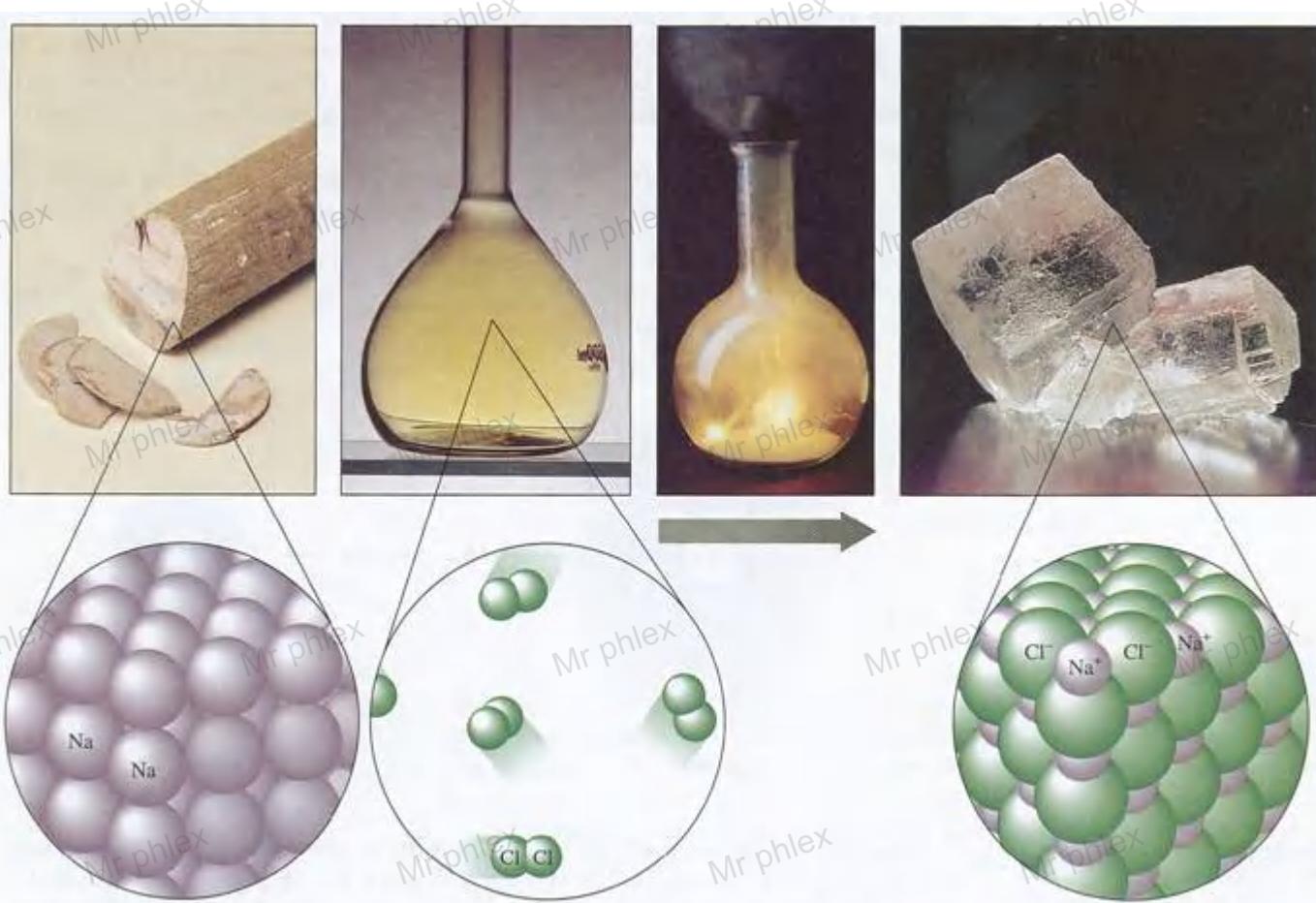
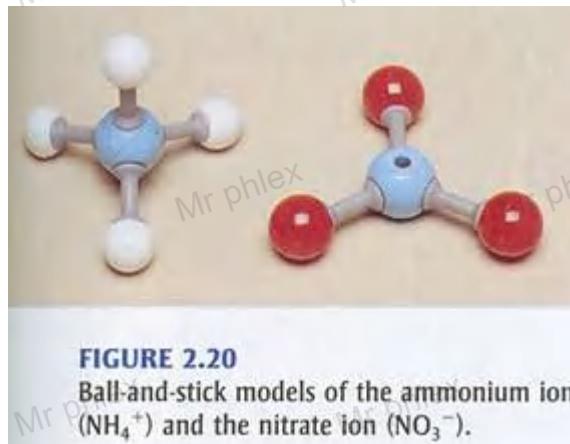


FIGURE 2.19

Sodium metal (which is so soft it can be cut with a knife and which consists of individual sodium atoms) reacts with chlorine gas (which contains Cl_2 molecules) to form solid sodium chloride (which contains Na^+ and Cl^- ions packed together).

- **Ionic Solids:** A solid consisting of oppositely charged ions is an ionic solid or a salt.
- **Types of Ions:**
 - **Simple Ion:** Any ion made from a single atom. Na^+ and Cl^- are good examples.
 - **Polyatomic Ion:** An ion in which two or more atoms are covalently bonded together into a molecule with a net charge. A good example of a compound made from two types of polyatomic ions is ammonium nitrate, NH_4NO_3 , which is made of ammonium ions, NH_4^+ , and nitrate ions, NO_3^- . These two ions are illustrated in Figure 2.20:



- **Metallic Bonding:** (not discussed in Chapter 2, so you don't need to know this yet.): Metal atoms tend to cluster into large aggregates, and the most loosely bound electrons are shared among all the atoms in an aggregate. This gives rise to metallic bonding, as distinct from covalent bonding or ionic bonding.

2.7 Introduction to the Periodic Table

- **What it is:** A Periodic Table is a chart that shows all the known elements giving lots of information about each and organizing them in a particular useful manner.
- **Where to find it:**
 - In textbooks: There are at least 2 versions of the periodic table in your text. (See the inside front cover and page 56.)
 - Posted in class: There is one hanging on the sidewall of D-108 near the door. There is also one posted in the lab (D-103).
 - On the web: If you do a Google search, you will find many different versions of the periodic table. Here is one example: <http://www.webelements.com/>.
- The Periodic Law: The Periodic Law states that the chemical properties of the elements are a periodic function of their atomic numbers.
- Arrangement of the Periodic Table:
 - Columns: The elements in a given column of the periodic table have similar chemical properties. The collection of elements in a column is called a group or a family.

- Rows: The elements in a given row of the periodic table are ordered by atomic number, without any gaps in the number sequence. These rows are also called periods.
- Chemistry of Selected Groups:
 - Metals: Most elements are classed as metals. They are located on the left hand side and in the center of the periodic table, and as you go down the table to heavier and heavier elements, they occur more and more toward the right hand side. For example, in Period 6 (elements with atomic number 55 through 86), fully 30 of the 32 elements are classed as metals. As elements, metals tend to occur as metallically bound solids that are good conductors of heat and electricity, they tend to be malleable and ductile so that they can be hammered into thin sheets or drawn into wires, they often appear shiny or lustrous, and chemically they tend to react by losing electrons to form positive ions.
 - Group 1 (Alkali Metals, such as sodium and potassium): These are all very active metals that readily form ions with +1 charges when they react with non-metals.
 - Group 2 (Alkaline Earths, such as magnesium and calcium): These are metals that form ions with +2 charges.
 - Groups 3-12 (Transition Metals): There are 10 groups of transition metals, but group to group differences among transition metals are not as pronounced as those among the main groups (Groups 1 and 2 and 13 through 18). They tend to have complex chemistries. Many of them have two or more ionic forms, for example: iron (Fe) can lose 2 electrons to form the Fe^{2+} ion, but it can also lose a third electron to form Fe^{3+} . Many of them form 2 or more different kinds of oxide, for example: titanium (Ti) forms TiO and TiO_2 . And many of them are capable of forming polyatomic anions, for example: chromium (Cr) can form the chromate (an)ion, CrO_4^{2-} .
 - Group 18 (Noble Gases, such as helium and argon): These elements all occur in nature as monatomic gases. They were thought never to form chemical bonds until the mid-1960's when several compounds of xenon and fluorine were successfully prepared.
 - Group 17 (Halogens, the elements fluorine, chlorine, bromine, and iodine): These non-metals can all form ions with -1 charges when they react with an active metal. They can also form covalent bonds with themselves and with other non-metals. As elements, they occur as diatomic molecules, such as Cl_2 .
 - Other Non-Metals: The non-metals other than the halogens are nearly all found in the upper right corner of the periodic table. The most important of these are carbon, nitrogen, oxygen, phosphorous, and sulfur. Like the halogens, they tend to accept electrons and form negative ions when they react with metals, and they tend to form covalent bonds when they react with each other.

- What about Hydrogen? The placement of hydrogen in the periodic table has always been a problem. In some respects its chemistry resembles the chemistry of the alkali metals, but it also behaves as a non-metal. As an element, it occurs as the diatomic gas, H₂, and it forms covalent bonds with carbon and other non metals. There are valid arguments for placing it in Group 17 above fluorine.

- Using the Periodic Table:

- As a Predictive Tool: Since its earliest days, the periodic table has been used successfully to predict the properties of unknown, undiscovered elements. When Mendeleev published the very first version of the periodic table, he had to leave several gaps in it where there were no known elements to fit particular combinations of period and group. For example, he could not fit any known element into Period 4 of Group 14. His answer was to predict that such an element could be found and that its chemical properties would resemble those of silicon (Period 3, Group 14) and tin (Period 5, Group 14) and that its physical properties (atomic mass, density, etc.) would be similar to its neighboring elements in Period 4. Given this road map of a prediction, other chemists soon discovered the element, germanium, and found that its actual properties were a close match for Mendeleev's predictions.
- As a Data Organizer: The periodic table summarizes and correlates a wide variety of information in a compact and easy to use format.
- As a Look-Up Tool: The periodic table charts every element by atomic number, atomic mass, name, chemical symbol, group, and period. Thus if you know some of this information about a given element, you can look up the rest in the periodic table.
- As a Learning Tool: The next section we will cover in General Chemistry is about Naming Simple Compounds. This is likely to be the most heavy duty memorization you will encounter all quarter. We will expect you to know names of elements, their chemical symbols, and the formulas and names of typical compounds they form when they react with other elements. The good news in all this is that of the 110 or so known elements, you will be held responsible for knowing only the 25 or so most important ones. And you can use the periodic table as a graphical device to help you organize and learn this information.

