6

Thermodynamics

Section-A : JEE Advanced/ IIT-JEE

A **1.** isolated **2.** endotherimic **3.** extensive

B **1.** T **2.** F

C

1. (a)	**2.** (d)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (c)
9. (b)	**10.** (a)	**11.** (b)	**12.** (a)	**13.** (b)	**14.** (c)	**15.** (b)	**16.** (c)

D

1. (b, d)	**2.** (b, c, d)	**3.** (a,d)	**4.** (a, b)	**5.** (a, c)	**6.** (a, c, d)	**7.** (a, b, c)

E
1. 101.19 kcal **2.** 54.20 kcal **4.** 41.104 kcal
5. – 22 kcal **6.** – 372.0 kcal/mole of ethane **7.** 3.94 kcal/cc **8.** 319.1 g
9. – 121 kJ/mole **10.** 82 kcal, 99 kcal **11.** 50.90 kJ **12.** – 55.7 kJ/mole
13. 0.2803 *x l* /hr, 5.461 *x l*/hr **14.** – 72. kJ/mole **15.** – 152 kJ/mole
16. – 266 kJ/mole **17.** ionic **18.** –2091.32 kJ **19.** 309.16 kJ
20. – 115.41 joules **22.** – 2035 kJ/mole
23. + 15.992 kJ/mole, +12.312 kJ/mole –3.688 kJ/mole, B > C > A
24. (ii) – 6.13 L atm, 620.7 J, (iii) 0, 0, 0 **26.** 9900 bar mL, 100 bar mL
27. (i) – 56.0304 L atm ; (ii) forward **28.** 557 kJ mol^{-1}

F
1. A - p, r, s; B - r, s; C -t; D - p, q, t
2. A - r, t; B - p, q, s; C -p, q, s; D - p, q, s, t

G **1.** (c) **2.** (b)

H **1.** (b) **2.** (a)

I **1.** 9 **2.** 2

Section-B : JEE Main/ AIEEE

1. (b)	**2.** (a)	**3.** (d)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (a)
8. (c)	**9.** (b)	**10.** (c)	**11.** (d)	**12.** (d)	**13.** (b)	**14.** (N)
15. (c)	**16.** (c)	**17.** (a)	**18.** (d)	**19.** (a)	**20.** (d)	**21.** (b)
22. (b)	**23.** (c)	**24.** (a)	**25.** (b)	**26.** (b)	**27.** (a)	**28.** (c)
29. (a)	**30.** (a)	**31.** (b)				

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **isolated**
2. **endothermic**
3. **extensive** (because its value does not depend on quantity of substance)

B. True/False

1. **True;** It only tells that if a process occurs the heat gained by one end would be exactly equal to heat lost by the other. It does not predict the direction.

2. **False;** $\frac{C_p}{C_v}$ for monoatomic gas = 1.66

$\frac{C_p}{C_v}$ for diatomic gas = 1.40

C. MCQs with One Correct Answer

1. **(a)** **TIPS/Formulae :**

Heat capacity at constant volume $(q_v) = \Delta E$

Heat capacity of constant pressure $(q_p) = \Delta H$

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

Δn = no. of moles of gaseous products − no. of moles of gaseous reactants $= 12 - 15 = -3$

$\Delta H - \Delta E = -3 \times 8.314 \times 298\,\text{J} = -7.43\,\text{kJ}$.

2. **(d)** **TIPS/Formulae :**

$\Delta H = \Delta E + \Delta nRT$ For $\Delta H \neq \Delta E, \Delta n \neq 0$

Where Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

(a) $\Delta n = 2 - 2 = 0$

(b) $\Delta n = 0$ ($\because$ they are either in solid or liquid state)

(c) $\Delta n = 1 - 1 = 0$ ($\because$ C is in solid state)

(d) $\Delta n = 2 - 4 = -2$

$\therefore$ (d) is correct answer

3. **(b)** $CO_{2(g)} + H_{2(g)} \longrightarrow CO_{(g)} + H_2O_{(g)}$, $\Delta H = ?$

$\Delta H = \sum \Delta H_f$ (Product) $- \sum \Delta H_f$ (reactant)

Given, $\Delta H_f CO_{2(g)} = -393.5$ kJ/mol

$\Delta H_f CO_{(g)} = -110.5$ kJ/mol

$\Delta H_f H_2O_{2(g)} = -241.8$ kJ/mol

$$\therefore \Delta H = [\Delta H_f CO_{(g)} + \Delta H_f H_2O_{(g)}] - [\Delta H_f CO_{2(g)} + \Delta H_f H_{2(g)}]$$

$$= [-110.5 + (-241.8)] - (-393.5 + 0) \qquad \left[\because \Delta H_f (H_2)_g = 0\right]$$

$= 41.2\,\text{kJ mol}^{-1}$

4. **(c)** In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

5. **(a)** Work is not a state function because it depends upon the path followed.

6. **(c)** **TIPS/Formulae :**

$\Delta H = \Delta U + P_2V_2 - P_1V_1$ Given, $\Delta U = 30.0$ L atm

$P_1 = 2.0$ atm, $V_1 = 3.0$ L, $T_1 = 95$ K

$P_2 = 4.0$ atm, $V_2 = 5.0$ L, $T_2 = 245$ K

$\Delta H = \Delta U + P_2V_2 - P_1V_1$

$= 30 + (4 \times 5) - (2 \times 3) = 30 + 20 - 6 = 44$ L atm.

7. **(b)** **TIPS/Formulae :**

ΔH_f° is the enthalpy change when 1 mole of the substance is formed from its elements in their standard states.

In (a) carbon is present in diamond however standard state of carbon is graphite. Again, in (d) CO (g) is involved so it can't be the right option. Further in (c) 2 moles of NH_3 are generated. Hence the correct option is (b).

8. **(c)** $\Delta H = nC_p\Delta T$ solution; since $\Delta T = 0$ so, $\Delta H = 0$

9. **(b)** $\Delta S = \dfrac{\Delta Q_{rev.}}{T}$; $75 = \dfrac{30 \times 10^3}{T}$ $\therefore T = 400$ K

10. **(a)** $\Delta S_{(A \to B)} = \Delta S_{(A \to C)} + \Delta S_{(C \to D)} - \Delta S_{(B \to D)}$

$= 50 + 30 - 20 = 60$ e.u.

