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DEPARTMENT OF PURE AND APPLIED SCIENCE

FACULTY OF SCIENCES

COURSE CODE: CHM201

COURSE TITLE: PHYSICAL CHEMISTRY II

CHM 201

PHYSICAL CHEMISTRY II

**COURSE TEAM: Professor Nnabuk Okon Eddy, MRSC (Course Writer) -
University of Nigeria, Nsukka,**

**Prof. Benedict Ita (Course Editor)
University of Calabar, Calabar.**

**Dr. Emeka C. Ogoko
Head of Department Pure and Applied Science,
National Open University of Nigeria**

**National Open University of Nigeria
Headquarters**

Plot 91, Cadastral Zone,

Nnamdi Azikiwe Expressway, Jabi - Abuja

National Open University of Nigeria

Liaison Office

14/16 Ahmadu Bello Way

Victoria Island, Lagos

Email: centralinfo@nou.edu.ng

URL: www.nou.edu.ng

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COURSE GUIDE

INTRODUCTION

This course is titled, physical Chemistry II. The course is designed to introduce the students to essential aspects of physical chemistry including kinetic theory of gases, behaviour of gases, introduction to thermodynamics, phase equilibria and chemical kinetics. Under gases, the basic principles of kinetic theory of gas and their relationship with pressure, kinetic energy, temperature, collision number and molecular speed are highlighted. Associated equations have been derived and explained. Under the behaviour of gases, equation of states and the various gas laws, their application and worked examples have been analysed. Thermodynamic section treats thermodynamic laws (zeroth, first, second and third law of thermodynamics). Consequences of these laws are also treated in this book. Some of them include adiabatic and isothermal expansion of a gas, ideal and real gases, entropy change of an ideal gas, Carnot cycle, etc. Thermodynamic consideration of phase equilibria has also been treated.

COURSE DESCRIPTION

Kinetic theory of gasses, behaviour of real gases; The laws of thermodynamic, entropy and free energy, reactions and phase equilibrium; reaction rate laws for gases where the concentration of the reactions are the same. Mechanism and theories of unimolecular reactions.

COURSE AIM

The aim of the course is to bring the students to the knowledge of fundamental aspects, theory and laws in the different areas of chemical thermodynamics especially, equation of state, thermodynamic laws, thermodynamics and their consequences. Detailed analyses of phase, phase rule, vapour pressure and essential theories have also been included in the course. Finally, behaviour of gases, gas laws and kinetic theory of gas are also included in this course.

COURSE OBJECTIVES

- To introduce the student to kinetic theory of gases, basic postulates of kinetic molecular theory of gases and their applications to equilibrium properties of gases including temperature, pressure, collision number, kinetic energy and molecular speed
- To explain the various behaviour of gases through consideration of equation of states, ideal gas equation and other gas laws
- To encourage the student to solve qualitative and quantitative problems related to gas behaviour and kinetic theory.
- To introduce the students to the various terms in thermodynamics including thermodynamic system, boundary, surrounding, state functions, processes, etc.
- To introduce the various equations of state and their consequences in thermodynamics.
- To introduce and explain the laws of thermodynamics, their implications, applications and consequences.
- To explain the concept of the third law of thermodynamics
- To examine thermodynamic requirements for spontaneity of a chemical reaction
- To solve mathematical problems related to chemical thermodynamics.

WORKING THROUGH THIS COURSE

The course is structured into three Modules. Module 1 consists of three unit, Module 2 consists of four units while Module 3 consists of one unit. It is necessary that for the student to study and understand the content of all the units in the respective modules.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide
2. Study Units

STUDY UNITS

Module 1

Unit 1: Kinetic theory of gas

Unit 2: Behaviour of gas

Module 2

Unit 1: First law of thermodynamics

Unit 2: Consequences of first law of thermodynamics

Unit 3: Second, third and zeroth laws of thermodynamics

Unit 4: Zeroth and third law of thermodynamics

Module 3

Unit 1: Chemical kinetics

Module 1 is divided in three units. The unit introduces the students to gases, properties of gases and materials equilibria

Unit 1 identifies the basic postulates of kinetic theory and their applications in deriving equation for computation of gas pressure, kinetic energy, temperature, molecular speed and collision number.

Unit 2 treats Boyle's law, Charles' law, Dalton law, ideal gas equation and van der Waal forces as the fundamental equations of state. Mathematical and experimental implications of the equations have been considered in detail.

Unit 3 deals with phase equilibria including detailed qualitative and quantitative treatment of vapour pressure, phase systems, phase diagram and phase rule.

Module 2 is divided into four units

Unit 1 considers basic terms in chemical thermodynamics, their definitions and significance. These include a thermodynamic system, surrounding, boundary, classifications of thermodynamic properties, state functions, thermodynamic processes, reversible and irreversible

processes, etc. The unit also considers the First law of thermodynamics and its consequences. These include heat change or work done at constant pressure and volume, work done in isothermal expansion of ideal and real gases, relationship between pressure and volume during adiabatic expansion of gases, applications of the first law

Unit 2 deals with consequences of the first law of thermodynamics including thermodynamic work, Heat change at constant pressure and at constant volume, Work done in isothermal expansion of a gas, Work done in phase transition, Heat capacity, Adiabatic expansion of a gas and Joule Thompson experiment

Unit 3 introduces the concept of entropy in detail and provides statements of the second law of thermodynamics in various versions. Equation for entropy change of an ideal gas has been derived. General characteristics and principle of operation of heat engines have been outlined. Details treatment of the cyclic process (exemplified by the Carnot cycle) have been done. Equations for the efficiency of the Carnot cycle in terms of heat absorbed and temperature have also been derived.

Unit 4 discussed the zeroth and third laws of thermodynamics in detail. Consequences of the laws have also been highlighted.

Model 3 consists of one unit which discusses basic concepts of chemical kinetics including theoretical and experimental rate laws, order of reactions, molecularity of reaction, rate law for first and second order reactions, mechanism of reaction and finally theories of unimolecular reactions

. TEXTBOOKS AND REFERENCES

Textbooks referred to in the development of each unit are presented at the end of the units. However, a list of some General references is presented below:

1. Atkins, P. and De Paula, J. (2010). Atkins' Physical Chemistry. Ninth Edition. Oxford University Press. UK.
2. Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.
3. Levine, N. I. (2009). Physical Chemistry. 5th Edition. Higher Education. Boston.
4. Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70 % of the total course score.

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MODULE 1

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1.0 Introduction

There three states of matter are solid, liquid and gas. The distinction between the three named states of matter is based on the existence of micro properties and their relative rate of motion within a given system. The kinetic theory offers explanation on the different rate of movement of microscopic properties (atom, molecules, ions, charge, etc) within a given state of matter. Solids have definite shape and occupied volume. Liquids and gases take the shape and volume of the containing vessel. However, liquids differ from gases in that gas molecules are far apart, forces of cohesion is negligible within gas molecules, gas pressure is negligible and is related to the temperature of the gas. Liquid molecules are less closer to each other and move at lower speed compared to gas molecules.

2.0 Objectives

The objective of this section shall include the following,

- To understand the basic postulates of kinetic theory of gas
- To derive equation for pressure of gas using kinetic theory

- To derive equation for kinetic energy of gas using kinetic theory
- To derive expression for temperature of a gas and relate it to the average kinetic energy
- To derive expression for the various molecular speed components of gas including arithmetic (mean), most probable and root mean speed
- To derive expression for collision number of gas
- To solve qualitative and quantitative equations related to kinetic theory.

3.0 Main document

3.1 Postulates of kinetic theory of gases

According to the kinetic theory, gas consists of a large number of molecules or atoms (i.e sub-microscopic particles) that are in constant motion and whose collision with each other and with the wall of the container is responsible for its randomness. The theory assumes that gas pressure is due to collision impacts of gas molecules (moving at different velocities) on the wall of the container. The average kinetic energy exerted by the moving gas molecules is a measure of the temperature of a gas. Generally, kinetic theory of gases can be summarised as follows,

- i. The gas consists of very minute particles called molecules, which occupy a negligible volume compared to the volume of the container. This indicates that the average distance between gas molecules is large compared to their size.
- ii. Gas molecules are minute and are in constant random rapid motion and rectilinear motion
- iii. Gas molecules collide with each other and with the wall of the container. The molecules are considered to be perfectly spherical in shape because the collision between gas molecules are perfectly elastic (i.e change in momentum is zero).

- iv. Except during collision, forces of cohesion between gas molecules are negligible. This implies that relativistic and quantum mechanical effects are negligible and that the gas molecules can be treated as classical objects because the inter-particle distance is relatively larger than the thermal de Broglie wavelength (which justifies quantum mechanical treatment).
- v. The average kinetic energy of gas particles is a measure of the absolute temperature of the gas.
- vi. The elapsed time of a collision between a molecule and the container is negligible compared to the time between successive collisions.

It is significant to state that a gas molecule has mass, hence it can be affected by gravity. Also, because the number of gas molecules in a given system is always large and similar, statistical treatment can be applied to model their behaviour. In Chemistry, molecules can be treated under classical or quantum mechanical models. The classical approach is applicable to particles with relatively small distance or size (such as those within the thermal de Broglie wavelength) while classical theory negates the quantization principles. The absence of quantum effects in gas molecules implies that there is no molecular chaos and that the bulk properties are characterised by small gradients.

3.2 Equilibrium properties and kinetic theory of gas

The basic equilibrium properties that can be explained by the kinetic theory of gases are,

- i. Pressure of a gas
- ii. Temperature of a gas
- iii. Speed of a gas molecule: Most probable speed, arithmetic and root mean speed
- iv. Collision number

These properties are discussed separately in the following sub sections.

3.2.1 Kinetic theory and pressure of a gas

Consider a gas molecule of mass, 'm' under a motion with velocity given as v_x in the x-direction.

The molecules are contained in a cuboids of length, L and volume $V = L^3$ The momentum exerted by the gas molecule is given as,

$$1$$

where is the total change in momentum, p_i and p_f are the momentum before and after collision.

The elapsed time between collision on one side of the wall is given as,

$$2$$

where L is the distant between two sides of the container, hence 2L is the distant between collision. By definition, force is the rate of change of momentum, indicating that the force due to this particle is given as,

$$3$$

If the total number of molecules in the container is N, then the total force on N particle will be expressed as ,

$$4$$

The bar is used to indicate average molecular speed over N particle. Since there is no bias applicable to the motion of the gas molecules in any direction, it can be stated that the average square speed in any direction is the same. i.e . In a three dimensional system, the total square speed is given by Pythagoras theorem, which can be expressed as,

$$5$$

Since , , and the total force on N molecule can be expressed as,

$$6$$

Equation 6 expresses the force exerted on a cuboid of cross sectional area given by L^2 . Hence the gas pressure can be defined as force exerted divided by the area (equation 7).

7

The kinetic energy of the molecules can be written as $KE = \frac{1}{2} mv^2$ and from equation 7, $KE = 3PV/2$. Hence, KE

Question 1. Calculate the kinetic energy of an ideal gas occupying a volume of 22.4 dm^3 at stp.

Given,

$$P = 101325 \text{ Pa}$$

$$V = 22.4 \text{ dm}^3 = 0.0224 \text{ m}^3$$

But KE hence

3.2.2 Kinetic theory and temperature

Equation 7 can be re-written as,

8

Also, the ideal equation indicates that $PV = nRT$ or $PV = Nk_B T$. where k_B is the Boltzmann constant and T is the absolute temperature. Hence ,

or

From the above, and . Since the kinetic energy of the entire molecule is N times the kinetic energy of a single molecule, then, the total kinetic energy is $KE =$. Hence the kinetic energy per molecule and the temperature of the gas are expressed as follows,

9

10

Since $PV = Nk_B T$ and KE ($KE = 3PV/2$), equation 10 can also be linked to the ideal gas equation, indicating that ,

$$11a$$

$$11b$$

$$11c$$

$$11d$$

According to equation 11d, the product of the pressure and volume per mole of a gas is proportional to the average molecular (translational) kinetic energy. A mono atomic gas has three degree of freedom. Therefore, the average kinetic energy of N particle of mono atomic gas per degree of freedom per molecule is given as,

$$12$$

3.2.3 Kinetic theory and molecular speed

The kinetic energy of a gas is given as and . Therefore, the average molecular speed can be written as,

$$13$$

Where v_{rms} is the root mean speed of a gas molecule. The most probable speed and the arithmetic (mean) speed of a gas molecule are also expressed in equations 14 and 15

$$14$$

$$15$$

It should be noted that the v_{rms} is equal to the product of the most probable speed (v_p) and the square root of 3/2.

4.2.4 Collision with the container

A derivative defining the total number of collision per unit time per unit area can be written as,

1.0 Summary

The kinetic theory explains the macroscopic properties of gases (such as viscosity, pressure, temperature, pressure, etc) by considering their relationship with molecular composition and motion. The importance of the kinetic law to the behaviour of gases can not be over emphasised.

Conclusion

Postulate of the kinetic theory are very essential in understanding the behaviour of ideal gases, through which the expected behaviour of real gases can be extrapolated. The postulates offer avenues for estimation of fundamental macroscopic properties of gases such as pressure, kinetic energy, temperature, molecular speed and collision number.

2.0 Tutored marked assignment

1. Highlight the basic postulates of kinetic theory of gas
2. What is the relationship between gas pressure and kinetic energy of the gas molecules.
3. Use the kinetic energy theory to explain the behaviour of gas molecules with respect to classical and quantum mechanical concepts.
4. Derive expression for the pressure of gas molecule of mass m , confined to a cube of length, L
5. Derive expression for the kinetic energy of a gas molecule and for the temperature
6. Derive and expression for the most probable, mean and root mean speed of a gas. What is the relationship between them.

7.0 References

Atkins, P. and De Paula, J. (2010). Atkins' Physical Chemistry. Ninth Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco. New York.

Levine, N. I. (2009). Physical Chemistry. 5th Edition. Higher Education. Boston.

Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wiley and Sons Ltd. England.

MODULE 1

UNIT 2: Behaviour of gases

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10.2.1 Boyle's law

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1.0 Introduction

The kinetic theory is significant in explaining the behaviour of gas molecules. Gas molecules are subjected to continuous and rapid movement which operates through collision with each other and with the walls of the container. The collision of the molecules is elastic and does not defile the fundamental principle of classical theory of relativity. Based on established behaviour of gas molecules, it is evident that effects of its motion, collision and other behaviour are essential in establishing qualitative properties between macroscopic properties that characterised gas

molecules. For example, due to their collision, pressure is defined and due to kinetic energy, temperature is defined. The relationship between pressure and volume is given by Boyle's law while the relationship between volume and temperature is given by Charles' law. Fundamental equations of this nature are called equation of state. This section highlights the significance of equation of state and identifies the various equations as well as their significant.

2.0 Objectives

The objectives of this section shall include the following,

- To understand the concept of equation of state
- To establish the relationship and inter-relationship between various macroscopic properties of gas
- To understand the qualitative and quantitative information concerning gas laws including Boyle's , Charles, Dalton, Gay Lussac, Grahams laws, etc.

3.0 Main content

3.1 Equation of state

Equation of state is a thermodynamic model that relates two or more state functions. The state functions in the equation of state are variables that describe the state of matter under a given condition. Observable properties (pressure, temperature, mass, density, volume, etc) of gases are significant because their values determine the state of the gas. Therefore, variations in one or more property, while others are held constant, can provide useful information for predicting the state of a gas, through the establishment of the relationship between them. For example,

- i. If the pressure and temperature are held constant, the volume of the gas depends on the mass (i.e amount) indicating that the relationship between mass and volume of the gas (i.e density) can be verified.

- ii. If the mass and temperature are held constant, the product of the pressure and volume will be almost constant for real gas but exactly constant for ideal gas.
- iii. If the mass and the pressure are held constant, the volume will be directly proportional to temperature, indicating that the ratio of the volume to temperature will be constant.

Other properties of gases can be verified through other relationships and the necessary equations obtained from such verification constitute equation of state. The equation of state is also applicable to other states of matter. For example, equation of state for modelling the transition of solid from one crystalline state to another, equation of state for perfect fluid (in cosmology) and equation of state for modelling the interior of stars (which includes neutron stars, dense matter and radiation). However, since the behaviour of gases can easily be modelled, we shall concentrate on gases.

3.2 Gas laws

3.2.1 Boyle's law

Robert Boyle (1662) was the first to develop documented equation of state, which he obtained through series of experiments using J-shaped glass tube to study the variation of the volume of a fixed mass of a gas with pressure (at constant temperature). In support of Robert Boyle work, Edme Mariotte (1676) also confirmed the relationship between pressure and volume of a fixed mass of a gas at constant temperature. Boyle's law states that at constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure. Mathematically, Boyle's law can be expressed as follows,

1

2

Therefore, according to Boyle's law, the product of the pressure and volume for a given mass of a gas will always be constant provided the temperature is constant. It also implies that a plot of volume (V) against the inverse of pressure (1/P) and also a plot of pressure against volume, will follow predicted pattern as shown in the figures below (Fig. 1),

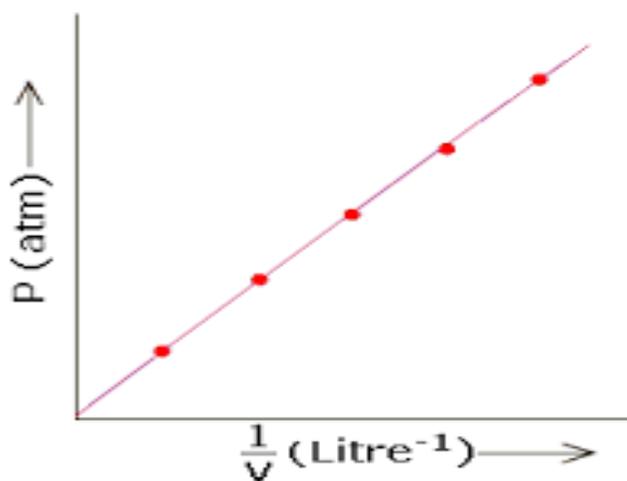


Fig. 1: Variation of pressure of ideal gas with the inverse of its volume according to Boyle's law

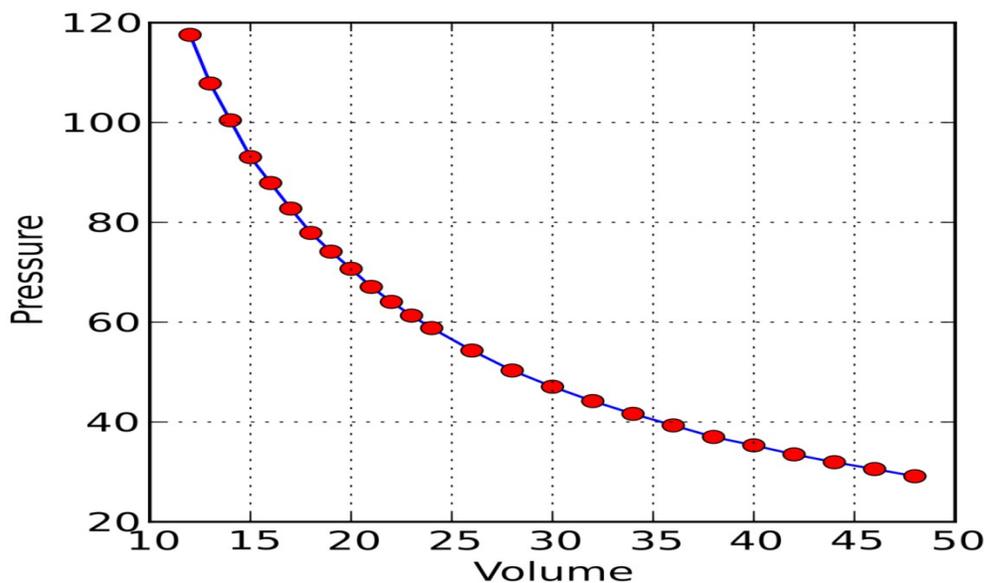


Fig. 2 Variation of pressure with volume according to Boyle's law

Question 5

(a) In an automobile combustion cylinder, fuel-air mixture in a cylinder of 1000 cm^3 capacity experience a temperature rise from 25 to $2200 \text{ }^\circ\text{C}$ before and after combustion. Calculate the peak pressure given that normal atmospheric pressure is 101325 Pa .

