# Solved Examples

## JEE Main/Boards

**Q.1** Calculate 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 kPa). The density of water and steam are 1000 kg $m^{-3}$ and 0.6 kg $m^{-3}$ respectively.

The latent heat of vaporization of water = $2.25 \times 10^6$ J $kg^{-1}$

**Sol:** Mass and density of water and steam is provided so from the given data calculate the increase in volume. Pressure term is given so by using pressure volume relationship calculate the work done by the system. Change in internal energy can be calculated using heat and work relation.

The volume of 1 kg of water

$$= \frac{1}{1000}\ m^3 \text{ and of 1 kg of steam} = \frac{1}{0.6}\ m^3$$

The increase in volume

$$= \frac{1}{0.6}\ m^3 - \frac{1}{1000}\ m^3 = (1.7 - 0.001\,m^3 \approx 1.7\,m^3)$$

The work done by the system is

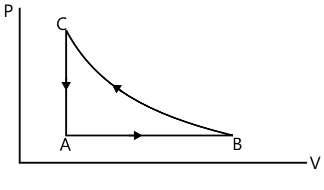
$$p\Delta V = (100kPa)(1.7m^3) = 1.7x10^5\ J.$$

The heat given to convert 1 kg of water into steam $= 2.25x10^6$ J.

The change in internal energy is

$$\Delta U = \Delta Q - \Delta W = 2.25\times10^6\,J - 1.7\times10^5\,J = 2.08\times10^6$$

**Q.2** Consider the cyclic process ABCA on a sample of 2.0 mol of an ideal gas as shown in figure. The temperatures of the gas at A and B are 300 K and 500 K respectively. A total of 1200 J heat is withdrawn from the sample in the process. Find the work done by the gas in part BC. Take R = 8.3 R = 8.3 $JK^{-1}$ $mol^{-1}$



**Sol:** The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Work done can be calculated by pressure volume relationship.

The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Hence,

$$W_{AB} = P_A(V_B - V_A) = nR(T_B - T_A)$$

$$= (2.0\text{ mol})(8.3\text{ J }K^{-1}\text{ mol}^{-1})(200K) = 3320\text{ J}.$$

The work done by the gas during the process CA is zero as the volume remains constant. From (i),

$$3320\text{ J} + W_{BC} = -1200\text{ J} = -4520\text{ J}$$

**Q.3** A mole of a monoatomic ideal gas at 1 atm and 273 K is allowed to expand adiabatically against a constant pressure of 0.395 bar until equilibrium is reached.

(a) What is the final temperature?

(b) What is the final volume?

(c) How much Work is done by the gas?

(d) What is the change in internal energy?

**Sol:** Let the initial and final volumes of the gas be $V_1$ and $V_2 m^3$ respectively. Given that the initial pressure ($P_1$) 1 x $10^5$ Pa, final temperature be $T_2$

We have, $P_1V_1 = n_1RT_1$

$$V_1 = \frac{1\ x8.314\ x273}{1\ x10^5} = 0.022697m^3$$

For an adiabatic expansion of 1 mole of monoatomic ideal gas against a constant external pressure ($P_2$), work done is given as

$$W = -P_2(V_2 - V_1) = Cv(T_2 - T_1) = \frac{3R}{2}(T_2 - T_1)$$

$$\text{Or} -0.395x10^5(V_2 - 0.022697) = \frac{3\times8.314}{2}(T_2 - 273) \quad \text{... (i)}$$

Again,

$P_2V_2 = nRT_2$;

$$0.395\times10^5\times V_2 = 1\times8.314\times T_2 \quad \text{... (ii)}$$

Solving eqns. (i) and (ii), we get,

(a) The final temperature, $T_2$= 207 K

(b) The final volume $V_2$= 0.043578 $m^3$

**Q.4** Metallic mercury is obtained by roasting mercury (II) sulphide in a limited amount of air. Estimate the temperature range in which the standard reaction is product-favored.

$$HgS(s) + O_2(g) \rightarrow Hg(l) + S\,O_2(g)$$

$\Delta H^o$= -238.6 kJ/ mole and $\Delta S^o$= + 36.7 J / mole K

**Sol:** Assume that ΔH and ΔS values do not depend on temperature. As ΔH° is negative and ΔS° is positive, using the equation ΔG° = ΔH° = TΔS° ΔG° Will be negative at all temperatures and so the reaction is product - favored at all temperatures. In this problem, both the factors ΔH° and ΔS° are favourable to spontaneity.

**Q.5** An ideal gas has a molar heat capacity at constant pressure $C_p = 2.5\,R$. The gas is kept in a losed vessel of Volume 0.0083 $m^3$, at a temperature of 300 K and a pressure of $1.6 \times 10^6\ Nm^{-2}$. An amount $2.49 \times 10^4$ J of Heat energy is supplied to the gas. Calculate the final temperature and pressure to the gas.

**Sol:** First calculate the number of moles (amount of gas) by using ideal gas equation, temperature can be calculated using internal energy and n. after calculating temperature pressure ($P_2$) can be calculated using following equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

We have, $C_v = C_p - R = 2.5R - R = 1.5R.$

The amount of the gas (in moles) is $n = \frac{PV}{RT}$

$$= \frac{\left(1.6\ x10^6\ \ N\ m^{-2}\right)\ x\left(0.0083\ m^3\right)}{(8.3\ J\ K^{-1}\ \ mol^{-1})\left(300K\right)} = 5.33\ mol$$

As the gas is kept in a closed vessel, its volume is constant,

Thus, we have

$$\Delta Q = n\ C_v\Delta T \qquad \text{or} \qquad \Delta T = \frac{\Delta Q}{nC_v}$$

$$= \frac{2.49\ x10^4\ J}{\left(5.3\ mpl\right)\left(1.5\ x8.3\ J\ K^{-1}mol^{-1}\right)} = 377K$$

The final temperature is 300 K + 377 K = 677K.

We have, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Here $V_1 = V_2$. Thus,

$$P_2 = \frac{T_2}{T_1}\ P_1 = \frac{677}{300}\ x1.6\ x10^6 N\ m^{-2} = 3.6\ x10^6 N\ m^{-2}.$$

**Q.6** Oxygen gas weighting 64 is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.

**Sol:** First find out value of n and then ΔS can be determined by using following equation

$$\Delta S = 2.303nR\ \log\left(\frac{P_1}{P_2}\right)$$

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$$n = \frac{w}{m.wt} = \frac{64}{32} = 2 \qquad = 2.303\ x2\ x8.314\ \log\left(\frac{1}{0.25}\right)$$

$$= 23.053\ J\ K^{-1}$$

**Q.7** An aluminium container of mass 100 g contains 200 g of ice at -20°C.Heat is added to the system at a rate of 100 cal $s^{-1}$. What is the temperature of the system after 4 minutes? Draw a rough sketch showing the variation in the temperature of the system as a function of time. Specific heat capacity of ice = 0.5 cal $g^{-1}\,{}^\circ C^{-1}$, specific heat capacity of aluminium = 0.2 cal $g^{-1\circ}\ C^{-1}$, specific heat capacity of water = 1 cal $g^{-1\circ}\ C^{-1}$, and latent heat of fusion of ice = 80 calg$^{-1}$.

**Sol:** Total heat supplied to the system in 4 minutes is Q = 100 cal $s^{-1}$ x 240 s = 2.4 x $10^4$ cal. The heat require to take the system from – 20°C to 0°C

= (100g) x (0.2 cag$^{-1}\,{}^\circ C^{-1}$ x (20°C) + (200g) x (0.5 cal$^{-1}\,{}^\circ C^{-1}$ x (20°C)

= 400 cal + 2000 cal = 2400 cal.

The time taken in this process $= \frac{2400}{100}\ S = 24\ s.$ The heat required to melt the ice at 0°C =(200g) x (80 cal$^{-1}$) = 16000 cal.

The time taken in this process $= \frac{1600}{100}\ S = 160\ s.$

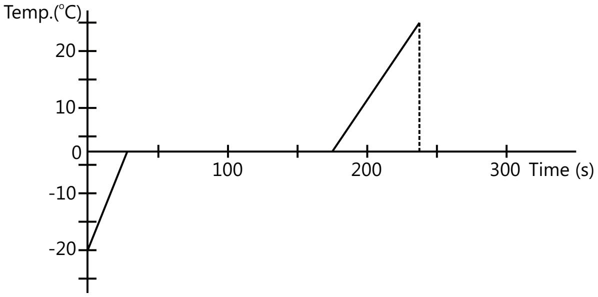
If the final temperature is $\theta$, the heat required to take the system to the final temperature is

= (100g) × (0.2 cal$^{-1}\,{}^\circ C^{-1}$) $\theta$ + (200g) × (0.5 cal$^{-1}\,{}^\circ C^{-1}$) $\theta$.

Thus, 2.4 x $10^4$ cal =2400 cal +16000 cal+(220 cal°C$^{-1}$) $\theta$

$$\text{Or, } \theta = \frac{5600\ cal}{200\ cal^\circ\ C^{-1}} = 25.5^\circ C.$$

The variation in the temperature as function of time is sketched in figure



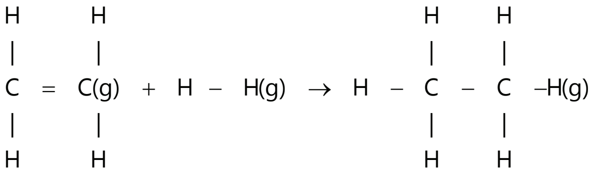
**Q.8** Calculate the enthalpy of the reaction

$$H_2C = CH_2(g) + H_2(g) \rightarrow CH_3 - CH_3(g)$$

The bond energies of

$C-H.C-C.C=C$ and $H-H$ are 99, 83,147 and 104 kcal respectively.

**Sol:** The reaction is:



$$\underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}}(g) + H - H(g) \rightarrow H - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - H(g)$$

$\Delta H$ = ?

$\Delta H$= Sum of bond energies of reactants – Sum of bond energies of products

$$= \left[\Delta H_{C=C} + 4\times\Delta H_{C-H} + \Delta H_{H=H}\right] - \left[\Delta H_{C-C} + 6\times\Delta H_{C-H}\right]$$

$$= \left(147 + 4\times 99 + 140\right) - \left(83 + 6\times 99\right) = -30 \text{ Kcal}$$

**Q.9** Calculate the heat of formation of acetic acid from the following data:

$$CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \text{... (i)}$$

$(\Delta H = -207.9 \text{ kcal})$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \text{... (ii)}$$

$(\Delta H = -94.48 \text{ kcal})$

$$H_2(g) + \frac{1}{2}O_2\ (g) \rightarrow H_2O(l) \qquad \text{... (iii)}$$

$(\Delta H = -68.4 \text{ kcal})$

**Sol: First method:** The required equation is $2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l);\ \Delta H = ?$ This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).

$$\left[2C + 2O_2 + 2H_2 + O_2 - CH_3COOH(l) - 2O_2\right.$$
$$\left.\rightarrow 2CO_2 + 2H_2O - 2CO_2 - 2H_2O\right]$$

$$\Delta H_{CH_3COOH(l)} = 2x(-94.48) + 2x(-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

**Second method:** From eqs. (ii) and (iii)

Enthalpy of $CO_2$ = -94.48 kcal

Enthalpy of $HO_2$= - 68.4 kcal

Enthalpy of $O_2$= 0 (by convention)

$\Delta H$ of eq. (i) = Enthalpies of products – Enthalpies of reactants

$$-207.9 = 2\ x(-94.48) + 2\ (-68.4) - \Delta H_{CH_3COOH(l)}$$

$$\Delta H_{CH_3COOH(l)} = -188.96 - 136.8 + 207.9$$

$$= -\ 325.76 + 207.9$$

$$= -\ 117.86 \text{ kcal}$$

**Q.10** 100 cm$^3$ of 0.5 N HCl solutions at 299.95 K were mixed with 100 cm$^3$ 0.5 N NaOH solution at 299.75 K in a thermos flask. The final temperature was found to be 302.65 K. Calculate the enthalpy of neutralization of HCl. Water equivalent of thermos flask is 44 g.

**Sol:** Here we are not provided with initial temperature. So by averaging the temperature of acid and base find out the initial temperature and thus rise in temperature and enthalpy of neutralization. The initial average temperature of the acid and the base.

$$= \frac{299.95 + 299.75}{2} = 299.85 \text{ K}$$

Rise in temperature = (302.65 – 299.85) = 2.80 K

Heat evolved during neutralization

= (100 – 100 + 44) × 4.184 × 2.8 = 2858.5 J

∴ Enthalpy of neutralization

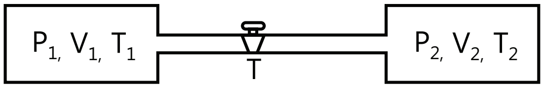
$$= -\frac{2858.5}{100}\times 1000\times\frac{1}{0.50} = -57.17 \text{kJ}$$

## JEE Advanced/Boards

**Q.1** Two vessels of volumes $V_1$ and $V_2$ contain the same ideal gas. The pressures in the vessels are $P_1$ and $P_2$ the temperatures are $T_1$ and $T_2$ respectively. The two vessels are now connected to each other through a narrow tube. Assuming that no heat is exchange between the surrounding and the vessels, find the common pressure and temperature attained after the connection.

**Sol:** In order to find out the common pressure and temperature attained after the connection, first we have to find out what is the amount of gas present in vessel one and two the formula to be used is

$$\gamma = \frac{C'_P}{C'_V} = \frac{n_1C'_p + n_2C'_p}{n_1C'_V + n_2C'_V}$$



The amount if the gas in vessel 1 is

$n_1 = \frac{P_1V_1}{RT_1}$ and that in vessel 2 is $n_2 = \frac{P_2V_2}{RT_2}$

If p′ and T′ be the common pressure and temperature after the connection is made, the amounts are

$n_1' = \frac{P'V_1}{RT'}$ and $n_2' = \frac{P'V_2}{RT'}$

We have $n_1 + n_2 = n_1' + n_2'$

$$\text{or} \quad \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2} = \frac{P'V_1}{RT'} + \frac{P'V_2}{RT'}$$

$$\text{or} \quad \frac{P'}{T'} = \frac{1}{V_1+V_2}\left(\frac{P_1V_1}{T_1} + \frac{P_2V_2}{T_2}\right)$$

$$\text{or} \quad \frac{T'}{P'} = \frac{T_1T_2(V_1+V_2)}{P_1V_1T_2 + P_2V_2T_1}. \quad \text{.... (i)}$$

As the vessels have fixed volume, no work is done by the gas plus the vessels system. Also no heat is exchanged with the surrounding. Thus, the internal energy if the total system remains constant.

The internal energy of an ideal gas is

$$T' = \frac{T_1\ T_2(\ P_1\ V_1 +\ P_2\ \ V_2)}{P_1\ V_1\ T_2\ +\ P_2\ V_2T_1}$$

The internal energy of the gases before the connection

$$= \frac{C_v\ P_1V_1}{R} + \frac{C_vP_2V_2}{R}$$

and after the connection $= \frac{C_v\ P'(V_1 +\ V_2)}{R}$

Neglecting the change in internal energy of the vessels (the heat capacity of the vessels is assumed negligible),

$$\frac{C_v\ P_1\ V_1}{R} + \frac{C_v\ P_2\ V_2}{R} = \frac{C_v\ P'(V_1 +\ V_2)}{R} \quad \text{Or,}$$

$$P' = \frac{p_1\ V_1 +\ \ p_2\ V_2}{V_1 +\ \ V_2}$$

From (i), $T' = \frac{T_1\ T_2(\ P_1\ V_1 +\ P_2\ \ V_2)}{P_1\ V_1\ T_2\ +\ P_2\ V_2T_1}$

**Q.2** 4 mole of an ideal gas having γ = 1.67 are mixed with2 mole of another ideal gas having γ = 1.4. Find the equivalent value of γ for the mixture.

**Sol:** The problem can be solved using the following two equations,

$$\gamma = \frac{C'_P}{C'_V} \qquad \text{And} \qquad C'_P = C'_V + R$$

$C'_V$ = Molar heat capacity of the first gas,
$C'_V$ = Molar heat capacity of the second gas,
$C_V^{'}$ = Molar heat capacity of the mixture
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and similar symbols for other quantities. Then,

$\gamma = \frac{C'_P}{C'_V} = 1.67$ and $C'_P = C'_V + R$

This gives $C_V^{'} = \frac{3}{2}R$ and $C'_p = \frac{5}{2}$ R.

Similarly, γ = 1.4. Gives $C'_V = \frac{5}{2}$ R. and $C_p^{'} = \frac{7}{2}R$.

Suppose the temperature of the mixture is increased by dT. The increase in the internal energy of the first gas $= n_1 C_v^{'}$ dT.

The increase in internal energy of the second Gas $= n_2 C_v^{'}$ dT and the increase in internal energy of the Mixture $= (n_1 + n_2)C_v^{'}$ dT

Thus, $(n_1 + n_2)C'_V dT = n_1C'_V dT + n_2C'_V dT;$

$$C'_V = \frac{n_1C'_V + n_2C'_V}{n_1 + n_2} \quad \text{...(i)}$$

$$C_P = C_V + R = \frac{n_1C'_V + n_2C'_V}{n_{1+}n_2}R$$

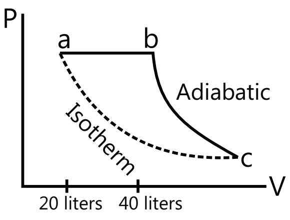
$$= \frac{n_1(C'_V + R) + n_2(C'_V + R)}{n_1 + n_2}$$

$$= \frac{n_1C'_p + n_2C'_p}{n_1 + n_2} \quad \textbf{... (ii)}$$

From (i) and (ii),

$$\gamma = \frac{C'_P}{C'_V} = \frac{n_1C'_p + n_2C'_p}{n_1C'_V + n_2C'_V} = \frac{4 \text{ x} \frac{5}{2} \text{ R} + 2 \text{ x} \frac{7}{2} \text{ R}}{4 \text{ x} \frac{3}{2} \text{ R} + 2 \text{ x} \frac{5}{2} \text{ R}} = 1.54$$

**Q.3** Two moles of helium gas (γ = 5/3) are initially at 27° and occupy a volume of 20 liters. The gas is first expanded at constant pressure until the volume is doubled. Then it undergoes



an adiabatic change until the temperature returns to its initial value. (a) Sketch the process in a p-V diagram (b) What is the final volume and pressure of the gas? (c) What is the work done by the gas?

**Sol:** (a) The process is shown in figure. During the part ab, the pressure is constant.

We have,

$$\frac{P_aV_a}{T_a} = \frac{P_bV_b}{T_b} \quad \text{or} \quad T_b = \frac{V_b}{V_a}T_a = 2T_a = 600\text{ K.}$$

During the part bc, the gas is adiabatically returned to the temperature $T_a$. The point  and the point  are on the same isotherm. Thus, we draw an adiabatic curve from b and an isotherm from a and look for the point of intersection c. That is the final state.

(b) From the isotherm ac,

$$P_aV_a = P_cV_c \qquad \text{...(i)}$$

and from the adiabatic curve bc,

$$P_bV_b^{\gamma} = P_cV_c^{\gamma} \quad \text{or } P_a\left(2V_a\right)^{\gamma} = P_cV_c^{\gamma} \qquad \text{...(ii)}$$

Dividing (ii) by (i),

$$2^{\gamma}\left(V_a\right)^{\gamma-1} = \left(V_c\right)^{\gamma-1};$$

$$V_c = 2^{\gamma/(\gamma-1)}\ V_a = 4\sqrt{2}V_a = 113\text{ liters}$$

From (i),

$$P_c = \frac{P_aV_a}{V_c} = \frac{nRT_a}{V_c}\frac{2\text{ mol x}\left(8.3\text{ J K}^{-1}\text{ mol}^{-1}\right)\text{x}\left(300\text{ K}\right)}{113\text{ x}10^{-3}\text{ m}^3}$$

$= 4.4 \times 10^4$ Pa.

(c) Work done by the gas in the part

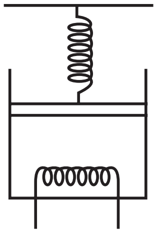
$$ab = P_a\left(V_b\ V_a\right) = P_bV_b - P_aV_a = nRT_2 - nRT_1$$

$$= 2\text{ mol} \times \left(8..3\text{ J K}^{-1}\text{mol}^{-1}\right) \times \left(600\text{ K} - 300\text{K}\right) = 4980\text{ J}$$

The net work done in the adiabatic part

$$bc = \frac{P_bV_b - P_cV_c}{\gamma - 1} = \frac{nR\left(T_2\ T_1\right)}{\gamma - 1} = \frac{4980\text{ J}}{5/3 - 1} = 7470\text{ J.}$$

The net work done by the gas = 4980 J + 7470 J = 12450 J



**Q.4** 2.00 mol of a monatomic ideal gas (U = 1.5 nRT) is enclosed in an adiabatic, fixed vertical cylinder fitted with a smooth, light adiabatic piston. The piston is connected to a vertical spring of spring constant 200 N $m^{-1}$ as shown in figure. The area of cross section of the cylinder is 20.0 $cm^2$. Initially, the spring is at 300 K. The atmospheric and the temperature of the gas is 300 K. the atmospheric pressure is 100 kPa. The gas is heated slowly for some time by means of an electric heater so as to move the piston up through 10 cm. Find (a) the work done by the gas (g) the final temperature of the gas and (c) the heat supplied by the heater.

**Sol:** (a) The force by the gas on the piston is F = $P_oA$ + kx. Where $P_0$ = 100kPa is the atmospheric pressure, A = $20cm^2$ is the area of cross section, k = 200 $Nm^{-1}$ is the spring constant and x is the compression of the spring. The work done by the gas as the piston moves through l = 10 cm is

$$W = \int_o^1 Fdx\ P_oAl + \frac{1}{2}\ kl^2$$

$$= (100 \times 10^3\text{Pa}) \times\ (20\text{ x}10^{-4}\text{ m}^2) \times (10 \times 10^{-2}\text{ m}) + \frac{1}{2}(200\text{ N m}^{-1}) \times (100 \times 10^{-4}\text{m}^2)$$

= 20 J + 1 J = 21 J.

