THERMODYNAMICS II & THERMOCHEMISTRY

CONTENTS

THERMODYNAMICS IInd & IIIrd LAW

THERMOCHEMISTRY

JEE (ADVANCED) SYLLABUS

First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy; Second law of thermodynamics, Entropy, Free energy, Criterion of spontaneity; Heat of reaction, fusion and vapourization, Hess's law.

JEE (MAIN) SYLLABUS

Thermal equilibrium, zeroth law of thermodynamics, concept of temperature. Heat, work and internal energy. First law of thermodynamics. Second law of thermodynamics: reversible and irreversible processes. Carnot engine and its efficiency.

Thermodynamics II law & Thermochemistry

IInd Law of thermodynamics :

Requirement : Ist law insufficient to Explain

Neutralization, Melting of ice > 0°

Combustion, Freezing of water < 0°

Fall of water, Boiling of water > 100° C

Cooling of a hot body, Free expansion of a gas, mixing of gases.

Spontaneous /Natural /Irreversible Processes :

If a system moves along in a direction on its own and system, surrounding interactions without the help of any external agency, then that direction is known as spontaneous direction and the process is knwon as a spontaneous process.

Limitation :

First law cannot predict the direction of any process. But in nature a process is found to have a specific direction at certain conditions.

1. Energy can be the factor : To achieve stability

* All exothermic processes are spontaneous.

* All endothermic processes are non spontaneous.

Exceptions

* melting of ice (above 0°C) although $\Delta H > 0$, $\Delta E > 0$

* Vaporization of water (above 100°C) $\Delta H > 0$, $\Delta E > 0$

* Spreading of ink in water $\Delta H = 0$, $\Delta E = 0$

* Mixing of two gases

* Endothermic solution of salt $\Delta H > 0$, $\Delta E > 0$

2. It is observed that nature tries to distribute energy and matter uniformaly (randomization)

Second law of thermodynamics :

Entropy of the universe is constantly inereasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \text{ for a spontaneous process.}$$

Where **(S)** = entropy is the measure of randomness or disorder. It is a state function and extensive property. Mathematically

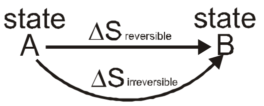
$$ds = \frac{dq_{rev}}{T} \text{ or } \Delta S = \int \frac{dq_{rev}}{T}, \quad \frac{dq}{T} \text{ is state function only for reversible process}$$

$$dS \propto dq_{rev}, \; dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.

- **Entropy Calculation :**

- **Calculation of ΔS_{system}**



As 'S' is a state function. Hence 'ΔS' will also be a state function.

$\therefore \quad \Delta S_{irrev} = \Delta S_{rev}$

$$\Delta S = \int_A^B \frac{dq_{rev}}{T} \text{ reversible path}$$

- **Entropy calculation for an ideal gas undergo in a process.**

State A $\xrightarrow{\Delta S_{irr}}$ State B

P_1, V_1, T_1 $\qquad$ P_2, V_2, T_2

As 'S' is a state function.So, ΔS will not depend upon path

$$\Delta S_{irrev} = \Delta S_{rev,\ system} = \int_A^B \frac{dq_{rev}}{T} \text{ rev path.}$$

from the first law

$dU = dQ + dw$

$dQ = dU - dw$

for reversible path

$dq = dq_{rev}$

$dq_{rev} = dU + P_{gas}\, dV \qquad \{P_{ext} = P_{gas} \text{ reversible}\}$

$$\Delta S_{rev,\ system} = \int_A^B \frac{dU + P_{gas}\ dV}{T}$$

for an ideal gas

$$\frac{P_{gas}}{T} = \frac{nR}{V} \ \& \ du = nc_V\, dT$$

$$\therefore \quad \Delta S_{sys} = \int_{T_1}^{T_2} \frac{nc_V\, dT}{T} + \int_{V_1}^{V_2} \frac{nRdV}{V}$$

$$\therefore \quad \boxed{\Delta S_{system} = nc_v\, \ell n \frac{T_2}{T_1} + nR\, \ell n \frac{V_2}{V_1}}$$

- **Calculation of $\Delta S_{surrounding}$:** As the surrounding is an infinite heat reservoir hence, no. amount of heat given to the surrounding can cause turbulance in it, hence all heat exhanges with surroundings are considered to be reversible.

$$\Delta S_{surrounding} = \int \frac{dq_{surrounding}}{T}$$

For $\quad$ surrounding T is constant

$$\therefore \quad \Delta S_{surr} = \frac{1}{T} \int dq_{surr} = \frac{q_{surrounding}}{T}$$

But according to the law of conservation of energy

$q_{surr} = -\, q_{system}$

$$\therefore \quad \Delta S_{surr} = \frac{-q_{system}}{T}$$

- ## Isothermal process :

(a) Reversible

$$\text{State A} \xrightarrow{Rev} \text{State B}$$

P_1, V_1, T $\qquad$ P_2, V_2, T

$$\Delta S_{\ system} = nC_V \ell n \frac{T_2}{T_1} + nR\ell n \frac{V_2}{V_1}$$

Since $T_1 = T_2$

$$\Delta S_{\ system} = nR\ell n \frac{V_2}{V_1}$$

$$\Delta S_{surrounding} = -\frac{q_{\ system}}{T}$$

du = dq + dw (since $T_1 = T_2$. So, du = 0)

$\therefore$ dq = – dw

$$\therefore\ q = -w \quad \text{as } w = -\, nRT\ell n \frac{V_2}{V_1}$$

$$q = nRT\ell n \frac{V_2}{V_1}$$

$$\therefore\ \Delta S_{sys.} = \frac{-nRT\ell n \frac{V_2}{V_1}}{T} = -nR\ell n \frac{V_2}{V_1}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$= nR\ell n \frac{V_2}{V_1} - nR\ell n \frac{V_2}{V_1} = 0$$

(b) Irreversible

$$\text{State A} \xrightarrow{irrev} \text{State B}$$

P_1, V_1, T $\qquad$ P_2, V_2, T

$$\Delta S_{system} = nR\ell n \frac{V_2}{V_1}$$

$$\Delta S_{Surrounding} = \frac{-q_{system}}{T}$$

q_{system} is calculated using FLOT

$q_{system} = P_{ext}(V_2 - V_1)$

$$\therefore\ \Delta S_{surrounding} = \frac{-p_{ext}(V_2 - V_1)}{T}$$

$$\Delta S_{universe} = nR\ell n\frac{V_2}{V_1} - \frac{-p_{ext}(V_2 - V_1)}{T}$$

$$= \frac{1}{T}\left[(nRT\ell n\frac{V_2}{V_1}) - P_{ext}\ (V_2 - V_1)\right] = \frac{1}{T}[W_{irrev} - W_{rev}] > 0$$

As irreversible work of gas is more than reversible work.

- ## Adiabatic Process (Isoentropic process)

(a) Reversible Adiabatic

State A $\xrightarrow{rev}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

$$\Delta S_{system} = nC_V\ \ell n\ \frac{T_2}{T_1} + nR\ \ell n\ \frac{V_2}{V_1}$$

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

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$(\Delta S)_{system} = nC_V\ell n\left(\frac{V_1}{V_2}\right)^{\gamma-1} + nR\ell n\frac{V_2}{V_1} = 0$$

$$\Delta S_{surr} = -\frac{q_{sys}}{T} = 0 \quad (q_{sys} = 0)$$

$$\therefore\ \Delta S_{universe} = 0 + 0 = 0$$

(b) Irreversible Adiabatic

State A $\xrightarrow{irre}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

$$\Delta S_{system} = nC_V\ \ell n\ \frac{T_2}{T_1} + nR\ \ell n\ \frac{V_2}{V_1} > 0 \quad [(T_2)_{irrev} > (T_2)_{rev}]$$

$$\Delta S_{surr} = -\frac{q_{sys}}{T} = 0$$

as q = 0

For irreversible expansion the decrease in temprature will be lesser as work done is lesser hence, decrease in entropy due to fall in temprature will be lesser in case of irrversible expansion. Hence, net entropy would increase.

- ## Isobaric process :

(a) Reversible Isobaric

State A $\xrightarrow{rev}$ State B

P, V_1, T_1 P, V_2, T_2

$$\Delta S_{sys} = \int\frac{dq_{rev}}{T} = \int\frac{nC_p dT}{T} = nC_p\ell n\frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{-dq_{sys}}{T} = -nC_p \ell n \frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irreversible Isobaric

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \frac{-nC_p(T_2 - T_1)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

- ## Isochoric Process

(a) Reversible Isochoric

$$\text{State A} \xrightarrow{rev} \text{State B}$$

P_1, V, T_1 $\quad$ P_2, V, T_2

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_v \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{-dq_{sys}}{T} = -nC_v \ell n \frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irreversible Isochoric

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_p \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \frac{-nC_v(T_2 - T_1)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

- ## Entropy Calculation for phase transformations

$$\Delta S_{fusion} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

for constant pressure $\Delta S_{fus.} = \frac{\Delta H_{fus}}{T}$

for constant volume $\Delta S_{fus.} = \frac{\Delta U_{fusion}}{T}$

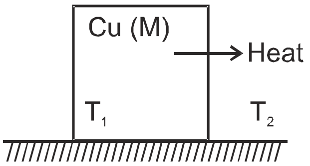
$$\Delta S_{vap} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

for constant Pressure, $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T}$

for constant Volume, $\Delta S_{vap} = \dfrac{\Delta U_{vap}}{T}$

- ## Entropy Calculation solid or liquid systems:

(a) 'Cu' block kept in open atmosphere



$T_1 > T_2$

$$\Delta S_{system} = \int_{T_1}^{T_2} \frac{msdT}{T} = m\ell n \frac{T_2}{T_1}$$

$\therefore$ $\Delta S_{surr} = \int \dfrac{dq_{surr}}{T} = \dfrac{q_{\ surr}}{T_2}$

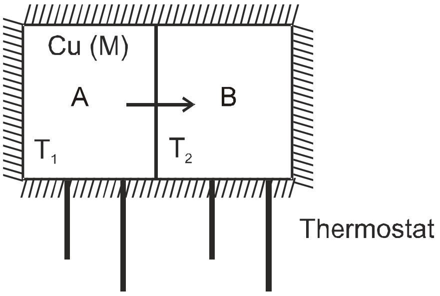
but $q_{\ surr} = -q_{system} = -ms(T_2 - T_1) = ms(T_1 - T_2)$

Hence, $\Delta S_{surr} = \dfrac{ms(T_1 - T_2)}{T_2}$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

$\therefore$ $\Delta S_{universe} = ms\ \ell n \dfrac{T_2}{T_1} + \dfrac{ms(T_1 - T_2)}{T_2} > 0$

(b) Two copper block kept in contact in thermostat



Two blocks are of same mass

$\Delta S_{surr} = 0$ (since no heat is lost to surrounding)

$\Delta S_{\ system} = \Delta S_A + \Delta S_B$

System will reach a common temperature (T_f)

and $T_1 > T_f > T_2$

$$\Delta S_{\ system} = \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T}$$

$$= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms\left[\ell n \frac{T_f}{T_1} + \ell n \frac{T_f}{T_2}\right]$$

$$\Delta S_{system} = ms\ell n \frac{T_f^{\ 2}}{T_1 T_2}$$

Since $T_f = \dfrac{T_1 + T_2}{2}$ $\therefore$ $\Delta S_{system} = ms\ell n \dfrac{(T_1 + T_2)^2}{4T_1T_2}$

SOLVED EXAMPLE

Ex-1. **(a)** One mole of an idal gas expands isothermally and reversibly at 25ºC from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas?

(ii) How much work is done by the gas?

(iii) What is q (surroundings)?

(iv) What is the change in the entropy of the surroundings?

(v) What is the change in the entropy of the system plus the surroundings?

(b) Also answer the questions opening a stopcock and allowing the gas to rush into an evacuated bulb of 10 L volume.

Sol. **(a)** (i) $\Delta S = 2.303\ nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76$ J/K.

(ii) $W_{rev} = -2.303 nRT \log \frac{V_2}{V_1}$

$= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1781$ J.

(iii) For isothermal process, $\Delta U = 0$ and heat is absorbed by the gas,

$q_{rev} = \Delta U - W = 0 - (-1718) = 1718$ J.

$\therefore$ $q_{rev} = 1718$ J. ($\therefore$ process is reversible)

(iv) $\Delta S_{surr} = -\frac{1718}{298} = -5.76$ J/K.

As entropy of the system increases by 5.76 J, the entropy of the surroundings decreases by 5.76J, since the process is carried out reversibly.

(v) $\Delta S_{sys} + \Delta S_{surr} = 0$..... for reversible process

(b) (i) $\Delta S = 5.76$ J/K, which is the same as above because S is a state function

(ii) $W = 0$ ($\because p_{ext} = 0$)

(iii) No heat is exchanged with the surroundings.

(iv) $\Delta S_{surr} = 0$.

(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process

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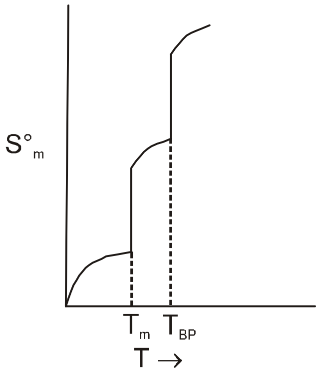
- ### Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Thus, absolute value of entropy unlike the absolute value of enthalpy for any pure substance can be calculated at any given temperature. In standard state (298 K, 1 atm), it is standard absolute entropy Sº.



$$\Delta S = S_{T(K)} - S_{0(K)} = \int_0^T \frac{nCdT}{T}$$

- **For chemical reaction**

$$aA + bB \longrightarrow cC + dD$$

$$\Delta S^0_{system} = (\Sigma\, n_i S^0_m)_{product} - (\Sigma\, n_i S^0_m)_{reactant}$$

where S^0_m = standard molar entropy. It can calculated using third law of thermodynamics.

$$\Delta S_{surr} = \frac{-Q_{system}}{T} = \frac{-\Delta H_{system}}{T}$$

* For a perfactly crystline substance at 0 K, entropy = 0

- **For phase transformations**

$$\Delta S_{fusion} = \int \frac{dp}{T} = \frac{1}{T}\int dp = \frac{Q}{T}$$

for constant pressure $\Delta S_{fus.} = \frac{\Delta H_{fus}}{T}$

for constant volume $\Delta S_{fus.} = \frac{\Delta U_{fusion}}{T}$

$$\Delta S_{vap} = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{Q}{T}$$

for constant Pressure, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$

for constant Volume, $\Delta S_{vap} = \frac{\Delta U_{vap}}{T}$

- **Gibb's free energy (G) :**

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb's so that entropy calculation for the surrounding need not be carried out.

It is a free energy at constant pressure.

$G = H - TS$

$dG = dH - TdS - SdT$

& $H = U + PV$

$dH = dU + PdV + VdP \quad \Rightarrow \quad dG = dU + PdV + VdP - TdS - SdT$

From Ist law of thermodynamics

$dq = dU + PdV$

& from 2nd law, $dq = TdS$

$dG = dq + VdP - TdS - SdT$

$dG = -SdT + VdP$

At constant temperature,

$dG = VdP$

For ideal gas, $V = \frac{nRT}{P}$

$$dG_m = V_m dP = \frac{RT}{P}\, dP$$

$$\int_1^2 dG_m = RT\int_{P_1}^{P_2}\frac{dP}{P}$$

$$G_{m_2} - G_{m_1} = RT\ell n\frac{P_2}{P_1}$$

Where G_m is free energy for 1 mole

If G_{m_1} is free energy for 1 mole in standard state and G_{m_2} is free energy for one mole in any other state.

$$G_m - G°_m = RT\ln\frac{P}{1} \qquad \& \; G - G° = nRT\ell n\frac{P}{1}$$

For the reaction, $aA(g) + bB(g) \rightleftharpoons C(g) + dD(g)$

$(\Delta G)_{reaction} = (\Sigma\Delta G)_{product} - (\Sigma\Delta G)_{reactant}$

$(\Delta G)_{reaction} = G_C + G_D - G_A - G_B$

$$G_C - G°_C = cRT\ln\frac{P_C}{1} \quad \Rightarrow \quad G_C = G°_C + cRT\ln P_C$$

Similarly, $G_D = G°_D + dRT\ln P_D$; $G_A = G°_A + aRT\ln P_A$, $G_B = G°_B + bRT\ln P_B$

$(\Delta G)_{reaction} = (G°_C + cRT\ln P_C) + (G°_D + dRT\ln P_D) - (G°_A + aRT\ln P_A) - (G°_B + bRT\ln P_B)$

$$= (\Delta G)°_{reaction} + RT\ln\frac{P^c{}_C.P^d{}_D}{P^a{}_A.P^b{}_B}$$

$$\boxed{\Delta G_{reaction} = \Delta G°_{reaction} + RT\ln Q}$$

Gibb’s Helmholtz Equation :

$dG = VdP - SdT$

At constant Pressure

$$dG = -SdT \quad \Rightarrow \quad \left(\frac{dG}{dT}\right)_P = -S \; \& \; \left(\frac{\partial\Delta G}{\partial T}\right)_P = -\Delta S$$

$$\& \qquad G = H - TS \quad \Rightarrow \quad \frac{G-H}{T} = -S$$

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

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

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

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

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$

$$\Delta S_{surr} = \frac{-Q_{system}}{T} = \frac{-\Delta H_{system}}{T}$$

$T\Delta S_{univ} = T\Delta S_{system} - \Delta H_{system}$

Introducing a new thermodyamic function G = Gibb's free energy (State function and an extensive property)

$G_{system} = H_{system} - TS_{system}$

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

$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$ .... (ii)

Comparing equation (i) and (ii)

$\Delta G_{system} = - T\Delta S_{universe}$

New criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 ⇒ process is spontaneous
(ii) If ΔG_{system} is > 0 ⇒ process is non spontaneous
(iii) If $\Delta G_{system} = 0$ ⇒ system is at equilibrium

So, at every temparature $\Delta G \neq 0$

ΔH_{system}	ΔS_{system}	$\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$
+ Ve	– Ve	+
– Ve	+ Ve	–
+ Ve	+ Ve	– Ve at high temprature
– Ve	– Ve	+ Ve at high temprature

ΔG^o = standrad free energy change :

When the reactants under standrad conditions gets converted into products which is also under standared condition, then the free energy change is known as ΔG^o (it is a constant) for 1 mole at 1 bar.

At standared conditions :

$\Delta G° = \Delta H° - T\Delta S°$

= constant for a GIVEN REACTION

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

$\Delta G°$ = (Gbb's energy of product) – (Gibb's energy of reactant)

$\Delta G° = \gamma G^0_{m,C} + \delta G^0_{m,D} - \alpha G^0_{m,A} - \beta G^0_{m,B}$, where G^0_m can not be calculated as H^0_m cannot be calculated.

hence, we can convert this relation in to Gibb's energy of formation of substance.

$\Delta G° = \gamma \Delta G^0_{f,C} + \delta \Delta G^0_{f,D} - \alpha \Delta G^0_{f,A} - \beta \Delta G^0_{f,B}$

ΔG^0_f : standared Gibb's energy of formation.

ΔG^0_f (elements in their standard states) = 0

$\Delta G° = \Delta G^0_{f,product} - \Delta G^0_{f,reac\,tan\,ts}$

For a reaction in progress

$\Delta G = \Delta G^o + RT\,\ell n\,Q$

Q is reaction quotient , $\Delta G > 0$ backward is feasible , $\Delta G < 0$ forward is feasible

At equilibrium $\Delta G = 0$ $\quad \therefore Q = K \quad \therefore \Delta G^o = - RT\,\ell n\,K$ at equilibrium

SOLVED EXAMPLE

Ex-2. K_a for CH_3COOH at 25ºC is 1.754×10^{-5} . At 50ºC, K_a is 1.633×10^{-5} What are ΔHº and ΔSº for the ionisation of CH_3COOH?

Sol. $(\Delta G^o)_{298} = -2.303RT \log K = -2.303 \times 8.314 \times 298 \times \log (1.754 \times 10^{-5}) = 27194$ J.

$(\Delta G^o)_{323} = 2.303 \times 8.314 \times 323 \times \log(1.633 \times 10^{-5}) = 29605$ J.

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

$27194 = \Delta H^o - 298\ \Delta S^o$

$29605 = \Delta H^o - 323\ \Delta S^o$

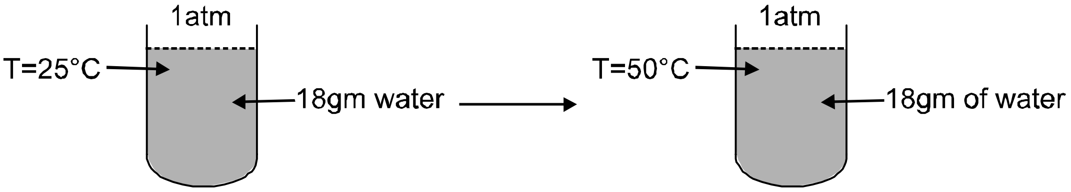
$\therefore \quad \Delta H^o = -1.55$ kJ/mol

$\Delta S^o = -96.44$ J/mol.K

Thermochemistry

❍ Enthalpy of a substance :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- H_m(substance) : For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as H_m (H_2O, g, 398 K, 1 atm). In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance. Standard state of any substance means.
  - ❍ For a **GAS** standard state means ideal gas at 1 bar partial pressure at any give temperature.
  - ❍ For a **LIQUID** – pure liquid at one bar pressure at 1 bar pressure at any given temperature.
  - ❍ For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at 1 bar pressure and at any given temperature
  - ❍ For any **SUBSTANCE or ION IN SOLUTION** – the species should be in unit molality (can also be taken as 1M concentration), at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at 398 K will be represented as $H°(H_2O$, g , 398 K) and molar standard enthalpy of liquid water at 398 K will be represented as $H_m°$ (H_2O, l, 398 K)
  (It is hypothetical but can be calculated).
- We cannot exactly calculate enthalpy content of a substance only the change in enthalpy can be calculated when substance is taken from one state to other.
  For example :



Let enthalpy content initially be $H^0_{m,1}$ & finally enthalpy content be $H^0_{m,2}$

Then, $\Delta H° = H^0_{m,2} - H^0_{m,1}$

= heat added at constant pressure to change temperature from 25°C to 50°C.

$= C_P\Delta T = (18 \text{ cal/mole °C}) (25°C) = 450$ cal

SOLVED EXAMPLE

Ex-3. Why does heat get released/absorbed during chemical reactions?

Sol. Because the reactants have a fixed enthalpy content before the reaction and when these are converted into the products which have a different enthalpy content. So, heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies $\Delta E \neq 0$.

If $H_{products} > H_{reactants}$

Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

and if $H_{products} < H_{reactants}$

Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction : $\boxed{\Delta H_{reaction} = H_{products} - H_{reactants}}$

$\Delta H°_{reactions} = H°_{products} - H°_{reactants}$

= positive – endothermic

= negative – exothermic

❍ Enthalpy of formation :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built.

- "The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value".The specified temperature is usually taken as 25°C.

A few exmaples are $\Delta H_f° (O_2, g) = 0$

$\Delta H_f°$ (C, graphite) = 0 $\Delta H_f°$ (C, diamond) $\neq 0$

$\Delta H_f° (Br_2$, liquid) = 0

$\Delta H_f°$ (S, rhombic) = 0 $\Delta H_f°$ (S, monoclinic) $\neq 0$

$\Delta H_f°$ (P, white) = 0 $\Delta H_f°$ (P, black) $\neq 0$

- "The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation". The chemical equations corresponding to enthalpy of formation of few substances are given below.

Enthalpy of formation of HBr(g) : $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(\ell) \rightarrow HBr(g)$

$$\Delta H_f°(HBr, g) = H_m^0(HBr, g) - \frac{1}{2}H_m^0(H_2, g) - \frac{1}{2}H_m^0(Br_2, \ell) \quad ...(1)$$

Enthalpy of formation of SO_2(g) : $S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g)$

$$\Delta H_f°(SO_2, g) = H_m^0(SO_2, g) - H_m^0(S, \text{rhombic}) - H_m^0(O_2, g) \quad ...(2)$$

But above equations cannot be for calculation of enthalpy of reaction as the molar enthalpies of different species can not be exactly known.

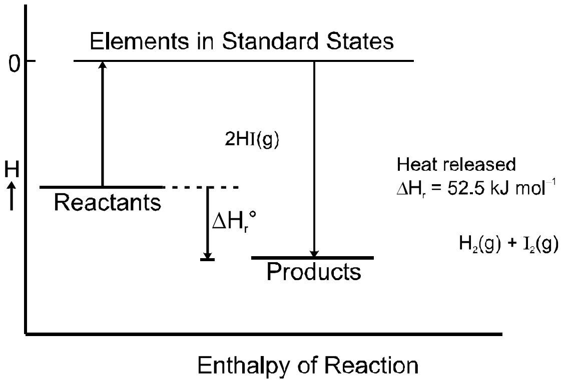
❍ Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r° = \Sigma \nu_B \Delta H_f°{}_{,products} - \Sigma \nu_B \Delta H_f°{}_{,reactants}$$

ν_B is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



Enthalpy of Reaction

SOLVED EXAMPLE

Ex-4. Calculate the standard enthalpy of reaction $ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$.
Given, ΔH_f° (ZnO, s) = – 350 KJ/mole, ΔH_f° (CO_2, g) = – 390 KJ/mole, ΔH_f° (CO, g) = – 110 KJ/mole.

Sol. $\Delta H^\circ = \{\Delta H_f^\circ(CO_2, g) - (\Delta H_f^\circ(ZnO, s) + \Delta H_f^\circ(CO, g))\}$

$\Delta H^\circ_{reaction} = -390 - (-350 - 110) = 70$ KJ

❍ Hess's Law of constant heat summation :

- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.
- Since $\Delta_r H$ stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products are written on the left hand side and reactants on the right hand side), then the numerical value of $\Delta_r H$ remains the same, but **its sign changes.**
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value $\Delta_r H$ for the reaction

$$C(graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

which is difficult to determine experimentally, can be estimated from the following two reactions for which $\Delta_r H$ can be determined experimentally.

$$C(graphite) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r H_1$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r H_2$$

Substracting the latter from the former, we get

$$C(graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

Consequently, $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

SOLVED EXAMPLE

Ex-5. Calculate heat of the following reaction at constant pressure,

$$F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$$

The heats of formation of F_2O (g), H_2O(g) and HF (g) are 5.5 kcal, –57kcal and –64 kcal respectively.

Sol. Given that

(i) $F_2(g) + \frac{1}{2}O_2(g) \rightarrow F_2O(g)$; $\Delta H = 5.5$ kcal

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H = -57$ kcal

(iii) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$; $\Delta H = -64$ kcal

F_2O and H_2O in eqns. (i) and (ii) and in the eqn. given in the problem are on the opposite sides, while HF in eqn. (iii) and in the eqn. given in the problem is on the same sides.

Thus applying, [– Eqn. (i) –Eqn. (ii) + 2 × Eqn. (iii)], we get

$$-F_2(g) - \frac{1}{2}O_2(g) - H_2(g) - \frac{1}{2}O_2(g) + H_2 + F_2(g) \rightarrow -F_2O(g) - H_2O(g) + 2HF(g);$$

$\Delta H = -5.5 - (-57) + 2 \times (-64)$

or $F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$; $\Delta H = -76.5$ kcal.

❍ Relation between energy and enthalpy of a reaction :

$$\mathbf{\Delta_r H = \Delta_r U + (\Delta v_g)RT}$$

where Δv_g is the change in the stoichiocmetric number of gaseous species in going from reactants to products. It should be noted that while computing Δv_g of a reaction, only the stoichiometric numbers of gaseous is counted and those of liquids and solids are completely ignored.

Kirchoff's equation (Variation of ΔH^o with temprature)

Since the enthalpy (or standard enthalpy) of a substance is dependent on state of the substance, value of enthalpy of a substance changes with temperature and hence the enthalpy change of reaction is also dependent on temperaturte at which the reaction is being carried out. This change is enthalpy change (or ΔE, of reaction is carried out at constant volume) is represented by **Kirchoff's Equations.**

$$\alpha P + \beta Q \longrightarrow \gamma R + \delta S$$

at temperature T_1 let the standard enthalpy of reaction be $\Delta H°_1$, then

$$\Delta H_1° = \gamma H°_m (R,T_1) + \delta H°_m (S, T_1) - \alpha H°_m (P, T_1) - \beta H°_m (Q, T_1)$$

If the same reaction is carried out at temperature T_2, then

$$\Delta H_2° = \gamma H°_m (R,T_2) + \delta H°_m (S, T_2) - \alpha H°_m (P, T_2) - \beta H°_m (Q, T_2)$$

Then, the change in enthalpy (or difference in enthalpy at these two temperatures)

$$\Delta H° = \Delta H_2° - \Delta H_1° = \gamma \{H_m° (R,T_2) - H_m° (R,T_1)\} + \{H_m° (\delta,T_2) - H_m° (\delta,T_1)\}$$
$$- \alpha \{H_m° (P,T_2) - H_m° (P,T_1)\} - \beta \{H_m° (Q,T_2) - H_m° (Q,T_1)\}$$

$H_m° (R, T_2) - H_m° (R,T_1) = C_{P,R} (T_2 - T_1)$ = Heat required at constant pressure to increase temperature of one mole of R from T_1 to T_2

Similarly

$$H_m° (S,T_2) - H_m° (S,T_1) = C_{P,S} (T_2 - T_1)$$
$$H_m° (P,T_2) - H_m° (P,T_1) = C_{P,P} (T_2 - T_1) \text{ and}$$
$$H_m° (Q,T_2) - H_m° (Q,T_1) = C_{P,Q} (T_2 - T_1)$$

so $\Delta H° = \Delta H_2° - \Delta H_1° = \gamma\, C_{P,R} (T_2 - T_1) + \delta C_{P,S}(T_2 - T_1) - \alpha\, C_{P,P} (T_2 - T_1) - \beta C_{P,Q}(T_2 - T_1)$

$$= [\gamma\, C_{P,R} + \delta C_{P,S} - \alpha\, C_{P,P} - \beta C_{P,Q}] (T_2 - T_1) = \Delta C_P (T_2 - T_1)$$

$$\Delta C_P = \gamma C_{P,R} + \delta C_{P,S} - \alpha C_{P,P} - \beta C_{P,Q}$$

= Difference in molar heat capacities of products and reactants.

so $\Delta H_2° = \Delta H_1° + \int \Delta C_P.dT$

For example for the reaction

$$N_2 (g) + 3H_2 (g) \longrightarrow 2NH_3 (g)$$
$$\Delta H_2° = \Delta H_1° + \Delta C_P (T_2 - T_1)$$

where $\Delta C_P = 2C_{P,NH_3} - C_{P,N_2} - 3C_{P,H_2}$

* for a constant volume reaction, $\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V .dT$

❍ Enthalpy of Combustion :

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

  For example, the standard enthalpy of combustion of methane at 298 K is – 890 kJ mol^{-1}. This implies the following reaction :

  $$CH_4 (g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O (\ell) \qquad \Delta H° = -890 \text{ kJ mol}^{-1}$$

  The standard enthalpy of combustion of methane at 298 K may be written as

  $$\Delta H_c° (CH_4, g, 298 K) = -890 \text{ kJ mol}^{-1}$$

- The data on the enthalpy of combustion can be determined experimentally.
- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of $CH_4(g)$:

  $$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$$

  First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane. Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :

  $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$

  $$\Delta H_C°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O , \ell) - \Delta H_f° (CH_4, g)$$

  therefore $$\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O , \ell) - \Delta H_C° (CH_4, g)$$

- The enthalpies of formation of CO_2 and H_2O can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the mesured value of $\Delta H_C°(CH_4, g)$, the enthalpy of formation of CH_4 can be calculated. The value is

  $$\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\ \Delta H_f°(H_2O , \ell) - \Delta H_C° (CH_4, g)$$

  $$= [-393 + 2(-285) - (-890)]\ kJ\ mol^{-1} = -73\ kJ\ mol^{-1}$$

  or, equivalently, we may add the following three chemical equations.

  $$C(graphite) + O_2 (g) \longrightarrow CO_2 (g) \qquad \Delta_C H° = -393\ kJ\ mol^{-1}$$

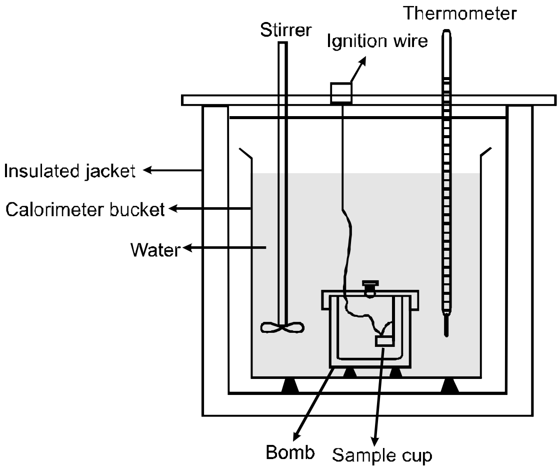
  $$2\ [H_2(g) + \frac{1}{2} O_2 (g) \longrightarrow H_2O(\ell)] \qquad \Delta_r H° = 2(-285)\ kJ\ mol^{-1}$$

  $$-[CH_4(g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2H_2O(\ell)] \qquad \Delta_r H° = -(-890)\ kJ\ mol^{-1}$$

  $$C(graphite) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta_f H° = -73\ kJ\ mol^{-1}$$

❍ Measurement of Enthalpy of Combustion :

Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure. The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container, as shown in figure. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.



Bomb calorimeter to determine enthalpy of combustion

If total heat capacity of calorimeter and all of its contents = C, rise in temperature = ΔT
then heat released = $q = C\Delta T$ of this heat is because of mass m of substance then :

due to 1 mole, heat released = $\left(\frac{M}{m}\right) q = \Delta E_C°$

(constant volume reaction).

Now, $\Delta H_C°$ can be calculated by using $\Delta H_C° = \Delta E_C° + \Delta n_g RT$.

Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.

SOLVED EXAMPLE

Ex-6. A gas mixture of 4 litres of ethylene and methane on complete combustion at 25ºC produces 6 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1464 and –976 kJ mol^{-1} at 25ºC. **[IIT 1991]**

Sol.

$$\overbrace{C_2H_4 \quad + \quad CH_4}^{4\ \text{lit.}} + O_2 \rightarrow CO_2 + H_2O$$

x lit. (4 – x)lit. 6 lit.
(say)

or x moles (4 – x) moles 6 moles

Applying POAC for C atoms,

$$2 \times x + 1 \times (4 - x) = 1 \times 6 \ ; \ x = 2 \text{ lit.}$$

Thus, the volume of C_2H_4 = 2 lit., and volume of CH_2 = 2 lit.

$\therefore$ volume of C_2H_4 in a 1 litre mixture = 2/4 = 0.5 lit.

and volume of CH_4 in a 1 litre mixture = 1 –0.5 = 0.5 lit.

Now, thermochemical reactions for C_2H_4 and CH_4 are

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O; \Delta H = -1464 \text{ kJ}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H = -976 \text{ kJ}$$

As ΔH values given are at 25ºC, let us first calculate the volume occupied by one mole of any gas at 25ºC (supposing pressure as 1atm)

Volume per mole at 25ºC = $\frac{298}{273} \times 22.4 = 24.4$ lit.

Thus, heat evolved in the combustion of 0.5 lit. of $C_2H_4 = -\frac{1464}{24.4} \times 0.5 = -30$ kJ

and heat evolved in the combustion of 0.5 lit.of $CH_4 = \frac{976}{24.4} \times 0.5 = -20$ kJ.

$\therefore$ total heat evolved in the combustion of 1 litre of the mixture = –30 + (– 20) = – 50 kJ.

