Physical Chemistry I

Answer the following questions on a hydrogen atom and a hydrogen molecule. Use the following values of physical constants if necessary: light velocity in vacuum $c_0 = 3.00\times10^{8}$ m s^{-1}, Planck constant $h = 6.33\times10^{-34}$ J s. The calculation result can be rounded to 2 significant digits.

I−a Fill ① ~ ⑥ with words, name, or values.

The energy levels of the electron in a hydrogen atom are given by the following equation, based on the ①'s atomic model that was named after a Danish physicist, with n to be ②.

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}$$

where m_e and e denote the electron rest mass and the elementary charge, respectively, and ε_0 is the electric permittivity in vacuum. $|E_1|$ corresponds to the minimum energy required to remove the electron from a hydrogen atom in the $n = 1$ state, which is called as ③ and is 2.18×10^{-18} J. The emission spectrum of a hydrogen discharge lamp contains spectral lines. The series of spectral lines observed in the visible (wavelength of approximately ④ nm to ⑤ nm) to near-ultraviolet region is called as ⑥.

I−b Derive an equation that gives the reciprocal of the emission wavelength λ when electronic transition of a hydrogen atom occurs from a level with ② of $n=a$ to $n=b$.

I−c Answer the longest wavelength of the ⑥ series lines. Explain how the line wavelength of transition to $n=b$ varies with $n=a$.

Physical Chemistry I

Let us discuss the electronic states of a hydrogen molecule cation H_2^+ based on the molecular orbital method with the linear combination of atomic orbitals (LCAO MO theory). We assume that the positions of the nuclei are fixed in space.

Atomic orbitals belonging to hydrogen atoms A and B are denoted as χ_A and χ_B, respectively, and the electronic Hamiltonian is represented as H. The atomic orbitals χ_A and χ_B are normalized. The LCAO MO of the system is written as ψ. With the coefficients of the atomic orbital c_A and c_B, ψ is given as $\psi = c_A\chi_A + c_B\chi_B$.

I－d Derive an expression of the electronic energy E of the system, with c_A, c_B, and integrals given in the following.

$$H_{ij} = \int \chi_i H \chi_j \mathrm{d}\mathbf{r} \quad (i,j = \mathrm{A},\mathrm{B})$$

$$S = \int \chi_\mathrm{A}\chi_\mathrm{B}\mathrm{d}\mathbf{r}$$

I－e By applying the variation principle on E derived in the question above, a simultaneous equation on c_A and c_B given in the following is obtained.

$$c_\mathrm{A}(H_\mathrm{AA} - E) + c_\mathrm{B}(H_\mathrm{AB} - SE) = 0$$

$$c_\mathrm{A}(H_\mathrm{AB} - SE) + c_\mathrm{B}(H_\mathrm{BB} - E) = 0$$

Solve this equation to obtain eigen energies E and corresponding coefficients c_A and c_B. The c_A and c_B values should be chosen as ψ to be normalized.

I－f The two molecular orbitals generated from the two pairs of $\{c_A, c_B\}$ obtained in the Question I－e are denoted as ψ_1, ψ_2. Describe difference in symmetries of ψ_1 and ψ_2, and its relevance to the eigen energies. Note that all the values of H_{ij} are negative.

(The end)

Physical Chemistry II

Answer the following questions about the phase transition of water.

II−a Fill in the blanks with the appropriate words or numbers for ① ~ ⑦. Water is in a liquid state under standard conditions (300 K, 1013 hPa). Under normal pressure, it becomes more stable in a solid state and turns into ice below ① K, and it becomes stable in a gaseous state and turns into water vapor above ② K. A state where two of the three phases—gas, liquid, and solid—coexist is called ③, and a state where all three phases coexist is called ④. In the case of water, this occurs at 273.16 K and 612 Pa. The ③ between the gas phase and the liquid phase is called the vaporization curve, which connects ④ and ⑤. The ⑤ for water is 647.14 K and 22.064 MPa, where the ⑥ of the gas and liquid phases become identical, resulting in a supercritical fluid state. The ③ between the liquid phase and the solid phase is called the melting curve, which, in the case of water, has an unusually negative coefficient. The ③ between the gas phase and the solid phase is called the ⑦.

