

50 minutes. Begin and end on the buzzer.

Answer all questions.

Write all your working on the question sheets.

Please write your name on each page.

This is a closed book exam.

You are allowed one side of a page of notes.

You are allowed a calculator but it is not essential.

Question 1 [39]

(a) What is the definition of thermal equilibrium between two systems, A and B? [4]

A and B are in thermal equilibrium if, when they are brought into thermal contact such that they can freely exchange energy (heat), there is no net energy/heat flow from one to the other.

(b) State the zeroth law of thermodynamics, in terms of three systems A, B and C. [2]

If A is in thermal equilibrium with each of B and C separately, then B is in thermal equilibrium with C.

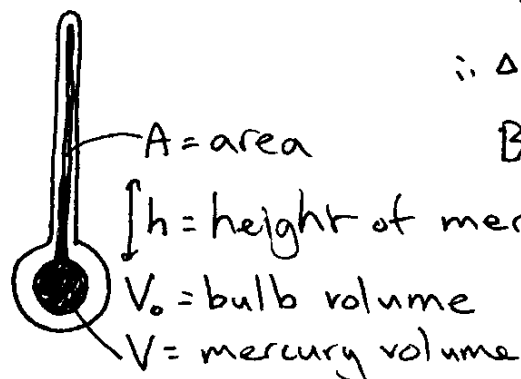
(c) Are the answers to (a) and (b) alone sufficient to prove that temperature is a unique scalar quantity (ie, one number) which is independent of the nature of the system? Y/N/(depends on the system). [2]

Yes!

(d) Can it be shown that there must exist an absolute zero of temperature from these two statements alone? [1].

No — [you need more, for instance a constant volume gas thermometer]

(e) A typical mercury-in-glass thermometer has a spherical bulb of volume 0.100 cm^3 connected to a closed capillary tube of cross-sectional area $1.80 \times 10^{-4} \text{ cm}^2$ filled with 0.1002 cm^3 of mercury at 0°C . The volume expansivity of mercury is $B = 180 \times 10^{-6} \text{ K}^{-1}$. If the thermometer is immersed in water at 10°C , how much will the height of the mercury in the capillary change (neglect expansion of the glass)? [6]



$$V = V_0 + Ah$$

$$\therefore \Delta V = A \Delta h \quad (\text{i}) \quad \text{if } \Delta h = \text{change in height when volume of Hg changes by } \Delta V$$

$$B = \frac{1}{V} \frac{\Delta V}{\Delta T} \quad (\text{ii})$$

\therefore from (i) and (ii),

$$\Delta h = \frac{\Delta V}{A} = \frac{BV \Delta T}{A}$$

$$= \frac{180 \times 10^{-6} \text{ K}^{-1} \times 0.1002 \text{ cm}^3 \times 10 \text{ K}}{1.80 \times 10^{-4} \text{ cm}^2}$$

$$r = 1.0 \text{ cm}$$

(f) What is the definition of the 'ideal gas' temperature scale as measured using a constant-volume gas thermometer? Define the terms you use. Why do we believe that such a thermometer measures absolute temperature? [6]

Definition: $T(K) = 273.16 \times \lim_{p \rightarrow 0} \frac{p}{p_0}$

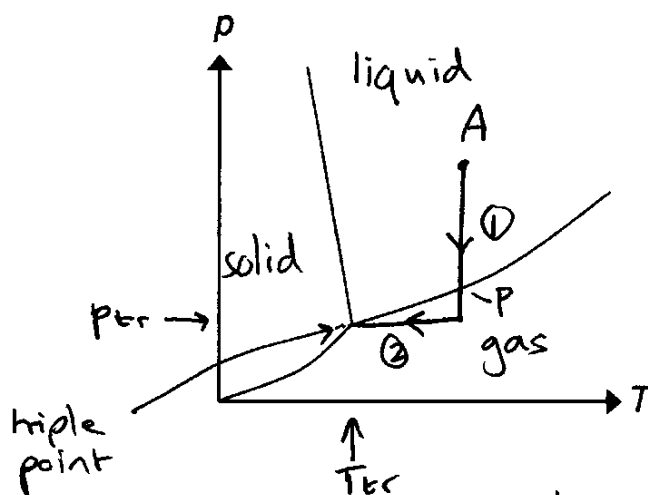
where p_0 = pressure measured when thermometer is dipped in a water triple-point cell
 p = pressure measured when in thermal equilibrium with system to be measured at temp. T .

