

EXAM 1

27 September 2001

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

Give units for all quantities!

Some data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

YOUR NAME SOLUTIONS

(1) 20 points

(a) Starting with the expression $pV = Nmc^2/3$ (where N = number of molecules of mass m in a volume V at a pressure p and temperature T), derive an expression for the average kinetic energy ϵ of molecules in terms of some or all of these variables and Boltzmann's constant k_B . Show work!

(b) The molar masses of H_2 and atomic S vapor are 0.002 and $0.032 \text{ kg mol}^{-1}$. Find ϵ and c for these two species at 10^5 Pa and 600 K .

(c) H_2 effuses at 10 times the rate of an unknown compound from the same container. Estimate the molar mass of the unknown compound.

$$\begin{aligned} a) \quad \epsilon &= \frac{1}{2} mc^2 \text{ so } pV = \frac{Nmc^2}{3} = \frac{2}{3} \epsilon \cdot N = nRT \therefore \epsilon = \frac{nRT}{N} \cdot \frac{3}{2} \\ &= \frac{nRT}{n \cdot N_A} \cdot \frac{3}{2} = \frac{3}{2} k_B T. \end{aligned}$$

$$b) \quad \text{Both have the same } \epsilon = \frac{3}{2} \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 600 \text{ K} = 1.24 \times 10^{-20} \text{ J}.$$

$$\epsilon = \frac{1}{2} mc^2 \text{ so } c = \sqrt{\frac{2\epsilon}{m}}.$$

$$m \text{ for } H_2 \text{ is } \frac{0.002 \text{ kg}}{N_A} = 3.32 \times 10^{-27} \text{ kg}; \quad c = 2730 \text{ m s}^{-1}.$$

$$m \text{ for S is 16 times greater and } c \propto \frac{1}{\sqrt{m}} \therefore c = \frac{2730}{4} \text{ m s}^{-1} = 683 \text{ m s}^{-1}.$$

$$c) \quad \text{Rate of effusion } \propto c \propto \frac{1}{\sqrt{m}} \therefore \text{unknown } m \text{ is 100 times greater} \\ \text{i.e. } 0.2 \text{ kg mol}^{-1}.$$

(2) 40 points

(a) Starting with the information that SF_6 has 15 vibrational modes, make an estimate of the heat capacity C_V at the high and low temperature limits for 1 mole of this gas.

(b) Use your estimate, or if you do not have one use C_V for 1 mol = 40 J K^{-1} , to calculate q , w , ΔU and ΔH when the temperature is reversibly lowered from 300 to 200 K and the initial pressure is 10^5 Pa . Assume SF_6 behaves perfectly and show work.

i) At constant volume.

ii) At constant pressure.

iii) Adiabatically.

a) Non-linear molecule has 3 degrees of translational freedom and three of rotational: each contributes $\frac{R}{2}$ to C_V so at low T , $C_V = \frac{3}{2}R + \frac{3}{2}R = 3R$.
At high T each vibrational mode contributes R so $C_V = 3R + 15R = 18R$.

b) Using $C_V = 3R = 24.9 \text{ J K}^{-1}$:

i) $w = 0$. $\Delta U = C_V \Delta T = -2490 \text{ J} = q + w = q$ here.

$$\Delta H = C_P \Delta T = (C_V + R) \Delta T = -3330 \text{ J}.$$

ii) $dw = -pdV$ so $w = -\int_{V_1}^{V_2} pdV = -p(V_2 - V_1)$ here (const. p).

$$pV_1 = nRT_1 \therefore V_1 = \frac{nRT_1}{p} = 0.02494 \text{ m}^3. \quad V \propto T \text{ at const } p \text{ so } V_2 = \frac{2}{3} V_1.$$

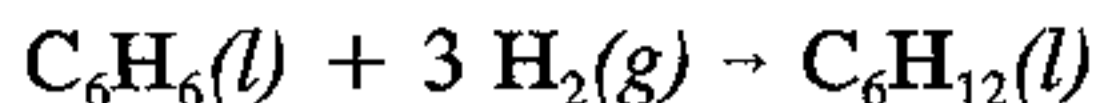
$$w = -10^5 \times (0.01663 - 0.02494) \text{ Pa m}^3 = +831 \text{ J}.$$

$$\Delta U, \Delta H \text{ same as in (i)} \therefore q = \Delta U - w = -3320 \text{ J}.$$

iii) $\Delta U, \Delta H$ same as in (i). $q = 0$ so $w = \Delta U$ here.

