

Solution
Assignment - I

Q.1.

Critical temp (T_c) = $\frac{8a}{27Rb}$. So gas having highest $a:b$ value will have highest T_c . $a:b$ values for A, B and C are 148.148, 400 and 187.5. So, B has highest T_c .

Molecular volume depends on radius and again $b \propto r^3$. So, the greater the 'b' value, the greater is volume. Hence 'C' has largest vol.

The less the values of 'a' and 'b', the more is ideal behaviour. So, A has most ideal behaviour.

Q.2.

For n mole van der Waals gas the equation of state is

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

Here $n = \frac{100}{44} = 2.273$; $a = 3.59 \text{ lit atm mole}^{-2}$, $b = 0.0427 \text{ lit mol}^{-1}$
 $V = 5 \text{ litre}$ $R = 0.082 \text{ lit atm deg}^{-1} \text{ mol}^{-1}$.

$$T = (273 + 40) \text{ K} = 313 \text{ K}$$

$$\begin{aligned} \text{Now, } P &= \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \\ &= \frac{2.273 \times 0.082 \times 313}{5 - 2.273 \times 0.0427} - \frac{2.273^2 \times 3.59}{5^2} \\ &= 11.899 - 0.742 = 11.157 \text{ atm} \end{aligned}$$

If it behave ideally, its pressure would have been

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{2.273 \times 0.082 \times 313}{5} = 11.668 \text{ atm.}$$

$P_{\text{real}} < P_{\text{ideal}}$ due to intermolecular attraction.

Q.3.

From this description it is clear that $32.8^\circ\text{C} \equiv 305.8 \text{ K}$ is its critical temp and 48.2 atm is critical pressure.

$$\text{So, } T_c = \frac{8a}{27Rb} = 305.8$$

$$P_c = \frac{a}{27b^2} = 48.2$$

$$T_c/p_c = \frac{8b}{R} = 6.344$$

or $b = 0.065 \text{ litre mole}^{-1}$
 $= 65 \text{ cm mole}^{-1}$

$$b = 4N_A \cdot A/3 \pi (2r)^3$$

N_A = Avogadro Number

$$r = 1.86 \text{ } \text{\AA}$$

diameter $2r = 3.72 \text{ } \text{\AA}$ = minimum distance of approach between the centres of two molecules.

Here, $a = 27b^2 \cdot p_c$

$$= 27 \times (0.065)^2 \times 48.2$$

$$= 5.498 \text{ litre}^2 \text{ atm mole}^{-2}$$

$$\therefore \text{Boyle's temperature} = \frac{a}{Rb} = \frac{5.498 \text{ litre}^2 \text{ atm mole}^{-2}}{0.082 \text{ litre atm mol}^{-1} \text{ deg}^{-1} \times 0.065 \text{ litre mol}^{-1}}$$

$$= 1031.5 \text{ deg (K)}$$

Q4.

For a Van der Waals gas

$$Z = \frac{Pv}{RT} = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{v}$$

$$\text{Putting } v \cong \frac{RT}{P}$$

$$Z = 1 + \left(b - \frac{a}{RT} \right) \frac{P}{RT} = 1 + \frac{bP}{RT} \left(1 - \frac{a}{RbT} \right)$$

$$\text{or } Z = 1.000054$$

$$\therefore \frac{a}{Rb} = \text{Boyle temp} = 107 \text{ K}, P = 1 \text{ atm}, T = 273 \text{ K}$$

$$\therefore 1.000054 = 1 + \frac{b \times 1}{0.082 \times 273} \left[1 - \frac{107}{273} \right]$$

$$\text{Solving, } b = 1.98 \times 10^{-3} \text{ litre mole}^{-1}$$

$$\text{But, } \frac{a}{Rb} = 107$$

$$\therefore \frac{a}{0.082 \times 1.98 \times 10^{-3}} = 107$$

$$\therefore a = 0.0173 \text{ litre}^2 \text{ atm mole}^{-2}$$

$$b = \frac{4}{3} \pi N_A \cdot \frac{4}{3} \pi (2)^3 = 1.98 \text{ cm}^3 \text{ mole}^{-1}$$

$$\therefore \gamma = 5.8 \times 10^{-9} \text{ cm}$$

$$\therefore \text{diameter} = 2r = 11.6 \times 10^{-9} \text{ cm} = 1.16 \text{ } \text{\AA}$$

85.

For a Van der Waals gas

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66$$

$$\text{or } V_C = \frac{RT_C}{2.66 P_C}$$

$$\text{For gas A, } v_c = \frac{0.082 \times 49}{2.66 \times 26} = 0.052 \text{ lit mol}^{-1}$$

$$\text{For gas B, } V_c = \frac{0.082 \times 304}{2.66 \times 72} = 0.130 \text{ litre mol}^{-1}$$

Now, at 25°C and 10 torr pressure

$$T = (273 + 25) \text{ K} = 298 \text{ K}, \quad 1 \text{ torr} = 1 \text{ mm of Hg} = \frac{1}{760} \text{ atm}$$

$$1000 \text{ torr} = \frac{1000}{760} = \frac{100}{76} \text{ atm}$$

$$= 0.013 \text{ atm} \quad 1.315 \text{ atm}$$

$$\text{Reduced temp of A} = \frac{298}{44} = 6.77$$

$$11 \quad 11 \quad f_B = \frac{298}{304} = 0.98$$

$$\text{Reduced pressure of A} = \frac{0.1315}{26} = 0.005$$

$$\text{of } B = \frac{0.315}{72} = 0.004375$$

$\therefore A$ is more ideal than B .

