KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Established Under Section 3 of UGC Act 1956)
Coimbatore – 641 021.
SYLLABUS
DEPARTMENT OF CHEMISTRY

Semester-II

17CHU201   PHYSICAL CHEMISTRY II (Chemical Thermodynamics and its applications)   5H-5C

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Instruction Hours/week:L: 5 T:0 P:0   Marks: Internal: 40 External: 60 Total:100

Scope
The course deals with the chemical thermodynamics, chemical equilibria and colligative properties. It helps the students to evaluate physical and chemical systems to determine how to control these systems.

Objectives
1. Students will explain and apply the concepts of thermodynamics to chemical and physical systems.
2. Students will be able to derive essential mathematical relationships in thermodynamics, and chemical equlibria.
3. List the colligative properties of solutions, explaining how and why each property is affected by an increase by the amount of solute

UNIT I
Chemical Thermodynamics: Intensive and extensive variables; state and path functions; isolated, closed and open systems.
First law: Concept of heat, Q, work, W, internal energy, U, and statement of first law; enthalpy, H, relation between heat capacities, calculations of Q, W, ΔU and ΔH for reversible, irreversible and free expansion of gases (ideal and Van der Waals) under isothermal and adiabatic conditions.

UNIT II
Thermochemistry: Heats of reactions: standard states; enthalpy of formation and enthalpy of combustion and its applications; effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions.
Second Law: Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics. Calculation of entropy change for reversible and irreversible processes.

UNIT III
Third Law: Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules. Free Energy Functions: Gibbs and Helmholtz energy; variation of S, G, A with T, V, P; Free energy change and spontaneity. Relation between Joule-Thomson coefficient and other thermodynamic parameters; inversion temperature; Gibbs-Helmholtz equation; Maxwell relations; thermodynamic equation of state.

Systems of Variable Composition: Partial molar quantities, dependence of thermodynamic parameters on composition; Gibbs Duhem equation, chemical potential of ideal mixtures, change in thermodynamic functions in mixing of ideal gases.

UNIT IV
Chemical Equilibrium: Criteria of thermodynamic equilibrium, degree of advancement of reaction, chemical equilibria in ideal gases. Thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient. Equilibrium constants and their quantitative dependence on temperature, pressure and concentration (LeChatelier Principle, Quantitatively). Free energy of mixing and spontaneity.equilibrium between ideal gases and a pure condensed phase.

UNIT V
Solutions and Colligative Properties: Dilute solutions; lowering of vapour pressure, Raoult's and Henry's Laws and their applications. Thermodynamic derivation using chemical potential to derive relations between the four colligative properties [(i) relative lowering of vapour pressure, ii) elevation of boiling point, (iii) Depression of freezing point, (iv) osmotic pressure] and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution.

Suggested Readings

Text Books:

1.   Peter, A. & Paula, J. de. (2011). *Physical Chemistry*. 9th Ed. Oxford University Press.
2.   Castellan, G. W. (2004). *Physical Chemistry*. 4th Ed. Narosa.

Reference Books:

1.   Engel, T. & Reid, P. (2012). *Physical Chemistry*. 3rd Ed. Prentice-Hall
2.   McQuarrie, D. A. & Simon, J. D. (2004). New Delhi: Molecular Thermodynamics Viva Books Pvt. Ltd.
3.   Assael, M. J., Goodwin, A. R. H., Stamatoudis, M., Wakeham, W. A. & Will, S. (2011). *Commonly Asked Questions in Thermodynamics*. NY : CRC Press.
4.   Levine, I .N. (2010). *Physical Chemistry*. 6th Ed. Tata McGraw Hill. •
5.   Metz, C.R. (2006). *2000 solved problems in chemistry*. Schaum Series

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LECTURE PLAN
DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. S. RAVI & Mr. M. DINESH KUMAR
SUBJECT NAME: Physical Chemistry II   SUB.CODE:17CHU201
SEMESTER: II   CLASS: I B.Sc (Chemistry)

S.No	Lecture duration period	Topics to be covered	Support material/ Page No.
		UNIT I	
1	1	Chemical Thermodynamics	T1: 719, T2: 42
2	1	Intensive and Extensive variables	T1: 721
3	1	State and Path functions	T1: 726
4	1	Isolated, Closed and Open systems	T1: 719, T2: 43
5	1	Concept of heat (Q) and Work(W)	T1: 722-723; T2:43-48
6	1	Internal Energy (U)	T1: 723; T2:51
7	1	Statement of First Law	T1: 725-726; T2: 64
8	1	Enthalpy H	T1: 727, T2: 51-55
9	1	Relation between heat capacities	T1: 728-729
10	1	Calculation of Q, W for reversible reactions	T1: 735-736; T2: 45-48
11	1	Calculation of ΔU & ΔH for reversible reactions	T1: 735-736
12	1	Calculation of Q, W for irreversible reactions	T1:736
13	1	Calculation of ΔU & ΔH for irreversible reactions	T1: 737
14	1	Free expansion of gases	T1: 746-747
15	1	Isothermal and adiabetic conditions	T1: 746-747
16	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 1=16		
		UNIT II	
1	1	Thermochemistry- Introduction	T1:751
2	1	Heat of Reactions	T1:752
3	1	Standard states	T1: 756
4	1	Enthalpy of formation	T1: 755-756; T2: 71
5	1	Enthalpy of combustion	T1: 757; T2: 75

6	1	Applications of enthalpy of combustion	T1: 756
7	1	Effect of temperature on reaction	T1:779-780; T2:78
8	1	Kirchoff's equation	T1:779-780
9	1	Effect of Pressure on enthalpy of reactions	T1:730
10	1	Concept of entropy	T1: 795
11	1	Thermodynamic scale of Temperature	T1: 794
12	1	Statement of second law of thermodynamics	T1: 789, T2:84
13	1	Calculation of entropy change for reversible processes	T1:797
14	1	Calculation of entropy change for irreversible processes	T1: 797
15	1	Recapitulation and discussion of important questions	
		Total No of Hours Planned For Unit 1I=15	
		UNIT III	
1	1	Statement of third law	T1:820; T2: 84
2	1	Concept of Residual entropy	T1: 820; T2: 97
3	1	Calculation of absolute entropy of molecules	T1: 799; T2:93
4	1	Free Energy functions	T1: 809
5	1	Gibbs and Helmholtz energy	T1: 816; T2: 98
6	1	Variation of S,G, A with T,V, P	T1: 811; T2:106-109
7	1	Free energy change and spontaniety	T1: 814, 843
8	1	Relation between Joule-Thomson Coefficient and other thermodynamic parameters	T1:731
9	1	Inversion Temperature	T1: 836
10	1	Gibbs-Helmholtz equation	T1:817
11	1	Maxwell relations and thermodynamic equation of state	T1:839
12	1	Partial Molar quantities	T1: 837
13	1	Dependence of thermodynamic parameters on composition	T1: 838; 843
14	1	Gibbs-Duhem equation, Chemical potential of ideal mixture	T1:807
15	1	Change in thermodynamic functions in mixing of ideal gases	T1: 807
16	1	Recapitulation and discussion of important questions	
		Total No of Hours Planned For Unit 1II=16	
		UNIT IV	
1	1	Criteria pf thermodynamic equilibrium	T1:832-846, T2: 175
2	1	Degree of advancement of reaction	T1:833
3	1	Chemical equilibria in solutions	T2: 179
4	1	Chemical equlibria in ideal gases	T1:834
5	1	Thermodynamic derivation of relation between Gibbs free energy of reactions and	T1: 844

		reaction quotient	
6	1	Equilibrium constant and its dependence on Temperature	T1: 843-845
7	1	Equilibrium constant and its dependence on concentration	T1: 835-836
8	1	Equlibrium constant and pressure	T1: 836-837
9	1	Le-Chatelier principle	T1:856
10	1	Free Energy of Mixing	T1: 839
11	1	Spontaniety of reaction	T1: 856-857
12	1	Equilibrium between ideal gases and a pure condensed phase	T1:841-843
13	1	Revision and discussion of important questions	
		Total No of Hours Planned For Unit 1V=13	
		UNIT V	
1	1	Dilute solutions, lowering of vapour pressure	T1: 812, T2:134
2	1	Rauolt's and Henry's law and their applications	T1:819-922
3	1	Thermodynamic derivation using chemical potential to deprive relations	T1: 837
4	1	Relative lowering of vapour pressure	
5	1	Colligative properties	T1:831-833
6	1	Elevation of boiling point	T1: 833
7	1	Depression of freezing point	T1:833
8	1	Osmotic pressure	T1:834
9	1	Applications in calculating molar masses of normal solutes	T1:839-844
10	1	Dissociated and associated solutes in solution	T1:875-876
11	1	Revision and discussion of questions	
12	1	Discussion of End Semester Exam Question paper	
13	1	Discussion of End Semester Exam Question paper	
14	1	Discussion of End Semester Exam Question paper	
		Total No of Hours Planned For Unit V=14	

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc Second Year), S.Chand and Co.Pvt.Ltd., New Delhi.

T2: Peter A and Paula J.de (2011), Physical Chemistry, 9th Edition., Oxford University Press.

Text Books:

1. Peter, A. & Paula, J. de. (2011). *Physical Chemistry*. 9th Ed. Oxford University Press.
2. Castellan, G. W. (2004). *Physical Chemistry.* 4th Ed. Narosa.

Reference Books:

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3. Assael, M. J., Goodwin, A. R. H., Stamatoudis, M., Wakeham, W. A. & Will, S. (2011). *Commonly Asked Questions in Thermodynamics*. NY : CRC Press.
4. Levine, I .N. (2010). *Physical Chemistry.* 6th Ed. Tata McGraw Hill. •
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COURSE CODE: 17CHU201   UNIT: I (Chemical Thermodynamics-First Law) BATCH-2017-2020

UNIT I

SYLLABUS

Chemical Thermodynamics: Intensive and extensive variables; state and path functions; isolated, closed and open systems.

First law: Concept of heat, Q, work, W, internal energy, U, and statement of first law; enthalpy, H, relation between heat capacities, calculations of Q, W, ΔU and ΔH for reversible, irreversible and free expansion of gases (ideal and Van der Waals) under isothermal and adiabatic conditions.

Chemical Thermodynamics

Introduction

In the study of chemistry the following fundamental questions need to be answered.

(i) Why does a reaction occur? That is, what is the driving force of a reaction?

(ii) How far a reaction can occur? That is, what is the extent (or progress) of the reaction?

(iii) How fast a reaction can occur? That is, what is the rate of the reaction?

We get the answer of the first two questions by the study of **thermodynamics**, while third question forms the domain of the study of chemical kinetics.

Terminology of thermodynamics

The term thermodynamics means *flow of heat*. In general it deals with the inter conversion of various kinds of energy in physical and chemical systems.

Thermodynamics

1. Predicts the feasibility of a physical process or chemical reaction under given condition of temperature and pressure.

2. Predicts whether a chemical reaction would occur spontaneously or not under a given set of conditions

3. Helps to determine the extent to which a reaction would take place.

Limitations of thermodynamics

1. It predicts the extent to which a reaction can take place .however it does not say anything about the rate.

2. It applies only to matter in bulk and not to individual atoms or molecules.

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Terms used in thermodynamics.

System and Surroundings:

Any part of the universe which is selected for thermodynamic study is called **system** and the rest of the Universe in its neighbourhood is known as **surroundings.**

The system may be water taken in a beaker, a balloon filled with air, an aqueous solution of glucose, a seed, a plant, a flower, a bird, animal cell etc**.**

For practical purposes the environment in the immediate vicinity of the system is called the surroundings. The boundary may be real or even imaginary

The system is separated from the surroundings by a real or imaginary **boundary** through which exchange of energy or matter may take place. This is illustrated in Fig.1.
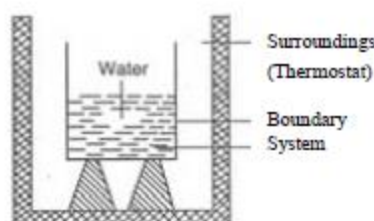
Fig. 1. Illustration of system, surroundings and boundary

Types of System

Homogeneous system: A system is said to be "homogeneous" if it consists of only one phase anduniform thought. Ex. a solution of sugar in water.

Heterogeneous system: When a system consists of two or more phases and is not uniform throughout it is called heterogeneous. Ex .Ice in water, chloroform in water.

Open system: A system which can exchange both energy and matter with the surroundings. Ex. beaker of water.

Closed system: A system which can exchange energy but not matter with the surroundings.Ex. Water in as stoppered bottle.

Isolated System: In system in which neither matter nor energy can exchange with its surroundings.
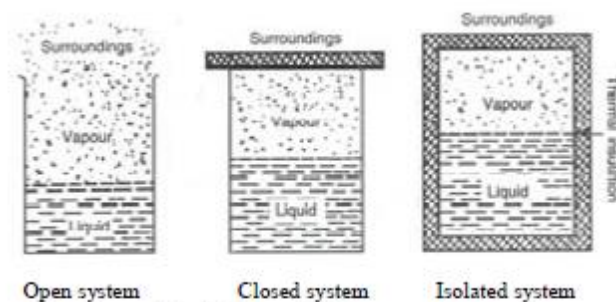
These are illustrated in the Fig.2.

Fig. 2. Types of systems

Properties of a system

The properties associated with a macroscopic system are called thermodynamic properties or variables.

Extensive properties: These are thermodynamic properties which depend on the quantity of matter specified in the system e.g. mass, volume energy etc.

Characteristics of an extensive property

- An extensive property of the entire system is greater than any of its smaller parts.
- The sum of the properties of subsystems is equal to the same property of the entire system. This means that the extensive properties are **additive.**

Intensive properties: These are thermodynamic properties which depend on characteristics of matter but independent of its amount e.g. pressure, temperature, viscosity, density melting point, boiling point etc.

Characteristics of an intensive property

- An intensive property of a homogeneous system is the same as that of any of its smaller parts.
- The intensive properties are non additive.

Illustration that volume is an extensive property but temperature is an intensive Property

Take 100 mL of water in a beaker (main system A) and note its temperature (say it is 25°C). Now divide water (the main system) into four parts as subsystems $A1$ (10 mL), $A2$ (20mL), $A3$ (30 mL), and $A4$ (40 mL). Here we observe that the volume of the main system A

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is larger than the volume of any individual subsystem. But the sum of the volumes ofsubsystems (10 mL + 20 mL + 30 mL+ 40 mL) is equal to the volume of the main system (100 mL). So *volume is an extensive property*.

Record the temperature of each subsystem. It is observed that the temperature of each subsystem*A1, A2, A3,* and *A4* is the same as it was for the main system. Therefore, *temperature is an intensive* property**.**

The ratio of two extensive properties is an intensive property. For example:

(1) Density is an intensive property

$$\frac{\text{Volume (extensive property)}}{\text{Mass (extensive property)}} = \text{Density (intensive property)}$$

(2) Molarity is an intensive property

Volume of solution (extensive property)/Mole of the solute (extensive property) = Molarity (intensive property)

Thermodynamic process:
The method by which the state of a system is changed is called a "Process". It can be affected by changing any one of the state variables *viz* P,T,C etc.

Isothermal process: It is a process carried out at constant temperature. Exchange of heat takes place between system and surroundings *dT = 0*

Adiabatic process: It is a process in which no exchange of heat takes place .The temperature of the system may increase or decrease during adiabatic process. *dQ =0*

Isobaric process: Carried out at constant pressure

Isochoric proces: Carried out at constant volume.

Reversible process

It is a process which takes place infinitesimally slowly so that the system is in thermodynamic equilibrium at any instant of the change. Since the process is carried out extremely slowly the properties of the system remain virtually unchanged and the direction

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maybe reversed by small change in a variable like temperature, pressure etc. The driving force is greater than the opposing force only by a infinitesimal quantity and hence the process would require infinite time for its completion.

Irreversible process

It is a process which takes place rapidly or spontaneously so that it is equilibrium with its surroundings. The driving force differs from the opposing force by a large amount and hence it cannot be reversed unless some external force is applied. All the natural process are irreversible.

Differences between reversible and irreversible process

Reversible Process	Irreversible process
Driving force and opposing force differ by small amount.	Driving force and opposing force differ by a large amount
It is a slow process	It is a rapid process
The work obtained is more	The work obtained is less
It is an imaginary process	It is a real process
5 It consists of many steps	It has only two steps i.e initial and final
It occurs in both the directions	It occurs in only one direction
It can be reversed by changing thermodynamic variables	It cannot be reversed

Illustrations of a reversible process

Let us consider a gas taken in a cylinder (Fig.3) which is fitted with a movable piston. Suppose that an external pressure (Pext) is applied on the gas by keeping sufficient quantity of sand grainson the piston. In this situation the pressure of the gas ($P1$) is balanced by the external pressure on the gas, that is, $P1 = P$ext

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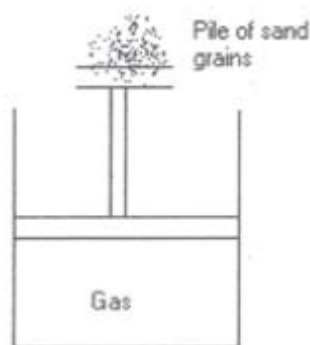COURSE CODE: 17CHU201   UNIT: I (Chemical Thermodynamics-First Law) BATCH-2017-2020

Fig. 3 Illustration of reversible process

Suppose that one grain of the sand is removed from the piston. The removal of the sand grainwill causes a very small decrease in the external pressure. Now the pressure of the gas becomes slightly greater than the external pressure. Because of this difference of pressure the gas will expand till the pressure of the gas becomes equal to the pressure on the gas. This expansion will result in an infinitesimally small work done by the gas on the surroundings.

The work is so small that no appreciable change is observed in the properties of the system or surroundings. On the other hand, if the same grain of sand is placed again on the piston, the external pressure will increase and the gas will be compressed to its initial stage. In this case also infinitesimally small work will be done by the surroundings on the system, which will not cause any appreciable change in the properties of the system and surroundings. Therefore, the change is said to be *reversible*. However, by removing the sand grains continuously from the piston (by lowering the pressure) the gas will expand by a definite volume

Irreversible process

A process is said to be *irreversible* if the change takes place in one direction. In an irreversible process the system cannot be brought back to its original state without affecting the surroundings. The entire natural changes are irreversible and hence spontaneous.

State variables of the system

A system can be described by its measurable properties such as temperature (T), pressure (P), volume (V) and amount (n = moles of various species present in the system). These measurable properties (T, P, V, n) are called *state variables*.

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Reason: If the state variables are fixed, the other properties of the system are also fixed. If the state variables are changed the properties of the system are accordingly changed. This implies that all the state variables are not independent. That is, the state of the system may be defined by fixing a certain minimum number of variables depending on the nature of the system.

State properties of the system and state functions

A property of the system which depends only on the state variables is called *state property* or state function. The change in a state property depends only on the initial and final states of the system. A state property is independent of the manner in which the change is brought about. This means that the state property does not depend on the path followed by the system. Thermodynamic properties namely energy *(U)*, enthalpy *(H)*, entropy (*S*), work function (*A*) free energy (G), volume *(V)*, pressure *(P)* and temperature (*T*) are state functions. A state function say energy (*U*) may be mathematically represented as $U = U (T, V, n)$. The mathematical representation is stated as *U* is a function of *T, V,* and *n*. That is, energy of the system depends on the state variables *T, V* and *n*. Similarly; volume of the system is a function of temperature (*T*), pressure *(P)* and amount *(n)*. That is, $V = V (T, P, n)$. For a system of constant composition (for a constant value of *n*) the volume of a gas is a function of temperature and pressure only i.e., $V = V (T, P)$.

We can understand the meaning of state functions and state property by taking an analogy. Suppose that one wants to climb a mountain peak l km above ground level. This decision defines the initial state (ground where $h = 0$) and the final state (peak where $h = h$). There may be various paths up to the mountain peak but the vertical height (*h*) of the peak from the ground is 1 km. The height of the mountain peak cannot be altered by choosing different paths though the actual distance travelled and the amount of work put in will be different if different paths are followed. Vertical distance in this analogy corresponds to a thermodynamic function.

Concept of internal energy, work and heat

Thermodynamics has been defined as the branch of science wherein we study the interconversions of heat, work and energy and various possible relations between these quantities. Therefore, it is essential to learn the meaning of these terms.

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Internal Energy: U or E

The energy stored in a substance by virtue of its constituent atoms and molecules is called Internal energy.It is the sum of vibrational energy, rotational energy, electronic energy etc.

Internal Energy change (ΔE)

It is the difference in the internal energies of initial and final states of the system.

$\Delta E = E_{final} - E_{initial}$

But for the chemical reactions

$\Delta E = E_{Products} - E_{Reactants}$

$\Delta E = E_P - E_R$

The total energy of all the molecules of the system is called *internal energy* or *intrinsic energy*. The internal energy is the cause of existence of various types of distinct substances. In thermodynamic studies one is more concerned with the change in internal energy (ΔU) rather than the absolute value of energy.

Importance of internal energy: The internal energy possessed by a substance differentiates it from other substances. For example, the allotropes of carbon namely graphite (C) and diamond (C), differ from each other because they possess different internal energies and have different structures. This is the reason that internal energy is also called *inherent energy* or *hidden energy* or more appropriately *intrinsic energy.*

Characteristics of internal energy

- Internal energy of a system is an *extensive* property. It depends on the amount of the substances present in the system. If the amount is doubled, energy is also doubled.
- Internal energy of a system is a *state property*. It depends only upon the state variables *(T,P, V, n)* of the system.
- The change in internal energy does not depend on the path by which the final state isreached.
- In a cyclic process, there is no energy change. ΔU (cycle) $= 0$

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Enthalpy or Heat content of a system (H)

It is "the heat content of the system: or "The sum of internal energy and pressure-Volume changework done) of s system , under a particular set of conditions"

Mathematically

$$H = E + PV$$

Unit: $KJ\ mol^{-1}$

Enthalpy change

It is the difference in the enthalpy of initial and final stages of the system.

$$\Delta H = H_{final} - H_{initial}$$

For the chemical reaction $\Delta H = H_P - H_R$

We know that $H = E + PV$

Then $\Delta H = E_2 + PV_2 - (E_1 + PV_1) = (E_2 - E_1) + P(V_2 - V_1)$

$$\Delta H = \Delta E + P\ \Delta V$$

At constant volume $\Delta V = 0$

$$\Delta H = \Delta E$$

There are three laws of thermodynamics: zeroth law, first law and second law.

Zeroth law of thermodynamics discusses about the thermal equilibrium between three bodies.

If two systems A and B are in thermal equilibrium with the system C, then A and B are in thermal equilibrium with each other..

First law of thermodynamics: (The law of conservation of energy)

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

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The mathematical form of **First law of thermodynamics** is

$$\Delta E = q - w$$

Where ΔE, q and w represent respectively the change in internal energy, quantity of heat supplied and work done. For a small change,

$$dE = dq - dw$$

Work done (dw) can be represented as PdV in terms of pressure-volume changes for the gas. i.e

$$dw = PdV$$

Path dependent function and its differential

A thermodynamic quantity is called a *path function* if its value depends on the path followed. For example, work done depends on the path followed by the system. For the same initial and final states of a system the work done is different under reversible and irreversible conditions as given below.

$$w_{reversible} \text{ (ideal gas)} = -2.303\, nRT \ln (P_1/P_2)$$

$$w_{irreversible} \text{ (ideal gas)} = - nRT \left(1- \frac{P_2}{P_1}\right)$$

It is clear from the above relations that w (reversible) $\neq$ w (irreversible)

Concept of work in thermodynamics

Work is a result of action against an opposing force. It is equal to the force multiplied by Displacement

$$w = -F \times \Delta x$$

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where$\Delta x$is the path length over which action is taken and F is the force against which work has to be done.

- If $F = 0$, then $w = 0$. That is, if there is no opposing force, then the motion itself cannot produce any work.
- If $\Delta x = 0$, then $w = 0$. That is, if there is no motion, even the strongest opposing force cannot generate any work.

Mechanical work involving gas

In a system when gases are involved, the mechanical work is equal to pressure (P)multiplied by change of volume (ΔV).

$$w = -F \times \Delta x$$

$$= \frac{F}{A} \times A \times \Delta x$$

$$= -P \times \Delta x$$

$$P = \frac{F}{A} = \text{Force per unit area} = \text{pressure}$$

$$\Delta V = A \times \Delta x = \text{Area} \times \text{displacement} = \text{change of volume}$$

Significance of minus sign in the expression $w = -P \times \Delta V$

- As per IUPAC recommendations the symbol w has to be used for work done on thesystem.
- During compression work is done on the system thus volume decreases and ΔV isnegative. Therefore, work done on the system is positive as is clear from the relation $w = -P \times \Delta V$
- During expansion volume increases and ΔV is positive so the work done on the system is negative as is clear from the relation $w = -P \times \Delta V$. But in this case work done by the system is positive during expansion as given by $-w = P \times \Delta V$.

