國立臺灣師範大學104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，否則不予計分。

Thermodynamics Part (35 分)[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. Thermodynamics: Write down the definition of enthalpy in terms of U, p, and V.
（簡答題 5 分，全對才給分）

2. Thermodynamics: Consider an adiabatic reversible process of a monoatomic ideal gas of 1 mole. The initial state is (V_1, T), where V and T are volume and temperature, respectively. The volume of the final state is V_2.

(a) The internal energy change, ΔU, of this process is:　（單選題 5 分）

(A) RT/2　(B) RT ln $(V_2/V_1)/2$　(C) RT $[(V_1/V_2)^{2/3}-1]/2$　(D) RT $[(V_1/V_2)^{3/2}-1]/2$
(E) RT　(F) RT ln (V_2/V_1)　(G) RT $[(V_1/V_2)^{2/3}-1]$　(H) RT $[(V_1/V_2)^{3/2}-1]$
(I) 3RT/2　(J) 3RT ln $(V_2/V_1)/2$　(K) 3RT $[(V_1/V_2)^{2/3}-1]/2$　(L) 3RT $[(V_1/V_2)^{3/2}-1]/2$
(M) 3RT　(N) 3RT ln (V_2/V_1)　(O) 3RT $[(V_1/V_2)^{2/3}-1]$　(P) 3RT $[(V_1/V_2)^{3/2}-1]$
(Q) 5RT　(R) 5RT ln (V_2/V_1)　(S) 5RT $[(V_1/V_2)^{2/3}-1]$　(T) 5RT $[(V_1/V_2)^{3/2}-1]$
(U) 7RT　(V) 7RT ln (V_2/V_1)　(W) 7RT $[(V_1/V_2)^{2/3}-1]$　(X) 7RT $[(V_1/V_2)^{3/2}-1]$
(Y) 0　(Z) none of the above.

(b) The entropy change, ΔS, of this process is:　（單選題 5 分）

(A) R/2　(B) R ln $(V_2/V_1)/2$　(C) R $[(V_1/V_2)^{2/3}-1]/2$　(D) R $[(V_1/V_2)^{3/2}-1]/2$
(E) R　(F) R ln (V_2/V_1)　(G) R $[(V_1/V_2)^{2/3}-1]$　(H) R $[(V_1/V_2)^{3/2}-1]$
(I) 3R/2　(J) 3R ln $(V_2/V_1)/2$　(K) 3R $[(V_1/V_2)^{2/3}-1]/2$　(L) 3R $[(V_1/V_2)^{3/2}-1]/2$
(M) 3R　(N) 3R ln (V_2/V_1)　(O) 3R $[(V_1/V_2)^{2/3}-1]$　(P) 3R $[(V_1/V_2)^{3/2}-1]$
(Q) 5R　(R) 5R ln (V_2/V_1)　(S) 5R $[(V_1/V_2)^{2/3}-1]$　(T) 5R $[(V_1/V_2)^{3/2}-1]$
(U) 7R　(V) 7R ln (V_2/V_1)　(W) 7R $[(V_1/V_2)^{2/3}-1]$　(X) 7R $[(V_1/V_2)^{3/2}-1]$
(Y) 0　(Z) none of the above.

3. Thermodynamics: 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. (X, Y)=

（單選題 5 分）

(A) (p,S)　(B) (p,V)　(C) (p,T)　(D)(V,S)　(E) (S,T)
(F) (S,p)　(G) (S,V)　(H) (V,T)　(I) (V,p)　(J) (T,S)
(K) (T,V)　(L) (T,p).

4. Thermodynamics: The Gibbs-Helmholtz equation is $(\partial(G/T)/\partial T)_p$= (單選題 5 分)

(A) U/T^2 (B) $(U-TS)/T^2$ (C) $-U/T^2$ (D) $-(U-TS)/T^2$
(E) H/T^2 (F) $(H-TS)/T^2$ (G) $-H/T^2$ (H) $-(H-TS)/T^2$
(I) A/T^2 (J) $(A-TS)/T^2$ (K) $-A/T^2$ (L) $-(A-TS)/T^2$
(M) G/T^2 (N) $(G-TS)/T^2$ (O) $-G/T^2$ (P) $-(G-TS)/T^2$.

