

Resource material for Ziauddin Examination Board



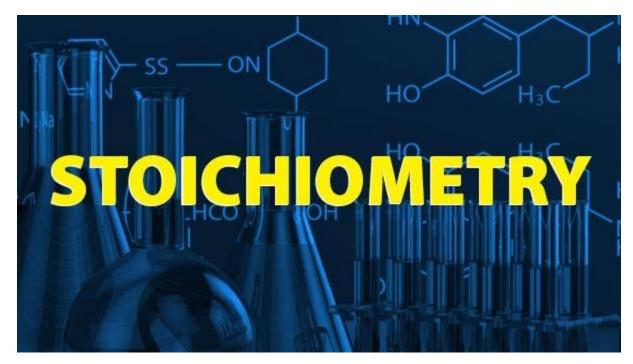
- Students will display a sense of curiosity and wonder about the natural world and demonstrate an increasing awareness that this has lead to new developments in science and technology. They will learn from books and other sources of information and reconstruct previously learned knowledge.
- Students will describe and explain common properties, forms, and interactions between matter and energy; their transformations and applications in biological, chemical and physical systems.
- Students will demonstrate an understanding of the impact of science and technology on society and use science and technology to identify problems and creatively address them in their personal, social and professional lives. They will explain how scientists decide what constitutes scientific knowledge; how science is related to other ways of knowing; and how people have contributed to and influenced developments in science.

CHAPTER CONTENT

S.no	Name of chapter
Chapter # 1	Stoichiometry
Chapter # 2	Atomic structure
Chapter # 3	States of Matter
Chapter # 4	Theories of covalent bonding & shapes of molecules
Chapter # 5	Chemical Equilibrium
Chapter # 6	Thermo chemistry
Chapter # 7	Chemical kinetics
Chapter # 8	Acid , Base & Salts
Chapter # 9	Solution & Colloids
Chapter # 10	Electrochemistry

CHAPTER 1

"STOICHIOMETRY"



INTRODUCTION:

Major concepts:

- Mole & Avogadro number calculations
- Percentage & composition of Empirical & molecular formula
- Stoichiometry
- Significant figures

Conceptual linkage This unit is built on,

- Atomic mass unit
- Mole concept
- Relative atomic mass & relative molecular mass
- Chemical calculations

Learning outcomes

Students will be able to	Analyzing	Applying	Understanding
• Construct mole ratios from balanced equations for use as conversion factors in stoichiometric problems.		~	
• Identify the limiting reagent in a reaction	~		
• Calculate the maximum amount of product(s) produced and the amount of any unreacted excess reagent.	~		
• Calculate theoretical yield, actual yield, percentage yield.		~	
• Calculate the theoretical yield and the percent yield when given the balanced equation, the amounts of reactants and the actual yield.			~
Determination of amount of reactant or product.	~		

SKILLS	Analyzing	Applying	Understanding
• Use the volume (22.4 L) of one mole of a gas at STP to work mole-volume problems.	~		
• Calculate the gram molecular mass of a gas from density measurements of gases at STP.	~		
• Use the mole to convert among measurements of mass, volume and number of particles.	~		
• Fine out the limiting reactant in a chemical reaction and do the related calculations.		~	
• Perform calculations based on moles, mass, volume and number of particles.			~

SOCIETY TECHNOLOGY AND SCIENCE

Students will be able to

> Understand that chemistry is quantitative science

Related video

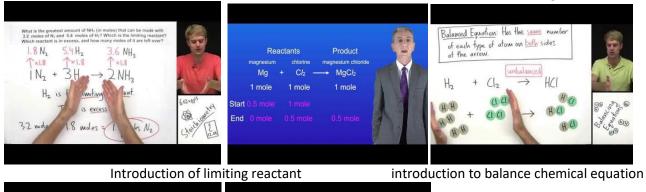




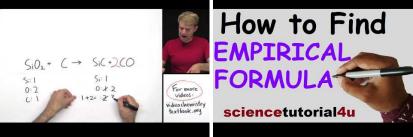
One mole of a substance is the amount of the substance which contain 6.022×10^{23} particles



calculation limiting reactant



Mole



Balance chemical equation-II

• . (New)

CHAPTER OVERVIEW

(THEORITICAL)

Mole

Mole

In <u>chemistry</u>, a standard scientific unit for measuring large quantities of very small entities such as <u>atoms</u>, <u>molecules</u>, or other specified particles.

How to find emprical formula

Avogadro's number

The number of atoms present in 12 g of carbon-12, which is 6.022×10 and the number of elementary entities (atoms or molecules) comprising one mole of a given substance.

Empirical formula

That formula which shows the simplest ratio of an atom in a molecule or compound.

Molecular formula

That formula which shows the actual number of an atom in a molecule or compound.

Stoichiometry

Stoichiometry is the study of the quantitative relationships or ratios between two or more substances undergoing a physical change or chemical change (chemical reaction).

Atomic mass

Atomic mass is defined as the average mass of an element.

Molecular mass

Molecular mass is a number equal to the sum of the atomic masses of the atoms in a molecule.

Chemical Reaction.

A process in which one or more substances, the reactants, are converted to one or more different substances, the products.

(NUMERICAL)

1. Calculation of formula mass or molecular mass.

Chloroform molecule, CHCl₃

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
С	1	×	12.01	=	12.01
н	1	×	1.008	=	1.008
CI	3	×	35.45	=	106.35
			Molecular ma	ass	119.37

Aspirin molecule, C9H8O4

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
С	9	×	12.01	=	108.09
н	8	×	1.008	=	8.064
0	4	×	16.00	=	64.00
			Molecular ma	ass	180.15

Exercise practice:

Calculate the molecular or formula mass of each of the following: (a) P_4 (b) H_2O

(c) Ca(NO₃)₂
(d) CH₃CO₂H (acetic acid)
(e) C₁₂H₂₂O₁₁ (sucrose, cane sugar).

References pages / sites. https://opentextbc.ca/chemistry/chapter/3-1-formula-mass-and-the-mole-concept/

2. Mole to mass calculation.

Mole-Mass Equation

 $mass = number of moles \times molar mass$

Example:

Calculate the mass of **3** moles of carbon dioxide gas, **CO**₂. (Relative atomic mass: C = 12; O = 16) *Solution:* mass of 1 mole of CO_2 = $(1 \times 12) + (2 \times 16)$ = 44 g

mass of 3 moles of CO_2 = 3 × 44 = 132g Answer

3. Mass to mole calculation

number of moles = $\frac{\text{mass}}{\text{molar mass}}$

Example:

Calculate the number of moles of magnesium oxide, MgO in 80 g of the compound. (Relative atomic mass: O = 16, Mg = 24) Solution: Mass of 1 mole of MgO = $(1 \times 24) + (1 \times 16)$ = 40 g number of moles = $\frac{mass}{molar mass}$ = $\frac{80}{40} = 2$ moles References pages / sites. https://www.onlinemathlearning.com/mole-calculation.html

Exercise practice:

• Calculate the mass of 3.5 moles of H_2 O. (Relative mass of H = 1 & O = 16)

- Calculate the no of moles calcium oxide,CaO in 24g of the compound.(Relative mass of Ca = 40 & O = 16)
- 4. Calculation of Empirical & Molecular formula.

Example :

Caffeine has the following percent composition: carbon 49.48%, hydrogen 5.19%, oxygen 16.48% and nitrogen 28.85%. Its molecular weight is 194.19 g/mol. What is its molecular formula?

Solution: (1) calculate the empirical formula, (2) compare "EFW" to molecular weight, (3) multiply empirical formula by proper scaling factor.

1) Calculate the empirical formula:

carbon: $49.98 \text{ g} \div 12.011 \text{ g/mol} = 4.16$ hydrogen: $5.19 \text{ g} \div 1.008 \text{ g/mol} = 5.15$ nitrogen: $28.85 \text{ g} \div 14.007 \text{ g/mol} = 2.06$ oxygen: $16.48 \text{ g} \div 15.999 \text{ g/mol} = 1.03$

Carbon: $4.16 \div 1.03 = 4.04 = 4$ hydrogen: $5.15 \div 1.03 = 5$ nitrogen: $2.06 \div 1.03 = 2$ oxygen: $1.03 \div 1.03 = 1$

2) Empirical formula is $C_4H_5N_2O$. The "empirical formula weight" is about 97.1, which gives a scaling factor of two.

3) The molecular formula is: C₄H₅N₂O times $2 = C_8H_{10}N_4O_2 < ---$ that's the molecular formula

Reference pages/sites https://www.chemteam.info/Mole/Empirical-MolecFormulas.html

5. Calculation of limiting reactant.

Problem #1: For the combustion of sucrose: $C_{12}H_{22}O_{11} + 12O_2 ---> 12CO_2 + 11H_2O$ There are 10.0 g of sucrose and 10.0 g of oxygen reacting. Which is the limiting reagent?

Solution path #1:

Calculate moles of sucrose:
 0.0 g / 342.2948 g/mole = 0.0292146 mol
 Calculate moles of oxygen required to react with moles of sucrose:
 From the coefficients, we see that 12 moles of oxygen are require for every one mole of sucrose. Therefore:

0.0292146 mol times 12 = 0.3505752 mole of oxygen required

3) Determine limiting reagent:

Oxygen on hand \Rightarrow 10.0 g / 31.9988 g/mol = 0.3125 mol

Since the oxygen required is greater than that on hand, it will run out before the sucrose. Oxygen is the limiting reagent

Student's Assessment

- How many carbon atoms are present in 0.5 moles of oxalic acid (C₂H₂O₄)?
- 0.5216g of a solid mixture containing Na₂SO₄ is dissolved in water and treated with an excess of BaCl₂, resulting in the precipitation of 0.6168g of BaSO₄. What percentage of the mixture was BaSO₄?
- Why do we need Mole concept?
- Why is Avogadro's number called a mole?
- What is the use of the mole concept?
- What does Avogadro's law state?
- How many moles are in a mole?
- What is the limiting reagent?
- What is the difference between limiting reactant and limiting reagent?
- Why is the limiting reactant important?
- Are limiting reactants present in all reactions?
- What is the benefit of having a limiting reagent?
- How many moles are in a mole?
- The molar mass of acetic acid as determined with a mass spectrometer is about 60g/mol. Using that information along with the simplest formula, determine the molecular formula of acetic acid.

Reference pages/sites

https://www.chemteam.info/Stoichiometry/Limiting-Reagent-Prob1-10.html https://byjus.com/chemistry/mole-concept-molar-mass-and-percentage-composition/

Practical # 01

- Determine the amount of ions in different salt solutions by gravimetrically.
- Determine the sugar level in blood sample by gravimetrically.

(Related videos links)

Mole : <u>https://youtu.be/4q2elWPfB6A</u>

https://youtu.be/z5yLuTcdwMo

limiting reactant :

https://youtu.be/6MHSBs-ed2I

https://www.youtube.com/watch?v=nZOVR8EMwRU

https://www.youtube.com/watch?v=MuzOmFhiE80

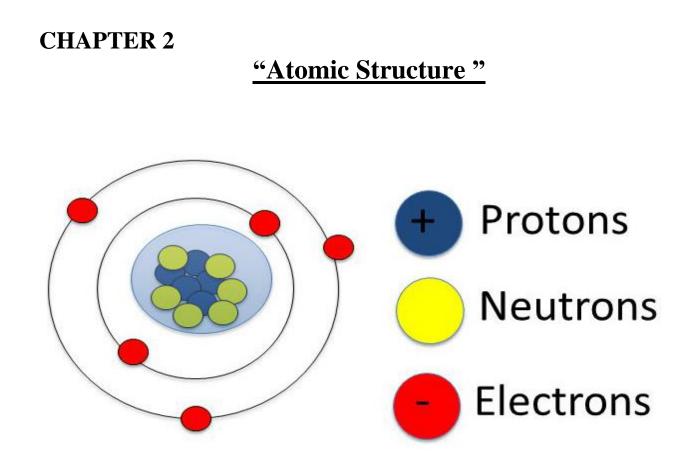
Stoichiometry

<u>https://www.youtube.com/watch?v=S6UQX7ZdkTg&list=PLaWEo7fLMF9b-imkPoVf3if-I7lrSlmpH</u> <u>https://www.youtube.com/watch?v=eNsVaUCzvLA</u> https://www.youtube.com/watch?v=yA3TZJ2em6g

Molecular & Empirical Formula

https://www.youtube.com/watch?v=lPLTLkn3dNU

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INTRODUCTION:

Major concepts:

- Fundamental particles
- Discharge tube experiment
- Application of Bohr's atomic model
- Plank's quantum theory
- X-Ray
- Quantum numbers & Orbitals.
- Electronic configuration
- Dalton's atomic theory
- Hydrogen spectrum series

Conceptual linkage

This unit is built on,

- Rutherford's Atomic Model.
- Bohr's atomic model
- Isotopes
- Concept of **S** & **P** sub shell

• Radioactivity

LEARNING OUTCOMES

Students will be able to	Remembering	Applying	Understanding
• Explain the sequence of filling of electrons in many electron atoms.		~	
Write electron configuration of atoms.		~	
• Describe the orbitals of hydrogen atom in order of increasing energy.			~
• Use the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule to write the electronic configuration of the elements.		~	
• . Describe the hydrogen atom using the Quantum Theory.			~
• Explain the significance of quantized energies of electrons.		~	
• Describe the general shapes of s, p, and d orbitals.			~
• Explain production, properties, types and uses of X-rays. (Understanding) Define photon as a unit of radiation energy.	~		
• Use Bohr's model for calculating radii of orbits.			 ✓
Summarize Bohr's atomic theory	v		

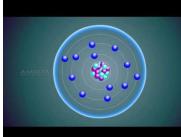
SKILLS	Analyzing	Applying	Understanding
• Calculate the frequency given the wavelength or wave numbers.		~	
• Calculate the energy of photon associated with a given wavelength or wave number of a radiation.		~	
• Calculate the energy differences between different energy level of hydrogen atom.	~		
• Knowing about the distribution of electrons in different orbitals			~
Observation of X-ray radiation in different medical field.			~

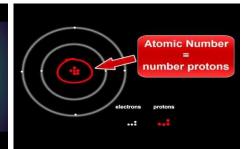
SOCIETY TECHNOLOGY AND SCIENCE

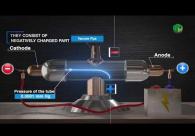
Students will be able to

- > Describe how making model helps better understand atom and molecules.
- Explain firework displays.

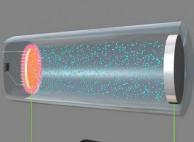
Related video



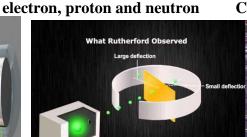




Atom and molecule



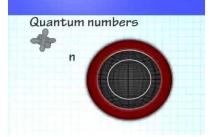
Cathod ray tube https://youtu.be/6gkjxPAYgy0



Rutherford experiment



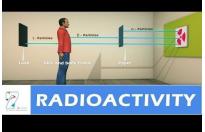
Bohr's atomic model



Quantum numbers



Dalton atomic theory



Radioactivity

Chapter overview

(THEORITICAL)

✤ Fundamental particles

There are three subatomic particles exist in atom

Electron

Electron was discovered by J.J Thomson. It is a negative charge particle whose mass is 9.11x10⁻³¹kg.

Proton

Proton was discovered by Goldstein. It is a positive charge particle whose mass is 1.6x10⁻²⁷kg.

Neutron

Neutron was discovered by James Chadwick. It is neutral charge particle.

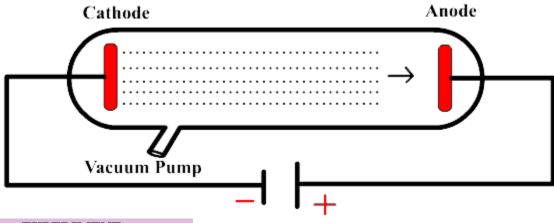
Dalton's atomic theory

The main points of Dalton's atomic theory are:

- Everything is composed of atoms, which are the indivisible building blocks of matter and cannot be destroyed.
- All atoms of an element are identical.
- The atoms of different elements vary in size and mass.
- Compounds are produced through different whole-number combinations of atoms.
- A chemical reaction results in the rearrangement of atoms in the reactant and product compounds.

Discharge tube experiment: DISCHARGE TUBE

Discharge tube is also called "CROOCK TUBE". It is made of a glass tube which consists of two metallic plates. One plate is connected to positive terminal of high voltage power supply and the other to negative terminal. The plate connected to the positive terminal is called "ANODE" the other connected to negative terminal is called "CATHODE". The tube is filled with any gas.



EXPERIMENT

In discharge tube experiment, at low pressure and at very high voltage, an electric current is passed. Due to passage of electric current, a stream of rays is passed in the tube originating from cathode. These rays are called "CATHODE RAYS".

PROPERTIES OF CATHODE RAYS

- These rays originate from cathode.
- Cathode rays travel in straight line.
- Cathode rays carry negative charge.
- Cathode rays are deflected by electric field.

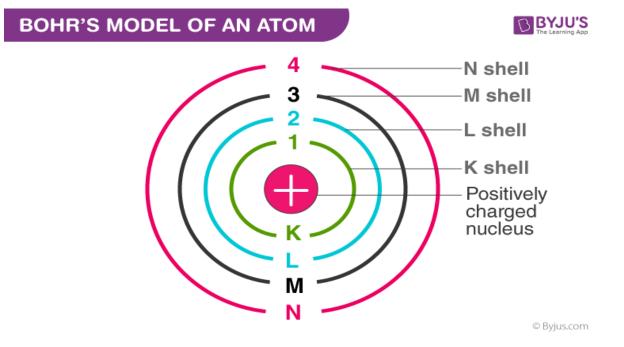
- Cathode rays are deflected by magnetic field.
- These rays consist of material particles.
- The ratio e / m of these particles was $1.76 \times 10^8 \text{ col} / \text{gm}$.
- Cathode rays consist of "electron".
- The rays, upon striking glass or certain other materials, cause them to glow

* Application's of Bohr's Atomic Model

Introduction to the Bohr Model

Bohr model of the atom was proposed by Neil Bohr in 1915. It came into existence with the modification of Rutherford's model of an atom. Rutherford's model introduced the nuclear model of an atom, in which he explained that a nucleus (positively charged) is surrounded by negatively charged electrons.

Bohr modified this atomic structure model by explaining that electrons move in fixed orbital's (shells) and not anywhere in between and he also explained that each orbit (shell) has a fixed energy level. Rutherford basically explained the nucleus of an atom and Bohr modified that model into electrons and their energy levels.

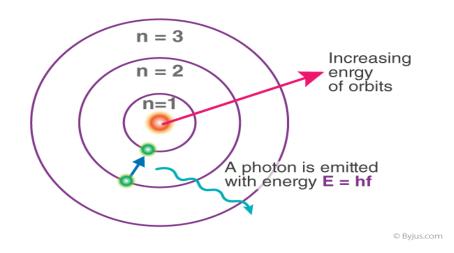


Bohr's Model of an Atom

Bohr's model consists of a small nucleus (positively charged) surrounded by negative electrons moving around the nucleus in orbits. Bohr found that an electron located away from the nucleus has more energy, and electrons close to the nucleus have less energy.

Postulates of Bohr's Model of an Atom

- In an atom, electrons (negatively charged) revolve around the positively charged nucleus in a definite circular path called as orbits or shells.
- Each orbit or shell has a fixed energy and these circular orbits are known as orbital shells.
- The energy levels are represented by an integer (n=1, 2, 3...) known as the <u>quantum number</u>. This range of quantum number starts from nucleus side with n=1 having the lowest energy level. The orbits n=1, 2, 3, 4... are assigned as K, L, M, N.... shells and when an electron attains the lowest energy level it is said to be in the ground state.
- The electrons in an atom move from a lower energy level to a higher energy level by gaining the required energy and an electron moves from a higher energy level to lower energy level by losing energy.



Limitations of Bohr's Model of an Atom

- Bohr's model of an atom failed to explain the Zeeman Effect (effect of magnetic field on the spectra of atoms).
- It also failed to explain the Stark effect (effect of electric field on the spectra of atoms).
- It violates the <u>Heisenberg Uncertainty Principle</u>.
- It could not explain the spectra obtained from larger atoms.

Reference page/site.

https://byjus.com/chemistry/bohrs-model/

✤ PLANK'S QUANTUM THEORY.

Before learning about Planck's quantum theory, we need to know few things.

As progress in the science field was happening, Maxwell's suggestion about the wave nature of electromagnetic radiation was helpful in explaining the phenomena such as interference, diffraction etc. However, he failed to explain various other observations such as the nature of emission of radiation from hot bodies, photoelectric effect i.e. ejection of <u>electrons</u> from a metal compound when electromagnetic radiation strikes it, the dependence of heat capacity of solids upon temperature, line spectra of atoms (especially hydrogen).

Black Body Radiation

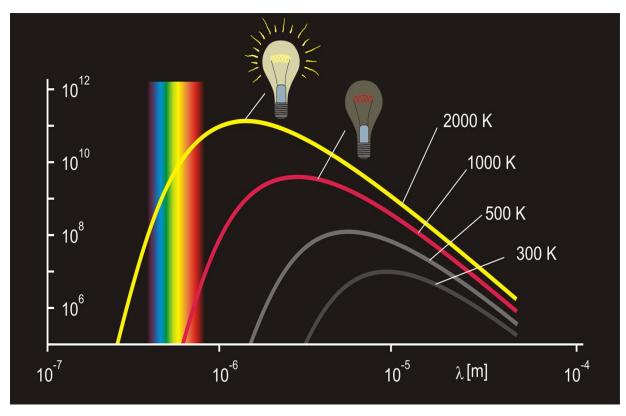
Solids, when heated, emit radiation varying over a wide range of wavelengths. For example: when we heat solid color, changes continue with a further increase in temperature. This change in color happens from a lower frequency region to a higher frequency region as the temperature increases. For example, in many cases, it changes from red to blue. An ideal body which can emit and absorb radiation of all frequencies is called a black body. The radiation emitted by such bodies is called black body radiation.

Thus, we can say that variation of frequency for a black body radiation depends on the temperature. At a given temperature, the intensity of radiation is found to increase with an increase in the wavelength of radiation which increases to a maximum value and then decreases with an increase in the wavelength. This phenomenon couldn't be explained with the help of Maxwell's suggestions. Hence, Planck proposed the Planck's quantum theory to explain this phenomenon.

Planck's quantum theory

According to Planck's quantum theory,

- 1. Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
- 2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of the radiation.



Meanwhile, the energy of radiation is expressed in terms of frequency as,

 $\mathbf{E} = \mathbf{h} \mathbf{v}$

Where,

 $\mathbf{E} = \text{Energy of the radiation}$

 $\mathbf{h} = \text{Planck's constant} (6.626 \times 10^{-34} \text{ J.s})$

v= Frequency of radiation

Interestingly, Planck has also concluded that these were only an aspect of the processes of absorption and emission of radiation. They had nothing to do with the physical reality of the radiation itself. Later in the year 1905, famous German physicist, Albert Einstein also reinterpreted Planck's theory to further explain photoelectric effect. He was of the opinion that if some source of light was focused on certain materials, they can eject electrons from the material. Basically, Planck's work led Einstein in determining that light exists in discrete quanta of energy, or photons.

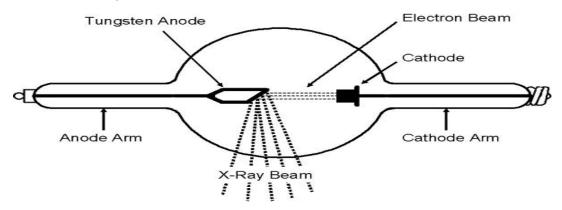
Reference page/site.

https://byjus.com/chemistry/planks-quantumtheory/#:~:text=Planck's%20quantum%20theory,radiation%20is%20known%20as%20quantum.

* X-Ray radiations.



X-Ray photons are <u>electromagnetic radiation</u> with wavelengths typically in the range 0.1 - 100 Å. X Rays used in diffraction experiments have wavelengths of 0.5 - 1.8 Å. X Rays can be produced by conventional generators, by synchrotrons, and by plasma sources. Electromagnetic radiation from nuclear reactions, called γ radiation, can also occur at the same energies as X rays, but γ radiation is differentiated from X ray radiation by the fact that it originates from nuclear reactions.



Reference page/site.

https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.orau.org%2Fptp%2Fcollection%2Fxra ytubescoolidge%2Fcoolidgeinformation.htm&psig=AOvVaw2cnpb0-JatfagU2p3WYa35&ust=1591674200656000&source=images&cd=vfe&ved=0CAIQjRxqFwoTCLiSiInq8 -kCFQAAAAdAAAABAD http://xrayweb.chem.ou.edu/notes/xray.html

♦ Quantum Numbers.

Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \dots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	$m_{\rm l}$	$-\ell,\ldots,-1,0,1,\ldots,\ell$
Spin Quantum Number	$m_{\rm s}$	+1/2, -1/2

The Principal Quantum Number

The first quantum number describes the electron shell, or energy level, of an atom. The value of n ranges from 1 to the shell containing the outermost electron of that atom

The Azimuthal Quantum Number

The second quantum number, known as the angular or orbital quantum number, describes the subshell and gives the magnitude of the orbital angular momentum through the relation. In chemistry and spectroscopy, $\ell = 0$ is called an s orbital, $\ell = 1$ a p orbital, $\ell = 2$ a d orbital, and $\ell = 3$ an f orbital.

The Magnetic Quantum Number

The magnetic quantum number describes the energy levels available within a subshell and yields the projection of the orbital angular momentum along a specified axis. The values of $m\ell$ range from – to ℓ , with integer steps between them. The s subshell ($\ell = 0$) contains one orbital, and therefore the $m\ell$ of an electron in an s subshell will always be 0.

The Spin Projection Quantum Number

The fourth quantum number describes the spin (intrinsic angular momentum) of the electron within that orbital and gives the projection of the spin angular momentum (s)

along the specified axis. Analogously, the values of m_s range from -s to s, where s is

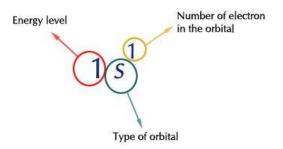
the spin quantum number, an intrinsic property of particles. An electron has spin $s = \frac{1}{2}$, consequently m_s will be \pm , corresponding with spin and opposite spin.

Reference page/site.

<u>https://courses.lumenlearning.com/introchem/chapter/quantum-</u> <u>numbers/#:~:text=To%20completely%20describe%20an%20electron,energy%20level%2C%20of%20an%20ato</u> <u>m.</u>

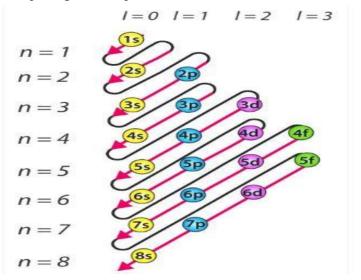
♦ Electronic configuration

The electron configuration of an element describes how electrons are distributed in its atomic orbitals.



Electron Configurations are useful for:

- Determining the valency of an element.
- Predicting the properties of a group of elements (elements with similar electron configurations tend to exhibit similar properties).
- Interpreting atomic spectra.



Examples

The electron configurations of a few elements are provided with illustrations in this subsection.

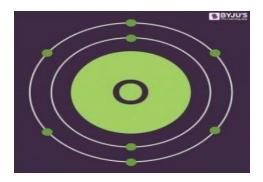
Electron Configuration of Oxygen

The atomic number of oxygen is 8, implying that an oxygen atom holds 8 electrons. Its electrons are filled in the following order: K shell - 2 electrons

L shell - 6 electrons

L shell - 6 electrons

Therefore, the electron configuration of oxygen is $1s^2 2s^2 2p^4$, as shown in the illustration provided below.



Electron Configuration of Oxygen

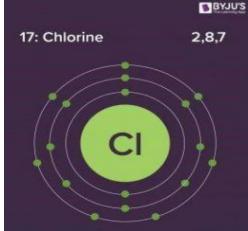
Chlorine Electronic Configuration

Chlorine has an atomic number of 17. Therefore, its 17 electrons are distributed in the following manner:

K shell -2 electrons L shell -8 electrons

M shell -7 electrons

The electron configuration of chlorine is illustrated below. It can be written as $1s^22s^22p^63s^23p^5$ or as [Ne] $3s^23p^5$



Electron Configuration of Chlorine

Quantum laws.

Aufbau Principle

- This principle is named after the German word 'Aufbeen' which means 'build up'.
- The <u>Aufbau principle</u> dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals.
- The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.
- According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p...

Pauli Exclusion Principle

• The Pauli exclusion principle states that a maximum of two electrons, each having opposite spins, can fit in an orbital.

- This principle can also be stated as "no two electrons in the same atom have the same values for all four quantum numbers".
- Therefore, if the principal, azimuthal, and magnetic numbers are the same for two electrons, they must have opposite spins.

Hund's Rule

- This rule describes the order in which electrons are filled in all the orbitals belonging to a subshell.
- It states that every orbital in a given subshell are singly occupied by electrons before a second electron is filled in an orbital.
- In order to maximize the total spin, the electrons in the orbitals that only contain one electron all have the same spin (or the same values of the spin quantum number).

Reference page/site.

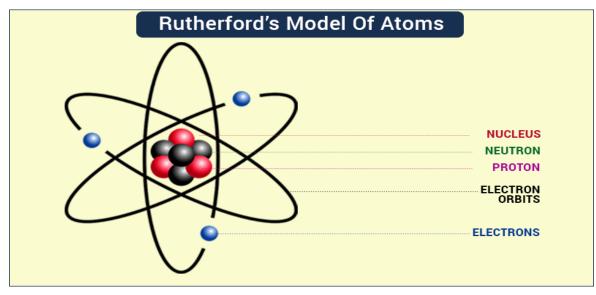
https://byjus.com/chemistry/electron-configuration/

* Rutherford atomic model

Rutherford Atomic Model – The plum pudding model is given by J. J. Thomson failed to explain certain experimental results associated with the atomic structure of elements. Ernest Rutherford, a British scientist conducted an experiment and based on the observations of this experiment he proposed the <u>atomic structure</u> of elements and gave **Rutherford Atomic Model**.

Rutherford's Alpha Scattering Experiment

Rutherford's conducted an experiment by bombarding a thin sheet of gold with α -particles and then studied the trajectory of these particles after their interaction with the gold foil.



Rutherford, in his experiment, directed high energy streams of α -particles from a radioactive source at a thin sheet (100 nm thickness) of gold. In order to study the deflection caused to the α -particles, he placed a fluorescent zinc sulphide screen around the thin gold foil. Rutherford made certain observations that contradicted <u>Thomson's atomic model</u>.

Observations of Rutherford's Alpha Scattering Experiment

The observations made by Rutherford led him to conclude that:

- 1. A major fraction of the α -particles bombarded towards the gold sheet passed through it without any deflection, and hence **most of the space in an atom is empty**.
- 2. Some of the α -particles were deflected by the gold sheet by very small angles, and hence the **positive** charge in an atom is not uniformly distributed. The positive charge in an atom is concentrated in a very small volume.
- 3. Very few of the α -particles were deflected back, that is only a few α -particles had nearly 1800 angle of deflection. So the **volume occupied by the positively charged particles in an atom is very small as compared to the total volume of an atom**.

Rutherford Atomic Model

Based on the above observations and conclusions, Rutherford proposed the atomic structure of elements. According to the Rutherford atomic model:

- 1. The positively charged particles and most of the mass of an atom was concentrated in an extremely small volume. He called this region of the atom as a nucleus.
- 2. Rutherford model proposed that the negatively charged electrons surround the nucleus of an atom. He also claimed that the electrons surrounding the nucleus revolve around it with very high speed in circular paths. He named these circular paths as orbits.
- 3. Electrons being negatively charged and nucleus being a densely concentrated mass of positively charged particles are held together by a strong electrostatic force of attraction.

Limitations of Rutherford Atomic Model

Although the Rutherford atomic model was based on experimental observations it failed to explain certain things.

- Rutherford proposed that the electrons revolve around the nucleus in fixed paths called orbits. According to Maxwell, accelerated charged particles emit electromagnetic radiations and hence an electron revolving around the nucleus should emit electromagnetic radiation. This radiation would carry energy from the motion of the electron which would come at the cost of shrinking of orbits. Ultimately the electrons would collapse in the nucleus. Calculations have shown that as per Rutherford model an electron would collapse in the nucleus in less than 10-8 seconds. So Rutherford model was **not in accordance with Maxwell's theory and could not explain the stability of an atom**.
- One of the drawbacks of the Rutherford model was also that he **did not say anything about the arrangement of electrons in an atom** which made his theory incomplete.
- Although the early atomic models were inaccurate and failed to explain certain experimental results, they were the base for future developments in the world of quantum mechanics.

Reference page/site.

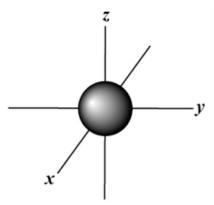
https://byjus.com/chemistry/rutherfords-model-of-atoms-and-its-limitations/

* Shapes of orbitals.

Atomic orbitals are mathematical functions that describe the wave nature of electrons (or electron pairs) in an atom.

The Shape of s Orbitals

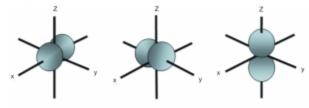
- The boundary surface diagram for the s orbital looks like a sphere having the nucleus as its centre which in two dimensions can be seen as a circle.
- Hence, we can say that s-orbitals are spherically symmetric having the probability of finding the <u>electron</u> at a given distance equal in all the directions.
- The size of the s orbital is also found to increase with the increase in the value of the principal quantum number (n), thus, 4s > 3s > 2s > 1s.



The Shape of s Orbitals

The Shape of p Orbitals

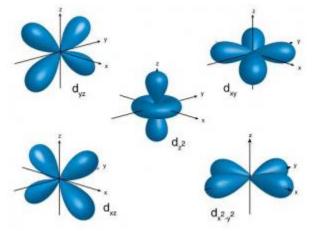
- Each p orbital consists of two sections better known as lobes which lie on either side of the plane passing through the nucleus.
- The three p orbitals differ in the way the lobes are oriented whereas they are identical in terms of size shape and energy.
- As the lobes lie along one of the x, y or z-axis, these three orbitals are given the designations $2p_x$, $2p_y$, and $2p_z$. Thus, we can say that there are three p orbitals whose axes are mutually perpendicular.
- Similar to s orbitals, size, and energy of p orbitals increase with an increase in the principal quantum number (4p > 3p > 2p).

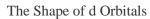


The Shape of p Orbitals

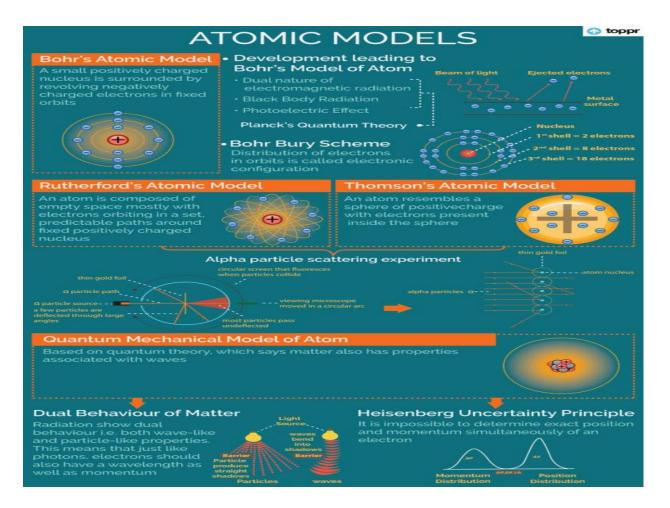
The Shape of d Orbitals

- The magnetic orbital <u>quantum number</u> for d orbitals is given as (-2,-1,0, 1,2). Hence, we can say that there are five d-orbitals.
- These orbitals are designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} .
- Out of these five d orbitals, shapes of the first four d-orbitals are similar to each other, which is different from the d_z^2 orbital whereas the energy of all five d orbitals is the same.



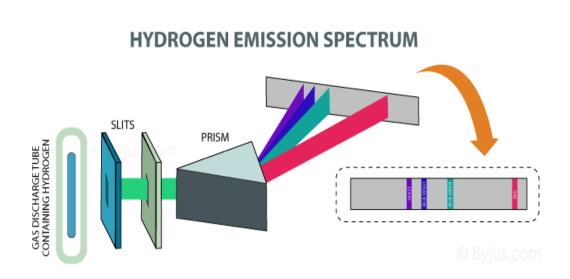


Reference page/site. https://byjus.com/chemistry/shapes-of-orbitals/



Hydrogen Spectrum introduction

We all know that electrons in an atom or a molecule absorb energy and get excited, they jump from a lower energy level to a higher energy level and they emit radiation when they come back to their original states. This phenomenon accounts for the emission spectrum through hydrogen too, better known as the <u>hydrogen emission</u> <u>spectrum</u>.



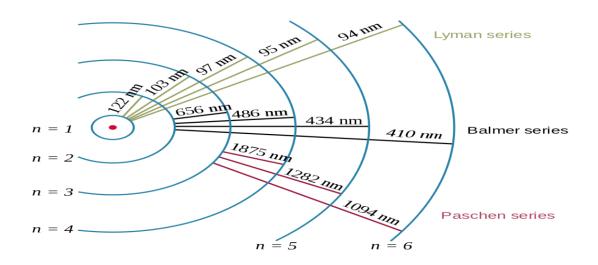
In the late 1800s, it was known that when a gas is excited using an electric discharge and the light emitted is viewed through a diffraction grating; the spectrum observed consists not of a continuous band of light, but of individual lines with well-defined wavelengths. Experiments have shown that the wavelengths of the lines were characteristic of the chemical element emitting the light. They were an atomic fingerprint which resulted from the internal structure of the atom.

What is Hydrogen spectrum?

The <u>hydrogen</u> spectrum is an important piece of evidence to show the quantized electronic structure of an atom. The hydrogen atoms of the molecule dissociate as soon as an electric discharge is passed through a gaseous hydrogen molecule. It results in the emission of electromagnetic radiation initiated by the energetically excited hydrogen atoms. The hydrogen emission spectrum comprises radiation of discrete frequencies. These series of radiation are named after the scientists who discovered them.

Hydrogen spectrum wavelength

When a hydrogen atom absorbs a photon, it causes the electron to experience a transition to a higher energy level, for example, n = 1, n = 2. When a photon is emitted through a hydrogen atom, the electron undergoes a transition from a higher energy level to a lower, for example, n = 3, n = 2. During this transition from a higher level to a lower level, there is the transmission of light occurs. The quantized energy levels of the atoms, cause the spectrum to comprise wavelengths that reflect the differences in these energy levels. For example, the line at 656 nm corresponds to the transition n = 3 n = 2.



