EDO UNIVERSITY IYAMHO

Department of Industrial Chemistry

CHM 211: Basic Physical Chemistry

Instructor: *Mr Inobeme Abel*, email: inobeme.abel@edouniversity.edu.ng

Lectures: Tuesday, 8.00am – 10.00 pm, LT5, phone: (+234) 8036237514

Office hours: Thursday, 2.00 to 4.00 pm, Office: F.O.S Rm 7.

General overview of lecture: This course introduces students to the basic concepts in Physical Chemistry. The topics covered include: Kinetic theory of gases; Behavior of real gases; the law of thermodynamics; Entropy and free energy in chemical reactions, Reactions and Phase equilibrium; photochemical reactions and catalysis and Basic electrochemistry. Practice problems and the practical applications of some of these concepts are also discussed.

Prerequisites: Basic Physical Chemistry is a course for students in the Department of Chemistry and Biochemistry. The intended learners for this course are expected to have passed their course in Introductory Chemistry which is a prerequisite to this. The course shall include lectures and imbedded practical exercises.

Learning outcomes: At the end of this course the students should be able to:

i. State the postulates of the kinetic theory of gases

ii. Differentiate ideal from non-ideal gases

iii. Explain the conditions that favor deviation of gases from ideal behavior

iv. Solve problems on Gibb's free energy; entropy and enthalpy

v. Differentiate between the various thermodynamic systems

vi. Apply the laws of thermodynamic to real life situation.

vii. Explain the concept of phase equilibria

Assignments:

Assessment for this course shall include three (3) assignments together with the mi-term test and final examination. Students will also be expected to make term paper presentation towards the end of the semester. Individual and group projects will also be assessed.

Grading:

Continuous assessment (CA) shall be assigned 30 % while the final examination takes 70%. Distribution of marks for the CA shall be as follows: 10% for home works; 10% for projects and 10% for midterm test. The Final exam is comprehensive.

Textbook: The recommended textbooks for this course are as follows:
Title: *Physical Chemistry*
Authors: Atkins, P. and De Paula, J.
Publisher: Freeman Publisher,
Edition: 8th ed
Year: 2006

Title: *Chemistry Precision and Design*

Author(s): Biddle, V. and Parker, G.
Publisher: Pensacola: Pensacola Christian College.
ISBN: 0-321-32221-5.
Year: 2000

Title: *Kinetics and Mechanism*
Author: Moore J.W. and Pearson, R.G.
Publisher: John Wiley,
Edition: 3rd ed
Year: 2000

Main Lecture: Below is a description of the contents.

Introduction

The kinetic theory of gases is a law that explains the behavior of a hypothetical ideal gas. The kinetic theory offers explanation on the different rate of movement of microscopic properties within a given state of matter. According to this theory, gases are made up of tiny particles which are in constant random, straight line motion. Gases move rapidly and continuously and make collisions with each other and the walls.

This theory was the first to describe gas pressure based on collisions with the walls of the container, rather than from static forces that push the molecules apart. This also account for how the different sizes of the particles contribute to their different, individual speeds.

Postulates

The kinetic molecular theory is a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of the individual gas particles (atoms or molecules). Basically, this theory is summarized thus:

1. *The gas consists of very minute particle called molecules; the volume occupied by the molecules is negligible compared to the volume of the container*. This means that the average distance between gas molecules is large compared to their size.

ii. Gas molecules are minute and are in constant random rapid motion and rectilinear motion

iii. *Gas molecules collide with each other and with the wall of the container*. *The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.* The molecules are considered to be perfectly spherical in shape because the collision between gas molecules are perfectly elastic (i.e change in momentum is zero).

iv. Except during collision, forces of cohesion between gas molecules are negligible. This implies that there are no interactive forces (forces of attraction or repulsion) between the particles of a gas.

v. *The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.* In other words, the average kinetic energy of gas particles is a measure of the absolute temperature of the gas and all gases at the same temperature have the same average kinetic energy.

However, the molecules in a real gas have finite volumes and also exert forces on each other. Thus *real gases* do not adhere strictly to these assumptions. These postulates explain clearly the behavior of ideal gases.

Formula of pressure of an ideal gas

Let's assume one molecule travelling towards the wall of the container

Given that it has a mass *m* and is moving with speed *v*, then its momentum is *mv*.

The molecule bounce off the wall hence travels away with the same momentum *mv*, assuming there is no loss in energy.

