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Chemical Thermodynamics

TOPIC 1

Generalised Terms and First Law of Thermodynamics

01 Which one among the following is the correct option for right relationship between C_p and C_V for one mole of ideal gas? **[NEET 2021]**

(a) $C_p + C_V = R$
(b) $C_p - C_V = R$
(c) $C_p = RC_V$
(d) $C_V = RC_p$

Ans. ***(b)***

For an ideal gas,

$$C_p - C_V = nR$$

(where, n = number of moles of gas, C_p, C_V = specific heat at constant pressure and volume, R = universal gas constant)

As $n = 1$, so $C_p - C_V = R$

02 The correct option for free expansion of an ideal gas under the adiabatic condition is **[NEET (Sept.) 2020]**

(a) $q = 0$, $\Delta T < 0$ and $w > 0$
(b) $q < 0$, $\Delta T < 0$ and $w = 0$
(c) $q > 0$, $\Delta T < 0$ and $w > 0$
(d) $q = 0$, $\Delta T = 0$ and $w = 0$

Ans. ***(d)***

For adiabatic process, $q = 0$

For adiabatic free expansion of an ideal gas, no work will be done, because, $dV = 0$.

$\therefore \quad w = pdV = 0$

For adiabatic free expansion of an ideal gas, no change in internal energy.

So, $dU = 0$ and $dT = 0 \quad [\because dU = nC_V\, dT]$

So, option (d) is correct.

03 Under isothermal condition, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is
(Given that 1 L bar = 100 J) **[NEET (National) 2019]**

(a) 5 kJ (b) 25 J (c) 30 J (d) −30 J

Ans. ***(d)***

Key Idea *For an isothermal irreversible expansion,* $W_{\text{irrev}} = -p_{\text{ext}}(V_2 - V_1)$

Given, $V_1 = 0.1\,\text{L}$, $V_2 = 0.25\,\text{L}$, $p_{\text{ext}} = 2\,\text{bar}$

We know that,

$$W_{\text{irrev}} = -p_{\text{ext}}(V_2 - V_1)$$

On substituting the given values in the above equation, we get

$$\begin{aligned} W_{\text{irrev}} &= -2\,\text{bar}\,(0.25 - 0.1)\,\text{L} \\ &= -2 \times 0.15\,\text{L bar} = -0.3\,\text{L bar} \\ &= -0.3 \times 100\,\text{J} \qquad [\because 1\,\text{L bar} = 100\,\text{J}] \\ &= -30\,\text{J} \end{aligned}$$

04 An ideal gas expands isothermally from $10^{-3}\,\text{m}^3$ to $10^{-2}\,\text{m}^3$ at 300 K against a constant pressure of $10^5\,\text{Nm}^{-2}$. The work done on the gas is **[NEET (Odisha) 2019]**

(a) + 270 kJ
(b) − 900 J
(c) + 900 kJ
(d) − 900 kJ

Ans. ***(b)***

For an isothermal irreversible expansion,

Work done $(W) = -p_{\text{ext}}(V_2 - V_1)$

where, V_1 = initial volume

V_2 = final volume

Given, $p_{\text{ext}} = 10^5\,\text{Nm}^{-2}$,

$V_1 = 10^{-3}\text{m}^3$, $V_2 = 10^{-2}\,\text{m}^3$

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

$$\begin{aligned} W &= -10^5\,\text{Nm}^{-2}(10^{-2}\text{m}^3 - 10^{-3}\text{m}^3) \\ &= -10^5\,\text{Nm}^{-2} \times 10^{-3}\,(10 - 1)\,\text{m}^3 \\ &= -900\,\text{Nm} = -900\,\text{J} \end{aligned}$$

05 A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be **[NEET 2017]**

(a) 1136.25 J
(b) − 500 J
(c) − 505 J
(d) + 505 J

Ans. ***(c)***

Key concept *According to first law of thermodynamics,*

$$\Delta U = q + w$$

where, ΔU = internal energy

q = heat absorbed or evolved, w = work done.

Also, work done against constant external pressure (irreversible process).

$$w = -p_{\text{ext}}\,\Delta V.$$

Work done in irreversible process,

$$\begin{aligned} w &= -p_{\text{ext}}\,\Delta V = -p_{\text{ext}}\,(V_2 - V_1) \\ &= -2.5\,\text{atm}\,(4.5\,\text{L} - 2.5\,\text{L}) \\ &= -5\,\text{L atm} = -5 \times 101.3\,\text{J} \\ &= -505\,\text{J} \end{aligned}$$

Since, the system is well insulated, $q = 0$

$\therefore \quad \Delta U = w = -505\,\text{J}$

Hence, change in internal energy, ΔU of the gas is − 505 J.

06 Which one of the following is correct option for free expansion of an ideal gas under adiabatic condition? **[CBSE AIPMT 2011]**

(a) $q \neq 0, \Delta T = 0, W = 0$
(b) $q = 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T < 0, W \neq 0$
(d) $q = 0, \Delta T \neq 0, W = 0$

Ans. *(b)*

In adiabatic process, heat exchange is constant, so $q = 0$ and for free expanion, $W = 0, \therefore \Delta T = 0$.

07 Which of the following are not state functions? **[CBSE AIPMT 2008]**

I. $q + W$ II. q
III. W IV. $H - TS$

(a) I and IV
(b) II, III and IV
(c) I, II and III
(d) II and III

Ans. *(d)*

The thermodynamic parameters which depend only upon the initial and final states of system, are called **state functions**, such as enthalpy $(H = q + W)$, Gibbs free energy $(G = H - TS)$, etc. While those parameters which depend on the path by which the process is performed rather than on the initial and final states, are called **path functions**, such as work done, heat, etc.

08 The work done during the expansion of a gas from a volume of $4\,\text{dm}^3$ to $6\,\text{dm}^3$ against a constant external pressure of 3 atm, is **[CBSE AIPMT 2004]**

(a) -6 J (b) -608 J
(c) $+304$ J (d) -304 J

Ans. *(b)*

Work done $(W) = -p_{\text{ext}}(V_2 - V_1)$

$$= -3 \times (6 - 4) = -6\,\text{L atm}$$
$$= -6 \times 101.32\ \text{J} \quad (\because 1\,\text{L atm} = 101.32\ \text{J})$$
$$= -607.92 \approx -608\ \text{J}$$

09 The molar heat capacity C of water at constant pressure is $75\ \text{JK}^{-1}\ \text{mol}^{-1}$, when 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is **[CBSE AIPMT 2003]**

(a) 4.8 K (b) 6.6 K
(c) 1.2 K (d) 2.4 K

Ans. *(d)*

According to heat capacity rule,

$$q = mc\Delta T, \quad c = \frac{q}{m(T_2 - T_1)}$$

Given that, $c = 75\ \text{JK}^{-1}\ \text{mol}^{-1}$

$$q = 1.0\ \text{kJ} = 1000\ \text{J}$$

Mass = 100 g water

Molar mass of water = 18 g

$$75 = \frac{1000}{5.55 \times \Delta T}$$

$$\left(\text{Number of moles} = \frac{100}{18} = 5.55\right)$$

$$\therefore \quad \Delta T = \frac{1000}{5.55 \times 75} = 2.4\ \text{K}$$

10 In a closed insulated container a liquid is stirred with a paddle to increase the temperature, which of the following is true? **[CBSE AIPMT 2002]**

(a) $\Delta E = W \neq 0, q = 0$
(b) $\Delta E = W = 0, q \neq 0$
(c) $\Delta E = 0, W = q \neq 0$
(d) $W = 0, \Delta E = q \neq 0$

Ans. *(a)*

In closed insulated container a liquid is stirred with a paddle to increase the temperature, therefore it behaves as adiabatic process, so for it $q = 0$.

Hence, from first law of thermodynamics

$$\Delta E = q + W$$

if, $q = 0$

$\therefore$ $\Delta E = W$ but not equal to zero.