Hydrogen transitions

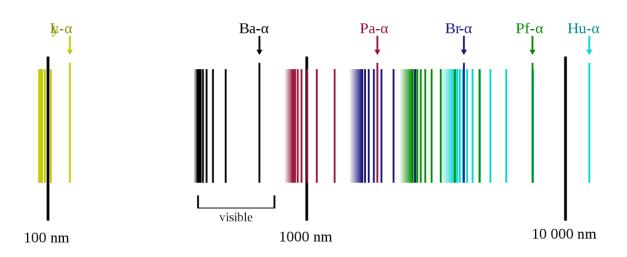
Hydrogen emission spectrum:

In the year 1885, on the basis of experimental observations, Balmer proposed the formula for correlating the wave number of the spectral lines emitted and the energy shells involved. This formula is given as:

$$\bar{v} = 109677(\frac{1}{2^2} - \frac{1}{n^2})$$

This series of the hydrogen emission spectrum is known as the Balmer series. This is the only series of lines in the electromagnetic spectrum that lies in the visible region. The value, 109,677 cm⁻¹, is called the Rydberg constant for hydrogen. The Balmer series is basically the part of the hydrogen emission spectrum responsible for the excitation of an <u>electron</u> from the second shell to any other shell. Similarly, other transitions also have their own series names. Some of them are listed below,

- Transition from the first shell to any other shell Lyman series
- Transition from the second shell to any other shell Balmer series
- Transition from the third shell to any other shell Paschen series
- Transition from the fourth shell to any other shell Bracket series
- Transition from the fifth shell to any other shell Pfund series



Hydrogen spectrum series

Johannes Rydberg, a Swedish spectroscopist, derived a general formula for the calculation of wave number of hydrogen spectral line emissions due to the transition of an electron from one orbit to another. The general formula for the hydrogen emission spectrum is given by:

$$\bar{v} = 109677(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2})$$

Where,

 $n_1 = 1, 2, 3, 4 \dots$

 $n_2 = n_1 + 1$

v= wave number of <u>electromagnetic radiation</u>. The value 109,677 cm⁻¹ is known as Rydberg constant for hydrogen.

(NUMERICALS)

Electronic configuration.

Example: Chlorine 17 1s²2s²2p⁶3s²3p⁵

Coefficients 1, 2, 2, 3, and 3 are energy levels of Cl. As you can see "p" sub shell can have maximum 6 electrons.

Superscripts 2, 2, 6, 2 and 5 are electrons in the sub shells "s" and "p".

Example: Bromine 35 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰4p⁵

As you can see "d" sub shell can have maximum 10 electrons.

Wave length & wave numbers.

Q. Calculate the wave number and wave length of a photon when the when the electron jumps from $n_2 = 4$ to $n_1 = 1$.

GivenLower energy level, $n_1 = 1$,Higher energy level, $n_2 = 4$ Required(a) Wave number \overline{v} (b) identification of the spectral lineFormula

$$\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where R is the Rydberg's constant and its value is 1.0974×10^7 m⁻¹. So put the values, Solution.

$$\bar{\nu} = 1.0974 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2} \right)$$

$$\bar{\nu} = 1.0974 \times 10^7 \left(1 - \frac{1}{16} \right)$$

$$\bar{\nu} = 1.0974 \times 10^7 \times \frac{15}{16}$$

$$\Rightarrow \bar{\nu} = 1.0974 \times 0.9375 \times 10^7 \Rightarrow \bar{\nu} = 1.0288125 \times 10^7 m^{-1}$$
Hence, there are about 10288125 wave in one meter length

Now, wavelength is the length of a wave in meters. Therefore, wavelength can be obtained by taking the reciprocal of the wave number.

$$\lambda = \frac{1}{1.0288125 \times 10^7} m = 0.972 \times 10^{-7} m$$

Exercise Practice.

- 1. Calculate the electronic configuration of the following.
- Na₁₁
- K₁₉
- S₁₆
 - 2. Calculate the wave number and wave length of a photon when the electron jump from n=3 to n=2.

Radioactivity:

- The process of emission of particles from nuclei because of the nuclear instability; is known as radioactivity.
- The substance that releases such energy/rays is known as radioactive substance.

There are three types of radioactive radiation.

Alpha (a) Particles

- Alpha particles are usually composed of two protons and two neutrons, which are tightly bound together.
- Alpha particles are being released during radioactive decay (or alpha decay) from the nucleus radio nuclides.
- The alpha particles are identical to the nucleus of either normal helium atom or doubly ionized helium atom.
- In comparison to other particles (i.e. Gamma and Beta), alpha particles are heavy and slow. Therefore, alpha particles have very small range in the air.
- Because of slow speed, Alpha particles have very weak penetrating powers; these particles are even stopped by a thin paper sheet (see image given above).
- Because of having the double positive charge, alpha particles are highly ionizing.

Beta (β) Particles

- Beta particles are the fast moving electrons emitted by some radio nuclides during the radioactive decay (also known as beta decay).
- Beta particles are of much lighter weight and carry a single negative charge.
- Beta particles are rarely ionizing than the alpha particles.
- Because of having lighter weight, beta particles can travel much farther than alpha particles; however, beta particles can be stopped by several sheet of papers or one sheet of aluminum.
- Beta particles are negatively charged and get attracted towards positively charged particles.

Gamma (y) Particles

- Gamma particles are the bundle of high energy namely electromagnetic energy (photon) emitted by the radioactive elements during the radioactive decay.
- Among all three particles (alpha, beta, and gamma), gamma particles are the most energetic photons.
- Gamma particles, which are the form of electromagnetic radiation(EMR), originate from the nucleus.
- The wavelengths of gamma are the shortest among all three.
- Gamma particles have no charge and they are neutral; therefore, they are unaffected by magnetic and electric fields.

Reference page/site.

https://www.tutorialspoint.com/chemistry_part2/chemistry_radioactivity.htm

Student's assessment

- What are subatomic particles?
- How do the atomic structures of isotopes vary?
- What are the shortcomings of Bohr's atomic model?
- How can the total number of neutrons in the nucleus of a given isotope be determined?
- Who proposed the principal quantum number?
- Why are there only 8 electrons in the outer shell?
- How do you find the principal quantum number?
- What are the principal energy levels?
- Which energy level has the least energy?
- Name three isotopes of oxygen.
- How isotopes are formed?
- Give some examples of stable isotopes.
- The unstable isotopes emit what rays?
- What are isobars?
- Give some examples of isobars.
- What is the electronic configuration of copper?

(Related videos)

Fundamental particles

https://youtu.be/I1VXM_b2KFY https://youtu.be/EMDrb2LqL7E Discharge tube https://youtu.be/vXOeehVTcRA https://youtu.be/Fal_QtW0MW4 Rutherford atomic model https://youtu.be/IQ1h_gdVIHg Bohr's atomic model https://youtu.be/fm2C0ovz-3M https://youtu.be/fm2C0ovz-3M https://youtu.be/WgJbBcVF12I Quantum numbers https://youtu.be/6gkjxPAYgy0 Dalton's atomic theory

https://youtu.be/AFlikHKYq8Q Radioactivity

https://youtu.be/Zc9xfUnrTxg

X-----X

CHAPTER 3



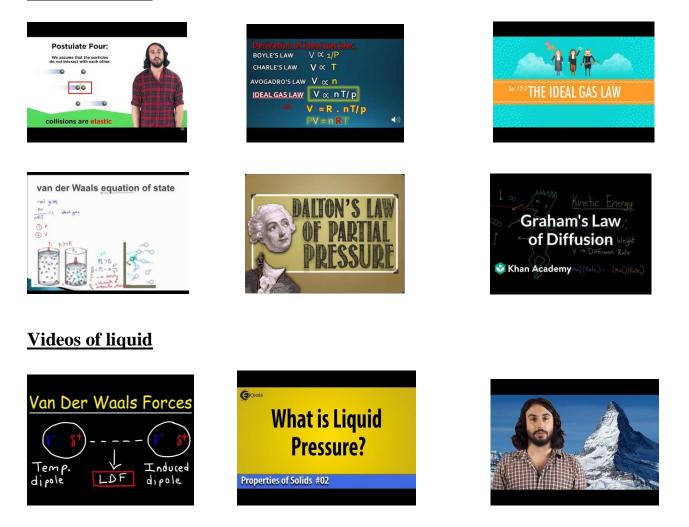
chapter	skills	understanding
GASES :		
Kinetic Molecular Theory of	Students will be able to:	Students will be able to:
Gases.	Interconvert pressure in pascals,	List the postulates of Kinetic
Absolute Temperature Scale on	kilopascals, atmospheres and bar.	Molecular Theory. (Remembering)
the Basis of Charles Law	(Applying)	Describe the motion of particles of
Avogadro's Law .	Calculate the partial pressure of a	a gas according to Kinetic Theory.
Ideal Gas Equation.	gas collected over water.	(Applying)
Deviation from Ideal Gas	(Applying)	State the values of standard
Behavior.	Calculate the new volume of a gas	temperature and pressure (STP).
Van der Waals Equation.	when the pressure of the gas	(Remembering)
Dalton's Law of Partial Pressure.	changes. (Applying)	Relate temperature to the average
Graham's Law of Diffusion and	Use the combined gas law in	kinetic energy of the particles in a
Effusion.	calculations. (Applying)	substance. (Applying)
Liquefaction of Gases	Determine the molar volume of	Use Kinetic Theory to explain gas
Fourth State of Matter: Plasma	the gas under various conditions.	pressure. (Applying)
Conceptual Linkages	(Applying)	Describe the effect of change in
This unit is built on	Apply the ideal gas laws to	pressure on the volume of gas.
• Physical Properties of Gases due	calculate the pressure or the	(Applying)
to Intermolecular Forces	volume of a gas. (Applying)	Describe the effect of change in
Boyle's Law		temperature on the volume of gas.
Charles' Law		(Applying)
LIQUIDS :	Identify types of intermolecular	Explain the significance of absolute
Kinetic Molecular Interpretation	attractions between the molecules	zero, giving its value in degree
of Liquids	of a liquid from a given list of	Celsius and Kelvin.
Intermolecular Forces (Van der	liquids based on its molecular	(Understanding)
Walls forces)	structures. (Applying)	State and explain the significance
Physical Properties of Liquids	Compare and explain the	of Avogadro's Law.
Energetics of Phase Changes	volatility of different liquids at	(Understanding)
Liquid Crystals	same temperature based on	

Concentual Links and	intermologylar forces	Derive Ideal Cas Ferration
Conceptual Linkages	intermolecular forces.	Derive Ideal Gas Equation using
This unit is built on	(Analyzing)	Boyle's, Charles' and Avogadro's
Physical Properties of Liquids due		law. (Understanding)
to Intermolecular Forces		Explain the significance and
Effects of Temperature and		different units of ideal gas constant.
Pressure on Vapor Pressure		(Understanding)
Effects of Temperature and		Distinguish between real and ideal
Pressure on Boiling Point		gases. (Understanding)
		Explain why real gases deviate
		from the gas laws. (Analyzing)
		Define and describe the properties
		of Plasma.(Applying)
		Derive new form of Gas Equation
		with volume and pressure
SOLIDS :		corrections for real gases.
Topics according to national	T ist as many second second	(Understanding)
curriculum.	List some common amorphous	State and use Graham's Law of
SOLIDS :	solids encountered in daily life.	Diffusion. (Understanding)
Kinetic Molecular Interpretation	(Applying)	State and use Dalton's Law of
of Solids	Explain why a compound like CaCl2 will fluctuate in mass from	Partial Pressures. (Understanding)
Types of Solids		Describe some of the implications
Properties of Crystalline Solids	day to day because of humidity.	of the Kinetic Molecular Theory,
Crystal Lattice	(Applying)	such as the velocity of molecules
Types of Crystalline Solids	Purify saline water by repeated	and Graham's Law. (Applying)
Concentual Linkages	freezing. (Applying)	Explain Und's method for the
Conceptual Linkages This unit is built on		liquefaction of gases.
		(Understanding)
Physical Properties of Solids		Define pressure and give its various units. (Remembering)
Amorphous Solids Crystalline Solids		Define and explain plasma
Allotropic Solids		formation. (Understanding)
Anonopic Solids		formation. (Onderstanding)
		Describe simple properties of
		liquids e.g., diffusion, compression,
		expansion, motion of molecules,
		spaces between them,
		intermolecular forces and kinetic
		energy based on Kinetic Molecular
		Theory. (Understanding)
		Explain applications of dipole-
		dipole forces, hydrogen bonding
		and London forces. (Applying)
		Explain physical properties of
		liquids such as evaporation, vapour
		pressure, boiling point, viscosity
		and surface tension.
		(Understanding)
		Use the concept of Hydrogen
		bonding to explain the following
		properties of water: high surface
		tension, high specific heat, low
L	1	tension, ingli specific ficut, iow

vapor pressure, high heat of
vaporization, and high boiling
point. And anomalous behaviour of
water when its density shows
maximum at 4 degree
centigrade(Applying)
Define molar heat of fusion and
molar heat of vaporization.
(Remembering)
Describe how heat of fusion and
heat of vaporization affect the
particles that make up matter.
(Understanding)
Relate energy changes with
changes in intermolecular forces.
(Applying)
Define dynamic equilibrium
between two physical states.
(Remembering)
Describe liquid crystals and give
their uses in daily life. (Applying)
Differentiate liquid crystals from
pure liquids and crystalline solids.
(Applying)
(**PP-JB)
Describe simple properties of
solids e.g., diffusion, compression,
expansion, motion of molecules,
spaces between them,
intermolecular tomes and kinetic
energy based on kinetic molecular
theory. (Understanding)
Differentiate between amorphous
Differentiate between amorphous
and crystalline solids
and crystalline solids. (Understanding) Describe
(Understanding) Describe
(Understanding) Describe properties of crystalline solids like
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point,
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal,
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy,
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism,
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature.
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding)
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding) Use oxygen and sulphur to define
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(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding) Use oxygen and sulphur to define allotropes. (Understanding) Explain the significance of the unit
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding) Use oxygen and sulphur to define allotropes. (Understanding) Explain the significance of the unit cell to the shape of the crystal
(Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding) Use oxygen and sulphur to define allotropes. (Understanding) Explain the significance of the unit

Name three types of packing
arrangements and draw or construct
models of them. (Applying)
Name three factors that affect the
shape of an ionic crystal.
(Understanding) Define lattice
energy. (Remembering)
Differentiate between ionic,
covalent, molecular and metallic
crystalline solids. (Applying)
Explain the low density and high
heat of fusion of ice.
(Understanding)
Define and ex lain molecular and
metallic solids. Understandin.

Videos of Gases

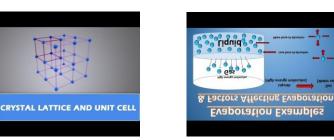


Videos of solid









Chapter overview

<u>GASES</u> : Express the five basic assumptions of the Kinetic Molecular Theory of Gases.

Key Points

Kinetic Molecular Theory states that gas particles are in constant motion and exhibit perfectly elastic collisions.

Kinetic Molecular Theory can be used to explain both Charles' and Boyle's Laws.

The average kinetic energy of a collection of gas particles is directly proportional to absolute temperature only.

Terms

macroscopic properties that can be visualized or measured by the naked eye; examples include pressure, temperature, and volume

ideal gas hypothetical gas whose molecules exhibit no interaction and undergo elastic collision with each other and the walls of the container

Basic Assumptions of the Kinetic Molecular Theory

By the late 19th century, scientists had begun accepting the atomic theory of matter started relating it to individual molecules. The Kinetic Molecular Theory of Gases comes from observations that scientists made about gases to explain their macroscopic properties. The following are the basic assumptions of the Kinetic Molecular Theory:

The volume occupied by the individual particles of a gas is negligible compared to the volume of the gas itself.

The particles of an ideal gas exert no attractive forces on each other or on their surroundings.

Gas particles are in a constant state of random motion and move in straight lines until they collide with another body.

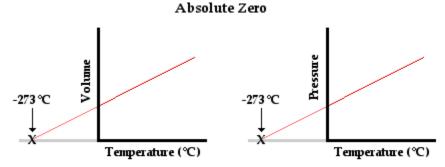
The collisions exhibited by gas particles are completely elastic; when two molecules collide, total kinetic energy is conserved.

The average kinetic energy of gas molecules is directly proportional to absolute temperature only; this implies that all molecular motion ceases if the temperature is reduced to absolute zero

Absolute Temperature Scale on the Basis of Charles Law .

Charles's Law states that the volume of a given mass of gas varies directly with the **absolute temperature** of the gas when pressure is kept constant. The **absolute**

temperature is temperature measured with the Kelvin scale. ...



A volume vs. temperature and a pressure vs. temperature plot will each have an x-intercept of -273 C. The volume and the pressure of a gas seem to reduce to 0 at a very specific temperature (assuming the gas remains as a gas).

Avogadro's Law

Avogadro's Law: The volume of a gas is directly proportional to the amount of gas. The typical *amount* of gas is in moles. Avogadro's Law assumes that temperature and pressure are constant.

Vn=k(constant)Vn=k(constant)

Where nn is in moles of gas.

As with the other gas laws (Boyle's and Charles'), Avogadro's Law is typically depicted when considering an initial set of conditions (condition 1) and a final set of conditions (condition 2).

V1n1=V2n2V1n1=V2n2

This is exactly like Charles' Law except the temperature (T) has been replaced with number of moles (n).

Also keep in mind that mass is proportional to moles which means the mass of the gas can also be used here:

V1m1=V2m2V1m1=V2m2

Where m is the mass of the gas. However, keep in mind that unlike for n, the two conditions compared with the mass must compare the same gas (as different gases have different molar masses).

GENERAL GAS EQUATION AND EQUATION OF STATE OF A GAS

According to Boyle's Law : Volume of a given mass of a gas is inversely proportional to pressure if temperature remains constant . V µ 1/P -----(1) According to Charles's law: Volume of a given mass of a gas is directly proportional to absolute temperature if pressure remains constant. V u T -----(2) According to Avogadro's law: Volume of a gas is directly proportional to no of moles. V μ n -----(3) Combining 1,2,and 3 **V μ T.n1/P. V μ nT/P** V= (constant) nT/P **PV/nT** = constant Here constant is R PV/nT = ROr PV= n RT This is the equation of state of a gas (Ideal Gas Equation) R= Universal gas constant Value of **R** is equal to **0.0821 dm³.atmosphere/mole.k** R has different values in different systems of unit **ANOTHER FORM:** As PV/nT = constantFor initial conditions: When temperature is T_1 and pressure is P_1 : $P_1V_1/T_1 = constant$ -----(a) Similarly for final conditions: $P_2V_2/T_2 = constant \dots (b)$ From equation (a) & (b) $P_1V_1/T_1 = P_2V_2/T_2$

Determine the volume of 2.00 moles of gases (ideal gas) at STP. STP = Standard Temperature and Pressure. <u>Known :</u> Moles of gas (n) = 2 moles Standard temperature (T) = 0 oC = 0 + 273 = 273 Kelvin Standard pressure (P) = 1 atm = 1.013 x 105 Pa

Universal gas constant (R) = 8.315 Joule/mole.Kelvin

Wanted: Volume of gases (V)

Solution :

Equation of Ideal gas law (in the number of moles, n)

PV = nRT $V = \frac{nRT}{P} = \frac{(2)(8.315)(273)}{1.013 \times 10^5} = \frac{(2)(8.315)(273)}{1.013 \times 10^5}$ $V = \frac{4539.99}{101300} = 0.0448 m^3 = 0.0448 \times 10^3 dm^3$ $V = 44.8 dm^3 = 44.8 \, liters$

DALTON'S LAW OF PARTIAL PRESSURE

PARTIAL PRESSURE

In a mixture of different gases which do not react chemically each gas behaves independently of the other gases and exerts its own pressure. This individual pressure that a gas exerts in a mixture of gases is called it's partial pressure.

DALTON'S LAW OF PARTIAL

PRESSURE

Based on this behaviour of gases, JOHN DALTON formulated a basic law which is known as "The Dalton's law of partial pressure" .

The law states that:

"If two or more gases (which do not react with each other) are enclosed in a vessel, the total pressure exerted by them is equal to the sum of their partial pressure". MATHEMATICAL

REPRESENTATION

Consider a mixture of three non-reacting gases **a**, **b** and **c**. Partial pressures of these gases are P_a , P_b and P_c . According to Dalton's law of partial pressure, their total pressure is given by:

 $\mathbf{P}_{total} = \mathbf{P}_a + \mathbf{P}_b + \mathbf{P}_c$

DALTON'S LAW IN THE LIGHT OF KINETIC MOLECULAR THEORY

According to kinetic molecular theory of gases there is no force of attraction or repulsion among the gas molecules. Thus each gas behaves independently in a mixture and exerts it's own pressure. In terms of KINETIC MOLECULAR THEORY, Dalton's law of partial pressure can be explained as:

"In a non-reacting mixture of gases, each gas exerts separate pressure on the container in which it is confined due to collision of it's molecules with the walls of container. The total pressure exerted by the gaseous mixture is equal to

the sum of collisions of the molecules of individual gas ."

EXPRESSION FOR PARTIAL PRESSURE

Consider a gaseous mixture of three different gases **a**, **b** and **c** enclosed in a container of volume Vdm³ at **T** Kelvin. Let the partial pressures of these gases are P_a , P_b and P_c respectively and total pressure of mixture is P_t . Let there are n_a , n_b and n_c moles of each gas respectively and the total number of

moles are **n**_{t.}



Three gases confined in a cylinder under similar conditions: Using equation of state of gas:

comp equation of state of gas.	PV = nRT
	OR
	P = nRT/V
For gas a	
	$P_a = n_a RT/V$ (i)
For gas b	
	$P_{b} = n_{a}RT/V$ (ii)
For gas c	
	$P_{c} = n_{c}RT/V$ (iii)
For any gas	
	$P_{gas} = n_{gas} RT/V$
	OR
	$\frac{P_{gas}}{n_{gas}} = RT/V$
	(a)

$$Pt = n_a RT/V + n_b RT/V + n_c RT/V$$
$$Pt = (n_a + n_b + n_c)RT/V$$
$$OR$$

But $n_t = n_a + n_b + n_c$

$$\frac{Pt = n_t RT/V}{n_t} = RT/V \dots \dots (b)$$

Comparing equation (a) and (b), we get,

$$\frac{\frac{Pt}{n_{t}}}{R} = \frac{\frac{P_{gas}}{n_{gas}}}{\frac{P_{gas}}{R}}$$
OR
$$\frac{P_{gas}}{P_{gas}} = \frac{n_{gas}}{n_{total}}$$

This expression indicates that the pressure of a gas is proportional to number of moles if confined under similar conditions.

Graham's Laws of Diffusion and Effusion

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Inter mixing of two or more gases to form a homogeneous mixture without any chemical change is called "DIFFUSION OF GASES". Diffusion is purely a physical phenomenon. Gases diffuse very quickly due to large empty spaces among molecules. Different gases diffuse with different rates (velocities).

GRAHAM'S LAW OF DIFFUSION

Graham's law is a quantitative relation between the density and rate of diffusion of gases.

STATEMENT

• The rate of diffusion of a gas is inversely proportional to the square root of its density.

$$\boldsymbol{r} \propto \frac{1}{\sqrt{d}}$$

• The comparative rates of diffusion of two gases are inversely proportional to the square root of their densities.

$$\frac{\boldsymbol{r}_1}{\boldsymbol{r}_2} \propto \sqrt{\frac{d_2}{d_1}}$$

MATHEMATICAL REPRESENTATION OF THE LAW

Consider two gases A and B having mass densities d1 and d2 and their rates of diffusions are r1 and r2 respectively.

According to Graham's law of diffusion: For gas A:

$$\mathbf{v}_{1} \propto \frac{\mathbf{I}}{\sqrt{d_{1}}}$$
OR
$$\mathbf{v}_{1} = \mathbf{K} \frac{\mathbf{I}}{\sqrt{d_{1}}}$$
.....(i)

For gas **B**:

$$r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$\mathbf{p}_2 = \mathbf{K} \frac{\mathbf{l}}{\sqrt{\mathbf{d}_2}}$$
.....(ii)

Dividing equation (i) by equation (ii)

$$\frac{\boldsymbol{v}_{1}}{\boldsymbol{v}_{2}} = \frac{\boldsymbol{k} \frac{1}{\sqrt{d_{1}}}}{\boldsymbol{k} \frac{1}{\sqrt{d_{2}}}}$$
OR
$$\frac{\boldsymbol{v}_{1}}{\boldsymbol{v}_{2}} = \frac{\frac{1}{\sqrt{d_{1}}}}{\frac{1}{\sqrt{d_{2}}}}$$
OR
$$\frac{\boldsymbol{v}_{1}}{\boldsymbol{v}_{2}} = \frac{\sqrt{d_{2}}}{\sqrt{d_{1}}}$$
OR
$$\frac{\boldsymbol{v}_{1}}{\boldsymbol{v}_{2}} = \sqrt{\frac{d_{2}}{\sqrt{d_{1}}}}$$
OR
$$\frac{\boldsymbol{v}_{1}}{\boldsymbol{v}_{2}} = \sqrt{\frac{d_{2}}{d_{1}}}$$

Since density **a** molecular mass, therefore, we can replace density **d** by Molecular mass **M**.

$$\frac{\boldsymbol{r_1}}{\boldsymbol{r_2}} \propto \sqrt{\frac{M_2}{M_1}}$$

Boyle's Law

Boyle's Law states that volume of a given amount of gas held at a constant temperature varies inversely the with pressure. The relationship between pressure and volume of Boyle's Law is expressed in mathematical terms as $P_1V_1 = P_2V_2$.

Formula and Derivation

As per Boyle's law, any change in the volume occupied by a gas (at constant quantity and temperature) will result in a change in the pressure exerted by it. In other words, the product of the initial pressure

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and the initial volume of a gas is equal to the product of its final pressure and final volume (at constant temperature and number of moles). This law can be expressed mathematically as follows:

 $\mathbf{P}_1\mathbf{V}_1=\mathbf{P}_2\mathbf{V}_2$

Where,

- P₁ is the initial pressure exerted by the gas
- V₁ is the initial volume occupied by the gas
- P₂ is the final pressure exerted by the gas
- V₂ is the final volume occupied by the gas

This expression can be obtained from the pressure-volume relationship suggested by Boyle's law. For a fixed amount of gas kept at a constant temperature, PV = k. Therefore,

 $P_1V_1 = k$ (initial pressure * initial volume)

 $P_2V_2 = k$ (final pressure * final volume)

 $\therefore \mathbf{P}_1 \mathbf{V}_1 = \mathbf{P}_2 \mathbf{V}_2$

This equation can be used to predict the increase in the pressure exerted by a gas on the walls of its container when the volume of its container is decreased (and its quantity and absolute temperature remain unchanged).

Example .1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

SOLUTION

Steps for Problem Solving	
Identify the "given"information	Given: $P_1 = 2.44$ atm and $V_1 = 4.01$ L
and what the problem is asking	$P_2 = 1.93$ atm
you to "find."	Find: $V_2 = ? L$
List other known quantities.	none
	First, rearrange the equation algebraically to solve for V2V2.
Plan the problem.	V2=P1×V1P2(11.4.4)(11.4.4)V2=P1×V1P2
Concel units and	Now substitute the known quantities into the equation and solve.
Cancel units and calculate.	V2=2.44atm×4.01L1.93atm=5.07L(11.4.5)(11.4.5)V2=2.44atm×4.01L1.93atm=5.07L

Steps for Problem Solving	
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

Charles' Law

Charles' Law states that the volume of a given mass of a gas is directly proportional to its Kelvin temperature at constant pressure.

Derivation of Charles Law

As we are aware of the fact that, at constant pressure, the volume of the fixed amount of the dry gas is directly proportional to absolute temperature according to Charle's law. We can represent the statement in the following manner.

V∝T

Since V and T are varying directly, we can equate them by making use of the constant k.

V/T=constant =k

In this, the value of k depends on the pressure of the gas, the amount of the gas and also the unit of the volume.

V*T=k----(1)

Let us consider V1 AND T1 to be the initial volume and the temperature respectively of an ideal gas.

Then we can write equation (1) as

V1/T1=k-----(2)

After it lets change the temperature of the gas to T2. Alternatively, its volume changes to V2 then we can write

V2/T2=k----(3)

Equating the above equations that is equation 2 and 3, we get

V1/T1=V2/T2

Charles Law Solved Problems

1. A gas occupies a volume of 400cm3 at 0-degree Celcius and 780mm of Hg. How many litres of volume will the gas occupy at 80-degree Celcius and 780mm Hg

Solution- According to the question, V1=400cm3

T1=0 degree Celcius= 0+273=273K

T2=80 DEGREE CELCIUS=80+273=353K

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You need to find the V2.

Here only the temperature is changing, the pressure remains constant

Using Charle's law, V1/T1=V2/T2

Putting the above values in the Charle's law we get,

400/273=V2/353

V2=400*353/273

V2=517.21CM3

Since 1 cubic centimeters = 0.001 litres,

Then 517.21cubic centimeters=517.21*10^-3=0.517 litres.

What is plasma?

<u>Plasma</u> is defined as a state of matter predominantly comprised of ions and electrons. An ion is formed when an atom or molecule gains or loses electrons,

LIQUIDS :

Kinetic - Molecular Interpretation Of Liquids.

Learning Objectives

To describe the unique properties of liquids.

To know how and why the vapor pressure of a liquid varies with temperature.

To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to four unique properties of liquids that intimately depend on the nature of intermolecular interactions:

surface tension, capillary action,

viscosity, and boiling point.

bonnig point.

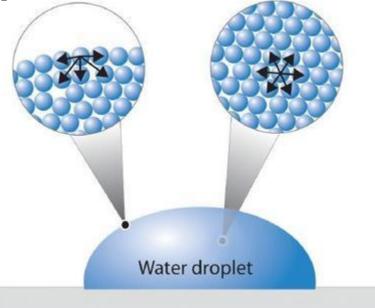
Surface Tension

Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces,

e.g., water with hydrogen bonds has a surface tension of $7.29 \times 10-2J/m27.29 \times 10-2J/m2$ (at 20°C), while mercury with metallic (electrostatic) bonds has as surface tension that is 6.5-times greater: $4.86 \times 10-1J/m24.86 \times 10-1J/m2$ (at 20°C).

presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has

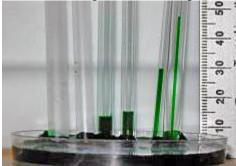
the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.



A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 10.1.310.1.3. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises. The height of the water does *not* depend on the angle at which the capillary is tilted.



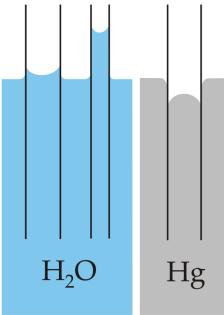
The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters.

action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary.

Cohesive forces bind molecules of the same type together

Adhesive forces bind a substance to a surface

Water has both strong adhesion to glass, which contains polar SiOHSiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 10.1.410.1.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex



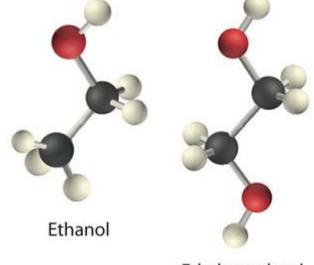
The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus. Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Polar substances are drawn up a glass capillary and generally have concave meniscuses and nonpolar substances general avoid the capillary and exhibit convex meniscuses.

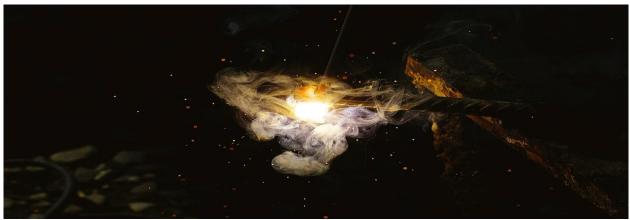
Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are

to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 10.1.110.1.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol (HOCH₂CH₂OH), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Ethylene glycol Comparison of structures of ethanol (left) with ethylene glycol



(right). (CC BY-SA-NC; anonymous by request)

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become "tangled" with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

Viscosity increases as intermolecular interactions or molecular size increases.

Boiling Points

The **vapor pressure** of a liquid is defined as the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system (discussed in more detail in next Sections of Chapter). As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 10.1.810.1.8 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm.

Intermolecular forces (Van der Waals Forces)

Van der Waals forces' is a general term used to define the attraction of intermolecular forces between molecules. There are two kinds of Van der Waals forces:

weak London Dispersion Forces

and stronger dipole-dipole forces.

Introduction

The chance that an electron of an atom is in a certain area in the electron cloud at a specific time is called the "electron charge density." Since there is no way of knowing exactly where the electron is located and since they do not all stay in the same area 100 percent of the time, if the electrons all go to the same area at once, a dipole is formed momentarily. Even if a molecule is nonpolar, this displacement of electrons causes a nonpolar molecule to become polar for a moment. Since the molecule is polar, this means that all the electrons are concentrated at one end and the molecule is partially negatively charged on that end. This negative end makes the surrounding molecules have an instantaneous dipole also, attracting the surrounding molecules' positive ends. This process is known as the London Dispersion Force of attraction.

The ability of a molecule to become polar and displace its electrons is known as the molecule's "<u>polarizability</u>." The more electrons a molecule contains, the higher its ability to become polar. Polarizability increases in the periodic table from the top of a group to the bottom and from right to left within periods. This is because the higher the molecular mass, the more electrons an atom has. With more electrons, the outer electrons are easily displaced because the inner electrons shield the nucleus' positive charge from the outer electrons which would normally keep them close to the nucleus.

When the molecules become polar, the melting and boiling points are raised because it takes more heat and energy to break these bonds. Therefore, the greater the mass, the more electrons present, and the more electrons present, the higher the melting and boiling points of these substances.

London dispersion forces are stronger in those molecules that are not compact, but long chains of elements. This is because it is easier to displace the electrons because the forces of attraction between the electrons and protons in the nucleus are weaker. The more readily displacement of electrons means the molecule is also more "polarizable."

Dipole-Dipole Forces

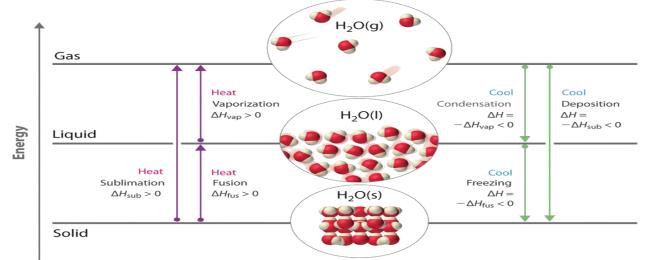
These forces are similar to London Dispersion forces, but they occur in molecules that are permanently polar versus momentarily polar. In this type of intermolecular interaction, a polar molecule such as water or H_2O attracts the positive end of another polar molecule with its negative end of its dipole. The attraction between these two molecules is the dipole-dipole force.

Energetics Of Phase Changes :

Learning Objectives

To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2 , as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes.



Energy Changes That Accompany Phase Changes

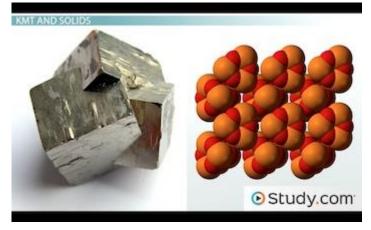
Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to

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allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very

SOLIDS :

KMT and Solids Now, let's check out some solids:



Pyrite crystals and phosphorus trioxide molecular structure

One of these images is of pyrite crystals in their naturally occurring cubic form; the other is the structure of phosphorus trioxide on the molecular scale. What **properties of solids** do you notice? Solid substances have definite shapes and volumes. Solid particles do move, but not very far! Solid particles have relatively little kinetic energy and vibrate in place. Because of this, they can't flow like liquids. Most solids are arranged in a tightly packed crystalline structure. The crystalline structure is an orderly, repeating arrangement of particles called a crystal lattice. The shape of the crystal shows the arrangement of the particles in the solid.

Some solids aren't crystalline-shaped. The ones that aren't are called amorphous solids. **Amorphous solids** don't have orderly internal structures. Examples of amorphous solids include rubber, plastic and glass. Wax is also an amorphous solid. It can be molded into any shape and remolded anytime it is warmed up a bit.

Intermolecular Forces

As previously noted, intermolecular forces are the attractive forces between particles. They are distinctly different from the bonds that occur within particles. The type of intermolecular forces present depends on the type of particles present.

Hydrogen bonds occur between polar molecules that contain an oxygen, nitrogen or fluorine atom covalently bonded to a hydrogen atom. The intermolecular attraction happens between the partially negatively charged oxygen, fluorine or nitrogen and the partially positively charged hydrogen of a neighboring molecule. Hydrogen bonds are relatively strong intermolecular forces. Types of Solids

There are five main types of solids, each of which has its own properties and structures. Let's have a look.

Ionic Solids

As we discussed at great length in <u>Ionic Compounds</u>, ionic solids consist of cations and anions held together by the strength of their opposite charges. The force that holds oppositely charged particles together is called an "electrostatic force."

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In <u>Ionic Compounds</u>, we treated all ionic solids as if they consisted of crystals in which all the ions had identical sizes. As you can probably guess, ions come in a wide variety of sizes. For example, in sodium chloride, the negatively charged chloride ions are much larger than the positively charged sodium ions. As a result, the structure of sodium chloride is a little different than you may have been led to expect. This is illustrated in the following figure:

The type of crystal structure of a particular ionic compound frequently depends on the ratio of the sizes of the anion and cation.

Metallic Solids

It was explained that metals are good conductors of electricity and heat, have high malleability (bendability), high ductility (can be made into wires), and are shiny. What we never explained was why metals exhibit these properties. As it turns out, the properties of metals stem from the nature of metallic bonds.

One very simple model used to explain bonding in metals is referred to as the electron sea theory. In the electron sea theory, the cations in a metallic solid remain in stationary crystalline positions while the valence electrons from each metal are free to wander throughout the entire solid:

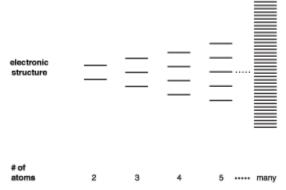


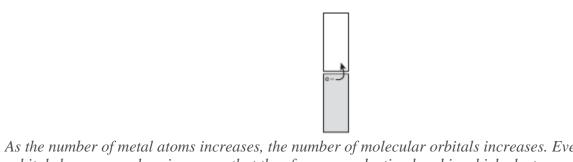
Figure 12.5*In the electron sea theory, the metal nuclei are locked in place and the electrons move freely through the solid.*

This theory does a good job of explaining the properties of metals. Because electrons are able to move freely throughout the entire solid, metals are excellent conductors of electricity. The high mobility of electrons also causes metals to conduct heat because they do a good job of dispersing energy. Because metal nuclei can move from place to place without causing bonds to be broken, metals are both malleable and ductile.

Though the electron sea theory accurately describes the properties of metals, it glosses over how the electrons are able to wander freely throughout the solid. After all, didn't we spend a great deal of time learning about how electrons exist within orbitals?

Think back to when we discussed hybrid orbitals (<u>Bonding and Structure in Covalent Compounds</u>). When an s-orbital and three p-orbitals overlap, they form four sp3 orbitals. If an s-orbital and two p-orbitals overlap, they form three sp2 orbitals.

In a metal, a similar thing happens. However, unlike covalent compounds, where only a few orbitals mix, all of the metal atoms mix their atomic orbitals (s-, p-, and d-orbitals) together to form a huge number of orbitals known as "molecular orbitals." These molecular orbitals are similar in energy to one another and form something called a conduction band:

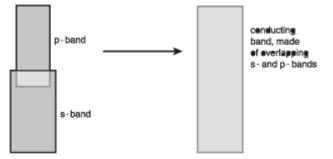


As the number of metal atoms increases, the number of molecular orbitals increases. Eventually, these orbitals become so close in energy that they form a conducting band in which electrons can easily jump from one orbital to another.

