Thermodynamics

1. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

2. The heat of neutralisation of strong base and strong acid is 57.0 kJ. Calculate the heat released when 0.5 mole of HNO_3 is added to 0.20 mole of NaOH solution.

3. Given

Reaction	**Energy Change (in kJ)**
$Li(s) \rightarrow Li(g)$	161
$Li(g) \rightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
$F(g) + e^- \rightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \rightarrow Li\,F(s)$	– 1047
$Li\,(s) + \frac{1}{2}F_2(g) \rightarrow Li\,F(s)$	– 617

Based on data provided, find the value of electron gain enthalpy of fluorine.

4. The standard enthalpy of formation of NH_3 is – 46.0 kJ/mol. If the enthalpy of formation of H_2 from its atoms is – 436 kJ/mol and that of N_2 is – 712 kJ/mol, find the average bond enthalpy of N – H bond in NH_3.

5. The enthalpy of neutralization of a weak acid in 1 M solution with a strong base is –56.1 kJ mol^{-1}. If enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is –57.3 kJ equiv^{-1}, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

6. The heat of sublimation of iodine is 24 cal g^{-1} at 50°C. If specific heat of solid iodine and its vapour are 0.055 and 0.031 cal g^{-1} respectively, Calculate the heat of sublimation of iodine at 100°C.

7. When 0.2 mole of anhydrous $CuSO_4$ is dissolved in water, the heat evolved is 1.451 kcal. If 0.2 mole of $CuSO_4.5H_2O$ is dissolved in water, the heat absorbed is 0.264 kcal. Calculate the molar heat of hydration of $CuSO_4$.

8. The specific heat of a monoatomic gas at constant pressure is 248.2 J kg^{-1} K^{-1} and at constant volume it is 149.0 J kg^{-1} K^{-1}. Find the mean molar mass of the gas.

9. The standard entropies of $CO_2(g)$, $C(s)$ and $O_2(g)$ are 213.5, 5.740 and 205 JK^{-1} respectively. Calculate the standard entropy of formation of $CO_2(g)$.

10. Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4(l)$ which in turn is produced from mineral rutile $TiO_2(s)$. Calculate the Gibb's free energy for the following reaction

$$TiO_2(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + O_2(g)$$

Given that: H_f° for $TiO_2(s)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are – 944.7, –804.2, 0.0, 0.0 kJ mol^{-1}

Also S° for $TiO_2(g)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are 50.3, 252.3, 233.0, 205.1 J mol^{-1} K^{-1} respectively.

11. One mole of CH_3COOH undergoes dimerization in vapour phase at 127°C as:

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

if dimer formation is due to two H-bonds involved in dimer, each of 33 kJ strength and the degree of dimerisation of acetic acid 98.2%. Calculate the change in standard entropy during dimerization.

12. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800ºC are given as :

$S_2(s) + 2O_2(g) \longrightarrow 2SO_2(g)$; $\Delta G = -544$ kJ

$2Zn(s) + S_2(s) \longrightarrow 2ZnS(s)$; $\Delta G = -293$ kJ

$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$; $\Delta G = -480$ kJ

Calculate the ΔG for the reaction :

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

13. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJmol^{-1} and 108.8 JK^{-1} mol^{-1}, respectively. Find the temperature at which Gibbs energy change (ΔG) for this transformation will be zero.

14. An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. Calculate the work done in kJ.

15. During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. Calculate the change in internal energy (in kJ)

SOLUTIONS

1. **(395)** Since, work is done against constant pressure and thus, irreversible.

