05

Chemical Thermodynamics

TOPIC 1

Generalised terms and First Law of Thermodynamics

01 For water $\Delta_{vap} H = 41 \text{kJ mol}^{-1}$ at 373 K and 1 bar pressure. Assuming that water vapour is an ideal gas that occupies a much larger volume than liquid water, the internal energy change during evaporation of water is .... kJ mol^{-1}.

$[\text{Use } R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}]$

[2021, 26 Aug Shift-II]

Ans. ***(38)***

$$H_2O(l) \longrightarrow H_2O(g)$$

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

ΔH = enthalpy of vaporisation

ΔU = change in internal energy

Δn_g = number of moles of water vapour

$R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$

$T = 373 \text{ K}$

$\therefore 41 \text{kJ} = \Delta U + RT$

$$\Delta U = 41 - 8.3 \times 373 \times 10^{-3} = 41 - 3.095$$

$$= 37.90 \text{ kJ mol}^{-1} = 38 \text{ kJ mol}^{-1}$$

02 A system does 200 J of work and at the same time absorbs 150 J of heat. The magnitude of the change in internal energy is .... J. (Nearest integer)

[2021, 25 July Shift-II]

Ans. ***(50)***

Work done by the system, $W = -200$ J

Heat absorbed, $q = +150$ J

According to first law of thermodynamics internal energy,

$\Delta U = q + W$

$$\Delta U = 150 + (-200)$$

$\{\Delta U = \text{Change in internal energy}\}$

$$= -50 \text{ J}$$

$$\text{Magnitude} = |-50 \text{ J}| = |\Delta U|$$

$$= 50 \text{ J}$$

03 At 25°C, 50 g of iron reacts with HCl to form $FeCl_2$. The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is ...... J. (Round off to the nearest integer)

$[\text{Given, } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$ Assume, hydrogen is an ideal gas$]$

[Atomic mass off Fe is 55.85 u]

[2021, 16 March Shift-II]

Ans. ***(2218)***

$$\underset{50\,g}{Fe(s)} + HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$$

(Moles of Fe = Moles of H_2)

$\text{moles} = \frac{50}{55.85}$ 0.8952 mol 0.8952 mol

$= 0.8952$ mol

Work done can be given by

$$W = -p_{ext}\Delta V = -\Delta n_g RT$$

where, Δn_g = {gaseous moles on product side} − {gaseous mole on reactant side}

$$= 0.8952 - 0$$

$$W = -0.8952 \times 8.314 \times 298$$

$$= -2217.92 \text{ J}$$

Closest integer = 2218

04 Five moles of an ideal gas at 293 K is expanded isothermally from an initial pressure of 2.1 MPa to 1.3 MPa against at constant external pressure 4.3 MPa. The heat transferred in this process is .... kJ mol^{-1}. (Rounded off to the nearest integer)

$[R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}]$

[2021, 25 Feb Shift-II]

Ans. ***(15)***

The gas performs isothermal irreversible work (W).

where, $\Delta U = 0$ (change in internal energy)

From, 1st law of thermodynamics,

$\Rightarrow$ $\Delta U = \Delta Q + W$

$\Rightarrow$ $0 = \Delta Q + W$

$\Rightarrow$ $\Delta Q = -W$

Now, $W = -p_{ext}(V_2 - V_1)$

$$= -p_{ext}\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right)$$

$$= -p_{ext} \times nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

Given, $p_{ext} = 4.3 \text{ MPa}, p_1 = 2.1 \text{ MPa},$

$p_2 = 1.3 \text{ MPa},$

$n = 5 \text{ mol},$

$T = 293 \text{ K}$

and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= -4.3 \times 5 \times 8.314 \times 293\left(\frac{1}{1.3} - \frac{1}{2.1}\right)$$

$$= -15347.70 \text{ J mol}^{-1}$$

$$= -15.347 \text{ kJ mol}^{-1}$$

$$\simeq -15 \text{ kJ mol}^{-1}$$

$\Rightarrow$ $\Delta Q = 15 \text{ kJ mol}^{-1}$

05 The ionisation enthalpy of Na^+ formation from $Na(g)$ is 495.8 kJ mol^{-1}, while the electron gain enthalpy of Br is –325.0 kJ mol^{-1}. Given, the lattice enthalpy of NaBr is –728.4 kJ mol^{-1}. The energy for the formation of NaBr ionic solid is (–) .... $\times 10^{-1}$ kJ mol^{-1}.

[2021, 25 Feb Shift-I]

Ans. ***(5576)***

$$Na(g) \xrightarrow{IE_1} Na^+(g)$$

$$[IE_1 = 495.8 \text{ kJ mol}^{-1}]$$

$$Br(g) \xrightarrow[\text{gain enthalpy}]{\text{Electron}} (EG)\, Br^-(g) \text{ [Gain enthalpy} = -325 \text{ kJ mol}^{-1}]$$

$$Na^+ + Br^- \xrightarrow[\text{energy}]{\text{Lattice}} (LE)\, NaBr(s)$$

$$[\text{Lattice energy} = -728.4 \text{ kJ mol}^{-1}]$$

$$\Delta H_{\text{Formation}} = IE_1 + \text{Gain enthalpy} + \text{Lattice energy}$$

$$\Delta H = 495.8 + (-325) + (-728.4)$$

$$= -557.6 \text{ kJ/mol}$$

$$= -5576 \times 10^{-1} \text{ kJ}$$

06 Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is **[2020, 4 Sep Shift-II]**

(a) $-RT \ln V_2 / V_1$ (b) $-RT(V_2 - V_1)$
(c) $C_V(T_2 - T_1)$ (d) zero

Ans. ***(d)***

Expansion of a gas in vacuum ($p_{ext} = 0$) is called free expansion. No work is done during free expansion, since as the expansion is done in vacuum that is in absence of external pressure, hence w will be

$$w = -p_{ext}\Delta V \Rightarrow w = 0$$

(Here, $p_{ext} = 0$), because expansion takes place in vacuum)

07 The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is ...., (Given : ΔH_{vap} for water at 373 K = 41kJ/mol, $R = 8.314$ $JK^{-1}mol^{-1}$)

[2020, 5 Sep Shift-I]

Ans. ***(189494)***

Given, $dH = 41 \text{ kJ/mol} = 41 \times 1000 \times 5$ J

[For 90 g or 5 mol $H_2O(l)$]

$$\begin{array}{lcc} & H_2O(l) \longrightarrow & H_2O(g) \\ t = 0 & \frac{90}{18} \text{ mol} & - \\ t = \infty & 0 & 5 \text{ mol} \end{array}$$

$$\Rightarrow \quad \Delta n_g = 5 \quad \because T = 373 \text{ K}$$

We know that,

$$dH = dU + \Delta n_g RT$$

dU = Internal energy change

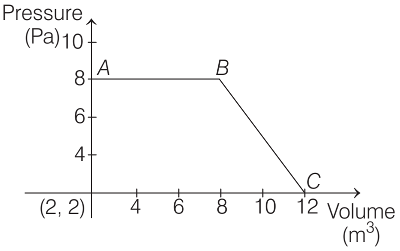
$$= dH - \Delta n_g RT$$

$$= 41 \times 1000 \times 5 - 5 \times 8.314 \times 373$$

$$= 189494.39 \text{ J} \simeq 189494.00 \text{ J}$$

08 The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is ....

[2020, 8 Jan Shift-I]



Ans. ***(48.00)***

Work done is equal to the area under pV-curve.

$$\therefore \text{Work done } (|W|) = \frac{1}{2}(6 + 10) \times 6$$

$$= 48.00 \text{ Pa. m}^3 = 48.00 \text{ J.}$$

09 At constant volume, 4 mol of an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is .... **[2020, 8 Jan Shift-II]**

Ans. ***(6.25)***

Given: $n = 4$ mol

$$\Delta T = 500 \text{ K} - 300 \text{ K} = 200 \text{ K}$$

$$\Delta U = 5000 \text{ J}$$

$$\Delta U = nC_V\Delta T$$

$$C_V = \frac{\Delta U}{n\Delta T} = \frac{5000}{4 \times 200} = \frac{50}{8} = 6.25$$

10 Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non- expansion work is zero)

[2019, 8 April Shift-I]

(a) Cyclic process : $q = -W$
(b) Adiabatic process : $\Delta U = -W$
(c) Isochoric process : $\Delta U = q$
(d) Isothermal process : $q = -W$

Ans. ***(b)***

From the 1st law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = change in internal energy

q = heat, W = work done

The above equation can be represented for the given processes involving ideal gas as follows:

(a) **Cyclic process** For cyclic process,

$$\Delta U = 0$$

$$\therefore \quad q = -W$$

Thus, option (a) is correct.

(b) **Adiabatic process** For adiabatic process,

$$q = 0 \Rightarrow \Delta U = W$$

Thus, option (b) is incorrect.

(c) **Isochoric process** For isochoric process,

$\Delta V = 0$. Thus, $W = 0 (\because W = p\Delta V)$.

$$\therefore \quad \Delta V = q$$

Thus, option (c) is correct.

(d) **Isothermal process** For isothermal process,

$$\Delta U = 0$$

$$\therefore \quad q = -W$$

Thus, option (d) is correct.

