

SEMESTER 2 EXAMINATION 2013-2014

Energy and Matter

Duration: 120 MINS (2 hours)

This paper contains 9 questions.

Answers to Section A and Section B must be in separate answer books.

Answer **all** questions in **Section A** and **only two** questions in **Section B**.

Section A carries 1/3 of the total marks for the exam paper and you should aim to spend about 40 mins on it.

Section B carries 2/3 of the total marks for the exam paper and you should aim to spend about 80 mins on it.

An outline marking scheme is shown in brackets to the right of each question.

A Sheet of Physical Constants is provided with this examination paper.

Only university approved calculators may be used.

A foreign language translation dictionary (paper version) is permitted provided it contains no notes, additions or annotations.

Useful formulae

Constants:

$$\text{Boltzmann constant } k_B = 1.3806503 \times 10^{-23} \text{ J K}^{-1}$$

$$\text{Avogadro number } N_A = 6.0221367 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Universal gas constant } R = k_B N_A = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{atomic mass unit to kg conversion : } 1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$$

Conversions:

$$0 \text{ K} = -273^\circ\text{C}$$

$$1 \text{ atm} = 101\,325 \text{ Pa} = 760 \text{ Torr}$$

$$1 \text{ Pa} = 10^{-5} \text{ bar} = 9.8696 \times 10^{-6} \text{ atm} = 7.5 \times 10^{-3} \text{ Torr}$$

Common integrals:

$$\text{Gaussian integral : } \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\text{Integration by parts : } \int_a^b f dg = [fg]_a^b - \int_a^b g df$$

Parametric differentiation for Gaussian Integrals :

$$x^{2n} e^{-\alpha x^2} = (-1)^n \frac{d^n}{d\alpha^n} e^{-\alpha x^2} \text{ and } \int \frac{\partial^n}{\partial \alpha^n} e^{-\alpha x^2} dx = \frac{d^n}{d\alpha^n} \int e^{-\alpha x^2} dx$$

Some identities of differential calculus :

$$d(fg) = f dg + g df$$

$$df(x, y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\text{chain rule: } \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x$$

$$\text{reciprocal: } \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x = 1$$

$$\text{reciprocity : } \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Thermodynamic potentials:

$$\text{Internal Energy: } U$$

$$\text{Enthalpy : } H = U + PV$$

$$\text{Helmholtz Free Energy : } F = U - TS$$

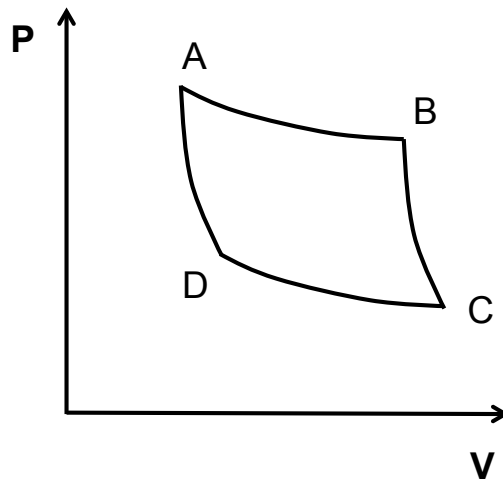
$$\text{Gibbs Free Energy : } G = U - TS + PV$$

Section A

- A1.** What is the volume occupied by 1 mol of gas at 10^{-10} Torr, the pressure of an “ultra high vacuum” chamber, at ambient temperature ($T = 300$ K)? [2]
- A2.** Mr. Boltzmann sits in his living room at 18°C . He decides he is rather cold and turns the heating up so that the temperature is 25°C . What happens to the total energy of the air in his living room? Justify your answer. [2]
- A3.** Thermodynamical systems can be subjected to transformation. Explain briefly what is meant by
- (a) The system is performing a reversible process. [1]
 - (b) The system is performing an irreversible process. [1]
 - (c) The system is in thermal equilibrium. [1]
- A4.** A mug of tea has been left to cool from 90°C to 18°C . If there is 0.2 kg of tea in the mug, and the tea has specific heat capacity of $4200 \text{ J K}^{-1} \text{ kg}^{-1}$,
- (a) calculate the tea’s entropy. [3]
 - (b) Consider the surroundings as a reservoir at 18°C ; calculate its entropy change. [3]
 - (c) Calculate the entropy change for the whole Universe. [1]
Comment on its sign. [1]

TURN OVER

A5. A Carnot engine has a cycle pictured below



- (a) What thermodynamic processes are involved at the boundaries AD, BC, AB, and CD? [2]
- (b) Where is work put in and where is it extracted? [2]
- (c) If the above is a system engine with $T_{in} = 450$ K operating at room temperature ($T = 300$ K), calculate the efficiency. [1]

Section B

B1. (a) Describe three properties that characterise black-body radiation. [3]

(b) Calculate the photon energy density of a black-body (Stefan-Boltzmann law) and derive a form for the constant σ . Follow the steps proposed:

(i) Calculate the energy stored in a cavity of volume $V = L^3$ as

$$U = \iiint dk_x dk_y dk_z E(\vec{k}) f(\vec{k}) = \int_0^\infty \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} g(\omega) d\omega$$

where $\beta = \frac{1}{k_B T}$, $\hbar = \frac{h}{2\pi}$ is the reduced Planck constant, and the so-called density of states is

$$g(\omega) = \frac{V \omega^2}{\pi^2 c^3}$$

Make use of the integral

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

[4]

(ii) Pose $u = \frac{U}{V} = \frac{4\sigma}{c} T^4$ and obtain a form for σ .

