

Physical Chemistry I

I – a

Fill in the blanks [A] to [J] with right words, phrases, numbers, or formulae.

Let us consider treatment of hydrocarbon molecules having π -electron bonds (π -bonds) with the simple Hückel molecular orbital method, one of the simplest quantum chemical method for polyatomic molecules. In this method, for the carbon atoms that form π -bonds, it is assumed that the valence atomic orbitals form [A] hybrid atomic orbitals to make σ -bonds, while the remaining [B] atomic orbitals that do not contribute to the [A] orbitals form π -bonds. We denote the [B] orbital of i -th carbon atom as χ_i , and then the following integrals

$$\int \chi_i^* \chi_j d\tau = S_{ij}$$

$$\int \chi_i^* H \chi_i d\tau = \alpha$$

$$\int \chi_i^* H \chi_j d\tau = \beta \quad (i \neq j)$$

are called [C] integral, [D] integral, and [E] integral, respectively, where H represents the π -electrons Hamiltonian. Under the Hückel approximation, S_{ij} is assumed to be unity if $i = j$ and zero if $i \neq j$. The quantities α and β both have negative values, and β is assumed to be zero if atoms i and j are not chemically bonded to one another. The α values are the same for any carbon atoms, and the β values are the same for any π -bonds.

When this method is applied to the simplest molecule having a π -bond, ethylene ($\text{CH}_2=\text{CH}_2$), the secular equation for the π -electrons is given as [F], and the solutions of the orbital energy are obtained as $E =$ [G] and [H] in ascending order of energy. Number of π -electrons in ethylene molecule is [I]. These electrons occupy the orbitals mentioned above in the order of energy from lower one to higher one, and as a result the total energy of π -electrons is [J].

I – b

Now we treat molecular orbitals of cyclopropenyl molecule C_3H_3 with Hückel molecular orbital method. Assume that the cyclopropenyl molecule has a geometry of equilateral triangle.

(1) Write a secular equation for π -electrons of cyclopropenyl molecule, and solve it to obtain the orbital energies. Draw rough sketches of the orbitals.

(2) Suppose that one of the carbon atoms in the cyclopropenyl molecule among the three is geometrically separated from, and does not interact with, the other two carbon atoms (schematically

represented as $\text{HC} \cdots \text{C}_2\text{H}_2$). Write secular equation for π -electrons of this system, and solve it to obtain the orbital energies. (The effects of A orbital changes along with the geometrical change can be neglected here.)

(3) How many π -electrons are there in a neutral molecule of cyclopropenyl? Based on the results of previous questions (1) and (2), discuss the stability of the ground state molecule from the viewpoint of π -electron energy.

(4) How many electrons are required to be withdrawn from the ground-state molecule of cyclopropenyl, to form a closed-shell electronic state? How many electrons are required to be added to the ground-state cyclopropenyl, to form a closed-shell electronic state?

(5) On the closed-shell cation and anion in the previous question (4), discuss their stabilities in terms of π -electron energies and Hückel rule (or aromaticity).

(6) Answer spin multiplicity of ground-state monovalent anion of cyclopropenyl molecule. Describe the reason for that also.

Physical Chemistry II

To design a pressure cooker, in which the boiling point of water $T_0 = 100\text{ }^\circ\text{C}$ (373 K) is shifted to $T_1 = 104\text{ }^\circ\text{C}$ (377 K) in the atmospheric pressure (101.3 kPa), thermodynamic calculation is made.

Consider two phases, L and G, which consist of the identical substance. Within a small change in temperature, T , and pressure, p , of the system, the relation

$$d\mu_L = d\mu_G$$

holds, where μ_L and μ_G are chemical potentials of the two phases, since the equilibrium of the system is maintained. Under the condition that the amount of the substance in the system stays constant, the small change of the chemical potential, $d\mu$, can be expressed as

$$d\mu = -\bar{S}dT + \bar{V}dp,$$

where \bar{S} and \bar{V} are molar entropy and molar volume, respectively.

II – a

To estimate pressure necessary for shifting the boiling point, derive the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}},$$

where $\Delta\bar{V}$ and $\Delta\bar{S}$ are the difference in the molar volumes and the difference in the molar entropies of the two phases, respectively.

II – b

The above equation is inconvenient to apply for the pressure cooker because of the entropy term, $\Delta\bar{S}$. Eliminate $\Delta\bar{S}$ using the relation

$$0 = \Delta H - T\Delta S,$$

where ΔH and ΔS are the enthalpy and entropy changes during the phase transition ($\Delta G = 0$), respectively.

II – c

Derive an equation to obtain the pressure change, Δp , necessary for the shifting of the boiling point from T_0 to T_1 , by integration of the equation derived in II – b with respect to T .

II – d

Calculate the pressure change, Δp , using the equation derived in II – c and evaluate the pressure necessary for the shifting of the boiling point to 104 °C. The answer should be given in the unit of kPa and rounded to two significant figures. The heat of vaporization and the volume change of water during vaporization are $\Delta\bar{H} = 40.7 \text{ kJ mol}^{-1}$ and $\Delta\bar{V} = 30.1 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, respectively. Use the approximation equation

$$\ln(1 + x) \approx x$$

which is applicable when x is small, if necessary.