(b) If the initial air fuel volume was 500 cm^3 in the above problem, calculate the new pressure,

Solution

Given,

$$P_1 = 101325 \text{ Pa}$$

$$T_1 = 25 \text{ }^\circ\text{C} = (273 + 25)\text{K} = 298 \text{ K}$$

$$T_2 = 2200 \text{ }^\circ\text{C} = (273 + 2200) \text{ K} = 2473 \text{ K}$$

$$P_2 = ?$$

From Boyle's law, $PV = K$ and from Charles, law, $V/T = K$. Since pressure is inversely proportional to volume, it also follow that $P/T = K$. Therefore, and $P_2 = P_1 T_1 / T_2$
 $= (101325 \text{ Pa} \times 298 \text{ K}) / 2473 \text{ K} = 12209.81 \text{ Pa} = 12.10 \text{ kPa}$

(h) The useful equation will be combine gas equation, which can be written as, or as,

Question 6

(a) 300 cm^3 of air at a pressure of 100 kPa is compressed to a volume of 200 cm^3 . What will be the pressure of the compressed air?

(b) What will be the volume that will be required to store 20 cm^3 of butane gas if it is to be compressed from 1.5 atm to 10 atm pressure?

(c) A 100 cm^3 gas syringe containing 80 cm^3 of gas that was compressed to 50 cm^3 . If the atmospheric pressure is 101325 Pa , calculate the pressure of the gas in the syringe after compression.

Solution

(a) From Boyle's law, $P_1V_1 = P_2V_2$. therefore, $P_2 = P_1V_1/V_2 = 100000 \text{ Pa} \times 300 \text{ cm}^3/200 \text{ cm}^3$
 $= 150\,000 \text{ Pa} = 150 \text{ kPa}$

(b) From Boyle's law, $P_1V_1 = P_2V_2$, therefore, $V_2 = P_1V_1/P_2$

$P_1 = 1.5 \text{ atm} = (1.5 \times 101325)\text{Pa} = 151987.5 \text{ Pa}$

$P_2 = 10 \text{ atm} = (10 \times 101325)\text{Pa} = 1013250 \text{ Pa}$

$V_1 = 20 \text{ cm}^3$

$V_2 = ?$

$V_2 = P_1V_1/P_2 = 151987.5 \text{ Pa} \times 20 \text{ cm}^3/1013250 \text{ Pa} = 3 \text{ cm}^3$

(c)

$V_1 = 80 \text{ cm}^3$

$V_2 = 50 \text{ cm}^3$

$P_1 = 101325 \text{ Pa}$

$P_2 = P_1V_1/V_2$) Boyle's law

$P_2 = (101325 \text{ Pa} \times 80 \text{ cm}^3)/50 \text{ cm}^3 = 162120 \text{ Pa} = 162.12 \text{ kPa}$

3.2.2 Charles law

The next level of development of equation of state for gases was pioneered by Jacques Charles (1787) and Josph Louis Gay-Lussac (1802). Charles found that the expansive behaviour of air and some gases over a range of temperature, followed a similar pattern. In repeating similar experiments, Gay-Lussac found that there is a linear relationship between volume and temperature. Charles law state that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature. Mathematically, Charles' law can be expressed as follows,

3

4

Hence, according to Charles' law (equation 18), the ratio of the volume of a fixed mass of a gas to its temperature, will always be a constant provided the pressure is held constant. This also

translates to interpreting a plot of V against T as linear with zero intercept and slope, equal to K . Graphical representation of Charles' law in various forms are presented in Fig. 3.

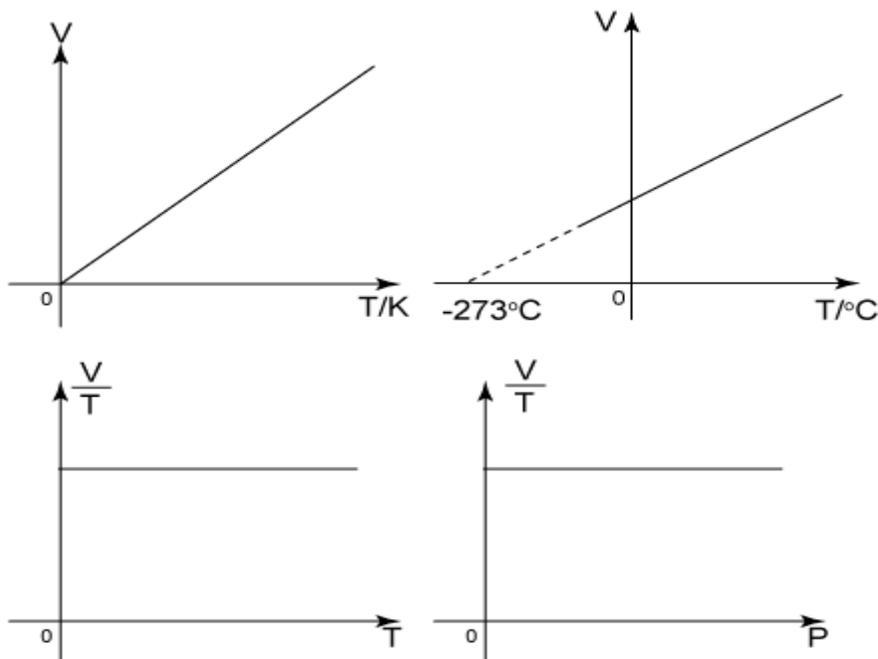


Fig. 3: Various plots representing Charles' law

The plots clearly reveal that according to Charles' law, plotting of values of volume against temperature give a linear relationship, which may be extrapolated to -273 K . Also, a plot of V/T against T or P is parallel to the x-axis.

3.2.3 Dalton law

Dalton law (1801) is concerned about the partial pressure exerted by gases in a mixture. The law states that for a mixture of gases which do not react chemically, the total pressure of the gas is the sum of the partial pressures exerted by the individual gases in the mixture. This implies that if the components of a gas mixture are A, B, C, D, \dots, N , then the total pressure of the gas will be expressed as

Question 3

- (a) A mixture of 6.5 mol of hydrogen gas and 3.5 moles of oxygen gas were contained in a 3 m^3 container at 273 K. Calculate the partial pressure of the individual gases.
- (b) Also calculate the total pressure of the gas mixture

Solution

- (a) According to Dalton law,

But the ideal gas law states that $PV = nRT$, Therefore,

and

- (b) According to Dalton law, the total pressure of the gas mixture is the sum of the partial pressures. Therefore,

Question 4

- (a) A given gas mixture consist of 2.24 mol of nitrogen and 1.37 mol of oxygen, use the ideal gas equation to calculate the total pressure of 10 m^3 of the gas mixture at 273 K.
- (b) Use the mole fraction of the respective components of the gas mixture to calculate the corresponding partial pressures.

Solution

(a) The total pressure in the gas mixture can be written as,

$$= 819.27 \text{ Pa}$$

(b) The mole fraction of nitrogen and oxygen can be calculated as follows,

The total pressure of the gas mixture is related to the mole fraction according to the following equations,

3.2.4 The ideal gas equation

The ideal gas equation was developed by Emile Clapeyron, who combined Boyle and Charles laws in 1834. The equation can be written according to equation 6,

$$6$$

where n is the number of moles of the gas and R is the universal gas constant, which is numerically equal to 8.314 J/mol/K

Question 1

Calculate the volume of 1 mol of an ideal gas at 1 atm pressure and at 0°C . Comment on our results, with respect to the expectation for all ideal gas

Solution

The needed equation is $PV = nRT$.

P is the pressure, given as 1 atm = 101325 Pa

n is the number of moles given as 1

R is the gas constant, which is numerically equal to 8.3144 J/K/mol

T is the temperature, given as $0^\circ\text{C} = 273\text{ K}$

Therefore,

The volume occupied by one mole of an ideal gas under standard temperature and pressure is the same for all gases and is called the molar volume of a gas.

Question 2

If the density of ethane is 1.264 g/dm^3 at 20°C , calculate the molar mass of ethane. Given that $H = 1.00794$ and $C = 12.0107$, compare the result obtained from your calculation with the actual molecular mass. Account for any difference, if it exists.

Solution

$1\text{ dm}^3 = 0.001\text{ m}^3$ of ethane weighs 1.264 g at 283 K (i.e., 20°C). Applying the ideal gas law, we have,

The formula of ethane is C_2H_6 indicating that its molar mass = $2(12.0107) + 6(1.00794) = 24.0214 + 6.04764 = 30.07\text{ g/mol}$. The difference between the two sets of values is 0.33 . This is due to the fact that in real gases, there exist intermolecular forces which are not taken into consideration in the ideal gas model.

Question 7

- (a) Define the term, equation of state and highlight the feature of state function with respect to equation of state.
- (b) Highlight the expectation in the property of a gas if the following variables are held constant,
- Pressure and temperature
 - Mass and temperature
 - Mass and pressure
- (c) State the three major equations of state that you know.
- (d) What is the relationship between the ideal gas equation and the van der Waals equation of state

Solution

(a) Equation of state is a thermodynamic model that relates two or more state functions. The state functions in the equation of state are variables that describe the state of matter under a given condition. Observable properties (pressure, temperature, mass, density, volume, etc) of gases are significant because their values determine the state of the gas.

- (b)
- If the pressure and temperature are held constant, the volume of the gas depends on the mass (i.e amount) indicating that the relationship between mass and volume of the gas (i.e density) can be verified.
 - If the mass and temperature are held constant, the product of the pressure and volume will be almost constant for real gas but exactly constant for ideal gas.
 - If the mass and the pressure are held constant, the volume will be directly proportional to temperature, indicating that the ratio of the volume to temperature will be constant.

- (c)
- Boyle's law states that at constant temperature, the volume of a fixed mass of a gas is inversely proportional to the pressure
 - Charles law state that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature.

iii. Dalton law of partial pressure states that for a mixture of gases which do not react chemically, the total pressure of the gas is the sum of the partial pressures exerted by the individual gases in the mixture.

(d) The ideal gas equation can be written as $PV = nRT$. Where P is the pressure, V is the volume, n is the number of moles, R is the universal gas constant and T is the temperature. The presence of intermolecular forces does not allow this equation to be applicable to real gas. Therefore, van der Waals equation modified the pressure term with a/V^2 and the volume by b. Hence according to van der Waals, (for 1 mol of a gas)

4.2.5 Van der Waal equation of state

In 1974, J. D. Van der Waals derived an equation of state that can be used to interpret the behaviour of real gases. This was necessary because most real gases do not obey the ideal gas equation. Therefore, van der Waal equation is a modification of the real gas equation and can be written as,

$$(for\ 1\ mol\ of\ a\ gas) \qquad \qquad \qquad 7$$

From the above, the pressure term is corrected by a/V^2 while the volume term is corrected by 'b'. This equation expects that for a real gas, the pressure will increase by a factor of a/V^2 while the volume will decrease by 'b', compared to ideal gas.

3.2.5 Law of diffusion/effusion of gas

Diffusion describes a process where particles of one gas are spread throughout another gas by molecular motion. A good example is when a container containing a gas such as ammonia is opened. The odour of ammonia will be perceived even at a reasonable distance from the point of opening because the ammonia gas is spread over the air. Not all gases diffuse at the same rate. It was Thomas Graham, a Scottish Chemist, who discovered that lighter gases diffuse at a faster rate than heavy gases. The law states that the rate of diffusion of all gases at constant temperature and pressure is inversely proportional to the square root of its molar mass. That is,

Effusion explains the escape of a molecule through a small hole in a container such that during the escape, there is no collision. As in diffusion, during effusion, the lighter molecule will escape first because it is characterised by higher speed, compared to the heavier molecule. Graham law is also applicable to effusion. From kinetic theory of gas, the average kinetic energy of a gas is a measure of the absolute temperature of that gas. Therefore, two gases at the same temperature will have the same kinetic energy. Hence,

9

10

11

12

Equation 23d reveals that the rate of diffusion of gases is inversely proportional to the molar mass or its density (since density is related to molar mass).

Question 8

The molar mass of hydrogen and oxygen gases are 1 g/mol and 16 g/mol. Calculate the relative rate of diffusion of the two gases.

Solution

The relative rate will be given as

$$= 4$$

Therefore, hydrogen gas will diffuses four time faster than oxygen.

Question 9

. Assuming a gas consist of three molecules with speed, 2, 3 and 4 m/s. Calculate the mean speed and the root mean speed of the gas.

Solution

- i. The mean speed is the average of the molecular speed of the gas molecules

$$= 3 \text{ m/s}$$

- ii. The root mean speed is square root of the average of the square of the molecular speed/ That is

$$= 3.11 \text{ m/s}$$

In practice, it is not possible to have a gas system that has three molecules only. Therefore the approach used above to calculate root mean speed may be very tedious when the number of molecules is large. In Equations 13 to 15 (in Module 1, unit), expressions for calculating root mean, arithmetic and most probable speed were given. In terms of the gas constant, molar mass and temperature, the root mean speed can also be expressed as,

$$13$$

The difference between equation 15 (of unit 1, module 1) and 13 above () is that the Boltzmann constant is substituted for the gas constant,

R is proportional to k_B . $R = Nk_B$, where N is the Avogadro's number. The $N = 6.022 \times 10^{23} \text{ mol}^{-1}$, $R = 8.314 \text{ J/mol/K}$.

Question 10

Helium molecule has a mass of 4.0026 g and is moving at a speed of 30 m/s. Calculate the classical kinetic energy of the gas.

Solution

The classical kinetic energy is given as, $KE = \frac{1}{2} mv^2$

$$= 1.80 \text{ kgm}^2/\text{s}^2 = 1.80 \text{ J}$$

Question 11

2.00 mol of Argon can effuse from an opening in a vessel in 3.626 seconds. 1.00 mol of gas X can effuse in 1.000 seconds. Use this information to identify gas X. (Given: Molar mass of argon gas = 39.95 g/mol. Also calculate the root mean speed of the Argon gas.

Solution

$$R_{\text{Ar}} = 3.626 \text{ second (2 moles)}$$

$$R_{\text{X}} = 1.000 \text{ second (1 mole)}$$

$$R_{\text{X}} = 2.000 \text{ second (2 moles)}$$

$$M_{\text{Ar}} = 39.95 \text{ g/mol}$$

Applying Grahams law,

The calculated molar mass correspond to xenon gas.

4.0 Summary

Gas laws are fundamental concepts that are needed to model the behaviour of gases. The basic gas laws have been developed into equations including, Boyle, Charles,-Gau Lussac, Dalton, combined and van der Waals equations. These laws rely on the effect of variation of parameters of thermodynamic significant. Thermodynamics can not be adequately resolved into meaningful models without considering these parameters. For example, pressure, volume, temperature, density, etc. In view of these and other advantages, the fundamental equations of state have been adequately analysed so that the objectives of the model can be appreciated by the students.

5.0 Conclusions

Fundamental treatments that transform equation of state to applicable forms are handled by gas laws including Boyle's, Charles, Dalton, Ideal gas equation, van der Waal and Grahams law of

diffusion. Although these laws are theoretical models that are applicable to ideal gases, there are necessary tools that are needed in predicting the most probable behaviour of a real gas through considerations of pressure, temperature, kinetic energy, molecular speed and collision number.

6.0 Tutoed marked assignment

1. What is the significant of equation of state in analysing the behaviour of gases?
2. Derive equations for Boyle's and Charles' laws and also derive an equation resulting from a combination of the two laws.
3. What is the difference between diffusion and effusion? Also derive an expression that relates the rate of diffusion of a gas to (i) Molar mass (ii) Vapour density.
4. What is the relationship between gas constant and Boltzmann constant? Calculate the numerical value of the Boltzmann constant.

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MODULE 1

MODULE 1

Unit 3: Phase equilibria

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1.0 Introduction

In the treatment of phase equilibrium, it is necessary to consider the various types of materials equilibrium that can be encountered. First an equilibrium may exist between a liquid and vapour due to evaporation and condensation. Equilibrium may exist between solid and vapour due to sublimation. Existence of equilibrium implies that boundaries may exist. Such boundaries may be between solid and gas, solid and liquid, liquid and gas. Two broad areas of science cover the existence of equilibrium and boundaries. These are vapour pressure and phase equilibria. Vapour pressure is the pressure exerted when an equilibrium is established between the number of

particles evaporating and condensing within a given system. Thermodynamic treatment are useful tools in analysing phase equilibria.

2.0 Objectives

Specific objectives for this section include the following,

- i. To understand what is phase equilibria
- ii. To know the meaning of vapour pressure
- iii. To differentiate between vapour pressure and atmospheric pressure
- iv. To understand the quantitative and qualitative relationship between vapour pressure and temperature
- v. To produce and understand phase diagrams of some components
- vi. To understand and apply phase rule in solving related problems

3.0 Main content

3.1 Vapour pressure

According to the kinetic theory, liquid consists of particles such as ions and molecules that are also in motion, The average energy of the particles in a liquid is a function of temperature. Increase in temperature will lead to increase in this average energy. Within the liquid system, some particles are more energetic than others resulting in arrangement, which drives the more energetic particle to be on the surface of the particles while the less energetic particles are in the bulk of the liquid. At reasonable energy function, these surface particles have the tendency to escape through process of evaporation. Evaporation is a surface process that involves escape of energetic molecules of liquid from the surface. Since the number of energetic particles can be increased by increase in temperature, evaporation will increase with increase in temperature. Evaporation differs from boiling in that it is a surface process while boiling involves the bulk

liquid. Besides, boiling occurs at a given temperature (depending on the atmospheric pressure) while evaporation increases with increase in temperature.

In a closed system (such as a closed container), the escaping energetic molecules will not be able to get into the atmosphere but will be found above the surface of the liquid. Some of them will have the opportunity of returning to the liquid and the process will continue until an equilibrium is approached when the number of particles leaving the surface of the liquid is balanced by the number of particles rejoining the surface. At equilibrium, the number of gaseous particles above the liquid surface is fixed and when they collide with each other and with the wall of the container, a pressure named saturated vapour pressure of the liquid will be exerted.

3.1.1 Effect of temperature on vapour pressure

This equilibrium involves the conversion of liquid to vapour as the forward reaction while the reverse reaction involves the reconversion of vapour to liquid is the reverse reaction. Consequently, the forward reaction will be endothermic because heat is needed to convert liquid to vapour while the reverse process is exothermic. According to Le Chatelier's principle, increase in temperature of a dynamic equilibrium favours the forward reaction as stated before.

