

CHM 3400 – Fundamentals of Physical Chemistry
Third Hour Exam

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

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

1. (24 points) The gas phase reaction



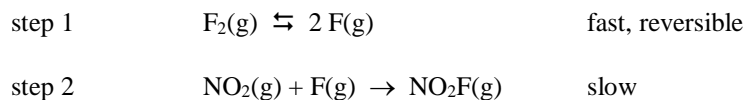
is an example of a second order heterogeneous reaction, with the rate of the reaction given by the expression

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

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 NO_2F 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

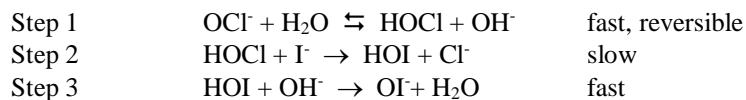


Find the rate law predicted by the above mechanism. Give your final expression for the rate law in terms of k_1 , k_{-1} , k_2 and concentrations of reactants and/or products.

2. (16 points) Consider the reduction reaction of 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 H_2O and 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 H_2O and 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-C₃H₆), with $[Ar] \gg [\text{cyclo-C}_3\text{H}_6]$, the following isomerization reaction will take place



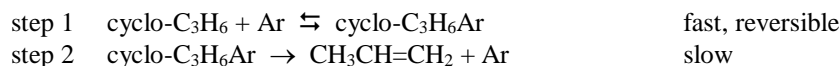
The reaction is first order and irreversible, with

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

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/cm³. After 100. seconds the concentration of cyclopropane has decreased to 6.44×10^{14} molecule/cm³. 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_{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⁻¹, and $k_b = 0.050$ min⁻¹. Find the following

a) t_{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.

Solutions.

1) a) $(\text{Rate})_0 = k[\text{NO}_2]_0[\text{F}_2]_0 = (38. \text{ L/mol}\cdot\text{s})(2.0 \times 10^{-4} \text{ mol/L})(5.0 \times 10^{-5} \text{ mol/L})$
 $= 3.8 \times 10^{-7} \text{ mol/L}\cdot\text{s}$

b) The easiest way to proceed is to make a table similar to the "ICE" table used in equilibrium problems

	Initial	Change	Equilibrium
NO_2	2.0×10^{-4}	$- 3.0 \times 10^{-5}$	1.7×10^{-4}
F_2	5.0×10^{-5}	$- 1.5 \times 10^{-5}$	3.5×10^{-5}
NO_2F	0.	3.0×10^{-5}	3.0×10^{-5}

where we have used the amount of NO_2F formed and the stoichiometry of the reaction to find the changes in the concentrations of NO_2 and F_2 .

Then $(\text{Rate}) = k[\text{NO}_2][\text{F}_2] = (38. \text{ L/mol}\cdot\text{s})(1.7 \times 10^{-4} \text{ mol/L})(3.5 \times 10^{-5} \text{ mol/L})$
 $= 2.3 \times 10^{-7} \text{ mol/L}\cdot\text{s}$

c) The overall rate of reaction is equal to the rate of the slow step (when there is a single slow step present in the mechanism), and so

$$\text{Rate} = k_2[\text{NO}_2][\text{F}]$$

F is a reaction intermediate. An expression for $[\text{F}]$ can be found from step 1 in the mechanism, which is fast and reversible.

$$k_1[\text{F}_2] = k_{-1}[\text{F}]^2$$

and so $[\text{F}]^2 = (k_1/k_{-1})[\text{F}_2][\text{F}] = (k_1/k_{-1})^{1/2} [\text{F}_2]^{1/2}$

Substituting gives the rate law $\text{Rate} = (k_1/k_{-1})^{1/2}k_2 [\text{NO}_2][\text{F}]^{1/2}$

2) a) Intermediates are HOCl and HOI

b) $\text{rate} = d[\text{Cl}^-]/dt = k_2 [\text{HOCl}] [\text{I}^-]$ (rate is equal to the rate of the slow step)

