

Chemical Kinetics Problem Set 2

(All questions are no-calculator friendly.)

- 1) Understanding the high temperature formation and breakdown of the nitrogen oxides is essential for controlling the pollutants generated from power plants and cars. The first-order breakdown of dinitrogen monoxide to its elements has rate constants 0.80 at 727°C and 1.20 at 827°C. What is the activation energy of this reaction?

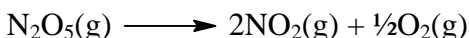
(Answer: about 40 kJ/mol)

- 2) The following rate constants were obtained for a first order reaction:

T(°C)	0	20	40	60
k(s ⁻¹)	2.46 x 10 ⁻⁵	4.75 x 10 ⁻⁴	5.76 x 10 ⁻³	5.48 x 10 ⁻²

- a) What would you graph to determine the E_a for this reaction? **(Answer: See your class notes)**
- b) The slope for your graph as plotted in part (a) is = -1.2 x 10⁴. What are the units associated with this slope?
- c) Calculate E_a for this reaction. **(Answer: E_a ≈ 1.0 x 10² kJ/mol)**
- d) What is the half-life of this reaction at 0°C? **(Answer: about 3 x 10⁴ seconds)**

- 3) Rate constants for the reaction



were determined at a series of temperatures. The data are given below,

T(°K)	298	308	318	328	338
k(s ⁻¹)	3.46 x 10 ⁻⁵	13.5 x 10 ⁻⁵	49.8 x 10 ⁻⁵	150 x 10 ⁻⁵	487 x 10 ⁻⁵

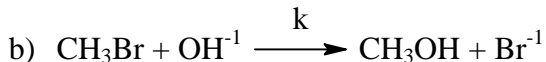
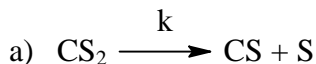
Construction of an Arrhenius plot from the above data would give a line with a slope = -1.2 x 10⁴. Determine the energy of activation for the above reaction.

(Answer: 1.0 x 10² kJ/mol)

- 4) Enzymes in the liver catalyze a large number of reactions that degrade ingested toxic chemicals. By what factor is the rate of a detoxification reaction changed if a liver enzyme lowers the activation energy of the reaction by 5 kJ/mol at 37°C?

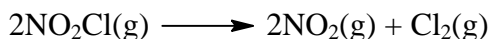
(Answer: The catalyzed reaction is about 7 times faster.)

- 5) Write a rate equation, showing the dependence of rate on reactant concentrations, for each of the following elementary reactions:

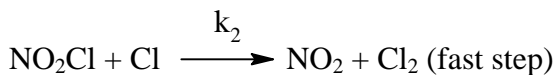
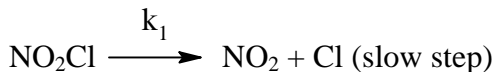


(Answers: (a) Rate = $k[\text{CS}_2]$; (b) Rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$)

- 6) The thermal decomposition of nitryl chloride, NO_2Cl ,



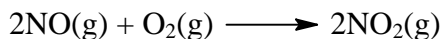
is thought to occur by the following mechanism:



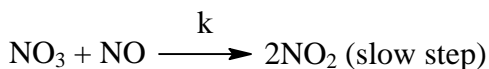
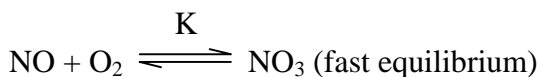
What rate law is predicted by this mechanism?

(Answer: Rate = $k_1[\text{NO}_2\text{Cl}]$)

- 7) The oxidation of nitric oxide by oxygen



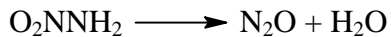
may have the following mechanism:



Derive the rate law from this mechanism. What will k_{observed} be in terms of the equilibrium constant (K) and the rate constant k?

