NATIONAL UNIVERSITY OF SINGAPORE

PC2230 THERMODYNAMICS AND STATISTICAL PHYSICS

(Semester II: AY 2006-07, 27 April 2007)

Time Allowed: 2 Hours

INSTRUCTIONS TO CANDIDATES

1. This examination paper contains **6 short-answer** questions in Part I and **3 long-answer** questions in Part II. It comprises **10** printed pages.
2. Answer **ALL** the 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.

IMPORTANT

Matriculation No.	Marks

PART I

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

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

1. Write down the general definitions, in terms of entropy, of (i) absolute temperature and (ii) pressure for a system, in equilibrium, specified by its energy E, volume V and the number of particles N.

2. (a) State the Clausius statement of the second law of thermodynamics.

(b) State the respective criteria, with reference to either the entropy, the Helmholtz function or the Gibbs function, for the equilibrium condition of a system

(i) at constant energy and volume,
(ii) at constant temperature and volume,
(iii) at constant temperature and pressure,
(iv) at constant enthalpy and pressure.

3. A paramagnetic crystal, in thermal equilibrium at temperature T, contains N atoms each with a spin of 1 and magnetic moment μ. Assuming only interactions of the dipoles with an applied magnetic field B, show that the mean magnetic moment of the crystal is given by

$$M = N\mu \frac{2\sinh x}{1+2\cosh x},$$

where $x \equiv \mu B/kT$.

4. In the Einstein model, a solid of N atoms is treated as $3N$ independent harmonic oscillators each with angular frequency ω. Assume the solid is in equilibrium at temperature T. Given that the mean energy is $\bar{\varepsilon} = -\partial(\ln Z)/\partial\beta$, where Z is the partition function, and $\beta = (kT)^{-1}$, show that the heat capacity at constant volume of the solid is

$$C_V = 3Nk\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right)-1\right]^2},$$

where the Einstein temperature Θ_E is given by $\hbar\omega = k\Theta_E$.

[Note: $(1-a)^{-1} = 1 + a + a^2 + \ldots$ for $|a| < 1$]

5. By writing $S = S(T, V)$, show that

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.$$

6. Consider the following chemical reaction involving the chemical species A, B, C, D, and E:

$$3A + 2B + 4C \rightleftharpoons 2D + 3E.$$

If the chemical potentials of A, B, C, D and E are -0.4, -0.3, 0.2, 0.1 and -0.2 eV respectively, in which direction (left or right) does the reaction proceed spontaneously? Explain your answer.

PART II

THIS PART OF THE EXAMINATION PAPER CONTAINS THREE LONG-ANSWER QUESTIONS AND COMPRISES THREE PAGES.

Answer any TWO questions.

1. (a) Consider a system in thermal contact with a heat reservoir at a temperature T. The pressure of the system is given by $P = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_\beta$ where Z is the partition function, $\beta = (kT)^{-1}$, and k the Boltzmann constant. Show that the pressure can be expressed, in terms of the Helmholtz function, as $P = -\left(\frac{\partial F}{\partial V}\right)_T$.

(b) Consider an ideal classical gas of N molecules, each of mass m, in an enclosure of volume V at temperature T.

(i) State the respective criteria for a gas to be considered as an ideal gas and as a classical gas.

(ii) The partition function of the gas is $Z(T,V,N) = [Z_1(T,V)]^N / N!$, where $Z_1\left(= Z_1^{\text{tr}} Z_{\text{int}}\right)$ is the single-molecule partition function. Here $Z_1^{\text{tr}}\left[= V\left(2\pi mkT/h^2\right)^{3/2}\right]$ is the translation partition function, and Z_{int} is the internal partition function of a molecule. Determine Z_{int} in terms of the energies of the internal motions of the molecules.

(iii) Find the Helmholtz function for the gas system.

(iv) Hence, derive the equation of state for an ideal classical gas.

2. (a) In the Planck law for black-body radiation, the spectral energy density, $u(\omega, T)$, is given by

$$u(\omega,T)\,\mathrm{d}\omega = \frac{\hbar\omega^3\,\mathrm{d}\omega}{\pi^2 c^3\left[\exp(\hbar\omega/kT)-1\right]}\,.$$

(i) Derive the Stefan-Boltzmann law.

(ii) Find the power radiated by the sun, per megacycle bandwidth, at a wavelength of 3 cm. Assume the sun, which has a radius of 7×10^8 m, to be a black body at a temperature of 6×10^3 K.

(b) (i) Use relevant $T\mathrm{d}S$ equations to determine the difference in the heat capacities, $C_P - C_V$, at temperature T, in terms of the volume expansivity $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, and the isothermal compressibility $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$.

(ii) Hence, determine whether C_p is always larger than C_V.

3. (a) Consider a two-phase single-substance system.

(i) State the equilibrium condition, in terms of the Gibbs function, for the two phases of the system.

(ii) Hence, use the equilibrium condition to derive the Clausius-Claypeyron equation, in terms of ΔS the change in entropy and ΔV the change in volume, as the substance undergoes a transformation from one phase to the other.

(iii) Express the Clausius-Claypeyron equation in terms of the latent heat of transformation when a given quantity of the substance is transformed from phase 1 to phase 2.

Question 3 continued on next page.

(b) At both the triple point as well as the ice point, ice and water are in equilibrium. However, the triple point temperature is higher than the ice point temperature. What are the physical reasons for the difference? Give a quantitative explanation for the difference.

[Note: specific volume of ice = 1.09070×10^{-3} m^3/kg; specific volume of liquid water = 1.00013×10^{-3} m^3/kg; triple point pressure = 611.3 Pa; latent heat of fusion of water = 3.35×10^5 J/kg]

(M.H. Kuok)

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