❍ Integral enthalpy of solution

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved ; Thus

$$HCl(g) + 10H_2O(\ell) \longrightarrow HCl\ (10H_2O) \qquad \Delta H_1 = -69.5 \text{ kJ mol}^{-1}$$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are

(i) $HCl(g) + 25\,H_2O(\ell) \longrightarrow HCl\ (25H_2O) \qquad \Delta H_2 = -72.3 \text{ kJ mol}^{-1}$

(ii) $HCl(g) + 40\,H_2O(\ell) \longrightarrow HCl\ (40H_2O) \qquad \Delta H_3 = -73.0 \text{ kJ mol}^{-1}$

(iii) $HCl(g) + 200\,H_2O(\ell) \longrightarrow HCl\ (200H_2O) \qquad \Delta H_4 = -74.2 \text{ kJ mol}^{-1}$

(iv) $HCl(g) + aq \longrightarrow HCl\ (aq) \qquad \Delta H_5 = -75.0 \text{ kJ mol}^{-1}$

Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).

❍ Enthalpy of Hydration :

Enthalpy of hydration is used in following two ways.

- Enthalpy of hydration of anhydrous or partially hydrated salts :

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by

$CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4.5\,H_2O(s)$

There is a almost invariably a liberation of heat in such reactions, i.e. the value of ΔH is negative.

$CuSO_4(s) + 800\,H_2O(\ell) \rightarrow CuSO_4\,(800\,H_2O)$ $\Delta H_r° = -\,68$ kJ mol^{-1}

$CuSO_4.5H_2O(s) + 795\,H_2O(\ell) \rightarrow CuSO_4\,(800\,H_2O)$ $\Delta H_r° = +\,10$ kJ mol^{-1}

by subtraction, we get

$CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4.5\,H_2O(s)$ $\Delta H_r° = -\,78$ kJ mol^{-1}

- Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqeous ion.

By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.

Enthalpy of hydration of Cl^- gaseous ions will be represented by :

$Cl^-(g) + aq. \longrightarrow Cl^-(aq)$ $\Delta H_r° = \Delta H_f°\,(Cl^-, aq)$

❍ Enthalpy of Neutralization :

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$ $\Delta H = -57.1$ kJ/mole $= -13.7$ kcal/mol

Remember :

- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to –13.7 kcal/mole or –57.1 kJ/mole.
- For any other combination of **acid and base** this heat is less than –13.7 kcal/mole or –57.1 kJ/mole.

❍ Enthalpy of Ionization :

- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.1 kJ mol^{-1}.
- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing there acids and bases this heat is known as enthalpy of ionization. Examples are :

$HCN + Na^+OH^- \rightarrow Na^+ + CN^- + H_2O$ $\Delta_r H° = -\,12$ kJ mol^{-1}

$CH_3COOH + Na^+OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$ $\Delta_r H° = -\,49$ kJ mol^{-1}

The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,

Ionization $HCN \longrightarrow H^+ + CN^-$ $\Delta H°_1 = x$

Neutralization $H^+ + OH^- \longrightarrow H_2O$ $\Delta H°_2 = -\,57.1$ kJ/mole

The complete reaction is obtained by adding the above two steps. Thus

$HCN + OH^- \longrightarrow H_2O + CN^-$ $\Delta H° = -\,12$ kJ/mole

Obviously, $\Delta H° = \Delta H°_1 + \Delta H°_2$

$\Delta H°_1 = \Delta H° - \Delta H°_2 = [-12 - (-57.1)] = 45.1$ kJ/mole

- **Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.**

SOLVED EXAMPLE

Ex-7. Enthalpy of neutralization of HCl by NaOH is –57.1 kJ/mol and by NH_4OH is –51.1 kJ/mol. Calculate the enthalpy of dissociation of NH_4OH.

Sol. Given that, $H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(\ell)$ $\Delta H = -51.1$ kJ/mole

We may consider neutralization in two steps.

(i) Ionization $NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$ $\Delta H_1 = ?$

(ii) Neutralization $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$ $\Delta H_2 = -57.1$ kJ/mole

Thus, $\Delta H = \Delta H_1 + \Delta H_2$

Therefore, $\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1} = 6.0$ kJ/mol

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Enthalpy of Transition :

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.

For example : $C(graphite) \rightarrow C(diamond)$ $\Delta H_{trs}^0 = 1.90 \text{ kJ mol}^{-1}$

so if $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_C^0 = -393.51 \text{ kJ mol}^{-1}$

and $C(diamond) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_C^0 = -395.41 \text{ kJ mol}^{-1}$

Subtracting, we have, $C(graphite) \rightarrow C(diamond)$ $\Delta H_{trs}^0 = 1.90 \text{ kJ mol}^{-1}$

Enthalpy of Precipitation :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.

For example : $BaCl_2(aq.) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$ $\Delta_r H^0 = -24.27 \text{ kJ mol}^{-1}$

SOLVED EXAMPLE

Ex-8. Calculate $\Delta H°$ for the reaction, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ at 25°C.

Given $\Delta_f H°(Ag^+, aq) = 105 \text{ kJ mol}^{-1}$, $\Delta_f H°(Cl^-, aq) = -167 \text{ kJ mol}^{-1}$ and $\Delta_f H°(AgCl, s) = -127 \text{ kJ mol}^{-1}$

Sol. For the reaction $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

we have $\Delta H° = \Delta_f H° (AgCl, s) - \Delta_f H°(Ag^+, aq) - \Delta_f H°(Cl^-, aq)$

$= [-127 - 105 - (-167)] \text{ kJ mol}^{-1} = -65 \text{ kJ mol}^{-1}$

❍ Enthalpy of Formation of ions :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as.

$\frac{1}{2} Cl_2(g) + aq \longrightarrow Cl^-(aq)$ $\Delta H_r° = \Delta H_f° (Cl^-, aq)$

By convention, the standard enthlpy of formation of H^+(aq) is taken to be zero.

We have seen that $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ $\Delta_r H^0 = -57.1 \text{ kJ mol}^{-1}$

For this reaction, $\Delta H_r^0 = \Delta H_f^0(H_2O, \ell) - \{\Delta H_f^0(H^+, aq) + \Delta H_f^0(OH^-, aq)\}$

Hence, at 25ºC, we get $\Delta H_f^0 (H^+, aq) + \Delta H_f^0(OH^-, aq) = \Delta H_f^0(H_2O, \ell) - \Delta H_r^0$

so $\Delta H_f^0(OH^-, aq) = \{-286.1 - (-57.1)\} \text{ kJ mol}^{-1} = -229.00 \text{ kJ mol}^{-1}$

- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with H^+ or OH^-. for example, the enthalpy of formation of Na^+ can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of NaOH. The two values are :
- The chemical equation for the formation of infinite dilute solution of NaOH(s) is

$NaOH(s) + nH_2O(\ell) \longrightarrow Na^+(aq) + OH^-(aq)$ $\Delta_{aq}H°(NaOH, s) = -44.50 \text{ kJ mol}^{-1}$

Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$\Delta_{aq}H°(NaOH, s) = \Delta_f H°(Na^+, aq) + \Delta_f H°(OH^-, aq) - \Delta_f H°(NaOH, s)$

or $\Delta_f H° (Na+, aq) = \Delta_{aq} H° (NaOH, s) - \Delta_f H°(OH°, aq) + \Delta_f H°(NaOH, s)$

$= [-44.50 - (-229.99) + (-425.61)] \text{ kJ mol}^{-1} = -240.12 \text{ kJ mol}^{-1}$

- Similarly, from NaCl(aq) or HCl(aq), the enthalpy of formation of Cl^-(aq) can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.

SOLVED EXAMPLE

Ex-9. The enthalpy of formation of $H_2O(l)$ is –285 kJ mol^{-1} and enthalpy of neutralization of a strong acid and a strong base is –55 kJ mol^{-1}. What is the enthalpy of formation of OH^- ions ?

Sol. Given that, $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$

$\Delta_f H$ 0 –285 kJ mol^{-1}

$\Delta_{neut}H = \Delta_f H(H_2O, \ell) - \Delta_f H(OH^-, aq)$

Hence $\Delta_f H\ (OH^-, aq) = \Delta_f H(H_2O, \ell) - \Delta_{neut}H$

$= [-285 - (-55)]$ kJ mol^{-1} = –230 kJ mol^{-1}

Ex-10. Calculate the enthalpy change when one mole of HCl(g) is dissolved in a very large amount of water at 25°C. The change in state is : $HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

Given : $\Delta_f H\ (HCl, g) = -92$ kJ mol^{-1} and $\Delta_f H°\ (Cl^-, aq) = -167$ kJ mol^{-1}

Sol. For the reaction, $HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

we have $\Delta H° = \Delta_f H°(Cl^-, aq) - \Delta_f H°(HCl, g)$

$\Delta H° = [-167 - (-92)]$ kJ mol^{-1} = – 75 kJ mol^{-1}

❍ Bond Enthalpies :

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound.for example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.

$H_2O(g) \to H(g) + OH(g)$ $\Delta H_r^0 = 501.87$ kJ mol^{-1}

However, to break the O–H bond in the hydroxyl radical required a different quantity of heat :

$OH(g) \to O(g) + H(g)$ $\Delta H_r^0 = 423.38$ kJ mol^{-1}

The bond enthalpy, ΔH_{OH}, is defined as the average of these two values, that is :

$$\Delta H_{OH} = \frac{501.87 mol^{-1} + 423.38 kJmol^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

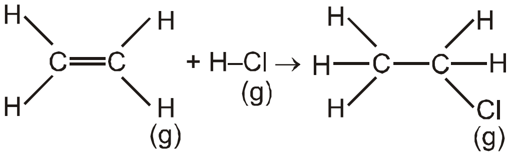
In the case of diatomic molecules, such as H_2, the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.

$H_2(g) \to 2H(g)$ $\Delta H_{H-H} = \Delta H_r^0 = 435.93$ kJ mol^{-1}

Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthaplies of the bond for a number of molecules in which the pair of atoms appears.

❍ Estimation of Enthalpy of a reaction from bond Enthalpies :

Let the enthalpy change for the gaseous reaction



be required from the bond enthalpy data. This may be calculated as follows :

$$\Delta H = \begin{pmatrix}\text{Enthalpy required to break reactants} \\ \text{into gasesous atoms}\end{pmatrix} - \begin{pmatrix}\text{Enthalpy released to form products} \\ \text{from the gasesous atoms}\end{pmatrix}$$

$= [4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-Cl}]_R + [-5\Delta H_{C-H} - \Delta H_{C-C} - \Delta H_{C-Cl}]_P$

$= (\Delta H_{C=C} + \Delta H_{H-Cl}) - (\Delta H_{C-H} + \Delta H_{C-C} + \Delta H_{C-Cl})$

SOLVED EXAMPLE

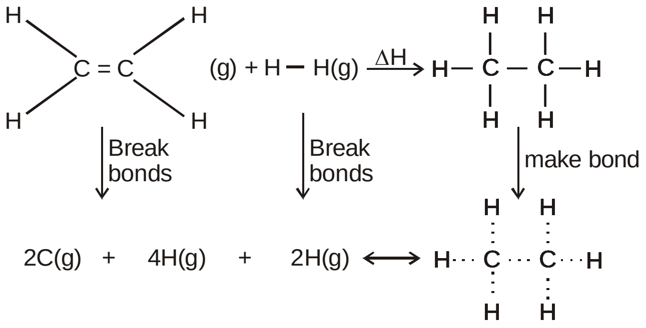
Ex-11. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

Data :

Bond	Bond enthalpy
C – C	336 kJ mol^{-1}
C = C	606 kJ mol^{-1}
C – H	410 kJ mol^{-1}
H – H	431 kJ mol^{-1}

Sol. Diagrammatically, we represent the given reaction as follows :



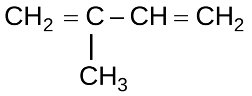
$\Delta H_r = (4\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-H}) - (6\Delta H_{C-H} + \Delta H_{C-C})$

$= (4 \times 410 + 606 + 431) - (6 \times 410 + 336)$

$= 2677 - 2796$

$= -119$ kJ/mol.

Ex-12. Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



$CH_2 = C(CH_3) - CH = CH_2$

Data Bond enthalpy of C – H bond = 413.38 kJ mol^{-1}

Bond enthalpy of C – C bond = 347.69 kJ mol^{-1}

Bond enthalpy of C = C bond = 615.05 kJ mol^{-1}

Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol^{-1}

Enthalpy of dissociation of $H_2(g)$ = 435.97 kJ mol^{-1}

Sol. For isoprene, we have to form

2C – C bonds ; 2C = C bonds and 8C – H bonds

Method-1 For which energy released is

$[2(+347.69) + 2(+615.05) + 8(+413.38)]$ kJ mol^{-1} = 5 232.52 kJ mol^{-1}

that is, ΔH (from gaseous atoms) = + 5232.52 kJ mol^{-1}

The reaction corresponding to this is

$5C(g) + 8H(g) \rightarrow C_5H_8(g)$ $\Delta_f H_1 = -5232.52$ kJ mol^{-1}

But we want $\Delta_f H$ corresponding to the following equation

$5C(graphite) + 4H_2(g) \rightarrow C_5H_8(g)$ $\Delta_f H = ?$

This can be obtained by the following manipulations :

$5C(g) + 8H(g) \rightarrow C_5H_8(g)$ $\quad \Delta_rH_2 = -5232.52$ kJ mol^{-1}

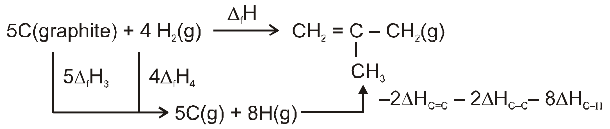
$5C(\text{graphite}) \rightarrow 5C(g)$ $\quad \Delta_rH_3 = 5 \times 718.39$ kJ mol^{-1}

$4H_2(g) \rightarrow 8H(g)$ $\quad \Delta_rH_4 = 4 \times 435.97$ kJ mol^{-1}

Adding, we get

$5C(\text{graphite}) + 4H_2(g) \rightarrow C_5H_8(g)$ $\quad \Delta_fH = 103.31$ kJ mol^{-1}

Method-2 Diagrammatically, the above calculations may be represented as follows.



Applying Hess's law, we get

$\Delta_fH = 5\Delta H_3 + 4\Delta H_4 - 2\Delta H_{C=C} - 2\Delta H_{C-C} - 8\Delta H_{C-H}$

$= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38)$ kJ mol^{-1}

$\Delta_fH = 103.31$ kJ mol^{-1}

Ex-13. Find the bond enthalpy of S – S bond from the following data :

$C_2H_5-S-C_2H_5(g)$ $\quad \Delta_fH° = -147$ kJ mol^{-1}

$C_2H_5-S-S-C_2H_5(g)$ $\quad \Delta_fH° = -201$ kJ mol^{-1}

$S(g)$ $\quad \Delta_fH° = 222$ kJ mol^{-1}

Sol. Given that

Method-1 (i) $4C(s) + 5H_2(g) + S(s) \longrightarrow C_2H_5-S-C_2H_5(g)$ $\quad \Delta_fH° = -147$ kJ mol^{-1}

(ii) $4C(s) + 5H_2(g) + 2S(s) \longrightarrow C_2H_5-S-S-C_2H_5(g)$ $\quad \Delta_fH° = -201$ kJ mol^{-1}

Subtracting Eq. (i) from Eq. (ii), we get

$C_2H_5-S-C_2H_5(g) + S(s) \longrightarrow C_2H_5-S-S-C_2H_5(g)$ $\quad \Delta_rH° = -54$ kJ mol^{-1}

Adding to this, the following equation

$S(g) \longrightarrow S(s)$ $\quad \Delta_fH° = -222$ kJ mol^{-1}

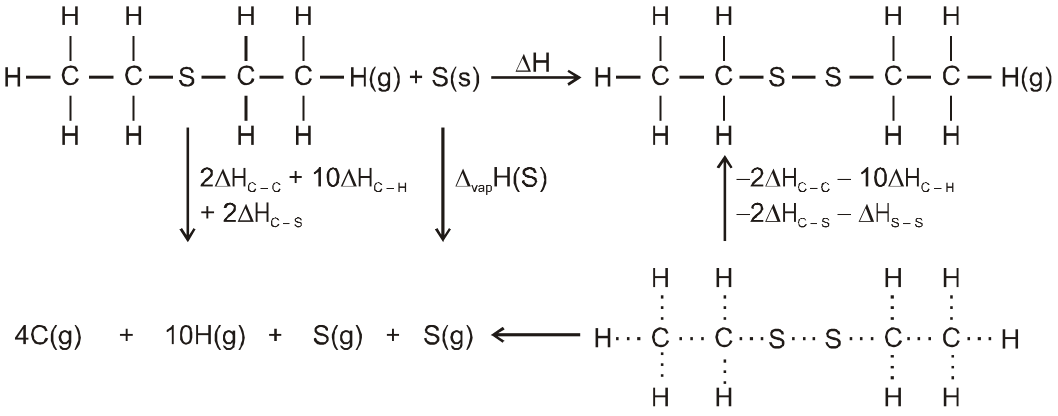
We get

$C_2H_5-S-C_2H_5(g) + S(g) \longrightarrow C_2H_5-S-S-C_2H_5(g)$ $\quad \Delta_rH° = -276$ kJ mol^{-1}

In the last equation 276 kJ of heat evolved because of the S–S bond formation.

Hence, the bond enthalpy of S – S is 276 kJ mol^{-1}.

Method-2 Diagrammatically, we may represent the above calculation as follows :



According to Hess's law

$\Delta_r H^\circ$ = Enthalpy involved in bond breaking Δ_{vap} H°(s) – Enthalpy involved in bond making

$\Delta_r H^\circ = [2\Delta H_{C-C} + 10\Delta H_{C-H} + 2\Delta H_{C-S} + \Delta_{vap} H(S)] + [-2\Delta H_{C-C} - 10\Delta H_{C-H} - 2\Delta H_{C-S} - \Delta H_{S-S}]$

$= \Delta_{vap} H^\circ(S) - \Delta H_{S-S}$

or $\Delta H_{S-S} = \Delta_{vap} H^\circ(S) - \Delta H^\circ$

$= \Delta_{vap} H^\circ(S) - [\Delta_f H^\circ(C_2H_5 - S - S - C_2H_5] - \Delta_f H^\circ(C_2H_5 - S - C_2H_5)]$

$= [222 - \{-201 - (-174)\}]\ \text{kJ mol}^{-1} = 276\ \text{kJ mol}^{-1}$

❍ Resonance Energy :

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$\Delta H^\circ_{resonance} = \Delta H^\circ_{f,\ experimental} - \Delta H^\circ_{f,\ calclulated}$

$= \Delta H^\circ_{combustion,\ calclulated} - \Delta H^\circ_{combustion,\ experimental}$

SOLVED EXAMPLE

Ex-14. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

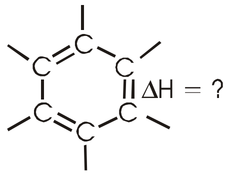
C – C = 83 kcal, C = C = 140 kcal, C – H = 99 kcal

Heat of atomisation of C = 170 .9 kcal

Heat of atomisation of H = 52.1 kcal

Sol. We have to calculate ΔH for the reaction

$6C\ (s) + 3H_2(g) \rightarrow C_6H_6\ (g)$



For reactants :

Heat of atomisation of 6 moles of C = 6 ×170.9 kcal

heat of atomisation of 6 moles of H = 6 × 52.1 kcal

For products :

Heat of formation of 6 moles of C – H bonds = – 6 × 99

Heat of formation of 3 moles of C–C = – 3 × 83

Heat of formation of 3 moles of C = C bonds = –3 × 140

on adding, we get heat of formation of C_6H_6, i.e.,

$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75$ kcal

MISCELLANEOUS SOLVED EXAMPLES

1. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.

(i) 18 g of graphite on complete combustion evolve 590 KJ heat

(ii) 15889 KJ heat is required to dissociate all the molecules of 1 litre water into H_2 and O_2.

(iii) The heat of formation of liquid benzene is 50 kJ/mol

(iv) Density of C_6H_6 (ℓ) = 0.87 g/mℓ

Sol. (i) $C(s) + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta H_f^\circ = -393.33$ KJ/mol

(ii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O\ (\ell)\ ;\ \Delta H_f^\circ = -286$ KJ/mol

(iii) $C_6H_6(\ell) + \frac{15}{2} O_2(g) \rightarrow 6CO_2\ (g) + 3H_2O\ (\ell)$

∴ $\Delta H^\circ = [6(-393.33) + 3\ (-286)] - 50 = -3268$ KJ/mole

∴ **Heat evolved from 87 g benzene = 3645 KJ** **Ans.** 3645 KJ

2. For the equations C(diamond) + $2H_2(g) \rightarrow CH_4(g)$ ΔH_1 ; $C(g) + 4H(g) \rightarrow CH_4(g)$ ΔH_2

Predict whether

(A) $\Delta H_1 = \Delta H_2$ (B) $\Delta H_1 > \Delta H_2$

(C) $\Delta H_1 < \Delta H_2$ (D) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

Ans. **(B)**

3. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25° C are -156 and + 49 KJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

= ΔH_F () – Δ H_f ()

= –156 – (+ 49) kJ = –205 kJ.

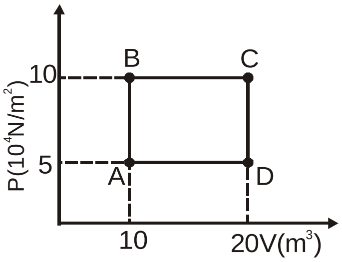
Given that,  + $H_2 \longrightarrow$  ΔH = 119 kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

= 3 × (–119) kJ = – 357 kJ.

$\therefore$ resonance energy of benzene = – 357 – (–205) kJ = –152 kJ mole^{-1} **Ans.** –152 kJ mole^{-1}

4. A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC. Then the temperature of the states A and B are (Given R = 8.3 joules/mol K) :



(A) T_A = 120.5 K, T_B = 120. 5K (B) T_A = 241 K, T_B = 241 K

(C) T_A = 120.5 K, T_B = 241 K (D) T_A = 241 K, T_B = 482 K

Sol. $$\frac{0.5\times10^5}{1.01\times10^5} \times 10 \times 10^3 = \frac{2\times1000}{2} \times 0.082\ T_A$$

$$\frac{1}{1.01} = 0.082\ T_A$$

T_A = 120.5 K

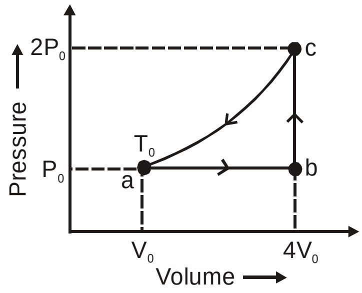
at constant volume

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$$T_B = \frac{P_B . T_A}{P_A} = \frac{10}{5} \times 120.5 = 241 \text{ K.}$$

Ans. **(C)**

5. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then, the change in the internal energy in expanding the gas from a to c along the path abc is :



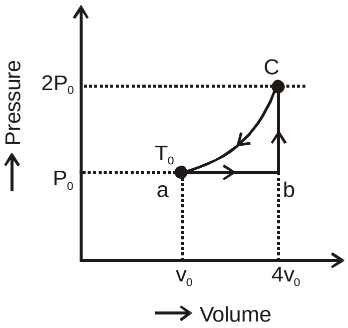
(A) 3 P_0V_0 (B) 6 RT_0

(C) 4.5 RT_0 (D) 10.5 RT_0

Sol. Pv = nRT at point C

$2P_0 \times 4v_0 = 1 \times RT_C$

$T_C = \left[\frac{8P_0V_0}{R}\right]$



at point a

$P_0V_0 = 1 \times RT_0$

$T_0 = \frac{P_0V_0}{R}$; $T_C = 8\,T_0$

Change in internal energy = $[nC_VdT]$

For path a to b = $1 \times \frac{3}{2} R \times [3T_0] = \frac{9}{2} RT_0$

For path b to c = $1 \times \frac{3}{2} R \times [4T_0] = 6T_0 R$

Total change = $\frac{9}{2} RT_0 + 6RT_0 = \frac{21RT_0}{2} = 10.5\, RT_0$.

So total change in internal energy

$\Delta U = 10.5\, RT_0$ **Ans. (D)**

6. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Then the enthalpy change during the process is (1L atm $\simeq$ 100 J)

(A) $\Delta H = 15$ kJ (B) $\Delta H = 15.7$ kJ

(C) $\Delta H = 14.4$ kJ (D) $\Delta H = 14.7$ kJ

Sol. $\Delta H = \Delta E + \Delta(PV)$ & $\Delta E = q + W = (50 \times 300 - 3 \times 100)$ J [as $T_f = 2 \times 300$ K = 600 K] = 14.7 kJ

$\Delta H = 14700 + 10 \times 100 = 15700$ J = 15.7 kJ. **Ans (B)**

7. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is : [R = 0.082 L atm mol^{-1} K^{-1} = 8.3 J mol^{-1}K^{-1}].

(A) 0 (B) $R\ell n\,(24.6)$ (C) $R\,\ell n\,(2490)$ (D) $3/2\, R\ell n\,(24.6)$

Sol. $\Delta S = nR\,\ell n\left(\frac{V_f}{V_i}\right) = R\ell n\left(\frac{P_i}{P_f}\right)$

$= R\,\ell n\left(\frac{300R}{1\,L \times 1\,atm}\right) = R\ell n\,(24.6)$ **Ans. (B)**

8. For a perfectly crystalline solid $C_{p.m.} = aT^3$, where a is constant. If $C_{p.m.}$ is 0.42 J/K–mol at 10 K, molar entropy at 10 K is :

(A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero

Sol. $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$

$S_m = \int_0^{10} \frac{C_{p.m.}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3}[10^3 - 0] = \frac{0.42}{3} = 0.14\,J/K-mol$ **Ans. (B)**

9. Given the following data :

Substance	**$\Delta H°$ (kJ/mol)**	**S°(J/mol K)**	**$\Delta G°$ (kJ/mol)**
FeO(s)	– 266.3	57.49	– 245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	– 110.5	197.6	– 137.15

Determine at what temperature the following reaction is spontaneous ?

$$FeO(s) + C\,(Graphite) \longrightarrow Fe(s) + CO(g)$$

(A) 298 K
(B) 668 K
(C) 966 K
(D) $\Delta G°$ is +ve, hence the reaction will never be spontaneous

Sol. $FeO\,(s) + C\,(graphite) \longrightarrow Fe\,(s) + CO\,(g)$

(1) $\Delta H = 0 + [-110.5] - (-266.3)$
$= -110.5 + 266.3$
$= +155.8$ kJ/mole

(2) $\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65$ J/mole

(3) $\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$
$T \times 161.65 \times 10^{-3} = 155.8 \quad \Rightarrow \quad T = 963.8$ K **Ans. (C)**

10. If ΔH_f^o for Ag^+ (infinitely diluted), NO_3^- (infinitely diluted), Cl^- (infinitely diluted) and AgCl(s) are 105.579, –207.36, –167.159 and –127.068 respectively. Calculate the enthalpy change for the reaction

$$AgNO_3(aq.) + HCl(aq.) \longrightarrow AgCl(s) + HNO_3\,(aq.)$$

(A) 21.471 KJ/mol (B) 145.688 KJ/mol (C) –65.488 KJ/mol (D) None

Sol. $\Delta H^o_{reaction} = [\Delta H_f\,(AgCl) + \Delta H_f\,(H^+) + \Delta H_f(NO_3^-)]$
$-[\Delta H^o_f\,(Ag^+)] + \Delta H^o_f\,(NO_3^-) + \Delta H^o_f\,(Cl^-) + \Delta H^o_f\,(H^+)]$
$= -127.068 - [105.579 - 167.159] = -65.488$ KJ / mol. **Ans. (C)**

11. What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

(A) 1294.0 cal, 11247 cal
(B) 921.4 cal, 11074 cal
(C) 1025.6 cal ; 12474.3 cal
(D) 1129.3 cal, 10207 cal

Sol. Mole of $H_2O = 1.39$
$Pv = nRT$
$1 \times v = 1.39 \times 0.082 \times 373$
$v = 42.51$ lit

$$w = P_{ext.}\,dv = 1 \times [42.80] \text{ atm} \times \text{lit.} = 42.80 \times 101.325 \text{ J} = \frac{42.80 \times 101.325}{4.2} = 1025.6 \text{ cal}$$

$\Delta H = \Delta U + [P\Delta v]. = 12470.6$ cal.
$\Delta U = \Delta H - P\Delta v = 13500 - 1025.6 = 12474.3$ cal **Ans. (C)**

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Introduction about entropy

A-1. The entropy of a gas increases on its expansion. Why ?

A-2. Entropy of the solutions is higher than that of pure liquid. Why ?

A-3.✍ What are the signs of ΔS for the system and for the surrounding in each of the following processes ?
(a) Water boils in a teakettle on a hot stove.
(b) Ice in an ice cube tray, left an a table melts.
(c) A cup of coffee is reheated in a microwave oven.

A-4. State the thermodynamic condition of spontaneous occurance of a process ?

A-5. If ΔH for a reaction has a positive value, how would you know the sign requirement of ΔS for it so that the reaction is spontaneous ?

Section (B) : Entropy Calculation

B-1. The entropy of vaporization of benzene is 85 JK^{-1} mol^{-1}. When 117 g benzene vaporizes at it's normal boiling point, calculate the entropy change of surrounding.

B-2.✍ Calculate standard entropy change in the reaction
$Fe_2O_3\,(s) + 3H_2\,(g) \longrightarrow 2Fe\,(s) + 3H_2O\,(\ell)$
Given : $S^o_m\,(Fe_2O_3, S) = 87.4$, $S^o_m\,(Fe, S) = 27.3$, $S^o_m\,(H_2, g) = 130.7$, $S^o_m\,(H_2O, \ell) = 69.9\ JK^{-1}\ mol^{-1}$.

B-3. Calculate the entropy change in surroundings when 1.00 mol of $H_2O\,(\ell)$ is formed under standard conditions at 298 K. Given $\Delta_rH^o = -286$ kJ mol^{-1}.

B-4.✍_ Order of increasing of entropy ammong given condition of substance is :
(I) 1 mole of $H_2O(l)$ at 298 k and 0.101 M Pa
(II) 1 mole of ice at 273 K and 0.101 M Pa
(III) 1 mole of $H_2(g)$ at 298 k and 1 atm
(IV) 1 mole of $C_2H_6(g)$ at 298 K and 1 atm

B-5. Oxygen & ozone are gases at standard temperature. Their molar entropies are in the sequence $O_2 < O_3$. Using molecular properties, explain why ozone is more disordered than oxygen.

B-6. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ($\Delta S_{system} + \Delta S_{surrounding}$) for given process.

Section (C) : Free energy

C-1. Comment on the following statements :
(a) An exothermic reaction is always thermodynamically spontaneous.
(b) Reaction with $\Delta G<0$ always have an equilibrium constant greater than 1.

C-2. What will be the states of a chemical reaction when :
(i) $\Delta G = 0$ (ii) $\Delta G > 0$ (iii) $\Delta G < 0$

C-3. A gaseous reactant A forms two different product, in parallel reaction, B and C as follows :

$A \longrightarrow B;\ \Delta H^o = -3\text{kJ},\ \Delta S^o = 20\text{JK}^{-1}$; $A \longrightarrow C;\ \Delta H^o = -3.6\ \text{kJ},\ \Delta S^o = 10\ \text{JK}^{-1}$

Discuss the relative stability of B and C on the basis of Gibb's free energy change at 27^{o}C.

C-4. With the following informations, determine standard Gibb's free energy of formation of $N_2O_4(g)$.

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ $\Delta G^o = 86.6$ kJ .....(i)

$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$ $\Delta G^o = -34.82$ kJ .....(ii)

$2NO_2(g) \longrightarrow N_2O_4(g)$ $\Delta G^o = -5.77$ kJ .....(iii)

C-5. For the equilibrium : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, equilibrium constant, $K = 1.8 \times 10^{-7}$. What is $\Delta G^0$for the reaction ?

C-6. Calculate the ΔG^o change at 300 K for the reaction;

$Br_2(\ell) + Cl_2(g) \longrightarrow 2BrCl(g)$. For the reaction $\Delta H° = 29.3$ kJ & the standard entropies of $Br_2(\ell)$, $Cl_2(g)$ & $BrCl(g)$ at the 300 K are 150, 220, 240 J mol^{-1}K^{-1} respectively.

C-7. The equilibrium constant of the reaction $2C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088K}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

PART - II : OBJECTIVE TYPE QUESTIONS

Section (A) : Introduction about entropy

A-1._ In which state, the matter have highest entropy

(A) Solid (B) Liquid (C) Gas (D) Equal in all

A-2. Predict which of the following reaction (s) has a positive entropy change ?

I. $Ag^+ (aq) + Cl^- (aq) \longrightarrow AgCl (s)$

II. $NH_4Cl (s) \longrightarrow NH_3 (g) + HCl (g)$

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

(A) I and II (B) III (C) II and III (D) II

A-3. Mixing of non-reacting ideal gases is generally accompanied by

(A) Decrease in entropy (B) Increase in entropy

(C) Change in enthalpy (D) Increase in free energy

A-4. Which of the following reactions is associated with the most negative change in entropy ?

(A) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ (B) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

(C) C (s, graphite) (s,) + $O_2 \longrightarrow CO_2(g)$ (D) $3C_2H_2(g) \longrightarrow C_6H_6(\ell)$

A-5. For the gas - phase decomposition, $PCl_5 (g) \overset{\Delta}{\rightleftharpoons} PCl_3 (g) + Cl_2 (g)$:

(A) $\Delta H < 0, \Delta S < 0$ (B) $\Delta H > 0, \Delta S > 0$ (C) $\Delta H > 0, \Delta S < 0$ (D) $\Delta H < 0, \Delta S > 0$

A-6. Which one of the following has ΔS^0 greater than zero.

(A) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ (B) $NaCl(aq) \rightleftharpoons NaCl(s)$

(C) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$ (D) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

A-7. For which reaction from the following, will be maximum entropy change :

(A) $Ca(s) + \frac{1}{2}O_2(g) \to CaO(s)$ (B) $CaCO_3(s) \to CaO(s) + CO_2(g)$

(C) $C(s) + O_2(g) \to CO_2(g)$ (D) $N_2(g) + O_2(g) \to 2NO(g)$

A-8. Which of the following statement is true. The entropy of the universe
(A) Increases and tends towards maximum value
(B) Decreases and tends to be zero
(C) Remains constant
(D) Decreases and increases with a periodic rate

Section (B) : Entropy Calculation

B-1. An isolated system comprises the liquid in equilibrium with vapours. At this stage the molar entropy of the vapour is :

(A) Less than that of liquid (B) more than that of liquid

(C) Equal to zero (D) Equal to that of liquid

B-2. When two mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is :

(A) $\frac{3}{2}R \ln 2$ (B) $-\frac{3}{2}R \ln 2$ (C) $5R \ln 2$ (D) $\frac{5}{2}R \ln 2$

B-3. In previous problem calcualte ΔS_{gas} if process is carried out at constant volume :

(A) $5R \ln 2$ (B) $\frac{3}{2}R \ln 2$ (C) $3R \ln 2$ (D) $-3R \ln 2$

B-4. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300ºC reversibly and isochorically ?

