國立臺灣師範大學 109 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 6 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。

Quantum mechanics (30 points)

1. Particle-in-a-box

(a) In quantum mechanics, the **operator of moment** of a wave is $\hat{p} = -i\hbar\frac{d}{dx}$, show the **operator of kinetic energy** of the wave (2 points)

(b) Write down the **Schrodinger equation** for particle-in-a-box in one-dimensional box (x) as $\hat{V} = \begin{cases} \infty, x < 0, x > l \\ 0, 0 \le x \le l \end{cases}$. (3 points)

(c) The wavefunction for the Schrodinger equation is $\sqrt{\frac{2}{l}}\sin\frac{n\pi x}{l}$, **find energy E.** (3 points)

2. Harmonic oscillator

(a) Write down the Schrodinger equation for harmonic oscillator in one-dimension space (x) as $\hat{V} = \frac{1}{2}kx^2$ (3 points)

(b) Plot the wavefunction of $\psi(z) = e^{-\frac{z^2}{2}}H_n(z)$ as n = 1, 2 and →∞. (3 points)

3. Hydrogen atom

(a) The Schrodinger equation for Hydrogen atom can be expressed as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2Z}{r}\psi + 2E\psi = 0$$

What terms are **kinetic energy** and what are **potential energy**. (4 points)

(b) The corresponded wavefunction can be separated into radial and angular parts as

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)\psi = RY$$

Show the Schrodinger can be rearranged in the radial and angular parts as (3 points)

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + 2Zr + 2Er^2\right] + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = 0$$

(c) Knowing that the Schrodinger equation in the angular part equals to $-l(l+1)$, that is

$$\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]=-l(l+1)Y$$

What is the **physical meaning of** l? l corresponds to what **property of the orbital**? (2 points)

(d) The wavefunction in the angular part can be further separated into the two variable as

$$Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)\ or\ Y=\Theta\Phi$$

Show the Schrodinger equation in the angular part can be further rearranged as (3 points)

$$\left[\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta\right]+\left[\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}\right]=0$$

(e) Knowing that the Schrodinger equation for $\Phi(\varphi)$ equals to $-m^2$, that is

$$\frac{d^2\Phi}{d\varphi^2}=-m^2\Phi$$

What is the **physical meaning of** m? m corresponds to what **property of the orbital**? (2 points)

(f) Substituting $-l(l+1)$, the Schrodinger equation in the radial part becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{-l(l+1)}{r^2}+\frac{2Z}{r}+2E\right]R=0$$

Solving the above radial equation by power series method can the energy

$$E=-\frac{Z^2me^4}{2n^2\hbar^2}$$

What is the **physical meaning of** n? n corresponds to what **property of the orbital**? (2 points)

Thermodynamics (35 points)

[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, μ: chemical potential, 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, E^θ: standard potential]

4. Thermodynamics: (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) $(RV_m+b)/(2pV_m-RT)$ (B) $(RV_m+2b)/(2pV_m-RT)$ (C) $(RV_m+3b)/(2pV_m-RT)$
(D) $(RV_m+4b)/(2pV_m-RT)$ (E) $(RV_m+b)/(2pV_m-2RT)$ (F) R/p
(G) $3R/(V_m-b)$ (H)$2R/(V_m-a)$ (I) $R/(V_m-b)$
(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. Thermodynamics : (單選題 5 分) 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. The entropy change, ΔS, of this process is:

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

6. Thermodynamics: (單選題 5 分) In thermodynamics, for an ideal gas, $(\partial U/\partial S)_V$=
(A) H (B) U (C) A (D) G (E) p (F) n (G) V (H) T (I) R (J) RT/p
(K) RT/V (L)$(RT)^2/p$ (M) $(RT)^2/V$ (N) $(pV)^2/T$ (O) $(PV)^2/R$ (P) –H
(Q) –U (R) –A (S) -G .

