Chem 338

Homework Set #10 solutions November 30, 2001

From Atkins: 10.1, 10.3, 10.4, 10.6, 10.7, 10.11, 10.15, 10.19, 10.20, 10.23

10.1) The rate of formation of C in the reaction $2A + B \rightarrow 3C + 2D$ is 2.2 mol L^{-1} s^{-1}.

State the rates of formation and consumption of A, B, and D.

rate of consumption of A = 2/3 (rate of formation of C) = 1.5 mol L^{-1} s^{-1}

rate of consumption of B = 1/3 (rate of formation of C) = 0.73 mol L^{-1} s^{-1}

rate of formation of D = 2/3 (rate of formation of C) = 1.5 mol L^{-1} s^{-1}

10.3) If the rate laws are expressed with (a) concentrations in molecules m^{-3}, (b) pressures in kPa, what are the units of the 2nd order and 3rd order rate constants? In both cases, the units of the rate itself must be in concentration or pressure per second:

a) For 2nd order: $r = k[A]^2$, k has units m^3 molecules^{-1} s^{-1}

For 3rd order: $r = k[A]^3$, k has units m^6 molecules^{-2} s^{-1}

b) For 2nd order: $r = k(P_A)^2$, k has units kPa^{-1} s^{-1}

For 3rd order: $r = k(P_A)^3$, k has units kPa^{-2} s^{-1}

10.4) The following initial rate data were obtained on the rate of binding of glucose with the enzyme hexokinase present at a concentration of 1.34 mmol L^{-1}. What is (a) the order of reaction with respect to glucose, (b) the rate constant?

$[C_6H_{12}O_6]$ (mmol L^{-1})	1.00	1.54	3.12	4.02
Initial rate (mol L^{-1} s^{-1})	5.0	7.6	15.5	20.0

The reaction of interest is: $C_6H_{12}O_6 + HK \rightarrow C_6H_{12}O_6\text{–}HK$

The rate law is assumed to have the form: $r = k\,[C_6H_{12}O_6]^x[HK]^y$

In the method of initial rates, this rate law becomes: $r_0 = k\,[C_6H_{12}O_6]_0^{\,x}[HK]_0^{\,y}$

There are two ways to go about this problem, taking simple ratios and graphically.

1) For each possible combination of experiments, construct the ratio of the intial rates:

e.g., $$\frac{r_{01}}{r_{02}} = \frac{[C_6H_{12}O_6]_{01}^{x}}{[C_6H_{12}O_6]_{02}^{x}}$$ (the *k*'s and the HK concentrations cancel out)

$$\frac{r_{01}}{r_{02}} = \frac{5.0}{7.6} = \left(\frac{1.00\times10^{-3}}{1.54\times10^{-3}}\right)^{x}$$

$$\ln\left(\frac{5.0}{7.6}\right) = x\ln\left(\frac{1.00\times10^{-3}}{1.54\times10^{-3}}\right)$$

$$x = 0.97$$

For the other combinations:

r01/r03 , x=0.99

r01/r04 , x=1.00

r02/r03 , x=1.01

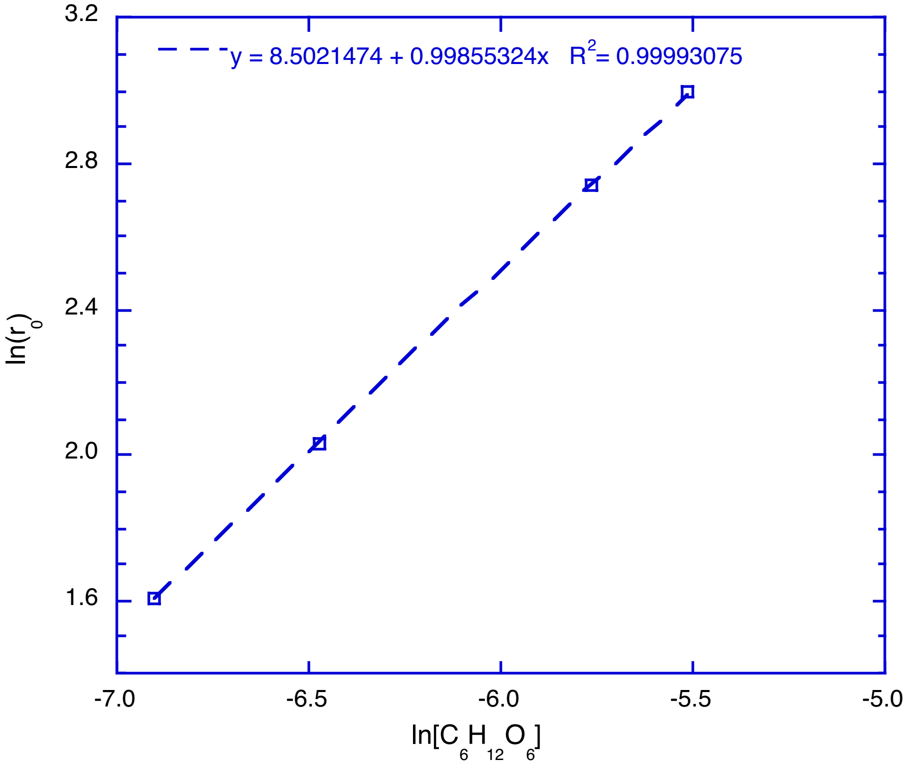
r02/r04 , x=1.01

r03/r04 , x=1.01

AVG order with respect to glucose = 0.998 = 1 (1st order in glucose)

The effective 1sts order rate constant is obtained by substitution for each combination, AVG k = 4920 mol^{-1} L s^{-1} (assumes the enzyme is in excess)

2) For a graphical (better) solution, plot $\ln r_0$ vs. $\ln[C_6H_{12}O_6]$. After fitting to a straight line, the slope will be *x* and the y-intercept will correspond to ln*k*.



Therefore:

x=0.9986 = 1 and k = exp(8.50215) = 4925 mol^{-1} L s^{-1}

(Note that these agree with the values obtained with the ratio method)

10.6) The rate constant for the 1st order decomposition of N_2O_5 in the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is $k = 3.38 \times 10^{-5}$ s^{-1} at 25°C.

a) What is the half-life of N_2O_5 ? What will be the total pressure, initially 500 Torr for the pure N_2O_5 vapor, a) 10 s, b) 10 min after initiation of the reaction?

a) For a 1st order reaction, $t_{1/2} = \dfrac{\ln 2}{k}$

$$\text{So, } t_{1/2} = \frac{\ln 2}{3.38\times 10^{-5}} = 2.05\times 10^{4}\ \text{s}$$

b & c) For a 1st order reaction, $[A] = [A]_0 e^{-kt}$, or in the present case if we assume the volume and temperature are held constant: $P_{N_2O_5} = P_{N_2O_5}^{t=o} e^{-kt}$ since then pressure is directly proportional to the number of moles of N_2O_5 (perfect gas).

After 10 s, the pressure due to N_2O_5 will be reduced to:

$$P_{N_2O_5} = (500\text{ Torr})\, e^{-kt} = (500)\exp[-(3.38\times 10^{-5})(10)] = 499.8\text{ Torr}$$

From the stoichiometry of the reaction, a loss of 0.2 Torr of N_2O_5 will be accompanied by an increase of 5/2 x 0.2 Torr = 0.5 Torr for the products

P(total) = 499.8 + 0.5 = 500.3 Torr (essentially unchanged)

After 10 min = 600 s,

$$P_{N_2O_5} = (500)\exp[-(3.38\times 10^{-5})(600)] = 490\text{ Torr}$$

The loss of 10 Torr of N_2O_5 is matched by an increase of 5/2(10) = 25 Torr in the products.

P(total) = 490 + 25 = 515 Torr

Note that you could also work this problem in terms of the fraction of N_2O_5 dissociated.

10.7) In the oxidation of ethanol, the molar concentration of ethanol decreased in a first-order reaction from 220 mmol L^{-1} to 56.0 mmol L^{-1} in 1.22×10^4 s. What is the rate constant of the reaction?

For a 1st order reaction, $[A] = [A]_o e^{-kt}$ or $\ln[A] = \ln[A]_o - kt$

Hence,

$$k = \frac{1}{t}\left(\ln[A]_o - \ln[A]\right)$$

$$= \frac{1}{1.22\times 10^4}[\ln(220) - \ln(56)] = 1.12\times 10^{-4}\text{ s}^{-1}$$

10.11) The formation of NOCl from NO in the presence of a large excess of chlorine is pseudosecond-order in NO. In an experiment to study the reaction, the partial pressure of NOCl increased from zero to 100 Pa in 522 s. What is the rate cosntant of the reaction given that the initial partial pressure of NO is 300 Pa?