5. Thermodynamics: Here is a Maxwell relation, $(\partial T/\partial p)_S=(\partial X/\partial Y)_p$ where S, V, and T are entropy, volume, and temperature, respectively. X and Y are thermodynamical quantities which are needed to be identified. Pressure is denoted by p. (X, Y)= (單選題 5 分)

(A) (p,S) (B) (p,V) (C) (p,T) (D)(S,V)
(E) (S,T) (F) (S,p) (G) (V,S) (H) (V,T)
(I) (V,p) (J) (T,S) (K) (T,V) (L) (T,p).

6. Thermodynamics: Consider a container of volume of V that is divided into two compartments of equal size. In the left compartment there is nitrogen at the pressure and temperature of p and T, respectively; in the right compartment there is hydrogen at the same temperature and pressure. What is the Gibbs free energy of mixing when the partition is removed. Assume that the gases are perfect. (單選題 5 分)

(A) nRT (B) 2nRT (C) nRT/2 (D) –nRT (E) -2nRT
(F) -nRT/2 (G) pV (H) 2pV (I) pV/2
(J) pV ln2 (K) 2pV ln2 (L) –pV (M) -2pV
(N) -pV/2 (O) -pV ln2 (P) -2pV ln2 (Q) 0.

7. Total energy (E) can be expressed as the sum of kinetic energy (T) and potential energy (V), i.e. E = T + V.

(a) In classical mechanics, what is T for a particle as it has mass m and moves in the moment of p? (3 分)

(b) In quantum mechanics, the operator for moment of a wave is $\hat{p} = -i\hbar\frac{d}{dx}$. Derive the operator for kinetic energy of the wave is $\hat{T} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$. (3 分)

(c) What are the differences between T in classical mechanics and $\hat{T}$ in quantum mechanics? (3 分)

(d) Schrodinger equation can be expressed as $\hat{H}\psi = E\psi$, where $\hat{H} = \hat{T} + \hat{V}$, $\hat{V}$ is operator for potential energy, E is energy and ψ is wave function. Write down Schrodinger equations for particle-in-a-box in one dimensional space as the box length is L and the related $\hat{V} = \begin{cases} \infty, x < 0, x > L \\ 0, 0 \le x \le L \end{cases}$. (3 分)

(e) Solve the Schrodinger and find E. (5 分)

(f) How E changes as L increase? (3 分)

(g) Write down Schrodinger equation for harmonic oscillator in one dimensional space. (3 分)

(h) Write down Schrodinger equation for Hydrogen atom in the three dimensional space. (3 分)

(i) What quantum numbers can we get by solving the Schrodinger equation in (h)? (3 分)

(j) The quantum numbers in (i) are related to which properties of the orbital? (6 分)

8. Given a set of experimental kinetic measurements of an irreversible elementary chemical reaction A+B→P, listed below:

$[A]_0$ / M	$[B]_0$ / M	Time elapsed for [B] drops down to 0.3679 $[B]_0$
0.5	1.0×10^{-3}	60
1.0	1.0×10^{-3}	30
2.0	1.0×10^{-3}	15
1.5	2.0×10^{-3}	?

(Hint: 1/e=0.3679)

(a) Obtain the rate constant (k) for this reaction. (6 分)

(b) Estimate the time elapsed for the reaction at the given condition shown in the last row of the above table. (2 分)

9. Nitrogen pentoxide decomposes according to the reaction $N_2O_5 \rightarrow 2NO_2 + (1/2)O_2$ with rate constant k. The measured rate at 150K and 300K are 3.0625×10^{-13} sec^{-1} and 3.5000×10^{5} sec^{-1}, respectively. Obtain the pre-exponential factor A for the Arrhenius equation (6 分) and estimate the reaction rate at 75K. (6 分)

10. Consider the chemical mechanism:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} X$$

$$X \xrightarrow{k_3} P$$

(a) Write the rate law for [X]. (i.e. $\frac{d[X]}{dt} = ?$) (3分)

(b) Knowing the fact that X is a short-lived intermediate, employ the steady-state approximation and show the rate law for [P] in terms of k_1, k_2, k_3, [A], and [B]. (i.e. $\frac{d[P]}{dt} = ?$) (7分)