CHM 5423 – Atmospheric Chemistry
Problem Set 3
Due date: Tuesday, February 19th. The first hour exam is on Thursday, February 21st. It will cover material from the first four handouts for the class.

Do the following problems. Show your work.

1) The chemical reaction

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \qquad (1.1)$$

plays an important role in ozone destruction. Because of this, it has been extensively studied both experimentally and theoretically.

The Arrhenius constants for the reaction are $A = 2.3 \times 10^{-11}$ $\mathrm{cm^3/molecule{\cdot}s}$ and $E_a = 1.67$ kJ/mol. Based on this information find the value for k for reaction 1.1 at T = 250. K and T = 300. K.

2) Baasandorj and coworkers (J.Phys.Chem.A 114 (2010) 4619-4633) studied the gas phase reaction of hydroxyl radical (OH) with $\mathrm{CH_2{=}CHF}$. A summary of their data is given below

| T(K) | 220. | 249. | 296. | 321. | 373. |
|---|---|---|---|---|---|
| $k(\mathrm{cm^3/molecule{\cdot}s})$ | $7.37 \times 10^{-12}$ | $6.31 \times 10^{-12}$ | $5.18 \times 10^{-12}$ | $4.92 \times 10^{-12}$ | $4.06 \times 10^{-12}$ |

a) Fit the above data to the Arrhenius equation. Find the values for A and $E_a$ corresponding to the data.

b) If you have done the fitting correctly you will have obtained a negative value for $E_a$, which is difficult to reconcile with a direct reaction. Consider the following mechanism for the reaction

$$\text{step 1} \quad \mathrm{OH} + \mathrm{CH_2{=}CHF} \rightleftarrows (\mathrm{OH\text{-}CH_2{=}CHF}) \qquad k_1,\ k_{-1} \qquad (2.1)$$

$$\text{step 2} \quad (\mathrm{OH\text{-}CH_2{=}CHF}) + \mathrm{M} \rightarrow \text{“product”} \qquad k_2 \qquad (2.2)$$

Find a general expression for the rate law predicted for the above mechanism.

c) Your general expression in b has the following low pressure ($[M] \rightarrow 0$) limiting behavior

$$d[\text{product}]/dt = (k_1k_2/k_{-1})\,[\mathrm{OH}][\mathrm{CH_2{=}CHF}] \qquad (2.3)$$

Assume that $k_1$, $k_{-1}$, and $k_2$ each obey the Arrhenius equation. For what conditions, if any, will the observed rate law for the reaction have a negative activation energy?

3) The general solution for second order heterogeneous kinetics for a reaction with stoichiometry and rate law

$$A + B \rightarrow \text{"products"} \qquad d[A]/dt = -\,k\,[A]\,[B] \qquad (3.1)$$

is, as discussed in class

$$kt = \frac{1}{([B]_0 - [A]_0)} \ln \frac{[A]_0\,[B]_t}{[B]_0\,[A]_t} \qquad [B]_0 \neq [A]_0 \qquad (3.2)$$

Show that in the limit $[B]_0/[A]_0 \rightarrow \infty$ eq 3.2 takes on the same form as the solution for a first order chemical reaction

$$[A]_t = [A]_0 \exp(-\,k_{obsd}t) \qquad (3.3)$$

and find an expression for $k_{obsd}$, the apparent first order rate constant.

4) The following question concerns the paper "Rate constant for the reaction of OH with $H_2$ between 200 and 480 K" by V. L. Orkin and coworkers (**J.Phys.Chem.A** (2006) **110**, 6978-6985). A copy of the paper is available at my website. Note that to answer some of the questions you may have to go to additional sources for information or perform calculations.

a) On page 6978 of the paper the main source of molecular hydrogen in the Earth's atmosphere is identified as photodissociation of formaldehyde

$$HCHO + hc/\lambda \rightarrow CO + H_2 \tag{4.1}$$

If photodissociation occurs at $\lambda$ = 350. nm, how much excess energy will be available for the photodissociation products? Where will that energy go? What will happen to the excess energy over time?

