HINTS & SOLUTIONS WORKBOOK - 2

Thermodynamics

Daily Tutorial Sheet	Level-0

Very Short Answer Type (1 Mark)

1. $\Delta H = \Delta U + \Delta n_g RT, \qquad \Delta n_g = 1-3 = -2$

2. $\Delta U = \dfrac{-22.3\,\text{kJ}}{0.532} \times 78$

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

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

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

3. **(iii)** $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$

$\Delta n_g = \left(n_p - n_r\right) = 1-3 = -2$

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

$\Delta H^\circ = -X - 2RT$

$\Delta H^\circ < \Delta U^\circ$, hence option (iii) is correct

4. Enthalpy change for the conversion of 1 mole liquid water at 10°C into 1 mole liquid water at 0°C,

$\Delta H_1 = C_p\,H_2O(\ell) \times \Delta T = -75.3\,\text{J mol}^{-1}\,\text{K}^{-1} \times 10\text{K} = -753\,\text{J mol}^{-1}$

Enthalpy of fusion,

$\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}} = -6.03\,\text{kJ mol}^{-1}$

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at 10°C,

$\Delta H_3 = C_p H_2O(s) \times \Delta T = -36.8\,\text{J mol}^{-1}\,\text{K}^{-1} \times 10\,\text{K} = -368\,\text{J mol}^{-1}$

$\Delta H_{\text{total}} = -\left(0.753 + 6.03 + 0.368\right)\text{kJ mol}^{-1} = -7.151\,\text{kJ mol}^{-1}$

5. Enthalpy change for the formation of 1 mole of $H_2O(\ell)$,

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell); \quad \Delta_f H^\circ = -286\,\text{kJ mol}^{-1}$

Energy released in the above reaction, is absorbed by the surroundings.

It means $q_{\text{surr}} = +286\,\text{kJ mol}^{-1}$

$\Delta S = \dfrac{q_{\text{surr}}}{T} = \dfrac{+286\,\text{kJ mol}^{-1}}{298\,\text{K}} = 0.9597\,\text{kJ K}^{-1}\,\text{mol}^{-1} = 959.7\,\text{J K}^{-1}\text{mol}^{-1}$

6. The two condition under heat becomes independent of path are

(i) when volume remains constant

(ii) when pressure remains constant

Short Answer Type-I (2 Marks)

7. **(A)** $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(\ell)$

58 gm butane $\longrightarrow$ 2658 kJ energy

11200 gm butane $= \frac{2658}{58} \times 11200\,\text{kJ}$ energy

$\therefore$ Number of days $= \frac{2658}{58} \times \frac{11200}{20000} = 26\,\text{days}$

(B) Number of days $= 26 \times 0.67 = 17\,\text{days}$

8. Given that, quantity of water = 18.0 g, pressure = 1 bar

As we know that, 18.0 g H_2O = 1 mole H_2O

Enthalpy change for vaporizing 1 mole of H_2O = 40.79 kJ mol^{-1}.

$\therefore$ Enthalpy change for vaporizing 2 moles of $H_2O = 2 \times 40.79$ kJ = 81.358kJ

Standard enthalpy of vaporization at 100°C and 1 bar pressure $\Delta_{vap}H^{-} = +40.79\,\text{kJ mol}^{-1}$

9. Given that $C_v =$ heat capacity at constant volume.

$C_p =$ heat capacity at constant pressure

Difference between C_p and C_v is equal to gas constant (R).

