國立成功大學

115學年度碩士班招生考試試題

編　號：35

系　所：化學系

科　目：物理化學

日　期：0203

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。

※ 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。

一、計算與簡答題: 80 %；每題 5 分 (只須寫答案，無須過程，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，自然對數(ln)和指數(exponential)值不須算出。

1. Evaluate the standard potential $E^{\varnothing}(Fe^{3+}, Fe^{2+})$ from $E^{\varnothing}(Fe^{3+}, Fe) = -0.04$ V and $E^{\varnothing}(Fe^{2+}, Fe) = -0.44$ V.

2. Methyl cyclohexane molecules may exist in one of two conformations, with the methyl group in either an equatorial or axial position. The equatorial form is lower in energy of 6.0 kJ mol^{-1} than the axial form. At a temperature of 500 K, please calculate the ratio of molecules population in the axial to equatorial states.

3. Suppose a 50 W electric heater immersed in 2.0 moles of ideal gas in a constant-volume adiabatic container was on for 12 s. It was found that the temperature of the gas rose by 5.0°C. Please calculate the C_p value of the ideal gas in $JK^{-1}mol^{-1}$ unit.

4. In the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$, please calculate the difference of molar enthalpy and internal energy ($\Delta H_m - \Delta U_m$) at 27°C.

5. When the pressure of carbon dioxide changes isenthalpically by –10 bar at 300 K, the change in temperature is –10 K. Evaluate the molar isothermal Joule coefficient (μ_T) of carbon dioxide.
(C_p of $CO_2 = 40.0\ JK^{-1}mol^{-1}$)

6. What temperature would be reported for the hot source if a thermodynamic efficiency of 0.50 for a Carnot engine was measured when the cold sink was at 27°C?

7. Suppose that 2.0 mol H_2 ideal gases, at 2.0 atm and 25°C and 4.0 mol N_2 ideal gases, at 3.0 atm and 25°C are mixed by removing the partition between them. Calculate $\Delta_{mix}G$.

8. Estimate the standard cell potential of a hydrogen fuel cell in which the reaction is
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$. (Hint: $\Delta_f G^{\varnothing}$ of $H_2O(l) = -240$ kJ/mol, 1 F ≈ 100,000 C)

9. A homonuclear diatomic molecule has a molecular-orbital configuration of
$(\sigma_{1s})^2\ (\sigma_{1s}^*)^2\ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py})^1(\pi_{2px})^1$. What is the molecule?

10. These two wavefunctions (sin x) and (sin 3x) are two are eigenfunctions of the kinetic energy hermitian operator for an electron confined to a one-dimensional quantum dot, and correspond to different eigenvalues. Please calculate the integral value of $\int_0^{2\pi} sin3x\ sinx\ dx$

11. The general unnormalized wavefunctions for a particle on a ring are

$Y_{ml}(\phi) = \exp(i\, ml\, \phi)$ (*ml* is the quantum number)

Please find the normalization constant for the $Y_{ml}(\phi)$.

12. β-Carotene is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If the length of the molecular box in B-carotene is L and the mass of an electron is m. Estimate the excitation energy of this molecule from its ground state to the next higher excited state. (Hint: 1-D box)

13. The MO energies of π-orbitals in benzene molecule are: $(\alpha + 2\beta)$, $2(\alpha+ \beta)$, $2(\alpha - \beta)$ and $(\alpha - 2\beta)$. The MO energies of π-orbitals in ethene molecule are $(\alpha+ \beta)$, and $(\alpha - \beta)$. Based on these data, please calculate the delocalization energy of the benzene molecule. ($\alpha < 0$, $\beta < 0$)

14. Based on Pauli exclusion principle, please write down the total function for the two electrons occupying different atomic orbitals ψ_a and ψ_b at triplet state (T_3).

15. For the reaction $2A + B \rightarrow$ products. The following mechanism is proposed:

$A + B \rightleftharpoons M$ (forward and reverse rate constants: k_1 and k_{-1})

$A + M \rightarrow$ products (rate constants: k_2)

Please use the steady-state approximation to derive the rate law.

16. The following data were collected in two studies of the reaction below.

$$2A + 2B \rightarrow X + Y$$

	$[B]_0 = 4.0\ M$	$[B]_0 = 8.0\ M$
	Experiment 1	Experiment 2
Time (s)	$[A]\ (/M) \times 10^{-2}$	$[A]\ (/M) \times 10^{-2}$
0	10.0	10.0
20	6.67	5.00
40	5.00	3.33
60	4.00	2.50
80	3.33	2.00
100	2.86	1.67
120	2.50	1.43

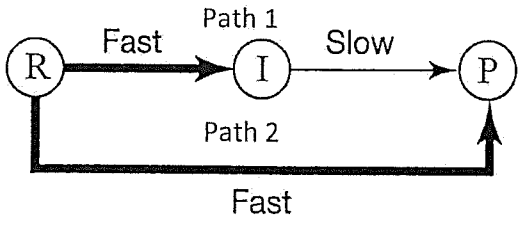
What is the rate law for this reaction?

二、問答題: 20 % (需寫出計算與推導過程否則不予計分)

1. (a) Calculate the steric factor P of the reactions in the following table. (3 %)
(b) Which reaction does proceed by a harpoon (魚叉) mechanism. Why? (4 %)

Reaction	A/(L·mol^{-1}·s^{-1})		E_a(kJ·mol^{-1})	*P*
	Experiment	Theory		
$2NOCl \rightarrow 2NO + Cl_2$	9.0×10^9	9.0×10^{10}	102.0	$P_1 = ?$
$2ClO \rightarrow Cl_2 + O_2$	6.0×10^7	3.0×10^{10}	0.0	$P_2 = ?$
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.0×10^{11}	2.0	$P_3 = ?$

2. (a) In the following reaction scheme, which path is the rate-determining? Why? (4 %)



(b) Draw the plots to demonstrate the concentration dependence of the molar conductivities of NaCl and CH_3COOH. (4 %)

3. A student was trying to determine the order of a chemical reaction. To accomplish this, the student graphed the concentration - time data using various plotting methodologies. The plots are shown below. What is the order of the reaction? Why? (5 %)