Unit 13 – Chapter 12: Kinetics **Name _____**

Review Problems **Period _____**

1. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide

$$2\ N_2O_{5(g)} \rightarrow 4\ NO_{2(g)} + O_{2(g)}$$

$[N_2O_5]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0750	8.90×10^{-4}
0.190	2.26×10^{-3}
0.275	3.26×10^{-3}
0.410	4.85×10^{-3}

Defining the rate as $-\Delta [N_2O_5]/\Delta t$, write the rate law and calculate the value of the rate constant.

2. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20^0C. The following data were collected with all concentration units in µmol/L. (A hemoglobin concentration of 2.21 µmol/L is equal to 2.21×10^{-6} mol/L.)

$[Hb]_0$ (µmol/L)	$[CO]_0$ (µmol/L)	Initial Rate (µmol/L · s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a) Determine the orders of this reaction with respect to Hb and CO.

b) Determine the rate law.

c) Calculate the value of the rate constant.

d) What would be the initial rate for an experiment with $[Hb]_0 = 3.36$ µmol/L and $[CO]_0 = 2.40$ µmol/L?

3. The following data were obtained for the reaction

$$2\ ClO_{2(aq)} + 2\ OH^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + ClO_2^-{}_{(aq)} + H_2O_{(l)}$$ where Rate = $\Delta[ClO_2]/\Delta t$

$[ClO_2]_0$ (µmol/L)	$[OH^-]_0$ (µmol/L)	Initial Rate (µmol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

a) Determine the rate law and the value of the rate constant.

b) What would be the initial rate for an experiment with $[ClO_2]_0 = 0.175$ mol/L and $[OH^-]_0 = 0.0844$ mol/L?

Integrated Rate Laws

3. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120 ± 1	0.91
300 ± 1	0.78
600 ± 1	0.59
1200 ± 1	0.37
1800 ± 1	0.22
2400 ± 1	0.13
3000 ± 1	0.082
3600 ± 1	0.050

Assuming that Rate = $\Delta[H_2O_2]/\Delta t$, determine that the rate law, the integrated rate law, and the value of the rate constant. Calculate $[H_2O_2]$ at 4000 seconds after the start of the reaction.

4. A certain reaction has the following general form: $aA \rightarrow bB$

At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}$ *M*, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of -2.97×10^{-2} min^{-1}.

a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

b) Calculate the half-life for this reaction.

c) How much time is required for the concentration of A to decrease to 2.50×10^{-3} *M*?

5. The rate of the reaction: $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ depends only on the concentration of nitrogen dioxide below 225^0C. At a temperature below 225^0C, the following data were collected:

Time (seconds)	$[NO_2]$ (µmol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate law, the integrated law, and the value of the rate constant. Calculate $[NO_2]$ at 2.70×10^4 seconds after the start of the reaction.

6. A certain reaction has the following general form: $aA \rightarrow bB$

At a particular temperature and $[A]_0 = 2.80 \times 10^{-3}$ *M*, concentration versus time data were collected for this reaction, and a plot of 1/[A] versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2}$ L/mol · s.

a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

b) Calculate the half-life for this reaction.

c) How much time is required for the concentration of A to decrease to 7.00×10^{-4} *M*?

7. The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3) surface

$$C_2H_5OH_{(g)} \rightarrow C_2H_{4(g)} + H_2O_{(g)}$$

was studied at 600 K. Concentration versus time data were collected for this reaction, and a plot of [A] versus time resulted in a straight line with a slop of -4.00×10^{-5} mol/L · s.

a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

b) If the initial concentration of C_2H_5OH was 1.25×10^{-2} *M*, calculate the half-life for this reaction.

c) How much time is required for all the 1.25×10^{-5} *M* C_2H_5OH to decompose?

8. At 500 K in the presence of a copper surface, ethanol decomposes according to the equation

$$C_2H_5OH_{(g)} \rightarrow CH_3CHO_{(g)} + H_{2(g)}$$

The pressure of C_2H_5OH was measured as a function of time and the following data were obtained:

Time (seconds)	**P_{C2H5OH} (torr)**
0	250.
100.	237
200.	224
300.	211
400.	198
500.	185

Since the pressure of a gas is directly proportional to the concentration of a gas, we can express the rate law for a gaseous reaction in terms of partial pressures. Using the above data, deduce the rate law, the integrated rate law, and the value of the rate constant, all in terms of pressure units in atm and time in seconds. Predict the pressure of C_2H_5OH after 900. seconds from the start of reaction. (*Hint*: To determine the order of the reaction with respect to C_2H_5OH, compare how the pressure of C_2H_5OH decreases with each time listing.)

9. The dimerization of butadiene $2\ C_4H_{6(g)} \rightarrow C_8H_{12(g)}$ was studied at 500. K and the following data were obtained:

Time (seconds)	$[C_4H_6]$ (µmol/L)
195	1.6×10^{-2}
604	1.5×10^{-2}
1246	1.3×10^{-2}
2180	1.1×10^{-2}
6210	0.68×10^{-2}

Assuming that Rate = $\Delta[C_4H_6]/\Delta t$, determine the form of the rate law, the integrated rate law, and the rate constant for this reaction. (These are actual experimental data, so they may not give a perfectly straight line.)

10. The rate of the reaction $O_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + O_{2(g)}$ was studied at a certain temperature.

