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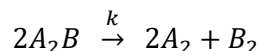
Problem 26. Chemical Kinetics

The decomposition reaction of a compound A_2B proceeds with the chemical equation

$$2A_2B \xrightarrow{k} 2A_2 + B_2$$

and the reaction rate equation follows $r = kc_{A_2B}^2$. The kinetic data of the system is given in the table below:

Temperature (K)	967	967	1030	1030
Initial concentration of A_2B (mmol dm^{-3})	156	39	7	49
First half-life of A_2B (s)	380	1520	1442	206

26-1 <u>**Calculate**</u> the activation energy E_A, and the reaction rate constant k at both 967 K and 1030 K.

The reaction is of second order with respect to A_2B, and the rate law is

$$\frac{dc_{A_2B}}{dt} = -2r = -2kc_{A_2B}^2 \ .$$

After integration, it yields

$$\frac{1}{c_{A_2B}(t)} - \frac{1}{c_{A_2B}(0)} = 2kt \ ,$$

and by imposing the half-life condition $c_{A_2B}(t_d) = c_{A_2B}(0)/2$ it yields the kinetic constant k as

$$k = \frac{1}{2c_{A_2B}(0)t_d} \ .$$

The values of k are taken as the mean between the two experiments at the same temperature, yielding for 967 K, with all units being mmol dm^{-3} s^{-1}

$$k(967 \ K) = \frac{k_1 + k_2}{2} = 8.43 \times 10^{-6} \ , \qquad k_1 = 8.43 \times 10^{-6} \ , \qquad k_2 = 8.43 \times 10^{-6} \ ,$$

while yielding for 1030 K, with all units being mmol dm^{-3} s^{-1}

$$k(1030 \ K) = \frac{k_1 + k_2}{2} = 4.95 \times 10^{-5} \ , \qquad k_1 = 4.95 \times 10^{-5} \ , \qquad k_2 = 4.95 \times 10^{-5} \ .$$

The activation energy is obtained from the classic Arrhenius form of the kinetic constant, and it is thus assumed as being independent from the temperature.

Taking the ratio of the kinetic constants at two temperatures the pre-exponential factor simplifies, yielding

$$\frac{k(967 \ K)}{k(1030 \ K)} = e^{-\frac{E_A}{R}\left(\frac{1}{967 \ K} - \frac{1}{1030 \ K}\right)} \ ,$$

thus

$$E_A = R \frac{\ln \frac{k(967 \ K)}{k(1030 \ K)}}{\frac{1}{1030 \ K} - \frac{1}{967 \ K}} = 232.7 \ kJ \ mol^{-1} \ .$$

26-2 If the initial concentration of A_2B at 1030 K is 54 mmol dm^{-3}, **calculate** the time taken for the conversion rate of A_2B to reach 37%.

The conversion rate is defined as the ratio of the depleted reactant with respect to the initial reactant, usually in a molar basis or molar concentration basis

$$\xi = \frac{c_{A_2B}(0) - c_{A_2B}(t)}{c_{A_2B}(0)}.$$

Thus, from the definition

$$c_{A_2B}(t) = c_{A_2B}(0)(1 - \xi),$$

which substituted in the rate law yields

$$t = \frac{1}{2c_{A_2B}(0)k} \frac{\xi}{1 - \xi} = 109.8 \ s$$

This value is consistent with the kinetic data, as in the fourth experiment at the specified temperature and with a similar initial concentration, the half-life (equivalent to ξ of 50%) is almost double as the calculated time.

26-3 The reaction, $A \rightarrow C$, can occur by two different mechanisms (Fig. 26):

(a) The reaction $A \overset{k_a}{\rightarrow} C$ occurs directly, and the half-life is not related to the initial concentration. At 294 K, the half-life is 1000 min, and at 340 K, the time needed for the concentration of A decreases to 1/1024 of the original concentration is 0.10 min.

(b) The reaction proceeds in two steps:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^*$$

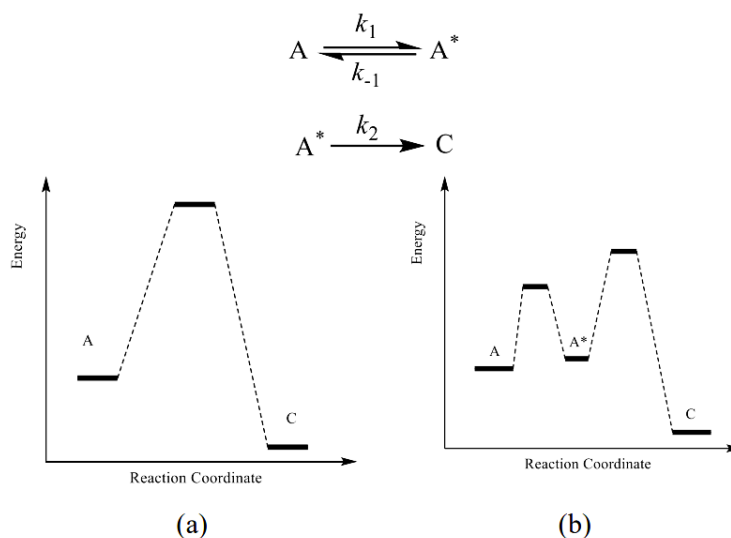$$A^* \overset{k_2}{\rightarrow} C$$

(a) (b)