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Characteristics of *w*

- A system does not possess any work. Work appears across the boundary duringchange only.
- The work is zero if there is no change.
- Work is path dependent quantity.
- Work is manifestation of energy.
- When work is done by the system its energy decreases.
- When work is done on the system its energy increases.

Expressions for work under different conditions

It has been stated that work is a path dependent quantity. It has different values if the change is brought under different experimental conditions. For example, for the changes between the same initial state and same final state of a system

(i) work done under isothermal condition is different from the work done underadiabatic condition.

(ii) work done under isothermal reversible condition is different from the work done under isothermal irreversible condition.

(iii) work done for free expansion is different from the work done under any otherCondition

(A) Work done under isothermal reversible condition

Let us consider *n* moles of a gas in a cylinder confined by a frictionless and weightless movable piston. Let us suppose that

Pext = External pressure acting on the gas

Pint = Internal pressure of the gas.

The change in the state of the gas will depend on the relative values of Pext and Pint. Thus

(a) When Pext>Pint the gas will be compressed

(b) When Pint >Pext the gas will expand

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When $P_{ext} = P_{int} \pm dP$, where dP is a small change in the pressure then the change isreversible. This type of situation is shown in Fig. 4. (a) for the expansion of a gas. In the figure the dotted lines show the position of the piston for a small volume change dV of the gas.
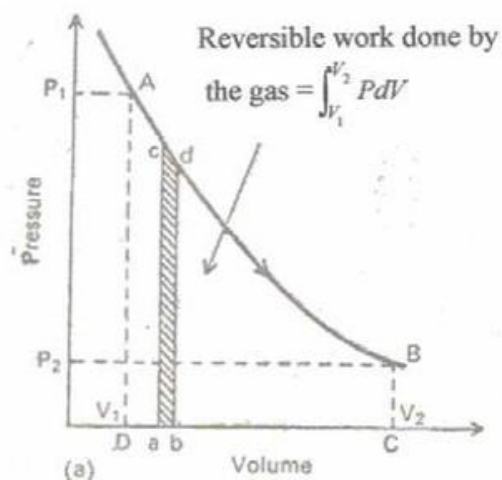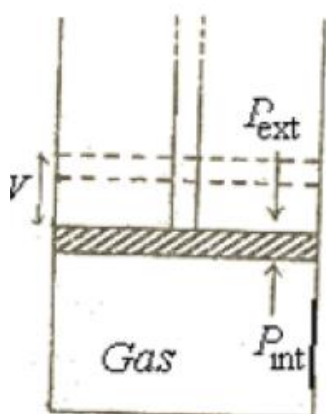

Fig. 4 (a) Reversible - isothermal expansion of an gas in a cylinder fitted with a movable piston expansion of an ideal gas.   Fig. 4 (b) Pressure versus volume ideal indicator diagram for reversible - isothermal

Work = Area ABCD

Calculation of work done for isothermal reversible process from *P* versus *V* indicator Diagram

When the change is isothermal and reversible the pressure and volume both are changed slowly so that equilibrium is maintained between the system and surrounding at each stage of the change. For such a process the variation of volume with pressure is shown by an indicator diagram in Fig. 4 (b).Suppose that the pressure is slightly lowered by dP(from c to d) so that there is infinitesimally small increase in volume by dV(from a to d). For such a small volume change.

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the small work done by the gas is given by

$$\bar{d}w \text{ (rev)} = (P - dP)\, dV$$

The change of pressure from point c to point d is very small as it is clear from the indicator diagram.

Therefore, it can be assumed that pressure on the gas $(P - dP)$ is very near to the pressure of the gas (P). That is,

$P - dP \approx P$ and thus work done by the gas is given by

$$-\bar{d}w \text{ (rev)} = P\, dV$$

From the indicator diagram it is seen that

$$P\, dV = ac \times ab = \text{Area of the thin strip abcd}$$

$$-dw(\text{rev}) = P\, dV = \text{Area abcd}$$

For a finite isothermal reversible change of state of the system, the total work done is equal to the sum of the areas of all such thin strips as *abcd*. Now the reversible change is very slow and continuous therefore, the work done by the gas is equal to the integral of *PdV*. Thus

$$-w(\text{rev}) = \int_{V_1}^{V_2} P dV = \text{Area ABCD}$$

Reversible work of expansion is the maximum work which can be obtained from a system.

(B) Work done under isothermal irreversible condition

Let us consider n moles of a gas in a cylinder confined by a frictionless and weightless movable piston. Let us suppose that the piston is held in position by a pin and the internal pressure of the gas is greater than the external pressure on the gas.

Concept of heat in thermodynamics

The change in the internal energy of the system due to difference of temperature of the system and its surroundings is called **heat**. The symbol of heat is q. Heat flows from higher temperature towards lower temperature. The energy of the system increases when it is brought into contact with the surroundings which is at a higher temperature. On the other

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hand, when the temperature of the system is higher than that of the surroundings the heat flows from the system to the surroundings and the internal energy of the system decreases.

Thus

When heat is absorbed by the system its energy increases. That is, ΔU is positive. Such a change is called *endothermic.*

When heat is given out by the system its energy decreases. That is, ΔU is negative. Such a change is called *exothermic.*

Characteristics of heat

1. A system does not possess any heat. It possesses only energy

2. The concept of heat comes into picture across the boundary during the change only.

3. If there is no difference of temperature between the system and surroundings there is no flow of heat.

4. Heat is a path dependent quantity.

5. Heat is manifestation of energy.

6. When heat flows into the system its energy increases.

7. When heat flows out of the system its energy decreases.

Sign conventions for heat (q)

When q has a positive value, then we say that heat is absorbed by the system from the surroundings. This change is endothermic

When q has a negative value, then we say that heat is given out by the system to the surroundings. This change is exothermic

Units of energy heat and work

The energy of a system is expressed as joules (J) or kilojoules (kJ). The change of energy is also expressed in J or kJ. Since heat and work are manifestation of energy, these are also expressed in the units of J or kJ.

Calories (cal) and kilocalories (kcal) are non-SI units of energy

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Characteristics of enthalpy

Enthalpy is an extensive property. Its value depends on the amount of the substances present in the system. Larger the amount larger is the value of *H*.

Enthalpy of a system is a state property. For a given amount of the system it depends only on the state variables (*T, P, V*). If the state variables are changed from *T*1, *P*1, *V*1 to *T*2, *P*2, *V*2 the enthalpy of a given amount (fixed *n*) of the system is changed from *H*1 to *H*2. The change in enthalpy is represented as*:*

$$\Delta H = H\,(T2,\ P2,\ V2) - H\,(\text{TI},\ P1,\ V1) \text{ when } n = \text{constant}$$

Since *T, P, V* are related by a suitable equation of state, out of *T, P, V,* if two are known the third is also known for a constant amount of the system. Therefore, enthalpy is considered as a function of *T* and *P* for a fixed amount, *i.e.,*

$$H = H\,(T,\ P)$$

and $$\Delta H = H\,(T2,\ P2) - H\,(TI,\ P1)$$

The change in enthalpy (ΔH) does not depend on the path by which the final state of the system is reached.

Sign conventions of ΔH

- When heat is absorbed by the system at constant pressure its enthalpy is increased so the value of *ΔH* is positive. When ΔH is positive, the process is said to be *endothermic*.
- When heat is liberated by the system at constant pressure its enthalpy is decreased so the value of ΔH is negative. When ΔH is negative, the process is said to be *exothermic*.

Heat capacity

The quantity of heat needed to cause unit rise in the temperature of a substance is called. Its *heat capacity*. It is denoted by symbol *C* and defined by

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$$\text{Heat capacity} = \frac{\text{Heat needed}}{\text{Increase of temperature}}$$

$$C = \frac{q}{\Delta T}$$

Units of heat capacity

Heat (q) is expressed in joules (J) and temperature in kelvin (K).

Therefore, heat capacity is expressed in the units of **joules per kelvin** (J K–1). Heat capacity is an extensive property because the heat needed to raise the temperature of the system depends on its size.

Calculation of thermodynamic properties from first law

(A) Calculation of w, q, ΔU and ΔH for isothermal and reversible changes in the states of an Ideal gas

Points to be remembered

Isothermal change: Temperature is constant

Reversible change: Change is slow but pressure and volume both are changed

Ideal gas: $PV = n\,RT$

(1) Calculation of w

For an infinitesimally small change in volume (dV) of a gas the small quantity of mechanical work (đw) is defined by

$$đw = -\,PdV$$

For an ideal gas $PV = nRT$ and $P = nRT/V$.

Thus

$$đw = -\,\frac{nRT}{V}\,dV = -\,nRT\,d\,ln\,V$$

For a finite reversible change of volume of a fixed amount of the gas from an initial volume of $V1$ to a final volume $V2$ at a constant temperature, the work is obtained by integrating

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equation (ii)

$$w = -nRT \int_{V_1}^{V_2} d \ln V$$

$$= -nRT \ln[V]_{V_1}^{V_2}$$

$$= -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2}$$

For an ideal gas at constant temperature, $P_1V_1 = P_2V_2$ and $V_2/V_1 = P_1/P_2$. Thus

$$w = -2.303 \, nRT \log \frac{P_1}{P_2} = 2.303 \, nRT \log \frac{P_2}{P_1}$$

The value of w can be calculated on substituting the values of *n, R, T, V₁,,V₂(or P₁, P₂)* in the above equation.

(2) Calculation of ΔU

The internal energy (U) of an ideal gas is a function of temperature only and isindependent of volume (***Joule's law***). Therefore, for an isothermal process when temperatureis constant internal energy of an ideal gas is also constant. Thus

$$U2 - U1 = \Delta U = 0 \dots \text{for an ideal gas at constant } T$$

(3) Calculation of q

From the first law of thermodynamics we have

$$\Delta U = q + w$$

For isothermal change, $\Delta U = 0$ for an ideal gas, therefore,

$$q = -w = 2.303 \, nRT \log \frac{V_2}{V_1} = 2.303 \, nRT \log \frac{P_1}{P_2}$$

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(4) Calculation of ΔH

Change of enthalpy = Final enthalpy – Initial enthalpy

$$\Delta H = H2 - H1$$
$$= (U2 + P2V2) - (U1 + P1V1)$$
$$= U2 - U1 + (P2V2 - P1V1)$$

For an ideal gas at constant temperature

$$U2 - U1 = \Delta U = 0$$

And $$P2V2 = P1V1$$

Therefore, $$\Delta H = 0$$

Summary: For isothermal reversible change of states of an ideal gas

$$(i) \quad w = -2.303 \, nRT \log \frac{V_2}{V_1} = -2.303 \, nRT \log \frac{P_1}{P_2}$$

$$(ii) \quad q = -w \quad (iii) \, \Delta U = 0 \quad and \quad (iv) \, \Delta H = 0$$

(B) Calculation of *w*, *q*, ΔU and ΔH for adiabatic and reversible changes in the states of an Ideal gas

Points to remember

Adiabatic change: $q = 0$
Reversible change: Change is slow and *T, P,* and V are changed
Ideal gas: $PV = n \, RT$

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(1) Calculation of q

The change is adiabatic, therefore, $q = 0$

(2) Calculation of ΔU

In adiabatic process there is change of temperature and for a small change of temperature (dT) the change of internal energy is given by

$$dU = C_V dT$$

For a finite change of temperature of a fixed amount of the gas from an initial value of $T1$ to a final value of $T2$ the change of internal energy is obtained on integrating equation.
Thus when Cv is constant

$$U2 - U1 = C\text{v} \, (T2 - T1)$$

Or, $\Delta U = C\text{v} \times \Delta T = n \, C\text{v}. \, \text{m} \times \Delta T$

Where, CV. m = molar heat capacity of the gas at constant volume and n is the amount of the gas

(3) Calculation of w

For a small change in volume (dV) of a gas the small quantity of mechanical work (dw) is given by d$w = - P dV$
For an ideal gas $PV = nRT$ and $P = nRT/V$. Thus

$$dw = -\frac{nRT}{V} \, dV$$

A direct calculation of work (w) is not possible because the integration of the above equations are difficult as in an adiabatic reversible process each one of T, P and V will change.

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Calculation of *w* from ΔU:

For adiabatic process $q = 0$ and first law of thermodynamic gives

$\Delta U = w$. Thus

$w = \Delta U = C\text{v} \times \Delta T = n\,C\text{v. m} \times \Delta T$

(4) Calculation of ΔH

$\Delta H = H2 - H1$

$= (U2 + P2V2) - (U1 + P1V1)$

$= (U2 - U1) + (P2V2 - P1V1)$

Since, $U2 - U1 = \Delta U = C\text{V}\,(T2 - T1)$

And $(P2V2 - P1V1) = (n\,RT2 - n\,RT1)$

Therefore,

$\Delta H = C\text{V}\,(T2 - T1) + n\,R(T2 - T1)$

$= (C\text{V} + n\,R)\,(T2 - T1)$

$= C\text{P}\,(T2 - T1)$

$= n\,C\text{P, m}\,(T2 - T1)$

Here,

$(C\text{V} + n\,R) = C\text{P} = n\,C\text{P. M}$

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POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is meant by a system in thermodynamics?

2. Point out the main differences between open, closed and isolated system

3. Point out the main differences between Reversible and irreversible process.

4. What do you understand by the state of a system. What are state variables

5. Define thermodynamics. What are its main objectives

6. Distinguish between State function and path function

7. Distinguish between Isothermal and adiabetic process

8. Define Zeroth law of thermodynamics.

9. Give in brief the objectives and limitations of thermodynamics

PART C (8 Mark Questions)

1. Derive an expression for the work done when a gas expands from volume V_1 to V_2 against external pressure P.

2. What are extensive and intensive variables. Give three examples of each of them.

3. State First Law of thermodynamics in two ways?   Derive its mathematical formulation.

4. Explain the fact that internal energy is a state function but work and heat are path functions.

5. Derive the relationship between the molar heat capacities C_v and C_v

6. Derive the expression for w, q, ΔU and ΔH when an ideal gas undergoes (i) isothermal reversible expansion (ii) isothermal irreversible expansion.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple Choice questions)

PHYSICAL CHEMISTRY II (CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS)

UNIT I

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	Which one of the following thermodynamic quantities is not a state function?	Gibbs free energy	work	entropy	internal energy	work
2.	At a constant temperature, an ideal gas is compressed from 6.0 liters to 4.0 liters by a constant external pressure of 5.0 atm. How much work is done on the gas?	w = +10 liter atm	w = -10 liter atm	w = +30 liter atm	w = -30 liter atm	w = +10 liter atm
3.	A system suffers an increase in internal energy of 80 J and at the same time has 50 J of work done on it. What is the heat change of the system?	+130 J	+30 J	-130 J	-30 J	+30 J
4.	A 5.000 g sample of methanol, CH_3OH, was combusted in the presence of excess oxygen in a bomb calorimeter conaining 4000 g of water. The temperature of the water increased from 24.000 oC to 29.765 oC. The heat capacity of the calorimeter was 2657 J/oC. The specific heat of water is 4.184 J/goC. Calculate E for the reaction in kJ/mol.	-314 kJ/mol	-789 kJ/mol	-716 kJ/mol	-121 kJ/mol	-789 kJ/mol

5.	A coffee cup calorimeter having a heat capacity of 451 J/oC was used to measure the heat evolved when 0.0300 mol of NaOH(s) was added to 1000 mL of 0.0300 M HNO3 initially at 23.000 oC. The temperature of the water rose to 23.639 oC. Calculate H (in kJ/mol NaNO3) for this reaction. Assume the specific heat of the final solution is 4.18 J/goC; the density of each solution is 1.00 g/mL; and the addition of solid does not appreciably affect the volume of the solution. $HNO_3(aq) + NaOH(s)$ $NaNO_3(aq) + H_2O(l)$	-63.7 kJ/mol	-151 kJ/mol	-2.55 kJ/mol	-98.6 kJ/mol	-98.6 kJ/mol
6.	The Ho for the following reaction at 298 K is -36.4 kJ. $1/2\ H_2(g) + 1/2\ Br_2(l)$ HBr(g) Calculate Eo at 298 K. The universal gas constant, R, is 8.314 J/mol K.	-35.2 kJ	+35.2 kJ	-36.4 kJ	-37.6 kJ	-37.6 kJ
7.	Calculate the amount of work done for the conversion of 1.00 mole of Ni to Ni(CO)4 in the reaction below, at 75oC. Assume that the gases are ideal. The value of R is 8.31 J/molK. Ni(s) + 4 CO (g)　　　Ni(CO)4(g)	1.80 x 103 J	8.68 x 103 J	-1.80 x 103 J	-8.68 x 103 J	8.68 x 103 J
8.	All of the following have a standard heat of formation value of zero at 25oC and 1.0 atm except:	N2(g)	Fe(s)	Ne(g)	H(g)	H(g)

9.	The entropy will usually increase when I. a molecule is broken into two or more smaller molecules. II. a reaction occurs that results in an increase in the number of moles of gas. III. a solid changes to a liquid. IV. a liquid changes to a gas.	I only	II only	III only	I, II, III, and IV	I, II, III, and IV
10.	The standard heat of combustion of ethanol, C2H5OH, is 1372 kJ/mol ethanol. How much heat (in kJ) would be liberated by completely burning a 20.0 g sample?	686 kJ	519 kJ	715 kJ	597 kJ	597 kJ
11.	Which statement is incorrect?	At constant pressure, H = E + PV	The thermodynamic symbol for entropy is S.	Gibbs free energy is a state function.	For an endothermic process, H is negative.	(d) For an endothermic process, H is negative.
12.	Which statement is false?	H is equal to E for the reaction:	The thermodynamic quantity most easily measured in a "coffee cup" calorimeter is H.	No work is done in a reaction occurring in a bomb calorimeter.	H is sometimes exactly equal to E.	H is equal to E for the reaction:
13.	Which of the following processes must violate the first law of thermodynamics? (There may be more than one answer!)	$W > 0$, $Q < 0$, and ?Eint $= 0$	$W > 0$, $Q < 0$, and ?Eint > 0	$W > 0$, $Q < 0$, and ?Eint < 0	$W > 0$, $Q > 0$, and ?Eint < 0	$W > 0$, $Q > 0$, and ?Eint < 0
14.	A spherical constant temperature heat source of radius r1 is at the center of a uniform solid sphere of radius r2. The rate at which heat is transferred through the surface of the sphere is proportional to	$r_{22} - r_{12}$	$r_2 - r_1$	$\ln r_1 - \ln r_2$	$1/r_2 - 1/r_1$	$r_{22} - r_{12}$
15.	What would be the most likely value for CT, the molar heat capacity at constant temperature?	0	$0 < CT < Cv$	$Cv < CT < Cp$	$CT = \infty$	0

16.	Which type of ideal gas will have the largest value for Cp – Cv?	Mono atomic	Diatomic	Polyatomic	The value will be the same for all.	The value will be the same for all.
17.	Consider the following processes that can be done on an ideal gas: constant volume, $\Delta V = 0$; constant pressure, $\Delta p = 0$; and constant temperature, $\Delta T = 0$. (a) For which process does W = 0? (b) For which process does Q = 0? (c) For which of these process does W + Q = 0? (d) For which of these process does $\Delta E_{int} = Q$?	$\Delta V = 0$	$\Delta p = 0$	$\Delta T = 0$	None of these	$\Delta V = 0$
18.	Consider an ideal heat pump and a perfect electric heater. The electric heater converts 100% of the electrical energy into heat energy; the heat pump converts 100% of the electrical energy into work, which then powers a Carnot refrigerator. Which is the more "efficient" way to heat a home? (Ignore maintenance or start-up costs.)	The electric heater is always more efficient.	The heat pump is always more efficient.	The heat pump is more efficient if the outside temperature is not too cold.	The heat pump is more efficient if the outside temperature is not too cold.	The heat pump is more efficient if the outside temperature is not too cold.
19.	A real engine operates at 75% of the efficiency of a Carnot engine operating betwen the same two temperatures. This engine has a power output of 100 W and discharges heat into the 27ºC low-temperature reservior at a rate of 300 J/s. what is the temperature of the high-temperature reservior?	27ºC	77ºC	127ºC	177ºC	127ºC
20.	A Carnot engine discharges 3 J of heat into the low temperature reservior for every 2 J of work output. (a) What is the efficiency of this Carnot engine?	01-Mar	02-May	03-May	02-Mar	01-Mar

21.	Which of the following is a consequence of the second law of thermodynamics?	Heat can flow only from high temperature to low temperature.	Objects in contact will tend to weird having the same temperature.	Any system that produces order from disorder must have	None of these	Any system that produces order from disorder must have
22.	A block of aluminum originally at 80° C is placed into an insulated container of water originally at 25℃. After a while the system reaches an equilibrium temperature of 31℃.	$\Delta S_{aluminum} > 0$	$\Delta S_{aluminum}$	$\Delta S_{aluminum} < 0$	None of these	$\Delta S_{aluminum} > 0$
23.	For which of the following process is the entropy change zero?	Isobaric	Isothermal	Adiabatic	Constant volume	Adiabatic
24.	How many microstates belong to the configuration of three particles in one container and seven in the other?	120	30240	3628800	6.3109	120
25.	A system is taken from state A to state B along two different paths 1 and 2. The heat absorbed and work done by the system along these paths are Q1 and Q2 and W1 and W2respectively. Then	Q1 = Q2	W1 + Q1 = Q2 + W2	W1 = W2	Q1 - W1 = Q2 - W2	Q1 - W1 = Q2 - W2
26.	When the gas expands under adiabatic condition, its temperature:	increases	decreases	does not change	none of the above	decreases
27.	In a reversible adiabatic change ΔS is	infinity	zero	equal to CvdT	equal to nRln V2/V1	zero
28.	If the temperature of source increases, the efficiency of a Carnot's engine:	decreases	increases	remains the same	may increase or decrease	increases
29.	If the temperature of the sink is decreased, the efficiency of a Carnot engine:	decreases	increases	remains the same	first increase and then decrease	increases
30.	Heat cannot flow by itself from a colder body to hotter body is a statement of:	2nd law of thermodynamics	conservation of momentum	conservation of mass	first law of thermodynamics	2nd law of thermodynamics
31.	A cycle consisting of one constant pressure, one constant volume and two isentropic processes is known as	Carnot cycle	Stirling cycle	Otto cycle	Diesel cycle	Diesel cycle

32.	The efficiency and work ratio of a simple gas turbine cycle are	low	very low	high	very high	very low
33.	The amount of heat required to raise the temperature of the unit mass of gas through one degree at constant volume, is called	specific heat at constant volume	specific heat at constant pressure	kilo Joule	none of these	specific heat at constant volume
34.	An adiabatic process is one in which	no heat enters or leaves the gas	the temperature of the gas changes	the change in internal energy is equal to the mechanical work done	all of the above	all of the above
35.	Which of the following is the lightest and most volatile liquid fuel?	Gasoline	Kerosene	Fuel oil	Petrol	Gasoline
36.	The processes occuring in open system which permit the transfer of mass to and from the system, are known as	flow processes	non-flow processes	adiabatic processes	none of these	flow processes
37.	Which of the following has the minimum atomic mass?	Oxygen	Sulphur	Nitrogen	Carbon	Carbon
38.	Work done in a free expansion process is	zero	minimum	maximum	positive	zero
39.	The pressure exerted by an ideal gas is _____ of the kinetic energy of all the molecules contained in a unit volume of gas.	one-half	one-third	two-third	three-fourth	two-third
40.	The compression ratio for petrol engines is	3 to 6	5 to 8	15 to 20	20 to 30	5 to 8
41.	The efficiency of Diesel cycle approaches to Otto cycle efficiency when	cut-off is increased	cut-off is decreased	cut-off is zero	cut-off is constant	cut-off is zero
42.	The atomic mass of oxygen is	12	14	16	32	16
43.	he ratio of specific heat at constant pressure (c_p) and specific heat at constant volume (c_v) is	equal to one	less than one	greater than one	none of these	greater than one
44.	Carbonization of coal consists of	drying and crushing the coal to a fine powder	molding the finely ground coal under pressure with or without a	heating the wood with a limited supply of air to temperature not less than 280°C	none of the above	none of the above

			binding material			
45.	If the value of $n = 0$ in the equation $pv^n = C$, then the process is called	constant volume process	adiabatic process	constant pressure process	isothermal process	constant pressure process
46.	The value of specific heat at constant pressure (c_p) is _____ that of at constant volume (c_v).	less than	equal to	more than	Zero	more than
47.	Which of the following is correct?	Absolute pressure = Gauge pressure + Atmospheric pressure	Gauge pressure = Absolute pressure + Atmospheric pressure	Atmospheric pressure = Absolute pressure + Gauge pressure	Absolute pressure = Gauge pressure - Atmospheric pressure	Absolute pressure = Gauge pressure + Atmospheric pressure
48.	Which of the following statement is incorrect?	The liquid fuels consist of hydrocarbons.	The liquid fuels have higher calorific value than solid fuels.	The solid fuels have higher calorific value than liquid fuels.	A good fuel should have low ignition point.	The solid fuels have higher calorific value than liquid fuels.
49.	Which of the following gas is mostly used in town for street and domestic lighting and heating?	Producer gas	Coal gas	Mond gas	Coke oven gas	Coal gas
50.	The value of gas constant (R) in S. I. units is	0.287 J/kgK	2.87 J/kgK	28.7 J/kgK	287 J/kgK	287 J/kgK
51.	The efficiency of Diesel cycle increases with	decrease in cut-off	increase in cut-off	constant cut-off	none of these	decrease in cut-off
52.	One kg of carbon monoxide requires _____ kg of oxygen to produce 11/7 kg of carbon dioxide gas.	All		11-Apr	09-Jul	04-Jul
53.	The absolute zero temperature is taken as	-273°C	273°C	237°F	-237°F	-273°C
54.	A series of operations, which takes place in a certain order and restore the initial conditions at the end, is known as	reversible cycle	irreversible cycle	thermodynamic cycle	none of these	thermodynamic cycle

55.	An isothermal process is governed by	Boyle's law	Charles' law	Gay-Lussac law	Avogadro's law	Boyle's law
56.	The sum of internal energy (U) and the product of pressure and volume ($p.v$) is known as	workdone	entropy	enthalpy	none of these	enthalpy
57.	The behavior of a perfect gas, undergoing any change in the variables which control physical properties, is governed by	Boyle's law	Charles' law	Gay-Lussac law	all of these	all of these
58.	A process of heating crude oil to a high temperature under a very high pressure to increase the yield of lighter distillates, is known as	cracking	carbonization	fractional distillation	full distillation	cracking
59.	The gas constant (R) is equal to the _____ of two specific heats.	sum	. product	. ratio	difference	difference
60.	When two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This statement is called	second law of thermodynamics	. Kelvin Planck's law	Zeroth law of thermodynamics	First law of thermodynamics	Zeroth law of thermodynamics
61.	In an irreversible process, there is a	no gain of heat	no loss of heat	loss of heat	. gain of heat	loss of heat

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UNIT II

SYLLABUS

Thermochemistry: Heats of reactions: standard states; enthalpy of formation and enthalpy of combustion and its applications; effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions.
Second Law: Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics. Calculation of entropy change for reversible and irreversible processes.

