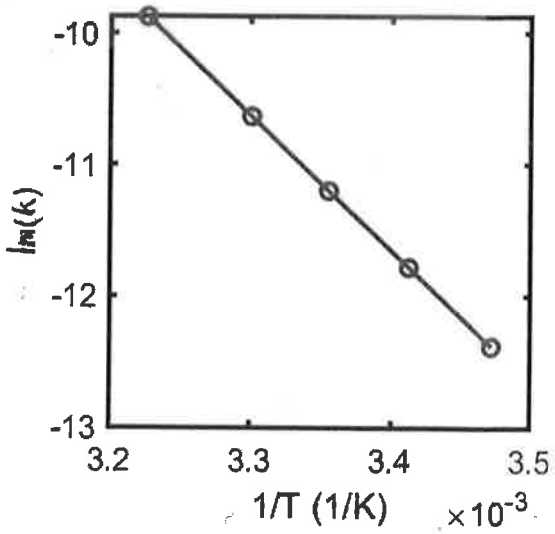
CHEM – C3220 – Kemiallinen dynamiikka

4. laskuharjoitus, vastaukset

1. Arrhenius-plot:



$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$

$k_k = -10197$

$k_p = 23.02$

$E_a = 10.197 \cdot 8.314 \text{ kJ/mol}$

$= 84.8 \text{ kJ/mol}$

$A = e^{23.02} \approx 9.9 \cdot 10^9$

2.

$$NH_4^+ + CNO^- \rightleftharpoons NH_3 + HNCO \quad \text{nopea}$$

$$NH_3 + HNCO \rightarrow (NH_2)_2CO \quad \text{hidas}$$

1. vaihe tasapainossa: $K_1 = \dfrac{[NH_3][HNCO]}{[NH_4^+][CNO^-]}$

$$R = \frac{d[(NH_2)_2CO]}{dt} = k_2[NH_3][HNCO]$$

$$= \underbrace{K_1 k_2}_{k}[NH_4^+][CNO^-]$$

Jos NH_4CNO:n konsentraatio tuplataan, reaktionopeus nelinkertaistuu

3. $[Br\cdot] = \left(\frac{k_1}{k_{-1}}[Br_2]\right)^{1/2} = \left(K_1[Br_2]\right)^{1/2}$ (2)

$$\frac{d[H\cdot]}{dt} = k_2[Br\cdot][H_2] - [H\cdot]\left(k_3[Br_2] + k_4[HBr]\right) = 0$$

$$[H\cdot] = \frac{k_2[Br\cdot][H_2]}{k_3[Br_2] + k_4[HBr]} = \frac{k_2\sqrt{K_1}[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]}$$

$$\frac{d[HBr]}{dt} = k_2[Br\cdot][H_2] + [H\cdot]\left(k_3[Br_2] - k_4[HBr]\right)$$

$$= k_2\sqrt{K_1}[H_2][Br_2]^{1/2} + \frac{k_2\sqrt{K_1}[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]}\left(k_3[Br]_2 - k_4[HBr]\right)$$

$$\frac{d[HBr]}{dt} = k_2\sqrt{K_1}[H_2][Br_2]^{1/2}\left(1 + \frac{k_3[Br]_2 - k_4[HBr]}{k_3[Br_2] + k_4[HBr]}\right)$$

$$= k_2\sqrt{K_1}[H_2][Br_2]^{1/2}\,\frac{2k_3[Br]_2}{k_3[Br_2] + k_4[HBr]}$$

$$= \frac{k'[H_2][Br_2]^{1/2}}{k_3 + k_4\frac{[HBr]}{[Br_2]}} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k_4}{k_3}\frac{[HBr]}{[Br_2]}}$$

5.

$$2A \rightarrow A_2 \; ; \; -\frac{dP_A}{dt} = kP_A^2$$

$$\left.\begin{aligned} P_A &= P_0 - 2x\frac{RT}{V} \\ P_{A_2} &= x\frac{RT}{V} \end{aligned}\right\} \quad P_T = P_A + P_{A_2} = P_0 - x\frac{RT}{V}$$

$$x\frac{RT}{V} = P_0 - P_T$$

$$P_A = P_0 - 2(P_0 - P_T) = 2P_T - P_0$$

$$\frac{1}{P_A} - \frac{1}{P_0} = kt \qquad k = 1{,}762 \cdot 10^{-5}\ \text{torr}^{-1}\,\text{s}^{-1}$$

4.

Lindemann: $$k = \frac{k_1 k_2 [A]^2}{k_2 + k_{-1}[A]} \approx k[A]$$

$$k = \frac{k_1 k_2 [A]}{k_2 + k_{-1}[A]} \qquad \frac{1}{k} = \frac{1}{k_1[A]} + \frac{k_{-1}}{k_1 k_2}$$

Kuvaaja ei ole suora, joten ei ole Lindemann-mekanismi.