Grade 11 Chemistry

Unit 3 –Unit 5 Full ppt

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Grade 11 Chemistry

UNIT 3

PHYSICAL STATES OF MATTER

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Introduction

- **Matter** is defined as anything occupying space and having mass, which is the material of the Universe.
- It exists in three common states: gas, liquid and solid
- The three physical states of water are:

  Steam (water vapor): gaseous state of water

  Water: liquid state of water

  Ice: solid state of water

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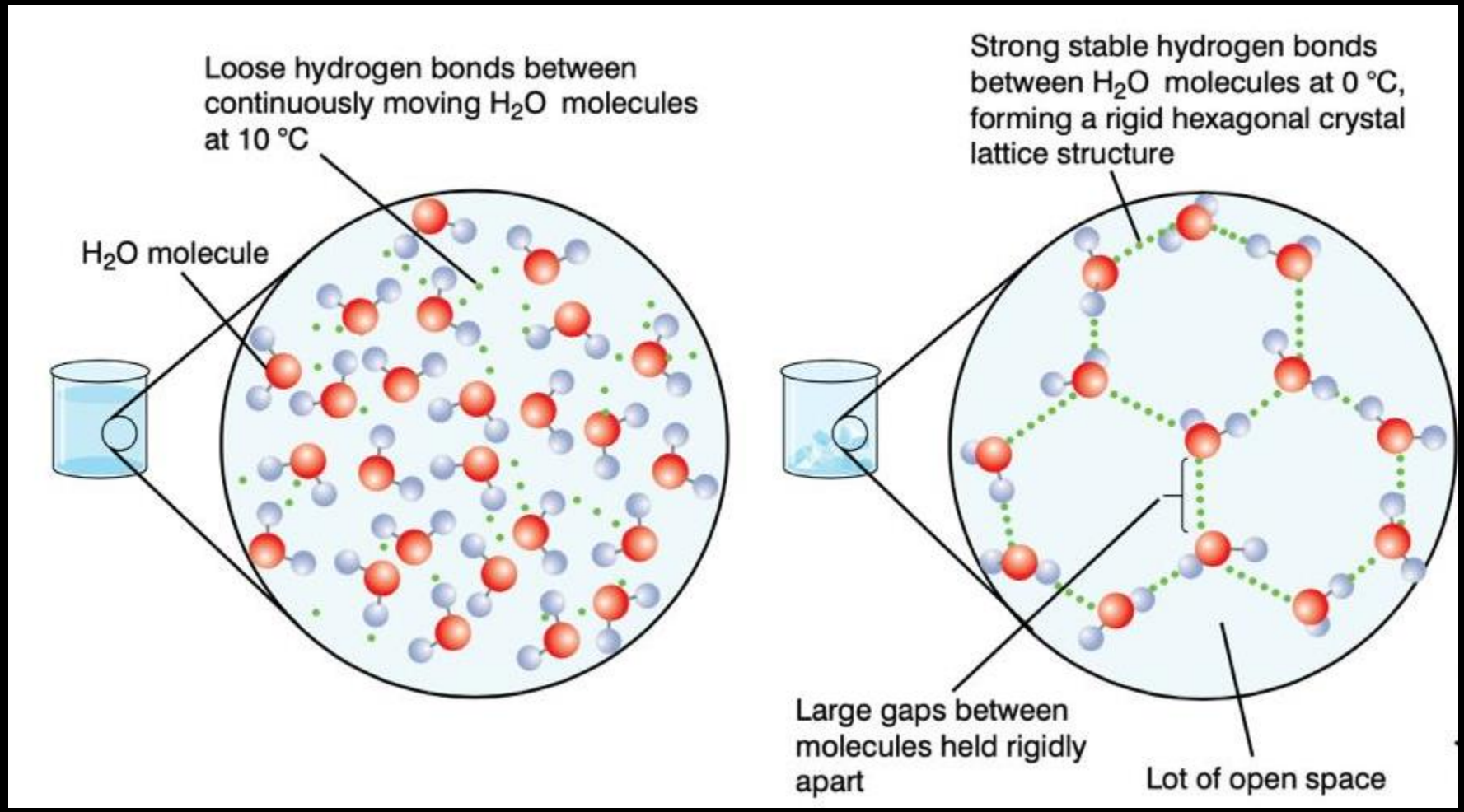
- Most solids change to liquids and most liquids change to gases as they are heated.
- Liquids and gases are known as **fluids** because they flow freely.
- Solids and liquids are referred to as **condensed states** because they have much higher densities than gases.
- Generally, the physical states of matter can be changed to solids, liquids, gases, or plasma by varying temperature and/or pressure.

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Solid

- A solid is rigid; it has a fixed volume and a fixed shape.
- Solids cannot be compressed.
- Solids have higher densities than liquids because their particles are usually packed closer than those in liquids.
- The tightly packed particles of solids are also highly organized.
- The particles of a solid, whether they are atoms, ions or molecules, only vibrate at a fixed point with respect to the neighboring particles.
- As a result, its particles stay in a fixed position.
- Metals, chalk, sand, soil, and stone are examples of solids.

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Liquid

- A liquid has a definite volume, but does not have a definite shape.
- It takes the shape of its container.
- It is very slightly compressible and has the ability to flow.
- In a liquid, particles vibrate about a point, and constantly shift their positions.
- Water, ethanol, mercury, bromine, and oil are examples of liquids

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Gas

- A gas has neither definite volume nor definite shape; it takes on the shape and volume of its container.
- Gas is highly compressible because most of the volume of a gas is composed of the large amounts of empty space between the gas particles.
- For example, air, hydrogen, oxygen, carbon dioxide, and nitrogen are gases

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Plasma

- Plasma is the fourth physical state of matter that exists at a high temperature (million degrees Celsius).
- At such high temperatures molecules cannot exist.
- Most or all of the atoms are stripped of their electrons and thus, exist in their ionized form.
- This state of matter, a gaseous mixture of positive ions and electrons, is called **plasma.**
- In another word, plasma is **an ionized gas**. Because of the extreme temperatures needed for fusion, no material can exist in the plasma state.
- Like gases, plasmas have no fixed shape and a fixed volume. They are also less dense than solids or liquids

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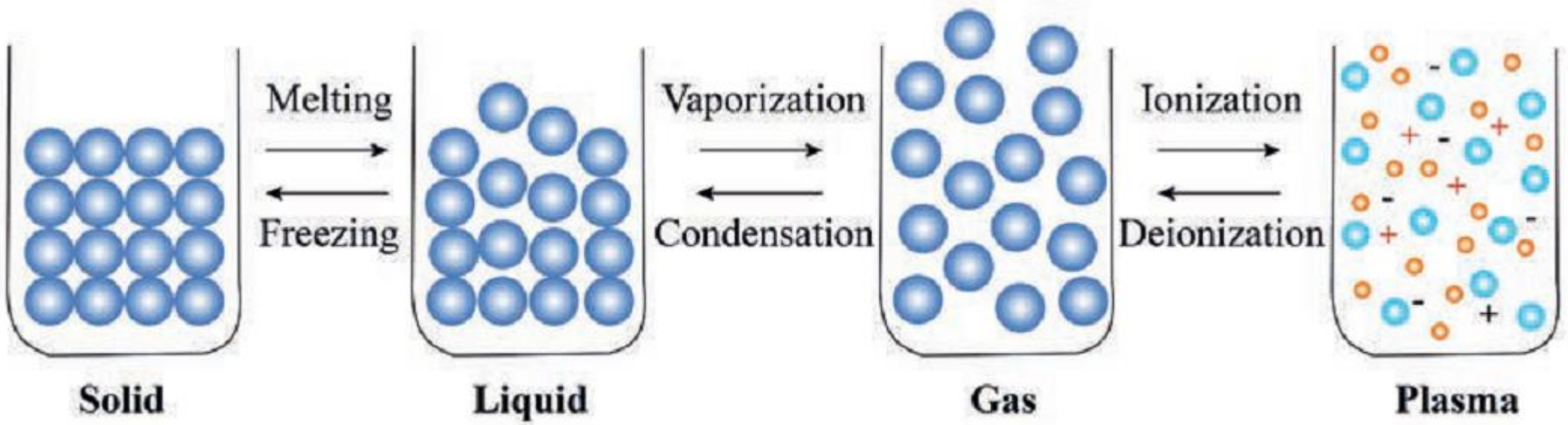


Figure 3.1: A particle diagram of a solid, liquid, gas and plasma

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kinetic theory and properties of matter

- The three states of matter in which substances are chemically the same but physically different are explained by the kinetic theory of matter.
- The kinetic theory of matter gives an explanation on the nature of the motion and the heat energy.
- According to the kinetic theory of matter, every substance consists of a very large number of very small particles called ions, atoms and molecules.
- The particles are in a state of continuous and random motion with all possible velocities.
- The motion of the particles increases with a rise in temperature.

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Generally, the kinetic theory of matter is based on the following assumptions:

1. All matter is composed of particles that are constantly moving.

2. All particles have kinetic energy (movement energy) and potential energy.

- **Molecules in the solid phase have the least amount of energy, while gas particles have the greatest amount of energy.**

3. The difference between the three states of matter is the energy contents they have and the motion of the particles. A change in phase may occur when the energy of the particles is changed.

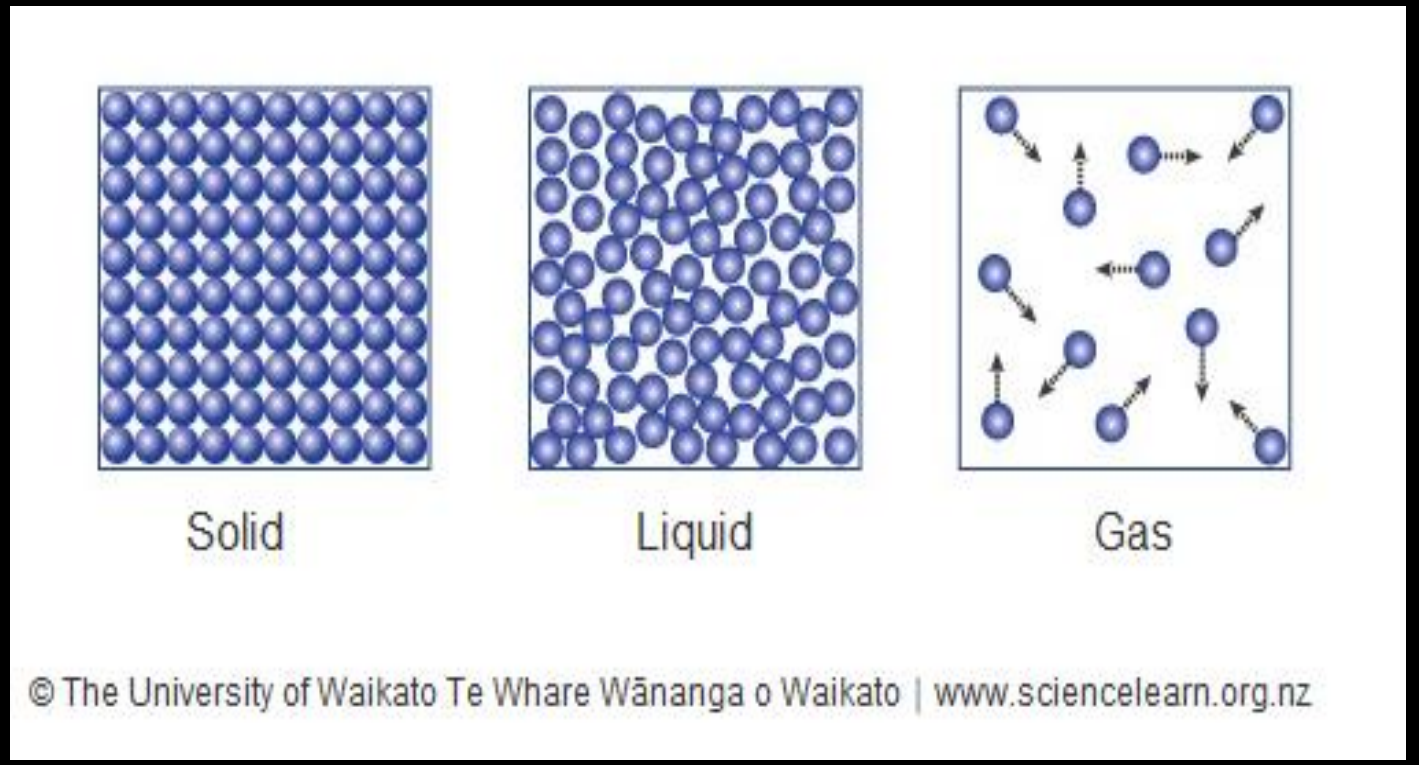
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4. The temperature of a substance is a measure of the average kinetic energy of the particles.

5. There are spaces between particles of matter. The average amount of empty space between molecules gets progressively larger as a sample of matter moves from the solid to the liquid and gas phases.

6. There are attractive forces between atoms/molecules, and these become stronger as the particles move closer together. These attractive forces are called **intermolecular forces.**

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Properties of Matter

- The properties of these three states of matter are explained in terms of the kinetic theory as follows:

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Properties of Gases

- From the kinetic molecular theory of gases, the following general properties of gases can be summarized.

1. Gases have no fixed shape and fixed volume. They assume the volume and shape of their containers.

2. Gases can be easily compressed. By applying pressure to the walls of a flexible container, gases can be compressed; the compression results in a decrease of its volume. This happens due to the large spaces between the particles of gases.

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3. Gases have low densities compared to liquids and solids. Because the particles of a gas are very far apart each other and the number of molecules per unit volume is very small.A small mass of a gas occupies a large volume and hence results in a very low density.

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4. Gases exert pressure in all directions. Gases that are confined in a container exert pressure on the walls of their container. This pressure is due to collisions between gas molecules and the walls of the container.

5. Gases easily flow and diffuse through one another. A gas moves freely and randomly throughout a given space.

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Properties of Liquids

Liquids have the following properties:

1. **Liquids have a definite volume, but have no definite shape.** They assume the shapes of their container. Lack of a definite shape for liquid substances arises from low intermolecular forces of attraction between their particles as compared to that of solids.

2. **Liquids have higher densities than gases.** Their density is a result of the close arrangement of liquid particles. Thus, the particles are closer in liquid than in their gaseous state. This accounts for the higher densities of liquids as compared to gases.

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3. Liquids are slightly compressible. The available free space between particles in liquids is very little as a result, liquids resist an applied external force

4. Liquids are fluids. A fluid is a substance that can easily flow. Most liquids naturally flow downwards due to gravitational force. But, the fluidity of liquids is much slower than gases.

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Properties of Solids

- Solids have the following properties:

1. Solids have a definite shape and definite volume, due to the presence of the strong force of attraction between the particles in a solid.

2. Solids generally have higher densities than gases and liquids. The particles of solids are very close to each other, and thus, there is almost no free space between the particles of solids. This closeness of particles makes solids to have more particles (mass) per unit volume.

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3. Solids are extremely difficult to compress because the high interparticle forces of attraction between the particles of solids are very strong due to a very short distance between them.

4. Solids are not fluids. Solids normally do not flow because particles of solids are rigidly held in position by strong forces that restrict them

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The Gaseous State

Assumptions of the kinetic molecular theory of gases:

1. A gas is a collection of particles (molecules) in constant, straight-line motion.

2. Gas particles do not attract or repel each other, they do not interact. The particles collide with each other and with the surfaces around them, but they bounce back from these collisions like pool balls.

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3. There is a lot of space between gas particles compared with the size of the particles themselves. In other word, the volume of the particles is negligible compared to the total volume of the gas.

- The molecules are so far apart, the total volume of the molecules is extremely small compared with the total volume of the gas.
- This assumption explains why gases are so easily compressed and why they can mix so readily.

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4. The average kinetic energy of gas particles is proportional to the temperature of the gas in kelvins.

- **This means that as the temperature increases, the particles move faster and therefore have more energy. The mathematically expressed as:**

$$\mathrm{KE} = \frac{1}{2}mv^2$$

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Generally, the gaseous state is characterized by the following physical properties:

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than solids and liquids.
- The volume and the shape of gases are not fixed. These take the volume and shape of the container.
- Gases mix evenly and completely.
- Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible.

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GAS lAWS

- The gas laws are the result of various research conducted for several centuries on the physical properties of gases.
- The first reliable measurement on the properties of gases was made by Robert Boyle in 1662 (an Anglo-Irish scientist).
- The observation of Boyle's and other scientists led to the development of the gas laws.
- The gas laws express mathematical relationships between the volume, temperature , pressure, and quantity of a gas.

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- **Pressure:** The pressure exerted by a gas sample is defined as the force per unit area that results from the collisions of gas particles with surrounding surfaces.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

- Pressure is one of the measurable properties of gases. Thus, the pressure of a gas can be expressed in unit of atmosphere, Pascal, torr, millimeter of mercury.
- The SI unit of pressure is Pascal (Pa).

$1\ \text{Pa} = 1\ \text{N/m}^2$ and

$1\ \text{atm} = 760\ \text{mmHg} = 76\ \text{cmHg} = 760\ \text{torr} = 101{,}325\ \text{Pa} = 101.325\ \text{kPa}$

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Volume: Volume is the space occupied by a substance.

- The SI unit of volume is the cubic meter (m^3).
- Volume is also expressed in cubic centimeter (cm^3) and cubic decimeter (dm3).
- Other common units of volume are milliliter (mL) and liter (L).

$$1\ cm^3 = (1\times10^{-2}\ m)^3 = 1\times10^{-6}\ m^3$$

$$1\ dm^3 = (1\times10^{-1}\ m)^3 = 1\times10^{-3}\ m^3 = 1\ L$$

A liter is equivalent to one cubic decimeter, as follows:

$$1\ L = 1000\ mL = 1000\ cm^3 = 1\ dm^3$$

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Temperature: Temperature is the degree of hotness or coldness of a body. Three temperature scales are commonly used.

- These are °F(degrees Fahrenheit), °C (degrees Celsius) and K(Kelvin).
- In calculations, the Kelvin scale is usually used.
- The three units are inter-converted by Equations 3.3 and 3.4:

$$K = °C + 273$$

$$°C = (°F - 32)\ 5/9$$

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Molar Volume and Standard Conditions:

- The conditions of a pressure of 1 atmosphere and a temperature of 0°C (273K) are called standard temperature and pressure (STP) for gases.
- At STP the volume of one mole of any gas is 22.4 liters. This volume is known as the molar volume of gases.