11 When 1 mole gas is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then, which statement is correct? **[CBSE AIPMT 2001]**

(a) $q = W = 500\ \text{J}, \ \Delta E = 0$
(b) $q = \Delta E = 500\ \text{J}, \ W = 0$
(c) $q = -W = 500\ \text{J}, \Delta E = 0$
(d) $\Delta E = 0, q = W = -500\ \text{J}$

Ans. *(b)*

We know that, $\Delta H = \Delta E + p\Delta V$

When, $\Delta V = 0$

$\therefore$ $\Delta H = \Delta E$

From first law of thermodynamics

$$\Delta E = q - W$$

In given problem $\Delta H = 500$ J

$$-W = -p\Delta V, \Delta V = 0$$

So, $\Delta E = q = 500$ J

12 In an endothermic reaction, the value of ΔH is **[CBSE AIPMT 1999]**

(a) zero (b) positive
(c) negative (d) constant

Ans. *(b)*

For endothermic reactions standard heat of reaction (ΔH) is positive because in these reactions total energy of reactants is lower than that of products, i.e. $E_R < E_P$

So, $\Delta H = E_P - E_R = +\text{ve}$

13 One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is $(R = 2\,\text{cal mol}^{-1}\text{K}^{-1})$ **[CBSE AIPMT 1998]**

(a) 163.7 cal (b) zero
(c) 1381.1 cal (d) 9 L atm

Ans. *(b)*

Isothermal process means temperature remains constant. At constant temperature, internal energy (ΔE) also remains constant. So, $\Delta E = 0$

14 During isothermal expansion of an ideal gas, its **[CBSE AIPMT 1991, 94]**

(a) internal energy increases
(b) enthalpy decreases
(c) enthalpy remains unaffected
(d) enthalpy reduces to zero

Ans. *(c)*

We know that,

$$H = E + W$$

Enthalpy = internal energy + pressure × volume

$$H = E + pV$$
$$\Delta H = \Delta E + \Delta(pV)$$
$$\Delta H = \Delta E + \Delta(n_g RT) \ (\because pV = nRT)$$

For isothermal expansion of ideal gas, $\Delta T = 0$

$$\therefore \quad \Delta H = \Delta E$$

TOPIC 2

Reactions Related to Enthalpies and Hess's Law

15 At standard conditions, if the change in the enthalpy for the following reaction is $-109\ \text{kJ mol}^{-1}$.

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that, bond energy of H_2 and Br_2 is $435\ \text{kJ mol}^{-1}$ and $192\ \text{kJ mol}^{-1}$ respectively, what is the bond energy (in kJ mol^{-1}) of HBr? **[NEET (Oct.) 2020]**

(a) 368 (b) 736 (c) 518 (d) 259

Ans. *(a)*

$$\underset{[H-H]}{H_2(g)} + \underset{[Br-Br]}{Br_2(g)} \longrightarrow \underset{[H-Br]}{2HBr(g)}$$

$$\Rightarrow \quad \Delta_r H = (\Sigma BE)_{Reactants} - (\Sigma BE)_{Products}$$

$$[\because BE = \text{bond energy}]$$

$$\Rightarrow -109 = [(BE)_{H_2} + (BE)_{Br_2}] - (BE)_{HBr} \times 2$$

$$= (435 + 192) - (BE)_{HBr} \times 2$$

$$\Rightarrow \quad (BE)_{HBr} = 368 \text{ kJ mol}^{-1}$$

16 The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is -200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[NEET 2018]**

(a) 800 kJ mol^{-1} (b) 100 kJ mol^{-1}

(c) 200 kJ mol^{-1} (d) 400 kJ mol^{-1}

Ans. *(a)*

Key Concept *Relation between heat of reaction* $(\Delta_r H)$ *and bond energies* (BE) *of reactants and products is given by*

$$\Delta_r H = \Sigma BE_{Reactants} - \Sigma BE_{Products}$$

The reaction of formation for XY is

$$\frac{1}{2}X_2(g) + \frac{1}{2}Y_2(g) \longrightarrow XY(g);$$

$$\Delta H = -200 \text{ kJ mol}^{-1}$$

Given, the bond dissociation energies of X_2, Y_2 and XY are in the ratio 1 : 0.5 : 1. Let the bond dissociation energies of X_2, Y_2 and XY are a kJ mol^{-1}, 0.5a kJ mol^{-1} and a kJ mol^{-1}, respectively.

$$\therefore \quad \Delta_r H = \Sigma BE_{Reactants} - \Sigma BE_{Products}$$

$$= \left[\frac{1}{2} \times a + \frac{1}{2} \times 0.5a\right] - [1 \times a]$$

$$-200 = \frac{a}{2} + \frac{a}{4} - a$$

$$-200 = \frac{2a + a - 4a}{4} = \frac{-a}{4}$$

$$a = 800 \text{ kJ mol}^{-1}$$

∴ The bond dissociation energy of

$$X_2 = a \text{ kJ mol}^{-1} = 800 \text{ kJ mol}^{-1}$$

17 Consider the following liquid-vapour equilibrium **[NEET 2016, Phase I]**

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

Which of the following relations is correct?

(a) $\dfrac{d\ln P}{dT} = \dfrac{-\Delta H_v}{RT}$

(b) $\dfrac{d\ln P}{dT^2} = \dfrac{-\Delta H_v}{T^2}$

(c) $\dfrac{d\ln P}{dT} = \dfrac{-\Delta H_v}{RT^2}$

(d) $\dfrac{d\ln G}{dT^2} = \dfrac{-\Delta H_v}{RT^2}$

Ans. *(c)*

The given phase equilibria is

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

This equilibrium states that, when liquid is heated, it converts into vapour but on cooling, it further converts into liquid, which is derived by Clausius Clapeyron and the relationship is written as,

$$\frac{d\ln p}{dT} = -\frac{\Delta H_v}{RT^2}$$

where, ΔH_v = Heat of vaporisation

18 The heat of combustion of carbon to CO_2 is -393.5kJ / mol. The heat released upon the formation of 35.2 g of CO_2 from carbon and oxygen gas is **[CBSE AIPMT 2015]**

(a) -315 kJ (b) $+315$ kJ

(c) -630 kJ (d) -3.15 kJ

Ans. *(a)*

Given, $C(s) + O_2(g) \longrightarrow CO_2(g)$;

$$\Delta_f H = -393.5 \text{ kJ mol}^{-1}$$

∵ Heat released on formation of 44 g or 1 mole

$$CO_2 = -395.5 \text{kJ mol}$$

∵ Heat released on formation of 35.2 g of CO_2

$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{g}} \times 35.2 \text{ g}$$

$$= -315 \text{ kJ mol}^{-1}$$

19 A reaction having equal energies of activation for forward and reverse reactions has **[NEET 2013]**

(a) $\Delta S = 0$

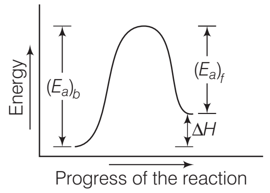
(b) $\Delta G = 0$

(c) $\Delta H = 0$

(d) $\Delta H = \Delta G = \Delta S = 0$

Ans. *(c)*

Energy profile diagram for a reaction is as



From the figure, it is clear that

$$(E_a)_b = (E_a)_f + \Delta H$$

[Here $(E_a)_b$ = activation energy of backward reaction and $(E_a)_f$ = activation energy of forward reaction].