(A) $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$ (C) $3R \ln\left(\frac{573}{473}\right)$ (D) $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$

B-5. If one mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is :

(A) zero (B) infinity (C) $\frac{5}{2}R \ln 3$ (D) $R \ln 3$

B-6. If $\Delta H_{vaporisation}$ of substance $X(\ell)$ (molar mass = 30 g/mol) is 300 J/g at it's boiling point 300 K, then molar entropy change for reversible condensation process is :-

(A) 30 J/mol.K (B) –300 J/mol.K (C) –30 J/mol.K (D) –10 J/mol.K

B-7. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and $\Delta H = -401.7$ J mol^{-1} for the transition. Assume the surroundings to be an ice-water. Both at 0ºC :
(A) – 1.09 JK^{-1} (B) 1.47 JK^{-1} (C) 0.38 JK^{-1} (D) None of these

B-8.✍ Given $\Delta_r S^o = -266$ and the listed [S^o_m values].
Calculate Sº for Fe_3O_4(s) :

$$4Fe_3O_4\,(s)\,[.............] + O_2\,(g)\,[205] \longrightarrow 6Fe_2O_3\,(s)\,[87]$$

(A) +111.1 (B) +122.4 (C) 145.75 (D) 248.25

B-9. For 1 mole of an ideal monoatomic gas on moving from one state to other, the temperature is doubled but pressure becomes $\sqrt{2}$ times. Then entropy change in the process will be

(R = 2 Cal/mol-K)

(A) R *l*n 2 (B) 2R *l*n 2 (C) 3R *l*n 2 (D) $\frac{R}{2}$ *l*n 2

Section (C) : Free energy

C-1._ Which of the following is incorrect regarding gibbs free energy
(A) it is a state function (B) it is extensive property
(C) it is macroscopic property (D) it is intensive property

C-2.✍ Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature ?
(A) $\Delta H > 0, \Delta S < 0$ (B) $\Delta H < 0, \Delta S > 0$ (C) $\Delta H < 0, \Delta S < 0$ (D) $\Delta H > 0, \Delta S < 0$

C-3. When reaction is at standard state at equilibrium, then :
(A) $\Delta H^o = 0$ (B) $\Delta S^o = 0$
(C) equilibrium constant K = 0 (D) equilibrium constant K = 1

C-4.✍ Which of the natural process is spontaneous
(A) Formation of curd from milk after doing initation.
(B) Conversion of C (graphite) → C (diamond) at 25ºC and latex.
(C) Formation of H_2 (g) and O_2 (g) from H_2O (ℓ)
(D) Formation of CrO_5 from H_2O_2 and $K_2Cr_2O_7$ in basic medium

C-5. What is the free energy change (ΔG) when 1.0 mole of water at 100ºC and 1 atm pressure is converted into steam at 100ºC and 1 atm pressure ?
(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero

C-6. The enthalpy change for a given reaction at 298 K is – x J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(A) can be negative but numerically larger than x/298
(B) can be negative but numerically smaller than x/298
(C) cannot be negative
(D) cannot be positive

C-7. A reaction has $\Delta H = -33$ kJ and $\Delta S = -58$ J/K. This reaction would be :
(A) spontaneous at all temperatures (B) non-spontaneous at all temperatures
(C) spontaneous above a certain temperature (D) spontaneous below a certain temperature

C-8. For a reaction A (g) $\rightleftharpoons$ B(g) at equilibrium. The partial pressure of B is found to be one fourth of the partial pressure of A. The value of $\Delta G°$ of the reaction A → B is
(A) RT ℓn 4 (B) – RT ℓn 4 (C) RT log 4 (D) – RT log 4

C-9.✍ If $\Delta G = -177$ K cal for (1) $2\,Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$

and $\Delta G = -19$ K cal for (2) $4\,Fe_2O_3(s) + Fe(s) \longrightarrow 3\,Fe_3O_4(s)$

What is the Gibbs free energy of formation of $Fe_3O_4(s)$?

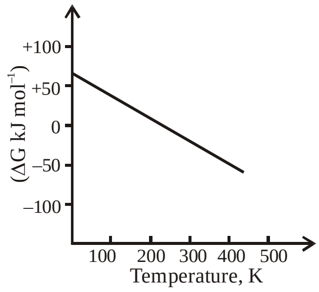
(A) + 229.6 kcal/mol (B) – 242.3 kcal/mol (C) – 727 kcal/mol (D) – 229.6 kcal/mol

C-10._ For a paticular reaction $\Delta H° = -76.6$ KJ and $\Delta S° = 226\ JK^{-1}$. This reaction is :

(A) Spontaneous at all temperatures (B) Non spontaneous at all temperatures

(C) Spontaneous at temperature below 66°C (D) Spontaneous at temperature above 66 °C

C-11. What can be concluded about the values of ΔH and ΔS from this graph?



(A) $\Delta H > 0,\ \Delta S > 0$

(B) $\Delta H > 0,\ \Delta S < 0$

(C) $\Delta H < 0,\ \Delta S > 0$

(D) $\Delta H < 0,\ \Delta S < 0$

C-12. For the reaction at 300 K

$$A(g) + B(g) \longrightarrow C(g)$$

$$\Delta U = -3.0\ \text{kcal} \quad ; \quad \Delta S = -10.0\ \text{cal/K}$$

value of ΔG is ?

(A) –600 cal (B) –6600 cal (C) –6000 cal (D) none

C-13. For the reaction that taking place at certain temperature $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, if equilibrium pressure is X bar, then $\Delta_rG°$ would be :-

(A) – 2 RT ln X (B) – RT (ln X – ln2)

(C) – 2 RT (ln X–ln 2) (D) – 0.5 RT (ln X–ln 2)

PART - III : MATCH THE COLUMN

1.

	Column–I	Column-II
(A)	Reversible adiabatic compression	(P) $\Delta S_{system} > 0$
(B)	Reversible vaporisation	(Q) $\Delta S_{system} < 0$
(C)	Adiabatic free expansion of ideal gas in vacuum	(R) $\Delta S_{surroundig} < 0$
(D)	Dissociation of $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	(S) $\Delta S_{surrounding} = 0$

2.✍

Column-I	Column-II
(A) Reversible adiabatic compression	(p) $\Delta S_{system} > 0$
(B) Reversible vaporisation of liquid	(q) $\Delta S_{system} < 0$
(C) $2N(g) \longrightarrow N_2(g)$	(r) $\Delta S_{surrounding} < 0$
(D) $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	(s) $\Delta S_{surrounding} = 0$

Exercise # 2

PART - I : ONLY ONE OPTION CORRECT TYPE QUESTION

1.✍_ Which of the following option the first compound has less entropy than second :
(A) (i) aqueous solution of 1 M of $MgCl_2$ (ii) aqueous solution of 1 M of NaCl
(B) (i) Br_2 liquid at 25ºC (ii) Br_2 liquid at 20ºC
(C) (i) HgO solid (ii) HgS solid
(D) (i) Br_2 liquid (ii) I_2 solid

2.✍_ Select the correct statement(s) :
S_1 : $AlCl_3$ when dissolve in H_2O its entropy decreases therefore it is a non-spontaneous process.
S_2 : When H_2 gas adsrobed at the surface of Pd, some amount of heat is released.
S_3 : Entropy of D_2 gas is greater than H_2 gas.
(A) S_1, S_2 & S_3 (B) S_1 & S_3 (C) S_2 & S_3 (D) S_1 & S_2

3._ Isoentropic process is
(A) adiabatic and irreversible process (B) isothermal and reversible process
(C) Adiabatic and reversible process (D) isothermal and reversible for which Q = 0

4.✍_ According to third law of thermodynamics
(A) The entropy of a substance at OK is zero.
(B) Entropy of hydrogen ion is zero at OK.
(C) Net change in entropy in coverssion $H_{2(g)}$ (130 K) $\rightarrow$ $H_{2(g)}$ (200K) is zero.
(D) Entropy generally decrease in combustion reactions.

5.✍ One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as (R = 2 calories/mol/K)

(A) $3 \ln \frac{298}{373} + 2 \ln 10$ (B) $5 \ln \frac{373}{298} + 2 \ln 10$

(C) $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$ (D) $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$

6. Select correct statements :
S_1 : For every chemical reaction at equilibrium, standerd gibbs energy of reaction is zero
S_2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing gibbs energy.
S_3 : Spontancity is related to change in entropy of universe.
(A) S_1 S_2 S_3 (B) only S_1 (C) S_2, S_3 (D) S_1, S_3

7.✍ Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the capturing of energy from the reaction is done through electrical process (non P–V work) then calculate maximum available energy which can be captured by combustion of 34.2 g of sucrose
Given : $\Delta H_{combustion}$ (sucrose) = – 6000 kJ mol^{-1}
$\Delta S_{combustion}$ = 180 J/K - mol and body temperature is 300 K
(A) 600 kJ (B) 594.6 kJ (C) 5.4 kJ (D) 605.4 kJ

8. For the hypothetical reaction , $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, Δ_rG and Δ_rS are 20 kJ/mole and –20 JK^{-1} mol^{-1} respectively at 200 K. If Δ_rC_p is 20 JK^{-1} mol^{-1} then Δ_rH at 400 K is :-
(A) 20 kJ/mole (B) 7.98 kJ/mole (C) 28 kJ/mole (D) 16 kJ/mole

PART - II : NUMERICAL TYPE QUESTIONS

1. The equilibrium constant for a reaction is 10. What will be the magnitude value of ΔG^o ?
$R = 8.31\ JK^{-1}\ mol^{-1}$, $T = 314$ K. (Approximate integer value in $KJ\ mol^{-1}$)

2._ For the reaction at 298 K

$$A\ (g) + B\ (g) \rightleftharpoons C\ (g) + D\ (g)$$

If $\Delta H^o = -29.8$ Kcal and $\Delta S^o = -0.1$ Kcal K^{-1} then calculate reaction constant (K) :

3.^ One mole of an ideal gas is expanded isothermally at 300 K until its volume is tripled. Find the values of ΔS_{total} under the condition.
Expansion is carried out irreversibly where 900 J of heat is less absrobed than expansion is carried out reversibly. (Approximate integer value, Used $e^{1.09} = 3$ & $8.314 \times 1.09 = 9$)

4.^✍ Calculate the magnitude of free energy in $KJ\ mol^{-1}$ when 1 mole of a an ionic salt MX (s) is dissolved in water at 27°C. Given
Lattice energy of MX = 780 $kJ\ mol^{-1}$
Hydration energy of MX = – 775.0 $kJ\ mol^{-1}$
Entropy change of dissolution at 27°C = 40 $J\ mol^{-1}\ K^{-1}$

5.✍_ For the formation of C (g) at 300 K.

$$A\ (g) + 3\ B\ (g) \rightarrow 2C\ (g)$$

Calculate the magnitude of ΔG^o (Kcal) if given data :

	A	B	C
ΔH_f^o (Kcal mol^{-1})	0	0	–10
ΔS_f^o (Cal $K^{-1}\ mol^{-1}$)	40	30	45

6._ The entropies of H_2 (g) and H (g) are 60 and 50 J $mole^{-1}\ K^{-1}$ respectively at 300 K. Using the data given below calculate the bond enthalpy of H_2 (g) in Kcal $mole^{-1}$.

$$H_2\ (g) \rightarrow 2H\ (g)\ ; \qquad \Delta G^o = 21.6\ KJ\ mole^{-1}$$

7.^ The standard free energy change for a reaction is – 213.3 $kJ\ mol^{-1}$ at 25°C. If the enthalpy change of the reaction is – 217.77 $kJ\ mole^{-1}$. Calculate the magnitude of entropy change for the reaction in Joule $mole^{-1}$.

8.^ Calculate the magnitude of standard entropy change for reaction $X \rightleftharpoons Y$ if $\Delta H^o = 25KJ$ and K_{eq} is 10^{-7} at 300K.

9.^ Calculate the magnitude of standard free energy of formation of ammonium chloride at 25°C (approximate integer in Kcal mol^{-1}), the equation showing the formation of NH_4Cl from its elements is $\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow NH_4Cl(s)$
For NH_4Cl, ΔH^0_f is – 313 $kJ\ mol^{-1}$, Also given that

$$S^0_{N_2} = 191.5\ JK^{-1}mol^{-1} \quad S^0_{H_2} = 130.6\ JK^{-1}mol^{-1}$$

$$S^0_{Cl_2} = 223.0 JK^{-1}mol^{-1} \quad S^0_{NH_4Cl} = 94.6\ JK^{-1}mol^{-1}$$

10.✍_ For the reaction $\frac{1}{2}\ N_2\ (g) + \frac{3}{2} H_2\ (g) \longrightarrow NH_3\ (g)$; $\Delta H = -30$ kJ to be at equilibrium at 477°C. If standard entropy of N_2 (g) and NH_3 (g) are 60 and 50 J $mole^{-1}\ K^{-1}$ respectively then calculate the standard entropy of H_2(g) in $Jmole^{-1}K^{-1}$.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.✍ In which of the following entropy increases :

(A) Rusting of iron (B) Melting of ice

(C) Crystallisation of sugar from solution (D) Vaporisation of camphor

2. Select the correct statement(s).

(A) In a reversible process, ΔG is always zero in a closed system.

(B) In a reversible process, ΔS_{univ} is always zero in a closed system.

(C) In a reversible process, ΔS_{sys} is always zero in a closed system.

(D) In a reversible process, ΔS_{sys} is always zero in an isolated system.

3._ Which of the following is false about molar entropy ?

(A) It is same for all type of gases

(B) For the gas of comparable mass. It decreases with the increases in atomicity.

(C) Under identical condition, it is greater for heavier gas.

(D) For ideal gas of comparable molar mass it decreases with the increase in thermo molecular attractions.

4.✍_ Which of the following statements is/are correct

(A) Reversible adiabatic process is iso entropie process

(B) ΔS_{system} for irreversible adiabatic compression is greater than zero

(C) ΔS_{system} for free expension in zero

(D) $\Delta S_{surrounding}$ for irreversible isothermal compression is greater than zero

5.✍ The normal boiling point of a liquid `X` is 400 K. Which of the following statement is true about the process X (l) $\longrightarrow$ X(g)?

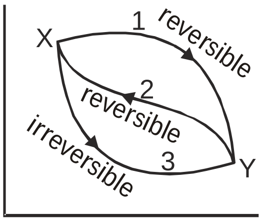
(A) at 400 K and 1 atm pressure $\Delta G = 0$ (B) at 400 K and 2 atm pressure $\Delta G = +$ ve

(C) at 400 K and 0.1 atm presure $\Delta G = -$ ve (D) at 410 K and 1 atm pressure $\Delta G = +$ ve

6. For isothermal expansion in case of an ideal gas :

(A) $\Delta H = 0$ (B) $\Delta E = 0$ (C) $\Delta G = -T.\Delta S$ (D) $T_{final} = T_{initial}$

7. Suppose a system make a transition from state X to state Y.



Given : $\Delta S_{XY} = 10$ J/K

(A) The state Y is more disordered than state X.

(B) ΔS_{XY} for path 1 and 3 is same.

(C) $\Delta S_{YX} = -10$ J/K

(D) The transition X $\rightarrow$ Y must be spontaneous.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

The reactions whose $\Delta G°$ are positive can not take place under standard state conditions. However another reaction whose $\Delta G°$ is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose $\Delta G°$ at 300 K are provided to answer following questions.

$A(g) + 3B(g) \longrightarrow 2C(g)$: $\Delta G° = +24$ kJ/mol ; $\Delta H° = -24$ kJ/mol

$3C(g) \longrightarrow 2D(g)$: $\Delta G° = -60$ kJ/mol ; $\Delta H° = -84$ kJ/mol

All data at 300 K temperature.

1. What is $\Delta S°$ at 300 K of reaction (in J/Kmole) :

$3A(g) + 9B(g) \longrightarrow 4D(g)$

(A) –640 (B) –480 (C) +640 (D) –240

2. Assuming $\Delta H°$ and $\Delta S°$ do not vary with temperature. At what temperature reaction $A(g) + 3B(g) \longrightarrow 2C(g)$ become spontaneous-

(A) 6250 K (B) 625 K (C) 150 K (D) 1000 K

Comprehension # 2

Dependence of Spontaneity on Temperature :

For a process to be spontaneous, at constant temperature and pressure, there must be decrease in free energy of the system in the direction of the process, i.e. $\Delta G_{P,T} < 0$. $\Delta G_{P,T} = 0$ implies the equilibrium condition and $\Delta G_{P,T} > 0$ corresponds to non-spontaneity.

Gibbs-Helmholtz equation relates the free energy change to the enthalpy and entropy changes of the process as :

$$\Delta G_{P,T} = \Delta H - T\Delta S \qquad ...(1)$$

The magnitude of ΔH does not change much with the change in temperature but the entropy factor $T\Delta S$ changes appreciably. Thus, spontaneity of a process depends very much on temperature.

For endothermic process, both ΔH and ΔS are positive. The energy factor, the first factor of equation, opposes the spontaneity whereas entropy factor favours it. At low temperature the favourable factor $T\Delta S$ will be small and may be less than ΔH, ΔG will have positive value indicating the nonspontaneity of the process. On raising temperature, the factor $T\Delta S$ increases appreciably and when it exceeds ΔH, ΔG would become negative and the process would be spontaneous.

For an exothermic process, both ΔH and ΔS would be negative. In this case the first factor of eq. 1 favours the spontaneity whereas the second factor opposes it. At high temperature, when $T\Delta S > \Delta H$, ΔG will have positive value, showing thereby the non-spontaneity of the process. However, on decreasing temperature, the factor $T\Delta S$ decreases rapidly and when $T\Delta S < \Delta H$, ΔG becomes negative and the process occurs spontaneously. Thus, an exothermic process may be spontaneous at low temperature and non-spontaneous at high temperature.

3.✍ When $CaCO_3$ is heated to a high temperature, it undergoes decomposition into CaO and CO_2 whereas it is quite stable at room temperature. The most likely explanation of it, is

(A) The enthalpy of reaction (ΔH) overweighs the term $T\Delta S$ at high temperature.

(B) The term $T\Delta S$ overweighs the enthalpy of reaction at high temperature.

(C) At high temperature, both enthalpy of reaction and entropy change become negative.

(D) None of these.

4.✍ For the reaction at 25°C, $X_2O_4(\ell) \longrightarrow 2XO_2(g)$

$\Delta H = 2.1$ Kcal and $\Delta S = 20$ cal K^{-1}. The reaction would be

(A) spontaneous (B) non-spontaneous (C) at equilibrium (D) unpredictable

5.✍ For the reaction at 298 K, $2A + B \longrightarrow C$
$\Delta H = 100$ kcal and $\Delta S = 0.050$ kcal K^{-1}. If ΔH and ΔS are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous ?
(A) 1000 K (B) 1500 K (C) 2000 K (D) 2500 K

6.✍ A reaction has a value of $\Delta H = -40$ kcal at 400K. Above 400 K, the reaction is spontaneous, below this temperature, it is not. The values of ΔG and ΔS at 400 K are respectively
(A) 0,– 0.1 cal K^{-1}
(B) 0,100 cal K^{-1}
(C) – 10 kcal, – 100 cal K^{-1}
(D) 0, – 100 cal K^{-1}

7.✍ The enthalpy change for a certain reaction at 300 K is – 15.0 K cal mol^{-1}. The entropy change under these conditions is – 7.2 cal K^{-1} mol^{-1}. The free energy change for the reaction and its spontaneous/non-spontaneous character will be
(A) – 12.84 kcal mol^{-1}, spontaneous
(B) 12.84 kcal mol^{-1}, non-spontaneous
(C) – 17.16 kcal $rnol^{-1}$, spontaneous
(D) None of these

Exercise # 3

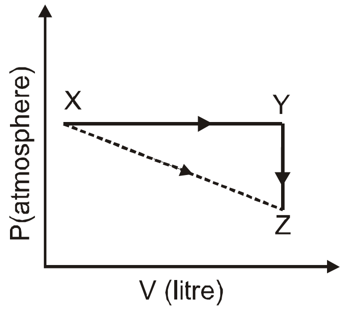
PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

*** Marked Questions may have more than one correct option.**

1. Match the transformation in **column I** with appropriate options in **column II.** **[JEE 2011, 8/180]**

Column I	Column II
(A) $CO_2(s) \longrightarrow CO_2(g)$	(p) phase transition
(B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	(q) allotropic change
(C) $2H\bullet \longrightarrow H_2(g)$	(r) ΔH is positive
(D) $P_{(white,\ solid)} \longrightarrow P_{(red,\ solid)}$	(s) ΔS is positive
	(t) ΔS is negative

2.* For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done]. **[JEE 2012, 4/136]**



(A) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$
(B) $w_{x\to z} = w_{x\to y} + w_{y\to z}$
(C) $w_{x\to y\to z} = w_{x\to y}$
(D) $\Delta S_{x\to y\to z} = \Delta S_{x\to y}$

3. For the process, $H_2O(\ell) \to H_2O(g)$
at T = 100 °C and 1 atmosphere pressure, the correct choice is : **[JEE(Advanced) 2014, 3/120]**
(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

4. Match the thermodynamic processes given under Column I with the expressions given under Column II.

[JEE(Advanced) 2015, 8/168]

	Column I		**Column II**
(A)	Freezing of water at 273 K and 1 atm	(P)	$q = 0$
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q)	$w = 0$
(C)	Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R)	$\Delta S_{sys} < 0$
(D)	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(S)	$\Delta U = 0$
		(T)	$\Delta G = 0$

5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is : (1 L atm = 101.3 J) **[JEE(Advanced) 2016, 3/124]**

(A) 5.763 (B) 1.013 (C) –1.013 (D) –5.763

6. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

[JEE(Advanced) 2017, 4/122]

(A) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

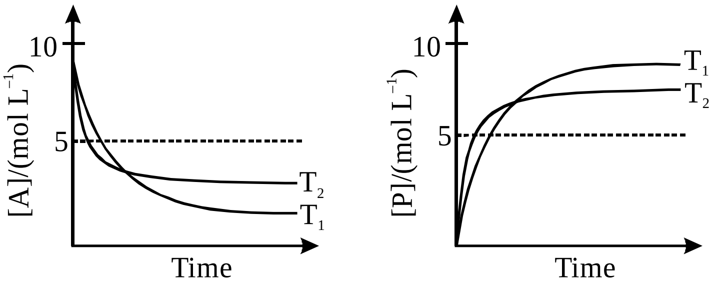
(B) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

(C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

(D) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

7. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below.

[JEE(Advanced) 2018]



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than $^{T_2}/_{T_1}$. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(A) $\Delta H^\theta < 0$, $\Delta S^\theta < 0$ (B) $\Delta G^\theta < 0$, $\Delta H^\theta > 0$

(C) $\Delta G^\theta < 0$, $\Delta S^\theta < 0$ (D) $\Delta G^\theta < 0$, $\Delta S^\theta > 0$

8. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :

$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$ **[JEE(Advanced) 2018]**

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is ___.

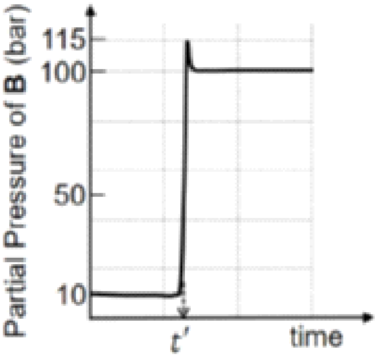
(Given : total pressure = 1 bar, R (universal gas constant) = 8 $JK^{-1}mol^{-1}$, ln(10) = 2.3. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + 1/2O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\theta = -\ 78,000\ J\ mol^{-1}$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$; $\Delta G^\theta = -\ 1,78,000\ J\ mol^{-1}$; G is the Gibbs energy)

9. Consider the reaction $A \rightleftharpoons B$ at 1000 K. At time t', the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of A was maintained at 1 bar. Given below is the plot of the partial pressure of B with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K?

[JEE(Advanced) 2020]



PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is : **[AIEEE 2011, 4/120]**

(1) 38.3 $J\ mol^{-1}K^{-1}$
(2) 35.8 $J\ mol^{-1}K^{-1}$
(3) 32.3 $J\ mol^{-1}K^{-1}$
(4) 42.3 $J\ mol^{-1}K^{-1}$

2. In view of the signs of Δ_rG^o for the following reactions :

$PbO_2 + Pb \rightarrow 2PbO$, $\Delta_rG^o < 0$

$SnO_2 + Sn \rightarrow 2SnO$, $\Delta_rG^o > 0$,

which oxidation states are more characteristics for lead and tin ? **[AIEEE 2011, 4/120]**

(1) For lead +2, for tin +2
(2) For lead +4, for tin +4
(3) For lead +2, for tin +4
(4) For lead +4, for tin +2

3. The incorrect expression among the following is : **[AIEEE 2012, 4/120]**

(1) $\frac{\Delta G_{system}}{\Delta S_{total}} = -T$
(2) In isothermal process, $w_{reversible} = -nRT \ln \frac{V_f}{V_i}$
(3) $\ln K = \frac{\Delta H^o - T\Delta S^o}{RT}$
(4) $K = e^{-\Delta G^o/RT}$

4. The following reaction is performed at 298 K

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of NO_2(g) at 298 K ? ($K_P = 1.6 \times 10^{12}$) **[JEE(Main) 2015, 4/120]**

(1) R(298) in $(1.6 \times 10^{12}) - 86600$ (2) $86600 + R(298) \ln (1.6 \times 10^{12})$

(3) $86600 - \dfrac{\ln\left(1.6 \times 10^{12}\right)}{R\,(298)}$ (4) $0.5\,[2 \times 86{,}600 - R\,(298) \ln (1.6 \times 10^{12})]$

5. For the reaction, A(g) + B(g) → C(g) + D(g), ΔH^o and ΔS^o are, respectively, –29.8 kJmol^{-1} and –0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298 K is:

[JEE(Main) 2016 Online (09-04-16), 4/120]

(1) 1 (2) 10 (3) 1.0×10^{-10} (4) 1.0×10^{10}

6. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following:

[JEE(Main) 2016 Online (09-04-16), 4/120]

(1) Both ΔH and ΔS are positive. (2) ΔH is negative while ΔS is positive.

(3) ΔH is positive while ΔS is negative. (4) Both ΔH and ΔS are negative.

7. $\Delta_f G°$ at 500 K for substance 'S' in liquid state and gaseous state are +100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to : (R = 2 cal K^{-1} mol^{-1})

[JEE(Main) 2018 Online (15-04-18), 4/120]

(1) 0.1 atm (2) 1 atm (3) 10 (4) 100 atm

8. Given

(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g)$; $\Delta_r G° = +\,1487.0$ kJ mol^{-1}

(ii) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$; $\Delta_r G° = -514.4$ kJ mol^{-1}

Free energy change, $\Delta_r G°$ for the reaction $2Fe_2O_3(s) + 6CO(g) \rightarrow 4Fe(s) + 6CO_2(g)$ will be

[JEE(Main) 2018 Online (15-04-18), 4/120]

(1) –112.4 kJ mol^{-1} (2) –56.2 kJ mol^{-1} (3) –168.2 kJ mol^{-1} (4) –208.0 kJ mol^{-1}

9. For which of the following processes, ΔS is negative ? **[JEE(Main) 2018 Online (16-04-18), 4/120]**

(1) C(diamond) → C(graphite) (2) N_2(g, 1 atm) → N_2(g, 5 atm)

(3) N_2(g, 273 K) → N_2(g, 300 K) (4) $H_2(g) \rightarrow 2H(g)$

10. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is :

[JEE(Main) 2019 Online Jan. 4/120]

(Specific heat of water liquid and water vapour are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1} ; heat of liquid fusion and vapourisation of water are 344 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively).

(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583)

(1) 7.90 kJ kg^{-1} K^{-1} (2) 2.64 kJ kg^{-1} K^{-1}

(3) 8.49 kJ kg^{-1} K^{-1} (4) 9.26 kJ kg^{-1} K^{-1}

11. A process has ΔH = 200 Jmol^{-1} and

ΔS = 40 JK^{-1}mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous : **[JEE(Main) 2019 Online Jan. 4/120]**

(1) 5 K (2) 4 K (3) 20 K (4) 12 K

12. For the reaction ; **[JEE(Main) 2020 Online Jan. 4/100]**

$A(l) \rightarrow 2B(g)$

ΔU = 2.1 kcal , ΔS = 20 cal K^{-1} at 300 K

Hence ΔG in kcal is_________ .

ANSWER KEY

EXERCISE - 1

PART - I

A-1. Because larger space creates more disorder.

A-2. Dissolution of solute makes the motion of solute particles free. Also the increased number of particles in mixed state increases disorderness.

A-3. (a) ΔS_{sys} is positive ; ΔS_{surr} is negative.
(b) ΔS_{sys} is positive, ΔS_{surr} is negative.
(c) ΔS_{sys} is positive, ΔS_{surr} is negative.

A-4. $\Delta G = (–)$ ve or $\Delta S_{total} > 0$

A-5. $\Delta G = \Delta H – T\Delta S$
For spontaneous reaction $\Delta G = (–)$ ve
$\therefore$ ΔS Should be positive

B-1. – 1.5 × 85 J/K

B-2. $– 215.2\ JK^{–1}\ mol^{–1}$

B-3. **Given :** $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l);\ \Delta_f H^o = –286\ kJ\ mol^{–1}$
T = 298 K
Asked : The entropy change for the reaction.= ?
Formula : $\Delta S_{surr} = \frac{q_{surr}}{T}$
Explanation : ΔS = Entropy change
T = Temperature in K [T = 298 K under standard conditions]
q_{surr} = Heat absorbed by the surrounding ($q_{surr} = +\ 286\ kJ\ mol^{–1}$)
Substitution & Calculation :

$$\Delta S_{surr} = \frac{286000}{298} = 959.73\ JK^{–1}.$$

Ans. Entropy change in surroundings = $959.73\ JK^{–1}$.

B-4. II < I < III <IV

B-5. Ozone has three atoms per molecule, whereas O_2 has only two.

B-6. 16 J/K

C-1. (a) When ΔH = – ve and $T\Delta S$ = – ve, also $T\Delta S > \Delta H$ then ΔG = + ve in such case, the reaction will not be spontaneous.
(b) $– \Delta G^o = 2.303\ RT \log K_c$.
If ΔG^o is negative (not to say that $\Delta G^o < 0$) then K_c will be +ve and will have value greater than one.

C-2. (i) Chemical reaction in equilibrium state
(ii) non-spontaneous
(iii) Spontaneous.

C-3. ΔG^o indicates that B is more stable than C.

C-4. 97.79 kJ

C-5. ΔG^0 of reaction is 38457 J/mol

C-6. –3.7 kJ

C-7. $\Delta H° = 9.04$ kJ/mol; $\Delta S° = -8.64$ J/mol^{-1} K^{-1}

PART - II

A-1.	(C)	**A-2.**	(C)	**A-3.**	(B)	**A-4.**	(D)	**A-5.**	(B)
A-6.	(C)	**A-7.**	(B)	**A-8.**	(A)	**B-1.**	(B)	**B-2.**	(C)
B-3.	(C)	**B-4.**	(C)	**B-5.**	(D)	**B-6.**	(C)	**B-7.**	(C)
B-8.	(C)	**B-9.**	(B)	**C-1.**	(D)	**C-2.**	(B)	**C-3.**	(D)
C-4.	(A)	**C-5.**	(D)	**C-6.**	(B)	**C-7.**	(D)	**C-8.**	(A)
C-9.	(B)	**C-10.**	(C)	**C-11.**	(A)	**C-12.**	(A)	**C-13.**	(C)

PART - III

1. (A) - S ; (B) - P,R ; (C) - P, S (D) - P, R **2.** (A) → (s); (B) → (p, r); (C) → (q); (D) → p, r)

EXERCISE - 2

PART - I

1.	(C)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(B)
6.	(C)	**7.**	(D)	**8.**	(A)				

PART - II

1.	6	**2.**	1	**3.**	$\Delta S_{total} = 3$ J K^{-1}	**4.**	– 7 kJ mol^{-1}.
5.	8	**6.**	8	**7.**	– 15	**8.**	51
9.	48	**10.**	40				

PART - III

1.	(ABD)	**2.**	(BD)	**3.**	(ABD)	**4.**	(ABD)	**5.**	(ABC)
6.	(ABCD)	**7.**	(ABC)						

PART - IV

1.	(A)	**2.**	(C)	**3.**	(B)	**4.**	(A)	**5.**	(C)
6.	(D)	**7.**	(A)						

EXERCISE - 3

PART - I

1. (A – p, r, s) ; (B – r, s) ; (C – t) ; (D – p, q, t) **2.** (AC)

3. (B) **4.** (A-R,T) (B-P,Q,S) (C-P,Q,S) (D-P,Q,S,T)

5. (C) **6.** (AB) **7.** (AC) **8.** (–14.6) **9.** 0.25

PART - II

1.	(1)	**2.**	(3)	**3.**	(3)	**4.**	(4)	**5.**	(1)
6.	(1)	**7.**	(1)	**8.**	(2)	**9.**	(2)	**10.**	(4)
11.	(1)	**12.**	–2.70 to –2.71						

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Calculation ΔU, ΔH & W

A-1. A mixture of 2 mole of CO and 1 mole of O_2, in a closed vessel is ignited to convert the CO to CO_2. If ΔH is the enthalpy change and ΔU is the change in internal energy then compare value of ΔH & ΔU :

A-2. For the reaction : $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$
if $\Delta U^o = -1373$ kJ mol^{-1} at 298 K. Calculate ΔH^o

A-3. 2 mole of zinc is dissolved in HCl at 25ºC. Calculate the work done in open vessel.

A-4. Ethyl chloride (C_2H_5Cl), is prepared by reaction of ethylene with hydrogen chloride:
$C_2H_4(g) + HCl\,(g) \rightarrow C_2H_5Cl(g)$ $\qquad \Delta H = -\,72.3$ kJ
What is the value of ΔE (in kJ), if 98g of ethylene and 109.5g of HCl are allowed to react at 300K.

Section (B) : Basics & Kirchoff's law

B-1. Classify the following processes as exothermic or endothermic :
(A) Burning of a match stick
(B) Melting of ice
(C) Molten metal solidifies
(D) Reaction between Na and H_2O
(E) Rubbing alcohol evaporates.

B-2. Diborane is a potential rocket fuel which undergoes combustion according to the reaction

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane

$2B(s) + (3/2)\,O_2(g) \longrightarrow B_2O_3(s)$ $\qquad \Delta H = -\,1273$ kJ mol^{-1}
$H_2(g) + (1/2)O_2(g) \longrightarrow H_2O(l)$ $\qquad \Delta H = -\,286$ kJ mol^{-1}
$H_2O(l) \longrightarrow H_2O(g)$ $\qquad \Delta H = 44$ kJ mol^{-1}
$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$ $\qquad \Delta H = 36$ kJ mol^{-1}

B-3. Predict the standard reaction enthalpy of $2\,NO_2(g) \rightarrow N_2O_4(g)$ at 100°C.
$\Delta H°$ at 25°C is –57.2 kj. mol^{-1} $C_p(NO_2) = 37.2$ j. mol^{-1} K^{-1} $C_p(N_2O_4) = 77.28$ J. mol^{-1} k^{-1}.

Section (C) : Enthalpy of formation & combustion

C-1. The heat of combustion of ethyl alcohol is –300 kcal. If the heats of formation of CO_2 (g) and $H_2O(\ell)$ are –94.3 and –68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.

C-2. From the following data at 25°C, Calculate the standard enthalpy of formation of FeO(s) and of $Fe_2O_3(s)$.

	Reaction	$\Delta_r H^o$ **(kJ/mole)**
(1)	$Fe_2O_3(s) + 3C(graphite) \rightarrow 2Fe\,(s) + 3CO(g)$	492
(2)	$FeO\,(s) + C(graphite) \rightarrow Fe(s) + CO(g)$	155
(3)	$C(graphite) + O_2(g) \rightarrow CO_2(g)$	–393
(4)	$CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g)$	–282

C-3. The standard enthalpy of decomposition of the yellow complex H_3NSO_2 Into NH_3 and SO_2 is + 40 kJ mol^{-1}. Calculate the standard enthalpy of formation of H_3NSO_2. $\Delta H^0_f(NH_3) = -\,46.17$ kJ mol^{-1}, $\Delta H^0_f(SO_2) = -\,296.83$

C-4.✍ When 12.0 g of carbon (graphite) reacted with oxygen to form CO and CO_2 at 25^0C and constant pressure, 252 kJ of heat was released and no carbon remained. If ΔH^0_f (CO,g) = – 110.5 $kJmol^{-1}$ and $\Delta H^0_f(CO_2,g)$ = – 393.5 kJ mol^{-1}, calculate the mass of oxygen consumed.

Section (D) : Bond enthalpy method & Resonance energy

D-1.✍ Calcualte the bond energy of Cl–Cl bond from the following data :
$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g); \Delta H = -100.3$ kJ. Also the bond enthalpies of C–H, C–Cl, H–Cl bonds are 413, 326 and 431 kJ mol^{-1} respectively.

