國立臺灣師範大學101學年度碩士班招生考試試題

科目：物理化學　　適用系所：化學系

注意：1.本試題共3頁，請依序在答案卷上作答，並標明題號，不必抄題。2.答案必須寫在指定作答區內，否則依規定扣分。

答題注意事項：作答時需按題號順序依次作答，每大題內的小題亦需按小題號順序作答，否則皆不予計分。

一、Quantum part:

1 . (A) (6 分)Write down the $2p_x$, $2p_y$ and $2p_Z$ orbitals from the following Tables

Angular wavefunctions:

$$Y_l^m(\theta,\phi)=\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}\text{, where}$$

$$P_0^0(\cos\theta)=1 \quad P_1^0(\cos\theta)=\cos\theta \quad P_1^1(\cos\theta)=\sin\theta \quad P_1^{-1}(\cos\theta)=-0.5P_1^1(\cos\theta)$$

Radial wavefunctions

$$R_1^0(\rho)=2\left(\frac{Z}{a}\right)^{3/2}e^{-\rho/2} \quad R_2^0(\rho)=\frac{1}{\sqrt{8}}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)e^{-\rho/2} \quad R_2^1(\rho)=\frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}$$

where $\rho=\dfrac{2Zr}{na_0}$

(B) (2 分)Why use p_x and p_y orbitals instead of p_1 and p_{-1} orbitals?

(C) (6 分)Show that these three orbitals are orthogonal

$$\int \sin\theta\cos\theta d\theta=\frac{\sin^2\theta}{2}$$

2. (A) (6 分)Which of the following molecules may show a pure rotational microwave or vibrational infrared absorption spectra (a) H_2, (b) CCl_4, (c) CH_2F_2

(B) (4 分)Classify each of the following molecules as a spherical, symmetrical, linear or asymmetric rotors (a) CO_2 (b) CH_3OH (c) benzene (d) methane. (4 分)How many normal modes of vibration for these molecules?

3. (A) (4 分)Derive the force constant expression for an oscillator modeled by Morse potential.
[Morse potential: $V(R)=hcD_e\{1-\exp(-a(R-R_e))\}^2$]

(B) (4 分)From (A), the Morse oscillator has a finite number of bound states. Find an expression for the maximum value of the vibrational quantum number.

二、Thermodynamics part:

[Notations H: enthalpy, U: internal energy, S: entropy, S_sur: entropy of surroundings, S_total=S+ S_sur, A: Helmholtz free energy, G: Gibbs free energy, p: pressure, T: temperature, V: volume, V_m: molar volume, n: number of moles, R: ideal gas constant, q: heat, w: work, $C_{V,m}$: molar heat

capacity at constant volume, $C_{p,m}$: molar heat capacity at constant pressure, rev: reversible]

1. (單選題 5 分, Choose the best answer.) In thermodynamics, ΔG (G denotes the Gibbs free energy) represents:
   (A). maximum additional (non-expansion) work at constant T and V.
   (B). maximum additional (non-expansion) work at constant T and P.
   (C). maximum additional (non-expansion) work at constant V and P.
   (D). maximum heat at constant T and V.
   (E). maximum heat at constant T and P.
   (F). maximum heat at constant V and P.
   (G). work at constant T and V.
   (H). work at constant T and P.
   (I). work at constant V and P.
   (J). maximum work at constant T and V.
   (K). maximum work at constant T and P.
   (L). maximum work at constant V and P.
   (M). minimum work at constant T and V.
   (N). minimum work at constant T and P.
   (O). minimum work at constant V and P.
   (P). heat at constant temperature(T) and volume (V).
   (Q). heat at constant T and pressure (P).
   (R). heat at constant V and P.
   (S). maximum work at constant T.
   (T). maximum work at constant P.
   (U). maximum work at constant V.

2. (單選題 5 分,Choose the best answer) The temperature dependence of molar internal energy of an ideal gas can be expressed by $U_m(T)=U_m(0)+f(T)$ where $U_m(0)$ is the molar internal energy at T=0. For a nonlinear polyatomic ideal gas, considering translation and rotation only, the f(T) can be approximately expressed in classical limit by
   (A) RT/2 (B) 2RT/2 (C) 3RT/2 (D) 4RT/2 (E) 5RT/2 (F) 6RT/2 (G) 7RT/2 (H) 8RT/2 (I) 9RT/2 (J) RT/3 (K) 2RT/3 (L) 4RT/3 (M) 5RT/3 (N) 7RT/3 (O) 8RT/3 (P) 5RT (Q) 6RT (R) 7RT (S) 8RT (T) 9RT.

