

EXAM 1

24 September 2004

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) 30 points

1 mol of $\text{SF}_6(\text{g})$ is held at a constant volume of 10^{-3} m^3 and the temperature is raised from 298 to 400 K. $C_v = (30 + 0.001 T^2) \text{ J K}^{-1}$.

a) assume ideal gas behavior to derive ΔU , ΔH , q and w .

b) assume the gas obeys the equation of state $p = (nRT/V) + an^2/V^2$ where $a = 1 \text{ Pa m}^6 \text{ mol}^{-2}$, and derive ΔU , ΔH , q and w .

$$\text{a) } C_v = \frac{dq}{dT} \text{ at const. } V = \left(\frac{\partial U}{\partial T} \right)_V \text{ because } \underline{w=0}$$

$$\Delta U = \int dU = \int C_v dT = \left[30T + \frac{0.001}{3} T^3 \right]_{298}^{400}$$
$$= 30(400 - 298) + \frac{0.001}{3} (400^3 - 298^3) = 3060 + 12572 \text{ J}$$
$$= \underline{15.6 \text{ kJ}}$$

$$\underline{q} = \Delta U \quad \Delta H = \Delta U + \Delta(pV)$$

$$\text{Here, } p_2 V_2 = nRT_2 \quad \therefore \Delta(pV) = nR(T_2 - T_1)$$
$$= 848 \text{ J}$$

$$\therefore \underline{\Delta H = 16.4 \text{ kJ}}$$

b) $q, w, \Delta U$ same as above.

$$\text{Initial } p_1 = \frac{nRT_1}{V_1} + \frac{an^2}{V_1^2} = \frac{1 \times 8.314 \times 298}{0.001} + \frac{1 \times 1^2}{(0.001)^2} \text{ Pa}$$
$$= 2.48 \times 10^6 + 10^6 \text{ Pa}$$
$$= 3.48 \times 10^6 \text{ Pa}$$

$$p_1 V_1 = 3480 \text{ J}$$

$$\text{Final } p_2 = 3.33 \times 10^6 + 10^6 \text{ Pa} = 4.33 \times 10^6 \text{ Pa}$$

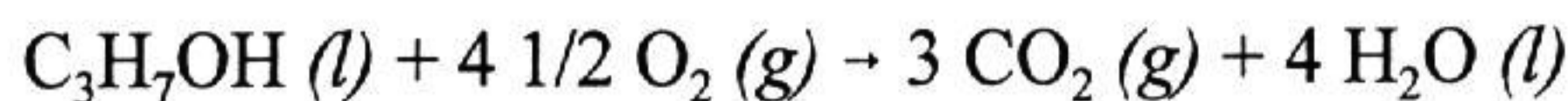
$$p_2 V_2 = 4330 \text{ J}$$

$$\Delta(pV) = 850 \text{ J} \quad (\text{a term cancels out})$$

$$\therefore \Delta H \text{ same as before, } \underline{16.4 \text{ kJ}}$$

(2) 40 points

Consider the combustion of propanol:



in a calorimeter at constant volume at 298 K. The heat released is $-1900.0 \text{ kJ mol}^{-1}$. Give answers to the nearest 0.1 kJ mol^{-1} .

a) Deduce ΔU and ΔH at 298 K.

b) Given that the enthalpies of formation of $\text{CO}_2 (g)$ and $\text{H}_2\text{O} (l)$ are -394.0 and $-286.0 \text{ kJ mol}^{-1}$, respectively, deduce $\Delta_f H_{298} (\text{C}_3\text{H}_7\text{OH})$.

c) The enthalpy of combustion of ethyl methyl ether, $\text{C}_2\text{H}_5\text{OCH}_3 (l)$, is $-1800.0 \text{ kJ mol}^{-1}$. Deduce ΔH_{298} for the isomerization reaction $\text{C}_2\text{H}_5\text{OCH}_3 (l) \rightarrow \text{C}_3\text{H}_7\text{OH} (l)$.

d) C_p for $\text{C}_2\text{H}_5\text{OCH}_3 (l)$ and $\text{C}_3\text{H}_7\text{OH} (l)$ are 150.0 and $165.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Find ΔH for the isomerization reaction of part (c) at 380 K.

a) const. vol. so $q = \Delta U = \underline{-1900 \text{ kJ mol}^{-1}}$.