11 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28$ JK^{-1} mol^{-1}, calculate ΔU and ΔpV for this process. ($R = 8.0$ JK^{-1} mol^{-1})

[2019, 8 April Shift-II]

(a) $\Delta U = 2.8$ kJ; $\Delta(pV) = 0.8$ kJ
(b) $\Delta U = 14$ J; $\Delta(pV) = 0.8$ J
(c) $\Delta U = 14$ kJ; $\Delta(pV) = 4$ kJ
(d) $\Delta U = 14$ kJ; $\Delta(pV) = 18$ kJ

Ans. ***(c)***

Given, $n = 5$ mol, $T_2 = 200$ K, $T_1 = 100$ K

$$C_V = 28 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta U = nC_V\Delta T = nC_V(T_2 - T_1)$$

$$= 5 \text{ mol} \times 28 \text{ JK}^{-1} \text{ mol}^{-1} \times (200 - 100) \text{ K}$$

$$= 14{,}000 \text{ J} = 14 \text{ kJ}$$

$$\Delta pV = nR\Delta T = nR(T_2 - T_1)$$

$$= 5 \text{ mol} \times 8 \text{ JK}^{-1} \text{ mol}^{-1} \times (200 - 100) \text{ K}$$

$$= 4000 \text{ J} = 4 \text{ kJ}$$

12 Among the following the set of parameters that represents path functions, is **[2019, 9 April Shift-I]**

(A) $q + W$ (B) q
(C) W (D) $H - TS$
(a) (A) and (D) (b) (A), (B) and (C)
(c) (B), (C) and (D) (d) (B) and (C)

Ans. ***(d)***

q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. $q + W$ and option (d), i.e. $H-TS$ are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

13 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10m^3 at 1000 K. Given R is the gas constant in $\text{JK}^{-1}\ \text{mol}^{-1}$, x is **[2019, 9 Jan Shift-I]**

(a) $\dfrac{2R}{4-R}$ (b) $\dfrac{4-R}{2R}$ (c) $\dfrac{4+R}{2R}$ (d) $\dfrac{2R}{4+R}$

Ans. ***(b)***

From the ideal gas equation,

$$pV = \Sigma nRT \qquad \ldots(\text{i})$$

Given: $p = 200$ Pa, $V = 10 \text{m}^3, T = 1000$ K

$n_A = 0.5$ moles, $n_B = x$ moles

On substituting the given values in equation (i), we get

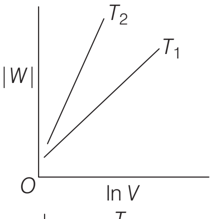
$$200 \times 10 = (n_A + n_B) \times R \times 1000$$

$$0.5 + x = \frac{200 \times 10}{R \times 1000}$$

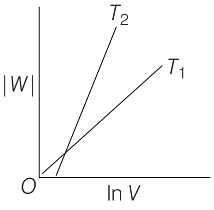
$$\frac{1}{2} + x = \frac{2}{R} = \frac{2}{R} - \frac{1}{2} = \frac{4-R}{2R}$$

14 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temp. T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (W) on the final volume (V) is **[2019, 9 Jan Shift-I]**

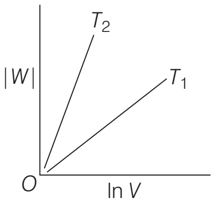
(a)



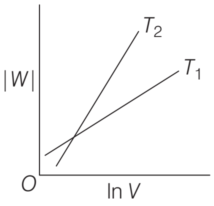
(b)



(c)



(d)



Ans. ***(c)***

For isothermal reversible expansion,

$$|W| = nRT \ln \frac{V_f}{V_i}$$

$$= nRT \ln \frac{V}{V_i}$$

where, V = final volume, V_i = initial final.

or $|W| = nRT \ln V - nRT \ln V_i$

On comparing with equation of straight line, $y = mx + c$, we get

$$\text{slope} = m = + nRT$$

$$\text{intercept} = - nRT \ln V_i$$

Thus, plot of $|W|$ with $\ln V$ will give straight line in which slope of $2(T_2)$ is greater than slope of $1(T_1)$ which is given in all options.

Now, if $V_i < 1$ then y intercept $(- nRT\ V_i)$ becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y-intercept goes above and other y-intercept goes below. Thus, option (b) and (d) are incorrect.

If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y-intercept. But they cannot give same y-intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then y-intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

15 An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J $\text{mol}^{-1}\text{K}^{-1}$, the temperature of Al increases by **[2019, 10 Jan Shift-II]**

(a) $\dfrac{3}{2}$ K (b) 1 K

(c) 2 K (d) $\dfrac{2}{3}$ K

Ans. ***(d)***

It is an irreversible isothermal compression of an ideal gas.

(i) $dE = dq + p(V_f - V_i)$

where, dE = Internal energy change

dq = amount of heat released

$\Rightarrow \quad 0 = dq + p(V_f - V_i)$

[$\because dE = 0$ for an isothermal process]

$\Rightarrow \quad dq = -4(1-5) = 16$ J

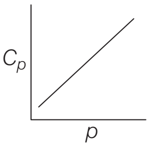
(ii) $dq = n \times C \times \Delta T$ (for Al)

$\Rightarrow 16 \text{ J} = 1 \text{ mol} \times 24 \text{ J mol}^{-1} \text{ K}^{-1} \times \Delta T$

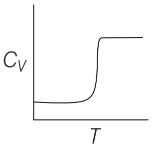
$\Rightarrow \quad \Delta T = \dfrac{16}{24} \text{ K} = \dfrac{2}{3} \text{ K}$

16 For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

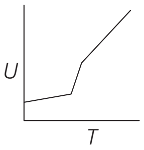
(a)



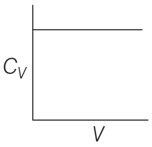
(b)



(c)



(d)



[2019, 12 Jan Shift-I]

Ans. ***(a)***

For diatomic ideal gases,

$$C_V = \frac{f}{2} R \text{ and } C_p = \left(\frac{f}{2} + 1\right) R$$

where, f = degree of freedom

f = translational degree of freedom + degree of freedom

$= 3 + 2 = 5$ [at normal temperature]

The explanation of various plots are as follows.

(a) We know that, C_p is heat capacity at constant pressure. Thus, it does not vary with the variation in pressure. Hence, plot given in option (a) is incorrect.

(b) In this plot, C_V first increases slightly with increase in temperature and then increases sharply with temperature. The sharp increase is due to increase in degree of freedom.

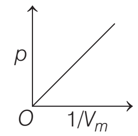
Thus, plot given in option (b) is correct.

(c) For ideal gases, Internal energy $(U) \propto T$

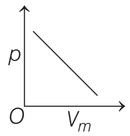
Thus, as temperature increases internal energy also increases. As temperature increases further degree of freedom also increases thus, there is slight variation in the graph. First translational degree of freedom is present followed by rotational and vibrational degree of freedom. Hence, plot given in option (c) is also correct.

(d) C_V is heat capacity at constant volume. Thus, it does not vary with variation in volume. Hence, plot given in option (d) is correct.

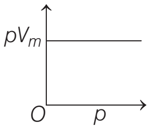
17 The combination of plots which does not represent isothermal expansion of an ideal gas is **[2019, 12 Jan Shift-II]**



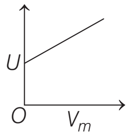
(a)



(b)



(c)



(d)

Ans. ***(c)***

In isothermal expansion, $pV_m = K$ (constant)

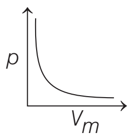
This relation is plotted in graph 'C'

Likewise, $p = \frac{K}{V_m}$

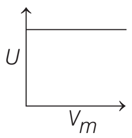
This relation is plotted in graph "A".

Thus, graph *B* and *D* are incorrect.

For them the correct graphs are:



and



for graph *B* for graph *D*

18 ΔU is equal to **[JEE Main 2017]**

(a) isochoric work (b) isobaric work
(c) adiabatic work (d) isothermal work

Ans. ***(c)***

According to first law of thermodynamics,

$$\Delta U = q + W = q - p\Delta V$$

In isochoric process $(\Delta V = 0)$, $\Delta U = q$
In isobaric process $(\Delta p = 0)$, $\Delta U = q$
In adiabatic process $(q = 0)$, $\Delta U = W$
In isothermal process $(\Delta T = 0)$ and $\Delta U = 0$
$\therefore$ ΔU is equal to adiabatic work.

19 A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of *q* and *W* for the process will be (R = 8.314 J / mol K, ln 7.5 = 2.01) **[JEE Main 2013]**

(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

Ans. ***(a)***

As the process is carrying out at constant temperature, therefore this type of expansion is called isothermal reversible expansion, for which, $\Delta U = 0$. Hence, $q = -W$

i.e., heat absorbed by the system is equal to the work done by the system.

Thus, $q = +208$ J, $W = -208$ J

20 An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, then which of the following statements is correct ? **[AIEEE 2006]**

(a) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(c) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
(d) $T_f = T_i$ for both reversible and irreversible processes

Ans. ***(a)***

In an ideal gas, there are no intermolecular forces of attraction.

Hence, $T_f = T_i$ for both reversible and irreversible processes.

21 An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **[AIEEE 2004]**

(a) -900 J (b) -900 kJ
(c) 270 kJ (d) 900 kJ

Ans. ***(a)***

Work done due to change in volume against constant pressure is

$$W = -p(V_2 - V_1)$$
$$= -1 \times 10^5 \text{ Nm}^{-2} (1 \times 10^{-2} - 1 \times 10^{-3}) \text{ m}^3$$
$$= -900 \text{ Nm} = -900 \text{ J} \qquad [1 \text{ Nm} = 1 \text{ J}]$$

22 The internal energy change when a system goes from state *A* to *B* is 40 kJ/mol. If the system goes from *A* to *B* by a reversible path and returns to state *A* by an irreversible path, what would be the net change in internal energy? **[AIEEE 2003]**

(a) 40 kJ (b) >40 kJ
(c) < 40 kJ (d) zero

Ans. ***(d)***

$\Delta E = 0$, in a cyclic process.

23 Heat required to raise the temperature of 1 mole of a substance by 1° is called **[AIEEE 2002]**

(a) specific heat
(b) molar heat capacity
(c) water equivalent
(d) specific gravity

Ans. ***(b)***

The amount of heat required to raise the temperature of one mole of substance through 1°C is called molar heat capacity.

$$C = \frac{q}{T_2 - T_1}$$

24 A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2. Work done is found to be $J(q_1 + q_2)$. This is in accordance with **[AIEEE 2002]**

(a) First law of thermodynamics
(b) Second law of thermodynamics
(c) Joules equivalent law
(d) None of the above

Ans. ***(c)***

Joules law suggests

$$J = \frac{\text{Mechanical work done by the system, } W}{\text{Net heat given to the system, } Q}$$

Hence, $J = \frac{W}{q_1 + q_2}$

Therefore, $W = J(q_1 + q_2)$

is constant with Joules law of equivalence.

TOPIC 2

Reactions Related to Enthalpies and Hess's Law

25 200 mL of 0.2 M HCl is mixed with 300 mL of 0.1 M NaOH. The molar heat of neutralisation of this reaction is – 57.1 kJ. The increase in temperature in °C of the system on mixing is $x \times 10^{-2}$.

The value of x is .... (Nearest integer)

[Given, specific heat of water = $4.18\ \text{J g}^{-1}\ \text{K}^{-1}$

Density of water = $1.00\ \text{g cm}^{-3}$]

(Assume no volume change on mixing) **[2021, 27 Aug Shift-I]**

Ans. ***(82)***

Millimoles of HCl $= 200 \times 0.2 = 40$

Millimoles of NaOH $= 300 \times 0.1 = 30$

Heat released $(q) = n \times$ molar heat

$$= \frac{30}{1000} \times 57.1 \times 1000 = 1713\ \text{J}$$

Mass of solution $= 500 \times 1 = 500$ g

We know that,

$$\Delta T = \frac{q}{mc} = \frac{1713\ \text{J}}{500\ \text{g} \times 4.18\ \text{J/g-K}}$$

$$= 0.8196\ \text{K} = 81.96 \times 10^{-2}\ \text{K}$$

$$x \approx 82$$

26 When 400 mL of 0.2 M H_2SO_4 solution is mixed with 600 mL of 0.1 M NaOH solution, the increase in temperature of the final solution is .... $\times 10^{-2}$ K. (Round off to the nearest integer).