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Energetics and dynamics of chemical reactions

Assignment - I

Solutions:

A-6

(a) Since compression factor is given as:

$$Z = \frac{V_m^o}{V_m} = \frac{0.9474 \text{ dm}^3 \text{ mol}^{-1}}{0.416 \text{ dm}^3 \text{ mol}^{-1}} = 2.277$$

$$Z > 1$$

So, repulsions dominant in these conditions.

(b) Critical compression factor (Z_c)

$$Z_c = \frac{p_c V_c}{R T_c}$$

Put the values of critical constants

$$Z_c = \frac{3}{8} = 0.375$$

A-7

Since the mass density ρ is related to the molar volume V_m by

$$V_m = \frac{M}{\rho}$$

Here M is the molar mass. Putting this relation into the perfect gas law gives:

$$pV_m = RT$$

$$\frac{pM}{\rho} = RT$$

$$M = \frac{\rho RT}{p} = \frac{(8.314 \text{ Pa m}^3 \text{ mol}^{-1}) \times [(100 + 273)\text{K}] \times (0.6388 \text{ kg mol}^{-1})}{16 \times 10^3 \text{ Pa}}$$

$$= 0.124 \text{ kg mol}^{-1} = 124 \text{ g mol}^{-1}$$

We can divide by the molar mass of phosphorus atoms to determine the number of atoms per gas molecule:

$$\frac{124 \text{ g mol}^{-1}}{31.0 \text{ g mol}^{-1}} = 4$$

So the desired formula is **P4**

A-8

The relation between pressure and temperature at constant volume can be derived from the perfect gas law:

$$pV = nRT$$

$$p \propto T$$

$$\begin{aligned} \frac{p_i}{T_i} &= \frac{p_f}{T_f} \\ p_f &= \frac{p_i T_f}{T_i} = \frac{125 \text{ kPa} \times (12 + 273) \text{ K}}{(25 + 273) \text{ K}} \\ &= 119.55 \text{ kPa} \end{aligned}$$

A-9

Since the van der Waals coefficients a and b are given as:

$$b = \frac{\overline{V}_C}{3}$$

&

$$a = 3P_C \overline{V}_C^2$$

$p_C = 45.6 \text{ atm}$, $\overline{V}_C = 98.7 \text{ cm}^3 \text{ mol}^{-1}$, and $T_C = 190.6 \text{ K}$

$$b = \frac{98.7 \text{ cm}^3 \text{ mol}^{-1}}{3} = 32.9 \text{ cm}^3 \text{ mol}^{-1} = 3.29 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

$$\begin{aligned} a &= 3 \times 45.6 \text{ atm} \times (98.7 \text{ cm}^3 \text{ mol}^{-1} \times 98.7 \text{ cm}^3 \text{ mol}^{-1}) = 1.33 \times 10^6 \text{ atm cm}^6 \text{ mol}^{-2} \\ &= 1.33 \text{ atm dm}^6 \text{ mol}^{-2} \end{aligned}$$

By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centers of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); that volume times the Avogadro constant is the molar excluded volume b

$$b = N_A \left(\frac{4\pi(2r)^3}{3} \right)$$

$$r = \frac{1}{2} \left(\frac{3b}{4\pi N_A} \right)^{1/3}$$

Putting the values of b and N_A ,

$$\begin{aligned} r &= \frac{1}{2} \left(\frac{3 \times 32.9 \text{ cm}^3 \text{ mol}^{-1}}{4\pi(6.022 \times 10^{23}) \text{ mol}^{-1}} \right)^{\frac{1}{3}} \\ &= \frac{1}{2} \left(\frac{98.7 \text{ cm}^3}{75.674 \times 10^{23}} \right)^{\frac{1}{3}} \\ &= \frac{1}{2} (13.04 \times 10^{-24} \text{ cm}^3)^{\frac{1}{3}} \\ &= 1.177 \times 10^{-8} \text{ cm} = 1.177 \times 10^{-8} \text{ m} \end{aligned}$$

A-10 Estimate the molar volume of chlorine gas on the basis of the perfect gas equation of state at 250 K and 150 kPa. Also calculate the percentage difference from the value predicted by the van der Waals equation. [Hint: For chlorine gas, $a = 6.260 \text{ atm dm}^6 \text{ mol}^{-2}$; $b = 5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$; $1 \text{ Pa} = 1.01 \times 10^{-5} \text{ atm}$].

For perfect gas equation,

$$V = \frac{RT}{p} = \frac{8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 250 \text{ K}}{1.48 \text{ atm}} = 13.86 \text{ dm}^3 \text{ mol}^{-1}$$

For van der Walls equation

$$p = \frac{RT}{V_m - b} - \frac{a}{V^2}$$

Rearranging for V_m ,

$$V_m = \frac{RT}{\left(p + \frac{a}{V^2} \right)} + b$$

Putting the values of a, b T and P,

$$\begin{aligned}V_m &= \frac{8.206 \times 10^{-2} \text{ dm}^3\text{atm K}^{-1}\text{mol}^{-1} \times 250 \text{ K}}{(1.48 \text{ atm}) + \left((6.260 \text{ atm dm}^6\text{mol}^{-2}) / (13.86)^2 \right)} + 5.42 \times 10^{-2} \text{ dm}^3\text{mol}^{-1} \\&= \frac{20.515 \text{ dm}^3\text{mol}^{-1}}{1.5126} + 5.42 \times 10^{-2} \text{ dm}^3\text{mol}^{-1} \\&= 13.616 \text{ dm}^3\text{mol}^{-1}\end{aligned}$$

Percentage difference

$$= \frac{(13.86 - 13.616)}{13.86} \times 100 = 1.76\%$$

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Energetics and dynamics of chemical reactions

Solutions Assignment - II

A-1

The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses (M) and their mass densities (ρ) by using $\rho = M/V_m$.