$C_p - C_v = nR$ (where, n = no. of moles)

$= 10 \times 4.184\,\text{J} = 41.84\,\text{J}$

10. In the first case, as the expansion is against constant external pressure

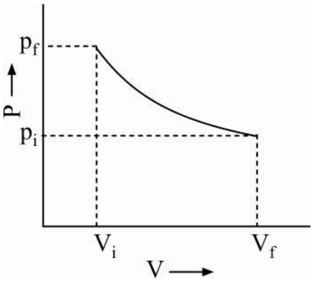
$W = -\rho_{ext}\left(V_2 - V_1\right) = -2\text{bar} \times \left(50 - 10\right)\text{L}$

$= -80\text{L bar}$ (1L bar = 100 J)

$= -80 \times 100\,\text{J} = -8\text{kJ}$

If the given expansion was carried out reversibly, the internal pressure of the gas should be greater than the external pressure at every stage. Hence, the work done will be more.

11. When compression is carried out in infinite steps with change in pressure, it is a reversible process. The work done can be calculated from p – V plot as shown in the given figure. Shaded area under the curve represents the work done on the gas.



12. No, enthalpy is one of the contributing factors in deciding spontaneity but it is not the only factor. Another contributory factor, entropy factor has also to be taken into consideration.

13. **(a)** The net enthalpy change, ΔH for a cyclic process is zero as enthalpy change is a state function, i.e., ΔH (cycle) = 0

(b) Gibbs energy for a reaction in which all reactants and products are in standard state $\Delta_r G^o$ is related to the equilibrium constant of the reaction as follows

$$\Delta_r G = \Delta_r G^o + RT\,\ln Q$$

At equilibrium, $0 = \Delta_r G° + RT \ln K$ $(\because \Delta_r G = 0)$ & $Q = k_{eq}$

or $\Delta_r G^o = -RT \ln K$

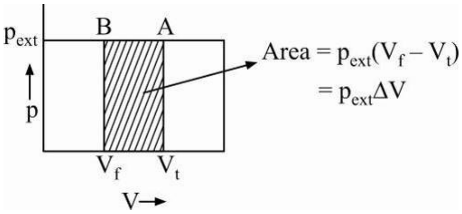
$\Delta_r G^o = 0$ when $K = 1$

For all other values of K, $\Delta_r G^o$ will be non-zero.

Short Answer Type-II (3 Marks)

14. Suppose total volume of the gas is V_i and pressure of the gas inside cylinder is p. After compression by constant external pressure, (p_{ext}) in a single step, final volume of the gas becomes V_f.

Then volume change, $\Delta v = (V_f - V_i)$



If W is the work done on the system by movement of the piston, then

$W = p_{ext}(-\Delta V)$

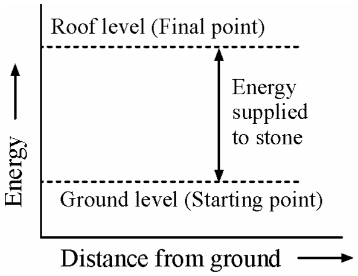
$W = -p_{ext}(V_f - V_i)$

This can be calculated from p – V graph as shown in the figure. Work done is equal to the shaded area ABV_fV_i

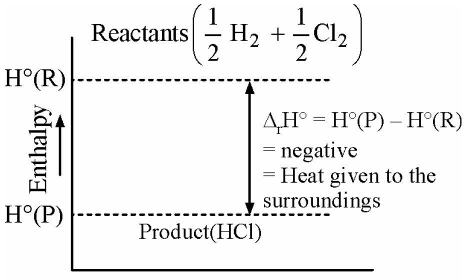
The negative sign in this expression is required to obtain conventional sign for W which will be positive. Because incase of compression work is done on the system, so ΔV will be negative.

15. Representation of potential energy/enthalpy change in the following processes

(a) Throwing a stone from the ground to roof.