$\Delta H°_f(CO) = - 110.53$ kJ/mol  $\Delta H°_f(HCHO) = - 108.57$ kJ/mol  $\Delta H°_f(H_2) = 0.0$ kJ/mol

b) The technique used in the experiments reported in the paper was flash photolysis. Briefly describe this technique. How was flash photolysis used to produce hydroxyl radicals in the experiment?

c) The method used to monitor OH radial concentration in the experiments was resonance fluorescence. Briefly describe this technique. How was this method applied in this paper to detect OH radicals?

d) The data obtained in this experiment was corrected for the effect of OH diffusion. What does this mean? Why is this an important correction? How was the correction carried out?

e) Use eq 15 on page 6983 to find the value for k for the reaction of $H_2$ with OH at T = 272. K, the estimated average temperature of the troposphere.

f) The authors report an estimated lifetime for $H_2$ of 10 years (note – remember the difference between lifetime and half-life for a chemical reaction). Assuming an average tropospheric temperature T = 272 K, and assuming that reaction of $H_2$ with OH is the only important process removing molecular hydrogen from the atmosphere, what is the value for [OH], the average value for the hydroxyl radical concentration in the troposphere? Give your answer in units of molecules/$cm^3$.

Solutions.

1) For a reaction obeying the Arrhenius equation we may say $k = A \exp(-E_a/RT)$

At T = 250. K, $k = (2.3 \times 10^{-11}\ \text{cm}^3/\text{molecule}\bullet\text{s}) \exp(-1670.\ \text{J/mol}/(8.314\ \text{J/mol}\bullet\text{K})\ (250.\ \text{K}))$

$= 1.03 \times 10^{-11}\ \text{cm}^3/\text{molecule}\bullet\text{s}$

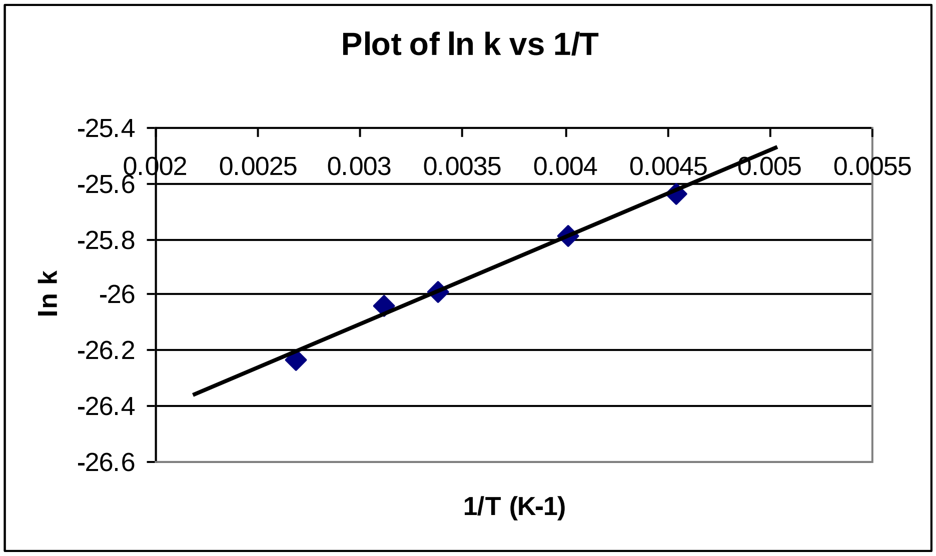
At T = 300. K, $k = (2.3 \times 10^{-11}\ \text{cm}^3/\text{molecule}\bullet\text{s}) \exp(-1670.\ \text{J/mol}/(8.314\ \text{J/mol}\bullet\text{K})\ (300.\ \text{K}))$

$= 1.18 \times 10^{-11}\ \text{cm}^3/\text{molecule}\bullet\text{s}$

Note that this is a weak dependence on temperature, which is often observed for reactions involving radicals such as Cl atoms.

2) ` a) The data are presented and plotted below

| T (K) | k(cm$^3$/molecule.s) | 1/T (K$^{-1}$) | ln k |
|---|---|---|---|
| 220. | $7.37 \times 10^{-12}$ | 0.004545 | - 25.634 |
| 249. | $6.31 \times 10^{-12}$ | 0.004016 | - 25.789 |
| 296. | $5.18 \times 10^{-12}$ | 0.003378 | - 25.986 |
| 321. | $4.92 \times 10^{-12}$ | 0.003115 | - 26.038 |
| 373. | $4.06 \times 10^{-12}$ | 0.002681 | - 26.230 |



Based on the best fit to the data I get $\ln k = (310.6\ \text{K})/T - 27.04$

So $E_a = -R\,(\text{slope}) = -(8.3145\ \text{J/mol}\cdot\text{K})\ (310.6\ \text{K}) = -2.58\ \text{kJ/mol}$

