NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: 405

COURSE TITLE: CHEMICAL THERMODYNAMICS

COURSE
GUIDE

CHM 405

CHEMICAL THERMODYNAMICS

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COURSE GUIDE

INTRODUCTION

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

The Journey to the study 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. This laid a foundation for an American mathematical physicist, Willard Gibbs to publish 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, and thus established the foundation of the science of chemical thermodynamics through their publication, "Thermodynamics and free energy of chemical substances ", which was responsible for supplanting the chemical affinity for the term free energy. E. A. Guggenheim also wrote a book tilted, *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 criterions for predicting the feasibility or spontaneousity 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 Helmoltz work function (as the major functions). Finally, thermodynamics is centered on application of two major laws (first and second law of thermodynamics) to these state functions.

COURSE DESCRIPTION

Chemical thermodynamics (CHM 405) is a 2 credit unit course, with the following content**;** Equations of state for gases, intermolecular forces, The laws of thermodynamics, internal energy and entropy; criteria for equilibrium, free energy; partial molar quantities, the chemical potential; Chemical equilibrium in ideal and non-ideal systems; The thermodynamics of mixtures; Statistical mechanics: microstates and randomness, probability and distribution functions; The Boltzmann distribution; Statistical thermodynamics of gases.

COURSE AIMS

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, thermochemisty,statistical thermodynamics and their consequences.

COURSE OBJECTIVES

- 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 bring the student to the understanding of the nature of intermolecular forces in gases and liquids as well as their consequences.
- To introduce and explain the first law of thermodynamics, its implication, applications and consequences.
- To explain the concept of thermochemistry, laws of thermochemistry, enthalpy changes associated with various reactions and associated theory
- To introduce and explain the concept of entropy and the second law of thermodynamics and associated thermochemical consequences.
- To explain the concept of the third law of thermodynamics
- To examine thermodynamic requirements for spontaneousity of a chemical reaction
- To analyse the concept of thermodynamics of mixtures
- To explain the concept of colligative properties and their applications in Chemistry
- To introduce the basic concepts in statistical thermodynamics
- To solve mathematical problems related to chemical thermodynamics.

WORKING THROUGH THIS COURSE

The course is structured into four models. All the Modules consist of three unit each except 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: Equation of state
Unit 2: Intermolecular forces
Unit 3: Concepts in chemical thermodynamics

Module 2

Unit 1: First law of thermodynamics
Unit 2: Thermochemistry
Unit 3: Second law of thermodynamics

Module 3

Unit 1: Third and zeroth laws of thermodynamics
Unit 2: Thermodynamic potentials
Unit 3: Maxwell equations

Module 4

Unit 1: Feasibility of chemical reactions

Unit 2: Thermodynamics of mixtures

Unit 3: Introduction to statistical thermodynamics

Module 1 is divided in three units. The unit introduces the students to the basic equations of state and intermolecular forces.

Unit 1 identifies the 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 details

In **unit 2**, treats intermolecular forces. Intermolecular forces have been classified based on different principles. London forces have been extensively discussed and compared. Relative strength of the various intermolecular and intramolecular forces have been examined.

Unit 3 considers basic terms in chemical thermodynamics, their definitions and significant. These include a thermodynamic system, surrounding, boundary, classifications of thermodynamic properties, state functions, thermodynamic processes, reversible and irreversible processes, etc.

Module 2 is also divided into three units.

Unit 1 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, application of the first law to the Joule-Thompson coefficient and the derivation of equation for the Joule-Thompson coefficient.

Unit 2 deals with concepts in thermochemistry. These included standard heat of reactions, thermochemical equations, thermochemical laws, Born Haber process, bond energy and lattice energy.

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 outline. Details treatment of the cyclic process (exemplified by the Carnot cycle) has been done. Equations for the efficiency of the Carnot cycle in terms of heat absorbed and temperature has been derived.

Module 3 is divided into three units

Unit 1 discussed the zeroth and third laws of thermodynamics in detail. Consequences of the laws have also been highlighted.

Unit 2 explores thermodynamic potentials and provides first principle derivation of equations for total differentiation of internal energy, enthalpy, Helmoltz work function and Gibb free energy.

Unit 3 presents Maxwell equations for various models. The equations are derived from first principle using different approaches. The applications of Maxwell equations in chemical sciences have been discussed in detail. Finally, derivation of entropy using Maxwell equation has been singled out and explained explicitly

Module 4 is also divided into three units

Unit 1 consists of one sub unit. The unit explicitly considers various concepts associated with feasibility of a chemical reaction. The Gibbs free energy and the Helmholtz work functions have been identified as the major functions that operate under constant pressure and volume respectively. The Gibb Duhem’s equation, effect of pressure and temperature on the Gibb free energy, partial molar quantities, Clausius equation and Clausius-Clayperon equations have also been discussed.Phase equilibrium and colligative properties have also been introduced to capture the interest of the students in this subject.

Unit 2 consists of one sub unit which explicitly treats thermodynamics of mixtures. Equations for thermodynamic functions of mixtures have been derived. These include equation for enthalpy, entropy, free energy, volume change and Helmholtz work functions of mixtures.

Unit 3 consist of one sub unit and introduces basic concepts in statistical thermodynamics such as properties of macroscopic state, postulates of statistical thermodynamics, partition function, distribution law (especially Boltzmann distribution law) and derivation of equation relating partition functions to some thermodynamic functions. The application of Stirling's approximation in solving some statistical thermodynamic equations have been explained.

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'PhysicalChemistry.NinthEdition.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.

MAIN COURSE

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UNIT 2: Intermolecular forces

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MODEL 2

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MODEL 2

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MODEL 3

UNIT 1: The Second law of thermodynamics

MODEL 3

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MODEL 3

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MODEL 1

UNIT 1: Equation of state

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    3.1.1 Boyle’s law
    3.1.2 Charles law
    3.1.3 Dalton’s law
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    3.1.5 van der Waal’s equation
4.0 Summary
5.0 Conclusion
6.0 Tutor mark assignment
7.0 References

1.0 Introduction

The Equation of state is a thermodynamic model that relates some state functions. The state functions in the equation of state 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, variation 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.

2.0 Objectives

At the end of this module, students are expected to understand the following;

i. To know the meaning of equation of state with respect to gases
ii. To follow the trend in the development of equation of state
iii. To know and apply Boyle's law in solving mathematical problems
iv. To know and apply Charles' law in solving mathematical problems
v. To know and apply Dalton law in solving mathematical problems
vi. To know and apply ideal gas law in solving mathematical problems
vii. To know and apply van der Waals equation in solving mathematical problems

3.0 Main text

3.1 Development of equation of state

3.1.1 Boyle's law

Robert Boyle (1662) was the first to develop a 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,

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

$$PV = K$$

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 patterns as shown in the figures below,

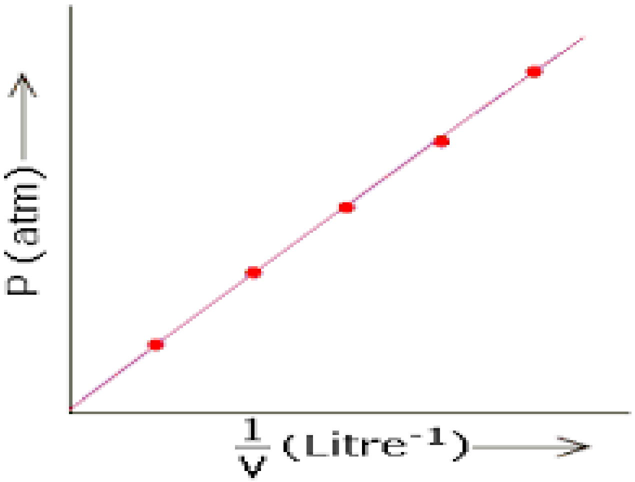


Fig. 1: Variation of pressure of ideal gas with the inverse of its volume according to Boyle's law

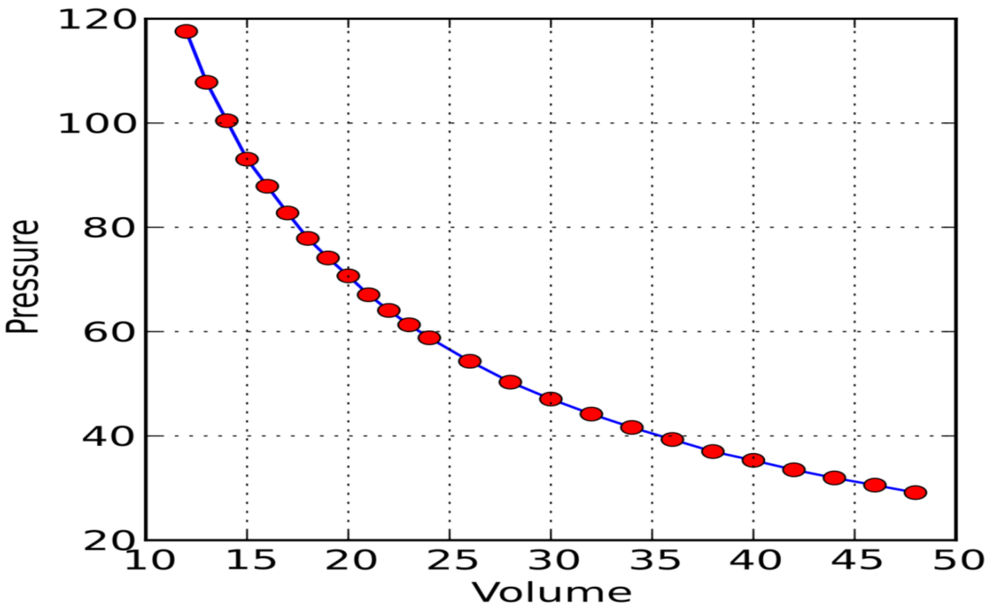


Fig. 2 Variation of pressure with volume according to Boyle's law

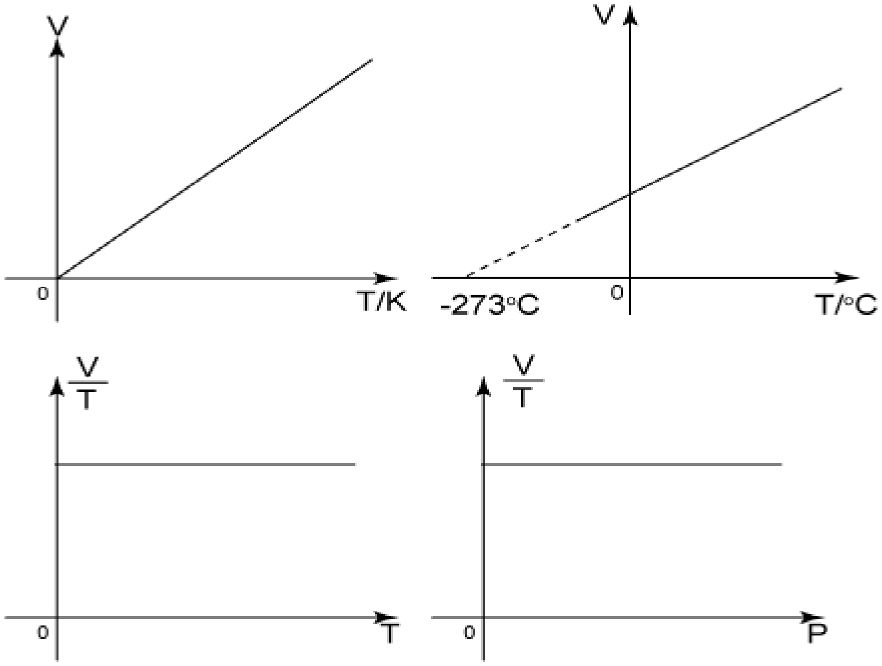
3.1.2 Charles law

The next level of development of equation of state for gases was pioneered by Jacques Charles (1787) and Jospeh 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 was a linear relationship between volume and temperature. Charles law states 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,

$$V \ \alpha \ T$$

$$\frac{V}{T} = K$$

Hence, according to Charles' law, 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 translate to interprets 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 below



Fig, 3: Various plots representing Charles' law

3.1.3 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 a components of a gas mixture are labeled as A, B, C, D.......N, then the total pressure of the gas will be expressed as

$$P_T = P_A + P_B + P_C + P_D \dots\dots\dots.. + P_N = \sum_{i=A}^{N} P_i$$

3.1.4 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 as,

$$PV = nRT$$

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

3.1.5 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 real gases do not obey the ideal gas equation and at high pressures or low temperatures. Therefore, van der Waal equation is a modification of the real gas equation and can be written as,

$$(\mathrm{PV})_{\mathrm{cor}} = \left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT} \text{ (for 1 mole of a gas)}$$

$$(\mathrm{PV})_{\mathrm{cor}} = \left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT} \text{ (for n moles of a gas)}$$

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 an ideal gas.

Solved problem 1

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

Solution

The needed equation is PV = nRT. Where

P is the pressure, given as 1 atm = 102325 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° C = 273 K

Therefore,

$$V = \frac{nRT}{P} = \frac{1 \times 8.3144\, JK^{-1}mol^{-1}}{102325\, Nm^{-2}} = 0.0224\, m^3 = 22.4\, dm^3$$

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

Solved problem 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 dm^3 = 0.001 m^3 of ethane weigh 1.264 g at 283 K (i.e, 20 ° C). Applying the ideal gas law, we have,

$$PV = nRT$$

$$PV = \frac{Mass\ of\ ethane}{Molar\ mass\ of\ ethane}(RT)$$

$$Molar\ mass\ of\ ethane = \frac{Mass\ of\ ethane\ \times R \times T}{P \times V}$$

$$Molar\ mass\ of\ ethane = \frac{1.264\ \times 8.3144\, JK^{-1}mol^{-1} \times 293\ K}{101325\ Nm^{-2} \times 0.001\ m^3} = 30.40\ g/mol$$

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 g/mol. The difference between the two set of values is 0.33. This is due to the fact that in a real gas, there exist intermolecular forces which are not taken into consideration in the ideal gas model.

Solved problem 3

(a) A mixture of 6.5 mol of hydrogen gas and 3.5 mol of oxygen gas was placed in a 3 m^3 container at 273 K. Calculate the partial pressures of the individual gases.

(b) Also calculate the total pressure of the gas mixture

Solution

(a) According to Dalton's law, $P_{Total} = P_{H_2} + P_{O_2}$

But the ideal gas law states that PV = nRT, therefore,

$P_{H_2} = \frac{n_{H_2}RT}{V}$ and $P_{O_2} = \frac{n_{O_2}RT}{V}$

$$P_{H_2} = \frac{6.5\ mol\ \times 8.314\, Jmol^{-1}K^{-1}\ \times 273\ K}{3\ m^3} = 4917.97\ Pa$$

$$P_{O_2} = \frac{3.5\ mol\ \times 8.314\, Jmol^{-1}K^{-1}\ \times 273\ K}{3\ m^3} = 2648.01\ Pa$$

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

$$P_{Total} = P_{H_2} + P_{O_2}$$

$$P_{Total} = \frac{n_{H_2}RT}{V} + \frac{n_{O_2}RT}{V}$$

$$P_{Total} = 4917.97\ Pa + 2648.01\ Pa = 7565.98\ Pa$$

Solved problem 4

(a) A given gas mixture consists 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,

$$P_{Total} = P_{N_2} + P_{O_2}$$

$$P_{Total} = \frac{n_{N_2}RT}{V} + \frac{n_{O_2}RT}{V} = \frac{RT}{V}\left(n_{N_2} + n_{O_2}\right)$$

$$= \frac{8.314\ J/mol/K \times 273\ K}{10\ m^3}\ (2.24 + 1.37)mol = 819.27 \text{ Pa}$$

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

$$X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2}} = \frac{2.24}{3.61} = 0.6205$$

$$X_{O_2} = \frac{n_{O_2}}{n_{N_2} + n_{O_2}} = \frac{1.37}{3.61} = 0.3795$$

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

$$P_{N_2} = X_{N_2}P_{Total} = 0.6205\ x\ 819.27\ Pa = 508.35\ Pa$$

$$P_{O_2} = X_{O_2}P_{Total} = 0.3795\ x\ 819.27 = 310.91\ Pa$$

Solved problem 5

(a) In an automobile combustion cylinder, fuel-air mixture in a cylinder of 1000 cm^3 capacity experiences a temperature rise from 25 to 2200 °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 Pa

T_1 = 25 °C = (273 + 25)K = 298 K

T_2 = 2200 °C = (273 + 2200) K= 2473 K

P_2 = ?

From Boyle's law, PV = K and from Charles, law, V/T = K. Since pressure is proportional to volume, it also follow that P/T = K. Therefore, $\frac{P_1}{P_2} = \frac{T_1}{T_2}$ and $P_2 = P_1T_2/T_1$

= (101325 Pa x 2473 K)/298 K = 840861. 49 Pa = 840.86 kPa

(h) The useful equation will be combined gas equation, which can be written as, $\frac{P_1V_1}{T_1} = K$ or as,

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

$$P_2 = \frac{P_1V_1T_2}{T_1V_2} = \frac{101325\, Pa \times 500\, cm^3 \times 2473\, K}{298\, K \times 1000 cm^3} = 420430.75\, Pa = 420.43\, kPa$$

Solved problem 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 contains 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 Pa x 300 cm^3/200 cm^3 = 150 000 Pa = 150 kPa

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

P_1 = 1.5 atm = (1.5 x 101325)Pa = 151987. 5 Pa

P_2 = 10 atm = (10 x 101325)Pa = 1013250 Pa

V_1 = 20 cm^3

V_2 = ?

$V_2 = P_1V_1/P_2$ = 151987.5 Pa x 20 cm^3/1013250 Pa = 3 cm^3

(c)

V_1 = 80 cm^3

V_2 = 50 cm^3

P_1 = 101325 Pa

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

P_2 = (101325 Pa x 80 cm^3)/50 cm^3 = 162120 Pa = 162.12 kPa

Solved problem 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,

i. Pressure and temperature
ii. Mass and temperature
iii. 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)

1. 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.
2. If the mass and temperature are held constant, the product of the pressure and volume will be almost constant for a real gas but exactly constant for ideal gas.
3. 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)

i. Boyle's law states that at constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure

ii. Charles law states 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 temperature, 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 a 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, $(\mathrm{PV})_{\mathrm{cor}} = \left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT}$

4.0 Summary

Gas laws are fundamental concepts in Chemical thermodynamics because they are useful in simplifying laws of thermodynamics and associated concept. The basic gas laws have been developed into equations including, Boyle, Charles,-Gay Lussac, Dalton, combined gas law and van der Waals equations. These laws rely on the effect of variation of parameters of thermodynamic significant.

5.0 Conclusion

Thermodynamics cannot be adequately resolved into meaningful models without considering the 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 cannot escape the students.

6.0 Tutor mark assignment

1. (a) List and state the gas laws that arises from the constancy of the following functions,

    i. The pressure and temperature are held constant
    ii. The mass and temperature are held constant
    iii. The mass and the pressure are held constant

(b) Write down the mathematical expressions for each of the gas law associated with the above and present expected graphs.

(c) Write and expression for ideal gas and van der Waals equations. Hence explain all the terms.

2. (a) Calculate the expected pressure exerted by a gas whose volume is 22.4 dm^3 at stp.

(b) What are the major differences between ideal gas and real gas. Hence what is the consequence of Van der Waals equation of state on the behavior of real gas, compared to ideal gas.

3.` (a) A sample of atmospheric air was found to contained 78 % N_2, 0.03 % CO_2, 16 % O_2, 1 % rare gases and 5 % gaseous impurities at stp. If 200 cm^3 of the air sample is analyzed, calculate the volume of the respective component of the air. Hence calculate the expected pressure 5 moles of the air will exert at stp.

(b) Use the kinetic theory to explain the consequences of forces of attraction and repulsion between gas molecules.

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UNIT 2: Intermolecular forces

1.0 Introduction

2.0 Objectives

3.0 Main content

- **3.1 Types of intermolecular forces**
- **3.2 The London forces**
- **3.3 Relative strength of inter and intra molecular forces**

4.0 Summary

5.0 Conclusion

6.0 Tutor mark assignment

7.0 References

1.0 Introduction

In molecules, two major forces of interaction can be identified. These are intramolecular forces and intermolecular forces. Intramolecular forces exist within molecules and influence their chemical properties while intermolecular forces exist within molecules and mediate interaction between molecules. Therefore, intermolecular forces affects the physical properties of molecules. They are weaker than intramolecular forces (i.e the bonding forces that keep molecules together). For example, water can exist as a liquid, solid (ice) and as a gas (steam). Experiment reveals that the bond angle, the dipole moment, the molecular shape and hydridization of the carbon are the same, irrespective of the physical state the water molecule assumed. These properties are controlled by intramolecular forces. However, the physical properties of water in each of these states differ significantly. The difference is attributed to intermolecular forces. Consequently, liquid water assumes the shape of the container but possess a definite volume, steam assumes the shape and volume of the container while ice has a definite shape and volume. Other effects of intermolecular forces are deviation of real gases from an ideal behavior, formation of condensed phases, molecular motion, melting and boiling point of some molecules.

2.0 Objectives

i. To know and understand the meaning of intermolecular forces and differentiate between inter and intra molecular forces.

ii. To be able to classify intermolecular forces based on different principles iii/ To understand the origin and the effect of dipole forces, dipole-dipole interaction and hydrogen bonding on molecules

i. To understand the origin and effect of ion-induced dipole force, ion-dipole forces and van der Waals forces on molecules

ii. To understand the different forms of London forces and their effects on molecules

iii. To know the relative strength of intra and inter molecular forces on molecules

3.0 Main text

3.1 Types of intermolecular forces

The major types of intermolecular forces that operate between molecules include the following;

i. Dispersion forces which operate as a London forces (named after Fritz London who first described these forces theoretically in 1930), as a weak intermolecular forces or as van der Waal's forces (named after the person who contributed to our understanding of non-ideal gas behaviour).

ii. Dipole-dipole interactions: Dipole-dipole is an electrostatic interaction existing between permanent dipoles in molecules. This interaction increases the force of attraction between molecules by reducing their potential energy. In dipole-dipole interaction, the positive end of one molecule will attract the negative end of the other molecule and influence its position. Therefore, dipole-dipole interaction is common in polar molecules. Hydrogen bonding is a special type of dipole-dipole interaction. However, some molecules are polar but due to their symmetry, the dipole moment cancels each other. Hence such molecules will not have permanent dipole moment. For example, CCl_4 and CO_2.

iii. Hydrogen bonds: This is a special case of dipole-dipole interaction that occurs when hydrogen atom is covalently bonded to an electronegative atom such as F, Cl, O, etc. In this case, the hydrogen will carry a partial positive charge while the electronegative element will carry a partial negative charge, leading to an electrostatic attraction between them. Hydrogen bonding has been found to influence properties of some compounds to a large extent. For example, the high boiling and melting point of water, compared to other hydride in similar groups, the solubility of ethanol in water compared to other alcohols.

Also, based on forces of attraction, intermolecular forces can be classified into the following three groups,

i. **Ion-induced dipole forces**: A charged ion, brought near a non-polar molecule can distort its electron cloud and induce a dipole moment. Therefore, ion-induced dipole interaction involves an ion and a non polar molecule interacting with each other.

ii. **Ion-dipole forces**: These involve ions and a polar molecule interacting such that the positive and negative groups come closer to each other. The difference between dipole-dipole interaction and ion-dipole interaction is that it involves interaction between ion and a dipole. This interaction is stronger than the one in dipole-dipole because it involves ions.

iii. **van der waals forces** (which include Keesom forces, Debye force and London dispersion forces): Van der Waals forces involve interaction between uncharged atoms or molecules. A Van der Waals force can influence the cohesion of condensed phases, physical adsorption of gases and universal force of attraction between macroscopic bodies

3.2 The London forces

The London force is also called induced dipole-induced dipole interaction. Its operates due to the non zero dipole moments in atoms or molecules. It is a dominant contributor to intermolecular forces. It originates from the non zero instantaneous dipole moments of all atoms and molecules. The inducement of the dipole (polarization) can come from the presence of polar molecule or by the repulsion of negatively charged electron clouds in non polar molecules. Since the London forces are caused by fluctuations of electron density in an electron cloud, the greater the number of electrons in an atom, the greater the effect of the London force. The London force is universal because all materials are polarizable and mediates in atom-atom interaction as well as macroscopic bodies in condensed systems.

Solved problem 1

Question 1

(a) Differentiate between inter molecular and intramolecular forces

(b) Highlight the effect of inter and intra molecular forces on the various physical states of water .

Solution

(a) Intramolecular forces exist within molecules and influence their chemical properties while intermolecular forces exist within molecules and mediate interaction between molecules.

Therefore, intermolecular forces affect the physical properties of molecules. They are weaker than intramolecular forces (I.e the bonding forces that keep molecules together).

(b) Water can exist as a liquid, solid (ice) and as a gas (steam). Experiment reveals that the bond angle, the dipole moment, the molecular shape and hydridization of the carbon are the same, irrespective of the physical state the water molecule assumed. These properties are controlled by intramolecular forces. However, the physical properties of water in each of these states differ significantly. The difference is attributed to intramolecular forces. Consequently, liquid water assumes the shape of the container but possess as a definite volume. Steam assumes the shape and volume of the container while ice has a definite shape and volume

Solved problem 2

(a) What is dipole-dipole interaction and its effect on the potential energy?

(b) Why is hydrogen bonding classified as dipole-dipole interaction?

(c) Explain why dipole-dipole interaction does occur in CCl_4 and CO_2.

Solution

(a) Dipole-dipole interactions is an electrostatic interaction existing between permanent dipoles in molecules. This interaction increases the force of attraction between molecules by reducing their potential energy.

(b) Hydrogen bonding is a special type of dipole-dipole interaction because the partial positive charge on hydrogen attracts the negative partial charge on the electronegative element that is bonded to hydrogen.

(c) CCl_4 and CO_2 are non polar and due to their symmetry, the dipole moment cancels each other. Hence they do not have permanent dipole moment and dipole-dipole interaction does not occur.

Solved problem 3

(a) Highlight the major features of the following intermolecular forces

  i. ion-induced dipole forces

ii. ion-dipole forces
iii. van der Waals forces

Solution

i. **Ion-induced dipole forces**: A charged ion, brought near a non-polar molecule can distort its electron cloud and induce dipole moment. Therefore, ion-induced dipole interaction involves an ion and a non polar molecule interacting with each other.

ii. **Ion-dipole forces**: These involve ions and a polar molecule interacting such that the positive and negative groups come closer to each other. The difference between dipole-dipole interaction and ion-dipole interaction is that it involve interaction between ion and a dipole. This interaction is stronger than the one in dipole-dipole because it involves ions.

iii. **van der Waals forces** (which include Keesom forces, Debye force and London dispersion force): Van der Waal forces involve interaction between uncharged atoms or molecules. This force can influence the cohesion of condensed phases, physical adsorption of gases and universal force of attraction between macroscopic bodies

3.3 Relative strength of inter and intra molecular forces

Intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds) are much weaker than intramolecular forces (covalent bonds, ionic bonds or metallic bonds). Dispersion forces are the weakest intermolecular forces (one hundredth-one thousandth the strength of a covalent bond), hydrogen bonds are the strongest of intermolecular forces (about one-tenth the strength of a covalent bond). Generally, the trend representing decreasing trend is dispersion forces < dipole-dipole interactions < hydrogen bonds Table 1 below, summarizes the relative strengths of the various forces.

