

CHM 3400 – Fundamentals of Physical Chemistry  
Third Hour Exam  
April 8, 2020

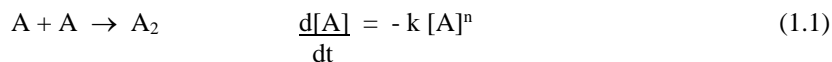
There are five problems on the exam. Do all of the problems. Show your work. Note that the exam must be turned in by 5:00pm on Thursday, April 9<sup>th</sup>. You do not need to submit a copy of the exam, as I will have that information. Also note that different students will have different questions.

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$R = 0.082057 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$	$N_A = 6.022 \times 10^{23}$
$R = 0.083145 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$	$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$
$R = 8.3145 \text{ J}/\text{mole}\cdot\text{K}$	$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$
$F = 96485. \text{ C}/\text{mol}$	$1 \text{ atm} = 760 \text{ torr}$
	$(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$

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1. (24 points) In a sample of pure molecules of A and an inert gas the following irreversible chemical reaction is found to occur



The rate law for the reaction is known to be homogeneous in A, but it is not known if the rate law is 1<sup>st</sup> order homogeneous, 2<sup>nd</sup> order homogeneous, or some other homogeneous rate law.

In a particular experiment, the initial concentration of A is  $[A] = 4.18 \times 10^{-3} \text{ mol/L}$ . After 100.0 s, the concentration of A is found to be  $[A] = 2.74 \times 10^{-3} \text{ mol/L}$ .

- Assuming the reaction obeys 1<sup>st</sup> order homogeneous kinetics, find  $[A]$  at  $t = 400.0 \text{ s}$ .
- Assuming the reaction obeys 2<sup>nd</sup> order homogeneous kinetics, find  $[A]$  at  $t = 400.0 \text{ s}$ .
- Experimentally it is found that  $[A] = (1.36 \pm 0.03) \times 10^{-3} \text{ mol/L}$  at  $t = 400.0 \text{ s}$ , where the  $\pm$  range is a measure of the uncertainty in the experimental result. Based on your answers in a and b, is the reaction 1<sup>st</sup> order homogeneous, 2<sup>nd</sup> order homogeneous, or some other order of homogeneous reaction? Justify your answer.

2. (12 points) The bromination of acetone reaction in aqueous solution is an irreversible reaction with the following stoichiometry.



The reaction is known to be catalyzed by hydrogen ion ( $\text{H}^+(\text{aq})$ ).

Under conditions where  $[\text{CH}_3\text{COCH}_3] \gg [\text{Br}_2]$  and  $[\text{H}^+] \gg [\text{Br}_2]$  reaction 2.1 follows zeroth order kinetics, that is

$$\begin{aligned} \frac{d[\text{Br}_2]}{dt} = -k & & [\text{Br}_2]_t = [\text{Br}_2]_0 - kt & & t < [\text{Br}_2]_0/k & & (2.2) \\ & & [\text{Br}_2]_t = 0 & & t \geq [\text{Br}_2]_0/k & & \end{aligned}$$

Define  $[\text{Br}_2]_0$  as the initial concentration of bromine. Find an expression for  $t_{1/2}$ , the half-life for bromine for the above reaction. Give your answer in terms of  $k$ ,  $[\text{Br}_2]_0$ , and/or other constants. Show your work.

3. (24 points) Consider a general irreversible reaction with stoichiometry



Experimentally, the above reaction is found to be second order heterogeneous, with

$$\frac{d[A]}{dt} = -k [A] [B] \quad [A]_0 \neq [B]_0 \quad (3.2)$$

As discussed in class, the dependence of concentration on time for this type of reaction is given by the expression

$$\frac{1}{([A]_0 - [B]_0)} \ln \left( \frac{[A]_t [B]_0}{[A]_0 [B]_t} \right) = kt$$

where  $[A]_0$  and  $[B]_0$  are initial concentrations and  $[A]_t$  and  $[B]_t$  are concentrations at time  $t$ .

In a particular experiment, the following are known

$$[A]_0 = 0.248 \text{ mol/L} \quad [B]_0 = 0.183 \text{ mol/L}$$
$$k = 4.70 \times 10^{-3} \text{ L/mol}\cdot\text{s}$$

- Find the value for  $[B]_t$  at long times (that is, for the case  $t \rightarrow \infty$ ).
- Find the value for  $[B]_t$  for  $t = 120. \text{ s}$

4. (24 points) In the lower atmosphere, the major initial reaction in the oxidation of alkenes is with OH radical, by the process



For propene, the observed value for the rate constant for this reaction at is  $k = 27.6 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$  at  $T = 290.0 \text{ K}$

