

## CY101 Assignment II September 2005

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1. The pseudo-first-order rate constant for the decomposition of NOCl (g) to NO(g) and Cl<sub>2</sub>(g) is measured and found to be  $1.96 \times 10^6 \text{ s}^{-1}$ . The actual rate limiting step is  $\text{Cl} + \text{NOCl} \rightarrow \text{Cl}_2 + \text{NO}$  which has rate constant  $k_2$ . The reaction is pseudo first order in chlorine atoms because the concentration of chlorine atoms is so much less than the concentration of NOCl.

a. Calculate the value of the rate constant  $k_2$ , with units, when  $p(\text{NOCl}) = 10.0 \text{ mol/m}^3$ .

$$\text{Ans: } k_2 = 1.96 \times 10^7 \text{ s}^{-1} \text{ (apparent 1st order)}$$

b. Calculate the value of the reaction rate, with units, when  $p(\text{NOCl}) = 10.0 \text{ mol/m}^3$  and  $p(\text{Cl}) = 1.0 \times 10^{-3} \text{ mol/m}^3$ .

$$\text{Ans: Rate} = 1.96 \times 10^4$$

$\text{mol m}^{-3} \text{ s}^{-1}$ .

$$\text{Rate} = k_2 [\text{Cl}] [\text{NOCl}]$$

$$k_2 = 1.96 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \times 10 \text{ mol m}^{-3}$$

$$= 1.96 \times 10^7 \text{ s}^{-1} \text{ (apparent 1st order)}$$

$$\text{Rate} = 1.96 \times 10^6 \times 10^3 \times 10 = 1.96 \times 10^4 \text{ mol m}^{-3} \text{ s}^{-1}$$

2. For  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ , determine the rate expression using the given data. Find  $k$  with units.

[N <sub>2</sub> ] (M)	[H <sub>2</sub> ] (M)	Initial rate (M / min)
0.10	0.10	0.0021
0.10	0.20	0.0084
0.20	0.40	0.0672

$$\text{Ans: Rate} = k[\text{N}_2] [\text{H}_2]^2, k = 2.1 (\text{M}^{-2} \text{min}^{-1}).$$

$$\text{Rate} = k [\text{N}_2]^a [\text{H}_2]^b$$

$$\left( \frac{0.0084}{0.0021} \right) = \left( \frac{0.20}{0.10} \right)^b$$

$$\therefore b = 2$$

$$\left( \frac{0.0672}{0.0084} \right) = \left( \frac{0.20}{0.10} \right)^a \left( \frac{0.40}{0.20} \right)^2$$

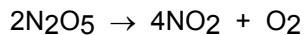
$$\therefore a = 1$$

$$\text{Rate} = k[\text{N}_2] [\text{H}_2]^2$$

$$k = 2.1 (\text{M}^{-2} \text{min}^{-1}).$$

3. N<sub>2</sub>O<sub>5</sub> gas decomposes according to the reaction  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ . The rate of reaction at 328 K is found to be  $0.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . What are the values of  $\frac{d[\text{N}_2\text{O}_5]}{dt}$ ,  $\frac{d[\text{NO}_2]}{dt}$ ,  $\frac{d[\text{O}_2]}{dt}$  ?

$$\text{Ans: } 1.5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}, 3 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}, 0.75 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}.$$



$$\frac{d[\text{N}_2\text{O}_5]}{dt} = 1.5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}$$

$$\frac{d[\text{O}_2]}{dt} = 0.75 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}$$

$$\frac{d[\text{N}_2]}{dt} = 3 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}$$