CHM 101 LECTURE NOTE

COURSE TITLE: INTRODUCTORY PHYSICAL CHEMISTRY

CREDIT UNIT: 03

PART TITLE: CHEMICAL EQUILIBRIUM

COURSE LECTURER: DR. S.A. AHMED

COURSE SYNOPSIS

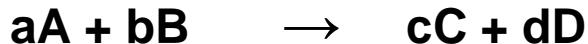
- The concept of equilibrium
- Equilibrium Law (Law of Mass action)
- Relationship between K_p and K_c
- Relationship between ΔG and K
- Effect of temperature on the equilibrium constant.
- Homogenous chemical equilibria
- Heterogeneous equilibria system
- Factors affecting equilibrium constants
- Chemical equilibrium in solution
 - water dissociation constant
 - hydrolysis and hydrolysis constant
- Solubility equilibria
- Common-ion effects

RECOMMENDED TEXTBOOKS/ REFERENCES

- 1. Principle of physical chemistry by J.M. Gross**
- 2. Physical chemistry by Atkins**
- 3. Essentials of physical chemistry by Bahl and Bahl**
- 4. Chemistry: The central science by Brown, Lemay,
Bursten and Murphy.**
- 5. Physical chemistry by K.K. Sharma and L.K.
Sharma**

Concept of Equilibrium

Consider this direct reaction,



The reaction stops when the reactants are used up.

However, for a reversible reaction like this



the equilibrium is attained when the rate of forward reaction is equal to the rate of backward reaction.

Chemical equilibrium is the state of a reversible reaction when the two opposing reactions occur simultaneously.

At equilibrium, the concentrations of reactants and products do not change with time.

The Equilibrium Law (Law of Mass action)

The law states that “at constant temperature, the rate at which a substance reacts is directly proportional to the active masses of the reactant”

Active mass is a thermodynamic quantity and it is expressed $a=fc$, where a -active mass, f - activity coefficient (fugacity), c - molar concentration.

For ideal gaseous and solution reaction, $f = 1$.

Therefore, the active mass is equal to molar concentration.

According to the law, $R_f \propto [A]^a[B]^b$

$$\Rightarrow R_f = K_f [A]^a[B]^b$$

Also, $R_b \propto [C]^c[D]^d$

$$\Rightarrow R_b = K_b [C]^c[D]^d$$

At equilibrium, $K_f [A]^a[B]^b = K_b [C]^c[D]^d$

$$\frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c$$

K_c is the equilibrium constant in term of concentration,

In term of activities,

$$K_A = \left\{ \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \right\},$$

The concept of activity addresses the deviation from ideal behaviour. Therefore, it can be defined as an idealized concentration. K_A is exact and does not depend on pressure.

In term of pressure,

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

where P_A^a , P_B^b , P_C^c and P_D^d are

the partial pressure of various gaseous species at equilibrium.

Relationship between K_p and K_c

In a gaseous reaction, the concentration of the gases at any given temp is expressed in term of their partial pressures.

Consider this gaseous reaction



the equilibrium constant in term of pressure is expressed as

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

where P_A^a , P_B^b , P_C^c and P_D^d are

the partial pressure of various gaseous species at equilibrium.

However, K_p and K_c are not numerically equal, the relationship can be derived as follow

For an ideal gases,

$$PV = nRT$$

$$\Rightarrow P = \frac{n}{V} RT$$

But $\frac{n}{V} = C$

$$\therefore P = CRT$$

$$K_p = \frac{C_C^c (RT)^c C_D^d (RT)^d}{C_A^a (RT)^a C_B^b (RT)^b}$$

$$= \frac{C_C^c C_D^d (RT)^{(c+d)}}{C_A^a C_B^b (RT)^{(a+b)}}$$

Recall that

$$K_c = \frac{C_C^c D_D^d}{A_A^a B_B^b}$$

$$\therefore K_p = K_c (RT)^{\Delta n}$$

Where $\Delta n = (c+d) - (a+b)$ i.e change in the amount of gaseous reagents

When Δn is positive, \Rightarrow the number of molecules of products are larger than those of the reactants i.e

$$K_p > K_c$$

When Δn is zero, \Rightarrow the number of molecules of products = the number of molecules of the reactants

i.e $K_p = K_c$

When Δn is negative, \Rightarrow the number of molecules of products are smaller than those of the reactants i.e

$$K_p < K_c$$

If the equilibrium constant is expressed in term of mole fractions, X it is related to K_p by

$$K_p = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K_p = \left(\frac{(X_C)(X_D)}{(X_A)(X_B)} \right) \times P^{(c+d)-(a+b)}$$

$$\therefore K_p = K_x P^{\Delta n}$$

where $\Delta n = (c+d) - (a+b)$

Relationship between ΔG and the equilibrium constant

The change in free energy of a reaction and the equilibrium constant K are related to each other by the expressions

$$\Delta G^\circ = -RT \ln K$$

Temperature dependence on the equilibrium constant

The value of equilibrium constant varies with temperature change. The relationship between the equilibrium constants at two different temperatures and the enthalpy change is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

Where K_{p_2} and K_{p_1} are the equilibrium constants at temperature T_2 and T_1 respectively.

In terms of change in internal energy (ΔE°), the equation becomes

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta E^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

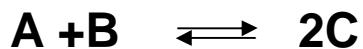
HOMOGENEOUS CHEMICAL EQUILIBRIUM

Homogenous equilibrium is an equilibrium in which the reactants and the products are in the same phase.

-Homogenous gaseous equilibria

Case I: The Hydrogen-Iodide system

Consider a reaction



if V (in dm³) is the total volume of the reaction mixture

then, $\frac{a - x}{V}$ $\frac{b - x}{V}$ $\frac{2x}{V}$

Hence, $K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$

$$K_c = \frac{4x^2}{(a-x)(a-b)}$$

volume

K_c is independent of the

In term of partial pressure,

$$K_p = \frac{P_c^2}{P_A \times P_B}$$

But $P_A = \frac{n_A}{N} \times P$, $P_B = \frac{n_B}{N} \times P$ **and** $P_C = \frac{n_C}{N} \times P$

Where $N = n_A + n_B + n_C$ = **total number of moles**,

P = total (external) pressures P_A , P_B & P_C are partial pressures of A, B and C respectively.

$$\therefore K_p = \frac{\left(\frac{n_C}{N} \times P\right)^2}{\left(\frac{n_A}{N} \times P\right) \times \left(\frac{n_B}{N} \times P\right)} = \frac{n_C^2}{n_A + n_B}$$

Examples:

1. A mixture of 1 mole of H_2 and 1 mole of I_2 in a flask was heated until the equilibrium is reached.

On analysis, the equilibrium mixture is found to contain 0.7mole of HI. Calculate the K_c

2. Consider this reaction



Given that the partial pressures of the following substances at 45°C are $P_{H_2} = 0.065\text{atm}$, $P_{I_2} = 0.45$

atm. and $P_{HI} = 0.245\text{ atm}$. Calculate (a) the equilibrium constant K_p for the reaction at 45°C (b) the equilibrium constant K_p for the backward reaction

3. K_c for this reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$

at 727°C is 16.7, calculate K_p for this reaction at 727°C .

N.B- Solutions to these examples shall be treated during the lecture hours

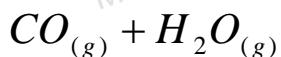
Exercises:

1. The K_p for this equilibrium reaction:

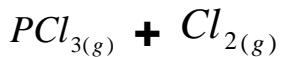


is 0.11 at 25°C , calculate K_c at this temperature.

2. The following results were obtained during analysis of a reaction



3. At 25°C and 4 atm., PCl_5 is 10% dissociated, calculate the K_p for this reaction,



Case II: $A \rightleftharpoons 2B$

e.g. Decomposition of N_2O_4 , i.e. $\cancel{N_2O_4} \rightarrow 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

$$\therefore K_c = \frac{4x^2}{(a-x)V}$$

In term of K_p ,

$$K_p = \frac{[NO_2]^2}{[N_2O_4]} = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

Also, while considering the equation, if x represent the degree of dissociation, then $2x$ of NO_2 will be produced, then $1-x$ of N_2O_4 will be left. then, the total number of moles present at equilibrium = $(1-x) + 2x = 1+x$.

$$\therefore P_{N_2O_4} = \left(\frac{1-x}{1+x} \right) P \quad \& \quad P_{NO_2} = \left(\frac{2x}{1+x} \right) P$$

So,

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{\left(\frac{2x}{1+x} \right)^2 P}{\left(\frac{1-x}{1+x} \right) P}$$

∴

$$K_p = \frac{4x^2 P}{1-x^2}$$

Examples:

- 1. N_2O_4 at 1 atm and 25°C dissociated by 18.5%, calculate its K_p at this temperature. If the atmospheric temperature was reduced to half its original value at the same temperature, calculate the degree of dissociation of the gas.**

- 2. N_2O_4 is 25% dissociated at 30°C and 1 atm., calculate**
 - (a) The equilibrium constant for the decomposition**
 - (b) The amount of NO_2 that would be attained if there had been 4 moles of N_2O_4 at the same temperature and pressure.**

N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

- 1. N_2O_4 is 25% dissociated at 37°C and 1 atm., calculate**
 - (i) The K_p and (ii) the % dissociation at 0.1 atm and 37°C**

2. An equilibrium mixture at 27°C contains N₂O₄ and NO₂ having 0.28 atm. and 1.1 atm. pressures respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the gases.

Case III:



e.g. synthesis of Ammonia



$$\frac{a-x}{V} \quad \frac{b-x}{V} \quad \frac{2x}{V}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)^3}$$

$$\therefore K_c = \frac{4x^2 V^2}{(a-x)(b-x)^3}$$

Also,

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

Examples:

1. In an experiment, H₂ and N₂ in the mole ratio 3:1 produced 0.0735mole fraction of NH₃ at 350°C and total pressure of 1013KNm⁻². Calculate K_p for the forward and reverse reactions

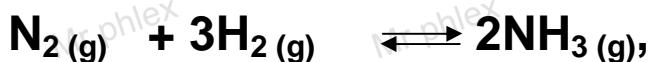
2. The K_p for this equilibrium reaction

N₂(g) + 3H₂(g) ⇌ 2NH₃(g) is 1.45 × 10⁻⁵ at 500°C. Calculate the partial pressure of NH₃ when the partial pressure of H₂ is 0.928atm and that of N₂ is 0.432atm.

Exercise:

1. The dissociation pressure of CaCO₃ is 342mmHg at 840°C and at 860°C, the dissociation pressure is 420mmHg. Calculate the heat of dissociation of the carbonate. Given that R=8.314KJmol⁻¹.

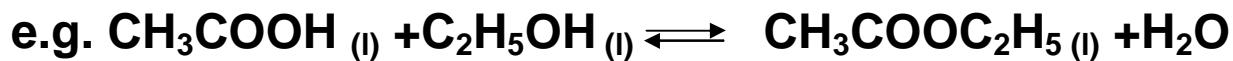
2. consider this reaction



The K_p is 1.64×10⁻⁴ at 400°C. calculate (i) the ΔG of the reaction (ii) ΔG when the partial pressure

of N₂, H₂ and NH₃ are 10atm, 30 atm and 3 atm respectively.