(b) The initial temperature is $T_1$= 300 K. Let the final temperature be $T_2$= 300 K. Let the final temperature be we have

$$nRT_1 = P_oV_o\text{and}nRT_1 = P_oV_o = \left(P_o + \frac{kl}{A}\right)\left(V_o + Al\right)$$

$$= nRT_1 + P_oAl + kl^2 + \frac{kl\ nRT_1}{AP_o} \quad \text{Or}$$

$$T_2 = T_1 + \frac{P_oAl + kl^2}{nR} + \frac{klT_1}{AP_o}$$

$$= \left(300k\right) + \frac{20\text{ J} + 2\text{J}}{\left(2.0\text{ mol}\right)\left(8.3\text{ J K}^{-1}\text{mol}^{-1}\right)} + \frac{\left(200\text{ N m}^{-1}\right)\text{x}\left(10\text{ x}10^{-2}\text{ m}\right)\text{x}\left(300\text{ K}\right)}{\left(20\text{ x}10^{-4}\text{ m}^2\right) \times \left(100 \times 10^3\text{ Pa}\right)}$$

= 300 K + 1.325 K 30 K $\approx$331K

(c) The internal energy is U = 1.5 nRT. The change in internal energy is $\Delta U = 1.5\ nR\Delta T$

$$= 1.5 \times \left(2.00\text{ mol}\right) \times \left(8.3\text{ J K}^{-1}\text{mol}^{-1}\right) \times \left(31\text{ K}\right) = 772\text{ J.}$$

$$\Delta Q = \Delta U + \Delta W = 772\text{J} + 21\text{J} = 793\text{J}$$

**Q.5** How much heat is produced in burning a mole of $CH_4$ under standard conditions if reactants and products are brought to 298 K and $H_2O$ (l) is formed? What is the maximum amount of useful work that can be accomplished under standard conditions by this system?

$$CH_4(g) + 2O_2(g) \quad \rightarrow \quad CO_2(g) + 2H_2O(l)$$

$$\Delta Hf^0 : -74.8 \qquad 0 \qquad -393.5 \quad -285.85\ KJ$$

$$\Delta Gf^0 : -50.8 \qquad 0 \qquad -394.4 \quad -236.8\ KJ$$

**Sol:** $\Delta H_f^{\circ} = (-393.5) + (2 \times -285.85) - 74.8 - 2 \times 0$ KJ/mole

Now the free energy change for a process, ΔG, equals the maximum useful work that can be done by the system at constant temperature and pressure.

$$\therefore \; W_{max} = \Delta G = (2 \times -236.8) + (-394.4) - 50.8 - 2 \times 0$$
$$= -817.2 JK \text{ mole } CH_4$$

**Q. 6** A heat engine operates between a cold reservoirs at temperature $T_2$ = 300 K and a hot reservoir at temperature $T_1$. It takes 200 J heat from the hot reservoir and delivers 120 J of heat to the cold reservoirin a cycle. What could be the minimum temperature of the hot reservoir?

**Sol:** The work done by the engine in a cycle is W = 200 J – 120 J = 80 J.

The efficiency of the engine is

$$n = \frac{W}{Q} = \frac{80\ J}{200\ J} = 0.40$$

From Carnot's theorem, no engine can have efficiency greater than that of a Carnot engine.

Thus, $T_1 \le \frac{300\ K}{0.60}$ or $T_1 \ge 500$ K

Or, $T_1 \le \frac{300\ K}{0.60}$ or $T_1 \ge 500$ K

The minimum temperature of the hot reservoir has to be 500K.

**Q.7** A gas mixture of 3.67 liter of ethylene and methane on complete combustion at 25°C produces 6.11 liter of $CO_2$. Find out the heat evolved on burning 1 liter of the gas mixture. The heats of combustion of ethylene and methane are- 1423 and – 891 kJ mol$^{-1}$ at 25°C.

**Sol:** $\underset{\text{a liter}}{C_2H_4} + 3O_2 \rightarrow \underset{\text{2a liter}}{2CO_2} + 2H_2O$;

$$\underset{(3.67-a)\text{liter}}{CH_4} + 2O_2 \rightarrow \underset{(3.67-a)\text{liter}}{CO_2} + 2H_2O$$

Given, 2a + 3.67 – a = 6.11; a = 2.44 liter

Volume of ethylene in mixture = 2.44 liter

Volume of ethylene in mixture = 1.23 liter

Volume of ethylene in 1 liter mixture

$$= \frac{2.44}{3.67} = 0.6649 \text{ litre}$$

Volume of ethylene in 1 liter mixture

$$= \frac{1.23}{3.67} = 0.3351 \text{ litre}$$

24.45 liter of gas at 25° C corresponds to 1 mole.

Thus, heat evolved by burning 0.6649 liter of ethylene

$$= \frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning 0.3351 liter of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning 1 liter mixture

= - 38.68 – 12.21 = - 50.90 kJ

**Q.8** The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are -13.7 and -12.7 kcal/eq. When one equivalent of NaOH is added to a mixture containing 1 equivalent of HA and HB; the enthalpy change was -13.5kcal. In what ratio is the base distributed between HA and HB?

**Sol:** Let x equivalent of HA and y equivalent of HB are taken in the mixture

x + y = 1 ... (i)

x × 13.7 + y × 12.7 = 13.5 ... (ii)

Solving eqs. (i) and (ii), we get

x = 0.8, y = 0.2

x: y = 4: 1

**Q.9** Given the following standard heats of reactions: (a) heat of formation of water = -68.3 kcal, (b) heat of combustion of $C_2H_2$ = 310.6kcal. Calculate the heat of the reaction for the hydrogenation of acetylene at constant volume and 25° C.

**Sol:** The required equation is

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g); \quad \Delta H = ?$$

Given, (a) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$

(ΔH =-68.3 kcal) ... (i)

(b) $C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

(ΔH =-310.6 kcal) ... (ii)

(c) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

($\Delta H$ =-337.2 kcal) ... (iii)

The required equation can be achieved by adding eqs. (i) and (ii) and subtracting (iii).

$$C_2H_2(g) + H_2(g) + 3O_2 - C_2H_4(g) - 3O_2$$
$$\rightarrow 2CO_2 + 2H_2O(l) - 2CO_2(g) - 2H_2O(l)$$

$$\text{or } C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$
$$\Delta H = -68.3 - 310.6 - (-337.2)$$
$$= -378.9 + 337.2 = -41.7\text{kcal}$$

We know that,

$\Delta H = \Delta E + \Delta nRT$ or $\Delta H = \Delta E - \Delta nRT$

$\Delta n$= (1 - 2) = -1, R = 2 × $10^{-3}$ kcal $mol^{-1}K^{-1}$and T

= (25 + 273) = 298K

Subtracting the values in above equation,

$\Delta E$ = -41.7 – (-1) (2 × $10^{-3}$)(298)

= -41.7 + 0.596 = -41.104kcal

**Q.10** Using the data (all values in kilocalorie per mole at 25°C). Given below, calculate the bond energy of C-C and C-H bonds.

$$\Delta H^o_{\text{combustion of ethane}} = -372.0$$

$$\Delta H^o_{(\text{combustion of propane})} = -530.0$$

$$\Delta H^o \text{ for } C_{(\text{graphite})} \rightarrow C(g) = +172.0$$

Bond energy of H–H Bond =+104.0;

$$\Delta H^0_f \text{ of } H_2O(l) = -68.0$$
$$\Delta H^0_f \text{ of } CO_2(g) = -94.0$$

**Sol:** $C_2H_6(g) + \frac{7}{2}O_2 \rightarrow 2CO_2(g) + 3H_2O(l);\ \Delta H = -372.0$

$$\Delta H^o_{f(C_2H_6)} = 2x(-94.0) + 3\ x(-68.0) + 372.0 = -\ 20\text{ kcal}$$

$$C_3H_8(g) + 5O_2 \rightarrow 3CO_2(g) + 4H_2O(l);\quad \Delta H = -530.0$$

$$\Delta H^o_{f(C_3H_8)} = 2\ x(-94.0) + 4\ x(-68.0) + 530.0 = -24\text{ kcal}$$

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g);\ \Delta H = -20.0$$
$$2C(g) \rightarrow 2C(s);\quad \Delta H = -344.0$$
$$6H(g) \rightarrow 3H_2(g);\ \Delta H = -312$$
$$\text{adding } 2C(g) + 6H(g) \rightarrow C_2H_6(g); \Delta H = -676\text{ kcal}$$

So, enthalpy of formation of 6C – H bonds and one C – C bond is – 676.0 kcal.

$$3C(s) + 4H_2(g) \rightarrow {}_3H_8(g);\quad \Delta H = -24.0$$
$$3C(g) \rightarrow 3C(s);\quad \Delta H = -516.0$$
$$8H(g) \rightarrow 4H_2(g);\quad \Delta H = -\ 416.0$$
$$\text{adding } 3C(g) + 8H(g) \rightarrow C_3H_8(g);\quad \Delta H = -956.0\text{ kcal}$$

So, enthalpy of formation of 8C – H and 2C – C bonds is-956 kcal

Let the bond energy of C – C be *x* and of C – H be y kcal.

In ethane $x + 6y = 676$
In propane $2x + 8y = 956$
So solving, $x = 82$ and $y = 99$

Thus, bond energy of C – C = 82 kcal and bond energy of C – H = 99 kcal.

## JEE Main/Boards

## Exercise 1

**Q.1** Predict sign of work done in following reactions at constant pressure.

| | Initial state | | Final state |
|---|---|---|---|
| (i) | $H_2O(g)$ | → | $H_2O$ (l) |
| (ii) | $H_2O(s)$ | → | $H_2O$ (g) |
| (iii) | $H_2O(l)$ | → | $H_2O$ (s) |
| (iv) | $CaCO_3(s)$ | → | CaO (s) + $CO_2$ (g) |

**Q.2** The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and $\Delta E$?

**Q.3** The enthalpy of combustion of glucose is -2808 kJ $mol^{-1}$ and 25˚C. How many grams of glucose do you need to consume [Assume wt = 62.5kg].

(a) To climb a flight of stairs rising through 3m.

(b) To climb a mountain of altitude 3000m?

**Q.4** Water expand when it freezes. Determine amount of work, in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1L of ice.

**Q.5** Lime is made commercially by decomposition of limestone, $CaCO_3$. What is the change in internal energy when 1.00 mole of solid $CaCO_3$ (V = 34.2ml) absorbs 177.9 kJ of heat and decomposes at 25˚C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and $CO_2$(g) (V=24.4L)?

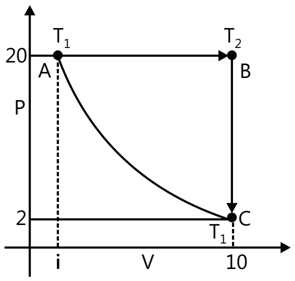
**Q.6** The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of $H_2$ at 1.5 atm pressure is $\Delta H = -0.31$ KJ. What is the $\Delta U$?

**Q.7** What is $\Delta E$ when 2.0 mole of liquid water vaporises at 100˚C? The heat of vaporisation, $\Delta H$ vap. of water at 100˚C is 40.66 $kJmol^{-1}$.

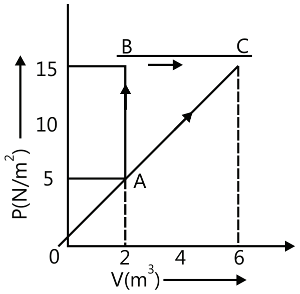
**Q.8** If 1.0 kcal of heat is added to 1.2 L of $O_2$ in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate $\Delta E$ and $\Delta H$ of the pressure.

**Q.9** 1 mole of ice at 0˚C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find $\Delta H$ and $\Delta E$ if the latent heat of fusion of ice is 80 Cal/gm and latent heat of vaporisation of liquid water at 0˚C is 596 Cal per gram and the volume of ice in comparison to that of water (vapour) is neglected.

**Q.10** The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 $kJmol^{-1}$. What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5A current in order to vaporise 7.8g of the sample at its boiling point?



**Q.11** Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext.pressure of 1 atm. Calculate q, w, $\Delta U$ & $\Delta H$. Calculate the corresponding value of all if the above process is carried out reversibly.



**Q.12** Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25˚C.

**Q.13** A real gas obeys the equation $P(V_m - b) - RT$, where (b - 0.1 L/mol), if 2 moles of gas is slowly compressed from 1.2 later to 0.6 litre at 300K then work done in the process is:

**Q.14** The moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas $C_V$ is 27.5 $JK^{-1}$ $mol^{-1}$ in this temperature range. Calculate q, w, $\Delta U$, $\Delta H$ and final V and final P.

**Q.15** 2 moles of an ideal gas undergoes isothermal compression along three different paths

(i) Reversible compression from $P_i$ = 2 bar and $V_i$ = 4L to $P_f$ = 20 bar

(ii) A single stage compression against a constant external pressure of 20 bar, and

(iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{gas} = P_{ext'}$ followed by compression against a constant pressure of 20 bar until $P_{gas} = P_{ext'}$.

**Q.16** One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from $T_1$ to $T_2$.

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

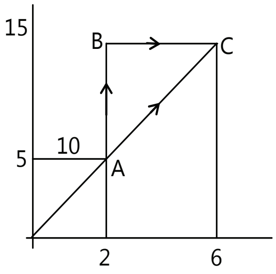
The steps are shown schematically in the figure show.

(a) Calculate $T_1$ and $T_2$.

(b) Calculate $\Delta E$, q and w in calories, for each step and for the cycle.

**Q.17** The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:

(a) Path along which work done is least.



(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.

(c) Amount of heat supplied to the gas to go from A to B, if internal energy change to gas is 10 J.

**Q.18** The standard enthalpy for the reaction $H_2(g)$ + 1/2 $O_2(g) \rightarrow H_2O(l)$ is - 285.76 kJ at 298 K. Calculate the value of ΔH at 373K. The molar heat capacities at constant pressure ($C_p$) in the given temperature range of $H_2(g)$, $O_2(g)$, and $H_2O(l)$ are respectively 38.83, 29.16 and 75.312 $JK^{-1}mol^{-1}$.

**Q.19** Methane (Considered to be an ideal gas) initially at 25˚C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by $C_p = 22.34 + 48.1 \times 10^{-3}$ T where $C_p$ is in $JK^{-1}$ $mol^{-1}$. Calculate molar (a) ΔH (b) ΔU.

**Q.20** One mole of NaCl(s) on melting absorbed 30.5 KJ of heat and its entropy is increased by 28.8 $JK^{-1}$. What is the melting point of sodium chloride?

**Q.21** Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increase in molar entropy? The molar heat capacity in $JK^{-1}mol^{-1}$ for the $O_2$ is $C_p$ = $25.5 + 13.6 \times 10^{-3}\ T - 42.5 \times 10^{-7}\ T^2$

**Q.22** Calculate $S_f^{\circ}$ at 298 K of ; (i) NaCl(s), (ii) $NH_4Cl(s)$ & (iii) diamond. The values of S˚ of Na, $Cl_2$, NaCl, $NH_4Cl$, $N_2$, $H_2$, diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $JK^{-1}mol^{-1}$ respectively.

**Q.23** A cannot cycle has an efficiency of 40%. Its low temperature reservoir is at 7˚C, what is the temperature of source?

**Q.24** Calculate entropy of a substance at 600 K using the following data.

(i) Heat capacity of solid from 0 K to normal melting point 200 K. $C_{pm}(s) = 0.035$ 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 from 200 K to normal boiling point 300K. $C_{pm}(l) = 60 + 0.016T$ $JK^{-1}mol^{-1}$.

(v) Heat capacity of gas from 300 K to 600 J at 1 atm. $C_{pm}(g) = 50.0$ $JK^{-1}mol^{-1}$.

**Q.25** Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (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 as stated. $\Delta H_{\text{combustion [glucose]}}$ = -2808 KJ

**Q.26** The entropies of $H_2(g)$ and H(g) are 130.6 and 114.6 J $mol^{-1}$ $K^{-1}$ respectively at 298 K. Using the data given below calculate the bond energy of $H_2$ (in kJ/mol):

$H_2(g) \rightarrow 2H(g)$; ΔG° = 406.62 kJ/mol

**Q.27** Calculate the heat produce when 3.785 lit of octane ($C_6H_{18}$) reacts with oxygen to form CO and water vapour at 25°C. The density of octane is 0.7025 g/ml. Heat of combustion of $C_6H_{18}$ is -1302.7 kcal/mol.

$\Delta H^{\circ}_r CO_2(g)$ = -94.05 kcal $mol^{-1}$;

$\Delta H^{\circ}_r CO(g)$ = -26.41 kcal $mol^{-1}$

$\Delta H^{\circ}_r H_2O(l)$ = -68.32 kcal $mol^{-1}$;

$\Delta H^{\circ}_r H_2O(g)$ = -57.79 kcal $mol^{-1}$

**Q.28** Calculate $\Delta H_1$ and $\Delta H_2$.

(i) Cis -2-butene→trans-2- butene, $\Delta H_1$

(ii) Cis -2-butene→1- butene, $\Delta H_2$

(iii) Trans-2- butene is more stable than Cis -2-butene

(iv) Enthalpy of combustion of 1- butene,

ΔH = -649.8 kcal/mol

(v) $9\Delta H_1 + 5\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans-2- butene, ΔH = -647.1 kcal/mol.

**Q.29** Calculate the bond energy of Xe – F from the following data

Ionization energy of Xe = 279 kcal/mol

Electron affinity of F = 85 kcal/mol

Bond energy of F - F = 38 kcal/mol and

Enthalpy change of reaction: $XeF_4(g) \rightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g)$, ΔH = 292 kcal

**Q.30** Using the data (all values are in kJ/mol at 25°C) given below:

$\Delta H^{\circ}_{\text{combustion}}$ (ethane) = -1559.8

$\Delta H^{\circ}_{\text{combustion}}$ (ethane) = -1410.9

$\Delta H^\circ_{combustion}$ (acetylene) = -1299.7

$\Delta H^\circ_{combustion}$ (acetaldyde) = -1192.3

$\Delta H^\circ_r$ $CO_2(g)$ = -393.5

$\Delta H^\circ_r$ of $H_2O(l)$ = -285.8

$\Delta H^\circ_r$ for C(graphite)→C(g) = -716.68

Bond energy of H - H = -435.94

Bond energy of O = O = -498.34

Calculate the following bond energies:

(i) C – C

(ii) C – H

(iii) C = O (iv) C = C (v) C = C

## Exercise 2

### Single Correct Choice Type

**Q.1** For which of the following change $\Delta H \neq \Delta E$?

(A) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

(B) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

(C) $C(s) + O_2(g) \rightarrow CO_2(g)$

(D) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

**Q.2** The reactions

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$.

has $\Delta H = -25$ kCal

| Bond | Bond Energy kCal |
|---|---|
| $\varepsilon_{C\text{-}Cl} \rightarrow$ | 84 |
| $\varepsilon_{H\text{-}Cl} \rightarrow$ | 103 |
| $\varepsilon_{C\text{-}H} \rightarrow$ | x |
| $\varepsilon_{Cl\text{-}Cl} \rightarrow$ | y |

x: y = 9: 5

From the given data, what is the bond enthalpy of Cl-Cl bond

(A) 70 kCal (B) 80 kCal

(C) 67.75 kCal (D) 57.75 kCal

**Q.3** Reactions involving gold have been of particular interest to a chemist. Consider the following reactions,

$Au(OH)_3 + 4HCl \rightarrow HAuCl_4 + 3H_2O, \Delta H = -28$ kCal

$Au(OH)_3 + 4\ HBr \rightarrow HAuBr_4 + 3H_2O,\ \Delta H = -36.8$ 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. What is the percentage conversation of $HAuBr_4$ into $HAuCl_4$?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

**Q.4** 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 vaporization 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) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

**Q.5** For the allotropic change represented by the equation C (graphite) → C (diamond),

H = 1.9 kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield $CO_2$, the enthalpy liberated in first case is

(A) Less than in the second case by 1.9 kJ

(B) More than in the second case by 11.4 kJ

(C) More than in the second case by 0.95 kJ

(D) Less than in second case by 11.4 kJ

**Q.6** $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g); \Delta H_1$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta H_2$

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g); \quad \Delta H_3$

The enthalpy of formation of $NCl_3$ (g) in the terms of $\Delta H_1$, $\Delta H_2$ and $\Delta H_3$ 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 of these

**Q.7** Ethanol can undergo decomposition to form two sets of products

$$C_2H_5OH\,(g) \rightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O\,(g) & \Delta H^o = 45.54\,kJ \\ \xrightarrow{2} CH_3CHO(g) + H_2\,(g) & \Delta H^o = 68.91\,kJ \end{cases}$$

If the molar ratio of $C_2H_4$ to $CH_3$ CHO is 8: 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is.

(A) 65.98 kJ (B) 48.137 kJ

(C) 48.46 kJ (D) 57.22 kJ

**Q.8** A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000K and rejects heat to a reservoir at $T_2$. A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at $T_2$ and rejects energy to a reservoir at 360K.If the efficiencies of engines A and B are the same then the temperature $T_2$ is

(A) 680 K (B) 640 K

(C) 600 K (D) None of these

**Q.9** The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300⁰C reversibly and isochorically

(A) $\frac{3}{2}R\ \text{In}\left(\frac{300}{200}\right)$ (B) $\frac{5}{2}R\ \text{In}\left(\frac{573}{273}\right)$

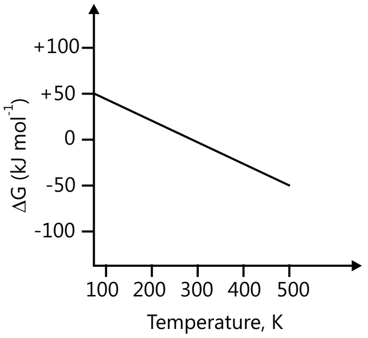
(C) $3R\ \text{In}\left(\frac{573}{273}\right)$ (D) $\frac{5}{2}R\ \text{In}\left(\frac{573}{473}\right)$

**Q.10** What is the free energy change (G) when 1.0 mole of water at 100⁰C and 1 atm pressure is converted into steam at 100⁰C and 2 atm pressure?

(A) Zero cal (B) 540 cal

(C) 517.13 cal (D) 510 cal

**Q.11** What can be concluded about the values of $\Delta H$ and $\Delta S$ 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) $\Delta H < 0,\ \Delta S < 0$

**Q.12** If $\Delta H_{vaporization}$ of substance X (l) (molar mass: 30 g/mol) is 300 J/mol 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) None of these

**Q.13** The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm is:

(A) 1.385 cal/K (B) -1.2 cal/K

(C) 1.2 cal/K (D) 2.77 cal/K

## Previous Years' Questions

**Q.1** Assuming that water vapour is an ideal gas, the internal energy (U)when 1 mol of water is vaporized at 1 bar pressure and 100⁰C, (Given: Molar enthalpy of vaporization of water at 1 bar and 373 K = 41 kJ mol $^{-1}$ an R=8.3 J mol$^{-1}$K$^{-1}$) will be ***(2007)***

(A) 4100 kJ mol$^{-1}$ (B) 3.7904 kJ mol$^{-1}$

(C) 37.904 kJ mol$^{-1}$ (D) 41.00 kJ mol$^{-1}$

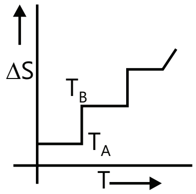
**Q.2** For the reaction, $2CO + O_2 \rightarrow 2CO_2; \quad \Delta H = \ 560kJ$

Two moles of CO and one mole of $O_2$ are taken in a container of volume 1L They completely form two moles of $CO_2$, the gases deviate appreciably from ideal behavior. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of $\Delta U$ at 00 K (1 L atm = 0.1 kJ) ***(2006)***

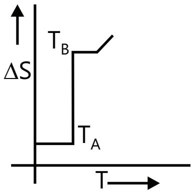
(A) 563 (B) 575 (C) 585 (D) 595

**Q.3** If for a given substance melting point is $T_8$ and freezing point is $T_A$, then correct variation shown by graph between entropy change and temperature is ***(2001)***

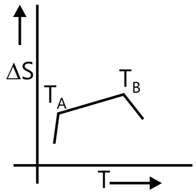
(A)



(B)



(C)



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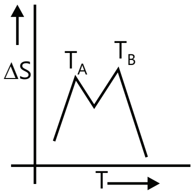


**Q.4** Identify the correct statement regarding a spontaneous process ***(2007)***

(A) For a spontaneous process in an isolated system, the change in entropy is positive.

(B) Endothermic processes are never spontaneous

(C) Exothermic process are always spontaneous

(D) Lowering of energy in the reaction process is the only criterion for spontaneity.