$A = \exp(-27.04) = 1.81 \times 10^{-12}\ \text{cm}^3/\text{molecule}\cdot\text{s}$

b) Basedon the mechanism

$$d[\text{product}]/dt = k_2\,[\text{OH-CH}_2\text{=CHF}][\text{M}]$$

If we make the steady state approximation for $\text{OH-CH}_2\text{=CHF}$, then

$$d[\text{OH-CH}_2\text{=CHF}]/dt \cong 0 = k_1[\text{OH}][\text{CH}_2\text{=CHF}] - k_{-1}[\text{OH-CH}_2\text{=CHF}] - k_2[\text{OH-CH}_2\text{=CHF}][\text{M}]$$

$$[\text{OH-CH}_2\text{=CHF}] = k_1[\text{OH}][\text{CH}_2\text{=CHF}]/(k_{-1} + k_2[\text{M}])$$

Substituting into our expression for rate gives

$$\frac{d[\text{product}]}{dt} = \frac{k_1k_2[\text{OH}][\text{CH2=CHF}][\text{M}]}{(k_{-1} + k_2[\text{M}])}$$

c) In the low pressure limit ($[\text{M}] \rightarrow 0$) the second term in the denominator becomes negligible, and the rate law reduces to a low pressure limiting law

$$d[\text{product}]/dt = (k_1k_2/k^{-1})[\text{OH}][\text{CH}_2\text{=CHF}][\text{M}] = k'[\text{OH}][\text{CH}_2\text{=CHF}][\text{M}]$$

Assume each individual rate constant fits an Arrhenius equation, so

$$k_1 = A\exp(-E_a/RT)$$

$$k_{-1} = B\exp(-E_b/RT)$$

$$k_2 = C\exp(-E_c/RT)$$

Then the apparent rate constant in the low pressure limit is

$$k' = \frac{[A\exp(-E_a/RT)][B\exp(-E_b/RT)]}{[C\exp(-E_c/RT]} = (AB/C)\exp[-(E_a + E_b - E_c)/RT]$$

which has the same form as the Arrhenius equation, but with an apparent activation energy

$$E' = E_a + E_b - E_c$$

If $E_c > (E_a + E_b)$, then $E'$ will be negative, as is observed in these experiments.

3) In the limit $[\text{B}]_0/[\text{A}]_0 \rightarrow \infty$, we have

$[\text{B}]_0 - [\text{A}]_0 \rightarrow [\text{B}]_0$ (since as $[\text{B}]_0/[\text{A}]_0 \rightarrow \infty$, $[\text{A}]_0/[\text{B}]_0 \rightarrow 0$)

$[\text{B}]_t/[\text{B}]_0 \rightarrow 1$ (since $[\text{B}]_t = [\text{B}]_0 - ([\text{A}]_0 - [\text{A}]_t)$, and the term involving A becomes small compared to $[\text{B}]_0$, so that $[\text{B}]_t \rightarrow [\text{B}]_0$)

Substituting these limiting values gives, in the limit $[\text{B}]_0/[\text{A}]_0 \rightarrow \infty$

$$kt = (1/[\text{B}]_0)\ln([\text{A}]_0/[\text{A}]_t)$$

Multiplying both sides of this equation by $[\text{B}]_0$ gives

$k[\text{B}]_0t = k_{obsd}t = \ln([\text{A}]_0/[\text{A}]_t)$ , where $k_{obsd} = k[\text{B}]_0$ is the observed rate constant for the reaction.

If we take the inverse ln of both sides of this equation, we get

$$\exp(k_{obsd}t) = [A]_0/[A]_t$$

This can be solved for $[A]_t$. The result is

$$[A]_t = \frac{[A]_0}{\exp(k_{obsd}t)} = [A]_0 \exp(- k_{obsd}t)$$

which is the expression expected for first order kinetics. Because of this, we call the experimental condition where $[B]_0/[A]_0 \rightarrow \infty$ pseudo-first order kinetics. Note the bimolecular rate constant is then $k_{bi} = k_{obsd}/[B]_0$.

4) a) As shown on the previous problem set, we may derive the following equation for the threshold wavelength for photodissociation

$$\lambda = \frac{hcN_A}{\Delta H°_{rxn}}$$

$$\Delta H°_{rxn} = [\ \Delta H°_f(CO) + \Delta H°_f(H_2)\ ] – [\ \Delta H°_f(HCHO)\ ]$$

$$= [\ (-110.53) + (0.0)\ ] – [\ (108.57)\ ] = - 1.96 \text{ kJ/mol}$$

The reaction is exothermic, and so any photon will have sufficient energy to photodissociate this molecule. (Note however that the energy barrier between the reactant and products means in practice this will not happen.)