Given, $\Delta V = (6-2) = 4\text{ L}$; $P = 1\text{ atm}$

$\therefore\ W = -1 \times 4\text{ L-atm} = -\dfrac{1\times 4\times 1.987}{0.0821}\text{ cal}$

(since $0.0821\text{ L-atm} = 1.987\text{ cal}$)

$= -96.81\text{ cal} = -96.81\times 4.184\text{ J}\ (\because 1\text{ cal} = 4.184\text{ J})$

$= -405.05\text{ J}$

Now from I^{st} law of thermodynamics

$q = \Delta U - W$

$800 = \Delta U + 405.05$

$\therefore\ \Delta U = 395\text{ J}$

2. **(11.4)** Given;

$$\underset{\substack{1\text{ mole}\\0.2\text{ mole}}}{NaOH}+\underset{\substack{1\text{ mole}\\0.5\text{ mole}}}{HNO_3}\rightarrow NaNO_3+\underset{\substack{\Delta H=57.0\text{ kJ}\\\Delta H=?}}{H_2O}$$

Given heat of neutralisation of strong acid by strong base $= 57.0\text{ kJ}$

$\because$ 0.2 mole NaOH is limiting reagent.

$\therefore$ Heat of neutralization $= 0.2\times 57 = 11.4\text{ kJ}$

3. **(–328)** Applying Hess's Law

$$\Delta_f H^\circ = \Delta_{sub}H + \frac{1}{2}\Delta_{diss}H + I.E. + E.A + \Delta_{lattice}H$$

$-617 = 161 + 520 + 77 + E.A. + (-1047)$

$E.A. = -617 + 289 = -328\text{ kJ mol}^{-1}$

$\therefore$ electron affinity of fluorine

$= -328\text{ kJ mol}^{-1}$

4. **(–964)** Given $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$;

$$\Delta H_f = -46.0\text{ kJ / mol}$$

$H + H \rightleftharpoons H_2;\ \Delta H_f = -436\text{ kJ / mol}$

$N + N \rightleftharpoons N_2;\ \Delta H_f = -712\text{ kJ / mol}$

$\Delta H_f(NH_3) = \frac{1}{2}\Delta H_{N-N} + \frac{3}{2}\Delta H_{H-H} - \Delta H_{N-H}$

$-46 = \frac{1}{2}(-712) + \frac{3}{2}(-436) - \Delta H_{N-H}$

On calculation

$\Delta H_{N-H} = -964\text{ kJ / mol}$

5. **(20)** $HA + aq \rightarrow H^+_{(aq)} + A^-_{(aq)}, \Delta H = x\text{ kJ mol}^{-1}$

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)}\ \Delta H = -57.3\text{ kJ mol}^{-1}$

Hence, $HA + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + A^-_{(aq)},$

$\Delta H = x - 57.3$

But $\Delta H = x - 57.3 = -56.1$ (given),

$x = 1.2\text{ kJ mol}^{-1}$

if no self ionization of HA occurs at all,

$\Delta H(\text{ionization}) = 1.5\text{ kJ mol}^{-1}$

Hence, % ionization in 1 M solution

$= \dfrac{(1.5-1.2)}{1.5}\times 100 = 20$

6. **(22.8)** $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

$\Delta H_2 - 24 = (0.031 - 0.055)(100-50)$

$\Rightarrow\ \Delta H_2 = 22.8\text{ calg}^{-1}$

7. **(–17.15)** (i)

$CuSO_4(s) + H_2O \longrightarrow CuSO_4(aq)$

$\Delta H = \dfrac{-1.451}{0.2} = -7.255\text{ k cal mol}^{-1}$

(ii) $CuSO_4.5H_2O(s) + H_2O \longrightarrow CuSO_4(aq)$

$\Delta H = \dfrac{0.264}{0.2} = 1.32\text{ k cal mol}^{-1}$

From (i) – (ii),

$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);$

$\Delta H = -28.575\text{ k cal mol}^{-1}$

8. **(83.8)** Molar heat capacity at constant pressure,

$C_p = 248.2\times M\text{ J kg}^{-1}$

where M is the molar mass of the gas.