The change in enthalpy when the transition occurs is

$$\begin{aligned}\Delta H &= H(\text{aragonite}) - H(\text{calcite}) \\ &= \{U(a) + pV(a)\} - \{U(c) + pV(c)\} \\ &= \Delta U + p\{V(a) - V(c)\} = \Delta U + p\Delta V\end{aligned}$$

The volume of 1.0 mol CaCO_3 (100 g) as aragonite is 34 cm^3 , and that of 1.0 mol CaCO_3 as calcite is 37 cm^3 . Therefore,

$$p\Delta V = (1.0 \times 10^5 \text{ Pa}) \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

(because $1 \text{ Pa m}^3 = 1 \text{ J}$).

Hence,

$$\Delta H - \Delta U = -0.3 \text{ J}$$

which is only 0.1 per cent of the value of ΔU . We see that it is usually justifiable to ignore the difference between the enthalpy and internal energy of condensed phases, except at very high pressures, when pV is no longer negligible.

A-2

This is an expansion against a constant external pressure; hence

$$w = -p_{ext} dV$$

The change in volume is the cross-sectional area times the linear displacement:

$$dV = (50.0 \text{ cm}^2) \times (15 \text{ cm}) \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 = 7.5 \times 10^{-4} \text{ m}^3,$$

$$\text{so } w = -(121 \times 10^3 \text{ Pa}) \times (7.5 \times 10^{-4} \text{ m}^3) = -91 \text{ J} \text{ (as } 1 \text{ Pa m}^3 = 1 \text{ J}).$$

A-3

(a) $w = -p_{\text{ex}} \Delta V = \frac{-(7.7 \times 10^3 \text{ Pa}) \times (2.5 \text{ dm}^3)}{(10 \text{ dm m}^{-1})^3} = \boxed{-19 \text{ J}}$

(b) $w = -nRT \ln \left(\frac{V_f}{V_i} \right) [2.11]$

$$w = - \left(\frac{6.56 \text{ g}}{39.95 \text{ g mol}^{-1}} \right) \times \left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \right) \times (305 \text{ K}) \times \ln \frac{(2.5 + 18.5) \text{ dm}^3}{18.5 \text{ dm}^3}$$
$$= \boxed{-52.8 \text{ J}}$$

A-4

Isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \approx -\frac{\Delta V}{V \Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V \kappa_T}$$

A density increase of 0.08 percent means $\Delta V/V = -0.0008$. So the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21 \times 10^{-6} \text{ atm}^{-1}} = \boxed{3.6 \times 10^2 \text{ atm}}$$

A-5

Since the volume is fixed, $w = 0$.

Since $\Delta U = q$ at constant volume, $\boxed{\Delta U = +2.35 \text{ kJ}}$.

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p \quad [\Delta V = 0].$$

From the van der Waals equation [Table 1.6]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{so} \quad \Delta p = \frac{R\Delta T}{V_m - b} \quad [\Delta V_m = 0 \text{ at constant volume}].$$

$$\text{Therefore, } \Delta H = \Delta U + \frac{RV\Delta T}{V_m - b}.$$

From the data,

$$V_m = \frac{15.0 \text{ dm}^3}{2.0 \text{ mol}} = 7.5 \text{ dm}^3 \text{ mol}^{-1}, \quad \Delta T = (341 - 300) \text{ K} = 41 \text{ K}.$$

$$V_m - b = (7.5 - 4.3 \times 10^{-2}) \text{ dm}^3 \text{ mol}^{-1} = 7.46 \text{ dm}^3 \text{ mol}^{-1}.$$

$$\frac{RV\Delta T}{V_m - b} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (15.0 \text{ dm}^3) \times (41 \text{ K})}{7.46 \text{ dm}^3 \text{ mol}^{-1}} = 0.68 \text{ kJ}.$$

$$\text{Therefore, } \Delta H = (2.35 \text{ kJ}) + (0.68 \text{ kJ}) = \boxed{+3.03 \text{ kJ}}.$$

A-6

SOLUTION: Because the reaction is carried out at a constant pressure of 1.00 bar, $\Delta H = q_p = -572 \text{ kJ}$. To calculate ΔU , we must first calculate ΔV . Initially, we have three moles of gas at 298 K and 1.00 bar, and so

$$V = \frac{nRT}{P} = \frac{(3 \text{ mol})(0.08314 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})}{1.00 \text{ bar}} \\ = 74.3 \text{ L}$$

Afterward, we have two moles of liquid water, whose volume is about 36 mL, which is negligible compared with 74.3 L. Thus, $\Delta V = -74.3 \text{ L}$ and

$$\begin{aligned}\Delta U &= \Delta H - P\Delta V \\ &= -572 \text{ kJ} + (1.00 \text{ bar})(73.4 \text{ L}) \left(\frac{1 \text{ kJ}}{10 \text{ bar}\cdot\text{L}} \right) = -572 \text{ kJ} + 7.43 \text{ kJ} \\ &= -565 \text{ kJ}\end{aligned}$$

The numerical difference between ΔH and ΔU in this case is about 1%.

