Date: ____________

THERMODYNAMICS

THERMODYNAMICS

"Thermodynamics is a macroscopic science that studies the relationship between heat, work and different forms of energy." In chemical systems it allows determination of the feasibility, direction, and equilibrium position of reactions.

SYSTEM AND SURROUNDING

"The part of universe which is under thermodynamic study is called system." "The remaining part of universe other than system is called surrounding."

BOUNDARY

The real or imaginary surface separating system from surrounding is called boundary.

Boundary can be rigid or flexible, diathermic or adiabatic.

Diathermic: Allows heat flow into or out of the system.

Date:

Adiabatic boundary: Prevents heat flow into or out of the system.

TYPES OF SYSTEM (Thermodynamic)

i. Open System $\Delta E \neq 0$, $\Delta m \neq 0$

A system in which both flow of mass and heat is possible.

Eg. Hot liquid placed in open vessel.

ii. Closed System $\Delta E \neq 0$, $\Delta m = 0$

A system in which flow of heat is possible but flow of mass is not possible.

Eg. Hot liquid placed in closed container

iii. Isolated System $\Delta E = 0$, $\Delta m = 0$

A system in which neither heat nor mass can flow in or out.

Eg. Hot liquid placed in a thermos flask.

OTHER TYPES OF SYSTEM

Homogeneous

A system uniform throughout consisting of one phase only is called homogeneous system.

Eg. Pure single solid, liquid or gas, A true solution of solid in liquid

Date:

Heterogeneous

A system consisting of two or more phases is called heterogeneous system.

Eg. Ice in contact with liquid water

STATE OF A SYSTEM

State of a system means condition of the system which is described in terms of certain observable properties such as T, P, V of the system.

STATE VARIABLES

The state variables (P, V, T, n) describes the condition of a system. On changing any one or more of these variables the state of system changes

STATE FUNCTION

A physical quantity is said to be state function if its value depends only upon initial and final state of system, and not upon path by which state is reached.

Eg. Temperature, Pressure, Volume, Enthalpy, Entropy, Internal energy, Gibbs free energy, mass, no. of moles

Date:

PATH FUNCTION

A quantity whose value depends not only the state of system but also on the path by which the state is reached is called path function.

Eg. work, Heat, heat capacity,

PROPERTIES OF SYSTEM

All macroscopic properties of a system irrespective of the fact whether they are state variable or not are divided into 2 types.

1. Intensive Properties

Independent of quantity of matter present in the system.

Eg. Pressure, Temperature, Refractive index, Density etc.

2. Extensive Properties

Depend on quantity of matter present in the system.

Eg. Mass, Volume, Heat capacity, Enthalpy, Gibbs free energy etc.

- Ratio of two extensive variables is an intensive variable

$$\underset{\text{(Intensive)}}{\text{Density}} = \frac{\text{Mass}}{\text{Volume}}$$

- By considering extensive properties for unit mass they can be converted to intensive properties.

THERMODYNAMIC EQUILIBRIUM

A system is said to be under thermodynamic equilibrium when none of the state variables (n, P, T, V) are changing and it satisfies the three equilibriums (Chemical, Mechanical, Thermal).

i. Chemical Equilibrium

There is no change in chemical composition of any part of the system with time. Dynamic equilibrium exists where rate of forward reaction equals rate of backward reaction.

ii. Thermal equilibrium T= constant

There is no flow of heat and the temperature of system remains constant.

iii. Mechanical equilibrium P=constant

There is no flow of matter from one part to another. No mechanical work is done by one part of the system on any other part of the system.

THERMODYNAMIC PROCESSES

i. Isothermal process dT=0

When temperature remains constant throughout the process, it is called isothermal process.

Eg. Freezing, melting, evaporation, condensation (Phase changes)

ii. Isobaric Process dP=0

When Pressure remains constant throughout the process; it is called isobaric process.

Eg. Expansion of gas in an open system
Boiling of water in open container

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3. Adiabatic Process $dq = 0$

When no heat can flow into or out of the system, process is adiabatic.

Eg. Joule Thomson effect, Tyre burst etc.

4. Isochoric Process $dV = 0$

When volume remains constant throughout the process, it is said isochoric.

