國立台灣科技大學一百學年度碩士班招生試題

系所組別： 材料科學與工程學系碩士班甲組

科　　目： 物理化學

（總分為100分）

總分 100 分，共八大題。選擇題務必於答案卷內依序作答，在試題內作答者不予計分。

一、選擇題：答案寫於答案紙內，其他方式作答不計分。

(21%) Choose the best answer in each problem. 3 points each. No penalty on the wrong guess. Be sure to answer all questions on the examination book, rather than problem sheet!

1. Transition state theory treats the physical or chemical rate constant as a function of temperature and (a) activation energy, (b) equilibrium constant, (c) Gibbs energy of activation, (d) molar enthalpy of change, (e) activation volume, of this process.

2. Heat capacity of materials, contributed by molecular/atomic vibration, is determined by temperature and Debye temperature, where Debye temperature is related to (a) size, (b) cohesive energy, (c) moment of inertia, (d) frequency, (e) lattice constant.

3. Which one of the followings does deal with the energy gap between bonding and antibonding orbitals in a conjugated molecule? (a) Hund's rule, (b) Heitler- London treatment, (c) valence- bond theory, (d) Heuckel MO theory, (e) Born- Oppenheimer approximation.

4. When the hydrogen atom is placed in a magnetic field, the energy of this dipole in a magnetic field is simply equal to magnetic field times (a) electric dipole moment, (b) magnetic quantum number, (c) electronegativity, (d) Bohr magneton, (e) magnetic moment.

5. For uncharged molecules, the net intermolecular energy is given by Lennard- Jones 6- 12 function. How many molecular parameters are incorporated within it?(a) 1, (b) 2, (c) 3, (d) 4, (e) 0.

6. The wave frequency of light emitted by a ruby laser is v. Assuming that the emission of photon of this wave frequency accompanied the transition of an electron from the n= 2 level to the n= 1 level of an infinite square well. The width of well is L. Suppose L is proportional to the mth power of v, then m= (a) -0.5, (b) -1, (c) 0, (d) 1, (e) 2.

7. Bohr's hydrogen atom model is used to describe the ionization of a dopant atom in silicon semiconductor. The ionization energy, E, of electron is related to the atomic radius of dopant, r. Suppose E is proportional to the nth power of r, then n= (a) -0.5, (b) -1, (c) 0, (d) 1, (e) 2.

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二、(7%) In the polymerization of styrene and ethylene, reactants (including monomers and initiators) go through a three-step reaction process as follows:

A (initiator) → B (activated initiating species)→ C (propagated chains)→ D (resulting terminated chains)

a) For radical polymerization, the first step, i.e., A to B, is a first-order reaction. The half-life of A is 10 hours at 126°C, and 1 hour at 147°C, respectively. Calculate the activation energy(in J/mol) of step 1 for A converted to B. (3 points)

b) If the first step is infinitely fast compared to the following two steps, consider merely species B, C, and D. The reaction rate constant is k1 for B to C (step 2), and k2 for C to D (step 3), separately. Sketch the graph of concentration of C versus time for finite k1 and k2 . (2 points)

c) Following the above b), give a condition for C (propagated chains) to be in a steady state, which is an ideal case. (2 points)

三、(7%) Vibrational spectroscopy is being widely used in materials analysis. The observed vibrational frequency of carbon monoxide, CO, is 6.42E13 Hz. (note:"E" means a power function of 10)

a) Give the vibrational energy values of two lowest quantized levels. (3 points)

b) Find the reduced mass (in kg) of CO. Given atomic mass, O: 15.994, C: 12.011. (2 points)

c) Find the force constant (in N/m) of this molecule modeled as a harmonic oscillator. (2 points)

*Useful Physical Constants

Planck constant= 6.626E-34 J-s　　Gas constant= 8.317 J/K/mol

四、You are responsible for the purchase of oxygen gas which, before use, will be stored at the pressure of 200 atm at 300K in a cylindrical vessel of a diameter 0.2 meters and height 2 meters. Would you prefer that the gas behavior ideally or as a van der Waals gas? The van der Waals constant for oxygen are a=1.36 (l^2xatm/$mole^2$) and b=0.0318 (l/mole). **(15 points)**

五、Describe the 1st Law of thermodynamics briefly, and express the relationship between the internal energy (U) and heat (q) or work (w) and explain the physical meanings of (q) and (w) for their direction. Then calculate the values of q and w, and the change in U, H, and S for one mole ideal gas undergoing a following process:

a. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to the triple its volume.

b. The gas is next heated reversibly to 400 K at constant volume.

c. The gas reversible expanded at constant temperature until its volume is again tripled.

d. The gas is finally reversibly cooled to 300 K at constant pressure.

(Assume the gas is an ideal gas, and c_v=1.5R; c_p=2.5R) **(20 points)**

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六、Please drive

(a) $\left(\frac{\partial A}{\partial T}\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$ (6 points)

(b) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (4 points).

七、Consider the reversible Cannot cycle with 1.75 mole of an ideal gas with $C_{V,m} = 3/2R$ as working substance. The initial isothermal expansion occurs at the hot reservoir temperature of T_{hot} = 920K from an initial volume of 4 L (V_a) to a volume of 11.5 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to T_{cold} = 375K. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by T_a = 920K and V_a = 4 L is reached.

a)Calculate w, ΔH, ΔS_{total} for the total cycle.(6 points)

b)Calculate maximum efficiency and amount of heat that is extracted from the hot reservoir to do 1000 J of work in the surrounding.(4 points)

八、A gas mixture with 3 mole of Ar, x moles of Ne, and y moles of Xe is prepared at 1 bar and 298K. The total number of moles in the mixture is four times that of Ar. At what value of x does ΔG_{mixing} have its minimum value? Calculate ΔG_{mixing} for this value of x.(10 points)