The Figure below shows the variation of saturated vapour pressure of water with temperature

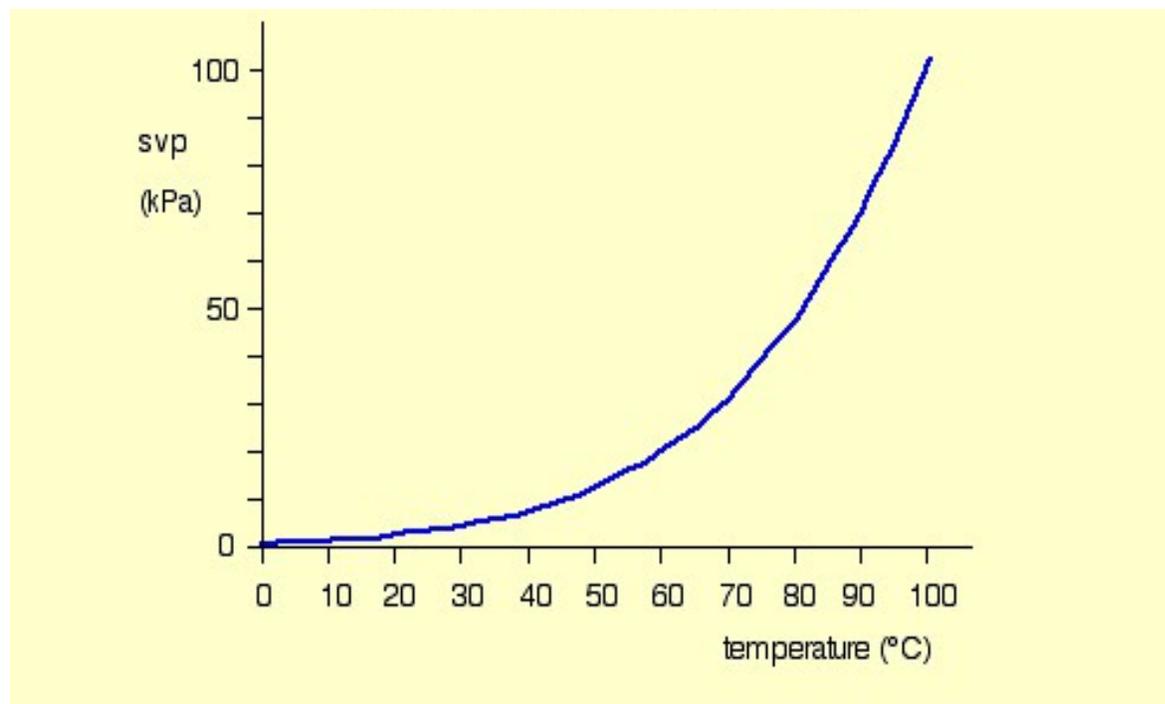


Fig. 1: Variation of saturated vapour pressure of water with temperature
(Source: <https://www.chemguide.co.uk/physical/phaseeqia/vapourpress.html#top>)

As shown in Fig. 1, the vapour pressure of any substance does not increase linearly with temperature. This is consequence of Clausius-Clayperon equation. The normal boiling point of a liquid is the temperature in which the prevailing vapour pressure of the liquid is equal to the ambient atmospheric pressure. At the boiling point, the vapour pressure has sufficient energy to overcome the atmospheric pressure and will cause the liquid to boil

Water has normal boiling point of 100 °C, which is the temperature at which it boils at a pressure of 101.325 kPa (i.e standard atmospheric pressure) as shown in the above plot. Similar information for some other liquids including methyl chloride, butane, neo-pentane, diethyl ether, methyl acetate, fluorobenzene and 2-heptene are shown in Fig. 2 below,

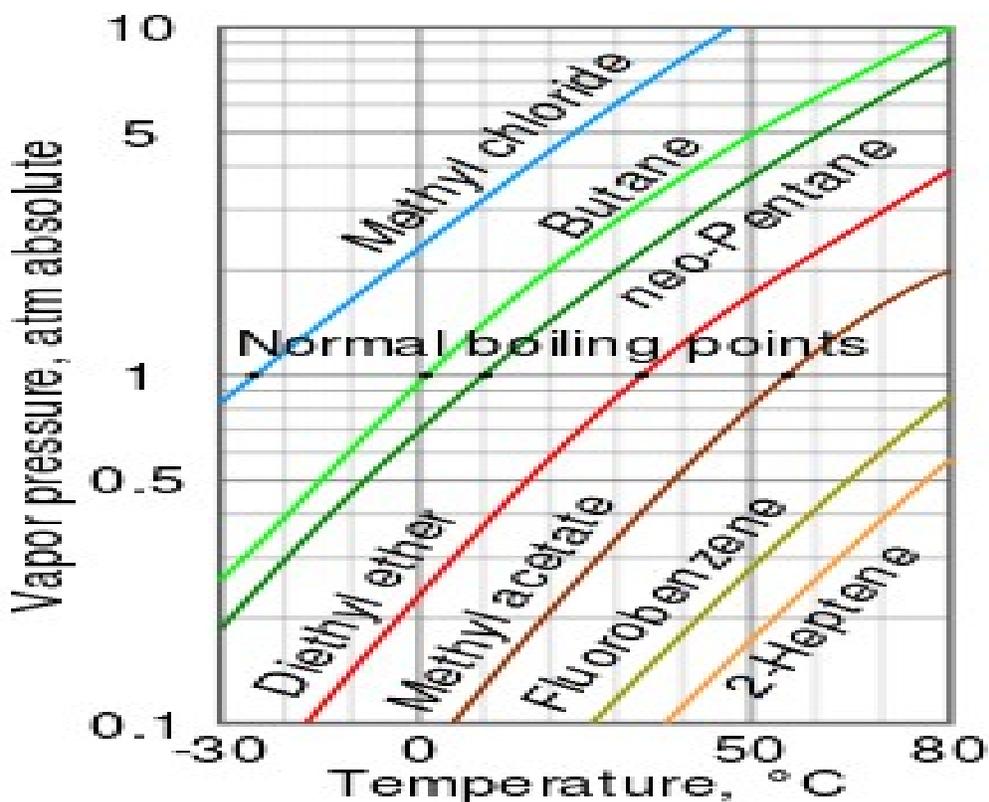


Fig. 2.: variation of saturated vapour pressure of methyl chloride, butane, neo-pentane, diethyl ether, methyl acetate, fluorobenzene and 2-heptene with temperature

(Source: https://en.wikipedia.org/wiki/Vapor_pressure)

From the above figure (Fig. 2), it can be deduced that the vapor pressures of liquids at ambient temperatures increase with decreasing boiling points. Also, at the normal boiling point of a liquid, the vapor pressure is equal to the standard atmospheric pressure which is 1 atmosphere (760 Torr or 101 325 kPa).

3.2 Raoult's law

For mixture of liquids, Raoult's law provides an avenue for estimating their vapour pressure. The law states that the pressure or fugacity (i.e activity) of a single-phase mixture is equal to the mole-weighted sum of the component pressure and can be written as,

where p_i and x_i are the vapour pressure and mole fraction of i th component of the liquid. Statements of the law can also be stated as follows,

- i. The partial pressure of each component of an ideal mixture of liquids is equal to the vapour pressure of the pure component multiplied by its mole fraction in the mixture.
- ii. The relative lowering of vapour pressure of a dilute solution containing non volatile solute is equal to the mole fraction of solute in the solution.

Systems that obeys Raoult's law are called ideal solutions while non ideal solutions do not obey the law.. For a two component systems, the Fig.3 below presents the nature of plots expected for systems that obeys Raoult's law.

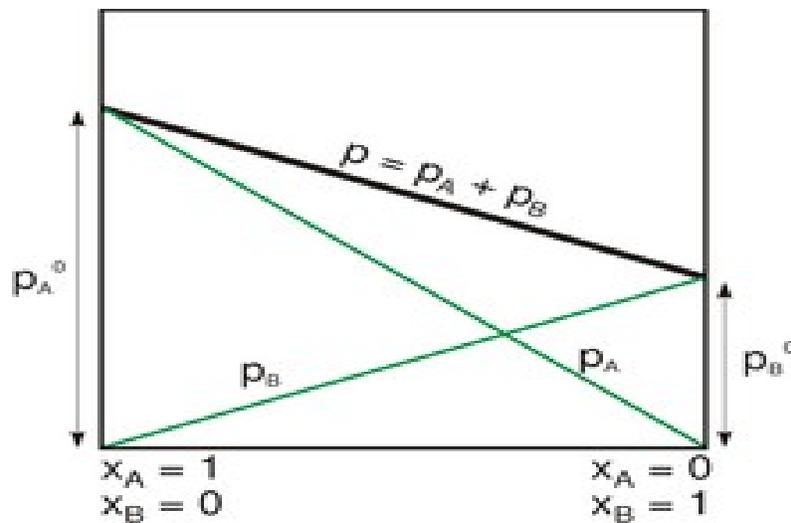


Fig. 3: Vapour pressure plots for a binary system obeying Raoult's law
(Source: https://en.wikipedia.org/wiki/Raoult%27s_law)

The Fig. 3 shows vapor pressure of a binary solution that obeys Raoult's law. The black line shows the total vapor pressure as a function of the mole fraction of component B, and the two green lines are the partial pressures of the two components.

3.2.1 Deviation from Raoult's law

Raoult's law is most applicable to non electrolytes and most applicable to non polar molecules with weak inter molecular attractions. Deviations from Raoult's law may be positive when the vapour pressure is higher than the expected. Positive deviation is associated with very weak intermolecular attraction in the solute than that of the solvent because the molecules will be held in the liquid phase less strongly than in the pure liquid. Azeotrope of 95 % ethanol and water is an example of this type of system. Since the vapour pressure of this azeotropic mixture is higher than the Raoult's predicted vapour pressure, the azeotropic liquid boils at a temperature that is much lower than that of either pure components. Other examples of systems that display negative deviation are,

- i. Chloroform (CHCl_3) and acetone (CH_3COCH_3) system due to hydrogen bond attraction between the two components
- ii. Hydrochloric acid-water exhibit large negative deviation due to ability of the mixture to evaporate without change of composition. Mixing of these components is exothermic and ionic bond is formed (i.e. $\text{H}_3\text{O}^+ - \text{Cl}$)

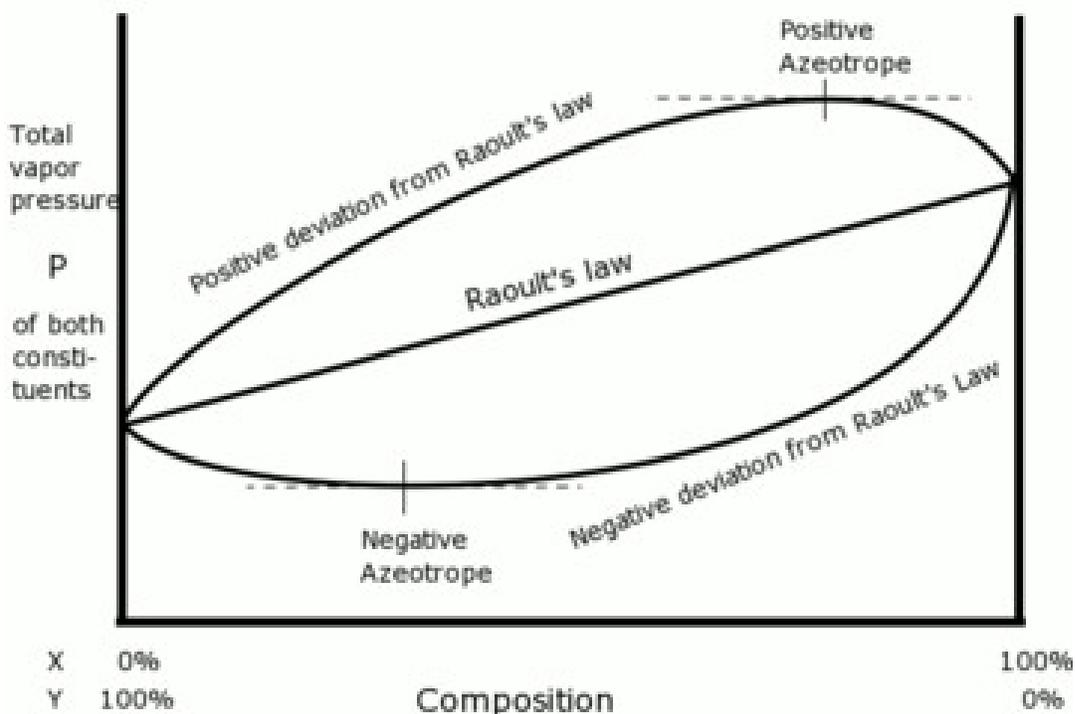
On the other hand, systems with negative deviations have vapour pressures that are lower than expected Raoult's vapour pressure. This deviation is associated with stronger intermolecular attraction between the constituents of the mixture than exists in the pure components. Hence, the molecules are "held in" the liquid more strongly when a second molecule is present. This means positive deviation arises when the cohesive forces between like molecules are stronger than adhesive forces between unlike molecules such that the differences in polarity enhances escape of liquid from the surface. Hence the observed vapour pressure will be greater than that predicted by Raoult's law. If the deviation is higher, the vapour pressure curve will display a maxima at a particular composition and forms positive azeotrope (as shown in Fig.4 below)

Trichloromethane (chloroform) and 2-propanone (acetone) mixture is an example of a system with negative deviation. It boils above the boiling point of either pure components. Others are

- i. Benzene and methanol mixture
- ii. Carbon disulphide and acetone mixture
- iii. Chloroform and ethanol mixture

If any of the above pair of compounds are mixed, the mixing is endothermic and is associated with the formation of weaker intermolecular forces with positive change in enthalpy

The significance of the negative and positive deviations is that they can be useful in the determination of thermodynamic activity coefficients of the components of the mixtures. Fig. 4 shows graphs depicting negative and positive deviations from the Raoult's law. In the graph, maxima and minima correspond to azeotrope and constant boiling mixtures.



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Fig. 4: Graphs showing positive and negative deviation from Raoult's law

(Source: https://en.wikipedia.org/wiki/Raoult%27s_law)

3.3 The Antoine equation

The Antoine equation was developed by a French engineer, Louis Charles Antoine in 1888. The equation is a semi empirical equation that describes the relationship between temperature and vapour pressure for pure components. It is an extension of Clausius-Clayperon equation. The original form of the Antoine equation can be written as,

$$2$$

where P is the vapour pressure, T is the temperature and A , B and C are component-specific constants. Closely related equation with C set as zero was also developed by Ernest Fedinard August. The August equation can be written according to equation 2 as

$$3$$

The equation shows that a linear relationship exists between \log_{10} of the vapour pressure and the inverse of temperature (compare this with the Arrhenius equation). Values of the constants, A , B and C for water and ethanol are presented in Table 1 below.

Table 1: Antoine constants for water and ethanol

Liquid	A	B	C	T _{Min} K	T _{Max} (K)
Ethanol	8.20417	1642.89	230.300	216	353
Ethanol	7.68117	1332.04	199.200	77	243
Water	8.07131	1730.63	233.426	274	373
Water	8.14018	1810.94	244.485	372	647

Solved problem1

The normal boiling point of ethanol is 78.32 °C. Use the Antoine equation to calculate the expected atmospheric pressure in mm/Hg.

From the above Table,

When $A = 8.20417$, $B = 1642.89$, $C = 230.300$ and $T = 78.32$ °C

Since

Which is simplified to give $P = 760 \text{ mm/Hg}$

Also, when $A = 7.68117$, $B = 1332.04$, $C = 199.200$ and $T = 78.32 \text{ }^\circ\text{C}$. Therefore,

The above equation is solved to give a value of $P = 761 \text{ mm/Hg}$

Solved problem 2

Use the Antoine equation and the data presented in Table 1 to calculate the normal boiling point of water.

Antoine equation is

Substitution of values presented in Table 1 to the equation yields the following solution

$$T_b = 100 \text{ }^\circ\text{C}$$

Also,

$$T_b = 100 \text{ }^\circ\text{C}$$

3.4 Solid vapour equilibrium

When a condensed phase is in equilibrium with its own vapour, equilibrium vapour pressure is defined. Therefore equilibrium solid such as crystal can attain equilibrium vapour pressure. This is the pressure when the rate of sublimation of a solid matches the rate of deposition of its vapour

phase. Although solid vapour pressure equilibrium is not commonly discussed, significant exception is dry ice. The vapour pressure of dry ice is 5.73 MPa at 253 K. This high vapour pressure explains why most sealed containers containing dry ice can rupture easily. Another example of solid that has significant vapour pressure is naphthalene.

The commonest method of calculating the sublimation pressure (i.e., the vapor pressure) of a solid is based on estimation of the sublimation pressure from extrapolated liquid vapor pressures (of the supercooled liquid), provided the heat of fusion is known, by using the modified form of the Clausius–Clapeyron equation given below

where p_s is the sublimation pressure of the solid component at the temperature $T_m > T$, p_l is the extrapolated vapour pressure of the liquid component at the temperature $T_m > T$, ΔH_f is the heat of fusion and R is the gas constant.

3.5 Phase equilibria

A phase is defined as a form of matter that is homogenous in a chemical composition and physical state. There are three typical phases, which correspond to the three states of matter, namely, solid, liquid and gas. For example, oil and water do not mix, hence they constitute a two phase system. Ice in water is another example of a two phase system (i.e liquid-solid phase). In each case, one component is separated from another by a distinct boundary. The number of component of a phase is the number of chemically independent constituents of the system, which reflects the minimum number of independent species necessary to define the composition of all the phases of the system. The number of degrees of freedom of a phase is the number of intensive variables which are dependent of each other.

There are two types of materials equilibrium: phase equilibrium and reaction equilibrium. Phase equilibrium refers to the transport of matter between phases (solid, liquid, or gas) of the system without conversion of one species to another. The crossing of any two-phase curve in a phase diagram is called a transition. A phase diagram is a graphical presentation of what phases are in existent at various pressures and temperatures. For example, the phase diagram for water is given in Fig. 5

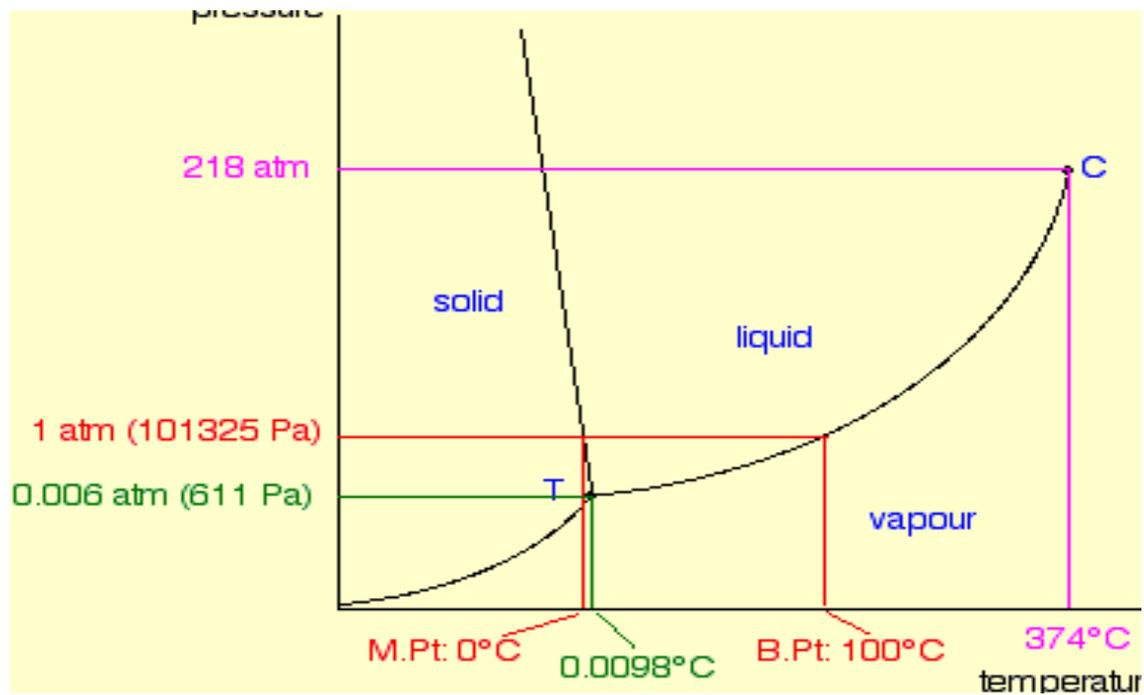


Fig. 5: Phase diagram for water

The phase diagram for the water displayed three equilibria, namely,

- i. Solid-liquid equilibrium, which slopes to the left
- ii. Liquid-vapour equilibrium, which tilt to the right
- iii. Solid-vapour equilibrium, which rises from the origin

In the above phase diagram, the normal melting and boiling points of water can be traced to where the 1 atmosphere pressure line crosses the solid-liquid and then the liquid-vapour equilibrium lines respectively. It can also be deduced from the phase diagram that water would first freeze to form ice as it crossed into the solid area. When the pressure fell low enough, the ice would then sublime to give water vapour. In other words, the change is from liquid to solid and from solid to vapour

The region where the three phases co-exist in equilibrium is called triple point. The triple point of water is 0.006 atm and at a temperature of 0.0098 °C. Another significant feature of the phase diagram is the critical point, marked as C. The critical point defines the temperature and pressure, beyond which gases can no longer be compressed. The triple point for water occurs at a very low pressure while the critical temperature is 374°C. Consequently, it is not possible to convert water vapour to a liquid water by compressing it above this temperature.

Fig. 6 shows phase diagram for carbon (IV) oxide. It is evident from the plot that the liquid solid equilibrium is tilt to the right. It can also be seen that the phase diagram for carbon (IV) oxide displays a triple point that is above atmospheric pressure unlike in water, where the triple point is below the atmospheric pressure. This implies that it is not possible to have liquid carbon (IV) oxide at pressures less than 5.11 atmospheres. At 1 atm pressure, carbon dioxide will sublime at a temperature of -78 °C, explaining why solid carbon (IV) oxide is often called dry ice. Liquid CO₂ can not be gotten under normal atmospheric condition, except solid and gas

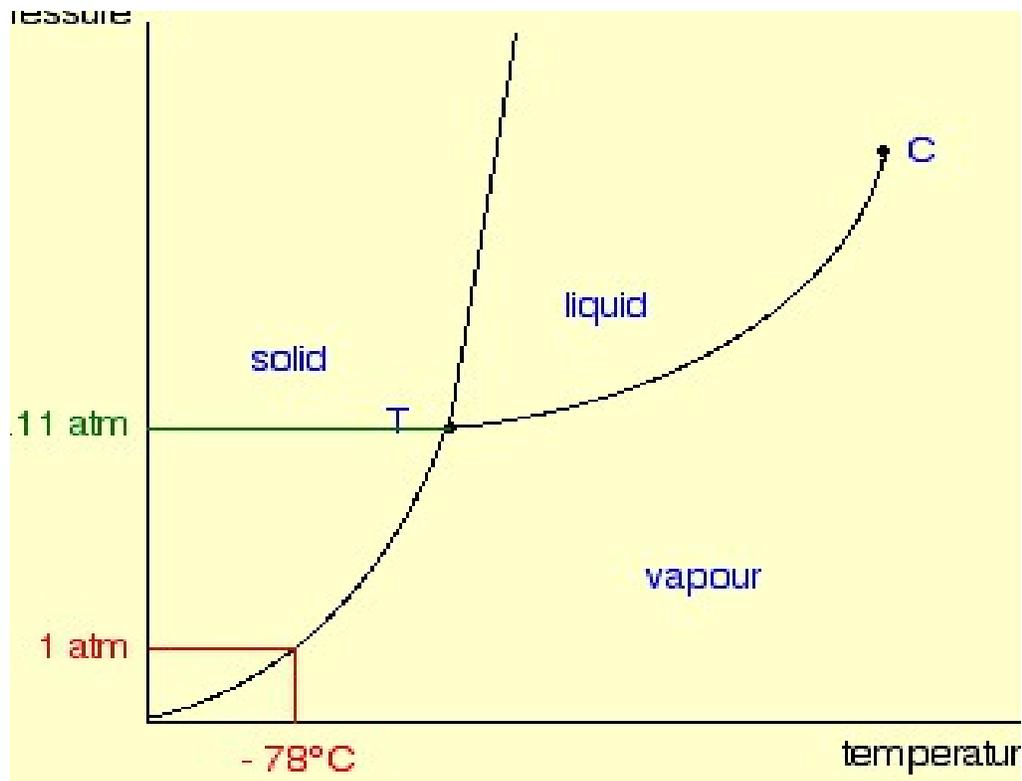


Fig. 6: Phase diagram of carbon (IV) oxide

3.6 Phase rule

The phase rule states that the number of degrees of freedom of a system in equilibrium is equal to the number of components minus the number of phases plus the constant two . This can be written as,

where F is the degree of freedom, P is the number of phases that can co-exist and C is the number of component making up the phase. The degrees of freedom represent the environmental conditions which can be independantly varied without changing the number of phases in the system. These conditions include temperature, pressure, chemical composition, pH, and oxygen fugacity

Solved problem 3

Water equilibrium consists of liquid water, vapour and ice, which all belongs to the same chemical component (i.e water, hence $C = 1$). The system has three physical phases that can co-exist (hence $P = 3$). Calculate the degree of freedom for this system and state the condition needed for the system to exist.