11. **(b)** $A \rightleftharpoons B$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\Delta G^\circ = -2.303\,RT\log_{10} K$

$-2.303\,RT \log_{10} K = \Delta H^\circ - T\Delta S^\circ$

$2.303\,RT \log_{10} K = T\Delta S^\circ - \Delta H^\circ$

$$\log_{10} K = \frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298} = 10$$

12. **(a)** Since, liquid is passing into gaseous phase so entropy will increase and at 373 K during the phase transformation it remains at equilibrium. So, $\Delta G = 0$.

13. **(b)** The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298K, Cl_2 is gas while Br_2 is liquid.

14. **(c)** The standard enthalpy of the combustion of glucose can be calculated by the eqn.

$C_6H_{12}O_6(s) + 6O_2(g) \to 6CO_2(g) + 6H_2O(l)$

$\Delta H_C = 6 \times \Delta H_f(CO_2) + 6 \times \Delta H_f(H_2O) - \Delta H_f[C_6H_{12}O_6]$

$\Delta H^\circ = 6(-400) + 6(-300) - (-1300) = -2900$ kJ/mol

For one gram of glucose, enthalpy of combustion

$$\Delta H^\circ = -\frac{2900}{180} = -16.11\,\text{kJ/gm}$$

15. **(b)** Given conditions are boiling conditions for water due to which

$\Delta S_{total} = 0$

$\Delta S_{system} + \Delta S_{surroundings} = 0$

$\Delta S_{system} = -\Delta S_{surroundings}$

For process, $\Delta S_{system} > 0$

$\Delta S_{surroundings} < 0$

16. **(c)** From 1st law of thermodynamics

$q_{sys} = \Delta U - w = 0 - [-P_{ext} \cdot \Delta V]$

$= 3.0\,\text{atm} \times (2.0\,\text{L} - 1.0\,\text{L}) = 3.0$ L-atm

$$\therefore \Delta S_{surr} = \frac{(q_{rev})_{surr}}{T} = -\frac{q_{sys}}{T}$$

$$= -\frac{3.0 \times 101.3\,\text{J}}{300\,\text{K}} = -1.013\,\text{J/K}$$

D. MCQs with One or More Than One Correct

1. **(b, d)** Properties independent of mass are intensive properties. Hence (b) and (d) which are independent of mass are the obvious choices.

2. **(b, c, d)** All combustion reactions are exothermic in nature.
3. **(a,d)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.
4. **(a, b)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.
5. **(a, c)** $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$ [Entropy is a state function, hence additive]

   $W_{x\to y\to z} = W_{x\to y}$ [Work done in $y \to z$, is zero because it is an isochoric process].
6. **(a, c, d)** $T_1 = T_2$ because process is isothermal.

   Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.

   In adiabatic process expansion occurs by using internal energy, hence, it decreases while in isothermal process temperature remains constant that's why no change in internal energy.
7. **(a, b, c)** Since the vessel is thermally insulated, $q = 0$

   Further since, $P_{ext} = 0$, so $w = 0$, hence $\Delta U = 0$

   Since $\Delta T = 0$, $T_2 = T_1$, and $P_2V_2 = P_1V_1$

   However, the process is adiabatic irreversible, so we can't apply $P_2V_2^{\gamma} = P_1V_1^{\gamma}$.

E. Subjective Problems

1. The required reaction in terms of dissociation energy is

$OH(g) \to O(g) + H(g); \quad \Delta H = ?$

This equation can be achieved by (a) reversing the equation (*i*), (b) dividing equation (*ii*) and (*iii*) each by 2, and (c) adding the three resulting equations.

$$OH(g) \to \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g); \quad \Delta H = +\,10.06\text{ kcal}$$

[Reversing eq (i)]

$$\frac{1}{2}H_2(g) \to H(g) \qquad \Delta H = -\,52.09\text{ kcal} \quad \left[\frac{1}{2}\text{Eq (ii)}\right]$$

$$\frac{1}{2}O_2(g) \to O(g); \qquad \Delta H = -\,59.16\text{ kcal} \quad \left[\frac{1}{2}\text{Eq (iii)}\right]$$

$$OH(g) \to O(g) + H(g); \qquad \Delta H = -\,101.19\text{ kcal (adding)}$$

Thus one mole of OH(*g*) needs 101.19 kcal of energy to break into oxygen and hydrogen gaseous atoms. Hence the bond energy of O–H bond is **101.19 kcal**.

2. The required equation is :

$2C_{(s)} + H_{2(g)} \to C_2H_2; \quad \Delta H = ?$

Write the thermochemical equations for the given data

(i) $C_2H_{2\,(g)} + \frac{5}{2}O_{2(g)} \to 2CO_{2(g)} + H_2O_{(\ell)};$

$\Delta H = -310.62\text{ kcal}$

(ii) $C_{(s)} + O_{2(g)} \to CO_{2(g)}; \quad \Delta H = -94.05\text{ kcal}$

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \to H_2O_{(\ell)}; \quad \Delta H = -68.32\text{ kcal}$

For getting the above required reaction, we will have to

NOTE:

(a) Bring C_2H_2 in the product that can be done by reversing the equation (i) to give equation (iv).

(b) Multiply equation (ii) by 2 to get 2C atoms in the reactants and thus equation (v) is obtained.

(c) Keep equation (iii) as such.

(d) Add equations (iv), (v) and (iii).

(iv) $2CO_2 + H_2O \to C_2H_2 + \frac{5}{2}O_2; \; \Delta H = 310.62\text{ kcal}$

(v) $2C + 2O_2 \to 2CO_2; \qquad \Delta H = -188.10\text{ kcal}$

(iii) $H_2 + \frac{1}{2}O_2 \to H_2O; \qquad \Delta H = -68.32\text{ kcal}$

On adding, $2C + H_2 \to C_2H_2; \; \Delta H = 54.20\text{ kcal}$

Hence the standard heat of formation of $C_2H_2(g)$

= **54.20 kcal**

3. If heat is absorbed at constant pressure, then

$q_p = \Delta E - (-P\Delta V)$ or $q_p = E_2 - E_1 - [-P(V_2 - V_1)]$

or $q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$

4. The given data can be written as follows

(i) $H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l); \quad \Delta H = -68.3\text{ kcal}$

(ii) $C_2H_2(g) + \frac{5}{2}O_2(g) \to H_2O(l) + 2CO_2(g);$

$\Delta H = -310.6\text{ kcal}$

(iii) $C_2H_4(g) + 3O_2 \to 2H_2O(l) + 2CO_2(g); \Delta H = -337.2\text{ kcal}$

The required thermochemical equation is

$C_2H_2(g) + H_2(g) \to C_2H_4(g)$

The required equation can be obtained by subtracting equation (*iii*) from the sum of equations (*i*) and (*ii*), thus ΔH of the required equation can be calculated as below.

