EXAM 2

15 October 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 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) *30 points*

i) A gas expanded adiabatically through a small nozzle through a pressure drop of 50 atm, and its temperature dropped by 6 K. Estimate the Joule-Thomson coefficient.

ii) Water has an isothermal compressibility of 5x 10^{-5} atm^{-1}. Assuming this is constant, what pressure increase is needed to decrease the volume of a sample of water by 1%?

i) $\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-6\,K}{-50\,atm} = 0.12\ K\,atm^{-1}$

or $1.2 \times 10^{-6}\ K\,Pa^{-1}$

ii) $\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \therefore \quad \int_{V_1}^{V_2} \frac{1}{V}\,dV = -\kappa_T \int_{p_1}^{p_2} dp$

$\therefore \quad \ln\left(\frac{V_1}{V_2}\right) = \kappa_T\,\Delta p.$

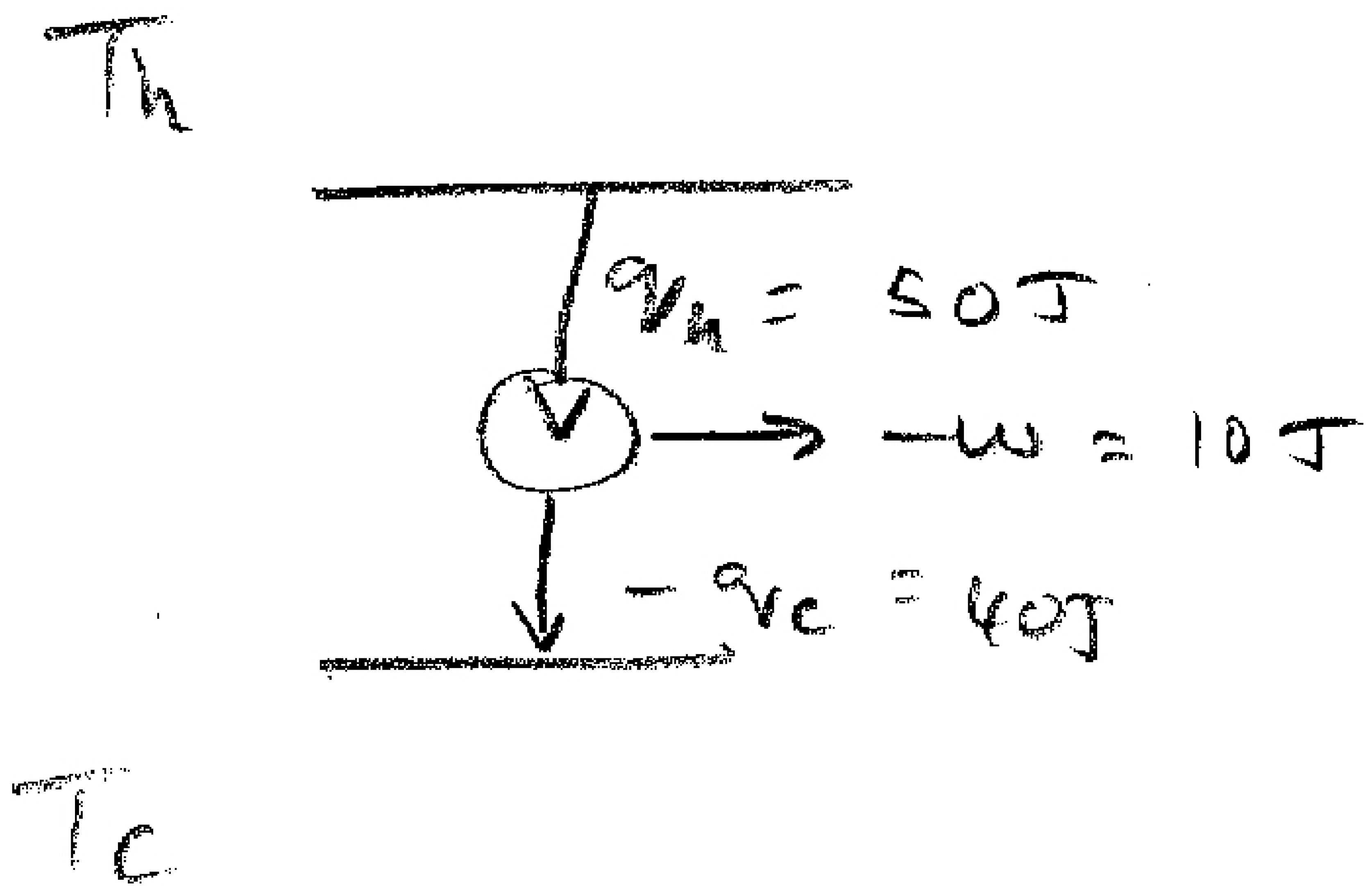
Here, $V_2 = 0.99\,V_1$ so $\ln\left(\frac{V_1}{V_2}\right) = 0.01$

$\Delta p = \frac{0.01}{5 \times 10^{-5}\,atm} = 200\ atm$

or $2 \times 10^{7}\ Pa$

(2) *24 points*

A Carnot cycle absorbs 50 J of heat at 450 K and rejects 40 J at a lower temperature. How much work is done on the surroundings, what is efficiency of this heat engine, and what is the lower temperature?



work on surroundings

$= -w_{system} = 10\,J$

$$\text{Efficiency} = \frac{-w}{q_h} = \frac{10}{50} = 0.2$$

$$\text{also} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{450\,K}$$

$$\therefore \quad 0.8 = \frac{T_c}{450\,K} \quad \therefore \; T_c = 360\,K.$$

(3) *46 points*

1 mol of perfect gas, with $C_V = 1.5\ R$, is initially at a pressure of 8×10^5 Pa and temperature of 330 K. It expands adiabatically against a constant external pressure of 3×10^5 Pa until it reaches a pressure of 3×10^5 Pa. Assume the surroundings remain at a constant temperature of 330 K. Deduce ΔS for the gas (the system) and ΔS for the surroundings, and hence prove whether this process is reversible or not. *Possibly helpful HINT: express w in terms of the final T and also in terms of pV work. If you have no answer for this assume T_{final} = 260 K (not the right value).*

$P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$. $\quad V_1 = \dfrac{nRT_1}{P_1} = 0.00343\ m^3$.

$w = -\int_{V_1}^{V_2} P_{ex} dV = -P_{ex}(V_2 - V_1)$.

Because $q = 0$, $w = \Delta U = C_V(T_2 - T_1) = 1.5R\,(T_2 - T_1)$.

$P_{ex}V_1 = 1029\,J$, $1.5RT_1 = 4115\,J$ so

$1029\,J - RT_2 = 1.5RT_2 - 4115\,J$

$\therefore T_2 = 247\,K$.

<u>Note</u> although $dq = 0$, $dS \neq 0$ because $dS \neq dq/T$, only dq_{rev}/T.

Overall change $P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$.

Consider reversible T change at const p

$dq_{rev} = C_p dT = (C_V + R)dT \therefore \Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T} = -6.02\ JK^{-1}$

Now let p change at const T, from 8 to 3×10^5 Pa, so V changes by a factor of 8/3. If this is done reversibly, $\Delta S = R\ln\left(\frac{V_f}{V_i}\right)$

$= 8.15\ JK^{-1}$.

Total ΔS reversible $= \Delta S$ all ways $= +2.13\ JK^{-1}$.

$\Delta S_{surr} = 0$ because $q_{surr} = 0$. $\Delta S_{univ} > 0$, so a spontaneous change.

(see homework problem 4.7)