Table 1: Relative strengths of intermolecular and intramolecular forces

B ond type	Dissociation energy (kcal/mol)
Ionic Lattice Energy	250–4000
Covalent Bond Energy	30–260
Hydrogen bonding	1–12 (about 5 in water)

Dipole–Dipole	0.5–2
London Dispersion Forces	<1 to 15 (estimated from the enthalpies of vaporization of hydrocarbons)

***Solved problem 4**

(a) London force is also called induced dipole-induced dipole interaction. Explain how it operates in atom or molecules with non zero dipole moments

(b) Give reasons why the London forces are said to be universal among all intermolecular forces

(c) Is intermolecular forces stronger than intra molecular forces?. Write an expression for the expected trend in the strength of intermolecular forces

(d) Complete the missing terms in the Table below

Bond type	**Dissociation energy (kcal/mol)**[9]
Ionic Lattice Energy	250–4000
	30–260
	1–12 (about 5 in water)
	0.5–2
	<1 to 15 (estimated from the enthalpies of vaporization of hydrocarbons)

Solution

(a) London forces originate from the non zero instantaneous dipole moments of all atoms and molecules. The inducement of the dipole (polarization) can come from the presence of polar molecule or by the repulsion of negatively charged electron clouds in non polar molecules. Since the London forces are caused by fluctuations of electron density in an electron cloud, the greater the number of electrons in an atom, the greater the effect of the London force.

(b) The London force is universal because all materials are polarizable and mediates in atom-atom interaction, macroscopic bodies in condensed systems.

(c) Intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds) are much weaker than intramolecular forces (covalent bonds, ionic bonds or metallic bonds). Dispersion forces are the weakest intermolecular force (one hundredth-one thousandth the strength of a covalent bond). Hydrogen bonds are the strongest intermolecular force (about one-tenth the strength of a covalent bond).

Generally, the trend representing decreasing trend is dispersion forces < dipole-dipole interactions < hydrogen bonds

(d)

Bond type	**Dissociation energy (kcal/mol)**[9]
Ionic Lattice Energy	250–4000
Covalent Bond Energy	30–260
Hydrogen bonding	1–12 (about 5 in water)
Dipole–Dipole	0.5–2
London Dispersion Forces	<1 to 15 (estimated from the enthalpies of vaporization of hydrocarbons)

4.0 Summary

Inter and intramolecular forces are the two major forces that determine the physical and chemical properties of molecules. Much researches have been carried out on intra molecular forces and molecular behaviour, especially, their stability. Little have been explored with respect to intermolecular forces compared to that of intramolecular forces. Nevertheless, the effect of intermolecular forces on some properties of molecules have been observed to be significant. Detailed study of intermolecular forces is beyond the scope of this course, however, the information provided reveals that intermolecular forces can influence some molecular properties to a large extent. For example melting point, macroscopic behaviour, solubility, etc

5.0 Conclusion

Intramolecular forces exist within molecules and influence their chemical properties while intermolecular forces exist within molecules and mediate interaction between molecules. He major intramolecular forces that operates in molecules are dispersion forces, hydrogen bonding and dipole –dipole interactions. However, based on force of attraction, intermolecular forces are classified into ion-induced dipole forces, ion-dipole forces and Van der Waals forces. Intermolecular forces can influence numerous physical properties of molecules and their relative strength vary.

6.0 Tutor mark assignment

1. Highlight the various forms of inter and intra molecular forces that is common in molecules.

2. What are the differences between inter and intra molecular forces and the relative strength of each of them.

3. With the aid of suitable equations, account for the forces responsible for the following

    i. Abnormal boiling point and freezing point of water compare to other hydrides in the same group

    ii High solubility of ethanol in water compared to other alcohol

4. What are the origin of London forces, Van der Waals force and induced-dipole forces?

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MODEL 1

UNIT 3: Basic concepts in thermodynamics

1.0 Introduction

Chemical thermodynamics is based on various technical terms which must be understood. Some of these terms have similar interpretations with their counterpart in classical chemistry while some are slightly modified to suit their applications in thermodynamics. In this section, basic thermodynamics terms are defined and explained so that the student can follow the successive modules in this course.

2.0 Objectives

(i) To know and understand what constitutes thermodynamic system, surrounding and boundary

(ii) To know and understand intensive and extensive properties of thermodynamics systems

(ii) To know what is thermodynamic state function and its major characteristics

(iii) To know the various ways of classifying thermodynamic processes

(iv) To understand the concept of reversible and irreversible processes

(v) To know the meaning of cyclic process in thermodynamics

(vi) To know thermodynamic definition of phase

3.0 Main content

3.1 Basic concepts in 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 surrounding 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 type of work that are associated with a chemical reaction are electrical and work of expansion. Chemical reactions can do work on their surroundings by driving an electric current through an external wire. Chemical reactions also do work on their surroundings when the volume of the system expands during the course of the reaction 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.

$$W = -Pdv \qquad 1$$

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 subsystems, 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, nor 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 dependent of the response of the system's property to the quantity of materials or matter in that system. Consequently, an extensive property of a system, thus define 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. E. g temperature, pressure, etc.

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 is a state function. Other examples of state function 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 a state function 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,

$$dy = \left(\frac{\partial y}{dz}\right)_x dz + \left(\frac{\partial y}{\partial x}\right)_z dx \qquad 2$$

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, $\frac{\partial^2 y}{\partial x \partial z} = \frac{\partial^2 y}{\partial z \partial x}$

3.1.4 Thermodynamic processes

Thermodynamic process is defined when there is an energetic changes 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. They include;

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 maintained by the atmospheric 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. This includes;

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 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 cannot be reversed by a very small change in some properties of the system.

3.1.6 Cyclic process

A cyclic process is a sequence of processes that leave 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 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 states 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) 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.

(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 and vice versa.

(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 1: First law of thermodynamics

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,

$$dU = \partial q + \partial W \qquad 3$$

where ∂q is the infinite quantity of heat absorbed. The ∂U is the infinite change in internal energy and ∂W is the work done. Equation 3 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 4,

$$\int_{U_1}^{U_2} \partial U = \int \partial q + \int \partial W = \Delta U = q + W \qquad 4$$

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.

2.0 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 grater 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 derived an expression for Joule-Thompson coefficient using exact differentiation approach and to know the significant 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,

$$F = PA \qquad 5$$

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

$$dW = Fdx \qquad 6$$

Substituting for F and dx in equation 6, we have,

$$dW = -PA\frac{dV}{A} = -PdV \qquad 7$$

Equation 7 can be simplified by integration, hence we have,

$$W = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1) \qquad 8$$

Returning to the mathematical expression of the first law, i.e, $\Delta U = \partial q + \partial W$, we can replace W with PdV and we have,

$$dU = \partial q + P\partial V \qquad 9$$

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 10.

$$U_2 - U_1 = q_P + + P(V_2 - V_1) \qquad 10$$

Rearrangement of equation 10 leads to equations 11 and 12

$$q_P = \quad U_2 - U_1 + P(V_2 - V_1) \qquad 11$$

$$q_P = \quad (U_2 + PV_2) - (U_1 + PV_1) \qquad 12$$

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 $(U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 = \Delta H$. 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 $U_2 - U_1 = q_v$, which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, $\Delta U = U_2 - U_1$

Solved problem 1

(a) From first principle, Show that thermodynamic work can be written in terms of pressure volume work.

(b) 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,

$$F = PA \qquad 5$$

The volume created as a results 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,

$$dW = Fdx \qquad 6$$

Substituting for F and dx in equation 6, we have,

$$\partial W = PA\frac{dV}{A} = P\partial V \qquad 7$$

Equation 7 can be simplified by integration, hence we have,

$$W = \int_{V_1}^{V_2} P\partial V = P(V_2 - V_1) \qquad 8$$

Returning to the mathematical expression of the first law, i.e, $\Delta U = dq + dW$, we can replace W with PdV and we have,

$$U = \partial q + P\partial V$$

(b) From the first law of thermodynamics, $U = \partial q + P\partial V$, therefore,

$$U_2 - U_1 = q_P + P(V_2 - V_1) \qquad 1$$

Rearrangement of equation 1 leads to equations 2 and 3

$$q_P = U_2 - U_1 + P(V_2 - V_1) \qquad 2$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1) \qquad 3$$

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, $U_2 + PV_2 = H_1$, $U_1 + PV_1 = H_1$, hence $(U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 = \Delta H$. 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 $U_2 - U_1 = q_v$, which translates to the statement that the heat absorbed at constant volume is equal to change in internal energy, $\Delta U = U_2 - U_1$

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, $0 = dq + PdV$ 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, dq = dw = PdV. From the ideal gas equation, PV = nRT or P = nRT/V .By substituting for P, the work done becomes,

$$dw = \frac{nRT}{V} dV \qquad 13$$

where n is the number of moles of the gas, R is the universal gas constant, Equation 13 can better be solved by integration over the appropriate limits as shown in equation 14,

$$w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRTln\left(\frac{V_2}{V_1}\right) = 2.303nRTlog\left(\frac{V_2}{V_1}\right) \qquad 14$$

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 14, we have,

$$w = 2.303nRTlog\left(\frac{P_1}{P_2}\right) = -2.303nRTlog\left(\frac{P_2}{P_1}\right) \qquad 15$$

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. 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, $(PV)_{cor} = \left(P + \frac{a}{V^2}\right)(V - b) = RT$. This gives, $P = \frac{RT}{V-b} - \frac{a}{V^2}$ and the work done is given as,

$$w = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2}\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)dV \qquad 16$$

$$= \int_{V_1}^{V_2}\frac{RT}{V-b}dV - \int_{V_1}^{V_2}\frac{a}{V^2}dV \qquad 17$$

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

$$W = RTln\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = 2.303RTlog\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \qquad 18$$

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,

$$W = PV = \frac{nRT}{P}.P = nRT \qquad 19$$

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 2 mol of an ideal gas change from 200 to 400 cm^3 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,

$0 = dq + PdV$ 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,

$$dw = \frac{nRT}{V} dV \qquad 1$$

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,

$$w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRTln\left(\frac{V_2}{V_1}\right) = 2.303nRTlog\left(\frac{V_2}{V_1}\right) \qquad 2$$

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,

$$w = 2.303nRTlog\left(\frac{P_1}{P_2}\right) = -2.303nRTlog\left(\frac{P_2}{P_1}\right) \qquad 3$$

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 $V_{cor} = V\text{-}b$. 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, $(\mathrm{PV})_{\mathrm{cor}} = \left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT}$. This gives, $\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V-b}} - \frac{\mathrm{a}}{\mathrm{V}^2}$ and the work done is given as,

$$w = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \left(\frac{\mathrm{RT}}{\mathrm{V-b}} - \frac{\mathrm{a}}{\mathrm{V}^2}\right) dV \qquad 4$$

$$= \int_{V_1}^{V_2} \frac{\mathrm{RT}}{\mathrm{V-b}} dV - \int_{V_1}^{V_2} \frac{\mathrm{a}}{\mathrm{V}^2} \mathrm{dV} \qquad 5$$

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

$$W = RTln\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = 2.303RTlog\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \qquad 6$$

(b) Given,

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

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

T = 298 K

N = 2 mol

$$w = 2.303nRTlog\left(\frac{V_2}{V_1}\right) = (2)(8.314J/K/mol)(298K)ln\left(\frac{0.4m^3}{0.2m^3}\right) = 3434.64\ \mathrm{J}$$

(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

$$w = 2.303nRTlog\left(\frac{V_2}{V_1}\right) = 2.303nRTlog\left(\frac{P_1}{P_2}\right)$$

Comparing the two equation, $\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{P_1}{P_2}\right)$, Therefore,

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(101325\ Pa)(0.2m^3)}{(0.4\ m^3)} = 50662.50\ Pa$$

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,

$$w = 2.303nRTlog\left(\frac{P_1}{P_2}\right)$$

That is ,

$$3434.64\ J = (2)(8.314\,J/mol/K)(298K)ln\left(\frac{101325\ \mathrm{Pa})}{P_2}\right)$$

$$\frac{3434.64\ J}{(2)(8.314\,J/mol/K)(298K)} = ln\left(\frac{101325\ \mathrm{Pa})}{P_2}\right)$$

$$\frac{3434.64\ J}{(2)(8.314\,J/mol/K)(298K)} = \ln(101325\ Pa) - ln(P_2)$$

$$ln(P_2) = ln(101325\ Pa) - \frac{3434.64\ J}{(2)(8.314\,J/mol/K)(298K)} = 50662.54\ Pa$$

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

$$C = \frac{dq}{dT} \qquad 20$$

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 stands 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,

$$C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \qquad 21$$

$$C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \qquad 22$$

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 23

$$q_P = dU + PdV \qquad 23$$

From equation 21, $C_P dT = q_p$ and from equation 22, $C_V dT = q_V$. Also from the ideal gas equation, PV = RT (for one mole of a gas), we have PdV = RdT. Hence subsisting for all this parameters into equation 23, we have,

$$C_P dT = C_V dT + RdT \qquad 24$$

Dividing the left and right hand sides of equation 24 by dT, gives equation 25

$$C_P = C_V + R \qquad 25$$

The implication of equation 25 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 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

$$C = \frac{dq}{dT} \qquad 1$$

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,

$$C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \qquad 2$$

$$C_V = \left(\frac{dq}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \qquad 3$$

(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 to the form given by equation 4

$$q_P = dU + PdV \qquad 4$$

From equation 2, $C_PdT = q_p$ and from equation 3, $C_VdT = q_V$. Also from the ideal gas equation, PV = RT (for one mole of a gas), we have PdV = RdT. Hence substtuting for all these parameters into equation 4, we have,

$$C_PdT = C_VdT + RdT \qquad 5$$

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

$$C_P = C_V + R \qquad 6$$

$$C_P - C_V = R \qquad 7$$

Equations 6 and 7 are for one mole but for n mole, the equation 7 becomes, $C_P - C_V = nR$

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 $\left(\frac{dH}{dT}\right)_P = 32.2$. However, $\left(\frac{dH}{dT}\right)_P = C_P$. Since, $C_P - C_V = nR$, then

$$C_V = C_P - nR = 32.2 - 3(8.314) = 7.258\,J/mol/K$$

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

$$C_V dT = -PdV \tag*{26}$$

From the ideal gas equation, PV = RT, indicating that P = RT/V. Substitution for P in equation 26 and rearrangement yields equation 27,

$$C_V dT = -\frac{RT}{V}.dV \ or \ C_V \frac{dT}{T} = -R\frac{dV}{V} \tag*{27}$$

The right hand side of equation 27 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,

$$C_V \int_{T_2}^{T_1} \frac{dT}{T} = R\int_{V_1}^{V_2} \frac{dV}{V} \tag*{28}$$

The result of the above integration is presented in equation 29,

$$C_V ln\left(\frac{T_2}{T_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \tag*{29}$$

The combine gas laws shows that $\frac{P_1.V_1}{T_{1.}} = \frac{P_2.V_2}{T_2}$. which implies that $\frac{T_2}{T_2} = \frac{P_2}{P_1}.\frac{V_2}{V_1}$. The step by step solution to equation 29 are presented in equations 30 to 37

$$C_V ln\left(\frac{P_2}{P_1}.\frac{V_2}{V_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \tag*{30}$$

$$C_V ln\left(\frac{P_2}{P_1}\right) + C_V ln\left(\frac{V_2}{V_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \tag*{31}$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) - C_V ln\left(\frac{V_2}{V_1}\right) \tag*{32}$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -(C_V + R)ln\left(\frac{V_2}{V_1}\right) \tag*{33}$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -C_P\ ln\left(\frac{V_2}{V_1}\right) \tag*{34}$$

$$ln\left(\frac{P_2}{P_1}\right) = \frac{C_P}{C_V} ln\left(\frac{V_1}{V_2}\right) \qquad 35$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}} \qquad 36$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\tau} \qquad 37$$

where $\tau = \frac{C_P}{C_V}$ = 5/3, (τ-1)/ τ = 2/3 , τ-1 = 2/3 τ =2/3 × 5/3 = 10/9

Solved problem 4

(a) Show that under adiabatic expansion of an ideal gas, the heat capacity at constant pressure (C_P) and at constant volume (C_V) are related to the pressure and volume in an exponential manner

(b) Calculate the ratio, $\frac{C_P}{C_V}$ for an ideal gas if the volume changes from 0.2 to 0.4 m^3 with a corresponding change in pressure from 101325 to 50663 Pa.

Solution

(a) Adiabatic process is a process that is carried out under constant heat transfer. 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

$$C_V dT = -PdV \qquad 1$$

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

$$C_V dT = -\frac{RT}{V}.dV \; or \; C_V \frac{dT}{T} = -R\frac{dV}{V} \qquad 2$$

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,

$$C_V \int_{T_2}^{T_1} \frac{dT}{T} = R\int_{V_1}^{V_2} \frac{dV}{V} \qquad 3$$

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

$$C_V ln\left(\frac{T_2}{T_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \qquad 4$$

The combined gas law shows that $\frac{P_1.V_1}{T_1.} = \frac{P_2.V_2}{T_2}$. which implies that $\frac{T_2}{T_2} = \frac{P_2}{P_1}.\frac{V_2}{V_1}$. The step by step solution to equation 4 are presented in equations 5 to 12

$$C_V ln\left(\frac{P_2}{P_1}.\frac{V_2}{V_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \qquad 5$$

$$C_V ln\left(\frac{P_2}{P_1}\right) + C_V ln\left(\frac{V_2}{V_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) \qquad 6$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -Rln\left(\frac{V_2}{V_1}\right) - C_V ln\left(\frac{V_2}{V_1}\right) \qquad 7$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -(C_V + R)ln\left(\frac{V_2}{V_1}\right) \qquad 8$$

$$C_V ln\left(\frac{P_2}{P_1}\right) = -C_P\ ln\left(\frac{V_2}{V_1}\right) \qquad 9$$

$$ln\left(\frac{P_2}{P_1}\right) = \frac{C_P}{C_V}\ ln\left(\frac{V_1}{V_2}\right) \qquad 10$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}} \qquad 11$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\tau} \qquad 12$$

where $\tau = \frac{C_P}{C_V}$. 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 m^3 with a corresponding changes in pressure from 101325 to 50663 Pa, the ratio, $\frac{C_P}{C_V}$, can be calculated using the equation,

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}}$$

$$ln\left(\frac{P_2}{P_1}\right) = \frac{C_P}{C_V}\ ln\left(\frac{V_1}{V_2}\right)$$

Therefore,

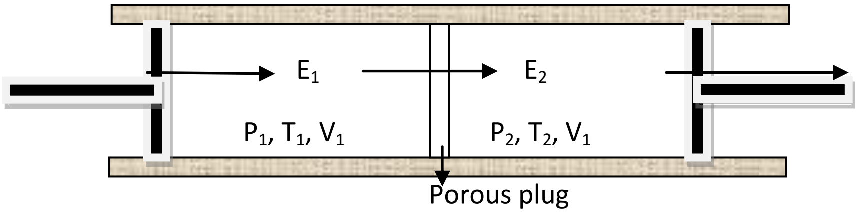
$$ln\left(\frac{50663\ Pa}{101325\ Pa}\right) = \frac{C_P}{C_V}\ ln\left(\frac{0.4\ m^3}{0.2\ m^3}\right)$$

$$ln\left(\frac{1}{2}\right) = \frac{C_P}{C_V}\ ln\left(\frac{2}{1}\right)$$

$$\frac{C_P}{C_V} = ln\left(\frac{1}{2}\right) - ln\left(\frac{2}{1}\right) = \ln\left(\frac{0.5}{2}\right) = -1.3863$$

3.1.7 Joule Thompson experiment

Joule-Thompson experiment attempts to measure the extent of deviation of the behaviour of a real gas from ideal gas. As shown below, the experiment is carried out in such a way that a piston moves from the left to the right hand side. Before the piston is 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 will start 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 will be zero and V_2 at the second chamber. The pressure and temperature at the second chamber ate 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 volumeV_1=$V_1$and volumeV_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 equals $P_1V_1 - P_2V_2$. 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,

$$U_2 - U_1 = P_1V_1 - P_2V_2 \qquad 38$$

Equation 38 simplifies to equation 39 upon re-arrangement,

$$U_2 + P_2V_2 = U_1 + P_1V_1 \qquad 39$$

From equation 39, 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,

$$\mu_{JT} = \lim_{\Delta P \to 0} \frac{T_2 - T_1}{P_2 - P_1} \qquad 40$$

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \qquad 41$$

Enthalpy is a state function and is a function of pressure and temperature, indicating that it can be written as, $H = f(P, T)$. As stated earlier, one of the major properties of a state function is that it gives exact differential. Consequently,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad 42$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -\left(\frac{\partial H}{\partial T}\right)_P dT \qquad 43$$

$$\mu_{JT} = \frac{\partial T}{\partial P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} = -\frac{1}{C_P}.\left(\frac{\partial H}{\partial P}\right)_T \qquad 44$$

Equation 44 gives various expressions for the μ_{JT}. However, in terms of measureable quantities, the Joule-Thompson coefficient can better be written as,

$$\mu_{JT} = \frac{\partial T}{\partial P} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} \qquad 45$$

where $T\left(\frac{\partial V}{\partial T}\right)_P - V = \left(\frac{\partial H}{\partial P}\right)$, 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, $\frac{\partial V}{\partial T} = \frac{V}{T}$, indicating that μ_{JT} would be equal to zero for ideal gas. Hence μ_{JT} is applicable to gases where there is molecular interaction. 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 the μ_{JT}.

The μ_{JT} for real gases can be developed using the Van der Waal's equation, $\left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT}$, which can be expanded and re-arranged to the form given below,

$$PV - bP + \frac{\mathrm{a}}{\mathrm{V}} - \frac{\mathrm{ab}}{\mathrm{V}^2} = \mathrm{RT} \qquad 46$$

From the gas law, we know that PV = RT, therefore, V = RT/P or 1/V = P/RT. Substituting for 1/V and neglecting the second order term of V^2 in equation 46, we have

$$PV - bP + \frac{\mathrm{aP}}{\mathrm{RT}} = \mathrm{RT} \text{ or } \mathrm{V} = \frac{\mathrm{RT}}{\mathrm{P}} - \frac{\mathrm{a}}{\mathrm{RT}} + \mathrm{b} \qquad 46$$

Therefore, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{\mathrm{R}}{\mathrm{P}} + \frac{\mathrm{a}}{\mathrm{RT}^2}$ and substituting for $\left(\frac{\partial V}{\partial T}\right)_P$ in equation 45, we have

$$\mu_{JT} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} = \frac{T\left(\frac{\mathrm{R}}{\mathrm{P}} + \frac{\mathrm{a}}{\mathrm{RT}^2}\right) - V}{C_P} \qquad 47$$

$$= \frac{T\left(\frac{\mathrm{R}}{\mathrm{P}} + \frac{\mathrm{a}}{\mathrm{RT}^2}\right) - \left(\frac{\mathrm{RT}}{\mathrm{P}} - \frac{\mathrm{a}}{\mathrm{RT}} + \mathrm{b}\right)}{C_P} = \frac{\frac{2\mathrm{a}}{\mathrm{RT}}}{C_P} - \mathrm{b} = \frac{2\mathrm{a}}{C_P\mathrm{RT}} - \mathrm{b} \qquad 48$$

From equation 48, we can examine what happens to the C_P at very low or high temperature. Consider that the temperature is very low, as T goes to 0, all terms with T in the denominator (equation 48) get very large. So the term associated with 2a/RT gets much larger than b. Hence we can neglect b at low temperature, which give us,

$$\mu_{JT} = \frac{2\mathrm{a}}{C_P\mathrm{RT}} \quad \text{(at very low temperature)} \qquad 49$$

In the above equation, μ_{JT} is positive, indicating cooling. On the other hand, when T is very large, all the terms related to T will become zero, hence,

$$\mu_{JT} = -\frac{\mathrm{b}}{C_P} \qquad \text{(At very high temperature)} \qquad 50$$

At very high temperature, μ_{JT} will be negative and points towards heating. An outstanding situation is obtained when μ_{JT} is set at zero, then equation 48 becomes $0 = \frac{2\mathrm{a}}{C_P\mathrm{RT}} - \mathrm{b}$, which can be solved for T. The value of T at this temperature is called inversion temperature, $\mathrm{T}_{\mathrm{Inversion}}$ and is given as,

$$T_{inversion} = \frac{2a}{bR} \times \frac{1}{C_P} \qquad 51$$

In summary, equation 49 shows that the Van der Waals constant, a is the only significant term at low temperature, equation 50 shows that the constant b is the only significant Van der Waal contributor at very high temperature. From equation 49 and 50, it is evident that the μ_{JT} must have a positive value at low temperature and a negative value at high temperature. Therefore, it must have an inversion temperature . At the inversion temperature (i.e the temperature at which μ_{JT} changes its sign to zero) the two constants (a and b) are significant but the pressure term is absent. At low temperature attractive forces dominate but at high temperature, forces of repulsion dominate.

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, $W = P_1V_1 - P_2V_2$,show that the process is isoenthalpy

(b) Define the term, Joule-Thompson coefficient. Hence show that $\mu_{JT} = \frac{\partial T}{\partial P} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P}$

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,

$$U_2 - U_1 = P_1V_1 - P_2V_2 \qquad 1$$

Equation 1 simplifies to equation 2 upon re-arrangement,

$$U_2 + P_2V_2 = U_1 + P_1V_1 \qquad 2$$

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

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

$$\mu_{JT} = \lim_{\Delta P \to 0} \frac{T_2 - T_1}{P_2 - P_1} \qquad 1$$

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \qquad 2$$

Enthalpy is a state function and is a function of pressure and temperature, indicating that it can be written as, $H = f(P,T)$. As stated earlier, one of the major properties of a state function is that it gives exact differentials. Consequently,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad 3$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -\left(\frac{\partial H}{\partial T}\right)_P dT \qquad 4$$

$$\mu_{JT} = \frac{\partial T}{\partial P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} = -\frac{1}{C_P}.\left(\frac{\partial H}{\partial P}\right)_T \qquad 5$$

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

$$\mu_{JT} = \frac{\partial T}{\partial P} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} \qquad 6$$

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 and is utilised 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 2: Thermochemistry

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1.0 Introduction

Thermochemistry is concerned with energy and heat accompanying a chemical reaction, physical transformations or both processes. During such changes, energy is either absorbed or given out. For example, the chemical reaction between hydrogen and oxygen gases during the formation of water is exothermic. However, the heat of vapourization of water is endothermic. Thermochemistry study these energy changes, particularly on the system's energy exchange with its surroundings. The heat that flows across the boundaries of a system (to the surrounding) undergoing a change is a fundamental property that characterizes the process. Thermochemistry offers a quantitative method of measuring the heat and enthalpy changes in a system during reaction or phase transition.