$\Delta H = [-68.3 + (-310.6)] - (-337.2)$

$= [-68.3 - 310.6] + 337.2$

$= -378.9 + 337.2 = -41.7\text{ kcal}$

ΔE, the heat of reaction for the hydrogenation of acetylene at constant volume is given by :

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

Here Δn = Moles of the gaseous products – Moles of the gaseous reactants

$= 1 - (1 + 1) = -1$

Substituting the values of ΔH, Δn, R and T in

$\Delta E = \Delta H - \Delta nRT = -41.7 - (-1 \times 2 \times 10^{-3} \times 298)$

$$\left[\begin{array}{l} \because R = 2\text{cal/degree/mole} \\ \quad = 2 \times 10^{-3}\text{ kcal/deg/mole} \end{array}\right]$$

$= -41.7 + 2 \times 10^{-3} \times 298$

$= -41.7 + 0.596 =$ **41.104 kcal**

5.

Bond	H–H	Cl–Cl	H–Cl
ΔH disso.	104 kcal	58 kcal	103 kcal

Formation of hydrogen chloride can be represented as

$H-H + Cl-Cl \rightarrow 2H-Cl$

Thus the reaction involves

Cleavage of one H – H bond, $\Delta H = 104$ kcal

Cleavage of one Cl – Cl bond, $\Delta H = 58$ kcal

Formation of two H – Cl bonds, $\Delta H = 2 \times -103$ kcal

$\therefore$ ΔH of the reaction $= (104 + 58) - 2(103)$

$= 162 - 206 = -44$ kcal

Now since the enthalpy of formation of a compound is the change in heat content accompanied in the formation of one mole of the compound, the enthalpy of formation of

HCl gas $= -\dfrac{44}{2} = $ **-22 kcal**

6. The required chemical reaction.

$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O; \Delta H = x$

Note that since 2 moles of ethane are reacting, the ΔH of the reaction will be ½x.

The thermochemical equations for the given data are written as below.

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g);$ $\Delta H = -94.1$ kcal

(*ii*) $H_2(g) + ½O_2(g) \longrightarrow H_2O(g);$ $\Delta H = -68.3$ kcal

(*iii*) $2C(s) + 3H_2(g) \longrightarrow C_2H_6(g);$ $\Delta H = -21.1$ kcal

We know that $\Delta H = H_{Products} - H_{Reactants}$

$$\Delta H = 4\Delta H_{CO_2} + 6\Delta H_{H_2O} - (2\Delta H_{C_2H_6} + 7\Delta H_{O_2})$$

$\Delta H = 4 \times -94.1 + 6 \times -68.3 - (2 \times -21.1 + 0)$

$= -376.4 - 409.8 + 42.2 = -744.0$ kcal/2 mole of ethane

= **-372.0 kcal/mole of ethane**

7. $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$

$2 \times 56 + 48 = 160$ $\quad 2 \times 27 = 54$

Heat of reaction = 399 – 199 = 200 kcal [Al & Fe are in their standard states]

Total weight of reactants = 160 + 54 = 214 g

$\therefore$ Fuel value/gram $= \dfrac{200}{214} = 0.9346$ kcal/g

Volume of Al $= \dfrac{54}{2.7} = 20$ cc

Volume of $Fe_2O_3 = \dfrac{160}{5.2} = 30.77$ cc

Total volume = 20 + 30.77 = 50.77 cc

$\therefore$ Fuel value per cc $= \dfrac{200}{50.77} =$ **3.94 kcal/cc**

8. 100 g of glucose = 1560 kJ

Energy utilised in body $= \dfrac{50}{100} \times 1560 = 780$ kJ

Energy left unutilised in body = 1560 – 780 = 780 kJ

Energy to be given out = 1560 – 780 = 780 kJ

Enthalpy of evaporation of water = 44 kJ/mole = 44 kJ/18 g of water [1 mole H_2O = 18g water]

Hence amount water to be perspired to avoid storage of energy $= \dfrac{18}{44} \times 780 =$ **319.1 g**

9. The required reaction is

$C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g), \quad \Delta H_1 = ?$ ...(1)

Cyclohexene Cyclohexane

The given facts can be written as :

$H_2(g) + ½O_2(g) \rightarrow H_2O, \quad \Delta H_2 = -241$ kJ/mol ...(2)

$C_6H_{10}(g) + \frac{17}{2}O_2 \rightarrow 6CO_2(g) + 5H_2O; \ \Delta H_3 = -3800$ kJ/mol ...(3)

$C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O, \ \Delta H_4 = -3920$ kJ/mol ...(4)

The required reaction (1) can be obtained by adding equations (2) and (3) and subtracing (4) from the sum of (2) and (3).

$C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$

$\Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4$

$= [-241 + (-3800)] - (-3920)$

$= (-241 - 3800) - (-3920)$

$= -4041 + 3920 =$ **-121 kJ/mole**

10. For C_3H_8 : $3C + 4H_2 \rightarrow C_3H_8; \Delta H_1 = ?$

For C_2H_6 : $2C + 3H_2 \rightarrow C_2H_6; \Delta H_2 = ?$

$\therefore \ \Delta H_1 = -[2(C–C) + 8(C–H)] + [3C_{s\rightarrow g} + 4(H–H)]$ ...(1)

$\therefore \ \Delta H_2 = -[1(C–C) + 6(C–H)] + [2C_{s\rightarrow g} + 3(H–H)]$ ...(2)

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

$\therefore$ By eq. (1) $\Delta H_1 = -(2x + 8y) + [3 \times 172 + 4 \times 104]$ ...(3)

$\Delta H_2 = -(x + 6y) + [2 \times 172 + 3 \times 104]$ ...(4)

Also given $C + O_2 \rightarrow CO_2; \Delta H = -94.0$ k cal ...(5)

$H_2 + ½O_2 \rightarrow H_2O; \Delta H = -68.0$ kcal ...(6)