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i. Boyle's Law

- The first quantitative experiments on gases were performed by Robert Boyle(1662).
- His experiment helped to understand the relationship between the volume and pressure of a fixed amount of a gas at constant temperature.
- On the basis of his experiments, Robert Boyle concluded that, at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume

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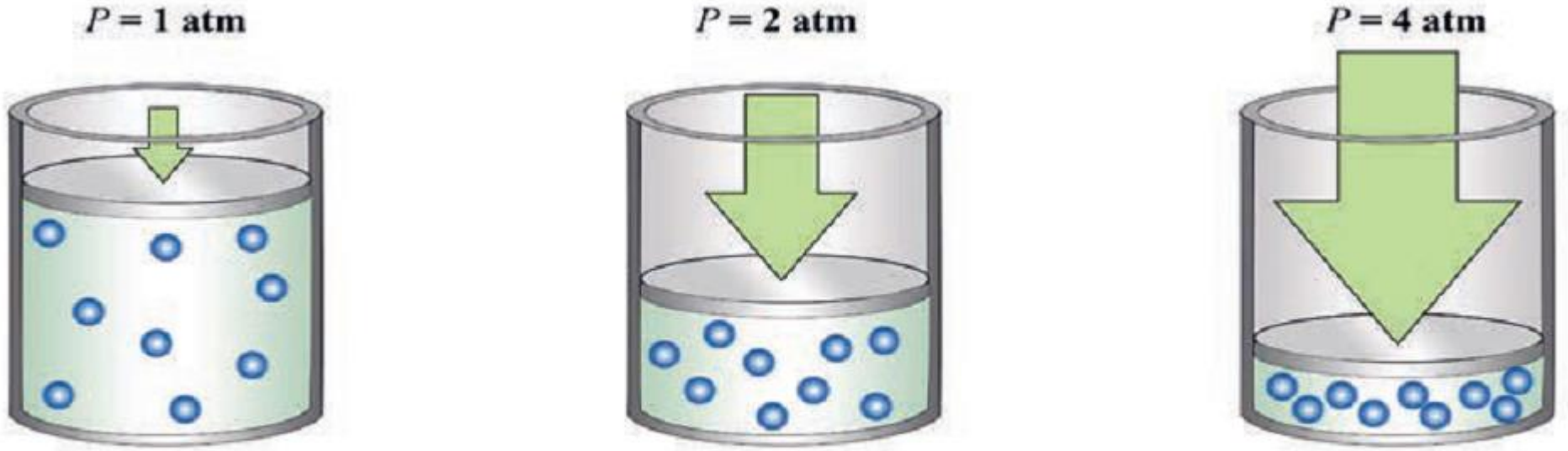


Figure 3.2: The relation between pressure and volume

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- He discovered that at constant temperature doubling the pressure on a sample of gas reduces its volume by one-half, and tripling the gas pressure reduces its volume to one-third of the original.
- Generally, the volume of a gas decreases, as the pressure on the gas increases.

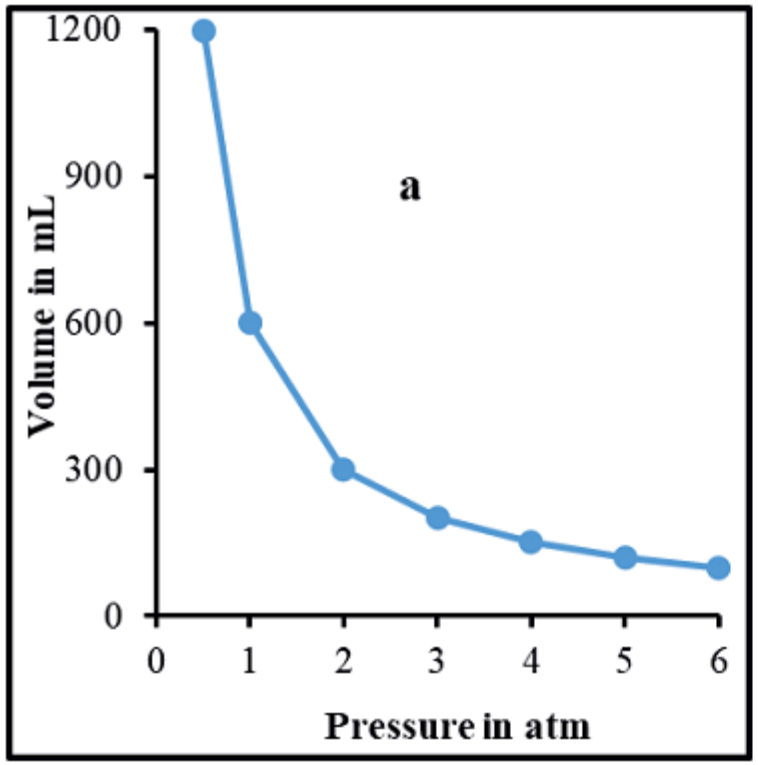
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Table 3.1: Pressure and volume data for a gas at constant mass and temperature

Pressure atm	Volume mL	*PV*
0.5	1200	600
1.0	600	600
2.0	300	600
3.0	200	600
4.0	150	600
5.0	120	600
6.0	100	600

Figure 3.3 (a and b) shows the graphical representation of the relationship between p and v, using the data of **Table 3.1**

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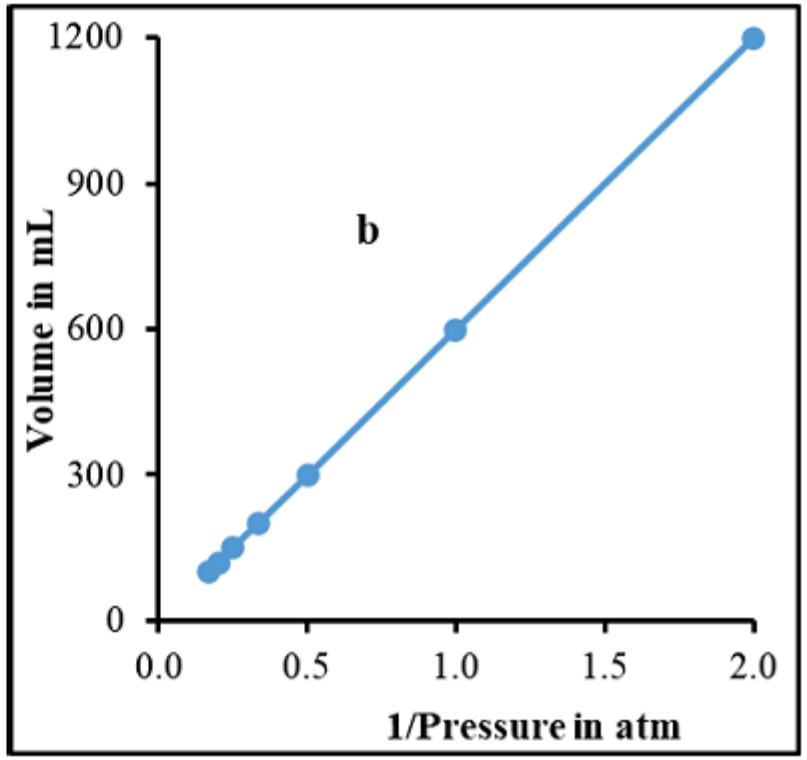


Figure 3.3: Graphs of Boyle's law, using Table 3.1 data: (a) V versus P and (b) V versus 1/P

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- Generally, Boyle's law states that the volume of a fixed mass of gas is inversely proportional to the pressure at a constant temperature. Mathematically this is written as:

$$V \propto \frac{1}{P}$$

$$V = k\left(\frac{1}{P}\right) \text{ or } PV = k$$

$$P_1V_1 = k = P_2V_2$$

$$P_1V_1 = P_2V_2$$

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Example 3.1

Sulfur dioxide (SO_2), that forms acid rain, is found in the exhaust of petrol and diesel vehicles, and power plants. Consider a 1.5 L sample of gaseous SO_2 at a pressure of 5.6 kPa. If the pressure is changed to 15.0 kPa at a constant temperature, what will be the new volume of the gas?

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Exercise 3.4

1. A certain gas occupies a volume of 10.0 m^3 at a pressure of 100.0 kPa. If its volume is increased to 20 m^3, what would be the new pressure of the gas assuming temperature remains constant?

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2. A cylinder equipped with a moveable piston has an applied pressure of 4.0 atm and a volume of 6.0 L. What is the volume of the cylinder if the applied pressure is decreased to 1.0 atm?

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ii. Charles' Law

- Scientists was Jacques Charles (a French physicist), who was the first person to fill a balloon with hydrogen gas and who made the first balloon flight.
- In 1787, Charles found that the volume of a gas at constant pressure increases linearly with the temperature of the gas.

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- For example, doubling the Kelvin temperature causes the volume of a gas to double, and reducing the Kelvin temperature by half causes the volume of a gas to decrease by half.
- This relationship between Kelvin temperature and the volume of a gas is known as **Charles' law.**

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- **Charles' law** states that the volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature.

$$V \propto T$$

$$k = VT$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

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Example 3.2

1. A sample of gas at 15 °C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38 °C and 1 atm?

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2. A sample of gas has a volume of 2.80 L at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume decreases to 2.57 L. What was its initial temperature (in kelvins and in Celsius)?

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Exercise 3.5

1. At constant pressure, by what fraction of its volume will a quantity of gas change if the temperature changes from -173 °C to 27 °C?

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2. At what temperature will the volume of a gas be
   a. halved,
   b. doubled, and
   c. tripled at constant pressure if the original temperature is 17 °C?

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3. At 25 °C and 1 atm a gas occupies a volume of 1.5 dm^3. What volume will it occupy at 100 °C and 1 atm?

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iii. Gay Lussac's Law

- Joseph Louis Gay-Lussac (a French scientist) studied how the pressure and temperature of a fixed amount of gas at constant volume are related.
- The relationship that he established is called **Gay-Lussac's law** or the **pressure-temperature law.**
- It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.
- **Mathematically:**

$$P \propto T$$

$$k = \frac{P}{T}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

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Example 3.3

At a temperature of 25 °C, the pressure of the gas in a deodorant can is 3 atm. Calculate the pressure of the gas when it is heated to 845 °C.

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Exercise 3.6

1. The pressure of a gas in a cylinder when heated to a temperature of 250 K is 1.5 atm. What is the initial temperature of the gas if its initial pressure was 1.0 atm?

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iv. The Combined Gas Law

- A sample of a gas can undergo simultaneous changes in temperature, pressure, and volume. In such cases, the three variables should be considered at the same time.

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- The three gas laws we have learned can be brought together into a single equation known as the **combined gas law** .

The combined gas law expresses the relationship between pressure, volume, and temperature of a fixed amount of gas.

Mathematically:

$$PV \propto T$$

$$\frac{PV}{T} = k$$

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

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Example 3.4

A sample of gas occupies 12.0 L at 240.0 °C under a pressure of 80.0 kPa. At what temperature would the gas occupy 15.0 L if the pressure were increased to 107.0 kPa?

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Exercise 3.7

1. If a 50 cm^3 sample of gas exerts a pressure of 60.0 kPa at 35 °C, what volume will it occupy at STP (0 °C and 1 atm)?

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2. A 280 mL sample of neon exerts a pressure of 660 torr at 26 °C. At what temperature in °C would it exert a pressure of 940 torr in a volume of 440 mL?

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v. Avogadro's law

- In 1811, Amedeo Avogadro (an Italian scientist) suggested that at the same temperature and pressure, equal volumes of gases contain equal numbers of moles.
- This observation is called Avogadro's law, shown as:

$$V \propto n$$

$$\frac{V}{n} = k$$

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- This equation states that for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles (molecules) of gas.
- In other words, equal numbers of molecules of different gases compared at the same temperature and pressure occupy equal volumes.

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- For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

- The volume occupied by a mole of gas at STP, is called **the standard molar volume.**
- It is nearly constant for all gases.
- The standard molar volume of an ideal gas is equal to 22.4 L per mole at STP.
- For an ideal gas: 1mol gas = 22.4 L gas

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Example 3.5

Suppose we have a 12.2 L sample containing 0.50 moles oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25 °C. If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

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Example 3.5

Suppose we have a 12.2 L sample containing 0.50 moles oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25 °C. If all this O_2 were converted to ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

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Exercise 3.8

One mole of a gas occupies 27.0 L, and its density is 1.41 g/L at a particular temperature and pressure. What is its molecular weight? What is the density of the gas at STP?

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vi. The Ideal Gas Equation

- An ideal gas is a hypothetical gas that obeys the gas laws.
- Real gases only obey the ideal gas laws closely at high temperature and low pressure.
- The ideal gas law is a combination of Boyle's law, Charles' law and Avogadro's law.

Boyle's law: $V \alpha P$(at constant T and n)

Charles' law: $V\alpha T$(at constant P and n)

Avogadro's law: $V \alpha n$(at constant P and T)

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- **This relationship indicates how the volume of gas depends on pressure, temperature and number of moles.**

$$V \propto n\frac{T}{P}$$

$$V = Rn\frac{T}{P}$$

At STP ($n = 1$ mol, $V = 22.4$ L, $T = 273$ K (0 °C) and $P = 1$ atm), the values of R can be calculated from the ideal gas equation:

$$R = \frac{PV}{nT} = \frac{1\text{ atm} \times 22.4\text{ L}}{1\text{ mol} \times 273\text{ K}} = 0.082\text{ atm.L/mol.K}$$

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Example 3.6

What pressure, in atm, is exerted by 54.0 g of Xe in a 1.00 L flask at 20.0 °C? (Molar mass of Xe = 131.3 g/mol)

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At STP, 0.280 L of a gas weighs 0.400 g. Calculate the molar mass of the gas.

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Exercise 3.9

1. The density of a gas at a pressure of 1.34 atm and a temperature of 303 K is found to be 1.77 g/L. What is the molar mass of this gas?

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2. A helium-filled weather balloon has a volume of 7240 ft^3. How many grams of helium would be required to inflate this balloon to a pressure of 745 torr at 21°C? (1 ft^3 = 28.3 L)

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vii. Graham's Law of Diffusion

- We have discussed that the gas molecules are in constant, rapid, random motion and occupy quickly throughout any container. This spreading of gas molecules throughout the container is called **diffusion.**

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- Thomas Graham (1805-869), a Scottish chemist, studied the rate of diffusion of different gases.
- He found that gases having low densities diffuse faster than gases that have higher densities.
- Based on his observations, in 1829, he postulated the relationship between the density of a gas and its rate of diffusion, which is known as **Graham's law of diffusion.**

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- **Graham's law of diffusion states that, at constant temperature and pressure, the rate of diffusion of a gas, r, is inversely proportional to the square root of its density, d, or molar mass, M.**

Mathematically it is expressed as:

$$r \ \alpha \ \sqrt{\frac{1}{d}} \qquad Or \qquad r \ \alpha \ \sqrt{\frac{1}{M}}$$

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For two gases (Gas 1 and Gas 2), their rates of diffusion can be given as:

$$r \ \alpha \ \sqrt{\frac{1}{d_1}} \quad Or \quad r \ \alpha \ \sqrt{\frac{1}{M_1}} \tag{3.19}$$

$$r \ \alpha \ \sqrt{\frac{1}{d_2}} \quad \text{Or} \quad r \ \alpha \ \sqrt{\frac{1}{M_2}} \tag{3.20}$$

By rearranging Equations 3.19 and 3.20 we obtainequation 3.21:

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \qquad Or \qquad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \tag{3.21}$$

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Example 3.7

1. Which gas will diffuse faster, oxygen or carbon dioxide? What is the relative rate of diffusion?

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2. The rate of diffusion of methane (CH_4) is twice that of an unknown gas What is the molecular mass of the gas?

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Exercise 3.10

1. A sample of ethane, C_2H_6, diffuses at a rate of 3.6×10^{-6} mol/h. An unknown gas, under the same diffuses at a rate of 1.3×10^{-6} mol/hr. Calculate the molar mass of the unknown gas.

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2. Which gas in each of the following pairs diffuses more rapidly, and what are the relative rates of diffusion?

a. Kr and O_2

b. N_2 and acetylene (C_2H_2)

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LIQUID STATE

- As in a gas, particles in a liquid are in constant motion.
- However, the particles in a liquid are closer together than those in a gas.
- The attractive forces between particles in a liquid are stronger than between particles of a gas.
- This attraction between liquid particles is caused by the intermolecular forces of attraction such as dipole dipole forces, London dispersion forces, and hydrogen bonding.
- Liquids are more ordered than gases because of the stronger intermolecular forces and the lower mobility of liquid particles.

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Energy Change in Liquids

- The process by which a liquid changes to a gas is known as **vaporization or evaporation.**
- **Evaporation** is the process by which molecules on the surface of a liquid break away and go into the gas phase.
- Molecules on the surface of a liquid are held less tightly than those in the interior, so the most energetic molecule can break away into the gas.

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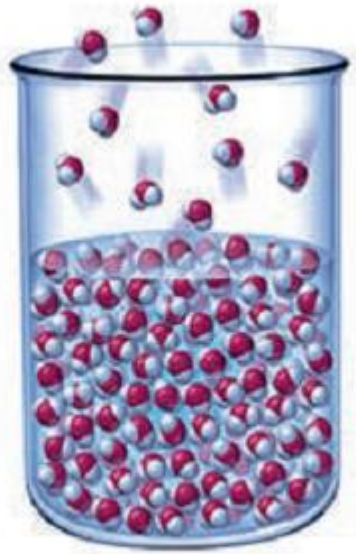


Figure 3.8: Evaporation of liquid

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- Evaporation is explained in terms of the energy that the molecules on the surface of the liquid have.
- In an open container, evaporation continues until all of the liquid enters the gas (vapor) phase (Figure 3.8).
- Most of the molecules that escape into the vapor phase do not collide with the surface of the liquid and return to the liquid phase.
- Instead, they will diffuse through the gas phase away from the container and equilibrium cannot be established.
- Under these conditions, the liquid will continue to evaporate until it has disappeared.

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- However, liquids in a closed container behave differently.
- The volume of the liquid decreases for some time, and then, remains unchanged.
- This is because in closed containers, the vapor cannot escape.
- As more molecules leave the liquid, more gaseous molecules collide with the container walls, with each other, and with the liquid surface and return to the original liquid state.

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- The process of when a vapor returns to the liquid state is called **condensation.**
- Evaporation and condensation are opposing processes.
- Evaporation is a liquid turning into a gas, and condensation is a gas turning into a liquid.