**Q.5** If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point then ***(2002; 2005)***

(A) $\Delta H$ is $-$ve, $\Delta S$ is $+$ve

(B) $\Delta H$ and $\Delta S$ both are +ve

(C) $\Delta H$ and $\Delta S$ both are -ve

(D) $\Delta H$ is $+$ve, $\Delta S$ is $-$ve

**Q.6** The enthalpy of vaporization of a liquid is 30 kJ $mol^{-1}$ and entropy of vaporization is 75 J $mol^{-1}$ K. The boiling point of the liquid at 1 atm is ***( 2004)***

(A) 250K (B) 400K

(C) 450K (D) 600K

**Q.7** The standard molar heat of formation of ethane, $CO_2$ and water (l) are respectively -2.1, -94.1 and -68.3 kcal. The standard molar heat of combustion of ethane will be, ***(1986)***

(A) -372 kcal (B) 162 kcal

(C) -240 kcal (D) 183.5 kcal

**Q.8** On the basis of the following thermochemical data:

$$(\Delta_f G^o H^+_{(aq)} = 0)$$

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq); \Delta H = 57.32 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \ ; \Delta H = -286.20 \text{kJ}$$

The value of enthalpy of formation of $OH^-$ ion at $25^0C$ is ***(2009)***

(A)-22.88 kJ (B) -22.8.88 kJ

(C) +228.88 kJ (D) -343.52 kJ

**Q.9** Standard molar enthalpy of formation of $CO_2$ is equal to ***(1997; 2001)***

(A) Zero

(B) The standard molar enthalpy of combustion of gaseous carbon

(C) The sum of standard molar enthalpies of formation of CO and $O_2$

(D) The standard molar enthalpy of combustion of carbon (graphite)

**Q.10** Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta diss \overset{\ominus}{H}} Cl(g) \xrightarrow{\Delta eg \overset{\ominus}{H}} Cl^-(g) \xrightarrow{\Delta hyd \overset{\ominus}{H}} Cl^-(aq)$$

The energy involved in the conversion of

$$\frac{1}{2}Cl_2(g) \text{ to } Cl^-(aq)$$

(Using the data $\Delta_{diss}HCl_2 = 240 \text{ kJmol}^{-1}$, $\Delta_{eq}H_{Cl} = -349 \text{ kJmol}^{-1}$, $\Delta_{hyd}H_{Cl} = -381 \text{kJmol}^{-1}$) will be ***(2008)***

(A) -610 $kJmol^{-1}$ (B)-850 $kJmol^{-1}$

(C) +120 $kJmol^{-1}$ (D) +152 $kJmol^{-1}$

**Q.11** 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 $\Delta_f H$ for the formation of XY is -200kJmole$^{-1}$. The bond dissociation energy of $X_2$ will be ***(2005)***

(A) 100 $kJmol^{-1}$ (B) 800 $kJmol^{-1}$

(C) 300 $kJmol^{-1}$ (D) 400 $kJmol^{-1}$

**Q.12** Using the data provided, calculate the multiple bond energy (kJ $mol^{-1}$) of a C=C bond in $C_2H_2$.That energy is (take the bond energy of a C – H bond as 350 kJ $mol^{-1}$)

$$2C(s) + H_2(g) \rightarrow C_2H_2(g) \ ; \Delta H = 225 \text{kJmol}^{-1}$$
$$2C(s) \rightarrow 2C(g); \quad \Delta H = 1410 \text{kJmol}^{-1}$$
$$H_2(g) \rightarrow 2H(g); \quad \Delta H = 330 \text{kJmol}^{-1}$$

***(2012)***

(A) 1165 (B) 837 (C) 865 (D) 815

**Q.13** In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria ***(2003)***

(A) $(dS)_{(V,E)} < 0, (dG)_{(T,P)} < 0$

(B) $(dS)_{(V,E)} > 0, (dG)_{(T,P)} < 0$

(C) $(dS)_{(V,E)} = 0, (dG)_{(T,P)} = 0$

(D) $(dS)_{(V,E)} = 0, (dG)_{(T,P)} > 0$

**Q.14** For a particular reversible reaction at temperature T, $\Delta H$ and $\Delta S$ were found to be both +ve. If is the temperature $T_e$ at equilibrium, the reaction would be spontaneous when ***(2003)***

(A) $T = T_e$ (B) $T_e > T$

(C) $T > T_e$ (D) $T_e$ is 5 time T

**Q.15** For which one of the following reactions, ΔH is not equal to ΔE **(1995)**

(A) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

(B) $C(g) + O_2(g) \rightleftarrows CO_2(g)$

(C) $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$

(D) $HCl(aq) + NaOH(aq) \rightleftarrows NaCl(aq) + H_2O$

**Q.16** A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0ºC. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: **(2013)**

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(A) $q = +208\ J,\ w = -208\ J$

(B) $q = -208\ J,\ w = -208\ J$

(C) $q = -208\ J,\ w = +208\ J$

(D) $q = +208\ J,\ w = +208\ J$

**Q.17** For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

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 $mol^{-1}$) **(2014)**

(A) -1366.95 kJ $mol^{-1}$ (B) -1361.95 kJ $mol^{-1}$

(C) -1460.50 kJ $mol^{-1}$ (D) -1350 kJ $mol^{-1}$

**Q.18** 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? $(K_p = 1.6 \times 10^{12})$ **(2015)**

(A) $R(298)\ in\ (1.6 \times 10^{12}) - 86600$

(B) $86600 + R(298)\ ln\ (1.6 \times 10^{12})$

(C) $86600 - \dfrac{ln\ (1.6 \times 10^{12})}{R(298)}$

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

**Q.19** 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: **(2016)**

(A) 676.5 (B) – 676.5

(C) –110.5 (D) 110.5

# JEE Advanced/Boards

## Exercise 1

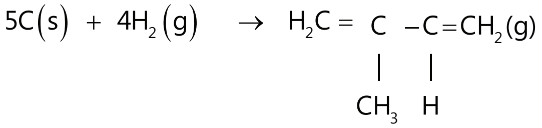
**Q.1** When 2 moles of $C_2H_6$ (g) are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of $C_2H_6$(g). Given $\Delta_f H$ for $CO_2$ (g) and $H_2O$ (l) are – 395 & 286 kJ respectively.

**Q.2** Calculate standard enthalpies of formation of carbon – di - sulphide. Given the standard enthalpy of combustion of carbon (s), sulphur (s) and carbon – di – sulphide are: -393.3, - 293.72 and – 1108.76 kJ $mol^{-1}$ respectively.

**Q.3** 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)** |
|---|---|
| (A) $Fe_2O_3(s) + 3C(g) \rightarrow 2Fe(s) + 3CO(g)$ | 492.6 |
| (B) $FeO(s) + C(g) \rightarrow Fe(s) + 3CO(g)$ | 155.8 |
| (C) $C(g) + O_2(g) \rightarrow CO_2(g)$ | -393.51 |
| (D) $CO + 11O_2(g) \rightarrow CO_2(g)$ | -282.98 |

**Q.4** Using bond enthalpy data, calculate enthalpy of formation of isoprene.



$$5C(s) + 4H_2(g) \rightarrow H_2C=\underset{CH_3}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}=CH_2(g)$$

Given: C – H = 98.8 k Cal; H – H = 104 k Cal;

C – C = 83 k Cal; C = C = 147 k Cal &

C(s) → C (g) = 171 k Cal

**Q.5** Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

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

Data:

| Bond | C – C | C = C | C – H | H - H |
|---|---|---|---|---|
| Bond Enthalpy | 336.81 kJ 1mol | 606.68 kJ 1mol | 410.87 kJ 1mol | 431.79 kJ 1mol |

**Q.6** Using the given data calculate enthalpy of formation of acetone (g). [All values in kJmol$^{-1}$] bond enthalpy of:

| | | |
|---|---|---|
| C- H = 413.4; | C – C = 347.0; | (C = 0 = 728.0; |
| (0 = 0) = 495.0; | H – H = 435.8; | $\Delta_{sub}H$ of C = 718.4 |

**Q.7** Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and $Na_2CO_3$ are mixed $\Delta_fH^o$ for $Ca^{2+}$ (aq), $CO_3^{-2}$ (ap) and $CaCO_3$ (s) are – 129.80, - 161.65, - 288.5 k Cal mol$^{-1}$ respectively.

**Q.8** The enthalpies of neutralization of NaOH & $NH_4OH$ by HCl are - 13680 Cal and - 12270 Cal respectively. What would be the enthalpy change if one gram equivalent of NaO H is added to one gram equivalent of $NH_4Cl$ in solution? Assume that $NH_4OH$ and NaCl are quantitatively obtained.

Q.9 1.00 Lit sample of a mixture of $CH_4$ (g) and $O_2$ (g) measured at 25° C and 740 bar was allowed to react at constant pressure in a Calorimeter which together with its contents had a heat capacity of 1260 Cal/K. The complete combustion of methane to $CO_2$ and $H_2O$ caused a temperature rise, in the Calorimeter, of$\Delta H^o_{comb}$ ($CH_4$) = -215 k Cal mol$^{-1}$.

**Q.10** Two solution initially 25°C were mixed in an adiabatic constant pressure Calorimeter one contains 400 ml of 0.2 M weak mono protic acid solution. The other contains 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2°C. How much heat is evolved in the neutralization of 1 mole of acid? Assume of solution 1.0 g/cm$^3$, and specific heat of solution 4.2 J/g-K Neglect heat capacity of the Calorimeter.

**Q.11** Calculate the electron gain enthalpy of fluorine atom using the following data. Make Born – Haber's cycle. All the values are in kJ mol$^{-1}$ at 25°C $\Delta H_{diss}$ ($F_2$) = 160, $\Delta_fH$ (NaF(s)) =571, I. E. [Na (g)] = 494, $\Delta H_{vap}$[Na(s)] = 101. Lattice enthalpy of NaF(s) = 894.

**Q.12** Calculate the enthalpy of combustion of methyl alcohol at 298 K from the following data

| Bond | C – H | C – O | O – H | O = O | C = O |
|---|---|---|---|---|---|
| Bond Enthalpy (kJ mol$^{-1}$) | 414 | 351.5 | 464.5 | 494 | 711 |

Resonance energy of $CO_2$ = - 143 kJ mol$^{-1}$

Latent heat of vaporization of methyl alcohol = 35.5 kJ mol$^{-1}$

Latent heat of vaporization of water = 40.6 kJ mol$^{-1}$

**Q.13** Calculate work done in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1atm to final pressure of 2 atm Initial temperature = 300 K.

(a) If process is carried out reversibly

(b) If process is carried out irreversible against 2atm external pressure.

Computer the final volume reached by gas in two cases and describe the work graphically.

**Q.14** One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure Calculate.

(a) Work done by the gas

(b) The heat exchanged by the gas in path CA and AB

(c) Net heat absorbed by the gas in the path BC.

(d) The max temperature attained by the gas during the cycle.

**Q.15** One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of $\Delta S_{gas}$ and $\Delta S_{total}$ under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly where 836.8 J of heat is less absorbed than in

(iii) Expansion is free.

**Q.16** The enthalpy change for vaporization of liquid 'A' at 200 K and 1 atm is 22kJ 1mol. Find out $\Delta S_{vaporization}$ for liquid 'A' at 200 K? The normal boiling point of liquid 'A' is 300 K.

$$A\,(l)\,\left[200\text{ K }1\text{ atm}\right] \rightarrow A\,(g)\,\left[200\text{ K }1\text{ atm}\right]$$

Given: $C_{p.m}(A, g)$ = 30 J 1 mol-K, $C_{p,,m}(A, l)$ = 40 J1mol – K;

Use: In (312) = 0.405

**Q.17** One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate $\Delta S_{system,}$ $\Delta S_{suit}$ and $\Delta S_{total}$ in

(i) When the process carried out reversibly.

(ii) When the process carried out irreversibly (one step)

**Q.18** Compute $\Delta_1 G$ for the reaction $H_2O$ (l, 1 atm, 323 K) → $H_2O$ (g, 1 atm, 323 K)

Given that: $\Delta_{vap}H$ at 373 K = 40.639 kJmol$^{-1}$, $C_p(H_2O,l)$ = 75.312 J K$^{-1}$ mol$^{-1}$,

$C_p(H_2O,G)$ = 33.305 J K$^{-1}$ mol$^{-1}$.

**Q.19** 10g of neon initially at a pressure of 506.625kPa and temperature of 473 K expand adiabatically to a pressure of 202.65kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.

(i) Expansion is carried out reversibly.

(ii) Expansion occurs against a constant external pressure of 202.65kPa.

(iii) Expansion is a free expansion.

**Q.20** At 298 K, $\Delta H^o_{combustn}$ (sucrose) = -5737 KJ$^{-1}$ mol and $\Delta G^o_{combustn}$ (sucrose) = -6333 KJ 1 mol.

**Q.21** The standard enthalpy of formation of FeO & $Fe_2O_3$ is – 65 kCal mol$^{-1}$ and -197 kCalmol$^{-1}$ 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 ration mixture, how much of thermal energy will be released per mole of the initial mixture?

**Q.22** The enthalpies of neutralization of a weak acid HA & a weak acid HB by NaOH are -6900 cal equivalent & -2900 cal equivalent respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was -3900 Calories. In what ratio is the base distributed between HA & HB?

**Q.23** Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 41.84 kJ of heat at

(a) Constant pressure.

(b) Constant volume

Given: $\Delta H^o_f$ (HgO$_{,}$(s) = -90.8 kJ mol$^{-1}$ & M (Hg) = 200.6 g mol$^{-1}$

**Q.24** For reduction of ferric oxide by hydrogen,

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$$

$\Delta H^o_{298}$ = -35.1 kJ. The reaction was found to be too exothermic to be convenient. It is desirable that $\Delta H^o$ should be at the most – 26kJ. At what temperature is it possible?

$C_P\left[Fe_2O_3\right]$ =104.5, $C_P\left[Fe(s)\right]$ =25.5,

$C_P\left[H_2(l)\right]$ = 75.3, $C_P\left[H_2(g)\right]$ = 28.9

(All in J/mol)

**Q.25** An intimate mix of ferric oxide and Al is used as solid rocket fuel. Calculate the fuel value per gm and fuel value per CC of the mix. Enthalpy of formation & densities are:

$\Delta H^o_f\left(Al_2O_3\right)$ = –399k Cal/mole;

$\Delta H^o_f\left(Fe_2O_3\right)$ = –199k Cal/mole,

Density of $Fe_2$ $O_3$ = 5.2 g/cc; density of Al = 2.7 g/cc.

**Q.26** Calculate the enthalpy change for the reaction

$$Xe\,F_4 \quad \rightarrow \quad Xe^+ + F^- + F_2 + F$$

The average Xe–F bond enthalpy is 34 K Cal/mol, first I E. of Xe is 279 k Cal/mol, electron affinity of is 85 k Cal/mol & bond dissociation enthalpy of $F_2$ is 38k Cal/mol.

**Q.27** Calculate the proton gain enthalpy of $NH_3$ (g) from the following data (in kJ/mole)

$\Delta H^o_{dissociation:}$ $H_2(g)$ = 218; $\Delta H^o_{dissociation:}$ $Cl_2(g)$ = 124

$\Delta H^o_{formation:}$ $NH_3(g)$ = -46; $\Delta H^o_f$:$NH_4$ Cl(s) = -314

Lattice enthalpy of $NH_4$ Cl(s) = -683

Ionization enthalpy of H = 1310

Electron affinity of Cl = 348.

**Q.28** During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition to $O_2$ and $N_2$. Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sacked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.

An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.

(i) If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?

(ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling-exhaling take?

$\Delta H^\circ_{comb}$(CO) = $-280\text{kJmol}^{-1}$. Neglect any use of Graham's Law.

**Q.29** Find the Bond enthalpy (in kJ/mol) of one "three centre two electron bond" in $B_2H_6$

{B-H-B→2B (g) +H (g)} from the given data.

$\Delta H^\circ_t [BH_3\ (g)] = 100$ kJ/mole

$\Delta H^\circ_t [B_2H_6\ (g)] = 36$ kJ/mole

$\Delta H_{atm} [B(s)] = 565$ kJ/mole

$\Delta H_{atm} [H_2\ (g)] = 436$ kJ/mole

**Q.30** The heat of neutralization of:

(i) $CHCl_2$–COOH by NaOH is 12830 cal;

(ii) HCl by NaOH is 13680 cal

(iii) $NH_4OH$ by HCl is 12270 cal.

What is the heat of neutralization of dichloroacetic acid by $NH_4OH$. Calculate also the heats of ionization of dichloroacetic acid and $NH_4OH$.

# Exercise 2

### Single Correct Choice Type

**Q.1** Hydrazine, a component of rocket fuel, undergoes combustion to yield $N_2$ and $H_2O$.

$N_2H_4(l) + O_2\ (g) \rightarrow N_2(g) + 2H_2O(l)$What is the enthalpy combustion of $N_2H_4$ (kJ/mole).

| Given Reaction | ΔH/kJ |
|---|---|
| $2NH_3(g) + 3N_2O(g) \rightarrow 4N_2(g) + 3H_2O(l)$ | 1011 kJ |
| $N_2O(g) + 3H_2(g) \rightarrow N_2H_4(l) + H_2O(l)$ | -317 kJ |
| $4NH_3(g) + O_2(g) \rightarrow 2N_2H_4(l) + 2H_2O(l)$ | 286 kJ |
| $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ | -385kJ |

(A) -620.5 (B) -622.75

(C) 1167.5 (D) +622.75

**Q.2** Find $\Delta_rU^\circ$ for the reaction $4HCl(g) + O_2(g) \rightarrow 2Cl_2 + 2H_2O(g)$ at 300 K. Assume all gases are ideal.

Given: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

$\Delta_rH^\circ_{300} = -184.5$ kJ/mole

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

$\Delta_rH^\circ_{300} = -483$ kJ/mole (Use R = 8.3 J/mole)

(A) 111.5 kJ/mole (B) -109.01kJ/mole

(C) -111.5 kJ/mole (D) None of these

**Q.3** The enthalpy changes at the following reactions at 27˚C are

$Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s)$

$\Delta_rH = -411$ kJmol

$H_2\ (g) + S(s) + 2O_2\ (g) \rightarrow H_2SO_4\ (l)$

$\Delta_rH = -811$ kJ/mol

$2Na(s) + S(s) + 2O_2\ (g) \rightarrow Na_2SO_4(s)$

$\Delta_rH = -1382$ kJ/mol

$1/2H_2\ (g) + 1/2Cl_2(g) \rightarrow HCl(g)$

$\Delta_rH = -92$ kJ/mol; R = 8.3 J/K-mol

From these data, the heat change of reaction at constant volume (in kJ/mol) at 27C for the purpose

$2NaCl(s) + H_2SO_4(l) \rightleftharpoons Na_2SO_4(s) + 2HCl(g)$ is

(A) 67 (B) 62.02 (C) 71.98 (D) None

**Q.4** For the reaction at 300K $A(g) + B(g) \rightarrow C(g)$

$\Delta E = -3.0$ kcal ; $\Delta S = -10.0$ cal/K; value of G is?

(A) -600 cal (B) -6600 cal

(C) -6000 cal (D) None

**Q.5** What is the free energy change ($\Delta G$) when 1.0 mole of water at $100^0$C and 1 atm pressure is converted into steam at $100^0$C and 1 atm pressure?

(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero

**Q.6** The enthalpy of tetramerization of X in gas phase (4X (g) → $X_4$(g)) is -100 kJ/mol at 300 K. The enthalpy of vaporisation for liquid X and $X_4$ are respectively 30 kJ/mol and 72 kJ/mol respectively. $\Delta S$ for tetramerization of X in liquid phase is -125 J/Kmol at 300 K, what is the $\Delta G$ at 300 K for tetramirization of X in liquid phase?

(A)-52 kJ/mol (B)-89.5 kJ/mol

(C) -14.5 kJ/mol (D) None of these

**Q.7** Standard entropy of $X_2$ $Y_2$ and $XY_3$ are 60, 40 and 50 $JK^{-1}mol^{-1}$, respectively. For the reaction

$\frac{1}{2}X_2+\frac{3}{2}Y_2 \rightarrow XY_3 \; \Delta H=-30\text{ kJ}$ to be at equilibrium, the temperature will be

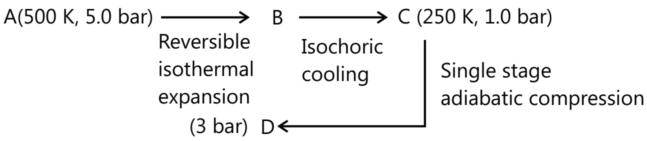
(A) 1250 K (B) 500 K (C) 750 K (D) 1000 K

**Q.8** When two equal sized pieces of the same metal at different temperatures $T_h$ (hot piece) and $T_c$ (cold piece) are brought into contract into thermal contact and isolated from its surrounding. The total change in entropy of system is given by

(A) $C\ln\frac{T_c+T_h}{2T_c}$ (B) $C\ln\frac{T_2}{T_1}$

(C) $C\ln\frac{(T_{c-}+T_h)^2}{2T_h.T_c}$ (D) $C\ln\frac{(T_{c-}+T_h)^2}{4T_h.T_c}$

**Q.9** Two moles of an ideal gas ($C_m$= 312 R) is subjected to following change of state.



The correct statement is 1 are:

(A) The pressure at B is 2.0 bar

(B) The temperature at D is 450 K

(C) $\Delta H_{CD}$ = 1000 R

(D) $\Delta U_{BC}$ = 375 R

### Multiple Correct Choice Type

**Q.10** From the following data at $25^0C$

| Reaction | $\Delta_r H^0$ kJ/mol |
|---|---|
| $\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g)\rightarrow OH(g)$ | 42 |
| $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g)$ | -242 |
| $H_2(g) \rightarrow 2H(g)$ | 436 |
| $O_2(g) \rightarrow 2O(g)$ | 495 |

Which of the following statement(s) is/ are correct:

(A) $\Delta_r H^0$ for the reaction $H_2O$ (g) → 2H (g) + O (g) is 925.5 kJ/mol

(B) $\Delta_r H^0$ for the reaction OH (g) → 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

**Q.11** Which is the following is true?

(A) For the reaction $CaCO_3$ (calcite) → $CaCO_3$ (aragonite)

Given: $\Delta_f G^0_{298}$ (calcite) = -1128.8 kJ/mol, $\Delta_f G^0_{298}$ (calcite) = -1127.75 kJ/mol,

Then calcite forms in thermodynamically more stable at standard conditions.

(B) For the reaction,

(a) C (diamond) +2$H_2$ (g) → $H_4$ (g) $\Delta H_1$

(b) C (g) + 4H (g) → $CH_4$ (g) $\Delta H_2$

Then more heat is evolved in reaction (b)

(C) $\Delta_f H^0$ ($I_2$, g) = $\Delta_{sub}$ H [$I_2$, s] at $25^0C$

(D) For the exothermic reaction

2 Ag (s) +11$O_2$(g) → 2$Ag_2O$(s) at 298 K.

$\Delta H < \Delta U$

**Q.12** Which of the following statement (s) is /are true?

(A) When $(\Delta_{system})_{TP}<0$; the reaction must be exothermic

(B) $\Delta 1_f H^0$ (S, monoclinic) ≠0

(C) If dissociation enthalpy of $CH_4$ (g) is 1656 kJ/mol and $C_2H_6$ (g) is 2812 kJ/mole, then value of C-C bond enthalpy will be 328 kJ/mole

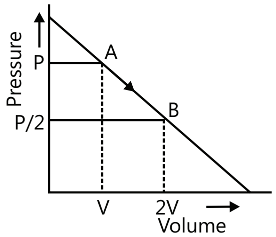
(D) If $H^+$(aq) + OH (aq) → $H_2O$(l)

$\Delta_r H^0$= -56 kJ/mol

$\Delta_f H^0(H_2O, g)$ = -242 kJ/mole; Enthalpy of vaporization of liquid water = 44 kJ/mol then $\Delta_f H^0(H_2O, g)$

= -142 kJ/mole;

**Q.13** An ideal gas is taken from state A (Pressure P, Volume V) to the state B (Pressure P/2, Volume 2V) along a straight line path in PV diagram as shown in the adjacent figure



Select the correct statement(s) among the following

(A) The work done by gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm

(B) In the T-V diagram, the path AB become part of the parabola

(C) In the P-T diagram, the path AB become part of the hyperbola

(D) In going from A to B the temperature T of the gas first increases to a maximum value then decreases.