(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$; $\Delta_r H^o = -92.32$ kJ mol^{-1}



Energy increases in (a) and it decreases in (b) process. Hence, in process (b), enthalpy change is the contributing factor to the spontaneity

16. The given diagram represent that the process is carried out in infinite steps, hence it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm to 1.0 atm 298 K.

$$W = -2303\,nRT\ \log\frac{\rho_1}{\rho_2}$$

$$W = -\ 2.303 \times 1\,mol \times 8.314\,J\,K^{-1}\,mol^{-1} \times 298\,K \log 2 \qquad \left(\because \frac{\rho_1}{\rho_2} = \frac{2}{1}\right)$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010 J$$

$$W = -1717.46\ J$$

17. As $\left(C_p - C_v\right) = R \quad \Rightarrow \quad C_p = C_v + R$

$\Rightarrow \qquad C_p = {}^{3}\!/_{2}R + R = {}^{5}\!/_{2}R$

Heat given at constant pressure

$$\left(\Delta H\right) = nC_p\Delta T = 1 \times {}^{5}\!/_{2}R \times \left(373 - 298\right)$$

$$\Rightarrow \qquad \left(\Delta H\right) = 1 \times {}^{5}\!/_{2} \times 1.987 \times 75 = 372.56\ cal$$

Work done in the process $= -P\Delta V$

$$= -P\left(V_2 - V_1\right) = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right) \qquad \text{(As, PV = nRT)}$$

$$= -\ nR\left(T_2 - T_1\right) = -1 \times 1.987 \times \left(373 - 298\right) = 149.05\,cal$$

From first law of thermodynamics

$$\Delta E = q + W = 372.56 - 149.05 = 223.51\,cal$$

18. $\because$ Work is carried out at constant P and thus irreversible.

Work done $= -P \times \Delta V = 1 \times \left(2.5 - 2.0\right) = -\ 0.5\,litre\,atm$

$$= -\frac{0.5 \times 1.987 \times 4.184}{0.0821}\ joule = -\ 50.63\,J$$

From I law of thermodynamics

$\because \qquad q = \Delta E - W$

$300 = \Delta E + 50.63$

$\therefore \qquad \Delta E = 249.37\ joule$

19. Volume of 1 mole liquid = 100 mL at pressure 1 bar

Volume of 1 mole liquid = 99 mL at pressure 100 bar

The process being irreversible as it is steeply changed from 1 bar to 100 bar

$\therefore \qquad w = -P\ (V_2 - V_1) = -100 \times (99 - 100) = 100$ bar mL

Also $\qquad \Delta E = q + w$

$\Delta E = w \qquad (\therefore\ q = 0$, adiabatic nature due to insulation)

$\therefore \qquad \Delta E = 100\,bar\ mL$

Also $\qquad \Delta H = \Delta E + P\Delta V = \Delta E + \left(P_2V_2 - P_1V_1\right)$

$= 100 + (100 \times 99 - 1 \times 100) = 9900$ bar mL

Long Answer Type (5 Marks)

20. $w = -2.303\,nRT\ \log\dfrac{V_2}{V_1}$

(i) where w is work done by the system under isothermal reversible conditions (work done by the system is negative)

$$-10\times10^3 = -2.303\times1\times8.314\times T\ \log\frac{P_1}{P_2} \qquad ......(i)$$

Also, $P_1V_1 = P_2V_2$ (at constant temperature)

$\therefore \quad 1\times10^7\times V_1 = P_2\times10\,V_1$

$\therefore \quad P_2 = \dfrac{1\times10^7}{10} = 10^6\,\text{Pa}$

From Eq. (i)

$$-10\times10^3 = -2.303\times1\times8.314\times T\log\frac{10^7}{10^6}$$

$T = 522.27\,\text{K}$

Using PV = nRT for one mol of gas

$1\times10^7\times V_1 = 1\times8.314\times522.27$

$\therefore \quad V_1 = 4.34\times10^{-4}\ \text{m}^3$

(ii) If 2 moles of gas have been used, the temperature would have been $\dfrac{522.27}{2} = 261.13\,\text{K}$

21. We know,

Path CA – Isothermal compression

Path AB – Isobaric expansion

Path BC – Isochoric change

Let V_1 and V_f are initial volume and final volume at respective points.