The balanced reaction is: $\mathrm{NO} + \frac{1}{2}\mathrm{Cl_2} \rightarrow \mathrm{NOCl}$

The rate for the production of NOCl is: $\frac{d[\mathrm{NOCl}]}{dt} = k[\mathrm{NO}]^2$, where k is the pseudo 2nd-order rate constant and Cl_2 is in large excess.

Using the integrated rate law for a 2nd-order reaction: $[\mathrm{NOCl}] = \dfrac{kt[\mathrm{NO}]_0^2}{1 + kt[\mathrm{NO}]_0}$

But for constant volume, the partial pressures are directly proportional to the molar concentrations, so we can use these directly in this expression:

$$P_{\mathrm{NOCl}} = \frac{ktP_{\mathrm{NO},0}^2}{1 + ktP_{\mathrm{NO},0}}$$

Solving for the rate constant k,

$$k = \frac{P_{\mathrm{NOCl}}}{t\left(P_{\mathrm{NO},0}^2 - P_{\mathrm{NOCl}}P_{\mathrm{NO},0}\right)} = \frac{100 \text{ Pa}}{522\left(300^2 - (100)(300)\right)}$$

$$= 3.19 \times 10^{-6} \ \frac{\text{Pa}}{\text{s Pa}^2} = 3.19 \times 10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$$

10.15) The half-life for ^{90}Sr = 28.1 yr. How much of 1.00 μg will remain after (a) 19 yr. and (b) 75 yr.

Each half-life decreases the concentration by 1/2:

$$[\mathrm{A}]_t = \left(\tfrac{1}{2}\right)^n [\mathrm{A}]_\mathrm{o} \quad , \text{ where } n \text{ is the number of half-lives}$$

Taking the natural log of both sides: $\ln[\mathrm{A}] = n \ln \tfrac{1}{2} + \ln[\mathrm{A}]_\mathrm{o}$

a) 19 yr = 0.6762 half-lives

$$\ln x = (0.6762)\ln \tfrac{1}{2} + \ln(1.00) = -0.4687$$

$$x = 0.63\ \mu\mathrm{g}$$

b) 75 yr. = 2.669 half-lives

$$\ln x = (2.669)\ln \tfrac{1}{2} + \ln(1.00) = -1.832$$

$$x = 0.16\ \mu\mathrm{g}$$

10.19) A rate constant is 1.78 x 10^{-4} L mol^{-1} s^{-1} at 19ºC and 1.38 x 10^{-3} L mol^{-1} s^{-1} at 37ºC. Evaluate the Arrhenius parameters of the reaction.

Starting from the relation derived from the Arrhenius equation (note: you should be able to easily derive this yourself!)

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{R \ln \frac{k_1}{k_2}}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{(8.3145)\ln \frac{1.78\times10^{-4}}{1.38\times10^{-3}}}{\left(\frac{1}{310} - \frac{1}{292}\right)}$$

$$= 85.63\times10^3 \ \mathrm{J/mol} = 85.6 \ \mathrm{kJ/mol}$$

using the 19ºC data:

$$A = \frac{k}{e^{-\frac{E_a}{RT}}} = \frac{1.78\times10^{-4}}{e^{-\frac{85.63\times10^3}{(8.3145)(292)}}} = 3.70\times10^{11} \ \mathrm{L\ mol^{-1}\ s^{-1}}$$

10.20) The activation energy for the decomposition of benzene diazonium chloride is 99.1 kJ/mol. At what temperature will the rate be 10% greater than its rate at 25ºC?

Starting with the relation: $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

if $k_2 = 1.10(k_1)$: $\ln\frac{1.10k_1}{k_1} = \ln(1.10) = \frac{E_a}{R}\left(\frac{1}{298} - \frac{1}{T_2}\right)$

Rearranging to solve for T_2:

$$T_2 = \frac{E_a}{\frac{E_a}{298} - R\ln 1.10}$$

$$= \frac{99.1\times10^3}{\frac{99.1\times10^3}{298} - (8.3145)\ln 1.10} = 299\text{ K}$$

10.23) Food rots about 40 times more rapidly at 25ºC than when it is stored at 4ºC. Estimate the overall activation energy for the processes responsible for its decomposition.

rate @ 25ºC = 40 x rate @ 4ºC :

$$\ln\frac{40k_4}{k_4} = \frac{E_a}{R}\left(\frac{1}{277} - \frac{1}{298}\right)$$

$$E_a = \frac{R\ln 40}{\left(\frac{1}{277} - \frac{1}{298}\right)} = 1.21\times10^5\text{ J / mol } = 121\text{ kJ / mol}$$