系別：化學工程與材料工程學系　　科目：物理化學

考試日期：3 月 10 日(星期日) 第 2 節　　　　本試題共 5 大題，2 頁

1. (a) What physical significance does the wavefunction in Schrödinger equation tell about the particle?　5%

   (b) An oxygen molecule is confined in a cubic box of volume 1.00 m^3. Assuming that the molecule has an energy equal to $\frac{3}{2} kT$ at T = 250 K, where k is the Boltzmann constant k = R/N$_{Avogadro}$, what is the value of $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ for this molecule?　　10%

   (c) What is its de Broglie wavelength?　5%

2. A sample of 4.0 mol O$_2$ with C_p = 29.355 J K^{-1} is originally confined in 20 dm^3 at 300 K and then undergoes adiabatic expansion against a constant pressure of 50 kPa until the volume has increased to 80 dm^3.

   (a) Calculate q, w, ΔT, ΔU, ΔH, and the final pressure of the gas p.　　12%

   (b) Calculate ΔS.　　　　　　　8 %

3. (a) What is the physical meaning of internal energy (usually termed as U) from molecular viewpoint?　　5%

   (b) Based on the explanation to question (a), why, the internal energy, can it be expressed as $U = U(T, V)$?　That means internal energy is a function dependent of both T (temperature) and V (volume) of a system.　5%

   (c) The heat capacity of a substance under constant volume condition is defined as $C_V \equiv \dfrac{dq_V}{dT}$.

   You are demanded to prove that $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$, knowing that the first law of thermodynamics and $U = U(T, V)$ when no extra work other than expansion work is concerned.　　10%

4. Refer you to next page for the data of the standard potential at 298K of the reduction half-reaction. Calculate

   (a) The emf of the cell Ag|AgCl(s)|AgCl(aq)|Ag at 25°C,　　5%

   (b) the solubility product of AgCl,　　and　　　10%

   (c) its solubility expressed in units of mol dm^{-3}.　　5%

5. The reaction mechanism below involves an intermediate A.

   　　A$_2$ ⇌ A + A (fast)

   　　A + B → P (slow)