Hence, the change in momentum during collision with the wall can be expressed as *2mv*

The force on the wall is the change in momentum divided by the time taken:

F= $\frac{2mv}{t}$ (*remember impulse (Ft) is equal to change in momentum*)

Since P=F/A

Pressure on the wall = $\frac{2mv}{tA}$

This can be simply: a molecule travel speed *v* will travel a distance *vt* in time *t*.

Over the area *A* of the wall, there will be a volume $A \times vt$ in which molecules liable to heat the wall can be found. If there are N molecules of gas per unit volume, the number of molecules hitting the wall is *NAvt*. Therefore for the gas,

Pressure on the wall = $\frac{2mv}{tA} \times NAvt = 2Nmv^2$

We have dealt with only one wall of the container. In fact there are six wall of area A(assuming the container is a cube), so on average only one-sixth of these molecules will hit any one wall. Our formula become

$P = \frac{1}{3}Nmv^2$

The molecules do not all travel with the same speed, so change in momentum and pressure they should exert will be averaged, hence we write a bar above v^2

Final equation becomes:

$P = \frac{1}{3}Nmv^2$

Connection between the average kinetic energy of molecules and temperature

We have known that $P = 1/3Nmv^2$

We also know that $pV = nRT$, so putting the two equations together:

$1/3Nmv^2 = RT/V$

N is the number of molecules per unit volume, so if we make V the volume of 1 mol of gas, then there must be 6.02×10^{23} particles present, i.e $N = L/V$

Putting this into the left hand side and rearranging we get

$mv^2 = 3RT/L$

but $R = Lk$ where k is boltzmanns constant, so

$mv^2 = 3kT$

given that the average kinetic energy is $mv^2/2$ we find

$1/2mv^2 = 3/2kT$

Behavior of Ideal Gases

A sample of gas has four basic physical properties: pressure (*P*), volume (*V*), temperature (*T*), and amount in moles (*n*). These properties are interrelated—when one changes, it affects one or more of the others.

NB:

1 atm = 760 mm Hg = 760 torr

1 atm = 14.7 psi = 101,325 Pa

The simple gas laws describe the relationships between pairs of these properties. For example, how does *volume* vary with *pressure* at constant temperature and amount of gas, or with *temperature* at constant pressure and amount of gas?

Such questions can be answered by experiments in which two of the four basic properties are held constant in order to elucidate the relationship between the other two.

Boyle's Law

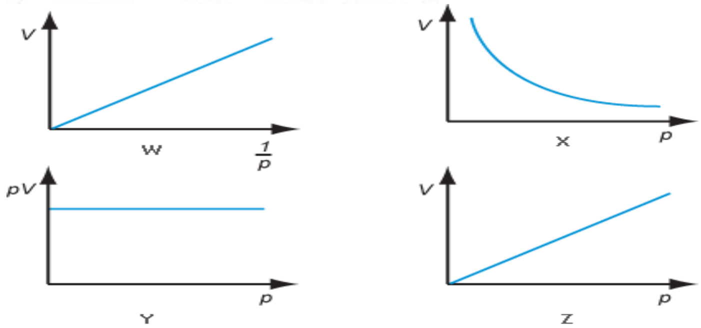
Robert Boyle in his law accounted for the relationship between the volume and pressure of a fixed mass of gas at constant pressure. This law was obtained after series of experiments he carried out to investigate relationship between volume and pressure of a fixed mass of gas. Edme Mariotte 1676 also carried out experiment which supported and confirmed the relationship between pressure and volume at constant temperature.

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

Mathematically, Boyle's law can be expressed as follows,

Graphical representation of Boyle's law

This implies that a plot of volume (V) against the inverse of pressure (1/P) and also a plot of pressure against volume will follow predicted pattern as represented below:

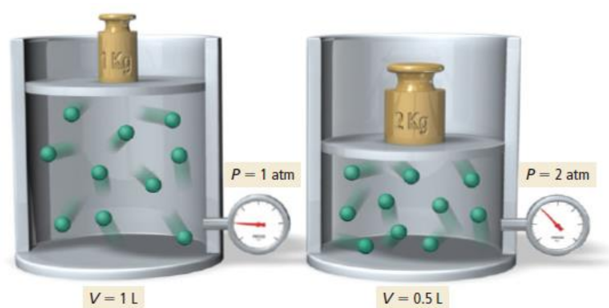


Graphical representation of Boyle's law

Molecular explanation for Boyle's law

The molecular reason for the pressure increase on a volume decrease is that the molecules are now in a smaller space, which produces more collisions per unit area and therefore greater pressure. If the volume of a gas sample is decreased, the same number of gas particles is crowded into a smaller volume, resulting in more collisions with the walls and therefore an increase in the pressure.

