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

YOUR NAME SOLUTIONS

(1) *30 points*

1 mol of $SF_6(g)$ is held at a constant volume of 10^{-3} m^3 and the temperature is raised from 298 to 400 K. $C_V = (30 + 0.001\ T^2)$ 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 Pa m^6 mol^{-2}, and derive ΔU, ΔH, q and w.

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

$$\Delta U = \int dU = \int C_V\, dT = \left[30T + \frac{0.001}{3}T^3\right]_{298}^{400}$$

$$= 30(400-298) + \frac{0.001}{3}(400^3 - 298^3) = 3060 + 12572 \text{ J}$$

$$= 15.6 \text{ kJ}.$$

$q = \Delta U$. $\Delta H = \Delta U + \Delta(pV)$.

Here, $p_2V_2 = nRT_2$ ∴ $\Delta(pV) = nR(T_2 - T_1)$ $= 848$ J

∴ $\Delta H = 16.4$ kJ.

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

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

$= 2.48 \times 10^6 + 10^6$ Pa

$= 3.48 \times 10^6$ Pa

$p_1V_1 = 3480$ J.

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

$p_2V_2 = 4330$ J

$\Delta(pV) = 850$ J (a term cancels out)

∴ ΔH same as before, 16.4 kJ.

(2) *40 points*

Consider the combustion of propanol:

$$C_3H_7OH\ (l) + 4\ 1/2\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 4\ H_2O\ (l)$$

in a calorimeter at constant volume at 298 K. The heat released is -1900.0 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 CO_2 *(g)* and H_2O *(l)* are -394.0 and -286.0 kJ mol^{-1}, respectively, deduce $\Delta_f H_{298}$ (C_3H_7OH).

c) The enthalpy of combustion of ethyl methyl ether, $C_2H_5OCH_3$ *(l)*, is -1800.0 kJ mol^{-1}. Deduce ΔH_{298} for the isomerization reaction $C_2H_5OCH_3\ (l) \rightarrow C_3H_7OH\ (l)$.

d) C_p for $C_2H_5OCH_3$ *(l)* and C_3H_7OH *(l)* are 150.0 and 165.0 J K^{-1} mol^{-1}, respectively. Find ΔH for the isomerization reaction of part (c) at 380 K.

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

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

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

$= -1903.7$ kJ mol^{-1}.

b) $\Delta H = 3 \times -394 + 4 \times -286 - \Delta_f H\ (C_3H_7OH) = -1903.7$ kJ mol^{-1}

$\therefore \Delta_f H\ (C_3H_7OH) = -422.3$ kJ mol^{-1}.

c) Hess cycle

$C_2H_5OCH_3 \xrightarrow{x} C_3H_7OH$

$C_2H_5OCH_3$ $+ 4\frac{1}{2}O_2$, -1800 kJ/mol $\rightarrow 3CO_2 + 4H_2O$

C_3H_7OH $+ 4\frac{1}{2}O_2$, -1900 kJ mol^{-1} $\rightarrow 3CO_2 + 4H_2O$

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

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

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

$= 104.9$ 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 $C_p = 29.0$ J K^{-1} mol^{-1} and find the final temperature of the air.

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

$\gamma = C_p/C_v = 1.402$.

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

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

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

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

$= 809$ K.