HOMOGENOUS (LIQUID) EQUILIBRIA



| | | | | |
|-----|-----|-----|---|---|
| t=0 | a | b | 0 | 0 |
| t=t | a-x | b-x | x | x |

$$K_c = \frac{\left(\frac{x}{V}\right) \times \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)}$$

$$\therefore K_c = \frac{x^2}{(a-x)(b-x)}$$

The equation above is the general expression for the liquid equilibria. However, in the example above where

water molecule is involved, the expression can be written as

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$\frac{K_c}{[H_2O]} = K' = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

The above expression is written in term of K' because the concentration of water is taken to be constant, K' has the unit of $[Concn]^{-1}$ but K_c has no unit.

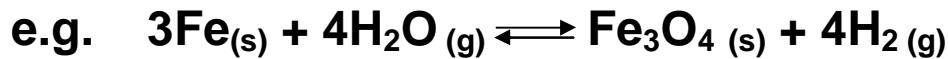
Example:

- 1. In an esterification process between 1 mole of ethanoic acid and 1 mole of ethanol at $25^\circ C$, 66.7% of the acid is esterified calculate the equilibrium constant and ΔG° .**
- 2. When 1 mole of ethanoic acid and 1 mole of ethanol were heated together at a temperature of**

25°C until the equilibrium is reached. Titration of the reaction mixture shows that 2/3 of the acid have been used up. Calculate the equilibrium constant.

HETEROGENEOUS EQUILIBRIA SYSTEM

Heterogeneous equilibrium is an equilibrium in which the reactants and the products are not in the same phase.



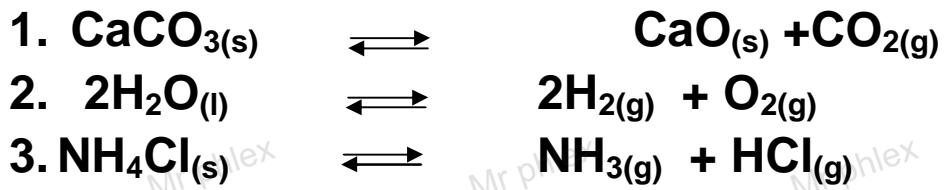
$$K_c = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4} = \frac{1 \times [\text{H}_2]^4}{1 \times [\text{H}_2\text{O}]^4} = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

N.B: the concentration of substances in solid phase is taken to be unity.

In term of K_p ,

$$K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

Exercises: Express the equilibrium constants K_p , for the following reactions.



Le-Chatelier's Principle

It states that “if a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the equilibrium will shift, so as to neutralize the effect of the change”.

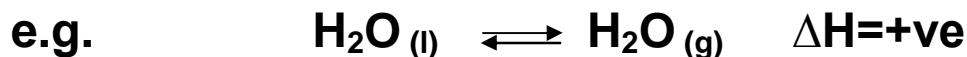
FACTORS AFFECTING EQUILIBRIUM

The factors are: temperature, concentration and pressure of the reactants and products, catalyst.

N.B: catalyst does not change the position of equilibrium, but affects the reaction equally in both directions.

1. Effect of temperature changes on equilibrium mixture: If a chemical system is in equilibrium and the temperature is lowered, the equilibrium position according to Le-Chatelier's Principle will shift so as to neutralize the cooling effect by releasing more heat.

Conversely, if the temperature is raised, the equilibrium position will shift so as to neutralize the heating effect by absorbing more heat.



Since the forward reaction is an endothermic, if the temperature is raised, more steam will be produced and the equilibrium position will shift to the right. On the other hand, if the temperature is lowered, the equilibrium position shifts to the left and more water will be formed as the steam condenses.

The table below summarises the effect of temperature change on the equilibrium position.

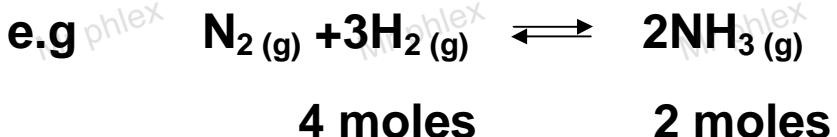
| Reversible reactions where forward rxn is endothermic | When the temp. of equilibrium system | |
|--|---|---|
| | increases | decreases |
| $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$ $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$ | Equilibrium position shifts to right, favouring forward rxn. K increases | Equilibrium position shifts to left, favouring backward rxn. K decreases |
| Forward rxn is exothermic | Equilibrium | Equilibrium |

| | | |
|--|---|---|
| $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$ | position shifts to left, favouring backward rxn. K decreases | position shifts to right, favouring forward rxn. K increases |
| $2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{H}_2\text{O}_{(\text{g})}$ | | |
| $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$ | | |

2. Effect of pressure changes on equilibrium mixture:

This effect occurs in gaseous state reactions in which the total numbers of moles of gaseous molecules on the left hand side of the equation differ from that on the right hand side of the equation.

When the pressure of a system at equilibrium is increased, then the reaction that involves a reduction in pressure will be favoured. This is in line with the Le-Chatelier's principle. Conversely, if the pressure is lowered for a system at equilibrium, the reaction that will increase the pressure will be favoured.



The forward reaction involves a decrease in the number of moles and hence, a decrease in the pressure of the system. Also, the backward reaction gives an increase in the number of moles, and hence an increase in the pressure of the system.

In the formation of ammonia, a high pressure will favour the forward reaction (where a reduction in volume occurs). This causes the equilibrium position to shift to the right. On the other hand, a low pressure will cause the equilibrium position to shift to the left, favouring the backward reaction.

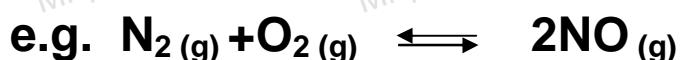
The table below summarises the effect of a change in pressure on the equilibrium position.

| Reversible reactions | Shift in equilibrium position when the pressure | |
|---|---|----------------------|
| 1. Forward rxns (decrease in vol) | Increases | decreases |
| $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$ $3\text{H}_{2(\text{g})} + \text{N}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$ $2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{CO}_{2(\text{g})}$ | right right right | Left Left Left |
| 2. Forward rxns (increase in vol) | Left | right |
| $\text{N}_2\text{O}_{4(\text{g})} \rightleftharpoons 2\text{NO}_{2(\text{g})}$ | | |

| | | |
|---|-------|-------|
| | | |
| 3.No change in volume $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{2(g)}$ $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)}$ $2H_{2(g)}$ | _____ | _____ |

NB: the value of K remain constant irrespective of the shift in the equilibrium position.

3. Effect of concentration changes on equilibrium mixture: if the concentration of any of the substances present is changed without a change in any of the other conditions. According to Le-chatelier's principle, the equilibrium position will move to increase the concentration of the added substance.



The addition of more reactants (either N_2 or O_2 or both) will upset the equilibrium. For the system to adjust, the equilibrium position will shift to the right thereby favouring the forward reaction. This results in a proportional increase in the concentration of the product.

Similarly, if the product formed is continually removed from the system, the equilibrium position will shift to the right to produce more of the product.

The effect of concentration change on equilibrium can be summarise in the table below

| Reversible reactions | Addition of reactants or removal of products | removal of reactants or addition of products |
|--|---|--|
| $\text{CaCO}_{3(\text{g})} \rightleftharpoons \text{CaO}_{2(\text{g})} + \text{CO}_{2(\text{g})}$ $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ $3\text{Fe}_{(\text{s})} + 4\text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{Fe}_{3\text{O}}_{4(\text{s})} + 4\text{H}_{2(\text{g})}$ | Equilibrium position shifts to the right | Equilibrium position shifts to the left |

NB: the value of K remain constant irrespective of the shift in the equilibrium position.

4. Effect of Catalyst: Addition of catalyst has no effect on either the equilibrium constant or shift. It only speed up the rate at which the equilibrium is reached.

CHEMICAL EQUILIBRIUM IN SOLUTION

a. Dissociation of water:



$$K = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

But $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ mol/dm³ at 25°C and
 $[\text{H}_2\text{O}] = \text{constant}$

$$\therefore K_w = [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

K_w is the water dissociation constant.

Examples

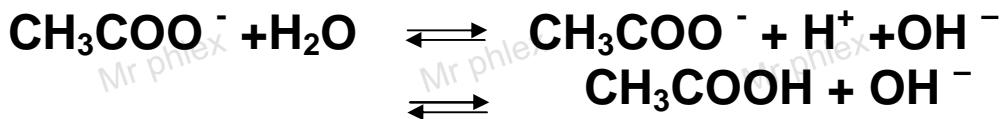
1. Calculate the $[\text{OH}^-]$ of the 0.01M HCl
2. Calculate the $[\text{H}^+]$ of the 0.0001M NaCl

(b). Hydrolysis and hydrolysis constant

when a salt of a strong acid and a strong base dissolved in water, the water remains neutral. However, when a salt formed from a strong acid and a weak base or vice versa is dissolved in water, it either make the water acidic or basic.

e.g. (a) salt of strong base-weak acid like sodium ethanoate

$(\text{CH}_3\text{COONa})$ react with water to give an alkaline solution.



As the CH_3COO^- consume the H^+ from water to form ethanoic acid, more of the water molecules dissociate to produce more of their ions.

At equilibrium,

$$K_a = \frac{[\text{HEt}][\text{OH}^-]}{[\text{Et}^-][\text{H}_2\text{O}]}$$

But

$$\frac{[\text{HEt}][\text{OH}^-]}{[\text{Et}^-]} = [\text{H}_2\text{O}] K_a = K_h$$

K_h is the hydrolysis constant, but $K_w = [\text{H}^+][\text{OH}^-]$

$$\therefore [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{K_w}{K_a}$$

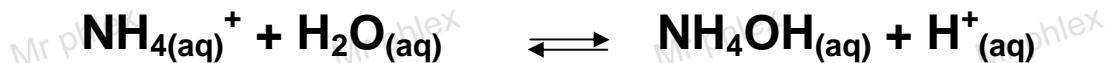
The hydrolysis constant K_h is related to the acid dissociation constant by the expression

$$K_h = \frac{K_w}{K_a}$$

The degree of hydrolysis, α , is the fraction of the salt which has undergone hydrolysis when equilibrium is reached and it is given by

$$\alpha = \sqrt{\frac{K_w}{K_h \times C}}$$

(b). salt of weak base-strong acid, e.g NH₄Cl.



$$\therefore K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

$$\text{but } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$\therefore K_h = \frac{K_w}{K_b}$$

c. Salt of weak acid-weak base, e.g CH₃COONH₄



The hydrolysis constant is given by

$$K_h = \frac{K_w}{K_a \times K_b}$$

and the degree of hydrolysis is given by

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Solubility Product

When a sparingly soluble salt e.g AgCl dissolves in water at a given temperature, a stage will be reached when it will not dissolve further and both the solid and solution will co-exist in equilibrium.