Diagrammatical representation of Boyle's law



Source: Atkins and Paula, 2006

Mathematical representation

From 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.

V α 1/p

V = kp

$K = P/V$

Therefore $P_1/V_1 = P_2/V_2$

Practice questions

1. A fixed mass of gas occupied a volume of 500cm3 at a pressure of 100mmHg. At what pressure will the volume be halved?
2. A mass of oxygen gas has a volume of 50L at a pressure of 10atm. What is the new volume of this gas under atmospheric pressure.

Charles law

Jacques Charles after series of experiments observed a related pattern in the expansive behavior of gases over a range of temperatures. This formed the basis of his law.

Charles law state that *the volume of a given mass of a gas is directly proportional to its absolute temperature provided the pressure is kept constant.* This law can be expressed mathematically as follows:

Mathematical representation

From 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.

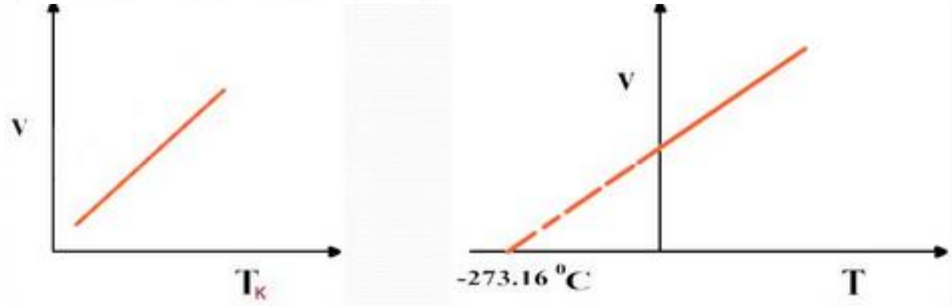
$V \alpha T$ (at constant pressure)

$V = kT$

Hence $\frac{V1}{T1} = \frac{V2}{T2}$

Graphical representation of Charles' law

Graphically, a plot of V against T as linear with zero intercept and slope, equal to K. the graphical representation of Charle's law is given below. An interesting feature emerges if we extend or *extrapolate* the line in the plot backwards from the lowest measured temperature. The extrapolated line shows that the gas should have a zero volume at -273C.



Source: https://images.search.yahoo.com/yhs/search

Significance of OK

At temperatures below OK, the extrapolated volumes would become negative. The fact that a gas cannot have a negative volume suggests that 0 K has a special significance.

In fact, 0 K is called absolute zero, and there is much evidence to suggest that this temperature cannot be attained. Temperatures of approximately 0.000001 K have been produced in laboratories, but 0 K has never been reached.

The Ideal Gas Law

Three fundamental laws that account for the experimental behavior of gases have been considered:

Boyle's law: $V = \frac{k}{P}$ (at constant T and n)

Charle's law: V = bT (at constant P and n)

Avogadro's law law: V = an (at constant T and P)

These relationships, which show how the volume of a gas depends on pressure, temperature, and number of moles of gas present, can be combined as follows:

$V = R\,(\frac{Tn}{P})$

Where *R* is known as the *universal gas constant*, a combined proportionality constant. The value of R depends on the unit of pressure and volume used in the expression. When the pressure is expressed in atmospheres and the volume in liters, *R* has the value 0.08206 L atm_K mol.

The ideal gas equation may be conveniently rearranged as :

$$PV= nRT$$

The ideal gas law is an *equation of state* for a gas, where the state of the gas is its condition at a given time. A particular *state* of a gas is described by its pressure, volume, temperature, and number of moles. In order to completely define the state of a gaseous system, any three of the properties are sufficient for the description, since the fourth can be determined from the equation connecting them. A gas that adheres to the ideal law is said to behave ideally. Ideal gas law is based on empirical measurements of the properties of gases. Real gases only tend to behave toward ideal when their pressure is low and temperature high.

Question

A sample of oxygen gas in a reaction vessel has a volume of 8.56 dm^3 at a temperature of 273K and a pressure of 1.5 atm. Calculate the number of moles of the gas present in the container.

Question

A fixed mass of methane gas has a volume of 7ml at a pressure of 1.68atm. The volume of the gas reduced to 4.0mL after compression at a fixed temperature. What is the final pressure of the gas.

