

UNIT – VII – THERMODYNAMICS

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UNIT – 7 – THERMODYNAMICS

II. WRITE BRIEF ANSWER TO THE FOLLOWING QUESTIONS.

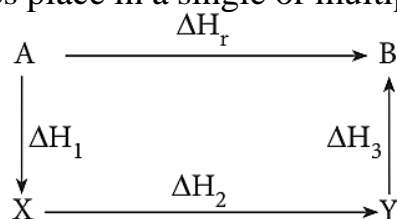
26.State the first law of thermodynamics. [GMQ-18, HY-19, SEP-21, HY-22]

The first law of thermodynamics, known as the law of conservation of energy, states that “the total energy of an isolated system remains constant though it may change from one form to another”. **The mathematical statement of the First Law as:** $\Delta U = q + w$

Where q - the amount of heat supplied to the system; w - work done on the system

27.Define Hess’s law of constant heat summation. (or) State Hess’s law. [QY-18,19, SEP-21, MAR-24]

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

28.Explain intensive properties with two examples.

The property that is independent of the mass or the size of the system is called an intensive property.

Examples : Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

29.Define the following terms: (a) isothermal process (b) adiabatic process (c) isobaric process (d) isochoric process

Isothermal process : An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surrounding and the temperature of the system remains constant.

For an isothermal process $dT = 0$

Adiabatic process: An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process.

For an adiabatic process $q = 0$

Isobaric process: An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an isobaric process $dP = 0$

Isochoric process: An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state.

For an isochoric process, $dV = 0$

30.What is the usual definition of entropy? What is the unit of entropy? [AUG-22]

✚ Entropy is a measure of the molecular disorderliness (randomness) of a system.

$$dS = dq_{rev} / T$$

✚ The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, the SI unit of entropy is JK^{-1} .

31.Predict the feasibility of a reaction when (i) both ΔH and ΔS positive, (ii) both ΔH and ΔS negative, (iii) ΔH decreases but ΔS increases [QY-22]

(i) Non-spontaneous

(ii) Non-spontaneous

(iii) Spontaneous

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32. Define Gibb's free energy. [CRT-22]

A thermodynamic potential that is used to measure the maximum amount of work done in any given thermodynamic system when the temperature and pressure of the system are kept constant.

$$G = H - TS$$

33. Define enthalpy of combustion.

The heat of combustion of a substance is defined as "The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen". It is denoted by ΔH_C .

34. Define molar heat capacity. Give its unit. [JUN-19]

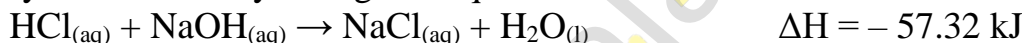
Molar heat capacity (c_m). It is defined as "The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin". The SI unit of molar heat capacity is $\text{JK}^{-1}\text{mol}^{-1}$.

35. Define the calorific value of food. What is the unit of calorific value?

The calorific value is defined as the amount of heat produced in calories (or joules) when one gram of the substance is completely burnt. The SI unit of calorific value is J kg^{-1} . However, it is usually expressed in cal g^{-1} .

36. Define enthalpy of neutralization.

The heat of neutralisation is defined as "The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution".



37. What is lattice energy? [QY-18, CRT-22]

Lattice energy is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance from one mole of crystal. It is also referred as lattice enthalpy.

38. What are state and path functions? Give two examples. [CRT, AUG-22, MAR-23]

State function: A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

Example: Pressure (P), Volume (V), Temperature (T), Internal energy (U), Enthalpy (H), free energy (G) etc.

Path functions: A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

Example: Work (w), Heat (q).

39. Give Kelvin statement of second law of thermodynamics. [QY-19]

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

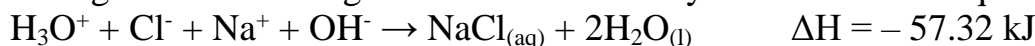
40. The equilibrium constant of a reaction is 10, what will be the sign of ΔG ? Will this reaction be spontaneous? [QY-22]

$$\Delta G = -2.303 RT \log K_{\text{eq}} \quad K_{\text{eq}} = 10$$

$\therefore \Delta G^\circ = -$ Ve value, so the reaction will be spontaneous.

41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

Strong acids and strong bases exist in the fully ionised form in aqueous solutions as below:



The H^+ ions produced in water by the acid molecules exist as H_3O^+ ions. Thus, enthalpy change of neutralisation is essentially due to enthalpy change per mole of water formed from H_3O^+ and

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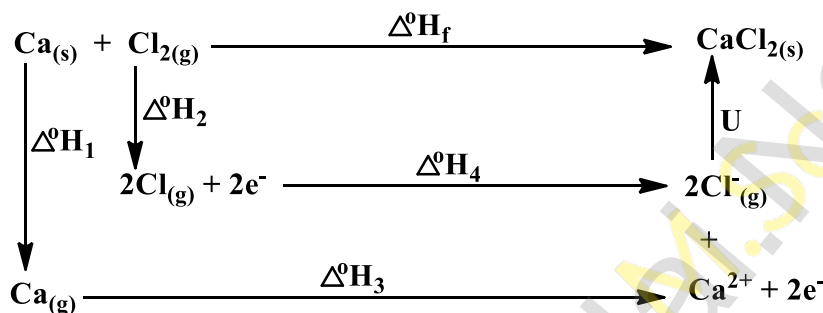
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OH⁻ ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralization of strong acid by strong base is a constant value which is equal to – 57.32 KJ.

42.State the third law of thermodynamics. [QY-18,19, MAR-19, CRT-22]

- ✚ The third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero.
- ✚ It can be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps.
- ✚ Mathematically, $\lim_{T \rightarrow 0} S = 0$ for a perfectly ordered crystalline state.

43.Write down the Born-Haber cycle for the formation of CaCl₂. [QY-22]



- ✚ $\Delta^{\circ}H_1$ - enthalpy change for the sublimation $\text{Ca}_{(s)}$ to $\text{Ca}_{(g)}$
- ✚ $\Delta^{\circ}H_2$ - enthalpy change for the dissociation of $\text{Cl}_{2(g)}$ to $2\text{Cl}_{(g)}$
- ✚ $\Delta^{\circ}H_3$ - Ionisation energy for $\text{Ca}_{(g)}$ to $\text{Ca}^{2+}_{(g)}$
- ✚ $\Delta^{\circ}H_4$ - electron affinity for the conversion of $2\text{Cl}_{(g)}$ to $2\text{Cl}^{-}_{(g)}$
- ✚ U - the lattice enthalpy for the formation of solid CaCl_2
- ✚ $\Delta^{\circ}H_f$ - enthalpy change for the formation of solid CaCl_2 directly from elements

$$\Delta^{\circ}H_f = \Delta^{\circ}H_1 + \Delta^{\circ}H_2 + \Delta^{\circ}H_3 + \Delta^{\circ}H_4 + U$$

44. Identify the state and path functions out of the following (a) Enthalpy, (b) Entropy, (c) Heat, (d) Temperature, (e) Work, (f) Free energy

State function: Enthalpy, Entropy, Temperature, Free energy

Path function: Heat, Work

45.State the various statements of second law of thermodynamics. [MAR-23]

Kelvin-Planck statement: It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

Clausius statement: It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

Entropy statement: The entropy of an isolated system increases during a spontaneous process

46.What are spontaneous reactions? What are the conditions for the spontaneity of a process? [HY-19, SEP-21, MAY-22]

A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction.