D-2. Calculate ΔH^o_r for the reaction $CH_2Cl_2\,(g) \longrightarrow C(g) + 2H(g) + 2Cl(g)$. The average bond enthalpies of C–H and C–Cl bonds are 414 kJ mol^{-1} and 330 kJ mol^{-1}.

D-3.✍ Calculate the enthalpy change (ΔH) of the following reaction
$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$ given average bond enthalpies of various bonds, i.e., C–H, C≡C, O = O, C = O, O–H as 414, 814, 499, 724 and 640 kJ mol^{-1} respectively.

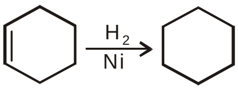
D-4. Find the enthalpy of S–S bond from the following data.

(i) $C_2H_5 - S - C_2H_5$ (g) $\Delta_f H^\circ = -150$ kJ/mol

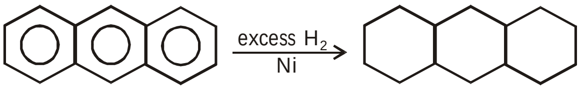
(ii) $C_2H_5 - S - S - C_2H_5$ (g) $\Delta_f H^\circ = -200$ kJ/mol

(iii) S (g) $\Delta_f H^\circ = 225$ kJ/mol

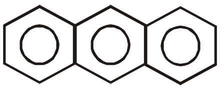
D-5. Use the following data to answer the questions below :



; ΔH = –28.6 Kcal mol^{-1} ;



; ΔH = –116.2 Kcal mol^{-1}

Calculate the resonance energy of anthracene, 

D-6.✍ Estimate the average S–F bond enthalpy in SF_6. The values of standard enthalpy of formation of SF_6(g), S(g) and F(g) are : – 1100, 274 and 80 kJ mol–1 respectively.

Section (E) : Enthalpy of solution & Born Haber's cycle

E-1. Calculate the standard enthalpy of solution of AgCl(s) in water ΔH^0_f (AgCl,s) = – 127.07 kJ mol^{-1}, ΔH^0_f (Ag^+, aq) = 105.58 kJ mol^{-1}, ΔH^0_f (Cl^-, aq) = –167.35 kJ mol^{-1}.

E-2._ Enthalpies of solution of $BaCl_2$ (s) and $BaCl_2.2H_2O$ (s) are – 20 kJ/mole and 8.0 kJ/mole respectively. Calculate heat of hydration of $BaCl_2$ (s).

E-3_.✍ Setup of Born-Haber cycle; calculate lattice energy of $MgO_{(s)}$. The given that - enthalpy of formation of $MgO_{(s)}$ = –602, sublimation of $Mg_{(s)}$ = 148 ; 1st & 2nd ionization energy of Mg = 738 & 1450 respectively.
For Oxygen bond dissociation energy = 498; 1st & 2nd electron gain enthalpy = –141 & 844 respectively (all unit in $kJmole^{-1}$).

Section (F) : Enthalpy of neutralization

F-1.✍_ 10 mL of each 1 M HCl and 1M H_2SO_4 are neutralized by 1 M NaOH solution that liberate the heat of a & b kJ/mol respectively. What is relation between a and b ?

F-2._ The enthalpy of neutralization of 1M HCl by 1M NaOH is – 57 kJ/mole. The enthalpy of formation of water is – 285 kJ/mole. The enthalpy of formation of OH^- ion is :

F-3.✍ The standard enthalpy of neutralization of KOH with HCN and HCl in dilute solution is –2480 cal.mol^{-1} and –13.68 kcalmol^{-1} respectively. Find the enthalpy of dissociation of HCN at the same temperature.

PART - II : OBJECTIVE TYPE QUESTIONS

Section (A) : Calculation ΔU, ΔH & W

A–1. The free energy change for a reversible reaction at equilibrium is :
(A) Positive (B) Negative (C) Zero (D) Cannot say

A–2. For a reaction, $2X(s) + 2Y(s) \rightarrow 2C(\ell) + D(g)$
The q_p at 27°C is – 28 Kcal mol^{-1}, the q_v is ----------- Kcal mol^{-1}
(A) – 27.4 (B) + 27.4 (C) – 28.6 (D) 28.6

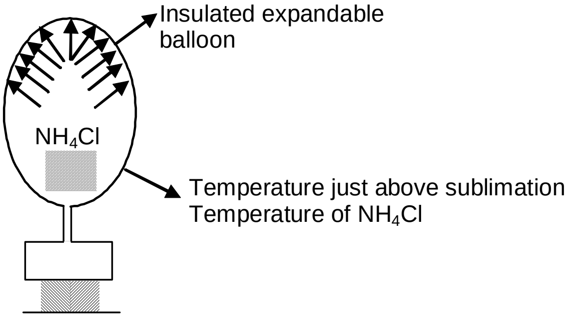
A-3.✍ Determine which of the following reactions at constant pressure represent surrounding that do work on the system :
I. $4NH_3\,(g) + 7O_2\,(g) \longrightarrow 4NO_2\,(g) + 6H_2O\,(g)$
II. $CO\,(g) + 2H_2\,(g) \longrightarrow CH_3OH\,(\ell)$
III. $C\,(s,\text{ graphite}) + H_2O\,(g) \longrightarrow CO\,(g) + H_2\,(g)$
IV. $H_2O\,(s) \longrightarrow H_2O\,(\ell)$
(A) III, IV (B) II and III (C) II, IV (D) I and II, IV

A-4. Consider the reaction at 300 K
$H_2\,(g) + Cl_2\,(g) \longrightarrow 2HCl\,(g)$; $\Delta H^o = -\,185$ kJ
If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is ΔU^o for this reaction ?
(A) 0 (B) – 185 kJ (C) 370 kJ (D) – 370 kJ

A-5._ A piece of NH_4Cl is kept inside a ballon filled with some air, having thermally insulated walls. The temperature is kept just above sublimation temperature of NH_4Cl.

$$NH_4Cl\,(s) \xrightarrow{\text{sublime}} NH_3\,(g) + HCl\,(g).$$

Which of the following is correct regarding this :



(A) q_{system} = positive (B) ΔU = negative (C) w = zero (D) ΔU = positive

Section (B) : Basics & Kirchoff's law

B-1. For which of the following change $\Delta H \neq \Delta E$?

(A) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ (B) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$
(C) $C(s) + O_2(g) \longrightarrow CO_2(g)$ (D) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

B-2_. Calculate the Standard internal energy of formation of liquid methyl acetate (CH_3COOCH_3) from its standard enthalpy of formation, which is –442.91 kJ mole^{-1} at 25ºC.

(A) –433 (B) +433 (C) –452.82 (D) 452.82

B-3. $2C + O_2 \rightarrow 2CO;\ \Delta H = -220\,kJ$ Which of the following statement is correct for this reaction

(A) Heat of combustion of carbon is 110 kJ (B) Reaction is exothermic
(C) Reaction needs no initiation (D) All of these are correct

B-4.✍ $C\ (s) + O_2\ (g) \longrightarrow CO_2,\ (g);$ $\Delta H = -94.3$ kcal/mol

$CO\ (g) + \frac{1}{2}O_2(g) \longrightarrow CO_2\ (g);$ $\Delta H = -\ 67.4$ kcal/mo!

$O_2(g) \longrightarrow 2O\ (g);$ $\Delta H = 117.4$ kcal/mol
$CO\ (g) \longrightarrow C\ (g) + O(g)\ ;$ $\Delta H = 230.6$ kcal/mol
Calculate ΔH for $C\ (s) \longrightarrow C\ (g)$ in kcal/mol.

(A) 171 (B)154 (C)117 (D)145

Section (C) : Enthalpy of formation & combustion

C-1. Study the following thermochemical equations :

$A \rightarrow B\ ;\ \Delta H = +\ 100$ kcal

$B \rightarrow C\ ;\ \Delta H = -\ 80$ kcal

The correct order of enthalpies of formation of A, B and C is -

(A) A < B < C (B) A < C < B (C) C < A < B (D) B < C < A

C-2.✍ Given, $H_2(g) + Br_2(g) \longrightarrow 2HBr(g), \Delta H^0_1$ and standard enthalpy of condensation of bromine is ΔH^0_2, standard enthalpy of formation of HBr at 25^{0}C is

(A) $\Delta H^0_1 / 2$ (B) $\Delta H^0_1 / 2 + \Delta H^0_2$
(C) $\Delta H^0_1 / 2 - \Delta H^0_2$ (D) $(\Delta H^0_1 - \Delta H^0_2) / 2$

C-3.✍ For the following reaction, $C\ (diamond) + O_2 \longrightarrow CO_2(g)\ ;\ \Delta H = -94.3$ kcal/mol
$C\ (graphite) + O_2 \longrightarrow CO_2(g)\ ;\ \Delta H = -97.6$ kcal/mol

The heat required to change 1 g of $C\ (diamond) \longrightarrow C\ (graphite)$ is

(A) 1.59 kcal (B) 0.1375 kcal (C) 0.55 kcal (D) 0.275 kcal

C-4. The standard heat of combustion of solid boron is equal to :

(A) $\Delta H^\circ_f\ (B_2O_3)$ (B) 1/2 $\Delta H^\circ_f\ (B_2O_3)$ (C) $2\Delta H^\circ_f\ (B_2O_3)$ (D) 1/2 $\Delta H^\circ_f\ (B_2O_3)$

C-5.✍ The heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 1350 kcal/mol. How much of heat will be liberated when 17.1 g of sucrose is burnt ?

(A) 67.5 kcal (B) 13.5 kcal (C) 40.5 kcal (D) 25.5 kcal

C-6. $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl\ (g);\ \Delta H_1$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g);\ \Delta H_2$

$H_2(g) + Cl_2(g) \rightarrow 2HCl\ (g)\ ;\ \Delta H_3$

The enthalpy of formation of NCl_3 (g) in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(A) $\Delta H_f = -\ \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(B) $\Delta H_f = \ \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(D) $\Delta H_f = \ \Delta H_1 + \Delta H_2 - \Delta H_3$

C-7.✍ When a certain amount of ethylene was combusted, 5644 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered into the reaction is :

(A) 268.8 ml (B) 268.8 L (C) 6226 × 22.4 L (D) 22.4 L

C-8._ The values of heat of combustion of ethane (C_2H_6) and ethyne (C_2H_2) are – 341 and – 310 Kcal respectively. Then which of the following is better fuel on mass basis :

(A) C_2H_2 (B) C_2H_6 (C) Both (A) & (B) (D) None of these

Section (D) : Bond enthalpy method & Resonance energy

D-1.✍ If enthalpy of dissociation of CH_4 and C_2H_6 are 320 and 600 calories respectively then bond energy of C–C bond is :

(A) 80 cal (B) 40 cal (C) 60 cal (D) 120 cal

D-2. If enthalpy change for hydrogenation of ethylene is –132 kJ/mole and enthalpy of formation 1,3-butadiene (g) and butane (g) are 115 kJ and –140 kJ/mole respectively then calculate resonance energy of 1,3-budadiene (in kJ).

(A) 9 (B) 18 (C) 4 (D) 10

D-3. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be

(A) – 44.0 kcal (B) – 22.0 kcal (C) 22.0 kcal (D) 44.0 kcal

D-4. AB, A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2, AB & B_2 are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from A_2 and B_2 is – 100 kJ/mol^{-1}. What is the bond enthalpy of A_2.

(A) 400 kJ/mol (B) 200 kJ/mol (C) 100 kJ/mol (D) 300 kJ/mol

Section (E) : Enthalpy of Solution & Born Haber's cycle

E-1. One mole of anhydrous $MgCl_2$ dissolves in water and librates 25 cal/mol of heat. $\Delta H_{hydration}$ of $MgCl_2$ = –30 cal/mol. Heat of dissolution of $MgCl_2.H_2O$ is

(A) +5 cal/mol (B) –5 cal/mol (C) 55 cal/mol (D) –55 cal/mol

E-2._ The enthalpy of solution of NaOH (s) in water is – 41.6 kJ/mole when NaOH is dissolved in water then the temperature of water :

(A) Increase (B) Decrease (C) Does not change (D) Fluctuates

E-3.✍_ The enthalpy change for the reaction of 5 liter of ethylene with 5 liter of H_2 gas at 1.5 atm pressure is $\Delta H = -\ 0.5$ kJ. The value of ΔU will be : (1 atm Lt = 100 J)

(A) – 1.25 kJ (B) + 1.25 kJ (C) 0.25 kJ (D) – 0.25 kJ

E-4_. For which one of the following reaction does the molar enthalpy change of a reaction corresponds to Lattice energy of KBr ?

(A) $KBr(s) \longrightarrow K(s) + \frac{1}{2}Br_2(g)$ (B) $KBr(g) \longrightarrow K(g) + Br(g)$

(C) $KBr(s) \longrightarrow K^+(g) + Br^-(g)$ (D) $KBr(g) \longrightarrow K^+(g) + Br^-(g)$

E-5_.✍ Calculate the lattice energy for the reaction

$Li^+(g) + Cl^-(g) \longrightarrow LiCl(s)$

given that

ΔH_{sub} (Li) = 160 ; ΔH_{diss} (Cl_2) = 244 ; IP(Li) = 520 ;

E_A (Cl) = –365 and ΔH_f (LiCl) = – 400 (all in kJ mole^{-1})

(A) –837 (B) –959 (C) –1567 (D) –37

Section (F) : Enthalpy of neutralization

F-1.✍_ The enthalpy of neutralization of which of the following acid & base is nearly – 13.6 kcal.

(A) HCN and NaOH (B) CH_3COOH and NH_4OH

(C) HCl and KOH (D) HCl and NH_4OH

F-2._ Equal volume of HCOOH and NaOH are mixed. If x is the heat of formation of water, then heat evolved of neutralization is :

(A) more than x (B) equal to x (C) twice of x (D) less than x

F-3. If heat of dissociation of $CHCl_2COOH$ is 0.7 kcal/mole then ΔH for the reaction :

$CHCl_2COOH + KOH \longrightarrow CHCl_2COOK + H_2O$

(A) – 13 kcal (B) + 13 kcal (C) – 14.4 kcal (D) – 13.7 kcal

PART - III : MATCH THE COLUMN

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1. Match the enthalpy change (ΔH) mentioned in list-II for 16 gm O_2 with the various reaction in list-I.

	List-I	**List-II (ΔH in kJ)**	
(P)	$2C_2H_2 + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$, ΔH– 2601 kJ	(1)	–285.8
(Q)	$H_2(g) + 1/2O_2(g) \longrightarrow H_2O(g)$, ΔH= – 285.8 kJ	(2)	–196.75
(R)	$3FeO(s) + 1/2O_2(g) \longrightarrow Fe_3O_4(s)$, ΔH = –302.4 kJ	(3)	–260.1
(S)	$C_{graphite} + O_2(g) \longrightarrow CO_2(g)$, ΔH = –393.5 kJ	(4)	–302.4

Code :

	P	**Q**	**R**	**S**
(A)	4	1	3	2
(B)	3	1	4	2
(C)	3	4	1	2
(D)	2	3	1	4

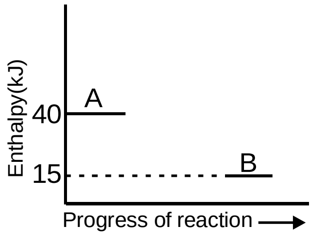
2.✍

Column - I	**Column - II**
(A) $C\ (s, graphite) + O_2(g) \longrightarrow CO_2(g)$	(p) $\Delta H^o_{combustion}$
(B) $C(s, graphite) \longrightarrow C(g)$	(q) $\Delta H^o_{formation}$
(C) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	(r) $\Delta H^o_{atomization}$
(D) $CH_4(g) \longrightarrow C(g) + 4H(g)$	(s) $\Delta H^o_{sublimation}$

Exercise # 2

PART - I : ONLY ONE OPTION CORRECT TYPE QUESTIONS

1. Look at the following diagram :



The enthalpy change for the reaction A → B will be

(A) – 25 kJ (B) – 40 kJ (C) + 25 kJ (D) – 65 kJ

2. In Haber's process of manufacturing of ammonia :

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)\ ;\ H^0_{25°C} = -92.2\ \text{kJ}$$

Molecule	$N_2(g)$	$H_2(g)$	$NH_3(g)$
C_P JK^{-1} mol^{-1}	29.1	28.8	35.1

If C_P is independent of temperature, then reaction at 100°C as compared to that of 25°C will be :

(A) More endothermic (B) Less endothermic (C) More exothermic (D) Less exothermic

3.✍ In the reaction $AB_2(\ell) + 3X_2(g) \rightleftharpoons AX_2(g) + 2BX_2(g)$ $\Delta H = -270$ kcal per mol. of $AB_2(\ell)$, the enthalpies of formation of $AX_2(g)$ & $BX_2(g)$ are in the ratio of 4 : 3 and have opposite sign. The value of ΔH_f^0 $(AB_2(\ell)) = +30$ kcal/mol. Then

(A) ΔH_f^0 $(AX_2) = -96$ kcal /mol (B) ΔH_f^0 $(BX_2) = +480$ kcal /mol

(C) $K_p = K_c$ & ΔH_f^0 $(AX_2) = +480$ kcal /mol (D) $K_p = K_c RT$ & $\Delta H_f^0(AX_2) + \Delta H_f^0(BX_2) = -240$ kcal /mol

4. The heat of formation of $C_2H_5OH(\ell)$ is – 66 kcal/mole. The heat of combustion of CH_3OCH_3 (g) is – 348 kcal/mole. ΔH_f for H_2O and CO_2 are –68 kcal/mole and –94 kcal/mole respectively. Then, the ΔH for the isomerisation reaction $C_2H_5OH(\ell) \longrightarrow CH_3OCH_3(g)$, and ΔE for the same are at T = 25°C

(A) ΔH = 18 kcal/mole, ΔE = 17.301 kcal/mole (B) ΔH = 22 kcal/mole, ΔE = 21.408 kcal/mole

(C) ΔH = 26 kcal/mole, ΔE = 25.709 kcal/mole (D) ΔH = 30 kcal/mole, ΔE = 28.522 kcal/mole

5. Caesium chlorides is formed according to the following equation $Cs(s) + 0.5\ Cl_2(g) \rightarrow CsCl(s)$. The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and –348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is –388.6 kJ mol^{-1}. Calculate the lattice energy of CsCl.

(A) 618.7 kJ mol^{-1} (B) 1237.4 kJ mol^{-1} (C) –1237.4 kJ mol^{-1} (D) –618.7 kJ mol^{-1}

6.✍ The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are –12250 cal/ mol and –13000 cal/ mol respecitively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was –12500 cal/ mol. In what ratio the acid is distributed between AOH and BOH?

(A) 2 : 1 (B) 2 : 3 (C) 1 : 2 (D) None of these

7. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of CH_3COOH will be :

(A) 57.1 kJ $equiv^{-1}$ (B) less than 57.1 kJ $equiv^{-1}$

(C) more than 57.1 kJ $equiv^{-1}$ (D) 13.7 kJ $equiv^{-1}$

8. Given $\Delta_{\text{ioniz}} H^\circ$ (HCN) = 45.2 kJ mol^{-1} and $\Delta_{\text{ioniz}} H^\circ$ (CH_3COOH) = 2.1 kJ mol^{-1}. Which one of the following facts is true ?

(A) pK_a (HCN) = pK_a (CH_3COOH) (B) pK_a (HCN) > pK_a (CH_3COOH)

(C) pK_a (HCN) < pK_a (CH_3COOH) (D) pK_a (HCN) = (45.17/2.07) pK_a (CH_3COOH)

9.✍ The average O–H bond energy in H_2O with the help of following data.

(1) $H_2O(\ell) \longrightarrow H_2O(g)$; ΔH = + 40.6 KJ mol–1
(2) $2H(g) \longrightarrow H_2(g)$; ΔH = – 435.0 KJ mol–1
(3) $O_2(g) \longrightarrow 2O(g)$; ΔH = + 489.6 KJ mol–1
(4) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$; ΔH = – 571.6 KJ mol–1

(A) 584.9 KJ mol^{-1} (B) 279.8 KJ mol^{-1} (C) 462.5 KJ mol^{-1} (D) 925 KJ mol^{-1}

10.✍ Enthalpy of polymerisation of ethylene, as represented by the reaction, $nCH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$ is –100 kJ per mole of ethylene. Given bond enthalpy of C=C bond is 600 kJ mol^{-1}, enthalpy of C–C bond (in kJ mol) will be :

(A) 116.7 (B) 350 (C) 700 (D) indeterminate

11.✍ The average energy required to break a P – P bond in P_4 (s) into gaseous atoms is 53.2 kcal mol^{-1}. The bond dissociation energy of $H_2(g)$ is 104.2 kcal mol^{-1}; ΔH_f^0 of $PH_3(g)$ from $P_4(s)$ is 5.5 kcal mol^{-1}. The P-H bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in $P_4(s)$]

(A) 85.2 (B) 57.6 (C) 76.9 (D) 63.3

PART - II : NUMERICAL TYPE QUESTIONS

1._ If heat of reaction for the given acid-base reaciton :
$HA + NaOH \rightarrow NaA + H_2O$; ΔH = – 4.7 kcal
The heat of dissociation of HA is______ .

2._ The enthalpy of combustion at 25ºC of H_2 (g), cyclohexane and cyclohexene are – 241, – 3920 and –3717 kJmole^{-1} respectively. The heat of hydrogenation of cyclohexene is (Kcal/mole) approximate integer :

3.^✍ When 0.36g of glucose was burned in a bomb calorimeter (Heat capacity 600 JK^{-1}) the temperature rise by 10 K. Calculate the standard molar enthalpy of combustion (MJ/mole).

4.^ For reduction of ferric oxide by hydrogen, $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(\ell)$;
ΔH°_{300} = – 26.72 kJ. The reaction was found to be too exothermic. To be convenient, it is desirable that ΔH° should be at the most – 26 kJ . At what temperature difference it is possible ?
$C_P[Fe_2O_3]$ = 105, $C_P[Fe(s)]$ = 25, $C_P[H_2O(\ell)]$ = 75, $C_P[H_2(g)]$ = 30 (all are in J/mol)

5.^ Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 are mixed. ΔH^0_f for Ca^{+2}(aq), CO^{-2}_3(aq) and $CaCO_3$(s) are – 129.80, – 161.7, – 288.50 kcal mol^{-1} respectively.

6. Calculate the enthalpy change of 1 mole of reaction

$$Na(s) + \frac{1}{2}Br_2(g) \longrightarrow NaBr(s) \text{ in kcal}$$

Given : ΔH_{sub} (Na) = 137 kJ mole^{-1} ; $\Delta H_{\text{bond dissociation}}$ (Br_2(g)) = 144 kJ mole^{-1}

$\Delta H_{\text{1st ionisation}}$(Na(g) = 496 kJ mole^{-1} ; $\Delta H_{\text{1st electron affinity}}$(Br(g) = –325 kJ mole^{-1}

$\Delta H_{\text{Lattice energy}}$ (NaBr) = +742

7_.✍ How many of the following have standard heat of formation is zero.

(i) $Br_{2(\ell)}$ (ii) $CO_{2\,(g)}$ (iii) $C_{(graphite)}$ (iv) $Cl_{2(\ell)}$
(v) $Cl_{2(g)}$ (vi) $F_{2(g)}$ (vii) $F_{(g)}$ (viii) $I_{2(g)}$
(ix) $S_{(monoclinic)}$ (x) $N_{2(g)}$ (xi) $P_{(Black)}$ (xii) $P_{(red)}$
(xiii) CH_4

8._ Standard enthalpy of combustion of cyclopropane is – 2091 kJ/mole at 25ºC then calculate the enthalpy of formation of cyclopropane. If $\Delta H_f^o\,(CO_2) = -\,393.5$ kJ/mole and $\Delta H_f^o\,(H_2O) = -\,285.8$ kJ/mole.

9._ Bond energies of $N \equiv N$; $H - H$ and $N - H$ bonds are 945, 463 & 391 kJ mol^{-1} respectively, the enthalpy of the following reactions is :

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

10._ The reaction of nitrogen with hydrogen to make ammonia has $\Delta H = -\,92$ kJ.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

What is the value of ΔU (in kJ) if the reaction is correct out at a constant pressure of 40 bar and the volume change is – 1.25 litre.

11. Calculate ΔU of reaction for the hydrogenation of acetalene at constant volume and at 77ºC.
Given that $-\Delta H_f\,(H_2O) = -678$ kcal mole; $\Delta H_{comb}(C_2H_2) = -310.1$ kcal/mole
$\Delta H_{comb}\,(C_2H_4) = -337.2$ kcal/Mole

12._ Calculate the C – C bond enthalpy from the following data :

(a) $C\,(s) \rightarrow C\,(g)$; $\Delta H = 170$ Kcal

(b) $\frac{1}{2} H_2\,(g) \rightarrow H\,(g)$; $\Delta H = 52$ Kcal

(c) Heat of formation of ethane = – 20 Kcal

(d) C – H bond enthalpy = 99 Kcal.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1._ Which of the following is(are) endothermic reaction :

(A) Combustion of methane
(B) Decomposition of water
(C) Dehydrogenation of ethane to ethylene
(D) Conversion of graphite to diamond

2._ Heat of reaction depend upon :

(A) Physical state of reactants and products
(B) Whether the reaction is carried out at constant pressure or at constant volume
(C) Method by which the final products are obtained from the reactants
(D) Temperature of the reaction

3._ Which of the following reaction cannot be used to define the heat of formation of CO_2 (g).

(A) $CO\,(g) + \frac{1}{2} O_2 \longrightarrow CO_2\,(g)$

(B) $C_6H_6\,(\ell) + \frac{7}{2} O_2\,(g) \longrightarrow 6CO_2\,(g) + 3H_2O\,(\ell)$

(C) $C\,(diamond) + 2O_2\,(g) \longrightarrow CO_2\,(g)$

(D) $C\,(graphite) + O_2\,(g) \longrightarrow CO_2\,(g)$

4. From the following data at 25°C

Reaction	**$\Delta_r H°$ kJ/mol**
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	–242
$H_2(g) \longrightarrow 2H(g)$	436
$O_2(g) \longrightarrow 2O(g)$	495

Which of the following statement(s) is/are correct:

(A) $\Delta_r H°$ for the reaction $H_2O(g) \longrightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

(B) $\Delta_r H°$ for the reaction $OH(g) \longrightarrow H(g) + O(g)$ is 502 kJ/mol

(C) Enthalpy of formation of H(g) is –218 kJ/mol

(D) Enthalpy of formation of OH(g) is 42 kJ/mol

5._ Heat of formation of CH_4 are :
If given heat :

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -394$ kJ

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$ $\Delta H = -284$ kJ

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$ $\Delta H = -892$ kJ

(A) – 70 kJ (B) – 16.7 kcal (C) – 244 kJ (D) – 50 kcal

6._ Heat of neutralization of the acid-base reaction is 57.32 kJ for :

(A) HCOOH + KOH (B) CH_3COOH + NaOH
(C) HNO_3 + LiOH (D) HCl + NaOH

7.✍_ For which of the following reaction $\Delta H^o_{reaction}$ is not equal to ΔH^o_f of product.

(A) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

(B) $N_2(g) + O_3(g) \longrightarrow N_2O_3(g)$

(C) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(\ell) + 2HCl(g)$

(D) $Xe(g) + 2F_2(g) \longrightarrow XeF_4(g)$

8.✍ Which of the reaction defines molar $\Delta H_f°$?

(A) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

(B) $\frac{1}{2}Br_2(\ell) + \frac{1}{2}H_2(g) \longrightarrow HBr(g)$

(C) $N_2(g) + 2H_2(g) + \frac{3}{2}O_2(g) \longrightarrow NH_4NO_3(s)$

(D) $\frac{1}{2}I_2(s) + \frac{1}{2}H_2(g) \longrightarrow HI(g)$

9._ If $\Delta H^o_{f(C_2H_6)}(g) = -85$ kJ mol^{-1}, $\Delta H^o_{f(C_3H_8)}(g) = -104$ kJmol^{-1}, ΔH^o for $C(s) \rightarrow C(g)$ is 718 kJmol^{-1} and heat of formation of H-atom is 218 kJmol^{-1} then :

(A) $\Delta H_{C-C} = 345$ kJ (B) $\Delta H_{C-H} = 414$ kJ (C) $\Delta H_{H-H} = 436$ kJ (D) $\Delta H_{H-H} = 218$ kJ

PART - IV : COMPREHENSION

Comprehension # 1

Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is

$H^+ (aq) + OH^- (aq) \longrightarrow H_2O (\ell)$; $\Delta_r H^o = -55.84$ kJ/mol

$\Delta H^o_{ionization}$ of aqueous solution of strong acid and strong base is zero.

When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base

$\Delta H^o_{neutrilization} = \Delta H^o_{ionization} + \Delta_r H^o$ $(H^+ + OH^- \rightarrow H_2O)$

1.✍ If enthalpy of neutralization of CH_3COOH by NaOH is –49.86 kJ/mol then enthalpy of ionzation of CH_3COOH is:

(A) 5.98 kJ/mol (B) –5.98 kJ/mol (C) 105.7 kJ/mol (D) None of these

2.✍ What is ΔH^o for complete neutralization of strong diacidic base $A(OH)_2$ by HNO_3 ?

(A) –55.84 kJ (B) –111.68 kJ (C) 55.84 kJ/mol (D) None of these

3.✍ Under the same condition how many mL of 0.1 M NaOH and 0.05 M H_2A (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature :

(A) 25 : 75 (B) 50 : 50 (C) 75 : 25 (D) 66.66 : 33.33

Comprehension # 2

Amount of heat evolved during complete combustion of liquid benzene can be calculated from the following data.

(i) 18 gm of graphite on complete combustion evolve 591 kJ heat

(ii) $\Delta H_f^o (H_2O, \ell)$ = – 286 kJ/mol

(iii) The heat of formation of liquid benzene is 50 kJ /mole

4. Heat of formation of $CO_2(g)$ from following data is-

(A) –286 kJ/mole (B) –590 kJ/mole (C) –394 kJ/mole (D) –3268 kJ/mole

5. Find heat evolved from combustion of 78 gm benzene

(A) 3272 kJ (B) 6345 kJ (C) 4536 kJ (D) 5364 kJ

Exercise # 3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is :

[JEE 2010, 3/163]

(A) $Br_2(g)$ (B) $Cl_2(g)$ (C) $H_2O(g)$ (D) $CH_4(g)$

2. The bond energy (in kcal mol^{-1}) of a C–C single bond is approximately : **[JEE 2010, 3/163]**

(A) 1 (B) 10 (C) 100 (D) 1000

3. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond C_2H_2. That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1}) **[JEE 2012, 3/136]**

$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H = 225$ kJ mol^{-1}

$2C(s) \longrightarrow 2C(g)$ $\Delta H = 1410$ kJ mol^{-1}

$H_2(g) \longrightarrow 2H(g)$ $\Delta H = 330$ kJ mol^{-1}

(A) 1165 (B) 837 (C) 865 (D) 815

4. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25ºC are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25ºC is

[JEE (Advance)2013, 2/120]

(A) +2900 kJ (B) – 2900 kJ (C) –16.11 kJ (D) + 16.11 kJ

Comprehension # 1

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 ºC was measured for the beaker and its contents (**Expt. 1)**. Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt. 2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6 ºC was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

5. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is :

[JEE (Advance)2015, 4/168]

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4

6. The pH of the solution after **Expt. 2** is **[JEE (Advance)2015, 4/168]**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0

7. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are **[JEE (Advance)2017]**

$\Delta_f G°$ [C(graphite)] = 0 kJ mol^{-1}

$\Delta_f G°$ [C(diamond)] = 2.9 kJ mol^{-1}

The standard state means that the pressure should be 1 bar , and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : 1 J = 1 kg m^2 s^{-2} ; 1 Pa = 1 kg m^{-1} s^{-2} ; 1 bar = 10^5 Pa]

(A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar

8. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. **[JEE(Advanced) 2019]**

(A) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$ (B) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

(C) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (D) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

9. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

At 298 K : $\Delta_f H^o(SnO2(s)) = -581.0$ kJ mol^{-1}, $fH^o(CO_2(g)) = -394.0$ kJ mol^{-1}

$S^o(SnO_2(s)) = 56.0$ j K^{-1}mol^{-1}, S^o (Sn(s)) = 52.0 j K^{-1} mol^{-1}

S^o(C (s)) = 6.0 JK^{-1} mol^{-1} , $S^o(CO_2(g)) = 210.0$ JK^{-1} mol^{-1}. **[JEE(Advanced) 2020]**

Assume that the enthalpies and the entropies are temperature independent.