Real Gas: Deviation from Ideal Behavior

In the postulates of the kinetic molecular theory, the volume occupied by the gas molecules and all the interactions between the molecules are ignored. However real gases have a volume which is not negligible.

Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. Real gas behavior differs from the predictions of the ideal gas law. Liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases is also explained.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures. Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior.

Real gases behave differently from ideal gases at high pressure and low temperature conditions, because under this situation the two fundamental assumptions behind the ideal gas laws (negligible volume and pressure) no longer hold.

The Van der Waals Equation

Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable. According to the kinetic theory gas particles occupy a negligible fraction of the total volume of the gas. It also assumes that the force of attraction between gas molecules is zero. The first assumption only holds when the pressure is low such as 1atm. The validity of the assumption fails when the gas is compressed at high pressure. Imagine for the moment that the atoms or molecules in a gas were all clustered in one corner of a cylinder, as shown in the figure below. At normal pressures, the volume occupied by these particles is a negligibly small fraction of the total volume of the gas. This no longer holds at high pressure. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures.

Values of constant *a* and b for common gases

a and *b* are experimental constants and their values vary with gases. The values of these constants for some gases are given below:

Gas	$a(L^2.atm)/mol^2$	b(L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387

CO	1.485	0.03985
CH_4	2.253	0.04278

The pressure term in Equation $(P + \frac{an^2}{v^2})$ corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, $\frac{n^2}{v^2}$ represents the concentration of the gas (n/Vn/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown below. The volume term V−nb corrects for the volume occupied by the gaseous molecules.

Practice question

A sample of gas has a volume of 2.80 L at an unknown temperature. When the sample is submerged in ice water at T = 0.00C its volume decreases to 2.57 L. What was its initial temperature (in K and in °C)?

Avogadro's law

Equal volume of all gases at the same temperature and pressure, contain the same number of moles.

V α n (T and P constant)

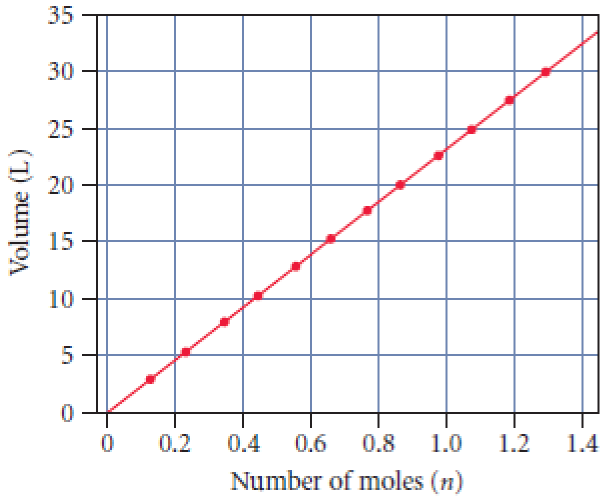
When the amount of gas in a sample is increased at constant temperature and pressure, its volume increases in direct proportion because the greater number of gas particles fill more space.

Avogadro's law can be used to compute the volume of a gas following a change in the amount of the gas *as long as the pressure and temperature of the gas are constant*. For these types of calculations,

Avogadro's law is expressed as

V1/n1 = V2/n2

Graphical representation



Source: Atkins and Paula, 2006

Practice questions

1. A 4.65-L sample of helium gas contains 0.225 mol of helium. How many additional moles of helium gas must be added to the sample to obtain a volume of 6.48 L? Assume constant temperature and pressure. (0.089moles)

2. A chemical reaction occurring in a cylinder equipped with a moveable piston produces 0.621 mol of a gaseous product. If the cylinder contained 0.120 mol of gas before the reaction and had an initial volume of 2.18 L, what was its volume after the reaction? (Assume constant pressure and temperature and that the initial amount of gas completely reacts.)

The Ideal Gas Law

The ideal gas equation was developed by Emile Clapeyron, who combined Boyle and Charles laws in 1834. This is written mathematically as

Derivation:

$V \alpha \frac{1}{P}$ (Boyle's law)

$V \alpha T$ (Charles' law)

$V \alpha n$ (Avogadro's law)

When the three expression above are combined we get

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

$PV = nRT$

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

The sign of proportionality can be replaced with an equals sign by incorporating *R*, a proportionality constant called the *ideal gas constant*:

$V = \frac{nRT}{P}$