Practice exam on kinetics
CHM 3400, Dr. Chatfield, Fall 2011

I suggest that you study for the exam and give yourself 1 ½ hours to take it. Making reference to equations in the text is fine. I suggest you not allow yourself to scour the text for information and approaches, though. Answers will be posted during the week of Nov. 28.

Suppose that the reaction: $A + B \rightarrow C$ has the rate law:

$$\text{rate} = -d[A]/dt = k[A]$$

The rate constant is $k = 0.032\ s^{-1}$ at 300 K. Initially, $[A] = 4.0 \times 10^{-3}$ mol L^{-1}.

(a) What is the order of reaction with respect to A? With respect to B?
(b)What is the concentration of A after ten seconds (at T = 300 K)?
(c) How long does it take for the concentration of A to fall to 1.0×10^{-3} mol L^{-1}?

(a) Order of rxn wrt A = 1
" " " B = 0

(b) $[A] = [A]_0 e^{-kt} = 2.9 \times 10^{-3}$ mol/L

$[A]_0$ = 4.0×10^{-3} mol/L, k = $0.032\ s^{-1}$, t = 10 s

(c) Two half lives required

$t_{1/2} = \frac{\ln 2}{k} = 21.7 s \Rightarrow$ time $= 2 t_{1/2} = 43.4 s$

2.

The rate constant for the reaction $2NO_2 \rightarrow 2NO + O_2$ is k = 0.522 L mol s^{-1} at 592 K and k = 5.030 L mol s^{-1} at 656 K. What is the activation energy, E_a, for the reaction? (Assume a one-step reaction.)

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln \frac{k(656K)}{k(592K)} = \frac{E_a}{R}\left(\frac{1}{592K} - \frac{1}{656K}\right)$$

5.030 L mol s^{-1}

$$E_a = R\left(\frac{1}{592K} - \frac{1}{656K}\right)^{-1} \ln \frac{k(656K)}{k(592K)} = 114 \text{ kJ/mol}$$

0.522 L mol s^{-1}

0.00831477 kJ K^{-1} mol^{-1}

3. A reaction 2A→B is second order in A and goes to completion in a reaction vessel of constant volume and temperature. The half-life of A is $t_{1/2}$ = 1 hr. Initially, only A is present and the pressure is 1 bar. Determine the total pressure after 2 hr and at equilibrium.

Pressure is proportional to concentration, so we can work in terms of p.

$$r = -\frac{1}{2}\frac{dp_A}{dt} = k\,p_A^2 \Rightarrow \frac{dp_A}{p_A^2} = -2k\,t \Rightarrow \int_{p_{A_0}}^{p_A} \frac{dp_A}{p_A^2} = -2k\int_0^t dt$$

$$(1) \quad \frac{1}{p_{A_0}} - \frac{1}{p_A} = -2kt$$

Obtain k from half-life:

$$\frac{1}{\underset{1\,\text{bar}}{p_{A_0}}} - \frac{1}{\frac{1}{2}p_{A_0}} = -2k\,\underset{1\,\text{hr}}{t_{1/2}} \Rightarrow k = \frac{1}{2}\ \text{hr}^{-1}\ \text{bar}^{-1}$$

From (1), $\frac{1}{p_A} = \frac{1}{p_{A_0}} + 2kt \Rightarrow p_A = \frac{p_{A_0}}{1+2ktp_{A_0}}$

$$p_B = \underset{0}{p_{B_0}} + \frac{1}{2}(p_{A_0} - p_A) = \frac{1}{2}(p_{A_0} - p_A)$$

After 2 hr: $p_A = 0.33$ bar, $p_B = 0.33$ bar $\Rightarrow \boxed{p_{tot} = 0.66\ \text{bar}}$

At equilibrium, all of A is converted to B.

$$p_A = 0 \quad p_B = \frac{1}{2}(p_{A_0} - p_A) = 0.5\ \text{bar} \quad \boxed{p_{tot} = 0.5\ \text{bar}}$$

4.

Consider the following overall reaction in basic aqueous solution:

$$I^-(aq) + OCl^-(aq) \rightleftharpoons OI^-(aq) + Cl^-(aq)$$

a. The following tables gives initial rate data. Determine the rate law for formation of $[OI^-]$ from these data. [NOTE: $[OH^-]$ will appear in the rate law even though it does not appear in the overall reaction. This is because the reaction occurs in basic solution and OH^- is involved in the mechanism.]