Thermochemistry has some basic advantages. First it can be used, along with other thermodynamic parameters to predict the spontaneity or feasibility of a given reaction. Based on the exchange *of heat between the system and the surrounding, chemical reactions can be classified into two, namely, exothermic and endothermic reactions. Endothermic reactions absorb heat from the surrounding while exothermic reactions release heat to the surrounding.

Thermochemistry offers a method of identifying exothermic or endothermic reaction through the bond energy of the reactant and that of the products. We shall see in this section that the heat of formation of an ionic compound can be estimated through the knowledge of reaction enthalpies of the various steps, into which the main reaction can be subdivided.

2,0 Objectives

i. To know and understand the various concepts and laws of thermochemistry

ii. To be able to understand the enthalpy changes associated with some chemical reactions such as neutralization, combustion, etc.

iii. To know and understand the concept of bond enthalpy, average bond enthalpy and their applications

iv. To understand the concept of lattice energy and their application

v. To know and apply the Bond Haber cycle in calculating the heat of formation or lattice energy of a compound

3.0 Main text

3.1 Thermochemical equations

In thermochemistry, some features of ordinary chemical reactions are modified. The following examples and highlights differentiate between ordinary chemical equation and thermochemical equations:

i. In thermochemical reactions, the physical state of the reactant and the products must be indicated. For example

Ordinary chemical equation: $2\ H_2 + O_2 \rightarrow 2\ H_2O$ 1

Thermochemical reaction: $2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}$ 2

ii. The heat change accompanying the reaction must be indicated. For example,

Ordinary Chemical equation: $2\ H_2 + O_2 \rightarrow 2\ H_2O$ 3

Thermochemical equation: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \quad \Delta H = -572\ \text{kJ}$ 4

In the above thermochemical equation, the enthalpy change during the reaction is -572 kJ/mol. The negative sign of the enthalpy change indicates that the reaction is exothermic. If the sign of the enthalpy change is positive (as in the equation below). It means that the reaction is endothermic:

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \quad \Delta H = 40.7 \text{ kJ} \qquad 5$$

In the first example, 572 kJ of heat is given off to the surrounding but in the second example, 40.7 kJ of heat is absorbed from the surrounding. The quantity 40.7 is known as the *enthalpy of vaporization* (often referred to as "heat of vaporization") of liquid water.

iii. If we multiply or divide the reactant by a factor, the product and the enthalpy change must also be multiplied by the same factor. For example, if we divide equation 4 by a factor of 2, we will have,

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ} \qquad 6$$

iv. The standard states as well as properties involved in the reaction must be represented. For example,

$$H_2O(l, 373 \text{ K}, 1 \text{ atm}) \rightarrow H_2O(g, 373 \text{ K}, 1 \text{ atm}) \quad \Delta H^0 = 40.7 \text{ kJ mol}^{-1} \qquad 7$$

The above equation shows that the standard state of water at 1 atm is the solid below 273 K, the liquid between 273 and 373 K and the gas above 373 K. A thermochemical quantity such as ΔH that refers to reactants and products in their standard states is denoted by ΔH^0. The standard state of a substance is the most stable state of that substance. For example, hydrogen gas, oxygen gas and graphite are the most stable states of hydrogen, oxygen and carbon and these are their respective standard states. If the reaction is taking place in solution, the concentration of the dissolved species must be specified. For example, the neutralization of water

$$H^+(aq, 1M, 298 \text{ K}, 1 \text{ atm}) + OH^-(aq, 1M, 298 \text{ K}, 1 \text{ atm}) \rightarrow H_2O(l, 373 \text{ K}, 1 \text{ atm}) \quad \Delta H = —56.9 \text{ kJ mol}^{-1}$$

Generally, since most thermochemical equations take place at standard conditions. specification of temperature, pressure is not necessary, provided. Thus for the above reaction, we can represent is as,

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta H^0 = —56.9 \text{ kJ mol}^{-1} \qquad 8$$

3.1.1 Standard enthalpies of reactions

As stated earlier, the enthalpy change for a chemical reaction is the difference between the enthalpy of the product and that of the reactant, thus,

$$\Delta H = H_{products} - H_{reactants} \qquad 9$$

If the reaction under consideration is for the formation of one mole of the compound from its elements in their standard states, the enthalpies of the elements can be set at zero and the heat of formation will become, $H_f° = \Sigma H_f°_{products} - \Sigma H_f°_{reactants} = \Delta H - 0$. For example, in the following reaction, $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $H_f° = \Sigma H_f°_{products} - \Sigma H_f°_{reactants} = -582 - 0 = -586$ kJ, which defines the *standard enthalpy of formation* of water at 298K.The value $H_f° = -586$ kJ tells us that when hydrogen and oxygen, at a pressure of 1 atm (respectively) and at 298 K react to form 1 mol of liquid water at 25°C and 1 atm pressure, 586 kJ will be given out to the surrounding. The negative sign indicates that the reaction is exothermic and that the enthalpy of the product is smaller than that of the reactants. Therefore, the standard enthalpy of formation of a compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states. In general, the *standard enthalpy change for a reaction* is given by $\Delta\Sigma H_f°_{products} - \Sigma H_f°_{reactants}$. where $\Delta\Sigma H_f°_{products}$ and $\Sigma H_f°_{reactants}$ are the sum of the standard enthalpies of formations of all products and reactants reapectively. This definition allows us to predict the enthalpy change of any reaction once the standard enthalpies of formation of the products and reactants are known.

3.1.2 Standard enthalpy of formation

Standard enthalpy of formation is the enthalpy change associated with the formation of one mole of the substance at standard temperature and pressure. In estimating the enthalpy of formation, the following information must be taken into consideration.

i. The thermochemical equation defining standard enthalpy of formation must be written in terms of one mole of the substance in question. For example,

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H° = -92.2 \text{ kJ} \qquad 10$$

The above equation shows that 1 mol of N_2 gas react with 2 mol of H_2 gas to form 2 mol of ammonia in an exothermic reaction, liberating 92.2 kJ of heat. This enthalpy change does not represent the standard enthalpy change since it is not the enthalpy change associated with the formation of 1 mol of ammonia. In order to write the thermochemical equation that shows the standard enthalpy change for the formation of ammonia, we divide the entire equation by a factor of 2, thus

$$\tfrac{1}{2} N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g) \quad \Delta H° = –46.1\ \text{kJ (per mole of } NH_3) \qquad 11$$

ii. The standard heat of formation of a compound should be considered based on the most stable form of the compound at 237 K and at 1 atmospheric pressure. This means for elements that exhibit allotropy, the most stable allotrope should be considered when defining standard enthalpy of formation of a compound involving such elements. For example, carbon can exist as diamond or graphite and the formation of CO_2 from each of these allotropes leads to the release of -393.5 and 395.8 kJ/mol of heat respectively (as shown in the equations below). However, since graphite is the most stable allotrope, the standard heat of formation of CO_2 will refer to the reaction involving graphite and not diamond

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H° \equiv H_f° = –393.5\ \text{kJ mol}^{-1} \qquad 12$$

$$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H° = –395.8\ \text{kJ mol}^{-1} \qquad 13$$

iii. If the product is not the stable one at 273 K, the physical state of the product must be indicated in the thermochemical equation representing standard enthalpy change. For example, water exists in gaseous and liquid states and the enthalpy changes for the two states are as shown in the equations below. However, the one associated with water in the aqueous phase is normally taken for standard enthalpy change.

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(aq)} \quad \Delta H° \equiv H_f° = –285.8\ \text{kJ mol}^{-1} \qquad 14$$

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H° = –241.8\ \text{kJ mol}^{-1} \qquad 15$$

It is significant to note that the differences in enthalpy value between the two states is -44 kJ/mol and this represents the heat of vaporization of water.

iv. The standard enthalpy change for the formation of most compounds are negative (i.e exothermic) but there are cases where the enthalpy change is positive. By convention, such endothermic process is expected to represent instability but there are some endothermic compounds that are stable.

v. Thermochemical equations representing the enthalpy change of the formation of some compounds may not be feasible. For example, direct reaction of graphite (carbon) with hydrogen gas, does not give methane as simplified in the equation below:

$$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad 16$$

vi. The standard enthalpy change associated with the formation of gaseous atom from the element is called heat of atomization. Heats of atomization are always positive and they are very useful in the calculation of bond energies.

vii. The standard enthalpy of formation of ions dissolved in water cannot be measured because this solution has several kinds of ions dissolved in it. Therefore, the general convention is to adopt a scale in which the enthalpy change of the $H^+_{(aq)}$ is defined as zero. Therefore ionic enthalpies are expressed such that $H_f°$ of the hydrogen ion at *unit activity* (1 M effective concentration) is defined as zero, as shown in the equation below,

$$½H_{2(g)} \rightarrow H^+_{(aq)} \quad \Delta H° \equiv H_f° = 0 \text{ kJ mol}^{-1} \qquad 17$$

Based on this, the enthalpy of formation of other ionic compounds can be calculated by combining it with the above equation. For example, in the formation of HCl, H_2 gas combine with Cl_2 gas as shown below:

$$½H_{2(g)} + ½Cl_{2(g)} \rightarrow HCl_{(aq)} \quad \Delta H° \equiv H_f° = -167 \text{ kJ mol} \qquad 18$$

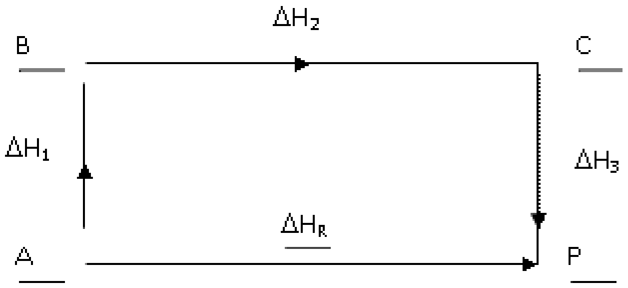
Since the enthalpy for the formation of $H^+_{(aq)}$ is zero, the enthalpy for the formation of HCl is -167 kJ/mol.

3.2 Laws of thermochemistry

Thermochemistry is based on the framework of two major laws, namely: Hess law and Laplace law. These laws are essential because they aid in thermochemical calculations.

The first thermochemical law was formulated by Hess in 1840. Germain Henri Hess (1802-1850) was a Swiss-born professor of chemistry at St. Petersburg, Russia. This principle, known as *Hess' law of independent heat summation* is a direct consequence of the enthalpy being a state function. Hess' law is one of the most powerful tools of chemistry. It allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from experimental data. ***Hess law states that the overall enthalpy of a chemical reaction is the sum of the enthalpies of the various steps into which the reaction can be subdivided***.

Let us consider a chemical reaction leading to the formation of a product C and the enthalpy of reaction is ΔH_R. If the different steps that bring about the product are A to B, B to C and C to P, characterised with enthalpies, ΔH_1, ΔH_2 and ΔH_3 . Then according to Hess law, $\Delta H_R = \Delta H_1 + \Delta H_2 + \Delta H_3$. This concept is demonstrated in the diagram shown below



3.3 Bond enthalpy

Chemical bonds hold compounds together. This maybe electrovalent or covalent. Most often, the reactants have their individual bonds associated with it. Therefore, before they can react, bonds have to be broken and before products formation, new bonds must be formed Bonds are broken in the reactants while new bonds are formed in the products. Bond enthalpy is the energy needed to break bond in gaseous molecules under standard condition. Due to some complications that may arise in using actual values of bond enthalpy, average bond enthalpies are often used. For example, water consists of two OH bonds and it has been found that the energy needed to break the first O-H bond is significantly higher than the energy needed to break the second O-H bond. Also, the energy needed to break OH bond in molecule such as ethanol is quite different from the energy needed to break the O-H bond in water and other molecules. Hence the use of average bond enthalpy is justified.

Let us consider the bond enthalpy associated with the breaking of H and O bonds in water and hydroxyl.

$$H_2O_{(g)} \quad \rightarrow \quad H_{(g)} \quad + \quad OH_{(g)} \quad \Delta H^0 \quad +502\ kJ/mol$$

$$OH_{(g)} \quad \rightarrow \quad H_{(g)} \quad + \quad O_{(g)} \quad \Delta H^0 \quad +427\ kJ/mol$$

$$\boldsymbol{H_2O_{(g)} \quad \rightarrow \quad H_{(g)} \ + \ H_{(g)} \ + \ O_{(g)} \quad \Delta H^0 \quad (502+427)\ kJ/mol \quad = 929\ kJ/mol}$$

Therefore, the average bond enthalpy for O-H is 929/2 = 464.50 kJ/mol. The average bond enthalpies and the corresponding bond lengths for some bonds are presented in the Table 2. All bond energies are obtained in the gaseous state so that the enthalpy change associated with the breaking and formation of intermolecular force can be eliminated.

Bond breaking is an exothermic process while the formation of new bond is an endothermic process. The amount of energy absorbed during the formation of bond is the same as the amount of energy liberated during the breaking of bond. This is the consequence of the second law of thermochemistry (i.e Laplace law), which states that the enthalpy change needed for the formation of a compound is the same as the enthalpy change (but with reverse sign) needed for the decomposition of the compound.

In the course of breaking bonds in the reactants and the formation of new bonds in the products the difference between the bond energies of the reactants and that of the products represents the enthalpy change of the reaction. That is,

$$H = \sum(bond\ breaking\ energies\ ) - \sum(bond\ forming\ energies)$$

Therefore, when $\sum(bond\ breaking\ energies\ ) > \sum(bond\ forming\ energies)$, the reaction is endothermic and when $\sum(bond\ breaking\ energies\ ) < \sum(bond\ frming\ energies)$, the reaction is exothermic. Bond breaking involves separation of atoms that were bonded in a molecule indicating that energy is required (i.e endothermic reaction). However bond forming involves bringing the atoms that are bonded by electrostatic attraction, hence energy is released.

Table 2: Average bond enthalpy and bond length for some bonds

Bond	Average bond enthalpy (kJ/mol)	Bond length (10^{-9} m)
H-H	436	0.074
C-C	347	0.154
C=C	612	0.134
C-H	413	0.108
O=O	498	0.121
O-H	464	0.096
C=O	746	0.120
Cl-Cl	243	0.199

Solved problem 1

Calculate the enthalpy change for the combustion of propane, which occurs according to the following equation,

$$C_3H_{8(g)} \quad + \quad 5O_{2(g)} \quad \rightarrow \quad 3CO_{2(g)} \quad + \quad 4H_2O_{(g)}$$

Given, $\Delta H_f^0\left(C_3H_{8(g)}\right) = -104.63\ kJ/mol,\ \Delta H_f^0\left(CO_{2(g)}\right) = -393.67\ kJ/mol,$ $\Delta H_f^0\left(4H_2O_{(l)}\right) = -287.20\ \ kJ/mol$

Solution

The standard enthalpy change of formation of an element in its most stable form is zero. There is no chemical change and so no enthalpy change when an element is formed from itself. Therefore $\Delta H_f^0\left(O_{2(g)}\right)$ is zero. Generally, the enthalpy change of the reaction is the difference between the enthalpy change of the product and that of the reactant. That is,

$$\Delta H^0_{reaction} \quad = \quad \sum \Delta H^0_{Product} \; - \; \sum \Delta H^0_{Reactant}$$

=[3(-393.67) + 4(-287.20)] – [-104.63] kJ/mol = (-1181.01- 1148.80) + 104.3

= -2225.51 kJ/mol

Solved problem 2

Given the following bond energies (in KJ/mol) ,calculate the heat of combustion of propene.

C=C = 613, C-C = 349, O=O = 496, O=C = 744, O-H = 464 and C-H = 452

Solution

The equation for the combustion is

$$CH_3CH = CH_2 \ + \ \frac{9}{2}O_2 \ \rightarrow \ 3CO_2 \ + \ 3H_2O$$

The change in enthalpy is given as,

$\Delta H = \sum(bond\ breaking\ energies\ ) - \sum(bond\ forming\ energies)$

Bond breaking energies are,

6C-H bonds = 6 x 456

C=C bond =1 x 613

4.5O=O bond = 4.5 x 498

$$\sum(bond\ breaking\ energies\ ) \ = 6(456) + 613 + 4.5(498) = 5590\ kJ/mol$$

Bond forming energies are

6C=O = 6 x 744 = 4464 kJ/mol

6O-H = 6 x 464 = 2784 kJ/mol

$$\sum(bond\ forming\ energies\ ) \ = 4464\ kJ/mol \ + 2784\ kJ/mol \ = 7248\ kJ/mol$$

$$\boldsymbol{\Delta H = (5590 - 7248) kJ/mol = \ -1658\ kJ/mol}$$

Solved problem 3

Given the following thermochemical equations,

$$S_{(s)} \ + \ \frac{3}{2}O_{2(g)} \ \ \rightarrow \ \ SO_{3(g)} \ \ \Delta H^{\theta} \ = \ -396\ kJ/mol$$

$$SO_{2(g)} \ + \ \frac{1}{2}O_2 \ \ \rightarrow \ \ SO_{3(g)} \ \ \Delta H^{\theta} \ = \ -99\ kJ/mol$$

Calculate the standard enthalpy change for the reaction, $S_{(s)} \ + \ O_{2(g)} \ \ \rightarrow \ \ SO_{2(g)}$

Solution

The second equation can be reversed and be added to the first equation as follows;

$SO_{3(g)} \rightarrow \ SO_{2(g)} \ + \ \ \frac{1}{2}O_{2(g)} \ \ \ \Delta H^{\theta} \ = \ +99\ kJ/mol$

$S_{(s)} \ + \ \frac{3}{2}O_{2(g)} \ \ \rightarrow \ \ SO_{3(g)} \ \ \Delta H^{\theta} \ = \ -396\ kJ/mol$

$$\boldsymbol{S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \quad \Delta H^{\theta} = (99 - 396) kJ/mol = -297\, kJ/mol}$$

Solved problem 4

Given the under listed thermochemical equations, calculate the standard enthalpy change for the reaction, $2C_{(s)} + 2H_{2(g)} \rightarrow C_2H_{4(g)}$

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^{\theta} = -395\, kJ/mol$ 1

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H^{\theta} = -287\, kJ/mol$ 2

$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H^{\theta} = -1416\, kJ/mol$ 3

Solution

The first step requires, reversing equation 3 and then multiplying equations 1 and 2 by a factor of 2. The three equations are then added together as follows,

$2C_{(s)} + \cancel{2O_{2(g)}} \rightarrow \cancel{2CO_{2(g)}} \quad \Delta H^{\theta} = -790\, kJ/mol$ 1

$2H_{2(g)} + \cancel{O_{2(g)}} \rightarrow 2\cancel{H_2O_{(g)}} \quad \Delta H^{\theta} = -574\, kJ/mol$ 2

$\cancel{2CO_{2(g)}} + \cancel{2H_2O_{(g)}} \rightarrow C_2H_{4(g)} + \cancel{3O_{2(g)}} \quad \Delta H^{\theta} = 1416\, kJ/mol$ 3

$$\boldsymbol{2C_{(s)} + 2H_{2(g)} \rightarrow C_2H_{4(g)} \quad \Delta H^{\theta} = (-790 - 574 + 1416) kJ/mol}$$
$$\boldsymbol{= 52\, kJ/mol}$$

Solved problem 5

Calculate the entropy change associated with the follow/ing reaction. Given that the entropy data for C_2H_4, H_2 and C_2H_6 are 219.56, 130.92 and 229.87 J/K/mol respectively. Based on the equation for the reaction, reconcile the expected direction of the entropy change with the calculated

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$

Solution

The entropy change for the reaction can be calculated using the following expression

$$\Delta S^0_{reaction} = \sum S^0_{Product} - \sum S^0_{Reactant}$$

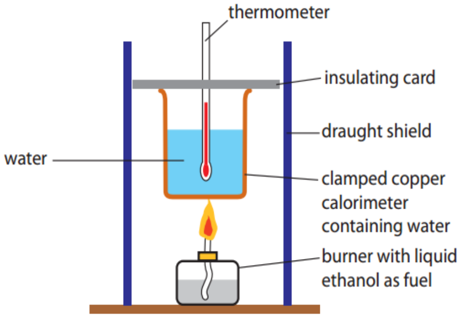
= (229.87) – (219.56+130.92) = -120.61 J/K/mol

From the equation for the reaction, two moles of gases reacted to give one mole of a gas. Therefore, there is a decreasing order hence the change in entropy is expected to be negative as obtained from the calculation.

Solved problem 6

(a) Define the term, enthalpy change of combustion

(b) The experimental set shown below was used to determine the heat of combustion of ethanol.



If the 0.46 g of ethanol was used to burn 200 g of water in the copper calorimeter and the resulting rise in temperature was 14 °C, calculate the heat of combustion of ethanol. (Heat capacity of water = 4.18)

Solution

(a) The heat produced when one mol of a substance is burn in excess oxygen is called the enthalpy change of combustion

(b) The heat of combustion of ethanol will be equivalent to the heat used in raising the temperature of the water by 1 mole of ethanol.

$$No\ of\ moles\ of\ ethanol\ used\ in\ the\ combustion = \frac{Mass\ of\ ethanol\ used}{Molar\ mss\ of\ ethanol}$$

$$= \frac{0.46}{46} = 0.01\ mol$$

$$Heat\ recieved\ by\ water = Mass\ of\ water\ x\ heat\ capacity\ x\ change\ in\ temperature$$

$$= -200 \times 4.18\ \times 14 = -11704\, J/mol/Deg$$

From the above, the combustion of 0.01 mol of ethanol produces -11704 J/mol/Deg of heat

therefore, the combustion of 1 mol of ethanol will produce (-11704/0.01) x 1 J/mol of heat =

1170400 J/mol of heat = -1170.40 kJ/mol. This is the heat of combustion of ethanol.

3.4 Born-Haber cycle

The Born-Haber cycle was developed by Max Born and Fritz Haber, who were German Chemists. The cycle analyse in detail enthalpies and lattice energy associated with the formation of ionic compounds from its constituent elements. Born-Haber cycle has found wider applications in calculating enthalpies and lattice energies of compounds that cannot be easily determined experimentally. Lattice energy is the enthalpy change involved in the formation of an ionic compounds from gaseous ions hence the process is exothermic. On the other hand, the endothermic process associated with the breaking of ionic compounds into gaseous ions is also equivalent to the lattice energy. Born-Haber cycle applies Hess law of thermochemistry to solve problems involving enthalpy change.

In order to analyse the Born-Haber cycle, let us consider the formation of $NaCl_{(s)}$. The steps involved are as follows,

i. Sodium atom in the solid state is changed into sodium atom in the gaseous state. The enthalpy change is called atomization energy, ΔH_{Atom}. i.e,

$$Na_{(s)} \quad \rightarrow \quad Na_{(g)} \quad \Delta H^0_{Atom} = +107\ kJ/mol$$

ii. Sodium ion in the gaseous state ionizes to lose one electron. The enthalpy change associated with the ionization is called ionization energy, ΔH_{IE},

$$Na_{(g)} \rightarrow Na^+_{(g)} + e^- \quad \Delta H^0_{IE} = +496\ kJ/mol$$

iii. Chlorine molecule dissociates into chlorine atoms in the gaseous state. The enthalpy change associated with this process is called dissociation energy, ΔH^0_D,

$$\frac{1}{2}Cl_{2(g)} \rightarrow \qquad Cl^-_{(g)}\Delta H^0_D = +243\ kJ/mol$$

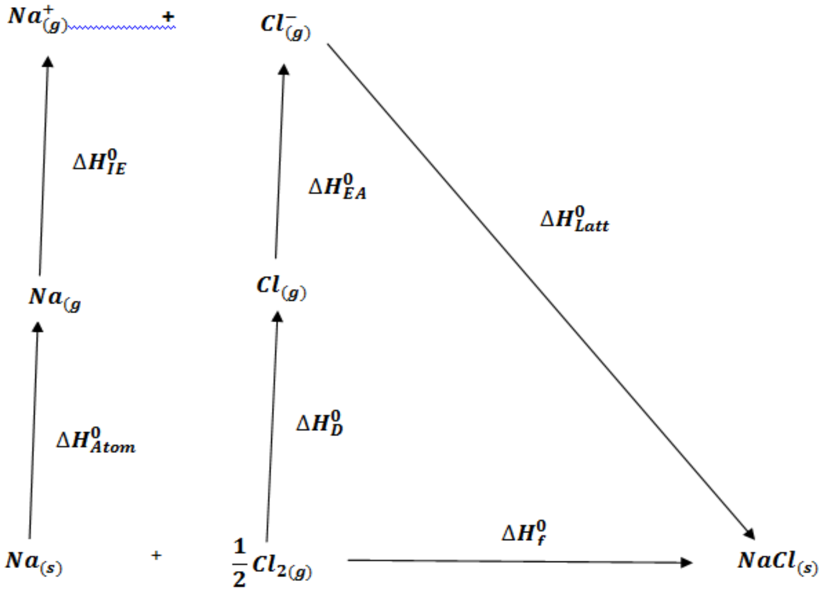
iv. The gaseous chlorine atom $Cl_{(g)}$in one electron from that was lost by sodium and become ionizes into chloride ion. The enthalpy change associated with the ionization is called electron affinity, ΔH^0_{EA}

$$Cl_{(g)} \ + \ e^- \ \rightarrow \ Cl^-_{(g)} \quad \Delta H^0_{EA} \ = \ -349\ kJ/mol$$

v. Sodium ion (formed in step ii) and chloride ion (formed in step iv) combine together to form one mole of NaCl. The enthalpy change associated with this combination is called lattice energy,

$$Na^+_{(g)} \ + \ Cl^-_{(g)} \ \rightarrow \ NaCl_{(s)} \quad \Delta H^0_{Latt} \ = ?$$

The entire steps involved in the formation of NaCl from its constituent elements can be represented in a cycle called Born-Haber cycle as shown in the figure below



From the above diagram , it is evident that the underlisted equation represent conservation principle, according to Hess law

$$\Delta H^0_f \ = \ \Delta H^0_{Atom} + \ \Delta H^0_{IE} \ + \ \Delta H^0_D \ + \ \Delta H^0_{EA} \ + \ \Delta H^0_{Latt}$$

Therefore, if the value of ΔH_f^0 is known, the ΔH_{Latt}^0 can easily be computed using the following equation,

$$\Delta H_{Latt}^0 = \Delta H_{Atom}^0 + \Delta H_{IE}^0 + \Delta H_D^0 + \Delta H_{EA}^0 - \Delta H_f^0$$

Substituting for the respective values of the enthalpy, the lattice energy becomes,

$$\Delta H_{Latt}^0 = 107 + \frac{1}{2}(243) + 496 - 349 + 411 = 786.5\ kJ/mol$$

Another method that can be used to calculate the lattice energy is the ionic model method. This method is based on the assumption that the crystal is formed from perfect spherical ions and that the only interaction is due to electrostatic force between the ions. For an ion pair, the energy needed to separate the ions depends on the sum of the ionic radii on the product of the ionic charges. Consequently, an increase in ionic charge will increase ionic attraction between them. In crystal, ions are surrounded by oppositely charge ions, hence the overall force of attraction between oppositely charged ion will overwhelm the force of repulsion between ions with same charge. The ionic model for calculating lattice energy can be expressed as follows,

$$\Delta H_{Latt}^0 = \frac{K_{mn}}{(R_{M^{n+}} + R_{X^{m-}})}$$

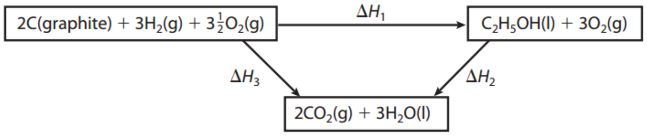
where K_{mn} is a constant, which depends on the geometry of the lattice, $R_{M^{n+}}\, and\ R_{X^{m-}}$ are ionic radius of the cation and anion respectively. In most cases, the ionic model has been found to yield theoretical values of lattice energy that are in good agreement with those calculated from Born-Haber cycle. Table 3 presents values of lattice energy calculated from Born-Haber cycle and ionic models for sodium and silver halides. The results generally show that the lattice energy obtained from experiment (i.e Born-Haber cycle) are relatively higher than those calculated from ionic model. The difference can be attributed to polarization effects. For example, the small positively charged sodium ion can distort the electron cloud of the large and squashy iodide ion leading to the introduction of some covalent character in the compound. Since the ionic model does not take the effect of polarization into consideration, values of lattice energy obtained from this model is expected to be relatively lower than those obtained from Born-Haber cycle, which is an experimental method. The differences between the two set of results seems to increase from Cl^- to I^- due to increasing strength of polarization. Generally, electronegativity of halides decreases from Cl^- to I^- which correspond to increase in covalent character, increase in ionic radii and expected increase in polarization.