Eg. Heating of substance in non-expanding chamber.

CYCLIC PROCESS $dE = 0, \ dH = 0$

The system undergoes a series of changes and finally returns to its initial state. The overall process is called cyclic process.

REVERSIBLE PROCESS

A process whose direction can be changed by an infinitesimal change to system or surrounding and which can be reversed by retracting the original path and system is restored to initial state.

Date:

- It involves slow changes.
- System should be in quasi static state (seems to be static but actually is not)
- Gives maximum work

IRREVERSIBLE PROCESS

- Direction of change can not be reversed by small changes in variables
- Irreversible processes are spontaneous
- Unidirectional
- $W_{irr} < W_{rev}$
- Natural processes are ~~sp~~ irreversible

Entropy increases in irreversible process

MODES OF ENERGY TRANSFER

i. Heat   ii. Work

i. **Heat** (q) unit = calorie or J (SI)

a form of energy flows from one system to another because of temperature difference between them. (moves from higher T to lower T).

ii. **Work** (W) unit = Joule (Newton meter)

Work is defined as movement against force. It is mode of energy transfer to or from a system with reference to surroundings.

ZEROTH LAW

"If two systems A and B are in thermal equilibrium with a third system C, then A and B will also be in thermal equilibrium with each other."

If $A = C$, $B = C$

then $A = B$

FIRST LAW (Law of conservation of energy)

(i) "Energy can neither be created nor destroyed but can be transformed from one form to another."

(ii) "Total mass and energy of an isolated system remains constant."

(iii) "It is impossible to construct a perpetual motion machine which could do work continuously without consuming energy." $(\Delta E = q + w)$

SECOND LAW

The entropy of the universe increases in every spontaneous process. Entropy of universe is continuously increasing.

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} > 0$$

Date:

THIRD LAW

(i) Every substance has a finite positive entropy but at absolute zero it may become zero, and does so become in case of perfectaly crystalline substance.

or

(ii) At absolute zero (K), entropy of a pure crystal is zero.

INTERNAL ENERGY

The energy stored within a substance or system is called internal energy. It is the sum of all types of energies associated with a system.

- Depends on chemical nature, amount, P, T of substance.
  Finding absolute value is not possible
- Only difference in energy is measured

$\Delta E = E_P - E_R$

- When $E_P > E_R$ = ΔE is positive and reaction is Endothermic
- when $E_P < E_R$ + ΔE is negative and reaction is Exothermic
- Extensive Property
- State function
- In case of ideal gas, its value depends only on temperature. When T = constant, $\Delta E = 0$ (for ideal gas)
- Determined by Bomb calorimeter.

$$\Delta E = \frac{C \times \Delta T \times M}{W}$$

C = Heat capacity of Bomb Calorimeter

ΔT = Rise in Temperature

M = Molecular mass of substance, w = Mass of substance taken

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ENTHALPY

Heat content of the system is called enthalpy. or
The amount of heat absorbed or evolved at constant pressure is called enthalpy ($\Delta H = q_p$).

$$H = E + PV$$

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

- In case of solids and liquids, change in volume is negligible, so

$$\Delta H \simeq E$$

- For gas phase reactions

$$\Delta H = \Delta E + \Delta n RT$$

Δn = difference in moles of gaseous reactants and products.

Standard enthalpy

Enthalpy change at standard conditions (1 atm pressure, 298 K Temperature) is called standard enthalpy (ΔH°).

ΔH for one mole of ideal gas (monoatomic)

$$\Delta H = \frac{5}{2} RT$$

HEAT CAPACITY

Amount of heat required to raise temperature of a system through one degree (K or °C).

Heat capacity ← $C = \dfrac{\overset{\rightarrow \text{heat absorbed.}}{q}}{\underset{\swarrow \text{mass}}{m}(T_2 - T_1)}$

- When mass is considered 1 mole, it is called molar heat capacity.

$$C = \frac{q}{dT}, \quad C = \frac{dq}{dT}$$

- When mass is considered 1 gram, it is called specific heat.
- Heat capacity at constant volume

$$C_v = \frac{dE}{dT}$$ (Rate of change of E with T at constant V)

- Heat capacity at constant Pressure

$$C_p = \frac{dH}{dT}$$ (Rate of change of H with T at constant P)

- Relationship between Cp and Cv.

$$C_p - C_v = R$$

$$C_p > C_v$$

- Extensive Property
- Path function.