The branch of chemistry dealing with the measurement and computation of energy changes (ΔU) and enthalpy changes (ΔH) of various types of physical transformations and chemical reactions is called ***thermochemistry.*** Now ΔU and ΔH are related to the heat exchanged between the system and the surroundings, therefore, these properties are also called as **heat of reactions**.

Types of heat of a reaction

Depending on the experimental conditions the heat of a reaction is classified as follows.

When the reaction is performed at constant volume the accompanying energy change (ΔU) is called ***heat of reaction at constant volume*** (qv)

$\Delta U = q$v = Heat of reaction at constant volume

When the reaction takes place at constant pressure the accompanying enthalpy change $(\Delta.H)$ is called the ***heat of reaction at constant pressure***

$\Delta H = q$p = Heat of reaction at constant pressure

Since most of the experiments are performed at constant pressure, the enthalpy change (ΔH) *is* used to describe the thermal changes in various types of chemical reactions and physical transformations.

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Standard States

You have seen that a system is described by the state variables. In order to compare the energies for different compounds, a standard set of conditions is chosen. This refers to the condition of 1 bar pressure at any specified temperature, with a substance in its most stable form.

Standard enthalpy of formation ($\Delta fH\upsilon$)

Standard enthalpy of formation is defined as *the heat absorbed or liberated when one mole of a substance is formed from its constituent elements in their respective standard states.* Standard enthalpy of formation is denoted by $\Delta fH\upsilon$ .and it is called standard *heat of formation* also.

It is expressed in the units of kJ mol–1.

For example, the standard enthalpy of formation of water is – 285.8 kJ mol–1.

It is written as $\Delta fH\upsilon$ (H2O) = – 285.8 kJ mol–1.

This enthalpy change is described as follows:

$$H_2(g) + \tfrac{1}{2} O_2 (g) \longrightarrow H_2O (l) \qquad \Delta_f H^\upsilon (H_2O) = - 285.8 \text{ kJ mol}^{-1}$$
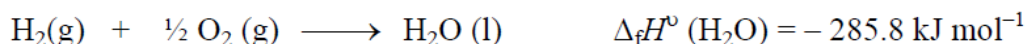
It is not always necessary to mention the standard conditions with the reactants and products in the balanced chemical equation, because $\Delta fH\upsilon$ itself tells that the value refers to standard state

Exothermic and Endothermic Reactions

Exothermic reactions are those reactions which proceed with the evolution of heat.

(i) Add a few cm3 of dilute hydrochloric acid in a test tube containing a few pieces of granulated zinc and observe the evolution of a gas. Feel the test tube. It would be hot.

(ii) You must have observed that when some water is added to quick lime to prepare white wash, a lot of heat is evolved.

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(iii) When a fuel like cooking gas or coal is burnt in air, heat is evolved besides light. Many chemical reactions lead to release of energy (heat) to the surroundings. We call these type of reactions as *exothermic reactions.*

Endothermic reactions are those reactions which proceed with the absorption of heat from the surroundings.

Let us now consider the following reactions:

(i) Add a small amount of solid ammonium chloride in a test tube half-filled with water. Shake and feel the test tube. It will feel cold.

(ii) Similarly repeat this experiment with potassium nitrate and feel the test tube, it will feel cold.

(iii) Mix barium hydroxide with ammonium chloride in small quantities in water taken in a test tube. Feel the test tube. It will be cold.

In all the above processes we see that heat is absorbed by the system from the surroundings. Such reactions are called *endothermic reactions.*
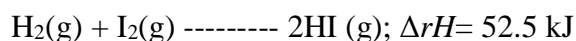
Enthalpy of reactions

The enthalpy of a reaction is defined as *the heat absorbed or liberated when the reactants are completely converted into products as represented by the balanced chemical equation at a given temperature and pressure.*

It is also called as the ***heat of reaction*** at constant pressure. Enthalpy of reaction is denoted by $\Delta rH$and expressed in the units of kJ mol^{-1}.

Let as denote total enthalpy of reactants as H reactants and total enthalpy of products as H products. The difference between these enthalpies, ΔH, is the enthalpy of the reaction

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$\Delta rH = H\text{products} - H\text{reactants}$

When Hproducts is greater than H reactants then ΔH is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,

$H_2(g) + I_2(g)$ --------- $2HI (g); \Delta rH = 52.5$ kJ

When Hproducts is less than Hreactants then ΔH is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example,

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O (l); \Delta rH = -890.4$ kJ
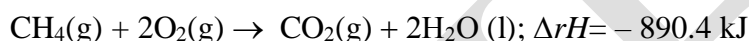
Enthalpy of a reaction changes with pressure and temperature. It is convenient to report enthalpies of the reactions in terms of standard state of substances as we have defined earlier. When substances are in their standard states, we call the enthalpy of reaction as *standard enthalpy of reaction*. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is denoted by $\Delta r H0$.

Enthalpy of formation ($\Delta fH°$)

The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $\Delta f H0$.

When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by $\Delta f H0$. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero.

For example:

$C (Graphite) + O_2(g) \rightarrow CO_2 (g) ; \Delta fH0 = -393.5$ kJ mol–1

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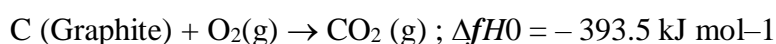
This means that carbon dioxide is formed from its elements in their most stable states. Carbon in the form of graphite and at room temperature and gaseous O_2 and CO_2 being at 1 bar.

Enthalpy of Combustion ($\Delta comb$ H°)

Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.

For example :

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) ; \Delta comb\ H^0 = -\ 1365.6\ kJ$$
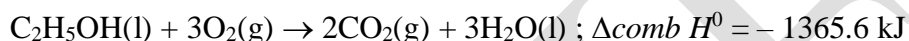
Enthalpy of combustion of C2H5OH(l) is – 1365.6 kJ mol^{-1}

Entropy concept - entropy change for an ideal gas.

Entropy:

Clausius introduced a new thermodynamic function called entropy. It is a measure of degree of disorder or randomness in a molecular system. It is also considered as a measure of unavailable form of energy.

The change in entropy ΔS of system is equal to the ratio of heat change 'q' to the temperature (T) of the reversible cyclic process.

$$\Delta S = \frac{q_{rev}}{T}$$

Unit: Cal /deg or $JK^{-1}\ mol^{-1}$

Significance of entropy:

Measure of disorder of the system: All spontaneous process are accompanied by increase in entropy as well as increases in the disorder .Increase in entropy implies increase in disorder.

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Measure of probability: An irreversible process tend to proceed from less probable state to more probable state. Since entropy increases in a spontaneous process, entropy may be defined as a function of probability of thermodynamic state.

Entropy and unavailable energy: When heat is supplied to the system, some portion of heat is used to do some work. This portion of heat is available energy. The remaining portion is called unavailable energy. Hence entropy is defined as unavailable energy per unit temperature.

$$Entropy = \frac{unavailable\ energy}{Temperature}$$

Entropy change for reversible and irreversible processes; entropy of phase transitions

Entropy change for a reversible (non spontaneous) process:

Consider an isothermal and reversible expansion of an ideal gas. If the system absorbs q amount of heat from the surroundings at temperature T, the increase in entropy of the system is given by

$$\Delta S_{system} = \frac{q}{T}$$

But the entropy of the surroundings decrease, because the surroundings loose the same of heat q i.e

$$\Delta S = \frac{-q}{T}$$

Hence, the net change in the entropy is given by

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$$\Delta S_{Total}= \Delta S_{System} + \Delta S_{surroundings}$$

$$\Delta S_{Total} = \frac{q}{T} + \left\{\frac{-q}{T}\right\}$$

$$\Delta S_{Total} = 0$$

i.e in a reversible isothermal process, there is no net change entropy.

Entropy change for a irreversible (spontaneous) process:

Consider a system maintained at higher temperature T1 and its surrounding maintained at a lower temperature T2.If q amount of heat passes irreversibly from the system to surrounding. then,

Decrease in entropy of the system,

$$\Delta S_{system} = \frac{-q}{T_1}$$

Increase in entropy of the surroundings.

$$\Delta S_{surroundings} = \frac{+q}{T_2}$$

Net change in entropy is given by

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$$

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$$\Delta S_{Total} = \frac{-q}{T_1} + \frac{q}{T_2}$$

$$= q \left| \frac{T_1 - T_2}{T_1 T_2} \right|$$

$$\text{Since } T_1 > T_2 : T_1 - T_2 \text{ is positive}$$

$$\Delta S_{Total} > 0$$

In an irreversible process the entropy of the system increases

Thermodynamic scale of temperature

Lord Kelvin defined the thermodynamic scale of temperature by assigning the triple point of water exactly equal to 273.16 K. On this scale one kelvin (1 K) is defined as the fraction 1/273.16 of the thermodynamic temperature of triple point of water. This temperature can be conveniently realized, maintained and measured in the laboratory. The measurement of temperature is independent of the method followed. That is, the temperature of a system is the same whether it is measured using a mercury thermometer or thermocouple or thermistor. The temperature on thermodynamic scale (kelvin scale) is always positive. There is no negative value of temperature on kelvin scale.

Comments: Triple point of water is the state when the three phases of water namely, solid (ice), liquid (water) and gas (vapour) exist together in equilibrium. The triple point of water is 273.16 K, which is greater than its melting point.

Zero value of kelvin temperature in terms of efficiency of Carnot cycle

Zero value of kelvin temperature is defined in terms of the efficiency (which isindependent of the working substance in the cycle) of Carnot cycle as

$$T_1 = T_2 (1 - \eta)$$

When $\eta = 1$

$$T_1 = T_2 (1 - 1) = 0 \text{ K}$$

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That is, the efficiency of the Carnot cycle is unity if the temperature of the surroundings (sink) is 0 K. In other words, we may state that the lowest temperature of thermodynamic scale corresponds to unit efficiency of Carnot cycle. This lowest temperature is written as $T = 0$ K which is equal to $-273.16\ ^{o}$C.

Temperature dependence of reaction enthalpy (Kirchhoff's equation)

Statement Variation of reaction enthalpy ($\Delta_r H$, heat of reaction) with temperature is called *Kirchhoff's equation.* It is stated as follows

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \Delta_r C_P$$

$$\mathrm{d}\Delta_r H = \Delta_r C_p\,\mathrm{d}T \qquad \text{at constant pressure}$$

Where

$\Delta_r H$= reaction enthalpy (heat of reaction at constant pressure)

and $\Delta_r C_p$ = reaction heat capacity at constant pressure

$$= \Sigma\ C_p(\text{products}) - \Sigma C_p\ (\text{reactants})$$

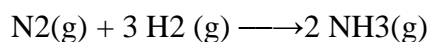Similarly, for the heat of reaction at constant volume the Kirchhoff's equation is given by

$$\mathrm{d}\Delta_r U = \Delta_r C_V \mathrm{d}T \text{ at constant volume}$$

Relevance of Kirchhoff's equation

Standard enthalpy of reaction (heat of reaction at 298K and at 1 bar) is calculated using the standard enthalpy of formation data of reactants and products given in the International tables. But when it is required to find the enthalpy of reaction at other temperatures then we use Kichhoff's equation.

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Derivation of Kirchhoff's equation

Let us consider a familiar reaction of synthesis of ammonia from nitrogen and hydrogen as represented by chemical equation

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

The standard enthalpy of this reaction is given by

$$\Delta_r H^0 = 2 \times H_m^{\Theta}(NH_3) - [H_m^{\Theta}(N_2) + 3 \times H_m^{\Theta}(H_2)]$$

On differentiating the above equation with respect to T at constant P, we get

$$\left(\frac{\partial \Delta_r H^{\Theta}}{\partial T}\right)_P = 2\left(\frac{\partial H_m^{\Theta}(NH_3)}{\partial T}\right)_P - \left[\left(\frac{\partial H_m^{\Theta}(N_2)}{\partial T}\right)_P + 3\left(\frac{\partial H_m^{\Theta}(H_2)}{\partial T}\right)_P\right]$$

By definition

$$\left(\frac{\partial H_m^{\Theta}}{\partial T}\right)_P = C_{p,m}^{\Theta} = \text{Standard molar heat capacity at constant pressure}$$

Therefore, $$\left(\frac{\partial \Delta_r H^{\Theta}}{\partial T}\right)_P = 2\,C_{p,m}^{\Theta}(NH_3) - [C_{p,m}^{\Theta}(N_2) + 3\,C_{p,m}^{\Theta}(H_2)]$$

$$= \Sigma\,C_p^{\Theta}\,(\text{products}) - \Sigma\,C_p^{\Theta}\,(\text{reactants})$$

$$= \Delta_r C_p^{\Theta}$$

Or, $$d\,\Delta_r H^0 = \Delta_r C_p^{\Theta}\,dT$$

It is differential form of Kirchhoff's equation

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SECOND LAW OF THERMODYNAMICS

Limitations of the first law of thermodynamics and Need of the second law

The first law of thermodynamics enables us to compute the energy changes (ΔU) and enthalpy changes (ΔH) for different types of chemical reactions and physical transformations. But this law is not capable of predicting the direction of a process. From the first law of thermodynamics we cannot get the answers of the following type of questions:

• Why do changes take place in a particular direction?
• How and why the systems are aware to proceed only in the particular direction?
• What are the driving forces which lead the process in a given direction?

Therefore, to answer such questions we need a second law of thermodynamics. This law introduces the concept of entropy and the methods of evaluating entropy changes which in turn act as driving force for spontaneous processes in isolated systems.

Different statements of the second law of thermodynamics

The second law of thermodynamics has been stated in different ways. But each statement is related to human experiences and is in agreement with experimental observations.

1. Heat cannot spontaneously pass from a colder to a warmer body. – *R.J.E. Clausius*

2. Every system left to itself changes rapidly or slowly in such a way to approach definite final state of rest. No system of its own will change away from the state of equilibrium except through the influence of external agencies –*G. N. Lewis*

3. Entropy is time's arrow. –*A. Edington*

4. The state of maximum entropy is the most stable state for an isolated system. –*Enrico Fermi*

5. In an irreversible process the total entropy of all bodies concerned is increased. –*G.N.*

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Lewis

6. The entropy function of a system of bodies tends to increase in all possible processes occurring in nature, if we include in the system all such bodies which are affected by the changes. – *M.N. Saha*

7. There exists a characteristic thermodynamic property called entropy. The difference in entropies of the system in states 1 and 2 is given by

$$S_2 - S_1 = \int \frac{dq_{rev}}{T} \qquad \text{over a reversible path}$$

$$S_2 - S_1 > \int \frac{dq_{irr}}{T} \qquad \text{over an irreversible path}$$

The entropy is property of state only. Its value for an isolated system never decreases. – *R. E. Gibson*

Concept of entropy

Entropy is a Greek word which stands for *trope* meaning chang*e;* a prefix 'en' is written to identify it as a thermodynamic property which belongs to the family of energy and enthalpy. This term was introduced by Clausius. He denoted entropy by the symbol S in the honour of Sadi Carnot (S from *Sadi).*

We know that energy is defined as the capacity of a system to do work. But entropy of a system is considered as an index of exhaustion of its capacity to do work. Thus entropy is a measure of unavailable portion of energy. On this basis entropy has been used to represent randomness. Greater is the randomness larger is the value of entropy. More regular is the molecular arrangement lower is the value of entropy. Thus, the entropy of a substance in gaseous state is greater than in the liquid state and that is greater than in its solid state. That is,

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S (gas) >*S* (liquid) >*S* (solid)

Characteristics of entropy

1. Entropy is an extensive property. Its value depends upon the amount of the substances present in the system.

2. Entropy of a system is a state function. It depends only on the state variables *(T, P, V, n)*. Thus, the change of entropy is given by $\Delta S = S$ (final) – S (initial)

3. Entropy change of system (ΔS system) does not depend on the path followed by the change,
but the entropy change of the surroundings (ΔSsurronnd1ngs) depends upon the path.

4. The total entropy change of an isolated system is equal to the sum of the entropy change of system and the entropy change of the surroundings.

$$\Delta S \text{ total} = \Delta S\text{system} + \Delta S\text{surroundings}$$

The total entropy change of an isolated system is also called the entropy change of the *univers*e (ΔSuniverse)

5. In a reversible process ΔSsystem = – ΔSurroundings

6. In an irreversible process $\Delta.S$ total > 0. This implies that in spontaneous changes there is increase of entropy of universe.

Entropy is the ratio of heat and temperature. Since heat is expressed as joule (J) and temperature is expressed in kelvin (K), therefore, the entropy and change in entropy is expressed as Joules per kelvin ≡J K–1

Notes
(i) If the amount of the substance is one mole, then entropy and its changes are expressed as joules per kelvin per mole (J K–1 mol–1).
(ii) Calories per kelvin = cal K–1 is the non-SI unit of entropy.

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Background of using $d\mathrm{S} = \dfrac{dq_{\mathrm{rev}}}{T}$ *as definition of entropy change of the system*

POSSIBLE QUESTIONS
PART B (2 Mark Questions)

1. What is meant by enthalpy of formation

2. Define enthalpy of combustion

3. What is meant by calorific value of foods and fuels.

4. What is meant by thermochemistry.

5. Briefly explain the terms enthalpy and enthalpy change. Is it intensive or extensive property.

6. State standard enthalpy of formation.

7. Explain the term entropy. Show that it is a state function.

8. What is meant by a thermochemical equation.

9. What is the unit of entropy.

PART C (8 Mark Questions)

1. Derive thermodynamically Kirchoff's equation

2. What is meant by enthalpy of combustion. How it is determined. What are its applications.

3. Explain that in a reversible process, there is no net entropy change.

4. What is meant by thermodynamic scale of temperature.

5. State and explain various statements of second law of thermodynamics.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple Choice questions)

PHYSICAL CHEMISTRY II (CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS)

UNIT II

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1.	What is the correct order, from highest to lowest molar heat value, for the three types of energy change?	Chemical, phase, nuclear	Phase, chemical, nuclear	Nuclear, phase, chemical	Nuclear, chemical, phase	Nuclear, chemical, phase
2.	Which metal requires the most energy to raise 1.00 g of it by 1.00°C? (Refer to Chemistry Data Booklet.)	Aluminum	Copper	Lead	Nickel	Aluminum
3.	What is the specific heat capacity of a substance if 2.41×10^4 J are needed to change the temperature of 105.0 g of it from 25.0°C to 250.0°C?	1.02 x 10-4 J/g°C	9.18 x 10-4 J/g°C	0.918 J/g°C	1.02 J/g°C	1.02 J/g°C
4.	Which statement about enthalpy is true?	Heat is given off to the surroundings in endothermic reactions.	Some substances have a negative specific heat capacity.	Specific heat capacity is the same for all liquids	The sign of ΔH is always negative in exothermic reactions	The sign of ΔH is always negative in exothermic reactions
5.	What happens to the value of ΔH for a thermochemical reaction if the reaction is reversed?	ΔH has the same numerical value, and the sign changes	ΔH has the same numerical value, and the sign remains the same	ΔH is the reciprocal of the original value, and the sign changes	ΔH is the reciprocal of the original value, and the sign remains the same	ΔH has the same numerical value, and the sign changes
6.	Which is an exothermic process?	Ice melting	Water boiling	. Water evaporating	Water vapour condensing	Water vapour condensing

#	Question					
7.	Which statement correctly describes an endothermic chemical reaction?	The products have higher potential energy than the reactants, and the ΔH is negative.	The products have higher potential energy than the reactants, and the ΔH is positive.	The products have lower potential energy than the reactants, and the ΔH is negative.	The products have lower potential energy than the reactants, and the ΔH is positive.	The products have higher potential energy than the reactants, and the ΔH is positive.
8.	Using the data below, what is the order of changes that occur when ethanol is heated from -25.0°C to 85.0°C?	Phase change, temperature change	Phase change, temperature change, phase change	Temperature change, phase change	Temperature change, phase change, temperature change	Temperature change, phase change, temperature change
9.	Which statement best describes the formation of methanol, $CH_3OH(l)$, from the elements?	It is endothermic and heat is absorbed	It is exothermic and heat is released.	It is exothermic and heat is absorbed.	It is exothermic and heat is released.	It is exothermic and heat is released.
10.	Which process results in the greatest endothermic change for 10.0g of H_2O?	Condensation	Melting	Solidification	Vaporization	Vaporization
11.	A small sample released 2.0 x 10^{10} kJ of energy while undergoing a change. What type of change most likely occurred?	Chemical	molecular	nuclear	physical	nuclear
12.	A substance increases in temperature by 255°C when a 983 g sample of it absorbs 83 200 J of heat. What is the specific heat capacity of the substance?	0.332 J/g°C	0.450 J/g°C	21.6 J/g°C	321 J/g°C	0.332 J/g°C
13.	What is the ΔH value for an exothermic energy change?	Always negative	Always positive	Could be positive or negative	Depends on the potential energy of the reactants	Always negative
14.	How much heat is required to vapourize 15.8 g $CH_3OH(l)$ at its boiling point? (ΔH_{vap} = 38.0 kJ/mol)	2.41 kJ	18.8 kJ	77.0 kJ	600. kJ	18.8 kJ

15.	Which of the following statements is true?	In an endothermic process heat is transferred from the surroundings to the system.	In an exothermic process heat is transferred from the surroundings to the system.	The surroundings will feel cooler in an exothermic process.	The surroundings will feel warmer in an endothermic process.	In an endothermic process heat is transferred from the surroundings to the system.
16.	Which of the following processes is exothermic?	Ether evaporating	Ice melting	Steam condensing	Water decomposing	Steam condensing
17.	As energy is added to a substance, the temperature remains constant. How may the substance be changing?	From a gas to a solid	From a liquid to a gas	From a liquid to a solid	In the amount of kinetic energy	From a liquid to a gas
18.	The addition of 9.54 kJ of heat is required to raise the temperature of 225.0 g of a liquid hydrocarbon from 20.5°C to 45.0°C. What is the heat capacity of this hydrocarbon?	0.94 J/g°C	1.73 J/g°C	1.88 J/g°C	9.42 J/g°C	1.73 J/g°C
19.	The ability to produce heat or do work	enthalpy	Energy	Potential	Heat	Energy
20.	Energy stored because of its composition	Kinetic	Potential	enthalpy	Combustion	Potential
21.	State change from solid to liquid	condensation	vaporization	boiling	Fusion	Fusion
22.	State change from liquid to gas	Combustion	vaporization	condensation	Fusion	vaporization
23.	Heat of enthalpy is a positive number	reaction is exothermic	reaction is potential	reaction is endothermic	reaction is kinetic	reaction is endothermic
24.	System plus the surroundings	Energy	Heat	Universe	enthalpy	Universe
25.	The SI unit for energy	calorimeter	joule	calorie	enthalpy	oule
26.	If the enthalpy change for 1 mole of water is 6.01, what is the change for 2 moles of water?	6.01	60.1	3.005	12.02	12.02

27.	If the enthalpy change for 1 mole of water is 6.01, what is the change for 3 moles of water?	18.03	18.04	18.02	18	18.03
28.	The heat required to melt one mole of a solid substance	enthalpy of combustion	enthalpy of vaporization	enthalpy of fusion	enthalpy of sublimation	enthalpy of fusion
29.	When the three types of energy changes are arranged in order of decreasing molar heat values, what is the correct order?	chemical, phase, nuclear	nuclear, phase, chemical	nuclear, chemical, phase	phase, chemical, nuclear	nuclear, chemical, phase
30.	The temperature remains constant as energy is added to a substance. How may the substance be changing?	from a gas to a solid	from a liquid to a gas	from a liquid to a solid	in the amount of kinetic energy	from a liquid to a gas
31.	Which metal requires the most energy to raise 1.00 g of it by 1.00°C?	aluminum	copper	lead	nickel	aluminum
32.	A substance has a molar heat of combustion of –810.4 kJ/mol. When 0.285 mol of the substance is burned in a calorimeter containing 8.60 kg of water, what is the increase of the water temperature?	0.156°C	6.41°C	7.89°C	12.8°C	6.41°C
33.	The addition of 9.54 kJ of heat is required to raise the temperature of 225.0 g of a liquid hydrocarbon from 20.5°C to 45.0°C. What is the heat capacity of this hydrocarbon?	0.94 J/g•°C	1.73 J/g•°C	1.88 J/g•°C	9.42 J/g•°C	1.73 J/g•°C
34.	If the molar heat of fusion of sodium is 2.63 kJ/mol, how much energy is needed to melt	2.63 kJ	2.93 kJ	20.6 kJ	473 kJ	20.6 kJ

	180.0 g of solid sodium at its melting point?					
35.	Which process is exothermic?	the boiling of liquid nitrogen	the freezing of water	the sublimation of dry ice	the vaporization of water	the freezing of water
36.	Which statement correctly describes the energy changes that take place when a solid changes to a liquid at constant temperature?	The potential energy increases, and the kinetic energy remains constant.	The potential energy remains constant, and the kinetic energy increases	The potential energy decreases, and the kinetic energy decreases	The potential energy increases, and the kinetic energy decreases	The potential energy increases, and the kinetic energy remains constant
37.	Why does warm water have a more rapid rate of evaporation than cold water?	It has a higher viscosity..	Its molecules have a higher average kinetic energy.	Its molecules have more attraction for one another.	D. More of its molecules have nearly the same kinetic energy	Its molecules have a higher average kinetic energy.
38.	If the heat of fusion of a substance is 20 kJ/mol, what heat is released when 1.0 mol of liquid at the melting point freezes?	10 kJ	20 kJ	40 kJ	80 kJ	20 kJ
39.	What does it mean if the ΔH value for a chemical reaction is positive?	kinetic energy is increasing in the system	potential energy is decreasing in the system	products have less potential energy than reactants	Reactants have less potential energy than products.	Reactants have less potential energy than products.
40.	During the production of a small amount of material, there is a large decrease in the temperature of the water in the calorimeter. What is the ΔH for the reaction?	large and positive	small and negative	small and positive	large and negative	large and positive
41.	What is 4.18 J?	The heat required to raise the temperature of one gram of water by one Celsius degree.	The heat required to raise the temperature of one mole of water by one Celsius degree.	The heat required to raise the temperature of one gram of substance by one Celsius degree.	The heat required to raise the temperature of one mole of substance by one Celsius degree.	The heat required to raise the temperature of one gram of water by one Celsius degree.