For temperature T_1 (For C) :

$PV = nRT_1$

$2\times10 = 1\times0.0821\times T_1$

$T_1 = 243.60$ K

For temperature T_2 (For C and B):

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

$$\frac{2\times10}{T_1} = \frac{20\times10}{T_2}$$

$\therefore \quad \dfrac{T_2}{T_1} = 10 \qquad \therefore \quad T_2 = 243.60\times10 = 2436.0$ K

Path CA : $W = +2.303\,nRT_1\ \log\dfrac{V_i}{V_f} = 2.303\times1\times2\times243.6\log\dfrac{10}{1} = +1122.02$ cal

$\Delta E = 0$ for isothermal compression; Also $q = W$

Path AB : $W = -P(V_f - V_i)$

$$= -20 \times (10 - 1) = -180 \text{ litre atm}$$

$$= \frac{-180 \times 2}{0.0821} = -4384.9 \text{ cal}$$

Path BC : $W = -P(V_f - V_i) = 0$ ($\because$ $V_f - V_i = 0$) since volume is constant

For monoatomic gas heat change at constant volume $= q_v = \Delta E$

Thus for path BC :

$$q_v = C_v \times n \times \Delta T = \Delta E$$

$$\therefore \quad q_v = \frac{3}{2}R \times 1 \times (2436 - 243.6) = \frac{3}{2} \times 2 \times 1 \times 2192.4 = 6577.2 \text{ cal}$$

Since process involves cooling

$$\therefore \quad q_v = \Delta E = -6577.2 \text{ cal}$$

Also in path AB, the internal energy in state A and state C is same. Thus during path AB, an increase in internal energy equivalent of change in internal energy during path BC should take place. Thus ΔE for path AB = +6577.2 cal

Now q for path $AB = \Delta E - W_{AB} = 6577.2 + 4384.9 = 10962.1$ cal

Cycle: $\Delta E = 0$;

$$q = -W = -[W_{\text{path CA}} + W_{\text{path AB}} + W_{\text{path BC}}]$$

$$= -[+1122.02 + (-4384.9) + 0]$$

$$\therefore \quad q = -W = +3262.88 \text{ cal}$$

22. For adiabatic expansion,

$$T^{\gamma}P^{1-\gamma} = \text{const.}$$

$$\Rightarrow \quad \left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$$

$$\gamma \times \log\frac{T_1}{T_2} = (1-\gamma)\log\frac{P_2}{P_1}$$

$$\Rightarrow \quad 1.4\log\frac{273}{T_2} = (1-1.4)\log\frac{1}{10}$$

$$\therefore \quad T_2 = 141.4 \text{ K}$$

Work done in adiabatic expansion in L atm $= \frac{nR}{(\gamma-1)}(T_2 - T_1) = \frac{14}{32} \times \frac{0.0821(141.4 - 273)}{(1.4-1)}$

$$w_{\text{rev.}} = -11.82 \text{ L atm}$$

In calorie $= \frac{14}{3} \times \frac{2 \times (141.4 - 273)}{(1.4-1)}$

$$w_{\text{rev.}} = -287.88 \text{ cal}$$

23. Initially n = 3 mole,

$$T_1 = 200\text{ K},\ P_1 = 2.0\text{ atm},\ C_v = 27.5\text{ JK}^{-1}\text{ mol}^{-1}$$

After compression

$$T_2 = 250\text{ K},\ P_2 = ?$$

$\therefore \quad C_P = 27.5 + 8.314\,JK^{-1}\,mol^{-1} = 35.814\,JK^{-1}\,mol^{-1}$

$\therefore \quad \frac{C_P}{C_v} = \frac{35.814}{27.5} = 1.30 = \gamma$

$\therefore \quad P_1^{1-\gamma} \cdot T_1^{\gamma} = P_2^{1-\gamma} \cdot T_2^{\gamma}$

