國立臺灣科技大學 108 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)

Useful physical constants: Planck constant= 6.626×10^{-34} J-s; Electron mass= 9.1×10^{-31} kg; Electron charge= 1.6×10^{-19} C; Boltzmann constant= 1.381×10^{-23} J/K= 8.61×10^{-5} ev/K; Gas constant= 8.314 J/mol-K; Atomic mass= 1.67×10^{-24} g

1.(12 points) Huckel molecular orbital theory deals with molecular orbitals occupied by delocalized pi-bonded electrons in so-called conjugate molecules.

(a) For ethylene (with 1 pi bond) and butadiene (with 2 pi-bonds), use bonding and antibonding orbitals to define highest occupied molecular level and lowest unoccupied molecular level. Draw schematically the Huckel orbital diagrams for two molecules, and indicate energy levels. (3 points)

(b) For ethylene and butadiene, how is the energy difference between two above molecular levels related to the resonance energy of each pi-bond? Which one of these two compounds holds the higher energy difference between two levels? (3 points)

(c) Crystalline carbon(diamond) and silicon in solid state are covalently bonded in three-dimensional network, with a large amount (approximately 10^{23}) of delocalized electrons that lead to the formation of bands. The ionization energy is 11.30 eV for carbon atom and 3.15 eV for silicon atom. Which one out of diamond and silicon possesses the higher energy difference between the lowest unoccupied and the highest occupied bands? Also give the reason leading to your judgement. (3 points)

(d) Compare the magnitude of bond energy (cohesive energy) and melting temperature of diamond to that of silicon. Why so? (3 points)

2. (13 points) The nitrogen and oxygen diffusion through a solid metal, vanadium(V), with body-centered cubic crystals, can be visualized as a series of gas molecule jumps into the interstitial void space in atoms. The activated complex theory leads to the representation of gas diffusion coefficient (D) by the Arrhenius equation:

$$D = A \exp(-E_a/RT)$$

where R= gas constant, T= temperature, E_a is activation energy equal to 152 (nitrogen in V) or 125 kJ/mol (oxygen in V), and A pre-exponential factor equal to 50.21×10^{-7} m^2/s (nitrogen in V) or 26.61×10^{-7} m^2/s (oxygen in V). Another more delicate theory, so-called transition-state theory, utilizes the free energy of activation and the frequency of transition state (i.e., jump state) to describe this rate process with visualizing a unimolecular reaction. Atomic weights of nitrogen and oxygen are 14.01 g/mol and 16.00 g/mol, respectively.

(a) Find the relationship between enthalpy of activation and activation energy, and calculate the activation enthalpy at 300K for nitrogen and oxygen in V, respectively. (3 points)

(b) Find the jump frequency for nitrogen and oxygen in V at 300K. (3 points)

(c) Use the pre-exponential factor in the activated complex theory to compare the activation entropy of nitrogen in V to that of oxygen in V, without calculating the real

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values of activation entropy. (3 points)

(d) Find the velocity of nitrogen and oxygen molecules at 300K in the open space, and also give a relationship between activation enthalpy of gas diffusion in V at 300K and gas velocity. (4 points)

3. (12 points) Scanning tunneling microscopy (STM) is an imaging technique based on detecting electrons tunneling across vacuum between a conducting sample and a conducting probe tip. The tunneling current is very sensitive to the distance between the tip and the sample. Suppose the kinetic energy of free electrons before leaving the probe tip is 5 eV and the potential barrier height between tip and conducting sample is 7 eV.