[2]

Give a numerical value for the calculated σ in SI units.

[3]

(c) Cosmic Microwave Background (CMB) radiation is considered to be the left-over of the Universe in the early stage of its history, right after the Big-Bang. It can be well described by considering the Universe as a black-body at a temperature of $T = 2.73$ K.

(i) What is the photon energy density u of the Universe?

[3]

(ii) What is the average power (energy per second) due to CMB radiation which lands on your outstretched palm (consider a palm to have a surface of $\approx 10 \text{ cm}^2$) ?

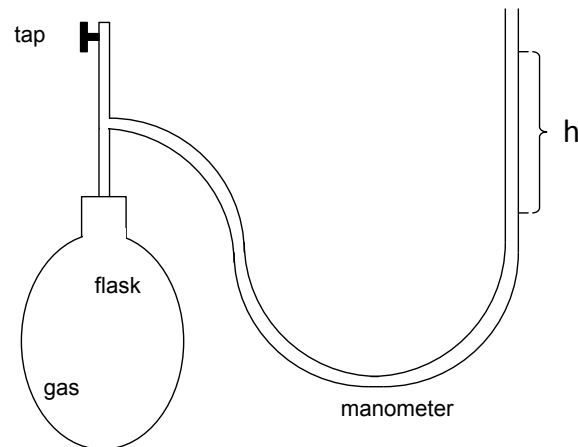
[3]

(iii) Given the average photon energy per photon to be $\approx 2.7 k_B T$, estimate the number of CMB photons which fall in your outstretched palm every second.

[2]

TURN OVER

B2. We aim at analysing a method to determine experimentally the ratio $\gamma = C_p/C_V$ for an ideal gas, proposed by Clément and Desormes in the 19th Century. The method consists of allowing an ideal gas to undergo a quasi-static adiabatic expansion followed by a constant volume process and read the changes in pressure through the changes in the height h of the liquid inside the manometer (see figure).



STEP 1) When the flask is closed, a mass of dry air of volume V_0 at atmospheric pressure P_0 is partly inside the flask, partly outside. The manometer is calibrated to measure h_0 .

STEP 2) Air from the outside is slowly pumped into the flask (to volume V_1). A tube manometer indicates the height h_1 .

STEP 3) Then the lid of the flask is quickly opened and closed, letting the pressure return momentarily to atmospheric. The sample expands adiabatically ($P_2 = P_0, T_2 < T_0, V_1 \rightarrow V_2$).

STEP 4) Finally, the sample is allowed to warm up slowly at constant volume V_3 to room temperature T_0 . A height h_3 is measured.

- (a) State what is meant by a (reversible) adiabatic transformation. Relate the pressure and the volume changes for an ideal gas undergoing an adiabatic expansion. Sketch this expansion on a P-V indicator diagram. [3]

Calling $(P_0, V_0), (P_1, V_1), (P_2, V_2), (P_3, V_3)$ the four steps described above, sketch the P-V diagram of the whole process and characterise these transformations. [3]

- (b) Compare the equation of state for this ideal gas at points $(P_0, V_0), (P_1, V_1)$ and (P_3, V_3) . Which quantity is conserved? [1]

Is the number of molecules conserved in the process? [1]

Derive an expression for $\gamma = \frac{C_p}{C_v}$ in terms of $P_0, P_1,$ and P_3 . [2]

Use the hydrostatic equilibrium equation to relate the pressures P and height h (depth). Write the explicit expression of γ in terms of $h_0, h_1,$ and h_3 . [2]

- (c) Starting from the first law of thermodynamics and the definition of C_p and C_v show that, in general

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$

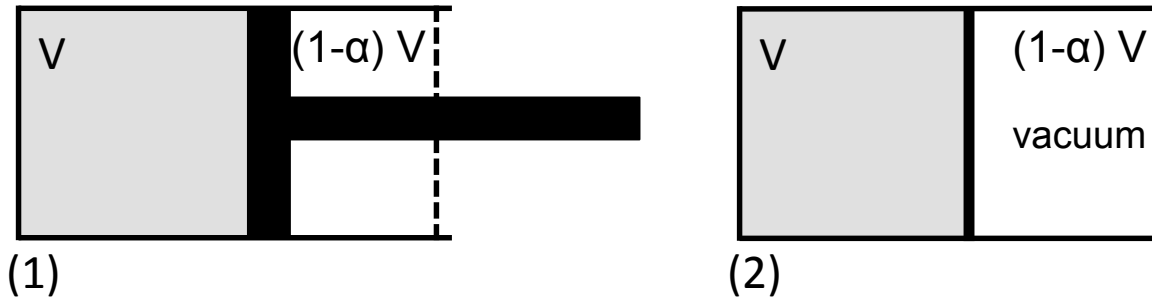
[6]