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- For instance, when liquid water is initially put into a closed container, more evaporation happens than condensation because there are so few gaseous water molecules in the space above the water (Figure 3.9a).
- However, as the number of gaseous water molecules increases, the rate of condensation also increases (Figure 3.9b).
- At the point where the rates of condensation and evaporation become equal (Figure 3.9c),**dynamic equilibrium** is reached and the number of gaseous water molecules above the liquid remains constant.

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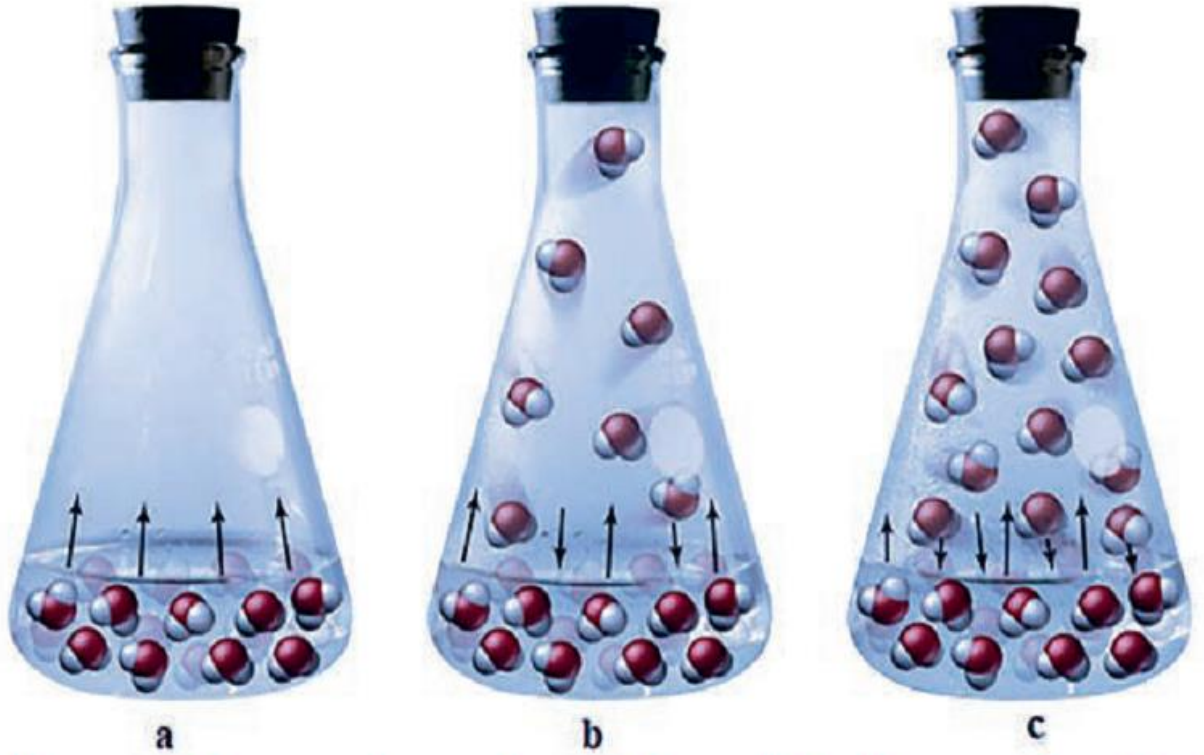


Figure 3.9: Evaporation and condensation: (a) when water is first put into a closed container, water molecules begin to evaporate; (b) Evaporation continues, but condensation also begins to occur; and (c) Dynamic equilibrium: rate of evaporation equals the rate of condensation

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The rate of evaporation of a liquid can be affected by these factors:

- **Temperature**
- **Intermolecular forces and**
- **Surface area of the liquid.**

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Temperature

- An increase in temperature increases the average kinetic energy of the molecules and thus increases the tendency to change into the gaseous state.
- Some liquids evaporate readily at room temperature. Such liquids are said to be **volatile.**
- Volatile liquids have relatively weak forces of attraction between particles.
- Liquids such as formaldehyde, ethyl alcohol, mercury, and benzene are volatile liquids.

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- Liquids that do not vaporize easily at a given temperature are said to be **nonvolatile.**
- They have relatively stronger attractive forces between their molecules.
- Liquids such as motor oil, edible oil, glycerin, water, and molten ionic compounds are nonvolatile.

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Vapor pressure

- The partial pressure of the vapor above a liquid is called **vapor pressure**.
- The vapor pressure of a liquid depends up on the temperature.
- At a given temperature, vapor pressure is constant.
- The vapor pressures of liquids always increase as temperature increases because the rate of evaporation increases with increasing temperature.

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Intermolecular forces

- Vapor pressure depends also on the intermolecular forces between the molecules of the liquid.
- The stronger the intermolecular forces, the lower will be the vapor pressure of the liquid because fewer molecules will have enough kinetic energy to overcome the attractive force at a given temperature.

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- For example, water and ethanol have relatively low vapor pressure because the very strong hydrogen bonding in these liquids account for their unusually low vapor pressures.
- However, liquids with low intermolecular forces have high vapor pressures at room temperature.
- For example, diethyl ether, a non-polar molecule with relatively weak dispersion forces, has a relatively higher vapor pressure.

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Surface area of the liquid

- Evaporation occurs at the liquids surface, where it interfaces with the air surrounding it.
- Liquid surface area is the amount of liquid that is exposed to the atmosphere (air).
- The number of liquid molecules present at the surface increases as the surface area of the container (or the surface area occupied by the liquid) increases.
- This, in turn, increases the number of molecules that separate from the liquid surface and change into gases at a specific moment, increasing the rate of evaporation.

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- **However, for liquids having the same surface area, the rate of evaporation depends on the two factors:**

  Temperature and

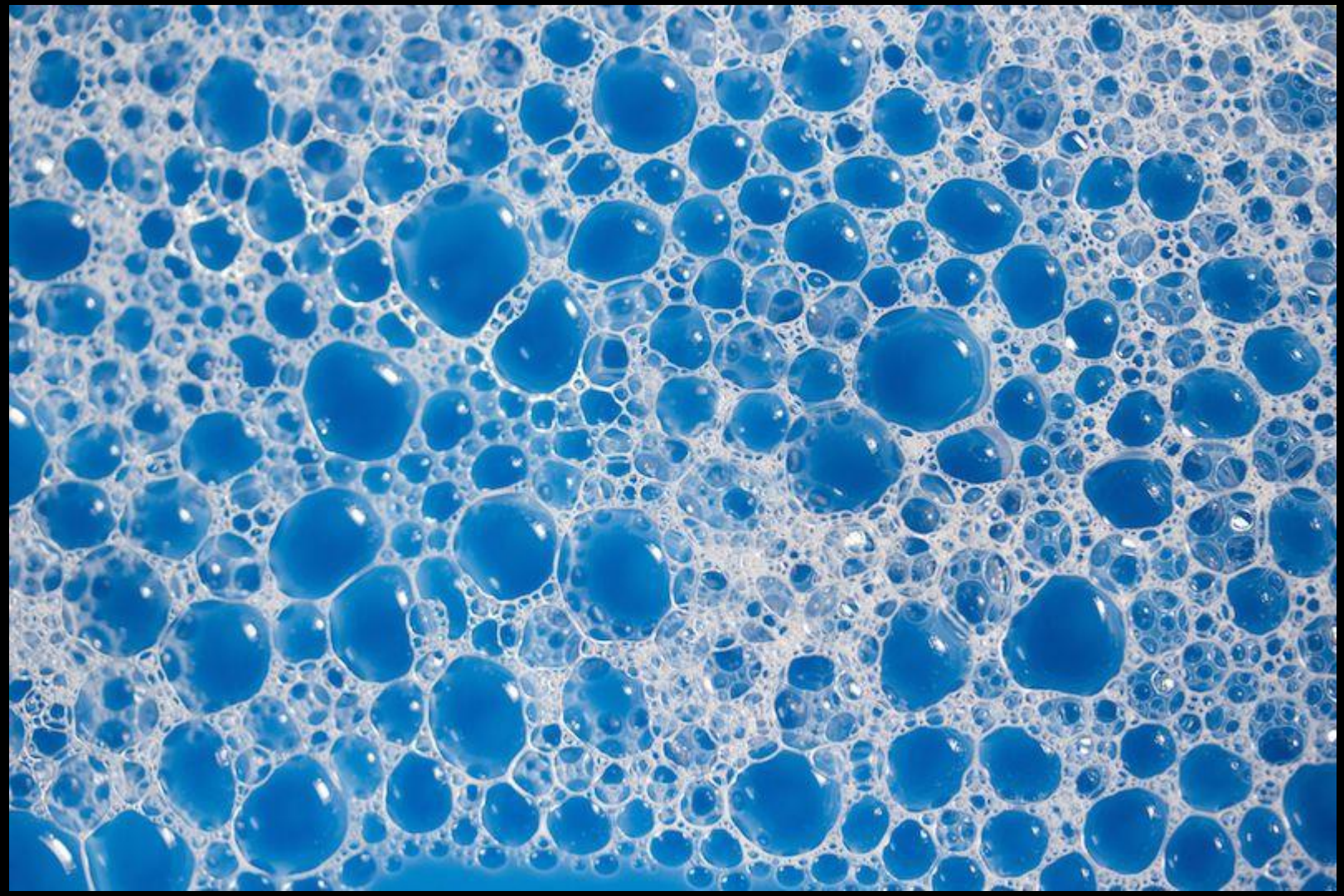
  The strengths of intermolecular attractions.

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Boiling and Boiling Point

- When heat energy is added to a liquid, it increases the kinetic energy of the molecules and the temperature of the liquid increases.
- Heating a liquid always increases its vapor pressure.
- When a liquid is heated to a sufficiently high temperature under a given applied (usually atmospheric) pressure, bubbles of vapor begin to form below the surface.
- If the vapor pressure inside the bubbles is less than the applied pressure on the surface of the liquid, the bubbles collapse as soon as they form.

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- On the other hand, if the temperature is raised sufficiently, the vapor pressure is high enough that the bubbles can persist and rise to the surface, and burst, releasing the vapor into the air.
- This process is called **boiling.** In short, boiling is the change of a liquid to bubbles of vapor that appear throughout the liquids.

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- It is the conversion of liquid to vapor within the liquid as well as at its surface.
- During evaporation, only molecules at the surface escape into the vapor phase.
- It is the formation of vapor bubbles within the liquid itself that characterizes boiling and distinguishes it from evaporation.

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- If the temperature of the liquid is increased, the equilibrium vapor pressure also increases.
- Finally, the boiling point is reached. The boiling point of a liquid is the temperature at which its vapor pressure equals the external atmospheric pressure.
- The normal boiling point is the temperature at which the vapor pressure of a liquid is equal to exactly one atmosphere.

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- For instance, water boils at 100 °C at 1.0 atmospheric pressure and thus, its normal boiling point of water is 100 °C.
- Nevertheless, the boiling point of water at 0.83 atm is 95 °C. Generally, when the pressure exerted on a liquid is varied, the boiling point of a liquid also varies

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- Note that as heat energy is added to vaporize a pure liquid at its boiling point, the temperature remains constant until the liquid is completely changed to vapor .
- Then, the temperature begins to rise after the liquid is completely changed to vapor.

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- **Boiling of a liquid requires a certain amount of heat energy to break the forces of attraction between the molecules.**
- **The amount of heat energy necessary to bring about the vaporization of a fixed amount of a liquid at a fixed temperature to the gaseous state is called the heat of vaporization.**

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- The **molar heat of vaporization** is the amount of heat needed to convert 1 mole of a liquid at its boiling point to a gas.
- It is equal to the amount of energy that is released when 1 mole of vapour condenses to liquid at the condensing point of a vapour.
- During condensation heat is released.
- Thus, the amount of heat realized when 1 mole of a gas is converted to a liquid at its condensation point is called the **molar heat of condensation(ΔHcond).**

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- **Molar heat of vaporization (ΔHvap) and molar heat of condensation (ΔHcond) are equal in magnitude but opposite in sign:**

$$\Delta H_{vap} = -\Delta H_{cond}$$

- **Note that vaporization is an endothermic process whereas condensation is an exothermic process.**

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SOLID STATE

- The temperature at which a pure liquid changes to a crystalline solid, or freezes, is called the freezing point;
- it is identical to the melting point.
- The melting or freezing occurs at the temperature where the liquid and solid are in dynamic equilibrium.

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- When a solid is continuously heated the ordered crystalline structure of solids will be disturbed.
- As a result, particles gradually get freedom of motion and melting (or fusion) take place.
- **Melting** is the process of converting solid into the liquid.
- The temperature at which a crystalline solid changes to a liquid or melts is called the **melting point.**

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- On the other hand, when a liquid is cooled, its molecules come closer to one another and thus, the intermolecular forces of attraction between them get stronger.
- As a result, its particles arrange themselves into a regular pattern and then converted to a solid.
- This process is called **freezing or solidification.**
- For instance, ice melts at 0 °C and water freezes at 0 °C.
- Ice and water coexist in equilibrium at 0 °C as follows:

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- **Unlike boiling points, melting points are affected only by large pressure changes.**
- **Note that both the melting point and the boiling point are characteristics of physical properties of a substance and can be used to help identify it.**

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- The amount of heat needed to convert one gram of solid to liquid at the melting point is called **heat of fusion.**
- The **molar heat of fusion** or **molar enthalpy of fusion** (ΔHfus) is the quantity of heat needed to convert one mole of a solid at its melting point to the liquid state.
- Melting requires the supply of energy; therefore, it is an endothermic process.
- During the process of solidification, the amount of heat liberated is exactly equal to the heat of fusion.
- The heat liberated is called **the heat of solidification** or **heat of crystallization.**

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- **The molar heat of crystallization (ΔHcryst) is the quantity of energy that is removed from one mole of a liquid to convert it to the solid state at its freezing point.**

$$\Delta H_{\text{cryst}} = -\Delta H_{\text{fus}}$$

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- Some solids have significant vapor pressure and thus, evaporate directly from the solid to the vapor state without passing through the liquid state.
- This process is called sublimation,i.e., the change of solid to vapor.
- The opposite of sublimation is deposition that is the change of vapor to solid.



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- The **enthalpy of sublimation, ΔHsub,** is the energy required to convert one mole of a substance from the solid to the gaseous state.
- Sublimation is an endothermic process.
- The **enthalpy of deposition, ΔHdep,** is the energy released when one mole of a substance from the gaseous state change to solid.
- The heat (enthalpy) of sublimation is related to the enthalpies of fusion and vaporization by:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

$$\Delta H_{sub} = -\Delta H_{dep}$$

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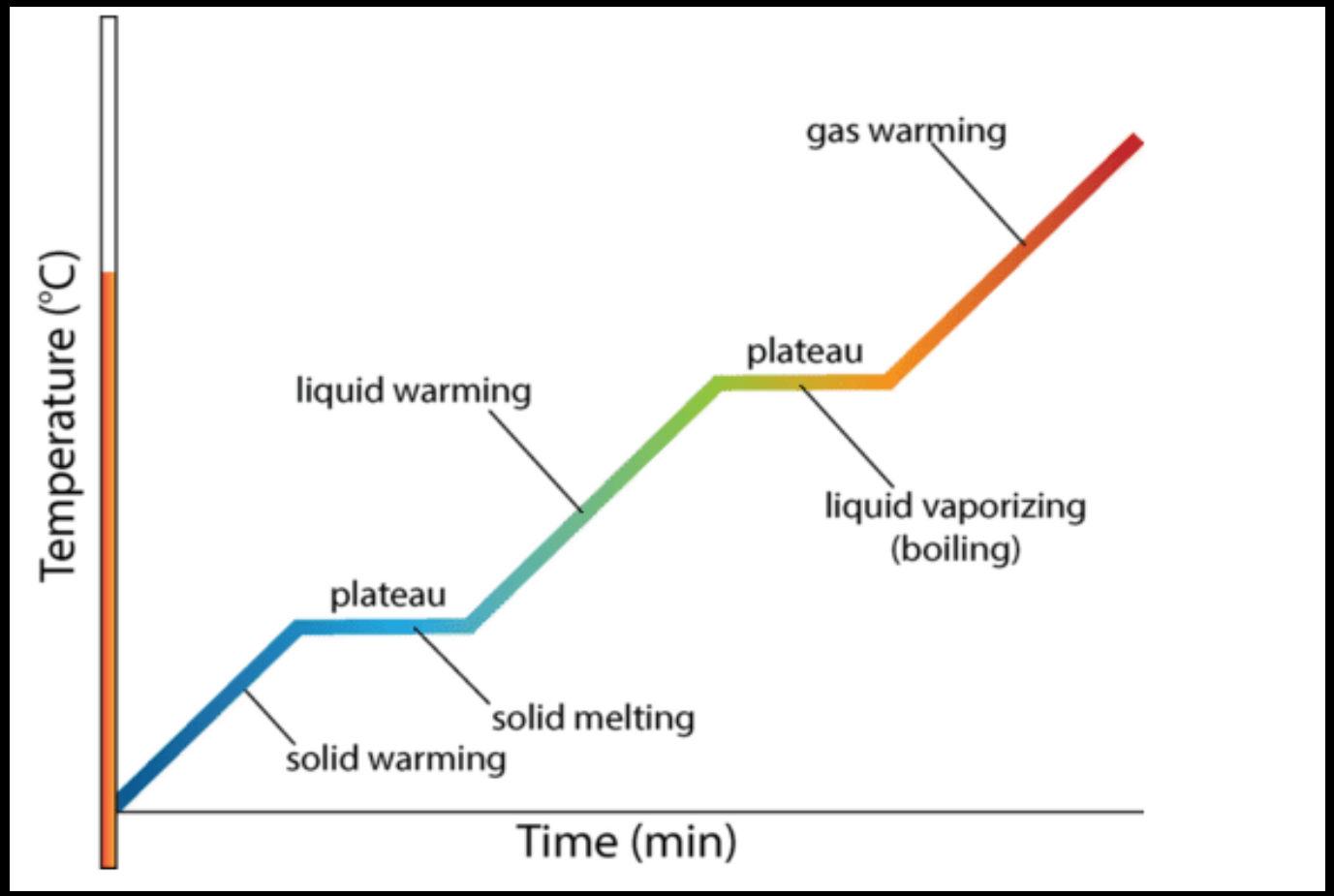
Heating curve

- **Heating curve** is a plot of the temperature versus the amount of heat added
- It is commonly used to show the relationship between phase changes and enthalpy for a given substance.
- There are two main observations that we can learn from the heating curve:

  regions where the temperature increases as heat is added and

  plateaus where the temperature stays constant.
- It is at plateaus that a phase change occurs.