**Q.14** The normal boiling point of a liquid 'A' is 350K. $\Delta H_{vap}$ at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume $\Delta H_{vap}$ to be independent of pressure).

(A) $\Delta S_{vaporisation} >$ 100 J/Kmole at 350 K and 0.5 atm

(B) $\Delta S_{vaporisation} >$ 100 J/Kmole at 350 K and 0.5 atm

(C) $\Delta S_{vaporisation} >$ 100 J/Kmole at 350 K and 2 atm

(D) $\Delta S_{vaporisation} >$ 100 J/Kmole at 350 K and 2 atm

**Q.15** Which statement is are correct?

(A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion

(B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase

(C) When an ideal gas is subjected to adiabatic expansion it gets cooled.

(D) Entropy increases in atomisation of dihydrogen

**Q.16** Which one is (are) correct statement?

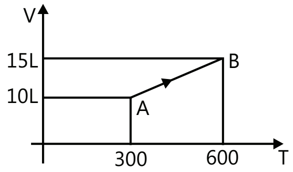
(A) $W_{adiabatic} > W_{isothermal}$ in an ideal gas compression from same initial state to same final volume

(B) The value of $\gamma^{\frac{C_p}{C_v}}$ remains constant for diatomic gas at all temperature

(C) Entropy increases when an ideal gas expanded isothermally

(D) $\Delta S_r$ and $\Delta H_r$ both are +ve for the decomposition of Mg $C_3$(s)

**Q.17** If one mole monoatomic ideal gas was taken through process AB as shown in figure, then select correct option(s).



(A) $W_{AB}$ = -2496.52J

(B) $q_{AB}$ = 5237.82 J

(C) $H_{AB}$=3741.3 J

(D) $S_{AB}$ is +ve

**Q.18** Which of the following statement(s) is/are correct?

(A) Reversible isothermal compression of an ideal gas represents the limiting minimum value of the work done (w) by the surrounding on the system for isothermal process.

(B) In an irreversible process, the cyclic integral of work is not zero.

(C) For thermodynamic changes in adiabatic process

$$T\left(\frac{C_{pm}}{R}\right)P=\text{constant}$$

**Q.19** Which of the following is true for reversible adiabatic process involving an ideal gas?

(A) Gas with higher Y has high magnitude of slope in a P (y-axis) vs T (x-axis) curve

(B) Gas with higher Y has high magnitude of slope in a V (y-axis) vs T (x-axis) curve

(C) Gas with higher Y has high magnitude of slope in a P (y-axis) vs V (x-axis) curve

(D) Gas with higher Y has high magnitude of slope in a P (y-axis) vs V (x-axis) curve

**Q.20** 100 ml 0.5 N $H_2SO_4$ (strong acid) is neutralised with 200 ml 0.2M $NH_4OH$ in a constant pressure Calorimeter which results in temperature rise of 1.4°C. If heat capacity of Calorimeter content is 1.5 kJ/°C. Which statement is /are correct

Given:

$$HCl + NaOH \rightarrow NaCl + H_2O + 57\text{ kJ}$$
$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O + 48.1\text{ kJ}$$

(A) Enthalpy of neutralisation of HCl v/s $NH_4OH$ is -52.5 kJ/mol

(B) Enthalpy of dissociation (ionization) of $NH_4OH$ is 4.5 kJ/mol

(C) Enthalpy of dissociation of $CH_3COOH$ is 4.6 kJ/mol

(D) $\Delta H$ For $2H_2O(l) \rightarrow 2H(aq.)+2OH^-$ is 114 kJ

**Q.21** Which of the following does not represent $\Delta H$ formation of the product.

(A) $\frac{1}{2}H_2(g)+(aq)\rightarrow H^+(aq)$

(B) $\frac{2}{3}O_3(g)\rightarrow O_2(g)\ e^-$

(C) $NH_4^+(g)+Cl^-(g)\rightarrow NH_4Cl(s)$

(D) $P_4(black)+5O_2(g)\rightarrow P_4O_{10}(s)$

(E) Reaction representing $\Delta H_{combustion}$ of C (graphite)

**Q.22** Which of the following statements is /are false?

(A) $\Delta S$ for $\frac{2}{3}N_2$ (g) × N (g) is positive

(B) $\Delta G_{system}$ is always zero for a reversible process in a closed system

(C) $\Delta G^0$ for an ideal gas is a function of temperature and pressure

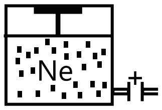
(D) Entropy of a closed system is always maximized at equilibrium

**Q.23** In isothermal ideal gas compression:

(A) W is +ve (B) $\Delta H$ is zero

(C) $\Delta S_{gas}$ is +ve (D) $\Delta G$ is +ve

**Q.24** A piston cylinder device initially contains $0.2\ m^3$ neon (assume ideal) at 200 kPa insideat $T_1{}^0C$. A valve is now opened and neon is allowed to escape until the volume reduces to half the initial volume. At the same time heat transfer with outside at $T_2{}^0C$ ensures a constant temperature inside. Select correct statement(s) for given process



(A) $\Delta U$ must be zero (B) $\Delta U$ cannot be zero

(C) q may be +ve (D) q may be –ve

### Assertion Reasoning Type

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I

(C) Statement-I is false, statement-II is true.

(D) Statement-I is true, statement-II is false

**Q.25 Statement-I:** There is no change in enthalpy of an ideal gas during compression constant temperature.

**Statement-II:** Enthalpy of an ideal gas is a function of temperature and pressure.

**Q.26 Statement-I:** Due to adiabatic free expansion, temperature of a real gas always increases.

**Statement-II:** If a real gas is at inversion temperature then no change in temperature is observed in adiabatic free expansion.

**Q.27 Statement-I:** $S_8$ (s) + $O_2$(g) → $SO_2$(g), represents complete combustion of $S_8$(s).

**Statement-II**: On complete combustion, the element from its amide, having maximum oxidation state.

**Q.28 Statement-I:** The enthalpy of neutralization of the reaction between HCl and NaOH is –

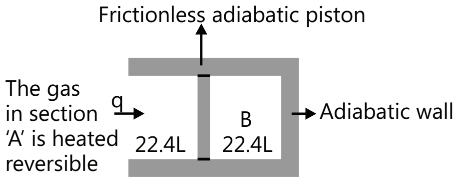
13.7kCal/mol. If the enthalpy of neutralization of oxalic acid ($H_2C_2O_4$) by a strong base in -25.4 kCal/mol, then the enthalpy changes ($\Delta H$) of the process

$H_2C_2O_4 \rightarrow 2H^+ + C_2O_4{}^{2-}$ is 11.7 kCal/mol.

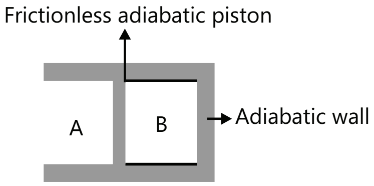
**Statement-II:** $H_2C_2O_4$ is a weak acid

### Comprehension Type

**Paragraph 1:** A cylindrical container of volume 44.8 liters is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3 K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes (1/8)th of initial volume.



Initial state



Initial state

Given: R = 2 cal/mol-K, $C_{vm}$ of monoatomic gas = $\frac{3}{2}$ R,
At 1 atm & $0^0$C ideal gas occupy 22.4 liter.

**Q.29** What will be the final pressure in container B?

(A) 2 atm (B) 8 atm
(C) 16 atm (D) 32 atm

**Q.30** Find temperature in container A will be

(A) 1638 K (B) 6988 K
(C) 3274 K (D) 51 K

**Q.31** Change in enthalpy for section A in k Cal

(A) 48.3 (B) 80.53
(C) 4.83 (D) 8.05

**Paragraph 2:** The vapor pressure of $H_2O$ (l) at 353 K is 532 mm Hg. The external pressure on $H_2O$ (l) taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (=0.9 kg) of $H_2O$ (l) at 33 K is increased to 1 atm. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of $H_2O$ (l) (=0.45 kg) is evaporated to form $H_2O$ (g) at 373 K. carefully observe the diagrams provided and form given data, answer the following questions

Given:

Specific heat of $H_2O$ = 4.2J/gm$^0$C

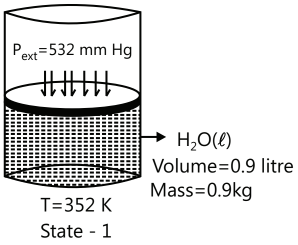
Use $H_{vap}$ at 373 K and 1 atm =+40 kJ/mol

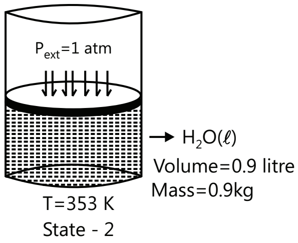
1L atm = 100 Joule

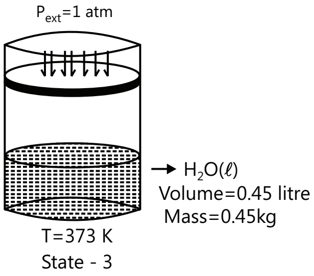
1 atm = 760 mm Hg

R = 8 Joule/mole K

(Assume internal energy of liquid to be dependent only on temperature).







**Q.32** ΔH When system is taken from state 1 to state 2 (Joule)?

(A) Zero (B) 0.27 (C) 27 (D) 90

**Q.33** Total change in ΔU going from state 1 to 3 (kJ)?

(A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

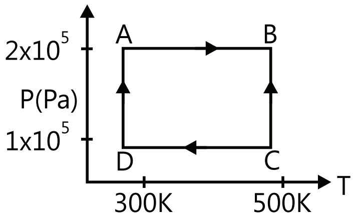
**Q.34** Total change in enthalpy going from state 1 to 3 (kJ)?

(A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

**Q.35** What is the work done in going from state 1 to state 3 in Joules?

(A) Zero (B) 74.6 (C) 90 (D) 31.5

**Paragraph 3:** Two moles of helium gas are taken over the ABCDA, as shown in the P-T diagram



**Q.36** Assuming the gas to be ideal the work done by the gas in taking it from A to B is

(A) 200 R (B) 300 R (C) 400 R (D) 500 R

**Q.37** The work done on the gas in taking it from D to A is-

(A) -414R (B) +414 R (C) -690 R (D) +690 R

**Q.38** The work done on the gas in the cycle ABCDA is-

(A) Zero (B) 276 R (C) 1076 R (D) 1904 R

## Match the Columns

**Q.39** Match the column I with column II:

| Column I (Ideal Gas) | Column II (Related equations) |
|---|---|
| (A) Reversible isothermal process | (p) W=2.303nRT log ($P_2/P_1$) |
| (B) Reversible adiabatic process | (w) W=n$C_{Vm}$ ($T_2$-$T_1$) |
| (C) Irreversible adiabatic process | (r) W=-2.303nRT log ($V_2/V_1$) |
| (D) Irreversible isothermal process | (s) $W = \int_{V_2}^{V_1} P_{ext}\, dV$ |

**Q.40** Match the column I with column II.

Note that column I may have more than one matching options in column II

| Column I | Column II |
|---|---|
| (A) Reversible adiabatic compression | (p) $\Delta S_{system} > 0$ |
| (B) Reversible vaporisation | (q) $\Delta S_{system} < 0$ |
| (C) Free expansion of ideal gas in vacuum | (r) $\Delta S_{surrounding} < 0$ |
| (D) Dissociation of $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ | (s) $\Delta S_{surrounding} = 0$ |

## Previous Years' Questions

**Q.1** The species which by definition has zero standard molar enthalpy of formation at 298 K is ***(2010)***

(A) $Br_2(g)$ (B) $Cl_2(g)$ (C) $H_2O(g)$ (D) $CH_4(g)$

**Q.2** The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given: $\Delta_r H^\circ_{298K} = -54.07$ kJ $mol^{-1,}$

$\Delta_r S^\circ_{298K} = 10\ JK^{-1}$ and $R = 8.314\ JK^{-1}\ mol^{-1}$; $2.303 \times 8.314 \times 298 = 5705$) ***(2007, 3M)***

(A) 5 (B) 10 (C) 95 (D) 100

**Q.3** For the process $H_2O$ (l) (1 bar, 373 K) $\rightarrow H_2O$ (G) (1 bar, 373 K), the correct set of thermodynamic parameters is ***(2007, 3M)***

(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

**Q.4** The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given that $\Delta S_{(A\rightarrow C)} = 50$ eu

$\Delta S_{(C\rightarrow D)} = 30$ eu

$\Delta S_{(D\rightarrow B)} = 20$ eu

where eu is entropy unit. Then $\Delta S_{(A\rightarrow B)}$ is ***(2006, 3M)***

(A) +100 eu (B) +60 eu

(C) -100 eu (D) -60 eu

**Q.5** A monatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas? ***(2006, 3M)***

(A) $\frac{4R}{2}$ (B) $\frac{3R}{2}$ (C) $\frac{5R}{2}$ (D) 0

**Q.6** Among the following, intensive property is (properties are): ***(2010)***

(A) Molar Conductivity (B) Electromotive force

(C) Resistance (D) Heat capacity

**Q.7** Among the following, the state function(s) is (are) ***(2009)***

(A) Internal energy

(B) Irreversible expansion work

(C) Reversible expansion work

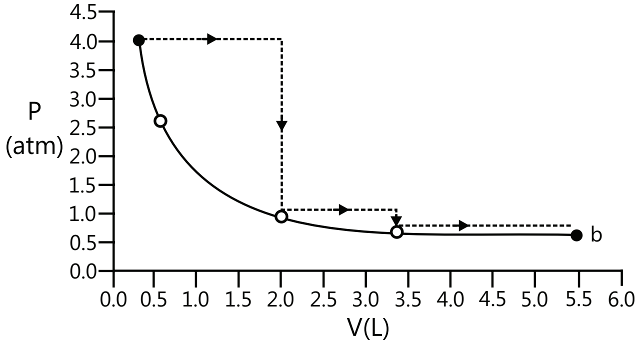
(D) Molar enthalpy

**Q.8** 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 $mol^{-1}$ is ***(2009)***

**Q.9** For the reaction, $2CO + O_2 \rightarrow 2CO_2$; $\Delta H = -560$ kJ. Two moles of CO and one mole of $O_2$ are taken in a container of volume 1 L. They completely form two moles of $CO_2$, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of $\Delta U$ at 500 K. (1 L atm = 0.1 kJ ) ***(2006, 3M)***

**Q.10** 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the $\Delta H$ and $\Delta U$. ***(2004, 2M)***

**Q.11** One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is **W**, and that along the dotted line path is $W_d$, then the integer closest to the ration $\frac{W_d}{W_s}$ is ***(2010)***



Read the following questions and answer as per the direction given below:

(A) Statement-I is true; statement-II is true; statement-II is the correct explanation of statement-I.

(B) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false; statement-II is true

**Q.12 Statement-I:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero

**Statement-II:** The volume occupied by the molecules of an ideal gas is zero. ***(2000, 2M)***

**Q.13 Statement-I:** For every chemical reaction at equilibrium, standard Gibbs' energy of reaction is zero.

**Statement-II:** At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs' energy. ***(2008, 3M)***

**Q.14 Statement-I:** There is a natural asymmetry between converting work to heat and converting heat to work.

**Statement-II:** No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. ***(2008, 3M)***

**Q.15** Match the transformations in column I with appropriation options in column II. ***(2011)***

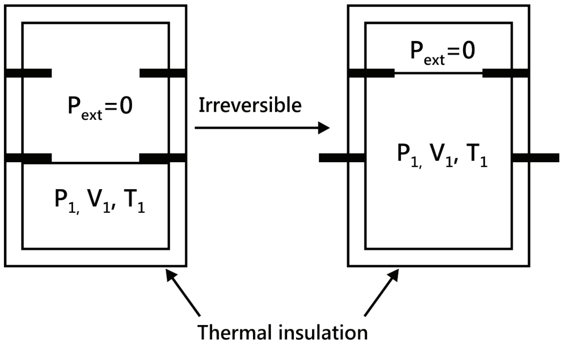
| **Column I** | **Column II** |
|---|---|
| (A) $CO_2(s) \rightarrow CO_2(g)$ | (p) Phase transition |
| (B) $CaCO_2(s) \rightarrow CaO(s) + CO_2(g)$ | (q) Allotropic change |
| (C) $2H \rightarrow H_2(g)$ | (r) ΔH is positive |
| (D) $P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$ | (s) ΔS is positive |
|  | (t) ΔS is negative |

**Q.16.** The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 250C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at $25^0C$ is ***(2013)***

(A) +2900 kJ (B) – 2900 kJ

(C) –16.11 kJ (D) +16.11 kJ

**Q.17** An ideal gas in a thermally insulated vessel at internal pressure = $P_1$, volume = $V_1$ and absolute temperature = $T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are $P_2$, $V_2$ and $T_2$, respectively. For this expansion, ***(2014)***



(A) q = 0 (B) $T_2 = T_1$

(C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^\gamma = P_1V_1^\gamma$

**Q.18** For the process $H_2O(l) \rightarrow H_2O(g)$ at T = 100°C and 1 atmosphere, the correct choice is ***(2015)***

(A) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} > 0$

(B) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$

(C) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} > 0$

(D) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} < 0$

**Q.19** 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 ($\Delta S_{surr}$) in $JK^{-1}$ is (1 L atm = 101.3 J) ***(2016)***

(A) 5.763 (B) 1.013

(C) -1.013 (D) -5.763

# MASTERJEE Essential Questions

## JEE Main/Boards

### Exercise 1

Q.1 Q. 10 Q. 11

Q. 15 Q. 16 Q. 17

Q. 28

### Exercise 2

Q. 3 Q. 8 Q. 11

Q.18 Q. 25 Q. 34

Q. 37

## JEE Advanced/Boards

### Exercise 1

Q. 3 Q. 6 Q.10

Q. 19 Q.22 Q. 24

Q. 28

### Exercise 2

Q. 7 Q.8 Q. 9

Q.10 Q.13 Q.16

Paragraph 2 Paragraph 3

## Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** (i) W, (ii)-W, (iii)-W (iv)-W

**Q.2** q=-65 J; w=20 J; Δ=-45J

**Q.3** (a) 0.47 gm, (b) 0.47 kg

**Q.4** -10 J

**Q.5** q=177.9kJ, W = 2.5 kJ; ΔE=175.4kJ

**Q.6** 0.3024 kJ

**Q.7** ΔE= 75.11 kJ

**Q.8** ΔE = 0.993 Kcal, ΔH = 1 Kcal

**Q.9** ΔH = 12168 calories; ΔE = 11623 calories

**Q.10** ΔE = 27.91 kJ $mol^{-1}$, t = 514 sec.

**Q.11** $W_{in}$ = 9353.25 $W_{in}$ =+17288.47 K, ΔU = ΔH = 0

**Q.12** W= -3.988 kJ

**Q.13** 4.59 kJ

**Q.14** q = 0; w = ΔU = 4.12 kJ; ΔH = 5.37 kJ $V_f$=11.8 $dm^2$, P= 5.21 atm

**Q.15** (i) 18.424 bar L;

(ii) 72 bar L.;

(iii) 40 bar L

Magnitude of work is maximum in single stage compression.

**Q.16** (a) T = 243.60 K; T = 2436.0 K,

(b) ΔE = 0; q = W= +3262.88 cal

**Q.17** (a) AC, (b) 170 J, (c) 10 J

**Q.18** $\Delta H_{373}$ ($H_2O$ (l) = -284.11 kJ

**Q.19** (a) 13.064 KJ $mol^{-1}$, (b) 10.587 kJ $mol^{-1}$

**Q.20** T = 1059 K

**Q.21** 21.18 $JK^{-1}$ $Mol^{-1}$

**Q.22** (i) -90.5

(ii) -374.5

(iii) -3.26 (all in J $mol^{-1}$ $K^{-1}$)

**Q.23** 196.66°C

**Q.24** 205.08 $JK^{-1}$ $mol^{-1}$

**Q.25** -2864.5 KJ

**Q.26** 436 kJ mol

**Q.27** Heat produced = -15549.7 kcal

**Q.28** $\Delta H_1$ = 0.96 kcal, $\Delta H_2$ = 1.74 kcal

**Q.29** Bond energy = 34 kcal/mol ; ΔH = 136

**Q.30** (i) 97.81 kJ (ii) 454.64 kJ

(iii) 804.26 kJ (v) 733.48 kJ

## Exercise 2

### Single Correct Choice Type

**Q.1** D **Q.2** D **Q.3** C **Q.4** B **Q.5** C **Q.6** A

**Q.7** B **Q.8** C **Q.9** C **Q.10** C **Q.11** A **Q.12** C

**Q.13** D

## Previous Years' Questions

**Q.1** C **Q.2** A **Q.3** A **Q.4** A **Q.5** B **Q.6** B

**Q.7** A **Q.8** B **Q.9** D **Q.10** A **Q.11** B **Q.12** D

**Q.13** B **Q.14** C **Q.15** C **Q.16** A **Q.17** A **Q.18** D

**Q.19** C

# JEE Advanced/Boards

## Exercise 1

**Q.1** -88 kJ mol

**Q.2** 128.02 kJ

**Q.3** -266.3 kJ 1mol and -824.2 kJ 1 mol

**Q.4** +20.6 k Cal

**Q.5** -120.08 kJ /mol

**Q.6** -192.3 kJ $mol^{-1}$

**Q.7** 2.95 kCal

**Q.8** -1410 Cal

**Q.9** 9.82 mol % $CH_4$

**Q.10** -31.5 kJ mole

**Q.11** -352 kJ $mol^{-1}$

**Q.12** -669.7 kJ $mole^{-1}$

**Q.13** (a) $T_2$ = 395.8; $V_2$=16.24L; $W_{rev}$=1194.72J.

(b) $V_{1/2}$=17.24 L $T_{1/2}$=420K

$W_{rev}$=1496.52J.