Date:

PRESSURE VOLUME WORK

$w = F \times d.$ $(F = P,\ d = dV)$

$\therefore w = P \cdot dV$ — dV ↓ change in volume.

Work done in isothermal reversible expansion

$$W_{max} = -2.303\, nRT \log \frac{V_2}{V_1} \quad \text{(In terms of } V\text{)}$$

$$W_{max} = -2.303\, nRT \log \frac{P_1}{P_2} \quad \text{(In terms of } P\text{)}$$

For isothermal reversible compression / ~~expansion~~

Value remain same with the sign changed.

Expansion = −ve

Compression = +ve

Work done in isothermal irreversible process

$$W = -P_{ext} \cdot dV \quad (P_{ext} = \text{external Pressure})$$

* In irreversible expansion, external pressure is less than gas pressure and work done is numerically less than work done in reversible expansion.

$$W_{irr} < W_{rev}$$

→ Difference of Pext and Pint is large as compared to reversible process.

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Work done in reversible adiabatic expansion

$$W = \frac{nR(T_2 - T_1)}{1-\gamma}$$

$T_2 > T_1$ (work done on gas)

$T_2 < T_1$ (work done by gas)

$\gamma = C_P/C_V$; $\gamma > 1$; $1-\gamma = -ve$

Work done in irreversible adiabatic expansion

$$w = -P_{ext}\,\frac{R[P_1T_2 - P_2T_1]}{P_1P_2}$$

Relation between Pressure and volume in adiabatic process

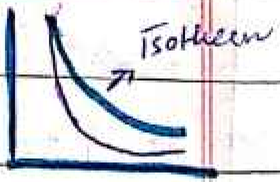
$$PV^{\gamma} = \text{constant}$$

This relation can be used to calculate work done in adiabatic expansion.

Relation between Temperature and volume in adiabatic expansion

$$TV^{\gamma-1} = \text{constant}$$

$\gamma = \frac{C_P}{C_V}$, $\gamma > 1$



For isothermal Process ; $P = \frac{1}{V}$

For adiabatic Process ; $P = \frac{1}{V^{\gamma}}$

$\gamma > 1$; $V^{\gamma} > V$, so adiabatic curve is steep than isotherm

JOULE THOMSON EFFECT

→ Adiabatic expansion of gas.

"Lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is called joule Thomson effect."

- Joule thomson expansion takes place at constant enthalpy.
- All gases show cooling except hydrogen and helium.
- Magnitude of effect is expressed in terms of Joule Thomson coefficient (u) which is the rate of change in temperature with pressure at constant enthalpy.

$$u = \left(\frac{dT}{dP}\right)_H$$

when

$u = +ve$ Gas shows cooling effect

$u = -ve$ Gas shows heating effect (H, He)

$u = 0$ Gas shows no Joule Thomson effect (Ideal gases)

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ENTROPY (S)

"It is a measure of degree of disorder or randomness in a system".

More heat, More randomness, Increased entropy.

- For any process

$$\Delta S = S_{final} - S_{initial}$$

- when $S_{final} > S_{initial}$, ΔS is positive and process is spontaneous.

Change in entropy is equal to heat energy absorbed or evolved divided by temperature.

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

when heat absorbed, ΔS = +ve (Increase entropy)

when heat evolved, ΔS = -ve (Decrease entropy)

Entropy change for different Processes

1. Isothermal Process

Change of entropy in terms of T and V.