42.	What is a positive molar heat of formation?	The heat absorbed when one mole of compound is formed from its elements.	The heat released when one mole of compound is formed from its elements.	The heat absorbed when one mole of elements is formed from the compound.	The heat released when one mole of elements is formed from the compound.	The heat absorbed when one mole of compound is formed from its elements.
43.	What change is probably happening when energy is added to a substance, but the substance's temperature does not rise?	gas to liquid	gas to solid	liquid to gas	liquid to solid	liquid to gas
44.	What occurs when solid A (50ºC) is placed in contact with solid B (80ºC)?	Heat energy flows from A to B as the average kinetic energy of the particles in A decreases.	Heat energy flows from A to B as the average kinetic energy of the particles in A increase.	Heat energy flows from B to A as the average kinetic energy of the particles in B decreases.	Heat energy flows from B to A as the average kinetic energy of the particles in B increases.	Heat energy flows from B to A as the average kinetic energy of the particles in B decreases.
45.	What characteristic(s) of water change(s) when its temperature is raised from 10ºC to 110ºC at standard pressure?	both kinetic and potential energy	intramolecular bonding only	kinetic energy only	potential energy only	both kinetic and potential energy
46.	What happens to the water in a calorimeter when an exothermic reaction occurs in it?	It absorbs heat, and a drop in temperature is observed.	It absorbs heat, and a rise in temperature is observed.	It releases heat, and a drop in temperature is observed.	It releases heat, and a rise in temperature is observed.	It absorbs heat, and a rise in temperature is observed.
47.	Which is true for an exothermic reaction?	The ΔH is positive.	The products have less potential energy than the reactants.	The reactants have more kinetic energy than the products.	The reactants are below the products in the potential energy diagram.	The products have less potential energy than the reactants.
48.	What is one result of a solid-liquid phase change?	A change in a substance's chemical bonding.	A change in a substance's mass.	A change in a substance's kinetic energy.	A change in a substance's potential energy.	A change in a substance's potential energy.
49.	At standard pressure, which is an example of a change in kinetic energy only?	carbon dioxide cooling from –80ºC to –100ºC	molten aluminum solidifying at 660ºC	steam condensing at 100ºC	water decomposing above 1 x 107ºC	carbon dioxide cooling from –80ºC to –100ºC

50.	Which statement is true?	An endothermic reaction is characterized by a negative value of ΔH.	An exothermic reaction transfers heat to the surroundings.	Heat is evolved when an endothermic reaction occurs.	The reaction vessel cools when an exothermic reaction occurs.	An exothermic reaction transfers heat to the surroundings.
51.	Which processes are exothermic? 1. boiling water 2. freezing water 3. condensation of steam 4. melting ice	1 and 3	1 and 4	2 and 3	2 and 4	2 and 3
52.	Which statement correctly describes an endothermic chemical reaction?	The products have higher potential energy than the reactants, and ΔH is negative.	The products have higher potential energy than the reactants, and the ΔH is positive.	The products have lower potential energy than the reactants, and the ΔH is negative.	The products have lower potential energy than the reactants, and the Δ H is positive.	The products have higher potential energy than the reactants, and the ΔH is positive.
53.	A small sample released 2.0 x 1010 kJ of energy while undergoing a change. What type of change most likely occurred?	chemical	molecular	nuclear	physical	nuclear
54.	A chemical reaction that absorbs heat from the surroundings is said to be _____ and has a _____ DH at constant pressure.	endothermic, positive	endothermic, negative	exothermic, negative	exothermic, positive	endothermic, positive
55.	If ?H value is less than zero than reaction will be	Exothermic	Endothermic	May be Exothermic or Endothermic	may not be Exothermic or Endothermic	Exothermic
56.	If internal energy of the system is increased	Change in state of the system is increased	Temperature of the system may rise	Chemical reaction may take place	All	All
57.	Which is true for a spontaneous endothermic	H<0	G<0	S<0	G>0	G<0

	process?					
58.	A reaction has values of ?H and ?S which are both positive. The reaction	Is spontaneous	Has an increasing free energy	Spontaneity is temperature dependent	Is non-spontaneous	Is non-spontaneous
59.	_____ is study about energy of a chemical system	thermochemistry	chemical kinetics	thermodynamics	stoichiometry	thermochemistry
60.	The environment in which a system is studied is	State function	surrounding	phase	state	phase
61.	Total energy of a system is	P.E + K.E	K.E + heat energy	P.E + heat energy	P.E + mechanical energy	P.E + K.E
62.	Mathematical form of first law of thermodynamics is	H=qp	E = q x v	E = q + W	q = E + W	E = q + W

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UNIT III

SYLLABUS

Third Law: Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules. Free Energy Functions: Gibbs and Helmholtz energy; variation of S, G, A with T, V, P; Free energy change and spontaneity. Relation between Joule-Thomson coefficient and other thermodynamic parameters; inversion temperature; Gibbs-Helmholtz equation; Maxwell relations; thermodynamic equation of state.
Systems of Variable Composition**:** Partial molar quantities, dependence of thermodynamic parameters on composition; Gibbs Duhem equation, chemical potential of ideal mixtures, change in thermodynamic functions in mixing of ideal gases.

Free energy and work function –concepts.

In order to find out the spontaneity of a process, we have to see the change in entropy of the system aswell as surroundings .It is difficult to find out entropy of the surrounding everytime. So new thermodynamic functions are introduced , which can be determined more conveniently.

1.Helmholtz free energy A or Helmholtz work function

2.Gibbs free energy G or free energy

Helmholtz free energy or work function A

The work function A is defined as A =E–TS

E- Energy content of the system

T- Absolute temperature

S- Entropy

For small change

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$$\Delta A = \Delta E - T\Delta S$$

By definition $\Delta S = \dfrac{q_{rev}}{T}$

$$\Delta A = \Delta E - q_{rev} \quad (1)$$

According to I law of thermodynamics

$$\Delta E = q_{rev} - w \quad (2)$$

Using 1 and 2 we get

$$\Delta A = - w_{rev}$$

- $\Delta A = W_{max}$

Thus the decrease in function A gives the maximum work that can be obtained during an isothermal and reversible change. W represents the total work i.e expansion, electrical work etc. so it is also called work function.

Gibbs free energy:

It is isothermally available energy present in the system

It is defined as $G = H - TS$

G – available energy

H – total energy

TS – unavailable energy

For a small change,

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$$\Delta G = \Delta H - T\Delta S$$

But $\Delta H = \Delta E + P\Delta V$

$$\therefore \Delta G = \Delta E + P\Delta V$$

By definition $\Delta A = \Delta E - T\Delta S$

$$\Delta G = \Delta E - T\Delta S + P\Delta V$$

$$\Delta G = \Delta A + P\Delta V$$

For reversible isothermal change.

$$\Delta A = -W_{max}$$

$$\Delta G = -W_{max} + P\Delta V \ \text{Or} \ -\Delta G = W_{max} - P\Delta V$$

For reversible isothermal change.

$$\Delta A = -W_{max}$$

$$\Delta G = -W_{max} + P\Delta V \ \text{Or} \ -\Delta G = W_{max} - P\Delta V$$

Where $P\Delta V$ is work of expansion

$$-\Delta G = W_{max} - W_{expansion}$$

$$W_{max} - W_{expansion} = \text{net or useful work}$$

$$-\Delta G = W_{useful}$$

The decrease of free energy of a process at constant temperature and pressure is useful work obtainable from the system.

Standard free energy change (ΔG)

The free energy change for a process at 25°C in which the reactants are converted into products in their standard states

Thus. $\Delta G^o = \sum G^0 (products) - \sum G^0 (reactants)$

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Gibbs –Helmholtz equation (in terms of free energy and enthalpy)

(Relation between ΔG and ΔH)

Free energy (G) is related with enthalpy (H) as

$\quad G = H - TS$ -------------------------------------- (1)

Enthalpy (H) is related with internal energy (E) as

$\quad H = E + PV$ ------------------------(2)

$\quad \therefore G = E + PV - TS$ ---------------(3)

Upon differentiation.

$\quad dG = dE + PdV + VdP - TdS - SdT$ --------------(4)

The first law of thermodynamics equation for an infinitesimal change may be written as

$\quad dq = dE + dW$-----------------(5)

If work done ,dW is only due to expansion than

$\quad dq = dE + PdV$-----------------(6)

For reversible process $dS = \dfrac{dq}{T}$ or $TdS = dq$

$\quad TdS = dq = dE = PdV$-----------------(7)

$\quad TdS = dq = dE = PdV$-----------------(7)

Combining (4) and (7) we get

$\quad dG = dE + PdV + VdP - (dE + PdV) - SdT$

$\quad dG = VdP - SdT$-----------------(8)

At constant pressure $dP = 0$ and the above equation 8 becomes

$\quad dG = -SdT$

$\qquad$ or

$\left(\dfrac{\partial G}{\partial T}\right)_P$ = -S -----------------(9)

Substituting   (9) in (1)

$\quad G = H - TS$

$\quad G = H + T \left(\dfrac{\partial G}{\partial T}\right)_P$ ------------------------ (10)

This is one form of Gibbs –Helmholtz equation.

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Let G_1 initial free energy of a system at T and G_1 and dG_1 = initial free energy of the system at $T + dT$ where dT is infinitesimally small and pressure is constant.

$$dG_1 = -S_1 dT$$ where S_1 is the entropy of the system in the initial state.

Now suppose that the free energy of the system in final state is G_2 at T. Let $G_2 + d\,G_2$ is the free energy of the system at T + dT in the final state then.

$$dG_2 = -S_2 dT$$ Where S_2 is the entropy of the system in the final state.

Subtracting (11) from (12)

$$dG_2 - dG_1 = -(S_2 - S_1)dT$$

$$d(\Delta G) = -\Delta S\, dT$$

At constant pressure

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S$$

We know $\Delta G = \Delta H - T\Delta S$

$$-T\Delta S = \frac{\Delta G - \Delta H}{T}$$

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

$$\boldsymbol{\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P}$$

This is called Gibbs - Helmoltz equation in terms of free energy and enthalpy at constant pressure.

MAXWELL RELATIONSHIP

     dE = q-PdV

     G = H – TS

     H = E + PV

     A + E – TS

Using the above fundamental equations any thermodynamic relationships can be derived.

Note: E, S, H, A, G, T, P, V are all state functions .

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dE = q – PdV

dE = TdS – PdV

At Constant volume

$$(dE)_v = TdS$$

Differentiating with respect to V at constant S

$$\frac{\partial^2 E}{\partial S\,\partial V} = \left(\frac{\partial T}{\partial V}\right)_S \; - - - - - (1)$$

At constant entropy

$$(dE)_s = -PdV$$

Differentiating with respect to S at constant V

$$\frac{\partial^2 E}{\partial V\,\partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \; - - - - - (2)$$

From equations 1 and 2

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

H = E + PV

dH = TdS + VdP

At constant pressure

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$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

Differentiating with respect to P at constant S

$$\frac{\partial^2 H}{\partial S\, \partial P} = \left(\frac{\partial T}{\partial P}\right)_S ----- (3)$$

At constant entropy

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

Differentiating with respect to S at constant P

$$\frac{\partial^2 H}{\partial P\, \partial S} = \left(\frac{\partial V}{\partial S}\right)_P ---- (4)$$

Since H is a state function and dH is an exact differential then from equation 3 and 4

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

$$G = H - TS$$
$$G = E + PV - TS$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

At constant pressure

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$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Differentiating with respect to P at constant T

$$\frac{\partial^2 G}{\partial T\,\partial P} = -\left(\frac{\partial S}{\partial P}\right)_T - - - - - (5)$$

At constant T

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Differentiating with respect to T at constant P

$$\frac{\partial^2 G}{\partial P\,\partial T} = \left(\frac{\partial V}{\partial T}\right)_P - - - - - (6)$$

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

$$A = E - TS$$

$$dA = -PdV - SdT$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Differentiating with respect to V at constant T

$$\frac{\partial^2 A}{\partial T\,\partial V} = -\left(\frac{\partial S}{\partial V}\right)_T - - - - - (7)$$

At Constant Temperature

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

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Differentiating with respect to T at constant V

$$\frac{\partial^2 A}{\partial V \, \partial T} = -\left(\frac{\partial P}{\partial T}\right)_V \; - - - - - (8)$$

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

$dE = q - PdV$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$
$H = E + PV$	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$
$G = H - TS$	$\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$
$A = E - TS$	$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

ADVANTAGES OF USING ΔA AND ΔG OVER ΔS

(i) Use of entropy change to predict the nature of a process requires the knowledge of the entropy changes for both the system and surroundings. But the change of Helmholtz energy or change of Gibbs energy of the system alone is sufficient to predict the direction of a process.

(ii) While using the entropy change it is required that energy and volume are constant (ΔS)U, V. >0. But it is not very convenient to maintain a constant energy condition in the laboratory. On the other hand, while using free energy change ΔA or ΔG only the state variables (*T, V,* or *T, P*) are to be kept constant, which are easy to maintain in the laboratory. Therefore, the use of ΔAs or ΔG is preferred over ΔS as a driving force to predict the direction of a process

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Advantages of using ΔG over ΔA

When ΔG is used to predict the direction of a process it is required to maintain constant temperature and constant pressure as (ΔG)T, P < 0 for a spontaneous process.. On the other hand, if ΔA is used to decide the direction of a process the temperature and volume are to be kept constant as $(\Delta A)_{T, V}$< 0 for spontaneous process. Since in the chemistry laboratoryusually the experiments are performed at constant temperature and constant pressure, therefore, the use of ΔG as driving force is preferred over the use of ΔA which requires thecondition of constant T and constant V.

Important deductions from equation dA = - PdV - SdT

Free energy change and spontaneous processes

We have already discussed that for a spontaneous process the total entropy change (ΔSuniverse) must be positive. Therefore, in view of the relation

$$\Delta G \text{ system} = - T\Delta S\text{universe},$$

the freeenergy change of the system must be negative. That is, at constant temperature and constantpressure the free energy of the system must decrease in a spontaneous process and

(ΔG)T, P < 0 .for a spontaneous process

A decreasing quantity must attain its minimum value at equilibrium after which there is no net change, therefore.

(ΔG)T, P = 0 at equilibrium

If there is increase in the free energy, the process is nonspontaneous (forbidden)

(ΔG)T, P > 0 nonspontaneous

These criteria may be summarized as follows

(i) ΔG is negative Spontneous process

(ii) ΔG is posiveNonspontneous process

(iii) ΔG is zero Equilibrium state

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Criteria of spontaneous process in terms of *ΔH* and *T ΔS*

A change is spontaneous only when *ΔG* is negative. Therefore, it is essential to learn the roles of *ΔH* and *T ΔS* in the relation *ΔG = ΔH – TΔ.S* and decide the direction of the change under differentsituations.

(1) When *ΔH* is negative and *ΔS* is positive

From the relation *ΔG = ΔH – TΔ.S*, it is clear that under the given situation *ΔG* is negative and therefore, the change is spontaneous. In other words, we may state that an exothermic reaction with positive entropy change is always spontaneous.

(2) When *ΔH* is positive and *ΔS* is negative

From the relation *ΔG = ΔH – TΔ.S*, it is clear that under the given situation *ΔG* is positive and therefore, the change is nonspontaneous (forbidden) in the desired direction. In other words, we may state that an endothermic reaction with negative entropy change is never Spontaneous. However, it may be spontaneous in the opposite direction

(3) **When both *ΔH* and *ΔS* are positive**

At lower temperature *TΔS* will be small therefore, *ΔH* will predominate. Thus *ΔG = ΔH – TΔS* will be positive and the change will be nonspontaneous. But at higher temperature *TΔS* will be larger than *ΔH*. Therefore, *ΔG = ΔH – TΔ.S* will be negative and the change will be spontaneous. In other words, we may state that an endothermic reaction with positive entropy change is spontaneous at high temperature but nonspontaneous at lower temperature.

(4) **When both *ΔH* and *ΔS* are negative**

At lower temperature *TΔS* will be small therefore, *ΔH* will predominate. Thus *ΔG = ΔH – TΔS* will be negative and the change will be spontaneous. But at higher temperature *TΔS* will predominate *ΔH*. Therefore, *ΔG = ΔH – TΔ.S* will be positive and the change will

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be nonspontaneous. In other words, we may state that an exothermic reaction with negative entropy change is spontaneous at lower temperature but nonspontaneous at higher temperature.

THIRD LAW OF THERMODYNAMICS

The first law of thermodynamics provides methods of calculation of the energy changes (ΔU) and enthalpy changes (ΔH). On the other hand, the second law of thermodynamics helps in the calculation of entropy changes (ΔS). But this law as such cannot be used to calculate the absolute value of entropy. Therefore, we need a new law of thermodynamics which can guide us to evaluate the absolute value of entropy of different type of substances. This new law is called the ***Third law of thermodynamics*** which is also called *Nernst heat theorem* in a limited perspective.

Nernst heat theorem

In 1906 Nernst stated the heat theorem that in the vicinity of absolute zero all processes should take place without any change in entropy and heat capacity. In terms of symbolic notations Nernst heat theorem may be stated as

$$\text{Lim } \Delta S \rightarrow 0 \text{ and Lim } \Delta CP \rightarrow 0$$
$$T \rightarrow 0 \qquad\qquad T \rightarrow 0$$

In 1913 Plank extended heat theorem in the form of third law of thermodynamics

Statement of the third law of thermodynamics

Every substance has a finite positive entropy but at 0 K (absolute zero) the entropy *may become zero and does so become in case of a perfectly crystalline substance*. This statement also implies that

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At absolute zero the entropy of a perfect crystal is zero

That is, when $T = 0$ K then $S = 0$

Molecular basis of third law of thermodynamics

We know that entropy is a measure of randomness. Greater the randomness larger is the value of entropy. Lower is radomness smaller is the value of entropy. If the randomness is reduced to zero the entropy is also reduced to zero. This implies that when there is perfect order in the system its entropy is zero. It is in tune with the third law of thermodynamics which states that at absolute zero the entropy of a perfect crystal is zero. This is true because at absolute zero of temperature there is complete order in a perfect crystal and no chaos hence entropy is zero. The correlation between entropy and molecular arrangement is given by Boltzmann equation

$$S = k \ln W \qquad \text{(i)}$$

Here, S = Entropy

$$k = \text{Boltzmann constant} = \frac{\text{Gas constant}}{\text{Avogadro constant}} = \frac{R}{N_A}$$

W = Number of ways of molecular arrangements

From equation (i) it is clear that larger is the value of W higher is entropy (S). At absolute zero (0 K ≡ 273.16 oC) all types of motions cease. Therefore, molecules (atoms and ions) can arrange themselves in one way only. That is, $W = 1$ and there is perfect order. Therefore,

$$S = k \ln W = k \ln 1 = k \times 0 = 0$$

Thus entropy is zero at absolute zero. At temperatures higher that 0 K, the molecules can have different types of motions and they arrange themselves in more than one ways. That is, $W > 0$ and therefore, $\ln W > 0$ and hence S is positive.

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Concept of residual entropy

There are certain substances which have positive entropy even at absolute zero. The value of entropy possessed by a substance at 0 K is called its **residual entropy**.

Origin of residual entropy

The residual entropy arises because the molecules can arrange themselves in more that one ways. For example, in case of carbon monoxide (CO) the molecules can have the following type of arrangements even at 0 K.

$$CO \quad CO \quad CO \quad CO$$
$$Or, \quad CO \quad CO \quad OC \quad CO$$
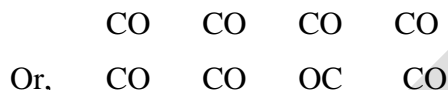
This suggests that each CO molecule can have two orientations. Thus $W = 2$ for each molecule.

Calculation of residual entropy

In a system containing one Avogadro number of molecules (one mole) the entropy is given by

$$S = N_A \times k \times 2.303 \log W = R \times 2.303 \log W$$

Now, $R = 8.314$ J K^{-1} mol^{-1}. Therefore, when $W = 2$ we shall have

$$S = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303 \log 2$$

$$= 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

The experimental value of residual entropy is lower 5.7 J K^{-1} mol^{-1}

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Remarks

Substances such as CO, N_2O, H_2O, H_2 have residual entropy. Therefore, in the reactions where one or more of such substances are involved the entropy change is finite even at absolute zero. This type of observation is called as exception to the third law or limitation of third law.

Evaluation of absolute entropy

The absolute entropy of a system can be evaluated using the relations derived from the second law of thermodynamics and then applying the third law. From the second law of thermodynamics we know that the entropychange of a system is related to its heat capacity at constant pressure by

$$S^o(T) = \int_{0K}^{TK} \frac{C_P}{T} \, dT \qquad \text{(iii)}$$

The value of absolute entropy $S_o(T)$ can be evaluated provided the integral on right side of equation (iii) is known.

Note: Absolute entropy $S_o(T)$ is also called ***third law entropy***, because it is calculated by assuming the validity of the third law of thermodynamics that at $T = 0$ K, $S_o(T) = 0$.

Discussion of absolute entropies

The values of absolute entropy of substances reveal the following interesting facts:

(1) The entropy of graphite (5.7 J K–1 mol–1) is greater than that of diamond (2.4 J K–1 mol–1).This is in tune with the fact that diamond has a compact structure than graphite. That is, there is less randomness in the lattice of diamond as compared to that in graphite.