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is **[AIEEE 2006]**

(R = 8.314 J K^{-1} mol^{-1})

(1) 1238.78 J mol^{-1} (2) -2477.57 J mol^{-1} (3) 2477.57 J mol^{-1} (4) –1238.78 J mol^{-1}

2. The standard enthalpy of formation ($\Delta H_f°$) at 398 K for methane, $CH_{4(g)}$ is 74.8 kJ mol^{-1}. The additional information required to determine the average energy for C - H bond formation would be :**[AIEEE 2007, 3/120]**

(1) the dissociation energy of H_2 and enthalpy of sublimation of carbon

(2) latent heat of vapourisation of methane

(3) the first four ionization energies of carbon and electron gain enthalpy of hydrogen

(4) the dissociation energy of hydrogen molecule, H_2

3. On the basis of the following thermochemical data : ($\Delta_f G^o H^+_{(aq)} = 0$) **[AIEEE 2009, 8/144]**

$H_2O(\ell) \longrightarrow H^+ (aq) + OH^- (aq.)$; $\Delta H = 57.32$ kJ

$H_2(g) + \frac{1}{2} O_2 (g) \longrightarrow H_2O (\ell)$; $\Delta H = -286.20$ kJ

The value of enthalpy of formation of OH^- ion at 25ºC is :

(1) –228.88 kJ (2) +228.88 kJ (3) –343.52 kJ (4) –22.88 kJ

4. The standard enthalpy of formation of NH_3 is – 46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is – 436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N – H bond in NH_3 is

[AIEEE 2010, 4/144]

(1) – 964 kJ mol^{-1} (2) + 352 kJ mol^{-1} (3) + 1056 kJ mol^{-1} (4) – 1102 kJ mol^{-1}

5. The value of enthalpy change (ΔH) for the reaction, $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ at 27°C is –1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be :

[AIEEE 2011, 4/120]

(1) –1369.0 kJ (2) –1364.0 kJ (3) –1361.5 kJ (4) –1371.5 kJ

6. Consider the reaction : $4NO_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$, $\Delta_r H = -111$ kJ.

If $N_2O_{5(s)}$ is formed instead of $N_2O_{5(g)}$ in the above reaction, the $\Delta_r H$ value will be:

(given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) **[AIEEE 2011, 4/120]**

(1) + 54kJ (2) + 219 kJ (3) – 219 kJ (4) – 165 kJ

7. For complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, $\Delta_C H$, for the reaction will be : (R = 8.314 kJ mol^{-1}) **[JEE(Main) 2014, 4/120]**

(1) – 1366.95 kJ mol^{-1} (2) – 1361.95 kJ mol^{-1} (3) – 1460.50 kJ mol^{-1} (4) – 1350.50 kJ mol^{-1}

8. The heat of atomixation of methane and ethane are 360 kJ/mol and 620 kJ/mol, respectively. The longest wavelength of light capable of breaking the C–C bond is :
(Avogadro number = 6.02×10^{23}, h = 6.62×10^{-34} J s) **[JEE(Main, Online) 2015, 4/120]**
(1) 2.48×10^{3} nm (2) 1.49×10^{3} nm (3) 2.49×10^{4} nm (4) 2.48×10^{4} nm

9. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE(Main) 2016, 4/120]**
(1) 676.5 (2) – 676.5 (3) –110.5 (4) 110.5

10. For a reaction, A(g) $\rightarrow$ A (l); $\Delta H = -3RT$. The correct statement for the reaction is :
[JEE(Main) 2017 Online (08-04-17), 4/120]
(1) $\Delta H = \Delta U \neq O$ (2) $|\Delta H| > |\Delta U|$ (3) $|\Delta H| < |\Delta U|$ (4) $\Delta H = |\Delta U| = O$

11. For which of the following reactions, ΔH is equal to ΔU ? **[JEE(Main) 2018 Online (15-04-18), 4/120]**
(1) $N_2(g) + 3H2(g) \rightarrow 2NH_3(g)$ (2) $2HI(g) \rightarrow H_2(g) + I_2(g)$
(3) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (4) $2NO_2(g) \rightarrow N_2O_4(g)$

12. The standard heat of formation $\left(\Delta_f H^0_{298}\right)$ of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are –1560, –393.5 and –286 kJ/mol, respectively is _______
[JEE(Main) 2020 Online Jan. 4/100]

13. The heat of combustion of ethanol into carbon dioxides and water is –327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is
(R = 2 cal mol^{-1} K^{-1}) **[JEE(Main) 2020 Online Sept. 4/100]**

14. The internal energy change (in J) when 90g of water undergoes complete evaporation at 100ºC is ____.
(Given : ΔH_{vap} for water at 373 K = 41 kJ/mol, R = 8.314 JK^{-1} mol^{-1})
[JEE(Main) 2020 Online Sept. 4/100]

ANSWER KEY

EXERCISE - 1

PART - I

A-1. $\Delta H < \Delta U$
A-2. –1368 kJ mol^{-1}
A-3. –4.955 kJ
A-4. –209.41
B-1. Exothermic A, C, D; endothermic : B, E
B-2. – 2035 kJ mol^{-1}
B-3. – 56.98 kJ mol^{-1}
C-1. (–94.1 kcal)
C-2. –266 kJ/mol and –825 kJ/mol
C-3. – 383 kJ mol^{-1}
C-4. 24 g
D-1. 243.7 kJ mol^{-1}
D-2. 1488 kJ mol^{-1}.
D-3. – 2573 kJ/mole
D-4. 275 kJ/mol
D-5. (–84 kcal / mol)
D-6. 309 kJ mol^{-1}
E-1. – 65.3 kJ mol^{-1}
E-2. – 28 kJ/mole
E-3. 3890 $kJmole^{-1}$
F-1. 2a = b
F-2. – 228 kJ/mole.
F-3. 11.2 Kcal

PART - II

A–1.	(C)	**A–2.**	(C)	**A-3.**	(D)	**A-4.**	(D)	**A-5.**	(B)
B-1.	(D)	**B-2.**	(A)	**B-3.**	(B)	**B-4.**	(D)	**C-1.**	(B)
C-2.	(D)	**C-3.**	(D)	**C-4.**	(B)	**C-5.**	(A)	**C-6.**	(B)
C-7.	(B)	**C-8.**	(A)	**D-1.**	(D)	**D-2.**	(A)	**D-3.**	(B)
D-4.	(A)	**E-1.**	(A)	**E-2.**	(A)	**E-3.**	(C)	**E-4.**	(C)
E-5.	(A)	**F-1.**	(C)	**F-2.**	(D)	**F-3.**	(A)		

PART - III

1. (B)

2. (A) → (p, q) ; (B) → (q, r, s) ; (C) → (p) ; (D) → (r)

EXERCISE - 2

PART - I

1.	(A)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(A)
6.	(A)	**7.**	(B)	**8.**	(B)	**9.**	(C)	**10.**	(B)
11.	(C)								

PART - II

1.	9	**2.**	9 Kcal/mole	**3.**	3	**4.**	9	**5.**	3
6.	7	**7.**	5	**8.**	53	**9.**	+ 93 kJ	**10.**	87
11.	40	**12.**	78 Kcal						

PART - III

1.	(BCD)	**2.**	(ABD)	**3.**	(ABC)	**4.**	(AD)	**5.**	(AB)
6.	(CD)	**7.**	(ABC)	**8.**	(BCD)	**9.**	(ABC)		

PART - IV

1.	(A)	**2.**	(B)	**3.**	(B)	**4.**	(C)	**5.**	(A)

EXERCISE - 3

PART - I

1.	(B)	**2.**	(C)	**3.**	(D)	**4.**	(C)	**5.**	(A)
6.	(B)	**7.**	(A)	**8.**	(AB)	**9.**	935		

PART - II

1.	(1)	**2.**	(1)	**3.**	(1)	**4.**	(2)	**5.**	(2)
6.	(3)	**7.**	(1)	**8.**	(2)	**9.**	(3)	**10.**	(2)
11.	(2)	**12.**	–192.50 or –85.00	**13.**	–326400.00				
14.	189000.00 to 190000.00								

Reliable Ranker Problems

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1._ Which of the following is true for an adiabatic process :

(A) $\Delta H = 0$ (B) $\Delta W = 0$ (C) $\Delta Q = 0$ (D) $\Delta V = 0$

2._ Which of the following is not a state function :

(A) ΔS (B) ΔG (C) ΔH (D) ΔQ

3._ The relation between ΔU and ΔH is :

(A) $\Delta H = \Delta U - P\Delta V$ (B) $\Delta H = \Delta U + P\Delta V$ (C) $\Delta U = \Delta V + \Delta H$ (D) $\Delta U = \Delta H + P\Delta V$

4._ The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25ºC is :

(A) $2.303 \times 298 \times 0.082 \log 2$

(B) $298 \times 10^7 \times 8.31 \times 2.303 \log 2$

(C) $2.303 \times 298 \times 0.082 \log 0.5$

(D) $8.31 \times 10^7 \times 298 - 2.303 \log 0.5$

5. The molar heat capacities at constant pressure (assumed constant with respect to temperature) at A,B and C are in ratio of 3 : 1.5 : 2.0 The enthalpy change for the exothermic reaction $A + 2B \longrightarrow 3C$ at 300 K and 310 K is ΔH_{300} and ΔH_{310} respectively then :

(A) $\Delta H_{300} > \Delta H_{310}$ (B) $\Delta H_{300} < \Delta H_{310}$ (C) $\Delta H_{300} = \Delta H_{310}$

(D) if $T_2 > T_1$ then $\Delta H_{310} > \Delta H_{300}$ and if $T_2 < T_1$ then $\Delta H_{310} < \Delta H_{300}$

6. Heat of combustion of ethanol at constant pressure and at temperature TK (= 298 K) is found to be $-q$ J mol^{-1}. Hence, heat of combustion (in J mol^{-1}) of ethanol at the same temperature at constant volume will be:

(A) $RT - q$ (B) $-(q + RT)$ (C) $q - RT$ (D) $q + RT$

7. Benzene burns according to the following equation at 300 K (R = 25/3 J mole^{-1}K^{-1})

$$2C_6H_6(\ell) + 15\,O_2\,(g) \rightarrow 12\,CO_2\,(g) + 6H_2O(\ell) \qquad \Delta H^o = -\,6547.5\text{ KJ}$$

What is the ΔE^o for the combustion of 1.5 mol of benzene

(A) –3271 kJ (B) –9813 kJ (C) –4905 kJ (D) –9810 kJ

8. Which statement regarding entropy is correct ?

(A) A completely ordered deck of cards has more entropy than a shuffled deck in which cards are arranged randomly.

(B) A perfect ordered crystal of solid nitrous oxide has more entropy than a disordered crystal in which the molecules are oriented randomly.

(C) 1 mole N_2 gas at STP has more entropy than 1 mole N_2 gas at 273 K in a volume of 11.2 litre.

(D) 1 mole N_2 gas at STP has more entropy than 1 mole N_2 gas at 273 K and 0.25 atm.

9. The enthalpy change for the reaction of 50 mL of ethylene with 50.0 mL of H_2 at 1.5 atm pressure is $\Delta H = -0.31$ KJ. What is the ΔE ?

(A) – 0.3024 (B) – 0.6048 (C) – 0.1.2 (D) None

10. 130 g of Zn is dissolved in dilute sulphuric acid in an open beaker at 27ºC. Find the work done in the process assuming isothermal operation.

(A) – 1200 cal (B) – 1800 cal (C) + 1800 cal (D) +1200 cal

11. The enthalpy of combustion of propane (C_3H_8) gas in terms of given data is :

Bond energy (kJ/mol)

ε_{C-H}	$\varepsilon_{O=O}$	$\varepsilon_{C=O}$	ε_{O-H}	ε_{C-C}
$+x_1$	$+x_2$	$+x_3$	$+x_4$	$+x_5$

Resonance energy of CO_2 is – zkJ/mol and $\Delta H_{vaporization}$ [$H_2O(\ell)$] is ykJ/mol.

(A) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - 4y - 3z$ (B) $6x_1 + x_5 + 5x_2 - 3x_3 - 4x_4 - 4y - 3z$

(C) $8x_1 + 2x_5 + 5x_2 - 6x_3 - 8x_4 - y - z$ (D) $8x_1 + x_5 + 5x_2 - 6x_3 - 8x_4 - 4y + 3z$

12. If x_1, x_2 and x_3 are enthalpies of H–H, O=O and O–H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen.

(A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$ (C) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (D) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

13. $NH_3(g) + 3Cl_2(g) \longrightarrow NCl_3(g) + 3HCl(g)\,;$ ΔH_1

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)\,;$ ΔH_2

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)\,;$ ΔH_3

The heat of formation of $NCl_3(g)$ in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) None

14. Find the enthalpy of S–S bond from the following data.

(i) C_2H_5–S–C_2H_5(g) $\Delta H^o_f = -147.2$ kJ/mol

(ii) C_2H_5–S–S–C_2H_5(g) $\Delta H^o_f = -201.9$ kJ/mol

(iii) S (g) $\Delta H^o_f = 222.8$ kJ/mol

(A) – 168.1 kJ/mol (B) + 168.1 kJ/mol (C) – 277.5 kJ/mol (D) + 277.5 kJ/mol

15. Given the following equations and ΔH^o values, determine the enthalpy of reaction at 298 K for the reaction :

$$C_2H_4\ (g) + 6F_2\ (g) \longrightarrow 2CF_4\ (g) + 4HF\ (g)$$
$$H_2\ (g) + F_2\ (g) \longrightarrow 2HF\ (g)\ ;\ \Delta H^o_1 = -537\ kJ$$
$$C\ (s) + 2F_2\ (g) \longrightarrow CF_4\ (g)\ ;\ \Delta H^o_2 = -680\ kJ$$
$$2C\ (s) + 2H_2\ (g) \longrightarrow C_2H_4\ (g)\ ;\ \Delta H^o_3 = 52\ kJ$$

(A) –1165 (B) –2486 (C) +1165 (D) +2486

16. Animals operate under conditions of constant pressure and most of the process that maintain life are isothermal (in a broad sense) . How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature) ? The entropy change is + 182. 4 JK^{-1} for the reaction stated above.

$\Delta H_{combustion}$ [glucose] = –2808 KJ

(A) – 2754.4 KJ (B) – 2864.5 KJ (C) – 56.5 KJ (D) – 2808 KJ

17. From the given table answer the following question :

	CO (g)	CO_2 (g)	H_2O(g)	H_2(g)
ΔH^o_{298}(–Kcal/ mole)	– 26. 42	– 94.05	– 57 .8	0
ΔG^o_{298}(–Kcal/ mole)	– 32 .79	– 94 .24	– 54 .64	0
S^o_{298}(– Cal/ K mol)	47.3	51.1	?	31.2

Reaction : $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2\ (g)$

Calculate $S^o_{298}\ [H_2O(g)]$

(A) – 119.47 Cal/ K mole (B) + 119.47 Cal/ K mole

(C) – 45.13 Cal/ K mole (D) + 45.13 Cal/ K mole

18. One gram sample of oxygen undergoes free expansion in insulated container from 0.75 L to 3.0 L at 298 K. Calculate ΔS, q, w, ΔH and ΔE.

(A) $\Delta S = 0.36\ JK^{-1}$, $\Delta E = 0$ (B) W = 227.97 J, $\Delta E = 0$

(C) q = – 227.97 J, $\Delta E = 0$ (D) W = 227.97 J, $\Delta H = 0$

19. Given that : $\Delta G_f°$ (CuO)=–30.4 kcal/mole

$\Delta G_f°$ (Cu_2O) = –34.98 kca/mole T = 298 K

Now on the basis of above data which of the following predictions will be most appropriate under the standard conditions and reversible reaction.

(A) Finely divided form of CuO kept in excess O_2 would be completely converted to Cu_2O

(B) Finely divided form of Cu_2O kept in excess O_2 would be completely converted to CuO

(C) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of CuO)

(D) Finely divided form of CuO kept in excess O_2 would be converted to a mixture of CuO and Cu_2O (having more of Cu_2O)

20. Calculate Δ_fG^o for (NH_4Cl, s) at 310 K.

Given : Δ_fH^o (NH_4Cl, s)=–314.5 kJ/mol; $\Delta_rC_p = 0$

$S^o_{N_2(g)} = 192\ JK^{-1}\ mol^{-1}$; $S^o_{H_2(g)} = 130.5\ JK^{-1}\ mol^{-1}$;

$S^o_{Cl_2}(g) = 233\ JK^{-1}\ mol^{-1}$; $S^o_{NH_4Cl(s)} = 99.5\ JK^{-1}\ mol_{/}^{-1}$

All given data are at 300 K.

(A) –198.56 kJ/mol (B) –426.7 kJ/mol (C) –202.3 kJ/mol (D) None of these

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. A coffee cup calorimeter initially contains 125 g of water, at a temperature of 24.2ºC. 8 g of ammonium nitrate (NH_4NO_3), also at 24.2ºC, is added to the water, and the final temperature is 18.2ºC. what is the heat of solution of ammonium nitrate in kJ/mol ? The specific heat capacity of the solution is 4.2 J/ºC g.

22. When 1.0 g of oxalic acid ($H_2C_2O_4$) is burned in a bomb calorimeter whose heat capacity is 8.75 kJ/K, the temperature increases by 0.312 K. The enthalpy of combustion of oxalic acid at 27ºC is :

23. Ethyl chloride(C_2H_5Cl), is prepared by reaction of ethylene with hydrogen chloride :

$$C_2H_4\,(g) + HCl\,(g) \rightarrow C_2H_5Cl\,(g) \qquad \Delta H = -\,72.3 \text{ kJ/mol.}$$

What is the value of ΔE (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K.

24. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27ºC in a cylinder fitted with a piston. Find the work done for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction.

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

25. When 0.1 mole of ice melt at 0ºC and at constant pressure of 1 atm 144 calories of heat are absorbed by the system. Calculate ΔH for the reaction (in Cal.).

PART - 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	: +3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	: 0	If none of the bubbles is darkened.
Negative Marks	: –1	In all other cases

1. A new flurocarbon of molar mass 102 g mol^{-1} was placed in an electrically heated vessel. When the pressure was 650 torr, the liquid boiled at 77ºC. After the boiling point had been reached, it was found that a current of 0.25 A from a 12.0 volt supply passed for 600 sec vaporises 1.8g of the sample. The molar enthalpy & internal energy of vaporisation of new flourocarbon will be :

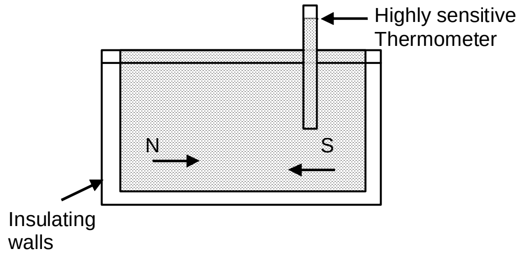
(A) ΔH = 102 kJ/mol, ΔE = 99.1 kJ/mol

(B) ΔH = 95 kJ/mol, ΔE = 100.3 kJ/mol

(C) ΔH = 107 kJ/mol, ΔE = 105.1 kJ/mol

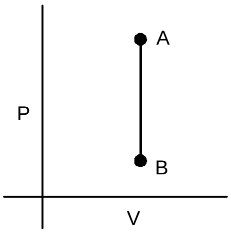
(D) ΔH = 92.7 kJ/mol, ΔE = 97.4 kJ/mol

2. Two opposite poles magnetic are moving towards each other very slowly in a water both. What will be the reading of thermometer.



(A) Increase (B) Decrease (C) No change (D) Data insufficient

3. Which of the following statements is/are correct regarding the following process :



(A) $dW = -P_{ext}.dv = 0$; Only if the system is undergoing only P–V work.
(B) $dW = -P_{ext}.dv = 0$; Irrespective of any type of work done by the system.
(C) $dU \neq dq_v$
(D) $dW \neq 0$

4. 1 mole of an ideal diatomic gas undergoes a reversible polytropic process (PV^2 = constant). The gas expand from initial volume of 1 litre and temp 300 K to find volume 3 lit. Calculate change in internal energy (approx.)
(A) –4.0 kJ (B) –4.2 kJ (C) –4.4 kJ (D) –4.6 kJ

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.
Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.
Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : –1 In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

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5. Which of the following statement(s) is/are ture?
(A) $\Delta E = 0$ for combustion of $C_2H_6(g)$ in a sealed rigid adiabatic container
(B) $\Delta_f H^o$ (S, monoclinic) $\neq 0$
(C) If dissociation energy of CH_4 (g) is 1656 kJ/mol and C_2H_6(g) is 2812 kJ/mol, then value of C—C bond energy will be 328 kJ/mol
(D) If $\Delta H_f(H_2O,g) = -242$ kJ/mol; $\Delta H_{vap}(H_2O, l) = 44$ kJ/mol then $\Delta_f H^o$ (OH^- ,aq.) will be – 142 kJ/mol

6. From the following data, mark the option(s) where ΔH is correctly written for the given reaction.
Given : $H^+ (aq) + OH^- (aq) \longrightarrow H_2O(\ell)$; $\Delta H = -57.3$ kJ
$\Delta H_{solution}$ of HA(g) = –70.7 kJ/mol
$\Delta H_{solution}$ of BOH(g) = 20 kJ/mol
$\Delta H_{ionization}$ of HA = 15 kJ/mol and BOH is a strong base.

Reaction	**ΔH_r (kJ/mol)**
(A) $HA(aq) + BOH(aq) \longrightarrow BA(aq) + H_2O$	–42.3
(B) $HA(g) + BOH(g) \longrightarrow BA(aq) + H_2O$	–93
(C) $HA(g) \longrightarrow H^+(aq) + A^- (aq)$	–55.7
(D) $B^+(aq) + OH^-(aq) \longrightarrow BOH(aq)$	–20

7. The value of $\Delta H_{transition}$ of C (graphite) $\longrightarrow$ C (diamond) is 1.9 kJ/mol at 25ºC entropy of graphite is higher than entropy of diamond. This implies that :
(A) C (diamond) is more thermodynamically stable then C (graphite) at 25ºC
(B) C (graphite) is more thermodynamically stable than C (diamond) at 25ºC
(C) diamond will provide more heat on complete combustion at 25ºC
(D) $\Delta G_{transition}$ of C (diamond) $\longrightarrow$ C (graphite) is –ve

8. Which of the following statement(s) is/are false ?
(A) All adiabatic processes are isoentropic (or isentropic) processes
(B) When $(\Delta G_{system})_{T,P} < 0$; the reaction must be exothermic
(C) $dG = VdP - SdT$ is applicable for closed system, both PV and non–PV work
(D) the heat of vaporisation of water at 100ºC is 40.6 kJ/mol. When 9 g of water vapour condenses to liquid at 100ºC of 1 atm, then ΔS_{system} = 54.42 J/K

9. For the reaction $2Ag_2O\ (s) \longrightarrow 4Ag(s) + O_2\ (g)$, ΔH is 61.17 kJ mol^{-1} and ΔS is 132 J K^{-1} mol^{-1}. Compute the temperature above which the given reaction will be spontaneous.
(A) T > 463.4 K (B) T > 190.25^0 C (C) T < 190.25^0 C (D) T < 463.4 K

10. Select the correct enthalpy at corresponding temperature using following datas
(i) Heat capacity of solid from 0 K to normal melting point 200 K
$C_{P,m}(s) = 0.035\,T$ JK^{-1} mol^{-1}.
(ii) Enthalpy of fusion = 7.5 KJ mol^{-1},
(iii) Enthalpy of vaporisation = 30 KJ mol^{-1}.
(iv) Heat capacity of liquid form 200 K to normal boiling point 300 K
$C_{P,m}(\ell) = 60 + 0.016\,T$ JK^{-1} mol^{-1}.
(v) Heat capacity of gas from 300 K to 600 K at 1 atm
$C_{P,m}(g) = 50.0$ JK^{-1} mol^{-1}.
(A) $S_{200\,(s)} = 7$ (B) $S_{300\,(\ell)} = 70.43$ (C) $S_{300\,(g)} = 170.43$ (D) $S_{600\,(g)} = 205.09$

11. Which of the following is/are correct. (Consider all gases are ideal & reaction occure at const. tempreture & pressure.

(A) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ (–ve P-V work)

(B) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ (–ve P-V work)

(C) $Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ (Non zero non P-V work)

(D) $NaCl(s) \xrightarrow{aq} Na^+(aq) + Cl^-(aq)$ (Non zero non P-V work)

12. 0.5 mole each of two ideal gases A $\left(C_{v,m} = \frac{5}{2}R\right)$ and B ($C_{v,m}$ = 3R) are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K and 250 K. Then for the process :
(A) $\Delta U = -100$ R (B) $\Delta U = -275$ R (C) $\Delta H = -375$ R (D) $\Delta H = -300$ R

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +3 If ONLY the correct numerical value is entered as answer.

  Zero Marks : 0 In all other cases.

13. Two moles of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)

Calculate the magnitude of work (W) done in L.atm

14. The enthalpy of combustion of mol. wt. 180 glucose is – 2808 KJmol^{-1} at 25ºC. X and Y grams of glucose do you need to consume respectively cases [Assume wt = 62.5 Kg].

(a) to climb a flight of stairs rising through 3M. (b) to climb a mountain of altitude 6000 M ?

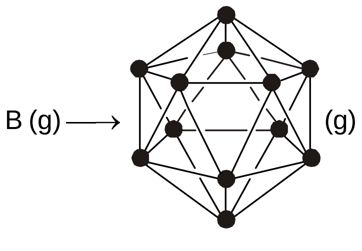
Assume that 25% of enthalpy can be converted to useful work.

X and Y are related as Y = mX; then find m/1000.

15. A sample of certain mass of an ideal polyatomic gas is expanded against constant pressure of 1 atm adiabatically from volume 2 L, pressure 6 atm and temperature 300 K to state where its final volume is 8L. Then calculate entropy change (in J / K) in the process. (Neglect vibrational degrees of freedom) [1L atm = 100 J, log 2 = 0.3, log 3 = 0.48, log e = 2.3] (aproximate integer)

16. The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are –94 & –68 kcal respectively. Given that heat of atomisation of C(s) & H_2(g) are 150 & 100 kcal respectively and C–H bond energy is 95 kcal. Calculate $\frac{\Delta H_{C\equiv C}}{22}$.

17. Boron exist in different allotropic forms. All allotropic form contains icosahedral units (icosahedral is a regular shape with 12 corners & 20 faces) with boron atoms at all 12 corners and all bonds are equivalent.



Calculate heat evolved at constant pressure (in kJ) per mole of boron atoms undergoing above change if ΔH_{BE}(B–B) = 200 kJ/mol. Report you Answer after dividing by 100

18. 1 mole of an ideal gas is allowed to expand isothermally at 27ºC till its volume is tripled . If the expansion is carried out reversibly then the $\Delta S_{universe}$ will be ?

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

1. Which of the following expression is correct ? **[NSEC–2002]**
(A) E = H + PV (B) H = E + PV (C) H = E – PV (D) P = E + HV

2. Iron metal is produced commercially by reducing iron (III) oxide in iron ore with carbon monoxide :
(a) Write down the balanced chemical equation for the above reduction of iron (III) oxide ?
(b) Enthalpies of formation for various substances at 25°C are given in the following table.

	$Fe_2O_{3(x)}$	$CO_{(g)}$	$Fe_{(x)}$	$CO2_{(g)}$
ΔH°_f (kJ/mol)	–824.2	–110.5	0	–393.5
S° [J/(K.mol)]	87.4	197.6	27.3	213.6

Calculate the standard free–energy change for this reaction at 25°C ?
(c) Is the reaction spontaneous at 25°C ?
(d) Does the reverse reaction become spontaneous at higher temperature ? Explain. **[NSEC–2002]**

3. If the bond energies are as follows **[NSEC–2008]**
(i) C–H = 413.8kJ (ii) Cl–Cl = 238.0 kJ (iii) C–Cl = 327.2 kJ (iv) H–Cl = 429.8 kJ
the enthalpy of the reaction : $CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$ will be
(A) +202.6 kJ (B) –202.6 kJ (C) +220.1 kJ (D) +870 kJ

4. The enthalpy changes for the following reactions are : **[NSEC–2012]**
$C_{diamond} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -395.3$ kJ mol^{-1}
$C_{graphite} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.4$ kJ mol^{-1}
The enthalpy change for the transition
$C_{diamond} \longrightarrow C_{graphite}$ will be :
(A) – 3.8 kJ mol^{-1} (B) + 3.8 kJ mol^{-1} (C) – 1.9 kJ mol^{-1} (D) + 1.9 kJ mol^{-1}

5. For a chemical reaction ΔH is negative and ΔS is positive. This reaction is **[NSEC–2013]**
(A) spontaneous at all temperatures (B) nonspontaneous at all temperature
(C) spontaneous only at high temperature (D) spontaneous only at low temperature

6. 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat energy. What is the enthalpy of vapourisation of ethanol ? **[NSEC–2013]**
(A) 43.42 kJ (B) 47.0 kJ (C) 21.75 kJ (D) 435.0 kJ

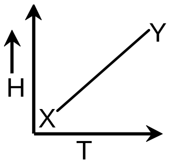
7. Two samples A and B of an ideal gas, initially at same temperature and pressure, are compressed from volume V to V/2, isothermally for A and adiabatically for B. The final pressure of A will be **[NSEC–2014]**
(A) greater than that of B (B) less than that of B (C) twice that of B (D) equal to that at B

8. The heat of formation of ethanol, from the following data is **[NSEC–2014]**
$C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$ –1368 kJ
$\Delta H_f CO_2(g) = -393.5$ kJ/mol; $\Delta H_f H_2O(\ell) = -286$ kJ/mol
(A) – 277 kJ/mol (B) – 1260.5 kJ/mol (C) – 688.5 kJ/mol (D) – 3013 kJ/mol

9. N_2 gas stored in a cylinder, fixed with a movable piston, undergoes adiabatic expansion. The statement that is true for the given situation is **[NSEC–2014]**
(A) q = W (B) ΔU = W (C) ΔU = 0 (D) ΔU = q

10. The enthalpy of vaporization of benzene is +35.3 kJ/mol at its boiling point of 80°C. The entropy change in the transition of vapour of liquid at its boiling point is **[NSEC–2014]**
(A) –100 (B) +100 (C) +342 (D) –342

11. The process in which an ideal gas undergoes change from X to Y as shown in the following diagram is



[NSEC–2015]

(A) isothermal compression (B) adiabatic compression
(C) isothermal expansion (D) adiabatic expansion

12. Glucose when dissolved in water leads to cooling of the solution. Suppose you take 250 mL water at room temperature in an open container (such as a bowl) made of thermally insulated material and dissolve a spoonful' of glucose in it. If you are able to accurately measure the heat absorbed by this solution in reaching back to room temperature (assuming negligible changes in the composition and the amount of solution during this process), you will be measuring **[NSEC–2015]**
(A) The enthalpy of dissolution of the glucose in water
(B) The Gibbs free energy of dissolution of the glucose in Water
(C) The work done by the atmosphere on the system during the dissolution process
(D) The heat capacity of the solution

13. An ideal gas taken in an insulated chamber is released into interstellar space. The statement that is nearly true for this process is **[NSEC–2015]**
(A) $Q = 0, W \neq 0$ (B) $W = 0, Q \neq 0$ (C) $\Delta U = 0, Q \neq 0$ (D) $Q = W = \Delta U = 0$

14. Standard molar enthalpy of formation of $CO_2(g)$ is equal to **[NSEC–2016]**
(A) Zero
(B) The standard molar enthalpy of combustion of carbon (graphite)
(C) The standard molar enthalpy of combustion of C(g)
(D) The standard molar enthalpy of combustion of CO(g)

15. For the conversion $CCl_4(\ell) \rightarrow CCl_4(g)$ at 1 bar and 350 K, the correct set of thermodynamic parameters is (Boiling point of CCl_4 is 77ºC) **[NSEC–2016]**
(A) $\Delta G = 0, \Delta S = +ve$ (B) $\Delta G = 0, \Delta S = -ve$ (C) $\Delta G = -ve, \Delta S = 0$ (D) $\Delta G = -ve, \Delta S = +ve$

16. Which reaction is spontaneous at all temperatures at standard pressure and concentration ?
(A) exothermic reaction with a decrease in entropy **[NSEC–2016]**
(B) exothermic reaction with an increase in entropy
(C) endothermic reaction with a decrease in entropy
(D) endothermic reaction with an increase in entropy

17. Given $\Delta_r H^o = -54.08 kJ\ mol^{-1}$ and $\Delta_r S^o = 10.0\ J\ mol^{-1}$ at 25ºC, the value of log10K for the reaction

$A \rightleftharpoons B$ is **[NSEC–2016]**
(A) 3.4 (B) 10 (C) 0.53 (D) 113

18. Three samples of 100 g of water (samples I, II and III), initially kept at 1 atm pressure and 298 K were given the following treatments.
Sample I was heated to 320 K and cooled to 298 K
Sample II was heated to 300 K, cooled to 273 K and heated to 298 K
Sample III was heated to 373 K and cooled to 298 K
At the end of these processes, the internal energy of **[NSEC–2017]**
(A) III is the highest
(B) II is the highest
(C) I and III are the same, II is lower than that of I and III
(D) I, II and III are the same

19. For the following spontaneous process $H_2O_{(l)} \rightarrow H_2O_{(s)}$ at 268 K, which of the following is true? **[NSEC–2017]**

(A) $\Delta S_{sys} < 0$ (B) $\Delta S_{sys} > 0$ (C) $\Delta S_{surr} < 0$ (D) $\Delta S_{sys} = -\Delta S_{surr}$

20. At constant volume, 6.0 mol of H_2 gas at 0ºC and 100 kPa was heated to 250 kPa. The molar heat of H_2 at constant pressure (C_P) = 28.9 J mol^{-1}. (Assume that the heat capacity values do not change with temperature). The final temperature of the H_2 gas and the change in entropy of the process are **[NSEC–2017]**

(A) 273ºC and 113 kJ mol^{-1} K^{-1} (B) 410ºC and 158.8 J mol^{-1} K^{-1}

(C) 682.5ºC and 113 J mol^{-1} K^{-1} (D) 682.5 K and 113 J mol^{-1} K^{-1}

21. Hydrazine used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equations

$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ ($\Delta H^o_{reaction} = -241$kJ/mol)

If ΔH^o (formation) of NH_3, H_2O_2 and H_2O are –46.1, –187.8 and –285.8kJ/mol respectively, ΔH^o for the decomposition of hydrazine into N_2 and H_2 is **[NSEC–2017]**

(A) 50.6 kJ/mol (B) 241 kJ/mol (C) –50.6 kJ/mol (D) 120.5 kJ/mol

22. At 298 K, change in internal energy for the complete combustion of fullerene, C_{60}(s), an allotrope of carbon, and the enthalpy of formation of CO_2(g) are –25970 kJ mol^{-1} and –393 kJ mol^{-1} respectively. The enthalpy of formation of C_{60}(s) at 298 K is **[NSEC–2018]**

(A) –2390 kJ (B) 4.95 × 104 kJ (C) 2.60 × 104 kJ (D) 2390 kJ

23. The lattice enthalpy and enthalpy of solution in water for solid NaCl are 753 kJ mol^{-1} and 5 kJ mol^{-1} respectively (Fig. above). If the solution enthalpies of Na+ and Cl^- are in the ratio 6 : 5, the enthalpy of hydration of Na+ ion is **[NSEC–2018]**

(A) 408 kJ mol^{-1} (B) –412 kJ mol^{-1} (C) –408 kJ mol^{-1} (D) –412 kJ mol^{-1}

24. For the reaction $4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$, $\Delta H_{reaction} = -112$ kJ. If the N_2O_5 is assumed to be formed in the reaction as a solid, $\Delta H_{reaction}$ will be ($\Delta H_{sublimation}$ of N_2O_5 is 54 kJ mol^{-1}) **[NSEC–2018]**

(A) – 220 kJ (B) – 4 kJ (C) – 166 kJ (D) – 332 kJ

25. 2.0 L of N_2 gas kept at 25ºC and 5 atm pressure were expanded isothermally against a constant pressure of 1 atm until the pressure of the gas reaches 1 atm. Assuming ideal behavior, reversible work of expansion in this process (in J) is close to **[NSEC–2018]**

(A) 810 J (B) –194 kJ (C) – 810 kJ (D) 3390 kJ

26. The daily energy requirement of a teenager is 7800 kJ. As calculated from the data given in the table below, the amount of glucose he has to consume (g) per day assuming that the entire energy he requires comes from the combustion of glucose is **[NSEC–2018]**

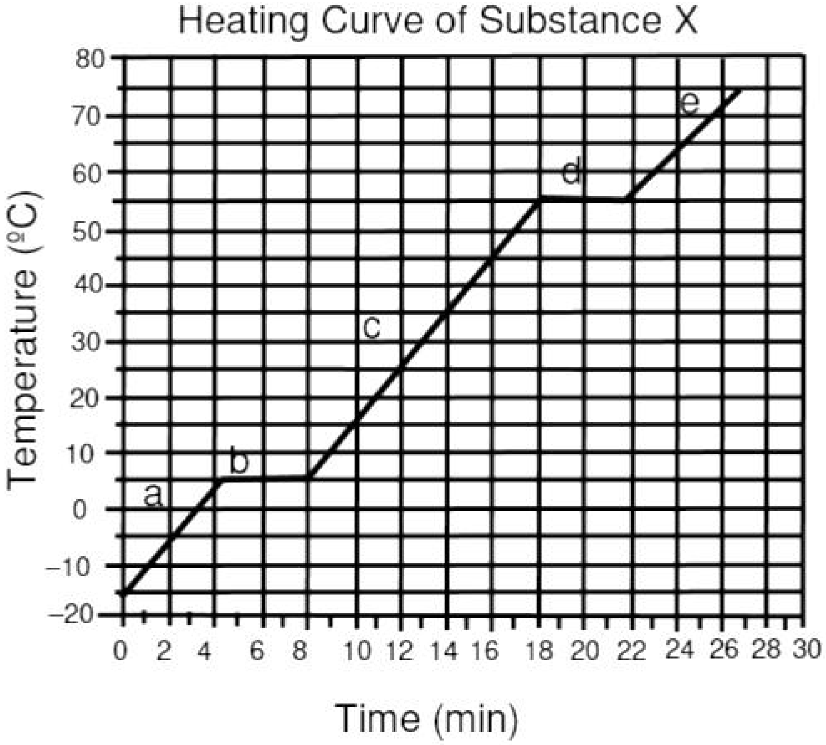
Molecule	**ΔH_f (kJ mol^{-1})**
$C_6H_{12}O_6$	– 1273
CO_2(g)	– 394
H_2O	– 286

(A) 262 (B) 500 (C) 131 (D) 250

27. The standard molar entropies of H_2(g), N_2(g) and NH_3(g) are 130, 190 and 193 J $mol^{-1}K^{-1}$ respectively. For the reaction $\frac{1}{2}N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g)$ ($\Delta H_{reaction} = -45$ kJ) to be in equilibrium, the temperature must be equal to **[NSEC–2018]**

(A) 464 K (B) 928 K (C) 737 K (D) 354 K

28. A substance X was heated at constant pressure and the temperature observed at various times of heating was plotted as given below **[NSEC–2018]**



Which of the following is/are correct ?