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$

Change of entropy in terms of P and T

$$\Delta S = 2.303\, nR \log \frac{P_1}{P_2}$$

In isothermal expansion

$V_2 > V_1$, $P_1 > P_2$, $\Delta S = +ve$

In isothermal contraction (compression)

$V_2 < V_1$, $P_1 < P_2$, $\Delta S = -ve$

ii. Isobaric Process

$$\Delta S = 2.303\, n C_p \log \frac{T_2}{T_1}$$

when $T_2 > T_1$, $\Delta S = +ve$

when $T_2 < T_1$, $\Delta S = -ve$

iii) Isochoric Process

$$\Delta S = 2.303\, n C_v \log \frac{T_2}{T_1}$$

iv) Entropy change during adiabatic expansion

In such process $q = 0$ at all stages. Hence $\Delta S = 0$. Thus reversible adiabatic processes are called isoentropic processes.

ENTROPY OF PHASE CHANGES

i. Entropy of melting or fusion

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

ΔH_m = Heat required to melt 1 mole at constant P, T_m = Melting point.

ii. Entropy of Boiling or vaporization

$$\Delta S_b = \frac{\Delta H_b}{T_b}$$

ΔH_b = Heat required to vaporise one mole of substance, T_b = Boiling point.

iii. Entropy of transition

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

ΔH_t = Heat required to change one allotropic form (1 mole) to another

T_t = Transition temperature.

iv. Entropy of Sublimation

$$\Delta S_s = \frac{\Delta H_s}{T_s}$$

Since, ΔH_f, ΔH_b, ΔH_t, ΔH_s are all positive, these processes are accompanied by increase in entropy and the reverse processes are accompanied by decrease in entropy. When gas is liquified or liquid is solidified, heat evolves, ΔH is negative and entropy decrease.

Absolute Entropy

"Absolute entropy of a pure substance at a given temperature is sum of all the entropy it acquire on warming from absolute zero ($S = 0$) to particular temperature."

Standard Entropy

"Absolute entropy of a substance at 25°C (298K) and 1 atm is called standard entropy (S°)."

$\Delta S_T = \Delta S_{sys} + \Delta S_{surrounding}$

$\Delta S_T > 0$ spontaneous, irreversible process

$\Delta S_T < 0$ non spontaneous, ~~irreversible~~

$\Delta S_T = 0$ Equilibrium (cyclic, reversible)

All natural processes are irreversible followed by increase in entropy.

Entropy of universe is increasing.

HEAT ENGINE

Machine which converts heat into work by using heat that flows out spontaneously from a high temperature source to a low temperature sink.

Efficiency of heat Engine

Ratio of the work obtained in a cyclic process to the heat taken from high temperature reservoir is called efficiency of heat engine.

$$\eta = \frac{W}{Q}$$

Carnot Cycle

In 1824, Sadi Carnot employed an imaginary reversible cycle to demonstrate maximum convertibility of heat into work.

Carnot cycle consist of four operations.

i- Isothermal expansion
ii- Adiabatic expansion
iii- Isothermal compression
iv- Adiabatic compression

Date:

Efficiency of Carnot cycle

$$\eta = \frac{W}{Q} = \frac{T_2 - T_1}{T_2}$$

Since, $\frac{T_2 - T_1}{T_2} < 1$, hence efficiency is always less than unity.

Larger the difference between T_2 and T_1, more heat converted into work by heat engine.

Carnot theorem

Every perfect engine working reversibly between same temperature limits has same efficiency independent of working substance.

Date:

FREE ENERGY

HELMHOLTZ FREE ENERGY

The maximum work obtainable from a system is given by Helmholtz free energy.

Change of internal energy determines change of Helmholtz free energy.

$$A = E - TS$$

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

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

S = Entropy, E = internal energy,

A = Helmholtz free energy.

GIBBS FREE ENERGY

The maximum useful work obtainable from a system is given by Gibbs free energy.

Change in Enthalpy determines change of Gibbs free energy.

$$G = H - TS$$

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

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

$\Delta G = -ve$ (Spontaneous process)

$\Delta G = +ve$ (Non Spontaneous)

$\Delta G = 0$ (Equilibrium)

GIBBS HELMHOLTZ EQUATION

In terms of free energy and enthalpy change

$$\Delta G = \Delta H + T d\left(\frac{\Delta G}{dT}\right)_P$$

$$\Delta A = \Delta E + T d\left(\frac{\Delta A}{dT}\right)_V$$

In terms of internal energy and work function at constant V

* Gibbs Helmholtz equation is used to calculate ΔH or ΔE without using calorimeter.