$C_2H_6 + (7/2)O_2 \rightarrow 2CO_2 + 3H_2O; \Delta H = -372$ k cal ...(7)

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O; \Delta H = -530$ k cal ...(8)

By inspection method : 2 × (5) + 3 × (6) – (7) gives

$2C + 3H_2 \rightarrow C_2H_6; \Delta H_2 = -20$ k cal ...(9)

and 3 × (5) + 4 × (6) – (8) gives

$3C + 4H_2 \rightarrow C_3H_8; \Delta H_1 = -20$ k cal ...(10)

$\therefore$ By eq. (3), (4), (9) and (10)

$x + 6y = 676$

$2x + 8y = 956$

$\therefore$ $x = 82$ k cal and $y = 99$ k cal

Bond energy of C–C bond = **82 k cal**

and Bond energy of C–H bond = **99 k cal**

11. Combustion of C_2H_4 and CH_4 takes place as follows :

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

1 vol. 2 vol.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 vol. 1 vol.

Let the vol. of CH_4 in mixture $= x\ l$

$\therefore$ Vol. of C_2H_4 in the mixture $= (3.67 - x)\ l$

Vol. of CO_2 produced by $x\,l$ of $CH_4 = x\,l$ and
Vol. of CO_2 produced by $(3.67 - x)\,l$ of $C_2H_4 = 2\,(3.67 - x)\,l$
∴ Total vol. of CO_2 produced $= x + 2\,(3.67 - x)$
or $6.11 = x + 2\,(3.67 - x)$ or $x = 1.23\,l$
∴ Vol. of CH_4 in the mixture $= 1.23\,l$
and Vol. of C_2H_4 in the mixture $= 3.67 - 1.23 = 2.44\,l$

Vol. of CH_4 per litre of the mixture $= \dfrac{1.23}{3.67} = 0.335\,l$

Vol. of C_2H_4 per litre of the mixture $= \dfrac{2.44}{3.67} = 0.665\,l$

Now we know that volume of 1 mol. of any gas at

$25°C\,(298\text{ K}) = \dfrac{22.4 \times 298}{273} = 24.45\,l$

[∵ Volume at NTP = 22.4L]

Heat evolved due to combustion of $0.335\,l$ of CH_4

$= -\dfrac{0.335 \times 891}{24.45} = -12.20\text{ kJ}$ [given, heat evolved by combustion of $1\,l = 891$ kJ]

Similarly, heat evolved due to combustion of $0.665\,l$ of C_2H_4

$= -\dfrac{0.665 \times 1423}{24.45} = -38.70\text{ kJ}$

∴ Total heat evolved = 12.20 + 38.70 = **50.90 kJ**

12. From the given data, we can write :

(*i*) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O;$ $\Delta H_1 = -285.8$ kJ/mol
(*ii*) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;$ $\Delta H_2 = -890$ kJ mol
(*iii*) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O;$ $\Delta H_3 = -1560$ kJ/mol
(*iv*) $C(s) + O_2 \rightarrow CO_2;$ $\Delta H_4 = -393.5$ kJ/mol
(*v*) $3C(s) + 4H_2 \rightarrow C_3H_8(g);$ $\Delta H_5 = -103.8$ kJ/mol

The required reaction is $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g),\ \Delta H = ?$

It can be obtained by the following calculations.

$3 \times (iv) - (v) + 5(i) - (iii) - (ii)$

In other words, $\Delta H = 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3$
∴ $\Delta H = 3(-393.5) - (-103.8) + 5(-285.8) + 890 + 1560$
$= -2609.5 + 2553.8 = \mathbf{-55.7\ kJ/mol}$

13. Combustion of CH_4 and C_4H_{10} takes place as follows
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,\ \Delta H = -809\text{ kJ mol}^{-1}$
$C_4H_{10} + 13/2\,O_2 \rightarrow 4CO_2 + 5H_2O,\ \Delta H = -2878\text{ kJ mol}^{-1}$
In order to get the same calorific output due to C_4H_{10},

the rate of supply of butane $= \dfrac{x \times 809}{2878} = \mathbf{0.281\,x\ l/hr}$

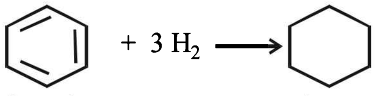
Rate of supply of oxygen $= 0.2803\,x \times \dfrac{13}{2} \times 3 = \mathbf{5.481\,x\ l/hr}$

14. $nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)_n$

NOTE : During the polymerisation of ethylene, one mole of ethylene breaks i.e. one C = C double bond breaks and the two CH_2 – groups are linked with C – C single bonds thus forming three single bonds (two single bonds are formed when each CH_2 – group of ethylene links with one CH_2 – group of another ethylene molecule). But in the whole unit of polymer, number of single C–C bonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 C–C single bonds
$= 2 \times 331 = 662$ kJ/mol of ethylene
Energy absorbed = Energy due to dissociation of 1 C=C double bond
= 590 kJ/mol of ethylene
∴ Enthalpy of polymerisation/mol of ethylene or
$\Delta H_{\text{polymerisation}} = 590 - 662$ kJ/mol $= \mathbf{-72\ kJ/mole}$

15. Standard enthalpy of hydrogenation of cyclohexene (–119kJ mol^{-1}) means the enthalpy of hydrogenation of one C = C double bond. Now benzene has three C = C double bonds, the enthalpy of the reaction would be $= 3 \times -119 = -357\text{ kJ mol}^{-1}$

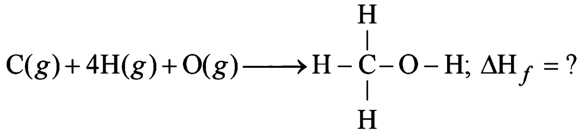


Actual enthalpy of the reaction can be evaluated as follows.

$$\Delta H_{(\text{Reaction})} = \Delta H_f^\circ(\text{Product}) - \Delta H_f^\circ(\text{Reactants})$$
$$= -156 - (49 + 0) = -205\text{ kJ mol}^{-1}$$

∴ Resonance energy $= \Delta H_{\text{Exp}} - \Delta H_{\text{cal}}$
$= -357 - (-205) = \mathbf{-152 kJ\ mol^{-1}}$

