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

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1. (24 points) The gas phase reaction

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g) \qquad (1.1)$$

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

$$\text{Rate} = -\frac{d[F_2]}{dt} = k[NO_2][F_2] \qquad (1.2)$$

where k = 38. L/mol·s at T = 27. °C

In a particular experiment (at T = 27. °C) the initial concentrations of reactants are $[NO_2]_0 = 2.0 \times 10^{-4}$ mol/L and $[F_2]_0 = 5.0 \times 10^{-5}$ mol/L.

a) What is R_0, the initial rate of reaction, for the above conditions.

b) What will be the rate of reaction in this experiment when the concentration of NO_2F in the system reaches the value $[NO_2F] = 3.0 \times 10^{-5}$ mol/L?

c) One mechanism proposed for the above reaction is the following

step 1	$F_2(g) \leftrightarrows 2\ F(g)$	fast, reversible
step 2	$NO_2(g) + F(g) \rightarrow NO_2F(g)$	slow

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.

$$I^- + OCl^- \rightarrow Cl^- + OI^- \qquad (2.1)$$

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

Step 1	$OCl^- + H_2O \leftrightarrows HOCl + OH^-$	fast, reversible
Step 2	$HOCl + I^- \rightarrow HOI + Cl^-$	slow
Step 3	$HOI + OH^- \rightarrow OI^- + H_2O$	fast

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

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

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_3H_6), with [Ar] >> [cyclo-C_3H_6], the following isomerization reaction will take place

$$\text{cyclo-}C_3H_6(g) \rightarrow CH_3CH{=}CH_2(g) \qquad (4.1)$$

The reaction is first order and irreversible, with

$$d[\text{cyclo-}C_3H_6]/dt = - k [\text{cyclo-}C_3H_6] \qquad (4.2)$$

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

a) In a particular experiment at T = 500. °C the concentration of cyclopropane initially present is $[\text{cyclo-}C_3H_6]_0$ = 6.83 x 10^{14} molecule/cm^3. After 100. seconds the concentration of cyclopropane has decreased to 6.44 x 10^{14} molecule/cm^3. 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

step 1	cyclo-C_3H_6 + Ar $\leftrightarrows$ cyclo-C_3H_6Ar	fast, reversible
step 2	cyclo-C_3H_6Ar $\rightarrow$ $CH_3CH{=}CH_2$ + Ar	slow

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

$$A \rightarrow I \quad k_a \qquad (5.1)$$

$$I \rightarrow P \quad k_b \qquad (5.2)$$

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

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

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

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

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) $[I]_{tmax}$, the concentration of intermediate present in the system at the maximum.