Table 3: Lattice energy for some sodium and silver halides calculated from Born-Haber cycle and ionic model methods

Compound	Born-Haber	Ionic model	% Difference
NaCl	790	769	2.7
NaBr	754	732	2.9
NaI	705	682	3.3
AgCl	918	864	5.9
AgBr	905	830	8.3
AgI	892	808	9.4

Solved problem 7

Consider the reaction pathways shown in the diagram below,



If ΔH_1 = -277 kJ/mol and ΔH_2 = -1367 kJ/mol , calculate ΔH_3

(b) State the standard conditions for reporting experimental data obtained for enthalpy change

Solution

(a) From the law of conservation of energy, the enthalpy change in a complete cycle is zero, therefore,

$\Delta H_1 + \Delta H_2 - \Delta H_3 = 0$ consequently, $\Delta H_3 = (\Delta H_1 + \Delta H_2) = (-277 - 1367) = -1644$ kJ/mol

(b) The standard conditions for enthalpy changes are:

i a temperature of 298 K or 25 °C

ii. a pressure of 100 kPa

iii. Concentration of 1 mol dm^3 for all solutions

iv, all substances in their standard states.

4.0 Summary

Thermochemistry studies the enthalpy change accompanying chemical reactions. It is based on two major laws. These laws can also be seen as extension of the first law of thermodynamics. The first law reveals that the total changes in enthalpies for a complete cycle is zero while the second law reveals that the heat of formation is the same as the heat of decomposition.

5.0 Conclusion

The study of thermochemistry is essential in identifying and solving some problems in thermodynamics. It has a wider application ranging from the calculation of enthalpy change to prediction of other parameters (such as heat of formation, etc).

6.0 Tutor mark assignment

1. What is thermochemistry? Hence differentiate between thermochemistry and thermodynamics

2. What is the advantages and disadvantages of using Born harber cycle to estimate the heat of formation of a compound?

3. State the basic thermochemical laws and list the features of thermochemical equations (Give suitable examples for each)

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MODEL 2

UNIT 3: The Second law of thermodynamics

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 cannot 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 cannot 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 cannot 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. 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 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, $dS \geq \frac{\delta q}{T}$, 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,

$$\frac{dq}{T} = \frac{dU}{T} + \frac{PdV}{T} = \frac{C_V dT}{T} + RT\frac{dV}{TV} \qquad 70$$

Simplification of equation 70 gives equation 71 and upon integration, equation 72 is obtained

$$dS = \frac{C_V dT}{T} + R\frac{dV}{V} \qquad 71$$

$$\int_{S_1}^{S_2} dS = C_V\int_{T_1}^{T_2}\frac{dT}{T} + R\int_{V_1}^{V_2}\frac{dV}{V} \qquad 72$$

The solution of equation 72 can be written as,

$$\Delta S = C_V[lnT]_{T_1}^{T_2} + R[lnV]_{V_1}^{V_2} \qquad 73$$

Hence

$$\Delta S = C_V ln\left(\frac{T_2}{T_1}\right) + Rln\left(\frac{V_2}{V_1}\right) \qquad 74$$

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 74 using this expression, we have,

$$\Delta S = C_V ln\left(\frac{P_2}{P_1}\right) + C_V ln\left(\frac{V_2}{V_1}\right) + Rln\left(\frac{V_2}{V_1}\right) \qquad 75$$

$$\Delta S = C_V ln\left(\frac{P_2}{P_1}\right) + (C_V + R)ln\left(\frac{V_2}{V_1}\right) \qquad 76$$

$$\Delta S = C_V ln\left(\frac{P_2}{P_1}\right) + C_P ln\left(\frac{V_2}{V_1}\right) \qquad 77$$

Equations 74 to 77 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 $T_2 = T_1$, $\Delta S = Rln\left(\frac{V_2}{V_1}\right)$

ii. Isobaric change: i.e $P_2 = P_1$ and $\Delta S = C_V ln\left(\frac{V_2}{V_1}\right)$

iii. Isochoric change: i.e $V_2 = V_1$ and $\Delta S = C_V ln\left(\frac{P_2}{P_1}\right)$ or $\Delta S = C_V ln\left(\frac{T_2}{T_1}\right)$

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 m^3 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,

$$\frac{dq}{T} = \frac{dU}{T} + \frac{PdV}{T} = \frac{C_V dT}{T} + RT\frac{dV}{TV} \qquad 1$$

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

$$dS = \frac{C_V dT}{T} + R\frac{dV}{V} \qquad 2$$

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dV}{V} \qquad 3$$

The solution of equation 3 can be written as,

$$\Delta S = C_V [lnT]_{T_1}^{T_2} + R[lnV]_{V_1}^{V_2} \qquad 4$$

Hence

$$\Delta S = C_V ln\left(\frac{T_2}{T_1}\right) + Rln\left(\frac{V_2}{V_1}\right) \qquad 5$$

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,

$$\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right) \ + \ C_V ln\left(\frac{V_2}{V_1}\right) \ \ + \ \ Rln\left(\frac{V_2}{V_1}\right) \qquad 6$$

$$\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right) \ \ + (C_V + \ R)ln\left(\frac{V_2}{V_1}\right) \qquad 7$$

$$\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right) \ + \ \ C_P ln\left(\frac{V_2}{V_1}\right) \qquad 8$$

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 $T_2 = T_1$, $\Delta S \ = \ Rln\left(\frac{V_2}{V_1}\right)$

Isobaric change: i.e $P_2 = P_1$ and $\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right)$

Isochoric change: i.e $V_2 = V_1$ and $\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right)$ or $\Delta S \ = \ C_V ln\left(\frac{T_2}{T_1}\right)$

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

$$\Delta S \ = \ Rln\left(\frac{V_2}{V_1}\right) = (8.314\, Jmol^{-1}K^{-1})ln\left(\frac{0.4\ m^3}{0.2\ m^3}\right) = 5.7628\, Jmol^{-1}K^{-1}$$

(d) For isobaric change, $\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right)$, therefore,

$$C_V \ = \frac{\Delta S}{ln\left(\frac{P_2}{P_1}\right)} \ = \ \frac{8.0\, Jmol^{-1}K^{-1}}{ln\left(\frac{101325\ Pa}{50662.50\ \mathrm{Pa}}\right)} = 11.5416 \ Jmol^{-1}K^{-1}$$

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

$$\Delta S \ = \ C_V ln\left(\frac{P_2}{P_1}\right) \ = \ C_V ln\left(\frac{T_2}{T_1}\right)$$

Since ΔS and C_V are known, then,

$$ln\left(\frac{T_2}{T_1}\right) \ = \frac{\Delta S}{C_V}$$

$$\frac{T_2}{T_1} = \exp\left(\frac{\Delta S}{C_V}\right)$$

$$T_2 \ = \ T_1 \exp\left(\frac{\Delta S}{C_V}\right) \ = (298\ K) \exp\left(\frac{8.0\, Jmol^{-1}K^{-1}}{11.5416\ \ Jmol^{-1}K^{-1}}\right) = \ \mathbf{501.17\, K}$$

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 $\Delta S = Rln\left(\frac{V_2}{V_1}\right)$ and the heat absorbed by n mole of a gas will be given by multiplying the entropy with T. Thus $q_2 = nRT_2 ln\left(\frac{V_2}{V_1}\right)$ is the heat absorbed at higher temperature. Therefore for reversible isothermal expansion in the Carnot cycle, $q_2 = nRT_2 ln\left(\frac{V_2}{V_1}\right) > 0$

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 $q_1 = nRT_1 ln\left(\frac{V_4}{V_3}\right) < 0$

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 $\in = \frac{w}{q_2}$. 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,

$$\in = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2} \tag{78}$$

Recall that heat absorbed or work done during isothermal expansion of an ideal gas is given as $W = nRTln\left(\frac{V_2}{V_1}\right)$, 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 $q_2 = nRT_2ln\left(\frac{V_2}{V_1}\right)$ while the heat given off during the fourth stage (isothermal compression) $q_1 = nRT_1ln\left(\frac{V_4}{V_3}\right)$. Substituting for q_2 and q_1 in equation 78, yields equation 79

$$\in = \frac{nRT_2ln\left(\frac{V_2}{V_1}\right) - nRT_1ln\left(\frac{V_4}{V_3}\right)}{nRT_2ln\left(\frac{V_2}{V_1}\right)} \tag{79}$$

$$\in = 1 - \frac{nRT_1ln\left(\frac{V_4}{3}\right)}{nRT_2ln\left(\frac{V_2}{V_1}\right)} \tag{80}$$

From Poison equation, which states that $T_2V_1^{k-1} = T_1V_4^{k-1}$ and that $T_2V_2^{k-1} = T_1V_3^{k-1}$, it follows that ($V_4/V_3$) = ($V_2/V_1$ hence equation 80 becomes,

$$\in = 1 - \frac{nRT_2ln\left(\frac{V_2}{V_1}\right)}{nRT_2ln\left(\frac{V_2}{V_1}\right)} \tag{81}$$

Hence,

$$\in = 1 - \frac{T_1}{T_2} = \frac{T_2 - T_1}{T_2} \tag{82}$$

Equation 82 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,

$$1 - \frac{T_1}{T_2} = 1 + \frac{q_1}{q_2} \tag{83}$$

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1} \; or \; \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \tag{84}$$

From equation 84, it can be seen that the sum of the quantity q/T for a Carnot cycle is zero. That is $\sum \frac{q}{T} = 0$. The quantity, dq/T is defined as the entropy. Therefore, it also follows from equation 84 that $\oint dS = 0$.If we follow a path, A to B (in state 1) and B to A (in state 2), the entropy change can be expressed as,

$$\oint dS = \int_A^B dS + \int_B^A dS = 0 \tag{85}$$

$$\int_A^B dS - \int_A^B dS = 0 \qquad 86$$

$$\int_A^B dS = \int_A^B dS \qquad 87$$

From the above, entropy is seen as a state function that does not depend on the path taken. Therefore, the change of the entropy between any two equilibrium states is independent of the path connecting those states.

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,

$$dq = dU + PdV$$

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

(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 $\Delta S = Rln\left(\frac{V_2}{V_1}\right)$ and the heat absorbed by n mol of a gas will be given by multiplying the entropy with T. Thus $q_2 = nRT_2 ln\left(\frac{V_2}{V_1}\right)$ is the heat absorbed at higher temperature. Therefore for reversible isothermal expansion in the Carnot cycle, $q_2 = nRT_2 ln\left(\frac{V_2}{V_1}\right) > 0$

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 $q_1 = nRT_1 ln\left(\frac{V_4}{V_3}\right) < 0$

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, $\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$, 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 $\varepsilon = w/q_2$. 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,

$$\in = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2} \qquad 1$$

Heat absorbed or work done during isothermal expansion of an ideal gas is given as $W = nRTln\left(\frac{V_2}{V_1}\right)$, 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 $q_2 = nRT_2 ln\left(\frac{V_2}{V_1}\right)$ while the heat given off during the fourth stage (isothermal compression) $q_1 = nRT_1 ln\left(\frac{V_4}{V_3}\right)$. Substituting for q$_2$ and q$_1$ in equation 1, yields equation 2

$$\in = \frac{nRT_2 ln\left(\frac{V_2}{V_1}\right) - nRT_1 ln\left(\frac{V_4}{V_3}\right)}{nRT_2 ln\left(\frac{V_2}{V_1}\right)} \qquad 2$$

$$\in = 1 - \frac{nRT_1 ln\left(\frac{V_4}{3}\right)}{nRT_2 ln\left(\frac{V_2}{V_1}\right)} \qquad 3$$

From Poison equation, which states that $T_2V_1^{k-1} = T_1V_4^{k-1}$ and that $T_2V_2^{k-1} = T_1V_3^{k-1}$, it follows that ($V_4/V_3$) = ($V_2/V_1$ hence equation 3 becomes,

$$\in = 1 - \frac{nRT_2 ln\left(\frac{V_2}{V_1}\right)}{nRT_2 ln\left(\frac{V_2}{V_1}\right)} \qquad 4$$

Hence,

$$\in = 1 - \frac{T_1}{T_2} = \frac{T_2 - T_1}{T_2} \qquad 5$$

(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,

$$1 - \frac{T_1}{T_2} = 1 + \frac{q_1}{q_2} \qquad 6$$

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1} \; or \; \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \qquad 7$$

(c) From equation 7, it can be seen that the sum of the quantity q/T for a Carnot cycle is zero. That is $\sum\frac{q}{T} = 0$. The quantity, dq/T is defined as the entropy. Therefore, $\oint dS = 0$, indicating that 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,

$$\in = 1 - \frac{T_1}{T_2} = \frac{T_2 - T_1}{T_2} = \frac{(900 - 300)K}{900\ K} = 0.6666$$

Therefore the efficiency of the cycle is 66. 67 %

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

$$0.6666 = \frac{400 + q_1}{400}$$

$$400 + q_1 = 400 \times 0.6666$$

$$q_1 = 400 \times 0.6666 - 400 = -133.33\, J$$

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,

$$Free\ energy\ change = \Delta H - T\Delta S \qquad 88$$

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

$$Free\ energy\ change = \Delta U - T\Delta S \qquad 89$$

At constant volume, the free energy is called Helmoltz 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.

Solved problem 4

(a) Consider the following reaction,

$$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$$

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, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. Therefore,

$\Delta G^0 = 58220\,J - 298\,K(176\,J/K)$ = 5772 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, $\Delta G^0 - RTlnk_{eq}$. Therefore,

$$lnk_{eq} = \frac{-\Delta G^0}{RT}$$

$$k_{eq} = Exp\left(\frac{-\Delta G^0}{RT}\right) = Exp\left(\frac{-5772\,J/mol}{(8.314\,Jmol^{-1}K^{-1} \times 300K}\right) = 0.9885$$

(c) From the equation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$, when $\Delta G^0 = 0$, then $\Delta H^0 = T\Delta S^0$, and

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{58220\,J}{176\,J/K} = 330.80\,K$$

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, $\geq \frac{\delta q}{T}$. 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, $\Delta S = Rln\left(\frac{V_2}{V_1}\right)$, $\Delta S = C_V ln\left(\frac{P_2}{P_1}\right)$ and $\Delta S = C_V ln\left(\frac{P_2}{P_1}\right) = C_V ln\left(\frac{T_2}{T_1}\right)$ 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, $\in = 1 - \frac{T_1}{T_2} = 1 + \frac{q_1}{q_2}$

ix. The free energy changes at constant pressure and at constant volume are $\Delta G = \Delta H - T\Delta S$ and $\Delta A = \Delta U - T\Delta S$

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, them entropy data are often used in combination with other thermodynamic parameters.

6.0 Tutor mark assignment

1. Derive an expression to show that the standard Gibb 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 3

UNIT 1: The Third law of thermodynamics

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

$$\Delta S = S - S_o = k_B ln\Omega$$

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 first 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, $\Delta S = S - S_o = k_B ln\Omega$ 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 $\Omega = 1$, hence $S = S - S_o = k_B ln 1 = 0$.

Therefore, the difference is zero indicating that $\Delta S = S - S_o = 0$ or $\Delta S = S - 0 = 0$ and S = 0.

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

$$\Delta S = \frac{dQ}{T}$$

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

$$dQ = C(X,T)dT$$

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 the above equation is divided by T, we have

$$\Delta S = \frac{C(X,T)dT}{T}$$

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

$$S(T,X) = S(T_0,X) + \int_{T_0}^{T} \frac{C(X,T)dT}{T}$$

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

$$S(T,X) = \int_{T_0}^{T} \frac{C(X,T)dT}{T}$$

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

$$\mathbf{S=2.303\ C_p \log T}$$

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.

Limitations of the third law of thermodynamics

i. Glassy solids even at 0 ^{o}K has entropy greater than zero.

ii. Solids having mixtures of isotopes do not have zero entropy at 0 ^oK. For instance, entropy of solid chlorine is not zero at 0^oK.

iii. Crystals of CO, N_2O, NO, H_2O, etc. do not have perfect order even at 0 ^oK thus their entropy is not equal to zero.

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 given system consists of 1 cm^3 matter with a mass of 1g, equivalent to 20 g/mol. If the system consist of 3 x 10^{23} identical atoms at 0 K and one atom absorb a photon of wavelength of 1 cm. Calculate

(a) The entropy change for the system

(b) The energy change of the system due to absorption of one mole

(c) The expected rise in the temperature of the system

Solution

Since system is at 0 K, then it is in its ground state and the atom is unique and the permutation of one unique atom among the 3 x 10^{23} gives N = 3 x 10^{23}. Therefore, since $k_B = 1.38 \times 10^{-23}$ JK^{-1}, then

(a) The entropy change for the system is

$$\Delta S = \frac{dQ}{T} = S - S_o = k_B ln\omega$$

$$= 1.38 \times 10^{23}\, JK^{-1} ln(3.0 \times 10^{-23}) = 7.46 \times 10^{-22}\, JK^{-1}$$

(b) The energy change will be given as

$$dQ = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} J.s \times 3.0\ 10^{8} m/s}{0.01\ m} = 2 \times 10^{-23}\, J$$

(c) The rise in temperature will be given as

$$T = \frac{Energy}{\Delta S} = \frac{2 \times 10^{-23}\, J}{7.46 \times 10^{-22}\, JK^{-1}} = 2.68 \times 10^{-22}\, K$$

Therefore the average temperature of the system over the range from $0 < S < 7.46 \times 10^{-23}$ J/K is $2.68 \times 10^{-22}\ K$. Although a single atom absorbs the photon it is the temperature and entropy changes that characterize the entire system

Solved problem 2

(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

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

(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^oK has entropy greater than zero.

ii. Solids having mixtures of isotopes do not have zero entropy at $0\ ^oK$. For instance, entropy of solid chlorine is not zero at 0^oK.

iii. Crystals of CO, N_2O, NO, H_2O, etc. do not have perfect order even at $0\ ^oK$ 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 and conclusions

i. The Third law of thermodynamics provide information on the calculation of absolute entropy of a system.

ii. **T**he 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, $S=2.303\ C_p \log T$

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MODEL 3

UNIT 2: Thermodynamic potentials

1.0 Introduction
2.0 Objectives
3.0 Main text
  3.1 Derivation of equations for thermodynamic potentials
    3.1.1 Total differentiation of internal energy, U
    3.1.2 Total differentiation of enthalpy, H
    3.1.3 Total differential of Helmholtz energy, A
    3.1.4 Total differential of Gibbs free energy, G
4.0 Summary
5.0 Conclusions
6.0 Tutor mark assignment
7.0 References

1.0 Introductions

Thermodynamic potentials include enthalpy, internal energy, Gibbs free energy and Helmoltz work function. These variables are state functions indicating that they give exact differentials and that mathematical manipulation of their differentials can give thermodynamic expressions for several variables such as heat capacity, pressure, surface work, etc.

It should be noted that a state of a thermodynamic system is defined by specifying a minimum number of state functions, which are the independent variables and also the dependent variables. A dependent variable is a function of independent variables and the total differential of a dependent variable will express an infinitesimal change of the variable in terms of the infinitesimal changes of the independent variables. An example of this type of problem and solution was presented during the derivation of an expression of the Joule-Thompson experiment. We shall use this approach to obtain useful expressions for the basic thermodynamic potentials.

2.0 Objectives

(i) To understand the concept of thermodynamic potentials and identify the fundamental potentials

(ii) To derive equations for the various thermodynamic potentials

(iii) To know the equation for total derivation of internal energy

(iv) To know the equation for total derivation of enthalpy

(v) To know the equation for total derivation of Helmholtz work function

(vi) To know the equation for total derivation of Gibbs free enrgy

3.0 Main text

3.1 Derivation of equations for thermodynamic potentials

3.1.1 Total differentiation of internal energy, U.

From the first law of thermodynamics, the internal energy of a system can be written as follows

$$dU = dq + dw \qquad 90$$

Since dq = Tds and if the work done is expansion work (as it is in most thermodynamic cases), then dw = -PdV and the above equation becomes,

$$dU = TdS - PdV \qquad 91$$

Therefore we state that for a close system, in which an expansion work is done, the internal energy is a function of two non dependent variables, namely, S and V. Hence we can state that U = f(S,V) and operation of the condition of exact differential gives,

$$dU = \left(\frac{\partial U}{\partial S}\right)_v dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad 92$$

Comparing equations 91 with 92 it can be shown that $\left(\frac{\partial U}{\partial S}\right)_v dS = TdS$, hence, $\left(\frac{\partial U}{\partial S}\right)_v = T$ and that $\left(\frac{\partial U}{\partial V}\right)_S dV = -PdV$, indicating that $\left(\frac{\partial U}{\partial V}\right)_S = -P$

3.1.2 Total differentiation of enthalpy, H

Enthalpy is a state function obtained at constant pressure and can be written as H = U + PV hence the differential of enthalpy will be given as $dH = dU + PdV + VdP$ However, $dU = TdS - PdV$, which yields the following equation, upon substitution,

$$dH = TdS - PdV + PdV + VdP \qquad 93$$

Hence,

$$dH = TdS + VdP \qquad 94$$

The above expression indicates that enthalpy can be expressed as a function of two independent variables, that is, H = f(S,P). Applying the condition of exact differential, we have,

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \qquad 95$$

Comparing equation 6 with 7, we have, $\left(\frac{\partial H}{\partial S}\right)_P dS = TdS$ and $\left(\frac{\partial H}{\partial P}\right)_S dP = VdP$. Hence, $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$

3.1.3 Total differential of Helmholtz energy, A

The thermodynamic definition of A is that A = U –TS, whose differential is dA = dU – TdS – SdT and by substituting for dU, we have, $dA = TdS - PdV - TdS - SdT$. Hence,

$$dA = -PdV - SdT \qquad 96$$

Equation 8 reveals that A is a function of V and T which are the independent variables that can be used deriving the exact differential parameters for A as follows,

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \qquad 97$$

Comparing equation 8 with 9 we have $\left(\frac{\partial A}{\partial V}\right)_T = -P$ and $\left(\frac{\partial A}{\partial T}\right)_V = -S$

The above derivation gives thermodynamic definition of entropy and another definition of pressure

3.1.4 Total differential of Gibb free energy, G

Classical definition of G is G = H –TS (i.e, dG = dH –TdS –SdT) but H = U + PV (or dH = dU + PdV +VdP) and dU = TdS –PdV. Combining these variables, we have,

$$dG = dH - TdS - SdT \qquad 98$$

$$dG = dU + PdV + VdP - TdS - SdT \qquad 99$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT \qquad 100$$

$$dG = VdP - SdT \qquad 101$$

Equation 13 clearly reveals that G = f(P,T), hence,

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \qquad 102$$

Comparison of equation 13 with 14 gives the following relations: $\left(\frac{\partial G}{\partial P}\right)_T dP = VdP$ and $\left(\frac{\partial G}{\partial T}\right)_P dT$ = SdT. Therefore, $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$. Hence through total differentiation of G, we have obtained another definition of V and S.

4.0 Summary

The following thermodynamic definitions of T, P, V and S are obtained from total differentiations of thermodynamic potentials,

(i) U: $\left(\frac{\partial U}{\partial S}\right)_v = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$

(ii) H: $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$

(iii) A: $\left(\frac{\partial A}{\partial V}\right)_T = -P$ and $\left(\frac{\partial A}{\partial T}\right)_V = -S$

(iv) G: $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$

5.0 Conclusions

Thermodynamic potentials include enthalpy, internal energy, Gibbs free energy and Helmholtz work function. They are sate functions which give exact differentials. They are useful equations that can be applied to solved numerous thermodynamics problems

6.0 Tutor mark assignment

1. what do you understand by the term, thermodynamic potentials?
2. Derive expression for total derivation of internal energy
3. Derive expression for total derivation of enthalpy
4. Derive expression for total derivation of Helmholtz work function
5. Derive expression for total derivation of Gibbs free enrgy

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MODEL 3

UNIT 3: Maxwell equation

1.0 Introduction

Maxwell equation are equations which employ the basic property of state functions (i,e exact differentiation) to derive thermodynamic equations that relate the differential of one sate function to another or to some physical properties.