16. The required thermochemical equation is



$$C(g) + 4H(g) + O(g) \longrightarrow H - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - O - H;\ \Delta H_f = ?$$

$$\Delta H_f = \left[\Delta H_{C(s)\to C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}\right]$$
$$-\left[3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{\text{vap.}CH_3OH}\right]$$
$$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$$
$$= \mathbf{-266\ kJ\ mol^{-1}}$$

17. **TIPS/Formulae :**

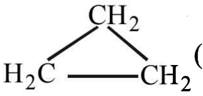
For ionisation $\Delta H_{\text{ionisation}} > \Delta H_{\text{Hydration}}$
Total hydration energy of Al^{3+} & $3Cl^-$ ions of $AlCl_3$ $(\Delta H_{\text{hydration}})$
= (Hydration energy of Al^{3+} + 3 × Hydration energy of Cl^-)
$= [-4665 + 3\,(-381)]\text{kJ mole}^{-1} = -5808\text{ kJ mole}^{-1}$

NOTE : This amount of energy is more than that required for the ionisation of Al into Al^{3+} (Ionisation energy of Al to Al^{3+} = 5137 kJ mol^{-1}). Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
$AlCl_3 + aq. \rightarrow AlCl_{3(aq.)};\ \Delta H = ?$

ΔH = Energy released during hydration
– Energy used during ionisation
$= -4665 - 3 \times 381 + 5137 = -671$ kJ/mol

Thus formation of ions will take place.

18.  $(g) \rightarrow CH_3CH=CH_2(g);$

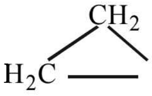
$\Delta H = -33.0\,kJ$ ...(i)

$C + O_2 \rightarrow CO_2(g); \Delta H = -393.5\,kJ$ ...(ii)

$H_2 + 1/2O_2 \rightarrow H_2O_{(l)}; \Delta H = -285.8\,kJ$ ...(iii)

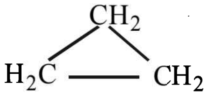
$3C + 3H_2 \rightarrow CH_3\text{–}CH=CH_2{}_{(g)}; \Delta H = 20.42\,kJ$ ...(iv)

The required reaction is

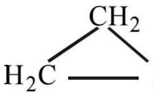
 $+ \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O; \quad \Delta H = ?$

To calculate the value of ΔH follow the following steps.

(iv) – (i) yields

$3C + 3H_2 \rightarrow$  $; \Delta H = 53.42\,kJ$ ...(v)

[3 × (ii) + 3 × (iii)] – (v) yields]

 $+ (9/2)O_2 \rightarrow 3CO_2 + 3H_2O;$

$\Delta H = \mathbf{-2091.32\ kJ}$

19. Given $S_{(s)} + 3F_{2(g)} \rightarrow SF_{6(g)}; \Delta H = -1100\,kJ$ .....(i)

$S_{(S)} \rightarrow S_{(g)}; \Delta H = 275\,kJ$ .....(ii)

$1/2\,F_{2(g)} \rightarrow F_{(g)}; \Delta H = 80\,kJ$ .....(iii)

To get $SF_{6(g)} \rightarrow S_{(g)} + 6F_{(g)}$ we can proceed as

(ii) + 6 × (iii) - (i)

$\therefore SF_{6(g)} \rightarrow S_{(g)} + 6F_{(g)}; \Delta H = 1855\,kJ$

Thus average bond energy for S-F bond $= \frac{1855}{6} = \mathbf{309.16\,kJ}$

20. **TIPS/Formulae :** For adiabatic expansion, we have

$$\ell n\frac{T_1}{T_2} = \frac{R}{C_v}\ell n\frac{V_2}{V_1} \text{ and } \Delta H = nC_p\Delta T.$$

$$\ell n\frac{300}{T_2} = \frac{8.31}{12.48}\ell n\frac{2.50}{1.25} \text{ Solving, we get, } T_2 = 188.5\,K$$

No. of moles of argon gas, $n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.082 \times 300} = 0.05$

Now we know that

$\Delta H = nC_p\Delta T = 0.05 \times 20.8(188.5 - 300) = \mathbf{-115.41\ Joules}$

$[\because C_p = C_v + R = 12.48 + 8.314 = 20.8]$

21. For following reaction

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$$

ΔG° can be calculated as follows :

$$\Delta G° = \Delta G_p° - \Delta G°_R = \left[\Delta G°CO_2 - \left(\Delta G°CO + \frac{1}{2}\Delta G°O_2\right)\right]$$

$$= -394.4 - (-137.2 + \frac{1}{2} \times 0) = -257.2\,kJ\,mol^{-1}$$

Since,

$\Delta G° = \Delta H° - T\Delta S^0$ or $-257.2 = \Delta H - 300(0.094)$

$\therefore \Delta H° = -285.4\,kJ/mol$

Since,

NOTE : ∴ ΔH° is negative, so the reaction is exothermic and since ΔG° is negative so the reaction is spontaneous.

22. The chemical reaction for combustion of diborane is

$$B_2H_6\,(g) + 3O_2\,(g) \longrightarrow B_2O_3\,(s) + 3H_2O\,(g), \Delta H = ?$$

For this the enthalpy change can be calculated in the following way.

$$\Delta H = [\Delta H_{B_2O_3(s)} + 3\Delta H_{H_2O(g)}] - \Delta H_{B_2H_6(g)};$$

$(\because \Delta H_f^\circ \text{ of } O_2 = 0)$

$\Delta H_{H_2O(g)}$ can be obtained by adding $\Delta H_{H_2O(\ell)}$ and $\Delta H_{H_2O(g)}$, i.e. $-286 + 44 = -242\,kJ\,mol^{-1}$

$\Delta H = [-1273 + 3 \times -242] - 36\,kJ\,mol^{-1} = -1273 - 726 - 36$

$= \mathbf{-2035\ kJ\ mol^{-1}}$

23. **TIPS/Formulae :**

$$\Delta G^\circ = -2.303RT\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

Calculation of ΔG values :