If $\quad (E_a)_b = (E_a)_f$

then $\quad \Delta H = 0$

20 Standard enthalpy of vaporisation $\Delta_{vap} H^\circ$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is (assume water vapour to behave like an ideal gas). **[CBSE AIPMT 2012]**

(a) $+37.56$ (b) -43.76

(c) $+43.76$ (d) $+40.66$

Ans. *(a)*

$$H_2O(l) \xrightarrow{100° C} H_2O(g)$$

$$\Delta_{vap} H^\circ = \Delta_{vap} E^\circ + \Delta n_g RT$$

$$\Delta_{vap} H^\circ = \text{enthalpy of vaporisation}$$

$$= 40.66 \text{ kJ mol}^{-1}$$

For the above reaction,

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

$$R = 8.314$$

$$T = 100° C = 273 + 100 = 373 \text{ K}$$

$$\therefore 40.66 \text{ kJ mol}^{-1} = \Delta_{vap} E^\circ + 1 \times 8.314 \times 10^{-3} \times 373$$

$$\Delta_{vap} E^\circ = 40.66 \text{ kJ mol}^{-1} - 3.1 \text{ kJ mol}^{-1}$$

$$= +37.56 \text{ kJ mol}^{-1}$$

21 Enthalpy change for the reaction,

$$4H(g) \longrightarrow 2H_2(g) \text{ is } -869.6 \text{ kJ}$$

The dissociation energy of H—H bond is **[CBSE AIPMT 2011]**

(a) -869.6 kJ (b) $+434.8$ kJ

(c) $+217.4$ kJ (d) -434.8 kJ

Ans. *(b)*

$$4H(g) \longrightarrow 2H_2(g), \Delta H = -869.6 \text{ kJ}$$

$$2H_2(g) \longrightarrow 4H(g), \Delta H = 869.6 \text{ kJ}$$

$$H_2(g) \longrightarrow 2H(g),$$

Dissociation energy of H—H bond

$$= \frac{869.6}{2} = 434.8 \text{ kJ}$$

22 From the following bond energies

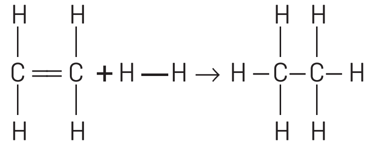
H—H bond energy : 431.37 kJ mol^{-1}

C═C bond energy : 606.10 kJ mol^{-1}

C—C bond energy : 336.49 kJ mol^{-1}

C—H bond energy : 410.50 kJ mol^{-1}

Enthalpy for the reaction,



$$H_2C{=}CH_2 + H{-}H \rightarrow H_3C{-}CH_3$$

will be **[CBSE AIPMT 2009]**

(a) 1523.6 kJ mol^{-1}

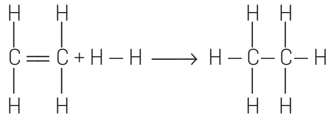
(b) -243.6 kJ mol^{-1}

(c) -120.0 kJ mol^{-1}

(d) 553.0 kJ mol^{-1}

Ans. *(c)*

For reaction,



$$CH_2{=}CH_2 + H-H \longrightarrow H-CH_2-CH_2-H$$

$\Delta H_{\text{reaction}}$

$$= \sum BE_{(\text{reactant})} - \sum BE_{(\text{product})}, \quad [BE = \text{bond energy}]$$

$$\Delta H_r = [4 \times BE_{(C-H)} + 1 \times BE_{(C==C)} + 1 \times BE_{(H-H)}] - [6 \times BE_{(C-H)} + 1 \times BE_{(C-C)}]$$

$$= (4 \times 410.50 + 1 \times 606.10 + 1 \times 431.37) - [(6 \times 410.50) + (1 \times 336.49)] \text{ kJmol}^{-1}$$

$$= [1642 + 606.1 + 431.37] - [2463 + 336.49] \text{ kJmol}^{-1}$$

$$= [2679.47] - [2799.49] \text{ kJmol}^{-1}$$

$$= -120.0 \text{ kJ mol}^{-1}$$

23 Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is **[CBSE AIPMT 2008]**

(a) 93 kJ mol^{-1} (b) –245 kJ mol^{-1}
(c) –93 kJ mol^{-1} (d) 245 kJ mol^{-1}

Ans. *(c)*

Given, $\Delta H_{H—H} = 434$ kJ / mol

$\Delta H_{Cl—Cl} = 242$ kJ / mol

$\Delta H_{H—Cl} = 431$ kJ / mol

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl, \Delta H_r = ?$$

$$\Delta H_r = \frac{1}{2} \times \Delta H_{H—H} + \frac{1}{2} \times \Delta H_{Cl—Cl} - \Delta H_{H—Cl}$$

$$= \frac{1}{2} \times 434 + \frac{1}{2} \times 242 - 431$$

$$= 217 + 121 - 431 = -93 \text{ kJ/mol}$$

24 Given that bond energies of H—H and Cl—Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is –90 kJ mol^{-1}. Bond enthalpy of HCl is **[CBSE AIPMT 2007]**

(a) 290 kJ mol^{-1}
(b) 380 kJ mol^{-1}
(c) 425 kJ mol^{-1}
(d) 245 kJ mol^{-1}

Ans. *(b)*

$$\Delta H_{\text{reaction}} = \Delta_{H-H} + \Delta H_{Cl-Cl} - 2\Delta H_{HCl}$$

or $$\Delta H_{H-Cl} = \frac{430 + 240 - (-90)}{2}$$

$$= \frac{760}{2} = 380 \text{ kJ mol}^{-1}$$

25 Consider the following reactions,

(i) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l), -x_1 \text{kJ mol}^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), x_2 \text{ kJ mol}^{-1}$

(iii) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(l) - x_3 \text{ kJ mol}^{-1}$

(iv) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l), + x_4 \text{ kJ mol}^{-1}$

Enthalpy of formation of $H_2O(l)$ is **[CBSE AIPMT 2007]**

(a) $-x_2$ kJ mol^{-1} (b) $+x_3$ kJ mol^{-1}
(c) $-x_4$ kJ mol^{-1} (d) $+x_1$ kJ mol^{-1}

Ans. *(a)*

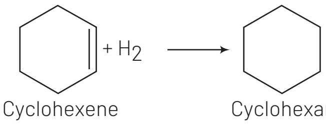
Enthalpy of formation The amount of heat evolved or absorbed during the formation of 1 mole of a compound from its constituent elements is known as **heat of formation**. So, the correct answer is

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta H = -x_2 \text{ kJ mol}^{-1}$$

26 The enthalpy of combustion of H_2, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ per mol respectively. Heat of hydrogenation of cyclohexene is **[CBSE AIPMT 2006]**

(a) –121 kJ per mol (b) + 121 kJ per mol
(c) + 242 kJ per mol (d) –242 kJ per mol

Ans. *(a)*



ΔH = [ΔH of combustion of cyclohexane – (ΔH of combustion of cyclohexene + ΔH of combustion of H_2)]

$$= -[-3920 - (-3800 - 241)] \text{ kJ}$$

$$= -[-3920 + 4041] \text{ kJ}$$

$$= -[121] \text{ kJ} = -121 \text{ kJ}$$

27 Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$? **[CBSE AIPMT 2006]**

(a) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(b) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$
(c) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$
(d) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

Ans. *(a)*

As we know that,

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

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

where, $\Delta n_g \rightarrow$ number of gaseous moles of product – number of gaseous moles of reactant

If $\Delta ng = 0$ (for reactions in which the total number of moles of gaseous products are equal to total number of moles of gaseous reactants), therefore $\Delta H = \Delta E$

So, for reaction (a) $\Delta n = 2 - 2 = 0$

Hence, for reaction (a), $\Delta H = \Delta E$

28 The absolute enthalpy of neutralisation of the reaction **[CBSE AIPMT 2005]**

$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$ will be

(a) less than – 57.33 kJ mol^{-1}
(b) – 57.33 kJ mol^{-1}
(c) greater than –57.33 kJ mol^{-1}
(d) 57.33 kJ mol^{-1}

Ans. *(a)*

Heat of neutralisation of strong acid and strong base is – 57.33 kJ. MgO is weak base while HCl is strong acid, so the heat of neutralisation of MgO and HCl is lower than –57.33 kJ because MgO requires some heat for ionisation, therefore the net released amount of heat is decreased.