2.0 Objectives

i. To derive the Maxwell equations using the principle of reciprocity

ii. To know the applications of the Maxwell equations

iii. To know the relationship between the Maxwell equation and Euler's test

3.0 Main text

3.1 Derivation of Maxwell equations

The Maxwell equations can be developed from thermodynamic potentials using the principle of reciprocity. Given an independent variable, x and y and f representing the total differential of a dependent state function such that:

$$df = adx + bdy \qquad 103$$

where a and b are functions of x and y. Based on equation 103, the reciprocity relation is given as:

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \qquad 104$$

The total differential equations that were derived for U, H, A and G are in form of equation 15. They include,

i. $dU = TdS - PdV$

ii. $dH = TdS + VdP$

iii. $dA = - PdV - SdT$

iv. $dG = VdP - SdT$

Therefore, applying the principle of reciprocity to the above equations, we have the following equations,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad 105$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad 106$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad 107$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad 108$$

3.2 Applications of the Maxwell equations

Equations 105 to 108 are the various forms of Maxwell equations corresponding to the thermodynamic potentials, U, H, A and G respectively. In order to apply the Maxwell equations, thermodynamic equation of state can be derived from the respective thermodynamic differentials as follows. The differential of internal energy is given as $dU = TdS - PdV$. If we divide this equation by dV, keeping T constant, we have,

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{dS}{dV}\right)_T - P \qquad 109$$

From the Maxwell equation, $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$, equation 23 becomes,

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad 110$$

Similarly, if we divide dU with dS, we have,

$$\left(\frac{dU}{dS}\right)_{P,T} = T - P\left(\frac{\partial V}{\partial S}\right)_P \qquad 111$$

Equation 111 can also be written as (note that $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$) follows,

$$\left(\frac{dU}{dS}\right)_{T,P} = T - P\left(\frac{\partial T}{\partial P}\right)_S \qquad 112$$

dH is given as $dH \ = TdS + VdP$, we can also apply the Maxwell equations by dividing the equation by dP ,

$$\left(\frac{dH}{dP}\right)_T \ = T\ \left(\frac{\partial S}{\partial P}\right)_T - \ V \qquad 113$$

Again, from the Maxwell equation, $\left(\frac{\partial V}{\partial T}\right)_P \ = -\left(\frac{\partial S}{\partial P}\right)_T$. Hence we have,

$$\left(\frac{dH}{dP}\right)_T \ = -T\left(\frac{\partial V}{\partial T}\right)_P - \ V \qquad 114$$

If we divide dH by dS, then we have,

$$\left(\frac{dH}{dS}\right)_{T,V} \ = T \ - \ V\left(\frac{\partial P}{\partial S}\right)_V \qquad 115$$

Since $\left(\frac{\partial T}{\partial V}\right)_S \ = - \ \left(\frac{\partial P}{\partial S}\right)_V$, equation 115 can also be written as,

$$\left(\frac{dH}{dS}\right)_{T,V} \ = T + \ V\left(\frac{\partial T}{\partial V}\right)_S \qquad 116$$

The differential of A is given as $dA \ = - PdV - SdT$, which is transformed to the underlisted equation, if it is divided by dT

$$\left(\frac{dA}{dT}\right)_P \ = -P\left(\frac{\partial V}{\partial T}\right)_P - \ S \qquad 117$$

But $\left(\frac{\partial V}{\partial T}\right)_P \ = -\left(\frac{\partial S}{\partial P}\right)_T$, therefore, $\left(\frac{dA}{dT}\right)_P$ can also be written as

$$\left(\frac{dA}{dT}\right)_{P,T} \ = \ P\left(\frac{\partial S}{\partial P}\right)_T - \ S \qquad 118$$

Similarly, if dA is divided by dV, we will have equation 118 which transforms to equation 119 upon substitution of the Maxwell equation, $\left(\frac{\partial T}{\partial V}\right)_S \ = - \ \left(\frac{\partial P}{\partial S}\right)_V$

$$\left(\frac{dA}{dT}\right)_P \ = -P - S\left(\frac{\partial T}{\partial V}\right)_S \qquad 119$$

$$\left(\frac{dA}{dT}\right)_P \ = -P + S\left(\frac{\partial P}{\partial S}\right)_V \qquad 120$$

Finally, $dG = VdP \ - \ \ SdT$ and by dividing dG with dT, we have

$$\left(\frac{dG}{dT}\right)_V \ = V\left(\frac{\partial P}{\partial T}\right)_V - \ S \qquad 121$$

But $\left(\frac{\partial P}{\partial T}\right)_V \ = \ \left(\frac{\partial S}{\partial V}\right)_T$ hence equation 121 becomes

$$\left(\frac{dG}{dT}\right)_V \ = V\left(\frac{\partial S}{\partial V}\right)_T - \ S \qquad 122$$

On the other hand, if we divide dG with dP, we have equation 123, which becomes equation 134 upon simplification ($\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$),

$$\left(\frac{dG}{dP}\right)_V = V - S\left(\frac{\partial T}{\partial P}\right)_S \qquad 123$$

$$\left(\frac{dG}{dP}\right)_V = V - S \left(\frac{\partial V}{\partial S}\right)_P \qquad 124$$

3.3 Maxwell’s equation and Euler’s test

Maxwell's equations can also be obtained using the principle of Euler's test for exact differentials, namely that mixed second derivatives of "nice" functions must be equal. Applying this principle to Gibb and Helmoltz free energy functions we have,

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V} \qquad 125$$

$$\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T \qquad 126$$

From the equation obtained for the total differentiation of A, $\left(\frac{\partial A}{\partial T}\right)_V$ = -S, therefore

$$\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V = \frac{\partial}{\partial V}(-S) = \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T = \frac{\partial}{\partial T}(-P) \qquad 127$$

From equation 127, we conclude that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ as gotten before. We can also extend the same analysis to Gibbs free energy as follows,

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial V} \qquad 128$$

From the above, we can apply the same principles of Euler’s test and the results obtained for Maxwell relation is consistent with those obtained through the principle of reciprocity.

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T \qquad 129$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial}{\partial P}(V) = \frac{\partial}{\partial T}(-S) \qquad 130$$

$$\left(\frac{\partial V}{\partial P}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_P \qquad 131$$

There is no restrained in using the Euler's principle to derive Maxwell equation from the other thermodynamic functions (i.e U and H). Without much explanation, the mathematical procedures are outlined for U as shown below

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \qquad 132$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V \qquad 133$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial S}(-P) = \frac{\partial}{\partial V}(T) \qquad 134$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad 135$$

Finally, similar procedures are outlined for H as shown below,

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} \qquad 136$$

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P \qquad 137$$

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial}{\partial S}(T) = \frac{\partial}{\partial P}(V) \qquad 138$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial P}\right)_S \qquad 139$$

3.4 Derivatives of entropy

We can derive further derivatives for entropy as follows. First we define entropy as dS = dq/T and heat capacity as C = dq/dT. Therefore dS/dT = (dq/T)/(dq/C) = C/T hence we obtained the following derivatives,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \text{ and } \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad 140$$

It can also be shown that

i. $\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{C_V}{T}\right)\left(\frac{\partial T}{\partial P}\right)_V$

ii. $\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{C_P}{T}\right)\left(\frac{\partial T}{\partial V}\right)_P$

4.0 Summary

The differential forms of the Maxwell equations include the following functions

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{dS}{dV}\right)_T - P \quad \text{and} \quad \left(\frac{dU}{dV}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{dU}{dS}\right)_{P,T} = T - P\left(\frac{\partial V}{\partial S}\right)_P \quad \text{and} \quad \left(\frac{dU}{dS}\right)_{T,P} = T - P\left(\frac{\partial T}{\partial P}\right)_S$$

$$\left(\frac{dH}{dP}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - V \quad \text{and} \quad \left(\frac{dH}{dP}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - V$$

$$\left(\frac{dH}{dS}\right)_{T,V} = T - V\left(\frac{\partial P}{\partial S}\right)_V \quad \text{and} \quad \left(\frac{dH}{dS}\right)_{T,V} = T + V\left(\frac{\partial T}{\partial V}\right)_S$$

$$\left(\frac{dA}{dT}\right)_P = -P\left(\frac{\partial V}{\partial T}\right)_P - S \quad \text{and} \quad \left(\frac{dA}{dT}\right)_{P,T} = P\left(\frac{\partial S}{\partial P}\right)_T - S$$

$$\left(\frac{dA}{dT}\right)_P = -P - S\left(\frac{\partial T}{\partial V}\right)_S \quad \text{and} \quad \left(\frac{dA}{dT}\right)_P = -P + S\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{dG}{dT}\right)_V = V\left(\frac{\partial P}{\partial T}\right)_V - S \quad \text{and} \quad \left(\frac{dG}{dT}\right)_V = V\left(\frac{\partial S}{\partial V}\right)_T - S$$

$$\left(\frac{dG}{dP}\right)_V = V - S\left(\frac{\partial T}{\partial P}\right)_S \quad \text{and} \quad \left(\frac{dG}{dP}\right)_V = V - S\left(\frac{\partial V}{\partial S}\right)_P$$

5.0 Conclusion

The differential forms of the Maxwell equation provide an avenue for deriving thermodynamic equation of states. These equations provide a link between thermodynamic parameters and some other variables such as pressure, temperature and volume.

6.0 Tutor mark assignment

1. Derive expression for the Maxwell equations using the principle of reciprocity

ii. What are the applications of the Maxwell equations

iii. Derive suitable expression to show the relationship between the Maxwell equation and Euler's test

7.0 References

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MODULE 4

UNIT 1: Feasibility of a chemical reaction

1.0 Introduction

The major objective of chemical thermodynamics is to use thermodynamic data to predict the direction of a chemical reaction. A spontaneous reactions can be defined as the one that can take place on its own without an external aid. So far, some thermodynamic state functions have been derived. These include internal energy, enthalpy, entropy, free energy and Helmholtz work function , It is significant to state that internal energy change is not a unique parameter for predicting the direction of a chemical reaction because it is a state function obtained at constant volume. Based on changes in enthalpy, chemical reactions can be classified as exothermic and endothermic. In exothermic reaction, heat is given off to the surrounding while heat is absorbed from the surrounding in endothermic reaction. Therefore, it is expected that exothermic reaction should be spontaneous while endothermic reactions should be non spontaneous. However, there are some exothermic reactions that are not spontaneous while some endothermic reactions are spontaneous. Hence, enthalpy data cannot be a unique data for predicting the spontaneity of a chemical reaction. Lastly, entropy data cannot be effectively used as a unique parameter for predicting the direction of a chemical reaction because the total entropy is the sum of the entropy of the system and that of the surrounding. Consequently, we that measure entropy are part of the surrounding indicating that there is a severe interferences in using entropy data alone for measuring the direction of a chemical reaction. A state function that has been found to be unique in predicting the direction of a chemical reaction is called the free energy. Fortunately, the free energy change is a state function obtained at constant pressure and is a function of enthalpy, entropy and temperature. At constant volume, the unique state function is Helmholtz work function.

2.0 Objectives

(i) To understand the concept of feasibility and spontaneousity of a chemical reaction
(ii) To understand the general condition for a reaction to be feasible
(iii) To understand the requirements for the feasibility of a chemical reaction
(iv) To find out the effect of temperature on the free energy change
(v) To find out the effect of pressure on the free energy change
(vi) To derive the relationship between free energy change and electromotive force
(vii) To know the relationship between boiling point elevation and mole fraction
(viii) To know the relationship between depression of freezing point and mole fraction
(ix) To know the relationship between free energy change and chemical potential
(x) To understand the concept of molar quantities
(xi) To know Gibbs Duhem equation
(xii) To know the conditions for phase equilibrium
(xiii) To know the equations that express chemical potentials of ideal gases
(xiv) To know the relationship between chemical potential and fugacity of ideal gases

3.0 Main text

3.1 Feasibility or spontaneity of a chemical reaction

Two thermodynamic functions are most dependent for predicting the direction of a chemical reaction. These are the change in Gibbs free energy (for reactions at constant pressure) and a change in Helmholtz free energy (for reactions at constant volume). The Helmholtz free energy depends on the internal energy (the sum total of all the kinetic and potential energies) while the Gibbs free energy is a function of enthalpy. Therefore, U can be expressed as,

$$dU = TdS - PdV + dW_{other} \qquad 141$$

where dW_{other} stands for other forms of work that are not PV work. Since A is a function of U and dA = -SdT – PdV, then we can also introduce similar term, to represent other forms of work, thus,

$$dA = -SdT - PdV + dW_{other} \qquad 142$$

At constant temperature, equation 142 becomes, $dA = -PdV + dW_{other} = dW_{All,reversible}$ indicating that at constant temperature the Helmholtz free energy gives all the reversible work (reversible work in this case, is the sum of PV work and all other forms of work).

We can also write similar expression for the change in Gibb free energy. Since dG = -SdT + VdP for pressure volume work. If we add other forms of work, we have,

$$dG = -SdT + VdP + dW_{other} \qquad 143$$

At constant temperature and pressure, equation 143 becomes

$$dG = dW_{other} = dW_{All,reversible} \qquad 144$$

From equation 144, it can be stated that at constant pressure and temperature, the change in Gibb free energy gives all the reversible work (except PV work)

For a thermodynamic process to be in equilibrium, then $dS \geq \frac{dq}{T}$ and or $TdS \geq dq$, which can be re-arranged to the following form,

$$0 \geq dq - TdS \text{ or } dq - TdS \leq 0 \qquad 145$$

The Helmholtz work function can be written as A = U + TS, which differentiate to the following form,

$$dA = dU - TdS - SdT \qquad 146$$

From the first law of thermodynamics, dU = dq – PdV, which fits into equation 146 to redefine dA as follows,

$$dA = dq - PdV - TdS - SdT \qquad 147$$

Rearranging equation, 147, we have,

$$dA = (dq - TdS) - PdV - SdT \qquad 148$$

Therefore, for a process at constant temperature and volume, the inequality becomes,

$$dA_{T,V} \ = dq - TdS \ \leq 0 \qquad 149$$

Hence, for a process at constant temperature and volume, the Helmholtz fee energy should be the minimum. Therefore, a system at constant temperature and volume is spontaneous if the Helmholtz free energy decreases (if the system is away from equilibrium).

We can also consider what is expected for a change in Gibbs free energy. The change in Gibb free energy can be written (note that G = H –TS, H = U + PV, U = dq - PdV) ,

$$dG = dH - TdS - SdT \qquad 150$$

$$dG = dU + PdV + VdP - TdS - SdT \qquad 151$$

$$dG = dq - PdV + PdV + VdP - TdS - SdT \qquad 152$$

$$dG = dq + VdP - TdS - SdT \qquad 153$$

Rearranging equation 153, we have,

$$dG = (dq - TdS) + VdP - SdT \qquad 154$$

Similarly, for a process at constant temperature and pressure, the inequality becomes,

$$dG_{T,P} \ = dq - TdS \ \leq 0 \qquad 155$$

Therefore, at constant temperature and pressure, the Gibb free energy seeks a minimum. Hence any spontaneous process occurring in a system of constant temperature and pressure, will decrease the Gibb free energy, if the system is away from equilibrium.

Solved problem 1

(a) Derive the inequality that is required for a thermodynamic process to be in equilibrium

(b) Show that a system at constant temperature and volume is spontaneous if the Helmholtz free energy decreases (provided the system is away from equilibrium)

(c) Show that any spontaneous process occurring in a system of constant temperature and pressure, will decrease the Gibbs free energy, if the system is away from equilibrium.

Solution

(a) For a thermodynamic process to be in equilibrium, then $dS \geq \frac{dq}{T}$ and or $TdS \geq dq$, which can be re-arranged to the following form,

$$0 \geq dq - TdS \text{ or } dq - TdS \leq 0$$

(b) The Helmholtz function can be written as A = U + TS, which differentiate to the following form,

$$dA = dU - TdS - SdT \qquad 1$$

From the first law of thermodynamics, dU = dq – PdV, which fits into equation 1 to redefine dA as follows,

$$dA = dq - PdV - TdS - SdT \qquad 2$$

Rearranging equation, 147, we have,

$$dA = (dq - TdS) - PdV - SdT \qquad 3$$

Therefore, for a process at constant temperature and volume, the inequality becomes,

$$dA_{T,V} = dq - TdS \leq 0 \qquad 4$$

Hence, for a process at constant temperature and volume, the Helmholtz fee energy should be the minimum. Therefore, a system at constant temperature and volume is spontaneous if the Helmholtz free energy decreases (if the system is away from equilibrium).

(c) The change in Gibbs free energy can be written (note that G = H –TS, H = U + PV, U = dq - PdV) ,

$$dG = dH - TdS - SdT \qquad 1$$

$$dG = dU + PdV + VdP - TdS - SdT \qquad 2$$

$$dG = dq - PdV + PdV + VdP - TdS - SdT \qquad 3$$

$$dG = dq + VdP - TdS - SdT \qquad 4$$

Rearranging equation 4, we have,

$$dG = (dq - TdS) + VdP - SdT \qquad 5$$

Similarly, for a process at constant temperature and pressure, the inequality becomes,

$$dG_{T,P} = dq - TdS \leq 0 \qquad 6$$

Therefore, at constant temperature and pressure, the Gibbs free energy seeks a minimum. Hence any spontaneous process occurring in a system of constant temperature and pressure, will decrease the Gibbs free energy, if the system is away from equilibrium.

3.1.1 Effect of temperature and pressure on G

It has been shown that the Gibbs free energy is a function of pressure and temperature and that dG = VdP – SdT. This fundamental equation can be examined under two major conditions, namely, at constant pressure and at constant temperature.

(i) Constant temperature: effect of pressure on G.

At constant temperature, dG = VdP. From the gas law, PV = RT implies that V = RT/P. Hence dG = RTdP/P If the change in pressure from P_1 to P_2 is accompanied by a corresponding change in free energy (from G_1 to G_2) respectively, then we can integrate the function as follows,

$$\int_{G_1}^{G_2} dG = G_2 - G_1 = \Delta G = \int_{P_1}^{P_2} \frac{dP}{P} \qquad 156$$

$$\Delta G = RTln\left(\frac{P_2}{P_1}\right) = 2.303RTlog\left(\frac{P_2}{P_1}\right) \qquad 157$$

(ii) Constant pressure: effect of temperature on G

At constant pressure, dG = -SdT, which rearranges to equation 158,

$$\left(\frac{dG}{dT}\right) = -S \qquad 158$$

For two states (1 and 2), the change in entropy can be written according to equation 159

$$\left(\frac{dG_2}{dT}\right) - \left(\frac{dG_1}{dT}\right) = -(S_2 - S_1) = -\Delta S \qquad 159$$

$$\frac{d}{dT}(\Delta G) = -\Delta S \qquad 160$$

However, $\Delta G = \Delta H - T\Delta S$, which implies that $-\Delta S = \frac{\Delta G - \Delta H}{T}$ and thus,

$$\frac{d}{dT}(\Delta G) = \frac{\Delta G - \Delta H}{T} \qquad 161$$

Equation 161 is called the Gibbs Helmholtz equation.

Lets take the differential of $\frac{d}{dT}\left(\frac{\Delta G}{T}\right)$ using the product rule, we have,

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{1}{T}\frac{d}{dT}(\Delta G) + (\Delta G)\frac{d}{dT}(1/T)) \qquad 162$$

The solution to the above problem is $\frac{1}{T}\frac{d}{dT}(\Delta G) - \frac{\Delta G}{T^2}$. But $\frac{d}{dT}(\Delta G) = \frac{\Delta G - \Delta H}{T}$. Therefore, equation 162 can be simplified into equation 163 and 164

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{1}{T}\left(\frac{\Delta G - \Delta H}{T}\right) - \frac{\Delta G}{T^2} \qquad 163$$

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{\Delta G}{T^2} - \frac{\Delta H}{T^2} - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2} \qquad 164$$

Since $\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$ and $\frac{d}{dT}\left(\frac{1}{T}\right) = -\frac{1}{T^2}$, then

$$\frac{d}{dT}\left[\frac{\Delta G/T}{1/T}\right]_P = \left(\frac{-\Delta H/T^2}{-1/T^2}\right) = \Delta H \qquad 165$$

From equation 165, a plot of $\frac{\Delta G}{T}$ versus $\frac{1}{T}$ would be linear with slope equal to ΔH

Solved problem 2

(a) Show that at constant temperature, the change in the Gibbs free energy is a function of pressure, hence calculate the change in Gibbs free energy for a reaction, whose pressure changes from 101325 Pa to 202650 Pa at 298 K

(b) Show that at constant pressure, $\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$, hence explain how you can use the derived equation to estimate the enthalpy change of a reaction.

(c) Use the equation that relates free energy change with electrode potential to derive an expression that relates the temperature coefficient of a cell with enthalpy change.

Solution

(a) The dG = VdP-SdT. At constant temperature, dT = 0 and dG = VdP. From the gas law, PV = RT implies that V = RT/P. Hence dG = RTdP/P, If the change in pressure from P_1 to P_2 is accompanied by a corresponding change in free energy (from G_1 to G_2) respectively, then we can integrate the function as follows,

$$\int_{G_1}^{G_2} dG = G_2 - G_1 = \Delta G = \int_{P_1}^{P_2} \frac{dP}{P} \qquad 1$$

$$\Delta G = RTln\left(\frac{P_2}{P_1}\right) = 2.303RTlog\left(\frac{P_2}{P_1}\right) \qquad 2$$

For a change in pressure from P_1(101325 Pa) to P_2(202650 Pa), the change in Gibb free energy is

$$\Delta G = RTln\left(\frac{P_2}{P_1}\right) = 8.314\, Jmol^{-1}K^{-1}(298\,K)ln\left(\frac{202650\,Pa}{101325\,Pa}\right) = 1717.32\,J/mol$$

(b) At constant pressure, dG = -SdT, which rearranges to equation 1,

$$\left(\frac{dG}{dT}\right) = -S \qquad 1$$

If two states (1 and 2) exist, the change in entropy can be written according to equation 2

$$\left(\frac{dG_2}{dT}\right) - \left(\frac{dG_1}{dT}\right) = -(S_2 - S_1) = -\Delta S \qquad 2$$

$$\frac{d}{dT}\,(\Delta G) = -\Delta S \qquad 3$$

However, $\Delta G = \Delta H - T\Delta S$, which implies that $-\Delta S = \frac{\Delta G - \Delta H}{T}$ and thus,

$$\frac{d}{dT}\,(\Delta G) = \frac{\Delta G - \Delta H}{T} \qquad 4$$

Equation 4 is called the Gibbs Helmoltz equation. The differentiation of $\frac{d}{dT}\left(\frac{\Delta G}{T}\right)$ using the product rule, gives

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{1}{T}\frac{d}{dT}\,(\Delta G) + (\Delta G)\frac{d}{dT}(1/T)) \qquad 5$$

The solution to the above problem is $\frac{1}{T}\frac{d}{dT}\,(\Delta G) - \frac{\Delta G}{T^2}$. But $\frac{d}{dT}\,(\Delta G) = \frac{\Delta G - \Delta H}{T}$. Therefore, equation 5 can be simplified into equation 6 and 7

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{1}{T}\left(\frac{\Delta G - \Delta H}{T}\right) - \frac{\Delta G}{T^2} \qquad 6$$

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{\Delta G}{T^2} - \frac{\Delta H}{T^2} - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2} \qquad 7$$

Since $\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$ and $\frac{d}{dT}\left(\frac{1}{T}\right) = -\frac{1}{T^2}$, then

$$\frac{d}{dT}\left[\frac{\Delta G/T}{1/T}\right]_P = \left(\frac{-\Delta H/T^2}{-1/T^2}\right) = \Delta H \qquad 8$$

From equation 8, a plot of $\frac{\Delta G}{T}$ versus $\frac{1}{T}$ would be linear with slope equal to ΔH

(c) The standard change in free energy is related to the electromotive force according to the following equation,

$$\Delta G = -nFE \qquad 1$$

where n is the number of charge transferred, F is the Faraday (which has a numerical value of 96 500 C) and E is the electromotive force. However, it is known that at constant pressure, the differential of the free energy change is given as, $\frac{d}{dT}\,(\Delta G) = \frac{\Delta G - \Delta H}{T}$, which indicate that if we substitute for the free energy change, we will have,

$$\frac{d}{dT}\,(-nFE) = -\frac{nFE - \Delta H}{T} \qquad 2$$

Simplification of equation 167 gives equation 168

$$nFT\frac{dE}{dT} = nFE + \Delta H \qquad 3$$

where $\frac{dE}{dT}$ is called temperature coefficient of the cell

3.1.2 Relationship between ΔG and electromotive force, E

The standard change in free energy is related to the electromotive force according to the following equation,

$$\Delta G = -nFE \qquad 166$$

where n is the number of charge transferred, F is the Faraday (which has a numerical value of 96 500 C) and E is the electromotive force. However, it is known that at constant pressure, the differential of the free energy change is given as, $\frac{d}{dT}\ (\Delta G) = \frac{\Delta G - \Delta H}{T}$, which indicate that if we substitute for the free energy change, we will have,

$$\frac{d}{dT}\ (-nFE) = -\frac{nFE - \Delta H}{T} \qquad 167$$

Simplification of equation 167 gives equation 168

$$nFT\frac{dE}{dT} = nFE + \Delta H \qquad 168$$

where $\frac{dE}{dT}$ is called temperature coefficient of the cell.

3.2 Calyperon and Clausius-Clayperon equation

For different phases in equilibrium, Clayperon equation gives the relationship between variables. These phases may include liquid-gas phase, solid-liquid phase, etc. In order to apply thermodynamics functions to a system in phase equilibrium, we first consider a liquid in equilibrium with its vapour such that an infinitesimal changes in temperature and pressure lead to T + dT and P + dP respectively. It follows that an infinitesimal change in pressure and volume is accompanied by infinitesimal change in Gibb free energy (dG = VdP-SdT). Therefore, the liquid and gas phases can be defined as follows,

$$dG_{(l)} = V_{(l)}dP - S_{(l)}dT \qquad 169$$

$$dG_{(g)} = V_{(g)}dP - S_{(g)}dT \qquad 170$$

At equilibrium, the free energy changes for the two phases are equal. That is $dG_{(l)} = dG_{(g)}$. Hence,

$$V_{(l)}dP - S_{(l)}dT = V_{(g)}dP - S_{(g)}dT \qquad 171$$

Rearrangement of equation 171 gives,

$$\frac{dP}{dT} = \frac{S_{(g)} - S_{(l)}}{V_{(g)} - V_{(l)}} = \frac{\Delta S}{\Delta V} \qquad 172$$

Also, at equilibrium, the change in Gibb free energy = 0 and we can state that, $\Delta G_{Vap} = \Delta H_{Vap} - T\Delta S_{Vap}$ and since $\Delta G_{Vap} = 0$, then, $\Delta S_{Vap} = \frac{\Delta H_{Vap}}{T}$. Substituting for ΔS_{Vap} in equation 172, we have

$$\frac{dP}{dT} = \frac{\frac{\Delta H_{Vap}}{T}}{\Delta V_{Vap}} = \frac{\Delta H_{Vap}}{T\Delta V_{Vap}} \qquad 173$$

The above equation is the Clayperon equation. Hence we conclude that the Clayperon equation gives the rate of change of vapour pressure with temperature.

$$\boldsymbol{\frac{dP}{dT} = \frac{\Delta H_{Vap}}{T\Delta V_{Vap}}}$$

This equation can be applied to any equilibrium between phases such as sublimation, fusion, etc. In the Clayperon equation given above, the change in volume is, $\Delta V_{Vap} = V_{(g)} - V_{(l)}$. It is significant to state that the volume occupied by a gas in a liquid-vapour phase is much larger than that occupied by the liquid. Then we can neglect $V_{(l)}$ and expressed the change in volume as $\Delta V_{Vap} = V_{(g)}$. From the gas equation, PV = RT, V = RT/P . Hence $V_{(g)} = \Delta V_{Vap} = RT/P$. Therefore, the Clayperon equation can be written as follows,

$$\frac{dP}{dT} = \frac{\Delta H_{Vap}}{T(RT/P)} = \frac{P(\Delta H_{Vap})}{RT^2} \qquad 174$$

Equation 175 can be re-arranged to the form given in equation 175

$$\frac{dP}{P} = \frac{\Delta H_{Vap}}{R}.\frac{dT}{T^2} \qquad 175$$

We can integrate equation 175 between the limits P_1 to P_2 and T_1 to T_2, as follows, $\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_{Vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$ and the solution is given as,

$$ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{Vap}}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} \qquad 176$$

$$ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{Vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad 177$$

Equation 177 is called the Clausius- Claperon equation and is useful in measuring vapour pressure of various liquids and solids.