[Use : $H^+(aq) + OH^+(aq) \longrightarrow H_2O$; $\Delta_y H = -57.1\ \text{kJ mol}^{-1}$]

Specific heat of $H_2O = 0.18\ \text{J K}^{-1}\ \text{g}^{-1}$, density of $H_2O = 1.0\ \text{g cm}^{-3}$.

Assume no change in volume of solution on mixing. **[2021, 27 July Shift-II]**

Ans. ***(82)***

$$\text{Molarity} = \frac{n \times 1000}{V(\text{mL})}$$

where, n = number of moles

V = volume of solution in mL

$$\text{Moles} = \frac{\text{molarity} \times \text{volume (mL)}}{1000}$$

1 mole of H_2SO_4 produces 2 moles of H^+

$$n_{H^+} = \frac{400 \times 0.2}{1000} \times 2 = 0.16\ \text{moles}$$

and 1 mole of NaOH produces 1 mole of OH^-.

$$n_{OH^-} = \frac{600 \times 0.1}{1000} = 0.06$$

n_{OH^-} is low.

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

Mol : 1 2 1 2

Now, 1 mole H_2SO_4 requires 2 moles NaOH, then 0.06 mole of NaOH will require = 0.03 moles of H_2SO_4

∴ 0.06 mole of OH^- reacts with 0.06 moleof H^+.

$$m = 1 \times 1000$$

Now, heat liberated from reaction

= heat gained by solution.

$$n \times \Delta H = m \times C_p \times \Delta T$$

$$0.06 \times 57.1 \times 10^3 = (1000 \times 1) \times 4.18 \times \Delta T$$

$$\Rightarrow \quad \Delta T = 0.8196\ \text{K}$$

$$= 82 \times 10^{-2}\ \text{K}$$

27 For water at 100°C and 1 bar, $\Delta_{\text{vap}} H - \Delta_{\text{vap}} U =$ .... $\times 10^2$ J mol^{-1}.

(Round off to the nearest integer)

[Use : $R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$]

[Assume volume of $H_2O(l)$ is much smaller than volume of $H_2O(g)$. Assume $H_2O(g)$ treated as an ideal gas] **[2021, 27 July Shift-I]**

Ans. ***(31)***

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Using formula, $\Delta H = \Delta U + \Delta n_g RT$

For 1 mole water,

$$\Delta n_g = 1$$

$$\therefore \Delta n_g RT = 1\ \text{mol} \times 8.31\ \text{J/mol K} \times 373\ \text{K}$$

$$= 3099.63\ \text{J}$$

$$\simeq 31 \times 10^2\ \text{J}$$

28 The Born-Haber cycle for KCl is evaluated with the following data :

$\Delta_f H°$ for KCl $= -436.7\ \text{kJ mol}^{-1}$

$\Delta_{\text{sub}} H°$ for K $= 89.2\ \text{kJ mol}^{-1}$,

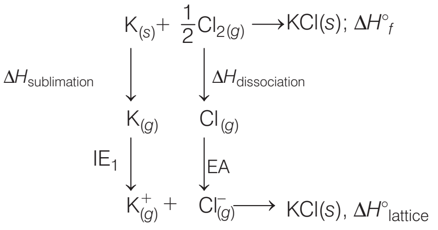
$\Delta_{\text{ionisation}} H°$ for K $= 419.0\ \text{kJ mol}^{-1}$;

$\Delta_{\text{electron gain}} H°$ for Cl(g) $= -348.6$ kJ mol^{-1}, $\Delta_{\text{bond}} H°$ for $Cl_2 = 243.0\ \text{kJ mol}^{-1}$

The magnitude of lattice enthalpy of KCl in kJ mol^{-1} is .... (Nearest integer) **[2021, 26 Aug Shift-I]**

Ans. ***(718)***

Born-Haber cycle for KCl is as follows



$$\therefore\ \Delta H_f^\circ = \Delta H_{\text{sublimation}} + \frac{1}{2}\Delta H_{\text{dissociation}}$$

$$+ IE_1 + EA + \Delta H_{\text{lattice}}$$

$$-436.7\ \text{kJ/mol} = 89.2\ \text{kJ/mol}$$

$$+ \frac{1}{2} \times (243\ \text{kJ/mol}) + 419\ \text{kJ/mol} + (-348.6\ \text{kJ/mol}) + \Delta H^\circ_{\text{lattice}}$$

$$\Rightarrow \quad \Delta H^\circ_{\text{lattice}} = -717.8\ \text{kJ/mol}$$

∴ Magnitude of lattice enthalpy of KCl in kJ/mol is 718 (nearest).

29 At 298 K, the enthalpy of fusion of a solid (X) is $2.8\ \text{kJ mol}^{-1}$ and the enthalpy of vaporisation of the liquid (X) is $98.2\ \text{kJ mol}^{-1}$. The enthalpy of sublimation of the substance (X) in kJ mol^{-1} is .... (Nearest integer) **[2021, 25 July Shift-I]**

Ans. ***(101)***

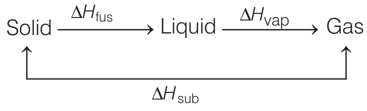
Given,

Enthalpy of fusion,

$$\Delta H_{\text{fus}} = 2.8\ \text{kJ mol}^{-1}$$

Enthalpy of vaporisation,

$$\Delta H_{\text{vap}} = 98.2\ \text{kJ mol}^{-1}$$



Using Hess's law,

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

$$= 2.8 + 98.2$$

$$= 101\ \text{kJ/mol}$$

30 At 298.2 K the relationship between enthalpy of bond dissociation (in kJ mol^{-1}) for hydrogen (E_H) and its isotope, deuterium (E_D), is best described by **[2021, 25 July Shift-I]**

(a) $E_H = \frac{1}{2} E_D$ (b) $E_H = E_D$

(c) $E_H \simeq E_D - 7.5$ (d) $E_H = 2E_D$

Ans. ***(c)***

Enthalpy of bond dissociation (kJ/mol) at 298.2 K

For hydrogen = 435.88 kJ/mol

For deuterium = 443.35 kJ/ mol

Hence, difference in energy of deuterium and hydrogen is approx. 7.50 kJ/mol

Therefore, equation is $[E_H \simeq E_D - 7.5]$

Here, deuterium is a heavy isotope of hydrogen that's why they required more enthalpy of bond dissociation, i.e. 7.5 kJ/mol.

31 If the standard molar enthalpy change for combustion of graphite powder is -2.48×10^2 kJ mol^{-1}, the amount of heat generated on combustion of 1 g of graphite powder is ...... kJ. (Nearest integer)

[2021, 22 July Shift-II]

Ans. ***(21)***

Standard molar enthalpy change for combustion of graphite powder, i.e. carbon-12 is -2.48×10^2 kJ mol^{-1}.

So, heat generated of 1g of graphite powder

$$= \frac{2.48 \times 10^2}{12}$$

$$= 20.66 = 21 \text{ kJ}.$$

Hence, amount of heat generated is 21 kJ.

32 For the reaction,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

the reaction enthalpy $\Delta_r H =$ .... kJ mol^{-1}

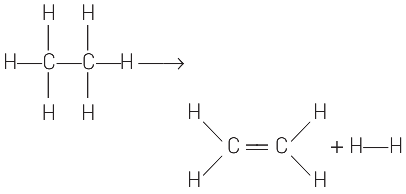
(Round off to the nearest integer).

[Given : Bond enthalpies in kJ mol^{-1} : C—C = 347, C$=$C = 611; C—H = 414; H—H = 436]

[2021, 18 March Shift-I]

Ans. ***(128)***

The equation representing various substances involved in chemical reaction is



Given bond enthalpies of various bonds in kJ mol^{-1} i.e. C—C = 347, C$=$C = 611, C—H = 414, H—H = 436

This reaction involves the breaking of 2C—H bonds and formation, of 1 C $=$ C bond and 1 H—H bond.

$$\Delta_r H =$$
$$[\text{Sum of bond ethalpies ofreactants}]$$
$$- [\text{Sum of bond enthalpies of products}]$$
$$= [1\Delta_{C\text{-}C} H + 6\Delta_{C\text{-}H} H]$$
$$- [1\Delta_{C=C} H + 4\Delta_{C—H} H + 1\Delta_{H—H} H]$$
$$= (357 + 6 \times 414) - [611 + 4 \times 414 + 436]$$
$$= 2831 - 2703$$
$$= 128 \text{ kJ/mol.}$$

33 The standard enthalpies of formation of Al_2O_3 and CaO are -1675 kJ mol^{-1} and -625 kJ mol^{-1} respectively.

For the reaction,

$3CaO + 2Al \longrightarrow 3Ca + Al_2O_3$ the standard reaction enthalpy $\Delta_r H°$ .... kJ.

(Round off to the nearest integer).

[2021, 17 March Shift-I]

Ans. ***(230)***

Given, $\Delta_f H^{\circ}_{Al_2O_3} = -1675$ kJ/mol

$\Delta_f H^{\circ}_{CaO} = -625$ kJ/mol

To find $\Delta_r H^{\circ}$ for the reaction

$3CaO + 2Al \longrightarrow 3Ca + Al_2O_3; \Delta_r H^{\circ} = ?$

$$\Delta_r H^{\circ} = \sum \Delta_f H^{\circ}_{\text{Product}} - \sum \Delta_f H^{\circ}_{\text{Reactant}}$$
$$= \{\Delta_f H^{\circ}_{Al_2O_3} + 3\Delta_f H^{\circ}_{Ca}\}$$
$$- \{3\Delta_f H^{\circ}_{CaO} + 2\Delta_f H^{\circ}_{Al}\}$$
$$= \Delta H_f^{\circ}(Al_2O_3) - 3 \times \Delta H_f^{\circ}(CaO)$$

We know, $\Delta_f H^{\circ}$ for elemental state = 0

$\Rightarrow \Delta_f H^{\circ}_{Ca} = 0, \Delta_f H^{\circ}_{Al} = 0$

Putting the value,

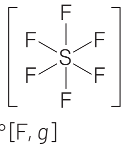
$$\Delta_r H^{\circ} = \{-1675 + 0\} - \{3(-625) + 0\}$$
$$= -1675 + 1905 = 230 \text{ kJ}$$

34 The average S—F bond energy in kJ mol^{-1} of SF_6 is .... (Rounded off to the nearest integer) [Given, the values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are -1100, 275 and 80 kJ mol^{-1} respectively.]

