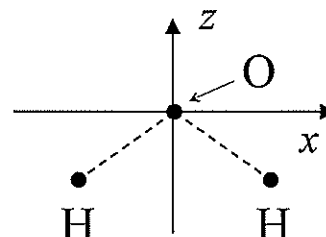## Physical Chemistry I

Answer the following questions concerning the water molecule (H_2O).

I — a

Consider H_2O aligned in the xz plane as shown in the right figure.

(1) Given that the two OH bonds are the same in length, the molecular structure of H_2O is invariant under some kinds of symmetry operation. In the right figure, the z axis corresponds to the C_2 rotation axis. Explain what is meant by the C_2 rotation.

(2) The water molecule is symmetric with respect to two kinds of reflection operation in the xz and yz mirror planes, denoted $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$, respectively. Counting the identity operation E as another symmetry operation, the H_2O molecule has four symmetry elements in total. Identify the point group to which H_2O belongs.

I — b

Let us focus on H_2, which is here viewed as a part of H_2O. We now introduce the bonding orbital φ_g and the anti-bonding orbital φ_u, which are derived as a superposition of two $1s$ atomic orbitals each associated with the H atoms in H_2. The right diagram shows that the bonding orbital φ_g is more stable in energy than the anti-bonding orbital φ_u, and φ_g is doubly occupied by a pair of electrons.
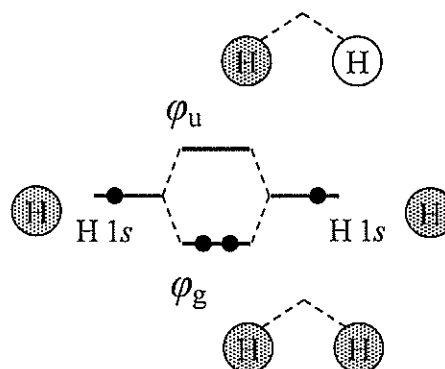
(1) The restriction that a single orbital cannot be occupied by more than two electrons is based on the ① principle. Answer what should be written in the blank ① .

(2) The bonding orbital φ_g and the anti-bonding orbital φ_u are represented with a linear combination of two hydrogenic $1s$ orbitals, $1s^A$ and $1s^B$, as follows:

$$\varphi_g = 1s^A + 1s^B, \quad \text{(with the same phase)}$$
$$\varphi_u = 1s^A - 1s^B, \quad \text{(with the opposite phase)}$$

where A and B represent each of the two H atoms in H_2. Show that φ_g and φ_u are orthogonal.

I — c

(1) The following relations are derived by applying each of the symmetry operations to the $2s$ and $2p_z$ atomic orbitals of the O atom:

$E\,(2s) = +1 \cdot (2s),$ $C_2\,(2s) = +1 \cdot (2s),$ $\sigma_{v(xz)}\,(2s) = +1 \cdot (2s),$ $\sigma_{v(yz)}\,(2s) = +1 \cdot (2s),$

$E\,(2p_z) = +1 \cdot (2p_z),$ $C_2\,(2p_z) = +1 \cdot (2p_z),$ $\sigma_{v(xz)}\,(2p_z) = +1 \cdot (2p_z),$ $\sigma_{v(yz)}\,(2p_z) = +1 \cdot (2p_z),$

Derive similar relations for the $2p_x$ and $2p_y$ atomic orbitals of the O atom.

(2) Using the character table shown below, it can be shown that the irreducible representations of the $2s$ and $2p_z$ atomic orbitals of the O atom are both assigned to a_1. Assign the irreducible representations of the $2p_x$ and $2p_y$ atomic orbitals of the O atom.

	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
a_1	1	1	1	1
a_2	1	1	−1	−1
b_1	1	−1	1	−1
b_2	1	−1	−1	1

(3) The irreducible representation of the bonding orbital φ_g of H_2 is assigned to a_1. Assign the irreducible representation of the anti-bonding orbital φ_u of H_2.

I — d

(1) It has been shown above that the $2s$ and $2p_z$ atomic orbitals of the O atom as well as the bonding orbital φ_g of H_2 are commonly of the a_1 symmetry. The supersession of these three orbitals leads to three molecular orbitals, as denoted ψ_1, ψ_2, and ψ_3 in the diagrams below.
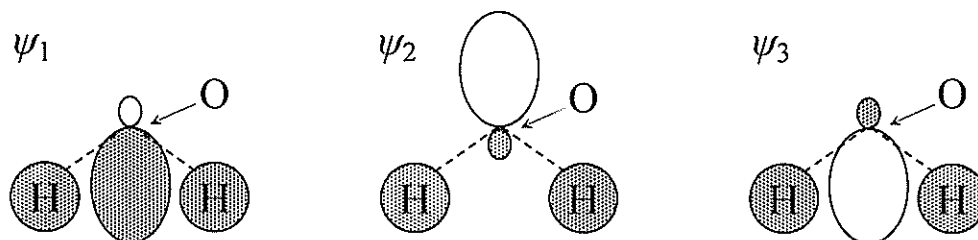
Describe the character of each of the orbitals ψ_1, ψ_2, and ψ_3 in terms of the bonding/anti-bonding nature in the OH bond.