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

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

Examples

1. Calculate the hydrolysis of a base whose dissociation constant is 1.75×10^{-5} .
2. The solubility of CuBr is found to be 2.0×10^{-4} mol/L at $25^\circ C$. calculate K_{sp} value for CuBr.
3. The solubility of $Mg(OH)_2$ at $25^\circ C$ is 0.00764g/L. what is the value of K_{sp} for $Mg(OH)_2$?

Exercises

1. Calculate the K_{sp} of AgCl whose solubility at $25^\circ C$ is 1.05×10^{-5} mol/L.
2. The solubility of $BaSO_4$ at $18^\circ C$ is 0.00233g/L. what is the value of K_{sp} for $BaSO_4$?

Common-ion Effect

When a soluble salt (say, A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB will be suppressed.



By the addition of the salt (AC), the concentration of A⁺ increases. In line with the Le-chatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A⁺ (i.e the degree of dissociation of AB will be reduced).

Thus, the reduction of the degree of dissociation of a salt by the addition of a common-ion is called the common-ion effect.

Examples

- 1. Calculate the [H⁺] when 0.1 mol acetic acid was treated with 0.2 mol acetate ion. The equilibrium constant is 1.8x 10⁻⁵.**
- 2. Calculate the [H⁺] when 1 mol of sodium formate was added to 0.5 mol formic acid. Given that K= 1.8x 10⁻⁵.**

Oxidation-Reduction Reactions

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Introduction

- Oxidation-reduction reactions are also known as redox reactions
- Def: Redox reactions describe all chemical reactions in which there is a net change in atomic charge
- It is a class of reactions that include:
 - formation of a compound from its elements
 - all combustion reactions
 - reactions that generate electricity
 - reactions that produce cellular energy

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Terminology

- The key idea is the net movement of electrons from one reactant to the other
- *Oxidation* is the loss of electrons
- *Reduction* is the gain of electrons
- *Oxidizing agent* is the species doing the oxidizing
- *Reducing agent* is the species doing the reducing

Redox Illustration



- Oxidation (electron loss by H_2)



- Reduction (electron gain by F_2)



H_2

- Oxidized

- Reducing agent

H_2

2e^- transfer

F_2

- Reduced

- Oxidizing agent

Oxidation Number

- Oxidation number (O.N.) is also known as oxidation state
- It is defined as the charge the atom would have if electrons were not shared but were transferred completely
- For a binary ionic compound, the O.N. is equivalent to the ionic charge.
- For covalent compounds or polyatomic ions, the O.N. is less obvious and can be determined by a given set of rules

Rules for Assigning an Oxidation Number

General Rules

1. For an atom in its elemental form (Na , O_2): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals to zero.
(equals to the ion's charge if it is a polyatomic ion)

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals
O.N. = -1 in combination with metals and boron
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides
O.N. = -2 in all other compounds (except with F)
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

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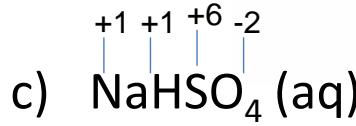
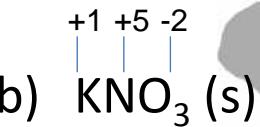
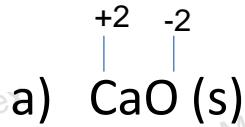
Example 1

- Determine the oxidation number (O.N.) of each element in these compounds:

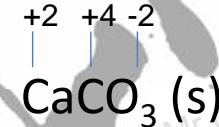
- $\text{CaO} (\text{s})$
- $\text{KNO}_3 (\text{s})$
- $\text{NaHSO}_4 (\text{aq})$
- $\text{CaCO}_3 (\text{s})$
- $\text{N}_2 (\text{g})$
- $\text{H}_2\text{O} (\text{l})$

Solution to Example 1

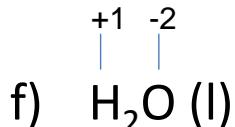
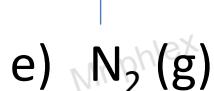
Simply apply the rules for assigning an oxidation number as described earlier



$$\text{S} = 0 - (+1) - (+1) - 4(-2) = +5$$



$$\text{C} = 0 - (+2) - 3(-2) = +4$$



Example 2

- Identify the oxidizing agent and reducing agent in each of the following:

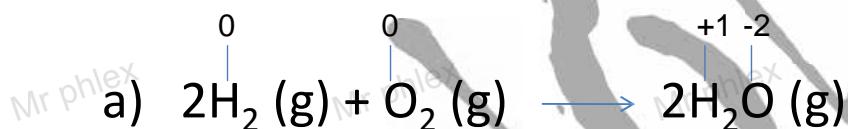


Solution to Example 2

Assign oxidation numbers and compare.

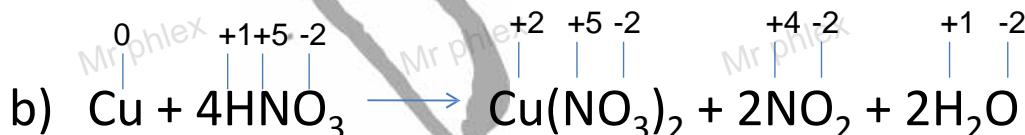
Oxidation is represented by an increase in oxidation number

Reduction is represented by a decrease in oxidation number



- O₂ was reduced (O.N. of O: 0 → -2); O₂ is the oxidizing agent

- H₂ was oxidized (O.N. of H: 0 → +1); H₂ is the reducing agent



- Cu was oxidized (O.N. of Cu: 0 → +2); Cu is the reducing agent

- HNO₃ was reduced (O.N. of N: +5 → +4); HNO₃ is the oxidizing agent

Balancing Redox Equations

- When balancing redox reactions, make sure that the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent
- Two methods can be used:
 1. Oxidation number method
 2. Half-reaction method

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Balancing Redox Equations

Method 1: Oxidation number method

1. Assign oxidation numbers to all elements in the reaction
2. From the changes in O.N., identify the oxidized and reduced species
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the O.N. changes
4. Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
5. Complete the balancing by inspection, adding states of matter

Example 3

- Use the oxidation number method to balance the following equations:



Part a: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements



- Step 2. Identify oxidized and reduced species
 - Al was oxidized (O.N. of Al: 0 \rightarrow +3)
 - H_2SO_4 was reduced (O.N. of H: +1 \rightarrow 0)
- Step 3. Compute e^- lost and e^- gained
 - In the oxidation: $3e^-$ were lost from Al
 - In the reduction: $1e^-$ was gained by H

Part a: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
 - Al lost $3e^-$, so the $1e^-$ gained by H should be multiplied by 3. Put the coefficient 3 before H_2SO_4 and H_2 .

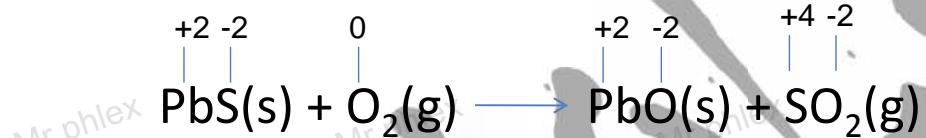


- Step 5. Complete the balancing by inspection



Part b: Solution to Example 3

- Step 1. Assign oxidation numbers to all elements



- Step 2. Identify oxidized and reduced species
 - PbS was oxidized (O.N. of S: -2 → +4)
 - O₂ was reduced (O.N. of O: 0 → -2)
- Step 3. Compute e⁻ lost and e⁻ gained
 - In the oxidation: 6e⁻ were lost from S
 - In the reduction: 2e⁻ were gained by each O

Part b: Solution to Example 3

- Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients
 - S lost $6e^-$, O gained $4e^-$ ($2e^-$ each O). Thus, put the coefficient $3/2$ before O_2 .
- PbS(s) + $3/2O_2(g)$ \longrightarrow PbO(s) + SO₂(g)
- Step 5. Complete the balancing by inspection



Balancing Redox Equations

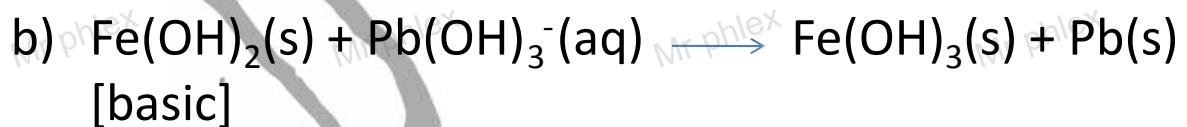
Method 2: Half-reaction method

1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species
2. Balance the atoms and charges in each half-reaction
 - Atoms are balanced in order: atoms other than O and H, then O, then H
 - Charge is balanced by adding electrons
 - To the left in reduction half-reactions
 - To the right in oxidation half-reactions
3. If necessary, multiply one or both half-reactions by an integer to make the number of e^- gained equal to the number of e^- lost
4. Add the balanced half-reactions, and include states of matter
5. Check that the atoms and charges are balanced

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Example 4

- Use the half-reaction method to balance the following equations:



Part a: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

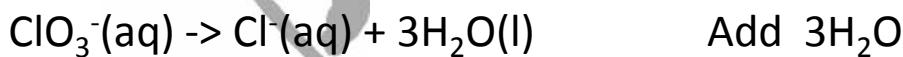


- Step 2. Balance atoms and charges in each half-reaction

– Atoms other than O and H

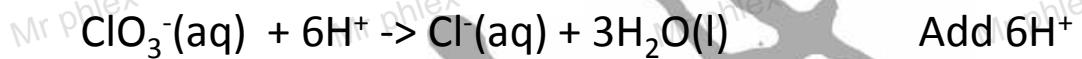


– Balance O atoms by adding H_2O molecules



Part a: Solution to Example 4

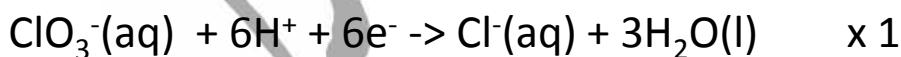
- Balance H atoms by adding H^+ ions



- Balance charge by adding electrons

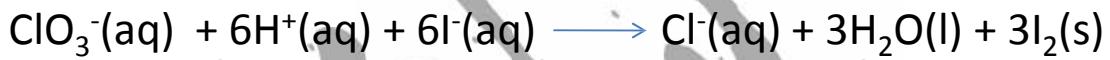


- Step 3. Multiply each half-reaction by an integer to equalize number of electrons



Part a: Solution to Example 4

- Step 4. Add the half-reactions together



- Step 5. Check that atoms and charges balance

– Reactants (Cl, 3O, 6H, 6I, -1) → products (Cl, 3O, 6H, 6I, -1)

- ClO_3^- is the oxidizing agent
- I^- is the reducing agent

Part b: Solution to Example 4

- The only difference in balancing a redox equation that takes place in basic solution is in Step 4.
- At this point, we add one OH^- ion to both sides of the equation for every H^+ ion present
- The H^+ ions on one side are combined with the added OH^- ions to form H_2O , and OH^- ions appear on the other side of the equation