[2021, 26 Feb Shift-II]

Ans. ***(309)***

$S(g) + 6F(g) \longrightarrow SF_6(g)$



So, $\Delta_f H°[S, g] + 6 \times \Delta_f H°[F, g]$

$$= \Delta_f H°[SF_6, g] + 6 \times E_{S-F}$$

[$\therefore E_{S-F}$ = Average S—F bond energy in SF_6]

$$275 + 6 \times 80 = -1100 + 6 \times E_{S-F}$$

$$\Rightarrow E_{S-F} = \frac{275 + 6 \times 80 + 1100}{6}$$
$$= 309.16 \text{ kJ mol}^{-1} = 309 \text{ kJ mol}^{-1}$$

35 Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1}, respectively. The hydration enthalpy of NaCl is

[2020, 5 Sep Shift-II]

(a) -780 kJ mol^{-1} (b) 780 kJ mol^{-1}

(c) -784 kJ mol^{-1} (d) 784 kJ mol^{-1}

Ans. ***(c)***

The enthalpy of solution of an ionic solid is numericlly equal to the sum of its hydration and lat energies,

i.e. $\Delta H^{\circ}_{sol} = \Delta H^{\circ}_{hydration} + \Delta H^{\circ}_{lattice}$

$$\therefore \begin{tikzcd} \text{NaCl}(s) \arrow[rr, "\Delta H = 4"] \arrow[dr, "\Delta H^{\circ} = 788"'] & & \text{NaCl}(aq) \\ & Na^+(g) + Cl^-(g) \arrow[ur, "\Delta H^{\circ}_{hyd}"'] & \end{tikzcd}$$

$$\Delta_{sol} H° = \Delta_{lattice} H° + \Delta_{hyd} H°$$
$$4 = 788 + \Delta_{hyd} H°$$
$$\Delta H_{hyd} H° = -784 \text{ kJ/mol}$$

36 The standard heat of formation $(\Delta_f H^{\circ}_{298})$ of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively is ....

[2020, 7 Jan Shift-II]

Ans. ***(192.50)***

$\Delta_f H°$ of ethane is $\Delta H°$ of the reaction :

$$2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g)$$

From $\Delta_c H°$ (heat of combustion) values,

$$\Delta_f H° = (2 \times \Delta_c H° \text{ of graphite})$$
$$+ (3 \times \Delta_c H° \text{ of } H_2) - (\Delta_c H° \text{ of } C_2H_6)$$
$$= (-2 \times 286) + (-393.5 \times 3)$$
$$- (-1560) \text{ kJ mol}^{-1}$$
$$= -192.50 \text{ kJ mol}^{-1}$$

37 The heat of combustion of ethanol into carbon dioxides and water is -327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is ($R = 2$ cal mol^{-1} K^{-1}) ....

[2020, 2 Sep Shift-II]

Ans. ***(326400)***

The combustion equation of ethanol (C_2H_5OH or C_2H_6O) is

$$C_2H_6O(l) + \left(2 + \frac{6}{9} - \frac{1}{2}\right)O_2(g) \xrightarrow{300K}$$

$$2CO_2(g) + \frac{6}{2}H_2O(l)$$

or $C_2H_6O(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta n_g = (2+0) - (0+3) = -1$$

$$\Rightarrow dq_p = du_v + \Delta n_g RT$$

$$\Rightarrow du_v = dq_p - \Delta n_g RT$$

$$= -327 - (-1) \times (2 \times 10^{-3}) \times 300$$

$$= -326.400 \text{ kcal} = -326400 \text{ cal}$$

$\because dq_p =$ Heat at constant pressure or enthapy change

$dU_v =$ Heat at constant volume or internal energy change

38 If enthalpy of atomisation for $Br_2(l)$ is x kJ/mol and bond enthalpy for Br_2 is y kJ/mol, the relation between them **[2020, 9 Jan Shift-II]**

(a) is $x < y$ (b) does not exist
(c) is $x > y$ (d) is $x = y$

Ans. ***(c)***

Atomisation of $Br_2(l)$

$$Br_2(l) \longrightarrow 2Br(g); \quad \Delta H = x \text{ kJ mol}^{-1}$$

which can be considered as sum of following :

$$Br_2(l) \longrightarrow Br_2(g);$$

$\Delta H =$ a positive value ...(i) (endothermic process)

$$Br_2(g) \longrightarrow 2Br(g); \Delta H$$

(bond enthalpy of Br_2) $= y$ ...(ii)

$\therefore x = y +$ (Positive value), and $x > y$.

39 For silver, C_p (J $K^{-1}mol^{-1}$) $= 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to **[2019, 8 April Shift-I]**

(a) 62 kJ (b) 16 kJ
(c) 21 kJ (d) 13 kJ

Ans. ***(a)***

According to Kirchoff's relation,

$$\Delta H = n\int_{T_1}^{T_2} C_p dT \quad \text{...(i)}$$

where, $\Delta H =$ Change in enthalpy.

$C_p =$ Heat capacity at constant pressure.

Given, $n = 3$ moles,

$T_1 = 300$ K,

$T_2 = 1000$ K,

$C_p = 23 + 0.01T$

On substituting the given values in Eq. (i), we get

$$\Delta H = 3\int_{300}^{1000}(23 + 0.01T)dT$$

$$= 3\int_{300}^{1000} 23dT + 0.01T\, dT$$

$$= 3\left[23T + \frac{0.01T^2}{2}\right]_{300}^{1000}$$

$$= 3\left[23(1000 - 300) + \frac{0.01}{2}(1000^2 - 300^2)\right]$$

$$= 3[16100 + 4550] = 61950 \text{ J} \approx 62 \text{ kJ}$$

40 The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to **[2019, 10 April Shift-II]**

(a) $-4\,RT$ (b) $3\,RT$
(c) $4\,RT$ (d) $-3\,RT$

Ans. ***(a)***

Key Idea The relation between ΔH and ΔU is

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

where, $\Delta n_g = \Sigma n_p - \Sigma n_R$

= number of moles of gaseous products − number of moles of gaseous reactants.

The general combustion reaction of a hydrocarbon is as follows :

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

For heptane, $x = 7$, $y = 16$

$\Rightarrow C_7H_{16}(l) + 11O_2(g) \longrightarrow 7CO_2(g) + 8H_2O(l)$

$\therefore \quad \Delta n_g = 7 - 11 = -4$

Now, from the principle of thermochemistry,

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

$$\Rightarrow \quad \Delta H - \Delta U = \Delta n_g RT = -4RT$$

41 Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and I_2(vap.) are 0.055 and 0.031 cal g^{-1} K^{-1} respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is **[2019, 12 April Shift-I]**

(a) 2.85 (b) 5.7
(c) 22.8 (d) 11.4

Ans. ***(c)***

Key Idea When q is the amount of heat involved in a system then at constant pressure

$$q = q_p$$

and $\quad C_p\Delta T = \Delta H$

Given reaction :

$$I_2(s) \longrightarrow I_2(g)$$

Specific heat of $I_2(s) = 0.055$ cal g^{-1} K^{-1}.

Specific heat of

I_2(vap) = 0.031 cal $g^{-1}K^{-1}$.

Enthalpy (H_1) of sublimation of iodine $= 24$ cal g^{-1}

If q is the amount of heat involved in a system then at constant pressure $q = q_p$ and

$$\Delta H = C_p\Delta T$$

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

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

$$H_2 = 24 + (0.031 - 0.055)(250 - 200)$$

$$H_2 = 24 + (-0.024)(50)$$

$$= 24 - 1.2 = 22.8 \text{ cal/g}$$

Thus, the enthalpy of sublimation of iodine at 250 is 22.8 cal/g.

42 Given :

(i) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);$

$\Delta_r H^\ominus = x$ kJ mol^{-1}

(ii) $C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);$

$\Delta_r H^\ominus = y$ kJ mol^{-1}

(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);$

$\Delta_r H^\ominus = z$ kJ mol^{-1}

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

(a) $y = 2z - x$ (b) $x = y - z$
(c) $z = x + y$ (d) $x = y + z$

[2019, 12 Jan Shift-II]

Ans. ***(d)***

Second equation given in this question is wrong. Hence, No answer in correct. If corrected second equation is given, i.e.

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

and if we take the above reaction in consideration then $x = y + z$ will be the answer as :

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

$\Delta_r H° = y$ kJ/mol

(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g),$

$\Delta_r H° = z$ kJ/mol

Summing up both the equation you will get equation (i)

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g),$

$\Delta_r H° = x$ kJ/mol

Hence, x, y and z are related as:

$$x = y + z$$

43 The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is

-3263.9 kJ mol^{-1} at 25° C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314$ JK^{-1} mol^{-1})

[JEE Main 2018]

(a) 4152.6 (b) -452.46
(c) 3260 (d) -3267.6

Ans. ***(d)***

Key Idea Calculate the heat of combustion with the help of following formula

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

where, ΔH_p = Heat of combustion at constant pressure

ΔU = Heat at constant volume (It is also called ΔE)

Δn_g = Change in number of moles (In gaseous state).

R = Gas constant; T = Temperature.

From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

Change in the number of gaseous moles i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now we have Δn_g and other values given in the question are

$\Delta U = -3263.9$ kJ/mol
$T = 25°\text{ C} = 273 + 25 = 298$ K
$R = 8.314$ JK^{-1}mol^{-1}

So, $\Delta H_p = (-3263.9) + (-1.5) \times 8.314 \times 10^{-3} \times 298$
$= -3267.6$ kJ mol^{-1}

44 Given,

$$C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g); \quad \Delta_r H° = -393.5 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta_r H° = -285.8 \text{ kJ mol}^{-1}$$

$$CO_2(g) + 2\ H_2O(l) \longrightarrow CH_4(g) + 2O_2(g); \quad \Delta_r H° = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction, **[JEE Main 2017]**

$$C_{(\text{graphite})} + 2\ H_2(g) \longrightarrow CH_4(g)$$

will be

(a) $+78.8$ kJ mol^{-1}
(b) $+144.0$ kJ mol^{-1}
(c) -74.8 kJ mol^{-1}
(d) -144.0 kJ mol^{-1}

Ans. ***(c)***

Based on given $\Delta_r H°$

$\Delta_f H° = H°_{CO_2} = -393.5$ kJ mol^{-1} ...(i)

$\Delta_f H° = H°_{H_2O} = -285.8$ kJ mol^{-1} ...(ii)

$\Delta_f H° = H°_{O_2} = 0.00$ (elements) ...(iii)

Required thermal reaction is for $\Delta_f H°$ of CH_4

Thus, from III

$$890.3 = [\Delta_f H°(CH_4) + 2\Delta_f H°(O_2)] - [\Delta_f H°(CO_2) + 2\Delta_f H°(H_2O)]$$
$$= \Delta_f H°(CH_4) + 0] - [-393.5 - 2 \times 285.5]$$