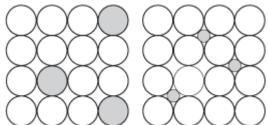
Chemistrivia

The molecular orbital theory that explains electron motion in metals is also referred to as "band theory."

Because there are more molecular orbitals in the conduction band than there are electrons, it doesn't take much energy to raise an electron from a filled orbital to an empty one with higher energy. When these electrons jump to empty orbitals, they are able to move freely around the metal.



In a metal, the difference in energy between filled orbitals and unfilled orbitals is very small. As a result, it's easy for electrons to jump to empty orbitals where they are free to move around the solid. There are typically several conducting bands in metals. One band (called the "s-band") is caused by an overlap between all of the s-orbitals in the metal. The other bands are called the "p-band" and "d-band" because they result from the overlap of p- and d-orbitals, respectively. Because these bands overlap in energy, they behave as one large, partially filled band:



When the *s*- and *p*-bands overlap in energy, they form a much larger band that makes it possible for metals to conduct electricity.

Other elements are sometimes added to metals to give them desired properties such as hardness, durability, or strength. The resulting material is referred to as an *alloy*.

There are two types of alloys:

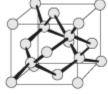
Substitutional alloys form when one of the atoms in a metal is replaced with a different element. For example, in sterling silver, some of the silver atoms are replaced with copper.

Interstitial alloys form when some of the spaces between the atoms in a metal are filled by smaller atoms. One of the most important interstitial alloys is carbon steel, in which carbon atoms are located between iron atoms.

Molecular Meanings

An **alloy** is a metallic material in which several elements are present. The elements added to a pure metal to form an alloy are selected to maximize a desired property.

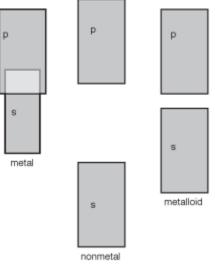
These two types of alloys are shown in the following figure.



The picture on the left represents a substitutional alloy; the picture on the right represents an interstitial alloy.

Network Atomic Solids

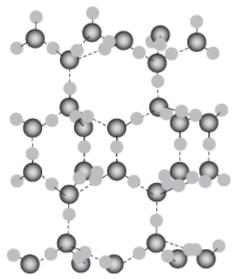
Network atomic solids are formed when many atoms are bonded together covalently to form one gigantic molecule. Unlike regular covalent molecules that are generally small, network atomic solids may grow quite large. One common example of a network atomic solid is a diamond:



The carbon atoms in a diamond are all held together by covalent bonds. As a result, diamonds can be thought of as being very large covalent molecules.

Network atomic solids have a wide number of varying properties. They are usually hard, owing to the strong bonds between neighboring atoms—for example, diamonds are (currently) the hardest known material. They also tend to have high melting and boiling points due to the very strong covalent bonds. Network atomic solids are frequently brittle because a small movement of atoms in the crystal tends to disrupt the network of covalent bonding. Aside from diamonds, some common network atomic solids are quartz (SiO2), graphite, and silicon.

When elements form network atomic solids, their atomic orbitals (s- and p-orbitals) overlap to form conducting bands in the same way that metals do. However, there is one major difference in the structure of the bands between metals, nonmetals, and metalloids. Whereas the s- and p-bands overlap in metals to form a giant conducting band, they don't for either nonmetals or metalloids, making it difficult for either to conduct electricity:



Left to right: the s- and p-bands for metals, nonmetals, and metalloids. Note the large energy gap between the s- and p-bands for nonmetals (causing them to be insulators) and the small energy gap for metalloids (making them semiconductors).

Because the s- and p-bands overlap in metals, they are good conductors of electricity. In nonmetals, there is a large energy gap between these bands (called, straightforwardly enough, the "band gap"), making it difficult for electrons to travel from one to another—as a result, they are good insulators. In metalloids, the band gap is small, which means that it is possible for electrons to jump from one band to another, causing them to conduct partially. This explains why metalloids are called "semiconductors."

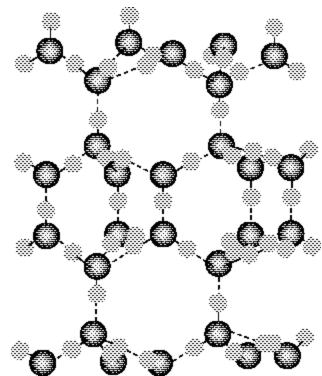
The Mole Says

A few network atomic solids, such as graphite, conduct electricity. However, these are much less common than insulating network atomic solids.

Molecular Solids

So far, we've talked about solids that are held together by chemical bonds. However, what happens when we make a solid from small covalent compounds, such as water, to form ice?

As it turns out, covalent molecules interact with one another through forces referred to as "intermolecular forces." Though we will spend more time speaking about intermolecular forces in Liquids and Intermolecular Forces, you can think of them as being Scotch tape in a world of Crazy Glue covalent bonds and ionic attractions. Though intermolecular forces don't possess nearly the strength of ionic attractions or covalent bonds, they are still strong enough to hold covalent molecules together in a solid. One example of a molecular solid is ice:



The dotted lines in this structure correspond to the intermolecular forces holding the water molecules together in the crystal.

Intermolecular forces are weaker than chemical bonds, making molecular crystals less tightly held together than other forms of crystals. As a result, molecular solids frequently have low melting points and are easily broken apart. Molecular solids are also extremely poor conductors of electricity. Aside from ice, other examples of molecular solids are sugar and dry ice.

Atomic Solids

Atomic solids are formed when the noble gases become cold enough to freeze. As with molecular solids, there are very weak intermolecular forces known as "London dispersion forces" that hold these atoms together. Because their interactions are extremely weak, frozen noble gases tend to be soft and have very low melting points. (See Liquids and Intermolecular Forces for more about London dispersion forces.)

Amorphous Solids

Some solids don't have a particular structure. Instead of being arranged into a regular crystal lattice, the atoms bond in irregular and nonrepeating patterns. These materials are referred to as amorphous solids.

As a result of this unusual bonding, amorphous solids have a very wide range of properties. Some amorphous solids, such as window glass, are hard, brittle, and have a high melting point, while other amorphous solids, such as rubber or plastic, are soft and have very low melting points

Crystal Lattice

Introduction

In a crystal lattice there is the parallelepiped constructed from vectors which correspond to translational periods called unit cells. These can be chosen in different ways. Commonly, unit cells are chosen so that its vertex coincides with one of the atoms of the crystal. Then lattice sites are occupied by atoms, and of the atoms of the crystal. Thus, the lattice sites are occupied by atoms, and vectors that connect the nearest equivalent atoms. The unit cell contains at least one atom of each of the types that

make up the crystal. Providing that the unit cell is made up of only one type of atom, it is called monatomic, anymore than that and it is polyatomic. Correspondingly a monatomic lattice is often identified as a simple lattice and a polyatomic one, a composite lattice. One such example is table salt, NaCl

SEVEN CRYSTAL SYSTEMS

A crystal system is a group of crystal structures that are organized according to their axial system used to describe their lattice. The following types are pictured and described below. CUBIC

This is the cubic crystal system. The cubic crystal system is also known as the isometric system. It is characterized by its complete symmetry. This system contains three crystallographic axes, which are perpendicular to each other, as well as all equal in length. These axes are all at angles 90° to one another. The cubic system contains one lattice point at each of its four corners, and has six faces. HEXAGONAL

The hexagonal crystal system contains four crystallographic axes. These consist of three equal horizontal axes at120° of each other. It has one vertical axis which is perpendicular to the other three, which maybe shorter or longer than the other three, horizontal axes. It is composed of eight faces. TETRAGONAL

A tetragonal crystal is a simple cubic shape that is extended along its vertical axis to create a rectangular prism. It consists of a square base and top, as well as three axes. These axes have one perpendicular and two horizontal with angels of 90°. Like the cubic system it is composed of six faces. RHOMBOHEDRAL

The rhombohedral is a trigonal system, that has a three-dimensional shape similar to a cube, but it has been inclined to one side making it oblique. It consists of three axes, one vertical and two horizontal all laid perpendicular to one another. These axes are at angles of 90° to one another. The rhobohedral is composed of six faces, although since the faces are not square they are more commonly known as rhombi.

ORTHORHOMBIC

Orthorhombic crystal systems consist of three axes. These axes are mutually perpendicular having all different lengths. Yet, the axes angles are all equidistant laying at 90° to each other. The orthorhombic has six faces.

MONOCLINIC

A monoclinic system has three unequal axes. The vertical and forward facing axes are inclined toward each other at an oblique angle, and the horizontal axis is perpendicular to the other two axes, this is known as the ortho axis. These angles are all arranged 90° to each other. A monoclinic system is made up of six faces.

TRICLINICA

triclinic system is made up of three unequal crystallographic axes. The axes intersect at oblique angles. These angles are 90° to one another. The triclinic system has six faces.

Reference pages

<u>GASES :</u>

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https://futurism.com/plasma-the-fourth-state-of-matter-2

LIOUIDS :

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SOLIDS:

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Principles_of_Modern_Chemis try_(Oxtoby_et_al.)/UNIT_3%3A_THE_STATES_OF_MATTER/10%3A_Solids%2C_Liquids%2C_ and Phase Transitions/10.1%3A_Bulk_Properties_of_Liquids - Molecular_Interpretation https://www.infoplease.com/math-science/chemistry/chemistry-types-of-solids

https://chem.libretexts.org/Bookshelves/Physical and Theoretical Chemistry Textbook Maps/Suppl emental Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_ Matter/Properties of Solids/Crystal Lattice

WORKSHEET :

Boyle's Law :

An introduction to the relationship between pressure and volume, and an explanation of how to solve gas problems with Boyle's Law

Example:

At 1.70 atm, a sample of gas takes up 4.25L. If the pressure in the gas is increased to 2.40 atm, what will the new volume be?

Understanding and applying Boyle's Law

Example:

A sample of Ne gas occupies 0.220L at 0.86 atm. What will be its volume at 29.4kPa?

Charle's Law :

What is the relationship between volume and temperature of a gas and how to solve problems using Charles' Law?

Example:

A balloon takes up 625L at 0° C. If it is heated to 80°C, what will its new volume be?

Understanding and applying Charles' Law

Example:

A gas at 40.0°C occupies a volume of 2.32L. If the temperature is raised to 75.0°C, what will the new volume be if the pressure is constant?

Ideal Gas Law :

Understanding and applying the ideal gas law

Example:

What is the pressure in atm of a 0.108 mol sample of the gas at a temperature of 20.0°C if its volume is 0.505L?

Sample problems for using the Ideal Gas Law, PV = nRT

Examples:

1) 2.3 moles of Helium gas are at a pressure of 1.70 atm, and the temperature is 41°C. What is the volume of the gas?

2) At a certain temperature, 3.24 moles of CO_2 gas at 2.15 atm take up a colume of 35.28L. What is this temperature (in Celsius)?

Graham's Law Of Diffusion:

1)If carbon dioxide molecules effuse at an average rate of 5 mol/s, at what rate would diatomic hydrogen molecules effuse in the exact same conditions?

2)Calculate the relative rates of diffusion of $H_2(g)$ and $Br_2(g)$ at the same temperatures.

Dalton's Law Of Partial Pressure:

1)What is the relationship between volume and temperature of a gas and how to solve problems using Charles' Law? Example: A balloon takes up 625L at 0°C. If it is heated to 80°C, what will its new volume be?

2)If I place 3 moles of N2 and 4 moles of 02 in a 35 L container at a temperature of 25° C, what will the pressure (in atm) of the resulting mixture of gases be?

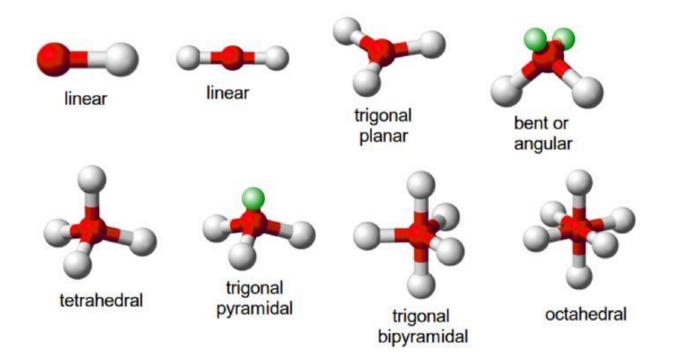
Practical # 02

- Determine the rate of diffusion by two different gas at constant volume.
- How to obtained serum from blood by centrifuging method.

CHAPTER 4

"THEORIES OF COVALENT BONDING & SHAPES OF MOLECULE"

Sir Rao Muzammil Ali & Ms Naheed Muneer Siddiqui



INTRODUCTION:

Major concepts:

- Shape of the molecule
- Types of chemical bond
- Theories of covalent bonding
- Effects of bonding on physical and chemical properties

Conceptual linkage

This unit is built on,

- Why do atoms form bond.
- Intermolecular forces
- Types of chemical bond

LEARNING OUTCOMES

• Use VSEPR and VBT theories to describe the shapes of simple covalent molecules.		~	
• Describe the features of sigma and pbonds.			~
• Describe the shapes of simple molecules using orbital hybridization.		~	
• Describe how knowledge of molecular polarity can be used to explain some physical and chemical properties of molecules.	~		
• Predict the molecular polarity from the shapes of molecules.		~	
• Define bond energies and explain how they can be used to compare bond strength of different chemical bonds.	•		
• Determine the shapes of some molecules from the number of bonded pairs and lone pairs of electrons around the central atom.	~		
• Describe the difference among molecular, network and metallic solids.			~
• Explain what is meant by the term ionic character of a covalent bond.			✓

SKILLS	Analyzing	Applying	Understanding
• Use balls and stick model to represent different molecular shapes			~
• Guess the physical state of molecule from its structure.	~		

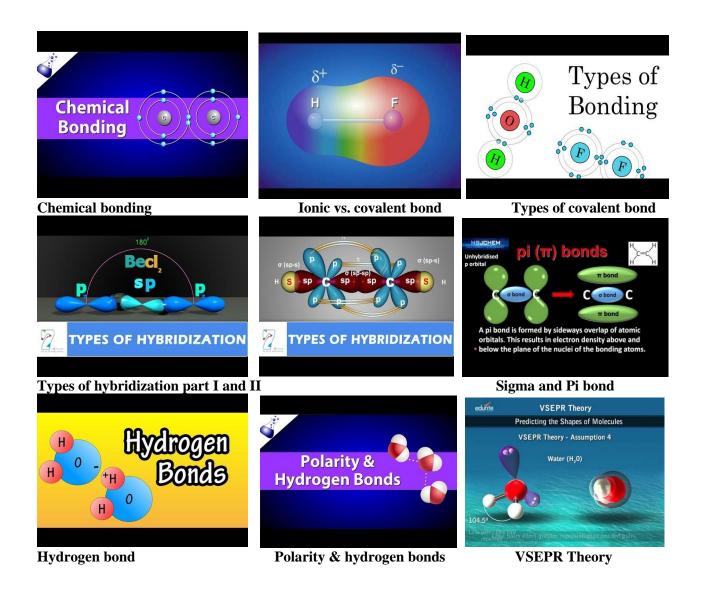
SOCIETY TECHNOLOGY AND SCIENCE

Students will be able to

Explain how hydrogen bond and covalent disulphide bridge are responsible for straight and curly hairs. (Applying)

Related videos

Sir Rao Muzammil Ali & Ms Naheed Muneer Siddiqui



Chapter overview

(THEORITICAL)

Chemical Bonding

Force of attraction between two or more than two atom in a molecule is known as chemical bonding. Chemical Bonding refers to the formation of a chemical bond between two or more atoms, molecules, or ions to give rise to a chemical compound. These chemical bonds are what keep the atoms together in the resulting compound.

Table of Content

- Lewis Theory
- Kossel's Theory
- <u>Types of Chemical Bonds</u>
- Ionic Bond

- Lewis Structures
- **Bond Characteristics**
- <u>Resonance in Chemical Bonding</u>
- London Dispersion Forces

The attractive force which holds various constituents (atom, ions, etc.) together and stabilizes them by the overall loss of energy is known as chemical bonding. Therefore, it can be understood that <u>chemical compounds</u> are reliant on the strength of the chemical bonds between its constituents; The stronger the bonding between the constituents, the more stable the resulting compound would be.

Important Theories on Chemical Bonding

Albrecht Kössel and Gilbert Lewis were the first to explain the formation of chemical bonds successfully in the year 1916. They explained chemical bonding on the basis of the inertness of noble gases.

Lewis Theory of Chemical Bonding

- An atom can be viewed as a positively charged 'Kernel' (the nucleus plus the inner <u>electrons</u>) and the outer shell.
- The outer shell can accommodate a maximum of eight electrons only.
- The eight electrons present in the outer shell occupy the corners of a cube which surround the 'Kernel'.
- The atoms having octet configuration, i.e. 8 electrons in the outermost shell, thus symbolize a stable configuration.
- Atoms can achieve this stable configuration by forming chemical bonds with other atoms. This chemical bond can be formed either by gaining or losing an electron(s) (NaCl, MgCl2) or in some cases due to the sharing of an electron (F2).
- Only the electrons present in the outer shell, also known as the <u>valence electrons</u> take part in the formation of chemical bonds. Gilbert Lewis used specific notations better known as Lewis symbols to represent these valence electrons.
- Generally, the valency of an element is either equal to the number of dots in the corresponding Lewis symbol or 8 minus the number of dots (or valence electrons).

Lewis symbols for lithium (1 electron), oxygen (6 electrons), neon (8 electrons) are given below:



Here, the number of dots that surround the respective symbol represents the number of valence electrons in that atom.

Kossel's theory of Chemical Bonding

- Noble gases separate the highly <u>electronegative</u> halogens and the highly electropositive alkali metals.
- Halogens can form negatively charged ions by gaining an electron. Whereas alkali metals can form positively charged ions by losing an electron.
- These negatively charged ions and positively charged ions have a noble gas configuration that is 8 electrons in the outermost shell. The general electronic configuration of noble gases (except helium) is given by ns²np⁶.
- As unlike charges attract each other these unlike charged particles are held together by a strong force of electrostatic attraction existing between them. For example, MgCl2, the magnesium ion, and chlorine ions are held together by force of electrostatic attraction. This kind of chemical bonding existing between two unlike charged particles is known as an electrovalent bond.

Explanation of Kossel Lewis Approach

In 1916 Kossel and Lewis succeeded in giving a successful explanation based upon the concept of an electronic configuration of noble gases about why atoms combine to form molecules. Atoms of <u>noble</u> <u>gases</u> have little or no tendency to combine with each other or with atoms of other elements. This means that these atoms must be having stable electronic configurations.

Due to the stable configuration, the noble gas atoms neither have any tendency to gain or lose electrons and, therefore, their combining capacity or valency is zero. They are so inert that they even do not form diatomic molecules and exist as monoatomic gaseous atoms.

Types of Chemical Bonds

When substances participate in chemical bonding and yield compounds, the stability of the resulting compound can be gauged by the type of chemical bonds it contains.

The type of chemical bonds formed vary in strength and properties. There are 4 primary types of chemical bonds which are formed by <u>atoms or molecules</u> to yield compounds. These types of chemical bonds include:

- Ionic Bonds
- Covalent Bonds
- Hydrogen Bonds
- Polar Bonds

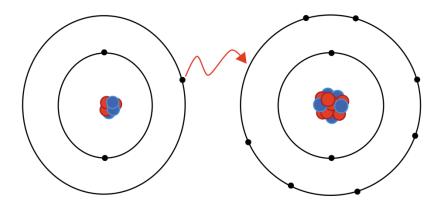
These types of bonds in chemical bonding are formed from the loss, gain, or sharing of electrons between two atoms/molecules.

Ionic Bonding

Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom or molecule to another. Here, an atom loses an electron which is in turn gained by another atom. When

such an electron transfer takes place, one of the atoms develops a negative charge and is now called the anion.

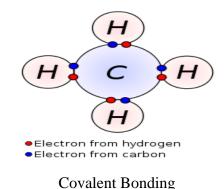
The other atom develops a positive charge and is called the cation. The <u>ionic bond</u> gains strength from the difference in charge between the two atoms, i.e. the greater the charge disparity between the cation and the anion, the stronger the ionic bond.



Types of Chemical Bonds – Ionic bonding

Covalent Bonding

A <u>covalent bond</u> indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of chemical bonding. The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.



Polar Covalent Bonding

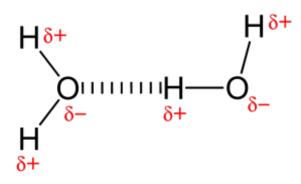
Covalent bonds can be either be Polar or Non-Polar in nature. In Polar Covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule.

A difference in charge arises in different areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged and the other end tends to be partially negatively charged.

Hydrogen Bonding

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a <u>hydrogen bond</u> and is responsible for many of the properties exhibited by water.



Hydrogen Bonding

What is Ionic Bond?

The bond formed as a result of strong electrostatic forces of attraction between a positively and negatively charged species is called an <u>electrovalent or ionic bond</u>. The positively and negatively charged ions are aggregated in an ordered arrangement called the crystal lattice which is stabilized by the energy called the Lattice enthalpy.

Conditions for the formation of an Ionic Bond

- The low ionization energy of the atom forming the cation.
- High electron gain enthalpy of the atom forming the anion.
- High negative lattice enthalpy of the crystal formed.

Generally, the ionic bond is formed between a metal cation and non-metal anion.

Writing Lewis Structures

The following steps are adopted for writing the Lewis dot structures or Lewis structures:

Step 1: Calculate the number of electrons required for drawing the structure by adding the valence electrons of the combining atoms. **For Example**, in methane, CH₄ molecule, there are 8 valence electrons (in which 4 belongs to carbon while other 4 to H atoms).

Step 2: Each negative charge i.e. for anions, we add an electron to the valence electrons and for each positive charge i.e. for cations we subtract one electron from the valence electrons.

Step 3: Using the chemical symbols of the combining atoms and constructing a skeletal structure of the compound, divide the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

Step 4: The central position in the molecule is occupied by the least <u>electronegative atom</u>. Hydrogen and fluorine generally occupy the terminal positions.

Step 5: After distributing the shared pairs of electrons for single bonds, the remaining electron pairs are used for multiple bonds or they constitute lone pairs.

The basic requirement is that each bonded atom gets an octet of electrons.

Example 1: Lewis formula for carbon monoxide, CO

Step 1: Counting the total number of valence electrons of carbon and oxygen atoms: C $(2s^22p^2) + O$ $(2s^22p^4) + 6 = 10$ that is, 4(C) + 6(O) = 10

Step 2: The skeletal structure of carbon monoxide is written as CO

Step 3: Drawing a single bond between C and O and completing octet on O, the remaining two electrons are lone pair on C.

$$: \stackrel{\oplus}{\mathbf{C}} - \stackrel{\ominus}{\mathbf{O}} :::$$

Step 4: This does not complete the octet of carbon, and hence we have a triple bond.

$$: \stackrel{\Theta}{C} \equiv \stackrel{\oplus}{O}:$$

Example 2: Lewis Structure of nitrite, NO₂⁻

Step 1: Counting the total number of valence electrons of one nitrogen atom, two oxygen atoms and the additional one negative charge (equal to one electron). Total Number of valence electrons is: N $(2s^22p^3) + 2O(2s^22p^4) + 1$ (negative charge) => 5+ 2(6) +1=18e⁻

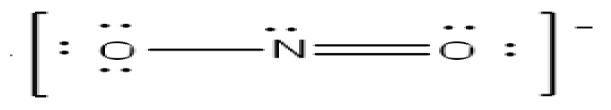
Step 2: The skeletal structure of nitrite ion is written as O-N-O

Step 3: Drawing a single bond between nitrogen and each oxygen atom: O - N - O

Step 4: Complete the octets of atoms.



This structure does not complete octet on N if the remaining two electrons constitute of a lone pair on it. Therefore, we have a double bond between one N and one of the two O atoms. The Lewis structure is



Problems:

- 1. Write the Lewis structure for the following.
- 2. CO_3^{2-} b) CN^{-} c) SO_5^{2-}

Bond Characteristics

Bond Length

During chemical bonding, when the atoms come closer to each other, the attraction takes place between them and the potential energy of the system keeps on decreasing till a particular distance at which the potential energy is minimum. If the atoms come more closer, repulsion starts and again the potential energy of the system begins to increase.

At equilibrium distance, the atoms keep on vibrating about their mean position. The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its **Bond length.**

It is expressed in terms of an angstrom (A^0) or picometer (pm). It is determined experimentally by x-ray diffraction or electron diffraction method or spectroscopic method. The bond length in chemical bonding is the sum of their ionic radii, in an ionic compound. In a <u>covalent compound</u>, it is the sum of their covalent radii. For a covalent molecule AB, the bond length is given by $d = r_a + r_b$

Factors Affecting the Bond length

- Size of the atoms: The bond length increases with increase in the size of the atom. HI > HBr > HCl > HF
- The multiplicity of Bond: The bond length decreases with an increase in bond order.
- **Type of hybridization:** A's' orbital is smaller in size, greater the 's' character, shorter is the bond length.

Bond Enthalpy

When atoms come close together the energy is released due to the chemical bonding between them. The amount of energy required to break one mole of bonds of a type so as to separate the molecule into individual gaseous atoms is called **bond dissociation enthalpy or Bond enthalpy.** Bond enthalpy is usually expressed in KJ mol^{-1.}

Greater is the bond dissociation enthalpy, greater is the bond strength. For <u>diatomic molecules</u> like H₂, Cl₂, O₂, N₂, HCl, HBr, HI the bond enthalpies are equal to their dissociation enthalpy.

In the case of polyatomic molecules, bond enthalpies are usually the average values, because the dissociation energy varies with each type of bond.

In H₂0, first O-H bond enthalpy = 502 KJ/mol; Second bond enthalpy = 427 KJ/mol Average bond enthalpy = (502 + 427) / 2 = 464.5 KJ/mol

Factors Affecting Bond Enthalpy in Chemical Bonding

Size of the Atom

Greater the size of the atom, greater is the bond length and less is the <u>bond dissociation enthalpy</u> i.e. less is the bond strength during chemical bonding.

Multiplicity of Bonds

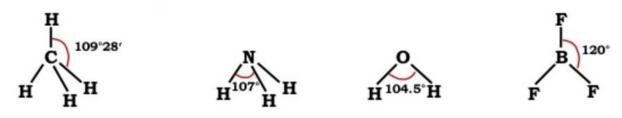
Greater is the multiplicity of the bond, greater is the bond dissociation enthalpy.

Number of Lone Pair of Electrons Present

More the number of lone pair of electrons present on the bonded atoms, greater is the repulsion between the atoms and thus less is the bond dissociation enthalpy of the chemical bond.

Bond Angle

A bond is formed by the overlap of atomic orbitals. The direction of overlap gives the direction of the bond. The angle between the lines representing the direction of the bond i.e. the orbitals containing the bonding electrons is called the **bond angle**.



Factors Affecting Bond Enthalpy in Chemical Bonding

Bond Order

In Lewis representation, the number of bonds present between two atoms is called the **bond order**. Greater the bond order, greater is the stability of the bond during chemical bonding i.e. greater is the bond enthalpy. Greater the bond order, shorter is the bond length.

Resonance in Chemical Bonding

There are molecules and ions for which drawing a single Lewis structure is not possible. For example, we can write two structures of O_3 .



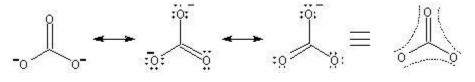
In (A) the oxygen-oxygen bond on the left is a double bond and the oxygen-oxygen bond on the right is a single bond. In B the situation is just the opposite. The experiment shows, however, that the two bonds are identical.

Therefore neither structure A nor B can be correct. One of the bonding pairs in ozone is spread over the region of all three atoms rather than localized on a particular oxygen-oxygen bond. This delocalized bonding is a type of chemical bonding in which bonding pair of electrons are spread over a number of atoms rather than localized between two.

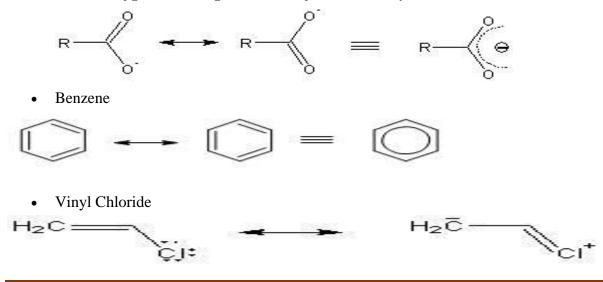
Structures (A) and (B) are called <u>resonating or canonical structures</u> and (C) is the resonance hybrid. This phenomenon is called resonance, a situation in which more than one canonical structure can be written for a species. The chemical activity of an atom is determined by the number of electrons in its valence shell. With the help of the concept of chemical bonding, one can define the structure of a compound and is used in many industries for manufacturing products in which the true structure cannot be written at all.

Some other examples:

•
$$CO_3^{2-}$$
 ion



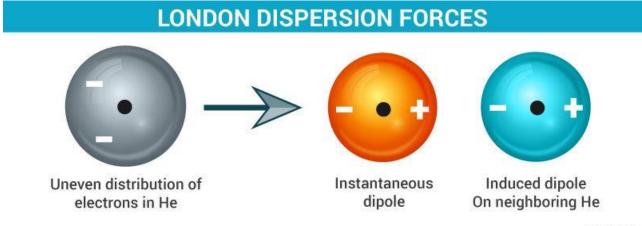
• Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance.



The difference in the energies of the canonical forms and resonance hybrid is called resonance stabilization energy.

London Dispersion Forces

Another form of chemical bonding is caused by London dispersion forces. These forces are weak in magnitude.



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Chemical Bonding – London Dispersion Forces

These forces occur due to a temporary charge imbalance arising in an atom. This imbalance in the charge of the atom can induce dipoles on neighbouring atoms. For example, the temporary positive charge on one area of an atom can attract the neighbouring negative charge.

FAQs on Chemical Bonding and Molecular Structure

Why atoms react and how?

Atoms having eight electrons in their last orbit are stable and have no tendency to react. Atoms having less than eight electrons, then react with other atoms to get eight electrons in their outermost orbit, and become stable. Atoms having slightly excess than eight electrons may lose them, to atoms, who, are short of eight. Atoms that cannot either loss or gain, may share to get octet configuration. Molecules short of octet configuration even after the reaction, may accept lone pair of electrons present in other atoms or molecules.

Name the forces that keep reacting atoms together?

In metals, outer orbitals of atoms overlap and so the electrons present in them do not belong to any particular atom but flows over to all atoms as well and binds them all together (metallic bonding). Atoms that have to lose and gain electrons, becomes ions and are held together by the electrostatic forces of attraction (Ionic Bond). When atoms equally give and share electrons, the shared electrons becomes the unifying force between them (covalent bond). Electron-deficient and free lone pair

containing molecules may again and satisfy the octet thirst of the electron-deficient atom. The shared electron bridges the electron-rich atom with electron-deficient atom (coordinate bond).

What are the hybridized orbitals? What are the uses of it?

Relatively similar energy sub-orbitals, may merge and form a new set of the same number of orbitals, having the property of all the contributing orbitals in proportion to their numbers. These orbitals are <u>hybridized orbitals</u>. They are useful in explaining the similarity in bond length, bond angles, structure, shape and Magnetic properties of molecules.

Sp³ and dsp² are four hybridized orbital. But one is the tetrahedral shape and other square planar. Why?

 Sp^3 orbitals are formed from the s -subshell with uniform electron distribution around the nucleus and of p-subshell with distribution in the three vertical axis. Hybridized orbitals, hence have their electron distribution in three dimensions, as tetrahedral directions.

In dsp^2 all the orbitals involved I hybridization have their electron distribution around the same plane. Hence the hybridized orbitals also are in the same plane giving rise to square planar geometry.

The oxygen molecule is paramagnetic. Is there an explanation?

Oxygen atom shares two electrons, each with another oxygen atom to form the oxygen molecule. Oxygen molecule exhibits paramagnetic nature indicating unpaired electrons. A <u>molecular orbital</u> <u>theory</u> has been proposed to explain this. According to this theory, atoms lose their orbitals and rather form an equal number of orbital covering the entire molecule and hence the name molecular orbital. Filling up of, these orbitals in increasing energy order leaves unpaired electron explaining the paramagnetic behaviour of oxygen molecule.

Reference page/site. https://byjus.com/jee/fajans-rule/

• VSEPR THEORY

VSEPR Theory is used to predict the shape of the molecules from the electron pairs that surround the central atoms of the molecule. The theory was first presented by Sidgwick and Powell in 1940. VSEPR theory is based on the assumption that the molecule will take a shape such that electronic repulsion in the valence shell of that atom is minimized.

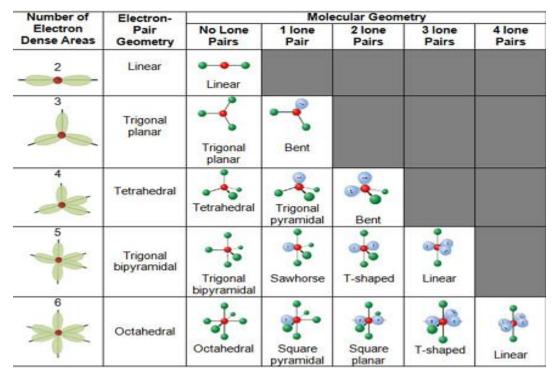
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- <u>Postulates</u>
- <u>Limitations</u>
- <u>Shapes of Molecules</u>
- What is VSEP Number?
- VSEPR Theory and Shapes of Molecules
- Frequently Asked Questions

What is VSEPR Theory?

The Valence Shell Electron Pair Repulsion Theory abbreviated as VSEPR theory is based on the premise that there is a repulsion between the pairs of <u>valence electrons</u> in all atoms, and the atoms will always tend to arrange themselves in a manner in which this electron pair repulsion is minimalized. This arrangement of the atom determines the geometry of the resulting molecule.

The different geometries that molecules can assume keeping with VSEPR theory can be seen in the illustration provided below.



VSEPR Theory – Different Geometries that Molecules can Assume

The two primary founders of the VSEPR theory are Ronald Nyholm and Ronald Gillespie. This theory is also known as the Gillespie-Nyholm theory to honour these chemists.

Also Read

- Chemical Bonding
- <u>Covalent Bond</u>
- <u>Hydrogen Bonding</u>
- <u>Hybridization</u>
- Molecular Orbital Theory

According to the VSEPR theory, the repulsion between two electrons is caused by the <u>Pauli exclusion</u> <u>principle</u> that has greater importance than electrostatic repulsion in the determination of molecular geometry.

Postulates of VSEPR Theory:

The postulates of the VSEPR theory are listed below

- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other <u>atoms belonging to the molecule</u> are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimizes the electronelectron repulsion between them and maximizes the distance between them.
- The valence shell can be thought of as a sphere wherein the electron pairs are localized on the surface in such a way that the distance between them is maximized.
- Should the central atom of the molecule be surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected.
- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each <u>resonance structure</u> of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules.
- If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the <u>energy of the molecule</u> will be low.

Limitations of VSEPR Theory:

Some significant limitations of the VSEPR theory include:

- This theory fails to explain isoelectronic species (i.e. elements having the same number of electrons). The species may vary in shapes despite having the same number of electrons.
- The VSEPR theory does not shed any light on the compounds of <u>transition metals</u>. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.
- Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Predicting the Shapes of Molecules:

The following steps must be followed in order to decide the shape of a molecule.

- The least <u>electronegative</u> atom must be selected as the central atom (since this atom has the highest ability to share its electrons with the other atoms belonging to the molecule).
- The total number of electrons belonging to the outermost shell of the central atom must be counted.
- The total number of electrons belonging to other atoms and used in bonds with the central atom must be counted.
- These two values must be added in order to obtain the valence shell electron pair number or the VSEP number.

What is VSEP Number?

The VSEP number describes the shape of the molecule, as described in the table provided below.

VSEP Number	Shape of the Molecule
2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal Bipyramidal
6	Octahedral
7	Pentagonal Bipyramidal

Each of these corresponding shapes can also be found in the illustration provided earlier. However, the VSEPR theory cannot be used to obtain the exact <u>bond angles</u> between the atoms in a molecule.

Now, we will discuss each shape in detail:

Linear Shape of Molecule:

- In this type of molecule, we find two places in the valence shell of the central atom.
- They should be arranged in such a manner such that repulsion can be minimized (pointing in the opposite direction).
- **Example:** BeF₂

Trigonal Planar Shape of Molecule:

- In this type of molecule, we find three molecules attached to a central atom.
- They are arranged in such a manner such that repulsion between the electrons can be minimized (toward the corners of an <u>equilateral triangle</u>).
- **Example:** BF₃

Tetrahedral Shape of Molecule:

- In two-dimensional molecules, atoms lie in the same plane and if we place these conditions on <u>methane</u>, we will get a square planar geometry in which the bond angle between H-C-H is 90^{0} .
- Now, if we consider all these conditions for a three-dimensional molecule, we will get a tetrahedral molecule in which the bond angle between H-C-H is 109⁰28' (toward the corners of an equilateral triangle) CH₄

Trigonal Bipyramid Shape of Molecule:

• Let's take an example of PF₅. Here, repulsion can be minimized by even distribution of electrons towards the corner of a <u>trigonal pyramid</u>. In trigonal bipyramid, three positions lie along the equator of the molecule. The two positions lie along an axis perpendicular to the equatorial plane.

How can the VSEPR Theory be used to Predict the Shapes of Molecules?

The strength of the repulsion between a lone pair and a bond pair of electrons lies in between the repulsion between two lone pairs and between two bond pairs. The order of repulsion between electron pairs as follows:

Lone Pair- lone pair > Lone Pair- bond- pair > Bond Pair- bond pair.

1. Total <u>number of electron pairs</u> around the central atom = $\frac{1}{2}$ (number of valence electrons of central atom + number of atoms linked to central atom by single bonds)

- For negative ions, add the number of electrons equal to the units of negative charge on the ions to the valence electrons of the central atom.
- For positive ions, subtract the number of electrons equal to the units of <u>positive charge</u> on the ion from the valence electrons of the central atom.

2. The number of Bond pair = Total number of atoms linked to central atom by single bonds.

3. Number of lone pairs = Total number of electron – No of shared pair

The electron pairs around the central atom repel each another and move so far apart from each another that there are no greater repulsions between them. This results in the molecule having minimum energy and maximum stability.

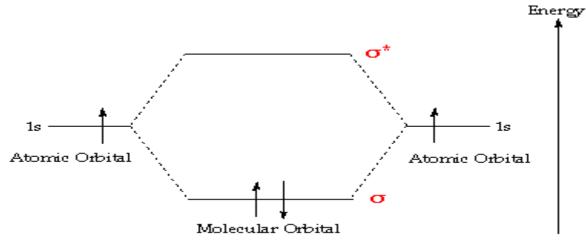
- The shape of a molecule with only two atoms is always linear.
- For molecules with three or more atoms, one of the atoms is called the central atom and other atoms are attached to the central atom.
- If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar as a result the shape of the molecule is symmetrical and the molecule is said to have regular geometry.
- If the central atom is linked to different atoms or is surrounded by bond pair as well as a lone pair of electrons, the repulsion between them is similar. As a result, the shape of the molecule has an irregular or distorted geometry.
- The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

Reference page/site

https://byjus.com/jee/vsepr-theory/

Molecular Orbital Theory

The molecular orbital theory states that each atom tends to combine together and form molecular orbitals. As a result of such arrangement, electrons are found in various atomic orbitals and they are usually associated with different nuclei. In short, an electron in a molecule can be present anywhere in the molecule.