Date: EQUATIONS

KIRCHOFF'S EQUATION

This equation tells the effect of temperature on heat of reaction(ΔH).

At constant Pressure

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

or

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

At constant volume

$$\Delta E_2 - \Delta E_1 = \Delta C_V (T_2 - T_1)$$

or

$$\Delta C_V = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}.$$

ΔH_1 = Heat of reaction at T_1 at constant P

ΔH_2 = Heat of reaction at T_2 at constant P

ΔE_2 = Heat of reaction at T_2 at constant V

ΔE_1 = Heat of reaction at T_1 at constant V

ΔC_p = Difference of heat capacities of products and reactaints at constand P

ΔC_V = Difference of heat capacities of products and reactants at constat V.

CLAPEYRON CLAUSIUS EQUATION

Clausius-Clapeyron equation is a mathematical relation dealing with transition state equilibrium between two phases of a single substance.

This equation gives variation of equilibrium pressure with temperature for any two phases of a single substance, existing in equilibrium with each other.

$$\frac{dP}{dT} = \frac{\Delta H_m}{T_m(V_B - V_A)}$$

i- For solid ⇌ liquid

$$\frac{dP}{dT} = \frac{\Delta H_f}{T_m(V_l - V_s)}$$

ΔH_f = molar heat of fusion
T_m = melting point of sol
V_l = molar V of liquid
V_s = molar V of solid

ii- For liquid ⇌ Vapour

$$\frac{dP}{dT} = \frac{\Delta H_v}{T_b(V_v - V_l)}$$

iii- For solid ⇌ vapour

$$\frac{dP}{dT} = \frac{\Delta H_s}{T_s(V_v - V_s)}$$

ΔH_s = Molar heat of sublimation.

Date:

Integrated form of Clausius clapeyron Eq.

$$\log \frac{P_2}{P_1} = \frac{DH}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Applications of Clausius clapeyron Eq.

1. Calculation of molal heat of vaporization
2. Calculation of boiling point or freezing point
3. Effect of pressure on boiling point
4. Calculation of molal elevation constant (K_b)

$$k_b = \frac{0.002T^2}{l_v}$$

l_v = latent heat of vaporization Per gram of solvent

T = Boiling point of solvent (Pure)

5. Calculation of molal depression constant (K_f)

$$K_f = \frac{0.002T^2}{l_f}$$

l_f = latent heat of fusion/g of solvent.

T = Freezing point of pure solvent

Date:

VANT HOFF ISOTHERM

- It gives the net work that can be obtained from a gaseous reactant when both the reactants and products are at suitable arbitrary pressure.
- It gives the mathematical relation between free energy change and ~~and~~ equilibrium constant of Reaction.

$$K_p = \frac{P_C \times P_D}{P_A \times P_B}$$

$$\Delta G^\circ = -RT \ln K_p$$

$$\Delta G^\circ = -2.303\, RT \log K_p$$

$K_p < 1$; $\ln K_p = -ve$; $\Delta G = +ve$ (Non spontaneous)

$K_p > 1$; $\ln K_p = +ve$; $\Delta G = -ve$ (Spontaneous)

$K_p = 1$; $\ln K_p = 0$; $\Delta G = 0$ (Equilibrium)

VANT HOFF ISOCHORE

$$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT}$$

$$\log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$ (integrated form)

⇒ (Vant Hoff isochore is derived by using Gibbs Helmhotz eq. and vant Hoff isotherm)

Date: ________

THERMOCHEMISTRY

Definition

"Thermochemistry is a branch of physical chemistry which deals with thermal or heat changes caused by chemical reactions."

- It is also termed as chemical energetics. It is based on 1st law of thermodynamics.

Thermochemical Equation

A chemical equation which gives all the information like energy changes associated with chemical reaction and phases of various reactants and products is called thermochemical equation.

Eg. $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H = -890\ kJ/mol$

Endothermic Reactions

The chemical reactions which proceed with absorption of heat energy are endothermic reactions.

$\Delta H = +ve$, $\Delta E = +ve$

$\Delta H = H_P - H_R$; $H_P > H_R$; $\Delta H = +ve$

Eg. 1. $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.5\ kJ/mol$.