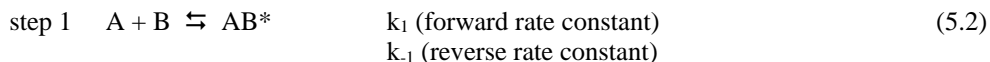
a) What is the value for  $t_{1/2}$ , the half-life for propene in the atmosphere, at  $T = 290.0 \text{ K}$ ? Assume that the concentration of OH radicals in the atmosphere is constant, with  $[\text{OH}] = 1.0 \times 10^6 \text{ molecule/cm}^3$ . Give your final value for  $t_{1/2}$  in units of hours.

b) The activation energy for the above reaction is  $E_a = -4.19 \text{ kJ/mol}$ . Based on this, and assuming the Arrhenius equation applies to this reaction, find the value for  $k$  for the above reaction at  $T = 240.0 \text{ K}$ .

c) The activation energy for the above reaction is negative. What, if anything, does this tell you about the mechanism for the reaction?

5. (16 points) In class we discussed the mechanism that corresponds to unimolecular reactions. Similar models have been developed for other general types of gas phase reactions.

Consider the following kinetic model for a gas phase recombination reaction.



In the above mechanism A and B are reactants (either atoms or small molecules), AB is the stable product molecule, and AB\* is an “energized” (unstable) product molecule. M is an inert solvent gas (Ar or N<sub>2</sub> would be common solvent gases). You may assume that [M] >> [A] and [M] >> [B]. You cannot assume any particular process in the mechanism is “fast” or “slow”.

a) Starting with the above model, find an expression for the rate of formation of stable product molecules, that is, find d[AB]/dt. Your final expression should be in terms of A, B, M, and/or rate constants only.

b) Based on your answer in a, discuss the rate law expected for this mechanism in the low pressure limit ( [M] → 0 ). You should determine the orders of reaction with respect to A, B, and M, and the overall order of reaction.

c) Based on your answer in a, discuss the rate law expected for this mechanism in the high pressure limit ( [M] → ∞ ). You should determine the orders of reaction with respect to A, B, and M, and the overall order of reaction.

### Solutions.

1) The general strategy for doing the first two parts of the problems is to first find the value for k, and then find the concentration at the indicated time.

a) If first order homogeneous, then

$$\ln([A]_t/[A]_0) = -kt$$

Rearranging gives

$$k = -(1/t) \ln([A]_t/[A]_0) = -(1/100.0 \text{ s}) \ln(2.74 \times 10^{-3}/4.18 \times 10^{-3}) = 4.224 \times 10^{-3} \text{ s}^{-1}$$

Since  $[A]_t = [A]_0 \exp(-kt)$

then  $[A]_t = (4.18 \times 10^{-3} \text{ mol/L}) \exp[-(4.224 \times 10^{-3} \text{ s}^{-1})(400.0 \text{ s})] = 0.77 \times 10^{-3} \text{ mol/L}$

b) If second order homogeneous, the

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Rearranging gives

$$\begin{aligned} k &= (1/t) [ (1/[A]_t) - (1/[A]_0) ] = (1/100.0 \text{ s}) [ (1/2.74 \times 10^{-3} \text{ mol/L}) - (1/4.18 \times 10^{-3} \text{ mol/L}) ] \\ &= 1.257 \text{ L/mol}\cdot\text{s} \end{aligned}$$

Since  $[A]_t = \frac{[A]_0}{1 + kt[A]_0}$

then  $[A]_t = \frac{(4.18 \times 10^{-3} \text{ mol/L})}{1 + (1.257 \text{ L/mol}\cdot\text{s})(400.0 \text{ s})(4.18 \times 10^{-3} \text{ mol/L})} = 1.35 \times 10^{-3} \text{ mol/L}$

c) Since the value in 1b is within the range  $(1.36 \pm 0.03) \times 10^{-3} \text{ mol/L}$ , the reaction is second order homogeneous.

2) Using the definition of half-life, we may say that when  $t = t_{1/2}$ ,  $[A]_t = [A]_0/2$ . Substituting into the equation for  $[A]_t$  gives

$$\frac{[Br_2]_0}{2} = [Br_2]_0 - kt_{1/2}$$

$$kt_{1/2} = [Br_2]_0 - \frac{[Br_2]_0}{2} = \frac{[Br_2]_0}{2}$$

$$t_{1/2} = \frac{[Br_2]_0}{2k}$$

3) a) Since the reaction is irreversible, then as  $t \rightarrow \infty$  the limiting reactant will be completely used up. Since B is the limiting reactant, that means  $[B]_t \rightarrow 0$  as  $t \rightarrow \infty$ .

b) The starting point for this problem is the equation for second order heterogeneous kinetics.

$$\frac{1}{([A]_0 - [B]_0)} \ln \left( \frac{[A]_t [B]_0}{[A]_0 [B]_t} \right) = kt$$