Features of Molecular Orbital Theory

- The atomic orbitals overlap to form new orbitals called **molecular orbitals**. When two atomic orbitals overlap they lose their identity and form new orbitals called **molecular orbitals**.
- The <u>electrons</u> in the molecules are filled in the new energy states called the Molecular orbitals similar to the electrons in an atom being filled in an energy state called atomic orbitals.
- The probability of finding the electronic distribution in a molecule around its group of nuclei is given by the molecular orbital.
- The two combining atomic orbitals should possess energies of comparable value and similar orientation. For example, 1s can combine with 1s and not with 2s.
- The number of molecular orbitals formed is equal to the number of atomic orbitals combining.
- The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals.

Reference page/site

https://byjus.com/jee/molecular-orbital-theory/

Hybridization

Hybridization is defined as the concept of mixing two atomic orbitals with the same energy levels to give a degenerated new type of orbitals. This intermixing is based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process provided they have equal energy.

During the process of hybridization, the atomic orbitals of similar energy are mixed together such as the mixing of two 's' orbitals or two 'p' orbital's or mixing of an 's' orbital with a 'p' orbital or 's' orbital with a 'd' orbital.

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- <u>Types</u>
- <u>sp Hybridization</u>
- <u>sp² Hybridization</u>
- <u>sp³ Hybridization</u>

What is Hybridization?

Redistribution of the energy of orbitals of individual atoms to give <u>orbitals of equivalent</u> <u>energy</u> happens when two atomic orbitals combine together to form hybrid orbital in a molecule. This process is called **hybridization**. The new orbitals thus formed are known as **hybrid orbitals**.

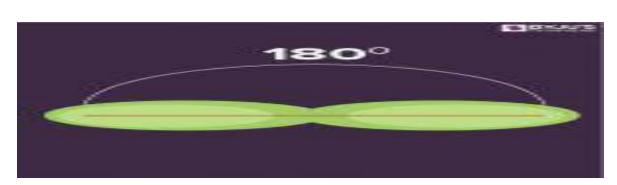
Types of Hybridization

Based on the <u>types of orbitals</u> involved in mixing, the hybridization can be classified as sp3, sp2, sp, sp3d, sp3d2, sp3d3. Let us now discuss the various types of hybridization along with their examples.

sp Hybridization

sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals**. It forms linear molecules with an angle of 180°

- This type of hybridization involves the mixing of one 's' orbital and one 'p' orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital.
- sp hybridization is also called diagonal hybridization.
- Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.



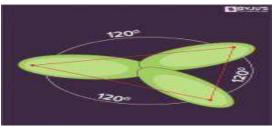
Examples of sp Hybridization:

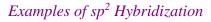
- All <u>compounds of beryllium</u> like BeF₂, BeH₂, BeCl₂
- All compounds of carbon-containing <u>triple Bond</u> like C₂H₂.

sp² Hybridization

 sp^2 hybridisation is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called sp^2 hybrid orbitals.

- sp² hybridization is also called trigonal hybridization.
- It involves mixing of one 's' orbital and two 'p' orbital's of equal energy to give a new hybrid orbital known as sp².
- A mixture of s and p orbital formed in trigonal symmetry and is maintained at 120° .
- All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has 33.33% s character and 66.66% 'p' character.
- The <u>molecules</u> in which the central atom is linked to 3 atoms and is sp2 hybridized have a triangular planar shape.



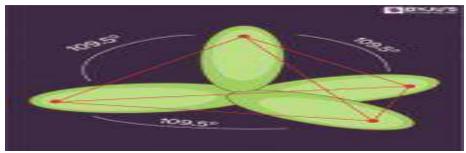


- All the compounds of Boron i.e. BF₃, BH₃
- All the <u>compounds of carbon</u> containing a carbon-carbon double bond, Ethylene (C_2H_4)

sp³ Hybridization

When one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization or sp**³. The new orbitals formed are called **sp**³ **hybrid orbitals**.

- These are directed towards the four corners of a regular <u>tetrahedron</u> and make an angle of 109°28' with one another.
- The angle between the sp3 hybrid orbitals is 109.28°
- Each sp³ hybrid orbital has 25% s character and 75% p character.
- Example of sp^3 hybridization: <u>ethane</u> (C₂H₆), methane.



Key Features of Hybridization

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals mixing.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if hybridization of the molecule is known.
- The bigger lobe of the hybrid orbital always has a positive sign while the smaller lobe on the opposite side has a negative sign.

Reference page/site.

https://byjus.com/jee/hybridization/

What is Valance Bond (VB) Theory

Many approaches have been put forth to explain the nature of bonding in coordination compounds. One of them is the Valence Bond (VB) Theory. The Valence Bond Theory was developed in order to explain chemical bonding using the method of quantum mechanics. This theory primarily focuses on the formation of individual bonds from the <u>atomic orbitals</u> of the participating atoms during the formation of a molecule.

What is Valance Bond (VB) Theory?

According to the valence bond theory,

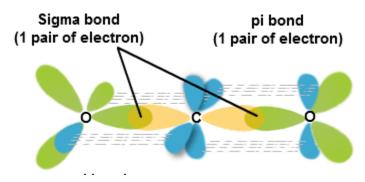
Electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap on the bond formation and the larger the overlap the stronger the bond. The metal bonding is essentially covalent in origin and metallic structure involves resonance of electron-pair bonds between each atom and its neighbors.

Postulates of Valence Bond Theory

The important postulates of the valence bond theory are listed below.

- 1. Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule.
- 2. The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.
- 3. Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.
- Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. <u>pi</u> <u>bonds</u> are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.

The formation of <u>sigma and pi bonds</u> is illustrated below.



Formation of Sigma and Pi Bonds – Valence Bond Theory (VBT)

Applications of Valence Bond Theory

- The maximum overlap condition which is described by the valence bond theory can explain the formation of covalent bonds in several molecules.
- This is one of its most important applications. For example, the difference in the length and strength of the chemical bonds in H₂ and F₂ molecules can be explained by the difference in the overlapping orbitals in these molecules.
- The covalent bond in an HF molecule is formed from the overlap of the 1s orbital of the hydrogen atom and a 2p orbital belonging to the fluorine atom, which is explained by the valence bond theory.

Limitations of Valence Bond Theory

The shortcomings of the valence bond theory include

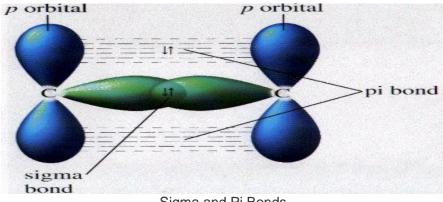
- Failure to explain the tetravalency exhibited by carbon
- No insight offered on the energies of the electrons.
- The theory assumes that electrons are localized in specific areas.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- No distinction between weak and strong ligands.
- No explanation for the colour exhibited by coordination compounds.

Reference page/site.

https://byjus.com/chemistry/valence-bond-theory/

Sigma and Pi bonds

Sigma and pi bonds are types of covalent bonds that differ in the overlapping of atomic orbitals. Covalent bonds are formed by the overlapping of atomic orbitals. Sigma bonds are a result of the head-to-head overlapping of atomic orbitals whereas pi bonds are formed by the lateral overlap of two atomic orbitals.



Sigma and Pi Bonds

The Sigma (σ) Bond

This type of covalent bond is formed by head-on positive (same phase) overlap of atomic orbitals along the internuclear axis. Sigma bonds are the strongest covalent bonds, owing to the direct overlapping of the participating orbitals. The <u>electrons</u> participating in a σ bond are commonly referred to as σ electrons.

Generally, all single bonds are sigma bonds. They can be formed via the following combinations of atomic orbitals.

S-S Overlapping

In this kind of overlapping, one 's' orbital from each participating atom undergoes head-on overlapping along the internuclear axis. An s orbital must be half-filled before it overlaps with another.

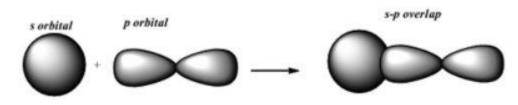


s-s Overlap in Sigma Bonds

The overlapping of two s orbitals resulting in a sigma bond is illustrated above. This type of overlap occurs in H_2 molecules, where each hydrogen atom has a half-filled s orbital.

S-P Overlapping

Here, one half filed s orbital overlaps with one half-filled p orbital along the internuclear axis, forming a covalent bond. This condition is illustrated below.

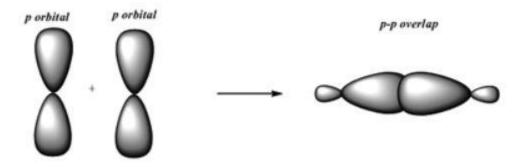


s-p Overlap in Sigma Bonds

This type of overlapping can be observed in <u>ammonia</u>. An NH_3 molecule features 3 sigma bonds, formed by the overlap of the $2p_x$, $2p_y$, and $2p_z$ orbitals belonging to the nitrogen atom and the 1s orbitals of the three hydrogen atoms

P-P overlapping

In this condition, one half-filled p orbital from each participating atom undergoes head-on overlapping along the internuclear axis. This type of overlapping is illustrated below.

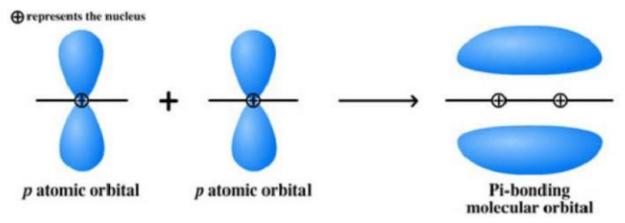


p-p Overlap in Sigma Bonds

A Cl_2 molecule features a p-p overlap of the $3p_z$ orbitals of two chlorine atoms. It is important to note that the head-to-head overlapping of two p orbitals gives a sigma bond whereas the lateral overlap of these orbitals leads to the formation of pi bonds.

The Pi (π) Bond

Pi bonds are formed by the sidewise positive (same phase) overlap of atomic orbitals along a direction perpendicular to the internuclear axis. During the formation of π bonds, the axes of the atomic orbitals are parallel to each other whereas the overlapping is perpendicular to the internuclear axis. This type of covalent bonding is illustrated below.



Pi Bonds

Pi Bonds are generally weaker than sigma bonds, owing to the significantly lower degree of overlapping. Generally, double bonds consist of one sigma and one pi bond, whereas a typical triple bond is made up of two π bonds and one σ bond. It is important to note that a combination of sigma and pi bonds is always stronger than a single sigma bond.

Difference Between Sigma and Pi Bonds

Sigma BondPi BondThe overlapping orbitals can be pure or hybridThe overlapping orbitals must be
unhybridizedThese bonds are strong and have high bond
energies.These bonds are relatively weak.Can exist independentlyMust exist along with a sigma bond.Has an impact on the shape of moleculesHas no role in determining the shape of
molecules

The key differences between sigma and pi bonds are tabulated below.

Reference page/site.

https://byjus.com/chemistry/sigma-and-pi-bond/

Hydrogen Bonding

Hydrogen bond or hydrogen bonding is a type of weak force that results in the formation of dipoledipole interaction between a hydrogen atom and an electronegative atom that is strongly bonded to another electronegative atom. The bond or bonds are mostly strong in comparison to normal dipoledipole and dispersion forces. However, they are weak compared to true covalent or ionic bonds.

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- <u>Conditions</u>
- <u>Effects</u>
- <u>Examples</u>
- <u>Strength of Hydrogen Bond</u>
- <u>Properties</u>
- <u>Types of H-Bond</u>

What are the Conditions for Hydrogen Bonding?

In a molecule, when a hydrogen atom is linked to a highly electronegative atom, it attracts the shared pair of electrons more and so this end of the molecules becomes slightly negative while the other end becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called the **hydrogen bond**.

As a result of hydrogen bonding, a hydrogen atom links the two <u>electronegative atoms</u> simultaneously, one by a covalent bond and the other by a hydrogen bond. The conditions for hydrogen bonding are:

- 1. The molecule must contain a highly electronegative atom linked to the hydrogen atom. The higher the electronegativity more is the polarization of the molecule.
- 2. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

Effects of Hydrogen Bonding on Elements

Association

The molecules of carboxylic acids exist as dimer because of the hydrogen bonding. The <u>molecular</u> <u>masses</u> of such compounds are found to be double than those calculated from their simple formula.

Dissociation

In aqueous solution, HF dissociates and gives the difluoride ion instead of fluoride ion. This is due to hydrogen bonding in HF. The molecules of HCl, HBr, HI do not form a hydrogen bond. This explains the non-existence of compounds like KHCl₂, KHBr₂, KHI₂.

Why do compounds having hydrogen bonding have high melting and boiling points?

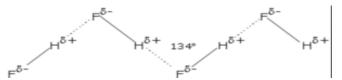
The compounds having hydrogen bonding show abnormally high <u>melting and boiling points</u>. The high melting and boiling point of the compound containing hydrogen bonds is due to the fact that some extra energy is needed to break these bonds.

- The unusually high boiling point of hydrogen fluoride among the halogen acid is due to the existence of hydrogen bonding.
- H₂O is a liquid whereas H₂S, H₂Se and H₂Te are all gases at ordinary temperature. In water, hydrogen bonding causes linkages in the water molecules which result in the boiling point of water is more than that of the other compounds.
- Ammonia has a higher boiling point than PH₃ because there is hydrogen bonding in NH₃ but not in PH₃.
- Ethanol has a higher boiling point than <u>diethyl ether</u> because there is hydrogen bonding in the ethanol.

Examples of Hydrogen Bonding

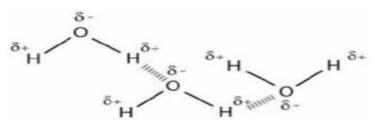
Hydrogen Bonding in Hydrogen fluoride

Fluorine having the highest value of electronegativity forms the strongest hydrogen bond.



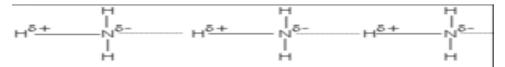
Hydrogen Bonding in Water

A water molecule contains a highly electronegative oxygen atom linked to the <u>hydrogen atom</u>. Oxygen atom attracts the shared pair of electrons more and this end of the molecule becomes negative whereas the hydrogen atoms become positive.



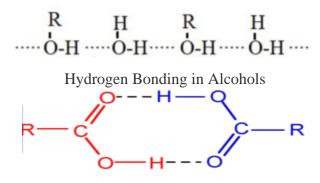
Hydrogen Bonding in Ammonia

It contains highly electronegative atom nitrogen linked to hydrogen atoms.



Hydrogen Bonding in Alcohols and Carboxylic acid

Alcohol is a type of an organic molecule which contains an -OH group. Normally, if any molecule which contains the hydrogen atom is connected to either oxygen or nitrogen directly, then hydrogen bonding is easily formed.



Hydrogen Bonding in Carboxylic acid

Hydrogen Bonding in Polymers

Hydrogen bonding is an important factor in determining the 3D structures and properties that are acquired by synthetic and natural proteins. Hydrogen bonds also play an important role in defining the structure of cellulose as well as derived polymers such as cotton or flax.

Strength of the Hydrogen bond

The hydrogen bond is a weak bond. The strength of hydrogen bond is in-between the weak <u>van der</u> <u>Waals forces</u> and the strong covalent bonds.

The dissociation energy of the hydrogen bond depends upon the attraction of the shared pair of electrons and hence on the electronegativity of the atom.

Properties of Hydrogen Bonding

- **Solubility:** Lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecule.
- **Volatility:** As the compounds involving hydrogen bonding between different molecules have a higher boiling point, so they are less volatile.
- **Viscosity and surface tension:** The substances which contain hydrogen bonding exists as an associated molecule. So their flow becomes comparatively difficult. They have higher viscosity and high surface tension.
- The lower density of ice than water: In the case of solid ice, the hydrogen bonding gives rise to a cage-like structure of water molecules. As a matter of fact, each water molecule is linked tetrahedral to four water molecules. The molecules are not as <u>closely packed</u> as they are in a liquid state. When ice melts, this case like structure collapses and the molecules come closer to each other. Thus for the same mass of water, the volume decreases and density increases. Therefore, ice has a lower density than water at 273 K. That is why ice floats.

Types of Hydrogen Bonding

There are two types of H bonds, and it is classified as the following:

- Intermolecular Hydrogen Bonding
- Intramolecular Hydrogen Bonding

Intermolecular Hydrogen Bonding

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called **intermolecular hydrogen bonding**.

For example – hydrogen bonding in water, alcohol, <u>ammonia</u> etc.

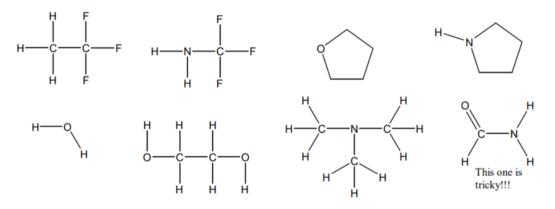
Intramolecular Hydrogen Bonding

The hydrogen bonding which takes place within a molecule itself is called **intramolecular hydrogen bonding.**

It takes place in compounds containing two groups such that one group contains hydrogen atom linked to an electronegative atom and the other group contains a highly electronegative atom linked to a lesser electronegative atom of the other group.

The bond is formed between the hydrogen atoms of one group with the more <u>electronegative atom</u> of the other group

Problem: Indicate which of the following molecules could form Hydrogen Bonds with other like molecules.



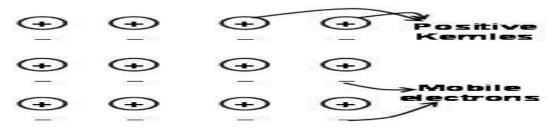
Symmetric Hydrogen Bond

This is a special type of hydrogen bond where the proton is usually placed in the middle between two identical atoms. The strength of the bond between each atom is equal. The symmetric hydrogen bond is a type of a three-centre four-electron bond. This bond is also much stronger compared to the "normal" hydrogen bond and its strength is almost similar to a covalent bond.

What is Metallic Bonding?

Metals are characterised by bright, lustre, high electrical and <u>thermal conductivity</u>, malleability, ductility and high tensile strength. A metallic crystal consists of a very large number of atoms arranged in a regular pattern.

Different model have been proposed to explain the nature of metallic bonding two most important modules are as follows



Reference page/site https://byjus.com/jee/hydrogen-bonding/

Student's assessment

- What is the premise of the VSEPR Theory?
- What would be the shape of the molecule if the VSEP number is 5?
- What are the advantages of the VSEPR theory?
- Explain sp3 Hybridization in Methane?
- Amide molecule looks sp3 hybridized but it is sp2, why?
- What results in sp, sp2 and sp3 hybridization?
- Explain the difference between molecular and hybrid orbitals?
- Draw the Lewis Structure of:

Carbon Tetrachloride (CCl4) Ammonia (NH₃)

Explain sp3 Hybridization in Methane?

- Amide molecule looks sp3 hybridized but it is sp2, why?
- What results in sp, sp2 and sp3 hybridization?
- Explain the difference between molecular and hybrid orbitals?

(Related videos)

Chemical bonding

https://youtu.be/g-tE6MN-wrE https://youtu.be/AHRkZHNxLoM https://youtu.be/4tvkUjceWBY https://youtu.be/OTgpN62ou24 https://youtu.be/DinMgWWwMUE

Hybridization

https://youtu.be/_gRWI5zUpHM https://youtu.be/jUhCHKVDjqc https://youtu.be/eGnbLEV9Be4

<u>Sigma and pi-bond</u> <u>https://youtu.be/_qzdRPv4Ns4</u> <u>https://youtu.be/jPUb8AHWK-s</u>

<u>Hydrogen bonding</u> <u>https://youtu.be/RSRiywp9v9w</u> <u>https://youtu.be/m-v5G8C70pc</u> <u>https://youtu.be/aZ8JxFwR_nY</u>

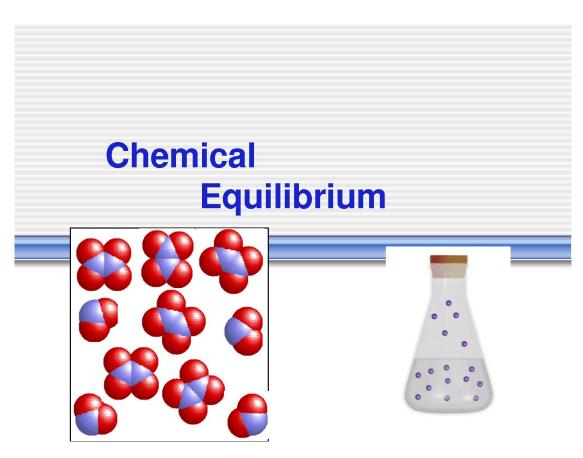
VSEPR THEORY

https://youtu.be/e99iaUKsucc

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CHAPTER 5

"CHEMICAL EQULIBERIUM"



Introduction

Major concept

- Reversible reaction & dynamic equilibrium
- > Factors effecting on equilibrium (Le-chatelier's principle)
- Industrial application of Le-chatlier principle (Haber & Contact process)
- > Solubility product and precipitation reaction.
- Common ion effect.
- ➢ Law of mass action

chapter

Chemical Equilibrium.

Topics according to national curriculum.

- Reversible Reactions and Dynamic Equilibrium
- Factors Affecting Equilibrium (Le-Chatelier's Principle).
- Industrial Application of Le-Chatelier's Principle (Haber's Process) Solubility Product and Precipitation Reactions
- Common Ion Effect
- Equilibrium Constant and its Derivation
- Law of Mass Action
- Equilibrium Calculations

skills

- Students will be able to:
 - Calculate the equilibrium constant for a reaction given the equilibrium concentrations of reactants and products. (Applying)
 - Calculate the concentration specified, given the equilibrium constant and appropriate information about the equilibrium concentrations. (Applying)

understanding

Students will be able to:

- Describe simple properties of solids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular tomes and kinetic energy based on kinetic molecular theory. (Understanding)
- Differentiate between amorphous and crystalline solids. (Understanding) Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding)
- Use oxygen and sulphur to define allotropes. (Understanding)
- Explain the significance of the unit cell to the shape of the crystal using NaCI as an example. (Applying)
- Name three types of packing arrangements and draw or construct models of them. (Applying)
- Name three factors that affect the shape of an ionic crystal. (Understanding)
- Define lattice energy. (Remembering)
 Differentiate between ionic, covalent, molecular and metallic crystalline solids. (Applying)
- Explain the low density and high heat of fusion of ice. (Understanding) Define and ex lain

	molecular and metallic solids. Understanding.

Related videos



Chapter overview

Reversible Reactions

Up until this point, we have written the equations for chemical reactions in a way that would seem to indicate that all reactions proceed completely until all the reactants have been converted into products. In reality, a great many chemical reactions do not proceed entirely to completion. A **reversible reaction** is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously. One example of a reversible reaction is the reaction of hydrogen gas and iodine vapor to from hydrogen iodide. The forward and reverse reactions can be written as follows.

Forward reaction : $H_2(g) + I_2(g) \rightarrow 2HI(g)$

Reverse reaction : $2HI(g) \rightarrow H_2(g) + I_2(g)$

In the forward reaction, hydrogen and iodine combine to form hydrogen iodide. In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. The two reactions can be combined into one equation by the use of a double arrow.

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

The double arrow is the indication that the reaction is reversible.

Dynamic Equilibrium

At dynamic equilibrium, reactants are converted to products and products are converted to reactants at an equal and constant rate. Reactions do not necessarily—and most often do not—end up with equal concentrations. Equilibrium is the state of equal, opposite rates, not equal concentrations.

LE CHATELIER'S PRINCIPLE

This page looks at Le Chatelier's Principle and explains how to apply it to reactions in a state of dynamic equilibrium. It covers changes to the position of equilibrium if you change concentration, pressure or temperature. It also explains very briefly why catalysts have no effect on the position of equilibrium.

Important: If you aren't sure about the words *dynamic equilibrium* or *position of equilibrium* you should read the <u>introductory page</u> before you go on

It is important in understanding everything on this page to realise that Le Chatelier's Principle is no more than a useful guide to help you work out what happens when you change the conditions in a reaction in dynamic equilibrium. *It doesn't explain anything*. I'll keep coming back to that point!

Using Le Chatelier's Principle

A statement of Le Chatelier's Principle

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

Using Le Chatelier's Principle with a change of concentration

Suppose you have an equilibrium established between four substances A, B, C and D.

A + 2B _____ C + D

Note: In case you wonder, the reason for choosing this equation rather than having just A + B on the lefthand side is because further down this page I need an equation which has different numbers of molecules on each side. I am going to use that same equation throughout this page.

What would happen if you changed the conditions by increasing the concentration of A? According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right. A + 2B \subseteq C + D

The position of equilibrium moves to the right if you increase the concentration of A.

This is a useful way of converting the maximum possible amount of B into C and D. You might use it if, for example, B was a relatively expensive material whereas A was cheap and plentiful.

What would happen if you changed the conditions by decreasing the concentration of A?

According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.

The position of equilibrium moves to the left if you decrease the concentration of A.

This is essentially what happens if you remove one of the products of the reaction as soon as it is formed. If, for example, you removed C as soon as it was formed, the position of equilibrium would move to the right to replace it. If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.

Important

This isn't in any way an *explanation* of why the position of equilibrium moves in the ways described. All Le Chatelier's Principle gives you is a quick way of working out what happens.

Note: If you know about equilibrium constants, you will find a <u>more detailed explanation</u> of the effect of a change of concentration by following this link. If you don't know anything about equilibrium constants, you should ignore this link.

If you choose to follow it, return to this page via the BACK button on your browser or via the equilibrium menu.

Using Le Chatelier's Principle with a change of pressure

This only applies to reactions involving gases:

A(g) + 2B(g) _____ C(g) + D(g)

What would happen if you changed the conditions by increasing the pressure?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the pressure is reduced again.

Pressure is caused by gas molecules hitting the sides of their container. The more molecules you have in the container, the higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.

In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right. By forming more C and D, the system causes the pressure to reduce.

Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules.

A(g) + 2B(g) _____ C(g) + D(g)

The position of equilibrium moves to the right if you increase the pressure on the reaction.

What would happen if you changed the conditions by decreasing the pressure?

The equilibrium will move in such a way that the pressure increases again. It can do that by producing more molecules. In this case, the position of equilibrium will move towards the left-hand side of the reaction. $A(g) + 2B(g) \longrightarrow C(g) + D(g)$

The position of equilibrium moves to the left if you decrease the pressure on the reaction.

What happens if there are the same number of molecules on both sides of the equilibrium reaction? In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium. Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

Important

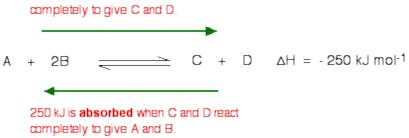
Again, this isn't an *explanation* of why the position of equilibrium moves in the ways described. You will find a rather mathematical treatment of the explanation by following the link below.

Note: You will find a <u>detailed explanation</u> by following this link. If you don't know anything about equilibrium constants (particularly K_p), you should ignore this link. The same thing applies if you don't like things to be too mathematical! If you are a UK A' level student, you won't need this explanation. If you choose to follow the link, return to this page via the BACK button on your browser or via the equilibrium menu.

Using Le Chatelier's Principle with a change of temperature

For this, you need to know whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):

A + 2B \longrightarrow C + D $\Delta H = -250 \text{ kJ mol}^{-1}$ This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction. The back reaction (the conversion of C and D into A and B) would be endothermic by exactly the same amount. 250 kJ is evolved when A and B react



What would happen if you changed the conditions by increasing the temperature?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the temperature is reduced again.

Suppose the system is in equilibrium at 300°C, and you increase the temperature to 500°C. How can the reaction counteract the change you have made? How can it cool itself down again?

To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the *back reaction* absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.

A + 2B _____ C + D ΔH = - 250 kJ mol⁻¹

The position of equilibrium moves to the left if you increase the temperature.

If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!

What would happen if you changed the conditions by decreasing the temperature?

The equilibrium will move in such a way that the temperature increases again.

Suppose the system is in equilibrium at 500°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the exothermic reaction. The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.



The position of equilibrium moves to the right if you decrease the temperature.

Summary

Increasing the temperature of a system in dynamic equilibrium favours the endothermic reaction. The system counteracts the change you have made by absorbing the extra heat.

Decreasing the temperature of a system in dynamic equilibrium favours the exothermic reaction. The system counteracts the change you have made by producing more heat.

Important

Again, this isn't in any way an *explanation* of why the position of equilibrium moves in the ways described. It is only a way of helping you to work out what happens.

Note: I am not going to attempt an explanation of this anywhere on the site. To do it properly is far too difficult for this level. It is possible to come up with an explanation of sorts by looking at how the rate constants for the forward and back reactions change relative to each other by using the Arrhenius equation, but this isn't a standard way of doing it, and is liable to confuse those of you going on to do a Chemistry degree. If you aren't going to do a Chemistry degree, you won't need to know about this anyway!

Le Chatelier's Principle and catalysts

Catalysts have sneaked onto this page under false pretences, because *adding a catalyst makes absolutely no difference to the position of equilibrium*, and Le Chatelier's Principle doesn't apply to them.

This is because a catalyst speeds up the forward and back reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. So why use a catalyst?

For a dynamic equilibrium to be set up, the rates of the forward reaction and the back reaction have to become equal. This doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

Le Châtelier's principle

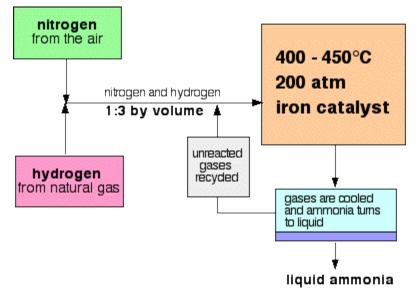
Le Châtelier's principle, chemical principle that states that if a system in equilibrium is disturbed by changes in determining factors, such as temperature, pressure, and concentration of components,

A brief summary of the Haber Process

The Haber Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.

 $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)} \Delta H = -92 \text{ kJ mal}^{-1}$

A flow scheme for the Haber Process looks like this:



Some notes on the conditions

The catalyst

The catalyst is actually slightly more complicated than pure iron. It has potassium hydroxide added to it as a promoter - a substance that increases its efficiency.

The pressure

The pressure varies from one manufacturing plant to another, but is always high. You can't go far wrong in an exam quoting 200 atmospheres.

Recycling

At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%.

Explaining the conditions

The proportions of nitrogen and hydrogen

The mixture of nitrogen and hydrogen going into the reactor is in the ratio of 1 volume of nitrogen to 3 volumes of hydrogen.

Avogadro's Law says that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. That means that the gases are going into the reactor in the ratio of 1 molecule of nitrogen to 3 of hydrogen.

That is the proportion demanded by the equation.

In some reactions you might choose to use an excess of one of the reactants. You would do this if it is particularly important to use up as much as possible of the other reactant - if, for example, it was much more expensive. That doesn't apply in this case.

There is always a down-side to using anything other than the equation proportions. If you have an excess of one reactant there will be molecules passing through the reactor which can't possibly react because there isn't anything for them to react with. This wastes reactor space - particularly space on the surface of the catalyst.

The temperature

Equilibrium considerations

You need to shift the position of the equilibrium as far as possible to the right in order to produce the maximum possible amount of ammonia in the equilibrium mixture.

The forward reaction (the production of ammonia) is exothermic.

 $N_{2(g)} + 3H_{2(g)}$ $\sim 2NH_{3(g)} \Delta H = -92 \text{ kJ mol}^{-1}$

According to Le Chatelier's Principle, this will be favoured if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat. In order to get as much ammonia as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450°C isn't a low temperature!

The pressure

Equilibrium considerations

 $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)} \Delta H = -92 \text{ kJ mol}^{-1}$

Notice that there are 4 molecules on the left-hand side of the equation, but only 2 on the right. According to Le Chatelier's Principle, if you increase the pressure the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again.

In order to get as much ammonia as possible in the equilibrium mixture, you need as high a pressure as possible. 200 atmospheres is a high pressure, but not amazingly high.

The catalyst

In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time. The catalyst ensures that the reaction is fast enough for a dynamic equilibrium to be set up within the very short time that the gases are actually in the reactor.

Precipitation and the Solubility Product

Learning Objectives

Define K_{sp} , the solubility product.

Explain solid/solution equilibria using KspKsp and Q_{sp} .

Calculate molarity of saturated solution from K_{sp} .

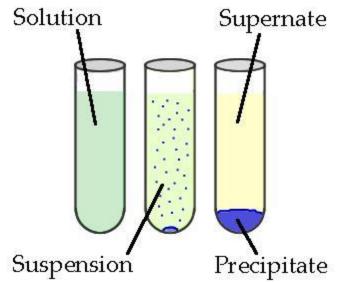
Calculate KspKsp from molarity of saturated solution.

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the

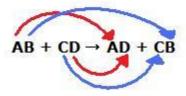
solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called **supernatant liquid** (or just the supernate). The two components of the mixture (precipitate and supinate) can be separated by various methods, such as filtration, centrifuging, or decanting.



The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as a double displacement reaction where the partners "switching; that is, the two reactants each "lose" their partner and form a bond with a different partner:



A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

 $CdSO4(aq)+K2S(aq) \rightarrow CdS(s)+K2SO4(aq)(16.3.1)(16.3.1)CdSO4(aq)+K2S(aq) \rightarrow CdS(s)+K2SO4(aq)$ Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Common Ion Effect

Skills to Develop

Recognize common ions from various salts, acids, and bases.

Calculate concentrations involving common ions.

Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp} 's are equilibrium constants in hetergeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

[Na+]+[K+]=[Cl-](1)(1)[Na+]+[K+]=[Cl-]

Consideration of charge balance or mass balance or both leads to the same conclusion.

Common Ions

When NaClNaCl and KClKCl are dissolved in the same solution, the Cl–Cl– ions are *common* to both salts. In a system containing NaClNaCl and KClKCl, the Cl–Cl– ions are common ions.

NaCl≓Na++Cl−NaCl≓Na++Cl−

 $KCl \rightleftharpoons K++Cl-KCl \rightleftharpoons K++Cl-$

 $CaCl2 \rightleftharpoons Ca2++2Cl-CaCl2 \rightleftharpoons Ca2++2Cl-$

AlCl3≓Al3++3Cl−AlCl3≓Al3++3Cl−

 $AgCl \rightleftharpoons Ag++Cl-AgCl \rightleftharpoons Ag++Cl-$

For example, when AgClAgCl is dissolved into a solution already

containing NaClNaCl (actually Na+Na+ and Cl–Cl– ions), the Cl–Cl– ions come from the ionization of both AgClAgCl and NaClNaCl. Thus, [Cl–][Cl–] differs from [Ag+][Ag+]. The following examples show how the concentration of the common ion is calculated.

What is the Law of Mass Action?

The law of mass action states that the rate of a reaction is proportional to the product of the concentrations of each reactant.

This law can be used to explain the behavior exhibited by solutions in <u>dynamic equilibria</u>. The law of mass action also suggests that the ratio of the reactant concentration and the product concentration is constant at a state of chemical equilibrium.

EQUILIBRIUM CONSTANTS: Kc

introducing equilibrium constants expressed in terms of concentrations, K_c. It assumes that you are familiar with the concept of a dynamic equilibrium, and know what is meant by the terms "homogeneous" and "heterogeneous" as applied to chemical reactions.

We need to look at two different types of equilibria (homogeneous and heterogeneous) separately, because the equilibrium constants are defined differently.

A homogeneous equilibrium has everything present in the same phase. The usual examples include reactions where everything is a gas, or everything is present in the same solution.

A heterogeneous equilibrium has things present in more than one phase. The usual examples include reactions involving solids and gases, or solids and liquids.

K_c in homogeneous equilibria

This is the more straightforward case. It applies where everything in the equilibrium mixture is present as a gas, or everything is present in the same solution.

A good example of a gaseous homogeneous equilibrium is the conversion of sulphur dioxide to sulphur trioxide at the heart of the Contact Process:

 $2SO_{2(g)} + O_{2(g)} = 2SO_{3(g)}$

A commonly used liquid example is the esterification reaction between an organic acid and an alcohol - for example: $CH_3COOH_{[1]} + CH_3CH_2OH_{[1]} \longrightarrow CH_3COOCH_2CH_3([1]) + H_2O_{[1]}$

Writing an expression for K_c

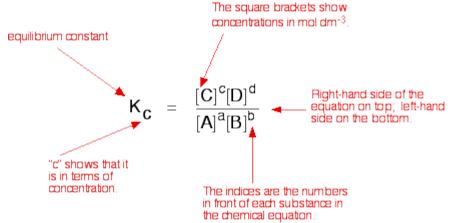
We are going to look at a general case with the equation:

aA + bB _____ cC + dD

No state symbols have been given, but they will be all (g), or all (l), or all (aq) if the reaction was between substances in solution in water.

If you allow this reaction to reach equilibrium and then measure the equilibrium concentrations of everything, you can combine these concentrations into an expression known as an *equilibrium constant*.

The equilibrium constant always has the same value (provided you don't change the temperature), irrespective of the amounts of A, B, C and D you started with. It is also unaffected by a change in pressure or whether or not you are using a catalyst.



Compare this with the chemical equation for the equilibrium. The convention is that the substances on the right-hand side of the equation are written at the top of the K_c expression, and those on the left-hand side at the bottom. The indices (the powers that you have to raise the concentrations to - for example, squared or cubed or whatever) are just the numbers that appear in the equation.

Reference pages

https://courses.lumenlearning.com/cheminter/chapter/reversible-reaction/

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_ Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Chemical_Equilibria/Principles_of_Chemical_Equi libria/Dynamic_equilibrium

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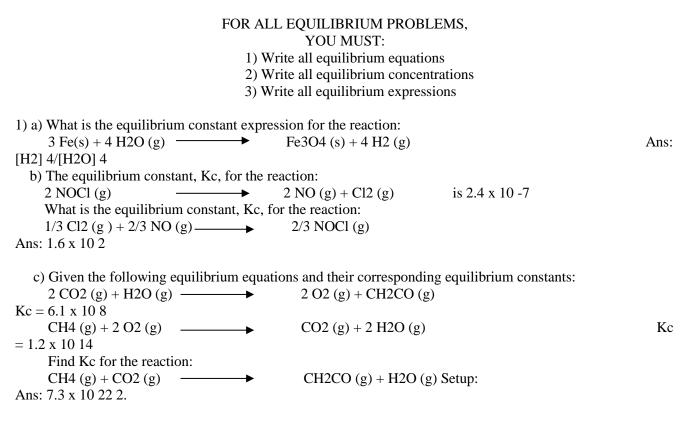
principle#:~:text=Le%20Ch%C3%A2telier's%20principle%20can%20be,one%20that%20gives%20off%20heat

WORKSHEET: CHEMICAL EQUILIBRIUM

Name

Sir Rao Muzammil Ali & Ms Naheed Muneer Siddiqui

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2) A mixture of 9.22 moles of A, 10.11 moles of B, and 27.83 moles of C is placed in a one-liter container at a certain temperature. The reaction is allowed to reach equilibrium. At equilibrium the number of moles of B is 18.32. Calculate the equilibrium constant for the reaction: A(g) + 2B(g) 3C(g)

Practical #03

To determine the equilibrium state between ferrous nitrate & sodium thiocyanate.