(3) 40 points

Consider the hydrogenation of benzene to form cyclohexane:

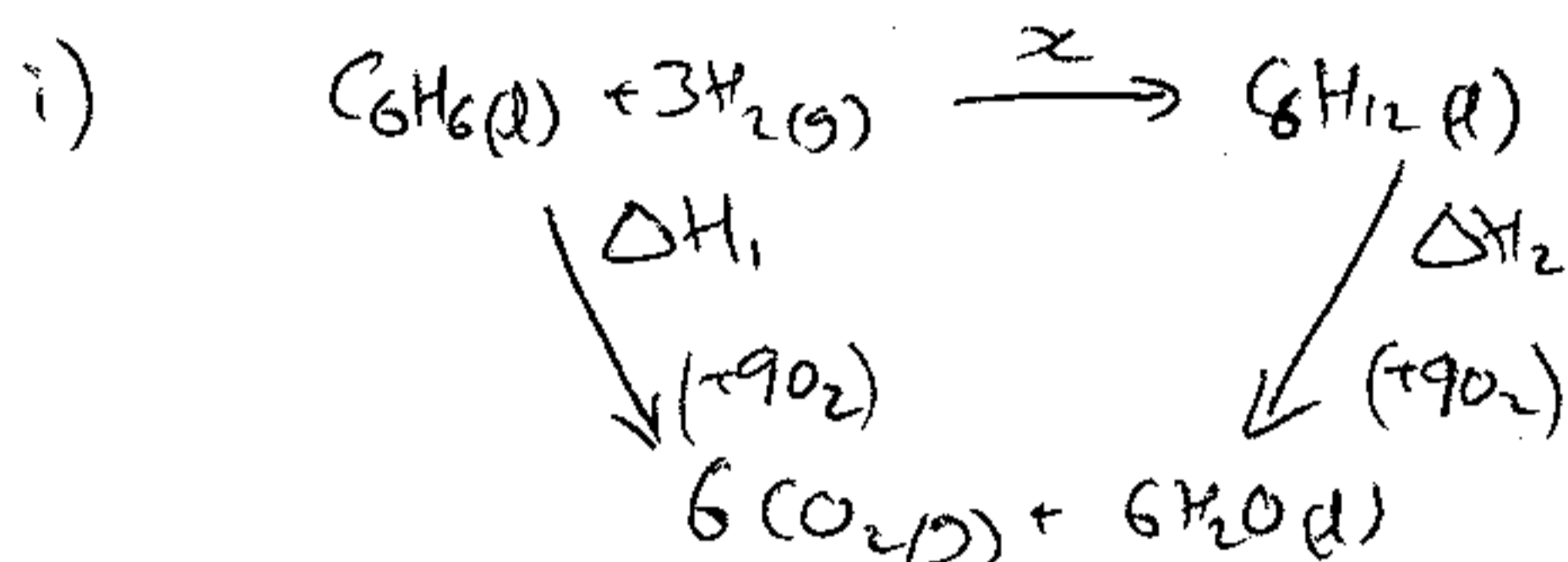


ΔH for combustion to $\text{CO}_2(g)$ and/or $\text{H}_2\text{O}(l)$ at 298 K for C_6H_6 , C_6H_{12} and H_2 is -3270, -4000 and -286 kJ mol^{-1} , respectively. C_p for C_6H_6 , H_2 and C_6H_{12} is $70 + 0.3 T$, $20 + 0.05 T$ and $110 + 0.2 T \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

i) Show that ΔH for hydrogenation at 298 K is -128 kJ mol^{-1} .

ii) Deduce ΔU for hydrogenation at 298 K.

iii) Deduce ΔH for hydrogenation at 1000 K.



$x + \Delta H_2 = \Delta H_1$ (Hess' Law)
 $\therefore x - 4000 \text{ kJ mol}^{-1} = -3270 + 3 \times (-286) \text{ kJ mol}^{-1}$
 $\therefore x = -128 \text{ kJ mol}^{-1}$

ii) $H = U + pV \therefore \Delta U = \Delta H - \Delta(pV) = \Delta H - RT \Delta n_{\text{gas}}$

$\Delta n_{\text{gas}} = -3$ so $\Delta U = -128 - \frac{8.314 \times 298 \times -3}{1000} \text{ kJ mol}^{-1} = -120.16 \text{ kJ mol}^{-1}$

iii) $\Delta H_{1000} = \Delta H_{298} + \int_{T_1}^{T_2} \Delta C_p \cdot dT$

$\Delta C_p = 110 + 0.2T - (70 + 0.3T + 3 \times (20 + 0.05T)) = -20 - 0.25T$

$\Delta H_{1000} = -128000 + \int_{298}^{1000} [-20T - 0.125T^2] \text{ J mol}^{-1}$

$= -128000 + \left\{ -2 \times 10^4 - (0.125 \times 10^5) + 5960 + 1.110 \times 10^4 \right\} \text{ J mol}^{-1}$

$= -128000 - 127900 \text{ J mol}^{-1}$

$= -255.9 \text{ kJ mol}^{-1}$