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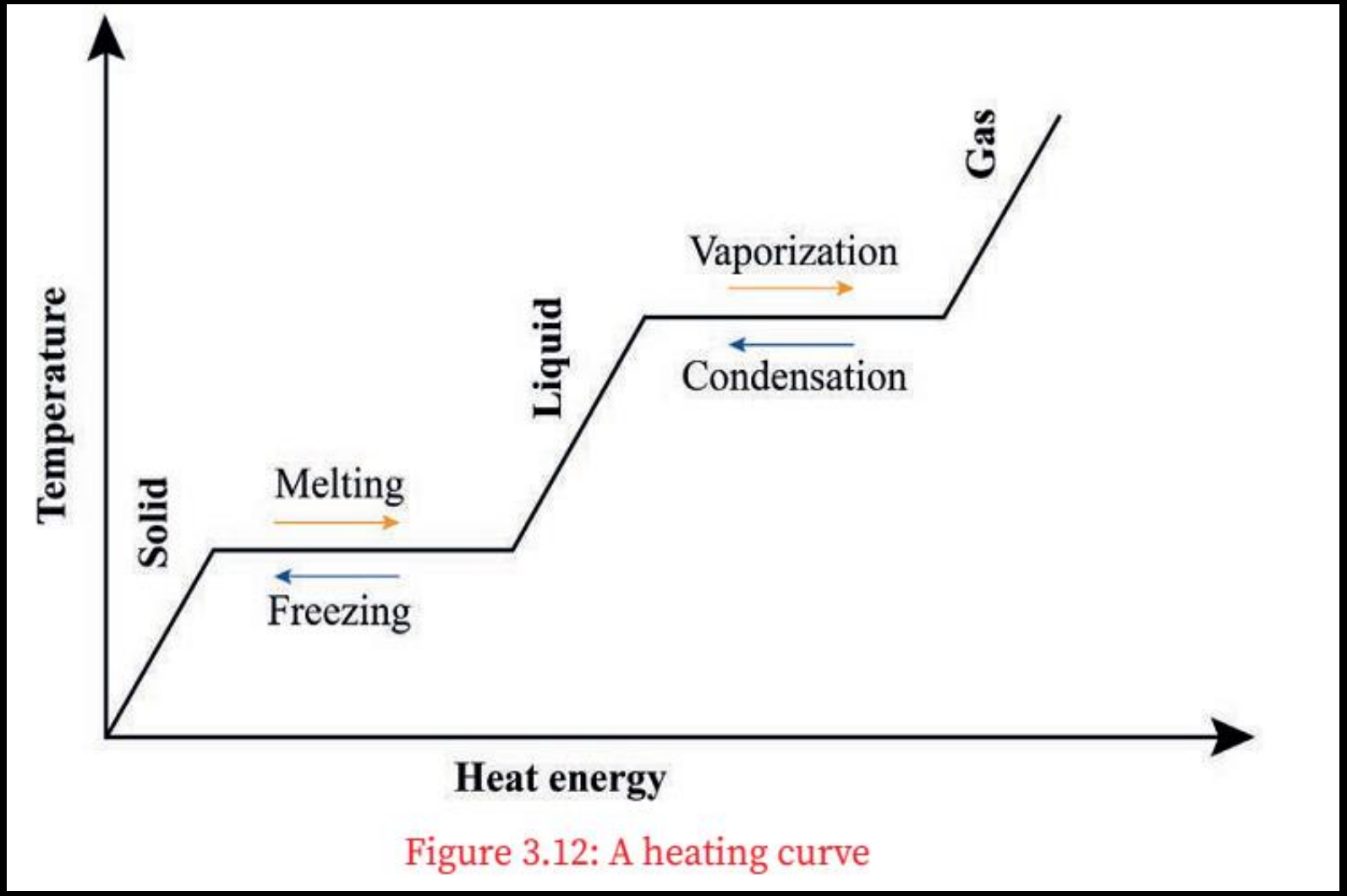


Figure 3.12: A heating curve

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The End

UNIT 4
CHEMICAL KINETICS

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Introduction

- Every chemical reaction proceeds at a different rate or speed.
- Some reactions proceed very slowly and may take a number of days to complete; while others are very rapid, requiring only a few seconds.
- For example, rusting of iron could start quickly, while ripening of fruits may be completed in a few days. On the other hand, weathering of stone may take more than a decade and the breakdown of plastics in the environment takes more than hundred years.
- However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds.

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- To be useful reactions must occur at a reasonable rate.
- The area of chemistry that is concerned with reaction rates is called **chemical kinetics.**
- The word **“kinetic”** suggests movement or change.
- **Chemical kinetics** refers to the rate of reaction, which is the change over times in the concentration of a reactant or a product.

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The Rate of reaction

- The rate of a chemical reaction measures the change in concentration of a reactant or a product per unit time.
- This means that the rate of a reaction determines how fast the concentration of a reactant or product changes with time.

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- For example, for a general reaction:

$$\text{Reactants} \rightarrow \text{Products}$$

- This equation tells us that, during the course of a reaction, reactant molecules are consumed while product molecules are formed.
- As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

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- **It is more convenient to express the rate in terms of change in concentration with time.**

$$\text{Rate of reaction} = \frac{\text{Change in concentration of substance}}{\text{change in time}} = \frac{\Delta c}{\Delta t}$$

Note that Δ denotes the difference between the final and initial state.

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- **Consider the progress of a simple reaction in which A molecules are converted to B molecules:**

A →B

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{A}]}{\Delta t} \quad \text{or rate} = \frac{\Delta[\text{B}]}{\Delta t}$$

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- in which, Δ[A] and Δ[B] are the changes in concentration ($molL^{-1}$) over a period Δt.
- Because the concentration of A decreases during the time interval, Δ[A] is a negative quantity.
- The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive.
- On the other hand, the rate of product formation does not require a minus sign because Δ[B] is a positive quantity (the concentration of B increases with time).

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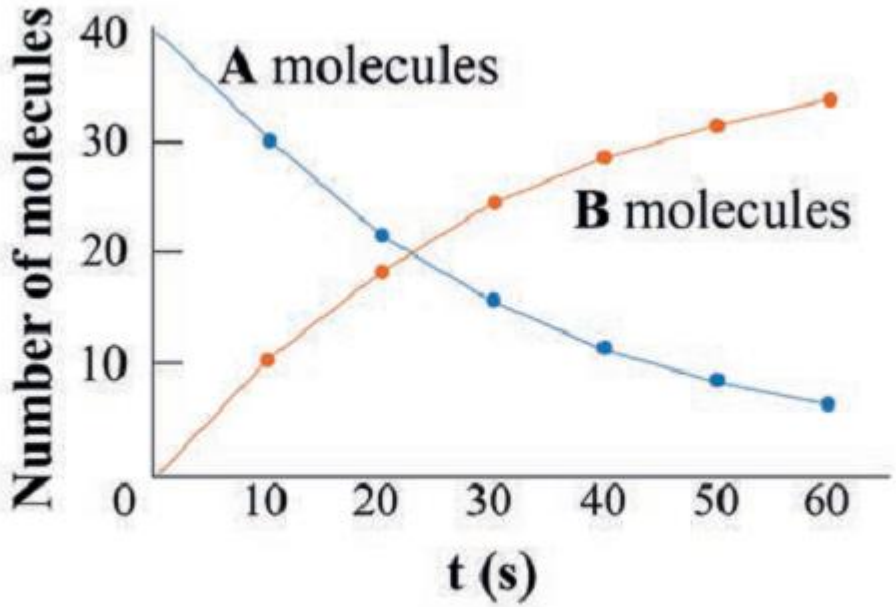


Figure 4.1: The rate of reaction A → B, represented as the decrease of A molecules with time and the increase of B molecules with time

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- For more complex reactions, we must be careful in writing the rate expression.
- Consider, for example, the reaction:

$$2A \rightarrow B$$

- Two moles of A disappear for each mole of B that forms, that is, the rate at which B forms is one half the rate at which A disappears.
- We write the rate as either:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \quad \text{or rate} = \frac{\Delta[B]}{\Delta t}$$

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Similarly, for the reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow \mathbf{c}\mathrm{C} + d\mathrm{D}$$

the rate is given by $\text{Rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$

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Example 4.1

1. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

   a. $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

   b. $3O_2(g) \rightarrow 2O_3(g)$

   c. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

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Exercise 4.1

3. Consider the reaction of:

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.037 mol $L^{-1}s^{-1}$.

a. At what rate is N_2O_5 being formed?

b. At what rate is NO_2 reacting?

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Exercise 4.1

4. Consider the reaction of:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078 mol $L^{-1}s^{-1}$.

a. At what rate is P_4 being formed?

b. At what rate is PH_3 reacting?

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Determination of Rate of Reaction

- Reaction rate is change in an observable property over time.
- This could be a colour change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).
- The observable (measurable) properties can be used to determine the change in concentration over time.

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- **Consider, for example, the thermal decomposition of gaseous dinitrogen pentoxide, N_2O_5, to give the brown gas nitrogen dioxide:**

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Colorless Brown Colorless

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

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Table 4.1: Concentrations (mol $L^{-1}s^{-1}$) as a function of time at 55 °C for the thermal decomposition of gaseous dinitrogen pentoxide (N_2O_5)

Time (s)	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

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The average rate of formation of O_2?

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The average rate of formation of NO_2?

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- The average rate of formation of NO_2 during the time period 300-400s is 3.7×10^{-5} $molL^{-1}s^{-1}$, which is four times the rate of formation of O_2,

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The average rate of formation of N_2O_5?

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- In general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds

What could be the possible reason for this decrease in the rate of reaction with time?

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Table 4.1: Concentrations (mol $L^{-1}s^{-1}$) as a function of time at 55 °C for the thermal decomposition of gaseous dinitrogen pentoxide (N_2O_5)

Time (s)	N_2O_5	NO_2	O_2
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300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

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Example 4.2

Using the data in **Table 4.1,** if $[N_2O_5] = 1.20 \times 10^{-2}$ mol L^{-1} at 300 s, calculate $[NO_2]$ and $[O_2]$ at t = 300 s.

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Example 4.2

Using the data in **Table 4.1,** if $[N_2O_5] = 1.20 \times 10^{-2}$ mol L^{-1} at 300 s, calculate $[NO_2]$ and $[O_2]$ at t = 300 s.

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- Often, chemists want to know the rate of a reaction at a specific time t rather than the rate averaged over a time interval Δt.
- For example, what is the rate of formation of NO_2 at time t= 350s? Such instantaneous rate is calculated from the slope of a tangent drawn at any points on the graph of concentrations versus time
- The slope of tangent taken at the initial point of the graph is assumed to be equal to its initial rate.
- In the initial rate the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts.

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Example 4.3

Consider the gas-phase reaction that occurs when we mix 1.000 moles of hydrogen and 2.000 moles of iodine chloride at 230 °C in a closed 1.000-liter container.

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g)$$

From the experimental data given in the table below, determine the instantaneous rate of reaction at time, $t = 2$ s.

Time (s)	0	1	2	3	4	5	6	7	8
[ICl] (mol L^{-1})	2.000	1.348	1.052	0.872	0.748	0.656	0.586	0.530	0.484
[H_2] (mol L^{-1})	1.000	0.674	0.526	0.436	0.374	0.328	0.293	0.265	0.242

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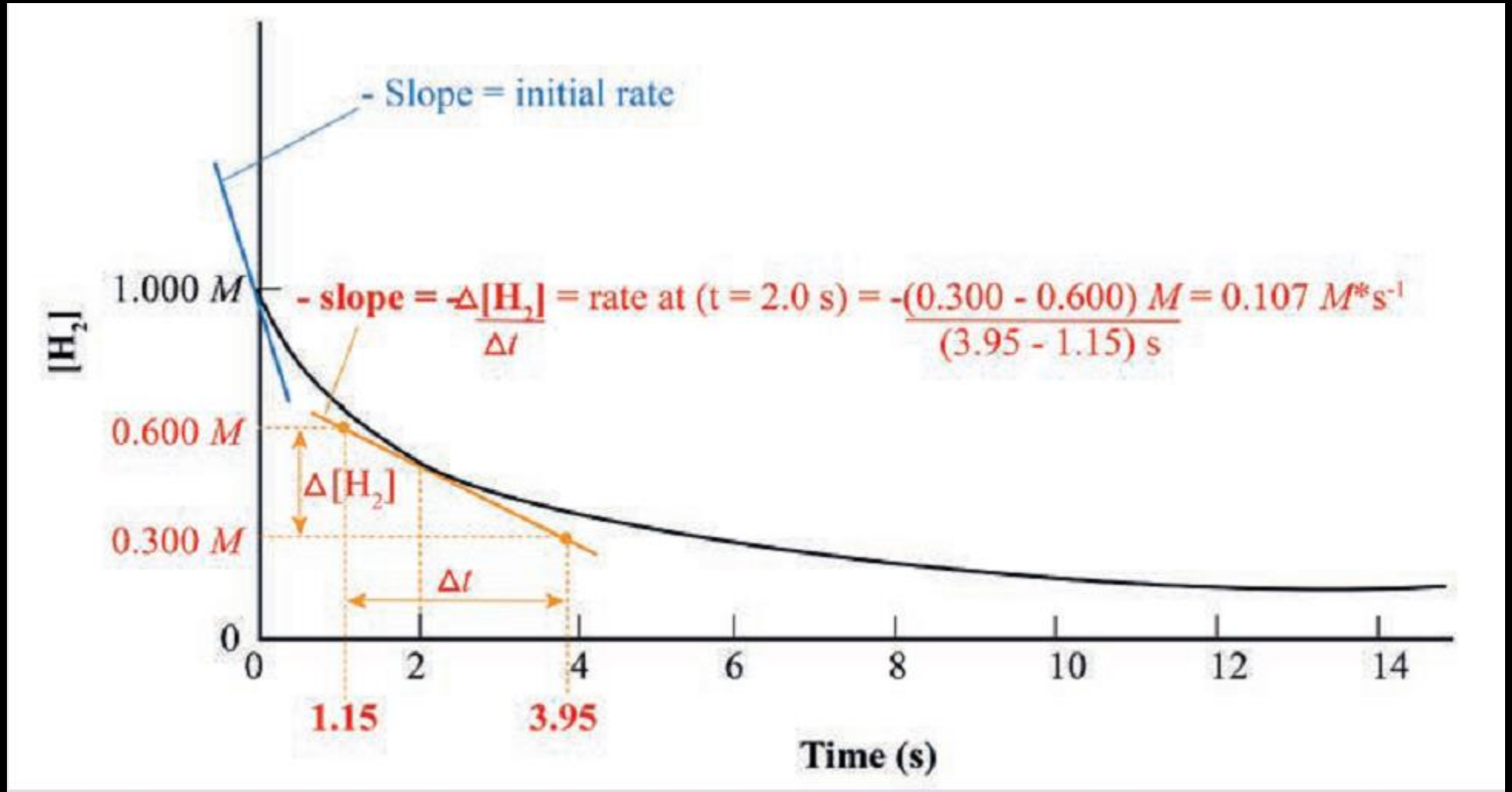


Figure 4.3: A plot of the hydrogen concentration versus time, using data of the above table

Exercise 4.2

1. Using the initial concentrations and the fact that $[O_2] = 0.64 \times 10^{-2}$ mol. L^{-1} at $t = 600$ s in **Table 4.1,** calculate $[N_2O_5]$ and $[NO_2]$ at $t = 600$ s.

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2. Consider the reaction:

$2C_2H_4(g) \rightarrow C_4H_8(g)$

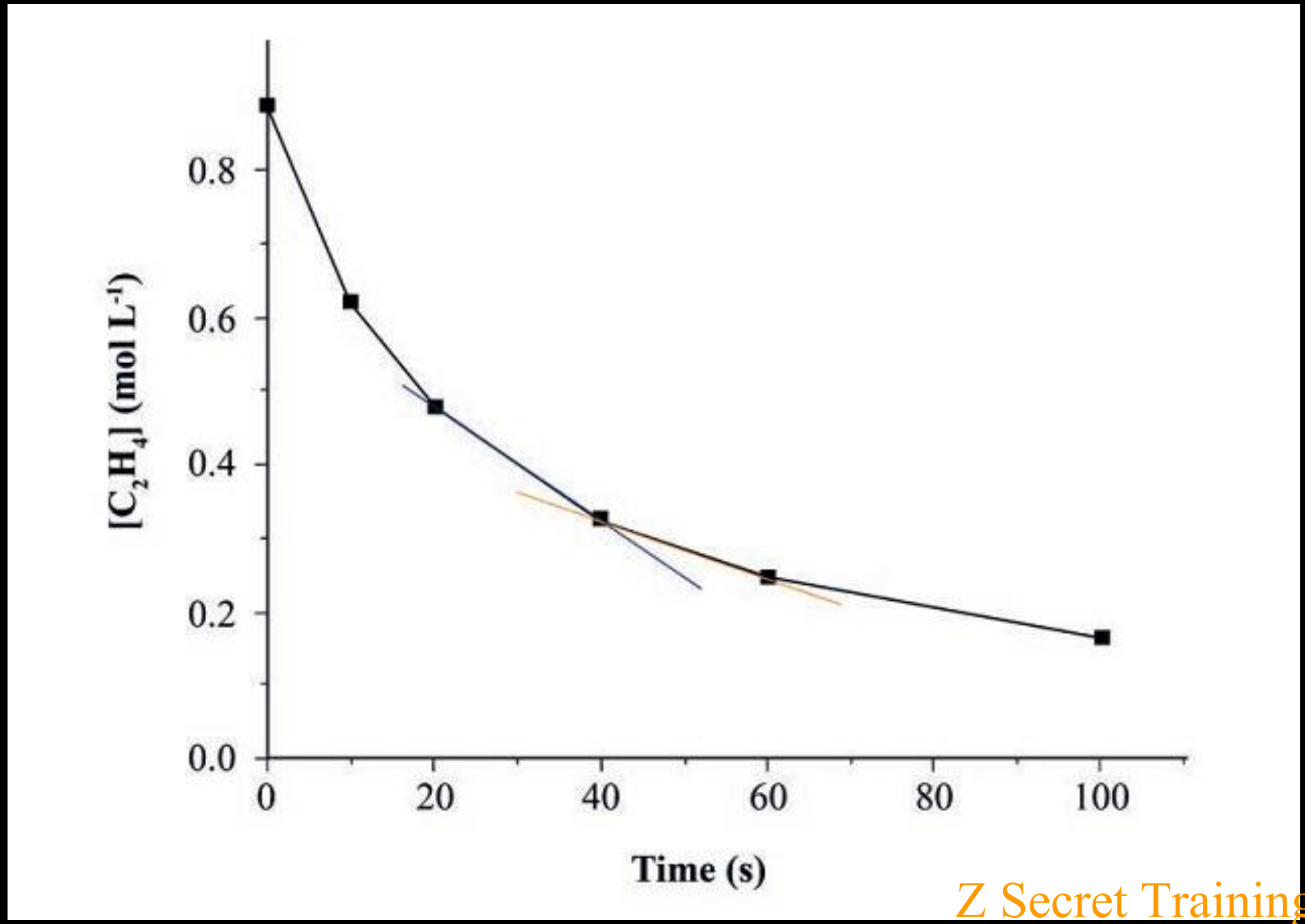
From the experimental data given in the table below, plot a graph for the consumption of ethylene, C_2H_4, versus time.

a. Calculate the rate of reaction between the time intervals 10 s to 30 s.

b. Calculate the rate of reaction at 45 s.