4. A first order reaction has activation energy of  $104,600 \text{ J mol}^{-1}$  and a pre-exponential factor  $A = 5 \times 10^{13} \text{ s}^{-1}$ , at what temperature will the reaction have a half-life of 30 days? Ans:  $T = 269.5 \text{ K}$

$$\frac{\ln 2}{t_{1/2}} = A \exp^{-E_a/RT}$$

$$\therefore T = 269.5 \text{ K}$$

5. A reaction follows the rate law.  $\sqrt{A} - \sqrt{A_0} = -\frac{kt}{2}$  find the order and units for k.

$$\text{Ans: order} = \frac{1}{2}, \text{ Units for k} = \text{mol}^{\frac{1}{2}} \text{ litre}^{-1/2} \text{ sec}^{-1}$$

$$\text{Substitute } n = \frac{1}{2} \text{ which gives } \sqrt{A} - \sqrt{A_0} = -\frac{kt}{2}$$

$$\text{Units for k} = \text{mol}^{\frac{1}{2}} \text{ litre}^{-1/2} \text{ sec}^{-1}$$

6. For a first order consecutive reaction,  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$  write down the rate expressions and obtain concentrations [A], [B] and [C] at time t in terms of  $[A]_0$ ,  $k_1$  and  $k_2$ . Obtain the same for B and C under steady state conditions. If  $[A]_0 = 100 \text{ M}$ ,  $k_1 = 0.04 \text{ min}^{-1}$ ,  $k_2 = 0.006 \text{ min}^{-1}$ , Calculate the concentrations of A, B and C at 5 min.

$$\text{Ans: } [A] = 81.87, [B] = 17.85, [C] = 0.278$$

Refer text book for the first part

$$[A] = 81.87, [B] = 17.85, [C] = 0.278$$

7. For a reaction  $A + B \xrightleftharpoons[k_{-1}]{k_1} C \xrightarrow{k_2} D$ , find rate expression for the formation of D applying steady state approximation. C is a reactive intermediate. Ans:

$$\frac{d[D]}{dt} = k_2 [C] = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2}$$

Using SSA

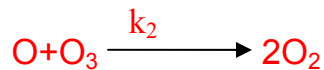
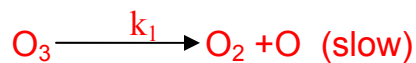
$$\frac{d[C]}{dt} = k_1 [A][B] - k_{-1} [C] - k_2 [C] = 0$$

$$[C] = \frac{k_1 [A][B]}{k_{-1} + k_2}$$

$$\frac{d[D]}{dt} = k_2 [C] = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2}$$

8. The decomposition of ozone  
 $2O_3 \rightarrow 3O_2$ , Experimental rate =  $-\frac{1}{2} \frac{d[O_3]}{dt} = k [O_3]$

Suggest a mechanism to account for the fact that it is not a bimolecular reaction.

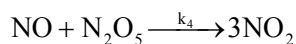
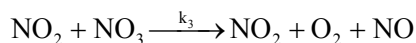
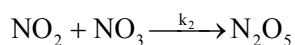
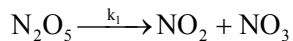
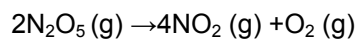


$$\frac{d[O]}{dt} = 0 = k_1 [O_3] - k_2 [O][O_3] \Rightarrow [O] = \frac{k_1}{k_2}$$

Total rate of disappearance of  $O_3$  :

$$-\frac{d[O_3]}{dt} = k_1 [O_3] + k_2 [O][O_3] = 2k_1 [O_3] = \text{exp. rate}$$

9. The following mechanism is suggested for the decomposition of  $N_2O_5$ .



Find the rate law consistent with this mechanism. Ans:  $\frac{d[N_2O_5]}{dt} = \frac{-2k_1 k_3 [N_2O_5]}{k_2 + k_3}$

$$\frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_2[NO_2][NO_3] - k_4[NO][N_2O_5]$$

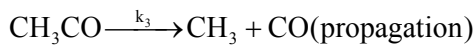
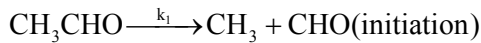
$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO_2][NO_3] = 0$$

$$\frac{d[NO]}{dt} = k_1[NO_2][NO_3] - k_4[NO][N_2O_5] = 0$$

$$\therefore \frac{d[N_2O_5]}{dt} = \frac{-2k_1k_3[N_2O_5]}{k_2 + k_3}$$

10. Pyrolysis (thermal decomposition in the absence of air) of acetaldehyde

$CH_3CHO(g) \xrightarrow{k} CH_4(g) + CO(g)$  is a chain reaction. The proposed Rice-Herzfeld mechanism is given below:



