SURREY SUPPLEMENT: CHEMICAL KINETICS

1) The rate equation for the reaction

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

is second order in NO(g) and first order in H_2(g).

a) Write an equation for the rate of appearance of N_2(g). **[rate = $k[NO]^2[H_2]$]**
b) If concentrations are expressed in moles/litre, what units would the rate constant, k, have? **[$M^{-2}s^{-1}$]**
c) Write an equation for the rate of disappearance of NO(g). Would k in this equation have the same numerical value as k in the equation of part (a)? **[rate = $k[NO]^2[H_2]$, NO.]**

2) For a reaction in which A and B form C, the following data were obtained:

[A] (M)	[B] (M)	Rate of reaction (M/s)
0.30	0.15	0.0007
0.60	0.30	0.0028
0.30	0.30	0.0014

a) What is the rate equation for the reaction? **[rate = k[A][B]]**
b) What is the numerical value of the rate constant, k? **[1.55×10^{-2} L/mol·s]**

3) For a reaction in which A and B form C, the following data were obtained:

[A] (M)	[B] (M)	Rate of reaction (M/s)
0.03	0.03	0.0003
0.06	0.06	0.0012
0.06	0.09	0.0027

a) What is the rate equation for the reaction? **[rate = $k[B]^2$]**
b) What is the numerical value of the rate constant, k? **[0.33 L/mol·s]**

4) In the study of a first order kinetics reaction for the decomposition of A to form products the following data were obtained:

[A] (mol/L)	1.00	0.80	0.60	0.35	0.15
Time (s)	0	110	255	525	950

a) Graphically determine the rate constant for this reaction. **[2.0×10^{-3} s^{-1}]**
b) What is the half-life of this reaction? **[350 s]**

5) In the study of a second order kinetics reaction for the decomposition of A to form products the following data were obtained:

[A] (mol/L)	0.50	0.40	0.30	0.20	0.10
Time (min)	0	50	130	300	800

a) Graphically determine the rate constant for this reaction. **[0.010 L/mol·min]**
b) How long does it take for the [A] to decrease to half of its original value? **[200 min]**
c) Would it take the same amount of time for [A] to subsequently decrease by another half? EXPLAIN. **[No]**

6) The single-step reaction

$NO_2Cl(g) + NO(g) \longrightarrow NO_2(g) + ONCl(g)$

is reversible; $E_{a,forward}$ = 28.9 kJ/mol and $E_{a,reverse}$ = 41.8 kJ/mol. Draw a potential energy diagram for the reaction. Indicate $E_{a,forward}$, $E_{a,reverse}$ and ΔH on the diagram. **[See end of problem set for answer.]**

7) The reaction:

$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$ is first order in C_2H_5Cl.

The rate constant is 3.5×10^{-8} sec^{-1} at 600 K and 1.6×10^{-6} sec^{-1} at 650 K. Calculate the energy of activation for this reaction. **[248 kJ/mol]**

8) For the reaction: $NO_2Cl(g) + NO(g) \longrightarrow NO_2(g) + ONCl(g)$, the pre-exponential factor A is 8.3×10^8 and the energy of activation is 28.9 kJ/mol. The rate equation is first order in NO_2Cl and first order in NO. What is the rate constant, k, at 500 K? **[7.9×10^5 s^{-1}]**

9) What is the energy of activation of a reaction that increases ten-fold in rate when the temperature is increased from 300 K to 310 K? **[178 kJ/mol]**

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

T (°C)	0	20	40	60
K (s^{-1})	2.46×10^{-5}	4.75×10^{-4}	5.76×10^{-3}	5.48×10^{-2}

a) Graphically determine the energy of activation (E_a) for this reaction. **[97.0 kJ/mol]**
b) What is the half-life of this reaction at 80°C? **[1.7 seconds]**

11) Rate constants for the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + ½O_2(g)$ were determined at a series of temperatures. The data are given below.

T (K)	298	308	318	328	338
K (s^{-1})	$3.46x10^{-5}$	$13.5x10^{-5}$	$49.8x10^{-5}$	$150x10^{-5}$	$487x10^{-5}$

Construct an Arrhenius plot and determine the energy of activation for the above reaction.
[102.6 kJ/mol]

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

a) $CS_2 \xrightarrow{k} CS + S$

b) $CH_3Br + OH^- \xrightarrow{k} CH_3OH + Br^-$
[See end of problem set for answers.]