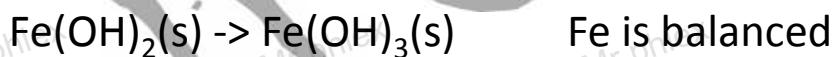
Part b: Solution to Example 4

- Step 1. Divide the reaction into half-reactions

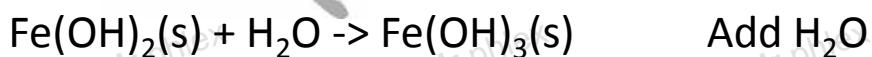
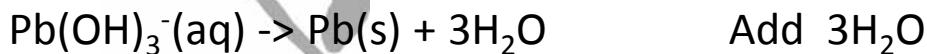


- Step 2. Balance atoms and charges in each half-reaction

- Atoms other than O and H

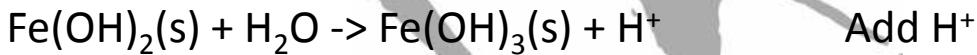
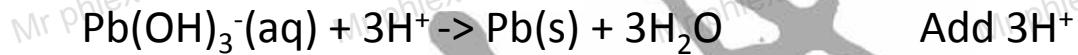


- Balance O atoms by adding H_2O molecules



Part b: Solution to Example 4

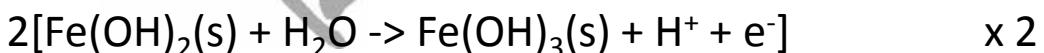
- Balance H atoms by adding H^+ ions



- Balance charge by adding electrons

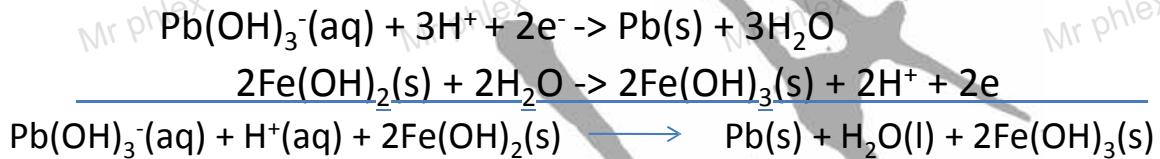


- Step 3. Multiply each half-reaction by an integer to equalize number of electrons



Part b: Solution to Example 4

- Step 4. Add the half-reactions together



- Step 4(basic). Add OH⁻

– Here, we add 1 OH⁻



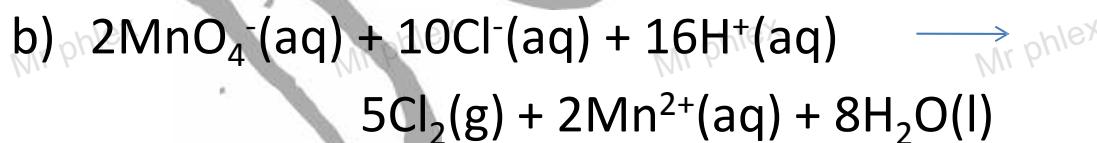
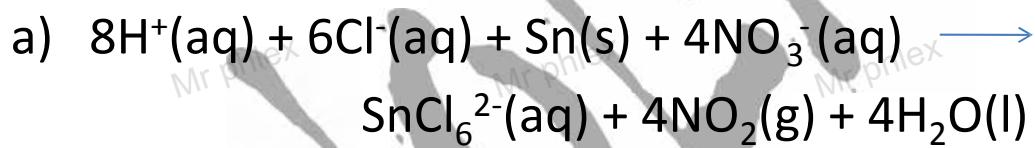
- Step 5. Check

– Reactants (Pb, 7O, 7H, 2Fe, -1) → products (Pb, 7O, 7H, 2Fe, -1)

- Pb(OH)₃⁻ is the oxidizing agent
- Fe(OH)₂ is the reducing agent

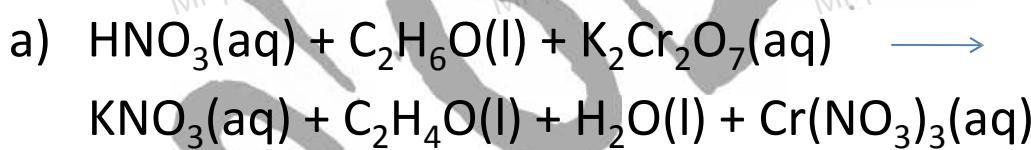
Practice Problem

1. Identify the oxidizing and reducing agents in the following:

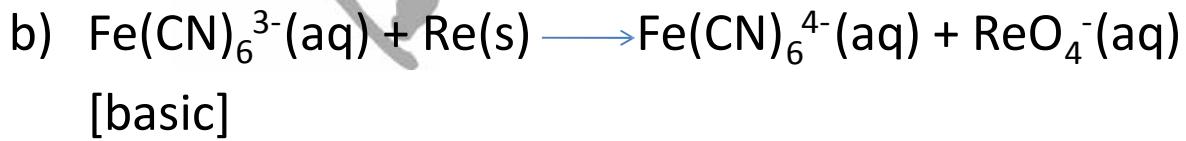


Practice Problem

2. Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents:



3. Use the half-reaction method to balance the following equations and then identify the oxidizing and reducing agents:



References

- Silberberg, Martin. Chemistry The Molecular Nature of Matter and Change. New York: McGraw-Hill Science/Engineering/Math, 2008.

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CHM 101: General Physical Chemistry

Thermochemistry and simple calculations based on Hess's law. Rate of reaction (Chemical kinetics)

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“Thermochemistry”



Thermochemistry

- This is a branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.
- In 1782 Antoine Lavoisier and Pierre-Simon Laplace laid the foundations of “thermochemistry”
- They showed that the heat evolved in a reaction is equal to the heat absorbed in the reverse reaction.



- Every substance has a definite amount of energy known as the intrinsic energy or internal energy, E.
- The exact value of internal energy cannot be determined but the change in internal energy, ΔE , can be accurately measured experimentally.

- When the internal energy of reactants (E_r) is greater than the internal energy of the products (E_p), the difference of internal energy, ΔE , is released as heat energy.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}} \text{ o (or } \Delta E = E_p - E_r)$$

- Such a reaction is called exothermic reaction.



- If the internal energy of the products (E_p) is greater than that of the reactants (E_r), heat is absorbed from the surroundings.
- Such a reaction is called endothermic reaction.
- The amount of heat released or absorbed in a chemical reaction is termed the heat of reaction.
- The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds.
- Thus, thermochemistry provides useful information regarding the bond energies.



Unit of Energy

- The energy changes are usually expressed as:
 - the calorie (cal.),
 - kilocalorie (1 kcal = 1000 cal),
 - Joule (J) and
 - kilojoule (kJ).
- It may be noted that 1 cal = 4.18 J and 1 kcal = 4.18 kJ.



ENTHALPY OF A REACTION

- Thermochemical measurements are made either at (a) constant volume or (b) constant pressure.
- The magnitudes of changes observed under the two conditions are different.
- The change in internal energy (ΔE) is the heat change accompanying a chemical reaction at constant volume because no external work is performed.
- However at constant pressure not only does the change in internal energy take place but work is also involved because of expansion or contraction.



- In the laboratory most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume
- The enthalpy of a system is defined as the sum of the internal energy and the product of its pressure and volume.

$$H = E + PV$$

- Like internal energy, change in enthalpy (ΔH) accompanying a process is what can be measured accurately not absolute H.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = H_p - H_r$$

- Therefore, internal energy is the heat change in a process at constant volume while enthalpy is the heat change in a process at constant pressure.



EXOTHERMIC AND ENDOTHERMIC REACTIONS

- Consider a general reaction at constant pressure,

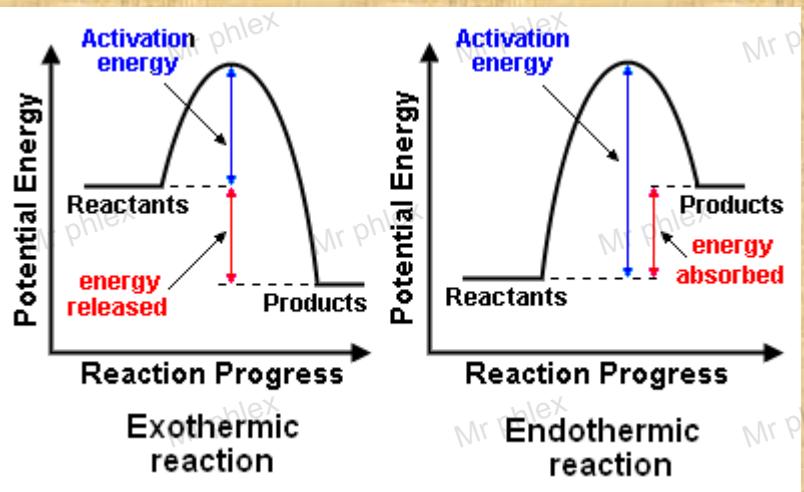


$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = (H_C + H_D) - (H_A + H_B)$$

- When ΔH is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed.
- In case ΔH is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.



- Such reactions which are accompanied by the evolution of heat energy are called Exothermic reactions.
- When ΔH is positive, the enthalpy or heat content of the reactants and an equivalent of heat is absorbed by the system from the surroundings.
- Such reactions which are accompanied by absorption of heat are called Endothermic reactions.
- Thus for an exothermic reaction $H_p < H_r$ and $\Delta H = - \text{ve}$, for an endothermic reaction $H_p > H_r$ and $\Delta H = +\text{ve}$.



EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

| Exothermic processes | Endothermic processes |
|---|---|
| Making ice cubes | Melting ice cubes |
| Formation of snow in clouds | Conversion of frost to water vapour |
| Condensation of rain from water vapour | Evaporation of water |
| Mixing sodium sulfite and bleach | Baking bread |
| Rusting iron | Cooking an egg |
| Burning sugar | Producing sugar by photosynthesis |
| Forming ion pairs | Separating ion pairs |
| Mixing water and strong acids | Mixing water and ammonium nitrate |
| Mixing water with an anhydrous salt | Making an anhydrous salt from a hydrate |
| Crystallizing liquid salts (as in sodium acetate in chemical handwarmers) | Melting solid salts |
| Nuclear fission | Reaction of barium hydroxide octahydrate crystals with dry ammonium chloride |
| Mixing water with calcium chloride | Reaction of thionyl chloride (SOCl_2) with cobalt(II) sulfate heptahydrate |



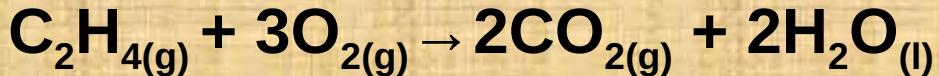
Example

- The heat of combustion of ethylene at 17°C and at constant volume is - 1389.9 kJ. Calculate the heat of combustion at constant pressure considering water to be in liquid state. ($R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$)



- **Solution**

The chemical equation for the combustion of ethylene is:



No. of moles of the gaseous products = 2

No. of moles of the gaseous reactants = 4

$$\therefore \Delta n = (2 - 4) = -2$$

We know that $\Delta H = \Delta E + \Delta nRT$ ($PV=nRT$)

Given that $\Delta E = -1389.9$ kJ

$$T = 273 + 17 = 290 \text{ K}$$

$$R = 8.314 \times 10^{-3} \text{ k J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned}\therefore \Delta H &= -1389.9 \text{ kJ} + ((8.314 \times 10^{-3}) \times -2 \times 290) \\ &= -1.384.72 \text{ kJ}\end{aligned}$$



Assignment

- The heat of combustion of carbon monoxide at constant volume and at 17°C is - 283.3 kJ. Calculate its heat of combustion at constant pressure ($R = 8.314 \text{ J degree}^{-1} \text{ mol}^{-1}$).



