EXAM 1

25 September 2003

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*

(a) Starting from the information that the weight of an object of mass m is mg, derive (***show work***) the result that a pressure p can support a column height h of incompressible fluid with density ρ, where p = ρgh.

(b) The air pressure inside a major hurricane is 9×10^4 Pa. Outside the pressure is 10^5 Pa. What height of water (density 1000 kg m^{-3}) in the storm can be supported by this pressure difference?

a) see notes

b) Pressure difference $p = 10^4 \text{ Pa} = \rho g h$

$$\therefore h = \frac{p}{\rho g} = \frac{10^4 \text{ Pa}}{1000 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}} = 1.02 \text{ m}.$$

(2) *40 points*

(a) Inside a diesel engine a mixture of fuel and air (average Cp 30 J K^{-1} mol^{-1}) in one of the cylinders is compressed reversibly and adiabatically such that its pressure increases from 10^5 Pa to 10^6 Pa. Initially the volume is 0.3 L and the temperature 350 K. What are the final temperature, w, q, ΔU and ΔH for the gas during this process?

(b) Now the gas mixture ignites and the temperature rises to 2500 K. The gas expands adiabatically against a constant pressure of 2 x 10^5 Pa until the volume is 0.3 L again. Assume Cp is 33 J K^{-1} mol^{-1}. What are w, q, ΔU and ΔH for the gas during this process? *[NOTE if you have no answer for part (a) you may assume the initial volume here is 0.1 L. This is not the true initial volume]*

a) $n = \frac{pV}{RT} = \frac{10^5 \text{ Pa} \times 3\times10^{-4} \text{ m}^3}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 350\text{K}} = 0.0103 \text{ mol}$

$\gamma = c_p/c_v = 30/(30-8.314) = 1.383$

$p_1V_1^\gamma = p_2V_2^\gamma \quad \therefore \quad \left(\frac{V_2}{V_1}\right)^\gamma = \frac{p_1}{p_2} = 0.1 \quad \therefore \quad \gamma \ln\left(\frac{V_2}{V_1}\right) = \ln 0.1 = -2.303$

$\therefore \frac{V_2}{V_1} = 0.1892 \quad \therefore V_2 = 5.676\times10^{-5} \text{ m}^3.$

$T = \frac{pV}{nR} = \frac{10^6 \times 5.676\times10^{-5}}{0.0103\times8.314} \text{ K} = 663 \text{ K}.$

$\Delta H = nC_p\Delta T = 0.0103 \times 30 \times (663-350) \text{ J} = 96.7 \text{ J}.$

$\Delta U = nC_v\Delta T = 0.0103 \times (30-8.314) \times \Delta T = 69.9 \text{ J}.$

$= q + w$ and $q = 0$ so $w = 69.9 \text{ J}.$

b) Const. p_{ex} so $w = -p_{ex}\Delta V = -2\times10^5 \text{ Pa } (3\times10^{-4} - 5.676\times10^{-5}) \text{ m}^3$

$= -48.6 \text{ J}$

$= \Delta U$ because $q = 0$.

$\Delta U = nC_v\Delta T = 0.0103 \times (33-8.314)\Delta T$ so $\Delta T = -191 \text{ K}.$

$\Delta H = nC_p\Delta T = 0.0103 \times (33) \times -191 \text{ J} = -64.9 \text{ J}.$

(3) *30 points*

At 298 K, 0.1 mol of CO (g) is burned in excess O_2 to make CO_2 (g) inside a sealed, rigid calorimeter, and 25 kJ of heat is given off.

(a) Calculate the molar ΔU and ΔH of combustion of CO (g) at 298 K.

(b) Given that the enthalpy of formation of CO_2 (g) is -400 kJ mol^{-1}, find the 298 K molar ΔH for

$$C\,(gr) + 1/2\, O_2\,(g) \rightarrow CO\,(g)$$

(c) Cp for C, O_2 and CO_2 may be expressed in the form $a + bT + c/T^2$ with the coefficients in the table. Use these data to deduce $\Delta_f H$ for CO_2 (g) at 3000 K.

species	a	b	c
C	8.5	0	0
O_2	30.0	4.2×10^{-3}	-1.7×10^{5}
CO_2	44.2	8.8×10^{-3}	-8.6×10^{5}

$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_2(g)$

a) $\Delta U = \frac{q_V}{n} = \frac{-25\text{ kJ}}{0.1\text{ mol}} = -250\text{ kJ mol}^{-1}$.

$H = U + pV$ so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$

$= \Delta U + RT\,\Delta n_{gas}$. $\Delta n_{gas} = -\frac{1}{2}$

$= \Delta U - \frac{1}{2}RT = -251.2\text{ kJ mol}^{-1}$.

b) Hess cycle

$C + O_2 \xrightarrow{x} CO + \frac{1}{2}O_2$

$C + O_2 \xrightarrow{-400} CO_2$; $CO + \frac{1}{2}O_2 \xrightarrow{-251.2} CO_2$

$x = -148.8\text{ kJ mol}^{-1}$.

c) CO_2 is formed by $C + O_2 \rightarrow CO_2$

$\Delta C_p = (44.2 - 30.0 - 8.5) + (8.8 - 4.2)\times10^{-3}\,T + (-8.6 + 1.7)\times10^{5}/T^2$

$= 5.7 + 4.6\times10^{-3}\,T - 6.9\times10^{5}/T^2$.

$\Delta H_{3000} = \Delta H_{298} + \int_{298}^{3000} \Delta C_p\, dT$

$= \Delta H_{298} + \left[5.7T + 4.6\times10^{-3}\frac{T^2}{2} + \frac{6.9\times10^{5}}{T}\right]_{298}^{3000}$

$= \Delta H_{298} + (15400 + 20496 - 2085)\text{ J mol}^{-1}$

$= \Delta H_{298} + 33.8\text{ kJ mol}^{-1}$

$= -366.2\text{ kJ mol}^{-1}$.