Time (s)	0	10	20	40	60	100
$[C_2H_4]$ (mol L^{-1})	0.884	0.621	0.479	0.328	0.250	0.169

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Conditions needed for a chemical reaction

- Chemical reactions are usually explained by the collision theory.
- The assumption of the collision theory is that chemical reactions take place due to collisions between molecules.
- **Conditions needed for a chemical reaction**

  Collisions between reactants

  Proper Orientation

  Activation energy

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1.Collisions between reactants

- The collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact).
- The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate } \alpha \ \frac{\text{number of collisions}}{\text{second}}$$

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2. Proper Orientation

- According to collision theory, the more collisions there are the faster the rate of reaction would be.
- However, not all collisions between reacting species result in a reaction.
- This is because collisions between reactants can be either effective or ineffective.
- **Effective collisions** are collisions that result in a reaction to form the desired products.
- **Ineffective collisions** are collisions that do not result in a reaction to form the desired products.
- Thus, the collision between molecules should have the proper orientation

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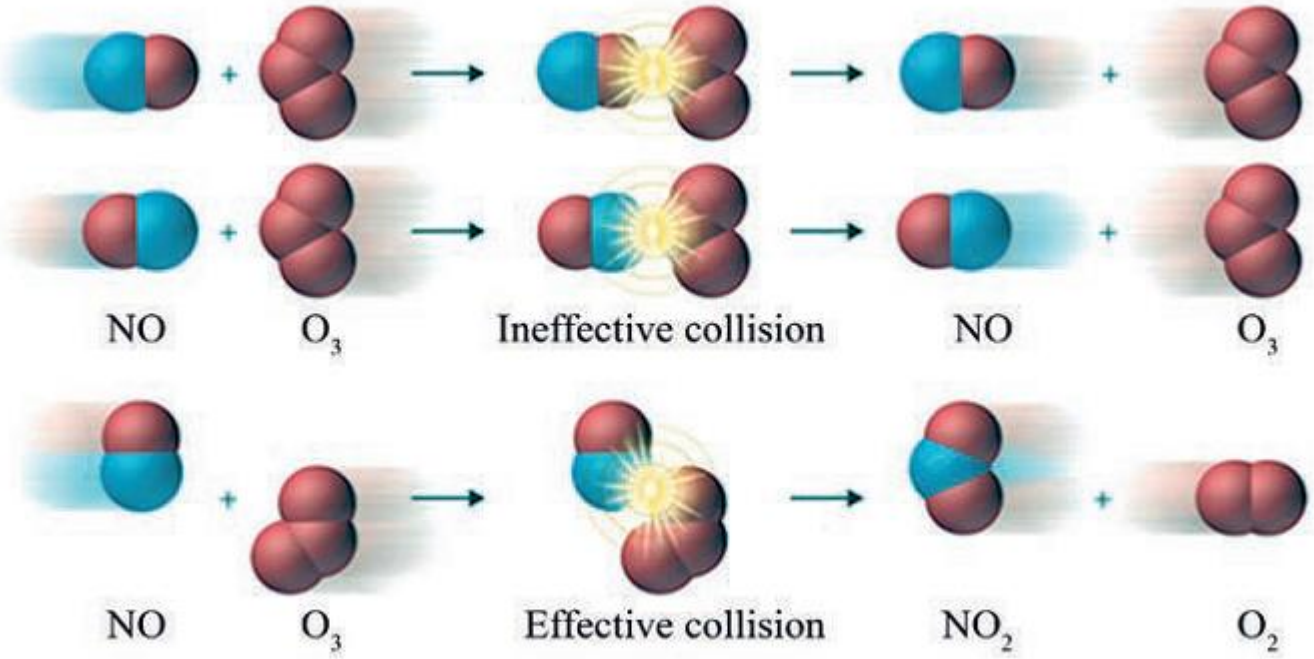


Figure 4.5: The effect of molecular orientation on the reaction of NO and O_3

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3. Activation energy

- If the collisions between the reactant molecules do not have sufficient energy, then no reaction will occur.
- Therefore, for the reaction to take place collision must always occur with sufficient energy to break the bonds in the reactants and form new bonds in the product.
- Thus, minimum amount of energy needed for the reaction is known as **activation energy, Ea.**

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- According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature.
- As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably.
- This causes the particles of the reactants to collide more frequently and with greater energy. This results in increase in reaction rate.

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factors that affecting the rate of a chemical reaction

- The rates at which reactants are consumed and products are formed during chemical reactions vary greatly.
- Even a chemical reaction involving the same reactants may have different rates under different conditions.
- factors that affecting the rate of a chemical reaction

Change in temperature,

Concentration,

Nature of reactant,

Surface area

Presence of a catalyst

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i. Nature of the reactants

- The rate of a reaction depends on the chemical nature of the substances in the reaction.
- Even similar reactions may have different rates under the same conditions.
- For example, if small pieces of the metal iron and sodium are left in air, the sodium reacts completely overnight, whereas the iron is barely affected

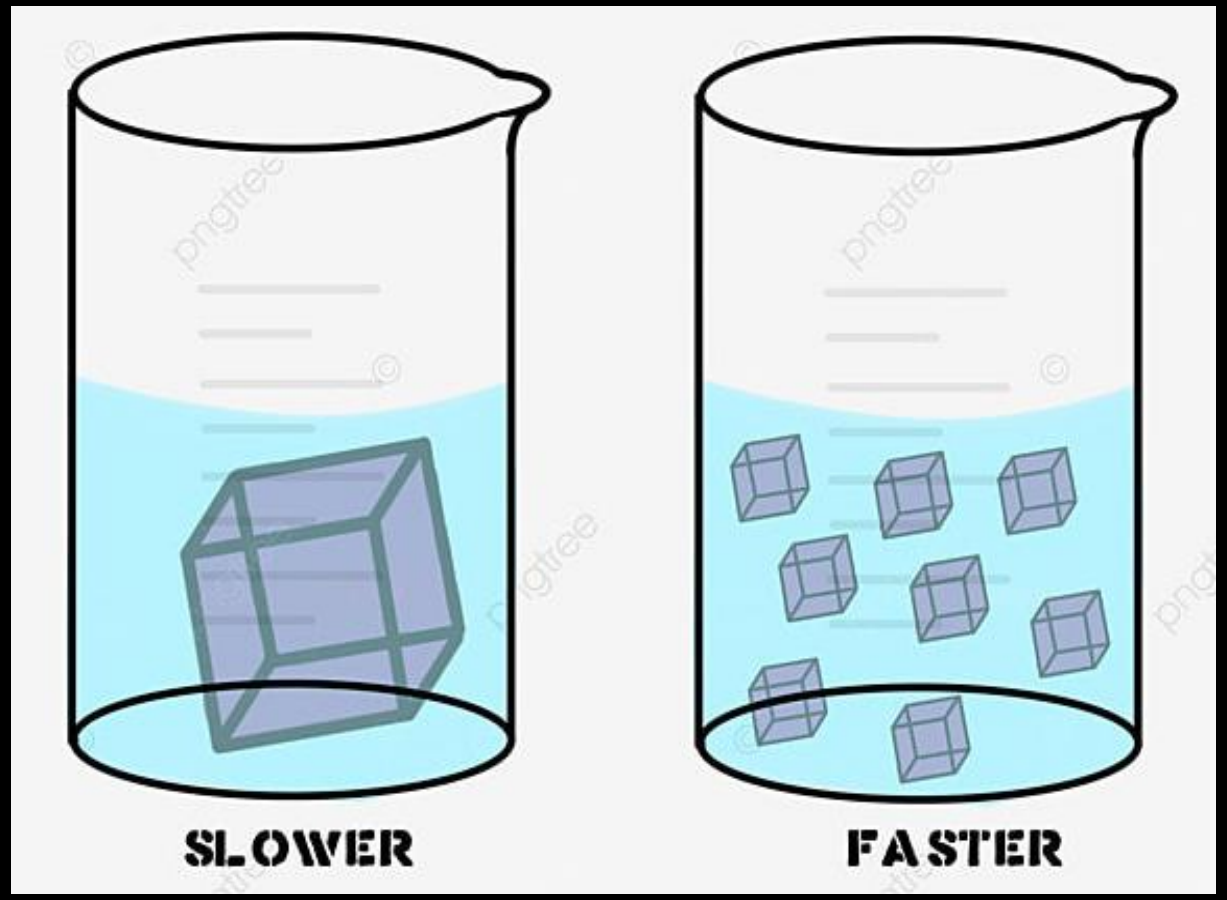
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ii. Surface Area of Reactants

- Reactions can be classified as homogeneous (same phase) and heterogeneous (different phases).
- the rate of reaction between two phases depends to a great extent on the surface area of contact between them.
- Finely divided solids, react more rapidly than the same amount of the substance in a large body because of the greater surface area available.

$$NO\ (g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g)$$

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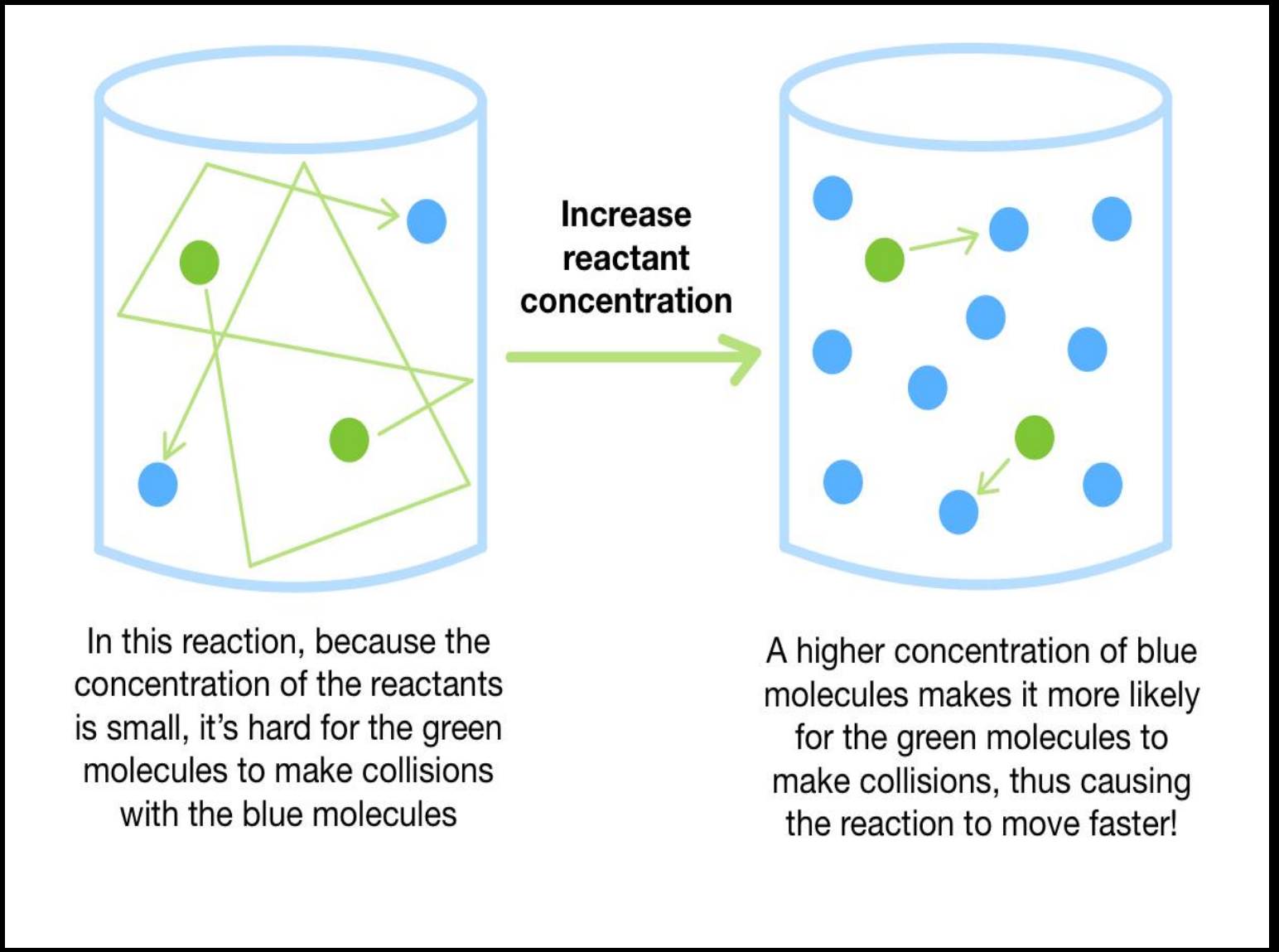


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iii. Concentration of Reactants

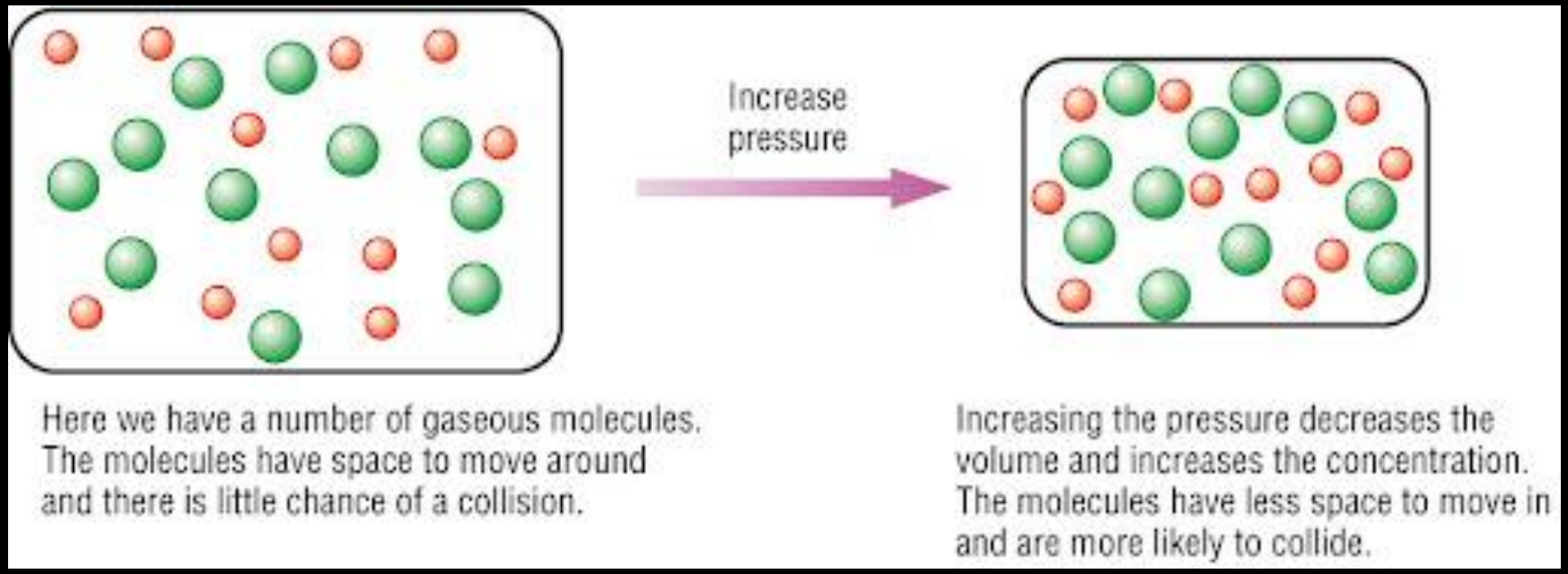
- At a fixed temperature, the rate of a given reaction depends on the concentration of the reactants.
- Reaction rates often increases when the concentration of one or more of the reactants increases.
- This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction.

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- **In the case of reactions that involve gaseous reactants, an increase in pressure can increase the concentration of the gases which may lead to an increase in the rate of reaction.**
- **However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.**



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iv. Temperature of Reactants

- Temperature usually has a major effect on the rate of reaction.
- Molecules at higher temperatures have more thermal energy.
- Generally, an increase in the temperature of a reaction mixture increases the rate of chemical reactions.
- This is because, as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases.
- So, they collide more frequently and with greater energy.

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- The effect of temperature on rate of reaction can be experienced in our daily life.
- For example, foods cook faster at higher temperature than at lower ones.
- In many cases, the rate of a reaction in a homogeneous system is approximately doubled by an increase in temperature of only 10 °C.

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v. Presence of a Catalyst

- A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy, Ea.
- An activation energy is the minimum energy required to start a chemical reaction.
- Catalysts are not used up by the reactions, rather they are recovered at the end of the reaction.
- Although a catalyst speeds up the reaction, it does not alter the position of equilibrium.