29 If the bond energies of H – H, Br – Br and H – Br are 433, 192 and 364 kJ mol^{-1} respectively, then $\Delta H°$ for the reaction $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ is **[CBSE AIPMT 2004]**

(a) –261 kJ (b) +103 kJ
(c) +261 kJ (d) –103 kJ

Ans. *(d)*

For reaction,

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g) \; \Delta H° = ?$$

$\Delta H° = -$[(2 × bond energy of HBr) – (bond energy of H_2 + bond energy of Cl_2)]

$$\Delta H° = -[2 \times (364) - (433 + 192)] \text{ kJ}$$

$$= -[728 - (625)] \text{ kJ} = -103 \text{ kJ}$$

30 For the reaction,

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

at constant temperature, $\Delta H - \Delta E$ is **[CBSE AIPMT 2003]**

(a) $+3RT$ (b) $-RT$
(c) $+RT$ (d) $-3RT$

Ans. *(d)*

For the reaction,

$$C_3H_8(g)+5O_2(g)\longrightarrow 3CO_2(g)+4H_2O(l)$$

Δn_g = number of gaseous moles of products – number of gaseous moles of reactants $=3-6=-3$

$\therefore \quad \Delta H=\Delta E+\Delta nRT$

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

$\therefore \quad \Delta H-\Delta E=-3RT$

31 For which one of the following equations ΔH°_r equal to ΔH°_f for the product? **[CBSE AIPMT 2003]**

(a) $Xe(g)+2F_2(g)\longrightarrow XeF_4(g)$

(b) $2CO(g)+O_2(g)\longrightarrow 2CO_2(g)$

(c) $N_2(g)+O_3(g)\longrightarrow N_2O_3(g)$

(d) $CH_4(g)+2Cl_2(g)\longrightarrow CH_2Cl_2(l)+2HCl(g)$

Ans. *(a)*

When one mole of a substance is directly formed from its constituent elements, then the enthalpy change is called **heat of formation**.

For the reaction,

$$Xe(g)+2F_2(g)\longrightarrow \underset{1\text{mol}}{XeF_4(g)}$$

$$\Delta H^\circ_{\text{react}}=\Delta H^\circ_f$$

32 Heat of combustion ΔH° for $C(s)$, $H_2(g)$ and $CH_4(g)$ are –94, –68 and –213 kcal/mol. Then, ΔH° for $C(s)+2H_2(g)\longrightarrow CH_4(g)$ is **[CBSE AIPMT 2002]**

(a) – 17 kcal/mol (b) – 111 kcal/mol

(c) – 170 kcal/mol (d) – 85 kcal/mol

Ans. *(a)*

For reaction,

$C(s)+2H_2(g)\longrightarrow CH_4(g),\ \Delta H^\circ=?$

$C+O_2\longrightarrow CO_2,\ \Delta H=-94\,\text{kcal} \quad \ldots\text{(i)}$

$2H_2+O_2\longrightarrow 2H_2O,$

$\Delta H=-68\times 2\,\text{kcal} \quad \ldots\text{(ii)}$

$CH_4+2O_2\longrightarrow CO_2+2H_2O,$

$\Delta H=-213\,\text{kcal} \quad \ldots\text{(iii)}$

On adding Eqs. (i) and (ii) and then subtracting Eq. (iii)

$=(-94)+(-2\times 68)-(-213)$

$=-230+213=-17\text{ k cal / mol}$

33 Enthalpy of the reaction,

$$CH_4+\frac{1}{2}O_2\longrightarrow CH_3OH, \text{ is}$$

negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct? **[CBSE AIPMT 2001]**

(a) $x>y$ (b) $x<y$ (c) $x=y$ (d) $x\geq y$

Ans. *(b)*

$$CH_4(g)+\frac{1}{2}O_2(g)\rightarrow CH_3OH(l)$$

$\therefore \quad \Delta H=-[(\Delta H_c \text{ of } CH_3OH)-(\Delta H_c \text{ of } CH_4)]$

$=-[(-y)-(-x)]=-[-y+x]=y-x$

$\therefore \quad x<y$

34 Change in enthalpy for reaction,

$$2H_2O_2(l)\longrightarrow 2H_2O(l)+O_2(g)$$

if heat of formation of $H_2O_2(l)$ and $H_2O(l)$ are –188 and –286 kJ/mol respectively is **[CBSE AIPMT 2001]**

(a) – 196 kJ/mol (b) + 196 kJ/mol

(c) + 948 kJ/mol (d) – 948 kJ/mol

Ans. *(a)*

$2H_2O_2(l)\longrightarrow 2H_2O(l)+O_2(g)\ \Delta H=?$

$\Delta H=[(2\times\Delta H_f \text{ of } H_2O(l))+(\Delta H_f \text{ of } O_2(g)]$

$-(2\times\Delta H_f \text{ of } H_2O_2(l))]$

$=[(2\times -286)+(0)-(2\times -188)]$

$=[-572+376]=-196\text{ kJ / mol}$

35 If ΔE is the heat of reaction for

$C_2H_5OH(l)+3O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l)$ at constant volume, the ΔH (heat of reaction at constant pressure), then the correct relation is **[CBSE AIPMT 2000]**

(a) $\Delta H=\Delta E+RT$

(b) $\Delta H=\Delta E-RT$

(c) $\Delta H=\Delta E-2RT$

(d) $\Delta H=\Delta E+2RT$

Ans. *(b)*

We know that, $\Delta H=\Delta E+\Delta n_gRT$

where, Δn_g = total number of moles of gaseous product – total number of moles of gaseous reactant

$=2-3=-1$

So, $\quad \Delta H=\Delta E-RT$

36 From the given reactions,

$$S(s)+\frac{3}{2}O_2(g)\longrightarrow SO_3(g)+2x\text{ kcal}$$

$$SO_2(g)+\frac{1}{2}O_2(g)\rightarrow SO_3(g)+y\text{ kcal,t}$$

he heat of formation of SO_2 is **[CBSE AIPMT 1999]**

(a) $(x+y)$ (b) $(x-y)$

(c) $(2x+y)$ (d) $(2x-y)$

Ans. *(d)*

$$S(s)+\frac{3}{2}O_2(g)\longrightarrow SO_3(g)+2x\,\text{kcal} \quad \ldots\text{(i)}$$

By inverting second equation we get,

$$SO_3(g)\longrightarrow SO_2(g)+\frac{1}{2}O_2(g)-y\,\text{kcal} \quad \ldots\text{(ii)}$$

On addition Eqs. (i) and (ii)

$$S(s)+O_2(g)\longrightarrow SO_2(g)+(2x-y)\text{ kcal}$$

Hence, heat of formation of SO_2 is $(2x-y)$ kcal.

37 Given that,

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

$$2CO(g)+O_2(g)\longrightarrow 2CO_2(g), \quad \Delta H^\circ=-y\text{ kJ}$$

The enthalpy of formation of carbon monoxide will be **[CBSE AIPMT 1997]**

(a) $y-2x$ (b) $2x-y$ (c) $\dfrac{y-2x}{2}$ (d) $\dfrac{2x-y}{2}$

Ans. *(c)*

$C+O_2\longrightarrow CO_2, \quad \Delta H^\circ=-x\text{ kJ} \quad \ldots\text{(i)}$

On reversing given second equation we get,

$2CO_2\longrightarrow 2CO+O_2, \quad \Delta H^\circ=+y\text{ kJ}$

or $\quad CO_2\longrightarrow CO+1/2O_2,$

$\Delta H^\circ=+y/2\text{ kJ} \quad \ldots\text{(ii)}$

From Eqs. (i) and (ii) (by addition)

$$C+\frac{1}{2}O_2\longrightarrow CO,$$

$$\Delta H^\circ=\frac{y}{2}-x=\frac{y-2x}{2}\text{ kJ}$$

38 If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1 atm pressure are 52, –394 and –286 kJ/mol, the enthalpy of combustion of ethene is equal to **[CBSE AIPMT 1995]**