The spontaneity of any process depends on three different factors.

- ✚ If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. (ΔH is negative)

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- ✚ If the entropy change of a process is positive, then the process may occur spontaneously. (ΔS is positive)
- ✚ The gibbs free energy which is the combination of the above two ($\Delta H - T\Delta S$) should be negative for a reaction to occur spontaneously, i.e. the necessary condition for a reaction to be spontaneous is $\Delta H - T\Delta S < 0$

47. List the characteristics of internal energy. [HY-19, CRT, MAY-22, MAR-24]

- ✚ The internal energy of a system is an extensive property.
- ✚ The internal energy of a system is a state function.
- ✚ The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$
- ✚ In a cyclic process, there is no internal energy change. $\Delta U_{(cyclic)} = 0$
- ✚ If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative. $\Delta U = U_f - U_i = -ve (U_f < U_i)$
- ✚ If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state (U_i), then ΔU would be positive. $\Delta U = U_f - U_i = +ve (U_f > U_i)$

48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.

Heat evolved at constant volume, is measured in a *bomb calorimeter*.

Apparatus Setup: The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

Experiment: A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started by striking the substance through electrical heating.

Calculation: A known amount of combustible substance is burnt in oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume (ΔU_c^0).

The amount of heat produced in the reaction (ΔU_c^0) is equal to the sum of the heat absorbed by the calorimeter and water.

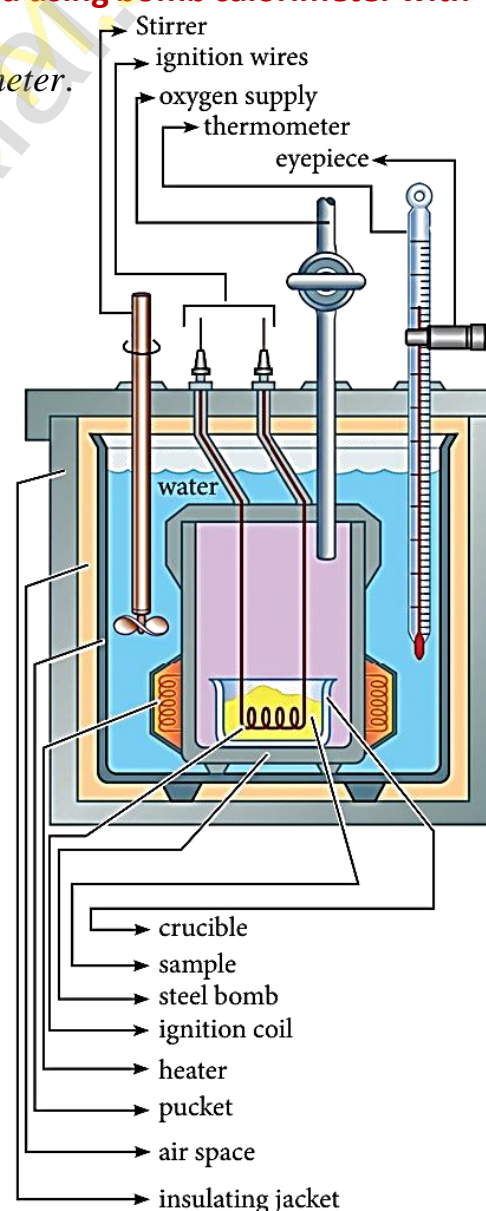
Heat absorbed by the calorimeter, $q_1 = k \cdot \Delta T$

where k is a calorimeter constant equal to $m_c C_c$ (m_c is mass of the calorimeter and C_c is heat capacity of calorimeter)

Heat absorbed by the water, $q_2 = m_w C_w \Delta T$

where m_w is molar mass of water C_w is molar heat capacity of water ($75.29 \text{ J K}^{-1} \text{ mol}^{-1}$)

Therefore $\Delta U_c = q_1 + q_2 = k \cdot \Delta T + m_w C_w \Delta T = (k + m_w C_w) \Delta T$



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Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known (-3227 kJmol^{-1}) The enthalpy of combustion at constant pressure of the substance is calculated from the equation

$$\Delta H^0_{C(\text{pressure})} = \Delta U^0_{C(\text{Vol})} + \Delta n_g RT$$

49. Calculate the work involved in expansion and compression process.

For understanding pressure volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A. The total volume of the gas inside is V_i and pressure of the gas inside is P_{int} .

If the external pressure P_{ext} is greater than P_{int} , the piston moves inward till the pressure inside becomes equal to P_{ext} . Let this change be achieved in a single step and the final volume be V_f .

In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F \cdot \Delta x \quad \text{-----(1)}$$

where dx is the distance moved by the piston during the compression and F is the force acting on the gas.

$$F = P_{\text{ext}} A \quad \text{-----(2)}$$

Substituting (2) in (1)

$$w = -P_{\text{ext}} A \Delta x$$

$$A \cdot \Delta x = \text{change in volume} = V_f - V_i$$

$$w = -P_{\text{ext}} \cdot (V_f - V_i) = -P_{\text{ext}} \cdot (-\Delta V) = P_{\text{ext}} \cdot \Delta V$$

Since work is done on the system, it is a positive quantity.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation.

$$w_{\text{rev}} = - \int_{V_i}^{V_f} P_{\text{ext}} dV$$

In a compression process, P_{ext} the external pressure is always greater than the pressure of the system. i.e $P_{\text{ext}} = (P_{\text{int}} + dP)$.

In an expansion process, the external pressure is always less than the pressure of the system. i.e $P_{\text{ext}} = (P_{\text{int}} - dP)$.

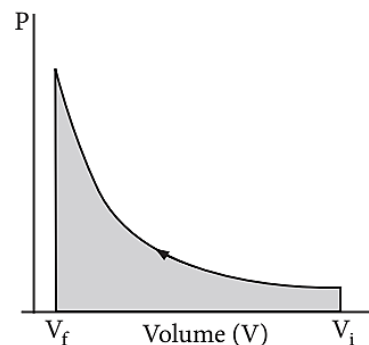
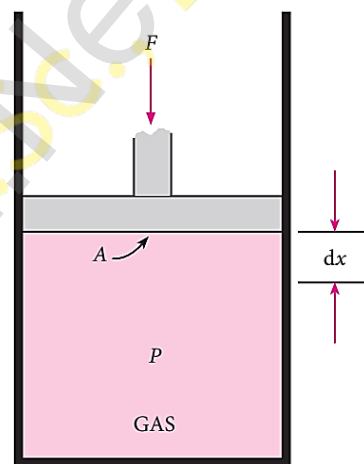
When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from V_i to V_f , the P-V plot looks like in image Work done on the gas is represented by the shaded area.