**Q.14** $w=P^0V^0$; $qCA= -\frac{5}{2}P^\circ V^\circ$ ; $qAB=3\ \ 3P^\circ V^\circ$ ;

$qBC\ -\frac{1}{2}P^\circ V^\circ\ \ T_{max}= \ =\frac{25}{8}\left(\frac{P^\circ V^\circ}{R}\right)$

**Q.15** (i) $\Delta S_{gas} = \Delta S_{surr}$ and $\Delta S_{total} = 0$,

(ii) $\Delta S_{total}$=2.808 $JK^{-1}$

(iii) $\Delta S_{total}$=9.134 $JK^{-1}$

**Q.16** 74.05 J/K

**Q.17** (i) Rev. Process $\Delta S_{sys} = \frac{3}{2}R$ in 10 ;

$\Delta S_{surr} = -\frac{3}{2}R$ ln 10;

(ii) In process $\Delta S_{sys} = -\frac{3}{2}R$ R ln 10 ; $\Delta S_{surr} = -\frac{3}{2}R$ (0.9)

$\Delta S_{total} = -\frac{3}{2}R\ (1.403)$

**Q.18** $\Delta G = 5.59$ kJ mol$^{-1}$

**Q.19** (i) $\Delta S_{sys} = 0$; $\Delta S = 0$ and $\Delta S_{total} = 0$;

(ii) $\Delta S_{total} = \Delta S_{sys} = 0.957$ JK$^{-1}$

(iii) $\Delta S_{sys} = \Delta S_{total} = 3.81$ JK$^{-1}$

**Q.20** 24kJ/mol

**Q.21** Heat released = 11.16 Kcal per mol of initial mixture.

**Q.22** 1: 3

**Q.23** (a) 92.435g (b) 93.715g

**Q.24** 404.18K

**Q.25** 0.9345 k cal g$^{-1}$, 3.94 k Cal cm$^{-3}$

**Q.26** 292 kCalmol

**Q.27** -718 kJmol

**Q.28** (i) 13 times, (ii) 21.54 sec

**Q.29** EB-H-B=455 kJmole

**Q.30** -11420 cal

## Exercise 2

### Single Correct Chioce Type

**Q.1** A
**Q.2** C
**Q.3** B
**Q.4** A
**Q.5** D
**Q.6** C
**Q.7** C
**Q.8** D
**Q.9** A

### Multiple Correct Chioce Type

**Q.10** A, D
**Q.11** A, B, C, D
**Q.12** B, C
**Q.13** A, B, D
**Q.14** A, C
**Q.15** A, C, D
**Q.16** A, C, D
**Q.17** B, D
**Q.18** A, B
**Q.19** C, D
**Q.20** A, B, D
**Q.21** A, B, C, D
**Q.22** B, C, D
**Q.23** A, B, D
**Q.24** B, C, D

### Assertion Reasoning Type

**Q.25** D
**Q.26** D
**Q.27** D
**Q.28** D

### Comprehension Type

**Paragraph 1:** **Q.29** D **Q.30** A **Q.31** B

**Paragraph 2:** **Q.32** C **Q.33** C **Q.34** B **Q.35** B

**Paragraph 3:** **Q.36** C **Q.37** B **Q.38** B

### Match the Columns

**Q.39** A $\rightarrow$ p, r, s; B $\rightarrow$ q, s; C $\rightarrow$ q, s; D $\rightarrow$ s

**Q.40** A $\rightarrow$ s; B $\rightarrow$ p, r ; C $\rightarrow$ p, s; D $\rightarrow$ p, r

## Previous Years' Questions

| | | | | | |
|---|---|---|---|---|---|
| **Q.1** B | **Q.2** C | **Q.3** A | **Q.4** B | **Q.5** A | **Q.6** A,B |
| **Q.7** A, D, C | **Q.8** 9 | **Q.9** -563 KJ | **Q.10** 9900 | **Q.11** 2 | **Q.12** B |
| **Q.13** D | **Q.14** B | **Q.15** A → p, r, s ; B → r, s ; C → t; D → p, q, t | | | **Q.16** C |
| **Q.17** C | **Q.18** B | **Q.19** C | | | |

# Solutions

## JEE Main/Boards

## Exercise 1

**Sol 1:** (i) $H_2O\ (g) \rightarrow H_2O(\ell)$

Volume of system ↓es

$W = -P\Delta V$

$\therefore W$ +ve

(ii) $H_2O(s) \rightarrow H_2O(g)$

V system ↓es

$W = -P\Delta V$

$\Delta V > 0,\ \therefore\ W$ –ve

(iii) $H_2O(s) \rightarrow H_2O\ (l)$

V↓es, $W = -\Delta V,\ \Delta V < 0$

$\therefore\ W$ +ve

(iv) $CaCO_3 \rightarrow CaO(s) + CO_2(s)$

V↑ es,

$\therefore\ \Delta V > 0 \therefore\ W < 0$

**Sol 2:** $Q = -65$ J

$W = 20$J

(Contraction work done system)

$\Delta E = Q + W$

$= 20 - 65 = -45$ J

**Sol 3:** $H_{\text{combustion}} = -2808$ kJ/mol

(i) Energy × Eff = Change in potential energy.

$\therefore \dfrac{\text{Mass of glucose}}{180} \times 2808 \times 10^3 \times \dfrac{25}{100}$

$= 62.25 \times 3 \times 9.8$

$= 0.47$ kg

**Sol 4:** $W = -P\Delta V$

$= -1 \times (1.1 - 1)$

$= -0.1$ atm

$= -0.1 \times 10^5 \times 10^{-3}\text{J} = -10\text{J}$

**Sol 5:** $\underset{34.2\text{ ml}}{CaCO_3} \xrightarrow{\quad} \underset{16.9\text{ ml}}{CaO} + \underset{24.4\text{ L}}{CO_2}$

$Q = +177.9$ kJ

$W = -P\Delta V$

$= -1 \times (24.4 + 16.9 \times 10^{-3} - 34.2 \times 10^{-3})$

$= -1 \times (24.4 - 17.3 \times 10^{-3})$

$= -2438.27$

$\therefore\ Q + W = \Delta E$

$177.9 \times 10^3 - 2438.27 = \Delta E$

$\therefore\ \Delta E = 175.462$ kJ

**Sol 6:** $W = -P\Delta V$

$= -1.5(50-50-50) \times 10^{-3}$

$= -1.5 \times -50 \times 10^{-3} \times 10^5 \times 10^{-3}$

$W = 15 = 0.0075$

$H = -0.31$

$\Delta V = \Delta H - \Delta(PV)$

$\Delta V = -0.31\ kJ + 0.15\ kJ = 0.3025$

**Sol 7:** $\Delta H_{vap} = 40.66\ kJ/mol$

$\Delta H_{gas} = 2 \times 40.66\ kJ$

$PV = nRT$

$1 \times V = 2 \times 0.0821 \times 373$

$V = 61.2466\ L$

$\Delta PV = 1(\Delta V) = 1(V_g - V_L)$

2 moles $\therefore$ Mass of $H_2O = 36g$

$d = 1\ gm/cm^3$

$\therefore\ V = 36\ cm^3 = 36 \times 10^{-3} L$

$$\therefore\ \Delta V = \frac{(61.2466 - 36 \times 10^{-3}) \times 10^2}{1000}$$

$V_L << V_g\ \Delta V = V_g$

$\Delta V = \Delta H - \Delta PV$

$= 81.32 - 6.125 = 75.1216$

**Sol 8:** $Q = 1\ Kcal$

$P = 1\ atm$

$W = -\int PdV = -\int dV = -P\Delta V$

$= -1(1.5 - 1.2) \times 10^5 \times 10^{-3}\ J$

$$= \frac{0.3 \times 10^2}{1000} kJ = 0.03\ kJ$$

$4.18\ J = 1\ cal$

$$\therefore\ 1J = \frac{1}{4.18} cal$$

$\therefore\ 0.03\ kJ = -7.18 \times 10^{-3}\ kcal$

$\Delta E = Q + W$

$= 1 - 7.8 \times 10^{-3}$

$= 0.993\ kcal$

$\Delta H = \Delta E + \Delta(PV)$

$= \Delta E + P\Delta V$

$= 0.993 + 7.8 \times 10^{-3}$

$= 1\ k\ Cal$

**Sol 9:** $V_{vapour} = \dfrac{nRT}{P} = \dfrac{1x0.0821 \times 273}{4.6 / 760}$

$= 3703.07\ L$

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

$0^oC \rightarrow 0^oC$

ice water

$\Delta H = nCp\Delta T$

$\Delta T = 0,\ \therefore\ \Delta H_{process} = 0$

$\Delta H_{total} = (80 + 596) \times 18 = 12168\ cal$

$\Delta E = \Delta H - (\Delta PV)$

$= \Delta H - P\Delta V$

$$= 12168 - \frac{4.6}{760} \times 3703.07$$

$= 12168 - 536.20$

$= 11623\ cal$

**Sol 10:** $\Delta H_{vap} = 30.84\ kJ/mol$

$$V_{vap} = \frac{1 \times 0.0821 \times 353}{1}$$

$= 28.9\ L$

$W = -P\Delta V = +PV_{vap}$

$= +0.0821 \times 353 = 2.89\ kJ$

$\Delta E = \Delta H - \Delta PV$

$= +30.84 - 2.89$

$= 27.91\ kJ/mol$

We know VIT = Q

$Q + W = \Delta E$

$\therefore\ Q = \Delta E - W$

$= \Delta E + \Delta PV = \Delta H$

$$\therefore 12 \times 0.5 \times t = 30.84 \times 10^3 \times \frac{7.8}{78}$$

$t = 514\ sec.$

**Sol 11:** $p_i = 4\ atm\ p_t = 1\ atm$

Const. external pressure of 1 atm.

$4V_i = 5 \times 0.082 \times 300$

$\therefore\ V_i = 30.79$

$V_t = 4\ V_i = 123.16$

$\Delta V = nC_v\Delta T$

$\Delta T = 0 \Rightarrow \Delta V = 0$

$\Delta H = nC_p\Delta T = 0$

$$W_{rev} = \int -PdV = -\int \frac{nRT}{V} dV = -nRT\ \lambda n\ V_2/V_1$$

$= -nRT\ ln\ 4 = -5 \times 8.314 \times 300\ ln\ 4 = -17228.47\ J$

$W_{air} = -P\Delta V = -P\Delta V = -1(123.16 - 30.79) \times 10^{-5} \times 10^{3}$

$= 9353.25$ J

**Sol 12:** $5 \times V_i = 1 \times V_f \quad \therefore \frac{V_f}{V_i} = 5$

$$w = -\int PdV = -\int \frac{nRT}{V}dV = -nRT\ \lambda n\ \frac{V_f}{V_i}$$

$= -1 \times 8.314 \times 298 \times \lambda n\ 5 = -3.988$ kJ

**Sol 13:** $P(V_m - b) = RT$

$$P = \frac{RT}{V_m - b}$$

$$w = -\int PdV = \frac{-RT}{\frac{V}{n}-b}dV = \int_{V_i}^{V_f}\frac{RT}{V-nb}dV$$

$$= -nRT\ \ell n\left(\frac{V_f - nb}{V_i - nb}\right)$$

$$= -2\times8.314\times300 \times \ell n\left(\frac{0.6-2\times0.1}{1.2-2\times0.1}\right)$$

$$= \frac{600}{1000}\times8.314\ \ell n\left(\frac{1.2-0.2}{0.6-0.2}\right) \text{kJ}$$

$$= 0.6\times8.314\ \ell n\left(\frac{1}{0.4}\right) = 4.59 \text{ kJ}$$

**Sol 14:** $2 \times V = 200 \times 3 \times 0.0821$

$V = 8.21 \times 3\ V_i = 24.63L$

$V^{r-1}$ = Constant

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{r-1}$$

$$\frac{200}{250} = \left(\frac{V_f}{24.63}\right)^{r-1}$$

$C_v = 27.5$

$C_P = V_c + R = 27 + 8.314$

$$r = \frac{C_P}{C_V} = \frac{27.5 + 8.314}{27.5} = 1.302$$

$$\left(\frac{200}{250}\right)^{\frac{1}{0.31}} = \frac{V_f}{24.63}$$

$V_f = 11.79$ L $V_f = 11.8$ dm$^2$

$\Delta V = n\ell\Delta T = 3 \times 27.5 \times 50 = 4215 = 9.12$ KJ

q = 0 (idealistic process)

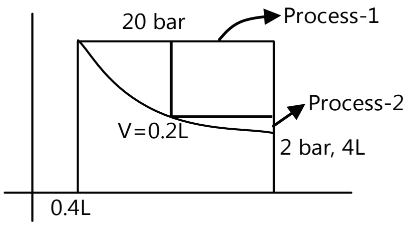
$\therefore \Delta V = W = 4.12$ kJ

$\Delta H = nC_P\,\Delta T = 3 \times 50 \times 35.81 = 5.37$ kJ

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$$

$$\therefore P_f = \frac{2\times24.63\times256}{200\times11.8};\ P_f = 5.21 \text{ atm}$$

**Sol 15:**



$$V_f = \frac{2\times4}{20} = 0.4$$

Process 1

$$W = -nRT\ln\frac{V_f}{V_i} = PV\ \ln\left(V_f / V_i\right)$$

$$= -2 \times 8.314 \times \ln\left(\frac{0.4}{4}\right)\times T$$

$W_{rev} = 18.424$ bar L

(ii) Single stage compression

$w = -P\Delta V = -20 \times (0.4 - 4)$

$= 3.6 \times 20 = 72$ bar lit

2 stage process

$W = -\sum P_1\ \Delta V_1$

$= -20 \times [0.4 - 0.8] - 10[0.8 - 4]$

$= 20 \times 0.4 + 10 \times 3.2$

$= 32 + 8 = 40$

Magnitude of work is in single stage conversion.

**Sol 16:** Momentum gas $C_V = \frac{3R}{2},\ r = \frac{5}{3}$

n = 1 mole

$P_1V_1 = nRT_1$

$2 \times 10 = 1 \times 0.0821\ T_1$

$\therefore T_1 = 243.60$ K

In step (BC)

W = 0

Volume const.

$\frac{P_2}{P_1} = \frac{T_2}{T_1}$ $\frac{20}{2} = \frac{T_2}{243.60}$

$\therefore T_2 = 2436$ K

W = 0 as dV = 0 $q = \Delta V = nC_V\,\Delta T$

$= \frac{3}{2}R \times 2 \times (-2436 + 243.6)$

= 3 × 8.314 × 2192.4

= – 54682.841 J

In process A – B

W = – PdV

$= -P\Delta V$

= – 20 × (10-1)

= – 180 bar lit

$= \frac{-180 \times 10^5 \times 10^{-3}}{4.18}$ cal.

$\Delta V = nC_V\Delta T$

$= \frac{3}{2}R \times 2 \times (2436 - 243.6) = 54682.841$ J

$Q = \Delta V - W$

$= \frac{54682.841}{4.18} + \frac{18000}{4.18} = 17388.24$ J

In process (CA)

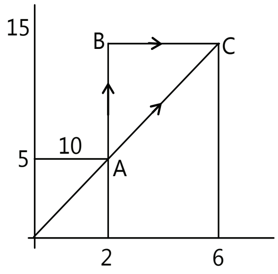
$\Delta T = 0 \Rightarrow \Delta V = 0$

$Q = W = -\int PdV = +PV\ \ln\frac{V_i}{V_f}$

$= +20 \times 1 \times \lambda n\left(\frac{20}{1}\right) = \frac{59.914 \times 100}{4.18}$

$W_{total} = \frac{5991.46}{4.17} - \frac{18000}{4.17} = -3262$ cal.

**Sol 17:**



Work done is area under the PV curve

∴ Work done under A–C curve is least.

$Q_{AC} = 200$ J

$W_{AC} = -\int PdV$

$\left(P = \frac{5}{2}V\right)$ along AC

$W_{AC} = -\int_2^6 \frac{5}{2}VdV$

$W_{AC} = -\frac{5}{4}V^2\Big|_2^6$

$= \frac{-5}{4}\left(6^2 - 4\right) = \frac{-5}{4} \times 4(9-1)$

= – 5 × 8 = –40

V = Q + W

$V_C - V_A = 200 - 40$

$V_C = 10 + 200 - 40$

$V_C = 170$ J

From A–B

W = 0 as $\Delta V = 0$

$\therefore Q = \Delta V = 10$ J

**Sol 18:** $H_2 + \frac{1}{2}O_2 \rightarrow H_2O\ (\ell)$

$\Delta H_{reac} = -285.76$

$\Delta H_{(373)} = \Delta H_{298} + \int_{298}^{373} nC_p\Delta T$

$\Delta H_{373} = -285.76 + \int 75.312 - 38.83 - \frac{29.16}{2}$

$= -285.76 \times 10^3 + 21.902\ T\ \Big|_{298}^{375}$

$= -285.76 \times 10^3 + 21.902 \times 75$

$\Delta H_{373} = -284.11$ kJ

**Sol 19:** $\Delta H = nCp\Delta T$

$10^5 \times V = 8.314 \times 298$ ;

V = 24.77 l, $T_f = 2T = 596$;

$V_f = 2V = 24.77 \times 2 = 49.54$;

$\Delta H = n\int Cp\Delta V = \int CpdT$ ;

$$= \int_{298}^{596} (22.34 + 4.81\times10^{-3}T)dT$$

$$= 22.34T + \frac{48.1}{2}\times10^{-3}T^2$$

$$= 22.34 \times 298 + \frac{48.1}{2}\times10^{-3}\,(596^2 - 298^2)$$

$$= 6657.32 + 6407.21$$

$\Delta H = 13.064$

$\Delta V = \Delta H - \Delta PV = H - P\Delta V$

$$= 13.064 - \frac{10^5\times24.77}{1000}\times10^{-3}$$

$$= 13.064 - 2.477 = 10.587$$

**Sol 20:** Q = 30.5 kJ

$\Delta S = 28.8$

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

$$28.8 = \frac{30.5\times10^3}{T} \qquad \therefore T = 1059K$$

**Sol 21:** $T_1 = 300$; $T_2 = 600$, P = 1 bar

$$\Delta S = \int n\frac{Cp}{T}\frac{dT}{T_1} + nR\ln\frac{P_2}{P_1}$$

$$\Delta S = \int n\frac{Cp\,dT}{T}$$

$$= \int\frac{n\times25.5 + 13.6\times10^{-3} - 42.5\times10^{-7}T^2}{T}$$

$$\Delta S = 25.5\ln\frac{T_2}{T_1} + 13.6\times10^{-3}\,T\Big|_{300}^{600}$$

$$-\,42.5\times10^{-7}\,(T_2^{\,2} - T_1^{\,2})$$

$$= 25.5\ln^2 + 13.6\times10^{-3}\times300$$

$$-\,42.5\times10^{-7}\,(600^2 - 300^2)$$

$$= 17.67 + 4.08 - 0.1475$$

$$= 21.18\ \text{J K}^{-1}\ \text{mol}^{-1}$$

**Sol 22:** $2Na + Cl_2 \rightarrow 2NaCl$

$\Delta S = 2\times S_{NaCl} - S_{Cl_2} - 2\times S_{Na}$

$= 2\times72 - 223 - 2\times51$

$\Delta S = -181/2 = -90.5$

$N_2 + 4H_2 + Cl_2 \rightarrow 2NH_4Cl$

$$\Delta S = \left(2\times S_{NH_4Cl} - S_{Cl_2} - S_{V_2} - 4S_{H_2}\right)/2$$

$= 2\times95 - 223 - 192 - 4\times131$

$= -749/2 = -374.5$

$C_{graphite} - C_{diamond}$

$\Delta S = S_{diamond} - S_{graphite}$

$= 2.43 - 5.69 = -3.26$

**Sol 23:** Efficiency = 40%

$$0.4 = 1 - \frac{T_L}{T_H}$$

$$\frac{T_L}{T_H} = 0.6$$

$$\frac{273+7}{T_H} = 0.6$$

$$\therefore T_H = \frac{280}{0.6} = 466.6\ K = 193.66^{o}C$$

**Sol 24:**

$$\int_0^{600} S = \int_0^{200} S + \frac{H_{fus}}{T} + \frac{T_{vap}}{T} + \int_{200}^{300} S + \int_{300}^{600} S$$

$$S_{600} = \int_0^{200}\frac{dT^{0.034T}}{T} + \frac{7.5\times10^3}{200} + \int_{200}^{300}\frac{60+0.016T}{T}$$

$$+ \frac{30\times10^3}{300} + \int_{300}^{600}\frac{50.dT}{T}$$

$$= 7 + 0.035\,(200-0) + 37.5 + 60\,\lambda n\left(\frac{300}{200}\right)$$

$$+\,0.016(300-200) + \frac{30000}{600} + 50\,\lambda n\left(\frac{600}{300}\right)$$

$$= 37.5\,T + 24.328 + 1.6 + 34.657 + 100 = 205.08J$$

**Sol 25:** $\Delta H_{combush} = -2808$

$\Delta S = 182.4$

T = 37° = 310 K

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

$$= \left(-2808 - \frac{310\times182.4}{1000}\right)KJ$$

$\Delta G = -2864.5$

**Sol 26:** $H_2 \rightarrow 2H$ $S^0$ 130.6 114.6

$\Delta S^o = 2 \times 114.6 - 130.6 = 98.6$

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

$406.62 \times 10^3 = \Delta H^o - 298 \times 98.6$

$$\Delta H^o = \left(406.62 + \frac{298 \times 98.6}{1000}\right) KJ$$

$\Delta H^o = 436$ KJ/mol $H_2$

**Sol 27:** $C_8H_{18} + 8.5\, O_2 \longrightarrow 8\, CO + 9\, H_2\, O(g)$

$V = 3.785 \times 10^3$ ml

d = 0.702 g/ml

$\therefore$ Mass $= 0.7025 \times 3.785 \times 10^3$ g $= 2658.9625$

$$\text{Moles} = \frac{2658.9625}{114} = 23.33 \text{ moles}$$

given

$C_8H_{18} + 12.5\ O_2 \rightarrow 8\ CO_2 + 9H_2O(\ell)$

$\Delta H = -130.27$

$\Delta H_{comb} = -n\Delta H_{f\ reactant} - n\Delta H_{f\ product}$

$-1302.7 = \Delta H_fC_8H_{18} + 12.5$

$\times\ O_2 - 8 \times \Delta HCO_2 - 9 \times \Delta H_fH_2O$

$\therefore\ \Delta H_f\ C_8H_{18} = 13027 + 8 \times (-94.05) + 9 \times (-68.32)$

$$\frac{\Delta H_{reactant}}{mol\ C_8H_{18}} = 8\ \Delta H_f\ (O)\ +\ 9\ + \Delta H_{H_2O(g)}\ - 8.9 \times\ \Delta H_{f\ O_2}$$

$- \Delta\, \Delta H_{f\ C_8H_{18}}\ + 64.58$

$= 8 \times (-26.41) + 9 \times (-57.79) - 666.80$

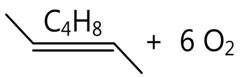
$\therefore\ \Delta H$ for given conditions =

$\Delta H_{reac} \times 23.33$

$= -666.80 \times 23.32 = -15549.7$

**Sol 28:** cis–2–butene → trans–2–butene $\Delta H < 0$

cis–2–butene = trans-2-butene – $\Delta H_2$



trans–2-butene → $4CO + 4H_2O$

Trans $\Delta H^o{}_{cumb} = \underbrace{4\Delta H_{CO_2} + 4\Delta H_{H_2O}}_{\Delta H} + \Delta H_fC_4H_8$

trans

$\Delta H^o{}_{comb} = 4\Delta H_{CO_2}\ +\ 4\Delta H_{H_2O}\ - \Delta H_{f_{C_4H_8}}$