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(2) The absolute entropies of halogens (Cl_2 = 223 JK–1 mol–1, Br_2 = 152 JK–1 mol–1, I_2 = 117JK–1 mol–1) confirm the trend S(gas) >S(l) >S(s) which suggests that there is more randomness in gas as compared to liquid and solid

(3) The entropy hence randomness increases with increasing molar mass in a family of compounds. This is clear from the trends in the $S\upsilon$values of alkanes.

Alkane	CH4	C2H6	C3H8	C4H10
$S\upsilon$/ JK–1 mol–1	186.2	229.5	270.9	310.8

(4) The entropy of hydrogen (130.6 JK–1 mol–1) is greater than the entropy of helium (126 JK–1 mol–1) though the molar mass of He is twice the molar mass of H2. This suggests that inH2 (a diatomic molecule) the entropy arises due to translational, rotational and vibrational motions of the H–H system, while in He (a monotomic molecule) there is only translational motion

Applications of the combined form of first and second laws of thermodynamics

The relation $Td S = dU + PdV$ is useful to derive various other thermodynamic relations.

(A) Thermodynamic equation of state

A relation between the change in a thermodynamic property (say U) and state variables (PVT) s called thermodynamic equation of state.

The combined form of first and second laws of thermodynamics states that

$$Td S = dU + PdV \qquad or$$

$$dS = \frac{1}{T}\,dU + \frac{1}{T}\,PdV \qquad\qquad (i)$$

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Energy of a given amount of a system is a function of temperature and volume, $U = U(T, V)$, and its total differential is given by

$$d\mathbf{U} = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (ii)$$

Therefore,
$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV \quad (iii)$$

From equation (iii) it is seen that entropy is a function of T and V and $S = S(T, V)$ The total differential of S is given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad (iv)$$

On comparing the coefficients of dT in equations (iii) and (iv), we get

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \qquad (v)$$

On differentiating equation (iv) with respect to V at constant T, we get

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} \qquad (vi)$$

On comparing the coefficients of dV in equations (iii) and (vi), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \qquad (vii)$$

On differentiating equation (vii) with respect to T at constant V, we get

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$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\right]_V$$

$$= -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \quad \text{(viii)}$$

Now S is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

In view of the above condition equations (vi) and (viii) give

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \quad \text{(ix)}$$

Now U is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

In view of the above equality condition, equation (ix) gives

$$-\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V = 0$$

Or, $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{(x)}$$

Equation (x) is called ***thermodynamic equation of state***. It provides an expression for the internal pressure $(\partial U/\partial V)_T$ in terms of state variable of a system. This equation is valid for both the ideal and nonideal systems.

Joule's Law

Joule's law states that the internal energy of an ideal gas is independent of its volume at a constant temperature. Mathematically it is expressed as

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \dots \textit{Joule's law}$$

This law also means that internal energy of a given amount of an ideal gas depends on its

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temperature only. Thus at a constant temperature there is no change in the internal energy of an ideal gas as the volume is changed.

From this experiment Joule argued as follows.

(i) There is no change of temperature showing that there is no exchange of heat between the system and surroundings. That is, $q = 0$.

(ii) The gas expands into an evacuated vessel where $P_{ext} = 0$. Therefore, no work is done in the process and $w = -P_{ext} \times \Delta V = -0 \times \Delta V = 0$.

(iii) From the first law of thermodynamics, therefore, it is obvious that $\Delta U = q + w = 0 + 0 = 0$ or $dU = 0$. Thus

$$dU = C_V \, dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

Or,

$$\left(\frac{\partial U}{\partial V}\right)_T dV = -C_V \, dT$$

Now, $dT = 0$ (because there is no change of temperature in Joule's experiment) but $C_V \neq 0$, therefore, $C_V \, dT = 0$. Thus

$$\left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

Now, $dV \neq 0$ (as the gas expands and occupies both the bulbs). Therefore, the above equation is valid only when

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \dots \textit{Joule's law}$$

Physical interpretation of Joule's law:

The derivative $(\partial U/\partial V)_T$ is called **internal pressure.** . It is a measure of the molecular force of attraction. For a nonideal gas obeying van der Waals equation of state the internal pressure is given by $(\partial U/\partial V)_T = a/V^2$. When the molecular force of attraction is strong, the internal pressure is large. In an ideal gas the molecular force of attraction is absent, therefore, its internal pressure is zero. Thus $(\partial U/\partial V)_T = 0$ is a thermodynamic definition of an ideal gas.

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Joule – Thomson Coefficient

The change of temperature with change of pressure of a gas at constant enthalpy is called*Joule – Thomson coefficient.* It is denoted by the symbol _J-T and defined as

μ*J-T*= $(\partial T/\partial P)_H$

Significance of Joule – Thomson coefficient μ*J-T* = $(\partial T/\partial P)_H$

➢ Joule-Thomson effect and the value of μ*J-T* form the basis of liquefaction of gases.

➢ A positive value of the Joule-Thomson coefficient (μ*J-T*) corresponds to a cooling effect when a compressed gas is allowed to pass through small holes

➢ A negative value of the Joule-Thomson coefficient (μ*J-T*) corresponds to a heating effect when a compressed gas is allowed to pass through small holes

➢ A zero value of the Joule-Thomson coefficient (μ*J-T*) corresponds to no thermal change when a compressed gas is allowed to pass through small holes

Summary of the significance of the values of Joule-Thomson Coefficient (μ$_{J-T}$)

Sign of the value of the (μ$_{J-T}$)	Effect observed
Positive	Cooling
Negative	Heating
Zero	Neither cooling nor heating

Inversion temperature:

The temperature at which the Joule-Thomson coefficient is zero is called the *inversion temperature*. At this temperature neither cooling nor heating effect is observed during Joule Thomson expansion, below this temperature, cooling effect is observed while above this temperature, heating effect is observed.

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In chemistry we are most interested in mixtures of components because we want to study reactions, to minimally go from reactant to product. This introduces another variable, **xi,** the partial molar fraction, **xi = ni/nTot**, in this case **nTot = £i ni**is a simple sum, it makes no difference what else is in mix, just sum all the components, and compare each to the total. This concept of partial molar contribution is not limited to number of moles, but with other properties it can be affected by intermolecular interactions.

Ideal gases, **PTot = £i Pi** and **Pi = xi PTot** brings partial pressures, works because ideal gases do not interact, each *contributes to total pressure* in same way. Same works for volume: **VTot = £i Vi**but if we talk about mixtures of interacting substances this changes.

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POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is third law of thermodynamics?

2. Differentiate between Gibbs free energy and Helmholtz free energy.

3. Show that the change in free energy is equal to net work done.

4. Explain the terms "free energy" and Maximum work function".

5. Show that $\Delta A < 0$ is criterion for spontaneity and equilibrium

6. Show that $\Delta G < 0$ is criterion for spontaneity and equilibrium.

7. What is meant by residual entropy

8. Write the significance of Gibbs-Dehum equation.

9. What is meant by partial molar quantity of gases.

PART C (8 Mark Questions)

1. What is Nernst heat theorem? State third law of thermodynamics. Briefly describe its importance.

2. What is residual entropy. How the concept of residual entropy originated. How is it calculated.

3. Derive Gibbs-Helmholtz equation in terms of free energy and enthalpy change at constant pressure. .

4. What are the applications of Gibbs-Helmholtz equation

5. State third law of thermodynamics. How does this law help in the determination of absolute entropies of chemical compounds at any desired temperature.

6. Explain in detail about the chemical potential of ideal gas mixtures.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple Choice questions)

PHYSICAL CHEMISTRY II (CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS)

UNIT III

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	Work function in thermodynamics is called	Helmholtz free energy	Gibbs free energy	entropy	Residual entropy	Helmholtz free energy
2.	For a process occurring at constant temperature, the decrease in the work function A is equal to	Maximum work done by the system	Minimum work done by the system	entropy	Residual entropy	Maximum work done by the system
3.	The maximum useful work obtained in a system is equal to	Helmholtz free energy	Gibbs free energy	entropy	Residual entropy	Gibbs free energy
4.	The Gibbs free energy G is given by	G = H-TS	G = H+TS	G= A-TS	G = A +TS	G = H-TS
5.	The Helmholtz free energy A is given by	A = U -TS	A = U+ TS	A = G - TS	A = G + TS	A = U –TS
6.	The Helmholtz free energy A is	Path function	State function	Intensive property	Extensive property	State function
7.	The Gibbs free energy A is	Path function	State function	Intensive property	Extensive property	State function
8.	For a process occurring at constant temperature and constant pressure, the decrease in Gibb's free energy is equal to	Maximum useful work	Minimum useful work	Work function	Maximum entropy	Maximum useful work
9.	Maximum useful work is equal to	Total work minus PV work	Total work plus PV work	Total work plus work of expansion	Total work minus entropy	Total work minus PV work
10.	According to the Nerst heat theorem	Temperature is lowered to absolute zero, the entropy change of the reaction tends to be zero	Temperature is lowered to 298 K, the entropy change of the reaction tends to be zero	Temperature is increased to 303 K, the entropy change of the reaction tends to be zero	Temperature is lowered to 298 K, the heat capacity of the reaction tends to be zero	Temperature is lowered to absolute zero, the entropy change of the reaction tends to be zero

11.	According to the Nerst heat theorem	Temperature is lowered to absolute zero, the difference in the heat capacities of the products and reactants tends to be zero	Temperature is lowered to 298 K,, the difference in the heat capacities of the products and reactants tends to be zero	Temperature is lowered to 298 K, the entropy change of the reaction tends to be zero	Temperature is increased to 303 K, the entropy change of the reaction tends to be zero	Temperature is lowered to absolute zero, the difference in the heat capacities of the products and reactants tends to be zero
12.	Nernst heat theorem is not applicable to gases because	Gases do not exist at the absolute zero	Gases do exist at the absolute zero	Gases do not exist at 298 K	Gases do not exist as molecules	Gases do not exist at the absolute zero
13.	Temperature is lowered to absolute zero, the entropy change of the reaction and the difference in the heat capacities of the products and reactants tends to be zero	Nerst heat theorem	Le-Chatelier's principle	Kirchoff's theorem	Gibbs theorem	Nerst heat theorem
14.	Nernst heat theorem is applicable only to	Liquids	gases	Solids	Plasma	solids
15.	According to third law thermodynamics, the entropy of all perfectly crystalline solids at the absolute zero is taken as	Zero	unity	100	1000	zero
16.	According to third law thermodynamics, the entropy is taken as zero at absolute zero temperature for	Liquids	gases	Perfectly crystalline Solids	Plasma	Perfectly crystalline Solids
17.	Entropy calculated by using third law of thermodynamics is	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann entropy	Thermal entropy
18.	Entropy calculated by using statistical mechanics is	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann entropy	Statistical entropy
19.	Entropy calculated by using the equation S = kln W is	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann entropy	Statistical entropy
20.	The entropy of the crystalline substance possesses at T=0 is called	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann entropy	Residual entropy
21.	Residual entropy can be calculated using the equation	S = kln A	S = kln G	S = kln E	S = kln W	S = kln W
22.	In the equation S = kln W , S is called	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann entropy	Statistical entropy
23.	In the equation S = kln W , W is called	Thermal entropy	Statistical	Residual	Thermodynamic	Thermodynamic

#	Question	A	B	C	D	Answer
			entropy	entropy	probability	probability
24.	In the equation S = kln W , k is called	Thermal entropy	Statistical entropy	Residual entropy	Boltzmann constant	Boltzmann constant
25.	The crystal which do not show zero entropy at 0 K is	CO crystal	Solid KMNO$_4$	nitrogen	Sodium chloride	CO crystal
26.	The crystal which do not show zero entropy at 0 K is	NO crystal	Solid KMNO$_4$	nitrogen	Sodium chloride	NO crystal
27.	The crystal which do not show zero entropy at 0 K is	H$_2$ crystal	Solid KMNO$_4$	nitrogen	Sodium chloride	H$_2$ crystal
28.	The residual entropy of CO is	5.85 J/K Mol	58.5 J/K Mol	585 J/K Mol	5585 J/K Mol	5.85 J/K Mol
29.	Under what conditions change in work function is equal to change in Gibbs free energy i.e. dA = dG	When there is no change in volume	When there is no change in enthalpy	When there is no change in temperature	When there is no change in pressure	When there is no change in enthalpy
30.	Residual entropy is	The entropy possessed by the crystalline substance when T =0	The entropy arising out of defects in crystalline substance	The entropy which is in excess over the normal value	The remaining entropy of a substance	The entropy possessed by the crystalline substance when T =0
31.	Which of the following is not a state function	H	S	U	W	W
32.	Partial molar property of a substance is also called	Chemical potential	Gibbs free energy	Helmholtz free energy	Residual entropy	Chemical potential
33.	Partial molar free energy of a substance is also called	Chemical potential	Gibbs free energy	Helmholtz free energy	Residual entropy	Chemical potential
34.	Gibbs free energy G is equal to chemical potential for	One mole of a substance	One gram of a substance	One mole fraction of a substance	two mole of a substance	One mole of a substance
35.	Producer gas is obtained by	carbonization of bituminous coal	partial combustion of coal, coke, anthracite coal or charcoal in a mixed air steam blast	passing steam over incandescent coke	passing air and a large amount of steam over waste coal at about 650°C	partial combustion of coal, coke, anthracite coal or charcoal in a mixed air steam blast
36.	Otto cycle is also known as	constant pressure cycle	constant temperature	constant volume cycle	constant temperature and	constant volume cycle

			cycle		pressure cycle	
37.	or a perfect gas, according to Boyle's law (where p = Absolute pressure, v = Volume, and T = Absolute temperature)	v/T = constant, if p is kept constant	p v = constant, if T is kept constant	T/p = constant, if v is kept constant	p/T = constant, if v is kept constant	p v = constant, if T is kept constant
38.	In an irreversible process, there is a	no loss of heat	no gain of heat	gain of heat	loss of heat	loss of heat
39.	The area under the temperature-entropy curve (T – s curve) of any thermodynamic process represents	heat absorbed	either heat absorbed or heat rejected	none of these	heat rejected	either heat absorbed or heat rejected
40.	When two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This statement is called	Kelvin Planck's law	Zeroth law of thermodynamics	First law of thermodynamics	Second law of thermodynamics	Zeroth law of thermodynamics
41.	For the same compression ratio, the efficiency of dual combustion cycle is	less than Diesel cycle	greater than Diesel cycle	greater than Diesel cycle and less than Otto cycle	less than Diesel cycle and greater than Otto cycle	greater than Diesel cycle and less than Otto cycle
42.	Kelvin-Planck's law deals with	conversion of heat into work	conversion of work into heat	conservation of work	conservation of heat	conversion of heat into work
43.	Those substances which have so far not been resolved by any means into other substances of simpler form are called	molecules	elements	compounds	atoms	elements
44.	The specific heat at constant volume is	he amount of heat required to raise the temperature of 1 kg of water through one degree	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant pressure	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume	the amount of heat required to lower the temperature of unit mass of gas through one degree, at constant volume	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume
45.	The measurement of a thermodynamic property known as temperature is based on	Zeroth law of thermodynamics	First law of thermodynamics	Third law of thermodynamics	Second law of thermodynamics	Zeroth law of thermodynamics
46.	The gas constant (R) is equal to the _____ of two specific heats.	difference	product	ratio	sum	difference

No.	Question	A	B	C	D	Answer
47.	Otto cycle efficiency is higher than Diesel cycle efficiency for the same compression ratio and heat input because in Otto cycle	maximum temperature is higher	combustion is at constant volume	expansion and compression are isentropic	heat rejection is lower	heat rejection is lower
48.	What is the name of the following statement: "When two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other"?	First Law of Thermodynamics	Second Law of Thermodynamics	Mechanical equivalent of heat	Zeroth Law of Thermodynamics	Zeroth Law of Thermodynamics
49.	An aluminum plate has a circular hole. If the temperature of the plate increases, what happens to the size of the hole?	Increases	Decreases	Stays the same	Increases the top half of the hole	Increases
50.	Which of two temperature change are equivalent?	1 K = 1 F	1 F = 1 C	1 Re = 1F	1 K = 1 C	1 K = 1 C
51.	The state of an ideal gas was changed three times at three different temperatures. The diagram represents three different isothermal curves. Which of the following is true about the temperature of the gas?	T1 > T2 > T3	T1 > T2 < T3	T1 < T2 < T3	T1 > T2 = T3	T1 < T2 < T3
52.	The temperature of an ideal gas increases from $20°C$ to $40°C$ while the pressure stays the same. What happens to the volume of the gas?	It doubles (B) (C)	It quadruples	It is cut to one-half	it slightly increases	it slightly increases
53.	A container with rigid walls filled with a sample of ideal gas. The absolute temperature of the gas is doubled. What happens to the pressure of the gas?	Doubles	Quadruples	Triples	Decreased to one-half	Doubles
54.	The absolute temperature of an ideal diatomic gas is quadrupled. What happens to the average speed of molecules?	Quadruples	Doubles	Triples	Increases by a factor of 1.41	Doubles
55.	The average molecular kinetic energy of a gas depends on	Pressure	Volume	Temperature	Number of moles Radiation	Temperature
56.	The process of heat transfer from object to another because of molecular motion and interaction is called:	Convection	Conduction	Induction	Reduction	Conduction

57.	A closed system is one in which	mass does not cross boundaries of the system, though energy may do so	mass does not cross boundaries of the system, though energy may do so	neither mass nor energy crosses the boundaries of the system	thermodynamic reactions take place	mass does not cross boundaries of the system, though energy may do so
58.	Maximum useful work is equal to	Total work minus PV work	Total work plus PV work	Total work plus work of expansion	Total work minus entropy	Total work minus PV work
59.	Which of the following gas is mostly used in town for street and domestic lighting and heating?	Producer gas	Coal gas	Mond gas	Coke oven gas	Coal gas

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UNIT IV

SYLLABUS

Chemical Equilibrium: Criteria of thermodynamic equilibrium, degree of advancement of reaction, chemical equilibria in ideal gases. Thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient. Equilibrium constants and their quantitative dependence on temperature, pressure and concentration (LeChatelier Principle, Quantitatively). Free energy of mixing and spontaneity.equilibrium between ideal gases and a pure condensed phase.

Criteria of thermodynamic equilibrium:

When the rate of the forward reaction is equal to the rate of the reverse reaction, then the reaction is said to be in equilibrium. Chemical equilibrium is a dynamic equilibrium. Eventhough the forward and backward reactions are continuously taking place, it will appear to us as if the reaction is at rest.

In case of a reaction, all moles of reactant that get used up show up as product, weighted by the stoichiometric coefficients, via, if we express the reaction of reactants and products (Xi) as

$\alpha A + \beta B + . . \rightarrow \gamma C + \delta D + . .$ then short form $0 = \Sigma_\iota \, v_\iota X_i$ (*where v_ι for react -, prod +*)

if reaction proceeds infinitesimally, then dn_i balance out, dG only depend on that, *const T,P*

$dG = \Sigma_\iota \, \mu_\iota dn_i$ if let ξ = measure of extent of reaction: $n_i = n_i{}^{init} + v_\iota \, \xi \rightarrow dn_\iota = v_\iota d\xi$

$dG = (\Sigma_\iota \, v_\iota \, \mu_\iota) \, d\xi = \Delta G_{react} \, d\xi$ or rearrange: $(\partial G/\partial \xi)_{T,P} = (\Sigma_\iota \, v_\iota \, \mu_\iota) = \Delta G_{react}$

at const T,P $\Delta G_{react} < 0$ spontaneous reaction, see μ_ι depend on other components

$(\partial G/\partial \xi)_{T,P} < 0 \rightarrow$ reaction - spontaneous as written

$(\partial G/\partial \xi)_{T,P} > 0 \rightarrow$ reaction - spontaneous in opposite direction than written

$(\partial G/\partial \xi)_{T,P} = 0 \rightarrow$ reaction – at equilibrium, no change

obviously important to determine ξ at equilibrium, mathematically straightforward

$(\partial G/\partial \xi)_{T,P} = 0 = (\Sigma_\iota \, v_\iota \, \mu_\iota)$ so substitute in chemical potentials and solve

Where is ξ? Consider $\mu_A{}^{mix} = \mu_A{}^{pure}(T,P) + RT \ln x_A$ each depends on ξ

Plug these into the sum and get terms at standard conditions $\rightarrow \Delta G^\circ_{react}$

And get terms in the log forms depend on x_i 's related to the ξ

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Degree of advancement of reaction:

Equilibrium constant

Canonical example reaction:
$$\alpha A(g) + \beta B(g) \rightleftharpoons \gamma C(g) + \delta D(g)$$

$$\Delta G_R = \sum_i v_i \Delta G_{f,i} = \gamma \mu_C^\circ + \gamma RT \ln \frac{P_C}{P^\circ} + \delta \mu_D^\circ + \delta RT \ln \frac{P_D}{P^\circ}$$

$$-\alpha \mu_A^\circ - \alpha RT \ln \frac{P_A}{P^\circ} - \beta \mu_B^\circ - \beta RT \ln \frac{P_B}{P^\circ}$$

Separate out terms in standard conditions, combine ln terms, note P° ref to std state: 1 bar

$$\Delta G_R = \Delta G_R^\circ + \gamma RT \ln \frac{P_C}{P^\circ} + \delta RT \ln \frac{P_D}{P^\circ} - \alpha RT \ln \frac{P_A}{P^\circ} - \beta RT \ln \frac{P_B}{P^\circ}$$

$$= \Delta G_R^\circ + RT \ln \frac{\left(\frac{P_C}{P^\circ}\right)^\gamma \left(\frac{P_D}{P^\circ}\right)^\delta}{\left(\frac{P_A}{P^\circ}\right)^\alpha \left(\frac{P_B}{P^\circ}\right)^\beta}$$

Where:
$$\Delta G_R^\circ = \gamma \mu_C^\circ (T) + \delta \mu_D^\circ (T) - \alpha \mu_A^\circ (T) - \beta \mu_B^\circ (T) = \sum_i v_i \Delta G_{f,i}^\circ$$

Products of pressures is reaction quotient of pressures (note all ref to P°)

$$Q_P = \frac{\left(\frac{P_C}{P^\circ}\right)^\gamma \left(\frac{P_D}{P^\circ}\right)^\delta}{\left(\frac{P_A}{P^\circ}\right)^\alpha \left(\frac{P_B}{P^\circ}\right)^\beta}$$

simplifies to
$$\Delta G_R = \Delta G_R^\circ + RT \ln Q_P$$

So if start out with lots of reactant, large A and B, small C and D, then Q will be small <<1

And ln term will be negative and large, so ΔG_{rxn} **< 0**, spontaneous forward

if C,D large partial P, then Q large >>1, and ln term pos, so ΔG_{rxn} **> 0**, not spont. (reverse)

Now at equilibrium: ΔG_{rxn} **= 0**, then $0 = \Delta G_{rxn}^\circ + RT \ln Q_P$ or ΔG_{rxn}° **= - RT ln Q_P**

Let **$Q_P = K_P$** for **$\Delta G_{rxn} = 0$** → pressure equilibrium constant

$$\ln K_P = -\frac{\Delta G_R^\circ}{RT}$$

or **K_P = exp (-ΔG_{rxn}° / RT)**

Note K_P does not depend on pressure, since each partial pressure is referenced to std P°

Chemical equilibria in ideal gases:

$$\frac{1}{2} N_2(g,T,p) + 3/2\, H_2(g,T,p) = NH_3(g,T,p)$$

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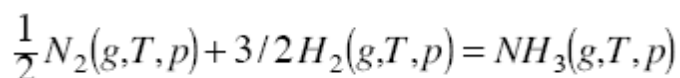
What are p_{N_2}, p_{H_2}, and p_{NH_3} at equilibrium?

Let's look at a more general case

$$v_A \ A(g, \ T, \ p) \ + \ v_B \ B(g, \ T, \ p) \ = \ v_C \ C(g, \ T, \ p) \ + \ v_D \ D(g, \ T, \ p)$$
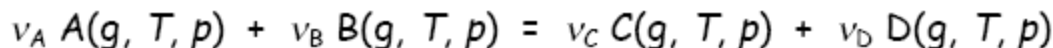
The v_i's are the stoichiometric coefficients.

Let's take a mixture of A, B, C, and D with partial pressures

$$p_A = X_A p, \ \ p_B = X_A p, \ \ p_C = X_C p, \text{ and } \ p_D = X_D p$$

Is this mixture in equilibrium?

We can answer by finding ΔG if we allow the reaction to proceed further.