In general case we can write, $P_{\text{ext}} = (P_{\text{int}} \pm dP)$. Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{\text{rev}} = - \int_{V_i}^{V_f} P_{\text{int}} dV$$

For a given system with an ideal gas, $P_{\text{int}} V = nRT$

$$P_{\text{int}} = \frac{nRT}{V} \quad w_{\text{rev}} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V} \right) = -nRT \ln \left(\frac{V_f}{V_i} \right) = -2.303 nRT \log \left(\frac{V_f}{V_i} \right)$$



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- ✚ If $V_f > V_i$ (expansion), the sign of work done by the process is negative.
- ✚ If $V_f < V_i$ (compression) the sign of work done on the process is positive.

50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation. [HY-18, SEP-20, QY-22]

When the system at constant pressure undergoes changes from an initial state with H_1, U_1, V_1 and P parameters to a final state with H_2, U_2, V_2 and P parameters, the change in enthalpy ΔH , is given by $\Delta H = \Delta U + P\Delta V$

$$\text{In the initial state } H_1 = U_1 + PV_1 \quad \text{-----(1)}$$

$$\text{In the final state } H_2 = U_2 + PV_2 \quad \text{-----(2)}$$

change in enthalpy is (2) - (1)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \quad \text{-----(3)}$$

As per first law of thermodynamics, $\Delta U = q + w$

Equation (3) becomes

$$\Delta H = q + w + P\Delta V \quad [\because w = -P\Delta V]$$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p \quad \text{-----(4)}$$

q_p is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature and pressure with V_i and V_f as the total volumes of the reactant and product gases respectively, and n_i and n_f as the number of moles of gaseous reactants and products, then,

$$\text{For reactants (initial state) : } PV_i = n_i RT \quad \text{-----(5)}$$

$$\text{For products (final state) : } PV_f = n_f RT \quad \text{-----(6)}$$

$$\text{Equation (6) - (5) } \quad P(V_f - V_i) = (n_f - n_i) RT$$

$$P\Delta V = \Delta n_{(g)} RT \quad \text{-----(7)}$$

Substituting in (7) in (3)

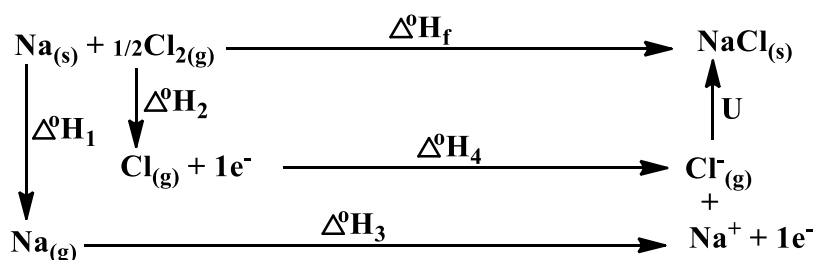
$$\Delta H = \Delta U + \Delta n_{(g)} RT \quad \text{-----(8)}$$

51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



$\Delta^{\circ}H_f$ = heat of formation of sodium chloride = $-411.3 \text{ kJ mol}^{-1}$

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$\Delta^\circ H_1$ = heat of sublimation of $\text{Na}_{(g)} = 108.7 \text{ kJ mol}^{-1}$

$\Delta^\circ H_2$ = ionisation energy of $\text{Na}_{(g)} = 495.0 \text{ kJ mol}^{-1}$

$\Delta^\circ H_3$ = dissociation energy of $\text{Cl}_{2(g)} = 244 \text{ kJ mol}^{-1}$

$\Delta^\circ H_4$ = Electron affinity of $\text{Cl}^-_{(g)} = -349.0 \text{ kJ mol}^{-1}$

U = Lattice energy of NaCl

$$\Delta^\circ H_f = \Delta^\circ H_1 + \Delta^\circ H_2 + \frac{1}{2}\Delta^\circ H_3 + \Delta^\circ H_4 + U$$

$$U = \Delta^\circ H_f - (\Delta^\circ H_1 + \Delta^\circ H_2 + \frac{1}{2}\Delta^\circ H_3 + \Delta^\circ H_4)$$

$$U = (-411.3) - (108.7 + 495.0 + 122 - 349) = (-411.3) - (376.7) = -788 \text{ kJ mol}^{-1}$$

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-

52. List the characteristics of Gibb's free energy. [HY-19, SEP-21, HY,AUG-22, CRT-23]

Free energy is defined as $G = H - TS$. 'G' is a state function.

G-Extensive property; ΔG -intensive property when mass remains constant between initial and final state of systems.

'G' has a single value for the thermodynamic state of the system.

G and ΔG values correspond to the system only.

Process	Spontaneous	Equilibrium	Non-Spontaneous
ΔG	-Ve	Zero	+Ve

Gibbes free energy and the net work done by the system,

For any system at constant pressure and temperature,

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

$$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S$$

From first law of thermodynamics

$$\Delta U = q + w$$

From second law of thermodynamics

$$\Delta S = \frac{q}{T} \quad \Delta G = q - w + P\Delta V - T\left(\frac{q}{T}\right)$$

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

$$-\Delta = -w - P\Delta V$$

But $-P\Delta V$ represents the work done due to expansion against a constant external pressure.

53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

$n = 2$ mole; $V_i = 500\text{ml} = 0.5\text{lit}$; $V_f = 2\text{Lit}$; $T = 25^\circ\text{C} = 298\text{K}$

$$w = -2.303 nRT \log\left(\frac{V_f}{V_i}\right) = -2.303 \times 2 \times 8.314 \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times 0.6021 = -6871 \text{ J} = -6.871 \text{ KJ}$$

54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K⁻¹. Calculate the enthalpy of combustion of the gas in kJ mol⁻¹.

$T_i = 298\text{K}$; $T_f = 298.45\text{K}$; $k = 2.5\text{KJ K}^{-1}$; $m = 3.5\text{g}$; $M_m = 28$

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Heat evolved = $k\Delta T = k(T_f - T_i) = 2.5 \text{ KJ K}^{-1}(298.85 - 298)\text{K} = 1.125 \text{ KJ}$

$$\Delta H_c = \frac{1.125}{3.5} \times 28 \text{ KJ mol}^{-1} = 9 \text{ KJ mol}^{-1}$$

55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

$T_{\text{sys}} = 77^\circ\text{C} = (77 + 273) = 350\text{K}$; $T_{\text{surr}} = 33^\circ\text{C} = (33 + 273) = 306\text{K}$; $q = 245\text{J}$;

$$\Delta S_{\text{sys}} = \frac{q}{T_{\text{sys}}} = \frac{-245}{350} = -0.7 \text{ JK}^{-1}; \quad \Delta S_{\text{surr}} = \frac{q}{T_{\text{surr}}} = \frac{+245}{306} = +0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -0.7 \text{ JK}^{-1} + 0.8 \text{ JK}^{-1} = 0.1 \text{ JK}^{-1}$$

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.