7. Thermodynamics: (簡答題 5 points 全對才給分! 計分只看最後答案!)
Electrochemistry: Given that $Cu^{+2}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$ E^θ=+0.3 V; $Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$ E^θ=+0.5 V, what is E^θ of this reaction (in V): $Cu^{+2}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$?

8. Thermodynamics: (簡答題 5 points 全對才給分! 計分只看最後答案!)
For a chemical reaction, what is the mathematical relation between equilibrium constant K and its standard reaction Gibbs free energy $\Delta_r G^\theta$?

9. Thermodynamics: (簡答題 5 points 全對才給分! 計分只看最後答案!)
For phase equilibrium, write down the Clapeyron equation.

10. Thermodynamics: (簡答題 5 points 全對才給分! 計分只看最後答案!)
Gibbs-Duhem equation: Suppose that n_A=0.1 n_B and a small change in composition results in μ_A changing by $d\mu_A$=+12 J/mol, by how much will μ_B change (in J/mol)?

Kinetics (35 points)

11. The one-dimensional velocity distribution of gaseous molecule is given below:

$$F(v_x)dv_x = \sqrt{\frac{m}{2\pi k_B T}}\exp\left(-\frac{mv_x{}^2}{2k_B T}\right)dv_x$$

(a) Find the mean one-dimensional velocity, $\langle v_x \rangle$. (3 points)

(b) Find the fraction of molecules in a gas that have $v_x^2 > \frac{2k_B T}{m}$ (Use error function, $\mathrm{erf}(x)$, to express your answer, where $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt$. 6 points)

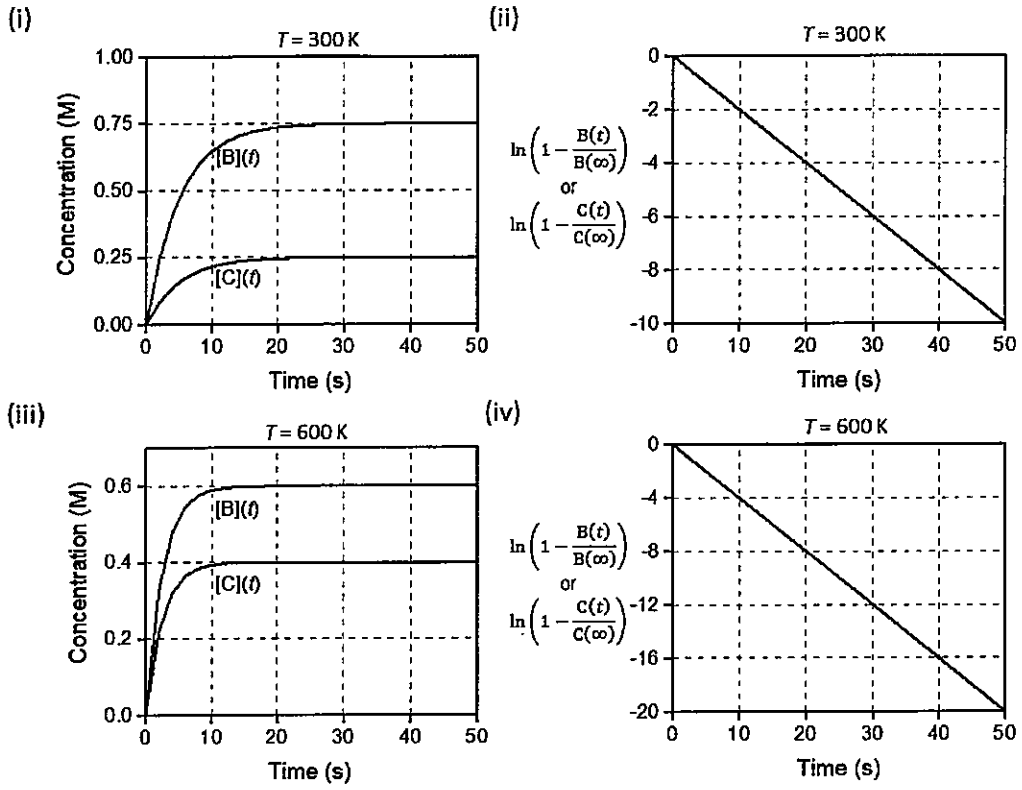
(c) What is the temperature dependence of the fraction in (b)? (2 points)