Solution.

Applying the phase rule, the degree of freedom is

Therefore, the degree of freedom for water is zero and the system can only exist at only one temperature and pressure.

Water phase system

Analysis of various equilibria in water phase system as shown in Fig. 7. Reveals useful information.

The number of component for the water system is calculated to be zero. That means the general phase rule for water can be written as,

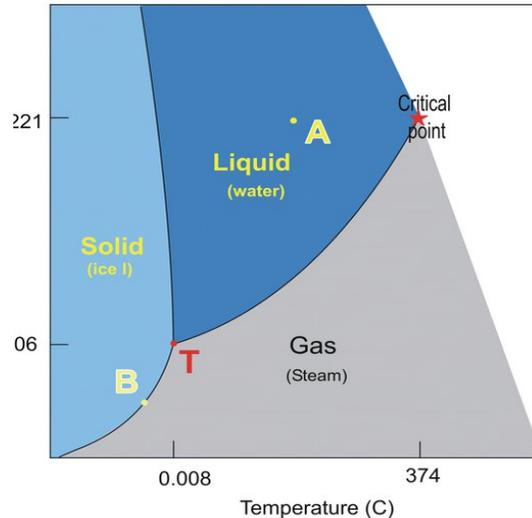


Fig. 7: Water phase equilibria

Source: <https://brocku.ca/earthsciences/people/gfinn/petrology/phaserul.htm>

1. **Point A:** From the graph, it can be seen that at point A, water only exist as liquid water, therefore $P = 1$ and the phase rule becomes, or $F = 2$. Therefore in order to maintain one phase of water (liquid water), two variables may change independently (i.e pressure and temperature)
- ii. **Point B:** This designate solid-gas equilibrium. This means two phases can co-exist hence $P = 2$ and the phase rule becomes or $F = 1$. Hence, since the degree of freedom is one, only one variable can be varied at a time. Thus the solid and gas phases must co-exit. This may be achieved by keeping temperature constant and vary as the pressure or by varying the temperature, when the pressure is kept constant.
- iii. **Point T :** This is the triple point where liquid water, vapour and ice co-exist, indicating that $P = 3$ and from the phase rule, hence $F = 0$. Therefore, in order to maintain Ice-liquid water-vapour equilibrium, no variable can be varied. It occurs at constant temperature and pressure. A change in any variable will change the co-existence of this equilibrium.

4.0 Summary

Phase equilibria covers significant features that are relevant in chemistry, geology, astrology, fluid engineering and other life science. Among all equilibria, liquid phase equilibria have received wider attention because fluid and fluids mixtures are widely handled in life and can easily be quantified or understudied. Gas phase equilibrium is rare and exceptional. Nevertheless, they are in existent.

5.0 Conclusion

Vapour pressure is the pressure exerted when the number of energetically active molecules escaping from the surface of the liquid through evaporation is balanced by those returning to the liquid through condensation. When the vapour pressure and the prevailing atmospheric pressure are equal, the associated temperature is the boiling point of that liquid. Solid displayed vapour pressure due to sublimation and the balanced between this pressure and the prevailing atmospheric pressure may be likely be associated with melting point. Evaporation and condensation is a surface process that seems to occur at all temperatures, therefore adequate knowledge of the chemistry at the surface and associated boundaries are essential.

6.0 Tutor marked assignment

1. Differentiate between evaporation and boiling
2. What are the factors responsible for positive and negative deviations from Raoult's law?
3. Differentiate between ideal and real solution
4. State the phase rule and use its rule to analyse the expected degree of freedom for the following water equilibria,
 - i. Liquid-gas equilibrium'
 - ii. Solid-liquid equilibrium
 - iii. Liquid-vapour-ice equilibrium

5. Sketch phase diagrams for water and carbon (IV) oxide. What are the differences and similarities between water and carbon (IV) oxide in terms of
 - i. Critical temperature and pressure
 - ii. Triple point
 - iii. Solid-liquid equilibrium
6. Given that the atmospheric pressure is 780 mm/Hg, use the data presented in Table 1 to calculate the boiling point of ethanol in degree Celsius.

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Model 2

Unit 1: Thermodynamics

1.0 Introduction

2.0 Objectives

3.0 Main content

3.1 Basic concepts in thermodynamics

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1.0 Introduction

The word thermodynamics is coined from two words; thermo, meaning heat and dynamics, meaning motion. Therefore, thermodynamics literally means heat in motion but technically, thermodynamics is the study of heat change accompanying chemical and physical changes. Chemical thermodynamics is therefore a branch of thermodynamics that study heat change accompanying chemical reactions.

The beginning of thermodynamics dates back to 1865, when a German Chemist, Rudolf Clausius suggested that the principles of thermochemistry could be applied to the principles of thermodynamics. Consequently, a foundation was laid for an American mathematical physicist, Willard Gibbs to published a work on the equilibrium of heterogeneous substances in which a graphical approach to the measurement of thermodynamic equilibrium of a chemical reaction was first revealed. The work of Gibbs was strongly supported and improved upon by Clausius and Sadi Carnot.

In the 20th century Gilbert Lewis and Merle Randall applied the principles developed by Gibbs to chemical processes, which led to the authentication of the science of chemical thermodynamics through their publications, “Thermodynamics and free energy of chemical substances “, which captured the chemical affinity for the term free energy. E. A. Guggenheim also wrote a book titled, *Thermodynamics by the methods of Willard Gibbs*, which threw more light to the science of chemical thermodynamics. In the light of these and other historical developments in the science of thermodynamics, Lewis, Randall, and Guggenheim are considered as the founders of modern chemical thermodynamics.

The major objective of chemical thermodynamics is to establish conditions or criteria for predicting the feasibility or spontaneity of chemical reactions, phase changes and solution formations. In order to do these, chemical thermodynamics operates with some functions, called state functions which include internal energy, enthalpy, entropy, Gibb free energy and Helmholtz work function (as the major functions). Finally, thermodynamics is centered on applications of two major laws (first and second laws of thermodynamics) to these state functions.

2.0 Objectives

- To understand the meaning of some thermodynamic terms

- To understand the concept behind thermodynamic state function
- To understand the concept of thermodynamic system
- To know and identify the various thermodynamic processes
- To understand the concept of a thermodynamic phase

3.1 Definition of terms in chemical thermodynamics

3.1.1 Thermodynamic system

Thermodynamic system is the part of the universe chosen for thermodynamic study. Thermodynamic system is usually separated from the surrounding by the boundary. The surrounding is the immediate vicinity outside the boundary. The system can interact with the surrounding through exchange of heat or matter. This means the system will either do work on the surroundings or has work done on it by its surrounding. The figure below (Fig.1) illustrates the nature of arrangement of a typical thermodynamic system, boundary and surrounding.

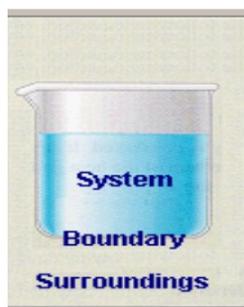


Fig. 1: Typical arrangement pattern for thermodynamic system, surrounding and boundary

The commonest types of work that are associated with a chemical reaction are electrical and expansion work. Chemical reactions can generate work on their surroundings by driving an electric current through an external wire. Work can also be derived from chemical reactions and passed to their surroundings when the volume of the system expands. The amount of work of

expansion done by the reaction is equal to the product of the pressure (against which the system expands) and the change in the volume of the system.

1

This type of work is called pressure volume work. The negative sign in the above equation justifies the fact that the internal energy of the system decreases when the system does work on its surroundings.

For some purposes we may wish to treat the system as being divided into sub-systems, or to treat the combination of two or more systems as a super system. If over the course of time matter is transferred in either direction across the boundary, the system is open; otherwise it is closed. If the system is open, matter may pass through a stationary boundary, or the boundary may move through matter that is fixed in space. If the boundary allows heat transfer between the system and surroundings, the boundary is diathermal. An adiabatic boundary, on the other hand, is a boundary that does not allow heat transfer. An isolated system is one that exchanges no matter, heat, or work with the surroundings, so that the mass and total energy of the system remain constant over time.

3.1.2 Property of thermodynamic system

Thermodynamic systems can be classified into two major groups depending on the dependence of the respond of the system's property to the quantity of materials or matter in that system. Consequently, an extensive property of a system, thus defined the property of a system that depends on the quantity of matter or materials in that system while an intensive property is a property that does not depend on the quantity of materials or matter in that system. For example, temperature and pressure are examples of intensive properties

3.1.3 Thermodynamic state function

Thermodynamic functions are obtained when some thermodynamic properties are manipulated mathematically. A state function describes the property of a system that depends only on the initial and final states of the system and not on the path that the system takes to arrive at that state. For example, if we measure the temperature of water in a beaker as 80 °C. It does not provide information on how the water was heated or cooled to the required temperature but it only provides information on the state of the water at the point of measurement. Temperature change is a state function. Other examples of state functions are internal energy, enthalpy, entropy, free energy, etc. For a state function, any change in its system is the difference between the final state and the initial state and not on the path taken.

One of the major properties of state functions is that it gives exact differentials. For example, if a state function $y = f(x,z)$ then by the theory of exact differentials we have,

$$2$$

For a state function, the second derivative is independent of the path of differentiation indicating that whether we start it with x or z , the result will still be the same. This is the principle of reciprocity. For example,

3.1.4 Thermodynamic process

Thermodynamic process is defined when there is an energetic change within the system. These changes will involve a change from initial state to a final state. Thermodynamic processes can be grouped into three major classes, namely

- i. Pressure-volume
- ii. Temperature-entropy
- iii. Chemical potential-particle number

3.1.4.1 Pressure – volume: This is concerned with the transfer of mechanical or dynamic energy as the result of work. It includes

- i. An isobaric process occurs at constant pressure. An example of this process is the work done in a movable piston in a cylinder which is caused by the atmospheric pressure and the pressure inside the cylinder even if it is isolated from the atmosphere. This makes the system to be dynamically connected, by a movable boundary, to a constant-pressure reservoir.
- ii. An isochoric process is a process that is carried out at constant volume. It is also known as isometric or isovolumetric. In this process, the work done is zero since the change in volume is equal to zero (see equation 1). This implies that for this process, any heat energy transferred to the system externally will be absorbed as internal energy. Therefore, $dQ = dU$

3.1.4.2 Temperature – entropy: The temperature-entropy conjugate pair is concerned with the transfer of thermal energy as the result of heating. It involves

- i. An isothermal process is a process which occurs at a constant temperature. For example a system immersed in a large constant temperature bath. Any work or energy done by the system will be lost to the bath, but its temperature will remain constant. In other words, the system is thermally connected by conductive boundary to a constant temperature reservoir.
- ii. An adiabatic process is a system which is thermally insulated from its environment and its boundary is a thermal insulator. This implies that there is no energy added or subtracted from the system by heating or cooling. For a reversible process, this is identical to an isentropic process.

- iii. An isentropic process is a process that is carried out at constant entropy. For a reversible process this is identical to an adiabatic process. If a system has an entropy which has not yet reached its maximum equilibrium value, a process of cooling may be required to maintain the system at that entropy.

3.1.4.3 Chemical potential - particle number: This conjugate system is concerned with the transfer of energy via particle transfer.

- i. In a constant chemical potential process the system is particle-transfer connected, by a particle-permeable boundary, to a constant chemical potential reservoir.
- ii. In a constant particle number process there is no energy added or subtracted from the system by particle transfer. The system is particle-transfer-insulated from its environment by a boundary that is impermeable to particles, but permissive of transfers of energy as work or heat. These processes are the ones by which thermodynamic work and heat are defined, and for them, the system is said to be closed.

3.1.5 Reversible and irreversible processes

In thermodynamics, a reversible process is a process whose direction can be reversed by means of infinitesimal changes in some properties of the system. The entropy of a system and that of the surrounding for a reversible change is constant and during the change, the system is in thermodynamic equilibrium. On the other hand, an irreversible process is the process, whose direction can not be reversed by a very small change in some properties of the system.

3.1.6 Cyclic processes

A cyclic process is a sequence of processes that leaves the system in the same state in which it started. This means that in a cyclic process, the system starts in a particular state and returns to

that state after undergoing a few different processes. For a cyclic process, its initial and final internal energies are equal. So the total internal-energy change in any cyclic process is zero. If the cycle goes clockwise, the system does work. This is the case for an engine. If the cycle goes anti-clockwise, work is done on the system at every cycle as in a refrigerator and air conditioner.

3.1.7 A Phase

A phase is a region of the system in which each intensive property (such as temperature and pressure) has at each instant either the same value throughout (homogeneous phase), or else a value that varies continuously from one point to another (heterogeneous phase).

An interface is a surface where two different phases meet. Since there are three state of matter, we can have solid phase, liquid phase and gaseous phase, which could present homogenous or heterogeneous phases, depending on the number of phases that are involved. A uniform phase may be either isotropic, exhibiting the same values of these properties in all directions, or (anisotropic) as in the case of some solids and liquid crystals.

4.0 Summary

- (i) A thermodynamic system is the part of the universe chosen for thermodynamic study. A thermodynamic system is usually separated from the surrounding by the boundary. The surrounding is the immediate vicinity outside the boundary.
- (ii) Thermodynamic properties are generally classified as extensive and intensive. When the property depends on the quantity of matter or materials in that system, it is called extensive property. On the other hand, intensive properties are those properties that do not depend on the quantity of matter or materials the system contain

- (iii) A state function describes the property of a system that depends only on the initial and final states of the system and not on the path that the system takes to arrive at that state. The major property of state function is that it gives exact differentials.
- (iv) Thermodynamic processes include pressure-volume, temperature-entropy and chemical potential-particle number.
- (v) In thermodynamics, a reversible process is a process whose direction can be reversed by means of infinitesimal changes in some properties of the system. If the system behaves otherwise, then it is an irreversible process.
- (vi) A cyclic process is a sequence of processes that leave the system in the same state in which it started.
- (vii) A phase is a region of the system in which each intensive property (such as temperature and pressure) has at each instance either the same value throughout (homogeneous phase), or else a value that varies continuously from one point to another (heterogeneous phase).

5.0 Conclusion

Thermodynamics offers an avenue for exploring properties of chemical system by considering the variation of certain basic functions with reference to established or standardized conditions. The study of thermodynamics embodied a system, the surrounding and the boundary. Through the understanding of the operation of these three components of thermodynamics, much can be understudied with good degree of accuracy.

6.0 Tutor mark assignment

1. Thermodynamic processes can be grouped into three major classes, namely
 - i. Pressure-volume

- ii. Temperature-entropy
- iii. Chemical potential-particle number

Enumerate the various components of each of the listed process

- 2. What are the basic features of thermodynamic cyclic processes ?
- 3. Under what condition can a thermodynamic process be said to be reversible or irreversible ?
- 4. What are the basic properties of thermodynamic state functions ?

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Model 2

Unit 2: First law of thermodynamics

1.0 Introduction

2.0 Objectives

3.0 Main content

3.1 Consequences of the first law of thermodynamics

3.1.1 Thermodynamic work

3.1.2 Heat change at constant pressure and at constant volume

3.1.3 Work done in isothermal expansion of a gas

3.1.4 Work done in phase transition

3.1.5 Heat capacity

3.1.6 Adiabatic expansion of a gas

3.1.7 Joule Thompson experiment

4.0 Summary

5.0 Conclusion

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7.0 References

1.0 Introduction

The first law of thermodynamics is sometimes called the law of conservation of energy because it accounts for the input and output energies when a system does work. The law can be stated as follows,

“The change in internal energy of a system, when heat is absorbed will lead to work done by the system or against the system”

From the statement of the law expressed above, three set of parameters are significant. These are heat, internal energy and work. Mathematically, the first law can be expressed as follows,

where q is the infinite quantity of heat absorbed. The U is the infinite change in internal energy and W is the work done. The sign shows that q and W are not exact differential while U is an exact differential. Equation 1 is the differential form of the first law of thermodynamics. If the equation is integrated, in a closed system, we will have the integrated form of the equation according to equation 2,

2

The above equation indicates that whenever there is a change in internal energy of a system, heat will be absorbed and work will be done on the system or by the system. The sign of W is positive when the heat absorbed leads to increase in internal energy and negative when the heat absorbed leads to decrease in internal energy. Therefore, positive heat is energy entering the system, and negative heat is energy leaving the system. Positive work is work done against the system, and negative work is work done by the system on the surroundings.

Heat refers to the transfer of energy across the boundary caused by a temperature gradient at the boundary. Work refers to the transfer of energy across the boundary caused by the displacement of a macroscopic portion of the system on which the surroundings exert a force, or because of other kinds of concerted, directed movement of entities (e.g., electrons) on which an external force is exerted.

8.0 Course objectives

- i. To know the first law of thermodynamics
- ii. To show that thermodynamic work is PV work
- iii. To show that heat absorbed at constant volume is equal to change in internal energy
- iv. To show that the heat absorbed at constant pressure is equal to change in pressure

- v. To know what is heat capacity and derive the equations for heat capacity at constant volume (C_V) and heat capacity at constant pressure (C_P)
- vi. To be able to prove that C_P is always greater than C_V by an amount equal to the gas constant
- vii. To be able to derive an equation for the work done during isothermal expansion of ideal and real gases
- viii. To be able to derive the relationship for the adiabatic expansion of an ideal gas
- ix. To be able to understand the Joule-Thompson experiment and show that the experiment is associated with constant enthalpy change
- x. To be able to derive an expression for Joule-Thompson coefficient using exact differentiation approach and to know the significance of the coefficient with respect to cooling upon expansion and vice versa.

3.0 Main text

3.1 Consequences of the first law of thermodynamics

3.1.1 Thermodynamic work

Thermodynamic work is usually considered as the work done by expansion of a gas. In order to gain insight into this concept, let us consider a piston (whose cross sectional area is A), compressing a gas (at pressure, P and volume, V). If the piston moves a distance called dx , then it can be stated that the force acting on the piston is given as,

3

The volume created as a result of this compression will be given as $dV = A dx$, indicating that $A = dV/dx$ or $dx = dV/A$. The work done is equal to the product of the applied force and the distance moved,

4

Substituting for F and dx in equation 4, we have,

5

Equation 5 can be simplified by integration, hence we have,

6

Returning to the mathematical expression of the first law, i.e., we can replace W with PV and we have,

7

3.1.2 Heat change at constant pressure and at constant volume

Equation 9 provides the basis for several transformational applications of the first law. Let us start by considering the two major conditions under which experimental study can be carried out. These are at constant pressure and at constant volume. At constant pressure, the heat absorbed is q_p and the pressure will be constant at, P , the volume will change from V_2 to V_1 while the internal energy will change from U_1 to U_2 (note that internal energy is a state function). Therefore, the first law is slightly modified to equation 8.