Solution of Assignment - II

Q. 7.

It is an irreversible expansion and the work is

$$W = P(V_2 - V_1) = P \left[\frac{nRT_2}{P} - \frac{nRT_1}{P} \right]$$

$$W = nR(T_2 - T_1) = 3 \times 1.987 (353 - 293) \text{ cal}$$

$$W = 357.66 \text{ cal}$$

Again $\int_{V_1}^{V_2} dV = \int_{T_1}^{T_2} nC_V dT = n \int_{T_1}^{T_2} C_V dT$

$$\text{or } \Delta V = 3 \int_{T_1}^{T_2} 7.5 dT + 3 \times 3.2 \times 10^{-3} \int_{T_1}^{T_2} T dT$$

Here $T_1 = 293 \text{ K}$ and $T_2 = 353 \text{ K}$

$$\text{So, } \Delta V = 3 \times 7.5 (353 - 293) + 3 \times 3.2 \times 10^{-3} \left(\frac{353^2}{2} - \frac{293^2}{2} \right)$$

$$\text{or } \Delta V = 1350 + 186.06 = 1536.06 \text{ cal}$$

$$\Delta H = \Delta U + P(V_2 - V_1) = 1536.06 + 357.66 \\ = 1893.72 \text{ cal}$$

We know when only mechanical work is done then heat absorbed at constant pressure $= \Delta H$
 So, heat absorbed $\therefore = 1893.72 \text{ cal.}$

Q. 8.

$$\text{Molar volume of Cu, } \bar{V}_m = \frac{63.5}{8.93} \text{ cc} = 7.11 \text{ cm}^3 = 7.11 \times 10^{-6} \text{ m}^3$$

$$\beta = 7.747 \times 10^{-6} \text{ Pa}^{-1} \quad \alpha = 49.2 \times 10^{-6} \text{ K}^{-1}$$

$$\text{Now } C_p - C_v = \frac{\alpha^2 \bar{V}_m T}{\beta} = \frac{(49.2 \times 10^{-6})^2 \times 7.11 \times 10^{-6} \times 298}{7.747 \times 10^{-6}} \\ = 0.662 \text{ J K}^{-1} \text{ mole}^{-1}$$

Q. 9.

$$\text{For a van der Waals gas } P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

This is a case of isothermal reversible expansion. So,

$$\text{work, } W = \int_{V_1}^{V_2} P dV$$

$$W = \int_{V_1}^{V_2} \left[\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right] dV$$

$$R = 0.08217 \text{ atm mol}^{-1} \text{ K}^{-1}$$

$$= nRT \ln \frac{V_2 - nb}{V_1 - nb} + n^2a \left[-\frac{1}{V_2} + \frac{1}{V_1} \right]$$

$$W = 2 \times 0.082 \times 300 \ln \frac{\frac{40 - 20 \times 0.057}{4 - 2 \times 0.057}}{2^2 \times 6.69 \left[\frac{1}{4} - \frac{1}{40} \right]}$$

$$= 108.548 \text{ litre-atm} = 2627 \text{ Cal}$$

Q. 10.

(i) This is a case of free expansion. For ideal gas in such case

$$W = 0, Q = 0; \Delta V = 0 \text{ and } \Delta H = 0.$$

Both the experiments (ii) and (iii) are done in a thermostat.

So, process is isothermal.

Hence, $\Delta V = \Delta H = 0$ for both experiments.

However expt. (ii) is irreversible and expt. (iii) is reversible.

So for (ii)

$$W = Q = P_{\text{ext}} (V_2 - V_1)$$

$$= P_2 \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right] = nRT \left[1 - \frac{P_2}{P_1} \right]$$

$$= 2 \times 1.987 \times 300 \left[1 - \frac{1}{2} \right]$$

$$R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$= 596.1 \text{ cal}$$

For case (iii) work is reversible, so,

$$W = Q = nRT \ln \frac{P_1}{P_2}$$

$$= 2 \times 1.987 \times 300 \ln \frac{2}{1}$$

$$= 826.37 \text{ cal.}$$

11.

$$C_V = 20.8 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$C_P = 29.1 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\gamma = \frac{C_P}{C_V} = \frac{29.1}{20.8} = 1.40$$

From adiabatic reversible equation,

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\therefore 1 \times 1 = P_2 \times 2^{1.4}$$

$$\therefore P_2 = 0.38 \text{ atm}$$

$$\text{Again, } T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\text{or } 273 \times 1 = T_2 \times 2^{0.4}$$

$$\text{or } T_2 = 206.9 \text{ K}$$

In adiabatic process, $\delta = 0$

$$W = C_V (T_1 - T_2)$$

$$= 20.9 (273 - 206.9)$$

$$= 1381.5 \text{ Joule}$$

$$W = -\Delta U$$

$$W = -n C_V (T_2 - T_1)$$

For 1 mole gas

$$W = C_V (T_1 - T_2)$$

$$\Delta U = C_V (T_2 - T_1) = -1381.5 \text{ Joule}$$

$$\Delta H = C_P (T_2 - T_1) = -1923.5 \text{ Joule.}$$

Q. 12.

This is a case of adiabatic compression. Had it been an ideal gas ΔU would have been $\Delta U = n C_V \Delta T = 5 \times 7 \times (400 - 300) = 3500 \text{ cal.}$

However, it is a real gas internal energy during compression has decreased to a certain extent.

$$\text{Hence, } \left(\frac{\partial U}{\partial V} \right)_T = \frac{n^2 a}{V^2} \text{ for real gas}$$

$$\text{or } \int dU = n^2 a \int_{V_1}^{V_2} \frac{dV}{V^2}$$

| For ideal gas

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$\text{or } \Delta U = m^2 a \left[-\frac{1}{V_1} + \frac{1}{V_2} \right]$$

$$= 5^2 \times 6.69 \left[-\frac{1}{10} + \frac{1}{100} \right]$$

$$= -15.05 \text{ liter atm} = -364 \text{ cal}$$

So, ~~internal~~ internal energy change = 364 cal.