I. Melting point of X is –5ºC

II. Solid and liquid forms of X coexist in the region b

III. Boiling point of X is 55ºC

IV. Solid and liquid forms of X coexist in the region d

(A) I and IV (B) II and III (C) III only (D) I, II and III

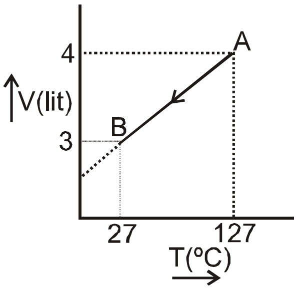
PART - 4 : ADDITIONAL PROBLEMS

SUBJECTIVE QUESTIONS

1. 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 litre to a volume of 10 litres at 27ºC. What is the maximum work done

2. Calculate work done by 1 mole of Ideal gas expand isothermally and irreversibly from pressure of 5 atm to 2 atm against a constant external pressure of 1 atm at 300 K temperature.

3. One mole of Ideal gas ($C_{P,m}$ = 15 JK^{-1} $mole^{-1}$) follow the process as shown in figure.



Predict the following :

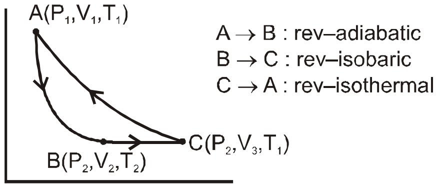
4. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.
(a) What is the final temperature ? (b) What is work done ?
Given $\gamma = 1.33$ and $C_V = 25.08\ \text{Jmol}^{-1}\text{K}^{-1}$ for CO_2.

5. (a) A certain mass of a gas initially at (1L, 5 atm, 300 K) is expanded reversibly and isothermally to a final volume of 5L, calculate work done by the gas and heat supplied in this process to the gas.
(b) Now,if the gas is restored to initial position by compressing it using an external constant pressure of 5 atm. Find work done on the gas in this process and heat rejected by gas
(c) In the above two processes, what is the net heat gained by surroundings?
[**Note :** From above question see that surroundings has done extra work on the system but system has returned that work in the form of heat to surroundings and work is considered on organized form of energy while heat as an unorganised form hence in the above process, there must be net increment in randomness of universe which will be called **Entropy,** soon.]

6. The molar heat capacity, C_v, of helium gas is 3/2 R and is independent of temperature. For hydrogen gas, C_v approaches 3/2 R at very low temperatures, equal 5/2 R at moderate temperatures and is higher than 5/2 R at high temperatures. Give a reason for the temperature dependence of C_v in case of hydrogen, in not more than two or three sentences.

7. There is 1 mol liquid (molar volume 100 ml) in an adiabatic container initial, pressure being 1 bar Now the pressure is steeply increased to 100 bar, and the volume decreased by 1 ml under constant pressure of 100 bar. Calculate ΔH and ΔE. [Given 1 bar = 10^5 N/m^2]

8. One mole of monoatomic gas was taken through a cyclic process as shown in figure.



Calculate $\sum\limits_{ABCA} \dfrac{dq_{rev}}{T}$.

9. One mole of ideal monoatomic gas was taken through isochoric heating from 100 K to 1000 K. Calculate ΔS_{system}, ΔS_{surr} and ΔS_{total} in
(i) when the process carried out reversibly
(ii) when the process carried out irreversibly (one step)

10. Following reaction occurs at 25°C :
$2NO\ (g, 1 \times 10^{-5}\ \text{atm}) + Cl_2\ (g, 1 \times 10^{-2}\ \text{atm}) \rightleftharpoons 2NOCl\ (g, 1 \times 10^{-2}\ \text{atm})$
Calculate $\Delta G°$ [R = 8 J/mole K]

11. For the reaction : $N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$
(i) In a mixture of 5 mol NO_2 and 5 mol N_2O_4 and pressure of 20 bar. Calculate the value of ΔG for the reaction. Given $\Delta G_f°\ (NO_2) = 50$ kJ / mol, $\Delta G_f°\ (N_2O_4) = 100$ kJ / mol and T = 298 K.
(ii) Predict the direction in which the reaction will shift, in order to attain equilibrium
[Given at T = 298 K, 2.303 RT = 5.7 kJ / mol.]

12. The difference between heats of reaction at constant presure and at costant volume for the reaction :
$2C_6H_6\ (\ell) + 15O_2\ (g) \longrightarrow 12CO_2\ (g) + 6H_2O\ (\ell)$ at 25ºC in kJ is :

13. Why is the enthalpy of sublimation equal to the sum of enthalpy of fusion and enthalpy of vaporisation ?

14. For a chemical reaction, ΔC_P is negative ($\Delta C_P < 0$).
The heat required to increase temperature of reactants of this reaction by a certain amount = q_1 and heat required to increase temperature of products of the same reaction by same amount = q_2, Relate q_1 and q_2

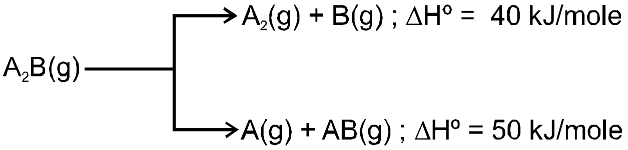
15. The specific heats of iodine vapour and solid are 0.031 calg^{-1}°C^{-1} and 0.055 calg^{-1}°C^{-1} respectively. If heat of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C ?

16. Find out the heat evolved in combustion if 112 litres (at STP) of water gas (mixture of equal volume of $H_2(g)$ and CO (g)).

$H_2(g) + 1/2\ O_2\ (g) \longrightarrow H_2O(g)$ $\Delta H = -\ 241.8$ kJ

$CO\ (g) + 1/2\ O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -\ 283$ kJ

17. Substance $A_2B(g)$ can undergoes decomposition to form two set of products :



If the molar ratio of $A_2(g)$ to A(g) is 5 : 3 in a set of product gases, calculate the energy involved in the decomposition of 1 mole of A_2B,

18. The ΔH^0_f (KF,s) is – 563 kJ mol^{-1}. The ionization enthalpy of K(g) is 419 kJ mol^{-1}. and the enthalpy of sublimation of potassium is 88 kJ mol^{-1}. The electron affinity of F(g) is 322 kJ mol^{-1} and F–F bond enthalpy is 158 kJ mol^{-1}. Calculate the lattice enthalpy of KF(s).

The given data are as follows :

(i) $K(s) + ½F_2(g) \rightarrow KF(s)$ $\Delta H^0_f = -\ 563$ kJ mol^{-1}

(ii) $K(g) \rightarrow K^+(g) + e^-$ $\Delta H^0_{Ioniz} = 419$ kJ mol^{-1}

(iii) $K(s) \rightarrow K(g)$ $\Delta H^0_{sub} = 88$ kJ mol^{-1}

(iv) $F(g) + e^- \rightarrow F^-(g)$ $\Delta H^0_{eg} = -\ 322$ kJ mol^{-1}

(v) $F_2(g) \rightarrow 2F(g)$ $\Delta H^0_{diss} = 158$ kJ mol^{-1}

(vi) $K^+(g) + F^-(g) \rightarrow KF(s)$ $\Delta H^0_L = ?$

ONLY ONE OPTION CORRECT TYPE

19. In thermodynamics, a process is called reversible when -
(A) surroundings and system change into each other
(B) there is no boundary between system and surroundings
(C) the surroundings are always in equilibrium with the system
(D) the system changes into the surroundings spontaneously

20. Two moles of an ideal gas expand spontaneously in vacuum. The work done is :
(A) 2 Joule (B) 4 Joule (C) Zero (D) Infinite

21. Temperature of 1 mole of a gas is increased by 2°C at constant pressure, then wark done is :
(A) R (B) 2R (C) R/2 (D) Data insufficient

22. Mechanical work is specially important in system that contain
(A) Solid-liquid (B) Liquid-Liquid (C) Solid-Solid (D) Gases

23. In the above questions out of the following which one is correct :
(A) Change in internal energy is zero. (B) Work involved is PV work.
(C) Work involved is non PV work. (D) $q \neq 0$

24. A piece of zinc at a temperature of 20°C weighing 65.38 g is dropped into 180 g of boiling water (T = 100°C). The specific heat of zinc is 0.4 J g^{-1} C^{-1} and that of water is 4.2 J g^{-1}°C^{-1}. What is the final common temperature reached by both the zinc and water ?
(A) 97.3 °C (B) 33.4 °C (C) 80.1 °C (D) 60.0°C

25. Which has maximum internal energy at 290 K ?
(A) Neon gas (B) Nitrogen gas (C) Ozone gas (D) All have equal value

26. A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr. by a mechanical linkage to a motor in the surrounding, for this process :

(A) $w < 0$; $q = 0$; $\Delta U = 0$
(B) $w > 0$; $q > 0$; $\Delta U > 0$
(C) $w < 0$; $q > 0$; $\Delta U = 0$
(D) $w > 0$; $q = 0$; $\Delta U > 0$

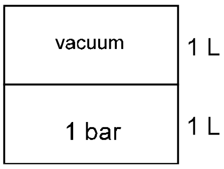
27. A balloon of 1 L volume is fill with O_2 gas, kept in a spaceship at STP. Now this spaceship is send in space & the balloon is released out of the spaceship. Then balloon expands upto bursting then calculate work done by balloon.

(A) 0
(B) 1
(C) 2
(D) 3

28. A system containing real gas changes it's state form state-1 to state-2.
State-1 (2 atm, 3L, 300 K)
State-2 (5 atm, 4L, 500 K)
If change in internal energy = 30 L atm then calculate change in enthalpy.

(A) 44 L atm
(B) 35 L atm
(C) 40 L atm
(D) None of these

29. A container of volume 2L is separated into equal compartments. In one compartment one mole of an ideal monoatomic gas is filled at 1 bar pressure and the other compartment is completely evacuated. A pinhole is made in the separator so gas expands to occupy full 2L and heat is supplied to gas so that finally pressure of gas equals 1 bar. Then



(A) $\Delta U = \Delta H = 150$ J
(B) $\Delta H = 250$ J
(C) $\Delta U = 100$ J
(D) $\Delta U = \Delta H = 0$

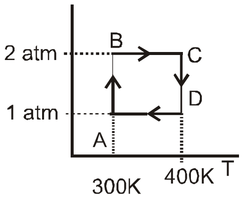
30. Which one of the following statement is false :

(A) work is a state function
(B) temperature is a state function
(C) change in the state is completely defined when the initial and final states are specified
(D) work appears at the boundary of the system.

31. Identify the state function among the following

(A) q
(B) q – w
(C) q/w
(D) q + w

32. Two moles of Helium gas undergo a reversible cyclic process as showin in figure. Assuming gas to be ideal, what is the net work involved in the cyclic process ?



(A) $-100\,R\ell n4$
(B) $+100R\ell n4$
(C) $+200R\ell n4$
(D) $-200R\ell n4$

33. Ice – Water mass ratio is mantained as 1 : 1 in a given system containing water in equilibrium with ice at constant pressure. If C_P (ice) = C_P (water) = 4.18 J mol^{-1} K^{-1} molar heat capacity of such a system is

(A) Zero
(B) Infinity
(C) 4.182 JK^{-1} mol^{-1}
(D) 75.48 JK^{-1} mol^{-1}

34. Two mole of an ideal gas is heated at constant pressure of one atomosphere from 27°C to 127°C. If $C_{v,m} = 20 + 10^{-2}\,T$ JK^{-1} mol^{-1}, then q and ΔU for the process are respectively :

(A) 6362.8 J, 4700 J
(B) 3037.2 J, 4700 J
(C) 7062.8, 5400 J
(D) 3181.4 J, 2350 J

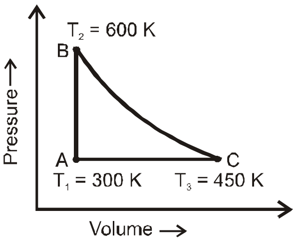
35. The increase in internal energy of 1 kg of water at 100°C when it is converted into steam at the same temperature and at 1 atm (100 k Pa) will be [The density of water and steam are 1000 kg/m^3 & 0.6 kg/m^3 respectively. The latent heat of vapourisation of water is 2.25×10^6 J/kg.]

(A) 2.08×10^6 J (B) 4×10^7 J (C) 3.27×10^8 J (D) 5×10^9 J

36. Consider a classroom that is roughly 5 m × 10m × 3m. Initially t = 27°C and P = 1 atm. There are 50 people in an insulated class loosing energy to the room at the average rate of 150 watt per person. How long can they remain in class if the body temperature is 42°C and person feels uncomfortable above this temperature. Heat capacity of air = (7/2) R.

(A) 4.34 minutes (B) 5.91 minutes (C) 6.86 minutes (D) 7.79 minutes

37. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure, the amount of heat added in the process AB and heat removed in the process CA are :



(A) q_{AB} = 450 R and q_{CA} = –450 R (B) q_{AB} = 450 R and q_{CA} = –225 R
(C) q_{AB} = 450 R and q_{CA} = –375 R (D) q_{AB} = 375 R and q_{CA} = –450 R

38. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. Ist sample using reversible isothermal process and IInd sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure. Then :

(A) Final volume of Ist sample < final volume of IInd sample
(B) Final volume of IInd sample < final volume of Ist sample
(C) Final volumes will be equal
(D) Information is insufficient

39. In the above problem :

(A) work done by gas in Ist sample > work done by gas in IInd sample
(B) work done by gas in IInd sample > work done by gas in Ist sample
(C) work done by gas in Ist sample = work done by gas in IInd sample
(D) none of these

40. 2 moles of ideal gas is expanded isothermally & reversibly from 1 litre to 10 litre. Find the enthalpy change in kJ mol^{-1}.

(A) 0 (B) 11.7 (C) – 11.7 (D) 25

41. One mole of an ideal monoatomic gas at temperature T and volume 1L expands to 2L against a constant external pressure of one atm under adiabatic conditions, then final temperature of gas will be :

(A) $T + \dfrac{2}{3 \times 0.0821}$ (B) $T - \dfrac{2}{3 \times 0.0821}$ (C) $\dfrac{T}{2^{5/3-1}}$ (D) $\dfrac{T}{2^{5/3+1}}$

42. The ratio of P to V at any instant is constant and is equal to 1, for a monoatomic ideal gas under going a process. What is the molar heat capacity of the gas.

(A) $\dfrac{3R}{2}$ (B) $\dfrac{4R}{2}$ (C) $\dfrac{5R}{2}$ (D) 0

43. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2} . The work is :

(A) – 900 J (B) – 900 kJ (C) 270 kJ (D) + 900 kJ

44. Consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; carried out at constant temperature and pressure. If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true ?

(A) $\Delta H = 0$ (B) $\Delta H = \Delta U$ (C) $\Delta H < \Delta U$ (D) $\Delta H > \Delta U$

45. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct ?

(A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(B) $(T_f)_{rev} = (T_f)_{irrev}$
(C) $T_f = T_i$ for both reversible and irreversible processes
(D) $(T_f)_{irrev} > (T_f)_{rev}$

46. When one mole of an ideal gas is comressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :

(A) $C_{p,m}$ ln 2 (B) $C_{v,m}$ ln 2 (C) R ln 2 (D) $(C_{v,m} - R)$ ln 2

47. Two mole of an ideal gas is expanded irreversibly and isothermally at 37ºC until its volume is doubled and 3.41 kJ heat is absorbed from surrounding. ΔS_{total} (system + surrounding) is :

(A) –0.52 J/K (B) 0.52 J/K (C) 22.52 J/K (D) 0

48. 1 mole of an ideal gas at 25°C is subjected to expand reversibly and adiabatically to ten times of its initial volume. Calculate the change in entropy during expansion (in J k^{-1} mol^{-1})

(A) 19.15 (B) – 19.15 (C) 4.7 (D) zero

49. What is the change in entropy when 2.5 mole of water is heated from 27ºC to 87ºC ? Assume that the heat capacity is constant. ($C_{p,m}$ (H_2O) = 4.2 J/g-K ln (1.2) = 0.18)

(A) 16.6 J/K (B) 9 J/K (C) 34.02 J/K (D) 1.89 J/K

50. $C_2H_6(g) + 3.5\, O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$
$\Delta S_{vap}(H_2O, \ell) = x_1$ cal K^{-1} (boiling point = T_1)
$\Delta H_f(H_2O, \ell) = x_2$
$\Delta H_f(CO_2) = x_3$
$\Delta H_f(C_2H_6) = x_4$
Hence, ΔH for the reaction is -

(A) $2x_3 + 3x_2 - x_4$ (B) $2x_3 + 3x_2 - x_4 + 3x_1T_1$
(C) $2x_3 + 3x_2 - x_4 - 3x_1T_1$ (D) $x_1T_1 + X_2 + X_3 - x_4$

51. Consider the ΔG^o_f and ΔH^o_f (kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas ?

(A) ZnO ($\Delta G^o = -318.4$, $\Delta H^o = -348.3$) (B) Cu_2O ($\Delta G^o = -146.0$, $\Delta H^o = -168.8$)
(C) HgO ($\Delta G^o = -58.5$, $\Delta H^o = -90.8$) (D) PbO ($\Delta G^o = -187.9$, $\Delta H^o = -217.3$)

52. If a refrigerator's door is opened, then we get

(A) Room heated (B) Room cooled
(C) More amount of heat is passed out (D) No effect on room

53. Which of the following statement (s) is/are correct?

Statement (i) : The entropy of isolated system with P–V work only, is always maximized at equilibrium.
Statement (ii) : It is possible for the entropy of close system to decrease substantially in an irreversible process.
Statement (iii) : Entropy can be created but not destroyed.
Statement (iv) : ΔS_{system} is zero for reversible process in an isolated system.

(A) Statement i, ii, iii, (B) Statement ii, iv (C) Statement i, ii, iv (D) All of these

54. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is **correct**, for the above process?
(A) The randomness of the universe decreases
(B) The randomness of the surroundings decreases
(C) Increase is randomness of surroundings equals to the decrease in randomness of system
(D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.

55. When CH_3OH (ℓ) is mixed in water :
(A) degree of Randomness (entropy) decreases due to formation of Hydrogen bond.
(B) Entropy of surrounding decreases
(C) Mixing is spontaoneous and reversible process
(D) All of the above are correct

56. Although graphite is thermodynamically most stable allotrope of Carbon but it has more entropy than diamond. Because :
(A) It has layer structure which slides on each other.
(B) In diamond Carbon is bonded with covalent bond.
(C) In graphite covalent bond only present within sheet and weak vanderwaal froce present between sheets which allow sliding easliy.
(D) Two types of bond lengths are present in graphite.

57. By how much does the entropy of 3 mole of an ideal gas change in going from a pressure of 2 bar to a pressure of 1 bar without any change in Temperature. If the surrounding is at 1 bar and 300 K. (Expansion is again of the constant external pressure of surrounding).
(A) + 7.29 J-K^{-1}
(B) + 4.82 J-K^{-1}
(C) – 5.29 J-K^{-1}
(D) – 8.35 J-K^{-1}

58. For a perfectly crystalline solid $C_{p,m} = aT^3 + bT$, where a and b constant. If $C_{p,m}$ is 0.40 J/K mol at 10 K and 0.92 J/K mol at 20 K, then molar entropy at 20 K is :
(A) 0.92 J/K mol
(B) 8.66 J/K mol
(C) 0.813 J/K mol
(D) None of these

59. For the hypothetical reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$
If Δ_rG^o and Δ_rS^o are 20 kJ/mol and –20 JK^{-1} mol^{-1} respectively at 200 K.
Δ_rC_p is 20 JK^{-1} mol^{-1} then Δ_rH^o at 400 K is :
(A) 20 kJ/mol
(B) 7.98 kJ/mol
(C) 28 kJ/mol
(D) None of these

60. ΔH = 30 kJ mol^{-1}, ΔS = 75 J / k / mol. Find boiling temperature at 1 atm.
(A) 400 K
(B) 300 K
(C) 150 K
(D) 425 K

61. Spontaneous adsorption of a gas on a solid surface is exothermic process because
(A) enthalpy of the system increases.
(B) entropy increases.
(C) entropy decreases.
(D) free energy change increases.

62. For a spontaneous reaction the ΔG, equilibrium constant (K) and E°_{cell} will be respectively
(A) – ve, > 1, + ve
(B) + ve, > 1, – ve
(C) – ve, < 1, –ve
(D) – ve, > 1, – ve

63. If ΔH is the change in enthalpy and ΔU the change in internal energy accompanying a gaseous reaction
(A) ΔH is always greater than ΔU
(B) $\Delta H < \Delta U$ only if the number of moles of the products is greater than the number of the reactants
(C) ΔH is always less than ΔU
(D) $\Delta H < \Delta U$ only if the number of moles of the products is less than the number of moles of the reactants

64. In the reaction $CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ $\Delta H = -265$ kcal
The enthalpies of formation of CO_2 and SO_2 are both negative and are in the ratio 4 : 3. The enthalpy of formation of CS_2 is +26kcal/mol. Calculate the enthalpy of formation of SO_2.
(A) – 90 kcal/mol
(B) – 52 kcal/mol
(C) – 78 kcal/mol
(D) – 71.7 kcal/mol

65. Heat of hydrogenation of ethene is x_1 and that of benzene is x_2. Hence, resonance energy is :

(A) $x_1 - x_2$ (B) $x_1 + x_2$ (C) $3x_1 - x_2$ (D) $x_1 - 3x_2$

66. Calculate the resonance energy of gaseous benzene from the given data

$\Delta H_{C-H} = 416$; $\Delta H_{C-C} = 331$; $\Delta H_{C=C} = 591$; ΔH_{sub} (C, graphite) = 718

ΔH_{diss} (H_2 , g) = 436 and ΔH_f (benzene, g) = 83 (all unit in kJ $mole^{-1}$)

(A) 354 (B) 271 (C) 437 (D) 83

67. Born-Haber cycle is used to determine :

(A) Lattice energy (B) Electron affinity (C) Crystal energy (D) All of these

68. Heat of neutralization of strong acid by a strong base is a constant value due to :

(A) salt formed does not hydrolysis

(B) only H^+ and OH^- ions react

(C) The strong base and strong acid react completely

(D) The strong base and strong acid react in aqueous solution

69. If $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O + q_1$

$H^+ + OH^- \rightarrow H_2O + q_2$

then the enthalpy change for the reaction

$CH_3COOH \rightarrow CH_3COO^- + H^+$ is equal to

(A) $(q_1 + q_2)$ (B) $(q_1 - q_2)$ (C) $(q_2 - q_1)$ (D) $-(q_1 + q_2)$

70. Enthalpy of neutralization of H_3PO_3 acid is – 106.68 kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is –55.84 kJ/mol. Calculate $\Delta H_{ionization}$ of H_3PO_3 into its ions :

(A) 50.84 kJ/mol (B) 5 kJ/mol (C) 2.5 kJ/mol (D) None of these

71. The difference between ΔH and ΔE (on a molar basis) for the combustion of n-octane (ℓ) at 25°C would be:

(A) – 13.6 kJ (B) – 1.14 kJ (C) – 11.15 kJ (D) + 11.15 kJ

72. The heat of formation of HCl at 348 K from the following data, will be

$0.5\ H_2(g) + 0.5\ Cl_2\ (g) \longrightarrow HCl \qquad \Delta H^\circ_{298} = -22060$ cal

The mean heat capacities over this temperature range are,

$H_2(g)$, $C_P = 6.82$ cal $mol^{-1}\ K^{-1}$; Cl_2 (g), $C_p = 7.71$ cal $mol^{-1}\ K^{-1}$; HCl (g), $C_P = 6.81$ cal $mol^{-1}\ K^{-1}$

(A) – 20095 cal (B) – 32758 cal (C) – 37725 cal (D) – 22083 cal

73. From the following data of ΔH, of the following reactions,

$$C(s) + \frac{1}{2}O_2\ (g) \longrightarrow CO\ (g) \qquad \Delta H = -110\ kJ$$

$$C(s) + H_2O\ (g) \longrightarrow CO\ (g) + H_2(g) \qquad \Delta H = 132\ kJ$$

What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, to maintain constant temperature :

(A) 0.5 : 1 (B) 1 : 0.6 (C) 0.8 : 1 (D) 1 : 1

74. When 12.0 g of carbon reacted with limited quantity of oxygen, 57.5 kcal of heat was produced, Calculate the number of moles of CO produced ($\Delta_f H$ (CO_2) = – 94.05 kcal, $\Delta_f H$ (CO) = – 21.41 kcal.

(A) 0.5 mol (B) 0.46 mol (C) 0.64 mol (D) 0.74 mol

75. The standard enthalpy of formation of FeO & Fe_2O_3 is – 65 kcal mol^{-1} and –197kcalmol^{-1} respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1. If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?

(A) 13.4 kcal/mole (B) 14.6 kcal/mole (C) 15.7 kcal/mole (D) 16.8 kcal/mole

76. Reactions involving gold have been of particular interest to alchemists. Consider the following reactions,

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O,$ $\Delta H = -28$ kcal

$Au(OH)_3 + 4\,HBr \longrightarrow HAuBr_4 + 3\,H_2O,$ $\Delta H = -36.8$ kcal

In an experiment, there was an absorption of 0.44 kcal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl. Then, the fraction of $HAuBr_4$ converted into $HAuCl_4$ (percentage conversion)

(A) 5% (B) 6 % (C) 7% (D) 8%

77. The average Xe–F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol. Then, the enthalpy change for the reaction

$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$ will be

(A) 367 kcal/mole (B) 425 kcal/mole (C) 292 kcal/mole (D) 392 kcal/mole

78. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true ?

(A) $x = y$ (B) $x = \frac{1}{2}y$ (C) $x = 2y$ (D) None of these

79. A solution is 500 ml of 2 M KOH is added to 500 ml of 2 M HCl and the mixture is well shaken. The rise in temperature T_1 is noted. The experiment is then repeated using 250 ml of each solution and rise in temperature T_2 is again noted. Assume all heat is taken by the solution

(A) $T_1 = T_2$ (B) T_1 is 2 times as large as T_2

(C) T_2 is twice of T_1 (D) T_1 is 4 times as large as T_2

80. 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution's temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mole of HCl. (Assuming density of sol. = 1 g/ml & specifice heat of water is 4.2 J/g-K) is

(A) -2.5×10^2 kJ/mole (B) -1.3×10^2 kJ/mole (C) -8.4×10^1 kJ/mole (D) -6.3×10^1 kJ/mole

81. Which of the following equation gives the values of heat of formation (ΔH_f^0)

(A) $C\,(\text{diamond}) + O_2(g) \longrightarrow CO_2\,(g)$ (B) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF\,(g)$

(C) $N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g)$ (D) $H_2(g) + F_2\,(g) \rightarrow 2HF\,(g)$

82. The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is

(A) 110.5 kJ (B) 676.5 kJ (C) – 676.5 kJ (D) – 110.5 kJ

83. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is - 200 KJ mol^{-1}. The bond dissociation energy of X_2 will be

(A) 100 KJ mol^{-1} (B) 200 KJ mol^{-1} (C) 300 KJ mol^{-1} (D) 800 KJ mol^{-1}

84. The enthalpy changes for the following processes are listed below:

$Cl_2(g) \rightarrow 2Cl(g)$; 242.3 kJ mol^{-1} ; $I_2(g) \rightarrow 2I(g)$; 151.0 kJ mol^{-1}

$ICl(g) \rightarrow I(g) + Cl(g)$; 211.3 kJ mol^{-1} ; $I_2(s) \rightarrow I_2(g)$; 62.76 kJ mol^{-1}

Given that the standard state for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl(g) is

(A) –16.8 kJ mol^{-1} (B) +16.8 kJ mol^{-1} (C) +244.8 kJ mol^{-1} (D) –14.6 kJ mol^{-1}

MATCH THE COLUMN

85. Match column-I to column-II standard entropy in J/K-molar at 298 K

Column-I	**Column-II**
(A) C (s, diamond)	(p) 5.7
(B) C (s, graphite)	(q) 2.37
(C) H_2 (g)	(r) 117.6
(D) H (g)	(s) 130.6

NUMERICAL TYPE QUESTIONS

86. A sample of 4 mole He is originally confined in 20 L at 270 K and then undergoes adiabatic expansion against a constant pressure of 125 mbar until the volume has increased by a factor of 3. calculate ΔT during process:

87. 10 litres of a monoatomic ideal gas at 0°C and 10 atm pressure is suddenly released to 1 atm pressure and the gas expands adiabatically against this constant pressure. The final volume (L) of the gas.

88.^ Two mole of an ideal gas originally at a volume of 8 L. at 1000 K, is allowed to expand adiabatically until final volume is 24 L. For the gas $C_V = 1.5$ R. Calculate values of ΔS for the process when :
(i) The expansion takes place reversibly.
(ii) The change in volume involves a free expansion.
Sum of ΔS of these two case is______ **.**
(Used : $e^{1.09} = 3$ and $1.09 \times 8.314 = 9$)

89. 150 mL of 0.5 N HCl solution at 25ºC was mixed with 150 mL of 0.5 N NaOH solution at same temperature. Calculate heat of neutralization of HCl with NaOH, if find temperature was recorded to be 29ºC.
(ρ_{H_2O} = 1g/mL) (Give your answer magnitude wise).

90. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increases from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is :

91. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is – 56.1 kJ mol^{-1}. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is – 57.3 kJ $equiv^{-1}$, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

92. A gas expands against a variable pressure given by $P = \frac{20}{V}$ bar. During expainsion from volume of 1 litre to 10 litre, the gas undergoes a change in internal energy of 400 J. Heat absorbed by the gas during expansion (in kJ) :

93. The molar enthalpy of vaporization of benzene at its boiling point (353K) is 29.7 KJ/mole.
For how long (minute) would a 11.4 Volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?

94. At 5 ×10^5 bar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature T. Find the value of $\left(\frac{\Delta U - \Delta H}{20}\right)$ for the conversion of 1 mole of graphite to 1 mole of diamond (in KJ) at temperature T. (1L.atm = 100 J)

95. 1 mole of an idal gas A ($C_{v,m}$ = 3R) and 2 mole of an ideal gas B are $\left(C_{V,m} = \frac{3}{2}R\right)$ taken in a container and expanded reversible and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. Find the magnitude value of $\Delta U/10R$ for the process is :

96. Two moles of an ideal gas is expanded isothermally and irreversibly at 27ºC from volume V_1 to 7.5 V_1 and 4.17 kJ heat is absorbed from surroundings. Determine ΔS_{sys} ? (Approximate integer in Cal)

97. The vapour pressure of liquid Hg at 433 K is 5 mm Hg. Calculate the free energy change accompanying the expansion of one mole of Hg vapour in equilibrium with liquid at 433 K to a pressure of 750 mm Hg at the same temperature assuming the vapour behaves like an ideal monoatomic gas in kJ $mole^{-1}$. (Approximate integer and $e^5 = 150$)

98. One litre sample of a mixture of CH_4 and O_2 measured at 32ºC and 760 torr, was allowed to react at constant pressure in a calorimeter. The complete combustion of CH_4 to CO_2 and water caused a temperature rise in calorimeter of 1 K. Calculate mole % of CH_4 in original mixture.
[Given : Heat of combustion of CH_4 is – 210.8 Kcal/mol. Total heat capacity of the calorimeter = 2108 cal/K]

99. Calculate the resonance energy of isoprene (C_5H_8) from the data given.
Given that $\Delta H_{C=C}$ = 615 $kJmole^{-1}$; ΔH_{c-C} = 348 kJ $mole^{-1}$; ΔH_{C-H} = 413 $kJmole^{-1}$; ΔH_{H-H} = 435 $kJmole^{-1}$
The standard heat of sublimation of graphite is 718 $kJmole^{-1}$ and heat of formation of $C_5H_8(g)$ is 79 $kJmole^{-1}$
(Give your answer in kcal $mole^{-1}$; approximate integer).

100.^ Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data. Predict your answer as $\frac{\Delta H}{100}$ (in KJ/mole).
(i) 18 g of graphite on complete combustion evolve 585 KJ heat
(ii) 15540 KJ heat is required to dissociate all the molecules of 1 litre water into H_2 and O_2.
(iii) The heat of formation of liquid benzene is 48 kJ/mol
(iv) Density of C_6H_6 (ℓ) = 0.87 g/mℓ

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

101. In which of the following system does non P–V work :
(A) Mixing of two ideal gases at constant pressure condition.
(B) Discharging of Galvanic cell.
(C) Isochoric heating of Ideal gas.
(D) Ejection of photoelectrons from electropositive metal.

102. Identify the following processes in which non P-V work is involved :
(A) Transfer of electron through a resistor.
(B) Stirring of liquid through mechanical agitator.
(C) Falling of an apple on Newton's head.
(D) Attraction of iron filings towards a magnet.

103. Which of the following are incorrect :

(A) Work done by the surrounding in case of infinite stage expansion is more than single stage expansion

(B) Irreversible work is always greater than reversible work. (with sign)

(C) On an ideal gas in case of single stage expansion and compression system as well as surrounding are restored back to their original states

(D) If a gas in thermodynamic equilibrium is taken from state A to state B, by four successive single stage expansions. Then we can plot 4 points on the P-V indicator diagram.

104. 4 KJ of heat is absorbed when 1 mol of ice melts at 0ºC and at constant pressure 1 atm. If molar volume of ice and water are 19 ml and 18 ml respectively, then

[Take 1 atm = 10^5 Pa]

(A) $\Delta H > \Delta U$ (B) $\Delta U > \Delta H$ (C) $\Delta U = 4.1$ KJ (D) $\Delta U = 4.0001$ KJ

105. 5 moles of a liquid L are converted into its vapour at its boiling point (273°C) and at a pressure of 1 atm. If the value of latent heat of vapourisation of liquid L is 273 L atm/mole, then which of the following statements is/are correct : Assume volume of liquid to be negligible and vapour of the liquid to behave ideally.

(A) Work done by the system in the above process is 224 L atm.

(B) The enthalpy change (ΔH) for the above process is 1365 L atm (with respect to magnitude only)

(C) The internal energy of the system increases in the above process.

(D) The value of ΔU for the above process is 1589 L atm.

106. Which of the following option show more entropy of first compound than second :

(A) (i) 1-hexene at 273 K and 1 atm (ii) Cyclohexane at 273 K and 1 atm

(B) (i) $\overset{12}{C}H_4$ at NTP (ii) $\overset{14}{C}H_4$ at NTP

(C) (i) SO_2 (g) at 300 K and 0.1 atm (ii) SO_2 (g) at 300ºC and 0.1 atm

(D) (i) C_2H_5OH (ℓ) at 46ºC and 1 atm (ii) CH_3OH (ℓ) at 46ºC and 1 atm

107. Consider the reactions

(i) $S\text{ (rhombic)} + 3/2\, O_2(g) \longrightarrow SO_3(g), \Delta H_1$

(ii) $S\text{ (monoclinic)} + 3/2O_2(g) \longrightarrow SO_3(g), \Delta H_2$

(iii) $S\text{ (rhombic)} + O_3(g) \longrightarrow SO_3(g), \Delta H_3$

(iv) $S\text{ (monoclinic)} + O_3(g) \longrightarrow SO_3(g), \Delta H_4$

(A) $\Delta H_1 < \Delta H_2 < \Delta H_4$ (magnitude only)

(B) $\Delta H_1 < \Delta H_3 < \Delta H_4$ (magnitude only)

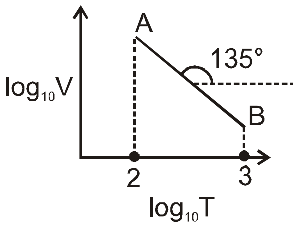
(C) $\Delta H_1 < \Delta H_2 = \Delta H_3 < \Delta H_4$ (magnitude only)

(D) $\Delta H_1 + \Delta H_4 = \Delta H_2 + \Delta H_3$

108. In an insulated rigid chamber some CO_2, CO and carbon is placed and O_2 is passed in the chamber. The mixture is ignited and combustion takes place. Which of the following is/are correct :

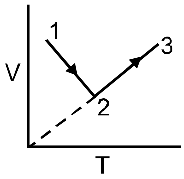
(A) $\Delta T_{\text{for system}} > 0$ (B) $\Delta T_{\text{for system}} < 0$ (C) $q_{\text{system}} = \text{zero}$ (D) $\Delta U = \text{zero}$

109. Three moles of an ideal diatomic gas undergoes a change in state from A to B reversibly as follows :
Which of the following statements is/are correct regarding the above process :



(A) Work done on the gas is 2700 R
(B) In the above process, pressure varies inversely with square of volume.
(C) Heat supplied to the gas is 4050 R
(D) Data insufficient for the calculation of work and heat supplied.