Thus for the equilibrium $B \rightleftharpoons A$

$$\Delta G_1^\circ = (-2.303 \times 8.314 \times 448)\log\frac{1.3}{95.2}$$

or $\Delta G_1^\circ = \mathbf{15.992\ kJ\,mole^{-1}}$

Similarly for the equilibrium $B \rightleftharpoons C$

$$\Delta G_2^\circ = (-2.303 \times 8.314 \times 448)\log\frac{3.5}{95.2}$$

or $\Delta G_2^\circ = \mathbf{12.312 kJ\ mole^{-1}}$

Similarly for equilibrium, $A \rightleftharpoons C$

$$\Delta G_3^\circ = -8.314 \times 448 \times 2.303 \times \log_{10}\frac{3.5}{1.3} = -3.688\,kJ\,mole^{-1}$$

Hence, we have that

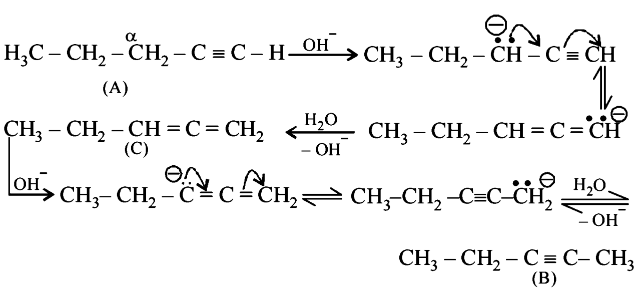
$B \rightleftharpoons A, \quad \Delta G_1^\circ = +15.992\ kJ\ mole^{-1}$

$B \rightleftharpoons C, \quad \Delta G_2^\circ = +12.312\ kJ\ mole^{-1}$

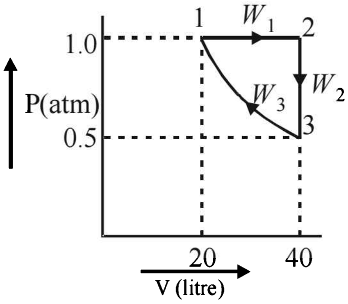
$A \rightleftharpoons C, \quad \Delta G_3^\circ = -3.688\ kJ\ mole^{-1}$

Thus, the correct order of stability, **B > C > A**

NOTE : Mechanism of isomerisation



24. (i)



(ii) Total work $(W) = W_1 + W_2 + W_3$

$$= -P\Delta V + 0 + 2.303nRT\log\frac{V_2}{V_1}$$

$$= -1\times 20 + 2.303\times 2\times 0.082\times 121.95\ \log 2$$

$$= -20 + 13.87 = \mathbf{-6.13\ L\ atm}$$

$$\begin{bmatrix} PV = nRT \\ T = \dfrac{PV}{nR} = \dfrac{.5\times 40}{2\times 0.082} \end{bmatrix} = 121.95\,\text{K}$$

Since the system has returned to its initial state i.e. the process is cyclic, so $\Delta U = 0$

$\Delta U = q + W = 0$, so $q = -W = -(-6.13)\,\text{L.atm} = \mathbf{620.7\ J}$

NOTE : In a cyclic process heat absorbed is completely converted into work.

(iii) Entropy is a state function and since the system has returned to its initial state, so $\mathbf{\Delta S = 0}$. Similarly $\mathbf{\Delta H = 0}$ and $\mathbf{\Delta U = 0}$ for the same reason i.e. U and H are also state functions having definite values in a given state of a system.

25. Helium molecule is monoatomic so it has just three degrees of freedom corresponding to the three translational motion at all temperature and hence C_v value is always 3/2 R. Hydrogen molecule is diatomic which are not rigidly held so they vibrate about a well defined average separation. For hydrogen molecule we have rotational and vibrational motion both besides translational motion. These two additional contributions increase its total heat capacity. Contribution from vibrational motion is not appreciable at low temperature but increases from 0 to R on raising temperature.

26. **TIPS/Formulae :** For adiabatic process, $W = P(V_2 - V_1)$

Here $P_1 = 1$ bar, $P_2 = 100$ bar, $V_1 = 100$ mL, $V_2 = 99$ mL; For adiabatic process, $q = 0 \backslash \Delta U = w$

$$\Delta U = q + W = q - P(V_2 - V_1) \text{ since } W = -P(V_2 - V_1)$$

$$= 0 - 100\,(99 - 100) = \mathbf{100\ bar\ mL}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

$$= 100 + [(100\times 99) - (1\times 100)]$$

$$= 100 + (9900 - 100) = \mathbf{9900\ bar\ mL}$$

27. (i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Initially $p_{N_2O_4} = p_{NO_2} = 10$

$$\text{Reaction quotient } = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{100}{10} = 10$$

$$\Delta G^\circ = 2\Delta G^\circ_{f(NO_2)} - \Delta G^\circ_{f(N_2O_4)} = 100 - 100 = 0$$

$$\Delta G = \Delta G^\circ - 2.303\,RT\log K_p$$

$$= 0 - 2.303\times 298\ \log 10 = \mathbf{-56.0304\ L\ atm.}$$

(ii) The negative value of ΔG indicates that the reaction is spontaneous & will lie in the right direction, (forward).

28. $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P \qquad (\because \Delta V = 0)$

or $\Delta U = \Delta H - V\Delta P = -560 - [1(40-70)\times 0.1]$

$$= -560 + 3 = -557\ \text{kJ mol}^{-1}$$

So the magnitude is **557** kJ mol^{-1}.

$\because \Delta G^\circ = -2.303RT\log K_p$ at equilibrium $\Delta G^\circ = 0$

$\therefore -2.303RT\log K_p = 0 \Rightarrow \log K_p = 0$ or $K_p = 1$

F. Match the Following

1. **A – p, r, s ; B – r, s ; C – t ; D – p, q, t**

(A) $CO_2(s) \rightarrow CO_2(g)$

It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.

(B) On heating $CaCO_3$ decomposes. So, process is endothermic.

The entropy increases as gaseous product is formed.

(C) $2H\bullet \rightarrow H_2(g)$

Entropy decreases as number of gaseous particles decreases.

(D) It is phase transition.

White and red P are allotropes.

Red P is more stable than white.

So ΔH is –ve.