Q. 13.

Joule Thomson coefficient

$$\mu = \left(\frac{dT}{dP} \right)_H = 0.0142 - 2.60 \times 10^{-4} P$$

$$\text{or } \int_{T_1}^{T_2} dT = 0.0142 \int_{P_1}^{P_2} dP - 2.60 \times 10^{-4} \int_{P_1}^{P_2} P dP$$

$$\left. \begin{array}{l} P_1 = 60 \text{ atm} \\ P_2 = 20 \text{ atm} \end{array} \right\}$$

$$\Delta T = -0.568 + 0.416 = -0.152 \text{ K}$$

Q. 14.

Case (a):

Isothermal expansion against 1 atm pressure

(i) Final temperature = Initial temp = $25^\circ\text{C} = 298 \text{ K}$

(ii) Heat absorbed = Work done

$$= RT \left[1 - \frac{P_2}{P_1} \right]$$

$$= 8.313 \times 298 \left[1 - \frac{1}{5} \right]$$

$$= 1981.82 \text{ Joule}$$

(iii) $\Delta U = 0$

(iv) $\Delta H = 0$

} as T is constant

Case (b)

Adiabatic reversible expansion:

$$T_1 P_1 \frac{1-\gamma}{\gamma} = T_2 P_2 \frac{1-\gamma}{\gamma}$$

$$298 \times 5 \frac{1-1.66}{1.66} = T_2 \quad [\because P_2 = 1 \text{ atm}]$$

$$\text{So, } T_2 = 157.15 \text{ K.}$$

(ii) Heat absorbed = 0.

$$(iii) \Delta U = C_V (T_2 - T_1)$$

$$= \frac{3}{2} \times 8.313 (157.15 - 298) \text{ Joule}$$

$$= -1756.34 \text{ Joule}$$

$$(iv) \Delta H = C_p (T_2 - T_1)$$

$$= \frac{5}{2} \times 8.313 (157.15 - 298) \text{ Joule}$$

$$= -2927.22 \text{ Joule.}$$

Q. 15.

monoatomic
Perfect gas = ideal gas monoatomic

Considering $PV = nRT$ equation,

$$\text{Temperature of state 1, } T_1 = \frac{PV}{nR}$$

$$= \frac{1 \times 1}{0.1 \times 0.082} = 121.95 \text{ K}$$

$$\text{Temperature of state 2, } T_2 = \frac{3 \times 1}{0.1 \times 0.082} = 365.85 \text{ K}$$

$$\text{, , State 3, } T_3 = \frac{3 \times 2}{0.1 \times 0.082} = 731.70 \text{ K}$$

$$\text{, , State 4, } T_4 = \frac{1 \times 2}{0.1 \times 0.082} = 243.90 \text{ K}$$

$$\text{Now } dG = dU + dW$$

$$= nC_V dT + \int_{V_1}^{V_2} P dV$$

In step 1:

$$W_1 = PdV = 0$$

$$dU_1 = 0.1 \times \frac{3}{2} \times 1.987 (365.85 - 121.95) \\ = 72.69 \text{ cal}$$

$$\text{So, } Q_1 = 72.69 \text{ cal.}$$

In step 2:

$$W_2 = \int_{V_1}^{V_2} PdV = P \int_{V_1}^{V_2} dV = P(V_2 - V_1) = 3(2-1) = 3 \text{ litr-atm} \\ = 72.6 \text{ cal}$$

$$dU_2 = 0.1 \times 1.987 \times \frac{3}{2} \times (731.70 - 365.85) = 109.04 \text{ cal}$$

$$Q_2 = 109.04 + 72.6 = 181.64 \text{ cal}$$

In Step 3:

$$W_3 = 0 \text{ as } dV = 0$$

$$dU_3 = 0.1 \times \frac{3}{2} \times 1.987 \times (243.9 - 731.7) = -145.38 \text{ cal}$$

$$\therefore Q_3 = -145.38 + 0 = -145.38 \text{ cal}$$

In Step 4:

$$W_4 = P \int_{V_1}^{V_2} dV = P_2(V_2 - V_1) = 1(1-2) = -1 \text{ litr-atm} = -24.2 \text{ cal}$$

$$dU_4 = 0.1 \times \frac{3}{2} \times 1.987 \times (121.95 - 243.9) \\ = -36.35 \text{ cal}$$

$$Q_4 = -36.35 - 24.2 = -60.54 \text{ cal}$$

S_g Total,

$$W = W_1 + W_2 + W_3 + W_4$$

$$= 0 + 72.6 + 0 - 24.2 = 48.4 \text{ cal}$$

$$Q = Q_1 + Q_2 + Q_3 + Q_4 = 72.69 + 181.64 - 145.38 - 60.54 = 48.41 \text{ cal}$$

$$dU = dU_1 + dU_2 + dU_3 + dU_4 = 72.69 + 109.04 - 145.38 - 36.35 = 0$$

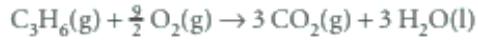
The process is cyclic so state functions will not change. As $dU = 0$, but $Q \neq 0$ and $W \neq 0$, so only U is a state function.

