Physical Chemistry I

I − a

Fill in the blanks ① to ⑧ with words or formulae.

We consider π orbitals of a 2-propenyl cation, $CH_2CHCH_2^+$, using the Hückel approximation. Three carbon atoms in the molecule are labelled as D, E, and F from left to right, and their 2p atomic orbitals are defined as φ_D, φ_E, and φ_F, respectively. The π orbitals are, then, written by the linear combination of the atomic orbitals as

$$\psi = c_D\varphi_D + c_E\varphi_E + c_F\varphi_F \,.$$

Here, we define

$$\int \varphi_i^*\varphi_j \mathrm{d}\tau = S_{ij}\,,$$

$$\int \varphi_i^* H\varphi_j \mathrm{d}\tau = \begin{cases} \alpha_i & (i = j) \\ \beta_{ij} & (i \neq j) \end{cases},$$

where i and j denote D or E or F, $\mathrm{d}\tau$ is the volume element, H is the hamiltonian, and S, α_i, and β_{ij} are called as ① integral, ② integral, and ③ integral, respectively.

In the Hückel approximation, it is assumed that S is given as

$$S_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases},$$

α_i is given as α independent of i, and β_{ij} becomes a non-zero value β when i and j are neighboring atoms; thus, β_{DF} is 0.

The total energy of the system ε and the orbital ψ can be obtained from the following three equations based on the ④ principle:

$$\frac{\partial\varepsilon}{\partial c_D} = 0, \quad \frac{\partial\varepsilon}{\partial c_E} = 0, \quad \text{⑤}.$$

To determine the orbital ψ, the ⑥ condition written as

$$\int \psi^*\psi \mathrm{d}\tau = 1\,,$$

is also imposed, where $\psi^*\psi$ is the ⑦ density. When electrons occupy the orbitals, the ⑧ exclusion principle should be satisfied.

I − b

(1) Explain what is the ④ principle.

(2) Explain the meaning of $\psi^*\psi \mathrm{d}\tau$, which is given by multiplying $\mathrm{d}\tau$ by the ⑦ density.

(3) Explain what is the ⑧ exclusion principle.

I − c

(1) On the basis of the description of I − a, write down the 3×3 secular determinant for the π orbitals of the 2-propenyl cation using ε, α, and β.

(2) Find three eigen-energies from the secular determinant obtained in (1).

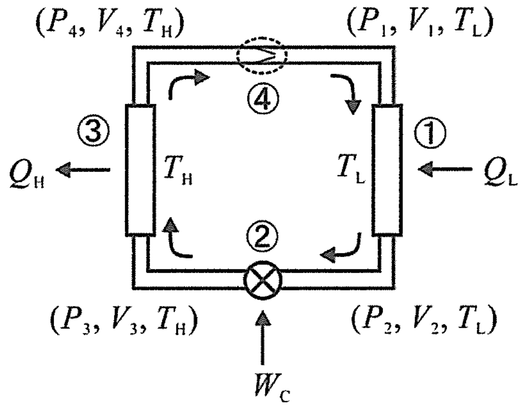
(3) From three π orbitals corresponding to the eigen-energies obtained in (2), find and write down the orbital ψ with the lowest eigen-energy using φ_D, φ_E, and φ_F.

(4) Draw a rough sketch of the π orbital obtained in (3).

I − d

The 2-propenyl cation is relatively stable comparing to other primary carbocations. Explain the reason of the stability on the basis of the result obtained in I − c.

Physical Chemistry II



We consider the reversed Carnot cycle that is a model of refrigerator. As shown in the figure, the state (P_1, V_1) at a low temperature (T_L [K]) receives the heat Q_L [J], and becomes the state (P_2, V_2) by the isothermal expansion in process ①. In process ②, the state (P_3, V_3) at a high temperature (T_H [K]) is formed due to the adiabatic compression by receiving the work W_C [J] from a compressor. The state (P_4, V_4) is formed due to the isothermal compression at a high temperature (T_H [K]) in process ③, and emits the heat Q_H [J]. Finally, the refrigerant recovers the state (P_1, V_1) at the low temperature (T_L [K]) by the adiabatic expansion with a reducing valve in process ④. Gas constant R is 8.31 [J K^{-1} mol^{-1}]. Absolute temperature is connected to Celsius temperature as T [K] = T_0 [°C] + 273 [K]. The refrigerant is an ideal gas whose amount is 1 [mol], and the equation of state becomes $PV = RT$. The energy change dU in the system is given by the sum of the heat dq and the work dw as dU = dq + dw. The change of the work is given by dw = −pdV. Answer the questions below. Use the significant figure of three.

I − a

Calculate the emitted heat Q_L [J] necessary for cooling the 10 g water from 25 °C to 10 °C. The heat capacity of water is 4.22 [J g^{-1} K^{-1}].

I − b

Derive a formula of pressure ratio P_2/P_1 for receiving the heat Q_L [J] in process ①. For the isothermal expansion, dU = 0.

I − c

In adiabatic compression process ②, the temperature is increased from T_L = 10 °C to T_H = 50 °C by receiving the work W_C [J]. The Poisson law described below holds in the adiabatic compression.

$$PV^{\gamma} = \text{const}$$

(1) Derive a formula for dV/dT in adiabatic compression process ②.

(2) Calculate the work W_C [J] by using the formula dV/dT obtained in question (1). $\gamma = 5/3$ for an ideal gas.

I − d

Calculate the heat Q_H [J] emitted in isothermal compression process ③. Use the heat Q_L [J] in isothermal expansion process ① obtained in question I − a. $V_4/V_3 = V_1/V_2$ holds in the reversed Carnot cycle of an ideal gas.