$\therefore \Delta_f H°(CH_4) = -74.8$ kJ / mol

45 The heats of combustion of carbon and carbon monoxide are -393.5 and -283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is **[JEE Main 2016]**

(a) 676.5 (b) -676.5 (c) -110.5 (d) 110.5

Ans. ***(c)***

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393.5 \text{ kJ mol}^{-1} \quad ...(i)$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2(g); \quad \Delta H = -283.5 \text{ kJ mol}^{-1} \quad ...(ii)$$

On subtracting Eq. (ii) from Eq. (i), we get

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

$$\Delta H = (-393.5 + 283.5) \text{ kJ mol}^{-1} = -110 \text{ kJ mol}^{-1} \text{ (approx.)}$$

46 For the complete combustion of ethanol,

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

the amount of heat produced as measured in bomb calorimeter is 1364.47 kJmol^{-1} at 25°C. Assuming ideality, the enthalpy of combustion, $\Delta_C H$ for the reaction will be
[$R = 8.314$ JK^{-1}mol^{-1}]

[JEE Main 2014]

(a) -1366.95 kJmol^{-1}
(b) -1361.95 kJmol^{-1}
(c) -1460.50 kJmol^{-1}
(d) -1350.50 kJmol^{-1}

Ans. ***(a)***

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

Amount of heat produced in bomb calorimeter,

$$\Delta u = -1364.47 \text{ kJmol}^{-1}$$

Enthalpy of a combustion reaction is

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

where, Δu = internal energy
Δn_g = moles of gas (products − reactants)
ΔR = Gas constant,
T = Temperature in K

As per equation,

$\Delta n_g = 2 - 3 = -1$
$T = 25°\text{ C} = 25 + 273\text{ K} \Rightarrow T = 298$ K

Thus, $\Delta H = -1364.47 + \left[\dfrac{(-1) \times 8.314 \times 298}{1000}\right]$

$\Delta H = -1364.47 - 2.477 = -1366.947$ kJmol^{-1}

Hence, the enthalpy of combustion, $\Delta_c H$ for the given reaction will be -1366.947 kJmol^{-1}.

47 The value of enthalpy change (ΔH) for the reaction

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

at 27°C is -1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be **[AIEEE 2011]**

(a) -1371.5 kJ (b) -1369.0 kJ
(c) -1364.0 kJ (d) -1361.5 kJ

Ans. ***(c)***

Relation between ΔH (enthalpy change) and ΔE (internal energy change) is

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

where, Δn_g = (moles of gaseous products) − (moles of gaseous reactants)

For the given reaction,

$$\Delta n_g = 2 - 3 = -1$$

$\Rightarrow \quad -1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$

$\therefore \quad \Delta E = -1364.0$ kJ mol^{-1}

48 Consider the reaction,

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g), \quad \Delta_r H = -111 \text{ kJ}.$$

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) **[AIEEE 2011]**

(a) -165 kJ (b) $+54$ kJ
(c) $+219$ kJ (d) -219 kJ

Ans. ***(a)***

$$\begin{tikzcd} \underbrace{4N_2(g)+O_2(g)} \arrow[rr, "\Delta H = -111\text{ KJ}"] \arrow[dr, "\Delta H = ?"'] & & 2N_2O_5(g), \\ & 2N_2O_5(s) \arrow[ur, "+54\text{kJ}"'] & \end{tikzcd}$$

From Hess law,

$$\Delta H_f + \Delta H_{\text{sub}} = \Delta H_{\text{reaction}} \ ;$$

$$\Delta H_f = \Delta H_{\text{reaction}} - \Delta H_{\text{sub}}$$

$$= -111\,\text{kJ} - (54\,\text{kJ})$$

$$= -111 - 54\,\text{kJ} = -165\,\text{kJ}$$

Thus, the enthalpy of formation, ΔH_f for $N_2O_5\,(s)$ is $-165\,\text{kJ}$.

49 The standard enthalpy of formation of NH_3 is -46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1}, the average bond enthalpy of N—H bond in NH_3 is **[AIEEE 2010]**

(a) -964 kJ mol^{-1} (b) $+352$ kJ mol^{-1}

(c) $+1056$ kJ mol^{-1} (d) -1102 kJ mol^{-1}

Ans. ***(b)***

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g),$$

$$\Delta_r H = -46\,\text{kJ mol}^{-1}$$

Bond enthalpy of $H_2 = 436\,\text{kJ mol}^{-1}$

[+ ve sign is taken because energy is supplied
to break the H—H bond into its atoms]

Similarly, bond enthalpy of

$$N_2 = +712\,\text{kJ mol}^{-1}$$

$$\Delta_r H = \left[\frac{1}{2}\text{BE}(N_2) + \frac{3}{2}\text{BE}(H_2)\right] - 3\,\text{BE(N—H)}$$

$$-46 = \left[\frac{1}{2}\times 712 + \frac{3}{2}\times 436\right] - 3\,\text{BE (N—H)}$$

$$-46 = (356 + 654) - 3\,\text{BE (N—H)}$$

$$3\,\text{BE (N—H)} = (1010) + 46$$

$$3\,\text{BE (N—H)} = 1056$$

$$\text{BE (N—H)} = 1056/3 = 352\,\text{kJ mol}^{-1}$$

50 On the basis of the following thermochemical data

$[\Delta_f G^\circ H^+(aq) = 0]$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);$$

$$\Delta H = 57.32\text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

$$\Delta H = -286.02\text{ kJ}$$

The value of enthalpy of formation of OH^- ion at 25°C is **[AIEEE 2009]**

(a) -22.88 kJ (b) -228.88 kJ

(c) $+228.88$ kJ (d) -343.52 kJ

Ans. ***(b)***

Consider the heat of formation of H_2O.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

$$\Delta H = -286.20\text{ kJ}$$

$$\Delta H_r = \Delta H_f(H_2O, l) - \Delta H_f(H_2, g) - \frac{1}{2}\Delta H_f(O_2, g)$$

$$= -286.20 = \Delta H_f(H_2O, l) - 0 - 0$$

$$\Delta H_f(H_2O, l) = -286.20$$

Now, consider the ionization of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$$

$$\Delta H = 57.32\text{ kJ}$$

$$\Delta H_r = \Delta H_f\,(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f(H_2O, l)$$

$$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.20)$$

Thus, $\Delta H_f(OH^-, aq) = 57.32 - 286.20$

$$= -228.80\text{ kJ.}$$

51 Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below

$$\frac{1}{2}Cl_2\ (g) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}}\ H^\ominus} Cl\ (g) \xrightarrow{\Delta_{EA}H^\ominus} Cl^-\ (g) \xrightarrow{\Delta_{\text{hyd}}\ H^\ominus} Cl^-\,(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2\ (g)$ to $Cl^-(aq)$

(using the data, $\Delta_{\text{diss}}\ H^\ominus_{Cl_2} = 240$ kJ mol^{-1}

$\Delta_{EA}H^\ominus_{Cl} = -349$ kJ mol^{-1},

$\Delta_{\text{hyd}}\ H^\ominus_{Cl} = -381$ kJ mol^{-1}) will be **[AIEEE 2008]**

(a) $+152$ kJ mol^{-1}

(b) -610 kJ mol^{-1}

(c) -850 kJ mol^{-1}

(d) $+120$ kJ mol^{-1}

Ans. ***(b)***

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

$$\Delta H = \frac{1}{2}\Delta H_{\text{diss}}\,(Cl_2) + \Delta H_{\text{EA}}\ Cl + \Delta H_{\text{hyd}}\,(Cl^-)$$

$$= \frac{240}{2} - 349 - 381 = -610\text{ kJ mol}^{-1}$$

52 Assuming that water vapour is an ideal gas, the internal energy change (ΔE) when 1 mole of water is vaporised at 1 bar pressure and 100°C, (Given : molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and $R = 8.3$ J mol^{-1} K^{-1}) will be **[AIEEE 2007]**

(a) 4.100 kJ mol^{-1} (b) 3.7904 kJ mol^{-1}

(c) 37.904 kJ mol^{-1} (d) 41.00 kJ mol^{-1}

Ans. ***(c)***

$$H_2O(l) \longrightarrow H_2O(g)$$

$$\Delta n_g = 1 - 0 = 1$$

$$\Delta E = \Delta H - \Delta n_g\,RT$$

$$= 41 - (1 \times 8.3 \times 373 \times 10^{-3})$$

$$[R = 8.3 \times 10^{-3}]$$

$$= 37.9\text{ kJ mol}^{-1}$$

53 $(\Delta H - \Delta E)$ for the formation of carbon monoxide (CO) from its elements at 298 K is ($R = 8.314$ JK^{-1} mol^{-1}) **[AIEEE 2006]**

(a) -1238.78 J mol^{-1}

(b) 1238.78 J mol^{-1}

(c) -2477.57 J mol^{-1}

(d) 2477.57 J mol^{-1}

Ans. ***(b)***

Calculate $\Delta H - \Delta E$ by using the formula,

$$\Delta H - \Delta E = \Delta n_g RT$$

$$= \frac{1}{2}\times 8.314 \times 298 = 1238.78\text{ J mol}^{-1}$$

$$\left[\begin{array}{c} C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \\ \Delta n_g = 1 - \frac{1}{2} = \frac{1}{2} \end{array}\right]$$

54 The enthalpy changes for the following processes are listed below

$Cl_2(g) = 2Cl(g)$, 242.3 kJ mol^{-1}

$I_2\ (g) = 2I\ (g)$, 151.0 kJ mol^{-1}

$ICl(g) = I(g) + Cl(g)$, 211.3 kJ mol^{-1}

$I_2(s) = I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation of ICl is **[AIEEE 2006]**

(a) -14.6 kJ mol^{-1}

(b) -16.8 kJ mol^{-1}

(c) $+16.8$ kJ mol^{-1}

(d) $+244.8$ kJ mol^{-1}

Ans. ***(c)***

$$\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g)$$

$$\Delta H = \left[\frac{1}{2}\Delta H_{s \to g} + \frac{1}{2}\Delta H_{\text{diss}}\,(Cl_2) + \frac{1}{2}\Delta H_{\text{diss}}\,(I_2)\right] - \Delta H_{ICl}$$

$$= \left(\frac{1}{2}\times 62.76 + \frac{1}{2}\times 242.3 + \frac{1}{2}\times 151.0\right) - 211.3$$

$$= 228.03 - 211.3$$

$$\Delta H = 16.73\text{ kJ mol}^{-1}$$

55 The standard enthalpy of formation (ΔH_f°) at 298 K for methane, $CH_4(g)$ is – 74.8 kJ mol^{-1}. The addition information required to determine the average energy for C—H bond formation would be **[AIEEE 2006]**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2

Ans. ***(a)***

Carbon is found in solid state. The state of substance affects the enthalpy change.

$$C(s) \longrightarrow C(g) \text{ sublimation,}$$

and $H_2(g) \longrightarrow 2H(g)$ dissociation are required for C—H bond.