For monoatomic ideal gas $C_V = \frac{3}{2} R$
 $R = 1.987 \text{ cal}$

CHM202
Energetics and dynamics of chemical reactions
Solutions Assignment - III

A-1

Answer The combustion reaction we require is



This reaction can be recreated from the following sum:

	$\Delta_r H^\circ / (\text{kJ mol}^{-1})$
$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$	-124
$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$	-2220
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	+286
$\text{C}_3\text{H}_6(\text{g}) + \frac{9}{2} \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$	<hr/> -2058

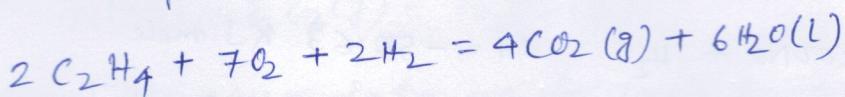
Assignment - III: Thermochemistry

Q. 2.

Given

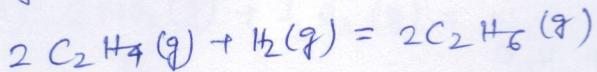
- (i) $C_2H_4(g) + 3O_2(g) = 2CO_2(g) + 2H_2O(l)$ $\Delta H = -337.3 \text{ Kcal}$
 (ii) $2H_2(g) + O_2(g) = 2H_2O(l)$ $\Delta H = -136.6 \text{ Kcal}$
 (iii) $C_2H_6(g) + 7O_2(g) = 4CO_2(g) + 6H_2O(l)$ $\Delta H = -745.6 \text{ Kcal}$

We multiply equn(i) by 2 and add the product with equn(ii) to get



$$\text{and } \Delta H = 2(-337.3) + (-136.6) = -811.2 \text{ Kcal}$$

If from this equn we subtract equn(iii) then we get,



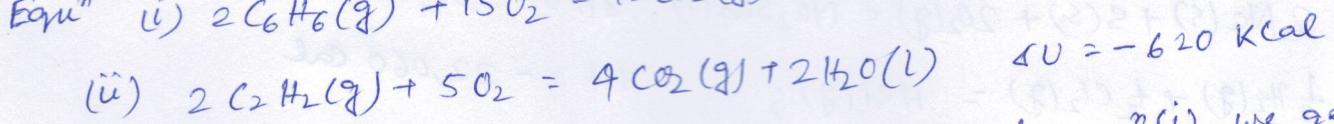
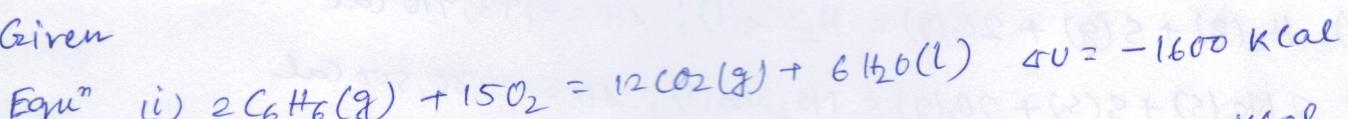
$$\Delta H = -811.2 - (-745.6) = -65.6 \text{ Kcal}$$

So, for $C_2H_4 + H_2 = C_2H_6$ reaction,

$$\Delta H = -\frac{65.6}{2} = -32.8 \text{ Kcal.}$$

Q. 3.

Given

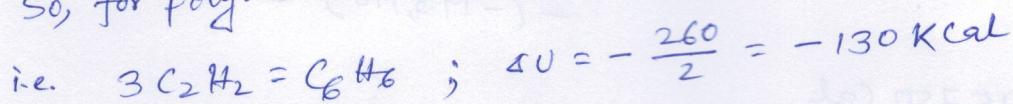


If we multiply equn (ii) with 3 and then subtract equn (i), we get



$$\Delta U = 3(-620) - (-1600) = -260 \text{ Kcal}$$

So, for polymerisation reaction



This is heat of reaction at constant volume.

Here $\Delta n = 1 - 3 = -2$.

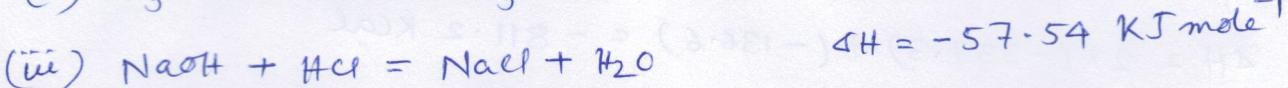
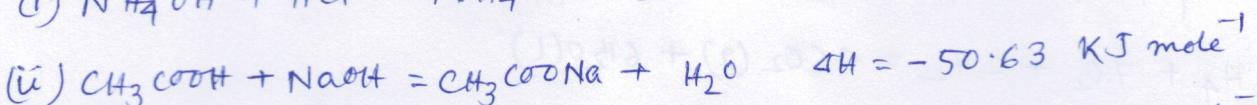
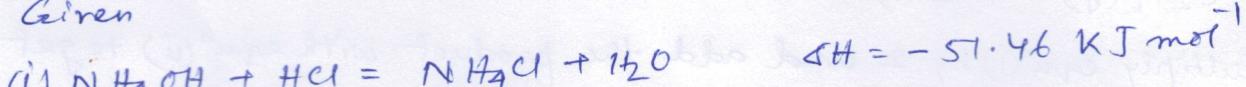
So, heat of reaction at constant pressure

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

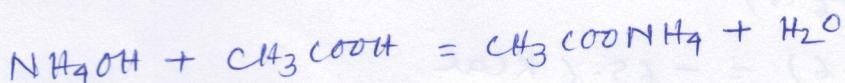
$$\text{or } \Delta H = -130,000 - 2 \times 1.987 \times 300 \\ = -131,192.2 \text{ cal} \approx -131.2 \text{ Kcal}$$