8

Rearrangement of equation 8 leads to equations 9 and 10

9

10

At this juncture, we define a state function call enthalpy, denoted as H . Enthalpy is the heat absorbed at constant pressure. It is a state function and can be represented as, $H = U + PV$. Therefore, $U_2 + PV_2 = H_2$, $U_1 + PV_1 = H_1$, hence $\Delta H = H_2 - H_1 = \Delta H$. Consequently, the heat absorbed at constant pressure is equal to change in enthalpy. As a consequence of the first law if the reaction is carried out at constant volume, dV will be equal to zero and we have, which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, $\Delta U =$

Solved problem 1

- From first principle, Show that thermodynamic work can be written in terms of pressure volume work.
- Show that the heat absorbed by a body at constant pressure and at constant volume is equal to change in enthalpy and change in internal energy respectively.

Solution

(a) Consider a piston (whose cross sectional area is A), compressing a gas (at pressure, P and volume, V). If the piston moves a distance called dx , then it can be stated that the force acting on the piston is given as,

$$F = PA$$

The volume created as a result of this compression will be given as $dV = Adx$, indicating that $A = dV/dx$ or $dx = dV/A$. Therefore the work done is equal to the product of the applied force and the distance,

$$dW = F dx \quad (1)$$

Substituting for F and dx in equation (1), we have,

$$dW = P dV \quad (2)$$

Equation 2 can be simplified by integration, hence we have,

$$W = \int P dV \quad (3)$$

Returning to the mathematical expression of the first law, i.e., $dU = dQ - dW$, we can replace dW with PdV and we have,

(b) From the first law of thermodynamics, $dU = dQ - dW$, therefore,

$$dU = dQ - PdV \quad (1)$$

Rearrangement of equation 1 leads to equations 2 and 3

$$dQ = dU + PdV \quad (2)$$

$$dQ = dH \quad (3)$$

At this juncture, we define a state function called enthalpy, denoted as H . Enthalpy is the heat absorbed at constant pressure. It is a state function and can be represented as, $H = U + PV$.

Therefore, $U_2 + PV_2 = H_2$, $U_1 + PV_1 = H_1$, hence $dH = H_2 - H_1 = \Delta H$. Consequently, we state that the

heat absorbed at constant pressure is equal to change in enthalpy. Let us consider the consequence of the first law if the reaction is carried out at constant volume. In this case, dV will be equal to zero and we have $dU = q$, which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, $\Delta U = q_v$

3.1.3 Work done in isothermal expansion of a gas

An ideal gas undergoing isothermal expansion is characterised by a constancy of temperature, hence the internal energy will be equal to zero and from the first law, we have, $dU = 0$ or $q = -w$ (if work is done by the system). It should be noted that the work done will be equal to the heat absorbed. Therefore, $q = w = PV$. From the ideal gas equation, $PV = nRT$ or $P = nRT/V$. By substituting for P , the work done becomes,

$$11$$

where n is the number of moles of the gas, R is the universal gas constant, Equation 11 can better be solved by integration over the appropriate limits as shown in equation 12,

$$12$$

From Boyle's law, we know that the pressure and volume of a gas are related according to the equation, $P_1V_1 = P_2V_2$. Therefore, $V_2/V_1 = P_1/P_2$ and by substitution to equation 12, we have,

$$13$$

The above derivation is true for an ideal gas. However, real gases do not show similar response to change in pressure or volume. While ideal gases obey the general gas law, real gases obey the Van der Waals equation. Therefore, the corrected pressure term is given as $P_{cor} = P + a/V^2$ and the corrected volume is $V_{cor} = V - b$. The a and b are the Van der Waal constant. Recall that for an ideal gas, $PV = RT$ (for 1 mole). Therefore for real gases, we have, $P(V - b) = RT - a/V$. This gives, $P = \frac{RT}{V - b} - \frac{a}{V^2}$ and the work done is given as,

The results of the above integration yields expression for the work done by a real gas thus,

$$= \quad \quad \quad 16$$

3.1.4 Work done in phase transition

In the absence of internal constraint, a system of two or more phases of a single substance is in an equilibrium state when each phase has the same temperature, the same pressure, and the same chemical potential. Phase transition is said to occur when substances change from one form to another. The transition may be accompanied by corresponding changes in some properties. For example vaporization of liquid occurs at constant pressure but the volume occupied by the vapour will be greater than the volume of the liquid, especially at higher temperature. Hence isothermal work done will be equal to PV and since the vapour will behave like a gas, the work can be expressed as follows,

Solved problem 2

- (a) Derive an expression for the work done in isothermal expansion of an ideal and real gases
- (b) If the volume of 2mol of an ideal gas change from 200 to 400 cm³ at 296 K, calculate the work done during the isothermal expansion of the gas.
- (c) What will be the final pressure of a gas after expansion if its initial pressure was 101325 Pa

Solution

- (a) An ideal gas undergoing isothermal expansion is characterised by a constancy of temperature, hence the internal energy will be equal to zero and from the first law, we have, $du = 0$ or $dq = -Pdv$ (if work is done by the system). It should be noted that the workdone will be equal to

the heat absorbed. Therefore, $q = w = PdV$. From the ideal gas equation, $PV = nRT$ or $P = nRT/V$. By substituting for P , the work done becomes,

$$(1)$$

where n is the number of moles of the gas, R is the universal gas constant, Equation 1 can better be solved by integration over the appropriate limits as shown in equation 2,

$$(2)$$

From Boyle's law, we know that the pressure and volume of a gas are related according to the equation, $P_1V_1 = P_2V_2$. Therefore, $V_2/V_1 = P_1/P_2$ and by substitution to equation 2, we have,

$$(3)$$

The above derivation is true for an ideal gas. However, real gases do not show similar response to change in pressure or volume. While ideal gases obey the general gas law, real gases obey the Van der Waals equation. Therefore, the corrected pressure term is given as $P_{cor} = P + a/V^2$ and the corrected volume is $V_{cor} = V - b$. Thus a and b are the Van der Waal's constant. Recall that for an ideal gas, $PV = RT$ (for 1 mole). Therefore for real gases, we have, . This gives, $P =$ - and the work done is given as,

$$(4)$$

$$(5)$$

The results of the above integration yields expression for the work done by a real gas thus,

$$= \quad (6)$$

(b) Given,

$$V_1 = 200 \text{ cm}^3 = 0.2 \text{ m}^3$$

$$V_2 = 400 \text{ cm}^3 = 0.4 \text{ m}^3$$

$$T = 298 \text{ K}$$

$$N = 2 \text{ mol}$$

(c) The pressure can be calculated from using the relation between volume and pressure. There are two approaches to this. Let us consider each approach.

Approach 1

Comparing the two equation, In, Therefore,

Note that this method uses Boyle's law which states that $P_1V_1 = P_2V_2$

Approach 2

The calculated value of the work done and the given pressure can be substituted into the equation,

That is ,

4.1.5 Heat capacity

The heat capacity of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change. Hence

18

Since q is a path function, the value of the heat capacity will depend on the specified conditions, which can either be at constant pressure or at constant volume. Consequently, when the heat is transferred at constant pressure, the heat capacity is called heat capacity at constant pressure and

is denoted by C_p while C_v will stand for heat capacity at constant volume. Equation 20 can be simplified based on the fact that the heat absorbed at constant pressure is equal to change in enthalpy and that the heat absorbed at constant volume is equal to change in internal energy. Therefore, we have the following expressions,

$$19$$

$$20$$

The relationship between C_p and C_v can be derived using the first law of thermodynamics. In order to do this, we modify the equation to the form given by equation 21

$$21$$

From equation 19, $C_p dT = q_p$ and from equation 20, $C_v dT = q_v$. Also from the ideal gas equation, $PV = RT$ (for one mole of a gas), we have $PdV = RdT$. Hence substituting for all these parameters into equation 21, we have,

$$22$$

Dividing the left and right hand sides of equation 22 by dT , gives equation 23

$$23$$

The implication of equation 23 is that the heat capacity at constant pressure is always greater than the heat capacity at constant volume by an amount equal to the gas constant (for 1 mole of a gas) or a multiple of the gas constant.

Solved problem 3

- (a) Define heat capacity and derive expressions for heat capacity at constant pressure (C_p) and at constant volume (C_v).
- (b) Show that for n moles of a gas, the C_p is always greater than C_v by multiple of R (where R is the gas constant).

(c) If enthalpy change of 3 mol of a gas at constant pressure is defined by the following differential equation, $H = 32.2T + 34$ (where T is temperature), what will be the estimated value of the heat capacity at constant volume for this system? [$R = 8.314 \text{ J/mol/K}$]

Solution

(a) The heat capacity of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change. Hence

$$(1)$$

Since q is a path function, the value of the heat capacity will depend on the specified conditions, which can either be at constant pressure or at constant volume. Consequently, when the heat is transferred at constant pressure, the heat capacity is called heat capacity at constant pressure and is denoted by C_p while C_v is the heat capacity at constant volume. Equation 1 can be simplified based on the fact that the heat absorbed at constant pressure is equal to change in enthalpy and that the heat absorbed at constant volume is equal to change in internal energy. Therefore, we have the following expressions,

$$(2)$$

$$(3)$$

(b) The relationship between C_p and C_v can be derived using the first law of thermodynamics. In order to do this, we modify the equation 3 to the form given by equation 4

$$(4)$$

From equation 2, $C_p dT = q_p$ and from equation 3, $C_v dT = q_v$. Also from the ideal gas equation, $PV = RT$ (for one mole of a gas), we have $PdV = RdT$. Hence substituting for all these parameters into equation 4, we have,

$$(5)$$

Dividing the left and right hand sides of equation 5, gives equation 6

$$(6)$$

$$(7)$$

Equations 6 and 7 are for one mole but for n mole, the equation 7 becomes,

The implication of the equations is that the heat capacity at constant pressure is always greater than the heat capacity at constant volume by an amount equal to the multiple of the gas constant

(c) Given

$H = 32.2T + 34$, then . However, . Since , then

3.1.6 Adiabatic expansion of a gas

As defined earlier, an adiabatic process is a process that is carried out under constant heat transferred. This implies that for an adiabatic change, the heat absorbed or given off, will be equal to zero and the first law of thermodynamics becomes, $U = -W$ or

$$24$$

From the ideal gas equation, $PV = RT$, indicating that $P = RT/V$. Substitution for P in equation 24 and rearrangement yields equation 25,

$$25$$

From the ideal gas equation, $PV = RT$, indicating that $P = RT/V$. Substitution for P in equation 1 and rearrangement yields equation 2,

$$(2)$$

The right hand side of equation 2 can be integrated within the expected limits of temperature (T_1 to T_2) and the left hand side within the limit of volume change (i.e V_1 to V_2). Hence we have,

$$(3)$$

The result of the above integration is presented in equation 4,

$$(4)$$

The combined gas law shows that $P_1 V_1 / T_1 = P_2 V_2 / T_2$, which implies that $P_2 = P_1 V_1 T_2 / (V_2 T_1)$. The step by step solution to equation 4 are presented in equations 5 to 12

$$(5)$$

$$(6)$$

$$(7)$$

$$(8)$$

$$(9)$$

$$(10)$$

$$(11)$$

$$(12)$$

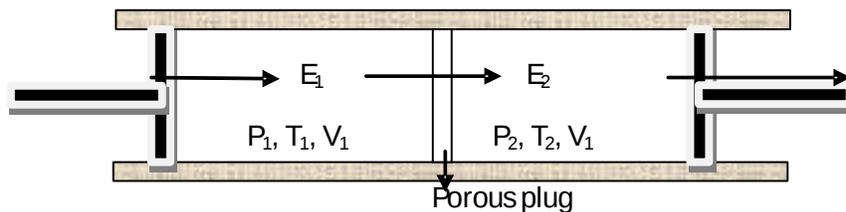
where $\gamma = C_p / C_v$. Equation 12 shows that the ratio of C_p to C_v are related to the volume and pressure exponentially.

(b) For a change in volume from 0.2 to 0.4 m³ with a corresponding changes in pressure from 101325 to 50663 Pa, the ratio, γ , can be calculated using the equation,

Therefore,

3.1.7 Joule Thompson experiment

Joule-Thompson experiment attempts to measure the extent of deviation of the behaviour of a real gas from ideality. As shown below, the experiment was carried out in such a way that a piston moves from the left to the right hand side. Before the piston was moved, the volume, pressure and temperature of the gas were V_1 , P_1 and T_1 . Before the start of the experiment, the volume of gas in the second chamber was zero. When the piston is moved, the gas started to move to the second chamber through the porous plug and eventually, all of the gas will be moved from the first to the second chamber. At this point, the volume of the gas in the first chamber becomes be zero and V_2 at the second chamber. The pressure and temperature at the second chamber were P_2 and T_2 respectively.



One of the most fascinating experiences in the Joule-Thompson experiment is that T_2 is not equal to T_1 . In some cases, it is higher and vice versa. The process starts with volume $V_1=V_1$ and volume $V_2=0$. It ends with volume, $V_1=0$ and volume $V_2 =V_2$. . The work done on the left chamber is: $W_1=-P_1(0-V_1)$ and the work done on the right chamber is $W_2 = -P_2(V_2-0)$. The total work done is the sum of the work done in the first and second chamber, hence it is equals to . The process is carried out at constant heat change (i.e adiabatic process) which implies that the

work done will be equal to the change in internal energy (consequence of the first law of thermodynamics). Therefore,

$$36$$

Equation 36 simplifies to equation 37 upon re-arrangement,

$$37$$

From equation 37, it is inferred that in the Joule-Thompson experiment, $H_1 = H_2$. Hence the process is isenthalpic. One of the major applications of the Joule-Thompson experiment is in the determination of the Joule-Thompson coefficient of a gas, μ_{JT} , which can be expressed as follows,

$$38$$

Since the experiment is carried out at constant enthalpy, the above expression can be written as ,

$$39$$

Enthalpy is a state function and is a function of pressure and temperature, indicating that it can be written as, . As stated earlier, one of the major properties of a state function is that it gives exact differential. Consequently,

$$40$$

Again, since the process is carried out at constant enthalpy, $dH = 0$ and equation 42 becomes 43 and upon rearrangement, equation 44 is obtained as

$$41$$

$$42$$

Equation 42 gives various expressions for the . However, in terms of measureable quantities, the Joule-Thompson coefficient can better be written as,

$$45$$

where $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$, which is a general thermodynamic relation. An ideal gas has no interactions between molecules (i.e forces of attraction and repulsion are absent). Therefore, for ideal gas, $\mu_{JT} = 0$, indicating that $\left(\frac{\partial T}{\partial P}\right)_H$ would be equal to zero for ideal gas. Hence μ_{JT} is applicable to gases where there is molecular interaction. The μ_{JT} can be positive or negative. When the ratio is positive, it means that the expansion of the gas will lead to cooling. It has been found that there is a certain temperature called the inversion temperature such that if the initial temperature, T_1 is above the inversion temperature, the final temperature, T_2 will be higher than the initial temperature and vice versa. This inversion temperature is found to depend on the pressure. Most real gases do not have zero value of μ_{JT} .

Solved problem 5

- (a) Given that in a Joule-Thompson apparatus, the total work done is the sum of the work done in the first and second chamber, that is, $W = W_1 + W_2$, show that the process is isoenthalpy
- (b) Define the term, Joule-Thompson coefficient. Hence show that

Solution

Joule Thompson process is carried out at constant heat change (i.e adiabatic process) which implies that the work done will be equal to the change in internal energy (consequence of the first law of thermodynamics). Therefore,

$$dU = -PdV \quad (1)$$

Equation 1 simplifies to equation 2 upon re-arrangement,

$$dU + PdV = 0 \quad (2)$$

From equation 2, it is inferred that in the Joule-Thompson experiment, $H_1 = H_2$. Hence the process is isenthalpic.

- (b) The Joule-Thompson coefficient of a gas, μ_{JT} , can be defined as

$$(1)$$

Since the experiment is carried out at constant enthalpy, the above expression can be written as ,

$$(2)$$

Enthalpy is a state function and is a function of pressure and temperature, indicating that it can be written as, . As stated earlier, one of the major properties of a state function is that it gives exact differentials. Consequently,

$$(3)$$

Again, since the process is carried out at constant enthalpy, $dH = 0$ and equation 3 becomes 4 and upon rearrangement, equation 5 is obtained

$$(4)$$

$$(5)$$

Equation 5 gives various expressions for the . However, in terms of measureable quantities, the Joule-Thompson coefficient can better be written as,

$$(6)$$

4.0 Summary

The first law is an extension of the law of conservation of energy, which states that energy is neither created nor destroyed but can change from one form to the other. In this case, heat is the form of energy which arises due to temperature differences and can undergo the change to internal energy. It can also be used in doing work (which maybe PV-work). It is a fundamental law in thermodynamics and guides the behaviour of ideal and real gases upon expansion under isothermal or adiabatic condition.

5.0 Conclusion

The first law identifies two major state functions, namely, enthalpy and internal energy, which are state functions obtained at constant pressure and constant volume respectively. It is a viable law that can be used to explain the heat capacity of the body under two unique experimental

conditions. It can also be used to derive the relationship between these heat capacities and the gas constant, R . The Joule-Thompson experiment, whose major contribution to thermodynamics is the knowledge of those gases that lead to cooling upon expansion, has been a guiding principle in the operation of numerous gas powered systems such as air conditioners, refrigerators, etc.

From the above summary, it can be stated that the first law of thermodynamics is a single sentence but its application is numerous and extensive. Therefore, the law provides the foundation upon which the listed objectives of these module stand.

6.0 Tutor mark assignment

1. What are the two major conditions feasible for the transfer of energy to a body? Hence derive expressions for the heat capacity arising from these conditions?
2. Derive suitable expression for adiabatic expansion of ideal gas
3. Show that the heat capacity at constant pressure is greater than the heat capacity at constant volume by a factor of R (R = gas constant)

7.0 References

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Model 2

UNIT 3: The Second law of thermodynamics

1.0 Introduction

2.0 Objectives

3.0 Main content

3.1 Statements of second law of thermodynamics

3.1.1 Entropy change of an ideal gas

3.1.2 Cyclic process: The Carnot cycle

3.2 Free energy

4.0 Summary

5.0 Conclusion

6.0 Tutor mark assignment

7.0 References/Further reading

1.0 Introduction

The first law of thermodynamics is the law of conservation of energy and it provides information on the energy changes during chemical reactions but does not provide information on the spontaneity of a chemical reaction. A spontaneous reaction is a reaction that can take place on its own without any external aid. Spontaneous processes relevant in chemical thermodynamics are irreversible. An irreversible process is a spontaneous process that can not be reversed. In addition, an irreversible process is a natural process, where reversibility is impossible.

The major thermodynamic functions obtained from the first law of thermodynamics are internal energy and enthalpy. Internal energy is a state function obtained at constant volume but most chemical reactions are carried out at constant pressure, which implies that internal energy can not be a unique data for predicting the spontaneity of a chemical reaction. Enthalpy is the heat absorbed at constant pressure. Enthalpy change can lead to an exothermic or endothermic reaction. It is expected that exothermic reactions should be spontaneous while endothermic

reactions should be non spontaneous. However, there are some exothermic reactions that are not spontaneous and there are some endothermic reactions that are spontaneous, indicating that enthalpy data can not be a unique function for predicting the direction of a chemical reaction.

From the above considerations, it is certain that there is need for a second law because the first law does not specify the direction of heat flow and the thermodynamic functions associated with the first law are enthalpy and internal energy changes, which are not unique in predicting the direction of a chemical reaction. The second law is concerned with entropy change during a chemical reaction. Entropy is defined as a measure of the degree of disorderliness of a system. This means a system gets more disordered as the entropy increases and becomes more ordered as the entropy decreases.

2.0 Objectives

- i. To know the concept of entropy
- ii. To know the various statements of the second law of thermodynamics
- iii. To derive expressions for entropy change of an ideal gas
- iv. To be able to define a cyclic process and understand the four stages involved in the Carnot cycle
- v. To derive an equation for calculating the efficiency of a Carnot cycle
- vi. To introduce free energy change and relate it to changes in enthalpy and entropy through Gibbs-Helmholtz equation

3.0 Main text

3.1 Statements of the second law

The second law of thermodynamics can be stated in the following ways

- i. The entropy of a natural system increases and tends toward a maximum

- ii. The entropy change, dS of an irreversible change of a closed system obeys the following inequality, $dS > dq/T$, where dq is the amount of heat transferred to the system and T is the absolute temperature
- iii. It is impossible to construct a device whose only effect, when it operates in a cycle, is heat transfer from a body to the device and the transfer by heat of an equal quantity of energy from the device to a warmer body.