Since the first step is fast and reversible

$$k_1 [\text{OCl}^-] [\text{H}_2\text{O}] = k_{-1} [\text{HOCl}] [\text{OH}^-]$$

$$[\text{HOCl}] = (k_1/k_{-1}) \frac{[\text{OCl}^-][\text{H}_2\text{O}]}{[\text{OH}^-]}$$

And so $\text{rate} = (k_1k_2/k_{-1}) \frac{[\text{I}^-][\text{OCl}^-][\text{H}_2\text{O}]}{[\text{OH}^-]} = k \frac{[\text{I}^-][\text{OCl}^-][\text{H}_2\text{O}]}{[\text{OH}^-]}$ where $k = (k_1k_2/k_{-1})$

3) $d[\text{A}]/dt = - k [\text{A}]^{1/2}$

So $d[\text{A}]/[\text{A}]^{1/2} = - k dt$

Integrating both sides of this equation gives

$$\int_0^t d[A]/[A]^{1/2} = -k \int_0^t dt$$

$$2 [A]_t^{1/2} - 2[A]_0^{1/2} = -kt$$

$$[A]_t^{1/2} = [A]_0^{1/2} - (kt/2)$$

$$[A]_t = \{ [A]_0^{1/2} - (kt/2) \}^2$$

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

and so $k = - (1/t) \ln \{ [A]_t/[A]_0 \} = - (1/100. \text{ s}) \ln(6.44/6.83) = 5.9 \times 10^{-4} \text{ s}^{-1}$

b) The overall rate is equal to the rate of the slow step, and so

$$\text{Rate} = k_2 [\text{cyclo-C}_3\text{H}_6\text{Ar}]$$

cyclo-C₃H₆Ar is a reaction intermediate. We can eliminate it from the expression for the rate by using step 1 in the mechanism, which is fast and reversible, and so rapidly establishes an equilibrium.

$$k_1 [\text{cyclo-C}_3\text{H}_6][\text{Ar}] = k_{-1} [\text{cyclo-C}_3\text{H}_6\text{Ar}]$$

$$[\text{cyclo-C}_3\text{H}_6\text{Ar}] = (k_1/k_{-1}) [\text{cyclo-C}_3\text{H}_6][\text{Ar}]$$

Substituting into our expression for rate gives us

$$\text{Rate} = (k_1 k_2/k_{-1}) [\text{cyclo-C}_3\text{H}_6][\text{Ar}] = k [\text{cyclo-C}_3\text{H}_6][\text{Ar}] \quad \text{where } k = k_1 k_2/k_{-1}$$

This predicts a reaction that is 1st order in cyclo-C₃H₆ and 1st order in Ar.

The observed rate law is 1st order in cyclo-C₃H₆, and since the argon concentration is constant, the prediction from the rate law is in accord with the observed rate law. To see if the reaction is also 1st order in argon, we would need to run the reaction at several different argon pressures.

5) a) $t_{\max} = \frac{\ln(k_a/k_b)}{(k_a - k_b)} = \frac{\ln(0.02/0.05)}{[(0.020 \text{ min}^{-1}) - (0.050 \text{ min}^{-1})]} = 30.54 \text{ min}$

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

When $t = t_{\max} = 30.54 \text{ min}$, then

$$[I]_{t_{\max}} = \frac{(0.020 \text{ min}^{-1})}{(0.050 \text{ min}^{-1}) - (0.020 \text{ min}^{-1})} \{ \exp[- (0.020 \text{ min}^{-1})(30.54 \text{ min})] - \exp[- (0.050 \text{ min}^{-1})(30.54 \text{ min})] \} (0.5000 \text{ mol/L})$$

$$= 0.109 \text{ mol/L}$$

The physical significance of this result is as follows. If the intermediate I was the substance we were interested in producing in a chemical reaction, then we would let the above reaction go for about 30 minutes and then quench it (by suddenly lowering the temperature, for example). We would be able to convert approximately 20% of the reactant molecule into intermediate by that process.