$n = 1 \text{ mole}$; $P = 4.1 \text{ atm}$; $V = 2 \text{ lit}$; $T = ?$; $q = 3710\text{J}$;

$$\Delta S = \frac{q}{T} = \frac{q}{\left(\frac{PV}{nR}\right)} = \frac{nRq}{PV} = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}} = 37.10 \text{ JK}^{-1}$$

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK⁻¹ mol⁻¹. Calculate the melting point of sodium chloride.

$\Delta H_f(\text{NaCl}) = 30.4 \text{ KJ} = 30400 \text{ J mol}^{-1}$; $\Delta S_f(\text{NaCl}) = 28.4 \text{ KJ}^{-1} \text{ mol}^{-1}$; $T_f = ?$;

$$\Delta S_f = \frac{\Delta H_f}{T_f}; \quad T_f = \frac{\Delta H_f}{\Delta S_f} = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ JK}^{-1} \text{ mol}^{-1}} = 1070.4 \text{ K}$$

58. Calculate the standard heat of formation of propane, if its heat of combustion is -2220.2 kJ mol⁻¹. The heats of formation of CO_{2(g)} and H_{2O(l)} are -393.5 and -285.8 kJ mol⁻¹ respectively.



$$\Delta H^\circ_f = -1180.5 - 1143.2 - (-2220.2) \text{ KJ mol}^{-1} = -103.5 \text{ KJ mol}^{-1}$$



Standard heat of formation of propane is $\Delta H^\circ_f(\text{C}_3\text{H}_8) = -103.5 \text{ KJ mol}^{-1}$

59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points (°C)	ΔH (kJ mol ⁻¹)
1	Ethanol	78.4	+42.4
2	Toluene	110.6	+35.2

For ethanol: $T_b = 78.4^\circ\text{C} = (78.4 + 273) = 351.4 \text{ K}$; $\Delta H_v(\text{ethanol}) = +42.4 \text{ KJ mol}^{-1}$;

$$\Delta S_v = \frac{\Delta H_v}{T_b} = \frac{+42.4 \text{ KJ mol}^{-1}}{351.4 \text{ K}} = \frac{+42400 \text{ J mol}^{-1}}{351.4 \text{ K}} = +120.66 \text{ JK}^{-1} \text{ mol}^{-1}$$

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For toluene: $T_b = 110.6^\circ\text{C} = (110.6 + 273) = 383.6 \text{ K}$; $\Delta H_v(\text{toluene}) = +35.2 \text{ KJ mol}^{-1}$;

$$\Delta S_v = \frac{\Delta H_v}{T_b} = \frac{+35.2 \text{ KJ mol}^{-1}}{383.6 \text{ K}} = \frac{+35200 \text{ J mol}^{-1}}{383.6 \text{ K}} = +91.76 \text{ JK}^{-1} \text{ mol}^{-1}$$

60. For the reaction $\text{Ag}_2\text{O(s)} \rightarrow 2\text{Ag(s)} + \frac{1}{2}\text{O}_2\text{(g)}$: $\Delta H = 30.56 \text{ kJ mol}^{-1}$ and $\Delta S = 6.66 \text{ JK}^{-1} \text{ mol}^{-1}$ (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

$\Delta H = 30.56 \text{ KJ mol}^{-1} = 30560 \text{ J mol}^{-1}$; $\Delta S = 6.66 \times 10^{-3} \text{ KJK}^{-1} \text{ mol}^{-1}$; $T = ?$ at which $\Delta G = 0$;

$$\Delta G = \Delta H - T\Delta S ; \Rightarrow 0 = \Delta H - T\Delta S ; \Rightarrow \Delta H = T\Delta S ; \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30.56 \text{ KJ mol}^{-1}}{6.66 \times 10^{-3} \text{ KJK}^{-1} \text{ mol}^{-1}} = 4589 \text{ K}$$

At 4589K; $\Delta G = 0$ the reaction is in equilibrium.

At temperature below 4598K, $\Delta H > T\Delta S$

$\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is non-spontaneous. In other words the reaction occurs in the backward direction.

61. What is the equilibrium constant K_{eq} for the following reaction at 400K. $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$, given that $\Delta H^\circ = 77.2 \text{ kJ mol}^{-1}$; and $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$.

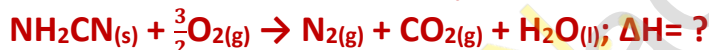
$T = 400 \text{ K}$; $\Delta H^\circ = 77.2 \text{ KJ mol}^{-1} = 77200 \text{ J mol}^{-1}$; $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$;

$$\Delta G^\circ = -2.303 RT \log K_{eq} ; \Rightarrow \log K_{eq} = -\frac{\Delta G^\circ}{2.303 RT} = -\frac{(\Delta H^\circ - T\Delta S^\circ)}{2.303 RT}$$

$$\log K_{eq} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right) = -\left(\frac{28400}{7659}\right) = -3.7080$$

$$K_{eq} = \text{antilog}(-3.7080) = 1.95 \times 10^{-4}$$

62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be $-742.4 \text{ kJ mol}^{-1}$, calculate the enthalpy change of the reaction at 298K.



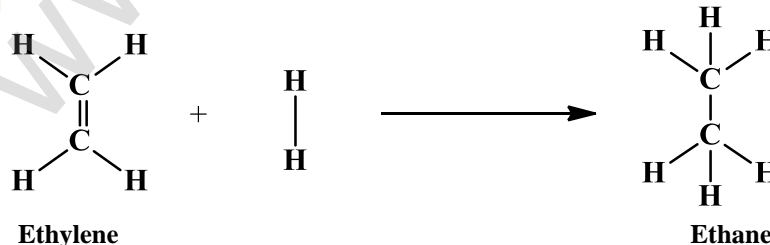
$T = 298 \text{ K}$; $\Delta U = -742.4 \text{ KJ mol}^{-1}$; $\Delta H = ?$;

$$\Delta H = \Delta U + \Delta n_g RT = \Delta U + (n_p - n_r) RT = -742.4 + \left[\left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298\right]$$

$$\Delta H = -742.4 + [(0.5) \times 8.314 \times 10^{-3} \times 298] = -742.4 + 1.24 = -741.16 \text{ KJ mol}^{-1}$$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C - H, C - C, C = C and H - H are 414, 347, 618 and 435 kJ mol^{-1} .