3.1.1 Entropy change of an ideal gas

An expression for entropy change of an ideal gas can be derived from the fundamental definition of entropy. That is $dS = dq/T$. From the first law of thermodynamics, we know that $dq = dU + PdV$ and that $dU = C_vdT$ while $P = RT/V$ (Note, $PV = RT$) which implies that change in entropy can be written as,

$$1$$

Simplification of equation 1 gives equation 2 and upon integration, equation 3 is obtained

$$2$$

$$3$$

The solution of equation 3 can be written as,

$$4$$

Hence

$$5$$

The combined gas law states that $P_1V_1/T_1 = P_2V_2/T_2$ which implies that $T_2/T_1 = (P_2/P_1).(V_2/V_1)$. If we substitute for T_2/T_1 in equation 5 using this expression, we have,

$$6$$

$$7$$

$$8$$

Equations 6 to 8 are the general expressions for the entropy change of an ideal gas under various conditions. Let us consider the expected change in entropy under the following conditions:

- i. Isothermal change: i.e $T_2 = T_1$,
- ii. Isobaric change: i.e $P_2 = P_1$ and

iii. Isochoric change: i.e $V_2 = V_1$ and or

Solved problem 1

- (a) What is entropy? . Hence state the second law of thermodynamics with respect to entropy change of natural processes
- (b) Derive mathematical equations for entropy changes of an ideal gas undergoing isothermal, adiabatic and isochoric changes
- (c) If the volume of an ideal gas changes from 0.2 to 0.4 m³ at stp, calculate the entropy change associated with the process.
- (d) If the pressure of an ideal gas under adiabatic process changes from 50662.50 to 101325 Pa and corresponding entropy change is 8.0J/mol/K, calculate the heat capacity at constant volume.
- (e) If the same gas in ‘d’ above undergoes isochoric change at initial temperature of 298 K, what will be its final temperature?

Solution

- (a) Entropy is a measure of the degree of disorderliness of a system. The second law of thermodynamics can be stated as follows, the entropy of a natural process increases and tends toward a maximum.
- (b) An expression for entropy change of an ideal gas can be derived from the fundamental definition of entropy. That is $dS = dq/T$. From the first law of thermodynamics, $dq = dU + PdV$ and $dU = C_vdT$ while $P = RT/V$ (Note, $PV = RT$) which implies that change in entropy can be written as,

$$(1)$$

Simplification of equation 1 gives equation 2 and upon integration, equation 3 is obtained

$$(2)$$

$$(3)$$

The solution of equation 3 can be written as,

$$(4)$$

Hence

$$(5)$$

The combined gas law states that $P_1V_1/T_1 = P_2V_2/T_2$ which implies that $T_2/T_1 = (P_2/P_1)(V_2/V_1)$. If we substitute for T_2/T_1 in equation 5 using this expression, we have,

$$(6)$$

$$(7)$$

$$(8)$$

Equations 6 to 8 are the general expressions for the entropy change of an ideal gas under various conditions. Under the required changes, the entropy changes are:

Isothermal change: i.e $T_2 = T_1$,

Isobaric change: i.e $P_2 = P_1$ and

Isochoric change: i.e $V_2 = V_1$ and or

(c) The stated change is under isothermal condition, hence,

$$5.7628$$

(d) For isobaric change, , therefore,

(e) The change in entropy under adiabatic and isochoric change will be the same, i.e

Since and are known, then,

3.1.2 Cyclic process: The Carnot cycle

A cyclic process operates through sequence of processes such that the state of the system remains unchanged at the end of the processes. This means that the internal energy change for a cyclic process is zero and from the first law of thermodynamics, it can be stated that the work done by a cyclic process is equal to the heat absorbed. In view of this, let us examine the mechanism of operation of a heat engine.

A heat engine is any device that can transform heat into work or mechanical energy. All the heat engines operate through the following consecutive steps;

- i Absorption of heat from a source at a relatively high temperature called hot reservoir
- ii. Performance of some mechanical work
- iii. Discard of heat at a lower temperature called the cold reservoir

Refrigerator and air conditioner are example of heat engines operating in reservoirs. They take heat from a hot place and give off heat to a cold place after doing work.

The commonest cyclic process is the Carnot cycle. The Carnot cycle consists of four different processes: two isothermal processes and two adiabatic processes. These are highlighted below:

- i. Reversible isothermal expansion: During this process, the gas expands isothermally at a higher temperature, T_2 and absorbs heat, q_2 . From equation 74, the entropy change for isothermal expansion of one mole of a gas is $R \ln \frac{V_2}{V_1}$ and the heat absorbed by n mole of a gas will be given by multiplying the entropy with T. Thus q_2 is the heat absorbed at higher temperature. Therefore for reversible isothermal expansion in the Carnot cycle,
- ii. Adiabatic expansion. In this stage, the gas is expanded adiabatically from a higher temperature, T_2 to a lower temperature, T_1 . The change in entropy is zero since the process is adiabatic.
- iii. Reversible isothermal compression: In this step, the gas is compressed isothermally to a lower temperature, T_1 and the heat given out is q_1 .
- iv. The gas is compressed adiabatically to its original state at a temperature, T_2

The thermal efficiency of a heat engine such as the Carnot cycle is defined as η . That is the ratio of the workdone to the heat absorbed at higher temperature. It has been stated that work done in a cyclic process is equal to the heat absorbed. In the Carnot cycle, the heat absorbed is $q_2 + q_1$.

Hence,

Recall that heat absorbed or work done during isothermal expansion of an ideal gas is given as , where V_1 and V_2 are the initial and final volume. In the Carnot cycle, the heat absorbed in the first stage (reversible isothermal expansion) is while the heat given off during the fourth stage (isothermal compression) . Substituting for q_2 and q_1 in equation 9, yields equation 10

$$10$$

$$11$$

From Poisson equation, which states that and that , it follows that $(V_4/V_3) = (V_2/V_1)$ hence equation 11 becomes,

$$12$$

Hence,

$$13$$

Equation 13 reveals that the efficiency of a Carnot cycle depends on the temperature of the hot (T_2) and cold (T_1) reservoirs. It follows that the efficiency of a Carnot cycle can be estimated using the quantities, q and through T . Therefore,

$$14$$

$$15$$

From equation 15, it can be seen that the sum of the quantity q/T for a Carnot cycle is zero. That is $\sum q/T = 0$. The quantity, dq/T is defined as the entropy.

Finally, the Carnot theorem states that all Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance.

Solved problem 2

- (a) Explain why the work done in a cyclic process is equal to the heat absorbed
- (b) What do you understand by heat engine, hence outline the fundamental mechanism of operation of a heat engine

(c) Discuss the thermodynamics of the four operation steps in a cyclic process

Solution

(a) A cyclic process operates through sequence of processes such that the state of the system remains unchanged at the end of the processes. This means that the internal energy change for a cyclic process is zero. From the first law of thermodynamics, the heat absorbed can be expressed by,

Therefore, if the change in internal energy is zero, then all the heat absorbed is used in doing work, i.e.

(b) A heat engine is any device that can transform heat into work or mechanical energy. All the heat engines operate through the following consecutive steps ;

- i Absorption of heat from a source at a relatively high temperature called hot reservoir
- ii. Performance of some mechanical work
- iii. Discard of heat at a lower temperature called the cold reservoir

(c) The thermodynamics of each operation steps in the Carnot cycle are highlighted below,

- i. Reversible isothermal expansion: During this process, the gas expands isothermally at a higher temperature, T_2 and absorbs heat, q_2 . From equation 74, the entropy change for isothermal expansion of one mole of a gas is $R \ln \frac{V_2}{V_1}$ and the heat absorbed by n mol of a gas will be given by multiplying the entropy with T . Thus $nRT \ln \frac{V_2}{V_1}$ is the heat absorbed at higher temperature. Therefore for reversible isothermal expansion in the Carnot cycle,
- ii. Adiabatic expansion. In this stage, the gas is expanded adiabatically from a higher temperature, T_2 to a lower temperature, T_1 . The change in entropy is zero since the process is adiabatic.
- iii. Reversible isothermal compression: In this step, the gas is compressed isothermally to a lower temperature, T_1 and the heat given out is $nRT_1 \ln \frac{V_2}{V_1}$
- iv. The gas is compressed adiabatically to its original state at a temperature, T_2

Solved problem 3

(a) Derive an expression for the efficiency of a Carnot cycle with respect to heat absorbed and with respect to the temperature of the hot and cold reservoir.

- (b) Show that for a Carnot cycle, $\eta = 1 - T_2/T_1$, where q is the heat absorbed and T is the temperature of the reservoir.
- (c) Show that the total entropy change in a Carnot cycle is zero
- (d) Calculate the efficiency of a Carnot cycle operating between the hot and cold reservoir at 300 and 900 K. Hence if the heat absorbed from the hot reservoir is 400 J, calculate the heat associated with the cold reservoir.

Solution

(a) The thermal efficiency of a heat engine such as the Carnot cycle is defined as $\eta = w/q_2$. That is the ratio of the work done to the heat absorbed at higher temperature. Work done in a cyclic process is equal to the heat absorbed. In the Carnot cycle, the heat absorbed is the sum of the heat absorbed at the higher and lower temperatures, i.e. $q_2 + q_1$. Hence,

$$(1)$$

Heat absorbed or work done during isothermal expansion of an ideal gas is given as $w = nRT \ln(V_2/V_1)$, where V_1 and V_2 are the initial and final volume. In the Carnot cycle, the heat absorbed in the first stage (reversible isothermal expansion) is q_2 while the heat given off during the fourth stage (isothermal compression) is q_1 . Substituting for q_2 and q_1 in equation 1, yields equation 2

$$(2)$$

$$(3)$$

From Poisson equation, which states that $PV^\gamma = \text{constant}$ and that $T_1V_1^\gamma = T_2V_2^\gamma$, it follows that $(V_4/V_3) = (V_2/V_1)$ hence equation 3 becomes,

$$(4)$$

Hence,

$$(5)$$

(b) Equation 5 reveals that the efficiency of a Carnot cycle depends on the temperature of the hot (T_2) and cold (T_1) reservoirs. It follows that the efficiency of a Carnot cycle can be estimated through the quantity, q and through T . Therefore,

$$(6)$$

$$(7)$$

(c) From equation 7, it can be seen that the sum of the quantity q/T for a Carnot cycle is zero. That is $\sum q/T = 0$. The quantity, dq/T is defined as the entropy. Therefore, the differential, because, Hence the total entropy change in the Carnot cycle is zero.

(d) The efficiency of a Carnot machine can be calculated from using the underlisted equation,

Therefore the efficiency of the cycle is 66.67 %

Since the efficiency can also be considered in terms of heat absorbed, then

The negative sign indicates that heat is given off.

3.2 Free energy

Two important thermodynamic functions are very essential in assessing the work done by a given system. Enthalpy is a state function obtained at constant pressure and fortunately, most chemical reactions occur at constant pressure. Enthalpy is the heat absorbed at constant pressure and it can be considered that enthalpy represent the necessary work put into a machine while entropy represent the disorderliness. Therefore, we can state that the free energy will be given as,

$$16$$

The above equation was obtained by Gibbs and is called Gibbs free energy. Similarly, at constant volume, the free energy is given as

$$17$$

At constant volume, the free energy is called Helmholtz free energy and is denoted by A . Therefore, at constant pressure, $G = H - TS$ and at constant volume, $A = U - TS$. The terms, H and

U represent the tendency towards orderliness while TS represents the tendency toward disorderliness.

Generally, when the change in free energy is zero, the reaction is at equilibrium. When the change is negative, the reaction is spontaneous in that direction and when it is positive, the reaction is not spontaneous in that direction.

Solved problem 4

(a) Consider the following reaction,

If the standard changes in enthalpy and entropy are 58220 J and 176 J/K, calculate the change in free energy of the reaction. Hence state whether the reaction is spontaneous or not.

(b) Calculate the equilibrium constant of the reaction at 300 K

(c) At what temperature will the standard change in free energy be equal to zero?.

Solution

(a) From the Gibb-Helmholtz equation, . Therefore,

$$= 5772 \text{ J}$$

Since the calculated value of standard free energy change is positive, the reaction is not spontaneous.

(b) The equilibrium constant is related to the standard change in free energy according to the equation, . Therefore,

(c) From the equation, , when , then , and

4.0 Summary and conclusion

- i. Entropy is a measure of the degree of disorderliness of a system. The second law deals with entropy change of a system
- ii. The entropy of a natural system increases and tends toward a maximum
- iii. The entropy change, dS of an irreversible change of a closed system obeys the following inequality, $dS \geq \frac{dq}{T}$ where dq is the amount of heat transferred to the system and T is the absolute temperature
- iv. It is impossible to construct a device whose only effect, when it operates in a cycle, is heat transfer from a body to the device and the transfer by heat of an equal quantity of energy from the device to a warmer body
- v. Entropy changes of an ideal gas for isothermal, isobaric and isochoric processes are, $nR \ln \frac{V_2}{V_1}$, $nC_p \ln \frac{T_2}{T_1}$ and $nC_v \ln \frac{T_2}{T_1}$ respectively.
- vi. A cyclic process operates through sequence of processes such that the state of the system remains unchanged at the end of the processes
- vii. The four stages involved in the Carnot cycle are isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression.
- viii. The efficiency of a Carnot cycle is related to the temperature and heat absorbed according to the equation, $\eta = 1 - \frac{T_2}{T_1}$
- ix. The free energy changes at constant pressure and at constant volume are ΔG and ΔA

5.0 Conclusions

The second law of thermodynamics is often called the law of entropy. Entropy itself is a measure of disorderliness or orderliness of a system. Thermodynamic parameters associated with a change from disorderliness to orderliness and vice versa are essential in measuring the direction

of a chemical reaction. Entropy data may not be unique in predicting the direction of a chemical reaction because we who measure the entropy are part of the surrounding. Therefore, since the total entropy is what is expected to be measured and the difficulty of measuring our entropy, then entropy data are often used in combination with other thermodynamic parameters.

6.0 Tutor marked assignment

1. Derive an expression to show that the standard Gibbs free energy is related to entropy at constant pressure
2. What are the four major properties of entropy?
3. Derive an expression for entropy change of an ideal gas
4. Highlight the four major stages in the Carnot cycle and state the direction or pattern of entropy for each of the stages.
5. Define the term, efficiency of a Carnot cycle and show that it can be expressed in terms of heat absorbed or temperature
6. What are the possible factors that can make a machine not to operate effectively as a Carnot cycle?

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MODEL 2

UNIT 4: The Third and zeroth laws of thermodynamics

2.0 Introduction

2.0 Objectives

3.0 Main content

3.1 The third law of thermodynamics

3.1.1 Limitations of the third law

3.2 The Zeroth law of thermodynamics

4.0 Summary

5.0 Conclusion

6.0 Tutor mark assignment

7.0 References/Further reading

1.0 Introduction

The third law of thermodynamics was developed between 1906 and 1912, by Walther Nernst. The law clarifies that the entropy change of a system at absolute zero is a well defined constant because at absolute zero, the system is in its ground state, which implies that the entropy is determined by only the degeneracy of its ground state. The first statement of the third law was stated in 1912 by Nernst, thus “ It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps. However, in 1923, Gilbert Lewis and Merle Randall gave an alternative version of the third law as follows,

“If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances”

Gilbert Lewis and Merle Randall law states not only ΔS will reach zero at 0 K, but S itself will also reach zero as long as the crystal has a ground state with only one configuration. Some crystals form defects which causes a residual entropy. This residual entropy disappears when the kinetic barriers to transitioning to one ground state are overcome.¹

Development of statistical mechanics has contributed to change of the third law from fundamental to derived law. The bases for its derivation is the statistical-mechanics definition of entropy for a large system according to the following equation

where k_B is the Boltzmann constant and Ω is the number of microstates consistent with the macroscopic configuration. The identification of this state is sustained but the reference state is absolute zero in which the entropy is S_0 .

The zeroth law was the last thermodynamic law to be formulated. However, since the first, second and third laws were already established, it was not possible to re-arranged the three laws, rather, the term, zeroth law was used. In this section, the zeroth law will only be stated.

2.0 Objectives

- i. To know the steps that led to the development of the third and the zeroth laws of thermodynamics
- ii. To be able to understand and state the third and zeroth laws of thermodynamics
- iii. To know the mathematical consequences of the third and zeroth laws of thermodynamics.
- iv. To apply the third and zeroth laws of thermodynamics in solving problems.
- v. To comprehend the major limitation of the third law of thermodynamics

3.0 Main text

3.1 The Third law of thermodynamics

In simple terms, the third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero. A perfect crystal is a crystal without crystal imperfection. Consequently, the third law provides an avenue for the determination of entropy at any other temperature. The entropy of a system, determined relative to this zero point, is then the *absolute* entropy of that system.

By implication, S is zero for ground state configuration that is unique. This means that for N identical particles lying within a matrix of a perfect crystal, the number of permutations of N particles, taking N at a time gives $N!$, hence $k \ln N!$. Therefore, the difference is zero indicating that $S = 0$ and $S = 0$.

From the second law of thermodynamics, the entropy of a system can be expressed as,

$$1$$

The rise in temperature due to the absorption of heat, dQ is related to the heat capacity according to the equation,

$$2$$

X is a factor which accounts for all parameters that are kept constant during the heat transfer. For example, if the pressure is kept constant, then C becomes the heat capacity at constant pressure, C_p . if equation 3 is divided by T , we have

$$3$$

Integration of the above equation from a reference temperature T_0 to an arbitrary temperature T gives the entropy at temperature T as,

$$4$$

If we chose the zero of the entropy through classical approach, then $S(0) = 0$, and the above equation becomes,

5

The most essential application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of substances at any temperature T .

$$S = 2.303 C_p \log T$$

where C_p is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range of 0 to T .

3.1.1 Limitations of the third law of thermodynamics

- i. Glassy solids even at 0°K has entropy greater than zero.
- ii. Solids having mixtures of isotopes do not have zero entropy at 0°K . For instance, entropy of solid chlorine is not zero at 0K .
- iii. Crystals of CO , N_2O , NO , H_2O , etc. do not have perfect order even at 0 K thus their entropy is not equal to zero.

3.2 The Zeroth law of thermodynamics

The zeroth law of thermodynamics states that “If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.” This implies that, if $A=B$ and $B=C$ then $A=C$. This may seem so obvious that it doesn't need stating but without this law we couldn't define temperature and we couldn't build thermometers.

Solved problems 1

- (a) What are major applications of the third law of thermodynamics? Hence, if the enthalpy of a system is defined by the equation, $H = 30T + 23.6$, calculate the absolute entropy of that system at 300 K.
- (b) State the third law of thermodynamics and list the major limitations of the third law
- (c) State the zeroth law of thermodynamics

Solution

The major application of the third law of thermodynamics is that it is used in the calculation of absolute entropies of the substance at any temperature T using the equation,

$$S = 2.303 C_p \log T$$

where C_p is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range of 0 to T .

From the given data, $H = 30T + 23.6$, $C_p = dH/dT = 30$ J, hence

$$S = 2.303(30 \text{ J})\log(300 \text{ K}) = 171.14 \text{ J/K}$$

- (b) The third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero. The major limitations of the third law are,
- i. Glassy solids even at 0°K has entropy greater than zero.
 - ii. Solids having mixtures of isotopes do not have zero entropy at 0 °K. For instance, entropy of solid chlorine is not zero at 0 K.
 - iii. Crystals of CO, N₂O, NO, H₂O, etc. do not have perfect order even at 0 °K thus their entropy is not equal to zero.
- (c) The zeroth law of thermodynamics states that “If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.”

4.0 Summary

- i. The Third law of thermodynamics provide information on the calculation of absolute entropy of a system.
- ii. The third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero.
- iii. The third law has some major limitations in imperfect crystals and for some condensed matter whose entropy reaches zero before the absolute zero temperature.
- (iv) The zeroth law of thermodynamics states that “If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

5.0 Conclusions

The third and zeroth laws of thermodynamics may have limited application but they are useful in predicting the thermodynamic behavior of systems at the limit of zero degree.