Result is independent of gas used \Rightarrow absolute temperature.

(g) The figure below shows a pressure-temperature phase diagram for water. Identify the triple point.

[2] Plot a point A on the diagram representing liquid water above the temperature of the triple point.

Plot a two-step process, the first of which is an isothermal decrease of pressure to the triple point pressure, and the second an isobaric temperature decrease to the triple point. Describe the various states of the water as a function of position on the path you have drawn. [8]



① isothermal pressure decrease.

Water goes from liquid to gas at point P.

② isobaric temperature decrease.

Water remains gaseous down to T_{tr} where it becomes a coexisting mixture of gas, liquid and solid.

A vessel contains a mixture of n_1 moles of nitrogen (molecular mass m_1) and n_2 moles of argon (molecular mass m_2) at temperature T and pressure p . Assume it is an ideal gas, and that the rotation of molecules is not quantized but internal vibrations are frozen out by quantization.

(h) What is the ratio of the rms velocity of a nitrogen molecule to that of an argon atom? (show your reasoning). [3] $\frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$ for every molecule, irrespective.

$$\therefore v_{rms} = \sqrt{\frac{3kT}{m}} \quad \therefore \frac{v_{rms}(\text{nitrogen})}{v_{rms}(\text{argon})} = \sqrt{\frac{m_2}{m_1}}$$

(i) What is the partial pressure of the nitrogen (ie, its contribution to the total pressure)? Explain. [3]

$$p_{\text{nitrogen}} = \frac{n_1}{n_1 + n_2} P$$

Total pressure = sum of contributions from each component gas calculated as if the other components were not present (Dalton's Law)

(j) What is the total internal energy of the gas, in terms of the gas constant R ? [4]

$$E_{int} = E_{N_2} + E_{Ar} = \frac{5}{2} n_1 RT + \frac{3}{2} n_2 RT$$

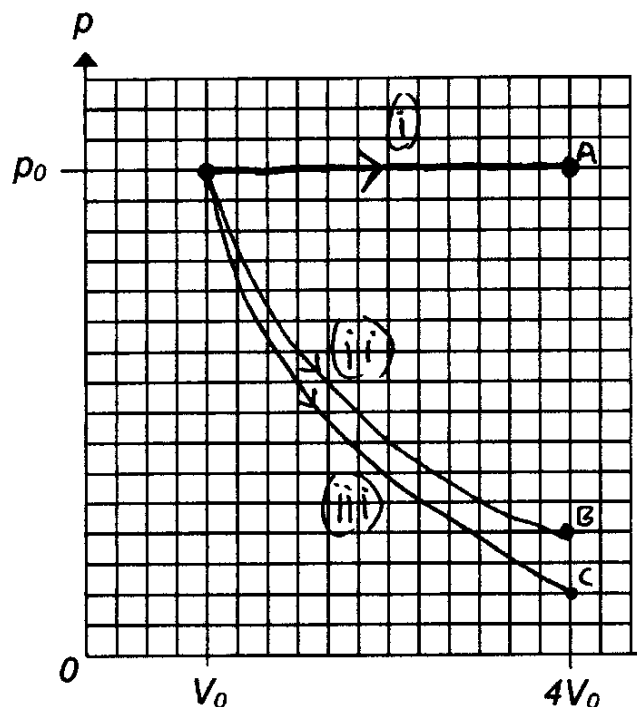
degrees of freedom: diatomic: v_x, v_y, v_z, w, w_z monatomic: v_x, v_y, v_z

$$= \left(\frac{5n_1 + 3n_2}{2} \right) RT$$

Question 2 [39]

An ideal gas, with $\gamma=1.5$, is contained in a cylinder with a vertically movable piston. The pressure can be controlled by adding and removing weights on the piston. The cylinder can be placed in contact with a thermal reservoir of adjustable temperature. The gas is expanded quasistatically from an initial state with volume V_0 , temperature T_0 , and pressure p_0 to each of three (different) final states A, B and C, all with volume equal to $4V_0$, under respectively (i) isobaric, (ii) isothermal and (iii) adiabatic conditions.