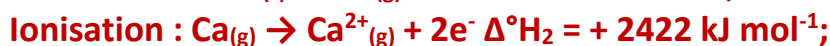
$E_{\text{C-H}} = 414 \text{ KJ mol}^{-1}$; $E_{\text{C-C}} = 347 \text{ KJ mol}^{-1}$; $E_{\text{C=C}} = 618 \text{ KJ mol}^{-1}$; $E_{\text{H-H}} = 435 \text{ KJ mol}^{-1}$;



$$\Delta H_r = \sum(\text{Bond energy})_r - \sum(\text{Bond energy})_p = (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}}) - (E_{\text{C-C}} + 6E_{\text{C-H}})$$

$$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414)) = 2709 - 2831 = -122 \text{ KJ mol}^{-1}$$

64. Calculate the lattice energy of CaCl_2 from the given data

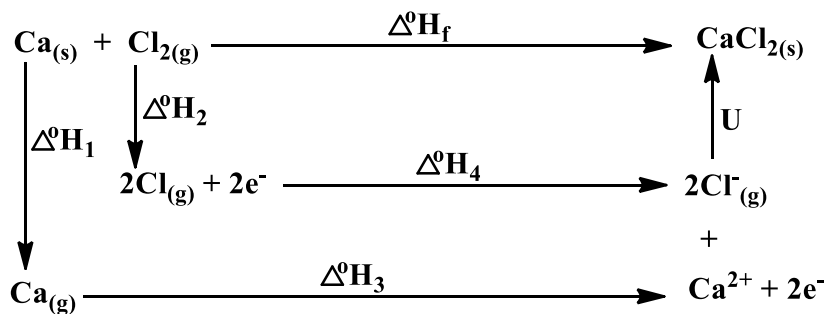


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Dissociation : $\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)}$ $\Delta^\circ\text{H}_3 = +242.8 \text{ kJ mol}^{-1}$;

Electron affinity : $\text{Cl}_{(g)} + e^- \rightarrow \text{Cl}^-_{(g)}$ $\Delta^\circ\text{H}_4 = -355 \text{ kJ mol}^{-1}$



$$\Delta^\circ\text{H}_f = \Delta^\circ\text{H}_1 + \Delta^\circ\text{H}_2 + \Delta^\circ\text{H}_3 + \Delta^\circ\text{H}_4 + U$$

$$U = \Delta^\circ\text{H}_f - (\Delta^\circ\text{H}_1 + \Delta^\circ\text{H}_2 + \Delta^\circ\text{H}_3 + 2\Delta^\circ\text{H}_4)$$

$$U = -795 - [121 + 2422 + 242.8 + (2 \times (-355))] = -795 - [2785.8 - 710] = -795 - 2075.8$$

$$U = -2870.8 \text{ KJ mol}^{-1}$$

65. Calculate the enthalpy change for the reaction $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ from the following data. $2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$; $\Delta\text{H} = -741 \text{ kJ}$; $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$; $\Delta\text{H} = -137 \text{ kJ}$; $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$; $\Delta\text{H} = -394.5 \text{ kJ}$

$$\Delta\text{H}_f(\text{Fe}_2\text{O}_3) = -741 \text{ KJ mol}^{-1}; \Delta\text{H}_f(\text{CO}) = -137 \text{ KJ mol}^{-1}; \Delta\text{H}_f(\text{CO}_2) = -394.5 \text{ KJ mol}^{-1};$$

$$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2; \Delta\text{H}_r = ? ;$$

$$\Delta\text{H}_r = \sum(\Delta\text{H}_f)_{\text{products}} - \sum(\Delta\text{H}_f)_{\text{reactants}}$$

$$\Delta\text{H}_r = [2\Delta\text{H}_f(\text{Fe}) + 3\Delta\text{H}_f(\text{CO}_2)] - [\Delta\text{H}_f(\text{Fe}_2\text{O}_3) + 3\Delta\text{H}_f(\text{CO})]$$

$$\Delta\text{H}_r = [0 + 3(-394.5)] - [-741 + 3(-137)] = [-1183.5] - [-1152] = -1183.5 + 1152 = -31.5 \text{ KJ mol}^{-1}$$

66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A), 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate ΔG° for the following equilibria.



$T = 175^\circ\text{C} = 175 + 273 = 448\text{K}$; Concentration of 1-pentyne [A] = 1.3%; Concentration of 2-pentyne [B] = 95.2%; Concentration of 1,2-pentadiene [C] = 3.5%;

$$\text{At equilibrium, B (95.2\%)} \rightleftharpoons \text{A (1.3\%)} \Rightarrow K_1 = \frac{1.3}{95.2} = 0.0136$$

$$\text{At equilibrium, B (95.2\%)} \rightleftharpoons \text{C (3.5\%)} \Rightarrow K_2 = \frac{3.5}{95.2} = 0.0367$$

$$\Delta\text{G}^\circ_1 = -2.303 \text{ RT} \log K_1 = -2.303 \times 8.314 \times 448 \times \log (0.0136) = +16010 \text{ J} = +16 \text{ KJ}$$

$$\Delta\text{G}^\circ_2 = -2.303 \text{ RT} \log K_2 = -2.303 \times 8.314 \times 448 \times \log (0.0367) = +12312 \text{ J} = +12.312 \text{ KJ}$$

67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

$$T = 33\text{K}; \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$$

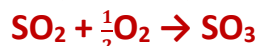
	N_2O_4	\rightleftharpoons	2NO_2
Initial no. of moles	100		0
Number of moles dissolved	50		-
No. of moles remaining	50		100
Total no. of moles	150 moles		

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$P_{N_2O_4} = \frac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} \cdot P$ $P_{N_2O_4} = \frac{50 \text{ mol}}{150 \text{ mol}} \cdot 1 \text{ atm} = \mathbf{0.333 \text{ atm}}$ $P_{NO_2} = \frac{n_{NO_2}}{n_{N_2O_4} + n_{NO_2}} \cdot P$ $P_{NO_2} = \frac{100 \text{ mol}}{150 \text{ mol}} \cdot 1 \text{ atm} = \mathbf{0.667 \text{ atm}}$	$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}}$ $K_P = \frac{(0.667)^2 \text{ atm}^2}{0.333 \text{ atm}} = \mathbf{1.336 \text{ atm}}$ $\Delta G^\circ = -2.303RT \log K_P$ $\Delta G^\circ = -2.303 \times 8.314 \times 33 \times \log(1.336)$ $\Delta G^\circ = \mathbf{-79.49 \text{ mol}^{-1}}$
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68. The standard enthalpies of formation of SO₂ and SO₃ are -297 kJ mol⁻¹ and -396 kJ mol⁻¹ respectively. Calculate the standard enthalpy of reaction for the reaction: [HY-22]



$$\Delta H_f(\text{SO}_2) = -297 \text{ KJ mol}^{-1}; \Delta H_f(\text{SO}_3) = -396 \text{ KJ mol}^{-1}; \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3; \Delta H_r = ? ;$$

$$\Delta H_r = \sum(\Delta H_f)_{\text{compound}} - \sum(\Delta H_f)_{\text{elements}}$$

$$\Delta H_r = [\Delta H_f(\text{SO}_3)] - [\Delta H_f(\text{SO}_2) + \frac{1}{2}\Delta H_f(\text{O}_2)]$$

$$\Delta H_r = [-396 \text{ KJ mol}^{-1}] - [-297 \text{ KJ mol}^{-1}] = -396 + 297 = \mathbf{-99 \text{ KJ mol}^{-1}}$$