6.0 Tutor marked assignment

1. State the third law of thermodynamics and highlight the major limitations to its applications
2. State the Zeroth law of thermodynamics and state one application of the law
3. Show that entropy change can be expressed as, $S = 2.303 C_p \log T$

7.0 References

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Model 3

Unit 1: Chemical kinetics

8.0 Introduction

9.0 Objectives

10.0 Main content

10.1 Derivation of integrated rate equation

10.1.1 Zero order reaction

10.1.2 First order reaction

10.1.3 Second order reaction

10.2 Effect of temperature on the rate of chemical reaction

10.3 Theories of chemical reaction

10.4 Elementary reaction

10.5 Molecularity of a reaction

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10.6.1 Arrhenius theory

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11.0 Summary

12.0 Conclusion

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14.0 References

1.0 Introduction

The rate of a chemical reaction can be defined as the rate of change of concentration of the reactant or the product. Before a chemical reaction starts, the concentration of the reactant will be zero at the initial time (i.e $t = 0$). However, when the reaction starts, the concentration of the reactant will decrease with time while that of the product will increase with time. Therefore, for a hypothetical reaction such as the one expressed in equation 1, the theoretical rate of the reaction can be expressed according to equation 2,

1

2

where a, b, c and d are the number of moles of A, B, C and D respectively and t is the time. If the concentration has a unit of moles and the time second, then the rate of reaction will have a unit of mole/second. Other units are g/s, lb/s, kg/day etc. Equation 2 reveals that the rate of a chemical reaction can be expressed in terms of decrease in concentration of the reactant (justifying the use of negative sign) or in terms of increase in concentration of the product (justifying the use of positive sign) with time. Let us consider the reaction between hydrogen and iodine, which leads to the formation of hydrogen iodide according to the following equation,

3

Before the reaction begins, the concentrations of hydrogen and iodine are maximum while that of hydrogen iodide is zero but when the reaction proceeds, concentrations of hydrogen and iodine begins to decrease while that of hydrogen iodide will begin to increase . According to the law of conservation of matter, matter can not be destroyed or created but can change from one form to another. Therefore, for every loss of x mole of reactant, x mole of product is formed. Therefore, the variation of concentration of reactants and product with time can be represented graphically as shown in Fig. 1

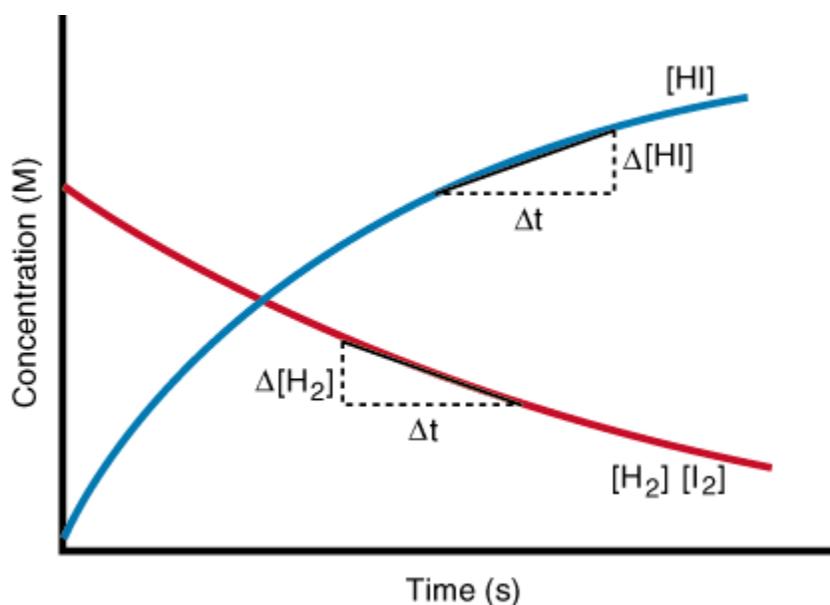


Fig. 1: Variation of concentrations of reactant and product with time

From equation 2 and Fig. 1, it is evident that the rate of formation of HI is twice the rate of disappearance of H_2 and I_2 . Applying equation 2, we can write the rate equation for this reaction as follows (equation 4),

4

Equation 4 also implies that the slope of either plots should give the value of the rate of reaction. Hence rate of reaction is the decrease in concentration of the reactant or increase in the concentration of the product with time.

The major short coming arising from the use of equations 2 in estimating the rate of a chemical reaction is that it is based on the expressed chemical equation and its stoichiometry. However, it has been found that the theoretical expressed rate equation may not always agree with the experimentally derived equation. An experimentally derived rate equation is called rate law. The essential features of a rate law for a given reaction can be written as,

$$5$$

where, k_n is the rate constant with respect to the overall order of reaction, x is the order of reaction with respect to the reactant, A while y is the order of reaction with respect to the concentration, B. The overall order of the reaction is the sum of the individual order (i.e $x + y = n$). An experimental derived equation such as the one expressed inequation 5 shows that the rate of reaction is proportional to the concentrations of reactant raised to certain power. If the order of reaction is 1,2,3,...n, the reaction is said to be first order, second order, third order,... n order. It is possible to have zero and even fractional order of reaction.

1.0 Objectives

The objectives of this unit shall include the following

- To introduce the student to the basic concept of chemical kinetics
- To know and define some terms associated with chemical kinetics
- To understand theoretical and experimental (rate law) rate equations and be able to differentiate between them
- To derive equation for zero, first and second order equations
- To understand details on theories of reactions including Arrhenius theory, collision theory and Transition state theory
- To understand the concept and application of molecularity of a reaction

- To comprehend unimolecular reaction theory.

3.0 Main content

3.1 Derivation of integrated rate equation

The rate equation is often represented as a differential equation, which indicates that it can be most useful if integrated. In this section, integrated rate equations are derived for some reactions orders.

3.1.1 Zero order reaction

A zero order reaction is characterised by a non dependency of the rate of the reaction on concentration. Example of a zero order reaction is the decomposition or cracking of ammonia using tungsten as a catalyst. The reaction proceeds independent of the concentration of ammonia. Generally, a first order reaction can be represented according to equation 6, which re-arranges to equation 7 ,

6

7

Integration of equation 7, within the concentrations limits, 'a₀' and '' (corresponding to time, t = 0 and t respectively) yields equations 8 and 9,

8

9

10a

10b

Equation 10 is the integrated rate law for a zero order reaction. In order to test whether a given reaction is a zero order, equation 10 is suitable. If equation 10 is linearised, it becomes , which

is in the form, $y = mx + C$, indicating that a plot of values of 'a' versus values of t should yield a straight line with slope and intercept equal to k_0 and a_0 (see Fig. 2).

The half life of a chemical reaction is the time taken for the concentration of the reactant to be reduced by half its initial value. This implies that if the initial concentration of the reactant was 'a', at half life, the concentration will become, $a_0/2$. Using this concept, the half life for a zero order reaction can be derived from equation 10 as follow,

11

12

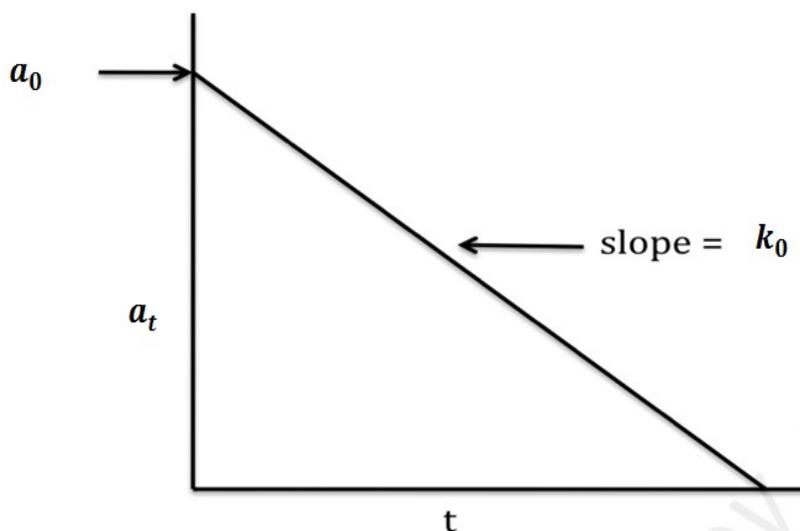


Fig.2: Variation of concentration with time for a zero order reaction

3.1.2 First order reaction

A first order reaction is a one in which the rate of reaction is proportional to the concentration of the reactant raised to the power of unity. Therefore, the rate law for a first order reaction, given as $A \rightarrow \text{product}$, can be written as,

13

14

where k_1 is the first order rate constant, $[A]$ is the concentration of the reactant and t is the time. If at time, $t = 0$ and at some other time, t , the concentrations of the reactant are ' a_0 ' and ' a_t ' respectively, then equation 14 can be integrated within these limits, yields equations 15 to 18 as the solutions,

15

16

17

18

Equation 18 is the integrated rate equation for a first order reaction. However, the equation can be simplified and re-presented in the forms expressed in equation 19 and 20,

19

20

Equations 19 and 20 are the various forms of integrated equation for a first order equation. From equation 19, a first order reaction can be tested and confirmed if a plot of $\ln \frac{a_0}{a_t}$ versus t gives a straight line. This approach follows the linearised model of the equation, thus, $\ln \frac{a_0}{a_t} = k_1 t$, which compares with the general linear model, $y = mx + C$. Such plots will give a negative slope equal to k_1 (see Fig.3)

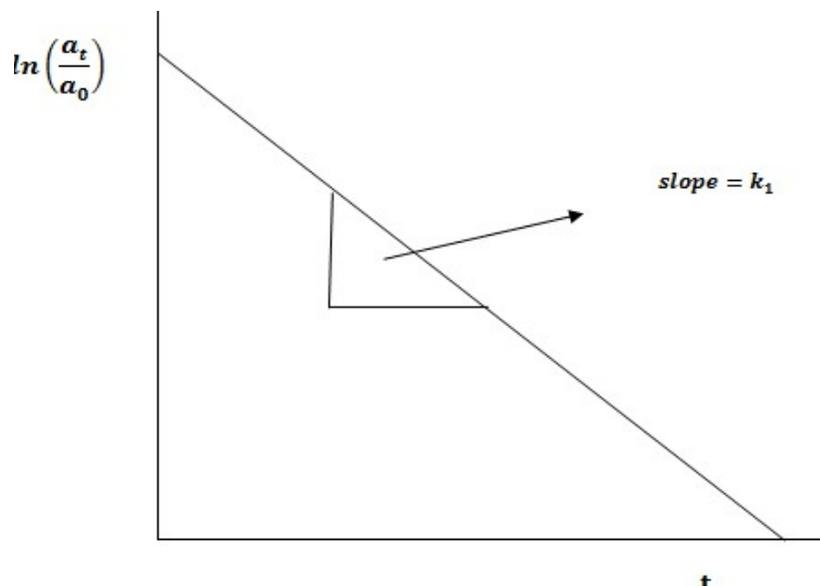


Fig. 3: Variation of $\ln \left(\frac{a_t}{a_0} \right)$ with t for a first order reaction

The life of a first order reaction can be derived using equation 19 since at half life, $a_t = a_0/2$, the equation becomes

$$21$$

$$22$$

$$23$$

Equation 23 reveals that the half life of a first order reaction is independent of the concentration of the reactant but is a function of the rate constant.

There are other ways of analysing a first order reaction. For example, consider a reactant, A giving a product, P upon reaction. If the number of moles of A reacting is a_0 at time, $t=0$ and the number of moles of product formed after some time, t , is x moles. Then at time t , the concentration of a is $(a_0 - x)$ while that of P is x . This indicates that an expression for a first order reaction can be written according to equations 24 and 25,

$$24$$

$$25$$

Rearrangement, integration and simplification of equation 25 yields equations 25 to 30

26

27

28

29

30

The mathematical significance of equation 30 is that a plot of $\ln(a_0 - x)$ versus t should be linear with slope equal to k_1 . This derivation also reveals that a first order equation can also be derived in terms of concentration of product (which is x), just as it was derived in terms of the concentration of the reactant. The expression for the half life of the reaction is the same as the one earlier derived (equation 23). This can be proved by inserting $x = a_0/2$ into equation 30. This gives hence as before.

Solved problem 1

(a) Given that for a zero order reaction, a reactant A decomposes to give a product, P.

Derive an integrated rate law for the reaction

(b) How can you test and confirm that a given reaction is zero order?

(c) Derive an expression for the half life of a zero order reaction hence, calculate the half life

of the reaction If the concentration of A changes from 0.1 M to 0.25 M after 30 minutes,

(d) Radioactivity of a sample ($z = 22$) decreases 90 % after 20 years. What will be the half-

life of the sample?

Solution

(a) The rate law for the reaction can be written as

1

2

Integration of equation 2, within the concentrations limits, 'a₀' and '' (corresponding to time, t = 0 and t respectively) yields equations 3 and 4, which simplifies to 5

3

4

5

Equation 10 is the integrated rate law for a zero order reaction.

(b) In order to test whether a given reaction is a zero order, equation 5 is suitable. If equation 10 is linearised, it becomes , which is in the form, $y = mx + C$, indicating that a plot of values of 'a' versus values of t should yields a straight line with slope and intercept equal to k_0 and a_0 (see Fig. 2).

(c) The half life of a chemical reaction is the time taken for the concentration of the reactant to be reduced by half its initial value. This implies that if the initial concentration of the reactant was 'a_t', at half life, the concentration will become, $a_0/2$. Using this concept, the half life for a zero order reaction can be derived from equation 5 as follow,

In order to calculate the half life, we need to know the values of a_0 ($a_0 = 0.1$ M, the initial concentration) and k_0 , the rate constant. Since a_0 , a_t and t are given, we can use equation 5 to calculate k_0 , that is

(d) A radioactive decay is a first order reaction. Therefore, the half life is given as $t_{1/2} = \frac{2.303}{k} \log \frac{a_0}{a_t}$. Hence we need to know the rate constant, which can be gotten from the equation, or

Let the initial concentration of the reactant be x M. That means the concentration after twenty years will be 90 % less, i.e $x - 90x/100 = (100x - 90x)/100 = 10x/100$. Hence $a_0 = x$, $a_t = (100x - 90x)/100$ and $t = 20$ years. Therefore

Therefore, the half life is

Solved problem 2

Given that for a first order reaction, the concentration of the reactant changes from 0.1 M to 0.025 M in 60 minutes. Calculate

- i. the rate of reaction, when the concentration of A is 0.05 M
- ii. The half life of the reaction

Solution

- i. A first order rate equation can be expressed as $\ln \frac{a_0}{a_t} = kt$, which translates to $k = \frac{2.303}{t} \log \frac{a_0}{a_t}$. From the question

(i.e initial concentration)

, that is the concentration after time, t

If these values are substituted into the rate equation, the rate constant becomes,

When the concentration of A = 0.05 M. It implies that $a_t = [0.05M]$ and since the reaction proceeds with the same rate constant and is a first order reaction, the rate can be expressed as

ii. The half life of a first order reaction is given as,

3.1.3 Second order reaction

A second order reaction can arise in two different ways. These are,

- (i) A single reactant, giving a product, P. That is $A \rightarrow \text{Product}$. The rate law in this case is
- (ii) Two reactants reacting to give a product, P such as $A + B \rightarrow P$. In this case, the rate law can be written as

From case 1, we have equation 31, which is integrated to give equation 32. Simplification of equation 32 gives equation 33 and 34

31

32

33

34

Equation 34 is the integrated rate equation for a second order reaction, involving one reactant. The unique feature of this equation is that it is a function of concentrations. From equation 34, a given reaction can be proven to be a second order if a plot of $\frac{1}{[A] - [A]_0}$ versus t gives a straight line. In this case, the slope will be $\frac{1}{[A]_0 - [A]}$ and the intercept will be $\frac{1}{[A]_0}$ (note, the linear form of equation 34 is $\frac{1}{[A] - [A]_0} = \frac{1}{[A]_0} + \frac{k}{[A]_0} t$).

Also, the half life of a second order reaction can be derived as follows, At half life, $a_t = a_0/2$ and $t = t_{1/2}$. Therefore, according to equation 34,

35

36

37

Therefore, the half life of a second order reaction depends on the initial concentration of the reactant and on the rate constant.

From case 2, the rate equation rearranges to

38

Let the initial concentrations of A and B be a_0 and b_0 . If x mole of the product is formed after time, t , concentrations of A and B will reduce to $(a_0 - x)$ and $(b_0 - x)$ respectively. By substituting for $[A]$ and $[B]$, equation 38 becomes,

39

40

Equation 40 can best be solved by treating it as a partial fraction,. This enables the equation to be splitted into two major part as follows,

41

There are two approaches that can be used to find the coefficients (C and D).In the first approach, the equation is simplified thus,

42

The LCM of the denominators in equation 41 is . Upon simplification, we have,

43

The first approach can be applied as follow. Putting $x = a_0$ into equation 42, we have, , which gives and . Again, putting $x = b_0$, into equation 42, we have, . This gives and

In the second approach, the equation is expanded and the constant terms and terms associated with the coefficient of x are used to approximate the constants, C and D . Expansion of equation 42 gives, , which rearranges to

$$43$$

Comparing the coefficients of x in the right and left hand side of equation 43, we have, $C + D = 0$ or $C = -D$. Similarly, comparing the coefficient of the constant, we have, . Since $C = -D$, we have, , This gives . Similarly, $C = -D$ also implies that $D = -C$ hence, since , we have, or and as before. Generally, the two methods gives the same solution. Substituting for C and D into equation 41 and resetting the original equation, we have,

$$44$$

Equation 44 can easily be integrated as follows,

$$45$$

The solution to equation 44 are gotten through the steps expressed below

$$46$$

$$47$$

$$48$$

$$49$$

$$50$$

Equation 51 can also be written as follows,

$$51$$

$$52$$

t

Equations 53 and 54 gives the integrated rate law for the second order reaction arising from two reactants combining to give a product.

Solved problem 3

Consider the following reaction, $2\text{Mg} + \text{O}_2 = 2\text{MgO}$. If the rate equation can be written as ,

The results of some three trial experiment generated the data given in the Table below

Experiment No	Initial [Mg] mol/L	Initial [O_2] mol/L	Measured rate (mol/Ls)
1	0.10	0.10	0.002
2	0.20	0.10	0.004
3	0.10	0.20	0.008

Answer the following questions

- What is the rate law for the reaction ?
- What is the overall order of the reaction
- Calculate the value of the rate constant, k_n

Solution

- The expected rate law should take the form, .
- From the data provided, when the concentration of O_2 is held constant at 0.10 mol, then we can obtained the order for Mg (using experiments 1 and 2) as follows,

This gives $2 = 2^1$ which means that the order of the reaction with respect to Mg is 1. Similarly, when the concentration of Mg is held constant in experiments 1 and 3, we have,

which gives, $2 = 2^2$ hence the order of the reaction with respect to oxygen is 2 and the overall order is 3rd order, i.e termolecular reaction.

- iii. Using data obtained from experiment 1, we can obtain the value of the rate constant. Thus,

, which gives $k_n = 2.0 \times 10^4$. This means that the rate equation can be re-written as

Solved problem 4

During the kinetic study of the reaction, $2A + B \rightarrow C + D$, following results were obtained:

Run	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate of formation of D/mol L ⁻¹ min ⁻¹
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

- (i) Determine the order of the reaction
(ii) Calculate the value of the rate constant
(iii) Write the rate law for the reaction

Solution

- (i) In runs I and IV, the concentrations of B are held constant at 0.01 mol. Therefore,

Which gives, $4^1 = 4^1$ hence the order with respect to A is 1. Similarly in runs II and III, concentrations of A is held constant, hence,

Which gives $2^1 = 2^2$, hence the order of the reaction with respect to B is II

The rate law for the reaction can be written as, , which gives overall order of 3. That is termolecular reaction.

