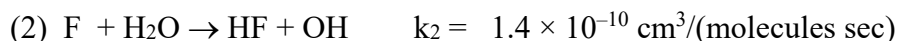
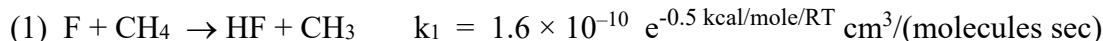


EXERCISES

Assume all reactions here are elementary

A. A fast flash of light creates an initial concentration of electronically excited X ($X^\#$), of 3.5×10^{-6} Molar. The rate constant for $X^\# \rightarrow X + h\nu$ is $1 \times 10^8 \text{ s}^{-1}$. What is the concentration of $X^\#$ after 2.5×10^{-8} seconds?

B.1 Calculate the rate of reactions (1) and (2) at 298 K, assuming $v_1 = k[F][CH_4]$ and $v_2 = k[F][H_2O]$



$$[\text{CH}_4] = 5 \times 10^{13} \text{ molecules/cm}^3$$

$$[\text{H}_2\text{O}] = 6 \times 10^{17} \text{ molecules/cm}^3$$

$$[\text{F}] = 1 \times 10^5 \text{ molecules/cm}^3 \quad \text{Note } 1 \text{ kcal/mole} = 4184 \text{ J/mole}$$

B.2 What is the ratio of the rate of reaction 1 to the rate of reaction 2? Does this ratio depend on $[F]$?

C. A unimolecular reaction has a rate constant $k(T) = A e^{-25 \text{ kcal/mole/RT}} \text{ sec}^{-1}$ which equals 0.01 sec^{-1} at 298 K. What is the rate constant at 500 K?

D.1 Consider the reaction $A \rightarrow B$ with $k = 10 \text{ sec}^{-1}$, $[A]_0 = 1 \text{ molar}$ and $[B]_0 = 0$. Use a spreadsheet to compute $[A]$ and $[B]$ at $t = 0, 0.01, 0.03, 0.1, 0.3, 1 \text{ sec}$. Plot $[A]$ and $[B]$ versus time on the same graph.

D.2 After how many lifetimes does $[A] = 0.9[A]_0$? $0.1[A]_0$?

D.3 Plot $\ln[A]$ vs time. Verify that the slope of this plot equals the rate constant from D.1.

The numbers below refer to the Exercises (not Problems) in *Physical Chemistry*, 8th Edition, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

22.1 22.3* 22.5-8

(For 22.7, note the "2" in front of the N_2O_5 when computing the rate constant !)

22.11 22.14

* The answer in the back of the book is not for this question! See answers to other Exercises for the correct answer.

Correct answer: $t_{1/2} = 1.02 \times 10^4$ seconds. $P(\text{N}_2\text{O}_5)$ is 499.7 Torr at 10 sec and 480. Torr at 10 minutes.

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, 9th Edition, by Peter Atkins and Julio De Paula. Numerical answers for the (a) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

21.2 21.4 21.7-10

(For 21.9, note the "2" in front of the N₂O₅ when computing the rate constant !)

21.12 21.14

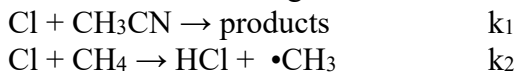
Problems

(treat all reactions in these Problems are elementary)

1) Using the data in the Excel spreadsheet provided:

- a) Verify that the disappearance of reactant A follows first order kinetics.
- b) determine the first order rate constant for loss of A

2) Consider the following reactions:



At what temperature does $k_2 = k_1$?

For both rate constants, see the 18th JPL Data Evaluation, Table 1.11. This is page 213 of the pdf file, marked in the file as page 1-199.

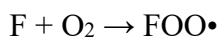
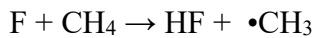
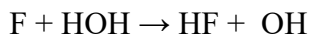
3) The gas phase reaction $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$ occurs with a rate constant

$$k = (8.3 \pm 2) \times 10^{-12} \text{ cm}^3/(\text{molecule sec}) \text{ at } 1000 \text{ K.}$$

In a laboratory reactor at 1000 K, $[\text{C}_2\text{H}_6]$ is initially 5.44×10^{12} molecules/cm³, and $[\text{O}]$ is initially 3.1×10^{11} molecules/cm³.

- a) Using the pseudo-1st order approximation, determine the time at which $[\text{O}] = 3.8 \times 10^{10}$ molecules/cm³.
- b) Using the exact expression for second order kinetics, determine the time at which $[\text{O}] = 3.8 \times 10^{10}$ molecules/cm³.
- c) What is the % difference in your answers in (a) and (b)? Is the difference meaningful?
- d) Compute $[\text{O}]$ when $t = 0.01$ sec.

4) Consider the following reactions occurring in the atmosphere at 230 K.



$$[O_2] = 1.0 \times 10^{17} \text{ molecules/cm}^3$$

$$[CH_4] = 3.0 \times 10^{13} \text{ molecules/cm}^3$$

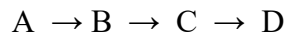
$$[HOH] = 4.0 \times 10^{12} \text{ molecules/cm}^3$$

For k_1 and k_2 , see the 18th JPL Data Evaluation, Table 1.10.
This is page 168 of the pdf file, marked as page 1-154.

- a) Under the conditions given above (with $[F] < \text{than } 10^5 \text{ molecules/cm}^3$ but unknown) what fraction of F reacts with CH_4 ?
- b) What is the lifetime of F with respect to reaction with:
 (i) HOH (ii) CH_4 (iii) O_2 ?
- c) What is the overall lifetime of F (considering all three reactions)?

HINT for c: Either the overall lifetime is the sum of the individual lifetimes, OR, the overall pseudo-1st order rate constant is the sum of the individual pseudo-1st order rate constants. Only one of these options makes physical sense!

5) The graph below shows concentration versus time for the consecutive elementary reactions:



with rate constants k_a k_b k_c

Initial concentrations are $[A]_0 = 1 \text{ molar}$, and $[B]_0 = [C]_0 = [D]_0 = 0$

Estimate the values of k_a , k_b , and k_c from the data in the graph.