$[I^-]_o$ (M)	$[OCl^-]_o$ (M)	$[OH^-]_o$ (M)	r_o (M s^{-1})
2.0×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}
4.0×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}
2.0×10^{-3}	3.0×10^{-3}	2.00	1.8×10^{-4}
4.0×10^{-3}	3.0×10^{-3}	1.00	7.2×10^{-4}

$$v = \frac{d[OI^-]}{dt} = k[I^-]^{\alpha}[OCl^-]^{\beta}[OH^-]^{\gamma}$$

Doubling $[I^-]$ alone doubles rate $\Rightarrow \alpha = 1$

Doubling $[I^-]$ and $[OCl^-]$ quadruples rate $\Rightarrow \beta = 1$

Doubling $[OCl^-]$ and $[OH^-]$ leave rate unchanged $\Rightarrow \gamma = -1$

b. The following mechanism has been proposed. Derive the rate law for the formation of OI^- based on this mechanism, applying the steady state approximation where needed. [NOTE: $[H_2O]$ and $[OH^-]$ may appear in your final rate law because both are present at substantial concentrations in basic, aqueous solution. Do not apply the steady state approximation to these species.]

$$OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-$$

$$I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$$

$$HOI + OH^- \xrightarrow{k_3} H_2O + OI^-$$

$$v = \frac{d[OI^-]}{dt} = k_3 \overset{\text{intermediate}}{[HOI]}[OH^-]$$

$$\text{s-s:} \quad \frac{d[HOI]}{dt} = 0 = k_2[I^-][HOCl] - k_3 \overset{\text{intermediate}}{[HOI]}[OH^-]$$

$$\frac{d[HOCl]}{dt} = 0 = k_1[OCl^-][H_2O] - k_{-1}[HOCl][OH^-] - k_2[I^-][HOCl]$$

$$[HOCl] = \frac{k_1[OCl^-][H_2O]}{k_{-1}[OH^-] + k_2[I^-]}$$

$$[HOI] = \frac{k_2[I^-][HOCl]}{k_3[OH^-]} = \frac{k_1k_2[OCl^-][I^-][H_2O]}{k_3[OH^-](k_{-1}[OH^-] + k_2[I^-])}$$

$$v = \frac{k_1k_2\cancel{k_3}[OCl^-][I^-][H_2O]\cancel{[OH^-]}}{\cancel{k_3}\cancel{[OH^-]}(k_{-1}[OH^-] + k_2[I^-])} = \frac{k_1k_2[OCl^-][I^-][H_2O]}{k_{-1}[OH^-] + k_2[I^-]}$$

c. State whether the rate law determined from the mechanism is consistent with the empirical rate law determined from the data in part (a). Discuss any restrictions necessary for the two rate laws to be consistent.

If $k_2[I^-] \ll k_{-1}[OH^-]$, as will be the case under sufficiently basic conditions, the rate law simplifies to:

$$v = \underbrace{\frac{k_1k_2}{k_{-1}}[H_2O]}_{k_{eff}}[I^-][OCl^-][OH^-]^{-1}$$

In aqueous solution, $[H_2O]$ is essentially constant, so it may be included in the effective rate constant, k_{eff}. Clearly, the mechanism is consistent with the data.

5. Suppose that an enzyme has a turnover number of 104 min^{-1} and a molar mass of 60,000 g/mol. How many moles of substrate can be turned over per hour per gram of enzyme if the substrate concentration is twice the Michaelis constant? (Assume that the substrate concentration is maintained constant, for example by a preceding enzymatic reaction.)

$$v = \frac{v_{max}[S]}{[S] + \underbrace{K_M}_{\frac{1}{2}[S]}} = \frac{2}{3}\underbrace{v_{max}}_{k_{cat}[E]_0} = \frac{2}{3} k_{cat}[E]_0$$

If $[S]$ is constant, $v = \frac{d[P]}{dt} = \frac{\Delta n_S \, L^{-1}}{\Delta t} = \frac{2}{3} k_{cat} \underbrace{[E]_0}_{n_{E_0} L^{-1}}$

$$\Delta n_S = \frac{2}{3} \underbrace{k_{cat}}_{10^4\,\text{min}^{-1}} n_{E_0} \underbrace{\Delta t}_{60\,\text{min}} = 6.67\ \text{mol}$$

$$n_{E_0} = 1\,\text{g} \cdot \frac{1}{6 \times 10^4}\ \text{mol g}^{-1} = (6 \times 10^4)^{-1}\ \text{mol}$$

$\boxed{\text{6.67 mol substrate turned over per hour per gram enzyme}}$