69. For the reaction at 298 K : 2A + B → C; ΔH=400 KJ mol⁻¹; ΔS = 0.2 KJ mol⁻¹ Determine the temperature at which the reaction would be spontaneous.

$$T = 298\text{K}; \Delta H = 400 \text{ KJ mol}^{-1}; \Delta S = 0.2 \text{ KJ K}^{-1} \text{ mol}^{-1}; \Delta G = \Delta H - T\Delta S; \text{ if } T = 2000\text{K};$$

$$\Delta G = 400 - (0.2 \times 2000) = 0$$

$$\Delta H = 400 \text{ KJ mol}^{-1} \text{ if } T > 2000\text{K} [\because \Delta G \text{ will be negative}]$$

The reaction would be spontaneous only beyond 2000K.

70. Find out the value of equilibrium constant for the following reaction at 298K, 2NH_{3(g)} + CO_{2(g)} ⇌ NH₂CONH_{2(aq)} + H₂O_(l) Standard Gibbs energy change, ΔG^o_r at the given temperature is -13.6 kJ mol⁻¹.

$$T = 298\text{K}; \Delta G^\circ_r = -13.6 \text{ KJ mol}^{-1} = -13600 \text{ J mol}^{-1};$$

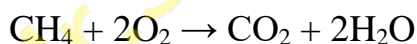
$$\Delta G^\circ = -2.303 RT \log K_{\text{eq}} \Rightarrow \log K_{\text{eq}} = \frac{\Delta G^\circ}{-2.303 RT} = \frac{(-13.6 \text{ KJ mol}^{-1})}{(-2.303 \times 8.314 \times 10^{-3} \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K})} = 2.38$$

$$K_{\text{eq}} = \text{antilog}(2.38) = \mathbf{239.88}$$

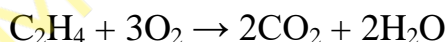
71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. (ΔH_c(CH₄)= - 890 kJ mol⁻¹ and (ΔH_c(C₂H₄)= -1423 kJ mol⁻¹.)

$$\Delta H_c(\text{CH}_4) = -890 \text{ kJ mol}^{-1}; \Delta H_c(\text{C}_2\text{H}_4) = -1423 \text{ kJ mol}^{-1};$$

Let the mixture contain x lit of CH₄ and (3.67 - x) lit of ethylene.



$$x \text{ lit} \qquad \qquad \qquad x \text{ lit}$$



$$(3.67 - x) \text{ lit} \qquad \qquad 2(3.67 - x) \text{ lit}$$

$$\text{Volume of carbondioxide formed} = x + 2(3.67 - x) = 6.11 \text{ lit.}$$

$$x + 7.34 - 2x = 6.11; \Rightarrow 7.34 - x = 6.11; \Rightarrow x = 7.34 - 6.11; \Rightarrow x = \mathbf{1.23 \text{ lit}}$$

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence,

$$\Delta H_c = \left[\frac{\Delta H_c(\text{CH}_4)}{22.4 \text{ lit}} \times (x) \text{ lit} \right] + \left[\frac{\Delta H_c(\text{C}_2\text{H}_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit} \right]$$

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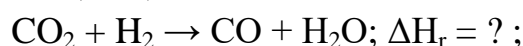
$$\Delta H_C = \left[\frac{-890 \text{ KJ mol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit} \right] + \left[\frac{-1423 \text{ KJ mol}^{-1}}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit} \right]$$

$$\Delta H_C = [-48.87 \text{ KJ mol}^{-1}] + [-155 \text{ KJ mol}^{-1}] = \mathbf{-203.87 \text{ KJ mol}^{-1}}$$

EVALUATE YOURSELF

1. Calculate ΔH°_f for the reaction $\text{CO}_{2(g)} + \text{H}_{2(g)} \rightarrow \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)}$ given that ΔH°_f for $\text{CO}_{2(g)}$, $\text{CO}_{(g)}$ and $\text{H}_2\text{O}_{(g)}$ are -393.5 , -111.31 and -242 kJ mol^{-1} respectively. [GMQ18]

$$\Delta H_f(\text{CO}_2) = -393.5 \text{ KJ mol}^{-1}; \Delta H_f(\text{CO}) = -111.31 \text{ KJ mol}^{-1}; \Delta H_f(\text{H}_2\text{O}) = -242 \text{ KJ mol}^{-1};$$



$$\Delta H_r = \sum(\Delta H_f)_{\text{products}} - \sum(\Delta H_f)_{\text{reactants}}$$

$$\Delta H_r = [\Delta H_f(\text{CO}) + \Delta H_f(\text{H}_2\text{O})] - [\Delta H_f(\text{CO}_2) + \Delta H_f(\text{H}_2)]$$

$$\Delta H_r = [(-111.31) + (-242)] - [(-393.5) + (0)] = -353.31 + 393.5 = \mathbf{+40.19 \text{ KJ mol}^{-1}}$$

2. Calculate the amount of heat necessary to raise 180 g of water from 25°C to 100°C . Molar heat capacity of water is $75.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\text{Number of moles of water, } n = \frac{180 \text{ g}}{18 \text{ g mol}^{-1}} = 10 \text{ mol}; \Delta H = ? ;$$

$$\text{Molar heat capacity of water, } C_p = 75.3 \text{ JK}^{-1} \text{ mol}^{-1}; T_2 = 100^\circ\text{C} = 373\text{K}; T_1 = 25^\circ\text{C} = 298\text{K};$$

$$\Delta H = n C_p (T_2 - T_1) = 10 \text{ mol} \times 75.3 \text{ JK}^{-1} \text{ mol}^{-1} \times (373 - 298)\text{K} = 56475\text{J} = \mathbf{56.475 \text{ KJ}}$$