12. A kinetic measurement was carried out at temperatures of 300 K and 600 K for the parallel reaction,

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

with initial concentration, $[A]_0 = 1.0$ M. The results are shown in the following figures:



Use the information in the figures:

(a) Find the rate constants k_1 and k_2 at 300 K and 600 K. (12 points)

(b) Find the activation energies for the elementary steps, $\mathrm{A} \rightarrow \mathrm{B}$ and $\mathrm{A} \rightarrow \mathrm{C}$. (6 points)

(c) Predict the final concentration of B, $\mathrm{B}(\infty)$, at 450K. (6 points)

Appendix: ln(x) table (partial):

x	ln(x)	x	ln(x)	x	ln(x)	x	ln(x)	x	ln(x)	x	ln(x)	x	ln(x)	x	ln(x)
0.26	-1.347	0.66	-0.416	1.06	0.058	1.46	0.378	1.86	0.621	2.26	0.815	2.66	0.978	3.06	1.118
0.27	-1.309	0.67	-0.400	1.07	0.068	1.47	0.385	1.87	0.626	2.27	0.820	2.67	0.982	3.07	1.122
0.28	-1.273	0.68	-0.386	1.08	0.077	1.48	0.392	1.88	0.631	2.28	0.824	2.68	0.986	3.08	1.125
0.29	-1.238	0.69	-0.371	1.09	0.086	1.49	0.399	1.89	0.637	2.29	0.829	2.69	0.990	3.09	1.128
0.30	-1.204	0.7	-0.357	1.10	0.095	1.50	0.405	1.90	0.642	2.30	0.833	2.70	0.993	3.10	1.131
0.31	-1.171	0.71	-0.342	1.11	0.104	1.51	0.412	1.91	0.647	2.31	0.837	2.71	0.997	3.11	1.135
0.32	-1.139	0.72	-0.329	1.12	0.113	1.52	0.419	1.92	0.652	2.32	0.842	2.72	1.001	3.12	1.138
0.33	-1.109	0.73	-0.315	1.13	0.122	1.53	0.425	1.93	0.658	2.33	0.846	2.73	1.004	3.13	1.141
0.34	-1.079	0.74	-0.301	1.14	0.131	1.54	0.432	1.94	0.663	2.34	0.850	2.74	1.008	3.14	1.144
0.35	-1.050	0.75	-0.288	1.15	0.140	1.55	0.438	1.95	0.668	2.35	0.854	2.75	1.012	3.15	1.147
0.36	-1.022	0.76	-0.274	1.16	0.148	1.56	0.445	1.96	0.673	2.36	0.859	2.76	1.015	3.16	1.151
0.37	-0.994	0.77	-0.261	1.17	0.157	1.57	0.451	1.97	0.678	2.37	0.863	2.77	1.019	3.17	1.154
0.38	-0.968	0.78	-0.248	1.18	0.166	1.58	0.457	1.98	0.683	2.38	0.867	2.78	1.022	3.18	1.157
0.39	-0.942	0.79	-0.236	1.19	0.174	1.59	0.464	1.99	0.688	2.39	0.871	2.79	1.026	3.19	1.160
0.40	-0.916	0.8	-0.223	1.20	0.182	1.60	0.470	2.00	0.693	2.40	0.875	2.80	1.030	3.20	1.163
0.41	-0.892	0.81	-0.211	1.21	0.191	1.61	0.476	2.01	0.698	2.41	0.880	2.81	1.033	3.21	1.166