X-----X

CHAPTER 6

"THERMOCHEMISTRY"



INTRODUCTION:

Major concepts:

- Energy in chemical reaction
- Thermodynamic
- Internal energy
- Laws of thermodynamics
- Standard state & standard enthalpy changes
- Heat capacity
- Hess's law
- Born Haber cycle
- Calorimetry

Conceptual linkage

This unit is built on,

• Exothermic & Endothermic reaction

LEARNING OUTCOMES

	Students will be able to	Remembering	Applying	Understanding
•	Define thermodynamics.	~		
•	Explain reaction pathway diagram in terms of enthalpy changes . (Born Haber's Cycle)		~	
•	Describe how heat of combustion can be used to estimate the energy available from foods.			v
•	Apply Hess's Law to construct simple energy cycles.			~
•	Specify conditions for the standard heat of reaction.		~	
•	Use the experimental data to calculate the heat of reaction using a calorimeter.		~	
•	Define bond dissociation energy.	~		
•	Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure.		~	
•	Name and define the units of thermal energy	~		
•	Define the terms system, surrounding, boundary, state function, heat, heat capacity,work done and enthalpy of a substance.	~		
•	Classify reactions as exothermic or endothermic.			v

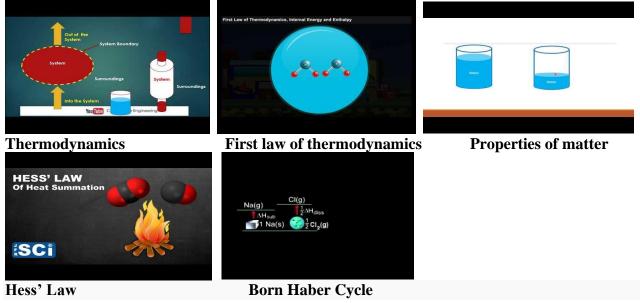
SKILLS	Analyzing	Applying	Understanding
• Use standard heat of formation to calculate the enthalpy change of reaction.		~	
• Determine the heat of a reaction which is experimentally inaccessible from the heats of a set of reaction which are experimentally measurable			
• Perform calculations involving energy cycles related to Hess's law.		~	
• Calculate lattice energy & enthalpy of formation of NaCl & MgO from given set of appropriate data.		>	

SOCIETY, TECHNOLOGY AND SCIENCE

Students will be able to

- ➤ Use of hot & cold pouches for cooling & heating.
- > Understand that transformation of matter is accompanied with changes in energy.

Related videos



(THEORITICAL)

THERMOCHEMISTRY

Thermochemistry is the study of the heat energy which is associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy,

Introduction:

In Physics, thermodynamics deals with temperature, heat and their relation to energy, radiation, work, and properties of matter. The energy can be of any forms such as electrical, mechanical, or chemical energy. William Thomson coined the term thermodynamics in 1749. It is derived from two Greek words "thermes" meaning heat, and "dynamikos" meaning powerful.

When we say the word dynamic we think of motion or movement and energy. Thus, the term thermodynamics means heat movement or heat flow.

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- <u>Thermodynamic Properties</u>
- What is Enthalpy?What is Entropy?

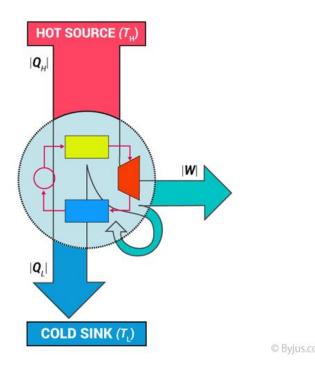
<u>Solved Problem on ThermodynamicsSummaryFAQs</u>

What is Thermodynamics?

Thermodynamics is the branch of Physics which is concerned with the relationship between other forms of energy and heat. We can define thermodynamics as:

The branch of Physics that deals with heat and temperature, and their relation to energy, work, radiation, and properties of matter.

To be specific, it explains how <u>thermal energy</u> is converted to or from other forms of energy and how matter is affected by this process. Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object. The faster these particles move, the more heat is generated.

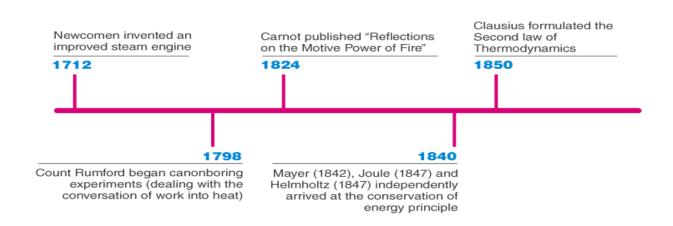


What is thermodynamic process?

A thermodynamic process is a passage of a thermodynamic system from an initial to a final state of thermodynamic equilibrium.

Thermodynamics Timeline

Thermodynamics has many sections under it and is considered as a broad subject because it deals with topics that exist all around us and thus classification becomes necessary.



Classical Thermodynamics:

In this section, the behaviour of matter is analyzed with a macroscopic approach. Units such as temperature and pressure are taken into consideration which helps the individuals to calculate other properties and to predict the characteristics of the matter that is undergoing the process.

Statistical Thermodynamics:

In this section, every molecule is under the spotlight i.e. the properties of each and every molecule and ways in which they interact are taken into consideration to characterize the behaviour of a group of molecules.

Pure Component Thermodynamics:

As the name itself states, this section tries to describe the behaviour of a system that has an unadulterated or pure constituent.

Solution Thermodynamics:

This section attempts to describe the behaviour of a system that contains more than one chemical in the mixture.

Laws of Thermodynamics.

The laws of thermodynamics define the fundamental physical quantities like energy, temperature and entropy that characterise thermodynamic systems at thermal equilibrium. The laws represent how these quantities behave under various circumstances.

How many laws of thermodynamics are there?

There are four laws of thermodynamics and are given below:

- Zeroth law of thermodynamics
- First law of thermodynamics

- Second law of thermodynamics
- Third law of thermodynamics

Zeroth Law of Thermodynamics

The Zeroth Law is the basis for the measurement of temperature. It states that:

Two bodies which are in thermal equilibrium with a third body are in thermal equilibrium with each other.

Zeroth Law Of Thermodynamics Examples:

- consider two cups *A* and *B* with boiling water.
- When a thermometer is placed in $\sup A$, it gets warmed up by the water until it reads 100°C.
- When it read 100° C, we say that the thermometer is in equilibrium with cup A.
- Now when we move the thermometer to cup *B* to read the temperature, it continues to read 100° C.
- The thermometer is also in equilibrium with cup B.
- From keeping in mind the zeroth law of thermodynamics, we can conclude that cup *A* and cup *B* are in equilibrium with each other.

The zeroth law of thermodynamics enables us to use thermometers to compare the temperature of any two objects that we like.

First Law of Thermodynamics

The first law of thermodynamics which is also known as the conservation of energy principle states that:

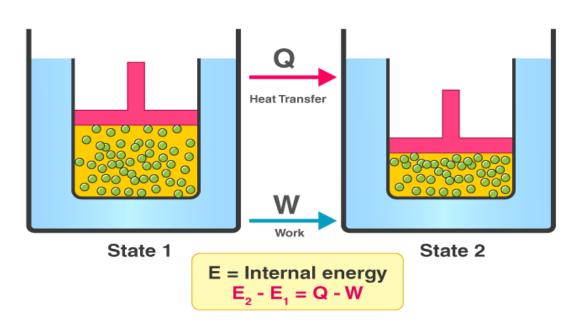
Energy can neither be created nor destroyed, but it can be changed from one form to another.

This law may seem abstract but if we look at a few examples of the first law of thermodynamics, we will get a clearer idea.

First Law Of Thermodynamics Examples:

- Fans convert electrical energy to mechanical energy.
- Plants convert the radiant energy of sunlight to <u>chemical energy</u> through photosynthesis. We eat plants and convert the chemical energy into kinetic energy while we swim, walk, breathe and when we scroll through this page.

Further on First Law of Thermodynamics



A thermodynamic system in an equilibrium state possesses a state variable known as the internal energy(E). Between two systems the change in the internal energy is equal to the difference of the heat transfer into the system and the work done by the system.

The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged between the system and the surroundings, it can't be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer. It redefines the conservation of energy concept.

First Law of Thermodynamics

The First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy.

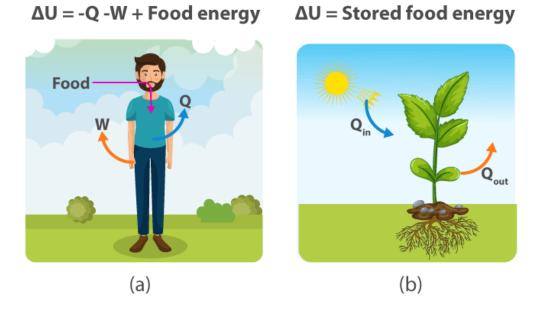
First Law of Thermodynamics Equation

The equation for the first law of thermodynamics is given as;

$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W}$

Where,

- $\Delta U =$ change in internal energy of the system.
- q = algebraic sum of heat transfer between system and surroundings.
- W = work interaction of the system with its surroundings.



Points to Remember

- For an isolated system, energy (E) always remains constant.
- Internal Energy is a point function and property of the system. Internal energy is an extensive property (mass-dependent) while specific energy is an intensive property (independent of mass).
- For an ideal gas, the internal energy is a function of temperature only.

First Law of Thermodynamics Limitations

The first law of thermodynamics states that whenever a system undergoes any thermodynamic process it always holds certain energy balance. However, the first law fails to give the feasibility of the process or change of state that the system undergoes.

For instance, the first law fails to explain why heat flows from hot end to cold end when a metallic rod is heated at one end and not on other and vice-versa. The first law only quantifies the energy transfer that takes place during this process. It is the second law of thermodynamics which provides the criterion for the feasibility of the various processes. We will take an example and understand the concept further.

First law of Thermodynamics for a Closed System

Work done for a closed system is the product of pressure applied and the change in volume that occurs due to applied pressure :

 $\mathbf{w} = -\mathbf{P} \Delta \mathbf{V}$

where P is the constant external pressure on the system, and ΔV is the change in volume of the system. This is specifically called "pressure-volume" work.

The internal energy of a system increases or decreases depending on work interaction that takes place across its boundaries. The internal energy would increase if work is done on the system and decreases if work is done by the system. Any heat interaction that takes place in the system with its surroundings also changes its internal energy. But since energy remains constant (from the first law of thermodynamics), the total change in internal energy is always zero. If energy is lost by the system, then it is absorbed by the surroundings. If energy is absorbed into a system, then it implies that the energy was released by the surroundings:

Δ Usystem = $-\Delta$ Usurroundings

where ΔU_{system} is the change in the total internal energy of the system, and $\Delta U_{surroundings}$ is the change in the total energy of the surrounding.

Also Read: Third Law of Thermodynamics

Carefully study the table given below:

Process	Sign Convention for heat(q)	Sign Convention for work(w)
Work done by the system	N/A	_
Work done on the system	N/A	+
Heat extracted from the system	-	N/A
Heat added to the system	+	N/A

Second Law of Thermodynamics

The second law of thermodynamics states that:

Energy in the form of heat only flows from regions of higher temperature to that of lower temperature.

Many individuals take this statement lightly and for granted, but it has an extensive impact and consequence. This is why it costs money to run an air conditioner. The human body obeys the second law of thermodynamics too.

Second Law Of Thermodynamics Examples

One of the examples of the second law of thermodynamics can be sweating in a crowded room. Assume yourself to be in a small room full of people. You are very likely to feel warm and start

sweating. Sweating is a mechanism the human body uses to cool itself. Here, the heat from your body is transferred to sweat. As the sweat absorbs more and more heat from the body it evaporates and transfers heat to the surrounding air, thereby, heating up the temperature of the room.

Different Statements of The Law

There are two statements on the second law of thermodynamics which are;

- 1. Kelvin- Plank Statement
- 2. Clausius Statement

Kelvin-Planck Statement

It is impossible for a heat engine to produce a network in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.

Exceptions:

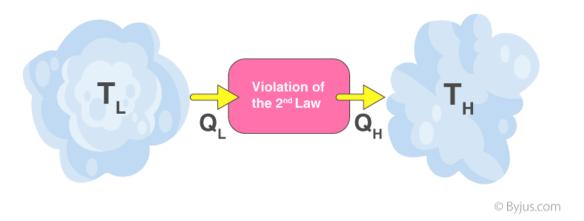
If $Q_2 = 0$ (i.e., $W_{net} = Q_1$, or efficiency=1.00), the heat engine produces work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement.

Clausius's Statement

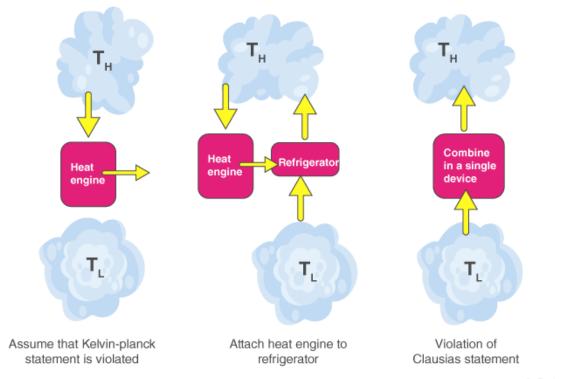
It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to warmer without consuming any work.

In other words, unless the compressor is driven by an external source, the refrigerator won't be able to operate.

Heat pump and Refrigerator works on Clausius's statement.



Both Clausius's and Kelvin's statements are equivalent i.e a device violating Clausius's statement will also violate Kelvin's statement and vice versa.



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In addition to these statements, a French physicist named Nicolas Léonard Sadi Carnot also known as"father of thermodynamics," basically introduced the Second Law of Thermodynamics. However, as per his statement, he emphasized the use of caloric theory for the description of the law. Caloric (self repellent fluid) relates to heat and Carnot observed that some caloric was lost in the motion cycle

Third Law of Thermodynamics

The Third Law states that:

The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K)

Entropy is sometimes called "*waste energy*" i.e., the energy that is unable to do work, and since there is no <u>heat energy</u> whatsoever at absolute zero, there can be no waste energy.

Third Law Of Thermodynamics Examples:

Let us consider steam as an example to illustrate the third law of thermodynamics step by step:

We know that steam is a gaseous state of water at higher temperatures. In this state:

- 1. The molecules within it move freely and have high entropy.
- 2. If one decreases the temperature below 100°C, the steam gets converted to water, where the movement of molecules is restricted, decreasing the entropy of water.

- **3.** When water is further cooled below 0°C, it gets converted to solid ice. In this state, the movement of molecules is further restricted and the entropy of the system reduces more.
- **4.** As the temperature of the ice further reduces, the movement of the molecules in them are restricted further and the entropy of the substance goes on decreasing.
- 5. When the ice is cooled to absolute zero, ideally the entropy should be zero. But in reality, it is impossible to cool any substance to zero.

Thermodynamic Properties:

Thermodynamic properties may be **extensive** or **intensive**.

• Intensive properties are properties that do not depend on the quantity of matter.

For example, pressure and temperature are intensive properties.

• In the case of extensive properties, their value depends on the mass of the system.

For example, volume, energy, and enthalpy are extensive properties.

What is Enthalpy?

Enthalpy is the measurement of energy in a thermodynamic system. The quantity of <u>enthalpy</u> equals the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.

Mathematically, the enthalpy, H, equals the sum of the <u>internal energy</u>, E, and the product of the pressure, P, and volume, V, of the system.

H = E + PV

What is Entropy?

The <u>entropy</u> is a thermodynamic quantity whose value depends on the physical state or condition of a system. In other words, it is a thermodynamic function used to measure the randomness or disorder of a system.

For example, the entropy of a solid, where the particles are not free to move, is less than the entropy of a gas, where the particles will fill the container.

Reference page/site

https://byjus.com/physics/thermodynamics/

Born Haber Cycle.

Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

Born Haber Cycle Examples

Example 1: Born Haber cycle of sodium chloride NaCl, (or any AB-type Mono-valent ionic solid).

The heat of formation of sodium chloride (ΔH_f^0) from the sodium metal and chlorine gas can be experimentally measured.

Na (s) + $\frac{1}{2}21 \operatorname{Cl}_2(g) \rightarrow \operatorname{NaCl}(s) \Delta H_f^0 = -411 \text{kJ/mol}$

The formation of ionic solid sodium chloride form solid sodium metal and gaseous chlorine is not a single step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

The processes or steps in the formation of sodium chloride are-

1. Solid sodium atom sublimes to gaseous atom by absorbing heat energy (ΔH_{sub}).

Na (s) \rightarrow Na (g),

Sublimation energy $\Delta H_{sub} = + 107 k J/mol$

2. Gaseous sodium atom absorbs the ionization energy to release one electron and forms gaseous sodium ion.

 $Na(g) \rightarrow Na^+(g) + 1e^-$,

Ionization energy $\Delta H_{IE} = +502 k J/mol$

3. Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of chlorine molecule.

 $Cl_2(g) \rightarrow 2Cl(g) \setminus frac\{1\}\{2\}21$

Bond dissociation energy of chlorine = $\frac{1}{2}21 \Delta H_{diss} = \frac{1}{2}21 242 = +121 kJ/mol$

4. Chlorine atom accepts an electron to form chloride ion and releases energy equivalent to electron affinity.

 $Cl(g) + 1e^{-} \rightarrow Cl^{-}(g)$

Electron affinity = ΔH_{EA} = -355kJ/mol

5. Gaseous sodium ion and gaseous chloride ion combine to form solid sodium chloride molecule and releases energy equivalent to lattice energy.

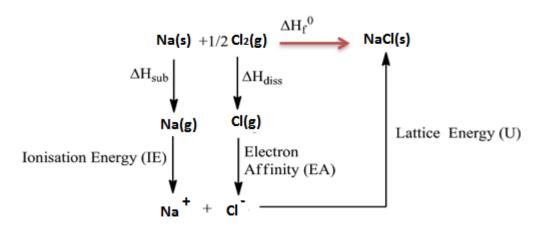
 $Na^+(g) + Cl^-(g) \rightarrow Na^+ Cl^-(s)$

Lattice energy = $\Delta H_{LE} = U = ?$

Summation of enthalpy of all the processes from step 1 to step 5) give the net enthalpy of formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid sodium chloride.

The enthalpies are represented as a cycle in the figure.

Born Haber Cycle for Sodium Chloride



So, $\Delta H_{f}^{0} = \Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}21 \Delta H_{dis} + \Delta H_{EA} + U \text{ or } \Delta H_{f}^{0} - (\Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}21 \Delta H_{dis} + \Delta H_{EA} + U) = 0$

411 + 107 + 502 + 121 - 355 + U = 0

Here, except lattice energy, all other enthalpies can be experimentally measured.

Lattice energy of the sodium chloride solid = $U = \Delta H_f^0 - (\Delta H_{sub} + \Delta H_{IE} + \frac{1}{2} \Delta H_{dis} + \Delta H_{EA})$.

= -411 -107 -502 -121 +355

= -786 kJ/mol

Example 2: Lattice energy of magnesium oxide (or any AB-type Divalent ionic solid).

The heat of formation of magnesium oxide (ΔH_f^0) from the magnesium metal and oxygen gas can be experimentally measured.

Mg (s) + $\frac{1}{2}21O_2(g) \rightarrow MgO(s)$

 $\Delta H_{\rm f}^{\ 0}$ = -602kJ/mol

The processes or steps in the formation of magnesium oxide are-

1. Solid magnesium atom sublimes to gaseous atom by absorbing heat energy (ΔH_{sub}).

Mg (s) \rightarrow Mg (g), Sublimation energy $\Delta H_{sub} = + 136 \text{kJ/mol}$

2. Gaseous magnesium atom releases two electrons in two steps with corresponding ionization energies.

 $Mg(g) \rightarrow Mg^+(g) + 1e^-$, Ionization energy $\Delta H^1_{IE} = +738 kJ/mol$

 $Mg^+(g) \rightarrow Mg^{2+}(g) + 1e^-$, Ionization energy ΔH^2_{IE} = +1450kJ/mol

So energy of ionization = $\Delta H_{IE} = 738 + 1450 = 2188$ kJ/mol

3. Diatomic oxygen breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of the chlorine molecule.

$$\begin{split} O_2(g) &\rightarrow 2O(g) \left\{1\right\}_{2}^{21} \text{ Bond dissociation energy of oxygen =} \left\{1\right\}_{2}^{21} \Delta H_{diss} = \left\{rac_{1}^{2}\right\}_{2}^{21} 498 = +249 \text{kJ/mol} \end{split}$$

4. Oxygen atom accepts two electrons to form oxide ion and releases energy equivalent to twoelectron affinities.

 $O(g) + 1e^- \rightarrow O^-(g)$ Electron affinity = $\Delta H^1_{EA} = -142 kJ/mol$

 $O^{-}(g) + 1e^{-} \rightarrow O^{2-}(g)$ Electron affinity = $\Delta H^2_{EA} = +798 \text{kJ/mol}$

Total energy released as electron affinity by the oxygen atom is = $\Delta H_{EA} = +656$ kJ/mol

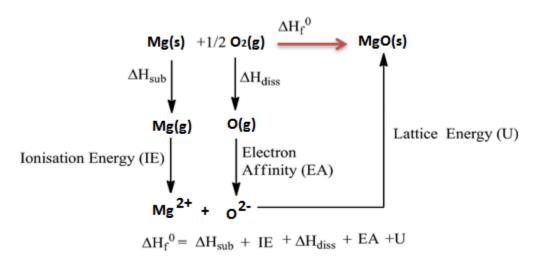
5. Gaseous magnesium ion and gaseous oxide ion combine to form solid magnesium oxide molecule and releases energy equivalent to lattice energy.

 $Mg^{2+}(g) + O^{2-}(g) \rightarrow Mg^{2+}O^{2-}(s)$ Lattice energy = $\Delta H_{LE} = U = ?$

Summation of enthalpy of all the processes from the starting step to the final step gives the net enthalpy of formation of solid crystalline magnesium oxide from magnesium and oxygen in their standard conditions of solid and gas respectively. This should be equal to the experimentally measured enthalpy of formation of solid magnesium oxide.

The enthalpies are represented as a cycle in the figure.

Born Haber Cycle for Magnesium Oxide



So, $\Delta H_{f}^{0} = \Delta H_{sub} + \Delta H_{IE} + \langle frac \{1\} \{2\} 21 \ \Delta H_{dis} + \Delta H_{EA} + U \text{ or } \Delta H_{f}^{0} - (\Delta H_{sub} + \Delta H_{IE} + \langle frac \{1\} \{2\} 21 \ \Delta H_{dis} + \Delta H_{EA} + U) = 0$

602 + 136 + 2188 + 249 + 656 + U = 0

Here, except lattice energy, all other enthalpies can be experimentally measured.

Lattice energy of the magnesium oxide solid = $U = \Delta H_f^0 - (\Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}21 \Delta H_{dis} + \Delta H_{EA})$.

= -602 - 136 - 2188 - 249 - 656 = -3831kJ/mol

Reference page/site

https://byjus.com/jee/born-haber-cycle/

Hess's Law

Hess's law also known as Hess's law of constant heat summation states, "at constant temperature, heat energy changes (enthalpy- Δ Hrec) accompanying a chemical reaction will remain constant, irrespective of the way the reactants react to form product".

Hess law is based on the state function character of enthalpy and the first law of thermodynamics. Energy (enthalpy) of a system (molecule) is a state function. So, enthalpy of reactant and product molecules is a constant and does not change with origin and path of formation.

Importance of Hess Law

Every substance (atom/ molecules) possess energy within. The internal energy depends on the nature of force existing in the substance and the temperature. When the substance undergoes chemical reactions, some of the bonds connecting some atoms are broken and some bonds are made new. The breaking and making of bonds involve energy.

So, in reactions, product substances may have either less or the same or more energy than the reacting substances. Reactions accordingly may release heat to become exothermic or absorb heat and endothermic. Reactants may further react to give the product;

- 1. In single-step or
- 2. In multi-steps or
- 3. Along with other products.

Knowledge of the energy changes in any reaction is essential for the manipulation of the reactants and products in a chemical process to our requirement.

Heat energy changes of reactions measured at constant volume are called internal energy change ΔE and energy measured at constant pressure is called <u>enthalpy change</u> ΔH .

The experimental measurements give only the net value of all reactions or products formed. It is not possible to measure experimentally the enthalpy change of an intermediary reaction step or any intermediary product.

For example, carbon reacts with oxygen to form carbon dioxide in excess oxygen. Carbon and oxygen combine to form carbon dioxide directly or in two steps -initially form carbon monoxide and then go to carbon dioxide. Measurement will give the energy changes for the formation of carbon dioxide only and not for carbon monoxide.

Similarly, measuring the enthalpy of formation of benzene, from carbon and hydrogen is not possible, because carbon and hydrogen may combine to form not only benzene but also other types of hydrocarbons in the given conditions.

Hess's law is useful and is the only way of calculating such non-measurable enthalpy changes in physical and chemical changes.

Forms of Hess Law

Hess law is stated in many different ways.

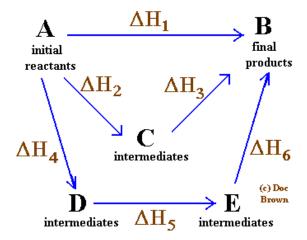
For multi-step reactions:

If reactants react to form products not in a single step but in a number of consecutive steps involving many intermediary products, the sum of all the reactants, products and the corresponding energy changes will give the reactant, products and heat energy changes of the overall reaction. So, like molecules, heat energy changes also can be subjected to mathematical operations.

For multi-different reactions:

If the reactants and products of a required chemical reaction can be obtained by the summation of many other chemical reactions, the enthalpy of the required reaction of reactants to the products also can be obtained by the sum of the enthalpy changes of all those chemical reactions.

a) Hess law and multi-step reaction:



Reactant can form product B by following three different steps. C, D and E are intermediates in the other stepwise reactions. Hess law states that the enthalpy of the reaction (Δ H1) is the same irrespective of the path.

So, the enthalpy of direct single-step reaction and other paths giving intermediates C, D and E should be the same. $\Delta H1 = \Delta H2 + \Delta H3 = \Delta H4 + \Delta H5 + \Delta H6$.

Example: Carbon reacts with oxygen to form carbon dioxide releasing 94.3kcals of heat in a single step. Carbon can also react in a two-step process of forming an intermediate carbon mono-oxide, which again is converted to carbon dioxide. ($\Delta H = -$ Heat released)

 $C + O_2 \rightarrow CO + 26.0$ kcals

 $CO + O_2 \rightarrow CO_2 + 68.3 kcals$

On adding the two reactions, $C + O_2 \rightarrow CO_2 + 94.3$ kcals

As per Hess law, $\Delta H = \Delta H1 + \Delta H2 = -26.0 + 68.3 = 94.3$ kcals

Net reaction enthalpy of both reactions is the same as that of single-step formation. So, enthalpy of reaction does not change on the path followed by the reactants.

b) Hess law and multi-different reactions:

Combustion of carbon, sulphur and carbon disulphide are exothermic with an enthalpy of-393.5kJ, -296.8kJ and -1075kJ.

Reactions are-

 $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5 \text{ kJ} \dots (1)$ $S(s) + O_2(g) \rightarrow SO_2(g) + 296.8 \text{ kJ} \dots (2)$ $CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) + 1075.0 \text{ kJ} \dots (3)$

These reactions and enthalpy changes can be treated as algebraic equations to get the heat of formation of carbon disulphide even without doing experiments.

Equation 1: $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5 \text{ kJ}$ 2x equation 2:2S(s) + 2O₂(g) \rightarrow 2SO₂(g) + 593.6 kJ

Reverse of equation3: $CO_2(g) + 2SO_2(g) \rightarrow CS_2(l) + 3O_2(g) - 1075.0 \text{ kJ}$

Adding the three reactions: C (s) + 2S (s) \rightarrow CS₂ (l) -87.9 kJ

Formation of carbon disulphide is an endothermic reaction.

Application of Hess law of Heat Summation

Hess law of heat summation is an efficient way to estimate heat changes that cannot be measured experimentally.

1. Enthalpy change in a physical change

Carbon and diamond are allotropes of carbon. But measuring the energy change in the conversion of graphite to diamond cannot be determined, as the process cannot be carried out. Still, the heat changes for this hypothetical physical change can be calculated using Hess law.

Graphite and diamond combine with oxygen with the heat of reaction as -393.4kJ and – 395.4kJ respectively.

C (graphite) + $O_2 \rightarrow CO_2 \Delta Hgr = -393.4 kJ$

C (diamond) + $O_2 \rightarrow CO_2 \Delta H di = -395.4 kJ$

Reversing the combustion reaction of diamond as-

 $CO_2 \rightarrow C$ (diamond) + $O_2 \Delta Hdi = + 395.4 kJ$

Adding,

C (graphite) + $O_2 \rightarrow CO_2 \Delta Hgr = -393.4 kJ$

C (graphite) \rightarrow C (diamond) Δ Htr = +2.kJ

Enthapy change in the allotrope transition of graphite to diamond is endothermic of 2KJ.

2. Enthalpy change of chemical reaction

The bond energy of hydrogen, iodine and hydrogen iodide are 218, 107kJ and 299kJ respectively.

Estimate the enthalpy of hydrogen iodide formation. Is the reaction endothermic or exothermic?

Formation of hydrogen iodide from hydrogen and iodine follows the reaction-

 $\frac{1}{2}21H_2(g) + \frac{1}{2}21I_2(g) \rightarrow HI(g)$

Enthalpy of formation of hydrogen iodide is the heat changes occurring when one atom of hydrogen and one atom of iodine react to form one mole of hydrogen iodide in standard conditions (as gas). To get one atom of hydrogen or iodine the molecular bond has to be broken.

Heat of formation = Bond energy of HI – Bond dissociation of H_2 – Bond dissociation energy of I_2 .

= 299 - (218 + 107) = 299 - 325 = -26kJ

As the heat of formation is negative, the reaction is exothermic.

3. Enthalpy of formation

When carbon combines with hydrogen, many hydrocarbons can be formed. Hence the heat of formation of benzene cannot be determined experimentally. The heat change can be calculated by Hess law.

 $6C+3H_2 \rightarrow C_6H_6\,\Delta H \; C_6H_6 = ?$

Heat of formation of carbon dioxide and water are -393.5kJand -285.8KJ respectively. Heat of combustion of benzene is -3301kJ.

 $C + O_2 \rightarrow CO_2 \Delta H1 = -393.5 \text{kJ}....1$ $H_2 + O_2 \rightarrow H_2 O \Delta H2 = -285.8 \text{kJ}....2$ $C_6H_6 + 9O_2 \rightarrow 6CO_2 + 3H_2 O \Delta H3 = -3301 \text{kJ} \dots 3$ $6 \text{ x Reaction 1: } 6C + 6O_2 \rightarrow 6CO_2 6\Delta H1 = -2361 \text{kJ}....1$ $3 \text{ x Reaction 2: } 3H_2 + 3O_2 \rightarrow 3H_2 O 3\Delta H2 = -857.4 \text{kJ}....2$ Reverse of reaction 3: $6CO_2 + 3H_2O \rightarrow C_6H_6 + 9O_2 - \Delta H3 = +3301 \text{kJ} \dots 3$ Adding the three reactions- $6C + 3H_2 \rightarrow C_6H_6 \Delta H = +82.6 \text{kJ}$

Heat of formation of benzene is 82.6kJ

Reference page/site.

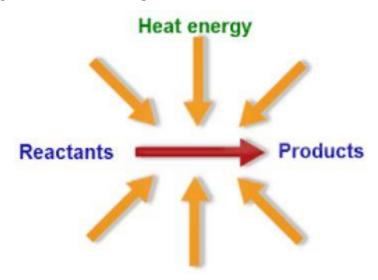
https://byjus.com/jee/hess-law-of-constant-heat-summation/

Exothermic Reaction.

An exothermic reaction is a reaction in which energy is released in the form of light or heat. Thus in an exothermic reaction, energy is transferred into the surroundings rather than taking energy from the surroundings as in an <u>endothermic reaction</u>. In an exothermic reaction, change in enthalpy (Δ H) will be negative.

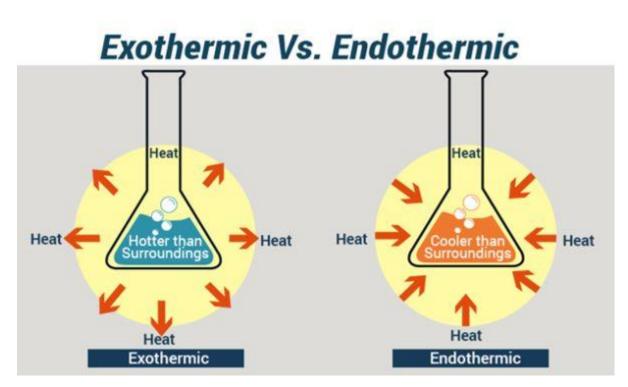
Endothermic Reaction.

Endothermic reactions are chemical reactions in which the reactants absorb heat energy from the surroundings to form products. These reactions lower the temperature of their surrounding area, thereby creating a cooling effect. Physical processes can be endothermic as well – Ice cubes absorb heat energy from their surroundings and melt to form liquid water (no chemical bonds are broken or formed).



How are Endothermic and Exothermic Reactions Different?

The terms 'Endo' and 'Exo' have Greek roots, meaning 'within' and 'out' respectively. As the names suggest, the primary difference between endothermic and exothermic reactions is that the former absorbs heat from the surroundings whereas the latter involves a release of heat.

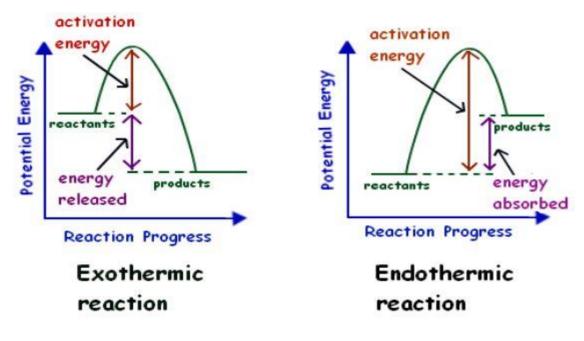


Some other differences between these types of chemical reactions are tabulated below.

Endothermic Reaction	Exothermic Reaction
The system absorbs heat from the surroundings	The system releases heat into the surroundings
The entropy of the surrounding decreases ($\Delta S < 0$)	The entropy of the surrounding increases (ΔS >0)
Enthalpy change (Δ H) is positive	ΔH is negative

Energy Level Diagram of an Endothermic Reaction

The simple energy level diagram of endothermic and exothermic reactions are illustrated below. The <u>activation energy</u> is the energy that must be provided to the reactants so that they can overcome the energy barrier and react.



Reference page/site.

https://byjus.com/chemistry/endothermic-exothermic-reactions-difference/

SI Unit of Heat

Generally, in the SI system, all forms of energy are measured in terms of joules. Notably, heat is a form of energy and therefore the si unit of heat is also joules (J) which is defined as the amount of energy needed to raise the temperature of a given mass by one degree. Usually, 4.184 joules of heat energy is necessary to increase the temperature of a unit weight (say 1 g) of water from 0 degrees to 1 degree Celsius.

Other Heat Units

In the CGS system, heat is expressed in the unit of calories which is further said to be the heat energy needed to increase the temperature of 1 gm of clean water by one degree Celsius. Sometimes kilocalorie (kcal) is also referred to as a unit of heat where 1 kcal = 1000 cal.

Additionally, the British thermal unit (BTU) which is part of the imperial system is also used to measure or calculate heat.

Units of Heat		
Calorie	1 cal	4184 J
Joules	1 J	0.000239006 kcal / 0.000947817Btu

BIO I Blu 1055.00 J

Reference page/site

https://byjus.com/physics/unit-of-heat/

(NUMERICALS)

"THERMODYNAMICS"

1. 3000 J of <u>heat</u> is added to a system and 2500 J of <u>work</u> is done by the system. What is the change in internal energy of the system?

<u>Data :</u>

Heat (Q) = +3000 Joule

Work (W) = +2500 Joule

Wanted: the change in internal energy of the system

Solution :

The equation of the first law of thermodynamics

 $\Delta U = Q \text{-} W$

The sign conventions :

Q is positive if the heat added to the system

W is positive if work is done by the system

Q is negative if heat leaves the system

W is negative if work is done on the system

The change in internal energy of the system :

 $\Delta U = 3000\text{-}2500$

 $\Delta U = 500$ Joule

Internal energy increases by **500 Joule.**

2. 2000 J of heat leaves the system and 2500 J of work is done on the system. What is the change in internal energy of the system?

<u>Known :</u> Heat (Q) = -2000 Joule Work (W) = -3000 Joule Wanted: The change in internal energy of the system

Solution :

 $\Delta U = Q-W$ $\Delta U = -2000-(-3000)$ $\Delta U = -2000+3000$ $\Delta U = 1000 \text{ Joule}$ Internal energy increases by **4500 Joule.**

Reference page/site

https://physics.gurumuda.net/the-first-law-of-thermodynamics-problems-and-solutions.htm

"Hess's law"

Example #1: Calculate the value of ΔH° for the following reaction:

 $P_4O_{10}(s) + 6PCl_5(g) ---> 10Cl_3PO(g)$

using the following four equations:

- a) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$ $\Delta H^\circ = -1225.6 \text{ kJ}$
- b) $P_4(s) + 5O_2(g) ---> P_4O_{10}(s)$ $\Delta H^\circ = -2967.3 \text{ kJ}$ c) $PCl_3(g) + Cl_2(g) ---> PCl_5(g)$ $\Delta H^\circ = -84.2 \text{ kJ}$
- d) $PCl_3(g) + \frac{1}{2}O_2(g) ---> Cl_3PO(g) \Delta H^\circ = -285.7 \text{ kJ}$

Solution:

1) We know that P_4O_{10} **MUST** be on the left-hand side in the answer, so let's reverse (b):

b) $P_4O_{10}(s) \rightarrow P_4(s) + 5O_2(g) \quad \Delta H^\circ = +2967.3 \text{ kJ}$

2) We know that PCl_5 **MUST** be on the left-hand side in the answer, so let's reverse (c) and multiply it by 6:

c) $6PCl_5(g) ---> 6PCl_3(g) + 6Cl_2(g) \Delta H^\circ = +505.2 \text{ kJ}$

3) We know that Cl₃PO MUST have a 10 in front of it:

d) $10PCl_3(g) + 5O_2(g) ---> 10Cl_3PO(g) \Delta H^\circ = -2857 \text{ kJ}$

4) Now, write all four equations, but incorporate the revisions:

a) $P_4(s) + 6Cl_2(g)> 4PCl_3(g)$	$\Delta H^{\circ} = -1225.6 \text{ kJ}$
b) $P_4O_{10}(s) \rightarrow P_4(s) + 5O_2(g)$	$\Delta H^\circ = +2967.3 \text{ kJ}$
c) $6PCl_5(g)> 6PCl_3(g) + 6Cl_2(g)$	$\Delta H^{\circ} = +505.2 \text{ kJ}$
d) 10PCl ₃ (g) + 5O ₂ (g)> 10Cl ₃ PO(g)	$\Delta H^{\circ} = -2857 \text{ kJ}$

5) Now, we will add all four equations as well as the ΔH° values. Notice the following:

- a) P₄(s) cancels out (see equations a and b)
- b) Cl₂ cancels out (see equations a and c)
- c) O_2 cancels out (see equations b and d)
- d) PCl₃ cancels out (see equations a+c and d)

6) The ΔH° values added together:

-1225.6 kJ + (+2967.3 kJ) + (+505.2 kJ) + (-2857 kJ) = -610.1 kJ

7) The answer:

 $P_4O_{10}(s) + 6PCl_5(g) ---> 10Cl_3PO(g)$

 $\Delta H^{\circ} = -610.1 \text{ kJ}$

Reference page/site https://www.chemteam.info/Thermochem/HessLawIntro1b.html

STUDENT"S ASSESMENT

(Theory base)

- What are the three laws of thermodynamics?
- What is the importance of thermodynamics?
- How is thermodynamics used in everyday life?
- Who is regarded as the Father of Thermodynamics?
- What is an example of negative work?
- Can energy be destroyed or lost?
- Fans convert electrical energy into mechanical energy this is explained by which law?
- What is the significance of internal energy?
- What factors affect internal energy?
- Is internal energy a state function?
- Why is entropy constant at the triple point of water?
- Does freezing increase entropy?
- Can entropy ever decrease?
- Can entropy be infinite?
- Can entropy be negative?
- What causes entropy?