1–butene Cis

$\Delta H_{f_{trans-2}} = \Delta H' + 649.8$ Kcal

$\Delta H_{f_{1-butene}} = \Delta H' + 647.1$ Kcal

$\Delta H_1 = \Delta H_{f_{trans}} - \Delta H_{f_{cis}}$

$\Delta H_2 = \Delta H_{f_{buten}} - \Delta H_{f_{cis}}$

$\Delta H_1 - \Delta H_2 = \Delta H_{f_{trans}}\ -\ \Delta H_{f_{cis}}$

$= 649.8 - 647.1$

$\Delta H_1 - \Delta H_2 = 2.7$

$\Delta H_1 + 5\Delta H_2 = 0$

$\Delta H_1 - \Delta H_2 = -2.7$

$$\Delta H_1 + \frac{9}{4}\Delta H_1 = -2.7$$

$\Delta H_1 = -0.964$ kcal

$$\Delta H_2 = \frac{9}{5} \times 0.964 \text{ kcal}$$

= 1.74 kcal

**Sol 29:** $Xe \rightarrow Xe^+ + e^-$ $\Delta H = 279$

$F + e^- \rightarrow F^-$ $\Delta H = -85$ kcal/mol

$F_2 \rightarrow 2F \Delta H = 38$ kcal/mol

$$\left.\begin{array}{l} Xe \rightarrow Xe^+ + e^- \\ F_2 \rightarrow 2F \\ 2F + e^- \rightarrow F + F^- \end{array}\right\} \text{Add}\, \Delta H$$

$\Delta H = -4 \times B.E._{\ Xe-F}$

$-\Delta H_{ion} - \Delta H_{+gain\ enthalpy} - \Delta H_{Bond\ energy}$

$292 = -4 \times x + 297 + 85 + 38$

$$x = \frac{292 - 279 + 85 + 38}{4} = 34$$

**Sol 30:** Combustion of ethane:

$$CH_3 - CH_3 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

$\Delta H^o{}_{comb} = E_{C-C} + 6E_{C-H}$

$$+\ \frac{7}{2}\, E_{O=O} - 2\,\Delta H_{f_{CO_2}}\ -\ 3\Delta H^o{}_{H_2O}$$

$$-1559.8 = E_{C-C} + 6E_{C-H} + \frac{7}{2}(498.34) - 2(-39.5) - 3(-285.8)$$

$E_{C-C} + 6E_{C-H} = -1460.01$ ...(i)

Combustion of Ethene:

$CH_2 = CH_2 + 3O_2$ ?→ $2CO_2 + 2H_2O$

$\Delta H^o_{Comb} = E_{C=C} + 4E_{C-H}$

$+ E_{O=O} - 2H_{f_{CO_2}} - 2\Delta H^o_{f_{H_2O}}$

$-1410.9 = E_{C=C} + 4E_{C-H}$

$+ 3(498.34) - 2(-393.5) - 2(-285.8)$

$E_{C=C} + 4E_{C-H} = -1274.48$ ....(ii)

Combustion of Acetylene:

$CH\equiv CH + 5/2\ O_2$ ?→ $2CO_2 + H_2O$

$\Delta H^o_{comb} = E_{C\equiv C} + 2E_{C-H} + 2E_{C-H}$

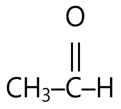
$+ 5/2E_{O=O} - 2\Delta H_{f_{CO_2}} - 2\Delta H_{f_{H_2O}}$

$-1299.7 = E_{C\equiv C} + 2E_{C-H}$

$+ 5/2(498.34) - 2(-393.5) - 2(-285.8)$

$E_{C\equiv C} + 2E_{C-H} = -1412.45$ .....(iii)

Combustion of Acetaldehyde:



$CH_3-\overset{\overset{O}{||}}{C}-H + 5/2\ O_2$ ?→ $2CO_2 + 2H_2O$

$\Delta H^o_{comb} = E_{C-C} + E_{C=O} + 4E_{C-H}$

$+ 5/2\ E_{o=o} - 2\Delta H_{f_{CO_2}} - 2\Delta H_{f_{H_2O}}$

## Exercise 2

### Single Correct Choice Type

**Sol 1: (D)** $\Delta H = \Delta E + \Delta n_g T$

Case–I = $\Delta n_g = 2 - 1 - 1 = 0$

Case–II = $\Delta n_g = 0 - 0 = 0$

Case–III = $\Delta n_g = 1 - 1 = 0$

Case–IV = $\Delta n_g = 2 - 3 - 1 = -2 \neq 0$

$\therefore$ In option (Δ) $\Delta H = \Delta E$

**Sol 2: (D)** $CH_4 + Cl_2$ ?→ $CH_3Cl + HCl$

$\Delta H = -25$

$-25 = 4 \times C - H + 4Cl$

$- Cl - 3 \times CH - 1C - Cl - 1\ H - Cl$

$-25 = 4x + y - 3x - 84 - 103$

$y - x = 162$

$x = \frac{9}{5}\ y$

$\frac{9}{5}\ x + \frac{1}{5}\ x = 162$

$\frac{14}{5}\ y = 162$

$y = 57.75$ k cal

**Sol 3: (C)** $Au(OH)_3 + HAuCl_4$

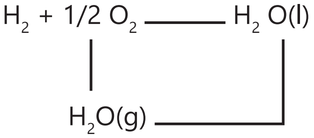
$\rightarrow HAuCl_4 + 3\ H_2O$

$36.8 + x \times -28 = 0.44$

$x(36.8 - 28) = 0.44$

$x = 0.05$

**Sol 4: (B)**

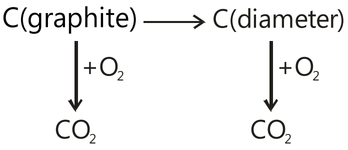


$\Delta H_{comb}$ = BE (H – 11) + ½ B.E (O =O – 2 × B.E (OH)

B.E. (vap)

$= x_1 + x/2 - 2 \times x_3 - x_4$

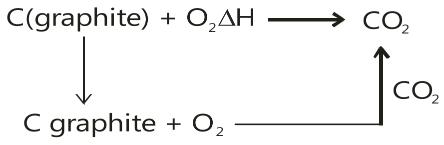
**Sol 5: (C)**



$\Delta H = 1.9$ kJ

C(graphite) + $O_2$ ?→ $CO_2$

$\Delta H = \Delta H_f CO_2$



$\Rightarrow \Delta H' = \Delta H_{fCO_2} + \Delta H_{c-c\ graphite}$

$\Delta H' = \Delta H_f - 1.9$

**Sol 6: (A)** $NH_3 + 3\ Cl_2 \rightarrow NCl_3 + 3HCl = -\Delta H_1$

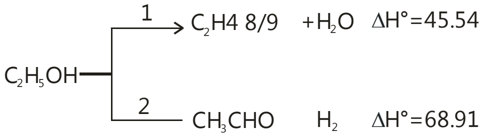
$N_2 + 3H_2 \rightarrow 2NH_3 = \Delta H_2$

$H_2 + Cl_2 \rightarrow 2HCl = \Delta H_3$

$-\Delta H_1 = 3\Delta H_f\ HCl + \Delta H_{fNC\ell_3} - \Delta H_f\ NO_3$

$\therefore\ \Delta H_{fNC\ell_3} = \frac{\Delta H_2}{2} - \frac{3\Delta H_3}{2} - \Delta H_1$

**Sol 7: (B)**



Molar ratio of $C_2\ H_4$ to $CH_3\ CHO$ = 8: 1

$\therefore$ Enthalpy per unit

8x t x = 0

$\therefore$ x = 1/9

$\therefore\ \Delta H = \frac{1}{9} \times 45.54_{4}\ \frac{8\times 68.91}{9} = 48.137$

**Sol 8: (C)** $E_1 = 1 - \frac{T_2}{1000}$

$E_1 = 1 - \frac{360}{T_2}$

$\therefore\ 1 - \frac{T_2}{1000} = 1 - \frac{360}{T_2}$

$\therefore\ (T_2)^2 = 360 \times 1000$

$T_2 = 600$

**Sol 9: (C)** Isochoric $\therefore\ V_1 = V_2$

$\Delta S = nC_v \ln \frac{T_2}{T_1} = nR \ln \frac{V_2}{V_1}$

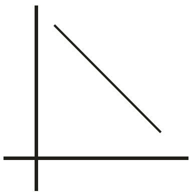
$\therefore\ \Delta S = 2 \times \frac{3R}{2} \ln\left(\frac{300+273}{200+273}\right)$

$= 3R \ln\left(\frac{573}{473}\right)$

**Sol 10: (C)** $\Delta G = \Delta dP = \int \frac{nRT}{P} dP$

$= nRT \ln \frac{P_2}{P_1} = 517.13$

**Sol 11: (A)**



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

$y = \Delta H - x\ \Delta S$

Slope is –ve

$\therefore\ \Delta S < 0$

$\therefore\ \Delta S > 0$ and intercept > 0

$\therefore\ \Delta H > 0$

**Sol 12: (C)** $\Delta H_{vap}$ = 300/g at T = 300 k

= 300 × 30 J/mol

$\Delta S\ \text{mole} = \frac{\Delta H_{moles}}{T} = \frac{300\times 30}{300} = 30$ J/mol

**Sol 13: (D)** $P \times 20 = 2 \times 0.0821 \times 243.6$ k

$P_i = 2$ atm $P_f = 1$ atm

$\Delta S = -4R \ln \frac{P_2}{P_1}$

$= 2 \times \frac{8.314}{4.19} \ln 2 = 2.77$

## Previous Years' Questions

**Sol 1: (C)** $H_2O_{(l)} \xrightarrow{\text{vaporization}} H_2O_{(g)}$

$\Delta n_g = 1 - 0 = 1$

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

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

$= 41 - 8.3 \times 10^{-3} \times 373 = 37.9\ \text{kJ mol}^{-1}$

**Sol 2: (A)** $\Delta H = \Delta U + \Delta(PV)$

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

$\Delta U = \Delta H - V\Delta P = -560 - 1 \times 30 \times 0.1$

Absolute value = 563 kJ.

**Sol 3: (A)** For a pure substance, $T_A$ and $T_B$ represent the same temperature. Hence, A is a correct choice.

**Sol 4: (A)** For a spontaneous process in an isolated system, the change in entropy is positive.

**Sol 5: (B)** For a reaction to be spontaneous, $\Delta G$ must be negative. According to the equation -

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

If $\Delta H$ and $\Delta S$ both are positive, than term T. $\Delta S$ will be greater than ΔH at high temperature and consequently ΔG will be negative at high temperature.

**Sol 6: (B)** $dS = \frac{dQ_{rev}}{T}$; $T = \frac{30\times10^3}{75}$; T = 400 K

**Sol 7: (A)** $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$ substitute the values.

**Sol 8: (B)** $H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l); \Delta H = -286.20kJ$

$\Delta H_r = \Delta H_f(H_2O, l) - \Delta H_f(H_2, g) - \frac{1}{2}\Delta H_f(O_2, g)$

$-286.20 = \Delta H_f(H_2O(l))$

So, $\Delta H_f(H_2O, l) = -286.20$

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\ \Delta H = 57.32$ kJ

$\Delta H_r = \Delta H_f^o(H^+, aq)\ \Delta H_f^o(OH^-, aq) - \Delta H_f^o(H_2O, l)$

$57.32 = 0 + \Delta H_f^o(OH^-, aq) - (-286.20)$

$\Delta H_f^o(OH^-, aq) = 57.32 - 286.20 = -228.88kJ$

**Sol 9: (D)** Standard molar heat enthalpy (H°) of a compound is equal to its standard heat of formation from most stable states of initial components.

**Sol 10: (A)** $\Delta H = \frac{240}{2} - 349 - 381$

= 120 – 349 – 381 = –610 kJ/mol

**Sol 11: (B)** $XY \longrightarrow X_{(g)} + Y_{(g)};\ \Delta H = +a$ kJ/mole ...(i)

$X_2 \longrightarrow 2X;\ \Delta H = +a$ kJ/mole ... (ii)

$Y_2 \longrightarrow 2Y;\ \Delta H = +0.5a$ kJ/mole ... (iii)

$\frac{1}{2}\times(ii) + \frac{1}{2}\times(iii) - (i)$, gives

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY;$

$\Delta H = \left(+\frac{a}{2} + \frac{0.5}{2}a - a\right)$kJ / mole

$+\frac{a}{2} + \frac{0.5a}{2} - a = -200$; a = 800

**Sol 12: (D)**

$$\begin{tikzcd} 2C(s) + H_2(g) \arrow[r] \arrow[d] & C_2H_2(g)\ \Delta H=225\text{ KJ/mol} \\ 2C(g) + 2H(g) \arrow[ur, "-(2\varepsilon_{C-H} + \varepsilon_{C=C})"'] & \end{tikzcd}$$

$\therefore \Delta H = +1410 + 330 - (350\times2) - \varepsilon_{C=C} = +225$

$\therefore \varepsilon_{C=C} = 1740 - 700 - 225 = +815$ KJ/mol.

**Sol 13: (B)** $(dS)_{V, E} > 0$, $(dG)_{T,P} < 0$

**Sol 14: (C)** ΔG = ΔH – TΔS [ΔH = +ve; ΔS = +ve]

$\Delta G = +ve - T_e(+ve)$

if $T > T_e$ then ΔG = –ve(spontaneous).

**Sol 15: (C)** In this reaction Δn = 2 – 4 = – 2 so ΔH ≠ ΔE

**Sol 16: (A)** The process is isothermal expansion Hence, q = - w ; Δu = 0

q = + 208 J

w = -208 J(expansion work)

**Sol 17: (A)** $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Bomb calorimeter gives ΔU of the reaction

So, as per question

$\Delta U = -1364.47\text{ kJ mol}^{-1}$

$\Delta n_g = -1$

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

$= -1364.47 - \frac{1\times8.314\times298}{1000}$

$= -1366.93\text{ kJ mol}^{-1}$

**Sol 18: (D)**

$2\Delta G^0_{f(NO_2)} - \left[2\Delta G^0_{f(NO)} + \Delta G^0_{f(O_2)}\right] = \Delta G^0_r = -RT\,\ell nK_p$

$2\Delta G^0_{f(NO_2)} - \left[2\times86,600 + 0\right] = -RT\ \ell\ nK_p$

$2\Delta G^0_{f(NO_2)} = 0.5\left[2\times86,600 - R(298)\ell n\left(1.6\times10^{12}\right)\right]$

**Sol 19: (C)** $C(S) + O_2(g) \rightarrow CO_2(g)$ ; $\Delta H = -393.5$ kJ / mol

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ ; $\Delta H = -283.5$ kJ / mol

$C(S) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ ; $\Delta H = -393.5 + 283.5$ kJ / mol

= –110 kJ / mol

# JEE Advanced/Boards

## Exercise 1

**Sol 1:** $2\ C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

$\Delta H_{comb}$ = ΔH for reactants – $\Delta H_f$ products

$3120 = 2 \times \Delta H_f\ (C_2\ H_6\ ) - 4 \times \Delta H$

$+\ CO_2 - 6\ \Delta HH_2O$

$\therefore\ \Delta\ H_f\ (C_2\ H_6) = \dfrac{3120-4\times395-6\times286}{2} = 88$ KJ

**Sol 2:** $\Delta H_f\ (Cs_2\ )$

$C + O_2 \rightarrow CO_2\ \Delta H_{comb.} = -393.3$

$S + O_2 \rightarrow SO_2\ \Delta H_{comb.} = 293.72$

$CS_2 + 2O_2 \rightarrow CO_2 + 2SO_2\ \Delta H_{comb.}$

$= -1108.76$

$\therefore\ C + S_2 \rightarrow CS_2$

$-\Delta H_3 + \Delta H_1 + 2\Delta H_2$

$= 1108.76 - 393.3 - 2 \times 293.72$

$\Delta H = 128.02$

**Sol 3:** $Fe_2O_3 + 3C \rightarrow 2F_e + 3CO$

$FeO + C \rightarrow Fe(s) + CO$

$C(g) + O_2 \rightarrow CO_2$

$CO + ½\ O_2 \rightarrow CO_2$

$Fe(s) + ½\ O_2 \rightarrow FeO$

$Fe + CO \rightarrow FeO + C\ \Delta H = -155.8$

$C + O_2 \rightarrow CO_2\ ; \Delta H = -393.51$

$CO_2 \rightarrow CO + ½\ O_2; \Delta H = +\ 282.98$

$Fe+CO+C+O_2+CO_2 \rightarrow\ FeO+C+CO_2\ +CO\ \ +H_2O_2+Fe+ \dfrac{1}{2}O_2 = FeO$

$\therefore\ \Delta H_f = -155.8 - 393.51 + 282.98 = -266.33$

$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$

$2Fe + 3CO \rightarrow Fe_2O_3 + 3C\ \Delta H = -492.6$

$3C + 3O_2 \rightarrow 3CO_2\ \Delta H = -3 \times 393.51$

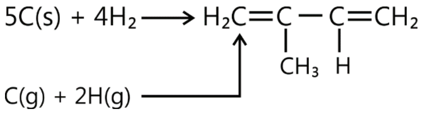
$3CO_2 \rightarrow 3CO + 3/2\ O_2\ \Delta x = +3 \times 282.8$

$\therefore$ Here $2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$

$\Delta H_2 = -492.6 - 3 \times 393.51 + 3 \times 282.98$

$= -824.2$

**Sol 4:**



$5C(s) + 4H_2 \longrightarrow H_2C{=}\underset{\displaystyle CH_3}{C}{-}\underset{\displaystyle H}{C}{=}CH_2$

$C(g) + 2H(g)$

ΔH atom

$= \Delta H_{C(S)\rightarrow C(B)} + \Sigma BE_{(Reactants)} - \Sigma BE_{(products)}$

$\Delta H_{formation}$

$= 5\times171+[4\times104–2\times83–2\times147–8\times98.8]$

= 20.6 K cal

**Sol 5:** $C_2\ H_4\ (g) + H_2\ (g) \rightarrow C_2\ H_6\ (g)$

$\Delta H_{reaction} = \Sigma BE_{reactants} - \Sigma BE_{products}$

$= 1 \times C = C + 4 \times C–H - 1 \times C - E + 6 \times (–H)$

$= 1 \times C = C - 1 \times C–C = 2 \times C–4$

$= 606.68 + 431.79 - 336 - 81 - 2 \times 410.87$

$= -120.08$

**Sol 6:**

$$\begin{tikzcd}
2C(g) + 2H_2 + 1/2\ O_2 \arrow[r, dash] \arrow[d, dash] & CH_3CHO(g) \\
2C(g) + 2H_2\ (g) + 1/2\ O_2(g) \arrow[ur, dash] &
\end{tikzcd}$$

$\therefore\ \Delta H_f = 2 \times \Delta H_{sub} + \Sigma BE_{reactants} - \Sigma BE_{products}\ = 2 \times 718.4$

$+ \left[2\times435.8+\dfrac{495}{2}-4\times413.4-728.0-347.0\right]$

$= -192.73$

**Sol 7:**

$$\begin{tikzcd}
CaCl_2 + Na_2\ CO_3 \arrow[r, dash] \arrow[d] & CaCO_3 + 2NaCl \\
Ca^{2+}_{-} + 2Cl^{-} + 2Na^{+} + CO_3^{2} \arrow[ur] &
\end{tikzcd}$$

$\Delta H_{reac.} = -288.5 + 129.80 + 1261.65$

= 2.98k cal

**Sol 8:** NaOH + HCl → NaCl (Strong acid–base)

$\therefore\ \Delta H^0 = -1368$ cal

$\Delta H\ NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

$\therefore\ \Delta H' = \Delta H - 1\Delta H_{diss} -12270$

$= -13680 + \Delta H_{diss}$

$\therefore \Delta H_{diss} = 1410$

**Sol 9:** $CH_4(g)+O_2(g)$ at $T = 298$ k $P = \frac{740}{766}$ atm

$v = 1$ L

$CH_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$PV = nRT$

$$\frac{740}{760} \times 1 = n \times 0.0821 \times 298$$

$\therefore n_E = 0.04$

$\Delta H_{rec} = 1260 \times 0.667$

$0.667 \times 1260 = n_{CH_4} \times \Delta H_{CO}$

$340 = n_{CH_4} \times 215 \times 10^3$

$n_{CH_4} = 0.0039$

$$\therefore n_{CH_4} = \frac{0.0039}{0.04} \times 100 = 9.82\%$$

**Sol 10:** $HA + NaOH \rightarrow NaA + H_2O$

$$\begin{array}{cc} \downarrow & \downarrow \\ 400\times0.2 & 100 \times 0.8 \end{array}$$

$V_t = 400 + 100 = 500$ cm$^3$

$n = 1$ g/cm$^3$

$$\therefore \Delta H = \frac{-500\times4.2\times\Delta T}{1000} = -31.5 \text{ KJ}$$

**Sol 11:**

$$\begin{tikzcd}
Na(s) \arrow[d] & + 1/2\, F_2 \arrow[d] \arrow[r] & NaF \\
Na(g) \arrow[d] & +\ 4F \arrow[d] & Na^+ + F^{-1} \arrow[u] \\
Na^+ & -\ F^- \arrow[ru] &
\end{tikzcd}$$

$$\therefore \Delta H_f = \Delta H_{sap} + \frac{\Delta BE}{2} + \text{I.E. } \Delta H_{EG} + \text{L.E.}$$

$$-57 = 101 + \frac{160}{2} + 494 + \Delta H_{EG}\ 894$$

$\Delta H_{EG} = -352$

**Sol 12:**

$$\begin{tikzcd}
CH_3OH + 3/2\, O_2 \arrow[r] \arrow[d] & CO_2 + 2H_2O \arrow[d] \\
CH_3O(g) + 3/2\, O_2 \arrow[r] & CO_2(g) + 2 \times H_2O(g)
\end{tikzcd}$$

Resonance eng of $CO_2$ + 43

$\therefore \Delta H_{cob} = +35.5+$

$\Sigma BE_{react} - \Sigma B.E._{products} - 40.0 \times 2$

$= 35.5 + 3/2 \times 494 + 351.5 + 464.5 + 3 \times 414 - 2 \times 711 - 143 - 2 \times 40.6 - 464.5 = -669.7$

**Sol 13:** (A) $C_V = 3$ R/2r = 5/3

$P_i = 1$ atm; $P_f = 2$ atm

$T_i = 300$ k

$1 \times V = 300 \times 1 \times 0.082$

$V_i = 24.63$

$1 \times (24.63)^r = 2 \times V_i^r$

$$\therefore W_{adiabatic} = \int -PdV = -\int \frac{CdV}{V^{1-r}} = 1194.72 \text{ J}$$

$P^{1-r}T^r = $ Const.

$$P_f^{1-\frac{5}{3}}T_f^{\frac{5}{3}} = P_i^{-\frac{2}{3}}T_f^{3}\,p_f$$

$$2^{-2300}\left(\frac{T}{300}\right)^5 = 1$$

$$\frac{T}{300} = 4^{\frac{1}{5}}$$

$$T = 4^{1/5} \times 300$$

$T_f = 395.85$

(B) $1 \times V_1 = 1 \times R \times T_1 = 300$ R

$P.V = nRT$

$nC_V\, \Delta T = -P_2(V_2 - V_1)$

$2 \times V_f = 1 \times R \times T_f$

$$1 \times \frac{3R}{2}(T_2 - T_1) = -2(V_2 - V_1)$$

$$\frac{3R}{2}(T_2 - 300) = T_f \times R + 2V_1$$

$$\frac{3R}{2}(T_2 - 300) = -T_f \times R + 2 \times 300 \text{ R}$$

$$\frac{3T}{2} - 450 = -T_f\, 1 + 600$$

$$\frac{5T}{2} = 1050$$

$T_f = \frac{2100}{5}$

$V_f = 420$ k

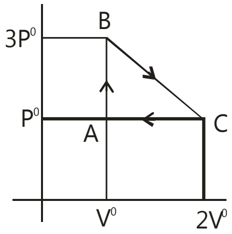
$T_f = \frac{R \times 420}{2} = 210\ R = 17.24$

