國立成功大學75學年度 化學研究所考試(試題) 共 2 頁 第 1 頁

1. Sketch the ESR spectrum for an unpaired electron in the presence of three protons for the following cases: (a) the protons are not equivalent, (b) the protons are equivalent, and (c) two protons are equivalent and the third is different. (3%)

2. For a particle in a cubic box, $E=\frac{h^2}{8ma^2}(n_1^2+n_2^2+n_3^2)$, calculate E for the first 5 states. What is the degeneracy for each energy level? (5%)

3. Tungsten has a body-centered cubic structure at room temperature. Since the density is 19.35 $g\,cm^{-3}$, what is the atomic radius? (atomic mass: W = 183.85) (6%)

4. The separation of the pure rotation lines in the spectrum of $C^{12}O^{16}$ is 3.86 cm^{-1}. Calculate (a) rotational constant B. (b) the equilibrium internuclear separation. Given: $B=\frac{h}{8\pi^2cI}$ where I is moment of inertia. (8%)

5. Dissolved in benzene, methyl iodide and pyridine react by a reaction first-order in each reactant with $k = 0.352\times10^{-4}\ L\,mol^{-1}s^{-1}$ at 40°C and $k = 1.46\times10^{-4}\ L\,mol^{-1}s^{-1}$ at 60°C. (a) What is activation energy E_a. (b) at 0°C how long does it take one-third of the pyridine to disappear by reaction in a solution initially one-molar in each reactant? (8%)

6. For the reaction: $2HI_{(g)} = H_{2(g)} + I_{2(g)}$. at 698.6K, $K_p = 1.83\times10^{-2}$. (a) How many grams of HI will be formed when 10g of I_2 and 0.2g of H_2 are heated to this temperature in a 3-L vessel? (b) What will be the partial pressures of H_2, I_2 and HI? (atomic mass: H = 1, I = 127) (8%)

7. At 90°C the vapor pressure of toluene is 400mm Hg, and that of o-xylene is 150 mm Hg. (a) What is the composition of a liquid mixture that will boil at 90°C when the pressure is 0.5 atm? (b) What is the composition of the vapour produced? (8%)

8. When pH = 4, for the reaction $Pb + PbO_{2(s)} + 2H_2SO_{4(aq.)} = 2PbSO_{4(s)} + 2H_2O_{(l)}$ at 25°C. Find the value of (a)ΔG° and (b)ΔG (when pH = 4). (8%)

Given: $PbO_{2(s)} + SO_4^{2-}{}_{(aq.)} + 4H^+_{(aq.)} + 2e^- = PbSO_{4(s)} + 2H_2O_{(l)}$ $E^\circ = 1.68V$

$PbSO_{4(s)} + 2e^- = Pb_{(s)} + SO_4^{2-}{}_{(aq.)}$ $E^\circ = -0.41V$

9. With the heats of formation and C_p for SO_2, O_2 and SO_3 listed below, calculate ΔH and ΔU at 425°C for the reaction $2SO_{2(g)} + O_{2(g)} = 2SO_{3(g)}$. (10%)

gas	$\Delta\bar{H}_f^\circ$ ($KJ\,mol^{-1}$)	C_p ($J\,mol^{-1}K^{-1}$)
O_2	0	$27.2 + 0.0042T$
SO_2	−297	$31.4 + 0.0272T$
SO_3	−395	$42.2 + 0.0272T$

10. For measuring the coefficient of viscosity (η) of a liquid, using the rate of settling ($\frac{dx}{dt}$) of a sphere (radius = r, density = ρ) in a liquid (density = ρ_0).
(a) Show that $\frac{dx}{dt} = \frac{2r^2(\rho-\rho_0)g}{9\eta}$, g is the acceleration of gravity. (b) A steel ball ($\rho = 7.86\ g\ cm^{-3}$) 0.2 cm in diameter falls 10 cm through a viscous liquid ($\rho_0 = 1.50\ g\ cm^{-3}$) in 25 s. What is the viscosity at this temperature? (10%)

11. Calculate (a) the root-mean-square, (b) mean, and (c) most probable speeds for oxygen molecules at 25°C. (atomic mass: O = 16) (10%)

12. Show the following equations: (16%)
(a) half-life $t_{1/2} \propto \frac{1}{(A)_0^{n-1}}$ for a reaction that is n^{th}-order in A.
(b) $x\hat{P}_x f(x) - \hat{P}_x x f(x) = i\hbar f(x)$
(c) Stirling's approximation $\ln N! = N\ln N - N$
(d) $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$