國立臺灣科技大學 109 學年度碩士班招生試題
系所組別：材料科學與工程系碩士班甲組
科　　目：物理化學

(總分為 100 分)

物理化學研究所考題

1. (10 points) Please drive

(a) $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$ (5 points)

(b) $\left(\frac{\partial [G/T]}{\partial T}\right)_P = -\frac{H}{T^2}$ (5 points)

where G, S, H, P, T and V are represented Gibbs energy, entropy, enthalpy, pressure, temperature and volume.

2. (20 points) An ideal gas undergoes a single-stage expansion against a constant external pressure $P_{external} = P_f$ at constant temperature from T, P_i, V_i, to T, P_f, V_f.

(a) What is the largest mass m that can be lifted through the height h in this expansion? (5 points)

(b) The system is restored to its initial state in a single-state compression. What is the smallest mass m' that must fall through the height h to restore the system to its initial state? (5 points)

(c) If $h = 15.5$ cm, $P_i = 1.75 \times 10^6$ Pa, $P_f = 1.25\times 10^6$ Pa, $T = 280$ K, and $n = 2.25$ mol, calculate the values of the masses in part (a) and (b). Molar gas constant $R = 8.314$ J K^{-1} mol^{-1}. (10 points)

3. (20 points) Consider a 20.0-L ideal gas sample of moist air at 60 °C and one atm in which the partial pressure of water vapor is 0.12 atm. Assume that dry air has composition 78.0 mole percent N_2, 21.0 mole percent O_2, and 1.0 mole percent Ar.

(1) What are the mole percentages of each of the gases in the sample? (4 point)

(2) The percent relative humidity is defined as %RH = $P_{H2O}/P^*_{H_2O}$ is the partial pressure of water in the sample and $P^*_{H_2O} = 0.197$ atm is the equilibrium vapor pressure of water at 60 °C. The gas is compressed at 60 °C until the relative humidity is 100%. What volume does the mixture contain now? (6 points)

(3) What fraction of the water will be condensed if the total pressure of the mixture is isothermally increased to 200 atm. (10 points)

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Useful physical constants:

Planck constant= 6.626x10^{-34} J-s; Electron mass= 9.1x10^{-31} kg; Electron charge= 1.6x 10^{-19} C; Boltzmann constant= 1.381x 10^{-23}J/K= 8.61x10^{-5} ev/K; Gas constant= 8.314 J/mol-K; Atomic mass= 1.67x10^{-24} g; Light speed= 3x10^{8} m/s

4. (12 points) Given the elementary reaction for hydroxyacid condensation:

$$2HO\text{-}R\text{-}COOH \rightarrow H(ORCO)_2OH + H_2O$$

(1) Write down the differential rate equation and initial condition for reactant of hydroxyacid. (3 points)

(2) Use the initial concentration of hydroxyacid ($[HO\text{-}R\text{-}COOH]_o$), and reaction rate constant(k), to find the reactant conversion, p, as a function of time(t).(5 points)

(3) Given the following data of reactant conversion(p) versus time(t):

t (minutes)	203	345
P	0.8161	0.883

Find mathematically the conversion (p) at t= 793 minutes. (4 points)

5. (13 points) An electron is confined in a finite one-dimensional potential energy well. The width of well(a) is 2 nm, and the height of the potential energy barrier 0.5 eV. (1 eV= 1.6x10^{-19} J). There are three energy levels in the well: E_1= 0.057 eV, E_2= 0.22 eV, and E_3= 0.45 eV.

(1) Find the electron momentum and wavelength in the ground state at energy= E_1. (5 points)

(2) Find the lowest excitation energy of electron, and the corresponding wavelength of irradiation light. (4 points)

(3) Then consider the electron in the finite three-dimensional potential well in the form of a cube with a length= 2 nm, with the barrier height= 0.5 eV in three dimensions. Find the lowest energy level and lowest excitation energy in the three-dimensional well. (4 points)

6. (13 points) Electron spin resonance (ESR) spectra are used to characterize free radicals in plastics, organic molecules in triplet states, and paramagnetic metal ions.

(1) For a free electron or the electron in hydrogen atom (spin quantum number= 1/2), give the magnitude of spin angular momentum. (3 points)

(2) Derive the possible values of spin magnetic moment from the spin angular momentum in part (1) of this problem. Given $he/(4\pi m_e)$= Bohr magneton= 9.274x10^{-24}J/T., where h= Planck constant, e= electron charge, and m_e= electron mass. (3 points)

(3) Find the microwave frequency required to excite the spin state in part (2)

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under the magnetic field= 0.339 T. (4 points)

(4) Regarding an organic molecule in a triplet state (spin quantum number= 1) for a pair of electrons. Give the possible values of the spin angular momentum in the direction of magnetic field. (3 points).

7. (12 points)The potential energy between $Na^+(g)$ and $Cl^-(g)$ consists of two parts: the attractive component, determined by the Coulombic electrostatic attractive force equal to $-e^2/(4\pi\varepsilon_o r^2)$, and the repulsive, which is negligible within an error of less than 10% for the ionic bonding. Note that ε_o = vacuum permittivity=$8.854\times10^{-12} C^2N^{-1}m^{-2}$, and r= interionic distance. The ionic radius of Na^+= 0.095 nm, and ionic radius of Cl^-= 0.181 nm. The ionization energy of Na= 5.14 eV, and electron affinity of Cl= -3.61 eV.

(1) Find the approximate interionic potential energy, which is equal to the negative value of the ionic bond energy of NaCl. (4 points)

(2) Lattice energy for the geometrical array (i.e., face- centered cubic packing) of ions in the solid state is equal to 1.75 times the bond energy for NaCl in part (1) of this problem. Calculate the lattice energy. (2 points)

(3) Binding (or cohesive) energy of solid is defined as the energy used to break the solid crystal into neutral free atoms. Calculate the binding energy for NaCl(s). (3 points)

(4) Compare the relative magnitude of binding (cohesive) energy of a family of covalently bonded solids such as diamond, silicon, and germanium, all of which have the same type of crystal lattice. Also give the reasoning for your answer. (3 points)