$\therefore\ W = -2\ (V_2 - V_1) = -2\ (210\ R - 300\ R)$

$= 180\ R = 1496.525$ J

**Sol 14:** $C_V = 3R/2\ n = 1$

Work done by gas = Area under P – V curve



= Area of ΔABC

$= \frac{1}{2} \times (3P^0 - P^0) \times (2V^0 - V_0)$

$= \frac{-2P^0V^0}{2} = -P_0V_0$

$\Delta V_{cycle} = 0$

$\therefore\ w_{d1} = Q_{process} = P_0V_0$

$W_{AB} = 0\ Q_{AB} = \Delta V_{AB} = nC_V\Delta T$

$= \frac{3R\Delta T}{2} = \frac{3}{2}\ \Delta PV$

$= \frac{3}{2} \times (3P_0V_0 - 2P_0V_0) = 3P_0V_0$

$W_{AC} = P_0 \times (V_0 - 2V_0) = P_0\ V_0$

$\Delta V_{AC} = NC_V\Delta T = \frac{3}{2}\ \Delta P_0\ V_0$

$\frac{3}{2}\ P_0\ (V_0 - 2V_0) = -\frac{3}{2}\ P_0\ V_0$

$\therefore\ Q = \Delta U - W$

$= -3/2\ P_0\ v_0 - P_0\ V_0$

$-5/2\ P_0\ V_0$

$Q_{AB} + Q_{BC} + Q_{CA} = Q_{plou} = P_0\ V_0$

$-5/2\ P_0\ V_0 + 3P_0\ V_0 + Q_{BC} = P_0\ V_0$

$\therefore\ Q_{BC} = \frac{P_0V_0}{2}$

at B temp $= \frac{3P_0V_0}{R}$

at Δ temp $= \frac{P_0V_0}{R}$

at B temp $= \frac{2P_0V_0}{R}$

from B – C

P – V curve is

$P = mV + C$

$(3P_0 = m\ V_0 + C) \times 2$

$P_0 = 2mV_0 + C$

$5P_0 = C$

$3P_0 = m\ V_0 + 5P_0$

$\therefore\ m = \frac{-2P_0}{V_0}$

$\therefore\ P = \frac{-2P_0}{V_0}\ V + 5P_0$

$\left(5P_0 - \frac{2P_0}{V_0}V\right)\ V = RT$

$T = R\left(5P_0V - \frac{2P_0}{V_0}V^2\right)$

$\frac{2T}{dV} = 0$ at $5P_0 - \frac{4P_0}{V_0}\ V = 0$

$\therefore\ V_0 = 5/4\ V$

$T = R\ [5\ P_0 \times 5/4\ V_0 - 2\ \frac{P_0}{V_0} \times \frac{25}{16}\ V_0]$

$T_{max} = R\left(\frac{25}{4} - \frac{25}{8}\right)\ P_0\ V_0 = \frac{25}{8}\ \frac{P_0V_0}{R}$

**Sol 15:** (i) $\Delta S_{gas} = nC_V\ \ln\ \frac{T_2}{T_1} + nR\ \ln\ \frac{V_2}{V_1}$

$\Delta S_{gas} = R \times \ln 3 = 9.13$

Reverse $\therefore\ \Delta S_{gas} = -\Delta S_{surr.}\ \therefore\ \Delta S_{total} = 0$

$\Delta S_{surr.} = -\frac{Q_{rev}}{T}$

$9.134 = \frac{-Q_{rev}}{298}$

$\therefore\ Q_{rev} = 2775.572$

$\therefore\ Q_{avg} = -2775.572 + 836.8$

$\therefore\ \Delta S_{total} = 9.134 + \frac{-2775.572}{278} + \frac{836.8}{298}$

$= \frac{836.8}{298} = 2.808$ J/k

(iii) In case of free expansion Q = 0

$\therefore \Delta S_{surr.} = 0$

$\therefore \Delta S_{system} = \Delta S_{total} = 9.134$ J

**Sol 16:** $Ag(\ell) \rightarrow Ag$

$\Delta H_{avg} = 22$ Kj

$$\Delta S_{300} = \frac{\Delta T}{T} = \frac{22\times10^3}{300} = \frac{220}{3}\ \text{J}$$

$$\int_{300}^{200} \Delta S = \int \frac{nC_p}{T} - nR\ dP$$

$\because P_2 = P_1 = 100$

$$\Delta S_{200}\ \frac{-220}{3} = C_P \ln \frac{T_2}{T_1} - C_P(\ell) \ln \frac{T_2}{T_1}$$

$$\Delta S_{-200/3} = (30 - 40) \ln \left(\frac{200}{300}\right)$$

$$\Delta S = \frac{220}{3} + 10 \ln (3/2)$$

= 22/3 + 10 × 0.405 = 74.05 J/k

V = constant

**Sol 17:** $\Delta S_{sys} = nC_V \ln T_2/T_1$

$$= 1 \times \frac{3R}{2} \ln (1000/10)$$

$$= \frac{3R}{2} \ln 10$$

$\therefore \Delta S_{total} = 0$

$\therefore \Delta S_{surr.} = \Delta S_{system} = -3/2k\ln (10)$

(ii) Irreversible Process

$\Delta S_{system} = -3/2\ R \ln (10)$

W + Q = ΔU

$W = 0$ as $dV = 0 \therefore Q = \Delta U = nC_V\ \Delta T$

$$= \frac{3R}{2} \times 900$$

$$\therefore \Delta S_{total} = \frac{3R}{2} (0.9 - \lambda n10)$$

$$= -\frac{3R}{2} \times 1.403$$

**Sol 18:**

$H_2O$ (1L, 1 atm, 323k) → $H_2O$ (g, 1 atm, 323 k)

$\Delta H_{vap}$ H at 373 = 40.639 = 2.1

$\Delta H_{373} = 40.639 \times 10^3$ J

$\Delta H_{323} = 38.54$ KJ

$$\Delta S_{373} = \frac{\Delta H_{vap}}{373} = \frac{40639}{373} = 108.95\ \text{J}$$

$$\int_{373}^{323} = \int_{373}^{323} \frac{nC_p dT}{T}$$

$= (33.305 - 75.312) \ln (T_2/T_1)$

$= -42.00 \ln (373/325)$

$\Delta S_{323} = 108.95 - 6.04$

= 102.349

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

$$= 38.54 - \frac{102.349\times323}{1000} = 5.54\ \text{kJ/mol}$$

**Sol 19:** Adiabatic expansion

$\therefore P = 0 \therefore \Delta S_{surr} = 0$

$\therefore \Delta S_{total} = \Delta S_{system}$

(i) Case:I: Reversible process,

$\therefore \Delta S_{system} = \Delta S_{total} = 0$

(ii) Case–II: Irreversible $P_{ext}$

= 262.65 KPa

$\Delta S_{system}$

Neon → monoatomic

$C_V = 3R/2\ r = 5/3$

$P^{1-r}$ = const.

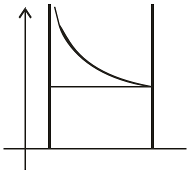
$P \propto T^{r/r-1}$

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{r/r-1}$$

$$\frac{202.65}{506.65} \left(\frac{T_2}{473}\right)^{\left(\frac{5/3}{2/3}\right)}$$

$\therefore T_f = 327.85$

$V_{ex} = 20.26$ J



PV = nRT

$$n \times \frac{3R}{2} \Delta T = -P_{ext} (V_2 - V_1)$$

$$n\times\frac{3R}{2}\Delta T = -P_{ext}\left(\frac{nRT_2}{P_2}-\frac{nRT_1}{P_1}\right)$$

$\therefore$ w = $nC_p$ ln $T_2/T_1$ – nP ln $(P_2/P_1)$

= –2.85 + 3.81 = 0.957 KJ

(iii) In case of free expansion

$\therefore$ $\Delta S = -ne\ \lambda n\ (P_2/P_1)$

$$= \frac{-10}{20}\times 8.314\ \lambda n\left(\frac{202.65}{506.625}\right) = 3.81\ J/k$$

**Sol 20:** $\Delta_r\ C_p = 0$

$\therefore$ $\Delta H^0_{298} = \Delta H^0_{373}$

$\Delta S^o_{298} = \Delta H^o_{373}$

P–V work = TΔ3°

$\therefore$ –6333 = –5737 – 298 → ΔS°

ΔS° = 2

Additional non-PV work

= (310 –298)× 2 = 24 kJ/mol

**Sol 21:** $\Delta H_{f\ FeO}$ = –65 k

$\Delta H_{f\ Fe2\ O3}$ = –197 k Cal

FeO + $Fe_2\ O_3$

2 1

initially

$$2FeO\ \frac{3}{2}O_2 \rightarrow Fe_2O_3$$

2–2x 1+ x

$$\text{Finally}\ \frac{1+x}{1-2x+2+x} = \frac{2}{3}$$

$$\frac{1+x}{3-x} = \frac{2}{3}$$

3 + 3x = 6 – 3x

$6x = 3 \Rightarrow x = 0.5$

$\therefore$ 1 mole of FeO ?→ converts to $Fe_2\ O_3$

$$\Delta H = \frac{\Delta H_{fFeO_3}}{2} - \Delta H_{FeO}$$

= –197/2 + 65 = –33.5

$\therefore$ ΔH/mole = –11.167

**Sol 22:** $\Delta H_{diss}$ $(H_A)$ = –6900 + 13400

$\Delta H_{diss}$ $(H_B)$ = –2900 + 13400

x – 6900 + (1 – x) x – 2900 = –3900

69 × x + (1 – x) × 29 = 39

40 x = 10

n = 0.25%

$\therefore$ 25% is given to HA and 75% to HB

**Sol 23:** $HgO \rightarrow Hg + \frac{1}{2}O_2$

At constant pressure

$\therefore$ ΔH = 41.84

$$\therefore\ 41.84 = \frac{m}{200.6}\times 90.8$$

$\therefore$ m = 92.435

(b) Δν = 41.84

ΔH = ΔU + ΔPT

= ΔU + ΔnRT

$$= \Delta U + \frac{m}{2\times 200.6}\times 8\times 314\times 298$$

$$\therefore\ \left(41.34+\frac{8.314\times 298\times m}{400.12\times 1000}\right) = \frac{m\times 90.8}{200.6}$$

$$41.84 = \left(\frac{90.8}{200.6}-\frac{1.238}{200.6}\right)m$$

41.84 = 0.446 n

m = 93.715 g

**Sol 24:** $Fe_2O_3 + 3H_2 \rightarrow 2\ Fe + 3H_2\ O(\ell)$

$\Delta H^\circ_{298}$ = –35.1

$\Delta H^\circ_{max}$ = –265

$$\int_{298}^{T}\Delta H\ =\ n(\Delta CP_{Products}-\Delta C_{rad})\ \ \Delta T = 0$$

$\Delta H_T - \Delta H_{298}$ (2 × 25.5 + 3 × 75.3

– 104.5 –3 × 28.9) [T – 28]

$$-26 + 35.1 = \frac{85.7}{10^3}\ (T_{-298})$$

$$\frac{9100}{85.7} = T-298$$

$T_f$ = 404.18 K

**Sol 25:** $2Al + 3/2\ O_2 \rightarrow Al_2O_3$

$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$

$Fe_2O_3 + 2Al \rightarrow Al_2\ O_3 + 2Fe$

$\Delta H^\circ_f = \Delta Hf_{A\ell_2O_3} - \Delta H_{fe_2O_3} = -399 + 199 = -200$ k cal/mol

2 mole of mixture

∴ Mole of $Fe_2O_3$ and ½ mole of $Al_2$

∴ Mass of $Fe_2O_3$ = 160

Mass of Al = 27 × 2 = 54

∴ Mass total = 214

∴ ΔH/mol = –200

$\Delta H/g = \frac{-200}{2 \times 214} = 0.9345$ g

Mole mix mass 2 mole of Al = 54 (g)

d = 2.7 g/cc

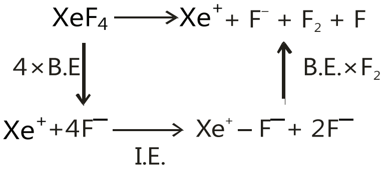
$\therefore V_1 = \frac{54}{2.7} = 20$

$V_2(Fe_2O_3) = \frac{160}{5.2} = 30.77$

$V_{total} = 50.77$ cc

$\therefore \Delta H = \frac{-200}{50.77} = 3.94$ k cal

**Sol 26:**

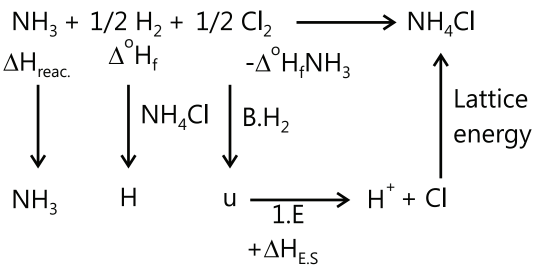


$+\Delta H_{EQ}$ = electron affinity= –85

= 4 × 34 + 279–85 – 38 = 292 k cal/mol

**Sol 27:** $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta^\circ H = -46 \times 2$

$\Delta H^\circ_f = -46$



$$\therefore \Delta H_{rea} = \frac{B.EH_2}{2} + \frac{B.E.C\ell}{2}$$

$+ I.E.H_2 + \Delta H_{E.G\,C\ell}$ + Lattice + Protein gain

$$-314 + 46 = \frac{218}{2} + \frac{124}{2} + 1310$$

– 348 + proton gain – 683

∴ Proton gain = –718 kJ/mol

**Sol 28:** $10^{-3} \times 1.2 \times 1 = 0.0820 \times 273 \times x$

$\therefore n_t = 0.5 \times 10^{-3}$

CO (will at) = ?

$CO + H_2O_2 = CO_2$ ; ΔH = –280 KJ

$\therefore n_{CO} + 280 \times 10^3 = 7$

$\therefore n_{CO} = \frac{7}{280} \times 10^{-3} = 2.5 \times 10^{-5}$

Proportion by volume

$\Rightarrow \frac{n_{CO}}{n_t} = \frac{2.5 \times 10^{-5}}{5 \times 10^{-3}} = 0.05$

$\frac{n_{CO}}{n_{CO_t}} = 0.001$ % y

$10^{-5} = 0.05 \times (1/2)$

After each cycle

$n_{CO_t} = \frac{1}{2} n_{CO}$

$\therefore \frac{n_{CO}}{n_{CO_t}} = \frac{1}{2} \ell n$

$2 \times 10^{-4} = (0.5)^n$

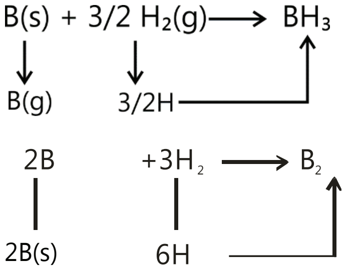
∴ n = 13

13 × x + 80 = 6 × 60

$x = \frac{360 - 80}{13}$

x = 21.54 sec

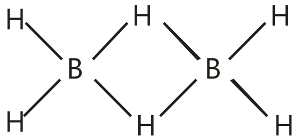
**Sol 29:**



$\Delta H^\circ_f = \Delta H\ B + 3/2\ \Delta H_6 H - 3 \times$ B.E. (B – H)

100 = 565 + 436 × 3/2 – 3 × x

∴ X= 373 H – = a



3 – centre, 2 – electron bond

$\Delta H^{O}_{f\,B_2H_6} - 36 = 2\times 565 + 436 \times 3 - 4 \times x$

**Sol 30:** $CHCl_2 - COOH$ by NaOH = 12850

HCl by NaOH is 13680

$NH_4OH$ by HCl is 12270

$CH\,Cl_2\,COOH + NaOH$

$\rightarrow CHCl_2\,COONa + H_2O$

$NH_4OH + HCl \rightarrow NH_4\,Cl + H_2O$

$NaOH + HCl \rightarrow NaCl + H_2 +$ (2) – (3) gives

$CHCl_2 + NH_4OH \rightarrow CH\,Cl_2\,COONa + NH_4\,Cl$

$\therefore \Delta H_{reac} = -12830 - 12270 + 413680 = -11420$

$\Delta H_{diss}$ of $CH\,C\lambda_2\,COOH = 13680 - 12830 = 850$

$\Delta H_{diss}\,NH_4\,OH = 13680 - 12270 = 1410$

# Exercise 2

## Single Correct Choice Type

**Sol 1 : (A)** $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\,H_2O\,(\ell)$

$a \rightarrow (1)\ 2NH_3 + 3N_2O \rightarrow 4N_2 + 3H_2O$

$b \rightarrow (2)\ N_2O + 3H_2 \rightarrow N_2H_4 + H_2O$

$c \rightarrow (3)\ 4NH_3 + O_2 \rightarrow 2N_2H_4(\ell) + 2H_2O(\ell)$

$d \rightarrow (4)\ H_2 + ½\,O_2\,(r) \rightarrow 2N_2H_4(\ell) + 2H_2O$

$4a = 1$

$b + 2c = -1$

$c + d/2 = 1$

$3a + b + 2c + d = 2$

$b + 2c = -1$

$c + d/2 = 1$

$3 \times ¼ - 1 + d = 2$

$d = 9/4$

$c = 1 - \frac{8}{9} = -\frac{1}{8}$

$b - \frac{2}{8} = -1$

$b = -1 + \frac{1}{4} = -\frac{3}{4}$

$\therefore \Delta H = \frac{1011}{4} + \frac{1}{8}$

$\times\ 286 - \frac{285\times 9}{4} + \frac{317\times 3}{4}$

$\Delta H = -620.5$

**Sol 2: (C)** $HCl + O_2 \rightarrow 2\,Cl_2 + 2H_2O$

$\Delta H_{reac.} = -2 \times \Delta H_1 + \Delta H_2$

$= 2 \times 184.5 + 483 = 114$

$\Delta H = \Delta V + \Delta ng$

$-114 = \Delta V + -1 \times 8.3 \times 300$

$\Delta V = -1115.5$

**Sol 3: (B)** $\Delta H_{reac.} = \Delta H_f + Na_2SO_4 + 2\Delta H\,HCl$

$-2\,\Delta H_f\,NaCl - \Delta H_f\,H_2SO_4$

$= -1382 - 2 \times 92 + 2 \times 441 + 811$

$\Delta V = \Delta H - ngRT = 62.02$

$\Delta H = -67$

**Sol 4: (A)** $A(g) + B(g) \rightarrow C$

$\Delta E = -3$ k Cal

$\Delta H = \Delta E + \Delta_{ng}R$

$= -3 - \frac{1\times 1.987\times 300}{1000}$

$\Delta H = -3.60$

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

$= -3.5 + \frac{300\times -10}{1000}$ 0.6 k cal $\Rightarrow$600 cal

**Sol 5: (D)** $\Delta S = \frac{\Delta H_{vap}}{T}$

$\therefore T\Delta S - \Delta H = -\Delta G = 0$

$\therefore \Delta G = 0$

**Sol 6: (C)**

$$\begin{tikzcd}
4x(g) \arrow[r] \arrow[d] & x_4(g) \arrow[d, "-\Delta Hvapo"] \\
x_4(l) & x_4(l)
\end{tikzcd}$$

$\Delta S = -125$ J/k

$– 100 \times 4 = –4 \times 30 – 32 + 4x$

$\Theta x = 52$

$\Delta G = \Delta H – 1\Delta S$

$= –52 – \left(\frac{–125 \times 300}{1000}\right)$

$= –52 + \frac{123 \times 3}{10}$

$\Delta H = –14.5$

**Sol 7: (C)** $\frac{1}{2} x_2 + \frac{3}{2} y_2 ?\rightarrow xy_3 \; \Delta H = –30$

Reactive at equals

$\therefore \Delta G = 0$

$\therefore \Delta H – T\Delta S = 0$

$\Delta H = T\Delta S$

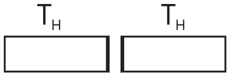
$\Delta S = \left(50 – \frac{3}{2} \times 40 – \frac{60}{2}\right)$

$–30 \times 10^3 = T \times (50 – 60 – 30)$

$T = \frac{30 \times 10^3}{40}$

$T = 750$ K

**Sol 8: (D)**



(Sizes here mass is equal)

$n \times C_P (T_f – T_H) + n \times C_P (T_f – T_C) = 0$

$\therefore 2 T_f = T_H + T_C$

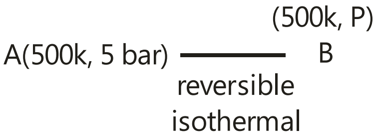
$T_f = \frac{T_H + T_C}{2}$

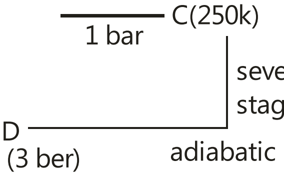
$\therefore \Delta S = C \ln \frac{T_2}{T_1}) H + C \ln \frac{T_2}{T_1} \lambda n$

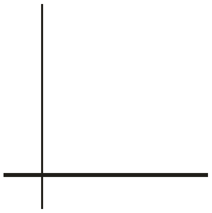
$= C \ln \left[\frac{T_f}{T_H}\right] + C \ln \frac{T_f}{T_H}$

$= C \ln \left[\frac{(T_H + T_C)^2}{T_H T_C}\right]$

**Sol 9: (A)** (V = 3/2 R)







$10^5 \times 5 \times V = 80314 \times 2 \times 500 \times 100$

$V_i = 8.31$

$4 \times 2 \times 10^{–3}$ m$^3$

$V_i = 16.628$ L

$\frac{P}{1} = \frac{500}{250}$

$\therefore P_B = 2$ bar

$P_V = \frac{3}{2} R, \; \frac{1}{r} = \frac{C_v}{C_p} = \frac{3R/2}{3R/2 + R} = \frac{3}{5}$

$r = 5/3$

$PV^r = $ Const.

$P\left(\frac{T}{P}\right)^r = $ const.

$P^{1–r}\, T^r = $ const.

