

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - DECEMBER 2001
PHYSICAL CHEMISTRY I - SCH 2104
TIME: 3 HOURS

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INSTRUCTIONS TO CANDIDATES

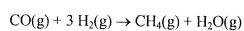
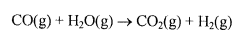
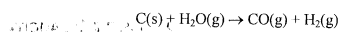
Answer **ALL** questions from Section A and **ANY THREE** from Section B.

Gas Constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Avogadro's Number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; 760 Torr = 1 atm; $0^\circ\text{C} = 273.15 \text{ K}$

SECTION A

- For neon the parameters of the Lennard-Jones (12,6) potential are $\epsilon = 4.92 \times 10^{-22} \text{ J}$ and $\sigma = 275 \text{ pm}$.
 - At what distance (other than infinity) is the potential zero? (4 marks)
 - What are the attractive and repulsive contributions to the energy at this distance? (6 marks)
- Using the formula for the sum to infinity of a geometric series, show that the partition function for a set of equally-spaced vibrational energy levels is given by
$$q_v = 1/(1 - e^{-hv/kT})$$
where hv is the spacing between successive levels, and deduce a formula for the occupancies of the individual levels. (10 marks)
- A flask containing several moles of acetic acid at its freezing point of 16.6°C is lowered briefly into an ice/water bath. When it is removed it is found that exactly 1 mol of acetic acid has frozen. Given that the enthalpies of fusion of water and acetic acid are 5.98 and $11.45 \text{ kJ mol}^{-1}$ respectively:
 - What is the change in entropy of the acetic acid? (3 marks)
 - What is the change in entropy of the water? (3 marks)
 - Calculate the change in entropy of the combined system water/acetic acid, and show that the process is irreversible. (4 marks)

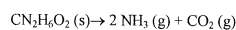
4. Methane may be produced from carbon by the following steps:



- (a) Calculate ΔH° for each of these reactions from the data below. (9 marks)
- (b) Give an equation for the overall reaction, calculate its standard enthalpy change from the data below, and show that Hess's Law holds. (5 marks)
- (c) If this reaction sequence were used to convert the carbon in coal to methane, would it be better to carry out the steps in three separate reactors in a single reactor? Explain. (4 marks)

Standard enthalpies of formation (KJ mol^{-1}): CO(g) -110.53; $\text{CO}_2\text{(g)}$ -393.51; $\text{CH}_4\text{(g)}$ -74.81; $\text{H}_2\text{O(g)}$ -241.82.

5. Ammonium carbamate decomposes according to the equation:



When an excess of ammonium carbamate is placed in a previously evacuated vessel, under conditions such that the partial pressure of ammonium carbamate is negligible, show that:

$$K = 4/27 (P/P^\circ)^3$$

where P is the total pressure. (6 marks)

6. An aqueous solution contains NaCl, NaBr, KCl and KBr. How many components are there in the solution? Explain. (4 marks)

SECTION B

7. (a) Explain how the nuclear motions of a molecule may be classified. How many modes of motion below to each type for a molecule of N atoms? Apply your formulae to determine the modes of nuclear motion for a diatomic molecule. (9 marks)
- (b) With reference to the Boltzmann distribution, and using the diagram on the next page, explain how the population of excited states is determined by the relative energy gaps for the types of excitation shown. (6 marks)



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8. The molar heat capacity of carbon dioxide gas may be represented by

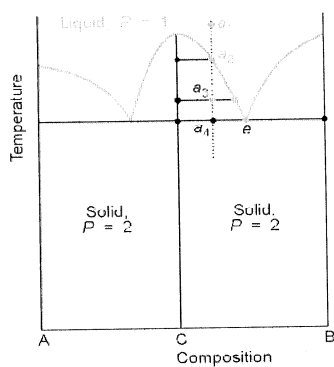
$$\bar{C}_p = \alpha + \beta T + \gamma T^{-2}$$

with $\alpha = 44.22 \text{ J K}^{-1} \text{ mol}^{-1}$, $\beta = 8.79 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$ and $\gamma = -8.62 \times 10^5 \text{ J K mol}^{-1}$.

- (a) How much heat is required to heat one mole of CO_2 gas from 300 K to 1000 K? (7 marks)
- (b) What is the change in entropy on heating one mole of CO_2 gas over the same temperature range? (8 marks)

9. The figure below is the solid/liquid phase diagram at constant pressure for the system A/B.

- (a) Explain the presence of a melting point maximum at the composition marked C. (3 marks)
- (b) How many phases are at equilibrium at the point marked e, and what are they? (4 marks)
- (c) State the Phase Rule, and apply it to the point e on the diagram. (3 marks)
- (d) Describe what happens on cooling along the isopleth marked $a_1 \dots a_4$. (5 marks)



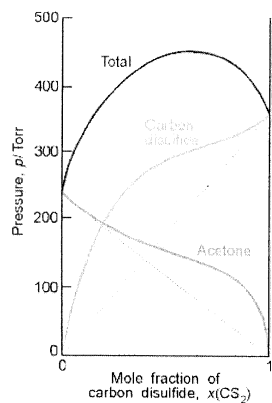
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10. The figure below shows the phase diagram for the system acetone/carbon disulphide at 298 K.

(a) Given that the standard enthalpies of evaporation of acetone and carbon disulphide are 29 and 27 kJ mol⁻¹ respectively, use the Clausius-Clapeyron equation and data from the graph to estimate their boiling points at 1 atm pressure. (6 marks)

(b) This system exhibits azeotropic behaviour. Estimate the azeotropic composition from the diagram. Is it a low-boiling or high boiling azeotrope? Explain. (4 marks)

(c) Use your results from (a) and (b) to sketch the acetone/carbon disulphide liquid/vapour phase diagram at 1 atm pressure. (5 marks)



11. The following data refer to three isomeric hydrocarbons C₂₀H₁₂ at 1000 K.

Species	ΔH_f° (formation) / (kJ mol ⁻¹)	S_m° / (J K ⁻¹ mol ⁻¹)
Perylene	253.2	987.9
Benzo(e)pyrene	253.2	993.7
Benzo(a)pyrene	262.4	999.4

What are the equilibrium mole fractions of these three isomers at 1000 K? (15 marks)

END OF QUESTION PAPER!!!!

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