

CHM 3400 – Fundamentals of Physical Chemistry  
Third Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

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$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$	$N_A = 6.022 \times 10^{23}$
$R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$	$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$
$R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$	$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$
$F = 96485 \text{ C}/\text{mol}$	$1 \text{ atm} = 760 \text{ torr}$
$(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$	

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1. (24 points) The gas phase reaction



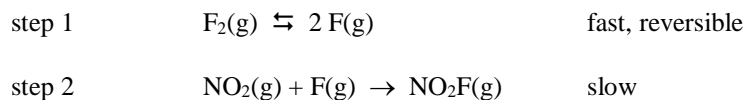
is an example of a second order heterogeneous reaction, with the rate of the reaction given by the expression

$$\text{Rate} = -\frac{d[\text{F}_2]}{dt} = k[\text{NO}_2][\text{F}_2] \quad (1.2)$$

where  $k = 38 \text{ L}/\text{mol}\cdot\text{s}$  at  $T = 27 \text{ }^\circ\text{C}$

In a particular experiment (at  $T = 27 \text{ }^\circ\text{C}$ ) the initial concentrations of reactants are  $[\text{NO}_2]_0 = 2.0 \times 10^{-4} \text{ mol/L}$  and  $[\text{F}_2]_0 = 5.0 \times 10^{-5} \text{ mol/L}$ .

- What is  $R_0$ , the initial rate of reaction, for the above conditions.
- What will be the rate of reaction in this experiment when the concentration of  $\text{NO}_2\text{F}$  in the system reaches the value  $[\text{NO}_2\text{F}] = 3.0 \times 10^{-5} \text{ mol/L}$ ?
- One mechanism proposed for the above reaction is the following

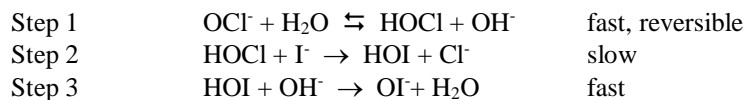


Find the rate law predicted by the above mechanism. Give your final expression for the rate law in terms of  $k_1$ ,  $k_{-1}$ ,  $k_2$  and concentrations of reactants and/or products.

2. (16 points) Consider the reduction reaction of  $\text{OCl}^-$  in a buffered aqueous solution.



One mechanism that has been proposed for this reaction is the following



a) List all of the reaction intermediates in the above reaction. Note that for a buffered aqueous solution  $\text{H}_2\text{O}$  and  $\text{OH}^-$  are not considered reaction intermediates as their concentrations are known and constant.

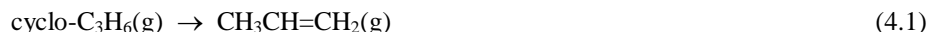
b) Find the rate law predicted for reaction 2.1 from the above mechanism. Give your final rate law in terms of rate constants, concentrations of reactants, concentrations of products, and/or the concentration of  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .

3. (16 points) Although rare, there are a few chemical reactions whose rate law is given by the expression

$$d[A]/dt = -k[A]^{1/2} \quad (3.1)$$

Find an expression for  $[A]_t$  for a reaction obeying the above rate law, in terms of  $k$ ,  $[A]_0$ , and  $t$ .

4. (20 points) In a gas mixture of argon (Ar) and cyclopropane (cyclo-C<sub>3</sub>H<sub>6</sub>), with  $[Ar] \gg [\text{cyclo-C}_3\text{H}_6]$ , the following isomerization reaction will take place



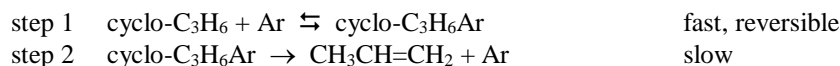
The reaction is first order and irreversible, with

$$d[\text{cyclo-C}_3\text{H}_6]/dt = -k[\text{cyclo-C}_3\text{H}_6] \quad (4.2)$$

where  $k$  is the first order rate constant for the isomerization reaction.

a) In a particular experiment at  $T = 500.^\circ\text{C}$  the concentration of cyclopropane initially present is  $[\text{cyclo-C}_3\text{H}_6]_0 = 6.83 \times 10^{14}$  molecule/cm<sup>3</sup>. After 100. seconds the concentration of cyclopropane has decreased to  $6.44 \times 10^{14}$  molecule/cm<sup>3</sup>. Based on this, find the value for  $k$ , the rate constant for the reaction (including correct units).

b) Consider the following two step mechanism for the above reaction



Find the rate law corresponding to the above two step mechanism. Is it consistent with the observed rate law for the reaction (yes/no and a brief explanation for your answer)?

5. (24 points) In class we discussed reactions where a reactant forms an intermediate, which then further reacts to form a final product. For the mechanism



where  $A$  = reactant,  $I$  = intermediate, and  $P$  = product, the general expressions for the concentration of the intermediate is

$$[I]_t = \frac{k_a}{(k_b - k_a)} [\exp(-k_a t) - \exp(-k_b t)] [A]_0 \quad (5.3)$$

By taking the derivative of the intermediate concentration with respect to time we can find  $t_{\text{max}}$ , the time at which the intermediate concentration reaches a maximum value

$$t_{\text{max}} = \frac{\ln(k_a/k_b)}{(k_a - k_b)} \quad k_a \neq k_b \quad (5.4)$$

Consider a system where  $[A]_0 = 0.5000$  mol/L,  $[I]_0 = [P]_0 = 0$ ,  $k_a = 0.020$  min<sup>-1</sup>, and  $k_b = 0.050$  min<sup>-1</sup>. Find the following

a)  $t_{\text{max}}$ , the time at which the concentration of the reaction intermediate reaches its maximum value.

b)  $[I]_{\text{max}}$ , the concentration of intermediate present in the system at the maximum.