110. Following graph is constructed for the fixed amount of the gas.



(A) From 1 - 2 pressure will increase
(B) From 2 - 3 pressure remains constant
(C) Gas pressure at (3) is greater at state (1)
(D) From 1 - 2 pressure will decrease

111. Choose the correct statement (s) :
(A) Temperature, enthalpy and entropy are state functions
(B) For reversible and irreversible both isothermal expansion of an ideal gas, change in internal energy and enthalpy is zero
(C) for a reaction in which $\Delta n_{gas} = 0$, entropy change is not always zero
(D) The entropy change associated with reversible isothermal expansion of an ideal gas is equal to 2.303 R $\log_{10}\frac{P_1}{P_2}$

112. One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. Then for this process(R = 2 calories/mol/K) (take calories as unit of energy and kelvin for temp)
(A) $\Delta H = 525$
(B) $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$
(C) $\Delta E = 525$
(D) ΔG of the process can not be calculated using given information.

113. Select the correct statements :
(A) All combustion reactions are exothermic
(B) Heat of combusiton are always exothermic
(C) $N_2 + O_2 \rightarrow 2NO$; $\Delta H = +$ ve
(D) $F_2 + \frac{1}{2}O_2 \rightarrow F_2O$; $\Delta H = +$ ve

COMPREHENSION

Comprehension # 1

A gaseous sample is generally allowed to do only expansion/compression type of work against its surroundings. The work done in case of an irreversible expansion (in the intermediate stages of expansion/compression the states of gases are not defined). The work done can be calculated using

$$dw = -P_{ext}\,dV$$

while in case of reversible process the work done can be calculated using

dw = – PdV where P is pressure of gas at some intermediate stages. Like for an isothermal reversible process. Since $P = \frac{nRT}{V}$, so

$$w = \int dw = -\int_{v_i}^{v_f} \frac{nRT}{V}\,.\,dV = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

Since dw = – PdV so magnitude of work done can also be calculated by calculating the area under the PV curve of the reversible process in PV diagram.

114. An ideal gaseous sample at initial state i (P_0, V_0, T_0) is allowed to expand to volume $2V_0$ using two different process; in the first process the equation of process is $PV^2 = K_1$ and in second process the equation of the process is $PV = K_2$. Then,

(A) work done in first process will be greater than work in second process (magnitude wise)

(B) The order of values of work done can not be compared unless we know the value of K_1 and K_2.

(C) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of K_1 and K_2.

(D) Ist process is not possible

115. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. Ist sample using reversible isothermal process and IInd sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then

(A) Final volume of Ist sample < final volume of IInd sample

(B) Final volume of IInd sample < final volume of Ist sample

(C) final volumes will be equal

(D) Information is insufficient

116. In the above problem

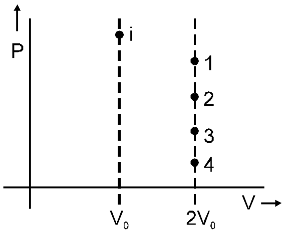
(A) work done by gas in Ist sample > work done by gas in IInd sample

(B) work done by gas in IInd sample > work done by gas in Ist sample

(C) work done by gas in Ist sample = work done by gas in IInd sample

(D) none of these

117. If four identical samples of an ideal gas initially at similar state (P_0, V_0, T_0) are allowed to expand to double their volumes by four different process.



I : by isothermal irreversible process

II : by reversible process having equation P^2V = constant

III : by reversible adiabatic process

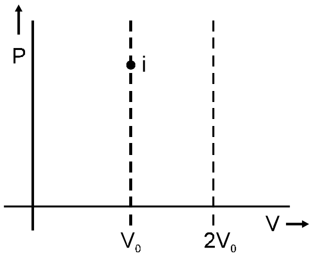
IV : by irreversible adiabatic expansion against constant external pressure.

Then, in the graph shown the final state is represented by four different points then, the correct match can be

(A) 1 – I , 2 - II, 3 – III, 4 - IV (B) 1 – II , 2 - I, 3 – IV, 4 - III

(C) 2 – III , 3 - II, 4 – I, 1 - IV (D) 3 – II , 1 - I, 3 – IV, 4 - III

118. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation PV^2 = constant then



(A) final temperature of both samples will be equal
(B) final temperature of first sample will be greater than of second sample
(C) final temperature of second sample will be greater than of first sample
(D) none of these.

Comprehension # 2

Phase transitions are ubiquitous in nature. We are all familiar with the different phase of water (vapour, liquid and ice) and with the change from one to another, the change of phase are called phase transitions. There are six ways a substance can change between these three phase ; melting, freezing, evaporating, condensing ; sublimination and decomposition.

At 1 atm pressure vaporisation of 1 mole of water from liquid (75ºC) to vapour (120ºC).

$C_v(H_2O, \ell)$ = 75 J mole^{-1} K^{-1} ; C_p (H_2O, g) = 33.3 J mole^{-1} K^{-1}
ΔH_{vap} at 100ºC = 40.7 kJ/mole.
Calculate change in internal energy when

119. Water liquid at 75°C to 100ºC ?
(A) 1875 J (B) 13125 J (C) – 1875 J (D) – 13125 J

120. Water liquid at 100°C to vapour at 100ºC ?
(A) 40700 J (B) 37598.878 J (C) 43801.1 J (D) 3101.2 J

121. Water vapour at 100ºC to 120ºC ?
(A) 666 J (B) 2998 J (C) 499.72 J (D) 166.28 J

Comprehension # 3

A gaseous mixture of propane, acetylene and CO_2 is burnt in excess of air. Total 4800 kJ heat is evolved. The total volume of CO_2 (g) after combustion is 224 liters at NTP.

The total evolved heat is used to perform two separate process :

(i) Vapourising 87.5% of water (liquid) obtained in the process of burning the original mixture.

(ii) Forming 3808 liters ethylene measured at STP from its elements.

ΔH_{H-H} = 435 kJ/mol ΔH_{C-H} = 416 kJ/mol ΔH_{C-C} = 347 kJ/mol

$\Delta H_{C=C}$ = 615 kJ/mol, $\Delta H_{C\equiv C}$ = 812 kJ/mol $\Delta H_{sublimation}$ of (C,s) = 718 kJ/mol

ΔH_f^o (CO_2, g) = –394 kJ/mol ΔH_f^o (H_2O, ℓ) = – 286 kJ/mol. ΔH_f^o (H_2O, g) = – 246 kJ/mol.

122. ΔH^o_{rxn} for $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$
(A) –220 kJ/mol (B) –180 kJ/mol (C) –250 kJ/mol (D) – 200 kJ/mol

123. Sum of enthalpies of combustion of $C_3H_8(g)$ and $C_2H_2(g)$ is :
(A) –2198 kJ/mol (B) – 3499 kJ/mol (C) –2798 kJ/mol (D) –3099 kJ/mol

124. Total moles of hydrocarbon gases taken in the initial mixture
(A) 3 (B) 4 (C) 2 (D) 5

RRP ANSWER KEY

PART- 1

1.	(C)	**2.**	(D)	**3.**	(B)	**4.**	(B)	**5.**	(C)
6.	(A)	**7.**	(C)	**8.**	(C)	**9.**	(A)	**10.**	(A)
11.	(A)	**12.**	(B)	**13.**	(B)	**14.**	(D)	**15.**	(B)
16.	(B)	**17.**	(D)	**18.**	(A)	**19.**	(B)	**20.**	(A)
21.	33.51	**22.**	–241.947	**23.**	– 209.41	**24.**	– 2.53 KJ	**25.**	1440 cal

PART- 2

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(B)	**5.**	(ABC)
6.	(ABC)	**7.**	(BCD)	**8.**	(ABCD)	**9.**	(AB)	**10.**	(ABCD)
11.	(ACD)	**12.**	(BC)	**13.**	– 6 L atm	**14.**	2	**15.**	3
16.	7	**17.**	5	**18.**	0				

PART- 3

1. (B)

2. Iron metal is produced commercially by reducing iron (**III**) oxide in iron ore with carbon monoxide.

(a) $Fe_2O_{3(S)} + 3CO_{(g)} = 2Fe_{(S)} + 3CO_2(g)$

(b) $\Delta G^o = \Delta H^o - T\Delta S^o$

Here $\Delta H^o = [2\Delta H^o_f (Fe) + 3\Delta H^o_f (CO_2)]$
$- [\Delta H^o_f (Fe_2O_3) + 3\Delta H^o_f (CO)]$

$\therefore\ \Delta H^o = -24.8$ kJ.

and $\Delta S^o = [2S^o (Fe) + 3S^o(CO_2)] -$
$[S^o (Fe_2O_3) + 3S^o(CO)]$

$\therefore\ \Delta S^o = +15.0$ J/K.

Therefore, $\Delta G^O = \Delta H^O - T\Delta S^o = -29.3$ kJ.

(c) As ΔG^O is negative, the reaction is spontaneous. This means that a mixture of $Fe_2O_{3(S)}$, $CO_{(g)}$, $Fe_{(S)}$ and $CO_{2(g)}$ with each gas at a partial pressure of 1 atm, will react at 250° C to produce more iron metal.

(d) Because ΔG^o is negative and ΔS^o is positive, ΔG^o will be negative at all temperatuers. The forward reaction is therefore spontaneous at all temperatures, and the reverse reaction does not become spontaneous at high temperatures.

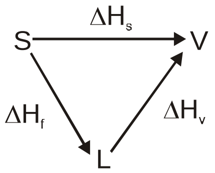
3.	(B)	**4.**	(C)	**5.**	(A)	**6.**	(A)	**7.**	(B)
8.	(A)	**9.**	(B)	**10.**	(A)	**11.**	(B)	**12.**	(A)
13.	(D)	**14.**	(B)	**15.**	(A)	**16.**	(B)	**17.**	(B)
18.	(D)	**19.**	(A)	**20.**	(D)	**21.**	(C)	**22.**	(D)
23.	(C)	**24.**	(A)	**25.**	All options are incorrect			**26.**	(B)
27.	(A)	**28.**	(B)						

PART- 4

1. –34.465 kJ
2. –0.7478 kJ
3. (i) Isobaric (ii) w = 830.865 J, q = –150 J
4. T_2 = 100 K, w = – 5.016 KJ
5. (a) – 816 J (b) + 2026 J (c) 1210 J
6. Hydrogen is diatomic so at high temperature rotational and vibrational motion also counts.
7. $\Delta H = 990$ J, $\Delta E = 10$ J
8. Zero
9. (i) Rev. Process $\Delta S_{system} = \frac{3}{2}R \ln 10$; $\Delta S_{surr} = -\frac{3}{2}R \ln 10$ $\Delta S_{Total} = 0$

(ii) Irr. Process $\Delta S_{system} = \frac{3}{2}R \ln 10$; $\Delta S_{surr} = -\frac{3}{2}R\,(0.9)$; $\Delta S_{total} = \frac{3}{2}R\,(1.403)$

10. – 43.92 KJ
11. (i) $\Delta G = 5.7$ kJ/mol (ii) backward shifting
12. – 7.432 kJ
13. Since, sublimation involves



According to Hess's law, $\Delta H_{(f)} + \Delta H_{(v)} = \Delta H_{(s)}$

14.	$q_1 > q_2$	**15.**	22.8 cal/g.	**16.**	1312 kJ	**17.**	43.73 kJ/mol		
18.	– 827 kJ mol^{-1}	**19.**	(C)	**20.**	(C)	**21.**	(B)	**22.**	(D)
23.	(C)	**24.**	(A)	**25.**	(C)	**26.**	(D)	**27.**	(A)
28.	(A)	**29.**	(B)	**30.**	(A)	**31.**	(D)	**32.**	(A)
33.	(B)	**34.**	(A)	**35.**	(A)	**36.**	(B)	**37.**	(C)
38.	(B)	**39.**	(A)	**40.**	(A)	**41.**	(B)	**42.**	(B)
43.	(A)	**44.**	(C)	**45.**	(D)	**46.**	(D)	**47.**	(B)
48.	(D)	**49.**	(C)	**50.**	(B)	**51.**	(C)	**52.**	(A)
53.	(D)	**54.**	(D)	**55.**	(B)	**56.**	(C)	**57.**	(B)
58.	(D)	**59.**	(A)	**60.**	(A)	**61.**	(C)	**62.**	(A)
63.	(D)	**64.**	(D)	**65.**	(C)	**66.**	(B)	**67.**	(D)
68.	(B)	**69.**	(C)	**70.**	(B)	**71.**	(C)	**72.**	(D)
73.	(B)	**74.**	(A)	**75.**	(A)	**76.**	(A)	**77.**	(C)
78.	(B)	**79.**	(A)	**80.**	(A)	**81.**	(B)	**82.**	(D)
83.	(D)	**84.**	(B)	**85.**	(A - q), (B - p), (C - s), (D - r)			**86.**	6
87.	64 L	**88.**	18	**89.**	– 16 Kcal.	**90.**	9	**91.**	20 %
92.	5	**93.**	9	**94.**	5	**95.**	96	**96.**	8 Cal
97.	18	**98.**	25%.	**99.**	5	**100.**	36 kJ	**101.**	(AB)
102.	(ABCD)	**103.**	(ACD)	**104.**	(BD)	**105.**	(ABC)	**106.**	(AD)
107.	(ABD)	**108.**	(ACD)	**109.**	(ABC)	**110.**	(ABC)	**111.**	(ABCD)
112.	(ABD)	**113.**	(BCD)	**114.**	(C)	**115.**	(B)	**116.**	(A)
117.	(B)	**118.**	(C)	**119.**	(A)	**120.**	(B)	**121.**	(C)
122.	(D)	**123.**	(B)	**124.**	(A)				

RRP SOLUTIONS

PART - 1

5. $\because\ \Delta_r C_p = 0, \quad \therefore\ \Delta H_{300} = \Delta H_{310}$

6. $C_2H_5OH\,(\ell) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(\ell)$

$\Delta n_g = 2 - 3 = -1$

so $\Delta U = \Delta H - \Delta n_g\, RT$

$= -q + RT$

7. From given reaction $\Delta n_g = 12 - 15 = -3$

so $\Delta E° = \Delta H° - \Delta n_g\, RT = -6542 + 3RT$

for 1.5 mole, $\Delta E° = \frac{1.5}{2}\,\{-6542 + 3RT\} = 4900.9$ kJ

8. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.

9. $C_2H_4 \quad + \quad H_2 \quad \longrightarrow \quad C_2H_6$

50 ml 50 ml 0

X X 50 ml

$\Delta H = \Delta U + P\,(\Delta V)$

$-0.31 = \Delta U + 1.5 \times 1.01 \times 10^5\,(-50 \times 10^{-6})$.

$\Delta U = -0.3024$ kJ.

10. Beaker is open and in open beaker external pressure remains constant.

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\,(g)$

$\frac{130}{65} = 2$ mole

$PV = nRT$

$P\Delta V = n_gRT$

$W = -n_gRT = 2 \times 2 \times 300 = -1200$ cal.

11. $C_3H_8(g) + 5O_2 \rightarrow 3CO_2(g) + 4H_2O(\ell)$

$$\Delta_C H = \begin{bmatrix} 8 \times B.E.(C - H) \\ + 2 \times B.E.(C - C) \\ + 5 \times B.E.(O = O) \end{bmatrix} - \begin{bmatrix} 6 \times B.E.(C = O) \\ + 8 \times B.E.(O - H) \\ + 3 \times |R.E.| \text{ of } CO_2 \\ + 4 \times \Delta_{vap} H(H_2O) \end{bmatrix}$$

12. $H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l) \quad ; \qquad \Delta H_{comb}\, H$

$\Delta H_{comb} = \Delta H_{H-H} + \frac{1}{2}\,\Delta H_{O=O} - 2\Delta H_{O-H} - \Delta H_{vap} = x_1 + \frac{x_2}{2} - 2x_3 - x_4$

13. $\frac{1}{2}\,N_2(g) + \frac{3}{2}\,Cl_2(g) \longrightarrow NCl_3(g)$

$\Delta H = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\,\Delta H_3$

14. $C_2H_5{-}S{-}C_2H_5 + S \longrightarrow C_2H_5{-}S{-}S{-}C_2H_5$

$\Delta H^o_f\,(C_2H_5{-}S{-}C_2H_5) = \Delta H^o_f\,(C_2H_5{-}S{-}S{-}C_2H_5) - \Delta H_{S-S} + \Delta H_{sub}\, S.$

$-201.9 = -147.2 - \Delta H_{S-S} + 222.8$

$\Delta H_{S-S} = 277.5$ kJ/mol

15. $\Delta H^o = 2 \times \Delta H_1^o + 2 \times \Delta H_2^o - \Delta H_3^o$

16. $\Delta G = \Delta H - T\Delta S = -2808 - 310 \times 182.4 \times 10^{-3} = -2864.5$ kJ

17. $\Delta S = 10.13 = 31.2 + 51.1 - 47.3 - S_{H_2O}$

$S_{H_2O} = 45.13$ cal/k mole.

18. Since, expansion occurred at constant temperature,

$$\Delta S = nR \ln \frac{V_2}{V_1} = \frac{1}{32} \times 8.314 \ln \frac{3.0}{0.75} = 0.36 \text{ JK}^{-1}$$

Since, this is case of free expansion, $P_{ext} = 0$. ⇒ $-W = P_{ext}\,\Delta V = 0,\ q = 0$
Also, since, $\Delta T = 0 \Rightarrow \Delta H = \Delta E = 0$.

19. (B) $Cu_2O(s) + \frac{1}{2}O_2(g) \rightleftharpoons 2CuO\ (s)$

$\Delta G^0_{reaction} = [2 \times (-30.4)] - [-34.98] = -25.82$ kcal

and $-25.82 \times 10^3 = 2.303 \times 2 \times 298 \log K$

∴ $K \approx 10^{19}$, a very high value, hence reaction will be almost complete with a trace of Cu_2O.

20. $\Delta_f S^o(NH_4Cl,s)$ at 300 K

$$= S^o_{NH_4Cl(s)} - \left[\frac{1}{2}S^o_{N_2} + 2S^o_{H_2} + \frac{1}{2}S^o_{Cl_2}\right] = -374 \text{ JK}^{-1}\text{ mol}^{-1}$$

$\Delta_f C_P = 0$

∴ $\Delta_f S^o_{310} = \Delta_f S^o_{300}$

$= -374$ JK^{-1} mol^{-1}

$\Delta_f H^o_{310} = \Delta_f H^o_{300} = -314.5$

$$\Delta_f G^o_{310} = \Delta_f H^o - 310\,\Delta S^o = -314.5 - \frac{310(-374)}{1000} = -198.56 \text{ kJ/mol.}$$

21. $\Delta H_{solution} = \dfrac{(125+8)\times 4.2 \times 6}{8} \times 80 = 33516$ J/mol or 33.51 kJ/mol.

22. $H_2C_2O_4(\ell) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell) + 2CO_2(g)$;

$\Delta n_g = 3/2$

$$\Delta U_c = -\frac{0.312 \times 8.75}{1} \times 90 = -245.7 \text{ kJ/mol}$$

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

$$= -245.7 + \frac{3}{2} \times \frac{8.314 \times 300}{1000} = -241.947 \text{ kJ/mol.}$$

23. $\Delta n_g = 1 - 2 = -1$
$\Delta E = \Delta H - \Delta n_g RT = \Delta H - RT = -72.3 + 8.314 \times 300 \times 10^{-3} = -69.806$ kJ/mole
so for 3 mole we will get $\Delta E = -69.806 \times 3$ kJ/mole = 209.42 kJ/mole

24. $W = -P_{ext}(\Delta V) = -(1 \text{ atm}) \times 500 \times 50 \times 10^{-3}$ L
$= -25$ L atm $= -25 \times 101.3 \times 10^{-3}$ kJ $= -2.53$ kJ

25. $H_2O\ (s) \longrightarrow H_2O\ (l)$, $\Delta H = 1440$ cal.

PART - 2

1. Molar mass = 102 gram/mole

P = 650 torr ; T = 77 + 273 = 350 K

Q = i × t = 0.25 × 600 = 150

E = Q × V = 150 × 12 = 1800 J

This heat is supplied to the system at constant pressure that's why this is used for change in enthalpy

∵ For vaporisation of 1.8 gram, amount of heat required q = 1800 J

∴ For vaporisation of 102 gram, amount of heat required $q = \frac{1800}{1.8} \times 102$ J

$= 102 \times 10^3$ J = 102 KJ/mole

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

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

For determination of ΔU per mol ($\Delta n_g = 1$)

$102 \text{ (KJ/mol)} = \Delta U + (1 \times 8.3 \times 350) \times 10^{-3} \Rightarrow \Delta U = 102 - 2.9 = 99.1$ KJ/mole

4. For polydropic process (n = 2)

$PV^2 = C$

$TV = C$

$T_1V_1 = T_2V_2$

$300 \times 1 = T_2 \times 3 \Rightarrow T_2 = 100$ K

$\Delta U = nC_{v,m}\,\Delta T$

$= 1 \times \frac{fR}{2}(T_2 - T_1) = 1 \times \frac{5\times R}{2} \times (100 - 300) = \frac{1\times 5\times R}{2} \times 200 = -500\,R = -4.2$ kJ

5. (A) ΔE will be – ve for combustion reactions

(B) ΔH_f° (S, rhombic) = 0

(C) $CH_4(g) \longrightarrow C(g) + 4H(g)$ $\Delta H = 1656$ kJ/mole $= 4\,\Delta H_{C-H}$

$C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ $\Delta H = 2812$ kJ/mole $= 6\,\Delta H_{C-H} + \Delta H_{C-C}$

so $\Delta H_{C-C} = (2812 - \frac{6}{4} \times 1656)$ kJ/mole = 328 kJ/mole

(D) Can not be concluded from given data.

6. (D) BOH (g) + aqueous $\longrightarrow B^+(aq) + OH^-(aq)$ $\Delta H = -20$ kJ/mole

7. More heat is evolved due to combustion of less stable form.

8. (A) Reversible adiabatic process is isoentropic (B) Reaction is spontaneous, need not be exothermic.

(C) Only when PV work is innvolved (D) $\Delta S_{system} = \frac{\Delta H_{system}}{T_b} = -\frac{40600}{373\times 2} = -54.42$ J/K

9. The given reaction will be spontaneous when ΔG would be negative when $\Delta H - T\Delta S$ is negative. That is,

$\Delta H - T\Delta S < 0$ or $T\Delta S > \Delta H$

or $T > \frac{\Delta H}{\Delta S}$ or $T > \frac{61170 \text{ J mol}^{-1}}{132 \text{ JK}^{-1}\text{ mol}^{-1}}$ or $T > 463.4$ K

10. $S_{200\,(B)} = \int_0^{200} \frac{C_P\,dT}{T} = 7 \text{ J mol}^{-1}\text{ K}^{-1}$

$S_{200\,(\ell)} = 7 + \frac{7500}{200} = 44.5 \text{ J mol}^{-1}\text{ K}^{-1}$

$$S_{300\,(\ell)} = 44.5 + \int_{200}^{300} \frac{C_P\,dT}{T} = 44.5 + 60 \ln \frac{300}{200} + 1.6 = 70.43 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$S_{300\,(g)} = 70.43 + \frac{30000}{300} = 170.43 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$S_{600\,(g)} = 170.43 + 50 \ln \frac{600}{300} = 205.09 \text{ JK}^{-1}\text{ mol}^{-1}$$

12. $\Delta H = (n_1C_{p,m_1} + n_2C_{p,m_2})\,\Delta T = \left(0.5\times\frac{7}{2}R+0.5\times 4R\right)(-100) = -\ 375\ R$ and $\Delta U = (0.5 \times \frac{5}{2}R + 0.5 \times 3R)$ $(-100) = -275\ R$.

13. (a) State A to state B (Isobasric expansion)
Wrok done by the gas = $W_1 = -\,p(V_B - V_A) = -\,1(40 - 20) = -\,20$L atm
(b) State B to state C (isochoric process)
Work done by the gas = $W_2 = 0.$ ($\because\ \Delta V = 0$)
(c) State C to state A (Isothermal compression)

Work done on the gas = $W_3 = -\,2.303\ nRT \log\frac{V_A}{V_C}$

$= -\,2.303\ pV \log\frac{V_A}{V_C}$ ($pV = p_AV_A = p_BV_B = nRT = 20$) $= -20\ \ell n(½) = 20 \times \ell n(B) = 14$

$\therefore$ total work done by the gas = $W_1 + W_2 + W_3 = -\,20 + 0 + 14 = -\,6$ L atm

14. (a) $0.25 \times 2808 \times \frac{x}{180} \times 10^3 = 62.5 \times 9.81 \times 3.$

x = 0.47 g.

(b) $0.25 \times 2808 \times 10^3 \times \frac{y}{180} = 62.5 \times 9.81 \times 6000.$

Y = 940 g.
Y = mX ⇒ 940 = m × 0.47 ⇒ m = 2000

15. $W = -\,P_{ext}(V_f - V_i) = -\,(1\text{ atm})\,(8 - 2)\text{ L} = -\,6\text{ L atm}$
as q = 0 so
$\Delta E = W \Rightarrow 3\,(8\,P_f - 12) = -\,6$

$8\,P_f = 12 - \frac{6}{3} = 10 \Rightarrow P_f = \frac{5}{4}$ atm

so, $\frac{T_f}{T_i} = \frac{\frac{5}{4}\times 3}{6\times 2} = \frac{10}{12}$

so $\Delta S = nC_{V,m}\,\ell n\left(\frac{T_f}{T_i}\right) + nR\,\ell n\left(\frac{V_f}{V_i}\right) = 3 \times \frac{12}{300} \ln\left(\frac{10}{12}\right) + \frac{12}{300} \ln 4$

= 3.312 J/K

Ans. 3 J/K

16. $H - C \equiv C - H + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O,$ $-\,312$ Kcal.

$-\,312 = [2(-\,94) + (-\,68)] - \Delta H_{f(C_2H_2)}$.

$\Delta H_{f(C_2H_2)}$ = 56 Kcal.

$$\begin{tikzcd}
2C\,(s) \arrow[d, "2\times150"] & +\ H_2\,(g) \arrow[d, "100"] \arrow[r] & C_2H_2\,(g),\quad 56 \\
2C\,(g) & +\ 2H\,(g) \arrow[ur, bend right] & H' = 0 - 2\times95 - x
\end{tikzcd}$$

56 = [(2 × 150) + 100] – [(2 × 95) + x].
x = 154 Kcal.

$$\frac{\Delta H_{C\equiv C}}{22} = 7$$

17. Heat evolved per mol of 'B' atoms = $\frac{5}{2} \times 200 = 500$ kJ

18. In isothermal reversible process.

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

$q = -w = 2.303\ RT \log \frac{V_2}{V_1}$

$= 2740.6$ J/mole

$\Delta S_{surr.} = \frac{q_{rev}}{T} = \frac{2740.6}{300} = 9.135$ J/K mole

$\Delta S_{surr.} = -\Delta S_{system} = -9.135\ JK^{-1}\ mole^{-1}$

$\Delta S_{universe} = 0$

PART - 3

4. $C_{diamond} + O_2(g) \longrightarrow CO_2(g)\ \ \Delta H = -395.3$ KJ/mol.
$C_{graphite} + O_2(g) \longrightarrow CO_2(g)\ \ \Delta H = -393.4$ KJ/mol.
Substracting eq. (B) from eq. (A)
$C_{diamond} \longrightarrow C_{graphite}\ \ \Delta H = ?$
$\therefore \Delta H = -395.3 - (-393.4)$
$= -1.9$ KJ/mole

5. $\Delta G = \Delta H - T\Delta S$
= (–) (+)
= (–) spontaneous at all temperature.

6. Enthalpy of vapourisation, $\Delta H_{vap} = \frac{5.89}{\left(\frac{6.24}{46}\right)}$ kJ/mol = 43.42 kJ/mol

PART - 4

1. $W = -2.303\ nRT \log \frac{V_2}{V_1} = -2.303 \times 6 \times 8.314 \times 300 \log \frac{10}{1}$

= –34464.8 Joule = 34.465 kJ

2. $\int dW = -\int P_{ext}\, dv$

$W_{irr} = -P_{ext}[V_2 - V_1] = -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right) = -P_{ext} \times nRT\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$

$= -1 \times 1 \times .082 \times 300\left(\frac{1}{2} - \frac{1}{5}\right) = -1 \times .082 \times 300 \times \frac{3}{10} = -7.38$ L.atm $= -747.8$ J

$W_{irr} = -0.7478$ KJ

3. (i) $\left(\frac{Pv}{nRT}\right)_A = \left(\frac{Pv}{nRT}\right)_B$

$\frac{P_A \times 4}{nR \times 400} = \frac{P_B \times 3}{nR \times 300} = \frac{P_A}{100} = \frac{P_B}{100} \Rightarrow P_A = P_B$ Hence process is isobaric.

(ii) $W = -P_{ext}(V_2 - V_1) = -\left(\frac{nRT_A}{V_A}\right)(V_B - V_A) = -\left(\frac{1 \times .082 \times 300}{3}\right)(3 - 4) \times 101.325$ J

$= 830.865$ J

$q_{AB} = nC_P(T_2 - T_1) = 1 \times 15 \times (300 - 400) = -150$ J

4. (a) $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$300 \times V^{1/3} = T_2 \times (27\,V)^{1/3} \Rightarrow T_2 = 100$ K

(b) $\Delta E = q + W$

For reversible adiabatic process,

$q = 0$

$\Delta U = W$

$\Rightarrow W = nC_V\Delta T$

$\Rightarrow W = 1 \times 25.08 \times (100 - 300) = -5.016$ kJ

5. $PV = nRT \Rightarrow 5 \times 1 = n \times 0.082 \times 300 \Rightarrow n = 0.203.$

	Initial	**Final**
(a)	V = 1 L.	V_2 = 5 L.
	P = 5atm	T = 300 K
	T = 300 K	

$w = -2.303\ nRT \log\frac{V_2}{V_1} = -2.303 \times 0.203 \times 8.314 \times 300 \log 5 = -816$ J

w = – 816 J and q = –w = 816 J

So, work done by the gas = 816 J.

(b) $w = -P_{ext}(V_2 - V_1) = -5[1-5] = +20 \times 101.325$

w = 2026 J.

(c) $q_1 = -w_1 = +816$ J

$q_2 = -w_2 = -2026$ J

$q_1 + q_2 = -1210$ J

So,Net heat released by the system = –1210

Net Heat gained by the surroundings = 1210

6. Helium (He) gas is monoatomic and it has three translational degree of freedom. Hence, the contribution of each translational degree of freedom towards C_v being R/2, so the **total contribution towards $C_v = 3 \times R / 2$.** Hydrogen molecule is diatomic. At low temperature, rotational and vibrational contribution for H_2 are zero. So, C_v for H_2 at low temperature continues to be 3R/2. At moderate temperature, rotational contribution (= 2 × R / 2) also becomes dominant and hence total contribution towards $C_V = \frac{3R}{2} + R = \frac{5R}{2}$. At even high temprature, vibrational contribution (= 1 × R) also becoms significant. Hence total contribution towards $C_V = \frac{3R}{2} + R + R = \frac{7R}{2}$

7. $\Delta U = q + W$

for adiabatic process $q = 0$, hence $\Delta U = W$ and $W = -p(\Delta V) = -P(V_2 - V_1)$

so, $\Delta U = -100\,(99 - 100) = -100\,(-1) = 100$ bar mL = 10 J

Now $\Delta H = \Delta U + \Delta(PV)$

Here ΔU already calculated above and

$\Delta PV = (P_2V_2 - P_1V_1)$

So, $\Delta H = 100 + (100 \times 99 - 1 \times 100) = 9900$ bar mL = 990 J

8. $dS = \dfrac{dq_{rev.}}{T} \quad \Rightarrow \quad \sum \dfrac{dq_{rev.}}{T} = \Delta S$

As 'S' being a state function, $\Delta S = 0$ in a cyclic process.

$\therefore \quad \sum \dfrac{dq_{rev.}}{T} = 0.$

9. (i) $\Delta S_{system} = nC_V \ln \dfrac{T_2}{T_1} = \dfrac{3}{2} R \ln 10$ and

$$\Delta S_{surr} = \int -\frac{dq_{sys}}{T} = \int_{T_1}^{T_2} -\frac{nC_V dT}{T} = -nC_V \ln \frac{T_2}{T_1} = -\frac{3}{2} R \ln 10$$

(ii) entropy is a state function.

$\Delta S_{system} = \dfrac{3}{2} R \ln 10.$

$\Delta S_{surr} = \dfrac{q}{T} = -\dfrac{nC_V(T_2 - T_1)}{T_2} = -\dfrac{3}{2} R \ (0.9).$

$\Delta S_{Total} = \dfrac{3}{2} R \ln 10 - \dfrac{3}{2} R(0.9) = \dfrac{3}{2} R(1.403)$

10. $2NO\ (9,\ 1 \times 10^{-5}\ \text{atm}) + Cl_2\ (9,\ 1 \times 10^{-2}) \rightleftharpoons 2NOCl\ (9,\ 1 \times 10^{-2})$

$$\Delta G^\circ = -2.303\ RT\left(\log \frac{(1 \times 10^{-2})^2}{(1 \times 10^{-5})^2 (1 \times 10^{-2})}\right) = -2.303\ RT\left[\log \frac{1 \times 10^{-2}}{1 \times 10^{-10}}\right]$$

$= -2.303\ RT\ [\log 1 \times 10^{8}] = -2.303 \times 8 \times 298 \times 8 = -43.92$ KJ.

11. (a) (i) ΔG^o for the reaction

$\Delta G^o reac. = 2\Delta G^o_f\,(NO_2) - \Delta G^o_f\,(N_2O_4)$

$100 - 100 = 0$

Now, $\Delta G = 2.303\ RT \log Q_P + \Delta G^o$

Here $Q_P = \dfrac{P^2_{NO_2}}{P_{N_2O_4}} = \dfrac{100}{10} = 10$ atm

So, $\Delta G = 2.303\ RT \log Q_P + 0 = 2.303\ RT \log Q_P = 2.303\ RT \log_{10} 10 = 2.303\ RT = 5.7$ kJ/mole

(ii) Since Q_P is more than K_P

(calculate K_P by putting the value of ΔG^o in the equation $\Delta G^o = 2.303\ RT \log K_P$ as $\Delta G^o = 0$ that's why K_P comes as 1.)

Hence, the reaction will proceed in backward direction.

12. $\Delta H = \Delta U + \Delta nRT$

$\Delta H - \Delta U = -3RT$

$= -3 \times 8.314 \times 298 = -7432\ J = -7.432\ kJ$

13. Since, sublimation involves

$$\begin{tikzcd} S \arrow[rr, "\Delta H_s"] \arrow[dr, "\Delta H_f"'] & & V \\ & L \arrow[ur, "\Delta H_v"'] & \end{tikzcd}$$

According to Hess's law, $\Delta H_{(f)} + \Delta H_{(v)} = \Delta H_{(s)}$

14. $\Delta C_p = -ve$; $C_{p\,(products)} < C_{p\,(Reactants)}$ so $q_2 < q_1$

15. $\Delta H_2 - 24 = -0.024 \times (523 - 473)$ cal/g.

$\therefore$ $\Delta H_2 = 22.8$ cal/g.

16. Equal volume of $H_2(g)$ & $CO(g)$

Total volume = 112 L

So, volume of CO = volume of H_2 = 56 L

Mole of CO = Mole of H_2 = 2.5 mole

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -241.8$ kJ

For 1 mole $\Delta H = -241.8$ kJ

For 2.5 mole $\Delta H = -241.8 \times 2.5$

Similarly, $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283$ kJ

$\Delta H = -283 \times 2.5$ kJ

Total Heat evolved = [–241.8 + (–283] 2.5 = – 1312 kJ

17. $\Delta_r H = \frac{5}{8} \times 40 + \frac{3}{8} \times 50 = 43.75$ kJ/mol

18. Equation (vi) can be generated by the following manipulations.

Eq. (i) – Eq. (ii) – Eq. (iii) – Eq. (iv) – ½ Eq. (v)

Carrying out the corresponding manipulations on ΔH^0_L, we get

$\Delta H^0_L = (-563 - 419 - 88 + 322 - 79)$ kJ mol^{-1}

$= -827$ kJ/mole

19. In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

20. (C) An ideal gas under going expansion in vacuum shows, $\Delta E = 0, W = 0$ and $q = 0$.