(2) Draw the diagram of the bonding orbital ψ_4 arising from the overlap between the $2p_x$ atomic orbitals of the O atom and the anti-bonding orbital φ_u of H_2.

I － e

The most stable electronic configuration of the water molecule is written as $(O\ 1s)^2\,(\psi_1)^2\,(\psi_2)^2$ $(\psi_4)^2\,(O\ 2p_y)^2$. The $2p_y$ atomic orbitals of the O atom ('O $2p_y$') is doubly occupied while it remains the form of the atomic orbital in the molecule. This type of orbital is thus often called the ② orbital.

(1) Answer what should be written in the blank ② .

(2) Let the bond order be defined as

(the number of electrons in the bonding orbitals － the number of electrons in the anti-bonding orbitals) / 2.

Using this definition, discuss that the two OH bonds in H_2O are single bonds.

Let us consider temperature variation of gases in the Joule-Thomson process. As shown in Figure, in the experiment of the Joule-Thomson process, two chambers A and B surrounded by adiabatic walls are connected to each other by a tube with a microporous partition, and the gases in chamber A with higher pressure are pushed into chamber B with lower pressure. Here, the microporous partition is inserted so that the gases can flow randomly, and you do not have to consider the effect explicitly in the following questions. It is known that the enthalpy of the transferred gases is invariant before and after the gas transfer.

Answer the following questions II-a to II-f. Define H as the enthalpy, S as the entropy, p as the pressure, T as the temperature, V as the volume, β as the bulk modulus, R as the gas constant, C_p as the specific heat at constant pressure, n as the molar amount. Note that the bulk modulus is defined as

microporous
partition

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and the specific heat at constant pressure C_p as

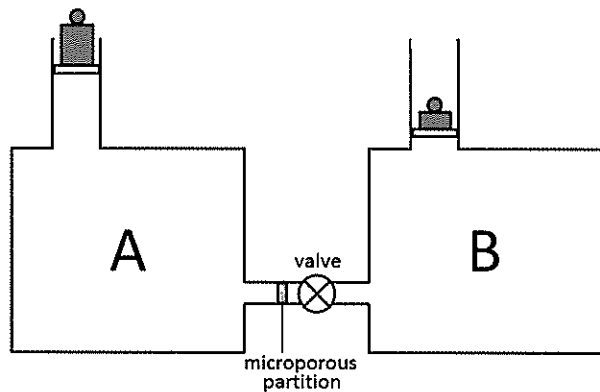$$C_p \equiv T\left(\frac{\partial S}{\partial T}\right)_p .$$

II-a

The exact differential of the Gibbs energy is expressed as

$$dG = -SdT + Vdp .$$

Write the corresponding Maxwell's relation. Moreover, show the equation

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\beta .$$

II-b

Using the exact differential of the enthalpy H

$$dH = TdS + Vdp,$$

show the equation

$$dH = C_p dT + V(1 - \beta T) dp \quad.$$

II-c

Express the Joule-Thomson coefficient $(\partial T/\partial p)_H$ using V, T, β and C_p.

II-d

Express the bulk modulus β for n-molar ideal gases using appropriate variables among V, T, n and R. Moreover, calculate the Joule-Thomson coefficient $(\partial T/\partial p)_H$ for n-molar ideal gases.

II-e

The equation of state for the n-molar van der Waals gases is given as

$$\left(p + \frac{n^2 a}{V^2} \right)(V - nb) = nRT.$$

The partial differential of the equation with respect to V under constant p leads to

$$\left(\frac{\partial T}{\partial V} \right)_p \cong \frac{T}{V - nb} - \frac{2na}{RV^2} \quad,$$

where the second- and higer-order terms concerning small van der Waals constants a and b are neglected. Calculate the bulk modulus β and the Joule-Thomson coefficient $(\partial T/\partial p)_H$ of the n-molar van der Waals gases. Here, by assuming $2na \ll RTV$, answer the first-order formula concerning a and b. Use appropriate variables among V, T, n, R, a, b and C_p in the answers.

II-f

Express the temperature T_{inv} where the sign of $(\partial T/\partial p)_H$ varies for n-molar van der Waals gases. Moreover, show the appropriate conditions in the Joule-Thomson process to reduce the temperature of chamber B with lower pressure.