Show that this mechanism is consistent with the experimental rate law  $\frac{d[CH_4]}{dt} = k[CH_3CHO]^{3/2}$

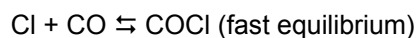
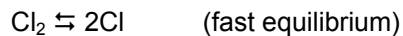
Intermediates:  $CH_3$  and  $CH_3CO$

$$\frac{d[CH_3]}{dt} = k_a[CH_3CHO] - k_b[CH_3][CH_3CHO] + k_c[CH_3CO] - 2k_d[CH_3]^2 = 0$$

Similarly using SSA for  $[CH_3CO]$  and substituting  $\therefore [CH_3] = \left[ \frac{k_a}{2k_d} \right]^{1/2} [CH_3CHO]^{1/2}$

$$\frac{d[CH_4]}{dt} = k_b[CH_3][CH_3CHO] = k_b \left( \frac{k_a}{2k_d} \right)^{1/2} [CH_3CHO]^{3/2} \quad \frac{d[CH_4]}{dt} = k_{obs} [CH_3CHO]^{3/2}$$

11. The reaction  $CO + Cl_2 \rightarrow COCl_2$  is thought to proceed by the following mechanism



Find the final rate expression using the mechanism. Ans:  $\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$

$$\frac{d[COCl_2]}{dt} = k_3[COCl][Cl_2]$$

Get [COCl] from pre equilibrium or SSA

$$\frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]}, \quad \frac{k_2}{k_{-2}} = \frac{[COCl]}{[Cl][CO]}$$

$$[COCl] = \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} [Cl_2] \right)^{\frac{1}{2}} [CO]$$

$$rate = \underbrace{k_3 \cdot \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{\frac{1}{2}}}_k [Cl_2]^{\frac{3}{2}} [CO]$$

12. The temperature coefficient of a reaction is the ratio of rate constants at two temperatures differing by 10K. For a typical  $E_a$  of 80 kJ mol<sup>-1</sup> and at temperature 300 K, show that the temperature coefficient is about 3.

$$k_T = Ae^{-E_a/RT}; \ln k_T = -\frac{E_a}{RT} + \text{constant}$$

$$\ln k_{T+10k} = -\frac{E_a}{R(T+10k)} + \text{const}$$

$$\ln \left( \frac{k_{T+10k}}{k_T} \right) = \frac{E_a}{R} \left( \frac{10}{T(T+10)} \right)$$

For typical  $E_a$  of 80 kJ mol and at T = 300K,

$$\frac{k_{T+10k}}{k_T} = e^{1.03} \approx 2.8$$

13. The frequency factor for an apparently unimolecular reaction at 473 K is  $2.5 \times 10^{18} \text{ s}^{-1}$ . Calculate  $\Delta S^{0\ddagger}$  and comment.

Ans:  $\Delta S^{0\ddagger} = -0.572 \text{ JK}^{-1}$ , may not be unimolecular as negative.

$$A = \frac{RT}{N_a h} \exp\left(\frac{\Delta S^{0\ddagger}}{R}\right) \exp(1 - \Delta n^\ddagger)$$

$$\Rightarrow \exp\left(\frac{\Delta S^{0\ddagger}}{R}\right) = A \left(\frac{N_a h}{RT}\right) e^{-1}$$

$$\frac{\Delta S^{0\ddagger}}{R} = \ln\left(\frac{AN_a h}{RT}\right) - 1$$

$$\Delta S^{0\ddagger} = \ln \left\{ \frac{(2.5 \times 10^{13})(6.022 \times 10^{-34})}{8.314 \times 473} \right\} - 8.314$$

$$= 7.742 \text{ Jk}^{-1} \text{ mol}^{-1} - 8.314 \text{ Jk}^{-1} \text{ mol}^{-1} = -0.572 \text{ Jk}^{-1}$$

May not be unimolecular as the value is negative.