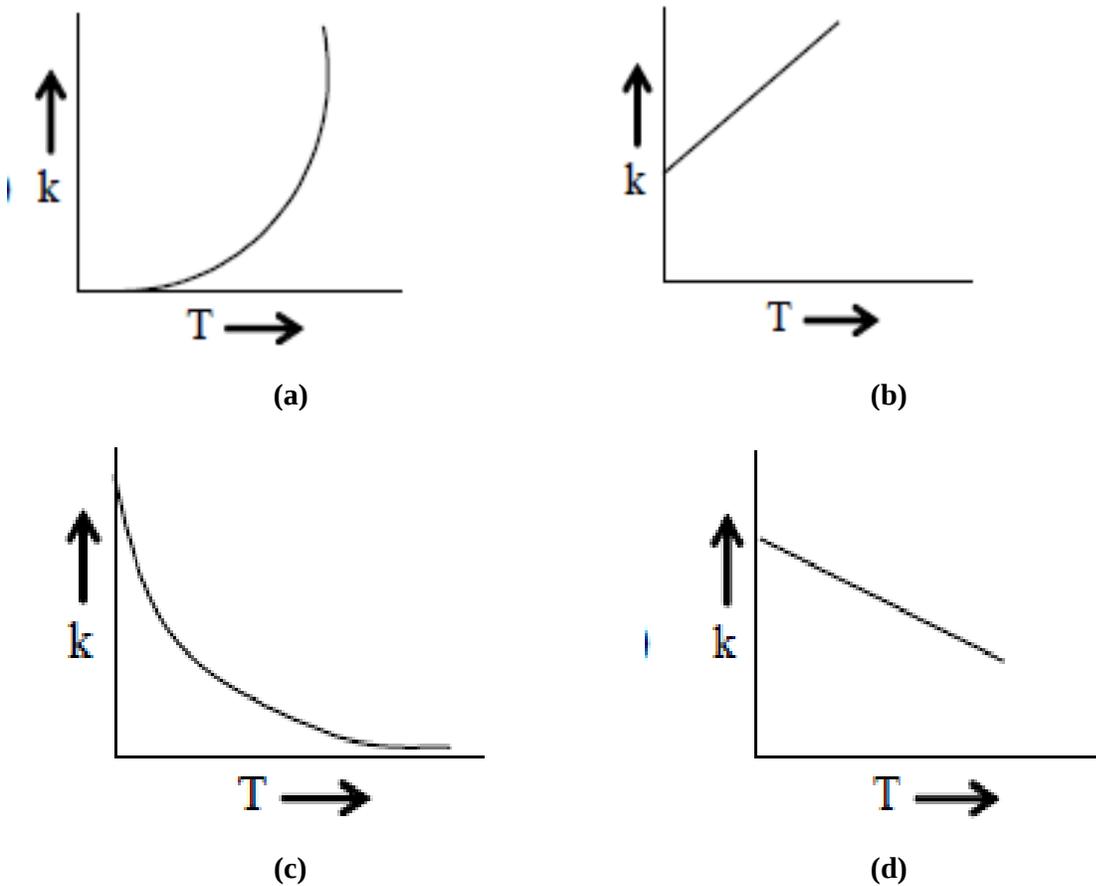
(ii) The rate constant can be obtained by substituting for the variables indicated in the rate law. If we choose run IV, we have

This gives $k_n = 6$

(ii) The rate law can be written as

3.2 Effect of temperature on the rate of reaction

It has long been established that temperature affects the rate of a chemical reaction. As a rule, reaction rate doubles for every 10°C rise in temperature. Increase in the rate of a chemical reaction will be accompanied by increase in the rate constant. Several reactions shows various respond to the variation of the rate of reaction with temperature. Fig. 4 shows different types of plots for the variation of rate of reaction with temperature. Figs. 4a and 4b clearly show that the rate of reaction increases with temperature while Fig. 4c and d show that the rate of reaction decreases with increase in temperature. Fig. 4a is a typical Arrhenius plot while others are anti-Arrhenius plots. The first empirical equation relating the rate constant of a chemical reaction with temperature was given by Hood who stated that the logarithm of the rate constant is proportional to the inverse of temperature as shown in equation 55,



Fig

. 4: Various types of variation of rate constant with temperature

As at then Hood's equation revealed that a plot of $\log k$ versus $1/T$ gives a straight line with slope and intercept equal to B and A . However, Hood was unable to give the physical significant of the constants, A and B . On the progressive path, Vant Hoff found that there exist a relationship between equilibrium constant and temperature while Arrhenius gave an equation for the variation of reaction rate constant with temperature (equation 56, which is rearranged to 57),

56

57

where k is the rate constant, T is the temperature, R is the Universal gas constant and E_a is the activation energy, defined as the minimum energy required for a reaction to proceed.

Integration of equation 57 yields the following results,

58

59

The constant included in equation 59 was found to be $\ln A$, where A is the Arrhenius or pre-exponential factor. Therefore, equation 59 becomes,

60

The exponential form of the Arrhenius equation can be written as, . Generally, from the Arrhenius equation, a plot of rate constant against the reciprocal of temperature is linear and is characterised by slope and intercept equal to $-E_a/R$ and $\ln A$ respectively (see Fig. 5). The Arrhenius equation can also be applied if the rate constants (k_1 and k_2) at two different temperatures (T_1 and T_2) are known. Inserting the corresponding rate constant and temperatures successively, into equation 60, gives the following expressions (equations 61 and 62):

61

62

Subtracting equation 61 from 62, gives equation 63 and equation 64 upon simplification

63

64

From equation 64, it is evident that Arrhenius equation can be used to estimate the value of the activation energy if the values of the rate constant at two different temperatures are known.

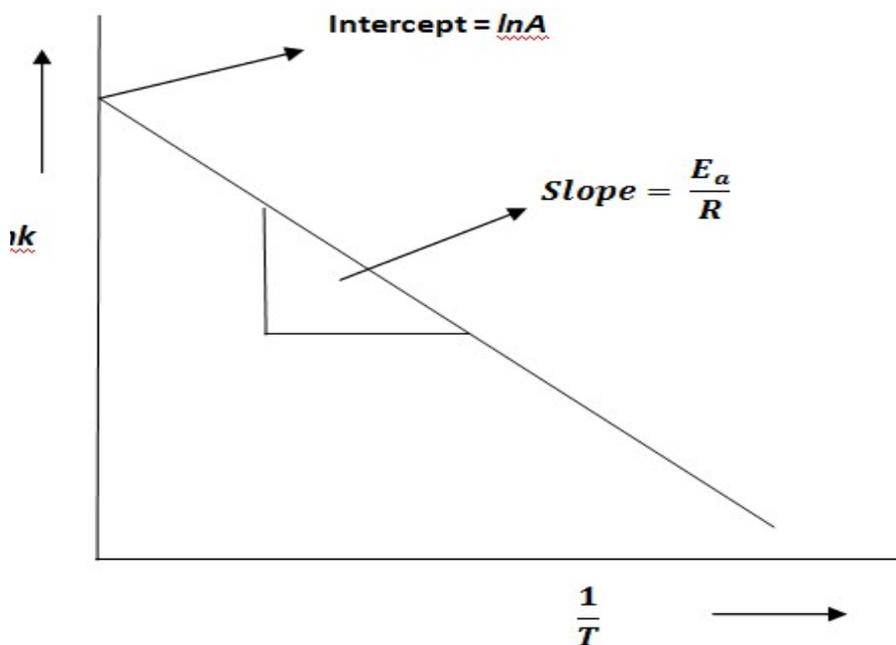


Fig. 5: Typical pattern of Arrhenius plot

Solved problem 4

Given that the rate constants for a first order reaction at 25 and 60 °C are 2×10^{-3} and 8×10^{-3} s/mol. Calculate the activation energy for the reaction.

Solution

The logarithm form of the Arrhenius equation can be used for the calculation. The equation is .

Substituting the given values to the equation, we have,

.3.3 Theories of chemical reaction

Theories of chemical reaction try to explain the various steps connected with the effect of variables such as energy and temperature on chemical reaction. Theories of chemical reactions uses established models to explain how the rate constant is related to thermodynamic variables, thus creating a link between chemical kinetics and thermodynamics. There are three major theories of chemical reactions. These are,

- (i) The Arrhenius theory
- (ii) The Collision theory
- (iii) The Transition state theory.

Each of these theories, its applications and limitations are examined closely in this section.

3.3.1 The Arrhenius theory

Arrhenius suggested that reaction occurs when molecules collide and that not all collision leads to chemical reaction. The collision that leads to chemical reaction are called effective collision. According to the Arrhenius concept, collision must produce energy equal to or higher than the minimum energy (activation energy) before it can be effective. This implies that there is an energy barrier that must be overcome (i.e the activation energy). In order to overcome this barrier, the energy produce by collision must be equal to or higher than the activation energy. According to Boltzmann equation, the fraction of molecules having energy, equal to or greater than the activation energy (i.e the fraction of molecules that have energy enough to be converted to the product) can be expressed as

65

where n is the number of molecules having energy equal to E_a and n_T is the total number of molecules. From equation 77, it is evident that the rate of reaction will be proportional to the

rate molecules are converted to products, which in turn is proportional to $\frac{1}{[A]}$. Hence it can be stated that the rate of the chemical reaction is proportional to $\frac{1}{[A]}$ as shown in equation 66,

66

It is known that the concentration of the reactant can significantly affect the rate of chemical reaction. Therefore,

67

68

where A is the Arrhenius or pre-exponential factor. Since the rate of a chemical reaction can also be expressed as $\text{rate} = k[\text{concentration of the reactant}]$, it implies that the rate constant, $k = \text{rate}/[\text{concentration of reactant}]$, hence $k = \frac{\text{rate}}{[A]}$. Therefore, equation 80 becomes,

69

Equation 81 is the Arrhenius equation, in which the Boltzmann constant, k is replaced with the gas constant, R . It can be seen from the above derivation that the probability of a molecule to go into a reaction is the function of its collision frequency.

The Arrhenius equation is widely applied in solving problems related to chemical system. However, it has some shortcomings. For example,

- i. the equation is most applicable to gaseous systems,
- ii. it doesn't explain how molecules becomes activated
- iii. It is unable to explain the physical meaning of the frequency factor, A

In view of these and other problems, the collision theory was introduced.

3.3.2 The Collision theory

The collision theory applies the assumptions of the Arrhenius equation but in addition, it has an additional assumption which requires that the molecule must be properly oriented at the point of collision. This implies that even if there could be several bonds in a molecule, the collision must take place at the appropriate bond. For example in the molecule shown below, the collision that will be effective in overcoming the energy barrier will be the one that takes place at the OH group. Therefore, even if the molecule has activation energy, it will not collide to produce product until it is properly oriented.

Introducing collision factor into the Arrhenius equation, the rate of reaction can be expressed according to equations 70 and 71

70

71

where $[A][B]$ is the concentration of the reactants and is related to the rate constant, k and to the rate of reaction. Generally, Rate of reaction = $k[A][B]$. Therefore, rate/ $[A][B]$ = k . This enables equation 83 to be written in the form shown in equation 72

72

The Arrhenius equation states that $k = A e^{-E_a/RT}$, which compares with the equation given by the collision theory to explain the physical meaning of 'A'. i.e. $k = Z e^{-E_a/RT}$, indicating that it represents effective collision in the system. However, it has been found that the theoretical value of k obtained through Z is often found to be higher than the experimental value. This difference is compensated by introducing a steric factor, which explains the probability that the molecule is properly oriented at the point of reaction. The collision number, which is the number of collision per unit

volume per unit time, is related to the average velocity of the molecule (v), the collision diameter (d_{AB}) and to the number of molecules. Therefore,

73

The velocity of the molecule is given as, $v = \sqrt{\frac{2E}{m}}$, where m is the reduced mass of the molecule. For two molecules consisting of A and B atoms with molecular mass given as M_A and M_B , the reduced mass is given as, $M_A M_B / (M_A + M_B)$. Inserting v into equation 73, we have,

74

From the Arrhenius equation, which states that $k = A e^{-E_a/RT}$ (equation 84), we can substitute for A and the results is given in equation 74,

75

From the above, it can be seen that the collision theory explains the Arrhenius factor but still suffer some setbacks because it is most applicable to gaseous reactions and does not provide a way to calculate the probability factor, P .

3.3.3 The Transition state theory

The transition state theory was developed in the 20th century by Eyring, an Irish Chemist. According to the transition state theory, a reaction forming a product, first form an intermediate which is in thermodynamic equilibrium with the molecules of the reactant. The only unique property of the intermediate is that it has an energy that is higher than the energy of either the reactant or the molecule and that it has a short life span. The intermediate is easily converted to the product. This implies that the rate of the reaction depends on two major factors, which are ,

- (i) The concentration of the activation complex
- (ii) The rate of dissociation of the activation complex into the product.

For a simple bimolecular reaction involving molecules A and B, then the reaction can be represented as follows,

76

The rate of reaction can be expressed as the product of the concentration of the intermediate and the frequency of decomposition of the activated complex (equation 77),

77

From equation 88, . According to Eyring, the specific rate (k) of any reaction is proportional to (Equation 78),

78

where R is the universal gas constant, T is the temperature, N is the Avogadro's number and h is the Planck constant. The constant, can be related to some changes in thermodynamic variables such as , and . Generally, the equilibrium constant, is related to and can be written as, indicating that

79

80

Substituting equation 80 into equation 78, gives equation 93, which simplifies to equation 94

81

82

Equation 82 is an expression for Eyring transition state equation. The Transition state equation has some similarities with the Arrhenius equation and can be used to explain Arrhenius parameters. Recall the Arrhenius equation, while the transition state equation can be expressed as . Then it is obvious that if we equate the two equation, some terms can be compared. i.e ,

It is evident from the above that A in the Arrhenius equation is related to entropy change while E_a is related to enthalpy change. That is $A = e^{\Delta S^\ddagger / R}$. Therefore, the Arrhenius factor can be estimated in terms of ΔS^\ddagger and the activation energy can be estimated in terms of ΔH^\ddagger . Generally, when volume and pressure are taken into consideration, then $\Delta H^\ddagger = \Delta U^\ddagger + P\Delta V^\ddagger$. For solids, change in volume is negligible, therefore, $\Delta H^\ddagger = \Delta U^\ddagger$ and $\Delta S^\ddagger = \Delta U^\ddagger / T$. However for gases, $PV = nRT$, therefore $\Delta H^\ddagger = \Delta U^\ddagger + P\Delta V^\ddagger = \Delta U^\ddagger + nR\Delta T$ and $\Delta S^\ddagger = \Delta U^\ddagger / T + nR$.

3.4 Elementary reaction

Different elementary steps combine to give a complex reaction. An elementary step has one transition step, no intermediate and can not be broken down into simpler reactions (Fig. 6a)

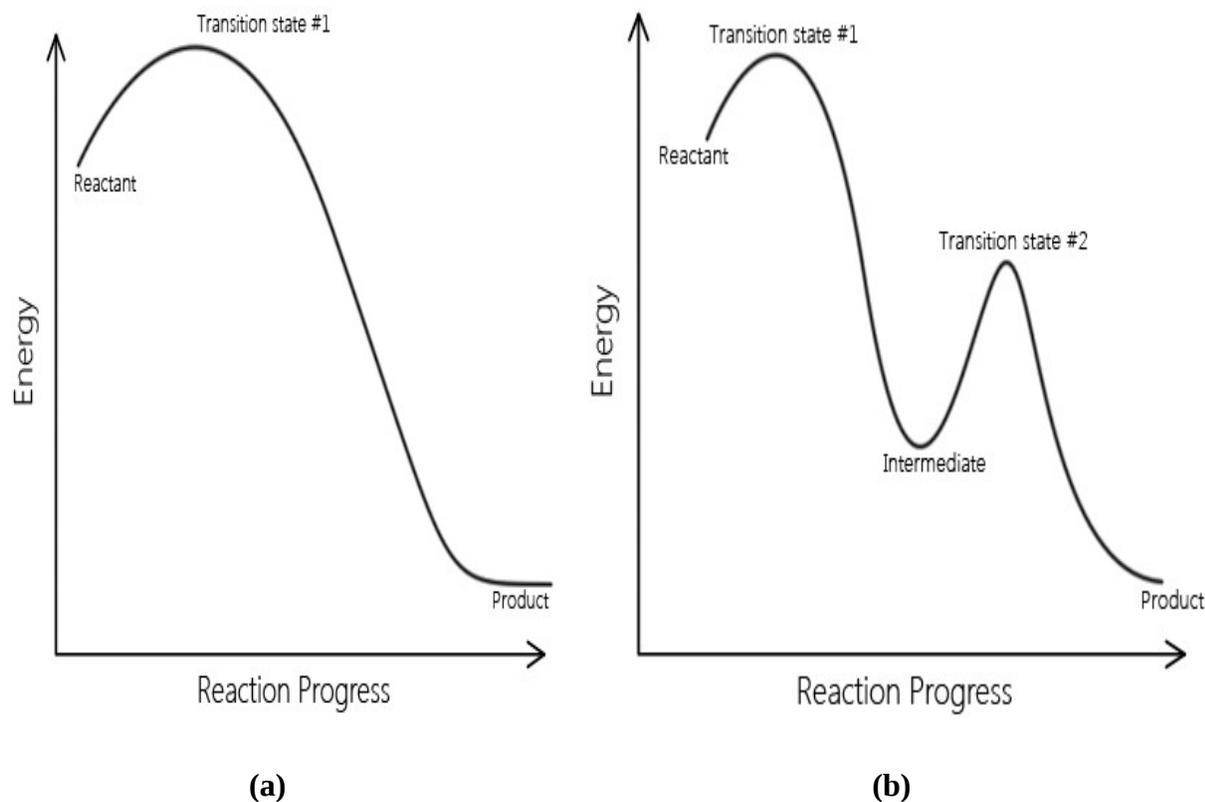


Fig. 6: Reaction profile diagram for (a) elementary step (b) non elementary step reactions

Non-elementary reactions can be described by multiple elementary reaction steps. A set of elementary reactions comprises of a reaction mechanism, which predicts the elementary steps

involved in a complex reaction. Fig. 6b shows a reaction coordinate of a complex reaction, which involves an intermediate and multiple transition A complex reaction can be explained in terms of elementary reactions.

3.5 Molecularity of a reaction

Molecularity of a reaction is the number of molecules that react in an elementary reaction and is numerically equal to the sum of the stoichiometric coefficients of reactants in the elementary reaction. For reaction that proceeds via different steps, some of the steps may be fast and some may be slow. The slowest step is the rate determining or rate limiting step and the number of molecules associated with the slowest step is the molecularity of the reaction.

A reaction is said to be unimolecular, bimolecular or termolecular when one, two or three molecules comes together to form products respectively.

3.6 Unimolecular reaction

A unimolecular reaction occurs when a single molecule rearranges its atoms to produce one or more products. Example of a unimolecular reaction is the isomerization of cyclopropane to propene as shown below

Some common reactions in chemistry occur via unimolecular process. These include, radioactive decay, cis-trans isomerization, thermal decomposition, ring opening and racemization.

The basic theory in explaining the mechanism of a unimolecular reaction was proposed by Frederick Alexander Lindemann (1922), who stated that a unimolecular reaction occurs via bimolecular activation step, followed by a rate determining unimolecular step. According to

Lindemann, a molecule, 'A' reacting to give product will first undergo bimolecular activation to form an intermediate (step1) and the intermediate will decompose to give the product (step 2)

The law of mass action states that the velocity of a chemical reaction is proportional to the concentration of the reactants (the proportionality constant in this case is the rate constant). Therefore, applying the law of mass action to the above reactions, we have,

83

According to the steady state approximation, the rate of change of the concentration of the intermediate will approximately be zero. That is which implies that the right hand side of the equation can be written as,

84

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86

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However, the rate of the reaction is given as

88

If , then can becomes negligible and the rate becomes

89

where is an effective first order rate constant. is a function of pressure and equation 89 is prevalent at high pressure, in which collisional deactivation of A* is the rate determining step, resulting in a first order reaction. However, if , equation 88 becomes,

90

which suggest that bimolecular excitation is the rate determining step and is second order with respect to A. This option is prevalent at high pressure.

There are two major shortcomings. The first is that Lindemann did not take into account, the dependence of biomolecular activation on energy. The theory also neglect the internal degree of

freedom of the molecule and undermine the rate of molecular activation. Secondly, the particular motion required for the unimolecular deactivation was not taken into consideration. These shortcomings, initiated the modification of Lindemann mechanism by Hinshelwood. Hinshelwood accounted for internal degrees of freedom during the activation process and modeled the internal modes of A by a hypothetical molecule having 's' equivalent classical harmonic oscillators, and by considering thermal equilibrium and the strong collision assumption (i.e, the probability of deactivation is equal to the collision frequency and that each collision is efficient to deactivate). Without proof, Hinshelwood equation is written according to equation 91,

91

Hinshelwood equation has been found to bridge much gap that was created by the Lindemann theory.

4.0 Summary

Chemical kinetics is the study of the rate of chemical reactions or processes. This include the study of the effects of various variables, re-arrangement or orientation of molecules on the rate of chemical reaction. The rate of a chemical process can be approached in terms of the amount of product formed per unit time or the amount of reactant consumed per unit time. However, in some chemical processes, not all reactants are converted to product, some reactions may be characterised by side reactions or progress through the formation of an intermediate, in other cases, the orientation of the reactant molecules may affect the formation of product and hence the rate of chemical reaction.

5.0 Conclusions

Chemical kinetics can be viewed in terms of macroscopic and microscopic components. In the macroscopic level, the amount of reactant that has reacted or the amount of product formed as

well as the rate of their formation/consumption are considered. However, at the microscopic level, orientation of the molecules before collision, collision of the molecule and the availability of enough energy, needed to activate the reaction are the essential factors.

6.0 Tutor marked assignment

1. Explain the concept of elementary reaction using a suitable diagram
2. Derive an expression for a first order reaction given that a single reactant yields a single product.
3. Derive an expression for integrated second order reaction giving that a single reactant yields a product.
4. What is the definition of molecularity of a reaction? Giving a reaction splitted into three steps, which take 2, 3, 5 and 7 minutes to complete respectively. Calculate the molecularity of the reaction if 2, 4, 5 and 6 molecules are involved for the respective steps. Give reason for your answer.
5. (a) A reactant A undergoes first order kinetics. Show that the time variation of the reactant concentration at any time t is given by $\ln \frac{[A]_0}{[A]} = kt$ where $[A]_0$ is the initial concentration of the reactant and k is the first order rate constant. How can you prove that a given equation is first order? Hence derive an expression for the half life of the reaction.

(b) For a particular first order reaction at 300 K, the concentration of reactant is reduced to one half of its initial value after 5000 s. At 310 K, the concentration is halved after 1000s. Calculate:

(i) the rate constant for the reaction at 300 and 310 K

- (ii) the time required for the concentration to be reduced to one quarter of its initial value at 300 K
- (iii) the activation energy of the reaction.

7.0 References

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