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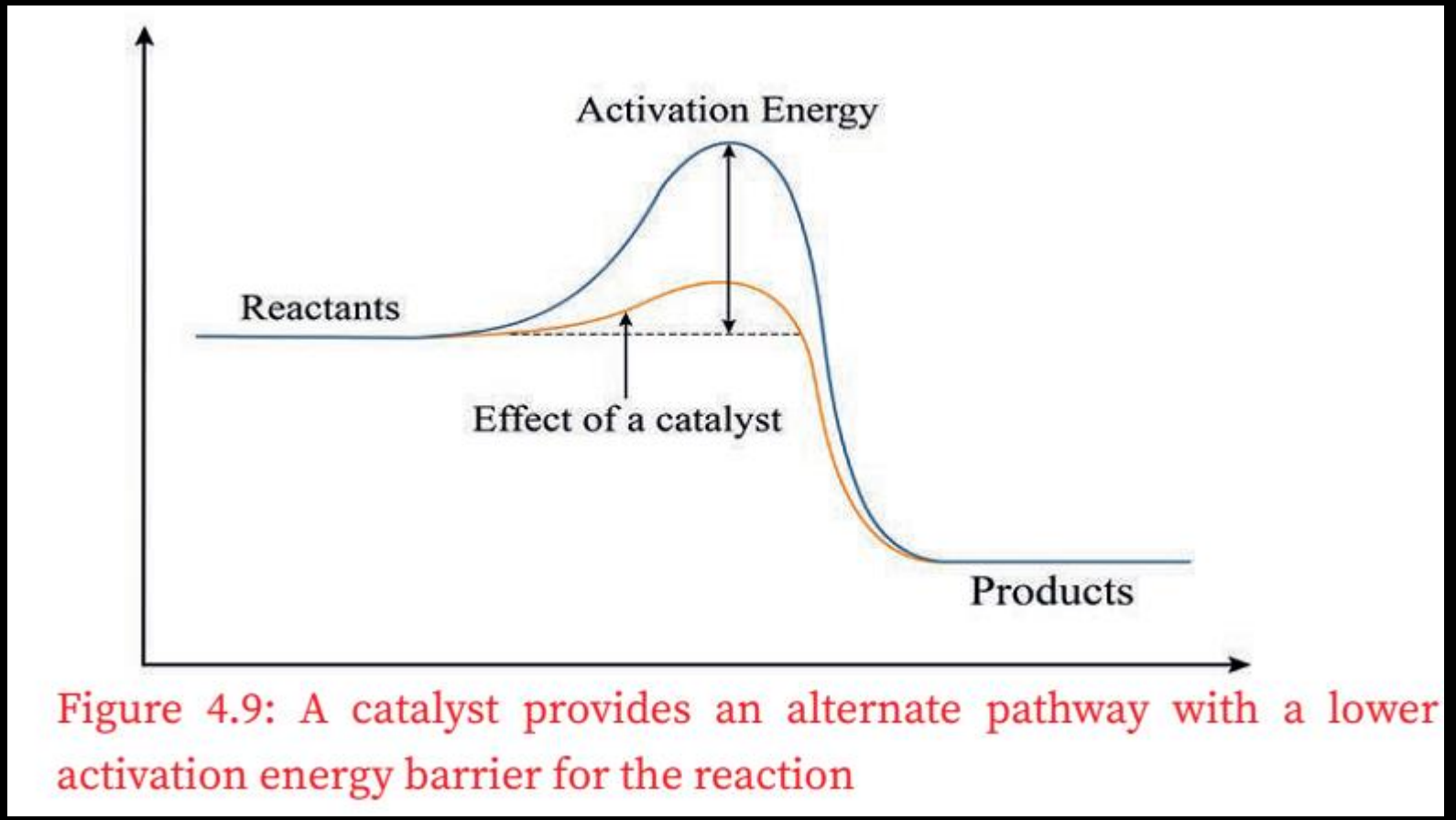


Figure 4.9: A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction

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Chemical catalysts can be either positive or negative.

- **Positive catalysts** increase the rate of reaction by lowering the Ea.

Example 4.4

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; $V_2O_5(s)$ as catalyst.

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- **Negative catalysts or inhibitors** decrease the rate of reaction by increasing the value of Ea.

Example 4.5

$OCl^-(aq) + I^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$; $OH^-(aq)$ as inhibitor.

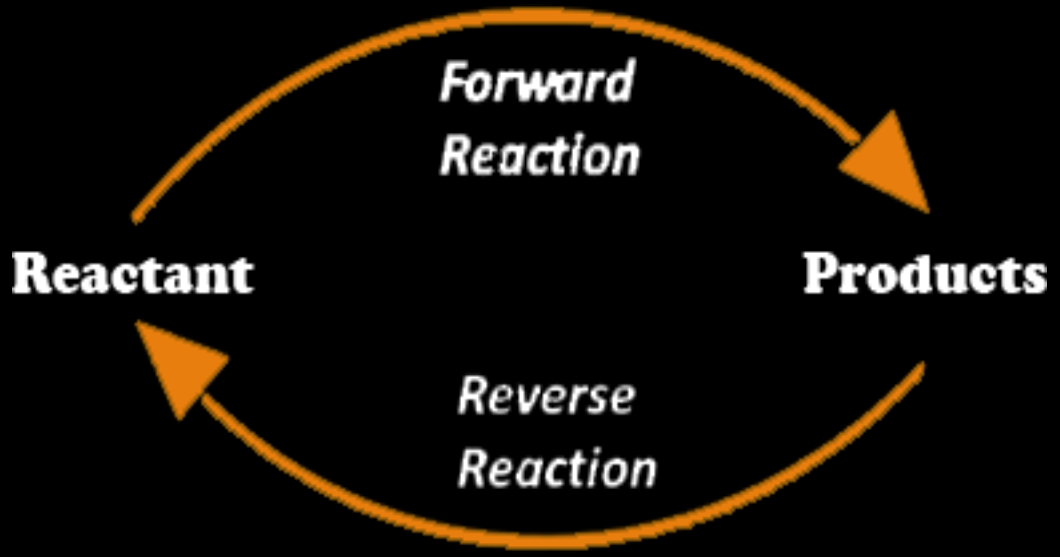
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- Example 4.4 represents **heterogeneous catalysts** as state of reactants and catalyst is different,
- while Example 4.5 represents **homogeneous catalyst** as both reactants and catalyst are in same state.
- A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar.
- The chemical reactions in living things are controlled by biochemical catalysts called **enzymes.**

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THE END

UNIT 5
CHEMICAL EQUILIBRIUM



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Introduction

- Do all reactions reach to completion?
- If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction it took?
- Why does the reaction reach to completion?
- Why does it attain equilibrium?

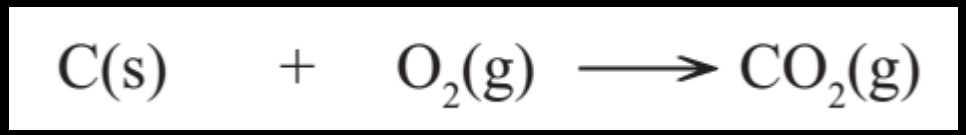
These questions can be answered after studying chemical equilibrium.

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Chemical equilibrium

Reversible and Irreversible reactions

- Many chemical reactions proceed to completion.
- In such types of reactions, the reactants, are converted to the products and the amount of reactants left after the reaction is very small.
- Such reactions are called **irreversible reactions** or **one-way reactions**.
- When the equation for an irreversible reaction is written, a single arrow (→) is used to indicate that the reaction proceeds in only one direction.



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- On the other hand, some reactions do not go to completion.
- Such reactions are called **reversible reactions or two-way reactions**.
- These reactions usually proceed both in the forward and reverse reactions.
- The reaction in which the original reactants form products is the **forward reaction** and the reaction in which the products are converted to the original reactant is the **reverse(backward) reaction**.
- When the equation for a reversible reaction is written, a **double arrow(⇌)** indicates the reaction that goes from reactants to products to the right and from the products to the reactants to the left



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Reversible reactions have the following general form:

$$aA + bB \rightleftharpoons cC + dD$$

In this reaction:

$$aA + bB \longrightarrow cC + dD \quad \text{Forward reaction}$$

$$cC + dD \longrightarrow aA + bB \quad \text{Reverse reaction}$$

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Attainment and Characteristics of Chemical Equilibrium

- For a reversible reaction, the rate with which the reactants form products is the forward reaction rate (rf)
- the rate with which the products combine to produce the original reactants is called the reverse reaction rate (rr).
- At the beginning of the reaction, the forward reaction has a high rate, but gradually decreases with time.
- The reverse reaction has a very small rate at the beginning, but gradually increases (as the products concentration increase)until equilibrium is established

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- **The equilibrium is attained when the rate of the two opposing reactions become equal.**
- **That is at equilibrium:**

Rate of forward reaction (rf)= Rate of reverse reaction(rr)

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Conditions of attainment of chemical equilibrium

- Chemical equilibria are dynamic equilibria,i.e., reactants and products are interconverted continually, even though the overall composition of the reaction mixture does not change.
- Once the equilibrium is established, a change in one direction is balanced by changes in the other direction.

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- To understand the concept, consider Figure 5.1, which shows the change in the reaction rate with time for the forward and reverse reactions.
- The rate of the forward reaction depends upon the concentration of reactants, whereas the rate of the reverse reaction depends upon the concentration of the products.
- Initially, only the reactants are present, therefore, the rate of the forward reaction is fast.
- The reaction in the reverse direction does not take place as no product is present yet.

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- As the reaction progresses, the concentration of the reactants decreases and hence, the rate of forward reaction also decreases.
- However, due to the increase in the concentration of products, the rate of the reverse reaction increases.
- As the reaction further progresses a point will be reached when the rate of forward reaction becomes equal to the rate of reverse reaction.
- When this stage is attained, the concentrations of reactants and products do not change.
- The reaction has reached chemical equilibrium.

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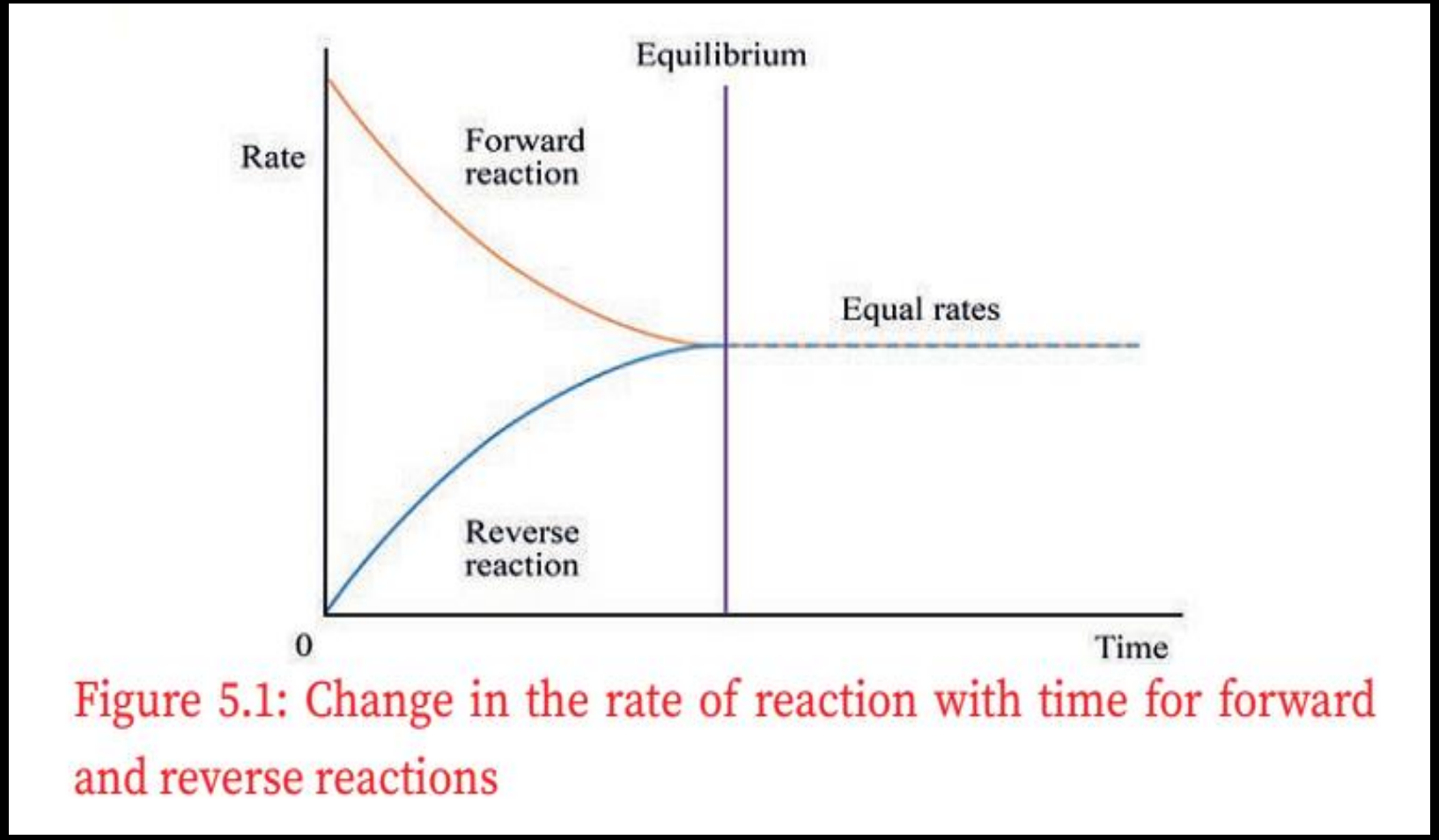


Figure 5.1: Change in the rate of reaction with time for forward and reverse reactions

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For example, synthesis of ammonia from nitrogen and hydrogen is a reversible process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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- At the beginning of the reaction, only nitrogen and hydrogen are present.
- As the reaction progresses, the concentrations of nitrogen and hydrogen decrease so the rate of formation of ammonia decreases.
- As more and more ammonia molecules are formed, some of the molecules start decomposing to give back nitrogen and hydrogen molecules.
- As the reaction progresses, the number of ammonia molecules increases, the rate of decomposition of ammonia also increases.
- As the reaction proceeds, the rate of formation of ammonia decreases while the rate of decomposition ammonia increases.
- At a given point the two rates become equal, and equilibrium is reached.

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- **Note that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal.**

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Generally, a reaction at equilibrium has the following characteristics:

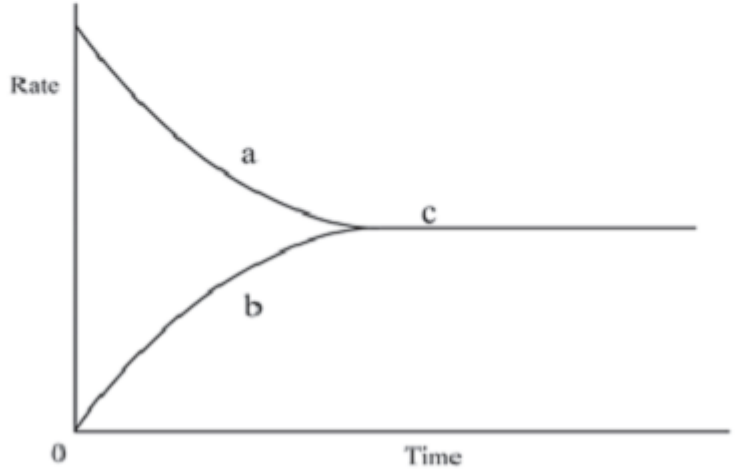
- The reaction is reversible in nature.
- There is no net change in the concentrations of the reactants and products of the reaction.
- The rates of the forward and reverse reactions are equal.
- The reaction should take place in a closed vessel to react at equilibrium.
- The equilibrium is dynamic in nature.
- The concentrations of reactants and products are generally not equal

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Exercise 5.2

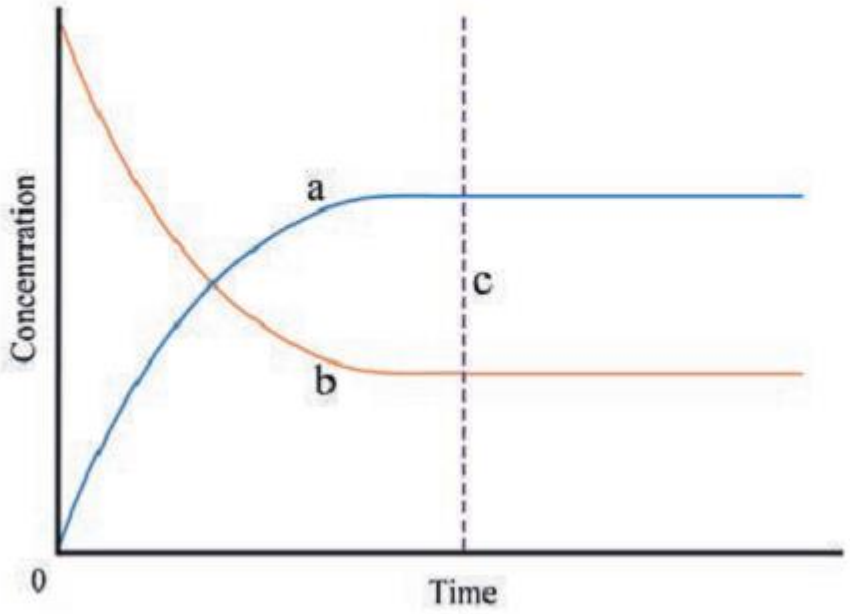
Answer the following questions

1. Explain trends of the rates of the forward and reverse reactions for the following graph, using the labels a, b and c.



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2. Explain what happens to the Concentration of the reactants and the concentration of the products in the graph using the labels a, b and c..



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3. What are the conditions that remain constant at equilibrium?

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Equilibrium Expression and Equilibrium Constant

a. Law of mass action

- Mathematically the equilibrium constant is written based on **the law of mass action** or **law of concentration action** proposed by Cato Maximilian Guldberg and Peter Waage, in 1864.
- **The law of mass action** states that "the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respective coefficient in the balanced chemical reaction."

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The general equation that represents a reversible reaction is:

$$aA + bB \rightleftharpoons cC + dD$$

- For the forward reaction A and B are reactants, and C and D are products.
- Assume that the reaction is homogeneous, in which all the reactants and the products are in the same state.
- The rate of forward reaction (rf) depends upon the concentrations of A and B as well as the rate of reverse reaction (rr) depends upon the concentrations of C and D.

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- **These relations are expressed as follows:**

$$r_f \alpha [A]^a[B]^b \quad \text{or} \quad r_f = k_f[A]^a[B]^b$$

$$r_r \alpha [C]^c[D]^d \quad \text{or} \quad r_r = k_r[C]^c[D]^d$$

At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction.