We can break the ln term into two parts, to get

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

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

$$\ln([A]_t/[B]_t) = kt ([A]_0 - [B]_0) - \ln([B]_0/[A]_0) = \phi$$

where we have defined  $\phi = kt ([A]_0 - [B]_0) - \ln([B]_0/[A]_0)$

Since  $\ln([A]_t/[B]_t) = \phi$

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

$$\frac{[A]_t}{[B]_t} = e^\phi$$

Now, the problem is that it looks like there are two unknowns in the above equation ( $[A]_t$  and  $[B]_t$ ). However, because of the stoichiometry of the reaction, the change in concentration of A and of B are the same, and so

$$[A]_0 - [A]_t = [B]_0 - [B]_t$$

$$[A]_t = ([A]_0 - [B]_0) + [B]_t$$

If we substitute this, we get

$$\frac{([A]_0 - [B]_0) + [B]_t}{[B]_t} = e^\phi$$

$$([A]_0 - [B]_0) + [B]_t = [B]_t e^\phi$$

$$([A]_0 - [B]_0) = [B]_t e^\phi - [B]_t = [B]_t (e^\phi - 1)$$

or, finally

$$[B]_t = \frac{([A]_0 - [B]_0)}{(e^\phi - 1)}$$

If we now substitute the information in the problem into the above equations, we get

$$\phi = (4.70 \times 10^{-3} \text{ L/mol}\cdot\text{s}) (120.0 \text{ s}) [ (0.248 \text{ mol/L}) - (0.183 \text{ mol/L}) ] - \ln [ (0.183)/(0.248) ]$$

$$= 0.3406 \quad \text{And so } e^\phi = e^{0.3406} = 1.4058$$

$$[B]_t = \frac{[(0.248 \text{ mol/L}) - (0.183 \text{ mol/L})]}{(1.4058 - 1)} = 0.1602 \text{ mol/L}$$

4) a) The reaction is second order heterogeneous – BUT we can assume [OH] is constant, and so

$$\frac{d[\text{alkene}]}{dt} = -k [\text{alkene}] [\text{OH}] = - (k [\text{OH}]) [\text{alkene}] = -k' [\text{alkene}] \quad k' = k [\text{OH}]$$

which is pseudo-first order kinetics.

Therefore  $t_{1/2} = \frac{\ln(2)}{k'}$   $k' = (27.6 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}) (1.0 \times 10^6 \text{ molecule}/\text{cm}^3)$   
 $= 27.6 \times 10^{-6} \text{ s}^{-1}$

$$t_{1/2} = \frac{\ln(2)}{27.6 \times 10^{-6} \text{ s}^{-1}} = 2.51 \times 10^4 \text{ s} = 6.98 \text{ hours}$$

b)  $\ln(k_2/k_1) = - (E_a/R) [ (1/T_2) - (1/T_1) ]$   
 $= - [ (-4190. \text{ J/mol}) / (8.3145 \text{ J/mol}\cdot\text{K}) ] [ (1/240.0 \text{ K}) - (1/290.0 \text{ K}) ]$   
 $= 0.362$

Taking the inverse ln of both sides of this equation gives

$$k_2/k_1 = e^{0.362} = 1.436 \quad k_2 = (1.436) k_1 = (1.436) (27.6 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s})$$

$$= 39.6 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$$

c) If the reaction took place in a single step, as written, the activation energy would have to be positive or zero (as can be seen in a diagram of energy vs extent of reaction). Since the activation energy for the reaction is negative, the mechanism must be a two step or multistep mechanism.

5) a)  $\frac{d[AB]}{dt} = k_2 [AB^*] [M]$

But  $\frac{d[AB^*]}{dt} = 0 = k_1 [A][B] - k_{-1} [AB^*] - k_2 [AB^*][M]$

$$k_1 [A][B] = k_{-1} [AB^*] + k_2 [AB^*][M] = (k_{-1} + k_2[M]) [AB^*]$$

$$[AB^*] = \frac{k_1 [A][B]}{(k_{-1} + k_2[M])}$$

and so  $\frac{d[AB]}{dt} = k_2 [M] \frac{k_1 [A][B]}{(k_{-1} + k_2[M])} = \frac{k_1 k_2 [A][B][M]}{(k_{-1} + k_2[M])}$

b) For  $[M] \rightarrow 0$ ,  $k_{-1} \gg k_2[M]$ , and so  $(k_{-1} + k_2[M]) \cong k_{-1}$

and so  $\frac{d[AB]}{dt} = \frac{k_1 k_2}{k_{-1}} [A][B][M]$  1<sup>st</sup> order in A, 1<sup>st</sup> order in B, 1<sup>st</sup> order in M, 3<sup>rd</sup> order overall

c) For  $[M] \rightarrow \infty$ ,  $k_2[M] \gg k_{-1}$ , and so  $(k_{-1} + k_2[M]) \cong k_2 [M]$

and so  $\frac{d[AB]}{dt} = \frac{k_1 k_2 [A][B][M]}{k_2 [M]} = k_1 [A][B]$  1<sup>st</sup> order in A, 1<sup>st</sup> order in B, 2<sup>nd</sup> order overall