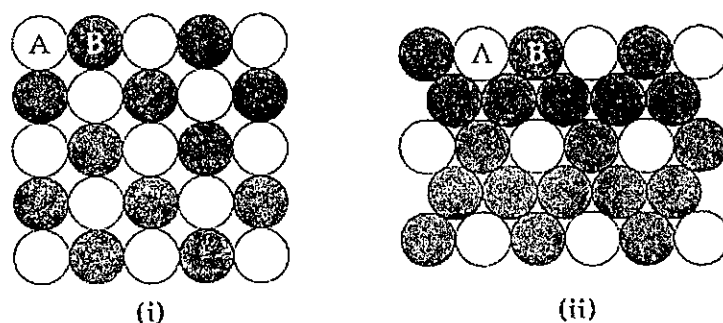


※ 注意：請於試卷上「非選擇題作答區」標明大題及小題題號，並依序作答。

- (15%) In 1858 J. Waterston found a clever way to estimate molecular sizes from macroscopic properties of a liquid, by comparing its surface tension and heat of vaporization. The surface tension of water, Σ , is the work per unit area needed to create more free surface. To define it, imagine breaking a brick in half. The two pieces have two new surfaces. Let Σ be the work needed to create these new surfaces, divided by their total area. The analogous quantity for liquid water is the surface tension. The heat of vaporization of water, Q_{vap} , is the energy per unit volume we must add to liquid water (just below its boiling point) to convert it completely to steam (just above its boiling point). That is, the heat of vaporization is the energy needed to separate every molecule from every other one. Picture a liquid as a cubic array with N molecules per centimeter in each of three directions. Each molecule has weak attractive forces to its six nearest neighbors. Suppose it takes energy ϵ to break one of these bonds. Then the complete vaporization of 1 cm^3 of liquid requires that we break all the bonds. The corresponding energy cost is $Q_{\text{vap}} \times (1 \text{ cm}^3)$. Next consider a molecule on the surface of the fluid. It has only five bonds—the nearest neighbor on the top is missing (suppose this is a fluid–vacuum interface). Draw a picture to help you visualize this situation. Thus to create more surface area requires that we break some bonds. The energy needed to do that, divided by the new area created, is Σ .
 - (5%) For water, $Q_{\text{vap}} = 2.3 \cdot 10^9 \text{ J/m}^3$, while $\Sigma = 0.072 \text{ J/m}^2$. Estimate N .
 - (5%) Assuming the molecules are closely packed, estimate the approximate molecule diameter.
 - (5%) What estimate for Avogadro's number do you get?
- (15%) The wave functions for a 1s and 2s orbitals in a hydrogen atom are $\psi_{1s}(r, \theta, \phi) = N_1 \exp(-r/a_0)$ and $\psi_{2s}(r, \theta, \phi) = N_2(2 - r/a_0) \exp(-r/2a_0)$, where a_0 is the Bohr radius and N_1 and N_2 are the suitable normalization constants.
 - (5%) Sketch wavefunction $\psi(r, \theta, \phi)$ and probability density $|\psi(r, \theta, \phi)|^2$ of 1s and 2s orbitals as a function of r along a particular direction, respectively.
 - (5%) Sketch the radial distribution functions $4\pi r^2 |\psi(r, \theta, \phi)|^2$ for 1s and 2s orbitals, respectively.
 - (5%) Sketch the wave function for an electron in the orbitals (i) 3s, (ii) $3p_x$, and (iii) $3d_{xz}$? Give the numbers of angular and radial nodes in each case.
- (10%) Consider the molecules H_2CCH_2 , H_2CCCH_2 , and H_2CCCCH_2 .
 - (3%) Draw Lewis structures for these molecules.
 - (3%) What is the hybridization at each C atom?
 - (2%) What type of bond connects the carbon atoms (single, double, etc.)?
 - (2%) Do all the hydrogen atoms lie in the same plane?
- (15%) The equipartition theorem states that in thermal equilibrium, any degree of freedom (such as a component of the position or velocity of a particle) which appears only quadratically in the energy has an average energy of $1/2 k_B T$ and therefore contributes $1/2 k_B$ to the system's heat capacity.
 - (3%) The kinetic energy of a particle of mass m free to undergo translation in three dimensions is $E_k = (1/2)mv_x^2 + (1/2)mv_y^2 + (1/2)mv_z^2$. What is the average kinetic energy of a particle free to move in three dimensions?
 - (3%) Use the equipartition theorem to show that for a monatomic perfect gas: $E_m(T) = E_m(0) + (3/2)RT$, $C_{V,m} = (3/2)R$, where $E_m(0)$ is the molar internal energy at $T = 0$, when all translational motion has ceased.
 - (3%) When the gas consists of molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as N_2 and CO_2 , can rotate around two axes perpendicular to the line of the atoms, so it has two rotational modes of motion, each contributing a term $1/2 k_B T$ to the internal energy. Show that $E_m(T) = E_m(0) + (5/2)RT$, $C_{V,m} = (5/2)R$ (linear molecule, translation and rotation only)