(Numerical base)

1. Calculate the reaction enthalpy for the formation of anhydrous aluminum chloride:

 $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$

from the following data:

 $2Al(s) + 6HCl(aq) ---> 2AlCl_3(aq) + 3H_2(g) \quad \Delta H^\circ = -1049 \text{ kJ}$

HCl(g)> HCl(aq)	$\Delta H^{\circ} = -74.8 \text{ kJ}$
$H_2(g) + Cl_2(g) 2HCl(g)$	$\Delta H^{\circ} = -185 \text{ kJ}$
AlCl ₃ (s)> AlCl ₃ (aq)	$\Delta H^\circ = -323 \text{ kJ}$

2. The heat of combustion for the gases hydrogen, methane and ethane are -285.8, -890.4 and -1559.9 kJ/mol respectively at 298K. Calculate (at the same temperature) the heat of reaction for the following reaction:

 $2CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$

The data given are these three reactions:

$$\begin{split} H_2 + \frac{1}{2}O_2 & ---> H_2O & \Delta H = -285.8 \text{ kJ} \\ CH_4 + 2O_2 & ---> CO_2 + 2H_2O & \Delta H = -890.4 \text{ kJ} \\ C_2H_6 + \frac{7}{2}O_2 & ---> 2CO_2 + 3H_2O & \Delta H = -1559.9 \text{ kJ} \end{split}$$

- **3.** 125 kJ of energy is added to a system while 104 kJ of work is done by the system. Calculate the change in internal energy (in kJ).
- **4.** You add coal to an old steam engine on a train. The coal adds 150kJ of energy into the engine. The engine then does 120kJ of work. What is the change in internal energy of the engine?

Practical # 04

- Determine the heat of Neutralization of HCL & NaOH.
- Determine the enthalpy change of NH₃Cl & CaCl₂.

Reference page/site

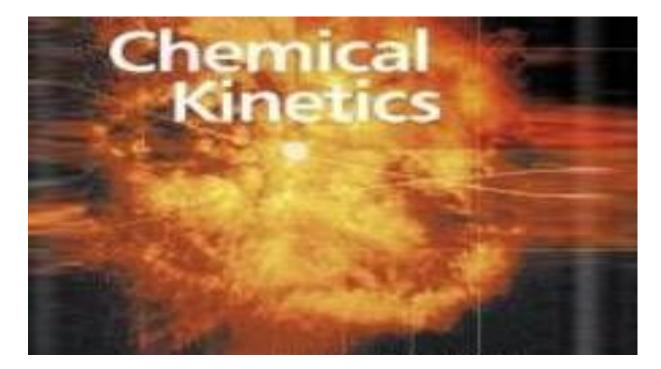
https://files.transtutors.com/cdn/uploadassignments/thermohw4_635730065490227326.pdf https://www.chemteam.info/Thermochem/Hess-3eq-prob1-10.html

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CHAPTER 7

"CHEMICAL KINETICS"



INTRODUCTION:

Major concepts:

- Chemical Kinetics
- Rates of Reactions
- Collision Theory, Transition State and Activation
- Catalysis
 - ✓ Characteristics of Catalysts
 - ✓ Homogeneous Catalysis
 - ✓ Heterogeneous Catalysis
 - ✓ Enzyme Catalysis

Conceptual linkage

This unit is built on,

- Rate law or Rate Expression
- Elementary and overall Rate Constant and Units
- Order of Reaction and its Determination
- Factors Affecting Rate of Reaction

LEARNING OUTCOMES

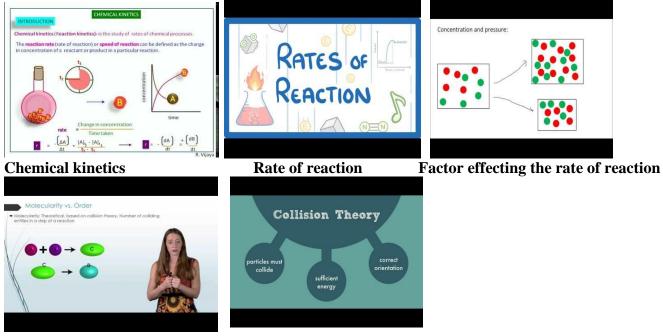
Students will be able to	Analyzing	Applying	Understanding
• Explain that a catalyst provides a reaction			
pathway that has low activation energy.	V		
• Explain why powdered zinc reacts faster.	~		
• Describe enzymes as biological catalysts.			~
• Define terms catalyst, catalysis, homogeneous catalysis and heterogeneous catalysis.			~
• Describe that increase in collision energy by increasing the temperature can improve the collision frequency.		~	
• Describe the role of the rate constant in the theoretical determination of reaction rate.		~	
• Explain the significance of the rate- determining step on the overall rate of a multi-step reaction.	~		
• Explain effects of concentration, temperature and surface area on reaction rates.		~	
• Given a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction.		~	
• Use the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration, size of molecules and.		~	
• Relate the ideas of activation energy and the activated complex to the rate of a reaction.		~	
• Explain what is meant by the terms activation energy and activated complex.			~
• Given the order with respect to each reactant, write the rate law for the reaction.		 ✓ 	
• Explain qualitatively factors affecting rate of reaction.		 ✓ 	
• Explain and use the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step.			~
Define chemical kinetics.			v

SKILLS	Analyzing	Applying	Understanding
• Show energy diagram that represent the activation energy and show the effects of catalyst.			~
• Calculate initial rate by using concentration data.		~	
• Deduce the order of reaction using the method of initial rates.	~		

SOCIETY, TECHNOLOGY AND SCIENCE Students will be able to

- > Describe how enzymes can be effective in removing stains from fabrics. (Applying)
- > Understand that chemistry deals with the transformation of matter.
- •

Related videos



Molecularity vs order

Collision Theory

(THEORITICAL)

Chapter overview

Chemical Kinetics

Chemical kinetics tell us the speed at which chemical species transform into new substances by breaking and reforming their molecular bonds. In other words, it studies the rates and processes of chemical reactions.



The kinetics determines how and how fast you get there, while thermodynamics determines the direction you are going and where you eventually end up.

Reference page/site

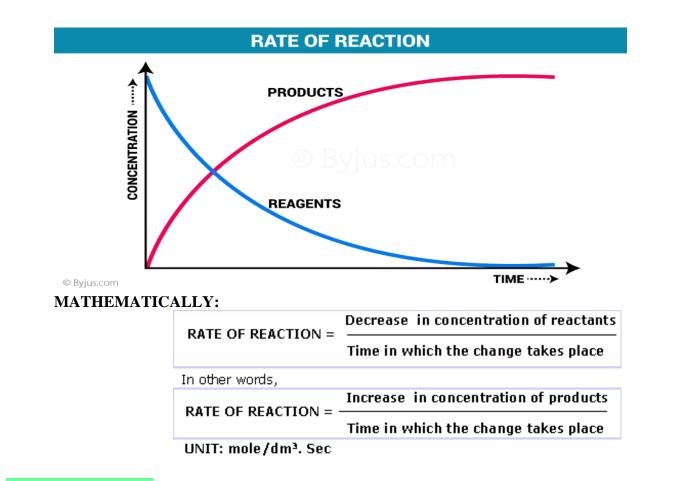
https://www.ansys.com/blog/chemical-kinetics-basics

RATE OF A CHEMICAL REACTION

"It is defined as the quantity of a reactant consumed or the quantity of a product formed in unit time."

In other words:

The conversion of the number of moles of reactants into products in unit time. The rate of reaction is not constant throughout the activity but decreases with time due to decrease in the concentration of reactants.



VELOCITY OF REACTION

Since the rate of reaction is not constant throughout the reaction, therefore, we cannot determine the uniform rate of reaction precisely.

Thus velocity of reaction may be defined as the rate of reaction at a particular given moment i.e. at a specific time.

If we consider a very small interval of time **dt** in which the change in concentration **dx** is taken to be nearly constant, then velocit reaction is given by:

**VELOCITY OF REACTION =
$$\frac{dx}{dt}$$**

Velocity of reaction is actually the instantaneous rate of reaction.

RATE EXPRESSION & RATE CONSTANT

Consider a general reaction:

Reactants -----> Products

According to the law of mass action, rate of reaction is directly proportional to active mass, hence for the above reaction:

Rate of reaction α [Reactants]

Rate of reaction = K[Reactants]-----(i)

This expression is called rate expression and ${f K}$ is called rate constant or velocity constant.

CHARACTERISTICS OF RATE CONSTANT

Sir Rao Muzammil Ali & Ms Naheed Muneer Siddiqui

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- (i) It has a fixed value at a particular temperature.
- (ii) Value of **K** varies with temperature.
- (iii) Value of **K** remains unaltered with the change in concentration of reactants.

ORDER OF REACTION

"The order of reaction is defined as the sum of all the exponents of the reactants involved in the rate equation."

It should be noted down that all the molecules shown in a chemical equation do not determine the value of order of reaction but only those molecules whose concentrations are changed are included in the determination the order of a reaction.

In other words:

"The number of reacting molecules whose concentration alters as a result of chemical reaction is termed as the order of reaction."

For example:

 $2NO + O_2 \longrightarrow 2NO_2$ dx/dt = k[NO]2[O2],

 $dx/dt = \kappa [NO] 2[O2]$, the reaction is of third order as 2 + 1 = 3

For a reaction maximum order is three and the minimum is zero.

FIRST ORDER REACTIONS

The reaction in which only one molecule undergoes a chemical change is called first order reactions. Example:

 $N_2 O_5 = 2NO_2 + \frac{1}{2}O_2$

SECOND ORDER REACTIONS

The reaction in which two molecules undergo a chemical change is called second order reactions. Example:

 $2CH3CHO \longrightarrow 2CH_4 + 2CO$

THIRD ORDER REACTIONS

The reaction in which only three molecules undergo a chemical change is called third order reactions. Example:

 $2NO + O_2$ $2NO_2$

SPECIFIC RATE CONSTANT

Rate constant determined when the concentration of each reactant is unity i.e. one mole/dm³ then **K** is called specific rate constant.

In other words:

Specific rate constant at a given temperature may be defined as the rate of reaction when the molar concentration of each reactant is unity.

MOLECULARITY OF REACTION

The total number of molecules taking part in the rate determining step of a chemical reaction is called "molecularity" of the reaction.

A reaction is unimolecular if only one molecule is involved in its rate-determining step.

A reaction is bimolecular if two molecules take part in its rate-determining step.

For example: $C_2H_5OH \square \square C_2H4 + H_2O$ Is a unimolecular reaction because only one molecule is

involved.

REMEMBER: The molecularity of a reaction can not always be predicted by the chemical equation alone, that every reaction must follow the rules of chemical kinetics.

ENERGY OF ACTIVATION

For a collision to be effective, the sum of energy of colliding molecules must equals or exceeds some minimum value called the activation energy of the reaction. It is the minimum energy needed to convert reactants into products.

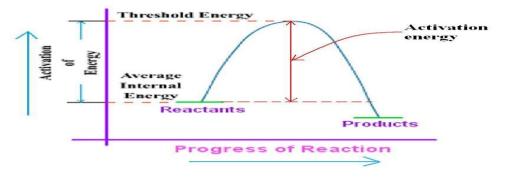
It is denoted by E_a The activation depends upon the nature of the chemical bonds undergoing rupture. Another definition of activation energy is that:

"The minimum energy which the reacting species must posses in order to be able to form an activated complex or transition state before proceeding to the products".

Reactions having higher activation energy are slow while those having high energy of activation proceed with slow speed.

EXPLANATION

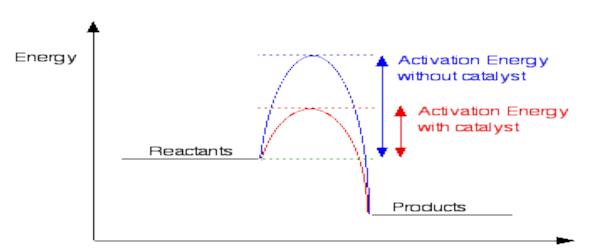
A reaction takes place when molecules of reacting substances collide together. But all the collision are not effective i.e. do not lead to the formation of product. It has been found that only those collisions are effective in which the colliding molecule possess a minimum amount of energy known as threshold energy. Before collision the molecules of reactants in their normal state do possess their respective internal energy, but their average internal energy is less than threshold energy. Now the molecules must acquire the difference of energy, to have effective collision. The excess energy that the reactant molecules, having average energy less than the threshold energy,must acquire in order to react and change into products is called activation energy. The speed of a reaction depends upon the activation energy of molecules.



Activation energy = Threshold energy – Average internal energy

ACTIVATION ENERGY AND RATE OF REACTION

The reactions having low activation energies take place with high speed. The reactions having high activation energies take place with slow speed.



Progress of reaction

ACTIVATION ENERGY AND TEMPERATURE

Reactions having low activation energies take place at low temperature Reactions having high activation energies take place at high temperature

ACTIVATION ENERGY AND CATALYST

The presence of positive catalyst increases the rate of a reaction by decreasing the energy of activation.

Reference page/site

Notes of city colligiate

Factors Affecting the Rate of Reaction

The various factions that can affect the rate of a chemical reaction are listed in this subsection.

Nature of the reaction

- The rate of reaction highly depends on the type and nature of the reaction. As mentioned earlier, few reactions are naturally faster than others while some reactions are very slow.
- The physical state of reactants, number of reactants, complexity of reaction and other factors highly influence the reaction rate as well.
- The rate of reaction is generally slower in liquids when compared to gases and slower in solids when compared to liquids. Size of the reactant also matters a lot. The smaller the size of reactant, the faster the reaction.

Effect of concentration on reaction rate

- According to the <u>collision theory</u>, the rate of reaction increases with the increase in the concentration of the reactants.
- As per the law of mass action, the chemical reaction rate is directly proportional to the concentration of reactants.

- This implies that the chemical reaction rate increases with the increase in concentration and decreases with the decrease in the concentration of reactants.
- Time plays a major role in changing the concentration of reactants and products. Therefore, even time is a vital factor affecting the reaction rate.

Pressure factor

- Pressure increases the concentration of gases which in turn results in the increase of the rate of reaction. The reaction rate increases in the direction of less gaseous molecules and decreases in the reverse direction.
- Thus, it can be understood that pressure and concentration are interlinked and that they both affect the rate of reaction.

How does temperature affect the reaction rate?

- According to collision theory, a chemical reaction that takes place at a higher temperature generates more energy than a reaction at a lower temperature.
- This is because colliding particles will have the required activation energy at high temperature and more successful collisions will take place.
- There are some reactions that are independent of temperature. Reactions without an activation barrier are examples of chemical reactions that are independent of temperature.

Reference page/site

https://byjus.com/chemistry/rate-of-reaction/

Collision Theory

According to the collision theory, *"the molecules of reactants are assumed to be hard spheres and the reactions are assumed to occur only when these spheres (molecules) collide with each other"*. So it was important to quantify the number of collisions occurring in order to form products so that we can have a clear picture of the reaction, and hence came the term collision frequency.

Collision Frequency can be understood as the number of collisions per second per unit volume of the reacting mixture. It is generally denoted by Z.

Let's consider the following bimolecular elementary reaction:

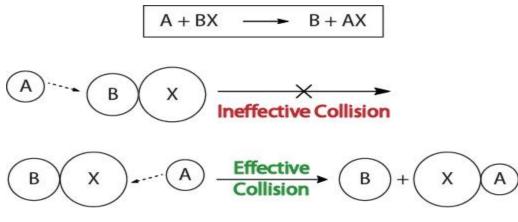
$P + Q \rightarrow Product$

Now as per the collision theory, the rate of the above reaction can be given by:

Rate= ZPQe-EaRT.....(1) Where:

- Z_{PQ} = collision frequency of reactants P and Q
- E_a = Activation Energy
- R = Universal Gas Constant

• T = Temperature in absolute scale



Reference page/site https://byjus.com/chemistry/the-collision-theory-of-chemical-reactions/

Catalyst

In Chemistry, catalysts are defined as those substances which alter the <u>rate of reaction</u> by changing the path of reaction. Most of the time a catalyst is used to speed up or increase the rate of the reaction. However, if we go into a more deeper level, catalysts are used to break or rebuild the chemical bonds between the atoms which are present in the molecules of different elements or compounds. In essence, catalysts encourage molecules to react and make the whole reaction process easier and efficient.

Some of the important characteristic features of catalysts are,

- A catalyst does not initiate a chemical reaction.
- A catalyst does not be consumed in the reaction.
- Catalysts tend to react with reactants to form intermediates and at the same time facilitate the production of the final reaction product. After the whole process, a catalyst can regenerate.

A catalyst can be either solid, liquid or gaseous catalysts. Some of the solid catalysts include metals or their oxides, including sulfides, and halides. Semi-metallic elements such as boron, aluminium, and silicon are also used as catalysts. Likewise, liquid and gaseous elements which are in pure form are used as catalysts. Sometimes, these elements are also used along with suitable solvents or carriers.

The reaction which involves a catalyst in their system are known as catalytic reactions.

Types of Catalysts with Examples

There are several types of catalysts that can be used depending on the need or requirement of the chemical reaction. They are as follows;

Positive Catalysts

Catalysts which increase the rate of a chemical reaction are positive catalysts. It increases the rate of reaction by lowering the activation energy barriers such that a large number of reaction molecules are converted into products, thereby the percentage of yield of products increases.

Example: In the preparation of NH_3 by <u>Haber's process</u> Iron oxide acts as a positive catalyst and increases the yield of ammonia in spite of less reaction of Nitrogen.

Negative Catalysts

Catalysts which decrease the rate of reaction and negative catalyst. It decreases the rate of reaction by increasing the activation energy barrier which decreases the number of reactant molecules to transform into products and hence the rate of reaction decreases.

Example: Decomposition of Hydrogen peroxide into water and oxygen is retarded by using Acetanilide, this acts as a negative catalyst to decrease the rate of decomposition of hydrogen peroxide.

Promoter or Accelerators

A substance which increases the catalyst activity are known as Promoters or accelerators.

Example: In Haber's process molybdenum or a mixture of potassium and Aluminium oxides act as Promoters.

Catalyst Poisons or Inhibitors

Substances which decrease the catalyst activity are known as catalyst poisons or inhibitors.

Example: In the hydrogenation of alkyne to an alkene, catalyst palladium is poisoned with barium sulphate in quinolone solution and the reaction is stopped at alkene level. The catalyst is known as Lindler's catalyst.

Catalysis

When a catalyst is used to increase the rate of a chemical reaction this phenomenon is known as catalysis.

Types of Catalysis

On the basis of nature and the physical state of substance employed in the chemical reaction, catalysis is of three types;

- Homogeneous catalysis
- Heterogeneous catalysis
- Autocatalysis

Types of Catalysis?

On the basis of nature and the physical state of substance employed in the chemical reaction, catalysis is of three types;

- Homogeneous catalysis
- Heterogeneous catalysis
- Autocatalysis

Homogeneous Catalysis

The catalysis in which the catalyst employed in the reaction and the reactants are in the same state of matter, that process is referred to as homogeneous catalysis.

Autocatalysis

In the autocatalytic reaction, there is no specific catalyst that is added. Instead, one of the products acts as a catalyst and increases the rate of formation of products.

Reference page/site https://byjus.com/jee/catalyst/

NUMERICALS

Rate of reaction.

Q)For decomposition of ethyl chlorocarbonate ($ClCO_2C_2H_5$)

 $ClCOOCH_2CH_3$ $CO_2 + ClCH_2CH_3$

 $K = 1.3 \times 10^{-3} \text{ s}^{-1}$ at 200C⁰. What is the initial rate when the initial concentration of ClCOOCH₂CH₃ is 0.25M?

<u>Data</u>

Rate constant(K)	$= 1.3 \text{ x } 10^{-3} \text{ s}^{-1}$
------------------	---

 $[ClCOOCH_2CH_3] = 0.25M$

Rate = ?

Solution:

ClCOOCH₂CH₃ ------

- CO_2 + $ClCH_2CH_3$

Rate = K [ClCOOCH₂CH₃]

Rate = $(1.3 \times 10^{-3}) (0.25)$

Rate =
$$3.25 \times 10^{-4} \text{ Ms}^{-1}$$

Order of Reaction:

Q) Following is given a data for the reaction; **A** + **B** ------ **C**, Find order of reaction.

S. No.	[A]	[B]	Rate
1.	0.1M	0.1M	8 x 10 ⁻⁴ M.s ⁻¹
2.	0.2M	0.1M	16 x 10 ⁻⁴ M.s ⁻¹
3.	0.1M	0.2M	16 x 10 ⁻⁴ M.s ⁻¹

Solution:

A + B ----- C Rate = K [A]^x [B]^y ----- (1) Put the value in above equation (i) $8x10^{-4} = K (0.1)^{x} (0.1)^{y}$ (ii) $16x10^{-4} = K (0.2)^{x} (0.1)^{y}$ (iii) $16x10^{-4} = K (0.1)^{x} (0.2)^{y}$ Divide equation (ii) by (i) $16x10^{-4} = K (0.1)^{x} (0.1)^{y}$ $2 = 2^{x}$ X = 1Divide equation (iii) by (i) $16x10^{-4} = K (0.1)^{x} (0.2)^{y}$ $8x10^{-4} = K (0.1)^{x} (0.2)^{y}$

 $2 = 2^{y}$

```
Y = 1
```

Put the value of 'x' and 'y' into equation (1) Rate = K [A]¹ [B]¹ Order of reation = x + y

= 1 + 1

Order of reaction = 2

Activation Energy.

For a chemical reaction; A \longrightarrow B, the threshold energy of reaction is **31KJ/mol**. The average internal energy of 'A' is **12KJ/mol**. Calculate the activation energy.

Data

Threshold energy = 31KJ/mol Internal energy = 12KJ/mol

Required

Activation energy = (Threshold energy) - (Internal energy of the reactants) AE=TE-IE

Activation energy = 31 - 12 = 19KJ/mol

Reference page

Personal notes

STUDENT"S ASSESMENT

Theoretical

- How can a positive catalyst alter the reaction?
- What is the role of catalyst poison in Rosenmund reaction?
- What are the key factors in heterogeneous catalysis?
- What is the role of promoters in Haber's process?
- What is the significance of autocatalysis?

Numerical

- 1. For a chemical reaction; A \longrightarrow B, the threshold energy of reaction is 40KJ/mol. The average energy of 'A' is 15KJ/mol. Calculate the activation energy.
- 2. Consider the following reaction: CH₃CHO \rightarrow CH₄ + CO

Experimentally this reaction is 2^{nd} order. The rate at a certain temperature is 0.18 mol/dm³.s, when [CH₃CHO] = 0.01 mol/dm³.

- Write rate expression for this reaction.
- Determine the rate constant
- Calculate the rate of reaction when $[CH_3CHO] = 0.02 \text{ mol/dm}^3$.
- **3.** Write the rate expression, find the value of rate constant and determine the order of reaction using the following data:

S. No.	[NO]	[O ₂]	Rate
1.	0.1M	0.1M	2 x 10 ⁻³ M.s ⁻¹
2.	0.2M	0.1M	8 x 10 ⁻³ M.s ⁻¹
3.	0.1M	0.2M	4 x 10 ⁻³ M.s ⁻¹

Practical # 05

- Show that the addition of catalyst effect the rate of reaction.
- Explore the effect of temperature and concentration on the rate of fading of methylene blue.
- Determine the rate of reaction and determination of density of blood sample.

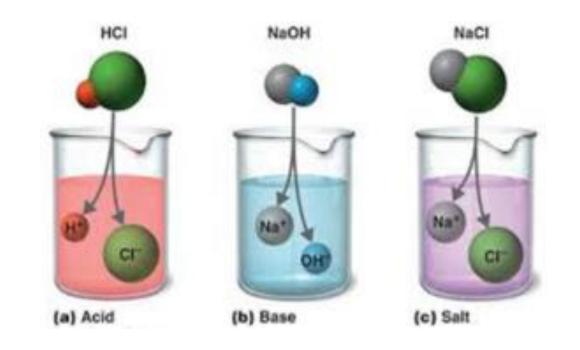
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X-----X

CHAPTER 8

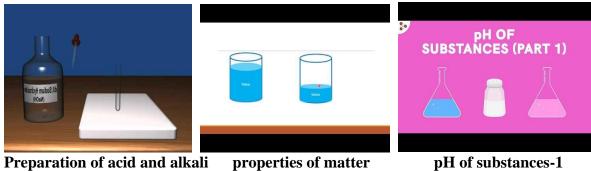
"ACIDS, BASES & SALTS"

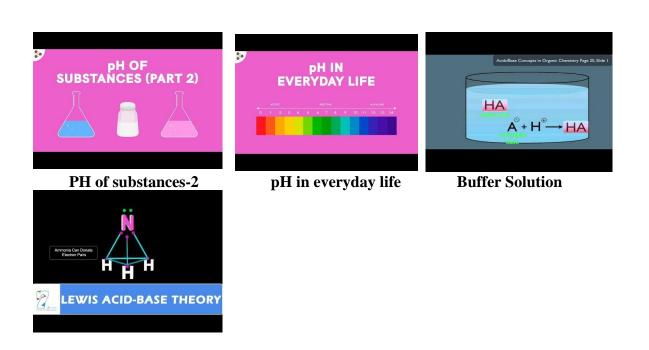


LEARNING OUTCOMES

Chapter content	Understand	Skills
 ACIDS , BASES & SALTS Acidic , Basic & Amphoteric substance. Bronsted-lowery definitions of acids & bases. Proton donors & Acceptor. Relative strength of acid and base. Conjugate acid-base pair. Expressing the strength of acid base & salt. Ionization equation of water. pH , pOH & pKw Acid ionization constant Ka & pKa. 	 Define Bronsted and Lowery concepts for acids and bases Define salts, conjugate acids and conjugate bases. Identify conjugate acid-base pairs of Bronsted-Lowery acid and base. Explain ionization constant of water and calculate pH and pOH in aqueous medium using given Kw values. 	 Calculate the fourth parameter when given three of four parameters— molarity of base, volume of base, molality of acid, volume of acid — used in a titration experiment, assuming a strong acid and strong base reaction. Calculate the [H301, given the Ka and molar concentration of weak acid. Calculate concentrations of ions of slightly soluble salts.
 Base ionization constant K_b & pK_b Leveling effect Relationship K_a & K_b Lewis definition of acid and base. Buffer solutions and their application. Salt hydrolysis. 	• Use the extent of ionization and the acid dissociation constant, Ka, to distinguish between strong and weak acids.	 Calculate Ka for the system, given the equilibrium concentrations of a weak acid and the [H301 in the solution. Perform acid-base titrations to calculate molality and strength of given sample solutions.

Related videos





Chapter overview.

"Theory"

Acid

Acid, any substance that in <u>water solution</u> tastes sour, changes the colour of certain indicators (e.g., reddens blue <u>litmus</u> paper), reacts with some <u>metals</u> (e.g., <u>iron</u>) to liberate <u>hydrogen</u>, reacts with <u>bases</u> to form <u>salts</u>, and promotes certain <u>chemical reactions</u> (acid catalysis).



Reference page/site https://www.britannica.com/science/base

Base

Base, in <u>chemistry</u>, any substance that in <u>water</u> solution is slippery to the touch, tastes bitter, changes the colour of indicators (*e.g.*, turns red litmus paper blue), reacts with <u>acids</u> to form salts, and promotes certain chemical reactions (base catalysis)



Reference page/site https://www.britannica.com/science/acid

Amphoteric

An amphoteric compound is one that can react with both acids and bases.

Reference page/site

https://www.chemicool.com/definition/amphoteric.html

Bronsted-Lowry Theory of Acid and Base

According to Bronsted-Lowry theory, acid is a substance which donates an H^+ ion or a proton and forms its conjugate base and the base is a substance which accepts an H^+ ion or a proton and forms its conjugate acid.

Bronsted-Lowry Acid

The Bronsted-Lowry acid is a substance which donates a proton or H⁺ ion to the other compound.

```
Acid \rightleftharpoons Proton + Conjugate base
```

A conjugate base can accept a proton and acid reforms.

$$HA(aq) \rightleftharpoons A^{-}(aq) + H^{+}(aq)$$

Bronsted-Lowry Base

The Bronsted-Lowry base is a substance which accepts a proton or H+ ion from other compounds.

```
Base + Proton \rightleftharpoons Conjugate acid
```

A conjugated acid can donate a proton and base reforms.

$B(aq) + H2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$

The Bronsted-Lowry theory of an acid-base reaction involves the transfer of protons or H^+ ions between the acid and base.

Note:

• Strong Bronsted-Lowry acids are those which have a strong tendency to give a proton and their corresponding conjugate base is weak.

• Weak Bronsted-Lowry acids will have a little tendency to donate a proton and their corresponding conjugated base is strong.

Reference page/site

https://byjus.com/jee/bronsted-lowry-theory/

conjugate acid-base pair.

Whenever an **acid** donates a proton, the **acid** changes into a **base**, and whenever a **base** accepts a proton, an **acid** is formed. An **acid** and a **base** which differ only by the presence or absence of a proton are called a **conjugate acid-base pair**.

Expressing the strength of acid and base. For Acid.

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a . For the reaction of an acid HA:

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

we write the equation for the ionization constant as:

$$K_{\rm a} = \frac{[{\rm H}_{3}{\rm O}^{+}][{\rm A}^{-}]}{[{
m H}{\rm A}]}$$

Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

% ionization =
$$\frac{[\mathrm{H}_3\mathrm{O}^+]_{\mathrm{eq}}}{[\mathrm{HA}]_0} \times 100$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

For Base

we can measure the relative strengths of bases by measuring their **base-ionization constant** (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

we write the equation for the ionization constant as:

				$K_{\rm b} =$	[HB ⁺][OH [B]	[]		
				Relative ac	d strength			
Stronger acids	H³O+	HCIO ₂	HF	H₂CO₃	сн _з соон	${\rm NH_4}^+$	HPO4 ²⁻	H ₂ O Weaker acids
K _a	1.0	10 ⁻²	10 ⁻⁴	10 ⁻⁶	10 ⁻⁸	10 ⁻¹⁰	10 ⁻¹²	10-14
			Rela	tive conjuga	ate base strenç	jth		
Weaker bases	H ₂ O	CIO ₂ ⁻	F	HCO ₃ ⁻	СН ₃ СОО⁻	NH ₃	PO ₄ ³⁻	OH ⁻ Stronger bases
K _b 1	10 ⁻¹⁴	10 ⁻¹²	10 ⁻¹⁰	10 ⁻⁸	10 ⁻⁶	10 ⁻⁴	10 ⁻²	1.0
		hows the re	elative stro	engths of c	<u>conjugate ac</u>	id-base p	airs, as indi	cated by their

ionization constants in aqueous solution.

	Acid			Base			
	perchloric acid sulfuric acid hydrogen iodide hydrogen bromide hydrogen chloride nitric acid hydronium ion hydrogen sulfate ion phosphoric acid	$HCIO_4$ H_2SO_4 HI HBr HCI HNO_3 H_3O^+ HSO_4^- H_3PO_4	Undergo complete acid ionization in water	Do not undergo base ionization in water	CIO_{4}^{-} HSO_{4}^{-} I^{-} Br^{-} CI^{-} NO_{3}^{-} $H_{2}O$ SO_{4}^{2-} $H_{2}PO_{4}^{-}$	perchlorate ion hydrogen sulfate ion iodide ion bromide ion chloride ion nitrate ion water sulfate ion dihydrogen phosphate ion	
ווומרמסוווץ מכום סורבוואמו	hydrogen fluoride nitrous acid acetic acid carbonic acid hydrogen sulfide ammonium ion hydrogen cyanide hydrogen carbonate ion	HF HNO_{2} $CH_{3}CO_{2}F$ $H_{2}CO_{3}$ $H_{2}S$ NH_{4}^{+} HCN HCO_{3}^{-}	1		F^{-} NO_{2}^{-} $CH_{3}CO_{2}^{-}$ HCO_{3}^{-} HS^{-} HN_{3} CN^{-} CO_{3}^{2-}	fluoride ion nitrite ion acetate ion hydrogen carbonate ion hydrogen sulfide ion ammonia cyanide ion carbonate ion	
	water hydrogen sulfide ion ethanol ammonia hydrogen methane	H_2O HS^- C_2H_5OH NH_3 H_2 CH_4	Do not undergo acid ionization in water	Undergo complete base ionization in water	OH^{-} S^{2-} $C_{2}H_{5}O^{-}$ NH_{2}^{-} H^{-} CH_{3}^{-}	hydroxide ion sulfide ion ethoxide ion amide ion hydride ion methide ion	

The chart shows the relative strengths of conjugate acid-base pairs.

Reference page/site

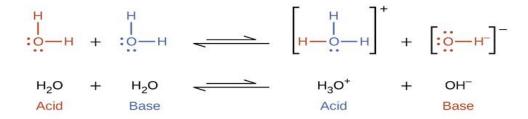
https://opentextbc.ca/chemistry/chapter/14-3-relative-strengths-of-acids-and-bases/

The Ion-Product Constant of Pure Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an auto ionization process:

$$2 H_2 O(l) \rightleftharpoons H_3 O^+(aq) + OH^-(aq)$$

In pure water, a very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **auto ionization**. The equilibrium constant K for this reaction can be written as follows:

$$K = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{OH}^{-}]}{[\mathrm{H}_{2}\mathrm{O}]^{2}}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[{\rm H_3O^+}] = [{\rm OH^-}] = 1.003 \times 10^{-7} \; M$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate [H2O] at 25°C from the density of water at this temperature (0.997 g/mL):

$$[H_2O] = mol/L = (0.997 \text{ g/mL}) \left(\frac{1 \text{ mol}}{18.02 \text{ g/}}\right) \left(\frac{1000 \text{ prL}}{L}\right) = 55.3 \text{ M}$$

With so few water molecules dissociated the equilibrium of the auto ionization reaction lies far to the left. Consequently concentration of water essentially unchanged by the auto ionization reaction & can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to arrange the equation to define a new equilibrium constant the ion-product constant of liquid water (K_w).

$$K = rac{K_w}{[\mathrm{H_2O}]^2}$$

 $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}][\mathrm{OH^-}]$

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25°C into this expression

$$K_w = (1.003 imes 10^{-7})(1.003 imes 10^{-7}) = 1.006 imes 10^{-14}$$

Reference page/site

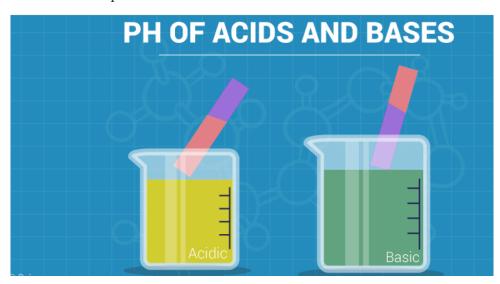
https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/ 16%3A_Acids_and_Bases/16.3%3A_Self-Ionization_of_Water_and_the_pH_Scale

рΗ

pH is defined as the negative logarithm of H^+ ion concentration. Hence the meaning of the name pH is justified as the power of hydrogen.

pH Chemistry

A pH scale is a tool for measuring acids and bases. The scale ranges from 0-14: Litmus paper is an indicator used to tell if a substance is an acid or a base. The color of the paper matches up with the numbers on the pH scale to indicate what kind of substance is being tested. For example, Vinegar is an acid and measures 2.4 on the pH scale.



pH of Acids and Bases - Red Litmus Test

pH of Acids and Bases

The pH of a solution varies from 0 to 14.

- Solutions having a value of pH ranging 0 to 7 on pH scale are termed as *acidic* and for the value of pH ranging 7 to 14 on pH scale are known as *basic* solutions.
- Solutions having the value of pH equal to 7 on <u>pH scale</u> are known as neutral solutions.

Solutions having the value of pH equal to 0 are known to be *strongly acidic solutions*. Further, the acidity decreases as the value of pH increases from 0 to 7 whereas, solutions with the value of pH equal to 14 are termed as *strongly basic solutions*.

The basicity decreases as the value of pH decreases from 14 to 7. The strength of <u>acids and</u> <u>bases</u> depends on the number of H^+ and OH^- ions produced. Acids furnishing more number of H^+ ions are known to be strong acids and vice versa.

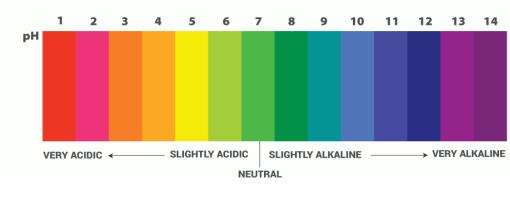
The degree of ionisation of acids and bases differ for different acids and bases. It helps in the determination of the strength of acids and bases. The strength of an acid depends on the concentration of hydronium ion (H_3O^+) too. With the help of the comparison between the concentration of hydronium ion and the hydroxyl ion, we can distinguish between acids and bases.

- For acidic solution: $[H_3O^+] > [OH^-]$
- For neutral solution: $[H_3O^+] = [OH^-]$
- *For basic solution:* [*H*₃*O*⁺] < [*OH*⁻]

Limitations of pH Scale

pH value of a solution does not instantaneously give us an idea of the relative strength of the solution.

- pH is zero for 1N solution of strong acid.
- pH is negative for concentrations 2N, 3N, ION of strong acids.
- At higher concentrations, in place of pH Hammett acidity functions are used.



pH Scale

pH Scale

The concentration of hydronium ion is conveniently expressed on a logarithmic scale. This scale is known as **pH scale**. <u>pH of acids and bases</u> is defined as the negative logarithm (with base 10) of activity of hydrogen ion (H^+).

Recommended Videos

1,40,950

How to Calculate pH?