3. From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



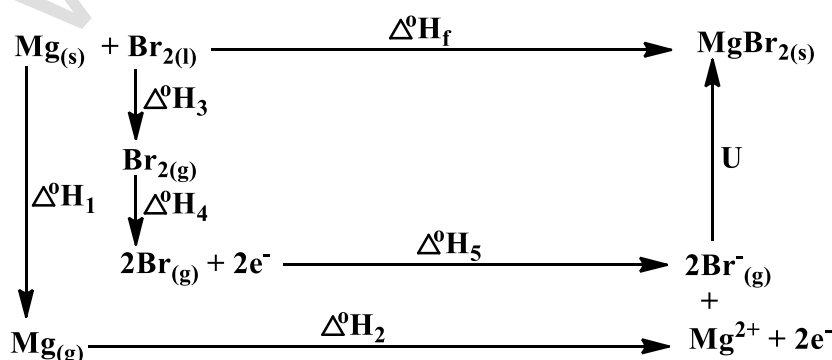
$$T = 25^\circ\text{C} = 298\text{K}; \Delta U = -3268.12 \text{ KJ mol}^{-1}; \Delta H = ? ;$$

$$\Delta H = \Delta U + \Delta n_g RT = \Delta U + (n_p - n_r) RT$$

$$\Delta H = -3268.12 + \left(6 - \frac{15}{2}\right) \times 8.314 \times 10^{-3} \times 298 = -3268.12 - (1.5 \times 8.314 \times 10^{-3} \times 298)$$

$$\Delta H = -3268.12 - 3.72 = \mathbf{-3271.84 \text{ KJ mol}^{-1}}$$

4. When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released. The heat of sublimation of Mg metal is 148 kJ mol^{-1} . The heat of dissociation of bromine gas into atoms is 193 kJ mol^{-1} . The heat of vapourisation of liquid bromine is 31 kJ mol^{-1} . The first and second ionisation energies of magnesium are $\text{IE}_1 = 737.5 \text{ kJ mol}^{-1}$ and $\text{IE}_2 = 1450.5 \text{ kJ mol}^{-1}$ and the electron affinity of bromine is $-324.5 \text{ kJ mol}^{-1}$. Calculate the lattice energy of magnesium bromide.



$$\Delta^\circ H_f = \Delta^\circ H_1 + \Delta^\circ H_2 + \Delta^\circ H_3 + \Delta^\circ H_4 + \Delta^\circ H_5 + U$$

$$U = \Delta^\circ H_f - (\Delta^\circ H_1 + \Delta^\circ H_2 + \Delta^\circ H_3 + \Delta^\circ H_4 + 2\Delta^\circ H_5)$$

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$$U = -524 - [148 + 2188 + 31 + 193 + (2 \times (-324.5))] = -524 - 1911 = -2870.8 \text{ KJ mol}^{-1}$$

5. An engine operating between 127°C and 47°C takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

$$T_h = 127^\circ\text{C} = 127 + 273 = 400\text{K}; T_c = 47^\circ\text{C} = 47 + 273 = 320\text{K}; \% \text{ efficiency } \eta = ? ;$$

$$\eta = \left[\frac{T_h - T_c}{T_h} \right] \times 100 = \left[\frac{400 - 320}{400} \right] \times 100 = \left[\frac{80}{400} \right] \times 100 = 20\%$$

6. Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea, H₂O, CO₂, NH₃ are 173.8, 70, 213.5 and 192.5 J mol⁻¹K⁻¹ respectively. Calculate the entropy change for this reaction.

$$S^\circ(\text{urea}) = 173.8 \text{ J mol}^{-1} \text{ K}^{-1}; S^\circ(\text{H}_2\text{O}) = 70 \text{ J mol}^{-1} \text{ K}^{-1}; S^\circ(\text{CO}_2) = 213.5 \text{ J mol}^{-1} \text{ K}^{-1};$$

$$S^\circ(\text{NH}_3) = 192.5 \text{ J mol}^{-1} \text{ K}^{-1}; \text{H}_2\text{N-CO-NH}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2; \Delta S^\circ_r = ? ;$$

$$\Delta S^\circ_r = \sum(S^\circ)_{\text{products}} - \sum(S^\circ)_{\text{reactants}}$$

$$\Delta S^\circ_r = [2S^\circ(\text{NH}_3) + S^\circ(\text{CO}_2)] - [S^\circ(\text{urea}) + S^\circ(\text{H}_2\text{O})]$$

$$\Delta S^\circ_r = [(2 \times 192.5) + 213.5] - [173.8 + 70] = 598.5 - 243.8 = + 354.7 \text{ J mol}^{-1}\text{K}^{-1}$$

7. Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol⁻¹.

$$T_b = 351\text{K}; \Delta H_{\text{vap}} = 39840 \text{ J mol}^{-1}; \Delta S_v = ? ;$$

$$\Delta S_v = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{39840}{351} = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

8. For a chemical reaction the values of ΔH and ΔS at 300K are - 10 kJ mol⁻¹ and -20 J deg⁻¹ mol⁻¹ respectively. What is the value of ΔG of the reaction? Calculate the ΔG of a reaction at 600 K assuming ΔH and ΔS values are constant. Predict the nature of the reaction.

$$\Delta H = -10 \text{ KJ mol}^{-1} = -10000 \text{ J mol}^{-1}; \Delta S = -20 \text{ J K}^{-1} \text{ mol}^{-1}; T = 300\text{K}; \Delta G = ? ;$$

$$\Delta G = \Delta H - T\Delta S = -10 \text{ KJ mol}^{-1} - (300 \times -20 \text{ J K}^{-1} \text{ mol}^{-1}) = (-10 \times 1000 + 6000) \text{ J mol}^{-1} = -4 \text{ KJ mol}^{-1}$$

$$\text{At } 600\text{K}, \Delta G = -10 \text{ KJ mol}^{-1} - (600 \times -20 \text{ J K}^{-1} \text{ mol}^{-1}) = (-10 \times 1000 + 12000) \text{ J mol}^{-1} = +2 \text{ KJ mol}^{-1}$$

GOVERNMENT QUESTIONS AND ANSWERS

1. Give the relation between enthalpy (H) and internal energy (U). [GMQ-18, HY-22, CRT-23]

$$H = U + PV$$

Considering the initial and final states of H, U and V as H₁, U₁ and V₁ and H₂, U₂ and V₂.

$$\text{Change in enthalpy is } (H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1) \quad \Delta H = \Delta U + P\Delta V$$

2. Write the relationship between ΔH and ΔU. [QY-18]

$$H = U + PV$$

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

$$\Delta H = \Delta U + \Delta n_g RT$$

3. State zeroth law of thermodynamics. [QY-18, SEP-20, CRT-23]

The law states that 'If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

4. Explain sign convention of heat. [MAY-22]

The symbol of heat is q.

+ If heat flows into the system from the surrounding, energy of a system increases. Hence it is taken to be positive (+q).

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✚ If heat flows out of the system into the surrounding, energy of the system decreases. Hence, it is taken to be negative ($-q$).