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

(A) $\rightarrow$ r, t

$H_2O(\ell) \rightleftharpoons H_2O(s)$

It is at equilibrium at 273 K and 1 atm

So ΔS_{sys} is negative

As it is equilibrium process so $\Delta G = 0$

(B) → p, q, s

Expansion of 1 mole of an ideal gas in vacuum under isolated condition

Hence, $w = 0$

and $q_p = C_p dT$ $(\because dT = 0)$

$\Rightarrow$ $q = 0$

$\Delta U = C_v dT$ $(\because dT = 0)$ $\Delta U = 0$

(C) → p, q, s

Mixing of two ideal gases at constant temperature

Hence, $\Delta T = 0$

$\therefore$ $q = 0;\ \Delta U = 0$

also $w = 0$ $(\Delta U = q + w)$

(D) → p, q, s, t

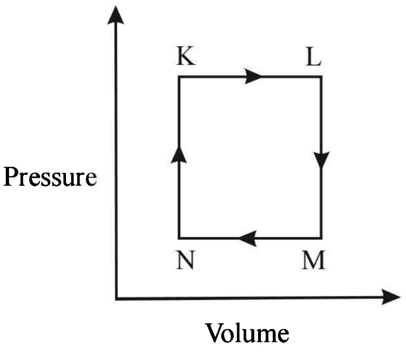
Reversible heating and cooling of gas follows same path also initial and final position is same.

$$\text{Hence, } \left.\begin{array}{l} q = 0 \\ w = 0 \end{array}\right\} \text{Path same}$$

$$\left.\begin{array}{l} \Delta U = 0 \\ \Delta G = 0 \end{array}\right\} \text{State function}$$

G. Comprehension Based Questions

1. **(c)**



$K \rightarrow L \Rightarrow$ V increasing at constant P

Hence T increases (Heating)

$L \rightarrow M \Rightarrow$ P decreasing at constant V

Hence T decreases (Cooling)

$M \rightarrow N \Rightarrow$ V decreasing at constant P

Hence T decreases (Cooling)

$N \rightarrow K \Rightarrow$ P increasing at constant V

Hence T increases (Heating)

2. **(b)** L to M and N to K, both are having constant volume therefore these processes are isochoric.

H. Assertion & Reason Type Questions

1. **(b)** By first law of thermodynamics $dq = dE + dW$. Under isothermal condition for ideal gas $dW = 0$ as volume occupied by the molecules of ideal gas is zero. Also $(dE)_T = 0$ as for ideal gas there is no change in internal energy at constant T due to no force of attraction between the molecules. $\therefore dq = 0 + 0 = 0$.

2. **(a)** Statement 1 is true because it is not possible to convert whole of heat to work. For such a conversion we need an efficiency of 100% but so far we have not been able to get such a machine (carnot engine).

Statement 2 is true because it is not possible to convert the whole of heat absorbed from a reservoir into work. Some of the heat is always given to the sink.

Also statement 2 is correct explanation for statement 1. Thus the correct choice is option (a).

I. Interger Value Correct Type

1. Energy released by combustion of 3.5 g gas

$$= 2.5 \times (298.45 - 298) \text{ kJ}$$

Energy released by 1 mole of gas $= \dfrac{2.5 \times 0.45}{3.5/28} = 9 \text{ kJmol}^{-1}$

2. $w_d = \left(-4 \times \dfrac{3}{2}\right) + (-1 \times 1) + \left(-\dfrac{2}{3} \times \dfrac{5}{2}\right) = -\left(6 + 1 + \dfrac{5}{3}\right)$

$w_d = -\dfrac{26}{3} \text{L atm}$

$w_s = -2.303 \text{ RT} \log \dfrac{5.5}{1/2} = -2.303 \text{ PV} \log 11$

$w_s = -4.606 \times 1.04 = -4.8 \text{ L atm}$

$$\frac{w_d}{w_s} = \frac{-\frac{26}{3}}{-4.8} = 1.80 \simeq 2.0$$

Section-B JEE Main/ AIEEE

1. **(b)** **TIPS/Formulae :**

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

Since $\Delta G = \Delta H - T\Delta S$ for an endothermic reaction,

ΔH = +ve and at low temperature ΔS = + ve

Hence $\Delta G = (+)\Delta H - T(+)\Delta S$

and if $T\Delta S < \Delta H$ (at low temp)

ΔG = +ve (non spontaneous)

But at high temperature, reaction becomes spontaneous i.e. ΔG = –ve.

because at higher temperature $T\Delta S > \Delta H$.

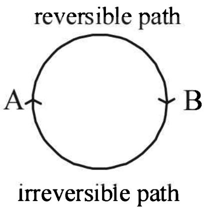
2. **(a)** According to first law of thermodynamics energy can neither be created nor destroyed although it can be converted from one form to another.

NOTE : Carnot cycle is based upon this principle but during the conversion of heat into work some mechanical energy is always converted to other form of energy hence this data violates 1st law of thermodynamics.

3. **(d)** ΔH negative shows that the reaction is spontaneous. Higher negative value for Zn shows that the reaction is more feasible.

4. **(b)** The heat required to raise the temperature of body by 1K is called thermal capacity or heat capacity.

5. **(c)** For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.



6. **(c)** $CH_2 = CH_2(g) + H_2(g) \rightarrow CH_3\text{-}CH_3$

Enthalpy change = Bond energy of reactants – Bond energy of products.

$$\Delta H = 1(C{=}C) + 4(C{-}H) + 1(H{-}H) - 1(C{-}C) - 6(C{-}H)$$
$$= 1(C{=}C) + 1(H{-}H) - 1(C{-}C) - 2(C{-}H)$$
$$= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175 = -125\text{ kJ.}$$

7. **(a)** For spontaneous reaction, dS > 0 and dG should be negative i.e. < 0.

8. **(c)** $\Delta G^\circ = -RT\ln K_c$ or $-\Delta G^\circ = RT\ln K_c$

9. **(b)** Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.