THERMOCHEMICAL EQUATIONS

- An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation.
- It must essentially :
 - be balanced;
 - give the value of ΔE or ΔH corresponding to the quantities of substances given by the equation;
 - mention the physical states of the reactants and products.
- The physical states are represented by the symbols (s), (l), (g) and (aq) for solid, liquid, gas and aqueous states respectively.

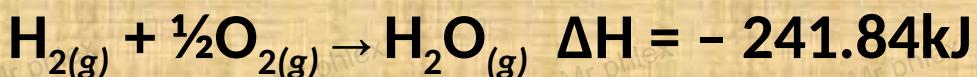
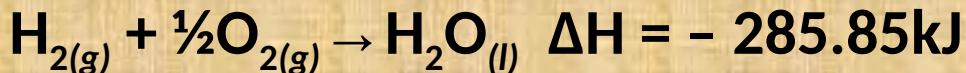


- The equation :



1 mole of H₂ with 0.5 mole of O₂, to form 1 mole of water with evolution of 285.85 kJ of at constant pressure.

- If two moles of hydrogen are burnt, the heat evolved would be (2×285.85) kJ
- It is not thermochemical equation because it doesn't specify whether H₂O is steam or liquid



- There is difference in the value of ΔH if water is in the liquid or gaseous state as shown above.



HEAT OR ENTHALPY OF REACTION

- Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products.



- The heat of reaction varies with the change in temperature. Thus, the temperature at which the reaction is taking place must be stated.
- The temperature of 298 K under pressure of one atmosphere has been fixed as the standard state.
- Thus the heat change accompanying a reaction taking place at 298 K and one atmospheric pressure is called the standard heat change or standard enthalpy change. It is denoted by ΔH° .



VARIATION OF HEAT (OR ENTHALPY) OF REACTION WITH TEMPERATURE

- The variation of heat change of reaction with temperature are represented by **Kirchoff's equations.**
- At constant volume,

$$\Delta E = E_2 - E_1$$

$$\left(\frac{d\Delta E}{dT} \right)_V = \left(\frac{dE_2}{dT} \right)_V - \left(\frac{dE_1}{dT} \right)_V$$

$$\left(\frac{dE}{dT} \right)_V = C_v$$

C_v is the constant volume heat capacity.

$$\left(\frac{d\Delta E}{dT} \right)_V = (C_v)_2 - (C_v)_1 = \Delta C_v$$

Integrating the above equation between temperatures T₁ and T₂, we have

$$\int_{E_1}^{E_2} d\Delta E = \int_{T_1}^{T_2} \Delta C_v dT$$

$$\int_{E_1}^{E_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_p dT$$

Similar process can be used to obtain the enthalpy



Exercise

- The heat of reaction $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{HCl}$ at 27°C is $- 22.1$ kcal. Calculate the heat of reaction at 77°C . The molar heat capacities at constant pressure at 27°C for hydrogen, chlorine and HCl are 6.82 , 7.70 and 6.80 cal mol $^{-1}$ respectively. (Ans = $- 22.123$ kcal)
- The heat of reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ at 27°C was found to be -21.976 kcal. What will be the heat of reaction at 50°C ? The molar heat capacities at constant pressure and at 27°C for nitrogen, hydrogen and ammonia are 6.8 , 6.77 and 8.86 cal mol $^{-1}$ degree $^{-1}$. (Ans = 22.192 kcal)



DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTION

- **HEAT OF FORMATION:** The change in enthalpy that takes place when one mole of the compound is formed from its elements. Denoted as ΔH_f
- **STANDARD HEAT OF FORMATION OF A COMPOUND:** The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure).
- **STANDARD HEAT OF REACTION (ΔH°) FROM STANDARD HEAT OF FORMATION (ΔH_f°):** The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.

$$\Delta H^\circ = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

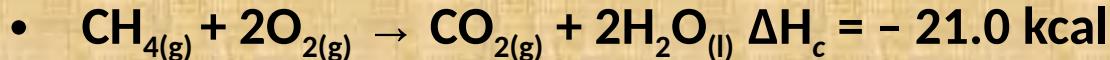


Excercise

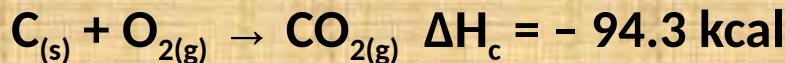
- Calculate ΔH° for the reaction: $\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightarrow \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$ given that ΔH of for $\text{CO}_{2(\text{g})}$, $\text{CO}_{(\text{g})}$ and $\text{H}_2\text{O}_{(\text{g})}$ are - 393.5, - 111.31 and - 241.80 kJ mol^{-1} respectively.
(Ans = 40.4 kJ)
- The standard heats of formation of $\text{C}_2\text{H}_5\text{OH}_{(\text{l})}$, $\text{CO}_{2(\text{g})}$ and $\text{H}_2\text{O}_{(\text{l})}$ are - 277.0, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction
(Ans = - 1366.5 kJ)



- **HEAT OF COMBUSTION:** the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.



- Now consider the chemical equations



- The ΔH_c for C is $- 94.3 \text{ kcal}$ and not $- 26.0 \text{ kcal}$ because the combustion is complete only in the first reaction.
- The heat of combustion of a substance (ΔH_c) is always negative since heat energy always evolved during the process of combustion.

- **APPLICATIONS OF THE HEAT OF COMBUSTION**

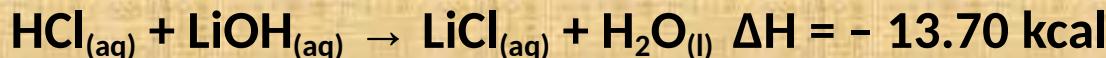
- Calculation of heat of formation
- Determination of calorific value of foods and fuels.
- Deciding constitution



- **HEAT OF SOLUTION:** the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.
- It is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.



- heat of solution of an electrolyte may be due to energy change involved during ionization or some hydrate formation as in case of sulphuric acid.
- **HEAT OF NEUTRALIZATION:** the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralized by one gram equivalent of a base or vice versa in dilute solution.



the heat of neutralization of a strong acid and strong base is -13.7 kcal, no matter which acid or base is employed because it is heat of formation of water from hydrogen and hydroxyl ions.



ENERGY CHANGES DURING TRANSITIONS OR PHASE CHANGES

- **HEAT OF FUSION:** the heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its melting point.



- **HEAT OF VAPOURISATION:** the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state at its boiling point.



- **HEAT OF SUBLIMATION:** the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.

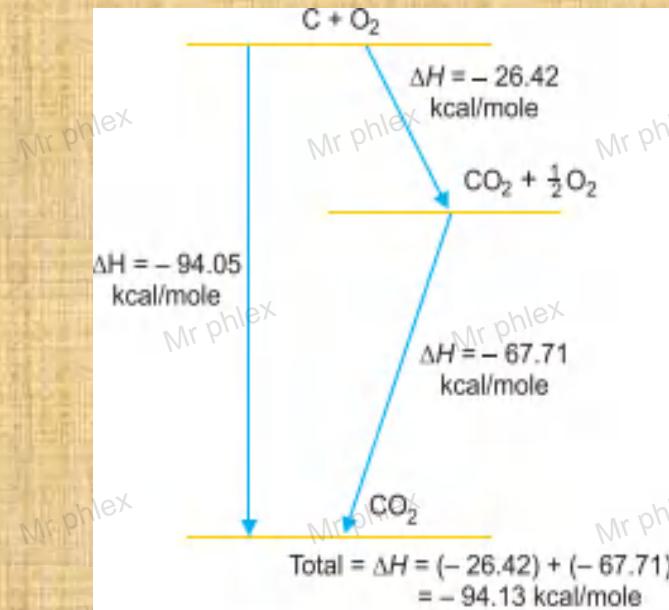
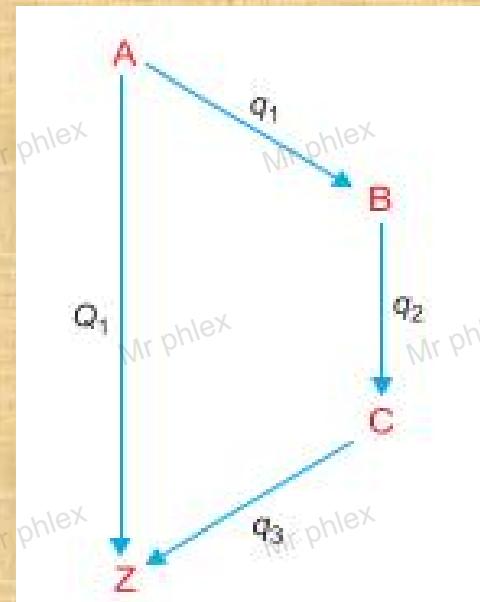


- **HEAT OF TRANSITION:** the change in enthalpy which occurs when one mole of an element changes from one allotropic form to another.



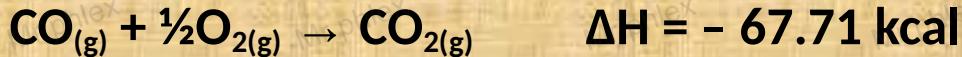
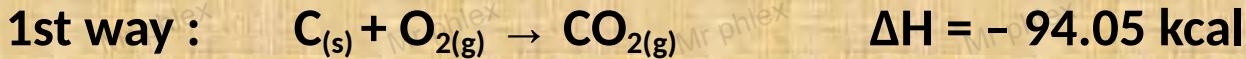
HESS'S LAW OF CONSTANT HEAT SUMMATION

- ΔE and ΔH depend only on the initial state and final state of the system and not the manner or the steps in which the change takes place.
- Hess's Law states that: *If a chemical change can be made to take place in two or more different ways whether in one, two or more steps, the amount of total heat change is same no matter by which method the change is brought about.*

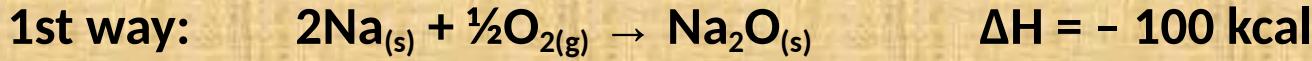


Illustration

- Burning of carbon to CO_2 .