5. If an automobile engine burns petrol at a temperature of 1089K (816°C) and if the surrounding temperature is 294K (21°C), calculate its maximum possible efficiency. [AUG-22, CRT-23]

$$T_n = 1089\text{K}; T_c = 294\text{K}; \% \text{ Efficiency} = \left(\frac{1089-294}{1089} \right) \times 100 = 73\%$$

6. Derive the relationship between C_p and C_v for an ideal gas. [QY-19, CRT-23]

From the definition of enthalpy

$$H = U + PV \quad \text{-----(1)}$$

for 1 mole of an ideal gas

$$PV = nRT \quad \text{-----(2)}$$

By substituting (2) in (1) $H = U + nRT \quad \text{-----(3)}$

Differentiating the above equation with respect to T,

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + nR \frac{\partial T}{\partial T}$$

$$C_p = C_v + nR \quad (1)$$

$$C_p - C_v = nR \quad \text{-----(4)}$$

$$\left[\begin{array}{l} \because \left(\frac{\partial H}{\partial T} \right)_P = C_p \\ \text{and} \left(\frac{\partial U}{\partial T} \right)_V = C_v \end{array} \right]$$

At constant pressure processes, a system has to do work against the surroundings. Hence, the system would require more heat to effect a given temperature rise than at constant volume, so C_p is always greater than C_v

7. A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system. [QY-19]

Given data $q = 400 \text{ J}$ $V_1 = 5\text{L}$ $V_2 = 10\text{L}$

$\Delta u = q - w$ (heat is given to the system (+q); work is done by the system (-w))

$$\begin{aligned} \Delta u &= q - PdV \\ &= 400 \text{ J} - 1 \text{ atm} (10-5)\text{L} \end{aligned}$$

$$= 400 \text{ J} - 5 \text{ atm L}$$

$$[\because 1\text{L atm} = 101.33 \text{ J}]$$

$$= 400 \text{ J} - 5 \times 101.33 \text{ J}$$

$$= 400 \text{ J} - 506.65 \text{ J}$$

$$= -106.65 \text{ J}$$

8. Calculate the mole fraction of methanol and water when 0.5 mole of methanol is mixed with 1.5 mole of water. [SEP-20]

0.5 mole of methanol is mixed with 1.5 mole of water.

The mole fraction of methanol in the above solution is = $\frac{\text{No. of moles of the methanol}}{\text{Total no. of moles of methanol and water}}$

$$= \frac{0.5}{1.5+0.5} = \frac{0.5}{2} = 0.25$$

The mole fraction of water in the above solution is = $\frac{\text{No. of moles of the water}}{\text{Total no. of moles of methanol and water}}$

$$= \frac{1.5}{1.5+0.5} = \frac{1.5}{2} = 0.75$$

UNIT – VII – THERMODYNAMICS

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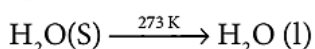
9. Distinguish between extensive and intensive properties. [SEP-20]

EXTENSIVE PROPERTIES	INTENSIVE PROPERTIES
The property that depends on the mass or the size of the system is called an extensive property	The property that is independent of the mass or the size of the system is called an intensive property.
Examples: Volume, Number of moles, Mass, Internal energy, etc.,	Examples : Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

10. Calculate the entropy change during the melting of one mole of ice into water at 0° C and 1 atm pressure. Enthalpy of fusion of ice is 6008 J mol⁻¹. [MAR-19, SEP-20, CRT-22, MAR-23]

$$\Delta H_{\text{fusion}} = 6008 \text{ J mol}^{-1}$$

$$T_f = 0^\circ \text{C} = 273 \text{ K}$$

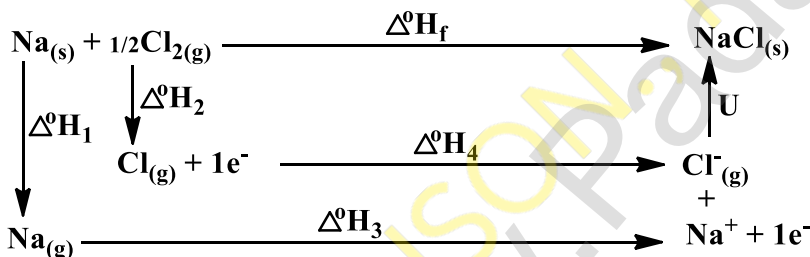


$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$\Delta S_{\text{fusion}} = \frac{6008}{273}$$

$$\Delta S_{\text{fusion}} = 22.007 \text{ J K}^{-1} \text{ mole}^{-1}$$

11. Calculate the lattice energy of formation of NaCl from the following data: [QY-19]



$$\Delta^\circ H_f = \text{heat of formation of sodium chloride} = -411.3 \text{ kJ mol}^{-1}$$

$$\Delta^\circ H_1 = \text{heat of sublimation of Na}_{(g)} = 108.7 \text{ kJ mol}^{-1}$$

$$\Delta^\circ H_2 = \text{ionisation energy of Na}_{(g)} = 495.0 \text{ kJ mol}^{-1}$$

$$\Delta^\circ H_3 = \text{dissociation energy of Cl}_{2(g)} = 244 \text{ kJ mol}^{-1}$$

$$\Delta^\circ H_4 = \text{Electron affinity of Cl}_{(g)} = -349.0 \text{ kJ mol}^{-1}$$

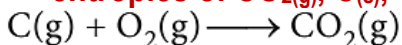
$$U = \text{Lattice energy of NaCl}$$

$$\Delta^\circ H_f = \Delta^\circ H_1 + \Delta^\circ H_2 + \frac{1}{2}\Delta^\circ H_3 + \Delta^\circ H_4 + U$$

$$U = \Delta^\circ H_f - (\Delta^\circ H_1 + \Delta^\circ H_2 + \frac{1}{2}\Delta^\circ H_3 + \Delta^\circ H_4)$$

$$U = (-411.3) - (108.7 + 495.0 + 122 - 349) = (-411.3) - (376.7) = -788 \text{ kJ mol}^{-1}$$

12. Calculate the standard entropy change for the following reaction (ΔS_r°), given the standard entropies of CO_{2(g)}, C_(s), O_{2(g)} as 213.6, 5.740 and 205 JK⁻¹ respectively. [MAR-19]



$$\Delta S_r^\circ = 213.6 - [5.74 + 205]$$

$$\Delta S_r^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ$$

$$\Delta S_r^\circ = 213.6 - [210.74]$$

$$\Delta S_r^\circ = \{S_{\text{CO}_2}^\circ\} - \{S_{\text{C}}^\circ + S_{\text{O}_2}^\circ\}$$

$$\Delta S_r^\circ = 2.86 \text{ JK}^{-1}$$

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13.Explain the measurement of heat change at constant pressure with a neat diagram. [JUN-19]

Heat change at constant pressure (at atmospheric pressure) can be measured using a coffee cup calorimeter. A schematic representation of a coffee cup calorimeter is given in Figure. Instead of bomb, a styrofoam cup is used in this calorimeter. It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding. This entire heat energy is absorbed by the water inside the cup. This method can be used for the reactions where there is no appreciable change in volume. The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where m_w is the molar mass of water and C_w is the molar heat capacity of water ($75.29 \text{ J K}^{-1} \text{ mol}^{-1}$)

14.Explain intensive properties with two examples. [HY-22]

The property that is independent of the mass or the size of the system is called an intensive property.

Examples: Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

