Chapter 12 Questions

Section 12.1

1) Consider the hypothetical aqueous reaction A (aq) --> B (aq). A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	0.031

a) Calculate the number of moles of B at each time in the table. Assume that there are no molecules of B at time zero.
b) Calculate the average rate of disappearance of A for each 10 min interval, in units of mol/s.
c) Between t = 10 min and t = 30 min, what is the average rate of appearance of B in units of M/s? Assume that the volume of the solution is constant.

2) For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the appearance of each product:
a) H_2O_2 (g) --> H_2 (g) + O_2 (g)
b) 2 N_2O (g) --> 2 N_2 (g) + O_2 (g)
c) N_2 (g) + 3 H_2 (g) --> 2 NH_3 (g)

3) The rate of disappearance of HCl was measured for the following reaction:
CH_3OH (aq) + HCl (aq) --> CH_3Cl (aq) + H_2O (l)
The following date were collected:

Time (min)	*[HCl] (M)*
0.0	*1.85*
54.0	*1.58*
107.0	*1.36*
215.0	*1.02*
430.0	*0.580*

Calculate the average rate of reaction, in M/s, for the time interval between each measurement.

4) Consider the combustion of C_2H_4:
C_2H_4 (g) + 3 O_2 (g) --> 2 CO_2 (g) + 2 H_2O (g)
If the concentration of C_2H_4 is decreasing at the rate of 1.8 M/s, what are the rate of change in the concentrations of oxygen, carbon dioxide and water vapor?

5) The reaction 2 NO (g) + Cl_2 (g) --> 2 NOCl (g) is carried out in a closed vessel. If the moles of NO are decreasing by 0.03 mol/min, what is the rate of consumption of chlorine?

Section 12.2 & 12.3

6) A reaction obeys the following rate law:
Rate = $k[A][B]^2$
a) If [A] changes, will the rate change? Will the rate constant change? Explain.
b) What are the reaction orders for A and B? What is the overall reaction order? What are the units of the rate constant?

7a) What is the difference between a rate constant and a rate law?
b) What are the units of the rate constant for a reaction in solution that has an overall reaction order of two?

8) Consider the following reaction
2 NO (g) + 2 H_2 (g) --> N_2 (g) + 2 H_2O (g)
a) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law.
b) If the rate constant for this reaction at 1000 K is 6.0 x 10^4 $M^{-2}s^{-1}$, what is the reaction rate when [NO] = 0.050 M and [H_2] = 0.10 M?
c) What is the reaction rate at 1000 K when the concentration of NO is doubled to 0.10 M, while the concentration of H_2 is 0.10 M?

9) Consider the following reaction
CH_3Br (aq) + OH^- (aq) --> CH_3OH (aq) + Br^- (aq)
The rate law for this reaction is first order for both reactants. When [CH_3Br] is 5.0 x 10^{-3} M and [OH^-] is 0.050 M, the reaction rate at 298 K is 0.0432 M/s.
a) What is the value of the rate constant?
b) What are the units of the rate constant?

10) The following data were collected for the rate of disappearance of NO in the reaction
2 NO (g) + O_2 (g) --> 2 NO_2 (g):

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	0.0126	0.0125	1.41 x 10^{-2}
2	0.0252	0.0250	1.13 x 10^{-1}
3	0.0252	0.0125	5.64 x 10^{-2}

a) What is the rate law for the reaction?
b) What are the units of the rate constant?
c) What is the average value of the rate constant calculated from the three sets of data?

11) For a reaction of the type A + B + C --> products, the following observations are made: Doubling the concentration of A doubles the rate, tripling the concentration of B has no effect on the rate and tripling the concentration of C increases the rate by a factor of 9.
a) What is the rate law for the reaction?
b) By what factor will the rate change if the concentrations of A, B and C are all halved?

12) Using the data below, determine the rate law and rate law constant.

Exp	$[BrO_3^-]$ (M)	$[Br^-]$ (M)	$[H^+]$ (M)	Initial Rate (M/s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	8.0×10^{-4}

13) The following data were measured for the reaction BF_3 (g) + NH_3 (g) --> F_3BNH_3 (g)

Exp.	$[BF_3]$ (M)	$[NH_3]$ (M)	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

a) What is the rate law for the reaction?
b) What is the overall order of the reaction?
c) What is the value of the rate constant for the reaction?

