EXAM 2

16 October 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 numerical quantities!

Some data: $R = 8.314$ J K^{-1} mol^{-1} 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}$ mol^{-1}
$k = 1.38 \times 10^{-23}$ J K^{-1} mol^{-1} 1 amu = 1.66×10^{-27} kg

Your name SOLUTIONS

(1) *26 points*

i) The Joule-Thompson coefficient for a gas is $\mu = (\partial T/\partial p)_H$. By considering H as a function of p and T, prove that $(\partial H/\partial p)_T = -C_p\,\mu$.

ii) Find an expression for ΔH when a real gas with $\mu = (a + bp)/C_p$ is compressed from pressure p_1 to p_2.

i) At constant H, $dH = 0 = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$

Divide by dT with H constant;

$$\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_H = -\left(\frac{\partial H}{\partial T}\right)_p = -c_p \quad \therefore \left(\frac{\partial H}{\partial p}\right)_T \frac{1}{\mu} = -c_p \,.$$

ii) $$\Delta H = \int dH = \int_{p_1}^{p_2} -c_p \cdot \mu\, dp = -\int_{p_1}^{p_2} (a+bp)\,dp$$

$$= a(p_1 - p_2) + \frac{b}{2}\left(p_1^2 - p_2^2\right) = (p_1 - p_2)\left(a + \frac{b}{2}(p_1 + p_2)\right)$$

(2) *26 points*

1 mol of water vapor at 373 K (the boiling temperature) is reversibly condensed and then cooled to 300 K at constant pressure. Find ΔS for this process.

Data: $\Delta_{vap}H = 41$ kJ mol^{-1} and $C_p(H_2O\ (l)) = 20 + 0.1T - 2000/T$ J K^{-1} mol^{-1}.

$$\Delta S_{condensation} = \frac{q_{rev}}{T} = \frac{-\Delta H_{vap}}{373K} = -109.9 \text{ JK}^{-1}\text{mol}^{-1},$$

$$\Delta S_{cooling} = \int \frac{dq_{rev}}{T} = \int_{373}^{300} \frac{C_p dT}{T} =$$

$$\int_{373}^{300} \frac{20}{T} + 0.1 - 2000T^{-2}\ dT = \left[20 \ln T + 0.1T + \frac{2000}{T}\right]_{373}^{300}$$

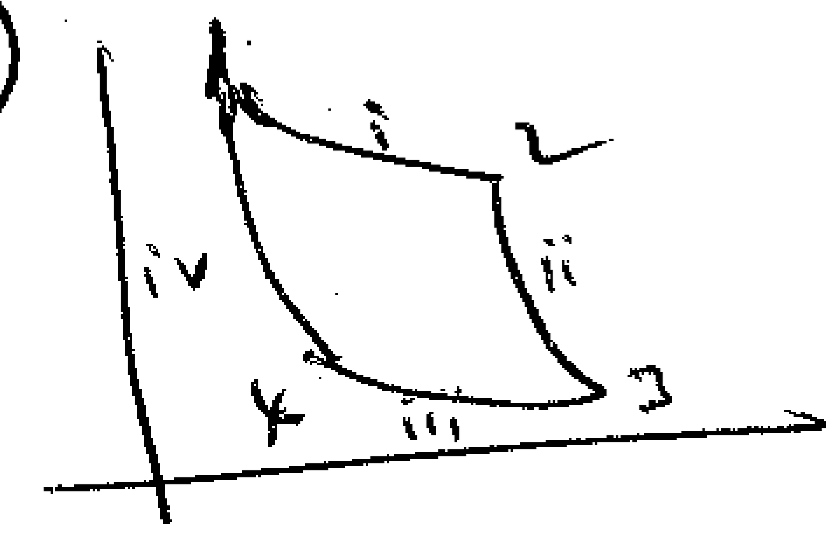
$$= -4.4 - 7.3 + 1.3 \text{ JK}^{-1}\text{mol}^{-1} = -10.4 \text{ JK}^{-1}\text{mol}^{-1}.$$

Total $\Delta S = -120.3 \text{ JK}^{-1}\text{mol}^{-1}.$

(3) *48 points*

1 mol of an ideal gas (the system) has $C_V = 15\ \mathrm{J\,K^{-1}}$. It is initially at 500 K and has a pressure of 10^6 Pa. It is taken around a reversible Carnot cycle, involving (i) isothermal expansion until the pressure is 10^4 Pa, (ii) adiabatic expansion until the temperature is 298 K, (iii) isothermal compression, and (iv) adiabatic compression to the initial T and p.

For each step (i)-(iv) calculate q, w, ΔU, ΔH, ΔG, ΔS and $\Delta S_{universe}$ (i.e. the total ΔS), and then determine the overall efficiency of this heat engine. ((i) and (iii) only)



i) Isothermal ideal gas $\Delta H = 0$, $\Delta U = 0 = q + w$.

$w = \int -p\,dV = -RT \ln \frac{V_2}{V_1}$.

$V \propto \frac{1}{p}$ at const T $\therefore \frac{V_2}{V_1} = \frac{p_1}{p_2} = 100$

$\therefore w = -RT \ln 100 = -19.14$ kJ ; $q = +19.14$ kJ.

$\Delta S = \frac{q_{rev}}{T} = \frac{19140\ \mathrm{J}}{500\ \mathrm{K}} = 38.3\ \mathrm{J\,K^{-1}}$, $\Delta G = \Delta H - T\Delta S = -19.14$ kJ. $\Delta S_{uni} = 0$.

ii) Adiabatic so $q = 0$ so $\Delta S = 0$. $\Delta U = C_V.(T_3 - T_2) = -3.03$ kJ.

$\Delta H = C_p(T_3 - T_2) = (C_V + R)(T_3 - T_2) = -4.71$ kJ.

$w = \Delta U - q = -3.03$ kJ. $\Delta S_{uni} = 0$ (reversible).

iii) Isothermal compression : p_4 and p_3 are not 10^4 or 10^6 Pa.

$p_2 V_2^\gamma = p_3 V_3^\gamma$ and $p_2 V_2 = RT_2$ and $p_3 V_3 = RT_3$ so $RT_2 V_2^{\gamma-1} = RT_3 V_3^{\gamma-1}$

or $T_2/T_3 = (V_3/V_2)^{\gamma-1}$

Similarly, for step (iv) $T_4/T_1 = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$ but $T_1 = T_2$ and $T_3 = T_4$ so $\frac{V_4}{V_1} = \frac{V_3}{V_2}$.

So $\frac{V_4}{V_1} = \frac{V_1}{V_2} = \frac{1}{100}$.

$w = -RT \ln\left(\frac{1}{100}\right) = 11.41$ kJ. $q = -11.41$ kJ. $\Delta S = -38.3\ \mathrm{J\,K^{-1}}$.

$\Delta G = \Delta H - T\Delta S = +11.41$ kJ, $\Delta S_{uni} = 0$.

ΔU, ΔH both zero.

iv) $q = 0$, $\Delta S = 0$, $\Delta U = +3.03$ kJ, $\Delta H = +4.71$ kJ. $w = 3.03$ kJ. $\Delta S_{uni} = 0$.

efficiency $= \frac{\text{work done by engine}}{\text{heat absorbed at high T}} = \frac{-(-19.14 - 3.03 + 11.41 + 3.03)}{19.14} = 0.40$.