56 Consider the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[AIEEE 2005]**

(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$ (d) $\Delta H = 0$

Ans. ***(b)***

According to relationship of ΔH and ΔE,

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

ΔH = enthalpy change (at constant pressure)

ΔE = internal energy change (at constant volume)

(given reaction is exothermic)

(Δn_g = moles of gaseous products – moles of gaseous reactants)

For the reaction

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

$$\Delta n_g = 2 - 4 = -2$$

Thus, $\Delta H = \Delta E - 2RT$

$\Rightarrow$ $\Delta H < \Delta E$

Note Numerical value of $\Delta H < \Delta E$ in exothermic reaction and when $\Delta n_g < 0$.

57 If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is – 200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) 400 kJ mol^{-1} (b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1} (d) None of these

Ans. ***(d)***

Formation of XY is shown as

$$X_2 + Y_2 \longrightarrow 2XY$$

$$\Delta H = [(BE)_{X—X} + (BE)_{Y—Y}] - [2(BE)_{X—Y}]$$

If (BE) of X—Y = a KJ/mol

then, (BE) of (X—X) = a and (BE) of

$$(Y—Y) = \frac{a}{2} \qquad \left[\because \frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY\right]$$

$$\therefore \qquad \Delta H_f (X—Y) = -200 \text{ kJ}$$

$$\therefore -400 \text{ (for 2 mol } XY) = \left(a + \frac{a}{2} - 2a\right)$$

$$-400 = -\frac{a}{2};\ a = +800 \text{ kJ}$$

The bond dissociation energy of $X_2 = 800$ kJ mol^{-1}.

58 The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol^{-1}, respectively. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) 110.5 kJ (b) 676.5 kJ
(c) – 676.5 kJ (d) – 110.5 kJ

Ans. ***(d)***

$$\text{I} \ C(s) + O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -393.5 \text{ kJ}$$

$$\text{II} \ CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -283.0 \text{ kJ}$$

[I – II] gives

$$\text{III} \ C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g),$$

$$[\Delta H = -393.5 + 283.0 \text{ kJ}] \quad \Delta H = -110.5 \text{ kJ}$$

The equation III also represents formation of one mole of CO and thus, enthalpy change is the heat of formation of CO(g).

59 The enthalpy change for a reaction does not depend upon the **[AIEEE 2003]**

(a) physical state of reactants and products
(b) use of different reactants for the same product
(c) nature of intermediate reaction steps
(d) difference in initial or final temperatures of involved substances

Ans. ***(c)***

Enthalpy change is state function and depends only on initial and final condition do not depend on path or nature of its intermediates.

60 If at 298 K, the bond energies of C—H, C—C, C$=$C and H—H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction,

$$H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3C{—}CH_3(g) \text{ at 298 K will be}$$

[AIEEE 2003]

(a) + 250 kJ (b) – 250 kJ
(c) + 125 kJ (d) – 125 kJ

Ans. ***(d)***

$$CH_2{=}CH_2 + H_2 \longrightarrow CH_3{—}CH_3$$

$$\Delta H = (BE)_{\text{reactants}} - (BE)_{\text{products}}$$

$$= 4(BE)_{C—H} + (BE)_{C=C} + (BE)_{H—H} - [6(BE)_{C—H} + (BE)_{C—H}]$$

$$= -125 \text{ kJ}$$

TOPIC 3

Entropy, Free Energy Change and Spontaneity

61 For the reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$, when $\Delta S = -176.0 \ JK^{-1}$ and $\Delta H = -57.8$ kJ mol^{-1}, the magnitude of ΔG at 298 K for the reaction is .... kJ mol^{-1}. (Nearest integer) **[2021, 1 Sep Shift-II]**

Ans. ***(5)***

Given, $\Delta H = -57.8 \text{ kJ mol}^{-1}$

$\Delta S = -176 \text{ JK}^{-1} \text{mol}^{-1}$

$T = 298$ K

Using Gibb's free energy relation

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

where, ΔG = change in Gibb's free energy

ΔH = change in enthalpy

T = temperature

ΔS = change in entropy

$$\Delta G = 57.8 \text{ kJ/mol} - [298 \text{ K} \times (-176 \text{ JK}^{-1}\text{mol}^{-1})]$$

$$= 57.8 \text{ kJ/mol} - \left(298 \times \frac{-176}{1000} \text{ kJ}\right) \quad [\because 1 \text{ kJ} = 1000 \text{ J}]$$

$$= -5.352 \text{ kJ/mol}$$

$$|\Delta G| = 5.352$$

Hence, answer is 5.

62 The incorrect expression among the following is **[2021, 31 Aug Shift-II]**

(a) $\dfrac{\Delta G_{\text{System}}}{\Delta S_{\text{Total}}} = -T$ (at constant p)

(b) $\ln k = \dfrac{\Delta H° - T\Delta S°}{RT}$

(c) $k = e^{-\frac{\Delta G°}{RT}}$

(d) For isothermal process, $W_{\text{reversible}} = -nRT \ln \dfrac{V_f}{V_i}$

Ans. ***(b)***

All the expression of thermodynamics are correct except

$$\ln k = \frac{\Delta H° - T\Delta S°}{RT}$$

As we know,

$$\Delta G = \Delta H - T\Delta S° \quad \text{...(i)}$$

Also $\quad \Delta G = -RT \ln K \quad$ ...(ii)

∴ From (i) and (ii)

$$-RT \ln K = \Delta H - T\Delta S°$$

$$\therefore \quad \ln K = \frac{-\Delta H}{RT} + \frac{\Delta S°}{R}$$

The corect expression is

$$\ln K = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} = \frac{\Delta H° - T\Delta S°}{RT}$$

63 Data given for the following reaction is as follows.

$$FeO(s) + C_{(\text{graphite})} \longrightarrow Fe(s) + CO(g)$$

Substance	$\Delta \boldsymbol{H}°$ (kJ mol^{-1})	$\Delta \boldsymbol{S}°$ (J mol^{-1} K^{-1})
FeO(s)	−266.3	57.49
$C_{(\text{graphite})}$	0	5.74
Fe(s)	0	27.28
CO(g)	−110.5	197.6

The minimum temperature in K at which the reaction becomes spontaneous is .... (Integer answer) **[2021, 27 Aug Shift-II]**

Ans. ***(964)***

$$FeO(s) + C_{\text{graphite}} \longrightarrow Fe(s) + CO(g)$$

$$\Delta H°_{\text{reaction}} = \Delta H°_{f\,(\text{product})} - \Delta H°_{f\,(\text{reactants})}$$

$$= [\Delta H°_{f\,(\text{Fe})} + \Delta H°_{f\,(\text{CO})}] - [\Delta H°_{f\,(\text{FeO})} - \Delta H°_{f\,(\text{C})}]$$

$$= [0 + (-110.5)] - [-266.3 - 0]$$

$$= 156 \text{ kJ}^{-1} \text{ mol}^{-1}$$

$$\Delta S°_{\text{reaction}} = \Delta S°_{\text{product}} - \Delta S°_{\text{reactant}}$$

$$= [\Delta S°_{(\text{Fe})} + \Delta S°_{(\text{CO})}] - [\Delta S°_{(\text{FeO})} - \Delta S°_{(\text{C})}]$$

$$= [27.28 + 197.6] - [57.49 + 5.79]$$

$$= 161 \text{ J K}^{-1} \text{ mol}^{-1}$$

According to Gibb's equation,

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

The reaction becomes spontaneous when $\Delta G°$ is atleast zero or negative.

$$0 = \Delta H° - T\Delta S°$$

$$T\Delta S° = \Delta H°$$

$$\Rightarrow \quad T = \frac{\Delta H°}{\Delta S°} = \frac{156 \text{ kJ mol}^{-1}}{161 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$= \frac{156000 \text{ mol}^{-1}}{161 \text{ J K}^{-1} \text{ mol}^{-1}} = 964 \text{ K}$$

The temperature at which reaction becomes spontaneous is 964 K.

64 For a given chemical reaction, $A \longrightarrow B$ at 300 K the free energy change is -49.4 kJ mol^{-1} and the enthalpy of reaction is 51.4 kJ mol^{-1}. The entropy change of the reaction is ...... JK^{-1}mol^{-1}. **[2021, 20 July Shift-II]**

Ans. ***(360)***

For the reaction, $A \xrightarrow{300\text{K}} B$

Gibb's free energy change

Given, $\Delta G = -49.4$ kJ/mol

Change in enthalpy

$\Delta H_{\text{reaction}} = 51.4$ kJ/mol

Change in entropy $\Delta S_{\text{reaction}} = ?$

According to Gibbs free energy,

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

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

$$= \frac{51.4 - (-49.4)}{300} \times 1000 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{\text{reaction}} = 336 \text{ J/mol K}$$

65 During which of the following processes, does entropy decrease?

A. Freezing of water to ice at 0°C.

B. Freezing of water to ice at −10°C.

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

D. Adsorption of CO(g) and lead surface.

E Dissolution of NaCl in water.

[2021, 17 March Shift-II]

(a) A, B, C and D (b) B and C

(c) A and E (d) A, C and E

Ans. ***(a)***

Entropy will decrease in A,B,C and D processes.

A, B → Freezing of water will decrease entropy as particles will move closer and forces of attraction will increase. This leads to a decrease in randomness. So, entropy decreases.

(A) Water $\xrightarrow{0°\text{C}}$ ice; $\Delta S = -\text{ve}$

(B) Water $\xrightarrow{-10°\text{C}}$ ice; $\Delta S = -\text{ve}$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta S = -\text{ve}$

Number of moles are decreasing

$$n = 2 - (3 + 1)$$

$$n = -2$$

So, entropy decreases.

(D) Adsorption; $\Delta S = -\text{ve}$

Adsorption will lead to a decrease in the randomness of gaseous particles.

So, entropy decreases.

(E) $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$; $\Delta S > 0$

The number of species on product side is more than the number of species on reactant side. So, entropy increases on dissolution of NaCl in water.

66 For a dimerisation reaction

$$2A(g) \longrightarrow A_2(g),$$

at 298 K, $\Delta U^{\ominus} = -20$ kJ mol^{-1}, $\Delta S^{\ominus} = -30$ JK^{-1} mol^{-1}, then the $\Delta G^{\ominus}$ will be .... J. **[2020, 5 Sep Shift-II]**

Ans. ***(13537.57)***

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

$$\Delta H = -20 \times 1000 - 1 \times 8.314 \text{ J/mol.K} \times 298 \text{ K}$$

$$= -22477.572 \text{ J}$$

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

$$\Delta G = -22477.572 + 298 \times 30$$

$$\Delta G = -13537.57 \text{ Joule}$$

67 For the reaction; $A(l) \longrightarrow 2B(g)$

$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K.