10. **(c)** $w = -P\Delta V = -10^{-5}(1\times10^{-2} - 1\times10^{-3}) = -900\text{J}$

11. **(d)** (i) $C + O_2 \rightleftharpoons CO_2, \Delta H = -393.5\text{ kJmol}^{-1}$

(ii) $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2,$

$\Delta H = -283.0\text{ kJmol}^{-1}$

Operating (i) - (ii), we have

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -110.5\text{ kJmol}^{-1}$$

12. **(d)** Enthalpy of reaction $(\Delta H) = E_{a_{(f)}} - E_{a_{(b)}}$

for an endothermic reaction ΔH = +ve hence for ΔH to be negative

$$E_{a_{(b)}} < E_{a_{(f)}}$$

13. **(b)** $\Delta H = \Delta U + \Delta nRT$ for $N_2 + 3H_2 \longrightarrow 2NH_3$

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

$\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT \quad \therefore \Delta U > \Delta H$

14. **(N)** $X_2 + Y_2 \longrightarrow 2XY, \Delta H = 2(-200).$

Let *x* be the bond dissociation energy of X_2. Then

$\Delta H = -400 = \xi_{x-x} + \xi_{y-y} - 2\xi_{x-y} = x + 0.5x - 2x = -0.5x$

or $x = \frac{400}{0.5} = 800\text{ kJ mol}^{-1}$

(In the question paper, this option was not mentioned. So the answer has been marked 'N')

15. **(c)** **NOTE :** In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So

$$T_f(\text{rev.}) < T_f(\text{irr.})$$

16. **(c)** The standard enthalpy of formation of CH_4 is given by the equation :

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

Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

17. **(a)** $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$

$$\Delta A = [\Delta I_2(s) \rightarrow I_2(g) + \Delta H_{I-I} + \Delta H_{Cl-Cl}] - 2[\Delta H_{I-Cl}]$$
$$= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$$

$$\Delta H_f^o(ICl) = \frac{33.46}{2} = 16.73\text{ kJ/mol}$$

18. **(d)** For the reaction, $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO$

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

$\Delta n = 1 - \frac{1}{2} = \frac{1}{2}; \Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298$

$$= 1238.78\text{ J mol}^{-1}$$

19. **(a)** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous reaction $\Delta G^\circ < 0$

or $\Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$

$$\Rightarrow T > \frac{179.3 \times 10^3}{160.2} > 1117.9\text{K} \approx 1118\text{K}$$

20. **(d)** Given $\Delta H = 41\ \text{kJ mol}^{-1} = 41000\ \text{J mol}^{-1}$

$T = 100°C = 273 + 100 = 373\ K, n = 1$

$\Delta U = \Delta H - \Delta nRT = 41000 - (2 \times 8.314 \times 373)$

$= 37898.88\ \text{J mol}^{-1} \simeq 37.9\ \text{kJmol}^{-1}$

21. **(b)** Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

22. **(b)** The energy involved in the conversion of

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

$$\Delta H = \frac{1}{2}\Delta_{diss}H^{(-)}_{Cl_2} + \Delta_{eg}H^{(-)}_{Cl} + \Delta_{hyl}H^{(-)}_{Cl}$$

Substituting various values from given data, we get

$$\Delta H = \left(\frac{1}{2} \times 240\right) + (-349) + (-381)\ \text{kJmol}^{-1}$$

$$= (120 - 349 - 381)\ \text{kJ mol}^{-1} = -610\ \text{kJ mol}^{-1}$$

i.e., the correct answer is (b)

23. **(c)** For a reaction to be at equilibrium $\Delta G = 0$. Since $\Delta G = \Delta H - T\Delta S$ so at equilibrium $\Delta H - T\Delta S = 0$ or $\Delta H = T\Delta S$

For the reaction

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3; \quad \Delta H = -30\text{kJ (given)}$$

Calculating ΔS for the above reaction, we get

$$\Delta S = 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right] JK^{-1}$$

$$= 50 - (30 + 60)\ JK^{-1} = -40\ JK^{-1}$$

At equilibrium, $T\Delta S = \Delta H$ $[\because \Delta G = 0]$

$$\therefore T \times (-40) = -30 \times 1000 \quad [\because 1kJ = 1000J]$$

or $T = \dfrac{-30 \times 1000}{-40}$ or 750 K

24. **(a)** Given, for reaction

(i) $H_2O(\ell) \longrightarrow H^+(aq.) + OH^-(aq.); \Delta H_r = 57.32\ kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell); \Delta H_r = -286.20\ kJ$

For reaction (i)

$$\Delta H_r = \Delta H°_f(H^+.aq) + \Delta H°_f(OH^-.aq) - \Delta H°_f(H_2O, \ell)$$

$$57.32 = 0 + \Delta H°_f(OH^-, aq) - \Delta H°_f(H_2O, \ell) \quad \ldots(iii)$$

For reaction (ii)

$$\Delta H_r = \Delta H°_f(H_2O, \ell) - \Delta H°_f(H_2, g) - \frac{1}{2}\Delta H°_f(O_2, g)$$

$$-286.20 = \Delta H°_f(H_2O, \ell)$$

On replacing this value in equ. (iii) we have

$$57.32 = \Delta H°_f(OH^-, aq) - (-286.20)$$

$$\Delta H°_f = -286.20 + 57.32 = -228.88\ kJ$$

25. **(b)** $N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = 2 \times -46.0\ \text{kJ mol}^{-1}$

Let x be the bond enthalpy of N – H bond then

[**Note :** Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

$\Delta H = \Sigma$ Bond energies of products

– Σ Bond energies of reactants

$2 \times -46 = 712 + 3 \times (436) - 6x; -92 = 2020 - 6x$

$6x = 2020 + 92 \Rightarrow 6x = 2112 \Rightarrow x = +352$ kJ/mol

26. **(b)** At equilibrium $\Delta G = 0$

Hence, $\Delta G = \Delta H - T_e\Delta S = 0$

$\therefore \Delta H = T_e\Delta S$ or $T_e = \dfrac{\Delta H}{\Delta S}$

For a spontaneous reaction

ΔG must be negative which is possible only if $\Delta H < T\Delta S$

or $T > \dfrac{\Delta H}{\Delta S}; \ T_e < T$

27. **(a)** Entropy change for an isothermal reversible process is given by

$$\Delta S = nR\ln\frac{V_2}{V_1} = 2 \times 8.314 \times 2.303 \log\frac{100}{10}$$

$$= 38.3\ \text{J mol}^{-1}\ K^{-1}$$

28. **(c)** $\Delta G° = \Delta H° - T\Delta S°; \ -RT\ \ell nK = \Delta H° - T\Delta S°$

$$\ell nK = -\frac{\Delta H° - T\Delta S°}{RT}$$

30. **(a)** $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

Bomb calorimeter gives ΔU of the reaction

Given, $\Delta U = -1364.47\ \text{kJ mol}^{-1}$

$\Delta n_g = -1$

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

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000} = -1366.93\ \text{kJ mol}^{-1}$$

31. **(b)** Given

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

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

$\therefore$ Heat of formation of CO = eqn(i) – eqn(ii)

$= -393.5 - (-283.5) = -110\ kJ$