Use the following steps as a guide to your answer:

- write the first law in differential form for a reversible process with respect to heat
- consider the internal energy as a function of V and T
- consider V as a function of T and P and apply the chain rule
- recognise C_p and C_v and obtain the final form
- find the result for the case of an ideal gas for 1 mole. [2]

TURN OVER

B3. Consider n moles of a gas, initially confined within a volume V and held at a temperature T . The gas is expanded to a total volume αV , where α is a positive constant, by (1) a reversible isothermal expansion or (2) removing a partition and allowing a free expansion in the vacuum. Both cases are depicted in the figure below:



- (a) • Describe a reversible isothermal process in terms of dQ , dW , and dU . [1]
 • Describe the free expansion (2) in terms of dQ , dW , and dU . Is it reversible? [1]
 • Does $dQ = TdS$ apply in (2)? [1]

Justify your answers.

- (b) Assuming the gas is ideal, derive an expression for the change of entropy of the gas in case (1). [1]
 (c) Derive the change of entropy of the gas undergoing the transformation (2). [2]
 (d) If now the gas obeys the Van der Waals equation

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

what is the entropy change ΔS for the isothermal process?

Use the following steps as a guide to your answer:

- Write the entropy as a general differential form, function of volume V and temperature T . How can we simplify this expression? [2]

- Use the Helmholtz free energy F to obtain the Maxwell relation relating the variation of S over V (which you don't know) to the variation of P over T , at constant volume (the variables of the equation of state). [2]
- Write dS as a function of the volume (times dV) and integrate dS over the change in volume. [2]

(e) Show that in the case (2), the temperature change of the gas is zero if the gas is ideal, and is proportional to $\frac{\alpha-1}{\alpha}$ if it follows the above Van der Waals equation of state.

Use the following steps as a guide to your answer:

- What thermodynamic quantity is conserved? [1]
- Consider the total internal energy and write its infinitesimal change as a function of temperature and volume $U = U(T, V)$.
- Rewrite the infinitesimal temperature change in terms of the infinitesimal volume change. Do you recognise any of the proportionality terms? [2]
- In order to calculate the variation of the internal energy with respect to the volume (at constant temperature), show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

[3]

Use the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ in order to rewrite the variation of S over V (which you don't know) into the variation of P over T , at constant volume, (the variables of the equation of state).

- Combine the above results and rewrite dT in terms of an explicit function of the volume (times dV), then integrate dT over the change in volume in the case of an ideal gas and in the case of a gas following the above Van der Waals equation of state. [2]

TURN OVER

B4. (a) State the Clausius-Clapeyron equation in terms of liquid and vapour phases at phase equilibria. [1]

(b) Sketch a P-T diagram in the case of a triple point. [1]

Along the boundary in the P-T diagram, we can write

$$\frac{d}{dT} = \left(\frac{\partial}{\partial T} \right)_P + \frac{dP}{dT} \left(\frac{\partial}{\partial P} \right)_T$$

(c) Using the expression for the latent heat in terms of vapour and liquid entropies, show that the temperature dependence of the latent heat of vaporisation L is given by the following expression

$$\frac{d}{dT} \left(\frac{L}{T} \right) = \frac{C_{P_V} - C_{P_L}}{T} + \left[\left(\frac{\partial S_V}{\partial P} \right)_T - \left(\frac{\partial S_L}{\partial P} \right)_T \right] \frac{dP}{dT}$$

here, S_V, S_L, C_{P_V} , and C_{P_L} are, respectively, the entropies and the heat capacities of vapour and liquid phases. [2]

(d) Show that

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

If the natural variables are T and P , which thermodynamic potential do you need? [1]

Write the differential of this thermodynamics potential as a function of T and P and identify the entropy S and the volume V . In order to prove the above result, find the relation between the partial derivatives of S and V as functions of P and T respectively. [2]

Using the above Maxwell relation and the result in (c), obtain the slope $\frac{dP}{dT}$ for an incompressible liquid. [4]

- (e) The saturated vapour of an incompressible liquid undergoes an adiabatic expansion;

What thermodynamic quantity is conserved? [1]

Give the differential of the conserved thermodynamic quantity in terms of temperature and pressure. Equating it to zero (it is conserved!), calculate the P-T slope $\frac{dP}{dT}$ in this case. [3]

- (f) "Liquid will condense out if the gradient of the expansion is smaller than the gradient of the phase boundary".

Explain the statement graphically on a P-T diagram. [2]

- (g) Using the results obtained in points (d) and (e), show that the condition in (f) implies that

$$C_{P_L} + T \frac{d}{dT} \left(\frac{L}{T} \right) < 0$$

[3]

END OF PAPER