Section 12.4

14a) What is a zero order reaction?
b) What quantity, when graphed versus time, will yield a straight line for a first order reaction?

15a) What is a first order reaction?
b) What quantity, when graphed versus time, will yield a straight line for a first order reaction?
c) Does the half-life of a first order reaction depend on the initial concentration?

16a) What is a second order reaction?
b) What quantity, when graphed versus time, will yield a straight line for a second order reaction?
c) Does the half-life of a second order reaction depend on the initial concentration? Explain.

17a) The thermal decomposition of N_2O_5 (g) is a second order reaction. The rate constant for the reaction is 5.1×10^{-4} $M^{-1}s^{-1}$ at 318 K. What is the half-life of the decomposition?
b) The gas phase decomposition of SO_2Cl_2 is first order in SO_2Cl_2. At 600 K, the half-life for the process is 2.3×10^5 s. What is the rate constant at this temperature?

18) Data for the decomposition reaction of N_2O is given below. Using the following kinetic data, determine the reaction and the magnitude of rate constant:

Time (hr)	$[N_2O]$ (M)	Time (hr)	$[N_2O]$ (M)
0	1.000	33	0.547
11	0.849	44	0.396
22	0.698	55	0.245

19) The first order rate constant for the reaction

$$N_2O_5 \text{ (g)} \rightarrow 2\ NO_2 \text{ (g)} + \tfrac{1}{2}\ O_2 \text{ (g)}$$

at 70 ^oC is 6.82×10^{-3} s^{-1}. Suppose we start with 0.0300 mol of N_2O_5 in a volume of 2.50 L.
a) How many moles of N_2O_5 would be left after 2.5 minutes?
b) How many minutes would it take for the quantity of N_2O_5 to drop to 0.005 mol?
c) What is the half-life of N_2O_5 at 70 ^oC?

20) Data for the decomposition reaction of SO_2Cl_2 is given below. Using the following kinetic data, determine the reaction and the magnitude of rate constant:

Time (s)	$[SO_2Cl_2]$ (M)
0	1.000
2500	0.947
5000	0.895
7500	0.848
10000	0.803

21) The gas phase decomposition of NO_2 is studied at 383 ^oC, giving the following data:

Time (s)	$[NO_2]$ (M)
0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

a) Is the reaction first order or second order with respect to the concentration of NO_2?
b) What is the value of the rate constant?

Section 12.5

22a) What is meant by the term elementary step?
b) What is the difference between a unimolecular and a bimolecular elementary step?
c) What is a reaction mechanism?

23) The following mechanism has been proposed for the reaction of NO with H_2 to form N_2O and H_2O:

$NO (g) + NO (g) \rightarrow N_2O_2 (g)$

$N_2O_2 (g) + H_2 (g) \rightarrow N_2O (g) + H_2O (g)$

a) Show the elementary steps of the proposed mechanism add to provide a balanced equation for the reaction.
b) Write a rate law for each elementary step in the mechanism.
c) Identify any intermediates in the mechanism.
d) The observed rate law is Rate $=k[NO]^2[H_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second step?

Section 12.6 & 12.7

26) For the elementary process, $N_2O_5 (g) \rightarrow NO_2 (g) + NO_3 (g)$, the activation energy, E_a, and the overall ΔE are 154 kJ/mol and 136 kJ/mol, respectively.
a) Sketch the energy profile for this reaction and label E_a and ΔE.
b) What is the activation energy of the reverse reaction?

27a) Based on their activation energies and energy changes, which of the following reactions would be the fastest and which would be the slowest? Assume that all collision factors are the same.

	E_a (kJ/mol)	ΔE (kJ/mol)
a	55	-45
b	65	-10
c	35	10

b) Which of the reactions in (a) will be the fastest in the reverse direction? Which will be the slowest?

28a) What part of the energy profile of a reaction is affected by a catalyst?
b) What is the difference between a homogeneous and a heterogeneous catalys?
c) Most heterogeneous catalysts of importance are extremely finely divided solid materials. Why is particle size important?