Similarly, $C_v = 149\times M\text{ J kg}^{-1}$

$C_p - C_v = R$

$\therefore\ 248.2\times M - 149M = 8.314$

$M = \dfrac{8.314}{248.2-149} = 0.0838\text{ kg/mol}$

Molar mass of the gas = 83.8 g/mol

9. **(2.76)** Given :

$\Delta S^\circ_{CO_2} = 213.5\text{ JK}^{-1}$;

$\Delta S^\circ_{C(s)} = 5.74\text{ JK}^{-1}$;

$\Delta S^\circ_{O_2} = 205\text{ JK}^{-1}$

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

Standard entropy of formation of $CO_2(g)$

$= \Delta S^\circ_{CO_2} - [\Delta S^\circ_{C(s)} + \Delta S^\circ_{O_2}]$

$= 213.5 - [5.740 + 205] = 2.76\text{ JK}^{-1}$

10. **(158)** ΔH° for reaction

$= \left[\overset{\circ}{H}_{TiCl_4}(l) + \overset{\circ}{H}_{O_2}(g) - \overset{\circ}{H}_{TiO_2} - \overset{\circ}{H}_{Cl_2}\times 2\right]$

$= \left[-804.2 + 0.0 - (-944.7) - 0.0\right] = 140.5\text{ kJ}$

Also, ΔS° for reaction

$= \left[\overset{\circ}{S}_{TiCl_4}(l) + \overset{\circ}{S}_{O_2}(g) - \overset{\circ}{S}_{TiO_2}(s) - \overset{\circ}{S}_{Cl_2}(g)\times 2\right]$

$= [252.3 + 205.1 - 50.3 - 2\times 233.0]$

$= -58.9\text{ J} = -0.0589\text{ kJ K}^{-1}$

Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= 140.5 - 298\times(-0.0589) = 158\text{ kJ}$

11. **(–104)** $2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$

$$\begin{array}{cc} 1 & 0 \\ 1-0.982 & \dfrac{0.982}{2} \end{array}$$

$$K = \frac{(CH_3COOH)_2}{(CH_3COOH)^2} = \frac{0.982}{2 \times (0.018)^2} = 1515.4$$

Now, ΔH° for dimerization $= -2 \times 33$ kJ $= -66$ kJ

Thus, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-2.303\ RT \log K^\circ = \Delta H^\circ - T\Delta S^\circ$

$-2.303 \times 8.314 \times 400 \times \log(1515.4)$

$= -66 \times 10^3 - 400 \times \Delta S^\circ$

$-242359.2 = -66000 - 400\ \Delta S^\circ$

$$\Delta S^\circ = -\frac{41640.8}{400} = -104\ JK^{-1}\ mol^{-1}$$

12. **(–731)** For the reaction

$2\ ZnS \rightarrow 2\ Zn + S_2$; $\Delta G_1^o = 293$ kJ ....(i)

$2\ Zn + O_2 \rightarrow 2\ ZnO$; $\Delta G_2^o = -480$ kJ ....(ii)

$S_2 + 2\ O_2 \rightarrow 2\ SO_2$; $\Delta G_3^o = -544$ kJ ....(iii)

ΔG^o for the reaction

$2\ ZnS + 3O_2 \rightarrow 2\ ZnO + 2SO_2$

can be obtained by adding eqn. (1), (2) and (3)

$\Rightarrow \Delta G^o = 293 - 480 - 544 = -731$ kJ

13. **(373.4)** $H_2O(l) \xrightleftharpoons{1atm} H_2O(g)$

$\Delta H = 40630\ J\ mol^{-1}$

$\Delta S = 108.8\ JK^{-1}\ mol^{-1}$

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

When $\Delta G = 0$,

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

$$T = \frac{\Delta H}{\Delta S} = \frac{40630\ J\ mol^{-1}}{108.8\ J\ mol^{-1}} = 373.4\ K.$$

14. **(–0.9)** $w = -P\Delta V$

$= -(1\ bar) \times (9\ L)$

$= -(10^5\ Pa) \times (9 \times 10^{-3})\ m^3$

$= -9 \times 10^2\ N\ m$

$= -900\ J = -0.9\ kJ$

15. **(8)** $w = 10$ kJ

$q = -2$ kJ

$\Delta U = q + w = -2 + 10 = 8$ kJ