Therefore, $r_f = r_r$ or $k_f [A]^a [B]^b = k_r[C]^c[D]^d$

k_f and k_r are constant. Therefore, the ratio of k_f to k_r is also constant.

$$\frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}$$

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- **These relations are expressed as follows:**

$$r_f \alpha [A]^a[B]^b \quad \text{or} \quad r_f = k_f[A]^a[B]^b$$

$$r_r \alpha [C]^c[D]^d \quad \text{or} \quad r_r = k_r[C]^c[D]^d$$

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$$\frac{k_f}{k_r} = \frac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b} = K_{eq}$$

The ratio of k_f and k_r is represented by K_{eq}, which is called equilibrium constant. [A], [B], [C] and [D] are concentrations of A, B, C, D, and A at equilibrium, respectively. When their concentrations are expressed in molarities, the K_{eq} is shown by K_C. When the reaction reactants and the products are gaseous, their concentrations can be expressed in terms of partial pressures. In such cases, the K_{eq} is denoted by K_p.

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b. Equilibrium constant

- In homogeneous reactions, all reactants and products are present in the same physical state.

While writing equilibrium constant expressions for such reactions, the following rules are followed.

- The concentrations of all the substances formed as products are written in the numerator (the top of the fraction).
- The concentrations of all the reactants are written in the denominator (the bottom of the fraction).
- The equilibrium concentrations of each species are raised to a power equal to the coefficient of that species written in the balanced chemical equation.

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For a general reaction at equilibrium:

$$aA + bB \rightleftharpoons cC + dD$$

The expression for K_C is: $K_C = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$

The unit of K_C depends upon the number of moles of the reactants and products involved in the reaction. Therefore, for the above general reaction, the K_C unit will be:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{\left[\text{mol L}^{-1}\right]^c \left[\text{mol L}^{-1}\right]^d}{\left[\text{Amol L}^{-1}\right]^a \left[\text{mol L}^{-1}\right]^b}$$

$$= \left(\text{mol L}^{-1}\right)^{(c+d)-(a+b)}$$

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Example 5.1

K_C expressions and units as well as K_C value determinations:

1. $NH_3(g) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$

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2. $HF\,(aq) \rightleftharpoons H^{+}(aq) + F^{-}(aq)$

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4. For the reaction

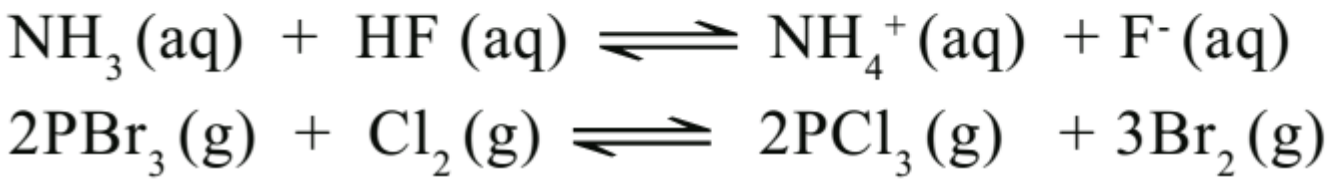
$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

An equilibrium mixture at 425 °C contains 4.79×10^{-4} mol/L of H_2, 4.79×10^{-4} mol/L of F_2 and 3.53×10^{-3} mol/L of HF. Determine the equilibrium constant of the reaction.

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Exercise 5.3

1. Write the equilibrium constant expressions (K_c) for the following reactions:



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2. For the reaction $N_2(g) + 3Cl_2(g) \rightleftharpoons 2NCl_3(g)$ an analysis of an equilibrium mixture is performed at a certain temperature. It is found that $[NCl_3] = 1.9 \times 10^{-1}$ M, $[N_2] = 1.4 \times 10^{-3}$ M, and $[Cl_2] = 4.3 \times 10^{-4}$ M. Calculate K_C for the reaction at this temperature

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C. Equilibrium constant expression involving partial pressure, K_P

- When all the reactants and the products are gases, their concentrations can be written in terms of partial pressures.
- In such cases the equilibrium constant is denoted by Kp, which is expressed as:

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

For the formation of ammonia: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p, will be:

$$K_P = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = \frac{[atm]^c [atm]^d}{[atm]^a [atm]^b} = (atm)^{(m+n)-(a+b)}$$

If the partial pressure is measured in kPa, then the unit of K_p will be $(kPa)^{(m+n)-(a+b)}$

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Example 5.2

K_P expressions and units as well as K_P value determinations:

1. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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2. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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4. The reaction for the formation of nitrosyl chloride was studied at 25 °C

$2NO\ (g) + Cl_2\ (g) \rightleftharpoons 2NOCl\ (g)$

At equilibrium, the partial pressures were found to be 1.2, 5.0×10^{-2} and 3.0×10^{-1} atm for NOCl, NO and Cl_2, respectively. Calculate the value of K_P for this reaction at 25 °C.

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Exercise 5.4

1. Write the equilibrium constant expressions (K_p) for the following reactions:

   a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

   b. $N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

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2. The following equilibrium pressures were observed at a certain temperature for the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$P_{NO_2} = 0.55$ atm

$P_{NO} = 6.5 \times 10^{-5}$ atm,

$P_{O_2} = 4.5 \times 10^{-5}$ atm

Calculate the value for the equilibrium constant at this temperature

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D. Equilibrium constant for heterogeneous reactions

- In heterogeneous reactions, the reactants and products are present in more than one physical state.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

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- When we write the equilibrium constant expression for heterogeneous reactions, we do not include the concentration of pure solids or pure liquids in the expression.
- This is because, the position of equilibrium does not depend on the amounts of pure solids or pure liquids present.
- The molar concentrations of pure solids and liquids are constant at a given temperature.

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Example 5.3

The equilibrium constant expressions for some heterogeneous reactions are shown below:

1. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

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2. $NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$

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Exercise 5.5

Write the equilibrium constant expression for the following reactions:

1. $Fe^{3+}(aq) + 3OH^{-}(aq) \rightleftharpoons Fe(OH)_3(s)$
2. $PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$
3. $2NBr_3(s) \rightleftharpoons N_2(g) + 3Br_2(g)$
4. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + Cl^{-}(aq)$

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E. Relation between K_C and K_P

For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

K_C and K_P expressions are:

$$K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

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

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Assume that all gaseous species behave like an ideal gas. Thus, according to the ideal gas equation, the partial pressure (P) of a gas is given by:

$$P = nRT/V \quad \text{and} \quad n/V = C$$

Where n is amount of the gaseous species in moles, R is gas constant, T is temperature in kelvin, V is volume of the reaction mixture and C is concentration in molarity.

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Thus, partial pressure of each species for the above general reaction is:

$$P_A = n_A RT/V = C_A RT$$

$$P_B = n_B RT/V = C_B RT$$

$$P_C = n_C RT/V = C_C RT$$

$$P_D = n_D RT/V = C_D RT$$

$$K_P = \frac{[n\mathrm{CRT}/\mathrm{V}]^c [n\mathrm{DRT}/\mathrm{V}]^d}{[n\mathrm{ART}/\mathrm{V}]^a [n\mathrm{BRT}/\mathrm{V}]^b} = \frac{C_C^c \, C_D^d}{C_A^a C_B^b} (\mathrm{RT})^n$$

Where $\Delta n = (c + d) - (a + b)$ for gaseous species

$$K_P = K_C (RT)^{\Delta n}$$

When the number of gaseous reactants and products are equal then, $a + b = c + d$

Therefore, $\Delta n = 0$ and, hence $K_p = K_c$

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Example 5.4

1. The equilibrium constant (K_p) for the reaction:

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is 1.8×10^{-3} kPa at 427 °C.

Calculate K_c for the reaction at the same temperature.

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2. What are the values of K_p and K_c at 1000 °C for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ if the pressure of CO_2 in equilibrium with $CaCO_3$ and CaO is 3.87 atm?

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3. At 400 °C, $K_c = 64$ for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

a. What is the value of K_p for this reaction?

b. If at equilibrium, the partial pressures of H_2 and I_2 in a container are 0.20 atm and 0.50 atm, respectively, what is the partial pressure of HI in the mixture?

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Exercise 5.6

1. At 327 °C, the equilibrium concentrations are

   $[CH_3OH] = 0.15$ M, $[CO] = 0.24$ M and $[H_2] = 1.1$ M for the reaction:

   $$CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2H_2\,(g)$$

   Calculate K_P at this temperature.

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2. At 1100 K, $K_P = 0.25$ for the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the value of K_C at this temperature?

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3. When 0.500 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3% of the N_2O_4 decomposes to NO_2. The decomposition reaction is: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Calculate K_c and K_p of the reaction at 400 K.

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Consider the reactions in which the product species in one equilibrium system are involved in the second equilibrium process.

$$A + B \rightleftharpoons C + D \qquad \text{(i)}$$

$$C + D \rightleftharpoons E + F \qquad \text{(ii)}$$

The equilibrium constant expressions for reaction (i) and (ii), respectively, are

$$K_1 = \frac{[C][D]}{[A][B]} \text{ and } K_2 = \frac{[E][F]}{[C][D]}$$

The overall reaction is given by the sum of the two reactions:

$$A + B \rightleftharpoons C + D$$

$$C + D \rightleftharpoons E + F$$

Overall reaction : $A + B \rightleftharpoons E + F$

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The equilibrium constant expression for the overall reaction is:

$$K_{overall} = \frac{[E][F]}{[A][B]} = K_1 \times K_2 = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]}$$

Note that if a reaction is the sum of two or more reactions, the equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of the individual reaction. That is: $K_{overall} = K_1 \times K_2 \times K_3 \ldots$

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Example: 5.5

1. Determine K_C for this reaction:

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$$

from the following information at 298 K.

$$2NO(g) \rightleftharpoons N_2(g) + O(g) \qquad \text{(i)} \quad K_1 = 2.4 \times 10^{30}$$

$$NO(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) \qquad \text{(ii)} \quad K_2 = 1.4$$

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Exercise 5.7

1. The following equilibrium constants were determined at 1123 K:

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $\quad K_{C1} = 1.4 \times 10^{12}$

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ $\quad K_{C2} = 5.5 \times 10^{1}$

Write the equilibrium constant expression K_c and calculate the equilibrium constant at 1123 K for the following reaction.

$C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$

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2. For the reaction:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

$K_p = 7.1 \times 10^4$ at 700 K.

What is the value of K_p for the following reactions at the same temperature?

a. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

b. $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons HBr(g)$

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3. Calculate a value for the equilibrium constant for the reaction:

$O_2(g) + O(g) \rightleftharpoons O_3(g)$ from the following information

$NO_2(g) \rightleftharpoons NO(g) + O(g)$ $\quad K_C = 6.8 \times 10^{-49}$

$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g)$ $\quad K_C = 5.8 \times 10^{-34}$

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Applications of Equilibrium Constant

- Useful information can be obtained from the value of equilibrium constant of a given reaction at a particular temperature.

The equilibrium constant of a reaction enables us to:

- predict the composition of an equilibrium mixture (or predict extent of reaction);
- predict the direction of the reaction
- calculate the equilibrium concentrations of reactants and products from initial concentrations.

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A. Predict the composition of an equilibrium mixture

- K_C or K_P value is used predict the extent of the reactions at equilibrium.
- Very large values of Kc or K_P indicate that at equilibrium the reaction system consists of mainly products and the equilibrium lies to the right, i.e., the reaction goes near to completion.
- An equilibrium mixture contains about as much product as can be formed from the given initial amounts of reactants.
- However, if Kc or KP values are very small, the equilibrium mixture consists of mainly reactants and the reaction lies far to the left.

Note that a reaction goes essentially to completion if K_C or $K_P > 10^{10}$ and not at all if K_C or $K_P < 10^{-10}$.

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Exercise 5.8

1. Predict whether the formation of product is favoured for the following reactions:

   a. $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ $\quad K_C = 3.6 \times 10^{8}$

   b. $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ $\quad K_C = 5.0 \times 10^{-3}$

   c. $2CO_2\,(g) \rightleftharpoons 2CO\,(g) + O_2\,(g)$ $\quad K_C = 4.45 \times 10^{-24}$

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2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent):

a. $CO + Cl_2 \rightleftharpoons COCl_2$ $\quad K_c = 13.8$

b. $2CO_2 \rightleftharpoons 2CO + O_2$ $\quad K_c = 2.0 \times 10^{-6}$

c. $2NOCl \rightleftharpoons 2NO + Cl_2$ $\quad K_c = 4.7 \times 10^{-4}$

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B. Predict the direction of the reaction

- To predict the direction of a reaction, we first calculate the reaction quotient (Q_C) and compare it with the value of the equilibrium constant.
- The **reaction quotient** is the ratio of concentrations of products to the concentrations of reactants each raised to the power equal to its stoichiometric coefficient.
- Q_C has the same form as K_C, but involves concentrations that are not necessarily equilibrium concentrations.

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For the general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

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

- Where [A], [B], [C] and [D] are concentrations at any stage during the reaction.
- At the initial stages of the reaction, the amount of product formed is low, therefore, the value of Q is small.
- As the reaction progresses, the value of Q also increases due to the increase in concentration of the products.
- When the reaction attains equilibrium, Q becomes equal to the equilibrium constant.

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To predict the direction of the reaction, Q is compared with Keq:

- **Q = Keq, the reaction is at equilibrium.**
- **Q < Keq, then the reaction will proceed to the right (the forward direction) to consume the reactants and to form more products until the equilibrium is reached.**
- **Q > Keq, the reaction will proceed to the left (the reverse direction) to reduce the products until the equilibrium is reached.**

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Example 5.6

1. At a certain temperature, the reaction:

   $CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$

   has an equilibrium constant $K_c = 13.8$. Is the following mixture an equilibrium mixture? If not, to which direction (forward or backward) will the reaction proceed to reach equilibrium?

   $[CO]_0 = 2.5$ mol L^{-1}; $[Cl_2]_0 = 1.2$ mol L^{-1}, and $[COCl_2]_0 = 5.0$ mol L^{-1}.

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Example 5.6

1. At a certain temperature, the reaction:

   $CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$

   has an equilibrium constant $K_c = 13.8$. Is the following mixture an equilibrium mixture? If not, to which direction (forward or backward) will the reaction proceed to reach equilibrium?

   $[CO]_0 = 2.5$ mol L^{-1}; $[Cl_2]_0 = 1.2$ mol L^{-1}, and $[COCl_2]_0 = 5.0$ mol L^{-1}.

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Exercise 5.9

1. At a start of a reaction, there are 0.0218, 0.0145, ad 0.0783 moles of H_2, I_2 and HI, respectively, in a 3.5 liter reaction vessel at 430 °C. Decide whether or not the reaction is at equilibrium. If not, predict in which direction the reaction will proceed. The equilibrium reaction is:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_C = 54.3 \text{ at } 430\ ^\circ C$$

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2. At a very high temperature, the following reaction has $K_C = 1.0 \times 10^{-13}$

$$2HF\,(g) \rightleftharpoons H_2\,(g) + F_2\,(g)$$

At a certain time, the concentrations of HF, F_2 and H_2 were 0.4 M, 0.004 M and 0.001 M, respectively. Is the system at equilibrium? If not, what must happen for the equilibrium to be reached?

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3. The decomposition of NOBr is represented by the equation:

$2NOBr\ (g) \rightleftharpoons 2NO\ (g) + Br_2\ (g)$ $\qquad K_C = 0.0169$

At equilibrium the concentrations of NO and Br_2 are 1.05×10^{-2} M and 5.24×10^{-3} M, respectively. What is the concentration of NOBr?

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C. Calculat the equilibrium concentrations

- Once equilibrium constant is determined for a reaction, it can be used to calculate the concentrations or partial pressures in an equilibrium mixture.

To calculate equilibrium concentrations, follow the following steps:

1. Write the balanced equation for the reaction and then the K_C or K_P expressions.

2. List the initial concentrations.

3. Calculate Q_C or Q_P to determine the direction of the reaction, if initial concentrations of the reactants and products are given.

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4. Define the change in concentration needed to reach equilibrium and find the equilibrium concentrations by using the change of the initial concentrations.

5. Substitute the equilibrium concentrations into the KC or KP expression, solve for the unknown.

6. Check whether the calculated equilibrium concentrations give the correct value of K_C or K_P.

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Example 5.7

1. The equilibrium constant, K_C is 69 for the following reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Given that 1 mole of H_2 and 2 moles of I_2 were added to a 500 mL reaction vessel. Determine the molar concentrations in the mixture at equilibrium.

1. The equation for the reaction is:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_C = \frac{[HI]^2}{[H_2][I_2]} = 69$$

$$[HI]_{initial} = [HI]_0 = 0$$

$$[H_2]_0 = \frac{1\ \text{mol}}{0.5\ \text{L}} = 2\frac{\text{mol}}{\text{L}} = 2\ \text{M}$$

$$[I_2]_0 = \frac{2\ \text{mol}}{0.5\ \text{L}} = 4\frac{\text{mol}}{\text{L}} = 4\ \text{M}$$

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2. No need to calculate Q_C since $[HI]_0 = 0$
3. Let the number of moles of H_2 (or I_2) consumed per liter to reach an equilibrium is x. Since the stoichiometric proportion of each reactant (H_2 and I_2) and the product HI is 1:2, for every x of both reactants consumed the concentration of HI formed is $2x$. These changes are shown here:

Concentration	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial	2.0 M		4.0 M		0
Change	$-x$		$-x$		$+2x$
Equilibrium	2.0 M-x		2.0 M-x		$2x$

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4. Substituting the equilibrium concentrations:

$$K_C = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

$$64 = \frac{(2x)^2}{(2.0\ \mathrm{M} - x)(4.0\ \mathrm{M} - x)} = \frac{(2x)^2}{x^2 - 6x + 8}$$

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By rearranging, we get:

$$4x^2 = 64x^2 - 384x + 512$$

By rearranging again, we get:

$$60x^2 - 384x + 512 = 0$$

This is a quadratic equation of the general formula $ax^2 + bx + c = 0$

The values of x can be obtained from the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this example a = 60, b = -384 and c = 512. Therefore:

$$x = \frac{-(-384) \pm \sqrt{(-384)^2 - 4(60 \times 512)}}{2 \times 60}$$

$$= \frac{384 \pm \sqrt{2.5 \times 10^4}}{120} = \frac{384 \pm 158}{120}$$

$x = 1.9$ M or 4.5 M

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But the change in concentration cannot be greater than the initial concentrations of the H_2, i.e., 2 M. Thus, only 1.9 is a reasonable value. Therefore, the equilibrium concentration of each species is:

$$[H_2] = 2.0 - x = 2.0\ \text{M} - 1.9\ \text{M} = 0.1\ \text{M}$$

$$[I_2] = 4.0 - x = 4.0\ \text{M} - 1.9\ \text{M} = 2.1\ \text{M}$$

$$[HI] = 2x = 2(1.9\ \text{M}) = 3.8\ \text{M}.$$

Check $K_C = \dfrac{[HI]^2}{[H_2][I_2]} = \dfrac{(3.8\ \text{M})^2}{0.1\text{M} \times 2.1\text{M}} = 68.76 \approx 69$

Therefore, the calculated equilibrium concentrations are correct.