If we rearrange the above equation for λ, and solve for ΔH°, we get

$$\Delta H° = \frac{hcN_A}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J•s})(2.998 \times 10^8\ \text{m/s})(6.022 \times 10^{23}\ \text{molecule/mol})}{(350. \times 10^{-9}\ \text{m})}$$

$$= 341.8 \text{ kJ/mol}$$

So the excess energy available is (341.8 + 1.96) = 343.7 kJ/mol. This energy will go into translational energy of the products, or internal energy (vibrational and rotational energy). Over time, collisions will thermalize the product molecules so that they eventually have an equilibrium energy consistent with the bath gas molecules.

b) In flash photolysis, a short duration pulse of light from a flash lamp or laser is used to photodissociate a precursor molecule, which generates the reactive species being studied. The progress of the reaction is followed in real time by monitoring the concentration of reactant species (or, less commonly, the concentration of the other reactant, or a product molecule concentration). This can be done using absorption spectroscopy, resonance fluorescence, or other detection technique.

In the present experiment the main method used to generate OH radical is photodissociation of water

$$H_2O + hc/\lambda \rightarrow H(^2S) + OH$$

In some experiments, hydroxyl radical was produced by the reaction of $O(^1D)$ atoms with hydrogen gas, with the oxygen atoms produced by the photodissociation of nitrous oxide

$$N_2O + hc/\lambda \rightarrow N_2 + O(^1D)$$

$$O(^1D) + H_2 \rightarrow H(^2S) + OH$$

c) In resonance fluorence a high intensity light source (usually a laser or resonance lamp) is used to excite an electronic transition in the molecule being studied, and the resulting fluorescence of the electronically excited molecules is measured. The technique has the advantages of being sensitive (fluorescence measurements are inherently more sensitive than absorption measurements) and specific for the molecule being studied (since the laser used to excite the molecule can be tuned to a specific transition).

In the present experiment light at 308 nm, generated in a microwave discharge lamp (with the discharge applied to a dilute mixture of water vapor helium), was used to electronically excite OH radicals. The resonance fluorescence signal was monitored using a multichannel scanner, averaging over 300-5000 flashes.

d) In flash photolysis experiments there will be a decrease in the signal generated from the hydroxyl radicals due to their ramdom motion outside the observation zone being monitored. This results in an apparent decrease in OH radical concentration with time that is not due to chemical reaction.

In the presen texpeiment a fairly complicated equation is used to apply a correction for diffusion.. This is necessary because in some experiments relatively high concentration of $H_2$ gas are used, and diffusion of OH radicals through $H_2$ is much faster than diffusion through argon or other carrier gases. Since the decay in OH concentration in the observation zone due to diffusion and that due to reaction are comparable in magnitude, this correction is particularly important. The authors claim that the maximum error in their experimental values for k due to errors in this correction is less than ~ 2% (but this may be optimistic).

e) The expression for the rate constant at this temperature is

$$k = (4.27 \times 10^{-13})\ (T/298)^{2.406} \exp(-\ 1240/T)$$

where the units for k are cm3/molecule•s. So at T = 272 K (a typical "average" temperature for the troposphere)

$$k = (4.27 \times 10^{-13})\ (272/298)^{2.406} \exp(-\ 1240/272) = 3.59 \times 10^{-15}\ \text{cm}^3/\text{molecule}\bullet\text{s}.$$

This is very close to the experimental value reported at this temperature (Table 1).

f) Since the lifetime is ~ 10 years, then

$$\tau = \frac{1}{k'} = \frac{1}{k\,[\text{OH}]}$$ , where k′ = k[OH] is the pseudo-first order rate constant

So $[\text{OH}] = \dfrac{1}{k\tau}$ $\tau = 10$ years (365.25 • 24 • 3600 s/year) = $3.16 \times 10^8$ s

and so the estimated average hydroxyl radical concentration in the troposphere is

$$[\text{OH}] = \frac{1}{(3.59 \times 10^{-15}\ \text{cm}^3/\text{molecule}\bullet\text{s})(3.16 \times 10^8\ \text{s})} = 9 \times 10^5\ \text{molecule/cm}^3$$

which is close to the average value we have been using. Because it is difficult to directly determine OH radical concentrations in the atmosphere, this indirect method has been commonly used to estimate average hydroxyl radical concentrations in the troposphere.