$\therefore \quad P_2^{1-\gamma} = P_1^{1-\gamma}\left(\frac{T_1}{T_2}\right)^{\gamma}$

$$(P_2)^{-0.3} = (2)^{-0.3} \times \left(\frac{200}{250}\right)^{1.30}$$

$\therefore \quad P_2 = 5.2\,atm$

Let the final pressure be P_2 and volume be V_2. $\left(\therefore V = \frac{nRT}{P} = \frac{3 \times 0.0821 \times 200}{2} = 24.63 \text{ litre}\right)$

Now for volume $V_2 : P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$\therefore \quad \left[\frac{V_2}{V_1}\right]^{\gamma} = \frac{P_1}{P_2}$

$\therefore \quad \left[\frac{V_2}{24.63}\right]^{1.3} = \frac{2}{5.2}$

$\therefore \quad V_2 = 11.8\,litre$

For adiabatic process $q = 0$

Since whole of the work done is made on the cost of internal energy of the system.

Thus $\quad \Delta E = W = +4.157\,kJ$

Also $\quad \Delta H = m \times C_p \times \Delta T = 3 \times 35.814 \times 50 = 5372.1 = 5.372\,kJ$

24. Let, ΔS_1 = Entropy change due to fusion of ice.

$$\Delta S_1 = \frac{\Delta H_f}{T_f} = \frac{6000 \text{ J}}{273.1} = 21.96 \text{ Jmol}^{-1}\text{K}^{-1}$$

ΔS_2 = Entropy change for heating 1 mole of water from 273.1 K to 373.1 K at constant pressure.

Then, $\Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \ln\frac{T_2}{T_1} = C_p \times 2.303 \log\frac{T_2}{T_1}$

$$= 75.2 \times 2.303 \log\frac{373.1}{273.1}$$

$$= 75.2 \times 2.303 \times 0.1354$$

$$= 23.45 \text{ J mol}^{-1} \text{ K}^{-1}$$

ΔS_3 = Entropy change due to conversion of water into steam, or entropy change when water is in equilibrium with vapour.

$$\Delta S_3 = \frac{\Delta H_v}{T_v} = \frac{40600}{373.1} \text{J mol}^{-1}\text{K}^{-1} = 108.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$\therefore \quad$ Total entropy change = $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$\Delta S = 21.96 + 23.45 + 108.8 = 154.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

25. We have to find out $\Delta H_p = nC_p\ dt$

No. of moles of Ar

$$n = \frac{PV}{RT} = \frac{1\times1.25}{0.082\times300} = 0.05$$

For adiabatic expansion,

$TV^{(\gamma-1)}$ = Constant

$C_p = C_v + R = 12.48 + 8.314 = 20.8$ Joules

$$\therefore \quad \frac{C_p}{C_v} = 1 + \frac{R}{C_v}$$

$$\Rightarrow \quad \gamma = 1+\frac{R}{C_v} \quad \Rightarrow \quad \gamma^{-1} = \frac{R}{C_v} \quad \Rightarrow \quad TV^{(R/C_v)} = \text{Constant}$$

$$\Rightarrow \quad T_1V_1^{(R/C_v)} = T_2V_2^{(R/C_v)} \quad \Rightarrow \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{R/C_v}$$

$$\Rightarrow \quad \ln\frac{T_1}{T_2} = \frac{R}{C_v}\ln\frac{V_2}{V_1} = \frac{8.314}{12.48}\ln\frac{2.50}{1.25}$$

Antilog 0.199 = 1.58

$$\Rightarrow \quad \log\frac{300}{T_2} = \frac{8.314}{12.48}\log 2 \quad \Rightarrow \quad \log\frac{300}{T_2} = 0.199 \quad \Rightarrow \quad \frac{300}{T_2} = 1.58 \quad \Rightarrow \quad T_2 = \frac{300}{1.58}$$

$T_2 = 189.87$ K

$\therefore \quad \Delta T = T_2 - T_1 = 189.87 - 300 = -110.13$

$\Delta H = 0.05 \times 20.8 \times (-110.13) = -114.53$ Joules