EXAM 2

19 October 2000

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!

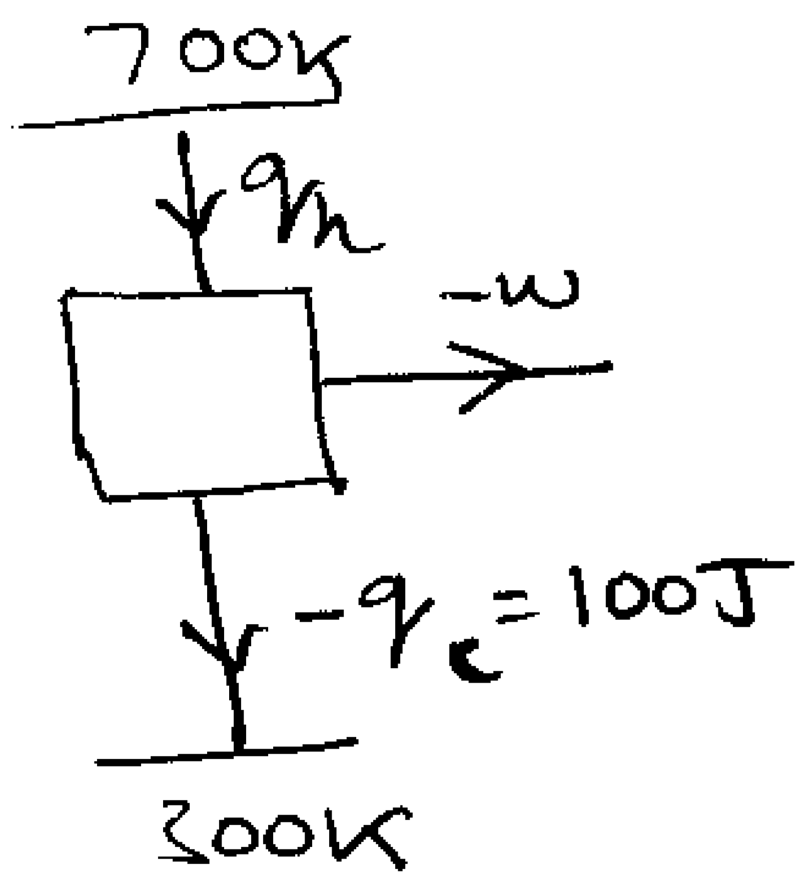
Some data: $R = 8.314\ J\ K^{-1}\ mol^{-1}$ 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}\ mol^{-1}$
$k = 1.38 \times 10^{-23}\ J\ K^{-1}\ mol^{-1}$ 1 amu = 1.66×10^{-27} kg

Your name SOLUTIONS

(1) *22 points*

An ideal Carnot engine operates in reverse, such that 100 J of heat are absorbed at 300 K and heat is rejected at 700 K. How much work must be done on the engine to accomplish this?

If the engine was working forwards.



Efficiency $\varepsilon = \frac{-w}{q_h} = \frac{T_h - T_c}{T_h} = \frac{700-300}{700} \approx 0.571$

$q_h = -w - q_c \quad \therefore \frac{-w}{-w-q_c} = 0.571 = \frac{w}{w+q_c}$

$\therefore \quad 0.429 w = -57.1$

$\therefore \quad w = -133\ J$

i.e. 133 J work must be done on engine to remove 100 J from 300 K.

(2) *30 points*

The isothermal compressibility is defined as $\kappa_T = -(1/V)(\partial V/\partial p)_T$. For a certain liquid, the volume is found to obey the following relationship:

actually it isn't – my mistake. Full credit either way you read the information.

$$V = V' \{1.2 - 0.1\,p + 0.003\,p^2\}$$

where p is the pressure in bar (1 bar = 10^5 Pa) and V' is the volume when p = 1 bar.

a) What is the numerical value of κ_T when p = 2 bar?

b) What is the % change in volume when the pressure is increased from 1 to 5 bar? *Note: κ_T varies with p.*

a) $\left(\frac{\partial V}{\partial p}\right)_T = V'(-0.1 + 0.006p)$

$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{0.1 - 0.006p}{1.2 - 0.1p + 0.003p^2} = 0.0870$ when $p = 2$.

b) $\left(\frac{\partial V}{\partial p}\right)_T = -V\kappa_T \therefore dV = -V.\kappa_T\,dp$

$\therefore \Delta V = -\int_1^5 V.\kappa_T.dp = V'\int_1^5 (-0.1 + 0.006p)dp$

$= V'\left[-0.1p + 0.003p^2\right]_1^5$

$= -0.328\,V'$.

Relative to using V = V' when p = 1, that's a 33% decrease.

If you used $\frac{\Delta V}{V_{init}} = \frac{-0.328}{1.103} = -0.297$, that's a 30% decrease.

(see for example exercises 3.12 and 3.13 from the homework).

(3) *48 points*

1 mol of an ideal gas (the system) has $C_V = 20\ J\ K^{-1}$. It is initially at 500 K and has a pressure of 10^4 Pa. It is expanded in two ways.

a) Reversibly and isothermally until the pressure is 5000 Pa.

b) Isothermally against a constant external pressure of 5000 Pa.

For each process calculate q, w, ΔU, ΔS, ΔH, ΔG, ΔS_{surr} and $\Delta S_{universe}$ (i.e. the total ΔS).

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

$P_{ex} = P = \frac{RT}{V}$; $dw = -P_{ex} dV = -\frac{RT}{V} dV$

$\therefore w = -\int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln\left(\frac{V_1}{V_2}\right) = -2881\ J$.

$\therefore q = +2881\ J$.

$\Delta S = \frac{q_{rev}}{T} = 5.763\ JK^{-1}$.

$\Delta G = \Delta H - T\Delta S = -2881\ J$.

Reversible so $\Delta S_{uni} = 0$ and $\Delta S_{surr} = -5.763\ JK^{-1}$.

b) Same final state as (a) so $\Delta U, \Delta H, \Delta S, \Delta G$ same as above.

$V_{init} = \frac{RT}{P} = 0.4157 m^3$. $V_{final} = 0.8314\ m^3$.

$w = -P_{ex} \cdot \Delta V = -2079\ J \therefore q = +2079\ J$.

$\Delta S_{uni} \neq 0$ for a non-reversible change (must be positive)

$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T} = \frac{-2079\ J}{500\ K} = -4.157\ JK^{-1}$.

$\Delta S_{uni} = 5.763 - 4.157\ JK^{-1} = +1.606\ J$.

(See problems 4.6 and 4.7 in the homework).