國立成功大學

114學年度碩士班招生考試試題

編　號：41

系　所：化學系

科　目：物理化學

日　期：0211

節　次：第 1 節

注　意：1.不可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

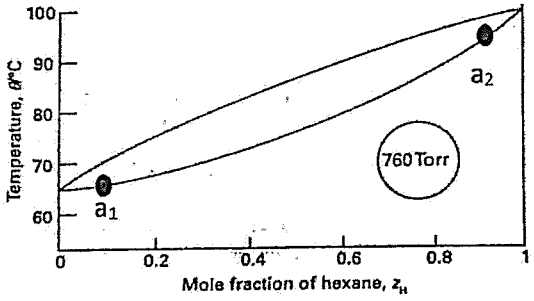
一、計算與簡答題: 70 %；每題 5 分 (**只須寫答案，答案 (數字和單位)正確才予計分**，氣體常數以 R 表示，普郎克常數以 h 表示，光速以 c 表示，自然對數(ln)值不須算出)。

(1). Given $CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$ equilibrium constant is K_a at T. What is ΔG at T for a solution in which the initial concentrations are:
$[CH_3CO_2H]_0 = 0.1$ M ; $[CH_3CO_2^-]_0 = 0.4$ M ; $[H^+]_0 = 0.5$ M.

(2). The Joule-Thomson coefficient for a real gas at 25°C and 1 atm is +0.25 K bar^{-1}. What is the final temperature of the gas when its pressure changes by –20 bar under isenthalpic conditions?

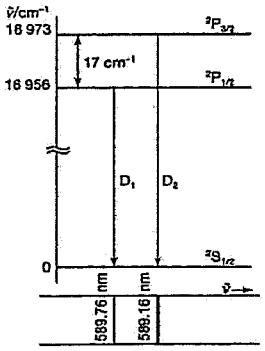
(3). At 1.0 atm, the melting of water at its normal melting point has $\Delta V = -1.6$ cm^3 mol^{-1} and $\Delta_{trs}H = 5.460$ kJ mol^{-1}. Please calculate the value of $(\delta\mu(l)/\delta T)_p - (\delta\mu(s)/\delta T)_p$.

(4). Please estimate minimum number of the theoretical plates is required to purification from a_1 composition to a composition with hexane molar fraction higher than a_2.



(5). Calculate the entropy change when n moles of argon at T_1°C in a container of V_1 dm^3 is allowed to expand to V_2 dm^3 and is simultaneously heated to T_2°C.

(6). It is known that the spin-orbital coupling energy $E_{j,l,s} = hcA\, l \bullet s$ and A is the spin-orbital coupling constant. From the right-hand figure, calculate the value of the spin-orbital coupling constant A.



(7). What is the average linear momentum of a free particle describe by the wavefunction
$\psi = A\exp(ikx) + B\exp(-ikx)$; (Hint: operator $p_x = \hbar/i\, d/dx$)

(8). A photon of radiation with wavelength λ ejects an electron from a metal with a kinetic energy of E_k. Calculate the maximum wavelength of radiation capable of ejecting an electron from the metal.

(9). Calculate the populations ratio of the J = 2 to J = 0 rotational states of HCl at T.
(Hint: $E_J = hcBJ(J+1)$; degeneracy of rotational state : 2J + 1)

(10). Draw the cross-sectional structures of the spherical micelle and liposome of a surfactant.

(11). Derive the rate law for the decomposition of ozone on the basis of the incomplete mechanism.

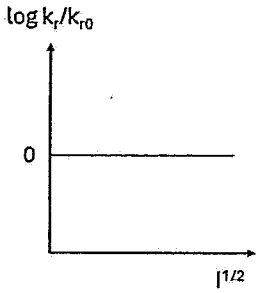
$O_3 \rightarrow O_2 + O$ k_a ; $O_2 + O \rightarrow O_3$ $k_{a'}$

$O + O_3 \rightarrow O_2 + O_2$

(12). For a reaction aA → products, $[A]_0 = 4.0\ M$, and the first three successive half-lives are 50, 100, and 200 min. Please calculate rate constant k.

(13). The enzyme carbonic anhydrase catalyzes the hydration of CO_2, in red blood cells to give bicarbonate (hydrogencarbonate) ion: $CO_2(g) + H_2O(1) \rightarrow HCO_3^-(aq) + H^+(aq)$. Based on the experimental data (where $[CO_2]$ unit in mmol dm^{-3} and reaction rate v unit in mmol dm^{-3} s^{-1}), we get the Lineweaver-Burk plot ($1/[CO_2]$ vs. $1/v$) with the slope of 40.0 and the y-intercept is 4.00. Please calculate the K_M.

(14). In the right figure shows the plot $\log(k_r/k_{r0})$ against $I^{1/2}$ for the hydrolysis reaction of $[CoBr(NH_3)_5]^{2+}$ in an aqueous solution. The slope of the straight is 0. Based on these results, what is the possible reactant for the hydrolysis of $[CoBr(NH_3)_5]^{2+}$



二、證明題: 30 %

(1). (a) Please briefly describe the isolation method to determine a complex rate law of a reaction:
A + 2B + 3C → product. (4 %)

(b) Derive the diffusion coefficient D = 1/3 λc for a gas,
(Hint: λ: mean free path; c: mean speed of gas molecule; Z_w = ¼ Nc; Taylor series; net flow: 2/3) (6 %)

(2). (a) For a black-body radiation from a source of temperature, T, is given by the Planck distribution: $\rho = (8\pi h\nu^3/c^3)/(\exp(h\nu/kT) - 1)$. Use this result to prove that $A/B = (8\pi h\nu^3/c^3)$ and B = B' (B, B' = coefficients of simulated emission and absorption; A: Einstein coefficient of spontaneous emission). (6 %)

(b). What are the two requirements for the laser action? (4 %)

(3). (a). We define the fugacity as: $f = \phi p$; ϕ: fugacity coefficient. Please derive: $\ln\phi = \int_0^p \frac{Z-1}{p} dp$ (7 %)

(b). If $\phi < 1$, use the >, = or, < to finish the following comparisons.

I. G_{real} ____ $G_{perfect}$; II. Z _____ 1 ; III. Joule-Thomson coefficient _____ 0. (3 %)