(a) –141.2 kJ/mol (b) –1412 kJ/mol

(c) +14.2 kJ/mol (d) +1412 kJ/mol

Ans. *(b)*

Combustion of hydrocarbon,

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

$\Delta_rH=\Sigma\Delta_fH_p-\Sigma\Delta_fH_r$

$=\{2\times\Delta_fH(CO_2)+2\times\Delta_fH(H_2O)\}$

$-\{\Delta_fH(C_2H_4)+3\Delta_fH(O_2)\}$

$=(2\times -394+2\times -286)-(52+3\times 0)$

$=-788-572-52=-1412\text{ kJ mol}^{-1}$

39 For the reaction, **[CBSE AIPMT 1991]**

$$N_2+3H_2\rightleftharpoons 2NH_3,\ \Delta H=?$$

(a) $\Delta E+2RT$ (b) $\Delta E-2RT$

(c) $\Delta H=RT$ (d) $\Delta E-RT$

Ans. *(b)*

According to enthalpy equation

$$\underset{\substack{\text{Enthalpy}\\\text{change}}}{\Delta H}=\underset{\substack{\text{Internal}\\\text{energy}}}{\Delta E}+\Delta n_gRT$$

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

$$\left[\Delta n = \underset{\text{Product mole}}{n_P} - \underset{\text{Reactant mole}}{n_R}\right]$$

$$= 2 - 4 = -2$$

$$\therefore \quad \Delta H = \Delta E + (-2)RT$$

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

40 Equal volumes of molar hydrochloric acid and sulphuric acid are neutralised by dilute NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true? **[CBSE AIPMT 1991]**

(a) $x = y$

(b) $x = \frac{1}{2}y$

(c) $x = 2y$

(d) None of the above

Ans. ***(b)***

$$HCl + NaOH \longrightarrow NaCl + H_2O + x \text{ kcal}$$

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + y \text{ kcal}$$

1 molar HCl = 1 g - equivalent of HCl

1 molar H_2SO_4 = 2 g - equivalent of H_2SO_4

so, $\quad y = 2x \Rightarrow x = \frac{1}{2}y$

41 If ΔH is the change in enthalpy and ΔE, the change in internal energy accompaning a gaseous reaction, then **[CBSE AIPMT 1990]**

(a) ΔH is always greater than ΔE

(b) $\Delta H < \Delta E$ only if the number of moles of products is greater than the number of moles of the reactants

(c) ΔH is always less than ΔE

(d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants

Ans. ***(d)***

Reactions in which there is a decrease in the number of moles of the gaseous components,
i.e. Δn_g is negative, the enthalpy change (ΔH) is lesser than the internal energy change (ΔE).

Reaction in which there is a increase in the number of moles of gaseous components i.e. Δng is positive, the enthalpy change is greater than the internal energy change.

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

TOPIC 3

Entropy, Free Energy Change and Spontaneity

42 For irreversible expansion of an ideal gas under isothermal condition the correct option is **[NEET 2021]**

(a) $\Delta U = 0$, $\Delta S_{\text{total}} = 0$

(b) $\Delta U \neq 0$, $\Delta S_{\text{total}} \neq 0$

(c) $\Delta U = 0$, $\Delta S_{\text{total}} \neq 0$

(d) $\Delta U \neq 0$, $\Delta S_{\text{total}} = 0$

Ans. ***(c)***

The change in internal energy depends on the temperature. For isothermal process, $\Delta T = 0$.

So, $\quad \Delta U = 0$.

With an expansion of an ideal gas, more space is available for the gaseous particles.

$\therefore$ Entropy of gas increases so, entropy of system is not zero.

i.e. $\quad \Delta S \neq 0$

43 If for a certain reaction $\Delta_r H$ is 30 kJ mol^{-1} at 450 K, the value of $\Delta_r S$ (in JK^{-1} mol^{-1}) for which the same reaction will be spontaneous at the same temperature is **[NEET (Oct.) 2020]**

(a) 70 (b) –33

(c) 33 (d) –70

Ans. ***(a)***

$\Delta G = \Delta H - T\Delta S$ (Gibbs equation)

For a spontaneous reaction,

$\Delta G < 0$, i.e. $T\Delta S > \Delta H$

$$\Rightarrow \quad T > \frac{\Delta H}{\Delta S} = \frac{30 \times 1000 \text{ J mol}^{-1}}{\Delta S}$$

[Given, $T = 450$ K]

$$\Rightarrow \Delta S > \frac{30 \times 1000 \text{ J mol}^{-1}}{450 \text{ K}}$$

$$= 66.67 \text{ J mol}^{-1}\text{K}^{-1}$$

When $\Delta S > 66.67$ J mol^{-1}K^{-1}, the reaction will be spontaneous.

So, from the options,
$\Delta_r S = 70$ J mol^{-1}K^{-1} indicates spontaneity of the reaction.

44 Hydrolysis of sucrose is given by the following reaction.

$$\text{Sucrose} + H_2O \rightleftharpoons \text{Glucose} + \text{Fructose}$$

If the equilibrium constant (K_C) is 2×10^{13} at 300 K, the value of $\Delta_r G^\ominus$ at the same temperature will be **[NEET (Sept.) 2020]**

(a) $8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$

(b) $8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln(3 \times 10^{13})$

(c) $-8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln(4 \times 10^{13})$

(d) $-8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$

Ans. ***(d)***

$$\text{Sucrose} + H_2O \rightleftharpoons \text{Glucose} + \text{Fructose}$$

For this equilibrium,

$\Delta_r G^\ominus = -RT \ln K_C$

Given, $K_C = 2 \times 10^{13}$ and $T = 300$ K

$\Rightarrow \Delta_r G^\ominus = -(8.314 \text{ J mol}^{-1}\text{K}^{-1}) \times (300 \text{ K}) \times \ln(2 \times 10^{13})$

45 For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, the correct option is **[NEET (Sep.) 2020]**

(a) $\Delta_r H > 0$ and $\Delta_r S < 0$

(b) $\Delta_r H < 0$ and $\Delta_r S > 0$

(c) $\Delta_r H < 0$ and $\Delta_r S < 0$

(d) $\Delta_r H > 0$ and $\Delta_r S > 0$

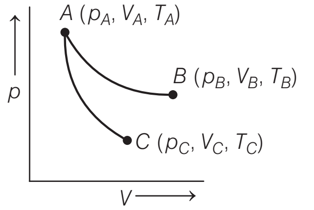
Ans. ***(c)***

In this reaction, combination of two Cl atoms takes place to give more stable Cl_2 molecule. So, the reaction is exothermic, i.e. $\Delta_r H < 0$.

Here, $\Delta n_g = 1 - 2 = -1$

So, entropy change of the reaction will be, $\Delta_r S < 0$.

46 Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure. **[NEET (Odisha) 2019]**



$AB \rightarrow$ Isothermal expansion

$AC \rightarrow$ Adiabatic expansion

Which of the following option is not correct?

(a) $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$
(b) $T_A = T_B$
(c) $W_{\text{isothermal}} > W_{\text{adiabatic}}$
(d) $T_c > T_A$

Ans. *(d)*

From first law of thermodynamics,

$$\Delta U = q + W$$

In adiabatic expansion, $q = 0$

$$\therefore \quad \Delta U = W$$

During expansion of a gas w is negative i.e $w < 0$ or $\Delta U < 0$.

We know that, $\Delta U = nC_V \Delta T$

$\therefore \quad nC_V \Delta T < 0$

or $\quad \Delta T < 0$

$\therefore \quad T_C - T_A < 0$

or $\quad T_C < T_A$

Thus, option (d) is incorrect while the remaining options are correct.

47 For an ideal solution, the correct option is **[NEET (National) 2019]**

(a) $\Delta_{\text{mix}} V \neq 0$ at constant T and p
(b) $\Delta_{\text{mix}} H = 0$ at constant T and p
(c) $\Delta_{\text{mix}} G = 0$ at constant T and p
(d) $\Delta_{\text{mix}} S = 0$ at constant T and p

Ans. *(b)*

Ideal solutions are those which obey Raoult's law over all concentration ranges at a given temperature, e.g. benzene-toluene, *n*-hexane-*n*-heptane, etc.