21. W_2 - $P(V_2 - V_1) = nR\Delta T = 1 \times R \times 2 = 2R$.

22. Mechanical work is important only in gases as they undergo appreciable change in volume.

24. Let final common temperature is T_f

Heat gained by Zinc piece = Heat lost by water

$0.4\,(T_f - 20) \times 65.38 = 4.2\,(100 - T_f) \times 180 \Rightarrow T_f = 97.3\ °C$

25. Internal energy of a gas $= \frac{f}{2}nRT$

Internal energy of a gas $\propto f$

26. Mechanical work is done on the system and internal energy increases.

27. $\because$ The process is of free expansion then W = 0.

29. Final temperature of gas must be double of the initial temperature

$\Delta H = \Delta U + \Delta\,(PV) = nC_V\,\Delta T + \Delta(PV)$ $\quad (\Delta T = T_f - T_i = 2T_i)$

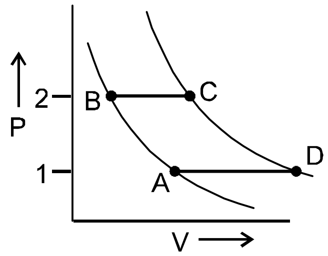
$$= \frac{nR}{(\gamma-1)}\,T_i + \Delta(PV) = \frac{3}{2} \times 100 + 100 = 250 \text{ J.}$$

30. Work is not a state function becuase it depends upon the path followed.

31. q + w = ΔU is a state function.

32. W_{Total} = area enclosed

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



$V_A = \frac{2R \times 300}{1} = \frac{600\,R}{1}$

$V_B = \frac{2R \times 300}{2} = \frac{300\,R}{1}$; $V_c = \frac{2\,R \times 400}{2} = \frac{400\,R}{1}$

$V_D = \frac{800R}{1}$

$W_{AB} = -nRT\,T_A \ln \frac{V_B}{V_A} = -2R\,(300)\ln\frac{1}{2} = 600\,R\ln 2$

$W_{BC} = -2(400 - 300)\,R = -\,200\,R$

$W_{CD} = -\,2\,R(400)\ln\frac{V_D}{V_C} = -\,800\,R\ln 2$

$W_{AD} = -1(600\,R - 800\,R) = 200\,R$

$W_{\ Total} = W_{AB} + W_{BC} + W_{CD} + W_{AD} = -\,200\,R\ln 2 = -\,100\,R\ln 4$

33. Since ice-water ratio is maintained as 1 : 1. So, $\Delta T = 0$.

34. (A) $w = -\,nR\,\Delta T = -2 \times 8.314 \times 100 = -1662.8$ J

$$\Delta U = n\int_{300}^{400} C_{V,m}\,dT = 2 \times \int_{300}^{400} (20 + 10^{-2}T)\,dT = 2\left[20 \times 100 + \frac{10^{-2}}{2}\left(400^2 - 300^2\right)\right] = 4700 \text{ J}$$

$4700 = q - 1662.8$

$\therefore \quad q = 6362.8$ J.

35. latent heat of vaporisation of water = 2.25×10^6 J/kg

$\Delta H = 2.25 \times 10^6$ J/kg.

work done = $-\,P_{ext}\,(V_2 - V_1)$

$\Delta H = 2.25 \times 10^6$ J/kg

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

(a) Now, volume of water $\quad V = \left(\frac{m}{d}\right) = \frac{1}{1000}\ M^3 = 1$ L

(b) volume of steam = $\frac{1000}{0.6} = 1666.67$ L

$2.25 \times 10^6 = \Delta U + 1\,[1666.67 - 1]\,101.325$

$\Delta U = 22.5 \times 10^5 - 1.68 \times 10^5 = 20.8 \times 10^5 = 2.08 \times 10^6$ J

36. Volume = $5 \times 10 \times 3 = 150\text{m}^3 = 150 \times 10^3$ L ; T = 27°C = 300 K ; P = 1 atm
$PV = nRT \Rightarrow 1 \times 150 \times 10^3 = n \times 0.082 \times 300 \Rightarrow n = 6097.6$
Total energy released per second = $150 \times 50 = 7500$ J/sec.
Amount of energy released by persons = energy gained by air $\Rightarrow [7500]\, t_{sec} = n\, C[dT]$

$$\Rightarrow \quad 7500\, t_{sec} = 6097.6 \times \frac{7}{2} \times 8.312 \times 15 \quad \Rightarrow \quad t_{sec} = 354.87 \text{ sec.} = \frac{354.87}{60} = 5.91 \text{ minutes.}$$

37. (C) At constant volume $\Delta U = q_v = nC_{vm}\,\Delta T = \frac{3}{2} R \times 300 = 450\,R$

at constant pressure $\Delta H = q_p = nC_{p,m}\,\Delta T = \frac{5}{2} R\,(-150) = -375\,R$

38. FACTUAL

39. FACTUAL

40. $\because \quad H = E + PV$ and $\Delta H = \Delta E + P\Delta V$
$P\Delta V = nRT.$
$\therefore \quad \Delta H = \Delta E + nR\Delta T$
For isothermal and reversible process
$\Delta T = 0.$
$\therefore \quad \Delta H = \Delta E + 0.$
$\because \quad \Delta E = 0.$
$\because \quad \Delta H$ is also equal to zero.

41. $\Delta U = W$
$nCv\,(T_2 - T) = -P \times (V_2 - V_1)$
$\frac{3}{2} R\,(T_2 - T) = -1 \quad \Rightarrow \quad \therefore \quad T_2 = T - \frac{2}{3 \times 0.0821}$

42. From first law of Thermodynamics, $\Delta E = q + w \Rightarrow nC_v dT = nCdT - PdV$ .....(A)
Now according to process, P = V and according to ideal gas equation, PV = nRT
We have , $V^2 = nRT$

On differentiating, $2VdV = nRdT$ and $PdV = VdV = \frac{nR\,dT}{2}$

So, from first equation we have, $nC_v dT = nCdT - \frac{nR\,dT}{2}$

So, $C_v = C - \frac{R}{2}$ Hence, $C = \frac{4R}{2}$

43. $W = -P\Delta V$
$= -1 \times 10^5\,(1 \times 10^{-2} - 1 \times 10^{-3})$
$= -1 \times 10^5 \times 9 \times 10^{-3} = -900$ J.

44. $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta n = 2 - 4 = -2$
$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT.$ $\therefore \quad \Delta H < \Delta U.$

45. In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e. q = 0 and secondary w_{rev} is always greater than w_{irr} therefore for reversible process there must be comparatively higher decreases in internal energy i.e. ΔU for reversible process will be more negative. Hence, final temperature in reversible process will be smaller than irreversible process.
$\therefore \quad (T_f)_{irrev} > (T_f)_{rev}$

46. $\Delta S = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_{v,m} \ln 2 + R \ln \left(\frac{1}{2}\right) = (C_{v,m} - R) \ln 2$

47. $\Delta S_{system} = nR \ln \frac{V_2}{V_1} = 2 \times R \times \ln 2 = 11.52$ J/K

$\Delta S_{surrounding} = -\frac{3.41 \times 1000}{310} = -11$ J/K

$\Delta S_{total} = +11.52 - 11 = +0.52$ J/K

48. $\Delta S = nC_v \ell n \frac{T_2}{T_1} + nR \ell n \frac{V_2}{V_1}$

For adiabatic process (Q = 0)

$\Delta E = W \quad \Rightarrow \quad nC_v \ell n \frac{T_2}{T_1} = -nR \ell n \frac{V_2}{V_1} \quad \therefore \quad \Delta S = 0.$

49. $\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} = 2.5 \times 18 \times 4.2 \ln \left(\frac{360}{300}\right) = 34.02$ J/K

50. $H_2O\ (l) \longrightarrow H_2O\ (g)\ \Delta H_{vap} = \Delta S_{vap} T_{B.P.} = x_1 T_1$

$\Delta H_f\ (H_2O,g) = \Delta H_f(H_2O,l) + \Delta H_{vap} = x_2 + x_1T_1$

$\Delta H_{reaction} = 2\Delta H_f, (CO_2, g) + 3\Delta H_f(H_2O, g) - \Delta H_f(C_2H_6,g)$

$= 2x_3 + 3\ (x_2 + x_1T_1) - x_4 = 2x_3 + 3x_2 + 3x_1T_1 - x_4.$

51. Lesser the ΔG^o_f, lesser its stability & easily it can decompose.

52. The compressor has to run for longer time releasing more heat to the surroundings.

53. All these are statements of second law of thermodynamics.

54. As dew formation is spontaneous process, therefore, entropy or randomness of the universe will increase. As randomeness of the system has decreased but randomness of the surrounding will increase larger so that change is positive.

57. $\Delta S\ (gas) = nR \ln \frac{P_1}{P_2} = 3 \times 8.314 \times \ln 2 = 17.29$ J/K

Since $\Delta T = 0$, therefore $\Delta U = 0$,

So, q = – W

$= nRT\left[1 - \frac{P_2}{P_1}\right]$

q = T × 12.47 J/K

$\Delta S_{surr} = -\frac{q}{T} = -12.47$ J/K

Change in $\Delta S = +4.82$ J/K

58. $0.40 = aT_1^3 + bT_1 \quad \Rightarrow \quad 0.40 = a \times (1000) + b \times 10 \Rightarrow 0.4 = 1000a + 10b$ ....(A)

$0.92 = aT_2^3 + bT_2 \quad \Rightarrow \quad 0.92 = a \times 8000 + 20b$ ....(B)

from Eqs. (A) and (B)

$a = 2 \times 10^{-5}, b = 0.038$

$S_m = \int \frac{aT^3 + bT}{T} . dT = \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1] = 0.427$ J/K-mol

59. (A) $\Delta G^{o}_{200} = \Delta H^{o}_{200} - T\,\Delta S^{o}_{200}$

$\Delta H^{o}_{200} = 20 - 4 = 16$ kJ/mol

$\Delta H^{o}_{T_2} = \Delta H^{o}_{T_1} + \Delta C_p[T_2 - T_1]$

$\Delta H^{o}_{400} = \Delta H^{o}_{200} + \frac{20 \times 200}{1000}$ kJ/ mol $= 16 + 4 = 20$ kJ/mol.

60. Given that, $\Delta H_{vaps} = 30$ kJ/mol $= 30 \times 10^3$ J/mol.
$\Delta S_{vaps} = 75$ J/mol.

We know that, $\Delta S = \frac{\Delta H_{vap}}{T_{B.P}}$

$\therefore$ $\Delta H = T\Delta S$ $\Rightarrow$ $30 \times 10^3 = T \times 75$.

T = 400 K.

61. In adsorption there is bond formation between the gases and solid surface which decrease the entropy.

62. For spontaneous process, $\Delta G = -$ ve, $K > 1$ and $E^0_{cell} = +$ ve.

63. If $\Delta n = -$ ve than $\Delta H < \Delta U$.

64. $CS_2\,(\ell) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g)$ $\Delta H = -256$ Kcal
Let $\Delta H_f\,(CO_2, g) = -4x$ and $\Delta H_f\,(SO_2, g) = -3x$
$\Delta H_{reaction} = \Delta H_f\,(CO_2, g) + 2\,\Delta H_f\,(SO_2 .g) - \Delta H_f\,(CS_2, \ell)$
$-265 = -4x - 6x - 26$
$x = +23.9$
$\therefore \Delta H_f\,(SO_2, g) = 3x =$ **–71.7 Kcal / mol.**

65. $CH_2 = CH_2 + H_2 \rightarrow CH_3\text{–}CH_3$ $\Delta H = X_1$
So, Hydrogenation energy of benzene sholud be $3x_1$
ΔH **calculated = $3x_1$**
So, Resonance energy = [$3x_1 - x_2$]

66. Required reaction $\Rightarrow 6C_{(graphite)} + 3H_{2(g)} \longrightarrow C_6H_{6(g)}$

1. $6C_{(g)} + 6H_{(g)} \longrightarrow C_6H_{6(g)}$
   $\Delta H_1 = -(6 \times \Delta H_{C-H} + 3\Delta H_{C=C} + 3\Delta H_{C-C}) = -(6 \times 416 + 3 \times 591 + 3 \times 331) = -5262$ kJ mole^{-1}
2. $6C_{(graphite)} \longrightarrow 6C_{(g)}$ $\Delta H_2 = 6 \times 718 = 4308$
3. $3H_{2(g)} \longrightarrow 6H_{(g)}$ $\Delta H_3 = 3 \times 436 = 1308$
   Adding (A) + (B) + (C)
   $6C_{(graphite)} + 3H_{2(g)} \longrightarrow C_6H_{6(g)}$
   $\Delta H = \Delta H^{\circ}_f(C_6H_6,(g)) = \Delta H_1 + \Delta H_2 + \Delta H_3 = 354$ kJ mole^{-1}
   Hence resonance energy = ΔH_f (cal.) – ΔH°_f(theo) = $354 - 83 = 271$ kJ mole^{-1}

68. In neutralization of strong acid and base only H^+ and OH^- ions react in every case. So, heat of neutralization is remain constant and equal to – 13.7 kcal (approximate).

69. Eqn. (ii) is for heat of neutralisation of strong acid with strong base. Eqn. (i) for weak acid with strong base. The difference $q_2 - q_1$ is heat of dissociation of weak acid.

70. $H_3PO_3 \longrightarrow 2H^+ + HPO_3^{2-}$; $\Delta_r H = ?$

$2H^+ + 2OH^- \longrightarrow 2H_2O$;
$\Delta_r H = -55.84 \times 2 = -111.68$
$-106.68 = \Delta_{ion}H - 55.84 \times 2$
$\Delta_{ion}\,H = 5$ kJ/mol.

71. $C_8H_{18}(\ell) + \frac{25}{2}O_2\,(g) \longrightarrow 8CO_2(g) + 9H_2O\,(\ell)$

$\Delta n_g = 8 - \frac{25}{2} = \frac{16-25}{2} = -\frac{9}{2} = -4.5$

$\Delta H - \Delta E = \Delta n_g RT = -\frac{4.5 \times 8.314 \times 298}{1000}$ **$= -11.15$ kJ**

72. $\Delta C_P = C_P\,(HCl) - \frac{1}{2}\,C_P\,(H_2) - \frac{1}{2}\,C_p\,(Cl_2) = 6.81 - \frac{1}{2} \times 6.82 - \frac{1}{2} \times 7.71$

$= 6.81 - 3.41 - 3.855 = -0.45$

$\Delta H_{348} = \Delta H_{298} + (\Delta C_P)\,(\Delta T) = -22060 + (-0.45) \times 50 = -22082.5$ cal

73. Let mixture contain x mole of steam & y mole oxygen then,
Here, temperature is constant. So, amount of heat released = amount of heat gain

$x \times 132 = y(220) \quad \Rightarrow \quad \frac{x}{y} = \frac{220}{132} = \frac{1.66}{1} \quad \Rightarrow$ **y : x = 1 : 0.6**

74. 12g C = 1 mole, suppose CO produced = x moles.
Then CO_2 produced = (1 – x) mole
$\therefore x(-21.41) + (1-x)(-94.05) = -57.5.$
This on solving gives x = 0.54 mole.

75. $FeO + Fe_2O_3$
2x x

$Fe + \frac{1}{2}O_2 \longrightarrow FeO \qquad \Delta H_f^o = -65$ Kcal/mole

$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3 \qquad \Delta H_f^o = -197$ Kcal/mole

$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$

$\Delta H = -197 + 65 \times 2 \Rightarrow \Delta H = -67$ Kcal/mole

$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$

$\frac{2}{3} \qquad\qquad \frac{1}{3}$

$\frac{2}{3} - 2x \qquad\qquad \frac{1}{3} + x$

$\frac{\frac{2}{3} - 2x}{\frac{1}{3} + x} = \frac{1}{2} \quad \Rightarrow \quad x = \frac{1}{5}$

So, energy released = $\frac{1}{5} \times 67 =$ **13.4 kcal/mole**

76.

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O, \qquad \Delta H = -28$ kcal

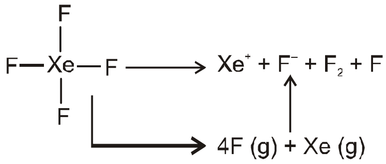
$HAuBr_4 + 3\,H_2O \longrightarrow Au(OH)_3 + 4\,HBr\,, \qquad \Delta H = +36.8$ kcal

$HAuBr_4 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O\,, \qquad \Delta H = +8.8$ kcal

When 100% conversion, heat absorbed = 8.8 Kcal

% conversion = $\frac{0.44}{8.8} \times 100 = 5\%$

77.



$\Delta H = 4E_{Xe-F} + \Delta H_{Ioni}\,[Xe \rightarrow Xe^{+}] - \Delta E_{F-F} - \Delta H_{eg}\,[F \rightarrow F^{-}]$
$= 4 \times 34 + 279 - 85 - 38 = 136 + 279 - 123 = 415 - 213$ **= 292 kcal/ mole.**

78. 1 M H_2SO_4 = 2g eq. of H_2SO_4

hence, $y = 2x$ or $x = \frac{1}{2}y$.

79. $Q = m\,S\,\Delta T_1 \quad \Rightarrow \quad \frac{Q_R}{2} = \frac{m}{2}\,S\,\Delta T_1 \quad \Rightarrow$ So, $\Delta T_1 = \Delta T_2$

80. Assuming density of solution is 1g/cc
and specipic heat is 4.2 J/g-K
$q = ms\Delta T = 100 \times 4.2 \times 3$
millimoles of acid nuetralized = 5

$\Delta H = -100 \times 4.2 \times 3 \times \frac{1000}{5} = -2.52 \times 10^{2}$ kJ/mole.

81. The amount of heat either evolved or absorbed when one gram mole of a substance is formed from its **constituent elements**, is known as the standard heat of formation (ΔH°_{f}).
Standard state temperature is 25C° or 298K and pressure of gaseous substance is one atmosphere.
Thus in given thermochemical equation '(B)' represents the standard heat of formation of HF.

$\frac{1}{2}H_{2(g)} + \frac{1}{2}F_2(g) \longrightarrow HF(g)$, ΔH°_{f} = ? (Standard heat of formation of HF(g))

82. $C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H = -393.5\ \text{kJ mol}^{-1}$ .... (A)

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)\ ;\ \Delta H = -283\ \text{kJ mol}^{-1}$ .... (B)

On subraction equation (B) from equation (A), we get $C(s) + O_2(g) \rightarrow CO(g)\ ;\ \Delta H = -110.5\ \text{kJ mol}^{-1}$.
The enthalpy of formation of carbon monoxide per mole $= -110.5\ \text{kJ mol}^{-1}$.

83. Let the bond dissociation energy of XY, X_2 and Y_2 be x,x and x, $\frac{x}{2}$ KJ/mol respectively,

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY;\ \Delta Hf = -200\ \text{KJ mol}^{-1}$.
ΔH reaction = [(sum of bond dissociation energy of all reactants) – (sum of bond dissociation energy of all product)]

$= \left[\frac{1}{2}\Delta H_{X2} + \frac{1}{2}\Delta H_{Y2} - \Delta H_{XY}\right] \quad = \frac{x}{2} + \frac{0.5x}{2} - x = -200 \quad \therefore \qquad x = \frac{200}{0.25} = 800\ \text{KJ mol}^{-1}$.

84. $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightarrow ICl(g) \qquad \Delta H_{f,\,ICl}(g) = \left[\frac{1}{2}\Delta H_{I_2(s)\rightarrow I_2(g)} + \frac{1}{2}\Delta H_{I-I} + \frac{1}{2}\Delta H_{Cl-Cl}\right] - \left[\Delta H_{I-Cl}\right]$

$= \left[\frac{1}{2} \times 62.76 + \frac{1}{2}151.0 + \frac{1}{2} \times 242.3\right] - \left[211.3\right] = 16.73$ kJ/mol.

86. $n = 4$

$V_1 = 20$ lit. $V_2 = 60$ lit

$\Delta W = -P_{ext}(V_2 - V_1)$

$$= -\frac{-125}{1000} \times (60-20) \times 100 = -500 \text{ J.}$$

In case of adiabatic process $\Delta q = 0$

$\Delta U = 0 + \Delta W$

$nCp\Delta T = \Delta W$

$$4 \times \frac{5}{2} \times R\Delta T = -500 \quad ; \quad \Delta T = -6 \text{ K}$$

87. This is adiabatic irreversible process so, for this process

PV^{γ} = Constant, is not applicable ; $W = -P_{ext}(V_2 - V_1)$

But for adiabatic process

$$W = dU = \left(\frac{P_2V_2 - P_1V_1}{\gamma - 1}\right)$$

$PV = nRT$ $\Rightarrow$ $10 \times 10 = n \times 0.082 \times 273 \Rightarrow n = 4.47$ moles

$$-P_{ext}(V_2 - V_1) = \left(\frac{P_2V_2 - P_1V_1}{\gamma - 1}\right) \Rightarrow -1 \times (V_2 - 10) = \frac{1 \times V_2 - 10 \times 10}{1.67 - 1}$$

$$\Rightarrow (10 - V_2) = \frac{V_2 - 100}{0.67} \Rightarrow 6.7 - 0.67\,V_2 = V_2 - 100$$

$$\Rightarrow 106.7 = 1.67\,V_2 \Rightarrow V_2 = 64$$

88. (i) In case of adiabatic reversible expansion, $dq_{rev} = 0 \Rightarrow \Delta S = 0$.

(ii) In case of free expansion (Adiabatically)

$W = 0$, $q = 0$, $\Delta U = 0$ $\Rightarrow$ $nC_V(T_2 - T_1) = 0$ $\Rightarrow$ $T_2 = T_1$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = 2R\ln(C) = \mathbf{18\ J/K.}$$

89. Total mass of solution = (150 + 150) = 300 g $\{\rho_{H_2O} = 1$ g/mL$\}$

$Q_{total} = mS\Delta T = 300 \times 1 \times (29 - 25) = 1200$ Cal

Since heat is liberated.

$$\text{Heat of neutralization} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1200}{150} \times 1000 \times \frac{1}{0.5} = 16 \text{ kcal}$$

Hence Heat of neutralization = –16 kcal

90. $n = \frac{3.5}{28}$

$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$

$C_V = 2.5$ kJ $k^{-1} = 2500$ JK^{-1}

$C_P = C_V + R = 2500 + 8.314 = 2508.314$ JK^{-1}

$Q_P = C_P\Delta T = 1128.74$ J

$$\Delta H = \frac{Q_P}{n} = \frac{1128.74}{3.5/28} = 9030 \text{ J mol}^{-1} = 9.030 \text{ KJ mol}^{-1} = 9 \text{ KJ mol}^{-1}.$$

91. $\Delta H_{ionization} = \Delta H_{neutralization}$ of WA + SB – $\Delta H_{neutralization}$ of SA + SB

$= -56.1 - (-57.3) = 1.2$ KJ eq^{-1}

Enthalpy of ionization for making 100% ionization when there is no ionization at all = 1.5 KJ eq^{-1}

$$\therefore \text{ \% of ionization} = \frac{1.5 - 1.2}{1.5} \times 100 = 20\%$$

92. $\Delta W = \int_{1}^{10} Pdv = -20\int_{1}^{10}\frac{dv}{V} = -20[\ell n(V)]_1^{10} = -20\ ln(10) = -4605\ J$

$\Delta q = \Delta U - \Delta W$

$= 400-(-4605) = 5005\ J \approx 5\ kJ.$

93. mole $= \frac{7.8}{78} = 0.1$

$\Delta H = n \times \Delta H_{vap}$

$= 0.1 \times 29.7\ KJ$

$= 2.97\ KJ$

$= 2970\ J$

ΔH = vaporization

$t = \frac{\Delta H}{v.i} = \frac{2970}{11.4 \times .5}$

t = 540 second

t = 9 minute

94. $C_{(graphite)} \longrightarrow C_{(diamond)}$

1 mole 1 mole

$\rho = 2\ g/cm^3$ $\rho = 3\ g/cm^3$

$V = \frac{12}{2}$ ml $V = \frac{12}{3}$ ml

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

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

$= -5\times10^5\left(\frac{12}{3} - \frac{12}{2}\right) \times 10^{-3}$ L.atm

$= -5\times 10^5 \times \frac{12}{6} \times 10^{-1}$ J= 100 KJ/mole

$= 10\times10^4$J = 100KJ/mole

$\frac{\Delta U - \Delta H}{20} = \frac{100}{20} = 5$ Ans.

95. Avg. $C_{V,\,m} = \frac{n_1C_{V,m_1} + n_2C_{V,m_2}}{n_1 + n_2} = \frac{1\times 3R + 2\times\frac{3}{2}R}{3} = 2\ R$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \Rightarrow 320 \times 1^{\frac{3}{2}-1} = T_2 \times (D)^{3/2-1} \Rightarrow T_2 = 160\ K$

$\Delta U = (n_1 + n_2)\ C_{V,avg}\ \Delta T = 3 \times 2R \times (160 - 320) = -960\ R$

$|(\Delta U/10R)| = |-960\ R/10R| = 96$

96. $\Delta S_{sys} = nRln\frac{V_2}{V_1} + nC_vln\frac{T_2}{T_1}$

$\Delta S_{system} = nR\ ln\frac{V_2}{V_1} = 2 \times 8.314\ ln\ 7.5 =$ **33.6 J** = 8 Cal.

97. $Hg(\ell) \rightarrow Hg(g)$ at 433 K and 4.19 mm of Hg is reversible and $\Delta G = 0$ but
ΔG for $Hg(g)$ (4.19 mm of Hg) $\rightarrow Hg(g)$ (760 mm of Hg)

with $\Delta G = nRT \ln \frac{P_2}{P_1}$

$\Delta G = 18$ J/mol.

98. Heat generated $= C_T\Delta T = 1260 \times 0.667$ cal.

$$\therefore \quad n_{CH_4} = \frac{2.108 \times 1}{210.8} = 0.01$$

$$n_{total} = \frac{PV}{RT} = 0.04 \qquad \therefore \qquad mol\% = \frac{0.01}{0.04} \times 100 = 25\% \text{ Ans.}$$

99. $2C_{(s)} \longrightarrow 5C_{(g)}$ $\quad \Delta H_1 = 5 \times 718 = 3590$
$4H_{2(g)} \longrightarrow 8H_{(g)}$ $\quad \Delta H_2 = 4 \times 435 = 1740$
$5C_{(g)} + 8H_{(g)} \longrightarrow C_5H_{8(g)}$ $\quad \Delta H_3 = -(8 \times 913 + 2 \times 348 + 2 \times 615) = -5230$
(A) + (B) + (C)
$5C_{(s)} + 4H_{2(g)} \longrightarrow C_5H_{8(g)}$ $\quad \Delta H_{rxn} = \Delta H_f(C_5H_8) = \Delta H_1 + \Delta H_2 + \Delta H_3 = 100$
so resonance energy = 79 – 100 = –21 kJ $mole^{-1}$
Hence resonance energy in Kcal$mole^{-1}$ = 5

100. (i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_f^o = -390$ KJ/mol ; $\quad \Delta H_f^o = \frac{585}{18} \times 12$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$; $\Delta H_f^o = -280$ KJ/mol ; $\Delta H_f^o = \frac{15540}{55.5}$

(iii) $C_6H_6(\ell) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$; $\quad \Delta H_f^o = -48$

$\therefore$ $\Delta H^o = [6(-390) + 3(-280)] - 48 = -3228$ KJ/ mol
Mass of benzene is = $0.87 \times 100 = 87$ g
$\therefore$ Heat evolved from 87 g benzene = 3600 KJ.

Hence, $\frac{\Delta H}{100} = 36$ kJ.

103. I – Work done by the system in case of infinite stage expansion is more than single stage expansion.
III – Single stage process is a irreversible process.
IV – We have 5 points on PV diagram.

104. $\Delta H = 4$ KJ
$\Delta H = \Delta U + \Delta(PV)$
$\Delta U = 4 - P(V_2 - V_1)$

$$= 4 - \frac{10^5(18-19)\times 10^{-6}}{10^3}$$

$= 4 + 1 \times 10^{-4}$
$= 4.0001$ KJ

105. $1 \times V_f = 5 \times R \times 546 = 224$ L
$W = -P_{ext}(\Delta V) = -1$ atm (224 L) = – 224 L atm
$\therefore$ work done by system = 224 L atm
Enthalpy change (ΔH) = q = 273 × 5 = 1365 L atm
$\Delta U = q + W = 1365 - 224 = 1141$ L atm.

109. From graph, slope = –1

$\therefore$ eq = $\log_{10}V + \log_{10}T$ = constant

$\therefore$ VT = constant or PV^2 = constant

$$C = C_V + \frac{R}{1-n} \quad \therefore C = \frac{5R}{2} + \frac{R}{1-2} = \frac{3R}{2}$$

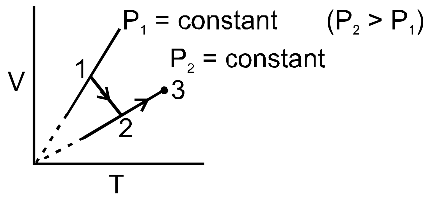
$$\therefore q = nC\Delta T = 3 \times \frac{3R}{2} \times (1000\text{-}100) = 4050\ R$$

$$\Delta U = nC_V\Delta T = 3 \times \frac{5R}{2} \times (1000 - 100) = 6750\ R$$

$$\therefore W = \Delta U - q = 6750\ R - 4050\ R = 2700\ R$$

110. V–T curve for a given mass of the gas is given

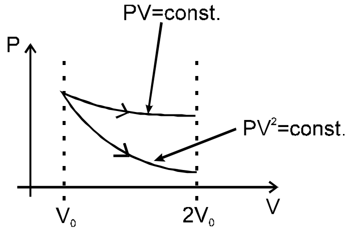
$$PV = nRT\ ;\ V = \left(\frac{nR}{P}\right)T$$



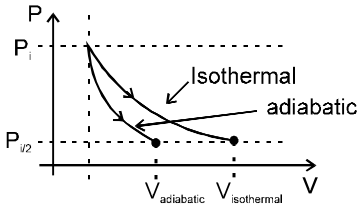
112. $\Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) = 5 \ln \frac{373}{298} + 2 \ln 10$

$\Delta H = nC_P\Delta T = n(C_V + R)\Delta T = 1 \times 7 \times 75 = 525$ cal

114. Work done in isothermal process will be more than PV^2 = const, process whatever be the value of K_1 and K_2 as is shown in the diagram.



115. Clearly $(V_f)_{\text{isothermal}} > (V_f)_{\text{adiabatic}}$



116. Work done in isothermal process is more than in adiabatic process as shown in the diagram above.

117. For isothermal irreversible process (T = constant)

$$P^\circ V^\circ = P' \, 2V^\circ \Rightarrow P = \frac{P^\circ}{2}$$

For $P^2 V$ = constant

$$P_o^2 V^\circ = P^2 \, 2V^\circ \Rightarrow P = \frac{P^\circ}{\sqrt{2}}$$

Final pressure of isothermal process > Final pressure of adiabatic process.
and Final pressure of irreversible adiabatic process > Final pressure of reversible adiabatic process.
So, final pressure order II > I > IV > III.

118.

$$\begin{tikzcd} & & P_1, V^\circ \\ P^\circ, V^\circ \arrow[r, "\text{irreversib le}", "\text{isothermal}"'] & 2V^\circ, \frac{P^\circ}{2} \arrow[ru, "\text{reversible adiabatic}"] \arrow[rd, "\text{reversible } PV^2 = K"'] & \\ & & P_2, V^\circ \end{tikzcd}$$

For reversible adiabatic,

$$\frac{P^\circ}{2}(2V^\circ)^\gamma = P_1 V_0^\gamma \Rightarrow P_1 = P^\circ 2^{\gamma-1}$$

For reversible $PV^2 = K$

$$\frac{P^\circ}{2}(2V^\circ)^2 = P_2 V_0^2 \Rightarrow P_2 = 2P^\circ$$

So, $P_2 > P_1$
Since final volume is same
$P \propto T$
So, $T_2 > T_1$

Sol. **(119 to 121)**

$H_2O\,(\ell, 75^oC) \xrightarrow{U_1} H_2O\,(\ell, 100^oC) \xrightarrow{U_2} H_2O\,(g, 100^oC) \xrightarrow{U_3} H_2O_{(g)}, 100^oC$

$U_1 = nC_{V,\,m(\ell)}, \Delta T = 1 \times 75 \times (100 - 75) = 1875$ J
$U_2 = n \times \Delta H_{vap} - \Delta n_g RT = 1 \times 40700 - 1 \times 8.314 \times 373 = 37598.878$ J
$U_3 = nC_{V,\,m(\ell)}\Delta T = n(C_{p,m(g)} - R)\,\Delta T$
$= 1 \times (33.3 - 8314) \times (120 - 100) = 24.986 \times 20 = 499.72$ J
$\Rightarrow P_2V_2 = P_1V_1$
The process is however adiabatic irriversible.
So we cannot apply $P_2V_2^\gamma = P_1V_1^\gamma$
Hence ans is (A) , (B), (C)

Sol. **(122 to 124)**

Let moles of $C_3H_8 = x$, moles of $C_2H_2 = y$

& moles of $CO_2 = z$.

Calculation of ΔH_f^o of C_3H_8 (g)

$$3C(s) + 4\,H_2\,(g) \longrightarrow C_3H_8(g)$$

ΔH_f^o of C_3H_8(g) = [3(718) + 4(435)] – [2(347) + 8 (416)]

= 3894 - 4022 = -128 kJ / mol.

Calculations of ΔH_f^o of $C_2H_2(g)$

$$2C\,(s) + H_2(g) \longrightarrow C_2H_2(g)$$

ΔH_f^o $C_2H_2(g)$ = [2(718) + (435)] – [(812) + 2(416)]

= (1436 + 435) – [1644]

= 227 kJ/mol.

Calculations of ΔH_f^o of $C_2H_4(g)$

$$2C\,(s) + 2H_2(g) \longrightarrow C_2H_4(g)$$

ΔH_f^o of $C_2H_4(g)$ = 2 (718) + 2 (435) – [615 + 4(416)]

= 2306 – 2279 = 27 kJ/mol.

Calculation of ΔH^o_{Comb} of C_3H_8 (g)

$$C_3H_8(g) + O_2(g) \longrightarrow 3CO_2(g) + 4H_2O\,(\ell)$$

ΔH^o_{Comb} of $C_3H_8 = [3\,\Delta H_{f^0}\,(CO_2) + 4\,\Delta H_{f^0}\,(H_2O, \ell)] - \Delta H_{f^0}\,(C_3H_8, g)$

$= [3\,(-394) + 4\,(-286)] - (-128) = -2198$ kJ/mol.

Calculation of ΔH^o_{Comb} of C_2H_2 (g)

$$C_2H_2(g) + 2.5O_2(g) \longrightarrow 2CO_2(g) + H_2O\,(\ell)$$

ΔH^o_{Comb} of $C_2H_2 = [2\,\Delta H_{f^0}\,(CO_2) + \Delta H_{f^0}\,(H_2O, \ell)] - \Delta H_{f^0}\,(C_2H_2)$

$= [2\,(-394) + (-286)] - 227$

$= -1301$ kJ/mol.

Now total heat released during combustion

$2198\,x + 1301\,y = 4800$ (i)

Combustion = $3x + 2y + z = 10$ (ii)

Total moles of $H_2O\,(\ell)$ formed = $4x + y$.

moles of $C_2H_4(g)$ to be prepared $= \frac{3808}{22.4} = 170$.

Total heat absorbed during evaporation of water formation of 170 moles C_2H_4 = 4800.

$[(4x + y) \times 0.875 \times 40] + (170 \times 27) = 4800$

$4x + y = 6$ (iii)

on solvent (i), (ii) and (iii)

we get x = 1, y = 2, and z = 3