   Deduce the rate law for the reaction in two ways by

   (a) assuming a pre-equilibrium, and　　10%

   (b) making a steady-state approximation.　10%

Table 7.2 Standard potentials at 298 K. (b) In electrochemical order

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$Ag^+ + e^- \to Ag$	+0.80	$I_2 + 2e^- \to 2I^-$	+0.54
$Ag^{2+} + e^- \to Ag^+$	+1.98	$I_3^- + 2e^- \to 3I^-$	+0.53
$AgBr + e^- \to Ag + Br^-$	+0.0713	$In^+ + e^- \to In$	−0.14
$AgCl + e^- \to Ag + Cl^-$	+0.22	$In^{2+} + e^- \to In^+$	−0.40
$Ag_2CrO_4 + 2e^- \to 2Ag + CrO_4^{2-}$	+0.45	$In^{3+} + 2e^- \to In^+$	−0.44
$AgF + e^- \to Ag + F^-$	+0.78	$In^{3+} + 3e^- \to In$	−0.34
$AgI + e^- \to Ag + I^-$	−0.15	$In^{3+} + e^- \to In^{2+}$	−0.49
$Al^{3+} + 3e^- \to Al$	−1.66	$K^+ + e^- \to K$	−2.93
$Au^+ + e^- \to Au$	+1.69	$La^{3+} + 3e^- \to La$	−2.52
$Au^{3+} + 3e^- \to Au$	+1.40	$Li^+ + e^- \to Li$	−3.05
$Ba^{2+} + 2e^- \to Ba$	+2.91	$Mg^{2+} + 2e^- \to Mg$	−2.36
$Be^{2+} + 2e^- \to Be$	−1.85	$Mn^{2+} + 2e^- \to Mn$	−1.18
$Bi^{3+} + 3e^- \to Bi$	+0.20	$Mn^{3+} + e^- \to Mn^{2+}$	+1.51
$Br_2 + 2e^- \to 2Br^-$	+1.09	$MnO_2 + 4H^+ + 2e^- \to Mn^{2+} + 2H_2O$	+1.23
$BrO^- + H_2O + 2e^- \to Br^- + 2OH^-$	+0.76	$MnO_4^- + 8H^+ + 5e^- \to Mn^{2+} + 4H_2O$	+1.51
$Ca^{2+} + 2e^- \to Ca$	−2.87	$MnO_4^- + e^- \to MnO_4^{2-}$	+0.56
$Cd(OH)_2 + 2e^- \to Cd + 2OH^-$	−0.81	$MnO_4^{2-} + 2H_2O + 2e^- \to MnO_2 + 4OH^-$	+0.60
$Cd^{2+} + 2e^- \to Cd$	−0.40	$Na^+ + e^- \to Na$	−2.71
$Ce^{3+} + 3e^- \to Ce$	−2.48	$Ni^{2+} + 2e^- \to Ni$	−0.23
$Ce^{4+} + e^- \to Ce^{3+}$	+1.61	$NiOOH + H_2O + e^- \to Ni(OH)_2 + OH^-$	+0.49
$Cl_2 + 2e^- \to 2Cl^-$	+1.36	$NO_3^- + 2H^+ + e^- \to NO_2 + H_2O$	−0.80
$ClO^- + H_2O + 2e^- \to Cl^- + 2OH^-$	+0.89	$NO_3^- + 4H^+ + 3e^- \to NO + 2H_2O$	+0.96
$ClO_4^- + 2H^+ + 2e^- \to ClO_3^- + H_2O$	+1.23	$NO_3^- + H_2O + 2e^- \to NO_2^- + 2OH^-$	+0.10
$ClO_4^- + H_2O + 2e^- \to ClO_3^- + 2OH^-$	+0.36	$O_2 + 2H_2O + 4e^- \to 4OH^-$	+0.40
$Co^{2+} + 2e^- \to Co$	−0.28	$O_2 + 4H^+ + 4e^- \to 2H_2O$	+1.23
$Co^{3+} + e^- \to Co^{2+}$	+1.81	$O_2 + e^- \to O_2^-$	−0.56
$Cr^{2+} + 2e^- \to Cr$	−0.91	$O_2 + H_2O + 2e^- \to HO_2^- + OH^-$	−0.08
$Cr_2O_7^{2-} + 14H^+ + 6e^- \to 2Cr^{3+} + 7H_2O$	+1.33	$O_3 + 2H^+ + 2e^- \to O_2 + H_2O$	+2.07
$Cr^{3+} + 3e^- \to Cr$	−0.74	$O_3 + H_2O + 2e^- \to O_2 + 2OH^-$	+1.24
$Cr^{3+} + e^- \to Cr^{2+}$	−0.41	$Pb^{2+} + 2e^- \to Pb$	−0.13
$Cs^+ + e^- \to Cs$	−2.92	$Pb^{4+} + 2e^- \to Pb^{2+}$	+1.67
$Cu^+ + e^- \to Cu$	+0.52	$PbSO_4 + 2e^- \to Pb + SO_4^{2-}$	−0.36
$Cu^{2+} + 2e^- \to Cu$	+0.34	$Pt^{2+} + 2e^- \to Pt$	+1.20
$Cu^{2+} + e^- \to Cu^+$	+0.16	$Pu^{4+} + e^- \to Pu^{3+}$	+0.97
$F_2 + 2e^- \to 2F^-$	+2.87	$Ra^{2+} + 2e^- \to Ra$	−2.92
$Fe^{2+} + 2e^- \to Fe$	−0.44	$Rb^+ + e^- \to Rb$	−2.93
$Fe^{3+} + 3e^- \to Fe$	−0.04	$S + 2e^- \to S^{2-}$	−0.48
$Fe^{3+} + e^- \to Fe^{2+}$	+0.77	$S_2O_8^{2-} + 2e^- \to 2SO_4^{2-}$	+2.05
$[Fe(CN)_6]^{3-} + e^- \to [Fe(CN)_6]^{4-}$	+0.36	$Sc^{3+} + 3e^- \to Sc$	−2.09
$2H^+ + 2e^- \to H_2$	0, by definition	$Sn^{2+} + 2e^- \to Sn$	−0.14
$2H_2O + 2e^- \to H_2 + 2OH^-$	−0.83	$Sn^{4+} + 2e^- \to Sn^{2+}$	+0.15
$2HBrO + 2H^+ + 2e^- \to Br_2 + 2H_2O$	+1.60	$Sr^{2+} + 2e^- \to Sr$	−2.89
$2HClO + 2H^+ + 2e^- \to Cl_2 + 2H_2O$	+1.63	$Ti^{2+} + 2e^- \to Ti$	−1.63
$H_2O_2 + 2H^+ + 2e^- \to 2H_2O$	+1.78	$Ti^{3+} + e^- \to Ti^{2+}$	−0.37
$H_4XeO_6 + 2H^+ + 2e^- \to XeO_3 + 3H_2O$	+3.0	$Ti^{4+} + e^- \to Ti^{3+}$	0.00
$Hg_2^{2+} + 2e^- \to 2Hg$	+0.79	$Tl^+ + e^- \to Tl$	−0.34
$Hg_2Cl_2 + 2e^- \to 2Hg + 2Cl^-$	+0.27	$U^{3+} + 3e^- \to U$	−1.79
$Hg^{2+} + 2e^- \to Hg$	+0.86	$U^{4+} + e^- \to U^{3+}$	−0.61
$2Hg^{2+} + 2e^- \to Hg_2^{2+}$	+0.92	$V^{2+} + 2e^- \to V$	−1.19
$Hg_2SO_4 + 2e^- \to 2Hg + SO_4^{2-}$	+0.62	$V^{3+} + e^- \to V^{2+}$	−0.26
		$Zn^{2+} + 2e^- \to Zn$	−0.76