類組：化學類　科目：物理化學(1004)　　※請在答案卷內作答

Problem 1 (30 分)

P-V isotherm diagram of Wan der Waals equation can be drawn from the following equation,

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

where $\overline{V} = \frac{V}{n}$ is molar volume, P is pressure, T is temperature, R is universal gas constant, a and b are Wan der Waals constants.

(a) (6 分) Explain physical meaning of $P \to 0$ at $\overline{V} \to \infty$ and give an example where this is applied.

(b) (6 分) Explain physical meaning of $P \to \infty$ at $\overline{V} \to b$ and give an example where this is applied.

(c) (6 分) Find $P = 0$ at which molar volume, and does this have correct physical meaning?

(d) (12 分) Find $P, \overline{V}, \ and\ T$ in terms of Wan der Waals constants at critical point (C.P.).

Problem 2 (40 分)

(a) (6 分) It is well-know that Schrödinger equation for hydrogen atom is given by

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{\sqrt{x^2 + y^2 + z^2}}\right]\Psi(x, y, z) = E\Psi(x, y, z)$$

where μ is reduce mass (approximately equal to electron mass). Is there any mathematic method with which solution can be written in form of $\Psi(x, y, z) = \eta(x)\xi(y)\varsigma(z)$? Give mathematic and physical explanation for yes or no.

(b) (6 分) By transforming above equation to spherical coordinate system (r, θ, ϕ), we obtain

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)P_{lm}(\theta)\Phi_m(\phi)$$

with energy solved as $E_n = -\frac{1}{2n^2}E_h$ (E_h is unit energy in atomic units), why Schrödinger equation can be written in separate form in spherical coordinate system? Give mathematic and physical explanation.

(c) (10 分) Calculate energy degeneracy for given principle quantum number n with and without considering electron spin wavefunction.

(d) (18 分) The probability finding the electron in a hydrogen atom somewhere in the spherical volume between *0* and a_0 (a_0 is Bohr radius) is given by

$$P_{nlm}(0 \le r \le a_0) = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\phi \int_0^{a_0} \left|\Psi_{nlm}(r, \theta, \phi)\right|^2 r^2 dr\ .$$

Calculate probability for $\Psi_{1s} = \Psi_{100} = \frac{2}{\sqrt{4\pi}}\left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)$.

注意：背面有試題

參考用

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Problem 3 (30 分)

Partition function for a molecule is given by

$$z = \sum_k \exp\left(-\frac{\varepsilon_k}{k_B T}\right),$$

where T is temperature, k_B is Boltzmann constant, and ε_k is energy level corresponding to the quantum state k that represents to sum over all quantum states for the molecule. In general, it is very difficult to obtain analytical expression for partition function. However, in the case of rigid rotor and harmonic oscillator approximation, we can. Derive analytical expressions for *the two of* following three cases (a) translational partition function, (b) rotational partition function and (c) vibrational partition function.

(a) (15 分) Use energy level for a particle in three-dimensional cubic box with length a,

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \quad n_x, n_y, n_z = 1,2,3,\cdots$$

(b) (15 分) Use rotational energy level for diatomic molecule,

$$\varepsilon_{JM} = \frac{J(J+1)\hbar^2}{2I}$$ where $J=0, 1, 2, \ldots$, and for given J, $M = -J, -(J-1), \ldots, 0, \ldots, (J-1), J$

(c) (15 分) Using vibrational energy level for diatomic molecule,

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right)$$ where $n = 0, 1, 2, \ldots$

注意：背面有試題