Q. 4.

Given

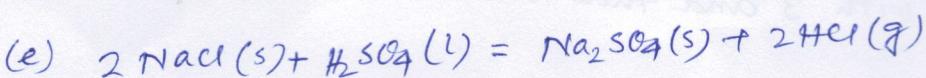
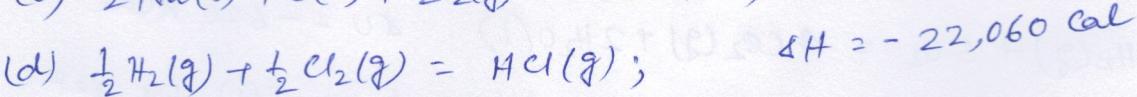
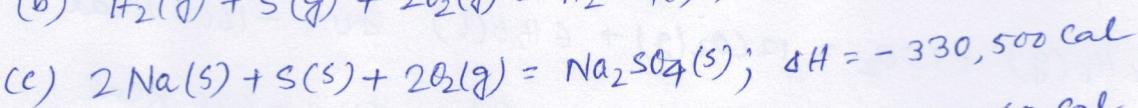
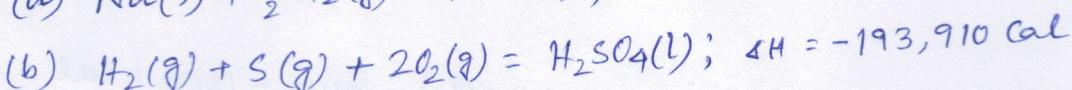
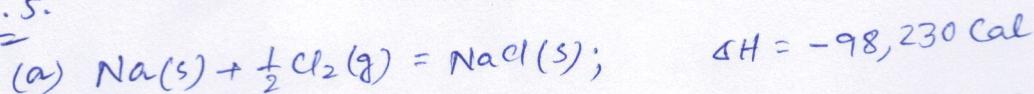


Adding (i) & (ii) and subtracting (iii) we get,



$$\Delta H = (-51.46) + (-50.63) - (-57.54) \\ = -44.55 \text{ KJ mole}^{-1}$$

Q. 5.



$$\text{Eqn}^n(e) = \text{Eqn}^n(c) + 2 \times \text{Eqn}^n(d) - 2 \times \text{Eqn}^n(a) - \text{Eqn}^n(b)$$

$$\text{so, } \Delta H \text{ for Eqn}^n(e) = -330,500 + 2 \times (-22,060) - 2(-98,230) \\ - (-193,910) \text{ cal}$$

$$= 15750 \text{ cal}$$

For eqnⁿ(e), Δn = Difference in no. of moles of gaseous products and reactants = 2 - 0 = 2

$$\therefore \Delta n = 2$$

$$\text{So, } \Delta H = \Delta U + \Delta n RT$$

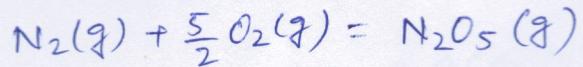
$$\therefore \Delta U = \Delta H - \Delta n RT$$

$$= 15750 - 2 \times 1.987 \times 298$$

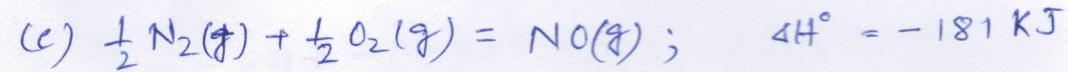
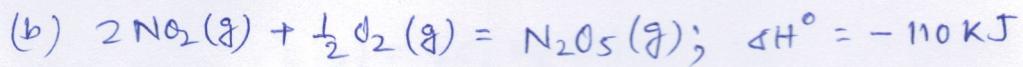
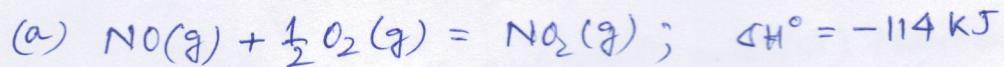
$$= 14565.75 \text{ cal.}$$

Q. 6.

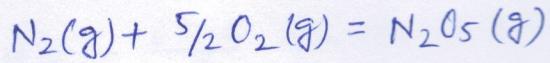
We have to find out ΔH° for the reaction



Since the given data are for 1 mole product, we write



Now equiⁿ(c) $\times 2 +$ equiⁿ(a) $\times 2 +$ equiⁿ(b) is



$$\begin{aligned} \text{So, } \Delta H^\circ \text{ for this reaction} &= 2(-181) + 2(-114) - 110 \\ &= -700 \text{ kJ} \end{aligned}$$

Sol. 1.

(a) The efficiency of heat Engine

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{500\text{K}}{1500\text{K}} = 0.5$$

$$\Rightarrow \boxed{\eta \% = 50\%}$$

(b) Maximum work done by for each 10kJ of heat

$$W = \eta Q_h = 0.5 \times 10\text{kJ} = 0.50\text{kJ}$$

(c) Since

$$\eta_{max} = \eta_{rev} \quad \& \quad |W_{max}| = |Q_h| - |Q_{c,min}|$$

$$\Rightarrow |Q_{c,min}| = 1.0\text{kJ} - 0.50\text{kJ}$$

$$= \underline{0.5\text{kJ}}$$

Sol. 2

Maximum possible Efficiency

$$\eta_{max} = 1 - \frac{T_c}{T_h} = 1 - \frac{(25+273)\text{K}}{(125+273)\text{K}}$$

$$= 1 - \frac{298\text{K}}{398\text{K}} = 0.2512$$

$$\boxed{\eta_{max}\% = 25.12\%}$$

Sol. 3.

