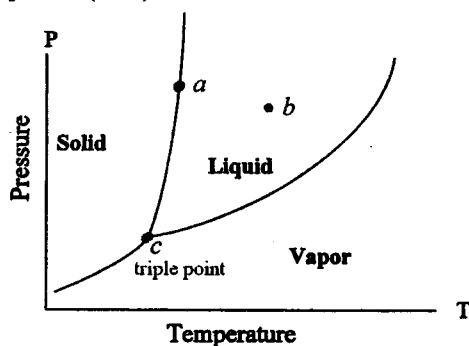


國立臺灣科技大學
九十四學年度碩士班招生考試試題

系所組別：高分子工程系碩士班丁組
科目：物理化學

總分 100 分

1. What is the **Gibbs's Phase Rule**? According to the unary system phase diagram as shown, determine the degree of freedom at indicated points. (10%)



- 2.(a) The van der Waal equation is usually used to describe the real gas behavior. And the formula can be expressed as:

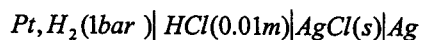
$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

The terms "a" and "b" are used to express in this equation. Can you show the relationship of a and b with P_{cr} and T_{cr} , where P_{cr} and T_{cr} are critical pressure and temperature, respectively? (15%)

- (b) A mass of 500g of gaseous ammonia is contained in a 30000 cm³ vessel immersed in a constant-temperature bath at 65°C. Calculate the pressure of the gas by each of following:

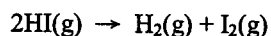
- (i) The ideal gas equation. (2%)
(ii) The van der Waal equation, where values of P_{cr} and T_{cr} for ammonia are 112.8 bar and 405.6K, respectively. (3%)

3. The emf of the cell



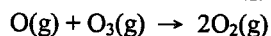
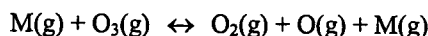
is 0.2002 V at 25 °C; $\partial E / \partial T$ is $-8.665 \times 10^{-5} V/K$. Write the cell reaction and calculate ΔG , ΔS , and ΔH . (12%)

4. The rate constant for the reaction for the reaction



is $1.22 \times 10^{-6} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 575 K and $2.50 \times 10^{-3} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 716 K. Estimate the value of E_a from these data. (7%)

5. The decomposition of ozone $2O_3 \rightarrow 3O_2(g)$ occurs by the reaction mechanism :



where M is a molecule that can exchange energy with the reaction ozone molecule through a collision, but M itself does not react. Use this mechanism to derive the rate law for $d[O_3]/dt$ assuming that the intermediate O(g) concentration can be treated by the steady-state approximation. (7%)

6. To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by $6.26 \times 10^{11} \text{ Hz}$. Calculate the bond length of $H^{35}Cl$. (7%)

7. Using the LCAO MO technique, determine which of the two arrangements, linear or the triangular H_3^+ , is the more stable state. (7%)

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8. One mole of $\text{H}_{2(g)}$ is heated from 300K to 500K at constant volume. Given that $C_p (\text{J/K-mol}) = 27.28 + 3.26 \times 10^{-3} T + 50000 T^{-2}$. Treating H_2 as an ideal gas,
- (a) calculate the entropy change ΔS in this process. (5%)
 - (b) If the initial pressure is 1 atm, what is the final pressure? (2%)
 - (c) Calculate the internal energy change ΔU in this process (3%)
9. A hydrogen atom in a one-dimensional box of $2 \text{ \AA}$ long.
- (a) Calculate the energy of level 2. (5%)
 - (b) How many levels are there with energy less than 1.0 eV? (5%)
10. The attractive energy between ions M^+ and A^- separated by a distance r is $(100/r)$, and the repulsive energy is $0.1/r^6$. The unit of energy is kJ/mol, and the unit of r is nm. Calculate (a) the equilibrium interionic distance and (b) the net energy at that distance. (10%)

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