編號： 47

國立成功大學 108 學年度碩士班招生考試試題

系　　所：化學系

考試科目：物理化學

考試日期：0224，節次：1

※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. (a) Derive dw_{add} (electronic work) = $\mu_A\, dn_A + \mu_B\, dn_B$ for a A ➔ 2B reaction at constant temperature and pressure. (4 %)
   (b) What is Gibbs-Duhem equation for this reaction? (2 %)
   (c) For this A ➔ 2B reaction, there are four electrons transferred and $\Delta_r H^0 = -50$ kJ and $\Delta_r S^0 = +200$ J/K. Please calculate the E^0_{max} and equilibrium constant of this reaction at 27°C. (4 %) (1 F ≈ 100,000 C)

2. (a) What is the thermodynamic criterion for the equilibrium between phase A and phase B? (2%)
   (b) In a phase diagram of a water, please derive the slope of water-ice boundary. (4 %)
   (c) Is the slope of water-ice boundary negative, positive? why? (2 %)
   (d) Why is the dp/dT slope for sublimation curve steeper than that for vaporization curve at similar temperature? (2 %)

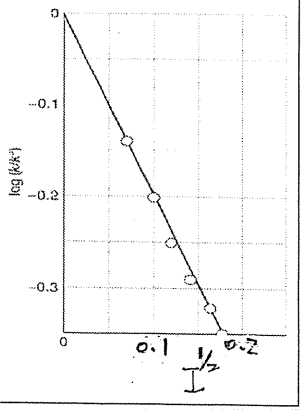
3. (a). Starting from the equation $dH = (\partial H/\partial T)_p\, dT + (\partial H/\partial p)_T\, dp$ to derive the $\mu_T = -\mu\, C_p$ (Hint: $\mu_T = (\partial H/\partial p)_T$) (4 %)
   (b). Based on the Joule-Thomson coefficient, please briefly describe the gas-liquefying process in the Linde refrigerator. (6 %)

4. (a) Derive the equation $\Pi = [J]RT$ (Π: osmotic pressure) (5 %)
   (b) For a regulation solution of a mixture A and B at constant pressure, please calculate the $\Delta_{mix}G$ and $\Delta_{mix}H$. (Hint: $\chi_A = n_A/n$; $n = n_A + n_B$; ξ: dimensionless parameter for a measurement of A-B interaction relative to A-A and B-B interactions). (2 %).
   (c) At large or small ξ value, the mixture will separate spontaneously into two phases. Why? (3 %)

5. (a). For the reaction between A and B ions, the rate constant is dependent on the ionic strength (I) of the solution. Use the following mechanism to derive the equation of $\log(k/k_0) = 2A Z_A Z_B I^{1/2}$.

   $$A + B \rightleftharpoons C^{\ddagger} \quad ; \quad C^{\ddagger} \longrightarrow \text{product}$$

   (Hint: $K = K_\gamma ([C^{\ddagger}]/[A][B])$; $\log \gamma_J = -A Z_J{}^2 I^{1/2}$) (6 %)
   (b). It is know that the A value is 0.509 in aqueous solution at 298 K. The right-hand figure shows the plot $\log(k/k_0)$ against $I^{1/2}$ for the hydrolysis reaction of $[FeBr(NH_3)_5]^{2+}$. The slope of the straight is –2.04. Based on these results, white the possible reaction equation for the hydrolysis of $[FeBr(NH_3)_5]^{2+}$. (4 %)



國立成功大學 108 學年度碩士班招生考試試題

6. (a) Please derive the Langmuir isotherm for adsorption. (Hint: θ = function of K and p). (4 %)
(b) The Langmuir-Hinshelwood mechanism of CO-oxidation reactions: the reaction takes place by encounters between CO and O_2 molecular adsorbed on the surface of Au-Ag nanoparticles. The second-ordered rate law:

$$CO + 1/2\ O_2 \longrightarrow CO_2 \ ;$$

Please derive the θ_{CO} and reaction rate v. (Hint: θ_A and v = functions of K_A, K_B, p_A, p_B, k) (6 %)

7. (a) For a reaction of A(aq) + 2 B(aq) → C(aq), the rate constant (k) is 0.0693 s^{-1} and the rate law is related to the [A]. When $[A]_0$ = 2.0 M, $[B]_0$ = 5.0 M, please calculate the [A], [B] after a reaction time of 30 s. (5 %)
(b) Please give the integrated rate law for the reaction A + 2B → P, $v = k_r [A][B]$ when $[A]_0 \neq [B]_0$, (5 %)

8. Write mathematical equations to describe the following physical properties and equations: (a) Normalization constant of a wavefunction; (b) de Broglie relation; (c) $\langle E_k \rangle$ of a wavefunction ψ in 1-dimension. (d) Schrödinger equation for a harmonic oscillator; (e) Schrödinger equation for a rotational motion. (10 %)

9. (a) Based on the property of the electron, please brief explain why the triplet (T_3) state is more stable than singlet state (S_1) when two electrons exists in different orbitals? (6 %)
(b) Give an equation to express the transition dipole moment between the initial and final states. Please briefly describe how to use the value of the transition dipole moment to predict an electron transition is forbidden or allowed. (4 %)

10. (a) Derive the energy of the spin-orbital coupling interaction:
$E_{l,s,j} = ½\ hcA\ \{ j(j+1) - l(l+1) - s(s+1) \}$ (A: spin-orbital coupling constant in a wavenumber unit.) (4 %)
(b) Draw a molecular orbital energy level diagram for O_2^{2+} molecule and predict the bond order and magnetism. Is the bond energy of the O_2^{2+} is higher than that of O_2? why? (6 %)