

Chem 312 – Spring 2008

Problem Set #7

Due Friday, 09 May, 10:10am in class.

Question 1

The data below apply to the reaction $(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$. Determine the order of the reaction, the rate constant, and the molar concentration of $(\text{CH}_3)_3\text{CBr}$ after 43.8 hours.

t (hours)	0	3.15	6.20	10.00	18.30	30.80
$[(\text{CH}_3)_3\text{CBr}]$ (10^{-2} M)	10.39	8.96	7.76	6.39	3.53	2.07

Question 2

The reaction $2\text{A} \rightarrow \text{P}$ has a third-order rate law with $k = 3.50 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. Calculate the time required for the concentration of A to change from 0.077 M to 0.021 M.

Question 3

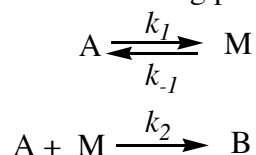
- (a) The reaction $2\text{H}_{(\text{g})} + \text{Ar}_{(\text{g})} \rightarrow \text{H}_{2(\text{g})} + \text{Ar}_{(\text{g})}$ is elementary with $k = 2.2 \times 10^8$ [units] at 3000 K. Write the rate law for this process (and figure out the units for k).
- (b) What is the relation among the various rates ($d[\text{species}]/dt$) for each species for the decomposition of $\text{N}_2\text{O}_{5(\text{g})}$ into $\text{N}_2\text{O}_{4(\text{g})}$ and $\text{O}_{2(\text{g})}$.
- (c) For gaseous reactions, the rate is often described in terms of dP_i/dt instead of dC_i/dt or dn_i/dt . Write an expression relating all three quantities. [C is concentration.]

Question 4

The rate constant for the decomposition of a certain substance is $1.70 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 24°C and $2.01 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 37°C . Evaluate the Arrhenius (pre-exponential) factor and the activation energy for the decomposition reaction.

Question 5

Consider the following proposed mechanism:



- (a) Write the overall chemical equation.
- (b) Write the rate expression, i.e., $d[\text{species}]/dt$, for all three species (A, M, B)
- (c) Assuming the steady state approximation for the intermediate M, rewrite the rate expression for A so that it does not contain any [M] terms.
- (d) Based on the following data measured using the method of initial rates, write an expression for the rate law.

Expt	$[\text{A}]_0$ (M)	Rate
1	0.20	4.6
2	0.40	9.3

- (e) Under what conditions does the rate expression you derived in (c) reduce to the experimentally measured rate law from (d)?