3.3 Chemical potential and Free energy

For a pure substance or for a system having the constant chemical composition, the infinitesimal change in Gibb free energy is given as, dG = VdP –SdT. However, if the component of the system vary, such that the number of moles are n_1, n_2.......n_i, the change in Gibbs free energy will be a function of different parameters and can be written as,

$$G = f(T, P, n_1, n_2, \ldots . n_i) \qquad 178$$

The total differential of equation 178 is given as,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_i} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_i} dn_2 \,..+ \left(\frac{\partial G}{\partial n_n}\right)_{P,T,n_i} dn_n \quad 179$$

The term, n_i is introduced to show that the quantities of all other components except the one in bracket are held constant. For a system whose composition is unperturbed, the change in composition is zero. That is $dn_1 = dn_2 = 0$ or $\Sigma dn_i = 0$. Therefore, under this condition, equation 179 will become,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP \qquad 180$$

If we compare the above equation with dG = VdP – SdT, then, $\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S$ and $\left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V$. Substitution of these function in equation 179 gives,

$$dG = -SdT + VdP + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_i} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_i} dn_2 \,..+ \left(\frac{\partial G}{\partial n_n}\right)_{P,T,n_i} dn_n \qquad 181$$

The coefficient of dn_i is called the chemical potential of the system. For example, $\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_i}$, $\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_i}$, $\mu_n = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_n}$. This implies that equation 181 can also be written as,

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \,..+ \mu_n dn_n \qquad 182$$

Finally, the summation, $\mu_1 dn_1 + \mu_2 dn_2 \,..+ \mu_n dn_n$ can be represented as $\Sigma \mu_i dn_i$, which transforms equation 182 to equation 183,

$$dG = -SdT + VdP + \sum \mu_i dn_i \qquad 184$$

From the above, we define the chemical potential of a chemical system as the rate of change of the Gibb free energy with the number of moles in that component, when the number of moles of all other components is held constant. Chemical potential is a force that drives chemical system to equilibrium, which indicates that the value of chemical potential throughout the system will be the same for a system in equilibrium. Chemical potential is also a measure of escaping tendency of a system, indicating that the higher the chemical potential, the higher the escaping tendency.

3.4 Gibb-Duhem equation

This equation shows the relationship between infinitesimal change in Gibbs free energy and chemical potential. Again, we can derive this equation by noting that $dG = -SdT + VdP + \sum \mu_i dn_i$.At constant temperature and pressure, dT = dP = 0 and the equation becomes,

$$dG = \sum \mu_i dn_i \qquad 185$$

Integration of equation 185 gives,

$$G = \sum \mu_i n_i \qquad 186$$

Again, if we differentiate equation 186, we have

$$dG = \sum(\mu_i dn_i + n_i d\mu_i) \qquad 187$$

Recall that $= -SdT + VdP + \sum \mu_i dn_i$. Hence if we equate this function with equation 187, we will have equation 188, which simplifies to equation 189

$$\sum(\mu_i dn_i + n_i d\mu_i) = -SdT + VdP + \sum \mu_i dn_i$$

$$\sum n_i d\mu_i = -SdT + VdP \qquad 188$$

The implication of equation 188 is that at constant temperature and pressure, if only the variation in composition, exists, we have the Gibb-Duhem equation given as

$$\sum n_i d\mu_i = 0 \ (T, P \ constant)$$

The Gibb-Duhem equation (given above), shows that with variation in composition, the chemical potential do not change. This equation can be used in solving some problems. For example, if we have a two component system, we can write the Gibb-Duhem equation as follows, $n_1 d\mu_1 + n_2 d\mu_2 = 0$. This equation can be rearranged according to equation 189,

$$d\mu_2 = \left(\frac{n_1}{n_2}\right) d\mu_1 \qquad 189$$

From equation 189, if we know the change in the chemical potential of one component, we can calculate the change in chemical potential of the other component.

3.5 Partial molar quantities

The chemical potential of a pure substance is defined by the equation,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \overline{G_i} \qquad 190$$

where G_i is called the partial molar free energy of component i. Similarly, we can define the partial molar volume (V_i) and the partial molar entropy ($\overline{S_i}$) as follows,

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \overline{V_i} \qquad 191$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j} = \bar{S}_\iota \qquad 192a$$

Since dG = VdP –SdT, at constant temperature, we have the following equation, $\left(\frac{\partial G}{\partial P}\right)_T = V$ which can be substituted to equation 191 to obtain equation 192b,

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_T = \bar{V}_\iota \qquad 192b$$

However, $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$ indicating that equation 192 simplifies to equation 193,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_\iota \qquad 193$$

Similarly, at constant pressure, dG = -SdT indicating that $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and that ,

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_T = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_P = -\bar{S}_\iota \qquad 194$$

Since $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,n_j}$ equation 194 becomes,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_\iota \qquad 195$$

Partial molar quantities are important in the study of the behaviour of non ideal mixtures.

3.6 Phase equilibria

Chemical potential can be applied in the study of phase equilibra. Let us consider a substance, i distributed between two phases, A and B. If μ_A and μ_B are the chemical potential of the substances in phases A and B respectively, then the number of moles of i transferred is dn$_i$. We can write the Gibbs-Duhem equation ($dG = \sum \mu_i dn_i$) for this system as $dG = \mu_A dn_i - \mu_B dn_i = dn_i\,(\mu_A - \mu_B)$ and at equilibrium dG = 0. Therefore, for an infinitesimal change in the number of moles dn$_i$ will not be equal to zero. Hence $\mu_A - \mu_B$ and $\mu_A = \mu_B$. This indicates that at equilibrium, and at constant temperature and pressure, the chemical potential of each component must be equal in all parts of the system.

3.7 Chemical potential of an ideal gas

The relationship between G of one mole of ideal gas at atmospheric pressure can be derived as follows;

$$dG = VdP - SdT \qquad 196$$

At constant temperature, $dG = VdP$. From the relation, PV = RT, V = RT/P and by substitution, we have, $= RT\frac{dP}{P}$. If we integrate this function, we have,

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} RT\frac{dP}{P} \qquad 197$$

The solution of equation 197 is

$$\Delta G = G_2 - G_1 = RTln\left(\frac{P_2}{P_1}\right) \qquad 198$$

Generally, the free energy of a gas is often defined with respect to the standard free energy, G^0 and is the free energy of one mole of a gas at one atmospheric pressure. Therefore, equation 198 becomes, $G - G^0 = RTln\left(\frac{P}{1}\right) = RTlnP$ indicating that G can be expressed as,

$$G = G^0 + RTlnP \qquad 199$$

Equation 199 forms the fundamental equation in analysing the chemical potential of an ideal gas. If there are n mumber of moles of the gas, the equation becomes,

$$G = G^0 + nRTlnP \qquad 200$$

Dividing both sides of equation 200 by n we have, $\frac{G}{n} = \frac{G^0}{n} + RTlnP$. Since the ratio, G/n defines chemical potential, we can state that the chemical potential of an ideal gas is given by,

$$\boldsymbol{\mu = \mu^0 + RTlnP}$$

3.7.1 Chemical potential of an ideal gas mixture

Consider a mixture of ideal gases, having total number of molecules n ($n = n_1 + n_2 + n_3 + ...$) and pressure P($P = P_1 + P_2 + P_3 +...$). For n number of molecules, the pressure and the volume are related according to the gas equation, PV = nRT. This indicates that V = nRT/P. This can be expressed as,

$$V = (n_1 + n_2 + n_3 + ..)\frac{RT}{P} \qquad 201$$

Differentiating equation 201 with respect to the number moles of any component, we obtain the following equations,

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_i} = \frac{RT}{P} \qquad 202$$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_i} = \frac{RT}{P} \qquad 203$$

$$\bar{V}_3 = \left(\frac{\partial V}{\partial n_3}\right)_{T,P,n_i} = \frac{RT}{P} \qquad 204$$

Generally, for an ith level, we can write an expression for the partial molar volume of any component of an ideal gas as follows;

$$\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \frac{RT}{P} \qquad 205$$

However, $\left(\frac{\partial V}{\partial n_i}\right)_{T,n_j} = \left(\frac{\partial \mu}{\partial P}\right)_{T,n_j}$ which transform equation 205 to, $\overline{V_i} = \left(\frac{\partial \mu}{\partial P}\right)_{T,P,n_j} = \frac{RT}{P}$. Therefore, $\partial\mu_i = RT\frac{dP}{P_i}$ and upon integration, we have, $\int \partial\mu_i = RT\int\frac{dP_i}{P_i}$, which gives the solution,

$$\mu_i = \mu_i{}^0 + RTlnP_i \qquad 206$$

where $\mu_i{}^0$ is the integration constant. Equation 206 provides a solution for calculating the chemical potential of any component of a mixture, using the partial pressure of the gas in the mixture. We can extend the usefulness of equation 206 further by nothing that the partial pressure, $P_i = C_iRT$. Therefore, by substitution, equation 206 becomes,

$$\mu_i = \mu_i{}^0 + RTln(C_iRT) = \mu_i{}^0 + RTlnRT + RTlnC_i$$

$$= \mu_{i(C)}{}^0 + RTlnC_i \qquad 207$$

where $\mu_{i(C)}{}^0 = \mu_i{}^0 + RTlnRT$. We can also simplify equation 206 using the relation, $P_i = X_iP$. where X_i is the mole fraction. By substitution, equation 206 gives,

$$\mu_i = \mu_i{}^0 + RTln(X_iP) = \mu_i{}^0 + RTln(X_i) + RTlnP$$

$$= \mu_{i(P)}{}^0 + RTlnX_i \qquad 208$$

Again, where $\mu_{i(P)}{}^0 = \mu_i{}^0 + RTln(P_i)$. The mole fraction of any component is always less than unity. This means the logarithm of X_i will be negative. Therefore, we conclude that the chemical potential of any gas in a mixture will a lways be less than the chemical potential of the pure gas under the same total pressure, P. Equation 208 will also be applicable to other type of solutions. In this case, chemical potential of the pure liquid and the mole fraction of the component in the solution will be the major parameters under consideration.

3.8 Chemical potential and fugacity

The equation, $\mu = \mu^0 + RTlnP$ is applicable to ideal gas. Real gas shows strong deviation from ideal gas indicating that this equation is not applicable. In 1870, Lewis found that to compensate for the imperfection of real gas, its chemical potential can be written as,

$$\mu = \mu^0 + RTlnf \qquad 209$$

where f is called fugacity. For ideal gas, P = f and the ratio, f/P = 1 but for real gas, f tend to P as P tend to zero. Thus the limit for real gases is $\lim_{P\to O}\frac{f}{P} = 1$.

The ration, f/P is called fugacity coefficient ($\gamma = f/P$) and is a measures of the deviation of real gas from ideal behaviour. For real gases mixture, the chemical potential of any component is expressed as,

$$\mu_i = \mu_i{}^0 + RTln\frac{f_i}{f_i^0} \qquad 210$$

Again, the ration of the fugacity of a given component, f_i to the fugacity at standard state, is called activity. That is $a = \frac{f_i}{f_i^0}$. Therefore, chemical potential can also be written as,

$$\mu_i = \mu_i{}^0 + RTlna \qquad 211$$

3.9 Colligative properties

Colligative properties are properties that depend on the number of solute particles added to the solvent and not on their identity. Addition of solute has the tendency of elevating the boiling point of a solvent, depressing the freezing point and it affects the osmotic pressure of the solution. In this section, we shall see how chemical potential can be used to study elevation of boiling point and depression of freezing point.

3.0.1 Elevation of boiling point

A liquid turns to vapour at its boiling point, which is constant at atmospheric pressure. However, in the presence of solute particles, the boiling point will be increased. Given a pure solvent A, addition of solute particles (B) to a solvent will increase the chemical potential of the pure liquid from $\mu_{A(l)}^0$ to $\mu_{A(l)}^0 + RTlnX_A$. The equation representing the increase in boiling point can be derived by considering the heterogenous equilibrium existing between the vapour and the liquid. Therefore the chemical potential of the vapour will be equal to the chemical potential of the gas at equilibrium:

$$\mu_{A\,(g)}^0 = \mu_{A\,(l)}^0 + RTlnX_A \qquad 212$$

where X_A is the mole fraction of the solvent which is related to that of the solute, X_B according to the equation, $X_A + X_B = 1$ hence $1-X_B = X_A$. Therefore, equation 212 can be written as, $\mu_{A\,(g)}^0 = \mu_{A\,(l)}^0 + RTln(1 - X_B)$ and upon rearrangement, equation 213 is obtained:

$$ln(1 - X_B) = \frac{\mu_{A\,(g)}^0 - \mu_{A\,(l)}^0}{RT} = \frac{\Delta G_{vap}}{RT} \qquad 213$$

ΔG_{vap} is related to enthalpy and entropy of vapourization according to the Gibb equation. Therefore, $\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$ and by substitution into equation 213, we have,

$$ln(1 - X_B) = \frac{\Delta G_{vap}}{RT} = \frac{\Delta H_{vap}}{RT} - \frac{\Delta S_{vap}}{R} \qquad 214$$

When X_B is equal to zero, the boiling point is that of the pure liquid and the temperature becomes T^0. Hence equation 214 becomes,

$$ln(1) = \frac{\Delta G_{vap}}{RT} = \frac{\Delta H_{vap}}{RT^0} - \frac{\Delta S_{vap}}{R} \qquad 215$$

Subtracting equation 215 from equation 214, we have,

$$ln(1 - X_B) = \frac{\Delta H_{vap}}{RT} - \frac{\Delta H_{vap}}{RT^0} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right) \qquad 216$$

The number of mole of B present in the system will often be two small compare to that of the solvent. Therefore, $ln(1\text{-}X_B) \approx X_B$ and equation 216 becomes,

$$X_B = = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T^0} - \frac{1}{T}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{T-T^0}{TT^0}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{\Delta T}{T^2}\right) \qquad 217$$

In the above equation, $TT^0$is equated to T^2 because $T \approx T^0$. From equation 217, we can make ΔT the subject of the equation and this represents the amount of elevation in temperature due to the addition of n_B mol of solute. Therefore,

$$\Delta T = \left(\frac{RT^2}{\Delta H_{vap}}\right) X_B \qquad 218$$

The terms in the bracket are a constant for a given system hence $\Delta T = K_B X_B$. K_B is called boiling point elevation or ebuloscopic constant. Also, X_B is proportional to molality (concentration in terms of number of moles of solute per kilogram). Therefore,

$$\boldsymbol{\Delta T = K_B M_B}$$

$$K_B = \frac{RT^2}{\Delta H_{vap}}$$

Depression of freezing point

Addition of a non-electrolyte to a pure solvent has the tendency of lowering the freezing point of a solvent. In this case, the heterogeneous equilibrium of interest is that between the pure liquid solvent and that of the solid. At the freezing point, the chemical potential of A in the two phases are equal and at equilibrium we have,

$$\mu^0_{A\,(S)} = \mu^0_{A\,(l)} + RTlnX_A \qquad 219$$

Equation 219 rearranged to equation 220 as follows,

$$ln(1 - X_B) = \frac{\mu^0_{A\,(S)} - \mu^0_{A\,(l)}}{RT} = \frac{\Delta G_{Fus}}{RT} = \frac{\Delta H_{Fus}}{RT} - \frac{\Delta S_{Fus}}{R} \qquad 220$$

When X_B is equal to zero, the freezing point is that of the pure liquid and the temperature becomes T^f. Hence equation 220 becomes,

$$ln(1) = \frac{\Delta G_{Fus}}{RT} = \frac{\Delta H_{Fus}}{RT^f} - \frac{\Delta S_{Fus}}{R} \qquad 221$$

Subtracting equation 221 from equation 220, we have,

$$ln(1 - X_B) = \frac{\Delta H_{Fus}}{RT} - \frac{\Delta H_{Fus}}{RT^f} = \frac{\Delta H_{Fus}}{R}\left(\frac{1}{T} - \frac{1}{T^f}\right) \qquad 222$$

The number of mole of B present in the system will often be two small compared to that of the solvent. Therefore, $\ln(1-X_B) \approx X_B$ and equation 222 becomes,

$$X_B = = \frac{\Delta H_{Fus}}{R}\left(\frac{1}{T^f} - \frac{1}{T}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{T-T^f}{TT^f}\right) = \frac{\Delta H_{Fus}}{R}\left(\frac{\Delta T}{T^2}\right) \qquad 223$$

Finally, the depression in freezing point is given as

$$\Delta T = \left(\frac{RT^2}{\Delta H_{Fus}}\right) X_B \qquad 224$$

The terms in the bracket are constant for a given system. Also, X_A is proportional to M_A Therefore, the freezing point depression is given by

$$\Delta T = K_B M_B$$

$$K_B = \frac{RT^2}{\Delta H_{Fus}}$$

where K_B is the freezing point depression constant or cryoscopic constant.

Solved problem 3

(a) 0.9 g of glucose was dissolved in 100 g of water. The freezing point of the glucose solution was determined to be 0.94 °C. Calculate the molar freezing point depression of water in the Kkg/mol.

(b) A salt is composed of cation, M^+ and anion X^-, and perfectly dissociate when dissolved in water. 2.0 g of this salt was disoloved in 100 g of water. The freezing point of the salt solution was determined to be -1.3 °C. Calculate the formula mass of the solute if the molar freezing point depression is 1.24 Kkg/mol.

Solution

(a) Depression of freezing point is given as $\Delta T = K_B M_B$. ΔT is the diference between the freezing point of the pure solvent and that of the solution. M_B is the molality of the solution(i.e concentration in mole per kg of the solution) and K_B is the depression point depression constant.

i.e the depression point associated with one mole of the solute (molar depression). From the question,

$$K_B = \frac{\varDelta T}{M_B}$$

$$\varDelta T = (0.00 - 0.94)\,℃ = (273 - 272.06) = 0.94\,K$$

$$M_B = \left(\frac{9.00g}{180\ g/mol}\right) \div 0.1\,kg\ = 5\,mol/kg$$

(molar mass of glucose = 180 g/mol, mass of water = 100 g = 0.1 kg)

Therefore,

$$K_B = \frac{0.94\,K}{5\,mol/kg} = 1.88\,Kkg/mol$$

(b) The freezing point depression of the salt is ΔT = 1.3 K. But $K_B = \frac{\varDelta T}{M_B}$

$$M_B = \left(\frac{2.00g}{X\ (in\frac{g}{mol})}\right) \div 0.1\,kg\ = \frac{20}{x}\ mol/kg$$

$$1.24\,Kkg/mol = \frac{x1.3\,K}{20\,mol/kg}$$

$$x = \frac{\left(1.24\frac{Kkg}{mol}\right)\left(20\frac{mol}{kg}\right)}{1.3\,K} = 19.08$$

4.0 Summary

(i) For a thermodynamic process to be in equilibrium, the inequality, $dS\ \geq \frac{dq}{T}$ and or $dq - TdS\ \leq 0$ must be satisfied.

(ii) For a process at constant temperature and volume, the Helmholtz fee energy should be the minimum since $dA_{T,V}\ = dq - TdS\ \leq 0$

(iii) For a process at constant temperature and pressure, the Gibb free energy seeks a minimum since $dG_{T,P}\ = dq - TdS\ \leq 0$. Therefore, any spontaneous process occurring in a system of constant temperature and pressure, will decrease the Gibb free energy, if the system is away from equilibrium.

(iv) At constant temperature, $\Delta G = RTln\left(\frac{P_2}{P_1}\right) = 2.303RTlog\left(\frac{P_2}{P_1}\right)$

(v) At constant pressure, $\frac{d}{dT}\left[\frac{\Delta G/T}{1/T}\right]_P = \left(\frac{-\Delta H/T^2}{-1/T^2}\right) = \Delta H$

(vi) The relationship between the change in free energy and electromotive force is ΔG = -nFE

(vii) Clausius Clayperon equation is $ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{Vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

(viii) The relationship between chemical potential and free energy change is $dG = -SdT + VdP + \sum \mu_i dn_i$

(ix) Gibb Duhem equation is $\sum n_i d\mu_i = 0\ (T, P\ constant)$

5.0 Conclusion

Most unique and widely applied thermodynamic function in predicting the direction of a chemical reaction is the standard Gibb free energy. It is a state function obtained at constant pressure and is related to enthalpy change (which defines the energy input) and entropy change (which represent frictional force or disorderliness). When the free energy change is negative, the reaction is spontaneous, when it is positive, the reaction is non spontaneous and when it is zero, the reaction is at equilibrium.

6.0 Tutor marked assignment

1. Derive expression to show the effect of change in pressure and temperature on the free energy change of a system. Hence explain how standard enthalpy change can be estimated graphically using data for standard free energy change at various temperature.

2. Derive Clausius-Clayperon equation and explain how the equation can be applied (graphically and non-graphically) to determine the enthalpy of vaporization of a liquid.

3. (a) What are the basic concepts behind colligative properties of a liquid. Hence state the four basic colligative properties of a liquid.

(b) The molar mass of a substances is 160 g/mol. When 5 g of this substance was dissolved in 100 g of water, the boiling point was elevated to 114 °C. Calculate the molar elevation point of the substance in Kkg/mol.

4. (a) What are the respective changes in sign of standard free energy change with respect to reaction that is spontaneous, non spontaneous and in equilibrium.

(b) Why is free energy data more unique that work function data in predicting the direction of a chemical reaction

7.0 References

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MODULE 4

UNIT 2: Thermodynamics of mixtures

1.0 Introduction

According to Dalton law of partial pressure, the total pressure of an ideal gas mixtures is the sum of the partial pressures of the various individual gases that constitute the mixture. This concept cannot be extended to thermodynamics functions because average thermodynamic function of a gas mixture may not necessarily be additives. This section considers detailed thermodynamic properties of ideal gas mixtures.

2.0 Objectives

i. To understand the concept of thermodynamics of mixture of ideal gases
ii. To derive expression for work done in mixing ideal gases
iii. To derive expression for entropy of mixing ideal gases
iv. To derive expression for free energy of mixing ideal gases
v. To derive expression for volume changes in mixing ideal gases
vi. To derive expression for enthalpy change of mixing ideal gases
vii. To derive expression for Helmholtz work function of mixing ideal gases

viii. To be able to solve problems related to thermodynamics of mixtures

3.0 Main text

3.1 Thermodynamics of mixtures of ideal gases

Thermodynamic properties of ideal gas mixtures are significant because they provide theoretical framework for the production of some industrial mixtures. In this section we will consider the following properties, viz, workdone in mixing ideal gases, change in entropy of mixing, change in free energies (both Gibbs and Helmoltz) with change of mixing, change in enthalpy of mixing and change in volume during mixing. The molar changes for each of these functions shall also be considered.

3.1.1 Work done in mixing ideal gases

In this section, we will first consider the work done and entropy change of mixing two ideal gases, A and B. It is worth noting that the work done in mixing the gases is equal to the sum of the work done by gas A and that done by gas B. Again, work done is equal to heat absorbed. Therefore, we state that the total work done in mixing gases A and B can be written as, $W = W_A + W_B = q$ hence,

$$dW = dq = W_A + W_B \qquad 225$$

$$= P_A dV_A + P_B dV_B \qquad 226$$

But $PV = nRT$ indicating that $P_A = n_AR/TV_B$ and $P_B = n_BRT/V_B$ hence substituting for P_A and P_B in equation 226, we have,

$$dW = n_A RT \frac{dV_A}{V_A} + n_B RT \frac{dV_B}{V_B} \qquad 227$$

We can integrate equation 227(for one mole of a gas) within some boundary conditions as follows,

$$\int dW = RT \int_{V_A}^{V_A+V_A} \left(\frac{dV_A}{V_A}\right) + RT \int_{V_B}^{V_A+V_B} \left(\frac{dV_B}{V_B}\right) \qquad 228$$

$$W = RT[lnV_A]_{V_A}^{V_A+V_A} + RT[lnV_B]_{V_B}^{V_A+V_A} \qquad 229$$

$$W = RTln\left(\frac{V_A+V_A}{V_A}\right) + RTln\left(\frac{V_A+V_A}{V_B}\right) \qquad 230$$

Applying Avogadro's law, which states that at constant temperature and pressure, equal volume of all gases contain the same number of molecules. This law allows us to substitute molecules or moles for volume, hence, $V_A = n_A$ and $V_B = n_B$. If this is done, then equation 230 becomes, 231

$$W = RTln\left(\frac{n_A+n_A}{n_A}\right) + RTln\left(\frac{n_A+n_A}{n_B}\right) \qquad 231$$

Again, mole fraction of A, in a mixture, A+B is given as $X_A = n_A/n_A + n_B$ and that of B is given as $X_B = n_B/n_A + n_B$. Therefore, introducing mole fractions into equation 231, we have,

$$W = RTln\left(\frac{1}{X_A}\right) + RTln\left(\frac{1}{X_B}\right) \qquad 232$$

$$W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right] \qquad 233$$

Therefore, we conclude that the work done in mixing ideal gases is respective sum of the product of the logarithm of the mole fraction, multiplied by RT. Therefore we have,

$$\boldsymbol{W = -RT[ln(X_A) + ln(X_B)]}$$

$$\boldsymbol{W = \frac{-RT\sum n_i ln(X_i)}{\sum n_i} = \frac{-RT\sum n_i ln(X_i)}{n}\ (workdone\ per\ mole. \sum n_i = n)}$$

$$\boldsymbol{W = -RT\sum\left(\frac{n_i}{n}\right) ln(X_i) = \sum X_i ln(X_i)\ \ (workdone\ per\ mole, \frac{n_i}{n} = X_i)}$$

2.1.2 Entropy of mixing

Equation 233 reveals that the work done in mixing two ideal gases is proportional to the reciprocal of their mole fractions. Since the work done is the heat absorbed, we can derive expression for the entropy of mixing the gases by dividing equation 233 by T, hence,

$$\Delta S_{mix} = R\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right] = -R[ln(X_A) + ln(X_B)] \qquad 234$$

If the number of molecules A and B are equal to n_A and n_B respectively, then the change in entropy of mixing can be written as follows

$$\Delta S_{mix} = -R[n_A ln(X_A) + n_B ln(X_B)] \qquad 235$$

From the above equation, we can deduce that for i number of molecules, the change in entropy of mixing is given as,

$$\Delta S_{mix} = -R\sum n_i ln(X_i) \qquad 236$$

If we are interested in the change in entropy per mole, equation 180 must be divided by the total number of moles (i.e $\sum n_i = n, also\ that$ $\mathrm{Xi} = \mathrm{ni/n}$. Therefore, equation 236 becomes,

$$\Delta S_{mix} = \frac{-R\sum n_i ln(X_i)}{\sum n_i} = \frac{-R\sum n_i ln(X_i)}{n} = -R\sum\left(\frac{n_i}{n}\right) ln(X_i) = -R\sum X_i ln(X_i) \qquad 237$$

From the above, we conclude that for mixtures of gases, the change in entropy of mixing is given as,

$$\boldsymbol{\Delta S_{mix} = -R\sum X_i ln(X_i)}$$

Solved problem 1

(a) Show that the work done in mixing two ideal gases, A and B can be written as,

$W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$.