2. Preparation of ozone

3. Evaporation of water;

Date: ____________

EXOTHERMIC REACTIONS

"The chemical reactions which proceed with the evolution of heat energy are exothermic."

$$\Delta H = -ve, \quad \Delta E = -ve$$

$\Delta H = H_P - H_R$; $H_P < H_R$; $\Delta H = -ve$

Eg. 1. $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H = -285.8 \, kJ$

2. Fermentation is also an exothermic reaction.

HEAT OF REACTION or ENTHALPY OF REACTION

"Heat of reaction or enthalpy of reaction is the amount of heat evolved or absorbed when quantities of substances indicated by chemical equation have completely reacted."

It is actually difference between enthalpies of products and reactants.

- $\Delta H = \Sigma H_P - \Sigma H_R$

⇒ It is determined by water and

- Bomb calorimeters.
- Heat of Reaction at constant V is

$$\Delta E = E_P - E_R = q_V$$

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Date:

- Heat of reaction at constant P

$\Delta H = H_P - H_R = q_p$

Factors which influence heat of reaction

i. Physical state of reactants and products

i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -57.8$ kcal

(ii) $H_{2(g)} + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -68.32$ kcal

Conversion of water(g) into steam, heat is absorbed(i). Conversion of steam into liquid, heat is evolved(ii)

ii. Allotropic forms of element.

Heat energy is also involved when one allotropic form of an element is converted into another.

$C_{(diamond)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = 94.3$ kcal

$C_{(amorphous)} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = 97.6$ kcal

* Difference in values is 3.3 Kcal which is the heat absorbed when 12g of diamond converted to 12g of amorphous C. This is termed heat of transition.

Date:

iii. Temperature

Variation of heat of reaction with temperature is given bay Kirchoff equation.

At constant Pressure

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

At constant volume

$$\Delta C_V = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

iv. Reaction carried out at constant Pressure or constant V.

When reactions carried out at constant volume, heat change is called internal energy of reaction at constant V.

When reactions carried out at constant pressure, heat change is called enthalpy of reaction.

$$\Delta H = \Delta E + \Delta n RT$$

Δn = no. of mole of Product − no. of mole of reactants.

v. Enthalpies of Solution.

$H_2S_{(g)} + I_{2(g)} \rightarrow 2HI + S$ $\Delta H = -17.3$ kcal

$H_2S + I_2 \rightarrow 2HI + S$ $\Delta H = -21.93$ kcal
(Sol)

Date:

TYDES OF HEAT OF REACTION

1. Heat of formation ΔH_f

"Change in enthalpy that takes place when one mole of the compound is formed from its elements."

→ Heat of formation may be +ve or -ve.

- ΔH = -ve exothermic compound (more stable)
- ΔH = +ve endothermic compound (Less stable)

Standard heat of formation

"Change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances taken in standard states (298K, 1atm)."

- Standard heat of formation of free element is taken as zero.

$$\Delta H^\circ = \Delta H_f^\circ - \Delta H_R^\circ$$

Standard heat of Reaction = standard heat of formation of Products − Standard heat of formation of Reactants

2. Heat of Combustion

Change in enthalpy of a system when one mole of substance is completely burnt in excess of air/oxygen.

ΔH_c is always -ve.

Date:

Application of heat of combustion

i. Calculation of heat of formation

ii. Calorific value of food and fuels

iii. Constitution of organic compounds

HEAT OF NEUTRALISATION

The change in heat content of a system when one gram equivalent of an acid is neutralised by one gram equivalent of base or vice versa in dil. soln.

Heat of neutralisation for strong acid and strong base is **-13.7 kcal** or **-57.3 kJ/mol**

It is always exothermic.

HEAT OF SOLUTION

The change in enthalpy when one mole of a substance is dissolved in specified quantity of solvent at given temperature.

For solid electrolytes

$\Delta H_{sol} = \Delta H_{Lattice} + \Delta H_{Hydration}$.

For liquid electrolytes

$\Delta H_{sol} = \Delta H_{Hydration}$

Date:

Heat of Hydration

The enthalpy change during hydration of one gm mole substance is called heat of hydration.