0.42	-0.868	0.82	-0.198	1.22	0.199	1.62	0.482	2.02	0.703	2.42	0.884	2.82	1.037	3.22	1.169
0.43	-0.844	0.83	-0.186	1.23	0.207	1.63	0.489	2.03	0.708	2.43	0.888	2.83	1.040	3.23	1.172
0.44	-0.821	0.84	-0.174	1.24	0.215	1.64	0.495	2.04	0.713	2.44	0.892	2.84	1.044	3.24	1.176
0.45	-0.799	0.85	-0.163	1.25	0.223	1.65	0.501	2.05	0.718	2.45	0.896	2.85	1.047	3.25	1.179
0.46	-0.777	0.86	-0.151	1.26	0.231	1.66	0.507	2.06	0.723	2.46	0.900	2.86	1.051	3.26	1.182
0.47	-0.755	0.87	-0.139	1.27	0.239	1.67	0.513	2.07	0.728	2.47	0.904	2.87	1.054	3.27	1.185
0.48	-0.734	0.88	-0.128	1.28	0.247	1.68	0.519	2.08	0.732	2.48	0.908	2.88	1.058	3.28	1.188
0.49	-0.713	0.89	-0.117	1.29	0.255	1.69	0.525	2.09	0.737	2.49	0.912	2.89	1.061	3.29	1.191
0.50	-0.693	0.9	-0.105	1.30	0.262	1.70	0.531	2.10	0.742	2.50	0.916	2.90	1.065	3.30	1.194
0.51	-0.673	0.91	-0.094	1.31	0.270	1.71	0.536	2.11	0.747	2.51	0.920	2.91	1.068	3.31	1.197
0.52	-0.654	0.92	-0.083	1.32	0.278	1.72	0.542	2.12	0.751	2.52	0.924	2.92	1.072	3.32	1.200
0.53	-0.635	0.93	-0.073	1.33	0.285	1.73	0.548	2.13	0.756	2.53	0.928	2.93	1.075	3.33	1.203
0.54	-0.616	0.94	-0.062	1.34	0.293	1.74	0.554	2.14	0.761	2.54	0.932	2.94	1.078	3.34	1.206
0.55	-0.598	0.95	-0.051	1.35	0.300	1.75	0.560	2.15	0.765	2.55	0.936	2.95	1.082	3.35	1.209
0.56	-0.580	0.96	-0.041	1.36	0.307	1.76	0.565	2.16	0.770	2.56	0.940	2.96	1.085	3.36	1.212
0.57	-0.562	0.97	-0.030	1.37	0.315	1.77	0.571	2.17	0.775	2.57	0.944	2.97	1.089	3.37	1.215
0.58	-0.545	0.98	-0.020	1.38	0.322	1.78	0.577	2.18	0.779	2.58	0.948	2.98	1.092	3.38	1.218
0.59	-0.528	0.99	-0.010	1.39	0.329	1.79	0.582	2.19	0.784	2.59	0.952	2.99	1.095	3.39	1.221
0.60	-0.511	1	0.000	1.40	0.336	1.80	0.588	2.20	0.788	2.60	0.956	3.00	1.099	3.40	1.224
0.61	-0.494	1.01	0.010	1.41	0.344	1.81	0.593	2.21	0.793	2.61	0.959	3.01	1.102	3.41	1.227
0.62	-0.478	1.02	0.020	1.42	0.351	1.82	0.599	2.22	0.798	2.62	0.963	3.02	1.105	3.42	1.230
0.63	-0.462	1.03	0.030	1.43	0.358	1.83	0.604	2.23	0.802	2.63	0.967	3.03	1.109	3.43	1.233
0.64	-0.446	1.04	0.039	1.44	0.365	1.84	0.610	2.24	0.806	2.64	0.971	3.04	1.112	3.44	1.235
0.65	-0.431	1.05	0.049	1.45	0.372	1.85	0.615	2.25	0.811	2.65	0.975	3.05	1.115	3.45	1.238