Hence, ΔG in kcal is .... **[2020, 8 Jan Shift-I]**

Ans. ***(2.70)***

Given: $\quad \Delta U = 2.1$ kcal

$$\Delta S = 20 \text{ cal K}^{-1} = \frac{20}{1000} \text{ kcal K}^{-1}$$

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

$$\therefore \quad \Delta n_g = 2 \text{ mol}$$

$$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$= \frac{2}{1000} \text{ kcal K}^{-1} \text{ mol}^{-1}$$

As we know,

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

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

$$\therefore \quad \Delta G = \Delta U + \Delta n_g RT - T\Delta S$$

$$\therefore\ \Delta G = 2.1 + \frac{2\times 2\times 300}{1000} - \frac{300\times 20}{1000}$$
$$= 2.1 + 1.2 - 6 = -2.70$$

68 The true statement amongst the following is **[2020, 9 Jan Shift-II]**

(a) S is not a function of temperature but ΔS is a function of temperature.
(b) Both ΔS and S are functions of temperature.
(c) Both S and ΔS are not functions of temperature.
(d) S is a function of temperature but ΔS is not a function of temperature.

Ans. ***(b)***

Statement (b) is a true statement whereas all other statements are incorrect.

By definition,

$$dS = \frac{dQ}{T} \quad\text{and}\quad \Delta S = \frac{\int dQ}{T}$$

$\therefore$ ΔS is a function of temperature :
S is also a function of temperature.

69 A process will be spontaneous at all temperature if **[2019, 10 April Shift-I]**

(a) $\Delta H > 0$ and $\Delta S < 0$
(b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$
(d) $\Delta H > 0$ and $\Delta S > 0$

Ans. ***(b)***

A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. $\Delta G < 0$.

Spontaneity of a process is decided by the value of ΔG, which can be predicted from the Gibb's equation, $\Delta G = \Delta H - T\Delta S$ for positive/negative signs of ΔH and ΔS at any/higher/lower temperature as:

ΔH	ΔS	**Comment on temperature** (T)	ΔG	**Comment on the process**
<0	>0	at any temp.	<0	spontaneous
>0	<0	at any temp.	>0	non-spontaneous
<0	<0	at lower temp.	<0	spontaneous
>0	>0	at higher temp.	<0	spontaneous

70 The incorrect match in the following is **[2019, 12 April Shift-II]**

(a) $\Delta G^\circ < 0, K > 1$ (b) $\Delta G^\circ = 0, K = 1$
(c) $\Delta G^\circ > 0, K < 1$ (d) $\Delta G^\circ < 0, K < 1$

Ans. ***(d)***

The incorrect match is $\Delta G^\circ < 0, K < 1$.

For an ideal gas $\Delta G^\circ = -RT\ln K$.

$$\therefore\quad \ln K = -\frac{\Delta G^\circ}{RT} \text{ and } K = e^{-\Delta G^\circ/RT}$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $\Delta G^\circ < 0$, $-\Delta G^\circ/RT = +\text{ve}$ and $e^{-\Delta G^\circ/RT} > 1$ and hence, $K > 1$. It means that the reaction occur spontaneously in the forward direction or products predominate over reactants.

(ii) If $\Delta G^\circ > 0$; $-\Delta G^\circ/RT = -\text{ve}$ and $e^{-\Delta G^\circ/RT} < 1$ and hence, $K < 1$. It means that the reaction is non-spontaneous in forward direction (i.e. product side) but spontaneous in reverse direction (i.e. reactants predominate over products or the reaction occurs rarely).

(iii) When $K = 1$, then $\Delta G^\circ = 0$. This situation generally occur at equilibrium.

71 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is (Specific heat of water liquid and water vapour are 4.2 $\text{kJK}^{-1}\text{kg}^{-1}$ and 2.0 $\text{kJK}^{-1}\text{kg}^{-1}$; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJkg^{-1} respectively).
($\log 273 = 2.436, \log 373 = 2.572, \log 383 = 2.583$)

(a) 9.26 $\text{kJ kg}^{-1}\text{K}^{-1}$ (b) 8.49 $\text{kJ kg}^{-1}\text{K}^{-1}$
(c) 7.90 $\text{kJ kg}^{-1}\text{K}^{-1}$ (d) 2.64 $\text{kJ kg}^{-1}\text{K}^{-1}$

[2019, 9 Jan Shift-II]

Ans. ***(a)***

The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:

$$\begin{tikzcd}
\underset{273\text{K}}{H_2O(s)} \arrow[r, "\Delta S_1"] & \underset{273\text{K}}{H_2O(l)} \arrow[r, "\Delta S_2"] & \underset{373\text{K}}{H_2O(l)} \arrow[d, "\Delta S_3"] \\
 & \underset{383\text{K}}{H_2O(g)} & \underset{373\text{K}}{H_2O(g)} \arrow[l, "\Delta S_4"']
\end{tikzcd}$$

$$\Delta S_1 = \frac{\Delta H_{\text{Fusion}}}{\Delta T_{\text{Fusion}}} = \frac{334\ \text{kJ kg}^{-1}}{273\ \text{K}}$$
$$= 1.22\ \text{kJ kg}^{-1}\ \text{K}^{-1}$$
$$\Delta S_2 = C\ln\frac{T_2}{T_1} = 4.2\ \text{kJ K}^{-1}\text{kg}^{-1}\ln\left(\frac{373\ \text{K}}{273\ \text{K}}\right)$$
$$= 4.2 \times 2.303\,(\log 373 - \log 273)\ \text{kJ K}^{-1}\text{kg}^{-1}$$
$$= 4.2 \times 2.303\,(2.572 - 2.436)$$
$$= 1.31\ \text{kJ K}^{-1}\text{kg}^{-1}$$
$$\Delta S_3 = \frac{\Delta H_{\text{vap.}}}{\Delta T_{\text{vap.}}} = \frac{2491\ \text{kJ kg}^{-1}}{373\ \text{K}}$$
$$= 6.67\ \text{kJ kg}^{-1}\text{K}^{-1}$$
$$\Delta S_4 = C\ln\frac{T_2}{T_1} = 2\ \text{kJ K}^{-1}\text{kg}^{-1}\ln\left(\frac{383\ \text{K}}{373\ \text{K}}\right)$$
$$= 2 \times 2.303\,(\log 383 - \log 373)\ \text{kJ K}^{-1}\ \text{kg}^{-1}$$
$$= 2 \times 2.303\,(2.583 - 2.572)\ \text{kJ K}^{-1}\ \text{kg}^{-1}$$
$$= 0.05\ \text{kJ K}^{-1}\ \text{kg}^{-1}$$
$$\Delta S_{\text{Total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$
$$= 1.22 + 1.31 + 6.67 + 0.05$$
$$= 9.26\ \text{kJ kg}^{-1}\ \text{K}^{-1}$$

72 A process has $\Delta H = 200\ \text{J mol}^{-1}$ and $\Delta S = 40\ \text{JK}^{-1}\ \text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous

(a) 20 K (b) 4 K (c) 5 K (d) 12 K

[2019, 10 Jan Shift-II]

Ans. ***(c)***

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

The process will be spontaneous, when
$\Delta G = -\text{ve}$, i.e. $|T\Delta S| > |\Delta H|$

Given : $\Delta H = 200\ \text{J mol}^{-1}$
and $\Delta S = 40\ \text{JK}^{-1}\ \text{mol}^{-1}$

$$\Rightarrow\quad T > \frac{|\Delta H|}{|\Delta S|} = \frac{200}{40} = 5\ \text{K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

73 The process with negative entropy change is

(a) synthesis of ammonia from N_2 and H_2
(b) dissociation of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$
(c) dissolution of iodine in water
(d) sublimation of dry ice

[2019, 10 Jan Shift-II]

Ans. ***(a)***

The explanation of all the options are as follows :

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$,
$$\Delta n_g = 2 - (1+3) = -2$$
So, ΔS is also negative (entropy decreases)

(b) $CaSO_4(s) \xrightarrow{\Delta} CaO(s) + SO_3(g)$,
$$\Delta n_g = (1+0) - 0 = +1$$
So, $\Delta S = +\text{ve}$

(c) In dissolution, $\Delta S = +\text{ve}$ because molecules/ions of the solid solute (here, iodine) become free to move in solvated/dissolved state of the solution,

$$I_2(s) \xrightarrow[\text{(KI)}]{\text{Water}} I_2(aq)$$

(d) In sublimation process, molecules of solid becomes quite free when they become gas,

$$\underset{\text{Dry ice}}{CO_2(s)} \longrightarrow CO_2(g)$$

So, ΔS will be positive.

74 For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is **[2019, 11 Jan Shift-I]**

(a) Y if $T = 280$ K
(b) X if $T = 350$ K
(c) X if $T = 315$ K
(d) Y if $T = 300$ K

Ans. ***(c)***

For a given value of T,

(i) If $\Delta_r G^\circ$ becomes < 0, the forward direction will be spontaneous and then the major and minor components will be Y and X respectively.

(ii) If $\Delta_r G^\circ$ becomes > 0, the forward direction will be non-spontaneous and then the major and minor components will be X and Y respectively.

(a) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 280 = 15$

i.e. $\Delta_r G^\circ > 0$0, major component $= X$;

(b) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 350 = -11.25$

i.e. $\Delta_r G^\circ < 0$, major component $= Y$

(c) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 315 = 1.875$

i.e. $\Delta_r G^\circ > 0$, major component $= X$

(d) $\Delta_r G^\circ = 120 - \frac{3}{8} \times 300 = 7.5$

i.e. $\Delta_r G^\circ > 0$, major component $= X$

75 Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is **[2019, 11 Jan Shift-I]**

(a) $^2C_p \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$

(b) $^2C_p \ln\left[\frac{T_1+T_2}{4T_1T_2}\right]$

(c) $C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$

(d) $^2C_p \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$

Ans. ***(c)***

At the thermal equilibrium,

$$\text{final temperature } T_f = \frac{T_1+T_2}{2}$$

$\Rightarrow$ for the 1st block, $\Delta S_{\text{I}} = C_p \ln \frac{T_f}{T_1}$

$\Rightarrow$ for the 2nd block, $\Delta S_{\text{II}} = C_p \ln \frac{T_f}{T_2}$

When brought in contact with each other,

$$\Delta S = \Delta S_{\text{I}} + \Delta S_{\text{II}} = C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2}$$

$$= C_p \ln\left(\frac{T_f}{T_1} \times \frac{T_f}{T_2}\right) = C_p \ln\left[\frac{T_f^2}{T_1T_2}\right]$$

$$= C_p \ln\left[\frac{\left(\frac{T_1+T_2}{2}\right)^2}{T_1T_2}\right] = C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$$

76 The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1}\text{mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is **[2019, 11 Jan Shift-II]**

(a) 2040.5 K
(b) 1890.0 K
(c) 2380.5 K
(d) 2480.3 K

Ans. ***(d)***

According to Gibbs-Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

For a reaction to be feasible (spontaneous)

$$\Delta_r G^\circ < 0$$

$$\Delta_r H^\circ - T\Delta_r S^\circ < 0$$

Given, $\Delta_r H^\circ = +\ 491.1 \text{ kJ mol}^{-1}$,

$\Delta_r S^\circ = 198 \text{ JK}^{-1}\text{mol}^{-1}$

$\therefore \quad 491.1 \times 10^3 - T \times 198 < 0$

$$T > \frac{491.1 \times 10^3}{198} = 2480.3 \text{ K}$$

$\therefore$ Above 2480.3 K reaction will become spontaneous.