13) The thermal decomposition of nitryl chloride, NO_2Cl,

$2NO_2Cl(g) \longrightarrow 2NO_2(g) + Cl_2(g)$ $\rightarrow$

is thought to occur by the following mechanism:

$NO_2Cl \xrightarrow{k_1} NO_2 + Cl\cdot$ (slow step)

$NO_2Cl + Cl\cdot \xrightarrow{k_2} NO_2 + Cl_2$ (fast step)

What rate law is predicted by this mechanism? **[rate = $k_1[NO_2Cl]$]**

14) The oxidation of nitric oxide by oxygen:

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

may have the following mechanism:

$NO + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_3$ (fast)

$NO_3 + NO \xrightarrow{k_3} 2NO_2$ (slow)

a) Derive the rate law from this mechanism. **[$rate = \frac{k_1 k_3}{k_2}[NO]^2[O_2]$]**

b) What will $k_{observed}$ be in terms of the rate constants in the elementary steps? **[$k_{obs} = \frac{k_1 k_3}{k_2}$]**

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

$$O_2NNH_2 \longrightarrow N_2O + H_2O$$

The experimental rate law is $rate = \frac{k[O_2NNH_2]}{[H_3O^+]}$.

Which of the following mechanisms seems appropriate?

a) $O_2NNH_2 \xrightarrow{k_1} N_2O + H_2O$

b) $O_2NNH_2 + H_3O^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2NNH_3^+ + H_2O$ (fast)

$O_2NNH_3^+ \xrightarrow{k_3} N_2O + H_3O^+$ (slow)

c) $O_2NNH_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H_3O^+$ (fast)

$O_2NNH^- \xrightarrow{k_3} N_2O + OH^-$ (slow)

$H_3O^+ + OH^- \xrightarrow{k_4} 2H_2O$ (fast)

[Mechanism (c), assuming that the [H_2O] is constant and gets incorporated into a rate constant.]

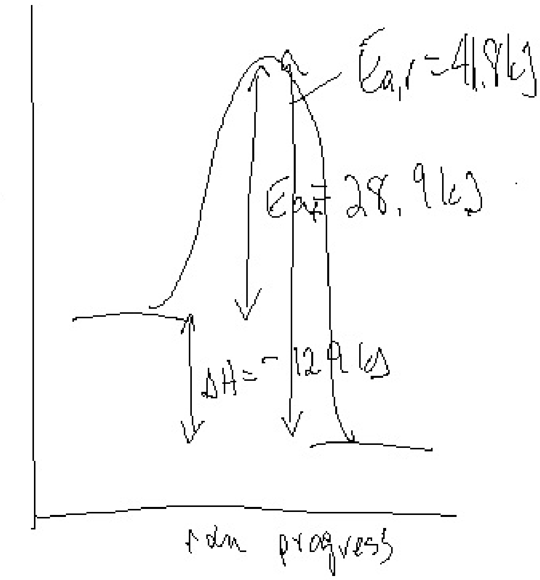
16) The catalytic destruction of ozone occurs via a two-step mechanism, where X can be any of several species:

$X + O_3 \xrightarrow{k_1} XO + O_2$ (slow)

$XO + O \xrightarrow{k_2} X + O_2$ (fast)

a) Write the overall reaction. **[$O + O_3 \longrightarrow 2O_2$]**
b) Write the rate law for each step. **[See end of problem set for answers.]**
c) What are the roles of X and XO in the mechanism above? **[X is a catalyst, XO is a reactive intermediate.]**
d) High-flying aircraft release NO into the stratosphere, which catalyzes this process. When O_3 and NO concentrations are 5×10^{12} molecules/cm^3 and 1.0×10^9 molecules/cm^3 respectively, what is the rate of O_3 depletion? The value of k for the rate-determining step is 6×10^{-15} cm^3/molecules·s. **[3.0×10^7 molecules/s]**

Answer to question 6:



Answers to question 12:

a) Rate = k[CS_2]
b) Rate = k[CH_3Br][OH^-]

Answers to question 16(b):

Rate = k_1[X][O_3] (first step)
Rate = k_2[XO][O] (second step)