We know $\mu_i(T,p)$ for an ideal gas in a mixture

and we know that $$G = \sum_i n_i \mu_i$$

$$\Rightarrow \quad \Delta G = \left[v_C \mu_C(g,T,p) + v_D \mu_D(g,T,p) \right] - \left[v_A \mu_A(g,T,p) + v_B \mu_B(g,T,p) \right]$$

But $\quad \mu_i(g,T,p) = \mu_i^{\circ}(T) + RT \ln p_i \qquad \left[\dfrac{p_i}{1 \text{ bar}} \text{ implied} \right]$

where $\mu_i^{\circ}(T)$ is the chemical potential of species "i" at 1 bar and in a pure (not mixed) state.

$$\therefore \quad \Delta G = \left[v_C \mu_C^{\circ}(T) + v_D \mu_D^{\circ}(T) \right] - \left[v_A \mu_A^{\circ}(T) + v_B \mu_B^{\circ}(T) \right] + RT \ln \left(\dfrac{p_C^{v_C} \, p_D^{v_D}}{p_A^{v_A} \, p_B^{v_B}} \right)$$

$$\Rightarrow \quad \Delta G = \Delta G^{\circ} + RT \ln Q$$

where $\quad \Delta G^{\circ} = \left[v_C \mu_C^{\circ}(T) + v_D \mu_D^{\circ}(T) \right] - \left[v_A \mu_A^{\circ}(T) + v_B \mu_B^{\circ}(T) \right]$

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and $Q = \dfrac{p_C^{v_C} p_C^{v_D}}{p_A^{v_A} p_B^{v_B}}$

$\Delta G°$ is the change in free energy associated with transforming pure reactants into pure products.

$$\Delta G° = \Delta G_{rxn}° = \Delta H_{rxn}° - T\Delta S_{rxn}°$$

Or $$\Delta G° = \Delta G_{form}°(\text{products}) - \Delta G_{form}°(\text{reactants})$$

If $\Delta G < 0$ then the reaction will proceed spontaneously to form more products

$\Delta G > 0$ then the backward reaction is spontaneous

$\Delta G = 0$ No spontaneous changes => Equilibrium

Define $Q_{eq} = K_p$ the equilibrium constant

$$K_p = \left(\frac{p_C^{v_C} p_C^{v_D}}{p_A^{v_A} p_B^{v_B}}\right)_{eq} = p^{\Delta v}\left(\frac{X_C^{v_C} X_C^{v_D}}{X_A^{v_A} X_B^{v_B}}\right)_{eq} = p^{\Delta v}K_X$$

and

$$\boxed{K_p = e^{-\Delta G°/RT}}$$

Note from this that $K_p(T)$ is not a function of total pressure p.

It is $K_X = p$ which is $K_X(p,T)$.

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Recall that all p_i values are divided by 1 bar, so K_p and K_x are both unit less

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Example: $H_2(g) + CO_2(g) = H_2O(g) + CO(g)$ *T=289k   P=1 bar*

	$H_2(g)$	$CO_2(g)$	$H_2O(g)$	$CO(g)$
Initial of moles	a	b	0	0
Moles at Eq.	a-x	b-x	x	x

Total moles at Eq. $= (a - x)+(b - x)+ 2x = a + b$

Mole fraction	$\dfrac{a-x}{a+b}$	$\dfrac{b-x}{a+b}$	$\dfrac{x}{a+b}$	$\dfrac{x}{a+b}$

$\Delta G^{\circ}_{form}(kJ/mol)$

0	-394.4	-228.6	-137.2

$$\therefore \quad \Delta G^{\circ}_{rxn} = 28.6\,kJ/mol \quad \Rightarrow \quad K_p = e^{-\frac{28,600\,kJ/mol}{(8.314\,J/K\text{-}mol)(298\,K)}} = e^{-11.54} = 9.7 \times 10^{-6}$$

$$K_p = \frac{p_{H_2O}\,p_{CO}}{p_{H_2}\,p_{CO_2}} = \frac{X_{H_2O}\,X_{CO}}{X_{H_2}\,X_{CO_2}} = \frac{x^2}{(a-x)(b-x)}$$

Let's take a = 1 mol and b = 2 mol

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We need to solve $$\frac{x^2}{(1-x)(2-x)} = 9.7 \times 10^{-6}$$

A) Using approximation method:

K << 1, so we expect x << 1 also.

Assume

$$1-x \approx 1, \ 2-x \approx 2 \implies \frac{x^2}{(1-x)(2-x)} \approx \frac{x^2}{2} = 9.7 \times 10^{-6}$$

$$x \approx 0.0044 \text{ mol} \ (\text{indeed} << 1)$$

B) Exactly: $$\frac{x^2}{x^2 - 3x + 2} = K_p = 9.7 \times 10^{-6}$$

$$x^2(1 - 9.7 \times 10^{-6}) + 3x(9.7 \times 10^{-6}) - 2(9.7 \times 10^{-6}) = 0$$

$$x = \frac{-3(9.7 \times 10^{-6})}{2(9.7 \times 10^{-6})} \pm \frac{\sqrt{9(9.7 \times 10^{-6})^2 + 4(1 - 9.7 \times 10^{-6})2(9.7 \times 10^{-6})}}{2(1 - 9.7 \times 10^{-6})}$$

The "-" sign gives a nonphysical result (negative x value)

Take the "+" sign only => x = 0.0044 mol (same)
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Effect of total pressure: example

$N_2O_4(g) = 2\ NO_2(g)$
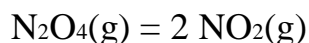
Initial mol #   n   0

\# at Eq.   n-x   2x   Total # moles at Eq. =

X_i's at Eq. $\dfrac{n-x}{n+x}$ $\dfrac{2x}{n+x}$ $n - x + 2x = n + x$

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{p^2 X_{NO_2}^2}{p X_{N_2O_4}} = p\frac{\left(\frac{2x}{n+x}\right)^2}{\left(\frac{n-x}{n+x}\right)} = p\frac{4x^2}{n^2 - x^2}$$

$$K_p = p\frac{4\alpha^2}{1-\alpha^2}$$ where $\alpha = x/n$ is the fraction reacted

$$(1-\alpha^2)\frac{K_p}{4p} = \alpha^2 \qquad \alpha^2\left(1+\frac{K_p}{4p}\right) = \frac{K_p}{4p} \qquad \alpha^2 = \frac{\frac{K_p}{4p}}{\left(1+\frac{K_p}{4p}\right)} = \frac{1}{\left(1+\frac{4p}{K_p}\right)} \qquad \alpha = \left(1+\frac{4p}{K_p}\right)^{-1/2}$$

$\therefore$ If p increases, α decreases

LeChatelier's Principle

A system in equilibrium will respond to counteract changes that affect the equilibrium. This is a statement of LeChatelier's principle. Using LeChatelier's principle, you can determine the effect of many external stimuli on chemical reactions. The stimuli to be considered here include temperature,

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pressure by changing the volume of the system, catalyst, and concentration. These stimuli are like levers that can control how much product you can get from a chemical reaction.

Effect of Concentration on K

Changing the concentrations of reactants and/or products in a chemical reaction does not change the value of K. Instead, the reaction shifts according to LeChatelier's Principle to establish a relative ratio of concentration according to K. K is unchanged. This technique is used frequently to obtain more products from a chemical reaction. There are two basic ways to form more product by changing concentrations: Add more reactants. Form more products. Take away products. Form more products. To obtain more reactants, remove reactants or add products.

Effect of Temperature on K

The effect of temperature depends on whether a reaction is exothermic (ΔHrxn>0), so you must first calculate or be given ΔHrxn. (Using standard conditions this would be ΔH°rxn) An exothermic reaction has a negative ΔHrxn value, and heat comes off as a product from the chemical reaction. Recall that you can increase the heat available by increasing the temperature.

$$A \leftrightarrow B + heat \qquad exothermic\ reaction\ (\Delta Hrxn < 0)$$

According to LeChatelier's Principle, adding heat pushes the reaction to form more reactants, which reduces the value of K at the higher temperature. The opposite holds for endothermic reactions where heat is a reactant. In this case, heat forms more products causing K to increase at the higher temperature.

Effect of Pressure on K

There are two methods to change the pressure on a system at equilibrium. Each method of changing pressure leads to a different analysis. When a system at equilibrium is squeezed to higher pressure by decreasing the volume, LeChatelier's Principle predicts that a reaction will shift to the side with fewer moles of gas. If both sides have the same number of moles of gas, there is no predicted change in K by increasing the pressure. Increasing the pressure on the reaction below by decreasing the volume results in a shift (according to LeChatelier's

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Principle) to form more reactants (the side with fewer moles of gas). This results in a decrease in equilibrium constant, K, at the higher pressure.

$$NaHCO_3(s) \leftrightarrow NaOH(s) + CO_2(g)$$
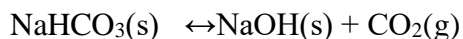
Effect on Catalyst on K

Catalysts do not change the value of the equilibrium constant, K. Catalysts change the rate (or speed) of approach to equilibrium based on the activation energy of the slow step in the mechanism. Catalysts can make it faster for a system to reach equilibrium. Catalysts, in an ideal sense, affect the kinetics of reaction, not the thermodynamics.

Equilibrium Constant and ΔG

At equilibrium the ΔG for a reversible reaction is equal to zero. Keq relates the concentrations of all substances in the reaction at equilibrium. Therefore we can write (through a more advanced treatment of thermodynamics) the following equation:

$$\Delta G\circ = -RT \ln Keq$$

The variable R is the ideal gas constant (8.314 J/K • mol), T is the Kelvin temperature, and lnKeq is the natural logarithm of the equilibrium constant.

When Keq is large, the products of the reaction are favored and the negative sign in the equation means that the ΔG∘ is negative. When Keq is small, the reactants of the reaction are favored. The natural logarithm of a number less than one is negative and so the sign of ΔG∘ is positive.

Consider an equilibrium reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

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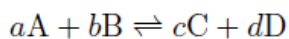
We do not specify any phases, as we will treat the reaction generally using activities. An equilibrium reaction is one that can proceed in both directions, as indicated by the $\leftrightarrow$ symbol replacing the usual $\longrightarrow$ in the chemical equation.

Recall that the molar free energy ΔG_j for compound j in the reaction in terms of its activity a_j as

$$\Delta G = \Delta G^0 + RT\ln a_j$$

Where $\Delta \bar{G}^{\circ}$ is the molar Gibbs free energy at a reference state, taken to be the standard state. Now the change in the Gibbs free energy of the reaction is

$$
\begin{aligned}
\Delta_r G &= c\Delta\bar{G}_C + d\Delta\bar{G}_D - a\Delta\bar{G}_A - b\Delta\bar{G}_B \\[4pt]
&= c\Delta\bar{G}_C^{\circ} + d\Delta\bar{G}_D^{\circ} - a\Delta\bar{G}_A^{\circ} - b\Delta\bar{G}_B^{\circ} \\[4pt]
&\quad + RT\left[c\ln a_C + d\ln a_D - a\ln a_A - b\ln b_B\right] \\[4pt]
&= \Delta_r G^{\circ} + RT\left[\ln a_C^c + \ln a_D^d - \ln a_A^a - \ln a_B^b\right] \\[4pt]
&= \Delta_r G^{\circ} + RT\ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right]
\end{aligned}
$$

At equilibrium, we need $\Delta_r G = 0$ at equilibrium. This gives the condition for chemical equilibrium

$$-\Delta_r G^{\circ} = RT\ln\left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right]$$

We define the equilibrium constant K as

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

which impmlies that

$$-\Delta_r G^{\circ} = RT\ln K$$

$$K = e^{-\Delta_r G^{\circ}/RT}$$

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EQUILIBRIUM OF GAS-PHASE CHEMICAL REACTIONS: IDEAL GASES

Consider a generic gas-phase reaction

$$a\mathrm{A}(g) + b\mathrm{B}(g) \rightleftharpoons c\mathrm{C}(g) + d\mathrm{D}(g)$$
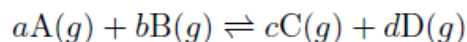
If we treat the gases as ideal gases, then recall that a

$$a_j = \frac{P_j}{P_j^\circ}$$

and the change in the molar Gibbs free energy when the pressure of an ideal gas changes from the standard value P° to some other pressure P at temperature T is

$$\Delta \bar{G} = \Delta \bar{G}^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

Let PA PB, PC, and PD be the partial pressures of each of the four species in the equilibrium state. The free energyof each species in the gas is defined as a free energy change with respect to its standard state. For gases, we haddefined this to be a partial pressure of 1 atm. Thus, let us the standard state partial pressure P° =1 atm. Then, inthe above reaction, a moles of A react, so the free energy of A is

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$$a\Delta G(A) = aRT \ln\left(\frac{P_A}{P^\circ}\right) + a\Delta_f G^\circ(A) \tag{9}$$

Similarly, for B, C, and D, we have

$$b\Delta G(B) = bRT \ln\left(\frac{P_B}{P^\circ}\right) + b\Delta_f G^\circ(B)$$

$$c\Delta G(C) = cRT \ln\left(\frac{P_C}{P^\circ}\right) + c\Delta_f G^\circ(C)$$

$$d\Delta G(D) = dRT \ln\left(\frac{P_D}{P^\circ}\right) + d\Delta_f G^\circ(D)$$

where $\Delta_f G^\circ(X)$ (X =A,B,C,D) is the standard energy of formation of X. Thus, the overall free energy change of for the reaction is

$$\Delta_r G = d\Delta G(D) + c\Delta G(C) - a\Delta G(A) - b\Delta G(B)$$

$$= d\Delta_f G^\circ(D) + c\Delta_f G^\circ(C) - a\Delta_f G^\circ(A) - b\Delta_f G^\circ(B)$$

$$+ dRT \ln\left(\frac{P_D}{P^\circ}\right) + cRT \ln\left(\frac{P_C}{P^\circ}\right) - aRT \ln\left(\frac{P_A}{P^\circ}\right) - bRT \ln\left(\frac{P_B}{P^\circ}\right)$$

The first line is just the standard free energy change $\Delta_r G^\circ$ for the reaction. The second line can be simplified giving

$$\Delta_r G = \Delta_r G^\circ + RT\left[d\ln\left(\frac{P_D}{P^\circ}\right) + c\ln\left(\frac{P_C}{P^\circ}\right) - a\ln\left(\frac{P_A}{P^\circ}\right) - b\ln\left(\frac{P_B}{P^\circ}\right)\right]$$

$$= \Delta_r G^\circ + RT\left[\ln\left(\frac{P_D}{P^\circ}\right)^d + \ln\left(\frac{P_C}{P^\circ}\right)^c - \ln\left(\frac{P_A}{P^\circ}\right)^a - \ln\left(\frac{P_B}{P^\circ}\right)^b\right]$$

$$= \Delta_r G^\circ + RT \ln\left[\frac{(P_D/P^\circ)^d (P_C/P^\circ)^c}{(P_A/P^\circ)^a (P_B/P^\circ)^b}\right]$$

Since the Gibbs free energy change $\Delta G = 0$ at equilibrium, we are left with

$$\Delta_r G^\circ = -RT \ln\left[\frac{(P_D/P^\circ)^d (P_C/P^\circ)^c}{(P_A/P^\circ)^a (P_B/P^\circ)^b}\right] \tag{10}$$

The quantity in brackets is called the *equilibrium constant*, K for the reaction:

$$K = \frac{(P_D/P^\circ)^d (P_C/P^\circ)^c}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \tag{11}$$

and is, itself, a thermodynamic quantity related to the standard Gibbs free energy change b

$$K = e^{-\Delta_r G^\circ / RT}$$

We can see that K is a direct measure of whether reactants, products or neither in particular is favored in anequilibrium state. If K is large (K ≫1), _rG∘ <0, and the reaction favors products and if K is very small (K ≪1),_rG∘ >0, and reactants are favored. For K near 1, there is likely to be roughly equal amounts of reactant andproduct in the equilibrium state.

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Note, also, that K can be a sensitive function of temperature, a point we will return to later. Also, due to thepresence of P∘ in the equation, K is a dimensionless quantity. Finally, since the reference partial pressure is P∘ = 1atm, if we insist that all partial pressures be expressed in atm, then we do not need to include the P∘ explicitly inthe equation for K and can simply write:

$$K = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

One use of equilibrium constants is the calculation of equilibrium compositions of reactions from given startingconditions.

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POSSIBLE QUESTIONS
PART B (2 Mark Questions)

1. What is Le-Chatlier's principle

2. State the law of mass action

3. Define the law of chemical equilibrium

4. What is the criteria for thermodynamic equilibrium

5. What is meant by free energy of mixing.

6. What are the optimum conditions to maximum yield of ammonia.

7. How increase of temperature affects an equilibrium reaction

8. How increase of concentration of the reactants affects an equilibrium reaction.

PART C (8 Mark Questions)

1. State and explain Le-Chatlier's principle

2. Derive the relationship between K_p and K_c.

3. What is meant by chemical equilibrium? Explain that chemical equilibrium is dynamic in nature.

4. Discuss any one application of Le-Chatlier's principle as applied to chemical equilibrium.

5. Explain the concept of chemical potential of a substance.

6. Explain the law of chemical equilibrium in detail

7. Explain the thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient

DEPARTMENT OF CHEMISTRY

Online questions (Multiple Choice questions)

PHYSICAL CHEMISTRY II (CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS)

UNIT IV

S.No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1.	Chemical equilibrium is	dynamic	static	invisible	dormant	dynamic
2.	A catalyst can	Alter the state of equilibrium	Cannot alter the state of equilibrium	Does not affect equilibrium	Decrease the rate of equilibrium	Cannot alter the state of equilibrium
3.	It is characterised by constant value of pressure at a given temperature	Chemical equilibrium	Chemical kinetics	polymerization	Formation of nano particles	Chemical equilibrium
4.	It is characterised by constant value of Concentration at a given temperature	Chemical equilibrium	Chemical kinetics	polymerization	Formation of nano particles	Chemical equilibrium
5.	It is characterised by constant colour at a given temperature	Chemical equilibrium	Chemical kinetics	polymerization	Formation of nano particles	Chemical equilibrium
6.	A reaction proceeds from the reactant towards the products it is called	Forward reaction	Backward reaction	Equilibrium reaction	Vibrant reaction	Forward reaction
7.	A reaction proceeds from the product towards the reactant it is called	Forward reaction	Backward reaction	Equilibrium reaction	Vibrant reaction	Backward reaction
8.	The two opposing reactions proceed simuntaneously at equal rate, the the system is said to be in	Chemical equilibrium	Steady state	Activated state	Inert state	Chemical equilibrium
9.	The rate at which a substance reacts is proportional to	The active mass	concentration	pressure	volume	The active mass

10.	The active mass of a solid substance	unity	concentration	pressure	volume	Unity
11.	The active mass of a solution	unity	Molar concentration	pressure	volume	Molar concentration
12.	The active mass of a gaseous substance is	unity	Molar concentration	Partial pressure	volume	Partial pressure
13.	The ratio of the rate constants of two opposing reactions	Equilibrium constant	Specific constant	Steady state constant	Van't of factor	Equilibrium constant
14.	Equilibrium constant is	The rate constant of the forward reaction	The rate constant of the backward reaction	The multiplication of the rate constants of two opposing reactions	The ratio of the rate constants of two opposing reactions	The ratio of the rate constants of two opposing reactions
15.	The equilibrium constant is a constant at a given	pressure	temperature	volume	concentration	temperature
16.	The equilibrium constant K_c refers to the equilibrium constant expressed in terms of	Molar concentration	Partial pressure	activities	Mole fraction	Molar capacities
17.	The equilibrium constant K_p refers to the equilibrium constant expressed in terms of	Molar concentration	Partial pressure	activities	Mole fraction	Partial pressure
18.	The equilibrium constant K_a refers to the equilibrium constant expressed in terms of	Molar concentration	Partial pressure	activities	Mole fraction	Activities
19.	The equilibrium constant K_x refers to the equilibrium constant expressed in terms of	Molar concentration	Partial pressure	activities	Mole fraction	Mole fraction
20.	If the equilibrium constant is expressed in terms of partial pressure , then it is written as	K_c	K_p	K_a	K_x	K_p
21.	If the equilibrium constant is expressed in terms of molar concentration , then it is written as	K_c	K_p	K_a	K_x	K_c
22.	If the equilibrium constant is expressed in terms of activity , then it is written as	K_c	K_p	K_a	K_x	K_a

23.	If the equilibrium constant is expressed in terms of mole fraction , then it is written as	K_c	K_p	K_a	K_x	K_x
24.	'dn' in the expression for the K_c and K_p is the	Difference in the number of moles of products and reactants	Difference in the number of mole fraction of products and reactants	Difference in the number of partial pressures of products and reactants	Product of the number of moles of products and reactants	Difference in the number of moles of products and reactants
25.	Unit of concentration in the expression of K_c is	Moles/litre	Moles^2/litre	Moles/litre^{-1}	Moles/litre^{-2}	Moles/litre
26.	The relation ship between K_p and K_c is	$K_p = K_c (RT)^{dn}$	$K_p = K_c (RT)$	$K_p = K_c (RT)^2$	$K_p = K_c (RT)^3$	$K_p = K_c (RT)^{dn}$
27.	Chemical potential of a substance is otherwise called	Gibbs free energy	Helmholtz free energy	Partial molar free energy	Duhem energy	Partial molar free energy
28.	When dG is negative, then it is a	Spontaneous in forward direction	222	Non-Spontaneous in forward direction	Non Spontaneous in reverse direction	Spontaneous in forward direction
29.	When dG is positive, then it is a	Spontaneous in forward direction	Spontaneous in reverse direction	Non-Spontaneous in forward direction	Non Spontaneous in reverse direction	Non-Spontaneous in forward direction
30.	When dG is less than zero, then it is a	Spontaneous in forward direction	Spontaneous in reverse direction	Non-Spontaneous in forward direction	Non Spontaneous in reverse direction	Spontaneous in forward direction
31.	When dG is greater than zero, then it is a	Spontaneous in forward direction	Spontaneous in reverse direction	Non-Spontaneous in forward direction	Non Spontaneous in reverse direction	Non-Spontaneous in forward direction
32.	When dG=0	Spontaneous in forward direction	Spontaneous in reverse direction	Non-Spontaneous in forward direction	The reaction will be in equilibrium	The reaction will be in equilibrium
33.	The reaction will be Spontaneous in forward direction, when the value of dG is	positive	negative	zero	fractions	negative
34.	The reaction will be in equilibrium, then the value of dG is	positive	negative	zero	insquares	zero

35.	The reaction will be Non-Spontaneous in forward direction, when the value of dG is	positive	negative	zero	fractions	Positive
36.	The reaction will be Spontaneous in forward direction, when the value of dG is	Greater than zero	Less than zero	zero	fractions	Less than zero
37.	The reaction will be Non-Spontaneous in forward direction, when the value of dG is	Greater than zero	Less than zero	zero	fractions	Less than zero
38.	An homogeneous equilibrium is	Reactants and products are in same phase	Reactants and products in different phases	The reactants and products are in two or more phases	Reactants and products are in different allotropic phase	Reactants and products are in same phase
39.	An heterogenous equilibrium is	Reactants and products are in same phase	Reactants and products in gaseous phases	The reactants and products are in two or more phases	Reactants and products are in different allotropic phase	The reactants and products are in two or more phases
40.	The reactants and products are in two or more phases, then the equilibrium is called	Homogenous	heterogenous	eutectic	Two phase system	heterogenous
41.	The reactants and products are in same phases, then the equilibrium is called	Homogenous	heterogenous	eutectic	Two phase system	Homogenous
42.	Formation of hydrogen iodide from hydrogen and iodine is an example for	Homogenous equlibrium	Heterogenous equilibrium	Eutectic system	Two phase system	Homogenous equilibrium
43.	Formation of ester from acid and alcohol is an example for	Homogenous equlibrium	Heterogenous equilibrium	Eutectic system	Two phase system	Homogenous equilibrium
44.	Decomposition of calcium carbonate in to calcium oxide and carbon di oxide is an example for	Homogenous equlibrium	Heterogenous equilibrium	Eutectic system	Two phase system	Heterogenous equilibrium

45.	If an equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress, the law is	Le-Chatelier Braun principle	Kirchoff principle	Gibbs-helmoltz equation	Duhem principle	Le-Chatelier Braun principle
46.	If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change	Le-Chatelier Braun principle	Kirchoff principle	Gibbs-helmoltz equation	Duhem principle	Le-Chatelier Braun principle
47.	In the Habers process for the synthesis of ammonia, the temperature should be	Very low	Moderate (773K)	Very high	high	Moderate (773K)
48.	In the Habers process for the synthesis of ammonia, the pressure should be	Very low	Moderate	Very high	high	Very high
49.	In the Habers process for the synthesis of ammonia, the concentration should be	Nitrogen should be more	Hydrogen should be more	Both nitrogen and hydrogen should be more	Ammonia should be more	Both nitrogen and hydrogen should be more
50.	In the Habers process for the synthesis of ammonia, the forward reaction is	endothermic	exothermic	intensive	extensive	exothermic
51.	In the Habers process for the synthesis of ammonia, the backward reaction is	endothermic	exothermic	intensive	extensive	endothermic
52.	In the Habers process for the synthesis of ammonia, the forward reaction is accompanied with	Increase in the number of moles	Decrease in the number of moles	Equal number of moles	Absorption of heat	Decrease in the number of moles
53.	In the synthesis of sulphur tri-oxide by contact process, the temperature should be	Very low	Moderate (873K)	Very high	high	Moderate (873K)
54.	In the synthesis of sulphur tri-oxide by contact process, the pressure should be	Very low	Moderate	Very high	high	Very high

55.	In the synthesis of sulphur tri-oxide by contact process, the concentration should be	High concentration of sulphur dioxide and oxygen	High concentration of sulphur dioxide	High concentration of oxygen	low concentration of sulphur dioxide and oxygen	High concentration of sulphur dioxide and oxygen
56.	In the synthesis of sulphur tri-oxide by contact process, the forward reaction is	endothermic	exothermic	intensive	extensive	endothermic
57.	In the synthesis of sulphur tri-oxide by contact process, the forward reaction is accompanied by	Increase in the number of moles	Decrease in the number of moles	Equal number of moles	Absorption of heat	Decrease in the number of moles
58.	The catalyst used in Habers process	Fe	Vanadium pentoxide	molybdenum	Iron & Molybdenum	Iron & Molybdenum
59.	The promoter used in Habers process	Fe	Vanadium pentoxide	molybdenum	Iron & Molybdenum	Molybdenum
60.	The promoter used in contact process	Fe	Vanadium pentoxide	molybdenum	Iron & Molybdenum	Vanadium pentoxide

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COURSE CODE: 17CHU201   **UNIT: V(Solution and Colligative Properties)**   **BATCH-2017-2020**

UNIT V

SYLLABUS

> **Solutions and Colligative Properties:** Dilute solutions; lowering of vapour pressure, Raoult's and Henry's Laws and their applications. Thermodynamic derivation using chemical potential to derive relations between the four colligative properties [(i) relative lowering of vapour pressure, ii) elevation of boiling point, (iii) Depression of freezing point, (iv) osmotic pressure] and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution.