For an ideal solution,

$$\Delta V_{\text{mix}} = 0, \Delta H_{\text{mix}} = 0,$$
$$\Delta G_{\text{mix}} < 0, \Delta S_{\text{mix}} > 0.$$

Hence, option (b) is correct.

48 In which case change in entropy is negative? **[NEET (National) 2019]**

(a) Expansion of a gas at constant temperature
(b) Sublimation of solid to gas
(c) $2H(g) \longrightarrow H_2(g)$
(d) Evaporation of water

Ans. *(c)*

The explanation of given statements are :

(a) Entropy is positive in case of expansion of a gas at constant temperature. It is because during expansion of gas volume increases and hence randomness increases.
(b) Entropy is positive in case of sublimation of solid to gas as gas is much disordered than a solid.
(c) Entropy is negative in case of $2H(g) \longrightarrow H_2(g)$ as the number of moles of gaseous reactants are more than that of gaseous products.
(d) Entropy is positive in case of evaporation of water as gas is much disordered than a liquid.

Hence, option (c) is correct.

49 For a given reaction, $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ JK^{-1} mol^{-1}. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature) **[NEET 2017]**

(a) $T < 425$ K
(b) $T > 425$ K
(c) all temperatures
(d) $T > 298$ K

Ans. *(b)*

According to Gibbs-Helmholtz equation,

Gibbs energy $(\Delta G) = \Delta H - T\Delta S$

Where, $\Delta H =$ Enthalpy change
$\Delta S =$ Entropy change
$T =$ Temperature

For a reaction to be spontaneous

$$\Delta G < 0.$$

$\therefore$ Gibbs -Helmholtz equation becomes,

$$\Delta G = \Delta H - T\Delta S < 0$$

or, $\quad \Delta H < T\Delta S$

or, $\quad T > \dfrac{\Delta H}{\Delta S} = \dfrac{35.5 \text{ kJ mol}^{-1}}{83.6 \text{ JK}^{-1}\text{mol}^{-1}}$

$$= \frac{35.5 \times 1000}{83.6} = 425 \text{ K}$$

$$T > 425 \text{ K}$$

50 The correct thermodynamic conditions for the spontaneous reaction at all temperatures is **[NEET 2016, Phase 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,d)*

We have the Gibbs Helmholtz reaction for spontaneity as

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

For reaction to be spontaneous, ΔG must be negative.

For this, ΔH should be negative and ΔS should be positive.

$\therefore \quad \Delta H < 0$

and $\quad \Delta S > 0.$

and also $\Delta S = 0$ shows ΔG a negative quantity.

51 For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by **[NEET 2016, Phase II]**

(a) $\Delta S = nR \ln\left(\dfrac{p_f}{p_i}\right)$
(b) $\Delta S = nR \ln\left(\dfrac{p_i}{p_f}\right)$
(c) $\Delta S = nRT \ln\left(\dfrac{p_f}{p_i}\right)$
(d) $\Delta S = RT \ln\left(\dfrac{p_i}{p_f}\right)$

Ans. *(b)*

Entropy change is given as,

$$\Delta S = nC_p \ln\frac{T_f}{T_i} + nR\ln\frac{p_i}{p_f} \qquad \ldots\text{(i)}$$

For isothermal process, $T_i = T_f$

$$\therefore \quad nC_p \ln\frac{T_f}{T_i} = nC_p \ln\frac{T_i}{T_i} = 0 \quad [\ln 1 = 0]$$

From Eq. (i)

$$\Delta S = nR\ln\frac{p_i}{p_f}$$

52 Which of the following statements is correct for a reversible process in a state of equilibrium? **[CBSE AIPMT 2015]**

(a) $\Delta G = -2.30\, RT \log K$
(b) $\Delta G = 2.30\, RT \log K$
(c) $\Delta G° = -2.30\, RT \log K$
(d) $\Delta G° = 2.30\, RT \log K$

Ans. *(a)*

Mathematical expression of the thermodynamic equilibrium is

$$\Delta G = \Delta G° + 2.303 RT \log Q$$

At equilibrium when $\Delta G = 0$ and $Q = K$

then $\Delta G = \Delta G° + 2.303\, RT \log K = 0$

$$\Delta G° = -2.303\, RT \log K$$

53 Which of the following statements is correct for the spontaneous absorption of a gas? **[CBSE AIPMT 2014]**

(a) ΔS is negative and therefore, ΔH should be highly positive
(b) ΔS is negative and therefore, ΔH should be highly negative
(c) ΔS is positive and therefore, ΔH should be negative
(d) ΔS is positive and therefore, ΔH should also be highly positive

Ans. ***(b)***

ΔS [change in entropy] and ΔH [change in enthalpy] are related by the equation $\Delta G = \Delta H - T\Delta S$

[Here, ΔG = change in Gibbs free energy]

For adsorption of a gas, ΔS is negative because randomness decreases. Thus, in order to make ΔG negative [for spontaneous reaction], ΔH must be highly negative. Hence for the adsorption of a gas, if ΔS is negative, therefore, ΔH should be highly negative.

54 For the reaction,

$$X_2O_4(l) \longrightarrow 2XO_2(g),$$

$\Delta U = 2.1\,\text{kcal}$,

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

Hence, ΔG is **[CBSE AIPMT 2014]**

(a) 2.7 kcal (b) – 2.7 kcal

(c) 9.3 kcal (d) – 9.3 kcal

Ans. ***(b)***

The change in Gibbs free energy is given by

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

where, ΔH = change enthalpy of the reaction

ΔS = change entropy of the reaction

Thus, in order to determine ΔG, the values of ΔH must be known. The value of ΔH can be calculated by using equation

$$\Delta H = \Delta U + \Delta n_g RT \qquad \text{...(i)}$$

where, ΔU = change in internal energy using

Δn_g = number of moles of gaseous products – number of moles of gaseous reactants

$$= 2 - 0 = 2$$

R = gas constant = 2 cal

given, $\Delta U = 2.1\,\text{kcal}$

$$= 2.1 \times 10^3\,\text{cal}$$

$$[\because 1\,\text{kcal} = 10^3\,\text{cal}]$$

By putting the values in eq. (i) we get,

$$\therefore \quad \Delta H = (2.1 \times 10^3) + (2 \times 2 \times 300)$$

$$= 3300\,\text{cal}$$

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

$$\Rightarrow \quad \Delta G = (3300) - (300 \times 20)$$

$$\Delta G = -2700\,\text{cal}$$

$$\therefore \quad \Delta G = -2.7\,\text{kcal}$$

55 In which of the following reactions, standard reaction entropy changes ($\Delta S°$) is positive and standard Gibbs energy change ($\Delta G°$) decreases sharply with increasing temperature? **[CBSE AIPMT 2012]**

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

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

(c) $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$

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

Ans. ***(a)***

Among the given reactions only in the case of

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

entropy increases because randomness (disorder) increases. Thus, standard entropy change ($\Delta S°$) is positive. Moreover, it is a combustion reaction and all the combustion reactions are generally exothermic, i.e. $\Delta H° = -\text{ve}$

We know that,

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

$$\Delta G° = -\text{ve} - T(+\text{ve})$$

Thus, as the temperature increases, the value of $\Delta G°$ decreases.