- Formation of Sodium hydroxide from Na:



Application of Hess's Law

- Determination of heat of formation of substances which otherwise cannot be measured experimentally
- Determination of Heat of Transition
- Determination of heats of various reactions



FURTHER EXAMPLES ON HESS'S LAW

Determine the heat of reaction for the reaction:



Using the following sets of reactions:



Hint: The three reactions must be algebraically manipulated to sum up to the desired reaction.

and.. the ΔH values must be treated accordingly.



Goal:



Using the following sets of reactions:



NH_3 : Reverse and x 2 $4\text{NH}_3 \rightleftharpoons 2\text{N}_2 + 6\text{H}_2 \quad \Delta H = +183.6 \text{ kJ}$

O_2 : Found in more than one place, SKIP IT (its hard).

NO : x2 $2\text{N}_2 + 2\text{O}_2 \rightleftharpoons 4\text{NO} \quad \Delta H = 361.2 \text{ kJ}$

H_2O : x3 $6\text{H}_2 + 3\text{O}_2 \rightleftharpoons 6\text{H}_2\text{O} \quad \Delta H = -1451.1 \text{ kJ}$



Goal:



NH₃: Reverse and x2 $4\text{NH}_3 \rightleftharpoons 2\text{N}_2 + 6\text{H}_2$ $\Delta H = +183.6 \text{ kJ}$

O₂: Found in more than one place, SKIP IT.

NO: x2 $2\text{N}_2 + 2\text{O}_2 \rightleftharpoons 4\text{NO}$ $\Delta H = 361.2 \text{ kJ}$

H₂O: x3 $6\text{H}_2 + 3\text{O}_2 \rightleftharpoons 6\text{H}_2\text{O}$ $\Delta H = -1451.1 \text{ kJ}$

Cancel terms and take sum.



Is the reaction endothermic or exothermic?



Determine the heat of reaction for the reaction:



Use the following reactions:



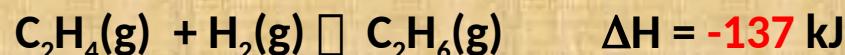
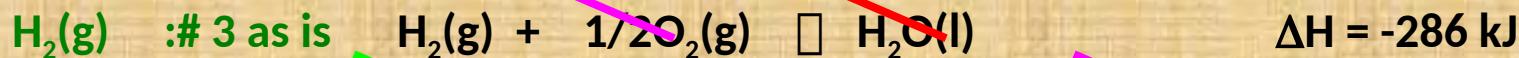
Consult your neighbor if necessary.



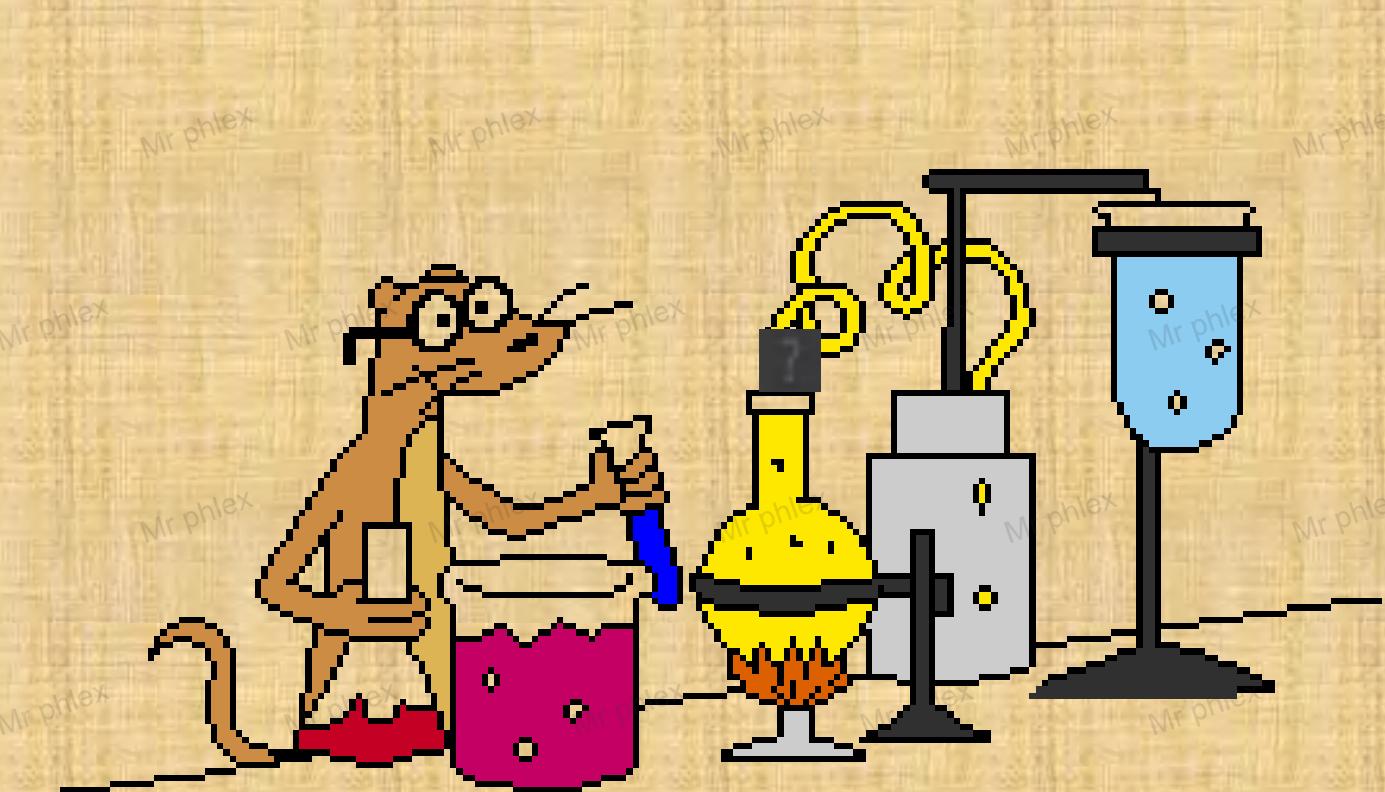
Determine the heat of reaction for the reaction:



Use the following reactions:



Rates of Reaction /Chemical Kinetics



- Most chemical reactions are spontaneous reactions. These reactions occur from left to right till all the reactants are converted to products.



- A spontaneous reaction may be slow or it may be fast. For example:

— *The reactions between aqueous sodium chloride and silver nitrate is a fast reaction.*

e.g. the precipitate of AgCl is formed as fast as AgNO₃ solution is added to NaCl solution.



— *On the contrary, the rusting of iron is a slow reaction that occurs over the years.*



- The branch of Physical chemistry which deals with the rate of reactions is called **Chemical Kinetics**
- The study of Chemical Kinetics includes :
 - *The rate of the reactions and rate laws.*
 - *The factors as temperature, pressure, concentration and catalyst, that influence the rate of a reaction.*
 - *The mechanism or the sequence of steps by which a reaction occurs.*



REACTION RATE

- The rate of a reaction tells as to what speed the reaction occurs.
- Consider a simple reaction



- The concentration of the reactant A decreases and that of B increases as time passes.
- The rate of reactions is defined as the change in concentration of any of reactant or products per unit time.
- For the given reaction, ***the rate of reaction*** may be equal to the rate of ***disappearance of A*** which is equal to the rate of ***appearance of B***.

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$



UNITS OF RATE

- Reactions rate has the units of concentration divided by time.
 - $[\text{mol dm}^{-3}] / \text{sec}$ or $\text{mol dm}^{-3} \text{ s}^{-1}$
 - $[\text{mol dm}^{-3}] / \text{min}$ or $\text{mol dm}^{-3} \text{ min}^{-1}$
 - $[\text{mol dm}^{-3}] / \text{hour}$ or $\text{mol dm}^{-3} \text{ h}^{-1}$ and, so on



Average Rate of Reaction

- Consider the reaction,



$$rate = -\frac{\Delta[\text{CO}]}{\Delta t} = -\frac{d[\text{CO}]}{dt}$$

- The concentration of CO was found experimentally every 10 seconds.

| | | | | | |
|--------------------------|-----|-------|------|------|-------|
| [CO] mol/dm ³ | 0.1 | 0.067 | 0.05 | 0.04 | 0.033 |
| Time (s) | 0 | 10 | 20 | 30 | 40 |

- Over the first 10 seconds, the average rate is

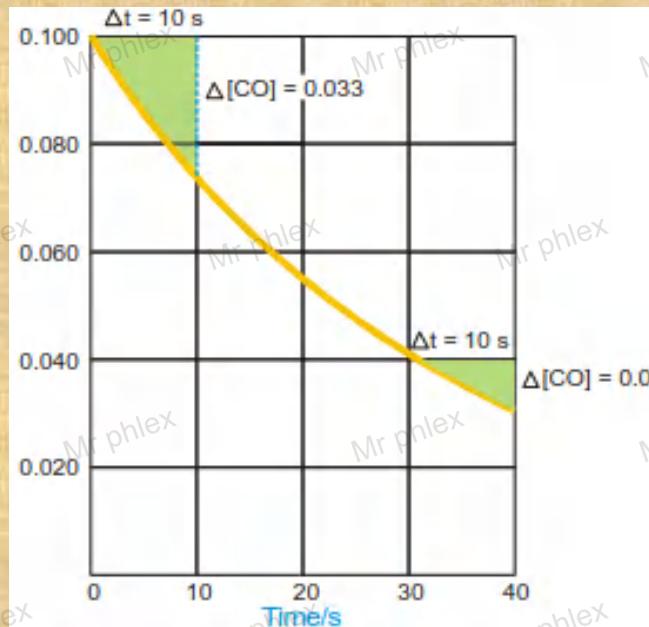
$$rate = -\frac{d[\text{CO}]}{dt} = -\frac{(0.067 - 0.1)}{10 - 0} = 0.0033 \text{ mol dm}^{-3} \text{ s}^{-1}$$



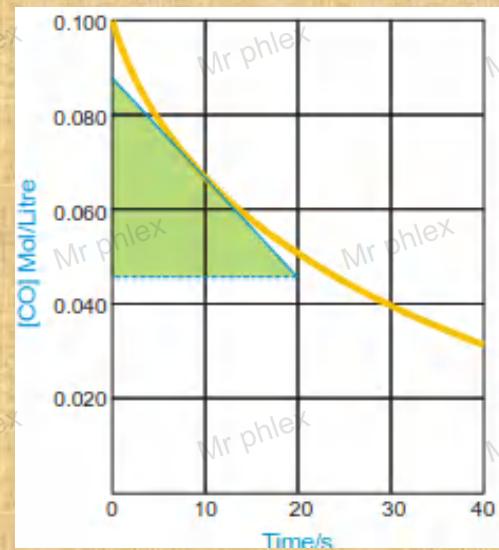
- In the time interval between 30 and 40 seconds, the average rate is much smaller.

$$\text{rate} = -\frac{d[\text{CO}]}{dt} = \frac{(0.033 - 0.04)}{40 - 30} = 0.0007 \text{ mol dm}^{-3} \text{ s}^{-1}$$

- So, a better way to estimate the rate of reaction, we need to make the time interval as small as possible.