(a) Describe and show each of these processes in the p - V diagram below. In each case, say how T and p should be changed or kept constant, if necessary. [9]



(i) to keep p const as V increases we must increase T , ie, heat the gas, leaving the same weight on the piston.

(ii) To keep T const, system must be left in contact with thermal reservoir at temperature T while the number of weights is decreased by a factor of 4.

(iii) The system must be thermally isolated, to prevent heat flow, as the weight is reduced appropriately.

(b) In each case, what is the ratio of the final to the initial pressure? [6]

(i) Isobaric = const. pressure, so $\frac{p_f}{p_i} = 1$

(ii) Isothermal: $pV = nRT = \text{const}$ so $\frac{p_f}{p_i} = \frac{V_i}{V_f} = \frac{1}{4}$

(iii) Adiabatic: $pV^\gamma = \text{const}$ so $\frac{p_f}{p_i} = \left(\frac{V_i}{V_f}\right)^\gamma = \left(\frac{1}{4}\right)^{1.5} = \frac{1}{8}$

(c) Order the three cases according to the work W done on the gas (be careful of signs). Explain. [4]

$W = - \int_{V_i}^{V_f} p dV$. In all cases here, W is negative.

$$[-W_{(i)}] > [-W_{(ii)}] > [-W_{(iii)}]$$

ie magnitude of W is as follows: isobaric > isothermal > adiabatic

(d) In which case(s) is there no change in internal energy, and why? [3]

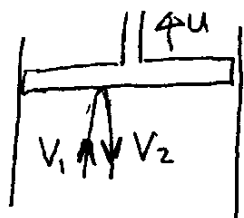
Case (i), isothermal: $E_{int} = \frac{q}{2} NkT = \frac{q}{2} pV = \text{const}$ if T is constant

[NB for an ideal gas, internal energy depends only on temperature]

(e) In which case(s) is the work done equal to the change in the internal energy of the ideal gas, and why? [3]

Case (iii), adiabatic: if no heat flows, by conservation of energy, $\Delta E_{int} = W$

(f) For the adiabatic case (iii), explain in terms of kinetic theory, (considering collisions of the molecules with the piston), why the temperature changes as the piston moves. [4]



If piston moves at speed u , molecules bounce off with smaller speed than they hit; $v_2 < v_1$.

\therefore Kinetic energy is transferred from molecules to piston

$\therefore E_{int}$ decreases $\rightarrow T$ decreases

The space occupied by the gas has a height h . We have derived before (from the variation of pressure with height) that the probability distribution function of the molecular gravitational energy $E_G = mgy$ has a Boltzmann form: $n(E_G) = A e^{\exp(-E_G/kT)}$ for $0 < y < h$.

(g) If $n(y)$ is the probability distribution function of heights within the cylinder, calculate the normalization constant A . [3]

$$1 = \int_0^h n(y) dy = \int_0^h A e^{-\frac{mgy}{kT}} dy = \left[A \left(-\frac{kT}{mg} \right) e^{-\frac{mgy}{kT}} \right]_0^h \therefore A = \frac{mg}{kT} \left(1 - e^{-\frac{mgh}{kT}} \right)$$

(h) Write down an expression for the mean value of E_G in the box [2] and evaluate it (integrating by parts.) [3]

$$\begin{aligned} \langle E_G \rangle &= \int_0^h E_G n(y) dy = \int_0^h A \cdot mgy \cdot e^{-\frac{mgy}{kT}} dy \\ &= kT \cdot (1 - e^{-\alpha}) [1 - e^{-\alpha} (1 + \alpha)] \quad \text{where } \alpha = \frac{mgh}{kT} \end{aligned}$$

Unsurprisingly, no one got this!

(i) Why does the equipartition theorem $\langle E \rangle = qkT/2$ not apply here - or does it? [2]

It doesn't apply because E is not a quadratic function of y , and because y doesn't range up to ∞ .