**14.** A dimerization reaction at 300 K follows Arrhenius equation, with  $A = 10^{5.61}$  and  $E_a = 65.4 \text{ kJ mol}^{-1}$ . Calculate the thermodynamic parameters of activation.

According to transition state theory

$$k = \underbrace{\left( \frac{RT}{N_a h} \right) e^{\left( \frac{\Delta S^{0\ddagger}}{R} \right)} e^{(1-\Delta n^\ddagger)}}_A e^{-\left( \frac{E_a}{RT} \right)}$$

$$\text{And } \Delta H^{0\ddagger} = E_a + (\Delta n^\ddagger - 1) RT$$

From here one can get  $\Delta S^{0\ddagger}$ ,  $\Delta H^{0\ddagger}$  and compute  $\Delta G^{0\ddagger}$ .

$$\text{Alternatively, } k = \frac{RT}{N_a h} e^{-\left( \frac{\Delta G^{0\ddagger}}{RT} \right)} = A e^{-\left( \frac{E_a}{RT} \right)}$$

$$\text{Get } \Delta G^{0\ddagger} \text{ from } A = \left( \frac{RT}{N_a h} \right) e^{\frac{\Delta S^{0\ddagger}}{R}} e^{(1-\Delta n^\ddagger)}$$

Get  $\Delta S^{0\ddagger}$ . Thus get  $\Delta H^{0\ddagger}$

$$\text{Here : } \Delta S^{0\ddagger} = -154.25 \text{ Jk}^{-1} \text{ mol}^{-1}, \Delta H^{0\ddagger} = 60.412 \text{ kJ mol}^{-1}, \Delta G^{0\ddagger} = 106.69 \text{ kJ mol}^{-1}$$

**15.** For the dissociation of HI at 556 K as per the reaction:  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , use collision theory and find the reaction rate constant assuming the steric factor to be unity. Given the data:

$$d_{\text{HI}} = 3.5 \text{ \AA}^0, M = 0.128 \text{ kg mol}^{-1}, E_a = 185 \text{ kJ mol}^{-1}$$

$$\text{Ans: } 7.25 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

Dissociation of HI at 556 K

Finding the number of molecules colliding as number  $\text{lit}^{-1}$

$$d_{\text{HI}} = 3.5 \text{ \AA}, \quad M = 0.128 \text{ kg mol}^{-1}, \quad N_A = 6.022 \times 10^{23} \text{ molecule dm}^{-3}$$

$$Z_{AA} = \pi (3.5 \times 10^{-19} \text{ dm})^2 \times \left( \frac{8 \times 8.314 \times 10^2 \text{ kg dm}^2 \text{ s}^{-2} \times 556 \text{ K}}{\pi \times 0.128 \text{ kg}} \right)^{1/2} (6.022 \times 10^{23} \text{ dm}^{-3})^2$$

$$= 3.0 \times 10^{34} \text{ s}^{-1} \text{ dm}^{-3} = 4.2 \times 10^{34} \text{ s}^{-2} \text{ dm}^{-3}$$

$$\mathbf{Z = 8.4 \times 10^{34} \text{ s}^{-1} \text{ dm}^{-3}}$$

$\text{Note: } 1 \text{ JK}^{-1} = 10^2 \text{ Kg dm}^2 \text{ s}^{-2}$

Finding the energy factor (q) and k: ( $E_a = 185 \text{ kJ mol}^{-1}$ )

$$q = \exp\left(-\frac{185 \times 10^3}{8.314 \times 556}\right) = 5.2 \times 10^{-8}$$

$$k = 8.4 \times 10^{34} \times 5.2 \times 10^{-8} = 4.37 \times 10^{17} \text{ molecules dm}^{-3} \text{ s}^{-1} = 7.25 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$