24) The following is a mechanism for a reaction:

$NO_2 + F_2 \rightarrow NOF_2 + O$ slow

$NO_2 + O \rightarrow NO_3$ fast

$NOF_2 + NO_2 \rightarrow NO_2F + NOF$ fast

$NO_3 + NOF \rightarrow NO_2F + NO_2$ fast

Determine the overall reaction, intermediates and a possible rate law.

25) Consider the following reaction:

$H_2 (g) + 2 ICl (g) \rightarrow 2 HCl (g) + I_2 (g)$

The rate law for the reaction is first order for both reactants. Which of the following mechanisms are consistent with the observed rate law?

a) $H_2 (g) + 2 ICl (g) \rightarrow 2 HCl (g) + I_2 (g)$ (termolecular reaction)

b) $H_2 (g) + ICl (g) \rightarrow HI (g) + HCl (g)$ (slow)
$HI (g) + ICl (g) \rightarrow HCl (g) + I_2 (g)$ (fast)

c) $H_2 (g) + ICl (g) \rightarrow HI (g) + HCl (g)$ (fast)
$HI (g) + ICl (g) \rightarrow HCl (g) + I_2 (g)$ (slow)

d) $H_2 (g) + ICl (g) \rightarrow HICl (g) + H (g)$ (slow)
$H (g) + ICl (g) \rightarrow HCl (g) + I (g)$ (fast)
$HICl (g) \rightarrow HCl (g) + I (g)$ (fast)
$I (g) + I (g) \rightarrow I_2 (g)$ (fast)

29) The rate of reaction

$CH_3COOC_2H_5 (aq) + OH^- (aq) \rightarrow CH_3COO^- (aq) + C_2H_5OH (aq)$

was measured at several temperatures, and the following date were collected:

Temp (^OC)	k ($M^{-1}s^{-1}$)
15	0.0521
25	0.101
35	0.184
45	0.332

Using these data, construct a graph of ln k versus 1/T. Using your graph, determine the value of E_a.

30) Given the following information, determine the activation energy of the reaction:

$2 N_2O_5 (g) \rightarrow 4 NO_2 (g) + O_2 (g)$

Temp (K)	*k (s^{-1})*
293	*2.0×10^{-5}*
303	*7.3×10^{-5}*
313	*2.7×10^{-4}*
323	*9.1×10^{-4}*
333	*2.9×10^{-3}*

31) The oxidation of SO_2 to SO_3 is catalyzed by NO_2. The reaction proceeds as follows:

NO_2 (g) + SO_2 (g) --> NO (g) + SO_3 (g)

2 NO (g) + O_2 (g) --> 2 NO_2 (g)

a) Show that the two reaction can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3.

b) Why do we consider NO_2 a catalyst and not an intermediate in the reaction?
c) Is this an example of a homogeneous or heterogeneous catalyst?

Review

1) Determine the empirical and molecular formula for adrenaline, a hormone secreted into the bloodstream in times of danger or stress: 59.0% C, 7.1% H, 26.2% O and 7.7% N, with a molar mass of 180 amu.

2) Write balanced net ionic equations for each of the following reactions:
a) solid calcium carbonate and aqueous hydrochloric acid
b) aqueous solutions of calcium bromide and lead (II) acetate
c) aqueous solutions of potassium hydroxide and chlorous acid
d) solid calcium and aqueous aluminum nitrate
e) liquid water and gaseous sulfur dioxide

3) Determine the standard heat of formation, standard entropy, and standard free energy for the formation of calcium carbonate from its elements. Then, show proof for the relationship $\Delta G = \Delta H - T\Delta S$.

4) The pH of an ammonia solution is 8.5. What is the concentration of the ammonia solution?

5) Ethanol, CH_3CH_2OH, is a common solvent in chemical plants. For ethanol, determine the molecule's
a) domain geometry
b) molecule shape
c) molecule polarity
d) intermolecular forces
e) melting point compared to water and oxygen

6) When solid calcium is dropped into liquid water, the chemical reaction caused the solution to become basic and a gas to be evolved. If 3.0 g of Ca is dropped into 145 mL of water and allowed to completely react, what is the pH of the solution, and what volume of gas would be evolved at a temperature of 17 ^{O}C and 725 torr?