(a) Maximum possible efficiency

$$\eta_{max} = 1 - \frac{T_c}{T_h} = 1 - \frac{(0+273)\text{K}}{(800+273)\text{K}} = 1 - \frac{273}{1073}$$

$$= 0.7455$$

$$\boxed{\eta_{max}\% = 74.55\%}$$

(b) As per part (c) of sol. 1, ~~from part~~ since $W_{max} = \eta_{max} Q_h$

$$|Q_{c,min}| = |Q_h| - |W_{max}|$$

$$= 1000 - 745.5\text{J}$$

$$= \underline{254.5\text{J}} \checkmark$$

$$= 0.7455 \times 1000\text{J}$$

$$= \underline{745.5\text{J}} \checkmark$$

Soln. 4

$$w = 2.50 \text{ kJ}$$

$$\eta = 45\%$$

$$\text{Work done for one cycle } w = 2.5 \text{ kJ} = \underline{\underline{2.5 \times 10^3 \text{ J}}}$$

$$\therefore \eta = \frac{w}{Q_H}$$

$$\Rightarrow Q_H = \frac{w}{\eta} = \frac{2.5 \times 10^3}{0.45} = 5.55 \times 10^3 \text{ J} = \underline{\underline{5.55 \text{ kJ}}}$$

$$\text{Since } |w| = |Q_H| - |Q_{C \text{ min}}|$$

$$\begin{aligned} \Rightarrow Q_C &= Q_H - w \\ &= (5.55 - 2.5) \text{ kJ} \\ Q_C &= \underline{\underline{3.05 \text{ kJ}}} \end{aligned}$$

Soln. 5

Given

$$1 h_p = 746 w$$

$$= 746 \text{ J/s}$$

$$0.1 h_p = 74.6 \text{ J/s}$$

$$\therefore Q_C = 74.6 \text{ J/s.}$$

$$Q_H = 500 \text{ J/s}$$

$$T_c = 20^\circ C = 293 K$$

$$\begin{aligned} \eta_{max} &= 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_c}{T_H} \\ \Rightarrow \frac{Q_C}{Q_H} &= \frac{T_c}{T_H} \end{aligned}$$

$$\begin{aligned} T_H &= \frac{Q_H}{Q_C} \times T_c \\ &= \frac{500}{74.6} \times \cancel{293} 20^\circ C \end{aligned}$$

$$\boxed{T_H = 134^\circ C}$$

Sol. 6

For path 'D'

$$\delta Q_{rev,D} = dU_D - \delta W_{rev,0} = C_V dT + P_1 dV \quad \text{--- (1)}$$

$$\Rightarrow \boxed{\Delta Q_{rev,D} = \int_{T_1}^{T_3} C_V dT + P_1 (V_2 - V_1)} \quad \text{--- (2)}$$

for Path 'E'

$$\delta W_{rev} = 0$$

$$\therefore \delta Q_{rev,E} = dU_E = C_V dT \quad \text{--- (3)}$$

$$\Rightarrow \boxed{\Delta Q_{rev,E} = \int_{T_3}^{T_1} C_V dT} \quad \text{--- (4)}$$

For complete process (path D+E)

$$Q_{rev,D+E} = Q_{rev,D} + Q_{rev,E} = P_1 (V_2 - V_1)$$

For calculating ΔS :

for path 'D' using eqn (1) $\Delta S_D = \int \frac{\delta Q_{rev,D}}{T}$

$$= \int_{T_1}^{T_3} \frac{C_V}{T} dT + P_1 \int_{V_1}^{V_2} \frac{dV}{T}$$

$$\boxed{\Delta S_D = \int_{T_1}^{T_3} \frac{C_V}{T} dT + nR \ln \frac{V_2}{V_1}} \quad \text{--- (5)}$$

For path 'E'

$$\text{since } \delta W_{rev} = 0$$

using eqn (3)

$$\text{At } \Delta S_E = \int \frac{\delta Q_{rev,E}}{T}$$

$$\boxed{\Delta S_E = \int_{T_3}^{T_1} \frac{C_V}{T} dT} \quad \text{--- (6)}$$

For complete process (path D+E)

$$\boxed{\Delta S_{D+E} = \Delta S_D + \Delta S_E = nR \ln \frac{V_2}{V_1}} \quad \text{--- (7)}$$

Sol. 7:

Given Eq.ⁿ: $P = \frac{RT}{V-b}$

Since $\delta Q_{rev} = dU - \delta W_{rev}$

Here, U is a function of only the temp.,
so $dU = 0$ for the expansion as U is independent
of volume.

$\therefore \delta Q_{rev} = -\delta W_{rev} = PdV$

$$= \frac{RT}{V-b} dV$$

So, change in Entropy

$$\Delta S = \int_1^2 \frac{\delta Q_{rev}}{T} = R \int_{V_1}^{V_2} \frac{dV}{V-b}$$

$$\boxed{\Delta S = R \ln \frac{V_2-b}{V_1-b}}$$

i.e. The entropy \uparrow when a gas expands into a vacuum.

Sol. 8.

Change in Entropy

$\Delta S = \frac{\Delta H_{rev}}{T} \Rightarrow$ First we need to change mass of water into mol.
by using its molar mass

$$5g \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g}} = \cancel{0.2775 \text{ mol}} \quad 0.2775 \text{ mol}$$

$$\therefore \Delta S = \frac{40.66 \text{ kJ/mol} \times \cancel{0.2775 \text{ mol}}}{373 \text{ K}} \quad 0.2775$$

$$\boxed{\Delta S = 30.25 \text{ J/K}}$$