The average rate is equal to the slope of the curve.



The slope of tangent at 10 seconds is equal to the instantaneous rate



Instantaneous Rate of Reaction

- The average rates obtained by finding the slope of the curve are not always useful.
- They cover a large time interval during which the rate of reaction changes significantly.
- So, a better way to estimate the rate of a reaction is to make the time interval as small as possible.
- If the interval is infinitesimally small (that is as Δt approaches zero), the rate is referred to as the instantaneous rate
- Thus at any time the instantaneous rate is equal to the slope of a straight line drawn tangent to the curve at that time

$$\text{rate} = - \frac{d[]}{dt}_t$$



RATE LAWS

- The rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

$$\text{rate} \propto [A]^n$$

$$\text{rate} = k[A]^n$$

- For a reaction $2A + B \rightarrow \text{products}$, the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as:

$$\text{rate} = k[A]^n[B]^m$$

The power (exponent) of concentration n or m in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant k is called the rate constant for the reaction.

- An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.



| REACTIONS | | RATE LAW |
|-----------|---|--|
| (1) | $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ | $\text{rate} = k[\text{N}_2\text{O}_5]$ |
| (2) | $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$ | $\text{rate} = k[\text{H}_2][\text{I}_2]$ |
| (3) | $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$ | $\text{rate} = k[\text{NO}_2]^2$ |
| (4) | $2\text{NO} + 2\text{H}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ | $\text{rate} = k[\text{H}_2][\text{NO}]^2$ |

- The rate law cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action.
- The rate law must be determined by experiment, however, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation.
- But usually the powers of concentration in the rate law are different from coefficients.



ORDER OF A REACTION

- The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

$$\text{rate} = k[A]^n[B]^m$$

Overall order of reaction = m + n

- The order of a reaction can also be defined with respect to a single reactant.
- Thus the reaction order with respect to **A** is **m** and with respect to **B** it is **n**.
- The overall order of reaction may range from 1 to 3 and can be fractional.



RATE LAW

$$\text{rate} = k[\text{N}_2\text{O}_5]$$

1

$$\text{rate} = k[\text{H}_2][\text{I}_2]$$

1 + 1 = 2

$$\text{rate} = k[\text{NO}_2]^2$$

2

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

1 + 2 = 3

$$\text{rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

1 + 1/2 = 1 1/2

- Based on the rate law above, reactions may be classified according to the order as:

- $m + n = 1$, it is first order reaction
- $m + n = 2$, it is second order reaction
- $m + n = 3$, it is third order reaction
- $m + n = 1\frac{1}{2}$ Fractional order

- Consider the reaction,



- The rate law for the equation above is given as

$$\text{Rate} = k[\text{NO}_2]^2$$

The reaction is zeroth order with respect to CO and second order with respect to $[\text{NO}_2]$. The overall reaction order is $2 + 0 = 2$

A zero order reaction is one whose rate is independent of concentration.

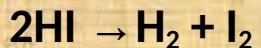


MOLECULARITY OF A REACTION

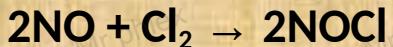
- Chemical reactions may be classed into two types:
 - Elementary reactions
 - Complex reactions
- An elementary reaction is a simple reaction which occurs in a single step while complex reaction involved two or more steps.
- The molecularity of an elementary reaction is defined as: the number of reactant molecules involved in a reaction.
- Unimolecular reactions : (molecularity = 1)



- Bimolecular reactions : (molecularity = 2)



- Termolecular reactions : (molecularity = 3)



- The term **molecularity** is often confused with order of a reaction.
- The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the molecularity of reaction.
- The sum of the powers to which the concentrations are raised in the rate law is known as the order of reaction.

Order of a Reaction

- It is the sum of powers of the concentration terms in the rate law expression.
- It is an experimentally determined value.
- It can have fractional value.
- It can assume zero value.
- Order of a reaction can change with the conditions such as pressure, temperature, concentration.

Molecularity of a Reaction

- It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction.

- It is a theoretical concept.
- It is always a whole number.
- It can not have zero value.

Molecularity is invariant for a chemical equation



PSEUDO-ORDER REACTIONS

- A reaction in which one of the reactants is present in a large excess shows an order different from the actual order.
- The experimental order which is not the actual one is referred to as the pseudo-order.
- Elementary reactions have similar molecularity and order, thus, pseudo-order reactions is known as pseudo molecular reactions.
- consider a reaction: $A + B \rightarrow \text{products}$
- If B is present in a large excess (i.e. its concentration remains practically constant in the course of reaction).

$$\text{rate} = k [A] [B]$$

$$\text{rate} = k' [A]$$

$$k' = k [B].$$

- Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a pseudo-first order.



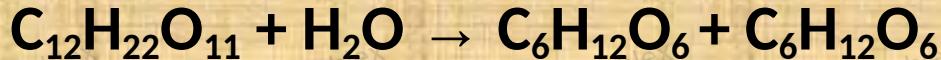
Examples of Pseudo-order Reactions

- Hydrolysis of an ester: hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.



$$\begin{aligned}\text{rate} &= k [\text{CH}_3\text{COOH}][\text{H}_2\text{O}] \\ &= k' [\text{CH}_3\text{COOH}]\end{aligned}$$

- Hydrolysis of sucrose: in the presence of a dilute mineral acid hydrolysis of sucrose produces glucose and fructose.



$$\begin{aligned}\text{rate} &= k [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}] \\ &= k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}]\end{aligned}$$



RATE LAWS

- **ZERO ORDER REACTIONS**

$A \rightarrow \text{Products}$

Initial conc.

$$[A_0]$$

Final conc.

$$[A_0] - [A_t]$$

$$[A_t]$$

$$-\frac{d[A]}{dt} = k_0[A]^0$$

$$-\frac{d[A]}{dt} = k_0[A]^0 = k_0$$

Upon integration

$$k_0 = \frac{[A]_t}{t}$$

$$[A]_t = k_0 t$$

the rate constant is equal to the rate of reaction at all concentrations.



• FIRST ORDER REACTIONS

$A \rightarrow \text{Products}$

Initial conc.

$$[A_0]$$

$$0$$

Final conc.

$$[A_0] - [A_t]$$

$$[A_t]$$

$$-\frac{d[A]}{dt} = k_1[A]^1$$

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[A]}{[A]} = -k_1 dt$$

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]} = - \int_0^t k_1 dt$$

$$\ln[A]_0 - \ln[A] = kt$$

$$\ln \frac{[A]_0}{[A]} = kt$$

Upon integration



• SECOND ORDER REACTIONS



Initial conc.

$$[A_0]$$

$$0$$

Final conc.

$$[A_0] - [A_t]$$

$$[A_t]$$

$$-\frac{d[A]}{dt} = k_2[A]^2$$

$$\frac{d[A]}{dt} = -k_2[A]^2$$

$$\frac{d[A]}{[A]^2} = -k_2 dt$$

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^2} = - \int_0^t k_2 dt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_2 t$$

Upon integration



• THIRD ORDER REACTIONS



Initial conc.

$$[A_0]$$

$$0$$

Final conc.

$$[A_0] - [A_t]$$

$$[A_t]$$

$$-\frac{d[A]}{dt} = k_3[A]^3$$

$$\frac{d[A]}{dt} = -k_3[A]^3$$

$$\frac{d[A]}{[A]^3} = -k_3 dt$$

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^3} = - \int_0^t k_3 dt$$

$$\frac{1}{2[A]_t^2} - \frac{1}{2[A]_0^2} = k_3 t$$

Upon integration



The units of rate constant for different orders of reactions are different.

- Units of Zero order Rate constant

For a zero order reaction, the rate constant k is given by the expression:

$$k_0 = \frac{[A]_t}{t}$$

[A]_t is in mol dm⁻³ while t is in sec, min, hr or years, thus the unit of k₀ is in mol dm⁻³ s⁻¹

- Units of first order Rate constant

$$k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$$

The unit of k₁ is in s⁻¹ since the ln [A]_t unit less

- Units of second order Rate constant

$$k_2 = \frac{[A]_0 - [A]_t}{[A]_t [A]_0 t}$$

The unit of k₂ is in mol⁻¹ dm³ s⁻¹

- Units of third order Rate constant

$$k_3 = \frac{[A]_0^2 - [A]_t^2}{[A]_t^2 [A]_0^2 t}$$

The unit of k₃ is in mol⁻² dm² s⁻¹



- Half-life is the time required for the concentration of a reactant to decrease to half its initial value.
- Half-life of Zero order Rate constant

$$t_{1/2} = \frac{[A]_0}{2k_0}$$

[A]_t is half of initial concentration

- Half-life of first order Rate constant

$$t_{1/2} = \frac{1}{k_1} \ln \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{1}{k_1} \ln 2 = \frac{0.693}{k_1}$$

- Half-life of second order Rate constant

$$t_{1/2} = \frac{\frac{1}{2}[A]_0}{\frac{1}{2}[A]_0[A]_0 k_2} = \frac{1}{[A]_0 k_2}$$

- Half-life of third order Rate constant

$$t_{1/2} = \frac{[A]_0^2 - \frac{1}{4}[A]_0^2}{\frac{1}{4}[A]_0^2 [A]_0^2 k_3} = \frac{3}{[A]_0^2 k_3}$$



EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

- As the temperature increases the rate of reaction also increases. As a rule, an increase of temperature by 10°C doubles the reaction rate.
- Arrhenius suggested a simple relationship between the rate constant, k , for a reaction and the temperature of the system.

$$k = Ae^{-\frac{E_a}{RT}}$$

This is called the Arrhenius equation in which A is an experimentally determined quantity, E_a is the activation energy, R is the gas constant, and T is Kelvin temperature.

- If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\frac{k_1}{k_2} = \frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



Exercises

- If 15% of a substance decomposes in first ten minutes in a first order reaction, calculate how much of it would remain undecomposed after one hour?
- A first order reaction is 15% complete in 20 minutes. What is the half-life period of the reaction?
- A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion ?
- The rate constant for a first order reaction is $1.54 \times 10^{-3} \text{ sec}^{-1}$. Calculate its half-life period.
- Calculate the activation energy of a reaction whose reaction rate at 27°C gets doubled for 10° rise in temperature ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