$3^{1–5/3}\, T^{5/3} = 1^{1–5/3} \times (25)^{5/3}$

$\therefore \frac{T}{250} = 3^{2/5} \left(\frac{T}{250}\right)^{5/3} = 3^{2/5}$

$T_f = 387.9$

$\Delta V_{BC} = HC_V\Delta T$

$= \frac{2 \times 3R}{2} \; (250 – 500)$

$= 3R \times 250 = 0750$ R

$\Delta H_{C\Delta} = nC_p\Delta T = 2 \times 5 \; \frac{R}{2} \; (357.90 – 250)$

### Multiple Correct Choice Type

**Sol 10: (A, D)** $H_2O\,(g) \rightarrow 2H(g) + O(g)$

$$\underbrace{H_2O\,(g) \longrightarrow H_2 + \tfrac{1}{2}\, O_2}_{\Delta H=242} \longrightarrow \underbrace{2H + O}_{\Delta H=436+395/2}$$

$$\therefore\ \Delta H_{total} = 242 + 436 + \frac{495}{2} = 925.5$$

$$\underbrace{OH \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}O_2}_{\Delta H = -42}\ \underbrace{\longrightarrow H + O}_{\Delta H = +\frac{436}{2} + \frac{495}{2}}$$

$$\therefore\ \Delta H_{total} = -42 + \frac{436+495}{2} = 423.5$$

$$\Delta H \text{ formation of } H = \frac{436}{2} = 218$$

$\Delta H_f$ OH = 42 – 0 – 0 = 42

**Sol 11: (A, B, C, D)** $CaCO_3$ (Calvin → $CaCO_3$/area)

$\Delta_f G^0$ (CalC) = –1128.8

$\Delta G^0 f$ = –1127.75

$\Delta G^0_{avg} > \Delta G^0_f$ (CalC)

∴ Cal is more stable

(b) C(Δiamond) + $2H_2 \rightarrow CH_4$

$C(g) + 4H(g) \rightarrow CH_4(g)$

More heat is evolved volume in case (b)

as C diamond → C(gas) ΔH > 0

(c) $\Delta_f H^0\ I_2(g) = \Delta_{surr.}\ H\ I_2(s)$ at 25° C

(d) 2Ag(s) = $112O_2$ (g) → $\Delta_{nges}$

= –ve + 1 × RT

∴ ΔV > ΔH

**Sol 12: (B, C)** (A) $(\Delta G_{system})<0$ then react must be is fare

ΔH – TΔS < 0

ΔH > 0

(B) $\Delta_f\ H^0$ (S, Momenta k) ≠ 0 true

$BE_{CH_4}$ = 1654

$$BE_{CH} = \frac{1654}{4}$$

$BE_{(C-C)} = B._{C2H6} - 6 \times B_{CH})$

$$28.2 - \frac{6 \times 1658}{4}$$

= 2812 – 2482= 328

(Δ) $H^0 + \Delta H^- \rightarrow H_2O(\ell)$

ΔH = –56 KJ

$H_2$ (g) + $O_2$ (l) → $\Delta H_f$ ($H_2O$)

$H_{vep}$ = 44 Kj cm

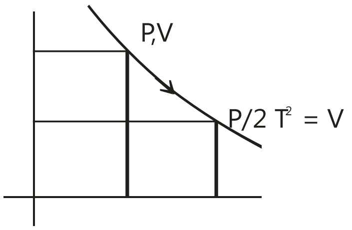
∴ $\Delta H_f$ ($H_2O$, ℓ) = –44 – 242

= –286

–56 = –286 ΔH ($OH^-$)

286 -56 = ΔH ($OH^-$) ; Hf($OH^-$)= 230

**Sol 13: (A, B, D)**



P = mV + C

$$\frac{P}{2}\ 2m\ V + C$$

$$mV = \frac{P}{2}$$

$$\therefore\ m = \frac{-P}{2V}$$

$$\text{Process} = \frac{-P}{2V}\ \text{volume} + \frac{3P}{2}$$

sw = –PdV

$$= \left(\frac{-P}{2V}x + \frac{3P}{2}\right) dV = -\frac{P}{fV^0}\ V^2 + \frac{3P}{2}\Bigg|_V^{2V}$$

$$= \frac{-P}{4V}\ (4V^0 - V^0) + \frac{3P}{2} \times V$$

$$= -\frac{3}{4}\ PV + \frac{3}{2}\ PV = \frac{3}{4}\ PV$$

PV λn 2

λn 2 < ¾ ∴ work done is higher

$$-\frac{2}{2V}\ x^2 + \frac{3}{2}\ PX = nRY$$

Parabolic bott

$$T = \frac{3PX}{2} - \frac{Px^2}{2V}$$

$$\frac{\delta T}{\delta x} = \frac{3P}{2} - \frac{Px}{V}$$

x = 3/2 V

$$\frac{\delta^2 T}{\delta x^2} = -P$$

T atomic max at 3/2 V

$V_{atm} = \frac{2V}{P}\left(\frac{3}{2}P - \text{pressure}\right)$

$\frac{2V}{P}\left(\frac{3P}{2} - \text{pressure}\right)$ Pressure = T

**Sol 14: (A, C)** Normal boiling point = 350 K

$\Delta H_{vap}$ = 3TKJ

at $\Delta S = \frac{350 \times 10^3}{350} = 100$ J

(i) $\Delta S$ at 1 atm 350 k = 100 J

at 0.5 350

$P < P_{vap}$ CHO mol

$\Delta S > \Delta S\text{vap} > 100$

(ii) as at 2 at 350 k

as $P > P_{vap}$

S < S val

**Sol 15: (A, C, D)** In adiabatic explained

w < 0,

Q = 0

$\therefore \Delta V = w$

$\Delta V < 0$

$w_{rev} < \Delta_{ice}$

$\therefore \Delta V_{rev} < \Delta_{avg}$

$\Delta T_{rev} < \Delta T_{ice}$

$\therefore T_{f\ rev} < T_{f\ ice}$

(ii) K.E = 3/2 nRT dependent on temperature if T is constant then KE is constant for adiabatic expansion of gas

$nC_V \Delta T = w < 0$

$H_2 \ ?\!\rightarrow \frac{1}{2} H$

$\Delta S > 0$, STV as no. of molecules hence no. of molecules.

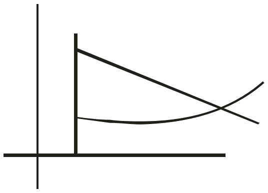
**Sol 16: (A, C, D)** At any common row on the p–v curve

$P(V)^r$

PV = C adiabatic

$P = C_1\, r - r$

$P = C_1\, V - r$



$\frac{\delta P}{\delta V} = -R$

$\frac{\delta P}{\delta V} = -r\,\frac{P}{V}$

r > 1

Slope of adiabatic C is more negative theorem slope of isothermal

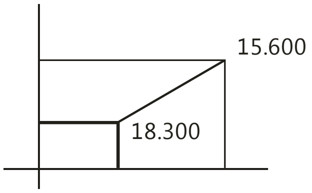
Adiabatic curve is above isothermal curve

Hence area under adiabatic curve > area under isothermal curve

Hence $w_{\text{adiabatic} >} w_{\text{isothermal}}$

$\delta = \frac{C_P}{C_v}$ not necessarily constant

**Sol 17: (B, D)**



$\Delta H_{AB} = nC_p\Delta T$

$= 1 \times \frac{5R}{2} \times 300 = 6235.5$ J

$\Delta S = nC_V \ln\frac{T_2}{T_1} - \ln R \ln\frac{V_2}{V_1}$

$= \frac{3R}{2}\ln 2 + R\ln\left(\frac{15}{10}\right)$

$\therefore \Delta S > 0$

V = mT + C

10 = 300 m + C

15 = 600 m + C

$m = \frac{5}{300}$

$10 = \frac{5}{300} \times 100 + C$

C = 5

$V = \frac{T}{300} + 5$

$PV = R (V - 5) \times 60$

$$P = R\left(60 - \frac{300}{V}\right)$$

$$w = \left(\frac{300}{V} - 60\right)$$

$= (300 \ln V - 60 V) R = -1488.88J$

$\Delta V = nC_V \Delta T$

$$= 1 \times \frac{3R}{2} \times 300 = 3746.3$$

$q = -w + Q$

$= 1491.8 + 3746.3 = 5237.82$

**Sol 18: (A, B)** Compressive $\therefore$ w +ve

(i) And reversible isothermal work is therefore the maximum value of isothermal work

(ii) Work is area under cyclic process

$S_{rev} \neq 0 \therefore w \neq 0$

For ideal gas $T^r p^{1-r} = 0$

$$T^{\frac{CP}{CV}} . T^{\frac{-e}{CV}} = 0$$

$$T^{\frac{CP}{R}} P^{-1} \text{ const.}$$

$$P = \frac{RT}{V_V - b} - \frac{a}{V^2}$$

$$w = -\int_{V_1}^{V_2} PdV$$

$$= -RT \ln\left[\left(\frac{V_2 - b}{V_1 - b}\right) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right]$$

**Sol 19: (C, D)** $P V^r = \text{const.}$

$\therefore P^{1-r} T^r = \text{const.}$

$V^{1+r} T^{-1} = \text{const.}$

$$PT^{\frac{r}{1-r}} = w$$

$P = G \times T$

$$\frac{rP}{rT} = \frac{r-1}{r}$$

$$\frac{rP}{rT} = \frac{r}{r_1} PT^{-r} = 1 + \frac{1}{r-1} PT^{-r}$$

$$\therefore \frac{rP}{rT} > 0$$

$$v^0 = \cos T^{\frac{1}{1+r} - 1}$$

$$\frac{rV}{rT} = \frac{1}{1+r} GT = \frac{-r}{1+r}$$

as r is $\frac{rV}{rT} = \frac{1}{1+r} VT^{-r} > 0$

$P = CV^{-r}$

$$\frac{rP}{rV} = -rCV^{-r}$$

**Sol 20: (A, B, D)** $H_2SO_4 + 2 (NH_4)OH \rightarrow (NH_4)_2 SO_4 + 2H_2O$

$\Delta H_{reac.} = 2 \times \Delta H_{dissociation}$ of $(NH_4)_2$ OH × moles of $NH_4OH$ + 2 × moles of dissociation of $H_2O$

Given $-1.5 \times 1.4 = -0.05 \times 57 \times 2 + 2 \times 0.2\ \Delta H_{diss.}$

$3.6 = 2 \times 0.2 \times 0.2 \times \Delta H$

$\therefore \Delta H_{diss} = 4.5$ KJ

$\Delta H_{reac}$ (HCl – NaOH) = –57 + 4.5 = –52.5

$\Delta H(CH_3COOH - NH_4\ OH) = -48.1$

$-48.1 = -57 + 4.5 + \Delta H_{diss}\ CH_3\ COOH$

$\therefore H_{diss}\ CH_3\ COOH = 4.4$ KJ

$\Delta H$ for $2H_2\ O\ (l) \rightarrow 2H^+ + 20\,H^-$

$= 2 \times 57 = 114$

**Sol 21: (A, B, C, D)** Only (g) + $O_2 \rightarrow CO_2$

Replacement $\Delta H_f$ of product

**Sol 22: (B, C, D)** $\Delta S$ for ½ $H_2 \rightarrow N$ is + ve true

as no. of molecules yes, entropy increase

$\Delta G_{system}$ is O for reversible process act standard conditions

$\Delta G^0$ i real = VdP – sdT

Function of P,V,T not just P and T at equilibrium $\Delta G$ is moles

Nothing fixed about $\Delta S$

**Sol 23: (A, B, D)** In isothermal gas cylinder,

(A) w + ve dV < 0 = w = –PdV

$\therefore$ w + ve

(B) $\Delta H = \Delta U = 0$ as $\Delta T = 0$

(C) $\Delta S = R \ln \frac{V_2}{V_1}$ , $= V_2 > V_1$

$\therefore \Delta S$ – ve

(D) $\Delta G = -T\Delta S > 0$ as $\Delta S < 0$

**Sol 24: (B, C, D)** 0.2 m$^3$ Ne at 200 kP at $T_i$

$V_f$ = ½ $VB_i$ = 0.1 m$^3$

Temperature constant inside as gas volume < and pressure is constant to maintain temperature to maintain air temperature

q may be +ve or – ve

$\Delta V \neq 0$ as $\Delta$ nRT $\neq 0$

## Assertion Reasoning Type

**Sol 25: (D)** HCl + NaOH = –13.7

$\therefore \Delta H_{rest}$ 0 × Alkali = –25%

$\Delta H_{diss}$ = +2 × 13.7 – 25% = 2

$\therefore H_2C_2O_4 \rightarrow 2H + C_2O_4$ $\Delta H$= 2 k cal

**Sol 26: (D)** $\Delta H = nC_p \Delta T$

(For ideal gas, ΔH is a function of compressor alone)

**Sol 27: (D)** Q = 0

w = ΔV

and w < 0, $\therefore \Delta U < 0$

No comments can be made about temperature T might not increase

**Sol 28: (D)** $\frac{1}{8} S_8 (s) + O_2 (g) ?\rightarrow SO_2 (g)$

S – (–2 × 2) = 0

S = 4

Max oxidation state = 6

Assertion is wrong

## Comprehension Type

### Paragraph 1:

| A | B |
|---|---|
| 22.4L | 22.4L |
| n | n |

**Sol 29: (D)** T = 27.3 k P = 1 atm

In container B

$V_f = \frac{V}{8} V_i = PV^r$ = const.

$$1 \times \left(\frac{V_i}{V_f}\right)^{5/3} \quad P_f \; r = 5/3$$

$P_f = (8)^{5/3}$

$P_f$ = 32 atm

In container A, $V_f = 22.4 + \frac{7}{8} \times 22.5$

$= \frac{15}{8} \times 22.4$

$V_f = \frac{15}{8} V_i$

$P_f$ = 8 atm

**Sol 30: (A)** $\dfrac{\frac{15}{8} \times 22.4}{T_f} = \dfrac{1 \times 22.4}{2 + .3}$

$C_f = \frac{273 \times 5}{8} 4 = 1638$

**Sol 31: (B)** $\Delta H_A = nC_P\Delta T = 1 \times \frac{5 \times 8.34}{2} \times (1638–27.5)$ = 80.53

### Paragraph 2:

**Sol 32: (C)** (i) T = 532 mm Hg = 0.4 atm T = 353 k

$V_i$ = 0.4 = 0.4 kg

$\Delta H = \Delta U + \Delta pV$

Dependent only on temperature

$\therefore \Delta H = \Delta pV$ = (1–0.7) × 0.9 L

= 0.3 × 0.9 L = 0.3 × 0.9 × 100 J= 27 J

**Sol 33: (C)** From 1 to 3

$\Delta U = \Delta$ (nCT)

$\Delta mCT = 0.9 \times C \times (373 - 353) + \frac{0.4 \times 40}{18} = 1075.6$

**Sol 34: (B)** $\Delta H = 1.8 \times 4.2 + \frac{450}{18} \times 80 = 1075.6$

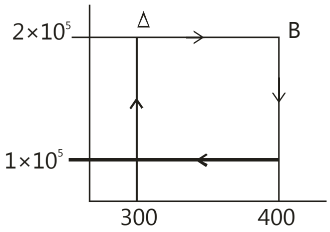
**Sol 35: (B)** Work done in 1 to 3

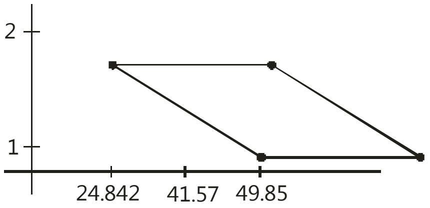
$w_{1–2}$ = 0 as ΔU = 0

$w_{2–3} = P_{ext}\, dU = \frac{0.45 \times 10^3}{18} \times \frac{0.0821 \times 373}{1000}$

$w_2$ (10 KJ)

**Paragraph 3:**





**Sol 36: (C)** w A–B –w = PCΔv = nRΔT

$= 2 \times 10^5 \times T$

= 2 × 8.314 × 200 = 400 R

**Sol 37: (B)** Work done= $-\ nRT\ ln\ \frac{V_2}{V_1}$

$= -nRT\ ln\ \frac{P_2}{P_1} = 2R \times 300\ ln \left(\frac{1}{2}\right)$

= + 600 R × ln 2 = + 414 R

**Sol 38: (B)**

Net work done in cycle

⇒ ln A – B = PΔV = nRΔT

2R × (500 – 300)

$B–C = -nRT\ ln\ \frac{P_2}{P_1} = 2R \times 500\ ln \left(\frac{1}{2}\right)$

= –2R 500 ln 2

C–D = PΔV – nRT = 2 × R (300 – 500)

D–A = –2R × 300 ln (1/2) = 2R × 300 λn 2

∴ Total mole = 2 R (500 – 300) –2R 500 λn 2

= 2R (500 – 300) + 2 × 300 λn 2

= 2R (300 – 500) ln

= 420 Rln 2

= 276 R

**Match the Columns**

**Sol 39:** A → p, r, s; B → q, s; C → q, s; D → s

(i) Reversible isothermal

$P = -nRT\ ln\ \frac{V_2}{V_1} = 2.303\ nRT\ log\ \frac{P_2}{P_1}$

(p, r)

(ii) Reversible adiabatic =

$w = \Delta U = nC_V\ (T_2 - T_1)$

qs

(iii) Irreversible adiabatic = $nC_V\ \Delta T = -P_{ex}\ dV$

(iv) Irreversible isothermal $w = -\int P_{ex} dV$

**Sol 40:** A → s; B → p, r; C → p, s; D → p, r

Irreversible adiabatic compression

(A) Q = 0, ∴ $\Delta S_{surr} = 0$, $\Delta S_{system} = 0$

(B) Reversible vap

$\Delta S_{system} > 0$

as gaseous

Reversible, process ∴ $\Delta S_{total} = 0$

∴ $\Delta S_{surr} < 0$

(C) free expansion of ideal gas

Q = w = 0

∴ $\Delta S_{surr.} = 0$

Expansion ∴ $\Delta S_{system} > 0$

(Δ) diss. of $CaCO_3$ (S) → CaO(s) + $CO_2$(g)

$\Delta S_{system} > 0$

$\Delta S_{system} + \Delta S_{surr} = 0$

∴ $\Delta S_{surr} < 0$

## Previous Years' Questions

**Sol 1: (B)** Elements in its standard state have zero enthalpy of formation. $Cl_2$ is gas at room-temperature, $\Delta H_f^o$ of $Cl_2$(g) is zero.

**Sol 2: (C)** $\Delta G^o = \Delta H^o - T\Delta S^o$

$= -54.07 \times 10^3 J - 298 \times 10 J = -57.05 \times 10^3\ J$

Also, $\Delta G^o = -2.303\ RT\ log\ K$

$$\Rightarrow\ log\ K = \frac{-\Delta G^o}{2.303\ RT} = \frac{57.05 \times 10^3}{5705} = 10$$

**Sol 3: (A)** At transition point (373 K, 1.0 bar), liquid remains in equilibrium with vapour phase, therefore $\Delta G = 0$. As vaporisation occur, degree of randomness increase, hence $\Delta S > 0$

**Sol 4: (B)** Entropy is a state function hence:

$$\Delta S_{A\to B} = \Delta S_{A\to C} + \Delta S_{C\to D} + \Delta S_{D\to B}$$

= 50 eu + 30 eu + (–20 eu) = 60 eu

**Sol 5: (A)** Given, $\frac{P}{V} = 1 \Rightarrow p = V$

Also from first law: $dq = C_v dT + pdV$

For one mole of an ideal gas: $pV = RT$

$\Rightarrow pdV + Vdp = RdT$

From (i) $pdV = Vdp$

Substituting in Eq. (ii) gives

$2pdV = RdT$

$\Rightarrow pdV = \frac{R}{2}dT \Rightarrow dq = C_v dT + \frac{R}{2}dT$

$$\Rightarrow \int \frac{dq}{dT} = C_v + \frac{R}{2} = \frac{3}{2}R + \frac{R}{2} = 2R$$

**Sol 6: (A, B)** Resistance and heat capacity are mass dependent properties, hence they are extensive.

**Sol 7: (A, D, C)** Internal energy, molar enthalpy are state function. Also, reversible expansion work is a state function because among the given initial and final states, there can be only one reversible path.

**Sol 8:** Temperature rise = $T_2 - T_1$ = 298.45 – 298 = 0.45K

q = heat-capacity × $\Delta T$ = 2.5 × 0.45 = 1.125 kJ

$$\Rightarrow \text{Heat produced per mol} = \frac{1.125}{3.5} \times 28 = 9 \text{ kJ}$$

**Sol 9:** $\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p$

$\Rightarrow \Delta U = \Delta H - V\Delta p$

= –560 – 1× 30 × 0.1 = –563 kJ

**Sol 10:** $\Delta U = q + W$

For adiabatic process, q = 0, hence $\Delta U = W$

$W = -p(\Delta V) = -p(V_2 - V_1)$

$\Rightarrow \Delta U = -100\ (99 - 100) = 100$ bar mL

$\Delta H = \Delta U + \Delta(pV)$

where, $\Delta pV = p_2V_2 - p_1V_1$

$\Rightarrow \Delta H = 100 + (100 \times 99 - 1 \times 100) = 9900$ bar mL

**Sol 11:** Work-done along dased path:

$$|-W| = \sum p\Delta V = 4\times1.5 + 1\times1 + \frac{2}{3}\times2.5 = 8.65 \text{ L atm}$$

Work-done along solid path: $-W = nRT \ln\frac{V_2}{V_1}$

$= p_1V_1 \ln\frac{V_2}{V_1} = 2 \times 2.3 \log\frac{5.5}{0.5}$

$= 2 \times 2.3 \log 11 = 4.79$

$$\Rightarrow \frac{W_d}{W_s} = \frac{8.65}{4.79} = 1.80 \approx 2$$

**Sol 12: (B)** Statement-I is true.

$dq = dE + p_{ext}dV = 0$

$\Delta T = 0 \therefore dE = 0;\ p_{ext} = 0 \therefore p_{ext}dV = 0$

Statement-II is true. According to kinetic theory of gases, volume occupied by molecules of ideal gas is zero.

However, statement-II is not the correct explanation of statement-I.

**Sol 13: (D)** Statement-I is false. At equilibrium, $\Delta G = 0$, $G \neq 0$.

Statement-II is true, spontaneous direction of reaction is towards lower Gibb's free energy.

**Sol 14: (B)** Statement-I is true, it is statement of first law of thermodynamics.

Statement-II is true, it is statement of second law of thermodynamics. However, statement-II is not the correct explanation of statement-I.

**Sol 15:** A $\to$ p, r, s; B $\to$ r, s; C $\to$ t; D $\to$ p, q, t

1. (A) $CO_2(s) \longrightarrow CO_2(g)$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence $\Delta S$ is positive

(B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, $\Delta S > 0$.

(C) $2H \longrightarrow H_2(g)$

A new H–H covalent bond is being formed, hence $\Delta H < 0$.

Also, product is less disordered than reactant, $\Delta S < 0$.

(D) Allotropes are considered as different phase, hence $P_{(\text{white, solid})} \longrightarrow P_{(\text{red, solid})}$ is a phase transition as well as allotropic change.

Also, red phosphorus is more ordered than white phosphorus, $\Delta S < 0$.

**Sol 16: (C)** Combustion of glucose

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\Delta H_{\text{combustion}} = \left(6 \times \Delta H_f CO_2 + 6 \times \Delta H_f H_2O\right)$$
$$- \Delta H_f C_6H_{12}O_6$$
$$= \left(6 \times -400 + 6 \times -300\right) - \left(-1300\right)$$

= -2900 kJ/mol

= -2900/180 kJ/g

= -16.11 kJ/g

Hence (C) is correct.

**Sol 17: (C)** Since container is thermally insulated. So, q = 0, and it is a case of free expansion therefore W = 0 and

$\Delta E = 0$

So, $T_1 = T_2$

Also, $P_1\ P_1 = P_2\ P_2$

**Sol 18: (B)** At 100°C and 1 atmosphere pressure

$H_2O(\ell) \rightleftharpoons H_2O(g)$ is at equilibrium. For equilibrium

$\Delta S_{\text{total}} = 0$ and $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

$\therefore\ \Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surrounding}} < 0$

**Sol 19: (C)** $\Delta E = q + w$

$0 = q - P_{\text{ext}}\ \Delta V$

$q = P_{\text{ext}}\ \Delta\ V = 3\ \text{atm}\ \left(2-1\right)L = 3\ \text{atm L}$

$= \left(3 \times 101.3\right)$ Joule

$$\Delta S_{\text{surr}} = -\frac{q}{T} = \frac{3 \times 101.3}{300} = -1.013\ \text{Joule/K}$$