The **colligative properties** of a solution are usually considered to be:

1. *Freezing-point depression*: the decrease in the freezing point of the solution, compared to pure solvent at the same pressure.

2. *Boiling-point elevation*: the increase in the boiling point of a solution containing nonvolatile solutes, compared to pure solvent at the same pressure.

3. *Vapor-pressure lowering*: the decrease in the vapour pressure of a solution containing nonvolatile solutes, compared to the vapour pressure of the pure solvent at the same temperature.

4. *Osmotic pressure*: the increase in the pressure of the solution that places the solvent in transfer equilibrium with pure solvent at the same temperature and pressure as the original solution.

Henry's Law

The most commonly used form of Henry's law states "the partial pressure (P) of the gas in vapour phase is proportional to the mole fraction (x) of the gas in the solution" and is expressed as p = KH .x Greater the value of KH, higher the solubility of the gas. The value of KH decreases with increase in the temperature. Thus, aquatic species are more comfortable in cold water [more dissolved O2] rather than Warm water.

Applications

1. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its

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solubility.

2. To minimise the painful effects (bends) accompanying the decompression of deep sea divers. O2 diluted with less soluble. He gas is used as breathing gas.

3. At high altitudes, the partial pressure of O2 is less then that at the ground level. This leads to low concentrations of O2 in the blood of climbers which causes anoxia

Methods of Expressing Concentration of Solutions

(i) Percentage by weight (w / w %)
It is defined as the amount of solute present in 100 g of solution. w / w % = weight of solute / weight of solution x 100

(ii) Percentage by volume (w / v%) It is defined as the weight of solute present in 100 mL of solution. w / v % = weight of solute /volume of solution x 100 or the volume of solute present in 100 mL of solution. v / v % = volume of solute / volume of solution x 100

(iii) Mole fraction (x) It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B are nA and nB respectively, the mole fraction of A will be

$$\chi_A = \frac{n_A}{n_A + n_B}$$

Similarly, $$\chi_B = \frac{n_B}{n_A + n_B} \quad \because \chi_A + \chi_B = 1$$

(iv) **Parts per million** (ppm)

It is defined as the parts of a component per million parts (10^6) of the solution. It is widely used when a solute is present in trace quantities.

ppm = number of parts of the component / total number of parts of all the components x 10^6

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(v) **Molarity** (M)

It is the number of moles of solute present in 1L(dm3) of the solution.

M = number of moles of solute / volume of solution (L)

M = mass of solute (in gram) x 1000 / mol. wt. of solute x volume of solution (in mL)

Molarity varies with temperature due to change in volume of solution.[When molarity of a solution is 1 M, it is called a molar solution. 0.1 M solution is called a decimolar solution while 0.5 M solution is known as semi molar solution]

Molarity = Percent by mass x density x 10 / molecular weight

Dilution law, M1 V1 = M2 V2 (for dilution from volume V1 to V2)

For reaction between two reactants, M1 V1 / n1 = M2 V2 / n2

where, n1 and n2 arc stoichiometric coefficient in balanced equation.

(vi) **Molality**(m)

It is the number of moles of solute per kilogram of the solvent.

Molality = mass of solute in gram / mol. wt. of solute x mass of solvent (in kg)

Molality is independent of temperature.

(vii) **Normality** (N) The number of gram equivalents of solute present in 1 L of solution.

Normality = number of grams equivalent of solute / volume of solution in L

Number of gramequivalents of solute = mass of solute in gram / equivalent weight

[Relationship between normality and molarity N x Eq. weight = M x mol. weight]

If two solutions of the same solute having volumes and molarities V1, M1 and V2, M2 are mixed, the molarity of the resulting solution is

$$M = \frac{V_1 M_1 + V_2 M_2}{V_1 + V_2}$$

$$\text{Similarly, Normality } (N) = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

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Lowering of vapour pressure of solvent in solution

All liquids exhibit tendency for evaporation. The gaseous state of a substance is called vapour. If the intermolecular forces of attraction are weak the liquids evaporate readily and are called volatile liquids. E.g Ethyl acetate is the most volatile liquid. Ethyl alcohol, acetone are also volatile liquids. Due to strong intermolecular forces of attraction, Lubricating oils are slightly volatile.

Concept of Vapour pressure of liquid

Liquid escapes from an open vessel by evaporation. If the vessel is closed, the process of evaporation continues
The molecules of liquid escaping from the surface of liquid remain in the container above the surface of liquid. These molecules of vapour are in continuous random motion.

They collide with each other, with the walls of the container and with the surface of the liquid and return to the liquid state. This is reverse of evaporation, called condensation.

After some time interval, equilibrium is established between two phases of the substance, liquid and its vapour. At this stage the rate of evaporation equals the rate of condensation.

The pressure exerted by vapor at this stage is called as Vapor pressure.Vapour pressure of a liquid, increases with the increase of temperature.

Note: If the boiling is carried out in an open atmosphere then external pressure is the atmospheric pressure.

Definition of Vapor pressure of Liquid

The vapour pressure of a substance is defined as the pressure exerted by the gaseous state of that substance when it is in equilibrium with the solid or liquid phase.

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Concept of Lowering of vapor pressure of solvent in solution

The vapour pressure of a liquid solvent is lowered when a non –volatile solute is dissolved in it to form a solution.

In case of pure solvent, its surface area is completely occupied by volatile solvent molecules. In case of solution of nonvolatile solute, its surface area is not completely available for volatile solvent but it is partly occupied by non volatile solute.

Hence, rate of evaporation of the solution will be less as compared to that of pure solvent Thus vapour pressure of solution is lower than that of the pure solvent.

Definition: The difference between vapour pressures of pure solvent and the vapor pressure of solvent from solution is called vapour pressure lowering
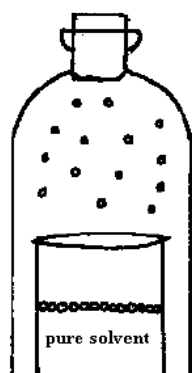
Evaporation of the
molecules of the
solvent from its surface
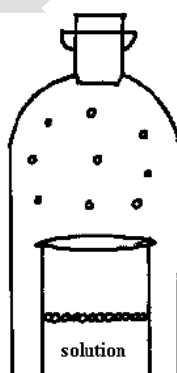
Evaporation of solvent from
solution

Thus lowering of vapour pressure of solvent takes place due to addition of non-volatile solute.

Mathematical Expression for lowering of vapour pressure

If is the vapour pressure of pure solvent is p01 and p is the vapour pressure of the solution of non volatile solute in the same solvent, then and the lowering of vapour pressure is,

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$\Delta p = p^0 1 -- p$

The relative lowering of vapour pressure: The relative lowering of vapour pressure for the given solution is the ratio of vapour pressure lowering of solvent from solution to the vapour pressure of pure solvent. Thus,

Relative lowering of vapour pressure $= \Delta P / P_1^0 = P_1^0 - P / P_1^0$

Raoult's Law

The partial vapour pressure of any volatile component of a solution is the product of vapour pressure of that pure component and the mole fraction of the component in the solution

The Raoult',s law can also be stated as "For a solution of two volatile liquids, the vapour pressure of each liquid in the solution is less than the respective vapour pressure of the pure liquids and the equilibrium partial vapour pressure of the liquid is directly proportional to its mole fraction.

For a solution containing two liquids A and B, the partial vapour pressure of liquid A

Is

$$p_A \propto \chi_A \quad \text{or} \quad p_A = k\chi_A$$

$$\text{where,} \quad \chi_A = \frac{n_A}{(n_A + n_B)} = \text{mole fraction of liquid } A$$

The proportionality constant is obtained by considering the pure liquid when $\chi A = 1$ then $k = P°A$, the vapour pressure of pure liquid, hence

$$p_A = p_A^° \chi_A$$

Similarly,

$$p_B = p_B^° \chi_B$$

The total vapour pressure of the solution,

$$P_T = p_A + p_B = p_A^° \chi_A + p_B^° \chi_B$$

$$= p_A^° + (p_B^° - p_A^°)\chi_B$$

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Relative Lowering of Vapour Pressure

It is the ratio of lowering in vapour pressure to vapour pressure of pure solvent. The relative lowering in vapour pressure of solution containing a nonvolatile solute is equal to the mole fraction of solute in the solution

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \chi_B$$

where, $\dfrac{p_A^\circ - p_A}{p_A^\circ}$ = relative lowering of vapour pressure

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

for dilute solutions, $n_B \ll n_A$. Hence,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_B}{n_A}$$

or

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$M_B = \frac{W_B}{W_A} \times M_A \times \frac{p_A}{(p_A^\circ - p_A)}$$

Above expression is used to find the molecular weight of an unknown solute dissolved in a given solvent. Where, WB and WA = mass of Solute and solvent respectively. MB and MA = molecular weight of solute and solvent respectively. Ostwald and Walker method is used to determine the relative lowering of vapour pressure.

Elevation in Boiling Point (ΔTb)

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. As the vapour pressure of a solution containing a nonvolatile solute is

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lower than that of the pure solvent, it boiling point will be higher than that of the pure solvent
as shown in figure. The increase in boiling point is known as elevation in boiling point, ΔTb
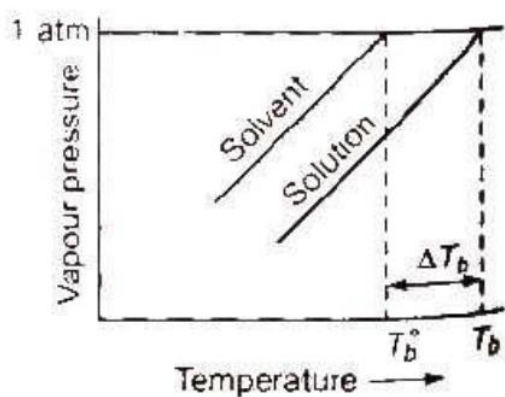
$$\Delta Tb = Tb - T°b$$

$$\Delta Tb = Kb\,m \text{ (where; m = molality)}$$

Kb is molal elevation constant or ebullioscopic constant. Molecular mass of solute can be
calculated as

$$\Delta T_b = \frac{K_b \cdot W_B \times 1000}{M_B \times W_A}$$

$$M_B = K_b \cdot \frac{W_B}{W_A} \times \frac{1000}{\Delta T_b}$$

where, WB and WA = mass of solute and solvent respectively.

Kb has units of K / m or K kg mol-1, for water, Kb = 0.52 K kg mol-1

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The boiling point elevation of a solution is determined by

(i) Landsberger's method

(ii) Cottrell's method

Depression in Freezing Point (ΔTf)

Freezing point of a liquid is the temperature at which vapour pressure of the solvent in its liquid and solid phase become equal. As we know that vapour pressure of solution containing non-volatile solute is lower than that of pure solvent, solid form gets separated out at a lower temperature as shown in the figure.
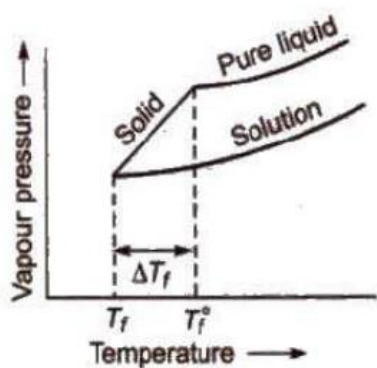
This decrease in freezing point of a liquid is known as depression in freezing point.

Depression in freezing point (ΔTf) = T°f– Tf

$$\Delta T_f = K_f \cdot m = K_f \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

Where, Kf is molal depression constant or cryoscopic constant.

Kf has units of K / m or K kg mol-1.

Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called antifreeze solution.

[Common salt (NaCI) and anhydrous CaC12 are used to clear snow on the roads because they depress the freezing point of water. The freezing point depression is determined by Beckmannmethod or Rast method.]

Calculations of molal elevation constant (Kb) and molal depression constant (Kf)

$$K_b = \frac{M_A R(T_b^{\circ})^2}{\Delta H_v}, \; K_f = \frac{M_A \cdot R(T_f^{\circ})^2}{\Delta H_f}$$

T_b° = boiling point of solvent
T_f° = freezing point of solvent
ΔH_f = molar enthalpy of fusion
ΔH_n = molar enthalpy of vaporisation

Semi permeable membrane:

It is a membrane which allows the solvent molecules, but not the solute molecules, to pass through it. The thin films of the copper ferrocyanide, deposited in pores of porous porcelain pot is the best semi permeable membrane. Cu_2 [Fe(CN)]6 Cellulose, cellulose nitrate, animal bladder, etc. are used as semi permeable membranes.

Osmosis

When a solution is separated from pure solvent by a semipermeable membrane as shown in figure, the solvent molecules pass through the membrane into the solution and dilute it.

Similarly, when two solutions of different concentrations are seperated by semipermeable membrane then the direction of flow of solvent molecules is from the solution of lower concentration to the solution of higher concentration.

Due to flow of solvent into the high concentrated solution, the solution gets diluted. The flow continues till the concentrations of the two solutions become equal.

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Osmosis between solvent & solution

Osmosis between 2 solutions of different concentration
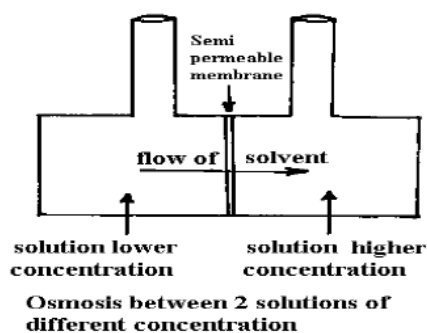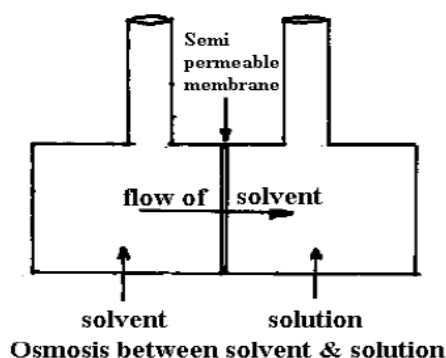
Definition of Osmosis

The spontaneous and unidirectional flow of solvent molecules through a semi permeable membrane, into the solution or flow of solvent from a solution of lower concentration to the solution of higher concentration through a semi permeable membrane is called osmosis

Osmotic Pressure

The excess of pressure on the side of solution that stops the net flow of solvent into solution through semi permeable membrane is called osmotic pressure.

Note: The osmotic pressure is not the pressure produced by solution. It exists only when the solution is separated from the solvent by the semi permeable membrane. The resulting osmosis produces an excess pressure (osmotic pressure) in the solution. The entry of the solvent into the solution causes its dilution and concentration changes.

Alternative Definition of Osmotic Pressure (π)

Osmotic pressure of a solution can also be defined as the excess mechanical pressure which must be applied on the side of solution to stop the flow of solvent molecules through semipermeable membrane into the solution.

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$$\text{Osmotic pressure } (\pi) = RCT; \left(C = \frac{n_B}{V} = \frac{W_B}{M_B V} \right)$$

$$M_B = \frac{W_B RT}{\pi V}$$

$$\pi = \frac{dRT}{M_B} : \left(d = \frac{W_B}{V} \right)$$

Where, d = density, R = solution constant, T = temperature, MB = molar mass of solute

Osmotic pressure can be determined by anyone of the method listed below

(i) Pfeffer's method

(ii) Berkeley and Hartley's method (very good method)

(iii) Morse and Frazer's method

On the basis of osmotic pressure, -the solution can be

(i)   **Hypertonic solution** A solution is called hypertonic if its osmotic pressure is higher than that of the solution from which it is separated by a semipermeable membrane. When a plant cell is placed in a hypertonic solution, the fluid from the plant cell comes out and cell shrinks, this phenomenon is called plasmolysis.

(ii)   **Hypotonic solution** A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semi permeable membrane.

(iii)   **Isotonic solution** Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBC's.

Two solutions are isotonic if they have the same molar concentration, e.g., if x % solution of X is isotonic with y % solution of Y, this means molar concentration of X = Molar concentration of Y

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Osmotic pressure method is the best method for determining the molecular masses of polymers since observed value of any other colligative property is too small to be measured with reasonable accuracy.

Abnormal Molecular Masses

In some cases, observed colligative properties deviate from their normal calculated values due to association or dissociation of molecules. As we know,

Colligative property $\propto 1 / MB$
Higher and lower values of molar mass is observed in case of association and dissociation respectively, e.g., in benzene, acetic acid gets associated, so, it's observed molecular mass is 120.

Similarly KCI undergoes dissociation in aqueous solution, so it's observed molecular mass is 37.25. These observed values are corrected by multiplying with vant Hoff factor (i).

Laws of osmotic pressure:

According to the theory, solute molecules in dilute solutions possess kinetic energy and move in random directions in the solution and behave like gas molecules.

On collision against semi permeable membrane, the solute molecules exert osmotic pressure equal to the pressure, which the solute molecules would exert if it were gas molecules at the same temperature and occupying the same volume as the solution.

Thus the osmotic pressure could be considered to be due to bombardment of solute particles on semi permeable membrane.

The osmotic pressure is thus directly proportional to the number of solute particles or the concentration of solute at constant temperature.

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State Van't Hoff – Boyle's Law and its mathematical expression.

At constant temperature the osmotic pressure of a dilute solution is directly proportional to its molar concentration or inversely proportional to the volume of the solution. **$\pi\ \alpha\ C$**

If n moles of solute is dissolved in V liters then

$$C = n/V$$

Hence, **$\pi\ \alpha\ n/V$ or $\pi\ \alpha\ 1/V$** for constant n hence ,

$$\pi V = \text{constant or } \pi/C = \text{constant}$$

State Van't Hoff – Boyle's Law and its math ematical expression

The concentration remaining constant ; the osmotic pressure of a dilute solution is directlyproportional to the absolute temperature. **$\pi\ \alpha\ T$** i.e.π/T = constant

Van't Hoff Factor (i)It is the ratio of observed value of colligative property to the calculated value of colligative property.

i = observed value of colligative property / calculated value of colligative property
or i = normal molecular mass / observed molecular mass
or i = number of particles after association or dissociation / number of particles initially So to correct the observed value of molar mass, vant Hoff factor (i) must be included in different expressions for colligative properties.

$$\Delta T_b = i\,K_b \cdot m$$
$$\Delta T_f = iK_f \cdot m$$
$$\pi = i\,CRT$$
$$\frac{\Delta p}{p_A^\circ} = ix_B$$

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Degree of Dissociation (α) and van't Hoff Factor (i)

(i) If one molecule of a substance gets dissociated into n particles or molecules and α is the degree of dissociation then

$$A \longrightarrow nP$$

Initially	1 mol	0
At eq.	$1 - \alpha$	$n\alpha$

Total number of moles at equilibrium

$$= 1 - \alpha + n\alpha$$

$$\therefore \quad i = \frac{1 - \alpha + n\alpha}{1}$$

$$\Rightarrow \quad \alpha = \frac{i - 1}{n - 1}$$
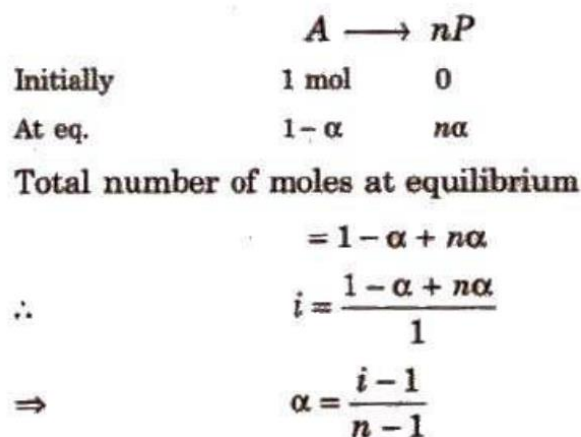
Degree of Association (α) and van't Hoff Factor (i)

If n molecules of a substance A associate to form An and α is the degree of association then

$$nA \longrightarrow A_n$$

Initially	1 mol	0
At equilibrium	$1 - \alpha$	$\dfrac{\alpha}{n}$

Total number of moles at equilibrium

$$= 1 - \alpha + \frac{\alpha}{n}$$

$$i = \frac{1 - \alpha + \dfrac{\alpha}{n}}{1}$$

$$\Rightarrow \quad \alpha = \frac{i - 1}{\dfrac{1}{n} - 1}$$
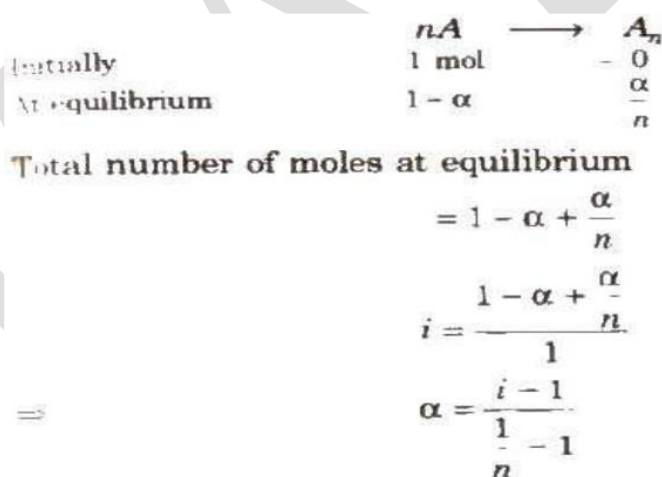
van't Hoff factor (i) > 1 for solutes undergoing dissociation and it is < 1 for solutes undergoing association

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POSSIBLE QUESTIONS
PART B (2 Mark Questions)

1. What are colligative properties

2. What is Van't Hoff factor

3. Define osmotic pressure

4. State Raoult's law

5. State and explain Henry law

6. What is meant by cryoscopic constant

7. State and explain ebulioscopic constant.

8. What is meant by osmosis.

9. At what temperature a liquid will boil.

PART C (8 Mark Questions)

1. Define osmotic pressure. How osmotic pressure is measured experimentally by Berkely and Hartely method. What are the advantages of this method over the other   methods?

2. Derive a relation between the relative lowering of vapour pressure and the molecular weight of the solute

3. Derive a relation between the osmotic pressure and the molecular weight of the solute.

4. what is meant by elevation of boiling point of a solution and how it is determined by Beckmann's method.