The activity has no units and is defined in terms of H⁺ ion concentration,

 $aH+ = [H^+]/mol L^{-1}$ Hence, the pH of a compound is given as,

pH = -log aH +

Example

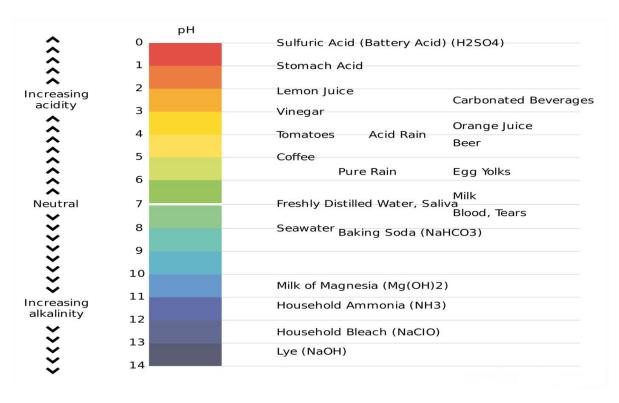
Thus, the pH of an acidic solution of $HNO_3 (10^{-3} \text{ M}) = 3$, a basic solution of KOH having $[OH^-] = 10^{-4} \text{M}$ and $[H_3O^+] = 10^{-10} \text{ M}$ will have a pH = 10. pH of acids is generally less than 7 whereas for bases it is greater than 7. At 298 K, ionic product of water, K_w can be given as:

 $K_w = [H_3O^+][OH^-] = 10^{-14}$

Taking the negative logarithm of RHS and LHS, we deduce

$$\begin{aligned} -\log K_w &= -\log ([H_3O^+] [OH^-]) = -\log 10^{-14} \\ &= >pK_w = -\log [H_3O^+] - \log [OH^-] = 14 \\ &= >pK_w = pH + pOH = 14 \end{aligned}$$

The value of pK_w controls the relative concentrations of hydrogen and hydroxyl ions as their product is always constant. pH of acids and bases can be roughly calculated with the help of pH scale while for accurate values we use pH meters.



pH Example Chart

pH Value and Nature of a Solution

- If [H+] > 10-7, pH is less than 7 and the solution is acidic.
- If [H+] = 10-7, pH is 7 and the solution is neutral.
- If [H+] < 10-7, pH is more than 7 and the solution is basic.

Importance of pH

- Only a narrow range of pH change can be sustained by a living organism, any further change in pH can make the living difficult. For example: in the case of <u>acid rain</u>, the pH of water is less than 7. As it flows into a river, it lowers the pH of river water which makes the survival of aquatic life difficult.
- We know that our stomach contains hydrochloric acid which helps in the digestion of food. When the stomach produces too much of hydrochloric acid during indigestion, we feel a lot of pain and irritation. Hence, we generally use antacids or a mild base which increases the pH of the acidic stomach and thus decreases the pain.
- Bacteria present in our mouth sometimes lower the pH of our mouth by producing acids through degradation of the food particle. Hence, we are instructed to clean our mouths with toothpaste (which are generally basic) to prevent their decay by maintaining the pH.

• We experience a lot of pain in case of bee-sting as the bee injects the methanoic acid through its sting. Hence, we are generally advised to apply <u>baking soda</u> or other mild bases on the surface as it helps in maintaining the pH of the surface.

Points to Remember on pH Scale

- pH of strong acid or base does not depend upon temperature.
- pH of weak acid decreases with increase in temperature due to increase in ionization.
- pH of weak base increases with increase in temperature due to increase in ionization or [OH-] ion concentration

Reference page/site

https://byjus.com/chemistry/ph-of-acids-and-bases/

The pOH Concept

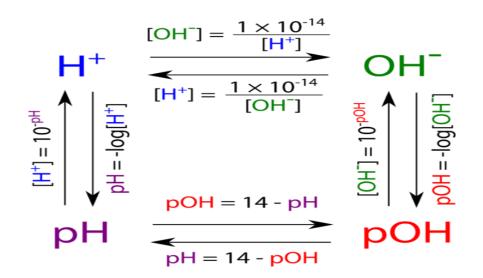
As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$pOH = -log[OH^{-}]$

The pH of a solution can be related to the pOH. Consider a solution with a pH = 4.0. The [H⁺] of the solution would be 1.0×10^{-4} M. Dividing K_w by this yields a [OH⁻] of 1.0×10^{-10} M. Finally the pOH of the solution equals $-\log (1.0 \times 10^{-10}) = 10$. This example illustrates the following relationship.

pH + pOH = 14

The pOH scale is similar to the pH scale in that a pOH of 7 is indicative of a neutral solution. A basic solution has a pOH of less than 7, while an acidic solution has a pOH of greater than 7. The pOH is convenient to use when finding the hydroxide ion concentration from a solution with a known pH.



Reference page/site

https://courses.lumenlearning.com/cheminter/chapter/the-poh-concept/

<u>Relationship between K_a & K_b</u>

As we known that Ka is directly proportional to the H^+ concentration and K_b is directly proportional to the OH^- concentration. As we know that H^+ and OH are related to each other too, so there must be some relation between Ka and K_b .

To find out their relation we have to study a reaction in which we can get both Ka and K_b , so that we can compare them with each other. And such a reaction can be provided by Brönsted acid base pair, so let's take an example of Brönsted acid base pair:

$$NH_{3(aq)} + H_2O_{(1)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$$

In this reaction NH_3 acts as base and it's conjugate acid is NH_4^+ . If we consider forward reaction, we can get the equation for K_b :

$$NH_{3(aq)} + H_2O_{(l)} \longrightarrow NH_4^+(aq) + OH^-(aq) \qquad -----(1)$$
$$K_b = [NH_4^+] [OH^-] / [NH_3]$$

If we write a reaction for dissociation of acid NH₄⁺, we can get the following equation for Ka :

$$NH_{4}^{+}{}_{(aq)} + H_{2}O_{(1)} \longrightarrow H_{3}O_{(aq)}^{+} + NH_{3(aq)} \qquad -----(2)$$
$$K_{a} = [H_{3}O^{+}] [NH_{3}] / [NH_{4}^{+}]$$

If we add equation 1 and 2, we will get a new equation:

$$2H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

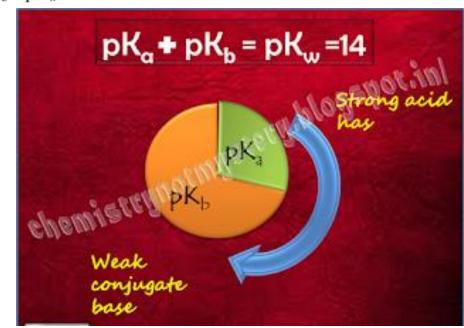
This is the dissociation reaction of water we have studied before and we know that:

$$K_w = [H_3O^+][OH^-]$$

Now you can see that if we multiply K_a and K_b we will get K_w

$$\begin{split} K_a \times K_b &= \{ [H_3O^+] [NH_3] / [NH_4^+] \} \{ [NH_4^+] [OH^-] / [NH_3] \} \\ K_a \times K_b &= [H_3O^+] [NH_3] [NH_4^+] [OH^-] / [NH_4^+] [NH_3] \\ K_a \times K_b &= K_w \end{split}$$

If we take (-log) of both sides, we will get:

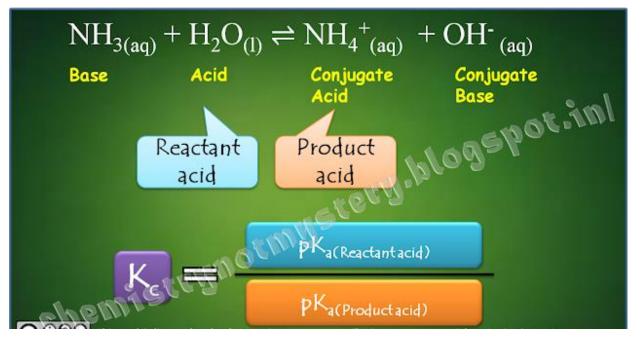


 $pK_a + pK_b = pK_w = 14$

A very important conclusion can be drawn from the above equation. If pK_a of an acid is lower then its conjugate base must have higher pK_b and vise versa, which means strong acid has a weak conjugate base.

We know that smaller the pK_a , the stronger the acid. Very strong acids have pK_a less than 1, moderately strong acids have pK_a in between 1 to 5 and weak acids have pK_a in between 5 to 14.

Always remember that there is an important difference between pH and pK_a, we use pH scale to measure the acidity and pK_avalue indicates the strength of an acid. The pH is the characteristic of a solution, it means we can get solutions of different pH by dissolving the same acid in different quantities, like 1×10^{-2} M solution of HCl has pH 2 and 1×10^{-4} M solution of HCl has pH 4(HCl is a strong acid which dissociates completely i.e. its α is 1). On the other hand, pK_a is the characteristic of the particular compound, for example, pK_a of HCl is -7, HF is 3.5×10^{-4} and pK_a of HCN is 4.9×10^{-10} . It tells us how readily the compound gives up a proton H⁺. By pK_a value you can also calculate the K_c



 $NH_{3(aq)} + H_{2}O_{(1)} \rightleftharpoons NH_{4}^{+}(aq) + OH^{-}(aq)$ $K_{c} = [NH_{4}^{+}][OH^{-}]/[NH_{3}][H_{2}O]$ -----(3)

If we write equation for reactant acid H₂O:

$$\begin{split} &H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)} \\ &K_{a \, (Reactant \, acid)} = [H^+][OH^-]/[H_2O] & -----(4) \end{split}$$

If we write equation for product acid ${\rm NH_4}^+$

$$\begin{split} \mathrm{NH_4^+}_{(\mathrm{aq})} &+ \mathrm{H_2O}_{(\mathrm{l})} \longrightarrow \mathrm{H^+}_{(\mathrm{aq})} + \mathrm{NH_3(\mathrm{aq})} \\ \mathrm{K_a} \left(\mathrm{Product} \ \mathrm{acid} \right) &= [\mathrm{H^+}] \left[\mathrm{NH_3} \right] / \left[\mathrm{NH_4^+} \right] & -----(5) \end{split}$$

When we compare equation 3, 4 and 5, we can infer that: $K_c = K_a$ (Reactant acid) / K_a (Product acid)

Now you are able to measure the strength of an acid, but what are the factors which make an acid strong or weak? Is it something which is hidden in its structure? In the next post we will try to reveal its secret.

Reference page/site.

https://www.chemistrynotmystery.com/2015/02/relation-between-ka-and-kb.html

Leveling effect

Leveling effect or solvent **leveling** refers to the **effect** of solvent on the properties of acids and bases. The strength of a strong acid is limited ("**leveled**") by the basicity of the solvent. Similarly the strength of a strong base is **leveled** by the acidity of the solvent.

Acids stronger than H₃O⁺ cannot be used in water. For example, water would react with sulfuric acid producing H₃O⁺. Virtually no sulfuric acid will remain if we wanted it to be available to react with another reagent

Lewis Acid

Lewis Acids are the chemical species which have empty orbitals and are able to accept electron pairs from Lewis bases. This term was classically used to describe chemical species with a trigonal planar structure and an empty p-orbital. An example of such a Lewis acid would be BR_3 (where R can be a halide or an organic substituent).

Water and some other compounds are considered as both Lewis acids and bases since they can accept and donate electron pairs based on the reaction.

Examples of Lewis Acids

Some common examples of Lewis acids which can accept electron pairs include:

- H^+ ions (or <u>protons</u>) can be considered as Lewis acids along with onium ions like H_3O^+ .
- The cations of d block elements which display high oxidation states can act as electron pair acceptors. An example of such a cation is Fe³⁺.
- Cations of metals such as Mg²⁺ and Li⁺ can form coordination compounds with water acting as the ligand. These aquo complexes can accept electron pairs and behave as Lewis acids.
- Carbocations given by H_3C^+ and other trigonal planar species tend to accept electron pairs.
- The Pent halides of the following group 15 elements can act as Lewis acids Antimony, Arsenic, and Phosphorus.

Apart from these chemical compounds listed above, any electron-deficient π system can act as an acceptor of electron pairs – exons, for example.

Lewis Base

Atomic or molecular chemical species having a highly localized HOMO (Highest Occupied Molecular Orbital) act as Lewis bases. These chemical species have the ability to donate an electron pair to a given Lewis acid in order to form an adduct, as discussed earlier.

The most common Lewis bases are <u>ammonia</u>, alkyl amines, and other conventional amines. Commonly, Lewis bases are anionic in nature and their base strength generally depends on the pK_a of the corresponding parent acid. Since Lewis bases are electron-rich species that have the ability to donate electron-pairs, they can be classified as nucleophiles. Similarly, Lewis acids can be classified as electrophiles (since they behave as electron-pair acceptors).

Examples of Lewis Bases

Examples of Lewis bases which have an ability to donate an electron pair are listed below.

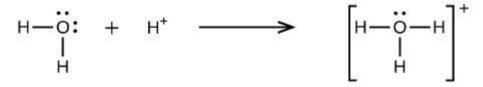
- Pyridine and the derivatives of pyridine have the ability to act as electron pair donors. Thus, these compounds can be classified as Lewis bases.
- The compounds in which Oxygen, Sulfur, Selenium, and Tellurium (which belong to group 16 of the Periodic Table) exhibit an oxidation state of -2 are generally Lewis bases. Examples of such compounds include water and ketones.
- The simple anions which have an electron pair can also act as Lewis bases by donating these electrons. Examples of such anions include H⁻ and F⁻. Even some complex anions, such as the sulfate anion (SO₄²) can donate pairs of electrons.
- The π -systems which are rich in electrons (such as benzene, ethyne, and ethene) exhibit great electron pair donating capabilities.

Weak Lewis acids have strong conjugate Lewis bases. Apart from this, many chemical species having a lone pair of electrons such as CH₃⁻ and OH⁻ are identified as Lewis bases due to their electron pair donating capabilities.

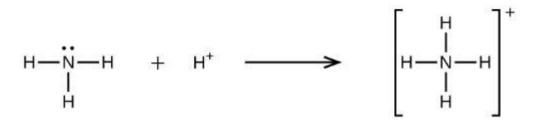
Chemical Reactions Between Lewis Acids and Bases

Reactions with the H+ ion

The H⁺ ion acts as a Lewis acid and H₂O acts as a Lewis base. The reaction between the water molecule and the proton yields a hydronium ion (H₃O⁺), as illustrated below.



Here, the oxygen atom donates an electron pair to the proton, forming a coordinate covalent bond in the process. The resulting Lewis acid has a +1 charge associated with it. Another example of a reaction in which the H⁺ ion acts as a Lewis acid is its reaction with ammonia (NH₃) to form an ammonium ion (NH₄⁺).



In this reaction, the proton receives an electron pair from the nitrogen atom (belonging to the ammonia molecule). The formation of a coordinate covalent bond between the two results in the formation of a Lewis adduct (the ammonium cation).

Reaction between Ag+ and Ammonia

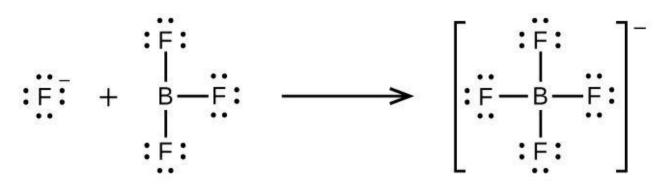
In this reaction, two Lewis bases form an adduct with one Lewis acid, as illustrated below.



Here, ammonia acts as a Lewis base and the silver ion acts as a Lewis acid. Each nitrogen atom donates an electron pair to Ag^+ , resulting in two separate coordinate covalent bonds. The adduct formed from the Lewis acid and base has the chemical formula $Ag(NH_3)_2^+$.

Reaction between the Fluoride Ion and Boron Trifluoride

This reaction features the formation of a coordinate bond between the fluoride anion (F-) and boron trifluoride (BF₃).



Here, F- acts as an electron pair donor whereas BF_3 accepts the electron pair. The reaction between the Lewis acid and base results in the formation of an adduct with the chemical formula BF_4 -.

Applications of Lewis Acids and Bases

Some important applications of Lewis acids and bases are provided below.

Lewis acids play a vital role as a catalyst in the <u>Friedel-Crafts reaction</u> – AlCl₃ accepts a lone pair of electrons belonging to the chloride ion leading to the formation of AlCl₄⁻ in the Friedel-Crafts alkylation process.

This also leads to the formation of the highly electrophilic carbonium ion which acts as a strong Lewis Acid. The chemical reaction can be written as follows.

$\mathbf{RCl} + \mathbf{AlCl}_3 \longrightarrow \mathbf{R}^{\scriptscriptstyle +} + \mathbf{AlCl}_{4^{\scriptscriptstyle -}}$

In the field of organic chemistry, Lewis acids are widely used to encourage many cationic or pseudo-cationic chemical reactions.

Lewis bases have immense applications in the modification of the selectivity and the activity of metallic catalysts. For the production of pharmaceuticals, asymmetric <u>catalysis</u> is an important part of enantioselective synthesis. In order to enable asymmetric catalysis, chiral Lewis bases are often used to confer chirality on catalysts.

Several Lewis bases have the ability to form many bonds with Lewis acids. These compounds are also called 'multidentate Lewis bases' or 'chelating agents' and have a wide range of industrial and agricultural applications.

Reference page/site

https://byjus.com/chemistry/lewis-acids-and-bases/

Buffer Solutions

Buffers are solutions that resist a change in pH on dilution or on addition of small amounts of <u>acids</u> or alkali. Solutions of a <u>weak acid</u> and its conjugate base or weak base and its conjugate acid are able to maintain pH and are buffer solutions.

Types of Buffer Solution

The two primary types into which buffer solutions are broadly classified into are acidic and alkaline buffers.

Acidic Buffers

As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong base. An aqueous solution of an equal concentration of <u>acetic acid</u> and sodium acetate has a pH of 4.74.

- pH of these solutions is below seven
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

Alkaline Buffers

These buffer solutions are used to maintain basic conditions. Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with strong acid. The aqueous solution of an equal concentration of ammonium hydroxide and <u>ammonium chloride</u> has a pH of 9.25.

- The pH of these solutions is above seven
- They contain a weak base and a salt of the weak base.
- An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

Mechanism of Buffering Action

In solution, the salt is completely ionized and the weak acid is partly ionized.

- $CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$
- $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

On Addition of Acid and Base

1. On addition of acid, the released protons of acid will be removed by the acetate ions to form an acetic acid molecule.

 $H^+ + CH_3COO^-$ (from added acid) $\rightleftharpoons CH_3COOH$ (from buffer solution)

2. On addition of the base, the hydroxide released by the base will be removed by the hydrogen ions to form water.

 $HO^- + H^+$ (from added base) $\rightleftharpoons H_2O$ (from buffer solution)

Preparation of Buffer Solution

If the dissociation constant of the acid (pK_a) and of the base (pK_b) are known, a buffer solution can be prepared by controlling the salt-acid or the salt-base ratio.

As discussed earlier, these solutions are prepared by mixing of weak bases with their corresponding conjugate acids, or by mixing weak acids with their corresponding conjugate bases.

An example of this method of preparing buffer solutions can be given by the preparation of a <u>phosphate</u> buffer by mixing HPO_{4^2} and H_2PO^4 . The pH maintained by this solution is 7.4.

Handerson-Hasselbalch Equation

Preparation of Acid Buffer

Consider an acid buffer solution, containing a weak acid (HA) and its salt (KA) with a strong base(KOH). Weak acid HA ionizes, and the equilibrium can be written as-

 $HA + H_2O \leftrightarrows H^{\scriptscriptstyle +} + A^{\scriptscriptstyle -}$

Acid dissociation constant = $Ka = [H^+] [A^-]/HA$

Taking, negative log of RHS and LHS:

$$-\log Ka = -\log [H+] - \log \left(\frac{[A^-]}{[HA]}\right)$$

$$pKa = pH - \log \left(\frac{[salt]}{[acid]}\right)$$

pH of acid buffer = pKa + ([salt]/[acid])

The equation is the <u>Henderson-Hasselbalch equation</u>, popularly known as the Henderson equation.

Preparation of Base Buffer

Consider base buffer solution, containing a weak base (B) and its salt (BA) with strong acid.

pOH, can be derived as above,

- pOH of a basic buffer = pKb + log ([salt]/[acid])
- pH of a basic buffer = pKa log ([salt]/[acid])

Significance of Handerson Equation

Handerson Equation can be used to:

- 1. Calculate the pH of the buffer prepared from a mixture of the salt and weak acid/base.
- 2. Calculate the pKa value.
- 3. Prepare buffer solution of needed pH.

Limitations of Henderson-Hasselbalch Equation

The Henderson - Hasselbalch equation cannot be used for strong acids and strong bases.

Buffering Capacity

The <u>number of mili moles</u> of acid or base to be added to a litre of buffer solution to change the pH by one unit is the Buffer capacity of the buffer.

 $B = millimoles /(\Delta pH)$

pH Maintenance

In order to understand how buffer solutions maintain a constant pH, let us consider the example of a buffer solution containing sodium acetate and acetic acid.

In this example, it can be noted that the sodium acetate almost completely undergoes ionization whereas the <u>acetic</u> <u>acid</u> is only weakly ionized. These equilibrium reactions can be written as:

- $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
- $CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$

When strong acids are added, the H^+ ions combine with the CH_3COO^- ions to give a weakly ionized acetic acid, resulting in a negligible change in the pH of the environment.

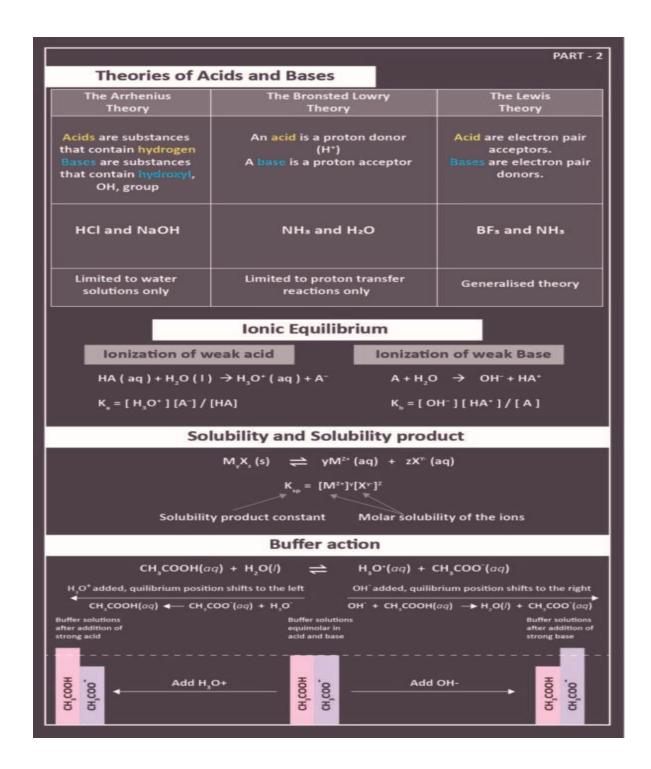
When strongly <u>alkaline</u> substances are introduced to this buffer solution, the hydroxide ions react with the acids which are free in the solution to yield water molecules as shown in the reaction given below.

 $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

Therefore, the hydroxide ions react with the acid to form water and the pH remains the same.

Uses of Buffer Solutions

- There exists a few alternate names that are used to refer buffer solutions, such as pH buffers or hydrogen ion buffers.
- An example of the use of buffers in pH regulation is the use of bicarbonate and carbonic acid buffer system in order to regulate the pH of animal blood.
- Buffer solutions are also used to maintain an optimum pH for enzyme activity in many organisms.
- The absence of these buffers may lead to the slowing of the enzyme action, loss in <u>enzyme properties</u>, or even denature of the enzymes. This denaturation process can even permanently deactivate the catalytic action of the enzymes.



<u>Reference page/site</u>

https://www.toppr.com/guides/chemistry/equilibrium/buffer-solutions/ https://byjus.com/jee/buffer-solutions/

Hydrolysis of Salts: Equations

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions would always be neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$\begin{aligned} \mathrm{HF}(aq) + \mathrm{NaOH}(aq) &\to \mathrm{NaF}(aq) + \mathrm{H_2O}(l) \\ \mathrm{HF}(aq) + \mathrm{OH^-}(aq) &\to \mathrm{F^-}(aq) + \mathrm{H_2O}(l) \end{aligned}$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting, to a small extent, with water, accepting a proton.

$$F^{-}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{-}(aq)$$

The fluoride ion is acting as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved into water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolyzing, but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ion.

$$F^{-}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{-}(aq)$$

Salts that are derived from the neutralization of a weak acid (HF) by a strong base (NaOH) will always produce salt solutions that are basic.

Salts That Form Acidic Solutions

Ammonium chloride (NH $_4$ Cl) is a salt that is formed when the strong acid HCl is neutralized by the weak base NH $_3$. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolyzing because it is the conjugate base of the strong acid HCl. In other words, the Cl - ion cannot accept a proton from water to form HCl and OH -, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid.

$$\mathrm{NH}_{4}^{+}(aq) + \mathrm{H}_{2}\mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{NH}_{3}(aq)$$

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of HCl by NaOH. A solution of NaCl in water has no acidic or basic properties, since neither ion is capable of hydrolyzing. Other salts that form neutral solutions include potassium nitrate (KNO ₃) and lithium bromide (LiBr). The **Table** below summarizes how to determine the acidity or basicity of a salt solution.

Salts formed from	Salt solution
Strong acid + Strong base	Neutral
Strong acid + Weak Base	Acidic
Weak acid + strong base	Basic

Reference page

<u>https://courses.lumenlearning.com/cheminter/chapter/hydrolysis-of-salts-</u> equations/#:~:text=Salt%20hydrolysis%20is%20a%20reaction,an%20acidic%20or%20basic%20solution.

(NUMERICALS)

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3} M$?

Show Answer

 $pH = -log[H_3O^+] = -log(1.2 \times 10^{-3}) = -(-2.92) = 2.92$

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Show Answer

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125 M$: $pOH = -log[OH^-] = -log 0.0125$ = -(-1.903) = 1.903

The pH can be found from the pOH:

pH + pOH = 14.00

pH = 14.00 - pOH = 14.00 - 1.903 = 12.10

calculate the pH of a buffer solution containing 0.100 mol dm⁻³ of ammonia and 0.0500 mol dm⁻³ of ammonium chloride.

Just put all these numbers in the K_a expression, and do the sum:

$$K_{a} = \frac{[NH_{3}][H^{+}]}{[NH_{4}^{+}]}$$
5.62 x 10⁻¹⁰ = $\frac{0.100 \times [H^{+}]}{0.0500}$

$$[H^{+}] = \frac{0.0500}{0.100} \times 5.62 \times 10^{-10}$$
= 2.81 x 10⁻¹⁰
pH = $-\log_{10}[H^{+}]$
= 9.55

Practical # 06

- Determine the molarity and solubility of given solution in given volume.
- Determine the concentration of hemoglobin in human blood.
- Determine the amount of acid in different fruits.

Related videos

https://youtu.be/1eePYyq2a6U https://youtu.be/Jfa2wxpJJBA https://youtu.be/Ne8xQ4LGLf0 https://youtu.be/mkAnvRIeATE https://youtu.be/r3hirzlWILM https://youtu.be/8U5tP6GL9wM https://youtu.be/LiEXkUkKQQA https://youtu.be/1AtNSTooA3A https://youtu.be/fUhPLe0NAvA

STUDENT"S ASSESMENT

- Calculate the pH and the pOH of each of the 0.003M solutions at 25 °C for which the substances ionize completely.
- What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52.
- The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3} M$ at 25 °C. What is the concentration of hydronium ions in the solution?
- What is pH scale in chemistry?
- What is the best pH for the human body?
- What is pH full form?
- Is pH of water important?
- What happens if your pH is too high?
- Use Lewis structures to classify the following acids as either nonmetal hydrides (*X*H) or nonmetal hydroxides (*X*OH)
- (a) HCN

(b) HNO₃

- (c) $H_2C_2O_4$
- Which of the following compounds can be Bronsted acids? Which can be Bronsted bases?

(a) H₂O

- (b) NH₃
- (c) HSO_4^-
- (d) OH^{-}
- What makes something an acid or a base?
- What is base and example?
- What is an acid and its properties?
- What is the main difference between an acid and a base?

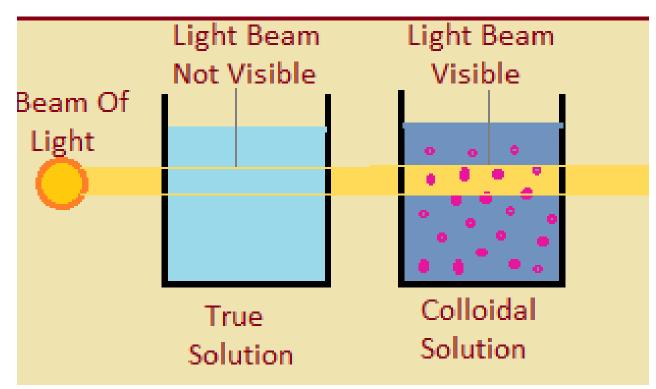
Reference page/site

https://byjus.com/chemistry/acids-and-bases/ https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/acidbase.php https://courses.lumenlearning.com/chemistryformajors/chapter/ph-and-poh/

X-----X

CHAPTER 9

"SOLUTION & COLLOIDS"



INTRODUCTION

CHAPTER CONTENT.

General properties	Raoult's law	Colligative properties	Colloids
Solution, suspension &	Non-volatile non	Vapour pressure lowering.	Properties of
colloids	electrolyte solutes in volatile solvents		colloids.
Hydrophilic & hydrophobic	When both	Boiling point elevation &	Types of
molecules.	components are	freezing point depression.	colloids.
	volatile.		
The nature of solution		Molar, mass determination	
		by lowering vapour	
		pressure.	
The effect on temperature &		Molar mass determination	
pressure on solubility.		by freezing point	
		depression	
		Osmotic pressure &	
		reverse osmosis.	

Major concepts:

- General properties of solution.
- ➢ Raoult's law
- > Colligative properties of non-electrolyte in solutions
- > Colloids

LEARNING OUTCOMES

Students will be able to	Analyzing	Applying	Understanding	Remembering
• List the characteristics of colloids and suspensions that distinguish them from solutions.		~		
• Define hydrophilic and hydrophobic molecules.				~
• Explain the nature of solutions in liquid phase giving examples of completely miscible, partially miscible and immiscible liquid-liquid solutions.		~		
• Explain the effect of temperature on solubility and interpret the solubility graph.	~			
• Express solution concentration in terms of mass percent, molality, molarity, parts per million, billion and trillion and mole fraction.				~
• Define the terms colligative.				v
• Describe on a particle basis why a solution has a lower vapor pressure than the pure solvent.		~		
• Explain on a particle basis how the addition of a solute to a pure solvent causes an elevation of the boiling point and depression of the freezing point of the resultant solution.		~		
• Describe the role of solvation in the dissolving process.			v	
• Define the term water of hydration.				~

• Explain concept of solubility and how it applies to solution saturation.	~		
• Distinguish between the soluation of ionic species and molecular substances.		~	
• List three factors that accelerate the dissolution process.		\checkmark	
• Define heat of solution and apply this concept to the hydration of ammonium nitrate crystals.	~		
• Explain how solute particles may alter the colligative properties.	~		
• Explain osmotic pressure, reverse osmosis, and give their daily life applications.	~		
• Describe types of colloids and their properties.	v		
List some colligative properties of liquids.		~	

SKILLS	Analyzing	Applying	Understanding
• Perform calculations involving percent (volume/volume) and percent (mass/volume) solutions.		~	
• Calculate the freezing point depression and the boiling point elevation of aqueous solutions.			
• Calculate molar mass of a substance using ebullioscopy and cryoscopy methods.		•	
• Calculate the percent of water in a given hydrate.		~	
• Explain the phenomenon freezing in a mixture of ice and salt.			 ✓

SOCIETY, TECHNOLOGY AND SCIENCE Students will be able to

Describe the effect of pressure on gas solubility and the effervescence observed when a bottle of carbonated drink is uncapped. (Applying)

(THEORITICAL)

Related videos



Solution, suspension and collides Properties of collides Molality and colligative properties



Colligative properties

Chapter overview

Solutions

A solution is a homogeneous mixture of two or more components. The dissolving agent is the solvent. The substance that is dissolved is the solute. The components of a solution are atoms, ions, or molecules, making them 10^{-9} m or smaller in diameter.

Example: Sugar and water.

Suspensions

The particles in <u>suspensions</u> are larger than those found in solutions. Components of a suspension can be evenly distributed by mechanical means, like by shaking the contents but the components will eventually settle out.

Example: Oil and water

Colloids

Particles intermediate in size between those found in solutions and suspensions can be mixed in such a way that they remain evenly distributed without settling out. These particles range in size from 10^{-8} to 10^{-6} m in size and are termed colloidal particles or colloids. The mixture they form is called a <u>colloidal</u> <u>dispersion</u>. A colloidal dispersion consists of <u>colloids</u> in a dispersing medium. **Example**: Milk

Reference page/site

https://www.thoughtco.com/solutions-suspensions-colloids-and-dispersions-608177

Hydrophilic molecule

A hydrophilic molecule or portion of a molecule is one whose interactions with **water** and other polar substances are more thermodynamically favorable than their interactions with oil or other hydrophobic solvents. They are typically charge-polarized and capable of hydrogen bonding.

Hydrophobic molecule

Hydrophobic molecules are molecules that do not have a charge, meaning they're nonpolar. Hydrophobic materials often do not dissolve in **water** or in any solution that contains a largely aqueous (watery) environment. Oil, waxes, and steroids are all examples of hydrophobic materials and molecules.

HYDROPHOBIC MOLECULES VERSUS HYDROPHILIC MOLECULES		
Hydrophobic molecules are molecules that do not dissolve in water	Hydrophilic molecules are molecules that can dissolve in water	
Called hydrophobes	Called hydrophiles	
Repel water molecules	Attract water molecules	
Nonpolar	Polar	
When added to water, Gibbs free energy gets a positive value	When added to water, Gibbs free energy gets a negative value	
When added to water, the entropy is decreased	When added to water, the entropy is increased	
Dissolving them in water is an endothermic reaction	Dissolving them in water is an exothermic reaction Visit www.pediaa.com	

solubility:

The amount of a substance that will dissolve in a given amount of a solvent to give a saturated solution under specified conditions.

Effect of Temperature on Solubility:

The solubility of solutes is dependent on temperature. When a solid dissolves in a liquid, a change in the physical state of the solid analogous to melting takes place. Heat is required to break the bonds holding the molecules in the solid together. At the same time, heat is given off during the formation of new solute -- solvent bonds.

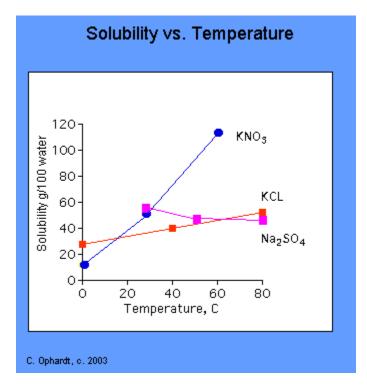
CASE I: Decrease in solubility with temperature:

If the heat given off in the dissolving process is greater than the heat required to break apart the solid, the net dissolving reaction is exothermic (energy given off). The addition of more heat (increases temperature) inhibits the dissolving reaction since excess heat is already being produced by the reaction. This situation is not very common where an increase in temperature produces a decrease in solubility.

CASE II: Increase in solubility with temperature:

If the heat given off in the dissolving reaction is less than the heat required to break apart the solid, the net dissolving reaction is endothermic (energy required). The addition of more heat facilitates the dissolving reaction by providing energy to break bonds in the solid. This is the most common situation where an increase in temperature produces an increase in solubility for solids.

The use of first-aid instant cold packs is an application of this solubility principle. A salt such as ammonium nitrate is dissolved in water after a sharp blow breaks the containers for each. The dissolving reaction is endothermic - requires heat. Therefore the heat is drawn from the surroundings, the pack feels cold.



Solubility of Gases vs. Temperature:

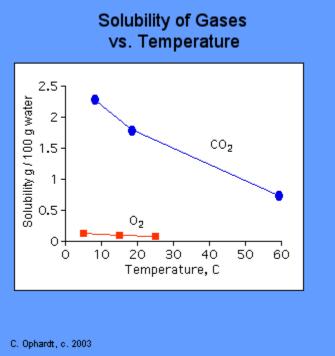
The variation of solubility for a gas with temperature can be determined by examining the graphic on the left.

As the temperature increases, the solubility of a gas decrease as shown by the downward trend in the graph .

More gas is present in a solution with a lower temperature compared to a solution with a higher temperature.

The reason for this gas solubility relationship with temperature is very similar to the reason that vapor pressure increases with temperature. Increased temperature causes an increase in kinetic energy. The higher kinetic energy causes more motion in molecules which break intermolecular bonds and escape from solution.

This gas solubility relationship can be remembered if you think about what happens to a "soda pop" as it stands around for awhile at room temperature. The taste is very "flat" since more of the "tangy" carbon dioxide bubbles have escaped. Boiled water also tastes "flat" because all of the oxygen gas has been removed by heating.

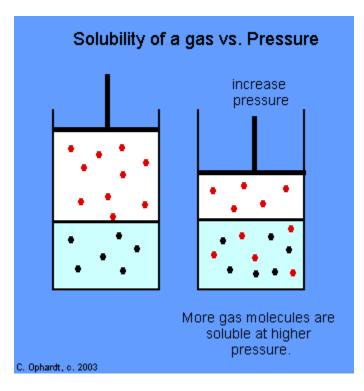


Gas Pressure and Solubility:

Liquids and solids exhibit practically no change of solubility with changes in pressure. Gases as might be expected, increase in solubility with an increase in pressure. **Henry's Law** states that: The solubility of a gas in a liquid is directly proportional to the pressure of that gas above the surface of the solution.

If the pressure is increased, the gas molecules are "forced" into the solution since this will best relieve the pressure that has been applied. The number of gas molecules is decreased. The number of gas molecules dissolved in solution has increased as shown in the graphic on the left.

Carbonated beverages provide the best example of this phenomena. All carbonated beverages are bottled under pressure to increase the carbon dioxide dissolved in solution. When the bottle is opened, the pressure above the solution decreases. As a result, the solution effervesces and some of the carbon dioxide bubbles off.



Reference page/site

http://chemistry.elmhurst.edu/vchembook/174temppres.html

Raoult's Law

Raoult's law has been named after François-Marie Raoult, a French chemist who while conducting an experiment found out that when substances were mixed in a solution, the vapour pressure of the solution decreased simultaneously. Raoult's law was established in the year 1887 and is also considered as the law of thermodynamics.

We will further take an in-depth look at Raoult's law and understand the principle behind the law as well as its application and limitations in this lesson.

Table of Content

- ٠
 - What is Raoult's Law?
- Importance of Raoult's law
- Limitations of Raoult's Law

What is Raoult's Law?

Raoult's law states that a solvent's partial <u>vapour pressure</u> in a solution (or mixture) is equal or identical to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution.

Mathematically, Raoult's law equation is written as;

 $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^0$

Where,

 $P_{\text{solution}} = \text{vapour pressure of the solution}$

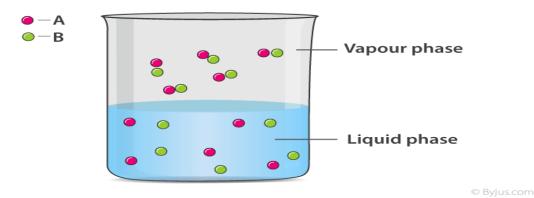
 X_{solvent} = mole fraction of the solvent

 $PO_{solvent} = vapour pressure of the pure solvent$

We will further understand the principle behind the law by looking at the example below.