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Exercise 5.10

1. For the equilibrium:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\quad K_C = 0.36$ at 100 °C

A sample of 0.25 mol N_2O_4 is allowed to dissociate and come to equilibrium in a 1.5 L flask at 100°C. What are the equilibrium concentrations of NO_2 and N_2O_4?

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2. At 400 °C, the equilibrium constant for the reaction is 64:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

A mixture of 0.250 mol H_2 and 0.250 mol I_2 was introduced into an empty 0.75 L reaction vessel at 400 °C, find the equilibrium concentrations of all components.

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5.2.6 Changing Equilibrium Conditions: Le-Chatelier's Principle

- Consider a chemical reaction that is initially at equilibrium.
- Often a change in conditions will displace the reaction from equilibrium.
- The reaction then shifts toward one direction or the other (left to right or right to left as the equation is written) as it changes to a new equilibrium state.
- The direction of an equilibrium reaction will shift when a change in conditions occurs is predicted by **Le Chatelier's principle.**

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- **Le Châtelier's principle** states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.
- The factors whose change may affect a reaction equilibrium include **concentration of a reactant** or **product**, **reaction volume** or **applied pressure**, and **temperature.**

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A. Effect of Change in The Concentration

When a system at equilibrium is disturbed by a change of concentration of one of the components, the system reacts in the direction that reduces the change. That is:

- If the concentration increases, the system reacts to reduces some of it.
- If the concentration decreases, the system reacts to produce some of it.

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Consider the general reaction:

$$A + B \rightleftharpoons C + D$$

- **An increase in the concentration of A or B, or both, shifts the equilibrium position to the right, that is, toward the formation of more products.**
- **Similarly, a decrease in the concentration of C or D, or both, shifts the equilibrium position to the right.**
- **However, an increase in the concentration of C or D, or both (or a decrease in A or B, or both) shifts the equilibrium position to the left.**

Note that adding or removing reactants or products changes the value of Q_C. It does not change the value of K_C.

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Consider the following reversible reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = \frac{[HI]^2}{[H_2][I_2]}$$

- If you wish to convert as much H_2 to HI as possible, you might increase the concentration of I_2.
- To understand the effect of this, first suppose that a mixture of H_2, I_2, and HI is at equilibrium.
- If I_2 is now added to this mixture, the equilibrium is disturbed.
- Thus, the reaction will now go in the direction that will use up some of the added I_2.
- Consequently, adding more I_2 has the effect of converting a greater quantity of hydrogen to HI.

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Exercise 5.11

A and B react to produce C according to the following chemical equation:

$$A + B \rightleftharpoons C$$

Amounts of A and B are added to an equilibrium reaction mixture of A, B, and C such that when equilibrium is again reached, the amounts of A and B are doubled in the same volume. How is the amount of C changed?

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B. Effect of Change in Pressure

- A change in pressure affects only equilibrium systems that involve gases.
- Pressure changes can occur in three ways:
  - Changing the concentration of a gaseous component
  - Adding an inert gas
  - Changing the volume of the reaction vessel.

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- **Adding an inert gas has no effect on the equilibrium position.**
- **The reason is that inert gas molecules do not take part in the reaction and therefore can not affect the equilibrium in any way.**
- **However, the addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.**

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- A pressure change obtained by changing the volume can affect the yield of product in a gaseous reaction if the reaction involves a change in total moles of gas.
- According to if a pressure at equilibrium is increased (volume decreased) then the reaction will proceed in the direction that relieves the pressure.
- Thus, an increase in pressure of the system at a constant temperature shifts the equilibrium in the direction that produces a smaller number of gaseous molecules, whereas a decrease in pressure shifts in the direction of greater number (moles) of gaseous molecules.

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For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The effect of pressure is decided by:

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

- If Δn > 0, the total moles of products is greater than the total moles of reactants. Lowering of pressure will favor the reaction in the forward direction.
- If Δn < 0, the total moles of products is less than the total moles of reactants. Increasing the pressure will favor the reaction in the forward direction.
- If Δn = 0, the change in pressure has no effect on the position of equilibrium.

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For example, in the formation of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta n = 2 - (1 + 3) = -2$$

Therefore, an increase in pressure at equilibrium will favor the forward reaction.

For the dissociation of dinitrogen tetroxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta n = 2 - 1 = 1$$

The decrease in pressure at equilibrium, favors the forward reaction.

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Exercise 5.12

1. Look at each of the following equations and decide whether an increase of pressure obtained by decreasing the volume will increase, decrease, or have no effect on the amounts of products.

   a. $CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$

   b. $2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$

   c. $C\,(s) + S_2\,(g) \rightleftharpoons CS_2\,(g)$

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C. Effect of Change in Temperature

- Temperature has a profound effect on most reactions.
- Reaction rates usually increase with an increase in temperature, meaning that equilibrium is reached sooner.
- Many reactions have very low rates at room temperature, but speed up at higher temperatures.
- Change of temperatures also changes the equilibrium constant values of a reaction.

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Consider the K_C values of the methanation reaction at different temperatures:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H° = -206.2 \text{ kJ}$$

K_C for methanation at different temperatures	
298	4.7×10^{27}
800	1.38×10^{5}
1000	2.54×10^{2}
1200	3.92

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Reversible reactions are endothermic in one direction and exothermic in the other.

Consider a general reaction:

$A + B \rightleftharpoons A + D +$ heat, which is an exothermic reaction.

- If we consider heat as a reaction component of the equilibrium system, a rise in temperature "adds" heat to the system and a drop in temperature "removes" heat from the system.
- As with a change in any other component, the system shifts to reduce the effect of the change.
- Therefore, an increase in temperature at a constant pressure and concentration favours the endothermic reaction.
- Whereas, a decrease in temperature favors the exothermic reaction.

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For example, formation of ammonia is an exothermic process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ \qquad \Delta H°_{rxn} = -92\ kJ$$

From the equation we can see that 92 kJ of heat is released when NH_3 is produced from N_2 and H_2. Therefore, the forward reaction is exothermic, while the reverse reaction is endothermic. Thus, an increase in temperature favors the decomposition of ammonia to N_2 and H_2, i.e, shifts the equilibrium to the left or reactant side. Whereas, a decrease in temperature favors the formation of ammonia (shifts the equilibrium to the right or product side).

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Exercise 5.13

Consider the possibility of converting CO_2 to CO by the endothermic reaction:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Is a high or a low temperature more favorable for the production of carbon monoxide? Explain.

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D. Effect of Catalyst

- A catalyst is a substance that increases the rate of a reaction but is not used up in the reaction.
- A catalyst is shown over the arrow in an equation for a chemical reaction and does not appear in an equilibrium constant or in the reaction quotients.

For instance, SO_3 is formed by the reaction of SO_2 with O_2:

$$2SO_2\,(g) + O_2\,(g) \xrightleftharpoons{\text{Catalyst}} 2SO_3\,(g) \qquad H°rxn = -197.6\ kJ/mol$$

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- Addition of a catalyst does not shift the equilibrium position.
- Because a catalyst increases the rates of both forward and reverse reactions by the same factor, it has no effect on the equilibrium composition of a reaction mixture.
- It speeds up reaching equilibrium but does not change either the value of the equilibrium constant or the equilibrium concentrations.

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Exercise 5.14

Predict the effect of the following changes on equilibrium;

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H°_{rxn} = 197.78\ kJ$$

a. increasing pressure at constant temperature

b. increasing temperature at constant pressure

c. adding a catalyst.

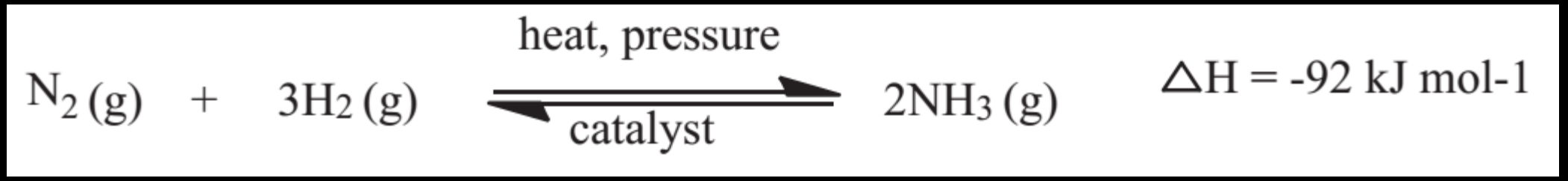
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5.2.7 Equilibrium and Industry

- Industrial processes are designed to give maximum possible yield of the products.
- The conditions for carrying out the reactions are varied based on Le Chatelier's principle.
- The following processes demonstrate application of Le Chatelier's principle in the industry.

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A. Haber Process for the Manufacture of Ammonia



- According to Le Chatelier's principle, the production of ammonia is favoured by high pressure and low temperature.
- However, the rate of the reaction at lower temperature is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia.

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As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	K_{eq}
25	6.4×10^{2}
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

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In the industrial production of NH_3 by Haber process, the reaction rate is increased by:

- adding a catalyst such as iron. It speeds up the reaction by lowering the activation energy so that the N_2 bonds and H_2 bond can be more readily broken.
- increasing reaction temperature. When temperature is increased, reactant molecules will get sufficient energy to overcome the energy barrier (activation energy) so that the reaction is faster at higher temperatures, but the yield of ammonia is lower at higher temperature.

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- At 200 °C and pressure above 750 atm, the yield of ammonia is almost 100 %, i.e., the reactants are completely converted to ammonia.
- Increasing the pressure increases the final yield of ammonia, however high pressures are expensive to produce and difficult to manage.
- So, the Haber process is carried out at pressures between 200 and 400 atm and a temperature of 500°C .

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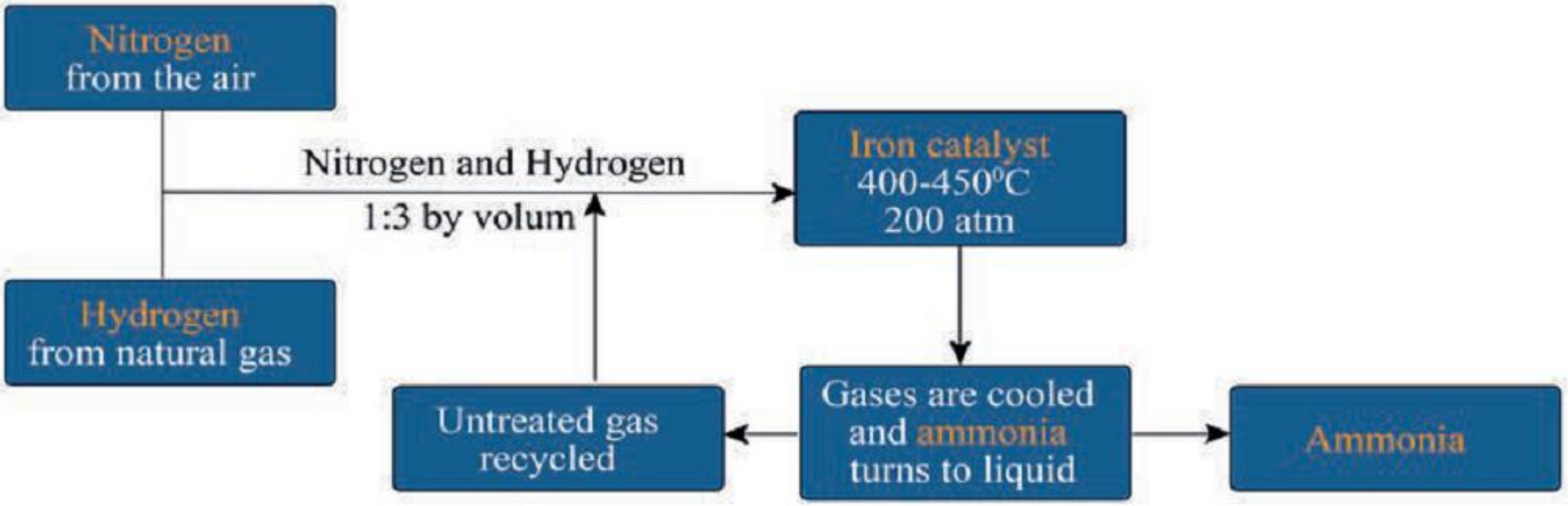


Figure 5.5: A flow diagram of the Haber process

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Exercise 5.15

Answers the following questions:

1. Which compound is manufactured by the Haber process?
2. What are the raw materials used in the Haber process?
3. What is the role of iron in the Haber process?

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B. Contact Process for the Manufacture of Sulphuric acid

The Contact process is the production of sulphuric acid, H_2SO_4, by the catalytic oxidation of sulphur dioxide, SO_2, to sulphur trioxide, SO_3. It is a reversible reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ}$$

The Contact process involves the following steps:

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i. Preparation of sulphur dioxide gas, SO_2, by burning pure sulphur in the presence of excess air:

$$S\,(s) \quad + \quad O_2\,(g) \longrightarrow SO_2\,(g)$$

To improve the efficiency of a catalyst (in the nest step), various impurities present in the mixture of SO_2 and air are first removed.

ii. Conversion of SO_2 to sulphur trioxide, SO_3

Oxidation of SO_2 to SO_3 takes place at 450 °C in the presence of a catalyst, a vanadium (V) oxide (V_2O_5):

$$2SO_2\,(g) \quad + \quad O_2\,(g) \xrightarrow[450\ ^oC]{V_2O_5} 2SO_3\,(g)$$

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iii. Converting sulfur trioxide into sulfuric acid, H_2SO_4

$SO_3(g)$ is dissolved in concentrated H_2SO_4 (98 %) to produce disulphuric acid or pyrosulpuric acid, also known as fuming sulphuric acid or oleum, $H_2S_2O_7$:

$$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$$

Converting sulfur trioxide to sulfuric acid cannot be done just by adding water, as the reaction is so uncontrollable that it creates a fog of sulfuric acid:

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iv. Dilution of $H_2S_2O_7$ to obtain H_2SO_4

A calculated amount of water is added to obtain sulphuric acid of desired strength:

$$H_2S_2O_7\,(l) + H_2O\,(l) \longrightarrow 2H_2SO_4\,(l)$$

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The oxidation of SO_2 to SO_3 (step ii) is an exothermic reaction. So, according to Le Chatelier's principle, higher temperatures will force the equilibrium position to shift to the left, favoring the production of SO_2, whereas lower temperatures would favor the production of SO_3. However, the rate of reaching equilibrium at the lower temperatures is extremely low. At higher temperature, equilibrium is reached rapidly but the yield of SO_3 is lower. The temperature about 450 °C is a compromising situation whereby a faster reaction rate results in a slightly lower yield.

Similarly, at higher pressures, the equilibrium position shifts to the least numbers of gaseous molecules, i.e., SO_3. In the Contact process, V_2O_5 is also used to speed up the rate of the reaction. Figure 5.6 shows the Contact process for the manufacture of H_2SO_4.

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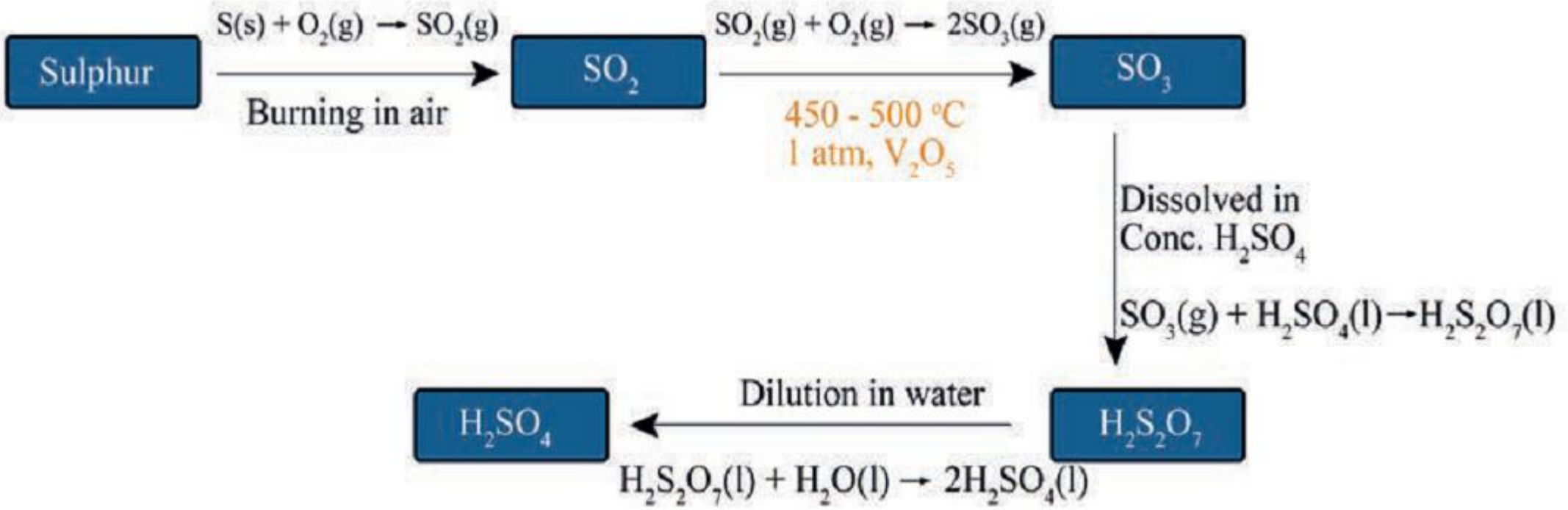


Figure 5.6: A flow diagram of the Contact process

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Exercise 5.16

Answer the following questions:

1. What is a mixture of H_2SO_4 and free SO_3?
2. What are the raw materials for making SO_2 in the Contact process?
3. Why is SO_3 not directly added to make H_2SO_4?

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