3. (單選題 5 分): The van't Hoff equation is d(ln K)/dT=
   (A) $-\Delta U/(RT^2)$ (B) $\Delta (U-TS)/(RT^2)$ (C) $\Delta U/(RT^2)$ (D) $-\Delta (U-TS)/(RT^2)$ (E) $-\Delta H/(RT^2)$ (F) $\Delta (H-TS)/(RT^2)$ (G) $\Delta H/(RT^2)$ (H) $-\Delta (H-TS)/(RT^2)$ (I) $-\Delta A/(RT^2)$ (J) $\Delta (A-TS)/(RT^2)$ (K) $\Delta A/(RT^2)$ (L) $-\Delta (A-TS)/(RT^2)$ (M) $-\Delta G/(RT^2)$ (N) $\Delta (G-TS)/(RT^2)$ (O) $\Delta G/(RT^2)$ (P) $-\Delta (G-TS)/(RT^2)$.

4. (單選題 5 分): For a van der Waals gas, $(\partial S/\partial V)_T$= ?[a and b are van der Waals coefficients]
(A)3R/(V_m-b) (B)2R/(V_m-a) (C) R/(V_m-b) (D) (RV_m+b)/($2pV_m$-RT) (E)(RV_m+2b)/($2pV_m$-RT) (F)(RV_m+3b)/($2pV_m$-RT) (G)(RV_m+4b)/($2pV_m$-RT) (H) (RV_m+b)/($2pV_m$-2RT) (I) R/p (J) 2R/p (K) R/(2p) (L) 3R/p (M) R/(3p) (N)4R/p (O)R/(4p) (P) a+bR (Q) a-bR (R) a-2bR.

5. (複選題 5 分,全對才給分！) For an ideal gas undergoing an adiabatic reversible change from (V_i, p_i, T_i) to (V_f, p_f, T_f), where i and f denote initial and final states, respectively, which ones of the following are correct? [$c=C_{V,m}/R$, $\gamma=C_{p,m}/C_{V,m}$]
(A)$V_iT_i^c=V_fT_f^c$ (B) VT^c=constant (C) $p_iV_i^c=p_fV_f^c$ (D)Entropy change is zero. (E) $V_iT_i^\gamma=V_fT_f^\gamma$.

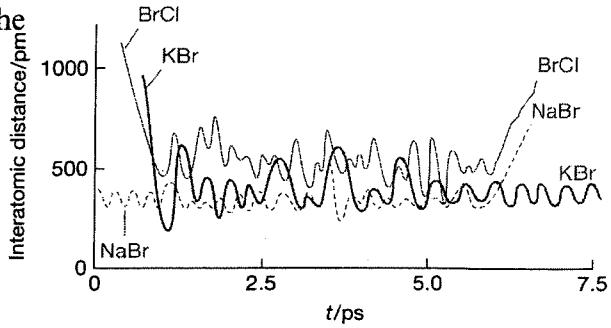
6. (填充題 5 分,全對才給分！): Clapeyron equation is an equation describing slopes of phase boundaries. Its mathematical form is usually expressed as $dp/dT = \Delta_{transition}X/\Delta_{transition}Y$ where X and Y are thermodynamical quantities which are needed to be identified. What is X? X=(6A) What is Y? Y=(6B).

三、Dynamics part:

1. (8 分)The rate of the reaction, A → B, can be expressed as $\frac{d[A]}{dt} = k[A]^{1/2}$.
(A) Derive the integrated rate equation for this reaction.
(B) Derive the half-life for this reaction in terms of k and [A].

2. (10 分)Derive the rate law for the decomposition of ozone in the reaction, $2O_{3(g)} \rightarrow 3O_{2(g)}$, on the basis of the following proposed mechanism:
1. $O_3 \rightarrow O_2 + O$ k_1
2. $O_2 + O \rightarrow O_3$ k_2
3. $O + O_3 \rightarrow O_2 + O_2$ k_3

3. (6 分)The figure displayed on the right represents the trajectory of a reaction of two diatomic molecules, which illustrates the relative distances between the atoms.
(A) Write the chemical equation for this reaction.
(B) Estimate the lifetime of the transition complex.
(C) Does this trajectory provide the information of activation energy? If yes, what is the activation energy of reaction?



4. (10 分)The pre-exponential factor A for a gas-phase reaction, A + A → A_2, is 4.0×10^5 $M^{-1}s^{-1}$ and its activation energy is 65.4 kJ/mol. Calculate the Gibbs energy of activation for this reaction at 300 K.