II−b Let's consider a phase transition from phase α (V_α) to phase β (V_β). When one of the phases involved in the phase transition is in the gas phase, the volume of the other phase can be neglected compared to that of the gas phase. Therefore, the Clausius-Clapeyron equation can be modified as follows using the ideal gas law. Here, P, T, R, and ΔH represent pressure, temperature, the gas constant, and the change in molar entropy, respectively.

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H}{T(V_\beta - V_\alpha)} = \frac{P\,\Delta H}{RT^2}$$

The molar enthalpy of vaporization near the ④ is 45.049 kJ mol^{-1}, and the molar enthalpy of sublimation is 51.12 $\text{J K}^{-1}\,\text{mol}^{-1}$. Calculate the slopes of the vaporization curve and the ⑦ in the pressure-temperature phase diagram near the ④. Assume that the gas constant R is 8.314 $\text{J K}^{-1}\,\text{mol}^{-1}$.

II−c Calculate the pressure [MPa] required to lower the melting point of ice by 1 K under normal pressure using the Clausius-Clapeyron equation. Assume the densities of water and ice near 0°C under normal pressure are 1.000 g/cm^3 and 0.917 g/cm^3, respectively, and the enthalpy of fusion is 6.01 kJ/mol. Use two significant digits in your answer.

Answer the following questions about molecular vibrations.

II−d Fill in the blanks with the appropriate words, numbers, or equations for $\boxed{\text{⑧}}$ ~ $\boxed{\text{⑬}}$.

Let’s consider the vibrations of a diatomic molecule. By modeling the chemical bond between the two atoms as a spring, we can denote the spring constant as k and approximate that it follows $\boxed{\text{⑧}}$’s law. This is known as the harmonic approximation. Let the masses of the two atoms be m_1 and m_2, respectively. Their reduced mass M is given by $\boxed{\text{⑨}}$. The vibrational frequency ω is given by

$$\omega = \sqrt{\frac{k}{M}} \qquad \text{(i)}$$

For example, in the case of HCl, k=516 N/m, and its vibrational frequency is $\boxed{\text{⑩}}$ Hz. Here, let the mass of hydrogen (H) be 1.67×10^{-27} kg, and the mass of chlorine (Cl) be 5.89×10^{-26} kg. In classical vibration, the energy can take continuous values, but in quantum theory, the vibrational energy can only take discrete values, as shown below.

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) \quad (n = 0, 1, 2, \cdots) \qquad \text{(ii)}$$

Here, n is called $\boxed{\text{⑪}}$. The state with $n = 0$ is called the $\boxed{\text{⑫}}$ state, and the state with $n = 1, 2, \cdots$ is called the $\boxed{\text{⑬}}$ states.

II−e Sketch the potential energy curve given by the harmonic approximation. Also, illustrate the vibrational energy levels given by the equation for $n = 0, 1, 2, \ldots$. Clearly indicate the spacing between the energy levels.

II−f The wave functions in the potential given by the harmonic approximation are expressed as a function of the displacement coordinate x by the equation

$$\psi_n(x) \propto H_n(x)e^{-x^2} \qquad \text{(iii)}$$

Here, H_n represents the Hermite polynomials, which are given for $n = 0, 1, 2$ as follows:

n	H_n
0	1
1	$2x$
2	$4x^2 - 2$

Add the shape of these wave functions to the potential energy diagram illustrated in Question II−e. Based on this, discuss why only transitions with $\Delta n = 1$ are allowed in the harmonic approximation. Assume that the electric dipole approximation holds for the transitions.

(The end)