

# 國立成功大學

## 113學年度碩士班招生考試試題

編 號：44

系 所：化學系

科 目：物理化學

日 期：0202

節 次：第 1 節

備 註：不可使用計算機

※ 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。

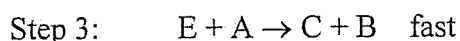
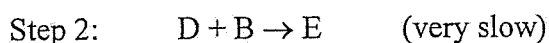
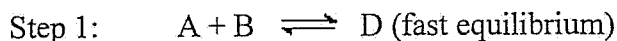
一、計算與簡答題:40分；每題5分(只需寫答案，答案正確才予計分，氣體常數以R表示，自然對數ln值不必算出)

(1). Calculate  $\Delta S$  for cooling 2.0 mol of an ideal monatomic gas from 27°C to 327°C at constant volume.

(2). What are the criteria for a spontaneous chemical reaction at all temperature?

(3). Given a reaction:  $HA \rightarrow H^+ + A^-$   $K_a = 1 \times 10^{-5}$  at 25°C; What is  $\Delta G^\circ$  at 25°C?

(4). The reaction:  $2A + B \rightarrow C$  has the following proposed mechanism.

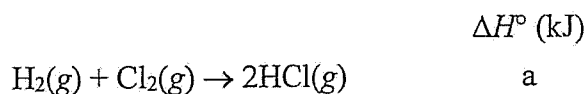


What should be the rate law of formation of C?

(5). For a chemical reaction with rate constant of  $50 \text{ M}^{-1}\text{s}^{-1}$ , please calculate the half-life ( $t_{1/2}$ ) at initial concentration of 0.2 M.

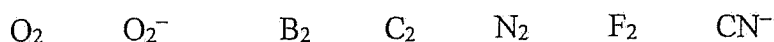
(6). For a particle in a cubic box ( $L_x = L_y = L_z$ ), how many degenerate energy levels have energy equal to  $14 h^2/8 \text{ mL}^2$ ?

(7). Using the following data reactions:



Please use the a, b, c values to give the energy of an H-Cl bond.

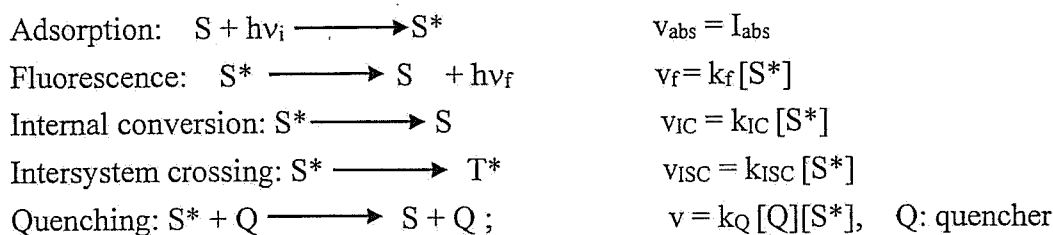
(8). Which of the following molecules or ions are paramagnetic? (全對才給分)



二、證明與計算題：60 分；每題 10 分（需有計算和推導過程才予計分）

1. (a). Please give the phenomenological equation for energy flux. (3 %)
- (b). Derive an equation for calculating the thermodynamic force of a concentration gradient. (4 %)
- (c). Please calculate the  $\partial c/\partial t$  values of a concentration gradient of  $c = c_0x$ . (3 %)

2. Consider the formation and decay of an excited singlet state:



How to use the intensities of fluorescence ( $I_f$ ) in the presence of the quencher at different concentration and fluorescence ( $I_f^0$ ) in the absence of quencher to obtain the quenching rate constant  $k_Q$ .

( $\tau_0$  is known and  $\tau_0 = 1/(k_f + k_{\text{IC}} + k_{\text{ISC}})$ ) (10 %)

3. (a) When two electrons in an atom occupy an orbital ( $\psi$ ), please write down the total wavefunction for the two electrons. Why the electrons must be paired? (4 %)
- (b). Is  $p_y \rightarrow p_z$  an allowed electric dipole transition in a molecule with  $C_{2v}$  symmetry? (6 %)

$C_{2v}$ ( $2mm$ )	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v$ ( $yz$ )		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

4. (a). The energy separation between  $m_I = +1/2$  and  $m_I = -1/2$  states of spin- $1/2$  nuclei ( $I = 1/2$ ) in a magnetic field  $B_0$  is  $\gamma\hbar B_0$ . Please prove the absorption intensity is proportional to  $\frac{\gamma\hbar B_0/kT}{2}$  (5 %)
- (b). It is known that the local magnetic field is

$$B_{\text{loc}} = \frac{-\gamma\hbar\mu_0(1 - 3\cos^2\theta)m_I}{4\pi R^3}$$

Please use this equation to explain why the NMR signal of the molecules in solid state is very broad. How to reduce the linewidths of the solid-state NMR spectrum? (5 %)

5. (a). What is Gibbs-Duhem equation? (3 %)
- (b). Give an equation to explain the relation between  $\Delta_r G$  and chemical potentials of reactants and products. (2%)
- (c). At constant pressure and temperature, prove the  $-\nu F E = \Delta_r G$ . ( $F$ : Faraday constant, 5 %)
6. (a). Please derive the Phase rule:  $F = C - P + 2$ ; and calculate the number of the intensive variables in a system with two components in a solid-liquid phase. (6 %)
- (b). Draw the  $C_p$  vs. Temperature diagrams to explain the first- and second-order phase transitions. (4 %)