Consider a solution of volatile liquids A and B in a container. Because A and B are both volatile, there would be both particles of A and B in the vapour phase.

Hence, the vapour particles of both A and B exert partial pressure which contributes to the total pressure above the solution.



Raoult's Law further states that at equilibrium,

$$P_A=\ P_A^{^\circ}x_A, P_B=\ P_B^{^\circ}x_B$$

Where PA is the partial pressure of A.

 P_A° is vapour pressure of pure A at that temperature.

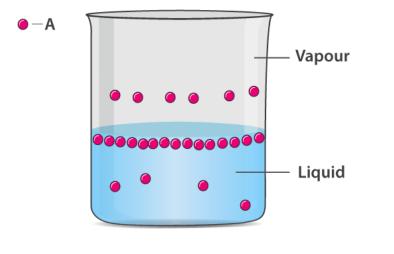
 x_A is mole fraction of A in the liquid phase.

Similarly $P_B, P_B^{\circ} x_B$

Hence $P_T = P_A + P_B \left(Dalton's Law \right) = P_A^{\circ} x_A + P_B^{\circ} x_B = P_A^{\circ} + x_B \left(P_B^{\circ} - P_A^{\circ} \right)$

What is the Importance of Raoult's law?

Assume that we have a closed container filled with a volatile liquid A. After some time, due to evaporation, vapour particles of A will start to form. Then as time passes, the vapour particles of A will be in dynamic equilibrium with the liquid particles (on the surface). The pressure exerted by the vapour particles of A at any particular temperature is called the vapour pressure of A at that temperature.



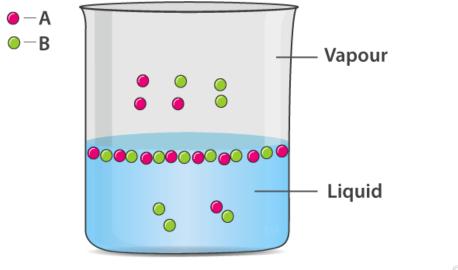
Vapour pressure is exhibited by all solids and liquids and depends only on the type of liquid and temperature.

Now imagine we are adding another liquid B (solute) to this container. This will result in B particles occupying the space between A particles on the surface of the solution.

For any given liquid there are a fraction of molecules on the surface which will have sufficient energy to escape to the vapour phase.

Since now we have a lesser number of A particles on the surface, the number of vapour particles of A in the vapour phase will be lesser. This will result in lower vapour pressure of A.

Now if we assume that B is volatile as well, we will have lesser number of B particles in the vapour phase as compared to pure liquid B.



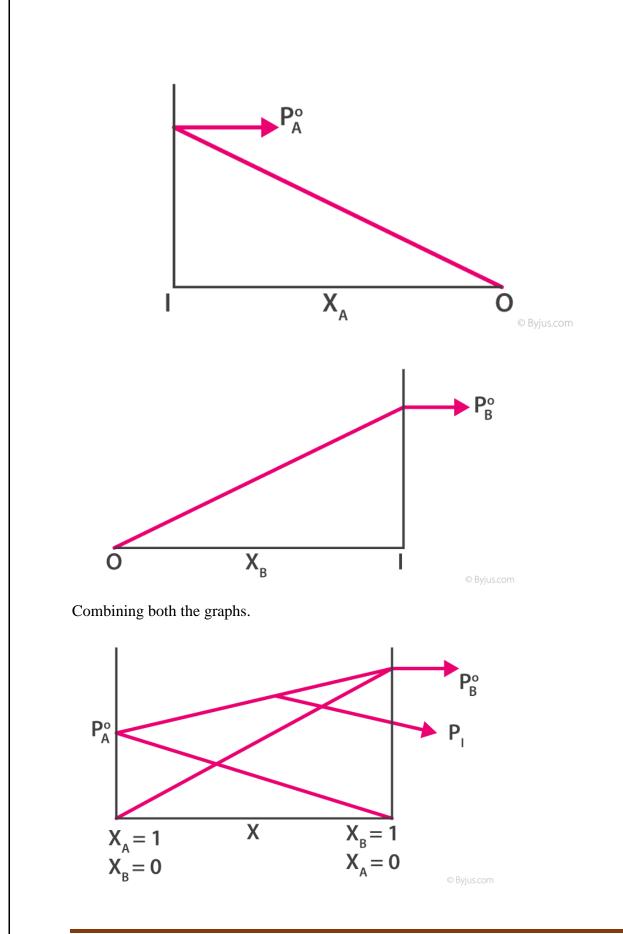
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This new pressure (partial pressure) of each (A and B) is given by Raoult's law and depends on the concentration of each component in the liquid phase.

 $P_A \propto X_A, P_B \propto X_B = X_A P_A^o = X_B P_B^o$

From Raoult's law it is evident that as the mole fraction of a component reduces, its partial pressure also reduces in the vapour phase.

The graphs below show pressure is the mole fraction for A and B.



In the above diagram, we have also added the graph for the total vapour pressure of solution i.e. $P_A + P_B$.

As far as the application of the law goes, it is also useful in calculating the molecular mass of an unknown solute.

Limitations of Raoult's Law

There are a few limitations to Raoult's law.

- Raoult's law is apt for describing <u>ideal solutions</u>. However, ideal solutions are hard to find and they are rare. Different chemical components have to be chemically identical equally.
- Since many of the liquids that are in the mixture do not have the same uniformity in terms of attractive forces, these type of solutions tends to deviate away from the law.

There is either a negative or a positive deviation. The negative deviation occurs when the vapour pressure is lower than expected from Raoult's law. An example of negative deviation is a mixture of chloroform and acetone or a solution of water and hydrochloric acid.

Alternatively, positive deviation takes place when the cohesion between similar molecules is greater or that it exceeds adhesion between unlike or dissimilar molecules. Both components of the mixture can easily escape from the solution. An example of positive deviation includes the mixtures of benzene and methanol or ethanol and chloroform.

Reference page/site <u>https://byjus.com/jee/raoults-</u> <u>law/#:~:text=Raoult's%20law%20states%20that%20a,mole%20fraction%20in%20the%20solution.</u>

Colligative Properties

A colligative property is one of the properties of a solution. It is applied only to solutions and it is usually dependent on the concentration or the ratio of the number of particles of the substances (solute and solvent) in a solution. Colligative property does not depend on the mass or the identity (nature) of the solute as in non-colligative property.

The word"colligative" has been adapted or taken from the Latin word "colligatus" which translates to "bound together". In the context of defining a solution, colligative property helps us to understand how the solvent's properties are linked to the concentration of solute in a solution.

What are Colligative Properties?

Dilute solution containing non-volatile solute exhibit some properties which depend only on the number of solute particles present and not on the type of solute present. These properties are called colligative properties. These properties are mostly seen in dilute solutions.

We can further consider colligative properties as those properties that are obtained by the dissolution of a non-volatile solute in a volatile solvent. Generally, the solvent properties are changed by the

solute where its particles remove some of the solvent molecules in the liquid phase. This also results in the reduction of the concentration of the solvent.

Meanwhile, when we talk about the given solute-solvent mass ratio, colligative properties are said to be inversely proportional to the solute molar mass.

Colligative Properties Examples

We can observe the colligative properties of solutions by going through the following examples. If we add a pinch of salt to a glass full of water its freezing temperature is lowered considerably than the normal temperature. Alternatively, its boiling temperature is also increased and the solution will have a lower vapour pressure. There are changes in its osmotic pressure as well.

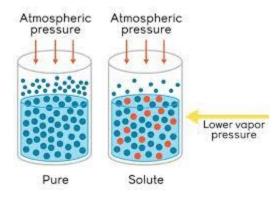
Similarly, if we add alcohol to water, the solution's freezing point goes down below the normal temperature that is observed for either pure water or alcohol.

Different Types of Colligative Properties of Solution

There are different types of colligative properties of a solution. These include, vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure.

Lowering of Vapour Pressure

In a pure solvent, the entire surface is occupied by the molecules of the solvent. If a non- volatile solute is added to the solvent, the surface now has both solute and solvent molecules; thereby fraction of surface covered by solvent molecules gets reduced. Since the vapour pressure of the solution is solely due to solvent alone, at the same temperature the vapour pressure of the solution is found to be lower than that of the pure solvent.



If P_0 is the vapour pressure of pure solvent and Ps is the vapour pressure of the solution. The difference Po – Ps is termed as lowering in vapour pressure. The ratio Po – Ps / Po is known as the relative lowering of vapour pressure.

Raoult, in 1886, established a relation between relative lowering in vapour pressure and mole fraction. The relationship is known as Raoult's law. It states that the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution

If n moles of solute is dissolved in N moles of the solvent, then according to Raoult's law

Po - Ps / Po = n / n + N

Elevation in Boiling Point

The boiling point of a liquid is the temperature at which the vapour pressure is equal to atmospheric pressure. We know that on the addition of a non-volatile liquid to a pure solvent, the vapour pressure of a solution decrease. Therefore to make vapour pressure equal to atmospheric pressure we have to increase the temperature of the solution. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed as elevation in boiling point.

If T^0 b is the boiling point of the pure solvent and Tb is the boiling point of the solution then elevation in boiling point is given as

∆Tb =T⁰b-Tb

Experimental results show that there is a relation between elevation in boiling point and molality 'm' of the solute present in solution

∆Tb ∝ m

∆Tb = kb m

Where,

kb = molal elevation constant

Substituting the value of 'm' in the above relation we get

ΔTb = 1000 x kb x m2 / M2 x m1

Where,

m2 = mass of solvent in g

M1 = mass of solvent in kg

M2 = molar mass of solute

Depression in Freezing Point

The freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour of the corresponding solid. According to Raoult's law when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at a lower temperature. The difference between the freezing point of the pure solvent and its solution is called depression in freezing point.

If T_{f}^{0} is the boiling point of the pure solvent and T_{f} is the boiling point of the solution then depression in freezing point is given as

$\Delta T_f = T_f^0 - T_f$

Just like elevation in boiling point, depression in freezing point is also directly related to molality 'm'.

 $\Delta T_{f} = 1000 \text{ x kf x m2} / \text{M2 x m1}$

Where,

k f = molal depression constant

m2 = mass of solvent in g

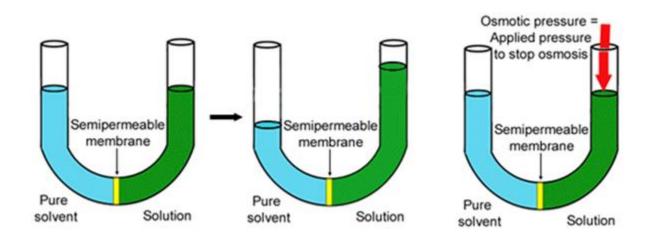
M1 = mass of solvent in kg

M2 = molar mass of solute

Osmotic Pressure

When a semipermeable membrane is placed between a solution and solvent, it is observed that solvent molecules enter the solution through the semipermeable membrane and the volume of the solution increases. The semi-permeable membrane allows only solvent molecules to pass through it but prevents the passage of bigger molecules like solute. This phenomenon of the spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution is called osmosis.

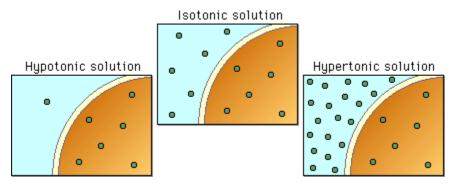
The flow of solvent molecules through the semipermeable membrane can be stopped if some extra pressure is applied from the solution side. This pressure that just stops the flow of solvent is called osmotic pressure of the solution.



Osmotic pressure is a colligative property as it depends on the number of solute present and not on the nature of the solute. Experimentally it was proved that osmotic pressure (π) is directly proportional to molarity(C) and temperature(T).

Different Solutions

- Isotonic solution: Two solutions having the same osmotic pressure at a given temperature are known as an isotonic solution. When such solutions are separated by a semi-permeable membrane than there is no osmosis.
- Hypotonic solution: A hypotonic solution has a lower osmotic pressure than that of the surrounding i.e, the concentration of solute particles is less than that of the surrounding. If the hypotonic solution is separated by semipermeable membrane then water moves out of the hypotonic solution.
- Hypertonic solution: A hypertonic solution has a higher osmotic pressure than that of the surrounding i.e, the concentration of solute particles is more than that of the surrounding. If the hypertonic solution is separated by semipermeable membrane then water moves inside the hypertonic solution.



For determining the molar mass, Osmotic pressure method has the advantage over other methods as pressure measurement is around room temperature. It is particularly useful for determination of the molar mass of biomolecules as they are unstable at higher temperatures.

Reference page/site

https://byjus.com/jee/colligative-properties/#:~:text=Colligative%20Properties-,Colligative%20Properties,and%20solvent)%20in%20a%20solution.

Colloids

A colloid is a mixture in which one substance of microscopically dispersed insoluble particles are suspended throughout another substance. Sometimes the dispersed substance alone is called the colloid. The colloid consists of a dispersed phase and a continuous phase.

Types of Colloids

- Sol It is a suspension of minute solid particles in a liquid.
- **Emulsion** It is a colloid between two or more liquid with one consisting a dispersion of another liquid.
- Foam It consists of gas dispersed in solid or liquid.
- Aerosol It consists of a minute liquid or solid particles in a gas.

Application of Colloids

Colloids are widely useful in industries, medical and domestic applications.

As food items: Syrup, Halwa, Soup belongs to a colloidal type of system.

Medicine: Colloidal silver in the name of Argyrols, it acts as antiseptic for eye infection.

In Purification of air by Cottrell precipitator:

This process involves coagulation of solution particle. Dust or smoke is passed through the inlet of an electrified chamber which has a central electrical plate which is provided with opposite charge of a dent a smoke particle when dust passes the particles are coagulated and pure air is passed through another outlet.

Tanning of leather:

Animal skins are very soft, when these are immersed in the solution of tannin which has the opposite charge of animal skin, particles are coagulated and the skin becomes hard this is known as tanning of leather.

Formation of delta:

It involves coagulation of clay particles of the river with an electrolyte of seawater.

Reference page/site

https://www.toppr.com/guides/chemistry/surface-chemistry/colloids/ https://byjus.com/jee/colloids/

(NUMERICALS)

1. The molal elevation constant for water is 0.513° C kg mol⁻. When 0.2mole of sugar is dissolved in 250g of water, calculate the temperature at which the solution boils under atmospheric pressure.

Solution:

The elevation in boiling point can be written as

 Δ Tb = moles of sugar x 1000 / weight of water in gram

ΔTb = 0.2 x 1000 / 250

∆Tb = 0.8

 \Rightarrow T⁰b-Tb = 0.8

For pure water, T⁰b =100°C

⇒ Tb= 0.8 + 100

=100.80⁰C

2. Is the graph of pressure vs mole fraction always a straight line?

Solution:

If the solution is ideal, the 3 graphs (P_A , P_B and P_T) will always be a straight line because

 $P_A = X_A P_A^o$ $P_B = X_B P_B^o$ $P_T = P_e^o x_e + P_m^o x_m$. P_e^o is vapour pressure of pure ethanol

 P^o_m is vapour pressure of pure methanol.

 $x_e \& x_m$ are mole fractions of ethanol and methanol.

No of moles of ethanol (n_e) $= \ \frac{60}{46} = \ 1.3 \, mol$

No of moles of methanol (n_m) = $\frac{40}{32} = 1.25 \, mol \ x_e = \frac{n_e}{n_e + n_m} = \frac{1.33}{(1.33 + 1.25)} = 0.51 \ x_m = 0.51$

$$\frac{n_B}{n_e + n_m} = \frac{1.25}{(1.33 + 1.25)} = 0.49$$

Therefore, $P_T = (0.51 imes 44.5) + (0.49 imes 88.7) = 66.2 \, mmHg$

Reference page/site

https://byjus.com/jee/colligative-properties/#:~:text=Colligative%20Properties-,Colligative%20Properties,and%20solvent)%20in%20a%20solution. https://byjus.com/jee/raoultslaw/#:~:text=Raoult's%20law%20states%20that%20a,mole%20fraction%20in%20the%20solution.

Students Assessments

- Is Raoult's law valid for all type of solutions?
- Calculate the molecular weight of sulfur if 35.5 grams of sulfur dissolve in 100.0 grams of CS₂ to produce a solution that has a boiling point of 49.48°C
- Is dust a colloid? If so, what type is it?
- Is whipped cream a colloid? if so, what type is it?
- What does Sol mean?
- When hit by light what happens to a colloidal mixture?
- What is the mixture considered if the particles are larger than the particles of a colloidal substance
- Which of the following is not a use of colloids?
- What are gels? Give an example.
- A small amount of electrolyte is needed for the formation of sol white large amount is required for coagulation of sol comment.

Practical #07

- How to increase the solubility of partial soluble salts.
- How to separate one liquid to another liquid by distillation method.
- Purification of dirty water.

Reference page/site

https://byjus.com/jee/colloids/

https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch15/colligative.php

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental _____Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Solutions_and_Mixtures/Co_____ lloid

https://www.toppr.com/guides/chemistry/surface-chemistry/colloids/

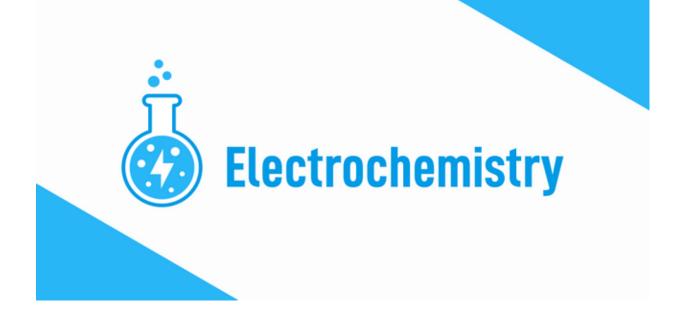
Related videos

https://youtu.be/UktHPe4oQLc https://youtu.be/Yo07oWNJgAA https://youtu.be/hOhgXRukRDg https://youtu.be/nCWSWbffQ8k

X-----X

CHAPTER 10

"ELECTROCHEMISTRY"



INTRODUCTION

CHAPTER CONTENT.

Oxidation-reduction Concept	Electrode Potential & Electrochemical	Batteries
	cell	
Oxidation & Reduction	Electrolytic cell	Primary batteries
Oxidation numbers	Voltaic cell	Secondary batteries
Recognition of redox reaction	Std state cell potential for voltaic cell	Fuel cell
Balancing redox reaction by	Std state reduction half cell potential.	
half reaction method.		
Oxidizing & reducing reagents	Std state cell potential for voltaic cell &	
	spontaneous reactions	

Major concepts:

- Oxidation Reduction concept
 Electrode, electrode potential & electrochemical series.
- > Types of electrochemical cells

LEARNING OUTCOMES

Students will be able to	Applying	Understanding	Remembering
• Give the characteristics of a Redox reaction.		 ✓ 	
• Determine the oxidation number of an atom of any element in a pure substance.	~		
• Define oxidation and reduction in terms of a change in oxidation number.	~		
• Use the oxidation-number change method to identify atoms being oxidized or reduced in redox reactions.	~		
• Use the oxidation-number change method to balance redox equations.	~		
• Balance redox reactions that take place in acid solutions.	~		
• Break a redox reaction into oxidation and reduction half reactions.	•		
• When given an unbalanced redox equation, use the half reaction method to balance the equation.	~		
• Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode).			~
• Identify the substance oxidized and the substance reduced in a dry cell.	~		
• Use the activity series of metals to predict the products of single replacement reactions.	~		
• Define cell potential, and describe how it is determined.		v	

• Describe the reaction that occurs when a lead storage battery is recharged.	✓	
• Explain how a fuel cell produces electrical energy.	v	
• Define the standard electrode potential of an electrode.		 ✓

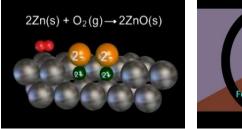
Skills	Applying	Analyzing	Understanding
• Use standard electrode potentials to calculate the standard emf of cell.	•		
• Predict the feasibility of an electrochemical reaction from emf data.		~	
• Calculate the amount of substance reduced when a quantity of another substance is oxidized in an electrochemical cell.	✓		
• Calculate the cell potential for an electrochemical cell under standard conditions.	v		
• Deduce the direction of flow of electrons in an electrochemical cell.		~	
• Calculate the quantity of charge passed in an electrochemical cell during electrolysis.	v		
• Calculate the mass or volume of substance liberated during electrolysis.	v		

SOCIETY, TECHNOLOGY AND SCIENCE

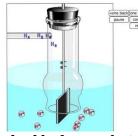
Students will be able to

- Explain how paints can protect metal surfaces from corrosion and other harmful agents. (Applying)
- > Provide examples of applications of oxidation-reduction reactions in daily life. (Applying)
- > Identify solar cells as the source of energy in future (Applying)
- Explain how batteries work. (Applying)
- > Explain many reactions as the result of electron transfer .

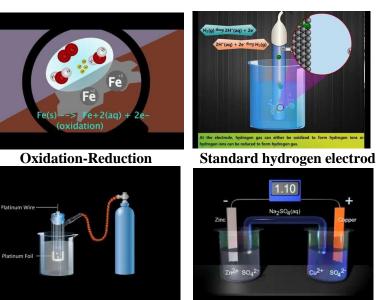
Related videos



Oxidation-reduction



Standard hydrogen electrod Chapter view

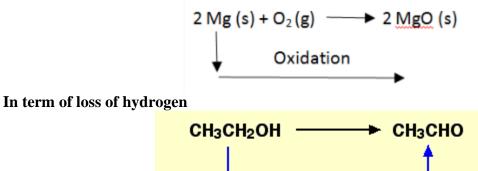


Glavanic cell with Zinc n Copper

(THEORY)

Oxidation

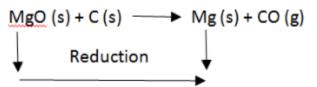
It is referred to gain of oxygen or loss of hydrogen and loss of electron.



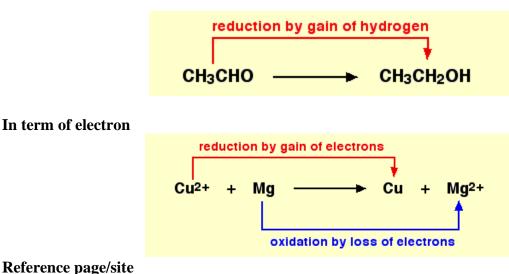
oxidation by loss of hydrogen

Reduction

It is referred to gain of hydrogen or loss of oxygen and gain of electron.



In term of gain of hydrogen



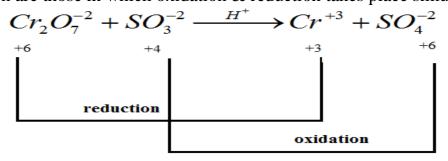
https://www.chemguide.co.uk/inorganic/redox/definitions.html https://byjus.com/chemistry/oxidation-and-reduction/

Oxidation numbers

Oxidation number, also called **Oxidation State**, the total **number** of electrons that an atom either gains or loses in order to form a chemical bond with another atom. **Oxidation number**.

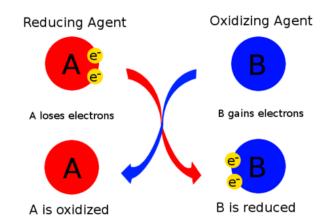
Redox reaction

Redox reaction are those in which oxidation & reduction takes place simultaneously.



Oxidizing & Reducing agent

- A reducing agent **reduces** other substances and **loses** electrons; therefore, its oxidation state **increases**.
- An oxidizing agent **oxidizes** other substances and **gains** electrons; therefore, its oxidation state **decreases**



Common oxidizing agents	Common reducing agents
O ₂	H ₂
O ₃	CO
F ₂	Fe
Br ₂	Zn
H ₂ SO ₄	Li
Halogens (they favor gaining an electron to obtain a noble gas configuration)	Alkali metals (they favor losing an electron to obtain a noble gas configuration)

Reference page/site

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Redox_Chemistry/Oxidizing_and_Reducing_Agents#:~:text=An%20oxidizing%20agent%2C %20or%20oxidant,reduced%20in%20a%20chemical%20reaction.&text=A%20reducing%20agent%2C%20or%2 Oreductant,known%20as%20the%20electron%20donor.

Electrolytic cell and voltaic cell (galvanic cell)

Voltaic cells use a spontaneous chemical reaction to drive an electric current through an external circuit. These cells are important because they are the basis for the batteries that fuel modern society. But they aren't the only kind of electrochemical cell. It is also possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells**. Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously.

Differences between electrolytic cell and voltaic cell

	Difference between electrolytic cell and galvanic cell		
S.no	Electrolytic cell	Galvanic cell	
1	Converts electrical energy into chemical energy.	Converts chemical energy into electrical energy.	
2	Electrical energy brings out a chemical reaction with the help of an external force.	Chemical energy generates electrical energy with the help of redox reaction.	
3	A cathode is negative and an anode is positive.	A cathode is positive and an anode is negative.	
4	Oxidation takes place at cathode and reduction at the anode.	Oxidation takes place at anode and reduction at the cathode.	
5	Both the anode and cathode are in the same container with an electrolytic solution.	Both the anode and cathode are in different containers known as a half cell which are connected by a salt bridge.	
6	Used in purifying copper and electroplating.	Used in batteries for example, batteries present in TV remotes.	

Reference page/site

https://www.student-baba.com/2020/03/difference-between-electrolytic-cell-and-galvinic-cell.html

Cell potential

The **cell potential**, Ecell, is the measure of the **potential** difference between two half **cells** in an electrochemical **cell**. The **potential** difference is caused by the ability of electrons to flow from one half **cell** to the other.

Standard cell potential

A **cell's standard** state **potential** is the **potential** of the **cell** under **standard** state conditions, which is approximated with concentrations of 1 mole per liter (1 M) and pressures of 1 atmosphere at 25°C. Write the oxidation and reduction half-reactions for the **cell**.

Standard Hydrogen Electrode

Standard Hydrogen Electrode is used as a reference electrode when calculating the standard electrode potential of a half cell.

What is a Standard Hydrogen Electrode?

The Standard Hydrogen Electrode is often abbreviated to SHE, and its standard electrode potential is declared to be 0 at a temperature of 298K. This is because it acts as a reference for comparison with any other electrode .

The redox half cell of the SHE is where the following reaction takes place:

 $2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$

The reaction given above generally takes place on a <u>platinum</u> electrode. The pressure of the hydrogen gas present in this half cell equals 1 bar.

Use of Platinum in the Standard Hydrogen Electrode

Platinum is used in the Standard Hydrogen Electrode due to the following reasons:

- Platinum is a relatively inert metal which does not corrode easily.
- Platinum has catalytic qualities which promotes the proton reduction reaction.
- The surface of platinum can be covered with platinum black, a fine powder of platinum. This type of platinum electrode is called a platinized platinum electrode.
- Platinum also improves the reaction kinetics by adsorbing hydrogen at the interface.

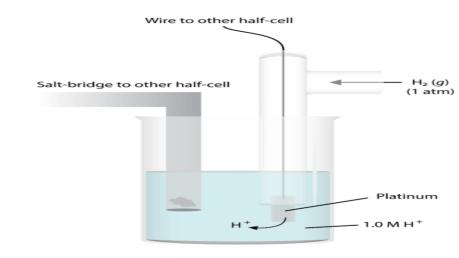
Standard Hydrogen Electrode Construction

The parts that make up a Standard Hydrogen Electrode are listed below.

- A platinum electrode which is covered in finely powdered platinum black (platinized platinum electrode).
- A hydrogen Blow.
- A solution of acid having a H⁺ molarity of 1 mole per cubic decimeter.
- The SHE also contains a hydroseal which is used to prevent the interference of oxygen.
- The other half-cell of the entire Galvanic cell must be attached to the Standard Hydrogen Electrode through a reservoir in order to create an ionically conductive path. This can be done through a direct connection, through a narrow tube, or even through the use of a salt bridge.

Standard Hydrogen Electrode Diagram

A labelled diagram of a standard hydrogen <u>electrode</u> is provided below. In the SHE illustrated, a salt bridge is used to link the SHE with the other half cell.



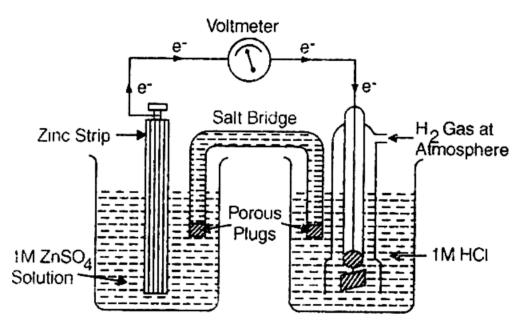
The platinized platinum surface has a very high adsorption activity. Therefore, this surface must be protected from atmospheric oxygen as well as from organic substances. Substances such as arsenic and sulfur compounds can deactivate or poison the catalyst.

Reference page/site

https://byjus.com/chemistry/standard-hydrogenelectrode/#:~:text=The%20Standard%20Hydrogen%20Electrode%20is,comparison%20with%20any%20other% 20electrode%20.&text=The%20reaction%20given%20above%20generally%20takes%20place%20on%20a%20p latinum%20electrode.

Electrode potential of zinc

In order to determine the electrode potential of zinc a voltaic cell is constructed by a zinc electrode(a zinc strip dipped in 1.00 molar solution of ZnSO₄) and hydrogen electrode. Salt bridge is made of potassium chloride (KCl) jelly which completes the circuit between half cells and prevents mixing of solutions.



The potentiometer reading gives the E.M.F. of the cell which is 0.76 Volt. Since hydrogen electrode has the potential of 0.00 Volt, hence potential of Zn electrode is 0.76 Volt.

0.76 - 0.00 = 0.76 Volt

In external circuit it is observed that the flow of electrons takes place from Zn to H.

Zn ; Z_n^{+2} (1.00M) $\stackrel{\bar{e}}{\longrightarrow} H^+$ (1.00M) ; H_2 (1.00 atmosphere) ; Pt

Thus it concludes that the electrons must have originated from Zn i.e. it is oxidized and it is anode and it is negative with respect to hydrogen electrode. Thus standard reduction potential of zinc is - 0.76V.

$$Z_n^{+2} + 2 \bar{e} \longrightarrow Zn$$
; $E = -0.76$ Volt

The standard oxidation potential of zinc is therefore + 0.76V.

 $\mathbf{E}_{red} = \mathbf{E}_{ox}$

Sir Rao Muzammil Ali & Ms Naheed Muneer Siddiqui

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- 0.76 Volt = +0.76 Volt

The negative sign shows that the reaction at Zn electrode occurs in the opposite direction and at Zn electrode oxidation takes place not reduction:

$$Zn - 2\bar{e} \longrightarrow Zn^{+2}; E = +0.76$$
 Volt

Reduction takes place on hydrogen electrode:

CELL REACTION

Adding two equations:

$$Zn - 2/\tilde{e} \longrightarrow Zn^{+2}; E = +0.76 \text{ Volt}$$

$$2H^{+} + 2/\tilde{e} \longrightarrow H_{2}; E^{\circ} = 0.00 \text{ Volt}$$

$$Zn + 2H^{+} \longrightarrow Zn^{+2} + H_{2}; 0.76 \text{ Volt}$$

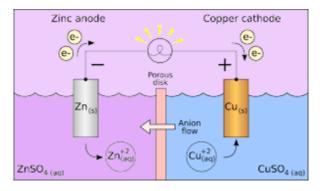
Reference page/site

http://www.citycollegiate.com/electrode_potential02.htm

Cathode and Anode

They are both defined by the flow of current. Therefore, a cathode is an electrode from which the current exits a polarized electrical device. Likewise, an anode is the electrode from which a current enters into a polarized electrical device.

The terms were *finalized in 1834 by William Whewell* who adapted the words from the Greek word (kathodos), 'descent' or 'way down'. William had consulted with Michael Faraday for the coining of the terms.



Cathode and Anode Example

Cathode

When we talk about cathode in chemistry, *it is said to be the electrode where reduction occurs*. This is common in an electrochemical cell. Here, the cathode is negative as the electrical energy that is supplied to the cell results in the decomposition of chemical compounds. However, it can also be positive as in the case of a <u>galvanic cell</u> where a chemical reaction leads to the generation of electrical energy.

In addition, a cathode is said to be either <u>hot cathode or a cold cathode</u>. A cathode which is heated in the presence of a filament to emit electrons by thermionic emission is known as a hot cathode whereas cold cathodes are not heated by any filament. A cathode is usually flagged as "cold" if it emits more electrons compared to the ones generated by thermionic emission alone.

Anode

In the most basic form, an anode in electrochemistry is the point *where an oxidation reaction occurs*. Generally, at an anode, negative ions or anions due to its electrical potential tend to react and give off electrons. These electrons then move up and into the driving circuit.

If we take a galvanic cell, the anode is negative in nature and the electrons mostly move towards the external part of the circuit. In an <u>electrolytic cell, it is again positive</u>. Additionally, an anode can be a plate or wire having an excess positive charge.

Difference Between Anode And Cathode

Here are some of the key differences between cathode and anode.

Anode	Cathode
The anode is the electrode where electricity moves into.	The cathode is the electrode where electricity is given out or flows out of.
The anode is usually the positive side.	A cathode is a negative side.
It acts as an electron donor.	It acts as an electron acceptor.
In an electrolytic cell, oxidation reaction takes place at the anode.	In an electrolytic cell, a reduction reaction takes place at the cathode.
In galvanic cells, an anode can become a cathode.	In galvanic cells, a cathode can become an anode.

Reference page/site

https://byjus.com/chemistry/cathode-and-anode/

What is a Battery?

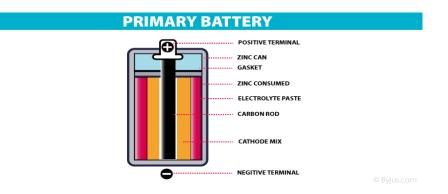
A Battery is a device consisting of one or more electrical cells that convert chemical energy into electrical energy. Every battery is basically a galvanic cell where redox reactions take place between two electrodes which act as the source of the chemical energy.

Battery types

Batteries can be broadly divided into two major types.

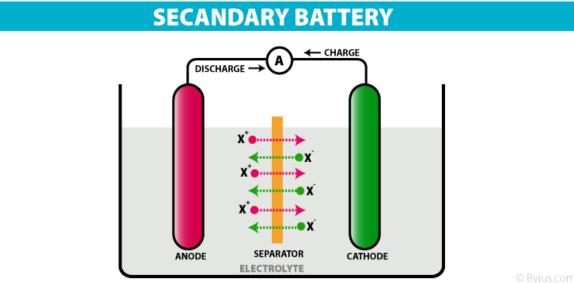
- Primary Cell / Primary battery
- Secondary Cell / Secondary battery

Primary Cell



Secondary Cell

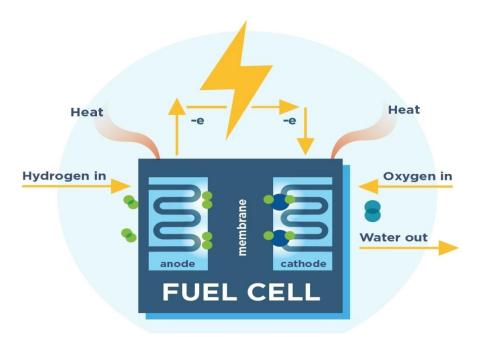
These are batteries that can be recharged after use by passing current through the electrodes in the opposite direction, i.e. from the negative terminal to the positive terminal.



Reference page/site https://byjus.com/chemistry/battery-types/

Fuel cells

A **fuel cell** is a device that converts chemical potential energy (energy stored in molecular bonds) into electrical energy. A PEM (Proton Exchange Membrane) **cell** uses hydrogen gas (H_2) and oxygen gas (O_2) as **fuel**. The products of the reaction in the **cell** are water, electricity, and heat.



Reference page/site https://byjus.com/chemistry/battery-types/

(NUMERICALS)

1. Calculate Oxidation number of Underlined element-

i) K ₂ <u>Cr</u> O ₄	ii) $K_2\underline{Cr}_2O_7$
2(+1)+x+4(-2)=0	2(+1)+2x+7(-2)=0
+2+x-8=0	+2+2x-14 =0
x=+6	2x-12=0

x=+6

O.No. of Cr = +6 O.No. of Cr = +6

2. Calculate oxidation number of underlined element in the Ion

i) <u>P</u> O4 ³⁻	ii) H <u>S</u> O ₃ ⁻
x+4(-2) = -3	+1+x+3(-2)=-1
x-8 =-3	+1+x-6= -1
x=-3+8	x=+4
x=+5	O.No. of 5 = +4

O.No. of P=+5

Reference page/site

https://chemistryonline.guru/solved-problems-oxidation-number/

Identify the oxidizing agent and the reducing agent in the following redox reaction:

 $MnO_4^- + SO_3^{2-} \to Mn^{+2} + SO_4^{2-}$

Solution

S is the reducing agent and Mn is the oxidizing agent.

Student's assessment

1. Which of the following is a strong reducing agent? Which of the following is a strong oxidizing agent?

NO-3, NO, N2H4, NH3

- 2. What is the oxidation state of the sulfur atom in the sulfate ion SO_4^{2-} .
- **3.** What is electrochemical cell?
- 4. Mention the names of anode and cathode of a daniel cell?
- **5.** What is salt bridge?
- 6. What is the direction of flow of electrons in an electrochemical cell?
- **7.** Define the term EMF?

Practical # 08

- Standardization of KMnO₄ by redox titration.
- Determine the amount of iron in ferrous gluconate by volumetric analysis.
- Determine the amount of iron in blood sample by volumetric analysis.
- How to coat one metal to another metal.

Related videos Oxidation and reduction <u>https://youtu.be/e6Xxz-VBE6s</u> <u>https://youtu.be/KmIj2eJPi5M</u> <u>https://youtu.be/VXvtkwubQQg</u>

Standard hydrogen potential https://youtu.be/k_vR0Eqb5gY https://youtu.be/ghvDcbCYJGU https://youtu.be/oBfNBuN8uFk

Zinc electrode potential https://youtu.be/0oSqPDD2rMA https://youtu.be/Doxrn05t08U

X-----X

What's New in it	What's New in it? "Although it is based on National curriculum and Sindh curriculum"		
"Although it is based on National curriculum an			
New Practical's	Topic		
 Determine the sugar level in blood sample by gravimetrically (NEW) How to obtained serum from blood by centrifuging method (NEW) Explore the effect of temperature and concentration on the same back in a back in the block. 	 X-Ray radiation Born Haber cycle Calorimetry Zeroth law of thermodynamic. Third law of 		
 rate of fading of methylene blue.(NEW) Determine the rate of reaction and determination of density of blood sample.(NEW) 	 thermodynamic. Handerson- Hasselbalch Equation PKa & PKb Fuel cell. 		
 Determine the concentration of hemoglobin in human blood (NEW) 			
• Determine the amount of acid in different fruits.(NEW)			
 How to separate one liquid to another liquid by distillation method(NEW) 			
 Purification method of dirty water. (NEW) Determine the amount of iron in blood sample by volumetric analysis(NEW) 			
• How to coat one metal to another metal.(NEW)			