(a) Find the momentum and wavenumber of free electrons before leaving the tip. (3 points)

(b) Suppose that the wave mechanics offers the wavefunction (ψ)of the electron in the gap (x) between sample and tip is given by ψ= B exp (-k x), where B is a constant evaluated with boundary conditions at x= 0, and k wavenumber in the gap. Find the numerical value of electron wavenumber and wavelength in the gap. (3 points)

(c) Find the probability density of electron wave at x= 0.5 nm. (3 points)

(d) By what factor would the STM current drop if the gap between probe and sample is moved from 0.5 nm to 0.6 nm? (3 points)

4. (13 points) The vibrational-rotational spectroscopy has been used to determine the bond length and bond vibrational frequency of diatomic gas molecules. CO has a vibrational force constant (k) of 1900 N/m, bond length of 1.13 Angstroms, and molecular weight of 28.01 g/mol.

(a) Find the moment of inertia of this molecule and the vibrational frequency of C=O bond. (4 points)

(b) Give the selection rule (for the change of vibrational and rotational quantum numbers) in spectral transition. (3 points)

(c) Find the highest wavenumber (defined as the ratio of linear frequency over light speed) of P- branch in spectral bands. (3 points)

(d) At higher temperatures, the molecular vibration is no longer harmonic, and the two-atom vibrational potential energy (V) vs. displacement from the equilibrium position (x) is modified as

$$V(x)= D\,[1- \exp(-ax)]^2$$

where D is dissociation energy and a constant. Show mathematically that k (force constant in harmonic vibration) is related to parameters in anharmonic vibration in this equation, $k= 2Da^2$. (3 points)

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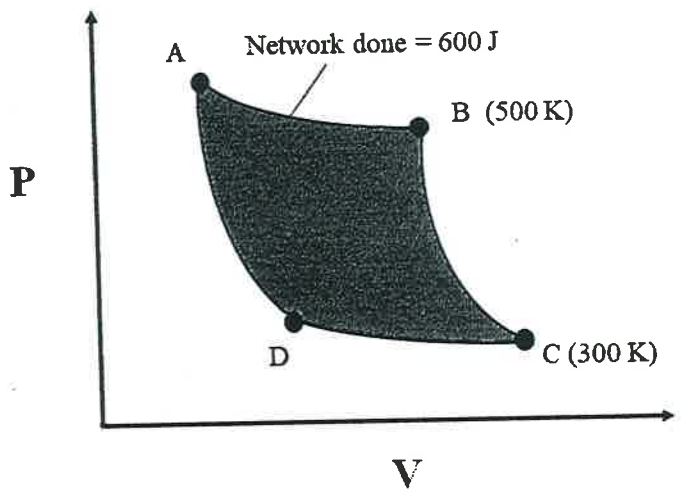
5. (15 points) Helium is compressed isothermally and reversibly at 100°C from 1 to 5 bar. Calculate (a) ΔG (3 points), (b) ΔA (3 points), (c) ΔH (3 points), (d) ΔU (3 points), and (e) ΔS (3 points) per mole, assuming helium is an ideal gas. (R=8.314 J/mol K, ln 5 = 1.609)

6. (12 points) The following diagram shows a reversible Carnot cycle for an ideal gas:
(a) How much heat is absorbed at 500 K? (3 points)
(b) How much heat is rejected at 300 K? (3 points)
(c) What is the entropy and Gibbs energy change in the process A→B (3 points)
(d) What is the entropy change in the entire cycle? (3 points)



7. (10 points) The ionization constant of an ion could be described by the equation $\ln K = 50 - 1860/T - 10 \ln T$ between 10°C and 50°C. Calculate values of ΔH^0 and ΔS^0 for the ionization at 37°C. (R=8.314 J/mol K, ln 10 = 2.30, ln 40 = 3.69, ln 50 = 3.91, ln 310 = 5.74) (10 points)

8. (13 points) (a) Derive an expression for dP/dT for a first-order phase transition. On the basis of the obtained expression, predict whether the melt point of ice rises or falls with increasing pressure. (8 points)
(b) The specific volumes of water and ice at 0°C and 1 atm pressure are 1.0001 cm^3g^{-1} and 1.0907 cm^3g^{-1}, respectively. The enthalpy of fusion of ice is 334 Jg^{-1}. Calculate the melting point of ice under a pressure of 15 MPa. (5 points)