56 The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is **[CBSE AIPMT 2012]**

(a) 10.52 cal/mol K (b) 21.04 cal/mol K

(c) 5.260 cal/mol K (d) 0.526 cal/mol K

Ans. ***(c)***

Molar entropy change for the melting of ice,

$$\Delta S_{\text{melt}} = \frac{\Delta H_{\text{fusion}}}{T} = \frac{1.435\,\text{kcal / mol}}{(0 + 273)\,\text{K}}$$

$$= 5.26 \times 10^{-3}\,\text{kcal/mol K}$$

$$= 5.26\,\text{cal/mol K}$$

57 If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be **[CBSE AIPMT 2011]**

(a) 1.0 J mol^{-1}K^{-1} (b) 0.1 J mol^{-1}K^{-1}

(c) 100 J mol^{-1}K^{-1} (d) 10 J mol^{-1}K^{-1}

Ans. ***(c)***

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

Given, $\Delta H_{\text{vap.}} = 30\,\text{kJ mol}^{-1}$

$$T = 27 + 273 = 300\,\text{k}$$

$\Delta G° = 0$ at equilibrium,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{30 \times 10^3\,\text{J mol}^{-1}}{300\,\text{K}}$$

$$= 100\,\text{J mol}^{-1}\,\text{K}^{-1}$$

58 The values of ΔH and ΔS for the reaction,

$C_{(\text{graphite})} + CO_2(g) \longrightarrow 2CO(g)$ are 170 kJ and 170 JK^{-1}, respectively. This reaction will be spontaneous at **[CBSE AIPMT 2009]**

(a) 710 K (b) 910 K

(c) 1110 K (d) 510 K

Ans. ***(c)***

Given, $\Delta H = 170\,\text{kJ} = 170 \times 10^3\,\text{J}$

$$\Delta S = 170\,\text{JK}^{-1};\ T = ?$$

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

For spontaneous reaction,

$$\Delta G < 0$$

$$\Rightarrow \quad 0 < 170 \times 10^3 - T \times 170\ ;\ T > 1000$$

$$\therefore \quad T = 1110\,\text{K}$$

59 For the gas phase reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

which of the following conditions are correct? **[CBSE AIPMT 2008]**

(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)***

From enthalpy equation,

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

For the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Δn_g = product mole – reactant mole

$\Delta n = 2 - 1 = 1$

Thus, the value of ΔH is positive or > 0.

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

For a spontaneous reaction, ΔG must be negative. Since in this reaction ΔH is positive, so for the negative value of ΔG, ΔS must be positive or > 0.

Hence, $\Delta H > 0, \Delta S > 0$

60 The enthalpy and entropy change for the reaction,

$$Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$$

are 30 kJ mol^{-1} and 105 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is **[CBSE AIPMT 2006]**

(a) 285.7 K (b) 273 K

(c) 450 K (d) 300 K

Ans. ***(a)***

At equilibrium Gibbs free energy change (ΔG) is equal to zero.

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

$$0 = 30 \times 10^3 \text{ (J mol}^{-1}) - T \times 105 \text{ (J K}^{-1} \text{ mol}^{-1})$$

$$\therefore \quad T = \frac{30 \times 10^3}{105} \text{ K} = 285.71 \text{ K}$$

61 Identify the correct statement for change of Gibbs free energy for a system (ΔG_{system}) at constant temperature and pressure. **[CBSE AIPMT 2006]**

(a) If $\Delta G_{\text{system}} > 0$, the process is spontaneous

(b) If $\Delta G_{\text{system}} = 0$, the system has attained equilibrium

(c) If $\Delta G_{\text{system}} = 0$, the system is still moving in a particular direction

(d) If $\Delta G_{\text{system}} < 0$, the process is not spontaneous

Ans. ***(b)***

If the Gibbs free energy for a system (ΔG_{system}) is equal to zero, then system is present in equilibrium at a constant temperature and pressure.

$$\Delta G = \Delta_r G^\circ + RT \ln K \ ; \ \Delta G = 0$$

$$\Delta_r G^\circ = -RT \ln K$$

K = equilibrium constant

If $\Delta G_{\text{system}} < 0$, then the process is spontaneous

62 Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction? **[CBSE AIPMT 2005]**

(a) Exothermic and decreasing disorder

(b) Endothermic and increasing disorder

(c) Exothermic and increasing disorder

(d) Endothermic and decreasing disorder

Ans. ***(c)***

If reaction is exothermic, therefore ΔH is negative and on increasing disorder, ΔS is positive thus, at these condition, ΔG is negative according to following equation.

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

ΔG = negative, and for spontaneous reaction ΔG must be negative.

63 A reaction occurs spontaneously if **[CBSE AIPMT 2005]**

(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve

(b) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve

(c) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve

(d) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is –ve

Ans. ***(b)***

The spontaneity of a reaction is based upon the negative value of ΔG and ΔG is based upon T, ΔS and ΔH according to following equation (Gibbs-Helmholtz equation)

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

If the magnitude of $\Delta H - T\Delta S$ is negative, then the reaction is spontaneous.

when $T\Delta S > \Delta H$ or we can say that ΔH and ΔS are positive, then ΔG is negative.

64 Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is **[CBSE AIPMT 2004]**

(a) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

(b) $\Delta S_{\text{system}} - \Delta S_{\text{surrounding}} > 0$

(c) $\Delta S_{\text{system}} > 0$

(d) $\Delta S_{\text{surrounding}} > 0$

Ans. ***(a)***

For spontaneous process, ΔS must be positive. In reversible process

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

Hence, system is present in equilibrium. (i.e. it is not spontaneous process)

While in irreversible process

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

Hence, in the process ΔS is positive.

65 Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are –382.64 kJ mol^{-1} and –145.6 JK^{-1}mol^{-1}, respectively. Standard Gibbs energy change for the same reaction at 298 K is **[CBSE AIPMT 2004]**

(a) – 221.1 kJmol^{-1} (b) – 339.3 kJ mol^{-1}

(c) – 439.3 kJ mol^{-1} (d) – 523.2 kJ mol^{-1}

Ans. ***(b)***

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \ldots\text{(i)}$$

Given that, $\Delta H^\circ = -382.64$ kJ mol^{-1}

$$\Delta S^\circ = -145.6 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= -145.6 \times 10^{-3} \text{ kJ K}^{-1}$$
$$T = 298 \text{ K}$$

On putting the given values in eq. (i) we get,

$$\text{or} \quad \Delta G^\circ = -382.64 - [298 \times (-145.6 \times 10^{-3})]$$
$$= -339.3 \text{ kJ mol}^{-1}$$

66 What is the entropy change (in J K^{-1} mol^{-1}) when one mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C) **[CBSE AIPMT 2003]**

(a) 2.198 JK^{-1}mol^{-1} (b) 21.98 JK^{-1}mol^{-1}

(c) 20.13 JK^{-1}mol^{-1} (d) 2.013 JK^{-1}mol^{-1}

Ans. ***(b)***

Given, $\Delta H_f = 6.0$ kJ mol^{-1}

$$T = 0 + 273 = 273 \text{ K}$$

$$\Delta S = \frac{\Delta H_f}{T} = \frac{6.0}{273} = 0.02198 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$(T = 0^\circ \text{C} + 273 = 273 \text{ K})$$

$$= 0.02198 \times 1000 \text{ JK}^{-1} \text{ mol}^{-1}$$
$$= 21.98 \text{ JK}^{-1} \text{ mol}^{-1}$$

67 The densities of graphite and diamond at 298 K are 2.25 and 3.31 g cm^{-3}, respectively. If the standard free energy difference (ΔG°) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is **[CBSE AIPMT 2003]**

(a) 9.92×10^6 pa

(b) 9.92×10^5 pa

(c) 9.92×10^8 pa

(d) 9.92×10^7 Pa

Ans. ***(c)***

$$\text{Volume of graphite} = \frac{\text{Mass}}{\text{Density}} = \frac{12}{2.25}$$

$$\text{Volume of diamond} = \frac{12}{3.31}$$

Change in volume,

$$\Delta V = \left(\frac{12}{3.31} - \frac{12}{2.25}\right) \times 10^{-3} \text{ L}$$
$$= -1.91 \times 10^{-3} \text{ L}$$

$$\Delta G^\circ = \text{work done} = -p\Delta V$$

$$p = -\frac{\Delta G^\circ}{\Delta V}$$
$$= \frac{1895 \text{ J mol}^{-1}}{1.91 \times 10^{-3} \times 101.3}$$
$$= 9794 \text{ atm}$$
$$[\because 1 \text{ atm} = 10^5 \times 1.013 \text{ Pa}]$$
$$= 9.92 \times 10^8 \text{ Pa}$$

68 2 moles of an ideal gas at 27°C temperature is expanded reversibly from 2 L to 20 L. Find entropy change (R = 2 cal/mol K). **[CBSE AIPMT 2002]**