5. Explain the applications in calculating molar masses of normal, dissociated and associated solutes in solution

DEPARTMENT OF CHEMISTRY

Online questions (Multiple Choice questions)

PHYSICAL CHEMISTRY II (CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS)

UNIT V

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1.	A liquid boils when its vapour pressure becomes equal to	One atmospheric pressure	Zero	Very high	Very low	One atmospheric pressure
2.	The elevation in boiling point is given by the formulae dt = $K_b$xw/m x 1/W, Kb is called	Boiling point constant	Ebullioscoic constant	Molal elevation constant	Depression in freezing point	Ebullioscoic constant
3.	In the calculation of depression of freezing point, K_f is called	Molal depression constant	Freezing point depression constant	Cryoscopic constant	Elevation of boiling point	Cryoscopic constant
4.	The ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a non-electrolyte solution is known as	Degree of dissociation	Degree of association	Activity coefficient	Van't Hoff factor	Van't Hoff factor
5.	Molal elevation constant is the boiling point elevation when ----- of the solute is dissolved in one kg of the solvent	One gram	One kg	One mole	One normal	One mole
6.	Freezing point depression is measured by	Beckmann method	Faraday's camphor method	calorimeter	polarimetry	Beckmann method
7.	In one molal solution that contains 0.5 mole of a solute there is	1000 g of the solvent	1000 ml of the solvent	500 ml of solvent	500 g of the solvent	500 g of the solvent

8.	The law of the relative lowering or vapour pressure was given by	Van't Hoff	Ostwald	Raoult	Henry	Raoult
9.	Which of the following is a colligative property	Molar refractivity	Optical rotation	Depression in freezing point	viscosity	Depression in freezing point
10.	Which of the following is a colligative property	Molar refractivity	Optical rotation	Osmotic pressure	viscosity	Osmotic pressure
11.	Which of the following is a colligative property	Molar refractivity	Optical rotation	Elevation in boiling point	viscosity	Elevation in boiling point
12.	Which of the following is a colligative property	Molar refractivity	Optical rotation	Lowering of vapour pressure of solvent	viscosity	Lowering of vapour pressure of solvent
13.	The number of moles of a solute per kilo gram of the solvent is called	formality	Normality	Molarity	Molality	Molality
14.	Which of the following does not depend upon the temperature	Molarity	Molality	formality	Normality	Molality
15.	The study of depression in freezing point of a solute is called	Osmotic pressure	ebullioscopy	cryoscopy	polarimetry	cryoscopy
16.	The liquid mixtures which distil with a change in composition are called	Azeotropic mixtures	Equilibrium mixtures	Zeotropic mixtures	Non scholarating mixtures	Zeotropic mixtures
17.	Lowering of vapour pressure is measured by	Beckmann method	Faraday's camphor method	Ostwald and Walkers method	polarimetry	Ostwald and Walkers method
18.	One of the applications of the colligative property is to determine the	Molecular weight of the substance	Refractive index	Melting point	density	Molecular weight of the substance
19.	Colligative property depends upon	No of solute particles present in the solution	Nature of the solute	Nature of the solvent	Molecular weight of the solvent	No of solute particles present in the solution
20.	Colligative properties are applicable only to	Concentrated solution	Dilute solution	Saturated solution	Isotonic solutions	Dilute solution
21.	The vapour pressure of a liquid of solution can be	Dialtometer	Pyrometer	manometer	Polarimeter	Manometer

	measured with the help of a					
22.	The relative lowering of vapour pressure depends only upon the	Melting point of solute	Boiling point of solvent	Molar concentration of the solvent	Mole fraction of the solute	Mole fraction of the solute
23.	Example for a semi permeable membrane	Parchment paper	Chromatography paper	Thin films	nanoparticles	Parchment paper
24.	The membrane which allows the flow of solvent molecules through it but not the solute molecules is called	Semipermeable membrane	Fully permeable membrane	Filter paper membrane	Animal cell membrane	Semipermeable membrane
25.	Pick up the semi permeable membrane	Collodion	Chromatography paper	Thin films	nanoparticles	Collodion
26.	Which is a semi permeable membrane	cellophane bag	Chromatography paper	Thin films	nanoparticles	cellophane bag
27.	Parchment paper is used as a	Semipermeable membrane	Chromatography paper	Thin films	nanoparticles	Semipermeable membrane
28.	Collodion is a	Semipermeable membrane	Chromatography paper	Thin films	nanoparticles	Semipermeable membrane
29.	When a solvent is separated from its solution by a semipermeable membrane, the molecules of the solvent diffuse through the semipermeable membrane, the phenomenon is	dialysis	Hydrolysis	Osmosis	vapourisation	Osmosis
30.	The pressure exerted by the solution column which just prevents the flow of solvent molecules into the solution through a semipermeable membrane	Internal pressure	External pressure	Osmotic pressure	Viscous pressure	Osmotic pressure
31.	The phenomenon by which the pure solvent molecules tend to diffuse though a semipermeable membrane	dialysis	Hydrolysis	Osmosis	vapourisation	Osmosis

	into the solution				
32.	The osmotic pressure is proportional to the molar concentration of the solute in the solution	Van't Hoff equation	Kirchoffs equatio	Gibbs eq uation	Helmholtz equation	Van't Hoff equation
33.	Osmotic pressure is directly proportional to the	Temperature of the solution	Volume of the solution	Pressure of the solution	Boiling point of the solution	Temperature of the solution
34.	Osmotic pressure is directly proportional to the	Molar concentration of the solution	Volume of the solution	Pressure of the solution	Boiling point of the solution	Molar concentration of the solution
35.	Molecular weight of a solute can be obtained from	Lowering of vapour pressure of the solvent	The transport number pf the solute	Infra red spectroscopy	Joule calorimeter	Lowering of vapour pressure of the solvent
36.	Molecular weight of a solute can be obtained from	Elevation of boiling point	The transport number pf the solute	Infra red spectroscopy	Joule calorimeter	Elevation of boiling point
37.	Molecular weight of a solute can be obtained from	Depression of freezing point	The transport number pf the solute	Infra red spectroscopy	Joule calorimeter	Depression of freezing point
38.	Molecular weight of a solute can be obtained from	Osmotic pressure	The transport number pf the solute	Infra red spectroscopy	Joule calorimeter	Osmotic pressure
39.	Two solutions having the same osmotic pressure at the same temperature is called	Isobaric solutions	Isotonic solutions	Isochoric solutions	Concentrated solutions	Isotonic solutions
40.	Isotonic solutions have the same osmotic pressure at the same	Pressure	Volume	Temperature	concentration	Temperature
41.	Isotonic solutions have at the same temperature	Pressure	Volume	Osmotic pressure	concentration	Osmotic pressure
42.	Osmotic pressure is determined by	Dialysis	Hydrolysis	Berkeley & Hartly method	Dialtometric method	Berkeley & Hartly method
43.	Beckmann thermometer is a	Absolute thermometer	Arbitrary thermometer	360 degree thermometer	Differential thermometer	Differential thermometer

44.	Example for a differential thermometer is	pyrometer	Cottrell thermometer	Beckmann thermometer	Oswald thermometer	Beckmann thermometer
45.	Beckmann thermometer is designed to measure	Small changes in temperature	Large difference in temperatures	Absolute temperature	Temperature in different pessures	Small changes in temperature
46.	In Beckmann thermometer, the scale is caliberated from	0K to 100K	0 to 360 K	298K to 373K	0 to 6K	0 to 6K
47.	Molal elevation constant is otherwise known as	Ebullioscopic constant	Cryoscopic constant	Osmotic pressure	Lowering of vapour pressure constant	Ebullioscopic constant
48.	The elevation in boiling point of a solution containing 1 gram mole of a solute per 1000 g of the solvent	Ebullioscopic constant	Cryoscopic constant	Osmotic pressure	Lowering of vapour pressure constant	Ebullioscopic constant
49.	The elevation in boiling point of a solution containing 1 gram mole of a solute per 1000 g of the solvent	Molal elevation constant	Cryoscopic constant	Osmotic pressure	Lowering of vapour pressure constant	Molal elevation constant
50.	Vapour pressure of a solution of a non-volatile solute is always	Lower than that of the solvent	Higher than that of the solvent	Equal to the solvent	Comparable to that of a solvent	Lower than that of the solvent
51.	The boiling point of a solution is always	Lower than that of the solvent	Higher than that of the pure solvent	Equal to the solvent	Comparable to that of a solvent	Higher than that of the pure solvent
52.	Molal depression constant is otherwise known as	Ebullioscopic constant	Cryoscopic constant	Osmotic pressure	Lowering of vapour pressure constant	Cryoscopic constant
53.	The depression in freezing point of a solution containing 1 gram mole of a solute per 1000 g of the solvent	Ebullioscopic constant	Cryoscopic constant	Osmotic pressure	Lowering of vapour pressure constant	Cryoscopic constant
54.	Abnormal molecular mass of a solute is due to	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	Association of molecules
55.	Abnormal molecular mass of a solute is due to	dissociation of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	dissociation of molecules
56.	The abnormal molecular mass of acetic acid in benzene is due	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	Association of molecules

57.	The abnormal molecular mass of benzoic acid in benzene is due	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	Association of molecules
58.	The abnormal molecular mass of chloro acetic acid in naphthalene is due	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	Association of molecules
59.	The value of Van't Hoff fator 'i' is greater than one, it is due to	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	Association of molecules
60.	The value of Van't Hoff fator 'i' is less than one, it is due to	Association of molecules	Evaporation of solvent	Condensation of the solvent	Volatility of the solvent	dissociation of molecules

Reg.No...............

[17CHU201]

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
SECOND SEMESTER
DEPARTMENT OF CHEMISTRY
INTERNAL EXAM - I
PHYSICAL CHEMISTRY-II (Chemical Thermodynamics and its applications)

Date   :
Sub code : 17CHU201

Time   : 2 hours
Marks : 50 marks

PART–A
Answer All the Questions   (20 x 1 = 20 marks)

1. Which one of the following thermodynamic quantities is not a state function?

    a. Gibbs free energy   b. work   c. entropy   d. internal energy

2. All of the following have a standard heat of formation value of zero at 25°C and 1 atm except

    a. $N_2(g)$ b. Fe(s)   c. Ne(g)   d. $H_2(l)$

3. The intensive property is

    a. mass   b. volume   c. energy   d. temperature

4. Which statement is incorrect?

    a. At constant pressure, H = E + PV   b. The thermodynamic symbol for entropy is S

    c. Gibbs free energy is a state function   d. for an endothermic process, ΔH is negative

5. Heat capacity is an ----------

    a. extensive property   b. intensive property   c. path function   d. state function

6. Which type of ideal gas will have the largest value for $C_p – C_v$?

    a. Mono atomic   b. Diatomic   c. Polyatomic   d. The value will be the same for all

7. For which of the following process is the entropy change zero?

    a. Isobaric   b. Isothermal   c. Adiabatic   d. Constant volume

8. A system is taken from state A to state B along two different paths 1 and 2. The heat absorbed and works done by the system along these paths are Q1 and Q2 and W1 and W2respectively. Then

    a. Q1 = Q2   b. W1 + Q1 = Q2 + W2   c. W1 = W2   d. Q1 - W1 = Q2 - W2

9. In a reversible adiabatic change ΔS is

    a. infinity   b. zero   c. equal to CvdT   d. equal to nRln V2/V1

10. In an isothermal process .... is constant

    a.pressure   b. temperature   c. volume   d. concentration

11. If pressure is constant the process is called ....

    a. isothermal   b. isobaric   c. isochoric   d. adiabatic

12. The gas constant (R) is equal to the _____ of two specific heats.

    a. Sum   b. Product   c. ratio   d. difference

13. When two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This statement is called

    a. Second law of thermodynamics   b. Kelvin Planck's law

    c. Zeroth law of thermodynamics   d. First law of thermodynamics

14. In an irreversible process, there is a

    a. no gain of heat   b. no loss of heat   c. loss of heat   d. gain of heat

15. First law of thermodynamics is the law of

    a. entropy   b. free energy   c. conservation of energy   d. none of these

16. A process during which there is no heat change is called

    a. adiabatic ,   b. reversible   c. irreversible   d. equilibrium

17. The equations showing the effect of temperature change on the heat of reaction is known as

    a. Arrhenius   b. Kirchoff's   c. Ostwald's   d. Faraday's

18. Standard heat of formation of an element is

    a. infinite   b. zero   c. 100 KJ   d. 200 KJ

19. The heat content of a system is called

    a. internal energy   b. enthalpy   c. free energy   d. entropy

20. A process in which a system comes to its initial position after a series of operations is called

    a. reversible   b. cyclic   c. adiabatic   d. irreversible

PART–B
Answer All the Questions   (3 x 2 = 6 marks)

21. What is meant by internal energy?

22. Give the mathematical equation for first law of thermodynamics

23. What is meant by enthalpy of formation?

PART–C

Answer All the Questions   (3 x 8 = 24 marks)

24. a) Explain open, closed and isolated systems in thermodynamics.

OR

   b) Derive expressions for w, q, dU and dH when an ideal gas undergoes isothermal reversible expansion.

25. a) Derive the relationship between heat capacities at constant pressure and constant volume

OR

   b) Distinguish between

   (i) Isothermal and adiabatic process. (ii) State and path function.

26. a) Derive thermodynamically Kirchoff's equation

OR

   b) What is meant by enthalpy of combustion. How to determine it. What are its applications

Part A

Answer All the questions (20 x 1 = 20 marks)

1. B. Work

2. D. Hydrogen (liquid)

3. D. Temperature

4. D. For an endothermic process, ΔH is negative

5. A. Extensive property

6. D. The value will be the same for all

7. C. Adiabetic

8. D. Q1-W1 = Q2-W2

9. B. Zero

10. B. Temperature

11. B. Isobaric

12. D. difference

13. C. Zeroth law of thermodynamics

14. C. Loss of heat.

15. C. Conservation of energy

16. A. Adiabetic

17. B. Kirchoffs

18. B. Zero

19. B. Enthalpy

20. A. Reversible

Part B

Answer All the questions (3 x 2 = 6 marks)

21. What is meant by Internal energy

The amount of energy stored by a substance by virtue of atoms or molecules.

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22. Give the mathematical equation of First law of thermodynamics.

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

The mathematical form of First law of thermodynamics is

$$\Delta E = q - w$$

where ΔE, q and w represent respectively the change in internal energy, quantity of heat supplied and work done.

23. What is meant by enthalpy of formation.

Standard enthalpy of formation is defined as *the heat absorbed or liberated when onemole of a substance is formed from its constituent elements in their respective standardstates.* Standard enthalpy of formation is denoted by $\Delta f H \upsilon$ .and it is called standard *heat of formation.*

Part C

Answer All the questions (3 x 8 = 24 marks)

24.a. Explain Open, closed and isolated stystems in thermodynamics

Open system: A system which can exchange both energy and matter with the surroundings. Ex. beaker of water.

Closed system: A system which can exchange energy but not matter with the surroundings.Ex. Water in as stoppered bottle.

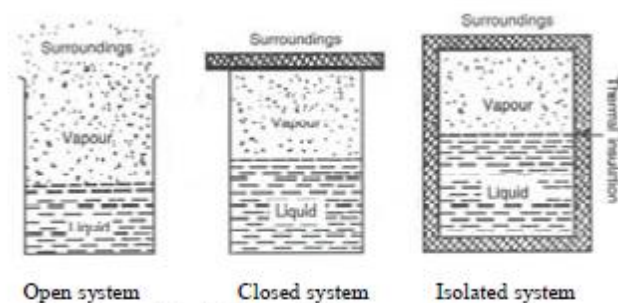Isolated System: In system in which neither matter nor energy can exchange with its surroundings.

Fig. 2. Types of systems

24.b. Derive expression for W, q, dU and dH when an ideal gas undergoes isothermal reversible expansion.

Calculation of *w*

For an infinitesimally small change in volume (dV) of a gas the small quantity of mechanical work (đw) is defined by

$$đw = -PdV$$

For an ideal gas $PV = nRT$ and $P = nRT/V$.

Thus

$$đw = -\frac{nRT}{V} dV = -nRT \, d \ln V$$

For a finite reversible change of volume of a fixed amount of the gas from an initial volume of $V1$ to a final volume $V2$ at a constant temperature, the work is obtained by integrating equation (ii)

$$w = -nRT \int_{V_1}^{V_2} d \ln V$$

$$= -nRT \, \ln[V]_{V_1}^{V_2}$$

$$= -nRT \, \ln \frac{V_2}{V_1} = nRT \, \ln \frac{V_1}{V2}$$

For an ideal gas at constant temperature, $P_1V_1 = P_2V_2$ and $V_2/V_1 = P_1/P_2$. Thus

$$w = -2.303 \, nRT \log \frac{P_1}{P_2} = 2.303 \, nRT \log \frac{P_2}{P_1}$$

The value of w can be calculated on substituting the values of n, R, T, V_1, V_2 (or P_1, P_2) in the above equation.

(2) Calculation of ΔU

The internal energy (U) of an ideal gas is a function of temperature only and is independent of volume (*Joule's law*). Therefore, for an isothermal process when temperature is constant internal energy of an ideal gas is also constant. Thus

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$U2 - U1 = \Delta U = 0$ … for an ideal gas at constant T

(3) Calculation of q

From the first law of thermodynamics we have

$\Delta U = q + w$

For isothermal change, $\Delta U = 0$ for an ideal gas, therefore,

$$q = -w = 2.303 \, nRT \log \frac{V_2}{V_1} = 2.303 \, nRT \log \frac{P_1}{P_2}$$

(4) Calculation of ΔH

Change of enthalpy = Final enthalpy – Initial enthalpy

$\Delta H = H2 - H1$

$= (U2 + P2V2) - (U1 + P1V1)$

$= U2 - U1 + (P2V2 - P1V1)$

For an ideal gas at constant temperature

$U2 - U1 = \Delta U = 0$

And $P2V2 = P1V1$

Therefore, $\Delta H = 0$

Summary : For isothermal reversible change of states of an ideal gas

$$(i) \quad w = -2.303 \, nRT \log \frac{V_2}{V_1} = -2.303 \, nRT \log \frac{P_1}{P_2}$$

$$(ii) \quad q = -w \quad (iii) \, \Delta U = 0 \quad and \quad (iv) \, \Delta H = 0$$

25.a. Derive the relationship between heat capacities at constant pressure and constant volume.

The heat capacity at constant pressure C_P is greater than the heat capacity at constant volume C_V, because when heat is added at constant pressure, the substance expands and work.

When heat is added to a gas at constant volume, we have

$Q_V = C_V \, OT = OU + W = OU$

because no work is done. Therefore,

$dU = C_V dT$, and $C_V = dU/dT$

When heat is added at constant pressure, we have

$$Q_P = C_P \, OT = OU + W = OU + P \, OV$$

For infinitesimal changes this becomes

$$C_P \, dT = dU + P \, dV \qquad\qquad = C_V \, dT + P \, dV \qquad\qquad .$$

From the ideal gas law, PV $= nRT$, we get for constant pressure

$$d(PV) = P \, dV + V \, dP = P \, dV \qquad\qquad = n \, R \, dT .$$

Substituting this in the previous equation gives

$$C_p \, dT = C_V \, dT + n \, R \, dT .$$

Dividing dT out, we get

$C_P = C_V + n \, R$.

For an ideal gas, the heat capacity at constant pressure is greater than that at constant volume by the amount n R.

25.b. Distinguish between (i) Isothermal and Adiabetic (ii) State and path functions.

   (i)   Thermodynamic process:

The method by which the state of a system is changed is called a "Process". It can be effected by changing any one of the state variables *viz* P,T,C etc.

Isothermal process: It is a process carried out at constant temperature. Exchange of heat takes place between system and surroundings *dT = 0*

Adiabatic process: It is a process in which no exchange of heat takes place .The temperature of the system may increase or decrease during adiabatic process. *dQ =0*

(ii) State and path functions.

     A property of the system which depends only on the state variables is called *state property* or state function. The change in a state property depends only on the initial and final

states of the system. A state property is independent of the manner in which the change is brought about. This means that the state property does not depend on the path followed by the system. Thermodynamic properties namely energy *(U)*, enthalpy *(H)*, entropy (*S*), work function (*A*) free energy (G), volume *(V)*, pressure *(P)* and temperature (*T*) are state functions. A state function say energy (*U*) may be mathematically represented as *U = U (T, V, n)*. The mathematical representation is stated as *U* is a function of *T, V,* and *n*. That is, energy of the system depends on the state variables *T, V* and *n*. Similarly; volume of the system is a function of temperature (*T*), pressure *(P)* and amount *(n)*. That is, *V = V (T, P, n)*. For a system of constant composition (for a constant value of *n*) the volume of a gas is a function of temperature and pressure only i.e., *V = V (T, P)*.

We can understand the meaning of state functions and state property by taking an analogy. Suppose that one wants to climb a. mountain peak l km above ground level. This decision defines the initial state (ground where *h = 0*) and the final state (peak where *h = h*). There may be various paths up to the mountain peak but the vertical height (*h*) of the peak from the ground is 1 km. The height of the mountain peak cannot be altered by choosing different paths though the actual distance travelled and the amount of work put in will be different if different paths are followed. Vertical distance in this analogy corresponds to a thermodynamic function.

If the property depends upon the path of the process, then it is called path function.

26.a. Derive thermodynamically Kirchoffs equation.

Temperature dependence of reaction enthalpy (Kirchhoff's equation)

Statement Variation of reaction enthalpy (ΔrH, heat of reaction) with temperature is called *Kirchhoff's equation.*It is stated as follows

$$\left(\frac{\partial \Delta_r H}{\partial T} \right)_P = \Delta_r C_P$$

$$\mathrm{d}\Delta_r H = \Delta_r C_p \, \mathrm{d}T \qquad \text{at constant pressure}$$

Where

ΔrH= reaction enthalpy (heat of reaction at constant pressure)

andΔrCp = reaction heat capacity at constant pressure

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$= \Sigma \, Cp(\text{products}) - \Sigma Cp \,(\text{reactants})$

Similarly, for the heat of reaction at constant volume the Kirchhoff's equation is given by

$d\Delta_r U = \Delta_r C_V dT$ at constant volume

Relevance of Kirchhoff's equation

Standard enthalpy of reaction (heat of reaction at 298K and at 1 bar) is calculated using the standard enthalpy of formation data of reactants andproducts given in the International tables. But when it is required to find the enthalpy of reaction at other temperatures then we use Kichhoff's equation.

Derivation of Kirchhoff's equation

Let us consider a familiar reaction of synthesis of ammonia from nitrogen and hydrogen as represented by chemical equation

$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$
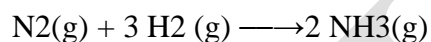
The standard enthalpy of this reaction is given by

$$\Delta_r H^\upsilon = 2 \times H_m^\Theta(NH_3) - [H_m^\Theta(N_2) + 3 \times H_m^\Theta(H_2)]$$

On differentiating the above equation with respect to T at constant P, we get

$$\left(\frac{\partial \Delta_r H^\Theta}{\partial T}\right)_P = 2\left(\frac{\partial H_m^\Theta(NH_3)}{\partial T}\right)_P - \left[\left(\frac{\partial H_m^\Theta(N_2)}{\partial T}\right)_P + 3\left(\frac{\partial H_m^\Theta(H_2)}{\partial T}\right)_P\right]$$

By definition

$$\left(\frac{\partial H_m^\Theta}{\partial T}\right)_P = C_{p,m}^\Theta = \text{Standard molar heat capacity at constant pressure}$$

Therefore, $$\left(\frac{\partial \Delta_r H^\Theta}{\partial T}\right)_P = 2\,C_{p,m}^\Theta(NH_3) - [\,C_{p,m}^\Theta(N_2) + 3\,C_{p,m}^\Theta(H_2)]$$

$$= \Sigma\, C_p^\Theta \text{ (products)} - \Sigma\, C_p^\Theta \text{ (reactants)}$$

$$= \Delta_r C_p^\Theta$$

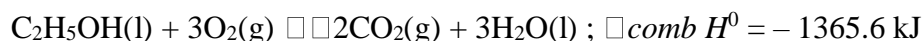Or, $$d\,\Delta_r H^0 = \Delta_r C_p^\Theta\, dT$$

It is differential form of Kirchhoff's equation

26.b. What is meant by enthalpy of combustion. How to determine it. What are its applications.

Enthalpy of Combustion ($\Delta comb\ H°$)

Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.

For example :

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $comb\ H^0 = -1365.6$ kJ

Enthalpy of combustion of $C_2H_5OH(l)$ is -1365.6 kJ mol^{-1}

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Applications

Humans have been making practical use of combustion for millennia. Cooking food and heating homes have long been two major applications of the combustion reaction. With the development of the steam engine by Denis Papin, Thomas Savery, Thomas Newcomen, and others at the beginning of the eighteenth century, however, a new use for combustion was found: performing work. Those first engines employed the combustion of some material, usually coal, to produce heat that was used to boil water. The steam produced was then able to move pistons and drive machinery. That concept is essentially the same one used today to operate fossil-fueled electrical power plants.

Before long, inventors found ways to use steam engines in transportation, especially in railroad engines and steam ships. However, it was not until the discovery of a new type of fuel—gasoline and its chemical relatives—and a new type of engine—the internal combustion engine—that the modern face of transportation was achieved. Today, most forms of transportation depend on the combustion of a hydrocarbon fuel such as gasoline, kerosene, or diesel oil to produce the energy that drives pistons and moves the vehicles on which modern society depends.

When considering how fuels are burned during the combustion process, "stationary" and "explosive" flames are treated as two distinct types of combustion. In stationary combustion, as generally seen in gas or oil burners, the mixture of fuel and oxidizer flows toward the flame at a proper speed to maintain the position of the flame. The fuel can be either premixed with air or introduced separately into the combustion region. An explosive flame, on the other hand, occurs in a homogeneous mixture of fuel and air in which the flame moves rapidly through the combustible mixture. Burning in the cylinder of a gasoline engine belongs to this category. Overall, both chemical and physical processes are combined in combustion, and the dominant process depends on very diverse burning conditions.