Figure 26 The potential energy profiles of the two mechanisms

The activation energies for the involved steps are:

$$E_{A,1} = 125.5 \text{ kJ mol}^{-1}, \ E_{A,-1} = 120.3 \text{ kJ mol}^{-1}, \ E_{A,2} = 167.4 \text{ kJ mol}^{-1}$$

Assume that the pre-exponential factors of these two mechanisms are the same, and both of the activation energies and the pre-exponential factors do not change with temperature. **Calculate** the ratio between the rates of the two mechanisms, r_B/r_A, at 500 K.

The mechanism (a) is of first order in A, as it is the only reaction order with half-life that is independent from the initial concentration, thus the rate law is

$$r_A = \frac{dc_A}{dt} = -k_a c_A \,.$$

After integration, it yields

$$\ln \frac{c_A(0)}{c_A(t)} = k_a t \,,$$

and by imposing the half-life condition $c_A(t_d) = c_A(0)/2$ it yields the kinetic constant k_a as

$$k_a(294 \, K) = \frac{\ln 2}{t_d} = 6.93 \times 10^{-4} \, min^{-1} \,.$$

For the second case, the time needed is obtained by setting $c_A(t) = c_A(0)/1024$, thus

$$k_a(340 \, K) = \frac{\ln 1024}{t} = 6.93 \times 10^{2} \, min^{-1} \,.$$

Taking the ratio of the kinetic constants at two temperatures the pre-exponential factor simplifies, yielding

$$\frac{k_a(294 \, K)}{k_a(340 \, K)} = e^{-\frac{E_A}{R}\left(\frac{1}{294 \, K} - \frac{1}{340 \, K}\right)} \,,$$

thus

$$E_A = R \frac{\ln \dfrac{k_a(294 \, K)}{k_a(340 \, K)}}{\dfrac{1}{340 \, K} - \dfrac{1}{294 \, K}} = 249.6 \, kJ \, mol^{-1} \,.$$

This value is consistent with the plots of Fig. 26, as the activation energy for mechanism (a) is roughly double the activation energies for mechanism (b).

The mechanism (b) is complex, with rate laws

$$r_B = \frac{dc_A}{dt} = -k_1 c_A + k_{-1} c_{A*}$$

$$\frac{dc_{A*}}{dt} = k_1 c_A - k_{-1} c_{A*} - k_2 c_{A*}$$

Assuming the pseudo-steady state condition on the intermediate A^*, it is possible to estimate its concentration on the basis that its formation ($k_1 c_A$) and depletion rates ($k_{-1} c_{A*} + k_2 c_{A*}$) balance each other:

$$\frac{dc_{A*}}{dt} = 0 \quad \rightarrow \quad c_{A*} = c_A \frac{k_1}{k_{-1} + k_2} \,,$$

thus

$$r_B = \frac{dc_A}{dt} = -\frac{k_1 k_2}{k_{-1} + k_2} c_A \,.$$

Then, from the equal pre-exponential assumption, the ratio r_B/r_A becomes

$$\frac{r_B}{r_A} = \frac{1}{k_a} \frac{k_1 k_2}{k_{-1} + k_2} = \frac{1}{e^{-E_A/RT}} \frac{e^{-E_{A,1}/RT} e^{-E_{A,2}/RT}}{e^{-E_{A,-1}/RT} + e^{-E_{A,2}/RT}} = \frac{e^{-(E_{A,1} + E_{A,2} - E_A)/RT}}{e^{-E_{A,-1}/RT} + e^{-E_{A,2}/RT}}$$

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yielding $r_B/r_A = 0.512$ for 500 K.

The ratio (also called "branching ratio") slightly decreases with increasing temperature, suggesting that the reaction rate from mechanism (b) is actually lower (almost half) than the reaction rate from mechanism (a). This is due to the intermediate effect, as with increasing temperature it can be shown that k_a is slightly lower than k_1, k_{-1} and k_2 which take an almost equal value k, yielding

$$r_B = -\frac{k}{2} c_A$$

which is almost half from $r_A = -k_a c_A$. This also shows consistency with the value of $r_B/r_A \approx 1/2$ at 500 K.