(b) If 0. 56 moles of gas A is mixed with 0.45 moles of gas B at 298 K, calculate the work done in mixing the two gases.

(c) Use the data given in option ‘b’ above to calculate the entropy change of mixing the two gases

Solution

The work done in mixing gas A with gas B is equal to the sum of the work done by gas A and that done by gas B. Again, work done is equal to heat absorbed. Therefore we state that the total work done in mixing gases A and B can be written as, W = W_A + W_B = q hence,

$$dW = dq = W_A + W_B \qquad 1$$

$$= P_A dV_A + P_B dV_B \qquad 2$$

But PV = nRT indicating that $P_A = n_A R/TV_B$ and $P_B = n_B RT/V_B$ hence substituting for P_A and P_B in equation 2, we have,

$$dW = n_A RT\frac{dV_A}{V_A} + n_B RT\frac{dV_B}{V_B} \qquad 3$$

We can integrate equation 3 (for one mole of a gas) within some boundary conditions as follows,

$$\int dW = RT\int_{V_A}^{V_A+V_A}\left(\frac{dV_A}{V_A}\right) + RT\int_{V_B}^{V_A+V_B}\left(\frac{dV_B}{V_B}\right) \qquad 4$$

$$W = RT[lnV_A]_{V_A}^{V_A+V_A} + RT[lnV_B]_{V_B}^{V_A+V_A} \qquad 5$$

$$W = RTln\left(\frac{V_A+V_A}{V_A}\right) + RTln\left(\frac{V_A+V_A}{V_B}\right) \qquad 6$$

Applying Avogadro’s law, which states that at constant temperature and pressure, equal volumes of all gases contains the same number of molecules. This law allows us to substitute molecules or moles for volume, hence, $V_A = n_A$ and $V_B = n_B$. If this is done, then equation 6 becomes equation 7

$$W = RTln\left(\frac{n_A+n_A}{n_A}\right) + RTln\left(\frac{n_A+n_A}{n_B}\right) \qquad 7$$

Again, mole fraction of A, in a mixture, A+B is given as $X_A = n_A/n_A + n_B$ and that of B is given as $X_B = n_B/n_A + n_B$. Therefore, introducing mole fractions into equation 7, we have,

$$W = RTln\left(\frac{1}{X_A}\right) + RTln\left(\frac{1}{X_B}\right) \qquad 8$$

$$W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right] \qquad 9$$

(b) The mole fractions of A and B can be calculated as follows,

$$X_A = \frac{n_A}{n_A + n_B} = \frac{0.56}{0.56 + 0.45} = 0.5545$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{0.45}{0.56 + 0.45} = 0.4455$$

Therefore, the work done in mixing the gases is given as

$$W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$$

$$= 8.314\,Jmol^{-1}K^{-1} \times 298\,K\left[ln\left(\frac{1}{0.5545}\right) + ln\left(\frac{1}{0.4455}\right)\right] = 3464.21\,Jmol^{-1}$$

(c) Since the work done in mixing the gas is $W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$. The work done is equal to the heat absorbed, hence W = q and $W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$. Entropy change is defined as q/T, therefore,

$$\Delta S_{mix} = \frac{q}{T} = \frac{W}{T} = R\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$$

$$\Delta S_{mix} = 3464.21\frac{Jmol^{-1}}{298K}K = 11.62\,J\,mol^{-1}$$

3.1.3 Free energy of mixing

We can also calculate the free energy of mixing two gases, A and B as follows: Let us consider the relationship between chemical potential and molar free energy, thus $\mu_{Pure} = G/n$. where μ is the chemical potential and n is the total number of moles. From the equation, $G = n\mu$ indicating that for more than one component, the Gibbs free energy will be, $G = \sum_i n_1 \mu_i$ The total G of gas A and B before mixing can be written as follow,

$$G_1 = n_A \mu_A^0 + n_B \mu_B^0 \quad 238$$

μ^0 is the chemical potential of the pure component. Then after mixing, the free energy will be

$$G_2 = n_A \mu_A + n_B \mu_B \quad 239$$

Then the change in free energy of mixing will be given as $\Delta G_{mix} = G_2 - G_1$, hence

$$\Delta G_{mix} = \left(n_A \mu_A + n_B \mu_B\right) - \left(n_A \mu_A^0 + n_B \mu_B^0\right) \quad 240$$

Generally, $\mu_i = \mu_i^0 + RTlnX_i$, where X_i is the mole fraction of i. Therefore, equation 240 becomes equation 241, which simplifies to equations 242 and 243

$$\Delta G_{mix} = n_A\left(\mu_A^0 + RTlnX_A\right) + n_B\left(\mu_B^0 + RTlnX_B\right) - \left(n_A \mu_A^0 + n_B \mu_B^0\right) \quad 241$$

$$\Delta G_{mix} = n_A \mu_A^0 + n_B \mu_B^0 - n_A \mu_A^0 - n_B \mu_B^0 + n_A RTlnX_A + n_B RTlnX_B \quad 242$$

$$\Delta G_{mix} = n_A RTlnX_A + n_B RTlnX_B \quad 243$$

Equation, 243 reveal that the change in Gibbs free energy for mixture of i number of ideal gases can be estimated from the following equation,

$$\Delta G_{mix} = RT \sum n_i lnX_i \quad 244$$

Consequently, the free energy change of mixing per mole can be obtained by dividing equation 244 by the total number of moles as follows,

$$\Delta G_{mix} = \frac{RT \sum n_i lnX_i}{\sum n_i} \quad 245$$

Note that mole fraction is given as $X_i = (n_i/n)$ and that $\sum n_i = n$. Therefore equation 245 can be written as,

$$\Delta G_{mix} = \frac{RT \sum n_i lnX_i}{n} = RT \sum \left(\frac{n_i}{n}\right) lnX_i = RT \sum X_i lnX_i \quad 246$$

Therefore, we conclude that for mixture of ideal gases, the free energy of mixing is the algebraic sum of the product of the mole fraction multiply by the natural logarithm of the mole fraction and by RT. That is

$$\Delta G_{mix} = RT \sum X_i lnX_i$$

3.1.4 Enthalpy of mixing

The change in enthalpy of mixing can be calculated using the Gibbs Helmoltz equation. Thus,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad 247$$

We know that $\Delta G_{mix} = RT\sum X_i lnX_i$ and that $\Delta S_{mix} = -R\sum X_i lnX_i$. Therefore, $-T\Delta S_{mix} = RT\sum X_i lnX_i$. Hence equation 247 becomes,

$$RT\sum X_i lnX_i = \Delta H_{mix} + RT\sum X_i lnX_i \qquad 248$$

The mathematical implication of equation 248 is that $\Delta H_{mix} = 0$. Hence we conclude that the change in enthalpy of mixing is zero. That is

$$\boldsymbol{\Delta H_{mix} = 0}$$

Solved problem 2

(a) Show that the free energy of mixing two ideal gases, A and B is a function of the mole fraction and the number of moles.

(b) Calculate the free energy of mixing gases A and B if their number of moles are 0.56 and 0.45 respectively. Hence state with reason, whether the mixing is spontaneous or not.

Solution

(a) The relationship between chemical potential and molar free energy, is $\mu_{Pure} = G/n$. where μ is the chemical potential and n is the total number of moles. From the equation, G = nμ indicating that for more than one component, the Gibbs free energy will be, $G = \sum_i n_1 \mu_i$ The total G of gas A and B before mixing can be written as follow;

$$G_1 = n_A\mu_A^0 + n_B\mu_B^0 \qquad 1$$

μ^0 is the chemical potential of the pure component. Then after mixing, the free energy will be

$$G_2 = n_A\mu_A + n_B\mu_B \qquad 2$$

Then the change in free energy of mixing will be given as $\Delta G_{mix} = G_2 - G_1$, hence

$$\Delta G_{mix} = (n_A\mu_A + n_B\mu_B) - (n_A\mu_A^0 + n_B\mu_B^0) \qquad 3$$

Generally, $\mu_i = \mu_i^0 + RTlnX_i$, where X_i is the mole fraction of i. Therefore, equation 3 becomes equation 4, which simplifies to equations 5 and 6

$$\Delta G_{mix} = n_A(\mu_A^0 + RTlnX_A) + n_B(\mu_B^0 + RTlnX_B) - (n_A\mu_A^0 + n_B\mu_B^0) \qquad 4$$

$$\Delta G_{mix} = n_A\mu_A^0 + n_B\mu_B^0 - n_A\mu_A^0 - n_B\mu_B^0 + n_ARTlnX_A + n_BRTlnX_B \qquad 5$$

$$\Delta G_{mix} = n_ARTlnX_A + n_BRTlnX_B \qquad 6$$

(b) The mole fractions of A and B can be calculated as follows,

$$X_A = \frac{n_A}{n_A + n_B} = \frac{0.56}{0.56 + 0.45} = 0.5545$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{0.45}{0.56 + 0.45} = 0.4455$$

Therefore,

$$\Delta G_{mix} = n_A RTlnX_A + n_B RTlnX_B$$

$$= 0.56(8.314\,Jmol^{-1}K^{-1})(298K)\ln(0.5545)\ \ 0.45(8.314\,Jmol^{-1}K^{-1})(298K)\ln(0.4455)$$

= -1719.62 J/mol

The mixing is spontaneous because ΔG_{mix} is negative.

3.1.5 Change in volume of mixing ideal gases

Recall that we have shown that for an infinitesimal change in free energy,

$$dG = VdP - SdT$$

At constant temperature, dV = 0 and we have,

$$dG = VdP \ or \ \left(\frac{dG}{dP}\right)_T = V$$

For a change in volume, ΔV

$$\left(\frac{d(\Delta G)}{dP}\right)_T = \Delta V$$

Since the total Gibbs free energy of mixing is $RT\sum X_i lnX_i$, then we have

$$\left(\frac{d(\Delta G_{\mathrm{mix}})}{dP}\right)_T = \Delta V_{\mathrm{mix}}$$

$$\left(\frac{d(\Delta G_{\mathrm{mix}})}{dP}\right)_T = \Delta V_{\mathrm{mix}} = \left(\frac{d(RT\sum X_i lnX_i)}{dP}\right)_T = 0$$

Hence we conclude that for mixtures of ideal gases, total volume do not change but equals to the sum of the volume of the individual component, after mixing.

3.1.6 Change in Helmholtz free energy of ideal gas mixture

A is defined as A = U + TS. But G = U + PV + TS = A + PV. Therefore, the underlisted equations are also true,

$$\Delta G = \Delta A + P\Delta V$$

$$\Delta G_{mix} = \Delta A_{mix} + P\Delta V_{mix}$$

However, $\Delta V_{mix} = 0$, which implies that the change in Helmoltz free energy of mixing ideal gas is equal to the change in Gibbs free energy of mixing. Hence,

$$\boldsymbol{\Delta A_{mix} = RT\sum X_i lnX_i}$$

Solved problem 3

(a) Show that for a mixture of two gases, A and B, the change in enthalpy of mixing is zero.

(b) Show that for a mixture of gases, the total volume do not change but is the sum of the volumes of the individual components.

(c) Show that the change in Helmholtz energy of mixing ideal gas is equal to the change in free energy of mixing.

Solution

(a) The change in enthalpy of mixing can be calculated using the Gibbs Helmoltz equation. Thus,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad 1$$

We know that $\Delta G_{mix} = RT\sum X_i lnX_i$ and that $\Delta S_{mix} = -R\sum X_i lnX_i$. Therefore, $-T\Delta S_{mix} = RT\sum X_i lnX_i$. Hence equation1 becomes,

$$RT\sum X_i lnX_i = \Delta H_{mix} + RT\sum X_i lnX_i \qquad 2$$

The mathematical implication of equation 192b is that $\Delta H_{mix} = 0$. Hence we conclude that the change in enthalpy of mixing is zero.

(b) For an infinitesimal change in free energy,

$$dG = VdP - SdT$$

At constant temperature, dV = 0 and we have,

$$dG = VdP \; or \; \left(\frac{dG}{dP}\right)_T = V$$

For a change in volume, ΔV

$$\left(\frac{d(\Delta G)}{dP}\right)_T = \Delta V$$

Since the total Gibb free energy of mixing is $RT\sum X_i lnX_i$, then we have

$$\left(\frac{d(\Delta G_{\text{mix}})}{dP}\right)_T = \Delta V_{\text{mix}}$$

$$\left(\frac{d(\Delta G_{\text{mix}})}{dP}\right)_T = \Delta V_{\text{mix}} = \left(\frac{d(RT\sum X_i lnX_i)}{dP}\right)_T = 0$$

Hence we conclude that for mixture of ideal gases, total volume do not change but is equal to the sum of the volumes of the individual component, after mixing.

(c) A is defined as A = U + TS. But G = U + PV + TS = A + PV. Therefore, the underlisted equations are also true,

$$\Delta G = \Delta A + P\Delta V$$

$$\Delta G_{mix} = \Delta A_{mix} + P\Delta V_{mix}$$

However, $\Delta V_{mix} = 0$, which implies that the change in Helmoltz free energy of mixing ideal gas is equal to the change in Gibbs free energy of mixing.

4.0 Summary and conclusion

i. The work done in mixing ideal gases is related to the mole fraction, the gas constant and the temperature, $W = RT\left[ln\left(\frac{1}{X_A}\right) + ln\left(\frac{1}{X_B}\right)\right]$

ii. The entropy of mixing ideal gases is related to the number of moles of the gases, mole fraction and gas constant, $\Delta S_{mix} = -R\sum n_i ln(X_i)$

iii. The change in free energy of mixing ideal gases is a function of the logarithm of the mole fraction, gas constant, temperature and total number of moles, i.e $\Delta G_{mix} = RT\sum n_i lnX_i$

iv. The enthalpy of mixing ideal gases is zero, i.e $\Delta H_{mix} = 0$.

v. The change in volume of mixing ideal gases is a function of the differential of Change in Gibb free energy to the differential of change in pressure and is equal to zero, i.e,

$$\left(\frac{d(\Delta G_{\text{mix}})}{dP}\right)_T = \Delta V_{\text{mix}} = \left(\frac{d(RT\sum X_i lnX_i)}{dP}\right)_T = 0$$

vi. The change in Helmholtz work function of mixing ideal gases is a function of the total number of moles, the gas constant, temperature and the logarithm of the total number of moles,

$$\Delta A_{mix} = RT \sum X_i lnX_i$$

It can be concluded that thermodynamic properties of mixtures do not respond to simple laws of addition but is a complex function of other properties.

5.0 Conclusions

Mixture of ideal gases often displayed properties that are not additives and that are mostly at variance from their initial state. Commonly accessible thermodynamic properties of ideal gas mixtures are related to enthalpy, entropy, free energy change, work done, Helmholtz work function and change in volume.

6.0 Tutor mark assignment

1. What are the major consequences of thermodynamics of mixture of ideal gas?
2. What are the changes expected for the underlisted properties when ideal gases are mixed;

i. work done

ii. Change in volume

iii. Free energy change

iv. Change in work function

v. Change in volume

vi. Change in entropy

vii. Change in enthalpy

3. Derive appropriate expression to show that the Helmoltz free energy of mixing ideal gases is given as $\Delta A_{mix} = RT \sum X_i lnX_i$

7.0 References

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MODULE 4

UNIT 3: Introduction to statistical thermodynamics

1.0 Introduction

Statistical thermodynamics is a branch of statistical mechanics, an aspect of theoretical physics that uses probability theory to study the average behaviour of a mechanical system where the state of the system is uncertain. The primary goal of statistical thermodynamics (also known as equilibrium statistical mechanics) is to explain the classical thermodynamics of materials in terms of the properties of their constituent particles and the interactions between them. In other words, statistical thermodynamics provides a connection between the macroscopic properties of materials in thermodynamic equilibrium, and the microscopic behaviours and motions occurring inside the material.

Every system consists of smaller particles which may include atom, molecules, ions, etc. These smaller particles constitute the microscopic component of the system. Virtually, all macroscopic systems are built up from the micro-components. In chemistry, the macroscopic system involves the study of bulk properties of matter which deals with samples in the dimension of the order, 10^{23} molecules or particles. The main theoretical framework for the study of bulk properties is thermodynamics (for equilibrium processes) or kinetics (for non equilibrium phenomena). However, the study of the micro systems operates on the framework of quantum/classical mechanics. Quantum mechanics deals with detailed arrangements and motion of molecules of matter while thermodynamics deals with the average behaviour of matter.

Concepts handled in macroscopic study include thermodynamic properties such as internal energy, enthalpy, entropy, heat capacities, Gibbs and Helmoltz free energies, etc. These concepts are governed by laws of thermodynamics. On the other hand, the microscopic study involves wave functions, particle momenta, kinetic and potential energies, etc.

Since the macroscopic systems are built from the microscopic systems, we can state that the properties of the macroscopic systems are related to those of the corresponding microsystems. Statistical thermodynamics seeks to study the link between the macro and the micro systems. This implies that statistical thermodynamics provides solutions for finding the properties of a bulk sample from the properties of molecules. Any principle or theory seeking to link macroscopic and microscopic properties must rely on statistics, hence statistical thermodynamics is a significant area in the physical sciences.

2.0 Objectives

i. To understand what is statistical thermodynamics and significance of partition function in statistical thermodynamics

ii. To know the properties of macroscopic systems

iii. To be able to state the basic postulates of statistical thermodynamics

iv. To know and apply the relationship between partition function and some thermodynamics functions including enthalpy, internal energy, heat capacity,etc.

v. To know and apply Stirling’s approximation in solving statistical thermodynamic problems

vi. To understand the concept of distribution law in statistical thermodynamics and know the basic approaches to the development of distribution law

vii. To know the major distribution laws, namely Maxwell Boltzmann, Bose-Einstein distribution and Femi-Dirac distribution laws

viii. To know and interprete expression for the Maxwell Boltzmann statistics

3.0 Main text

3.1 Properties of macroscopic system

Macroscopic systems exhibit three important properties which distinguish them from microscopic systems. These properties are

i. In macroscopic systems, there exist an irreversible process leading to equilibrium states in which the properties of the system do not depend on time (and there are no mass flows), $e^{-E_i\beta}$

ii. The equilibrium states are uniquely specified by a very small number of parameters (for one-component systems only three parameters are sufficient, e.g. T, V, N).

iii. Properties of macroscopic systems are in general random variables with small relative fluctuations.

Microstate is the microscopic state of the system specified by a small number of parameters that need to defined it

3.2 Fundamental postulates of statistical thermodynamics

The first postulate is the **Priori assumption**. This postulate states that all microstate of a given energy are equally probable and the equilibrium microstate must have overwhelming disorder number, Ω

_**Ergodic hypothesis**: An ergodic state is one that evolves over time to explore "all accessible" states: all those with the same energy and composition. In an ergodic system, the microcanonical ensemble is the only possible equilibrium ensemble with fixed energy. This approach has limited applicability, since most systems are not ergodic.

Principle of indifference: In the absence of any further information, we can only assign equal probabilities to each compatible situations.

Maximum information entropy: A more elaborate version of the principle of indifference states that the correct ensemble is the ensemble that is compatible with the known information and that has the largest Gibbs entropy (information entropy).

Solved problem 1

With the aid of a suitable plot (where necessary), discuss the two major postulates of statistical thermodynamics.

The first postulate is the **Priori assumption**. This postulate states that all microstates of a given energy are equally probable and the equilibrium microstate must have overwhelming disorder number, Ω. Fig. 1 presents the pattern of plot expected for the variation of Ω with microstates. The plot shows that at the equilibrium, maximum peak is obtained but at some other points, the microstates remain constant.

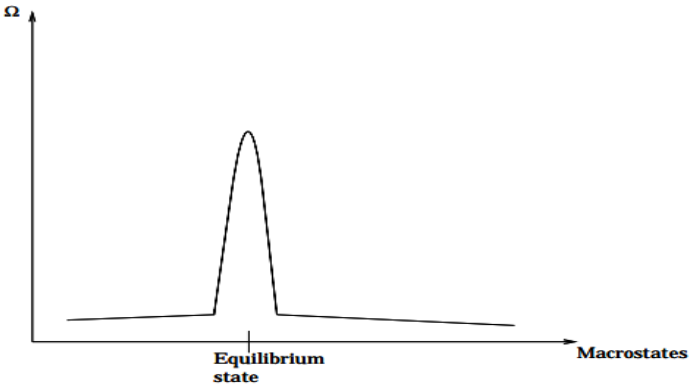


Fig. 1: Variation of Ω with microstate

The second postulate

The second postulate is the Postulate of ergodicity. This postulate states that the time-averaged properties of a thermodynamic system, i.e the properties manifested by the collection of molecules as they proceed through their natural dynamics, are equal to the properties obtained by weighted averaging over all microstates in the ensemble

3.3 Partition function

The probability of finding a system in the ith quantum state with energy E_i is proportional to the Boltzman factor ((exp(-E_i/kT)) and can be expressed as follows,

$$P_i = ce^{\frac{-E_i}{kT}} \qquad 1$$

where P_i is the probability of finding a system in the ith quantum state, E_i is the energy of ith quantum state, T is the equilibrium temperature, c is the probability constant and k is the Boltzmann constant. The Boltzmann constant has a numerical value, which can be calculated from the gas constant and Avogadro's number as follows;

$$k = \frac{R}{N} = \frac{8.314 \times JK^{-1}mol^{-1}}{6.023 \times 10^{23} mol} = 1.380 \times 10^{23} JK^{-1} \qquad 2$$

A close examination of equation 1 reveals that it conforms to some common equations in kinetics. For example,

i. The probability of finding a gas molecule with velocity, v_x in the x direction is given as

$$P_x \;\; \alpha \; e^{\frac{-mv_x^2}{2kT}} \;\; or \;\; P_x \;\; \alpha \; e^{\frac{-E_k}{kT}} \qquad 3$$

where E_k is the kinetic energy of the gas molecule {note, E_k = $E_k \; \frac{-mv_x^2}{2}$}

ii. The rate constant is related to the fraction of molecule having energy equal to or greater than the activation energy according to the following equation,

$$Rate \;\; \alpha \; e^{\frac{-E_a}{kT}} \;\; or \;\; Rate \;\; \alpha \; e^{\frac{E_a}{RT}} \qquad 4$$

The common term in the above equations is 1/kT, which can be symbolised as $\beta = 1/kT$. Hence equation 1 can be written as

$$P_i = ce^{-E_i\beta} \qquad 5$$

The probability constant, C can be derived by first assuming that the sum of probabilities over all possible quantum states is equal to unity. Therefore,

$$\sum_i P_i = 1 \qquad 6$$

It follows from equation 5 and 6 that

$$\sum_i P_i = 1 = c\sum_i e^{-E_i\beta} \qquad 7$$

Hence, $c = \frac{1}{\sum_i e^{-E_i\beta}}$. The denominator is a significant term and is given the special name, partition function. That is $c = \frac{1}{Q} = \frac{1}{\sum_i e^{-E_i\beta}}$. The symbol, Q means sum over states. Q is an important factor because most thermodynamic properties can be defined in terms of Q. It describes how energy is partitioned among the possible quantum states of the system. Q also connects the mechanical properties with thermodynamic properties. It connects the mechanical properties through the quantised energy, E_i and connects the thermodynamic properties through

Tlnβ = 1/kT. Therefore, Q = f(T,V,N). V and N are functions of mechanical variables while T is a function of thermodynamic variables.

It is worth stating that the normalization constant for a system in state having energy, E_i is 1/Q, Therefore, we can write the probability that the system is in state i, with energy Ei, as

$$P_i = \frac{e^{-E_i\beta}}{Q} \qquad 8$$

The importance of the molecular partition function is that it contains all the information needed to calculate the thermodynamic properties of a system of independent particles.

3.3.1 Partition function and internal energy.

The internal energy of a system is the sum total of all energies the system possesses. This will include all the kinetic and potential energy terms such as translational, rotational, vibrational, electronic, nuclear and mass energies contribution. It has been found that at 1000 K, the major contributors to the internal energy of a system are rotational, vibration and translational energies. For 1 mol of a gas, the contributions to the internal energy are summarised below,

Energy	**Contribution**
Translational energy ($E_{\text{thermal, Trans.}}$)	½ RT
Rotational energy ($E_{\text{thermal, Rot.}}$)	½ RT
Vibrational energy ($E_{\text{thermal, Vib.}}$)	$\frac{RTx}{e^{x}-1}$, where x = hυ/kT

An ideal molecule having N as the number of atoms, 3N degree of freedom, out of these, three degree of freedom will be assigned to translational motion leaving 3N-3 degree of freedom for rotational and vibrational motion. If the molecule is linear, will belong to translational motion, two for rotational motion, leaving 3N-5 for vibrational motion. On the other hand, for a non linear molecule, translational and rotational motions will take three degree of freedom, each, leaving 3N – 6 for vibrational motion.

