NATIONAL UNIVERSITY OF SINGAPORE

PC2230 Thermodynamics and Statistical Mechanics

(Semester II: AY2008-09, April)

Time Allowed: Two Hours

INSTRUCTIONS TO CANDIDATES

1. This examination paper contains **SIX SHORT** questions in Part I and **THREE LONG** questions in Part II. It comprises **NINE** printed pages.
2. Answer **ALL** questions in Part I. The answers to Part I are to be written on the question paper itself and submitted at the end of the examination.
3. Answer any **TWO** of the questions in Part II. The answers to Part II are to be written on the answer books.
4. This is a CLOSED BOOK examination. Students are allowed to bring in an A4-sized (both sides) sheet of notes.
5. The total mark for Part I is 48 and that for Part II is 52.

Matriculation No.	**Marks**

PART I

THIS PART OF THE EXAMINATION PAPER CONTAINS SIX (6) SHORT-ANSWER QUESTIONS FROM PAGE 2 TO 7.

Answer ALL questions. The answers are to be written on this question paper itself and submitted at the end of the examination.

1. Show that the work done on one mole of a perfect gas in an adiabatic quasistatic compression from volume V_1 to V_2 and pressure P_1 to P_2 is given by

$$W = \frac{P_1V_1}{\gamma-1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right] \quad , \quad \gamma = \frac{C_p}{C_v} \; .$$

2. At temperature T, a crystal with interstitial defects has n of its N atoms at the interstitial sites. The energy and entropy of the crystal are given respectively by

$$E(n) = n\varepsilon \quad , \quad S(n) = k \ln\left[\frac{N!}{n!(N-n)!}\right]^2 .$$

Write down the Helmholtz free energy $F(n)$ and hence determine the temperature dependence of the concentration n/N of the interstitial defects.

3. At room temperature T, the molar specific heat at constant volume of a diatomic gas has contributions from the translational and rotational motions. The rotational energy levels, whose spacing is small compared to kT, are given by

$$\varepsilon_r = \frac{\hbar^2}{2I} r(r+1) \quad , \quad \text{degeneracy} = 2r+1 \quad , \quad r = 0,1,2,..., \; .$$

Determine the molar specific heat of the gas.

4. The partition function for photons is given by

$$Z(T,V)=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\ldots\exp\{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)\}.$$

(i) Show that $Z(T,V)$ can be written as $Z(T,V)=\prod_{r=1}^{\infty}\frac{1}{1-\exp(-\beta\varepsilon_r)}$.

(ii) Show that the mean occupation number of the single photon state r is given by $\bar{n}_r=\frac{1}{\exp(\beta\varepsilon_r)-1}$.

$$\left[\text{Sum of n terms of geometrical series } S_n=\frac{a(1-r^n)}{1-r}\right]$$

5. The standard deviation Δn_i of the occupation number n_i of a quantal gas is given by

$$(\Delta n_i)^2 = kT\left(\frac{\partial \overline{n}_i}{\partial \mu}\right)_{T,V}.$$

(i) Obtain expressions for Δn_i for the Bose-Einstein and Fermi-Dirac statistics.

(ii) Comment on the relative fluctuation $\Delta n_i/\overline{n}_i$ for the two statistics.

6. The molar heat capacity at constant volume of a perfect gas of bosons, each of mass m, at a temperature T below the condensation temperature T_c is given by

$$C_v = 0.77 \times \frac{5}{2} R \left(\frac{T}{T_c} \right)^{\frac{3}{2}} .$$

For the gas at $T < T_c$, obtain expressions for

(i) the internal energy per mole E,

(ii) the entropy per mole in terms of E,

(iii) the Helmholtz free energy per mole in terms of E.

PART II

THIS PART OF THE EXAMINATION PAPER CONTAINS THREE (3) LONG QUESTIONS AND COMPRISES TWO PAGES.

Answer any TWO questions.

1. The statistical weight $\Omega(n)$ of a system of N spins $\frac{1}{2}$, each having a magnetic moment μ and located in a magnetic field B is given by

$$\Omega(n) = \frac{N!}{n!(N-n)!},$$

where n is the number of magnetic moments orientated parallel to B.

(i) Show that the total energy E, the entropy S and the absolute temperature T of the system are given respectively by

$$E = (N-2n)\mu B,$$

$$S = k\left[N \ln N - n \ln n - (N-n)\ln(N-n)\right],$$

$$\frac{1}{T} = \frac{1}{2\mu B} k \ln \frac{n}{N-n}.$$

(ii) Use the results of (i) to derive a relation expressing E as a function of T.

(iii) Show that the partition function for one magnetic moment is given by

$$Z_1 = 2\cosh\frac{\mu B}{kT}.$$

Use this result to find E as a function of T and compare with that of (ii).

2. (i) Consider a system in thermal contact with a heat bath at temperature T. Show that the partition function Z, the mean energy $\bar{E}$ and the standard deviation of the energy ΔE of the system are given respectively by

$$Z = \sum_r e^{-\beta E_r} \quad , \quad \bar{E} = -\frac{\partial \ln Z}{\partial \beta} \quad , \quad (\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} \, .$$

(ii) The partition function Z for a perfect classical gas is given by

$$Z = \frac{1}{N!} V^N \left(\frac{2\pi m}{\hbar \beta} \right)^{\frac{3}{2}N} .$$

Determine $\bar{E}$, ΔE and the relative fluctuation $\Delta E / \bar{E}$ for the gas. Comment on the result of $\Delta E / \bar{E}$.

3. Consider the dissociation gaseous reaction

$$2CO_2 \rightleftharpoons 2CO + O_2 .$$

(i) Express the chemical potential of CO_2 in terms of those of CO and O_2.

(ii) In what proportion, $dN(CO_2) : dN(CO) : dN(O_2)$ can the numbers of molecules of CO_2, CO and O_2 vary?

(iii) State the law of mass action and obtain the equilibrium constant $K_c(T)$ for the reaction.

(iv) Let f be the fraction of CO_2 molecules dissociated into CO and O_2 molecules when the system is in equilibrium. Derive the pressure dependence of f at a fixed temperature and comment on the dependence.

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