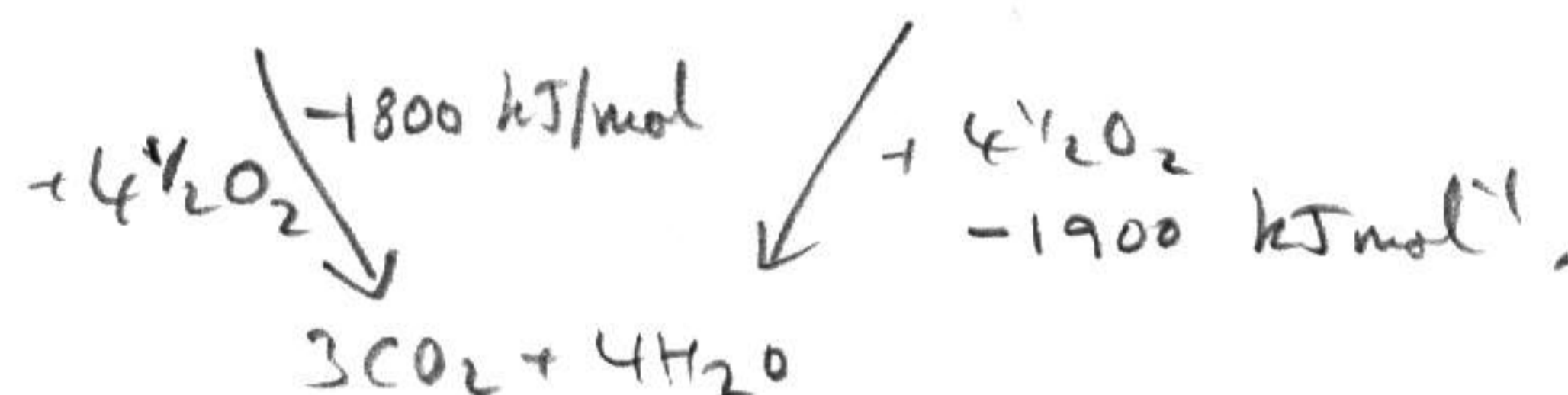
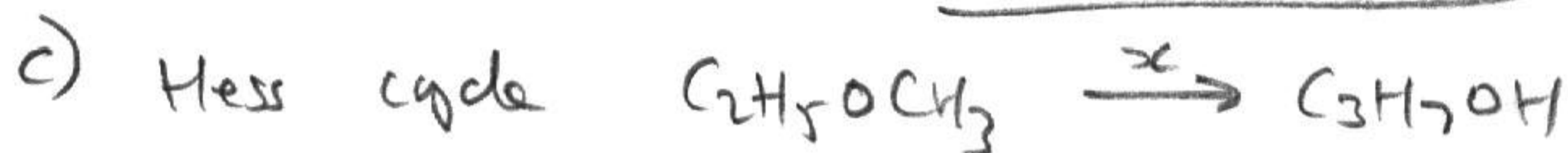
$$\Delta H = \Delta U + \Delta(pV) \approx \Delta U + \Delta n_{\text{gas}}(RT)$$

$$= -1900.0 \text{ kJ mol}^{-1} - \frac{1.5 \times 8.314 \times 298}{1000} \text{ kJ mol}^{-1}$$

$$= \underline{-1903.7 \text{ kJ mol}^{-1}}$$

b) $\Delta H = 3 \times -394 + 4 \times -286 - \Delta_f H (\text{C}_3\text{H}_7\text{OH}) = -1903.7 \text{ kJ mol}^{-1}$

$$\therefore \Delta_f H (\text{C}_3\text{H}_7\text{OH}) = \underline{-422.3 \text{ kJ mol}^{-1}}$$



$$x - 1903.7 = -1800.0 \therefore x = \underline{+103.7 \text{ kJ mol}^{-1}}$$

d) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ so $\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p = 165 - 150 = 15 \text{ J K}^{-1} \text{ mol}^{-1}$.

$$\Delta H_{380} = \Delta H_{298} + \int_{298}^{380} \Delta C_p \cdot dT = 103.7 + \frac{15(380-298)}{1000} \text{ kJ mol}^{-1}$$
$$= \underline{104.9 \text{ kJ mol}^{-1}}$$

(3) 30 points

Imagine you hold your finger over the end of a bicycle pump and compress the air, initially at 298 K and 10^5 Pa, reversibly and adiabatically to $1/12$ of its initial volume. Treat the air as an ideal gas with $C_p = 29.0 \text{ J K}^{-1} \text{ mol}^{-1}$ and find the final temperature of the air.

$$C_p - C_v = R \therefore C_v = 20.69 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\gamma = C_p / C_v = 1.402$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma = P_2 \left(\frac{V_1}{12}\right)^\gamma \quad ; \quad V_1^\gamma \text{ cancels so}$$

$$\therefore P_2 = P_1 \cdot 12^\gamma = 10^5 \text{ Pa} \times 12^{1.402} = 3.26 \times 10^6 \text{ Pa}$$

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} \text{ by ideal gas law}$$

$$\text{so } T_2 = \frac{P_2 V_2}{P_1 V_1} \cdot T_1 = \frac{32.6 \times \frac{1}{12} \times 298 \text{ K}}{1} = \underline{\underline{809 \text{ K}}}$$