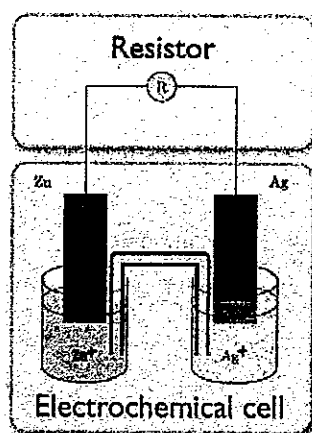
- (d) (3%) A non-linear molecule, such as CH_4 or H_2O , can rotate around three axes and, again, each mode of motion contributes a term $\frac{1}{2}k_B T$ to the internal energy. Show that $E_m(T) = E_m(0) + 3RT$, $C_{v,m} = 3R$ (non-linear molecule, translation and rotation only)
- (e) (3%) Use the equipartition theorem to calculate the contribution of molecular motion to the total energy of a sample of 10.0 g of (i) argon and (ii) carbon dioxide at 20°C . Hint: For (ii), take into account translation and rotation but not vibration. Boltzmann constant: $k_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$

5. (10%) Two patterns of packing for two different circles of the same size are shown here. For each structure
- (3%) draw the two-dimensional unit cell;
 - (3%) determine the angle between the lattice vectors, γ , and determine whether the lattice vectors are of the same length or of different lengths;
 - (4%) determine the type of two-dimensional lattice (Oblique, Square, Rectangular, Hexagonal, Rhombic lattices).



6. (15%) Boltzmann formula, $S = k_B \ln \Omega$, says that the entropy of a macroscopic state is proportional to the number of microstates of a system where all microstates are equiprobable. Calculate the number of microstates and residual entropy of the following systems, in terms of the ideal gas constant, $R = N_A k_B$, (N_A is Avogadro constant):
- (5%) A mole of monoxide crystal at $T = 0\text{K}$, assuming that each molecule can have two possible orientations CO or OC and also these two orientations have exactly the same energy.
 - (10%) A mole of ice crystal at $T = 0\text{K}$. Assume that there are exactly two OH bonds and two hydrogen bonds surrounding each oxygen atom as shown in the following figure, which will be called the chemical condition. (Hints: For a mole of ice, there are $2N$ hydrogen atoms. Along each O-H-O connection, the hydrogen can have possible choice of positions along its O-O axis. There are 2^{2N} microstates. However, the positions of four hydrogen atoms surrounding a particular oxygen atom are not independent. So you need to figure out the fraction of microstates that satisfies the chemical condition.)

7. (10%) Suppose we construct an electrochemical cell as shown in the following figure at the standard state ($\text{Zn}|\text{Zn}^{2+}(1\text{M})||\text{Cl}^-(1\text{M})|\text{AgCl}|\text{Ag}$). Assume that the extent of reaction is small enough to keep the concentrations essentially unchanged. During the discharge, heat will evolve from the resistor (R) and from the cell, and we would measure the heat change by placing the cell and resistor in separate calorimeters. If we take Q_C as the heat change in the cell and Q_R as that in the resistor, we find $Q_C + Q_R = -233 \text{ kJ/mol}$ independent of R . In the limit of infinite R , Q_C approaches -43 kJ/mol and Q_R tends toward -190 kJ/mol .



- (a) (6%) What are the enthalpy, entropy and Gibbs energy changes of the reaction, $\text{Zn} + 2\text{AgCl} \rightarrow \text{Zn}^{2+} + 2\text{Ag} + 2\text{Cl}^-$.
- (b) (4%) What is the maximal thermodynamic efficiency (i.e. converting the heat released to non-PV work) of this electrochemical cell?
8. (10%) The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C . The following data were collected, with all concentration units in $\mu\text{mol/L}$. (A hemoglobin concentration of $2.21 \mu\text{mol/L}$ is equal to $2.21 \times 10^{-6} \text{ mol/L}$.)

$[\text{Hb}]_0$ ($\mu\text{mol/L}$)	$[\text{CO}]_0$ ($\mu\text{mol/L}$)	Initial Rate ($\mu\text{mol L}^{-1} \text{ s}^{-1}$)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

- (a) (3%) Determine the orders of this reaction with respect to Hb and CO.
- (b) (3%) Determine the rate law.
- (c) (2%) Calculate the value of the rate constant.
- (d) (2%) What would be the initial rate for an experiment with $[\text{Hb}]_0 = 3.36 \mu\text{mol/L}$ and $[\text{CO}]_0 = 2.40 \mu\text{mol/L}$?

試題必須隨卷繳回