The major concern of statistical thermodynamics to internal energy is to explore the relationship between internal energy, U and the partition function, P_i. We start by defining the internal energy as the average energy. That is

U = average energy 9

If the total molecular energy is represented by E_i as indicated before, then U can be expressed as a probability function, thus,

$$U = \sum_i E_i P_i \qquad 10$$

$$U = \sum_i E_i \frac{e^{-E_i\beta}}{Q} \qquad 11$$

$$= \frac{1}{Q}\sum_i E_i\, e^{-E_i\beta} \qquad 12$$

Equation 12 can be written according to equation 13 and be simplified to equation14 by introducing the normalization factor, Q

$$E_i \frac{e^{-E_i\beta}}{Q} = -\frac{\delta}{\delta\beta} e^{-E_i\beta} \qquad 13$$

$$E_i \frac{e^{-E_i\beta}}{Q} = -\frac{1}{Q}\frac{\delta}{\delta\beta} e^{-E_i\beta} \qquad 14$$

Since we are dealing with systems that involve different states, it is ideal to consider the statistical thermodynamic parameter of such system as the summation of all possible contributions. Therefore we introduce the summation sign to both sides of equation 14 as follows,

$$\sum_i E_i \frac{e^{-E_i\beta}}{Q} = -\sum_i \frac{1}{Q}\frac{\delta}{\delta\beta} e^{-E_i\beta} \qquad 15$$

$$= -\frac{1}{Q}\sum_i \frac{\delta}{\delta\beta} e^{-E_i\beta} \qquad 16$$

$$= -\frac{1}{Q}\frac{\delta Q}{\delta\beta} = -\frac{\delta lnQ}{\delta\beta} \qquad 17$$

Therefore, $U = -\frac{\delta lnQ}{\delta\beta}$ 18

The expression in equation 18 gives the dependence of U on the partition function. Q is an extremely large dimensionless factor but its natural logarithm is relatively smaller. It also follows that other thermodynamic functions will also have some level of dependence on Q and we shall apprehend these as we progress.

We had defined the term, β ($\beta = 1/kT$)as a constant that is a function of temperature. This implies that we can also expresses the internal energy as a function of temperature. This also indicate that if we introduce differentials of temperature into equation 18, the significance of the equation will not be affected. Therefore,

$$-\frac{\delta lnQ}{\delta\beta} = -\frac{\delta lnQ}{\delta T} \cdot \frac{dT}{\delta\beta} \qquad 19$$

Recall that β = 1/kT, T = 1/kβ, then $\frac{dT}{\delta\beta}$ will be equal to $-kT^2$ and if we substitute for $\frac{dT}{\delta\beta}$ in equation 19, we have,

$$U = -\frac{\delta lnQ}{\delta\beta} = kT^2\frac{\delta lnQ}{\delta T} \qquad 20$$

Equation 20 simplifies the relationship between U, Q and T. This is a fundamental equation that can be used to analyse the relationship between Q and other thermodynamic parameters.

3.3.2 Partition function and Heat capacity

Heat capacity can be defined as the amount of heat transferred divided by the change in temperature. Mathematically, we express heat capacity as,

$$C = \frac{dq}{dT} \qquad 21$$

There are two major conditions under which heat can be transferred to a body, viz. constant volume and constant pressure. One of the major consequences of the first law of thermodynamics is that the heat absorbed at constant volume and at constant pressure is approximately equal to the change in internal energy and enthalpy change respectively. Therefore, we can define the heat capacity at constant volume and at constant pressure according to equations 22 and 23 respectively:

$$C_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v \qquad 22$$

$$C_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \qquad 23$$

Using equations 20 and 22, we can derive an expression for the relationship between C_v and Q. Therefore,

$$C_v = \left(\frac{dU}{dT}\right)_v = \frac{\partial}{\partial T}\left[kT^2\frac{\delta lnQ}{\delta T}\right] \qquad 24$$

Equation 24 can be differentiated using the product rule. For example, given a function, y = uv, where u and v are functions of x, then $\frac{dy}{dx}$ = V$\frac{dy}{dx}$ + U$\frac{dV}{dX}$. This means we first keep the first function and differentiate the other and reverse the order. The final differential is the summation of the two separate terms. From the present problem, we can state that u = kT^2 and v = $\frac{\delta lnQ}{\delta T}$. Therefore, du/dT = 2kT and $\frac{dv}{dT} = \left(\frac{\delta^2 lnQ}{\delta T^2}\right)$. Hence C_v can be expressed as follow

$$C_v = \left(\frac{dU}{dT}\right)_v = 2kT\left(\frac{\delta lnQ}{\delta T}\right) + kT^2\left(\frac{\delta^2 lnQ}{\delta T^2}\right) \qquad 25$$

Application of one of the principles of statistical thermodynamics, equation 25 simplifies to equation 26

$$C_v = \left(\frac{dU}{dT}\right)_v = 2kT\frac{\delta lnQ}{\delta T} + kT^2\frac{\delta^2 lnQ}{\delta T^2} \qquad 26$$

From thermodynamics, we know that C_p is always higher than C_v by an amount equal to the gas constant, R. therefore, having known C_v we can write an expression for C_p as follows,

$$C_p = C_v + R = \left[2kT\frac{\delta lnQ}{\delta T} + kT^2\frac{\delta^2 lnQ}{\delta T^2}\right] + R \qquad 27$$

3.3.3 Partition function and entropy

Mathematically, the entropy of a system is defined as the ratio of heat absorbed to the temperature. At constant volume, the heat absorbed is equal to the change in internal energy, hence

$$dS = \frac{dq}{dT} = \frac{dU}{dT} \qquad 28$$

The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. This implies that all pure compounds or a nice system have entropy equal to zero at 0 K. This law enables us to evaluate values of entropy from absolute zero temperature and at some other temperature, T as expressed below,

$$\int_0^T dS = S(T) = 0 + \int_0^T \frac{C_v}{T}\, dT \qquad 29$$

The first term in the right hand of equation 29 indicates zero entropy at 0 K while the second term stands for the entropy change between the temperatures, 0 and T. Substituting for C_v (equation 26) in equation 29, we have

$$\int_0^T dS = S(T) = \int_0^T \left[2k\frac{\delta lnQ}{\delta T} + kT\frac{\delta^2 lnQ}{\delta T^2}\right] dT \qquad 30$$

The above equation can be simplified by solving the integral in parts. The first part of the integral is $\int_{\mathbf{0}}^{\mathbf{T}} 2k\frac{\delta lnQ}{\delta T} dT = [2klnQ]_{\mathbf{0}}^{\mathbf{T}}$**.** However, the second part of the equation can be simplified by using the integration formula, $\int_0^T udv = uv - \int_0^T vdu$. In the above example, if u = T , then we will have dv = $\frac{\delta^2 lnQ}{\delta T^2}$ hence we obtain

$$k\int_0^T T\frac{\delta^2 lnQ}{\delta T^2} = \left[kT\frac{\partial lnQ}{\partial T}\right]_0^T - k\int_0^T \frac{\partial lnQ}{\partial T}.dT \qquad 31$$

$$= \left[kT\frac{\partial lnQ}{\partial T}\right]_0^T - [klnQ]_T^0 \qquad 32$$

Combining the solutions obtained from the two integrals, we have

$$S(T) = [2klnQ]_{\mathbf{0}}^{\mathbf{T}} + \left[kT\frac{\partial lnQ}{\partial T}\right]_0^T - [klnQ]_T^0 \qquad 33$$

$$= [klnQ]_{\mathbf{0}}^{\boldsymbol{T}} + \left[kT\frac{\partial lnQ}{\partial T}\right]_0^T \qquad 34$$

$$= klnQ + kT\frac{\partial lnQ}{\partial T} \qquad 35$$

Equation 35 can further be expressed in terms of the internal energy. From equation 24, $U = kT^2\frac{\delta lnQ}{\delta T}$, then $kT\frac{\delta lnQ}{\delta T}$ = U/T hence equation 35 becomes

$$S(T) = klnQ + \frac{U}{T} \qquad 36$$

Multiplying both sides of equation 36 by T, we have T$S(T) = kTlnQ + U\ or\ U - TS = kTlnQ$. From thermodynamics, the Helmholtz free energy is defined as A = U – TS hence $A = U - TS = kTlnQ$. This expression is significant because it provides the avenue for obtaining the relationship between Q and numerous thermodynamic functions. Let us examine the following functions

i. $$S = \left(\frac{\partial A}{\partial T}\right)_V = -\frac{\partial kTlnQ}{\partial T} \qquad 37$$

ii. $$P = \left(\frac{\partial A}{\partial V}\right)_{T,N} = -kT\left(\frac{\partial lnQ}{\partial T}\right)_{T,N} \qquad 38$$

iii. $$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial lnQ}{\partial N}\right)_{T,V} \qquad 39$$

From the above and other derivations obtained in this section, it is evident that partition function has a broad spectrum of applications in the study of statistical thermodynamics. However before we can proceed to other applications of partition function, it is necessary to consider some of the major physical and mathematical meanings and implications of statistical function. First we consider a system that consists of other subsystems, then to a good approximation and assuming that there is no interaction between them, some thermodynamics properties of that system can be said to be the sum of the properties of the various subsystems that made up the system. For example, consider two subsystems, A and B making up a system, then the energy of the system can be written as $E_{j,i}^{AB} = E_j^A + E_i^B$. However, the partition function for this system is the product of the partition function for each of the system. That is, $Q_{AB} = Q_A Q_B$. Hence since the respective energy for the sates A and B are known, we can write the partition function for the combined system as

$$Q_{AB} = \sum_{i,j} e^{-\beta\left(E_j^A + E_i^B\right)} \qquad 40$$

We therefore conclude that thermodynamic properties of a system are additives. These will include the Helmoltz free energy (A), entropy (S), internal energy (U), heat capacity and other thermodynamic properties. Let us consider A for example,

$$A_{AB} = -kTlnQ_{AB} \qquad 41$$

$$= -kTlnQ_AQ_B \qquad 42$$

$$= -kTlnQ_A - kTlnQ_B \qquad 43$$

$$= A_A + A_B \qquad 44$$

The partition function for one mole of a system is given by the expression,

$$Q(T,V,1) = q(T,V) \qquad 45$$

It also follows that the partition function for two moles of a system can also be written as

$$Q(T,V,2) = q(T,V)^2 \qquad 46$$

And for N molecules in a system, the partition function has a general expression given in equation 47

$$Q(T,V,2) = q(T,V)^N \qquad 47$$

Based on the assumption that molecules are indistinquishable, the partition function can better be written as follows,

$$Q(T,V,2) = \frac{q(T,V)^N}{N!} \qquad 48$$

The symbol $N!$, meaning N factorial means 1x 2x 3.......N. for example 3! = 1x 2 x3 = 6. As stated earlier, the internal energy of a system is the sum total of all he energies the molecules of that system possess. This will include energies due to rotational, vibrational, translational, electronic, nuclear and other motions. It therefore implies that molecular partition function can be written to include these contributions as follows,

$$q = q_{Trans}.q_{Rot}.q_{Vib}.q_{Elect}.q_{Nucl}..q_{Others} \qquad 49$$

Combination of equations 48 and 49 gives equation 50

$$Q = \frac{q^N}{N!} = \frac{q_{Rot}^N}{N!}.q_{Vib}^N.q_{Trans}^N.q_{Elect}^N.q_{Nucl}^N.q_{Others}^N \qquad 50$$

Solved problem 2

What is the relationship between partition function and the following thermodynamic parameters

i. Pressure
ii. Enthalpy

iii. Chemical potential

iv. Free energy change

v. Translational enthalpy

vi. Translational heat capacity

vii. Translational internal energy

Solution:

i. Pressure

H = E + PV and A = E – TS

Therefore, $T\left(\frac{dA}{dV}\right)_v = -P$ = -NRT$\left(\frac{dlnQ}{dN}\right)_T$

ii. Enthalpy, H = U + PV but $T\left(\frac{dA}{dV}\right)_v = -P$. Hence P = -NRT$\left(\frac{dlnQ}{dN}\right)_T$

Substituting for U and P, we have

$$H = NKT^2\left(\frac{dlnQ}{dT}\right)_V + NKT\left(\frac{dlnQ}{dV}\right)_T V$$

$$H = NKT\left[\left(\frac{dlnQ}{dT}\right)_V + V\left(\frac{dlnQ}{dV}\right)_T\right]$$

iii. Chemical potential, μ = $\left(\frac{dA}{dn_i}\right)_{T,V,P} = \frac{d}{dn_i}[NKTlnQ]_{T,V,P}$

iv. Free energy change, G = H-TS = U + PV – TS = A + PV

= $NKTlnQ + \left[NKT\left(\frac{dlnQ}{dV}\right)_T - lnQ\right]$

v. Translational enthalpy

H = U + PV = U + RT but U = 3/2 RT indicating that,

$$H_t = \frac{3}{2}RT + RT = \frac{5}{2}RT$$

vi. Translational heat capacity,

$C_{pt} = \frac{H_t}{dT} = \frac{5}{2}RT$

$C_{Vt} = \frac{U_t}{dT} = \frac{d}{dT}\frac{d}{dT}\left(\frac{3}{2}RT\right) \quad \frac{3}{2}R$

vii. Translational internal energy = $\frac{3}{2}RT$

3.4 Stirling's approximation

In solving statistical thermodynamics problems we may encounter large numbers of N, making it difficult to estimate $N!$. Fortunately, Stirling's approximation offers a short cut to this task by using a logarithm or exponential analytical methods as shown in equation 51 and 52 respectively

$lnN! = NlnN - N$ 51

$N! = N^N e^{-N}$ 52

3.5 Distribution law

There are three approaches that can be used to define a statistical thermodynamics system. These approaches give rise to three major ensembles, namely,

i. Microcanonical ensemble, which is applicable to isolated systems with fixed N and E
ii. Canonical ensemble, which is applicable to a system in heat bath at constant temperature and fixed N
iii. Grand canonical ensemble, which is applicable to open systems and nothing is fixed

Each of these ensembles can be modelled and the probability of finding a microstate in a given macro state has been discussed before. Basically, There are two major ways of applying the equation that gives the probability of finding a microstate. In the first approach particles that can occupy any of the accessible quantum states is considered. These particles are distinguishable and the approach is referred to as classical statistics. The probability of the system occupying a certain microstate is given as, $P_i = ce^{\frac{-E_i}{kT}}$. The distribution law that is applicable to this system is the Maxwell-Boltzman distribution law

In the second approach, the system is considered to be in a certain quantum state, i, which may be occupied by various numbers of particles (boson and femions). This system is governed by two statistical laws, namely,

i. Bose-Einstein distribution law
ii. Femi-Dirac distribution law

Consider the distribution of N particles over the energy level, E_i. The number of ways of arranging the first particle will be,

$$C_1 = \frac{N!}{n_1(N-n_1)!} \quad 90$$

Similarly, the number of ways of arranging the second particle is give as

$$C_2 = \frac{N-n_1!}{n_2(N-n_1-n_2)!} \quad 91$$

The total ways of arranging the entire i particles will be given by,

$$\Omega = \frac{N!}{n_1(N-n_1)!} \, x \, \frac{N-n_1!}{n_2(N-n_1-n_2)!} \, x \ldots ....$$

$$= \frac{N!}{\Pi n_i!} \qquad 92$$

where i is the level of distribution. If the level has a degeneracy , g_i, it implies that any of the n_i particles can enter into any of the level. Therefore the number of ways of distributing the particles into g_i level is $g_i^{n_i}$ and for all levels, the number of ways is given as $\Pi g_i^{n_i}$, Hence the total number of combination is given as

$$\Omega = N! \frac{\Pi g_i^{n_i}}{\Pi n_i!} \qquad 93$$

3.5.1 Maxwell-Boltzmann statistics

Given an energy level, E and N molecules is to be distributed over this energy level. Then for the first level, the number of ways of assigning n_1 particle is given as

$$\Omega_1 = \frac{N!}{n_1!\,(N-n_1)!} \qquad 94$$

Similarly, the number of ways of assigning n_2 molecules is given by,

$$\Omega_2 = \frac{N-n_1!}{n_2!\,(N-n_1-n_2)!} \qquad 95$$

Hence the total number of ways of assigning the molecules is given by the product of all the distributions

$$\Omega = \frac{N!}{n_1!\ (N-n_1)!} \, x \, \frac{N-n_1!}{n_2!\ (N-n_1-n_2)!} \ldots \ldots x..$$

$$= \frac{N!}{n_1 n_2 \ldots n_i} = \frac{N!}{\Pi n_i} \qquad 96$$

The symbol, Π means product of $n_1n_2.......n_i$. Level ith is assumed to has degeneracy , g_i, which implies that n_i molecule can enter into any of the g_i levels and the number of ways this can occur is given by $g_i^{n_i}$ and for all the molecules, we multiply all the respective functions together and have, $\Pi g_i^{n_i}$. Therefore, the total number of ways of assigning N molecules will involve multiplying equation 96 with the total number of ways the molecules can enter into the accessible quantum states and we have,

$$\Omega = \quad N! \, \Pi \frac{g_i^{n_i}}{n_i!} \qquad 97$$

From fundamental laws of statistical thermodynamics, $\sum n_i = N$ and $\sum n_i E_i = E$. E represent the total energy and N is the total number of molecules. From the logarithm of equation 97, we have,

$$ln\Omega = lnN! + \sum_i n_i lng_i - \sum \ln(n_i)! \qquad 98$$

We can apply the Stirling approximation theory, the above equation can be simplified to the under listed form,

$$ln\Omega = NlnN - N + \sum n_i lng_i - \sum[n_i \ln(n_i) - n_i] \qquad 99$$

Note the last term in equation 99 is equal to 1 (i.e, $\sum n_i = N$) hence the equation simplifies to,

$$ln\Omega = NlnN + \sum n_i lng_i - \sum n_i \ln(n_i) \qquad 100$$

$$\text{Or } ln\Omega = NlnN + \sum n_i ln\left(\frac{g_i}{n_i}\right) \qquad 101$$

If N is too large, then the term, NlnN will vanish and

$$d(ln\Omega) = \sum n_i d(lng_{i)} + lng_i(dn_i) - n_i d(lnn_i) - \ln(n_i)dn_i \qquad 102$$

$$= \sum_i ln\left(\frac{g_i}{n_i}\right) dn_i + \sum_i dln\left(\frac{g_i}{n_i}\right) n_i \qquad 103$$

Since $\sum dn_i = 0$ and $\sum dn_i E_i = 0$ at fixed N and E respectively, the above equation can be reduced to

$$\sum_i ln\left(\frac{g_i}{n_i}\right) dn_i = 0 \qquad 104$$

Introducing α and β as constants, thus, $\alpha \sum dn_i = 0$ and $-\beta \sum dn_i E_i = 0$ and combining these expression with equation 104, we have,

$$\sum_i ln\left(\frac{g_i}{n_i}\right) dn_i + \alpha \sum dn_i - -\beta \sum dn_i E_i = 0 \qquad 105$$

$$= \sum_i \left(ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta E_i\right) dn_i = 0 \qquad 106$$

Under the prevailing condition, that is the condition at which α and β are chosen, the above equation becomes,

$$ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta E_i = 0 \qquad 107$$

Hence, the microstate becomes,

$$n_i = g_i e^{\alpha} e^{-\beta E_i} \qquad 108$$

$$= \frac{Ng_i}{\sum g_i e^{-\beta E_i}} e^{-\beta E_i}$$

$$= \frac{Ng_i}{Q} e^{-\beta E_i} \qquad 109$$

The above equation gives the Maxwell-Boltzman distribution law. Q is the partition function.

Solved problem 3

Given four independent molecules, a, b, c and d, intended to be distributed among two energy states (the distribution is equally probable)

(a) Calculate the number of arrangements that can be achieved in the distribution.

(b) If the energy of the system is given as E = $3E_1 + E_3$, Calculate the number of complexions that will be achieved.

Solution

The number of arrangements is given as $\Omega = \frac{N!}{\Pi n_i!} = \frac{4!}{2!.2!}$ = 6. This can be illustrated as follows,

Molecules in state 1	**Molecules in state 2**
a, b	c,d
a,c	b,d
a,d	b,c
b, c	a,d
b.d	a,c
c.d	a, b

(b) If the energy is specified, the distribution can be illustrated as follows

E_4	-	-	-	-
E_3	d	c	b	a
E_2	-	-	-	-
E_1	a,b,c	a,b,d	a,c,d	b,c,d

In the first case, $n_1 = 3$, $n_2 = 0$, $n_3 = 1$ and $n_4 = 0$. Therefore, $\Omega = \frac{N!}{\Pi n_i!} = \frac{4!}{3!.1!}$ = 4

Solved problem 4

What are the major limitations of Maxwell-Boltzmann distribution law

There are two major limitations of Maxwell-Boltzmann statistics. They include:

- **i.** Boltzmann statistics is centred on the existence of large value of n_i. However, n_i is not always large.
- **ii.** Boltzmann statistics neglects some microstates, whereas the equilibrium distribution should be weighted against all possible micro states

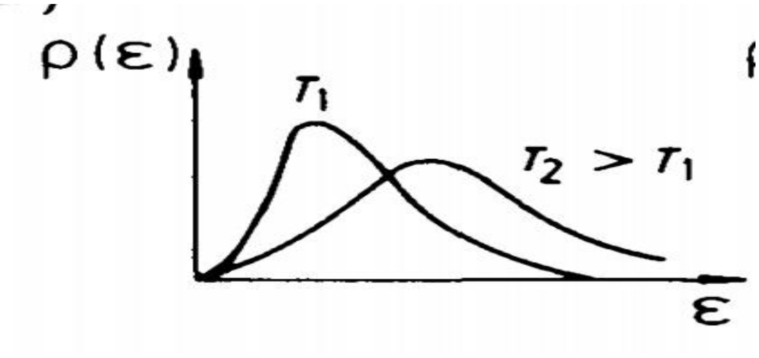
State the major difference between Maxwell-Boltzmann and Fermi-Dirac statistics. What will be the nature of energy distribution functions for the respective statistics, given two temperatures

Solutions

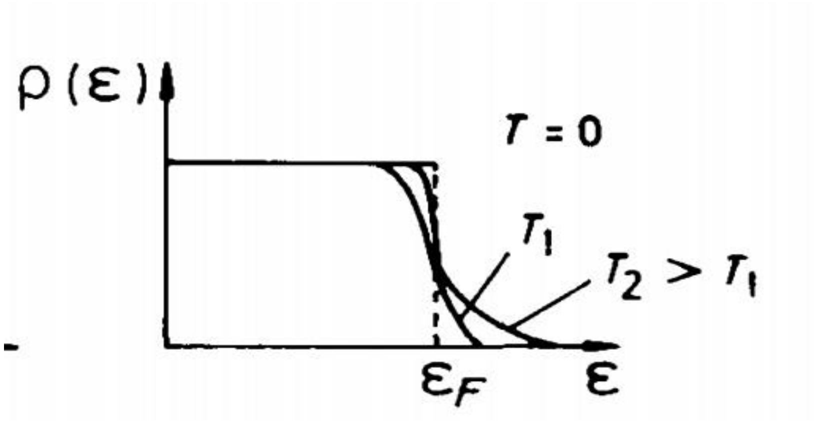
The Fermi-Dirac statistics has additional assumptions which include the following,

- i. Identical particles cannot be distinguished from one another: Principle of indistinguishibility
- ii. Pauli exclusion principle is applicable. i.e not more than one particle can occupy a quantum state

However, in the limit of non-degeneracy, Fermi-Dirac statistics becomes Maxwell-Boltzmann statistics. The expected plots for the energy functions for Maxwel-Boltzmann and Fermi-Dirac statistics are shown below:



(a) Maxwell-Boltzmann



(b) Fermi-Dirac

Solved problem 5

What are the features of Maxwell-Boltzmann statistics with respect to distnguishability of particle?

Solution

Maxwell-Boltzmann statistics: For a localised system, the particles are distinguishable and there is no limitation to the number of particles that can be accommodated in a singlet quantum state. The average number of particles that can accommodate an energy level, E_i is given as :

$$n_i = g_i e^{\alpha} e^{-\beta E_i}$$

4.0 Summary

i. Statistical thermodynamics uses statistics to connect macroscopic and microscopic properties of a system.

ii. The macroscopic system involves the study of bulk properties of matter which deals with samples in the dimension of the order, 10^{23} molecules or particles. The main theoretical framework for the study of bulk properties is thermodynamics (for equilibrium processes) or kinetics (for non equilibrium phenomena). However, the study of the micro systems operates on the framework of quantum/classical mechanics

iii. Statistical thermodynamics is a branch of statistical mechanics, an aspect of theoretical physics that uses probability theory to study the average behaviour of a mechanical system where the state of the system is uncertain

iv. Microstate is the microscopic state of the system specified by a small number of parameters that need to define it

v. Fundamental postulates in statistical thermodynamics are Priori assumption, ergodic, principles of indifference and maximum information entropy.

vi. The molecular partition function contains all the information needed to calculate the thermodynamic properties of a system of independent particles

vii. The relationship between partition function and internal energy is $U = -\frac{\delta lnQ}{\delta\beta} = kT^2\frac{\delta lnQ}{\delta T}$

viii. The relationship between partition function and C_V is $C_v = \left(\frac{dU}{dT}\right)_v = 2kT\frac{\delta lnQ}{\delta T} + kT^2\frac{\delta^2 lnQ}{\delta T^2}$

ix. The relationship between partition function and C_P is $C_p = C_v + R = \left[2kT\frac{\delta lnQ}{\delta T} + kT^2\frac{\delta^2 lnQ}{\delta T^2}\right] + R$

x. The relationship between partition function and entropy is $S = \left(\frac{\partial A}{\partial T}\right)_V = -\frac{\partial kTlnQ}{\partial T}$

xi. The relationship between partition function and pressure is $P = \left(\frac{\partial A}{\partial V}\right)_{T,N} = -kT\left(\frac{\partial lnQ}{\partial T}\right)_{T,N}$

xii. The relationship between partition function and chemical potential is $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial lnQ}{\partial N}\right)_{T,V}$

xiii. Stirling's approximation provides a means of simplifying statistical thermodynamics calculations when the value of N is too large. The approximation for N factorial are $lnN! = NlnN - N$ and $N! = N^N e^{-N}$

xiv. The three major ensembles in statistical thermodynamics are microcanonical ensemble, (which is applicable to isolated system with fixed N and E), canonical ensemble (which is applicable to a system in heat bath at constant temperature and fixed N) and grand canonical ensemble (which is applicable to open system and nothing is fixed)

xv. For n_i particles having energy, E_i and number of degeneracy, the Maxwell-Boltzmann statistics can be written as $n_i = g_i e^{\alpha} e^{-\beta E_i} = \frac{Ng_i}{\sum g_i e^{-\beta E_i}} e^{-\beta E_i} = \frac{Ng_i}{Q} e^{-\beta E_i}$, where Q is the partition function.

5.0 Conclusions

Statistical thermodynamics provides a method of linking the macroscopic and microscopic properties of a system. This makes the field to be significant because the behaviour of macroscopic systems depends on its microstates (molecules, ions, etc). The partition function in statistical thermodynamics is analogous to the Schrodinger equation in quantum chemistry because the partition function can be used to calculate all the statistical thermodynamic functions of a system just as the Schrodinger equation can be used to calculate all the quantum chemical parameters of a system.

6.0 Tutor mark assignment

1. What is statistical thermodynamics? The Schrodinger equation is used in quantum chemistry to calculate thermodynamics properties. Does statistical thermodynamics has such function? Explain in details.

2. List five basic properties of statistical thermodynamics microstate

3. What do you understand by the term, ensembles?

4. What are the major distribution laws in statistical thermodynamics? Hence state their basic features

7.0 References

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