$\Delta H_{Hydration} = -ve$ (mostly)

ENERGY CHANGES DURING PHASE CHANGES

i- Heat of fusion

Heat change when one mole of solid substance is converted into liquid state at its melting point.

$\Delta H_{fusion} =$ Always $+ve$

$H_2O_{(s)} \longrightarrow H_2O_{(l)}$ $\Delta H = 1.43 kcal$

* Fusion is an isothermal process. The temperature during phase change is constant.

ii- Heat of vaporization

Heat change when one mole of liquid is converted into vapour/gaseous state at its boiling point.

* Vaporization is also an isothermal process.

$H_2O_{(l)} \longrightarrow H2O_{(g)}$ $10.5 kcal$

Date:

Heat of Sublimation

It is change in enthalpy in converting one mole of solid directly into vapor at temperature below its melting point

$$\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fusion}$$

Heat of Atomization

Enthalpy change when bonds of one mole of substance are broken down completely to obtain atoms in gaseous phase.

Heat of Ionization

Quantity of heat absorbed when one mole of a substance is completely dissociated into its ions.

Heat of Transition

Enthalpy change when one mole of an allotropic form changes to another under constant temperature and pressure.

$$C_{(graphite)} \longrightarrow C_{Diamond} \quad \Delta H = 1.90\ KJ/mol$$

Calorimetry

Experimental measurement of heat of reaction or enthalpy change is called calorimetry.

Calorimeter

Apparatus used to measure heat absorbed or evolved in chemical reaction.

Bomb Calorimeter

Used to measure the heat of combustion of organic compounds.

Water Calorimeter

Used to measure heat changes accompanying chemical reactions taking place in solutions.

Date:

HESS'S LAW

(Law of constant heat Summation)

Presented by Hess (1840)

If a chemical reaction made to take place in a number of ways in one or in several steps, the total enthalpy change is always same.

$$\begin{tikzcd}
A \arrow[rrr, "Q"] \arrow[d, "q_1"'] & & & Z \\
B \arrow[r, "q_2"'] & C \arrow[r, "q_3"'] & D \arrow[ur, "q_4"'] &
\end{tikzcd}$$

$$Q = q_1 + q_2 + q_3 + q_4$$

Applications

⇒ Determination of enthalpies of formation of those compounds which can not be prepared easily. ~~using~~

⇒ Determination of enthalpies of extremely slow reactions

⇒ For determination of bond energies, lattice energies and resonance energy.

Date:

Levoiser and Laplace law

According to this law

Enthalpy of decomposition of a compound is numerically equal to enthalpy of formation of that compound with opposite sign.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -94.3\,kcal$

$CO_{2(g)} \longrightarrow C_{s} + O_{2g}$ $\Delta H = +94.3\,kcal$

BORN HABER CYCLE

Lattice enthalpy of an ionic compound is enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state. Since it is impossible to determine lattice enthalpies directly by experiment

* BORN HABER CYCLE is a series of steps (chemical processes) used to calculate lattice energy of ionic solids.

TROUTON'S RULE

According to this rule, ratio of heat of vaporization and normal boiling point of a liquid is approximately equal to 88 J/mole.

$$\frac{\Delta H_{vap}}{T_b \text{ (in K)}} = 88 \text{ J/mol}$$

UNITS

Heat (q)

1. Calorie (cal)

"amount of heat required to raise temperature of 1g of H_2O by 1°C is one calorie."

2. Joule (J) SI unit

1 J = 0.2390 cal

1 cal = 4.184 J

1 Kcal = 4.184 kJ

Work (W)

Joule (Newton meter)

$1\ J = 10^{7}$ ergs

$1\ erg = 10^{-7}\ J$

erg (unit of work in CGS system)

Internal Energy (E)

1. Joule (SI unit)
2. Calorie

Enthalpy

Kcal , kJ

Heat Capacity

$J K^{-1} mol^{-1}$ (SI)

$Cal K^{-1} mol^{-1}$

Date:

Entropy S (eu)

$cal\,mol^{-1}K^{-1}$

$J\,mol^{-1}K^{-1}$

1 eu = 4.184