(Answer: Rate = $kK[\text{NO}]^2[\text{O}_2]$ where $k_{\text{obs}} = kK$)

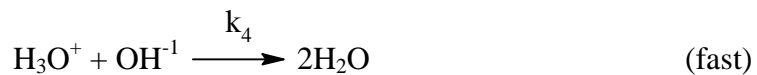
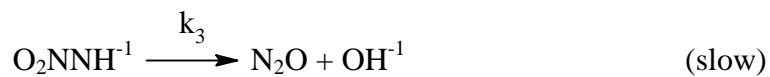
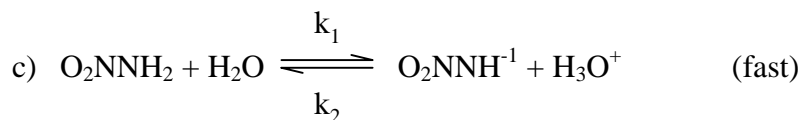
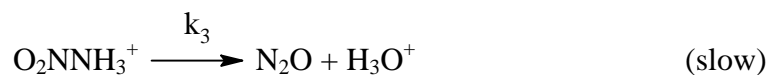
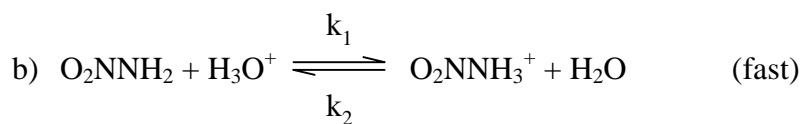
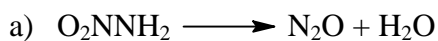
8) Nitramide, O_2NNH_2 , decomposes slowly in aqueous solution according to the equation



The experimental rate law is

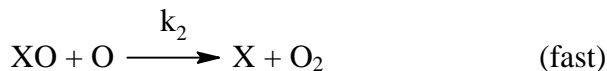
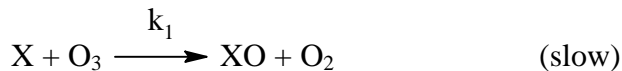
$$\frac{d[N_2O]}{dt} = k \frac{[O_2NNH_2]}{[H_3O^+]}$$

Which of the following proposed mechanisms is consistent with the experimental rate law?



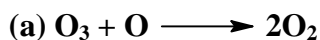
(Answer: Mechanism (c))

- 9) The catalytic destruction of ozone occurs via a two-step mechanism, where X can be any of several species:



- Write the overall reaction.
- Write the rate law for each step.
- What are the roles of X and XO in the mechanism above?
- High-flying aircraft release NO into the atmosphere, which catalyzes this process. When the O₃ and NO concentrations are 5.0 × 10¹² molecules/cm³ and 1.0 × 10⁹ molecules/cm³ respectively, what is the rate of O₃ depletion? The rate constant (k) for the process is 6.0 × 10⁻¹⁵ cm³/molecule-second.
- Is the O₃ concentration in part (d) reasonable for this reaction, given that the concentration of stratospheric O₃ never exceeds 10 mg/L?

(Answers:



(b) For step 1: rate = k₁[X][O₃]

For step 2: rate = k₂[XO][O]

(c) X is a catalyst and XO is an intermediate

(d) 3 × 10⁷ molecules/cm³-sec

(e) It is a reasonable value since 10 mg/L = 1.3 × 10¹⁷ molecules/cm³)

- 10) Acetone is one of the most important solvents in organic chemistry, used to dissolve everything from fats and waxes to airplane glue and nail polish. At high temperatures it decomposes in a first-order process to methane and ketene (H₂C=C=O). At 600°C, the rate constant is 8.7 × 10⁻³ s⁻¹.

- What is the half-life of the reaction at 600°C?
- How much time is required for 75% of a sample of acetone to decompose?
- How much time is required for 90% of a sample of acetone to decompose?

(Answers:

(a) t_{1/2} ≈ 80 seconds

(b) about 1.6 × 10² seconds

(c) about 2.5 × 10² seconds)