(a) 92.1 (b) 0 (c) 4 (d) 9.2

Ans. ***(d)***

$$\Delta S \text{ (entropy change)} = 2.303\, nR \log_{10} \frac{V_2}{V_1}$$
$$= 2.303 \times 2 \times 2 \times \log_{10} \frac{20}{2}$$
$$= 2.303 \times 2 \times 2 \times 1 = 9.212 \text{ cal}$$

69 Unit of entropy is **[CBSE AIPMT 2002]**

(a) $JK^{-1}\,mol^{-1}$
(b) $J\,mol^{-1}$
(c) $J^{-1}\,K^{-1}\,mol^{-1}$
(d) $JK\,mol^{-1}$

Ans. ***(a)***

Entropy change equal to change in heat per degree. $\Delta S = \frac{q}{T}$

q = required heat per mol
T = constant absolute temperature

Thus, unit of entropy is $JK^{-1}mol^{-1}$

70 $PbO_2 \rightarrow PbO, \Delta G_{298} < 0$

$SnO_2 \rightarrow SnO, \Delta G_{298} > 0$

Most probable oxidation state of Pb and Sn will be **[CBSE AIPMT 2001]**

(a) Pb^{4+}, Sn^{4+}
(b) Pb^{4+}, Sn^{2+}
(c) Pb^{2+}, Sn^{2+}
(d) Pb^{2+}, Sn^{4+}

Ans. ***(d)***

$\overset{+4}{Pb}O_2 \rightarrow \overset{+2}{Pb}O, \ \Delta G_{298} < 0$

For this reaction ΔG is negative, hence Pb^{2+} is more stable than Pb^{4+}.

$\overset{+4}{Sn}O_2 \rightarrow \overset{+2}{Sn}O, \qquad \Delta G_{298} > 0$

For this reaction ΔG is positive, hence Sn^{4+} is more stable than Sn^{2+} because for spontaneous change ΔG must be negative.

71 The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as

$$S_2(s) + 2O_2(g) \longrightarrow 2SO_2(g), \quad \Delta G = -544 \text{ kJ}$$

$$2Zn(s) + S_2(s) \longrightarrow 2ZnS(s), \quad \Delta G = -293 \text{ kJ}$$

$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s), \quad \Delta G = -480 \text{ kJ}$$

The ΔG for the reaction,

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

will be **[CBSE AIPMT 2000]**

(a) –357 kJ
(b) –731 kJ
(c) –773 kJ
(d) –229 kJ

Ans. ***(b)***

ΔG of formation of different substances are as

$2\,SO_2 = -544$ kJ
$2\,ZnS = -293$ kJ
$2ZnO = -480$ kJ

For the reaction,

$$2ZnS + 3\,O_2(g) \longrightarrow 2ZnO(s) + 2\,SO_2(g)$$

$$\Delta G = [(\Delta G_{(\text{products})} - \Delta G_{(\text{reactants})}]$$
$$= [(-480) + (-544) - (-293)]$$
$$= -1024 + 293$$
$$= -731 \text{ kJ}$$

72 The entropy change in the fusion of one mole of a solid melting at 27°C (latent heat of fusion is 2930 J mol^{-1}) is **[CBSE AIPMT 2000]**

(a) 9.77 J $K^{-1}\,mol^{-1}$
(b) 10.73 J $K^{-1}\,mol^{-1}$
(c) 2930 J $K^{-1}\,mol^{-1}$
(d) 108.5 J $K^{-1}\,mol^{-1}$

Ans. ***(a)***

$$\text{Entropy, } \Delta S_f = \frac{\Delta H_f}{T_f}$$
$$= \frac{\text{Fusion enthalpy}}{\text{Temperature}}$$
$$\Delta S_f = \frac{2930 \text{ J mol}^{-1}}{300 \text{ K}}$$
$$= 9.77 \text{ J K}^{-1} \text{ mol}^{-1}$$

73 Identify the correct statement regarding entropy. **[CBSE AIPMT 1998]**

(a) At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero
(b) At absolute zero temperature, the entropy of a perfectly crystalline substance is positive
(c) At absolute zero temperature, the entropy of all crystalline substances is to be zero
(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero

Ans. ***(a)***

"At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero." It is called **third law of thermodynamics**.

74 Given the following entropy values (in $JK^{-1}\,mol^{-1}$) at 298 K and 1 atm : $H_2(g)$: 130.6, $Cl_2(g)$: 223.0, $HCl(g)$: 186.7. The entropy change (in $JK^{-1}\,mol^{-1}$) for the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$, is **[CBSE AIPMT 1996]**

(a) +540.3
(b) +727.0
(c) –166.9
(d) +19.8

Ans. ***(d)***

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
$$\Delta_r S = \Sigma S_m{}^\circ(P) - \Sigma S_m{}^\circ(R)$$
$$\Delta_r S^\circ = 2 \times S_m{}^\circ(HCl) - [S_m{}^\circ(Cl_2) + S_m{}^\circ(H_2)]$$
$$= (2 \times 186.7) - (223 + 130.6)$$
$$= 373.4 - 353.6$$
$$= +19.8 \text{ JK}^{-1} \text{ mol}^{-1}$$

75 According to the third law of thermodynamics which one of the following quantities for a perfectly crystalline solid is zero at absolute zero? **[CBSE AIPMT 1996]**

(a) Free energy
(b) Entropy
(c) Enthalpy
(d) Internal energy

Ans. ***(b)***

Entropy is the degree of randomness or disorder of the system. When the temperature of the system is zero kelvin, then all the motion of molecules ceases. According to third law of thermodynamics "At absolute zero the entropy of a perfectly crystalline substance is taken as zero."

76 The correct relationship between free energy and equilibrium constant K of a reaction is **[CBSE AIPMT 1996]**

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

Ans. ***(a)***

The Gibbs free energy of a reaction, $\Delta_r G$ is related to the composition of the reaction mixture and the standard reaction Gibbs free energy $\Delta_r G^\circ$ as

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where, Q = reaction quotient

At equilibrium $Q = K$ and $\Delta_r G = 0$.
Therefore, the above reaction becomes

$$0 = \Delta_r G° + RT \ln K$$

$$\Delta_r G° = - RT \ln K$$

or $$\Delta_r G° = - 2.303\, RT \log K$$

K = equilibrium constant

77 Standard Gibb's free energy change for the isomerisation reaction $cis\text{-2-pentene} \rightleftharpoons trans\text{-2-pentene}$ is –3.67 kJ/mol at 400 K. If more *trans*-2-pentene is added to the reaction vessel, then **[CBSE AIPMT 1995]**

(a) more *cis*-2-pentene is formed
(b) equilibrium remains unaffected
(c) additional *trans*-2-pentene is formed
(d) equilibrium is shifted in forward direction

Ans. ***(a)***

According to Le-Chatelier's principle, when we increase the concentration of *trans*-2-pentene, then the reaction shifts in backward direction and hence, the concentration of *cis*-2-pentene increase to maintain the equilibrium constant K constant at given temperature.

78 Consider the following reaction occurring in an automobile

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

The sign of ΔH, ΔS and ΔG would be **[CBSE AIPMT 1994]**

(a) +, –, + (b) –, +, – (c) –, +, + (d) +, +, –

Ans. ***(b)***

The given reaction is combustion reaction, so it takes place by evolution of heat and hence, the sign of ΔH = negative and there is a increase in the number of moles of gaseous products, so entropy also increases and hence, ΔS = positive.

Thus,

$$\Delta G = \Delta H - T\Delta S = -\text{ve} - T(+\text{ve})$$
$$= -\text{ve at any temperature}$$

79 A chemical reaction will be spontaneous if it is accompanied by a decrease in **[CBSE AIPMT 1994]**

(a) entropy of the system
(b) enthalpy of the system
(c) internal energy of the system
(d) free energy of the system

Ans. ***(d)***

Gibbs free energy of a system will decide the spontaneity of a process.

If ΔG is negative, then the process is spontaneous.