77 The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $\Delta_r G^\circ = A - BT$

Where A and B are non-zero constants.

Which of the following is true about this reaction? **[2019, 11 Jan Shift-II]**

(a) Endothermic if, $A < 0$ and $B > 0$
(b) Exothermic if, $B < 0$
(c) Exothermic if, $A > 0$ and $B < 0$
(d) Endothermic if, $A > 0$

Ans. ***(d)***

According to Gibb's Helmholtz equation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

Given, $\quad \Delta_r G^\circ = A - BT$

On comparing above two equations, we get,

$$A = \Delta H^\circ \text{ and } \Delta S^\circ = B$$

We know that, if ΔH° is negative, reaction is exothermic and when it is positive, reaction is endothermic.

$\therefore$ If $A > 0$, i.e. positive, reaction is endothermic.

78 The following reaction is performed at 298K

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

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

(a) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(b) $86600 + R(298)\ln(1.6 \times 10^{12})$
(c) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
(d) $0.5[2 \times 86600 - R(298)\ln(1.6 \times 10^{12})]$

Ans. ***(d)***

For the given reaction,

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

Given, $\Delta G_f^\circ \text{(NO)} = 86.6 \text{ kJ / mol}$

$\Delta G_f^\circ (NO_2) = ? \quad K_p = 1.6 \times 10^{12}$

Now, we have,

$$\Delta G_f^\circ = 2\Delta G^\circ_{f(NO_2)} - [2\Delta G^\circ_{f(NO)} + \Delta G^\circ_{f(O_2)}]$$

$$= -RT\ln K_p = 2\Delta G^\circ_{f(NO_2)} - [2 \times 86{,}600 + 0]$$

$$\Delta G^\circ_{f(NO_2)} = \frac{1}{2}[2 \times 86{,}600 - R \times 298\ln(1.6 \times 10^{12})]$$

$$\Delta G^\circ_{f(NO_2)} = 0.5[2 \times 86{,}600 - R \times (298)\ln(1.6 \times 10^{12})]$$

89 The incorrect expression among the following is **[AIEEE 2012]**

(a) $\dfrac{\Delta G_{\text{system}}}{\Delta G_{\text{total}}} = -T$

(b) In isothermal process,
$W_{\text{reversible}} = -nRT \ln \dfrac{V_f}{V_i}$

(c) $\ln K = \dfrac{\Delta H° - T\Delta S°}{RT}$

(d) $K = e^{-\Delta G°/RT}$

Ans. ***(c)***

According to Gibbs Helmholtz equation,

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

(a) For a system, total entropy change $= \Delta S_{\text{total}}$

$$\Delta H_{\text{total}} = 0$$

$$\therefore \quad \Delta G_{\text{system}} = -T\Delta S_{\text{total}}$$

$$\therefore \quad \frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$$

Thus, (a) is correct.

(b) For isothermal reversible process, $\Delta E = 0$

By first law of thermodynamics, $\Delta E = q + W$

$$\therefore \quad W_{\text{reversible}} = -q = -\int_{V_i}^{V_f} p\,dV$$

$$\Rightarrow \quad W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$$

Thus, (b) is correct.

(c) $\Delta G° = \Delta H° - T\Delta S°$ ...(i)

Also, $\Delta G° = -RT \ln K$

$$\ln K = \frac{-\Delta G°}{RT}$$

$$\ln K = \frac{(\Delta H° - T\Delta S°)}{RT} \quad \text{[from Eq. (i)]}$$

Thus, (c) is incorrect.

(d) The standard free energy $(\Delta G°)$ is related to equilibrium constant K as

$$\Delta G° = -RT \ln K$$

$$\therefore \ln K = -\frac{\Delta G°}{RT} \Rightarrow K = e^{-\Delta G°/RT}$$

Thus, (d) is also correct.

80 The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of $10\,\text{dm}^3$ to a volume of $100\,\text{dm}^3$ at 27° C is **[AIEEE 2011]**

(a) $38.3\ \text{J mol}^{-1}\ \text{K}^{-1}$ (b) $35.8\ \text{J mol}^{-1}\ \text{K}^{-1}$
(c) $32.3\ \text{J mol}^{-1}\ \text{K}^{-1}$ (d) $42.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

Ans. ***(a)***

Entropy change for n moles of isothermal expansion of an ideal gas from volume V_1 to volume V_2 is

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

Here, $n = 2, V_2 = 100\ \text{dm}^3, V_1 = 10\ \text{dm}^3$

$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$

$$= 38.296\ \text{J mol}^{-1}\text{K}^{-1}$$

81 For a particular reversible reaction, at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when **[AIEEE 2010]**

(a) $T_e > T$ (b) $T > T_e$
(c) T_e is 5 times T (d) $T = T_e$

Ans. ***(b)***

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

Here, ΔG = Gibb's free energy
ΔH = Enthalpy change
ΔS = Entropy change
T = Temperature

As equilibrium, $\Delta G = 0$. Thus, $T\Delta S = \Delta H$, as ΔH and ΔS are +ve, for a reaction to be feasible (spontaneous), ΔG should be –ve. This can be possible only when

$$T\Delta S > T_e \Delta H \quad i.e., T\Delta S > T_e \Delta S$$

or $\quad T > T_e$

$[T_e$ = temperature at equilibrium$]$

82 In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are –166.2, –237.2 and –394.4 kJ mol^{-1}, respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be **[AIEEE 2009]**

(a) 80% (b) 87%
(c) 90% (d) 97%

Ans. ***(d)***

Percentage efficiency of the fuel cell

$$= \frac{\Delta G}{\Delta H} \times 100$$

The concerned reaction is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta G_r = [\Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, l)]$$
$$[-\Delta G_f(CH_3OH, l) - \frac{3}{2}\Delta G_f(O_2, g)]$$

$$= -394.4 + 2(-237.2) - (-166.2) - 0$$
$$= -394.4 - 474.4 + 166.2$$
$$= -702.6\ \text{kJ mol}^{-1}$$

Percentage efficiency

$$= \frac{702.6}{726} \times 100 = 96.78\% \approx 97\%$$

83 Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction, $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be **[AIEEE 2008]**

(a) 1250 K (b) 500 K
(c) 750 K (d) 1000 K

Ans. ***(c)***

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$$

$$\Delta S_{\text{reaction}} = S_{\text{products}} - S_{\text{reactants}}$$

$$\Delta S_{\text{reaction}} = 50 - \left(\frac{3}{2} \times 40 + \frac{1}{2} \times 60\right)$$

$$= -40\ \text{J mol}^{-1}$$

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

At equilibrium as $\Delta G = 0$

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

$$\Rightarrow \quad T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{40} = 750\ \text{K}$$

84 Identify the correct statement regarding a spontaneous process. **[AIEEE 2007]**

(a) For a spontaneous process in an isolated system, the change in entropy is positive
(b) Endothermic processes are never spontaneous
(c) Exothermic processes are always spontaneous
(d) Lowering of energy in the reaction process is the only criteria for spontaneity

Ans. ***(a)***

In an isolated system where either mass and energy are not exchanged with surrounding for that spontaneous process, the change in entropy is positive.

85 In conversion of limestone to lime,

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

the values of $\Delta H°$ and $\Delta S°$ are $+179.1\ \text{kJ mol}^{-1}$ and $160.2\ \text{J/K}$, respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **[AIEEE 2007]**

(a) 1008 K (b) 1200 K
(c) 845 K (d) 1118 K

Ans. ***(d)***

The entropy change can be given as

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

$$\Delta S = 160.2 \text{ J/K}$$

$$\Delta H = 179.1 \times 10^3 \text{ J/mol}$$

$$T = \frac{179.1 \times 10^3 \text{ J/mol}}{160.2 \text{ J/K}}$$

$$= 1117.97 \text{ K} \approx 1118 \text{ K}$$

86 For a spontaneous reaction, the ΔG, equilibrium constant (K) and E°_{cell} will be respectively **[AIEEE 2005]**

(a) $-$ ve, >1, $-$ ve
(b) $-$ ve, <1, $-$ ve
(c) $+$ ve, >1, $-$ ve
(d) $-$ ve, >1, $+$ ve

Ans. ***(d)***

The standard free energy related to equilibrium constant K as

$$\Delta G^\circ = -2.303\, RT \log K_{\text{eq}};$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

If a cell reaction is spontaneous (proceeding in forward side), it means

$$K_{\text{eq}} > 1$$

and $\qquad E^\circ_{\text{cell}} = +\text{ ve}$

Thus, $\qquad \Delta G^\circ = -\text{ve}$

87 In an irreverible 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 **[AIEEE 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) $(dS)_{V,E} = 0, (dG)_{T,p} > 0$

Ans. ***(b)***

An irreversible process
$\Rightarrow$ spontaneous process
$\Rightarrow (dS)_{V,E}$ (change in entropy) $= +\text{ve} > 0$
$\Rightarrow (dG)_{T,p}$ (change in Gibbs free energy) $-\text{ve} < 0$

88 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[AIEEE 2003]**

(a) $\Delta G = RT \ln K_c$ (b) $-\Delta G = RT \ln K_c$
(c) $\Delta G^\circ = RT \ln K_c$ (d) $-\Delta G^\circ = RT \ln K_c$

Ans. ***(d)***

Relationship between free energy and equilibrium constant,

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

89 A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then **[AIEEE 2002]**

	ΔH	ΔS
(a)	+ ve	+ ve
(b)	– ve	– ve
(c)	– ve	+ ve
(d)	+ ve	– ve

Ans. ***(a)***

For spontaneity, $\Delta G = -$ ve

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

ΔH, for endothermic process + ve
At lower temperature, ΔS + ve
Hence, $\qquad \Delta G = +$ ve
But at high temperature, $T\Delta S$ will be greater than ΔH.
Hence, $\Delta G = -$ve, spontaneous.