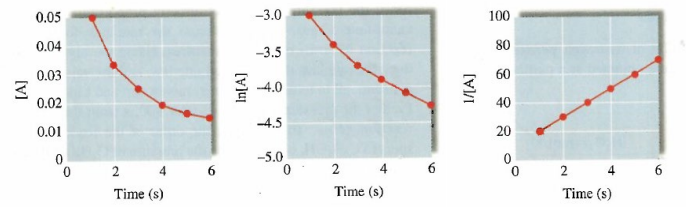
a) in the first set of experiments, NO_2 was in large excess, at a concentration of 1.0×10^{13} molecules/cm^3 with the following data collected:

Time (seconds)	[O] (atoms/cm^3)
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^9
3.0×10^{-2}	2.5×10^9

What is the order of the reaction with respect to oxygen atoms?

b) The reaction is known to be first order with respect to NO_2. Determine the overall rate law and the value of the rate constant.

11. Experimental data for the reaction $A \rightarrow 2B + C$ have been plotted in the following three different ways (with concentration unites in mol/L):



What is the order of the reaction with respect to A and what is the initial concentration of A?

12. Consider the data plotted in #11 when answering the following questions.

a) What is the concentration of A after 9 s?

b) What are the first three half-lives for this experiment?

13. The reaction $A \rightarrow B + C$ is known to be zero order in A and to have a rate constant of 5.0×10^{-2} mol/L · sec at 25^0C. An experiment was run at 25^0C where $[A]_0 = 1.0 \times 10^{-3}$ *M*.

a) Write the integrated rate law for this reaction.

b) Calculate the half-life for the reaction.

c) Calculate the concentration of B after 5.0×10^{-3} seconds has elapsed.

14. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ^{32}P to decay?

15. A first-order reaction is 75.0% complete in 320. s.

a) What are the first and second half-lives for this reaction?

b) How long does it take for 90.0% completion?

16. The rate law for the decomposition of phosphine (PH_3) is

$$\text{Rate} = -\Delta[PH_3]/\Delta t = k[PH_3]$$

It takes 120. seconds for 1.00 *M* PH_3 to decrease to 0.250 *M*. How much time is required for 2.00 *M* PH_3 to decrease to a concentration of 0.350 *M*?

17. Consider the following initial rate data for the decomposition of compound AB to give A and B:

$[AB]_0$ (mol/L)	Initial Rate (mol/L · sec)
0.200	3.20×10^{-3}
0.400	1.28×10^{-2}
0.600	2.88×10^{-2}

Determine the half-life for the decomposition reaction initially having 1.00 *M* AB present.

18. The rate law for the reaction $2\ NOBr_{(g)} \rightarrow 2\ NO_{(g)} + Br_{2(g)}$ at some temperature is

$$\text{Rate} = -\Delta[NOBr]/\Delta t = k[NOBr]^2$$

a) If the half-life for this reaction is 2.00 sec when $[NOBr]_0 = 0.900$ *M*, calculate the value of *k* for this reaction.

b) How much time is required for the concentration of NOBr to decrease to 0.100 *M*?

19. For the reaction A→ products, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[A]_0 = 0.10$ *M*. Calculate the concentration of A at the following times

a) 80.0 min

b) 30.0 min

20. Consider the hypothetical reaction $A + B + 2\ C \rightarrow 2\ D + 3\ E$ where the rate law is

$$\text{Rate} = -\Delta[A]/\Delta t = k[A][B]^0$$

An experiment is carried out where $[A]_0 = 1.0 \times 10^{-2}\ M$, $[B]_0 = 3.0\ M$, and $[C]_0 = 2.0\ M$. The reaction started, and after 8.0 seconds, the concentration of A is $3.8 \times 10^{-3}\ M$.

a) Calculate *k* for this reaction.

b) Calculate the half-life for this experiment.

c) Calculate the concentration of A after 13.0 seconds.

d) Calculate the concentration of C after 13.0 seconds.

Reaction Mechanisms

21. Write the rate laws for the following elementary reactions.

a) $CH_3NC_{(g)} \rightarrow CH_3CN_{(g)}$

b) $O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_{2(g)}$

c) $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$

d) $O_{3(g)} + O_{(g)} \rightarrow 2\ O_{2(g)}$

22. The mechanisms shown below have been proposed to explain the kinetics of the reaction

$2\ H_{2(g)} + 2\ NO_{(g)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)}$ Rate = $k\{NO]^2[H_2]$

Which of the following are acceptable mechanisms? Explain.

Mechanism 1:

$2\ H_{2(g)} + 2\ NO_{(g)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)}$

Mechanism 2:

$H_{2(g)} + NO_{(g)} \rightarrow H_2O_{(g)} + N_{2(g)}$ Slow

$N_{(g)} + NO_{(g)} \rightarrow N_{2(g)} + O_{(g)}$ Fast

$H_{2(g)} + O_{(g)} \rightarrow H_2O_{(g)}$ Fast

Mechanism 3:

$H_{2(g)} + 2\ NO_{(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$ Slow

$N_2O_{(g)} + H_{2(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$ Fast

23. A proposed mechanism for a reaction is

$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ Slow

$C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ Fast

$C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ Fast

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

24. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

$NO_2 + NO_2 \rightarrow NO_3 + NO$ Slow

$NO_3 + CO \rightarrow NO_2 + CO_2$ Fast

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

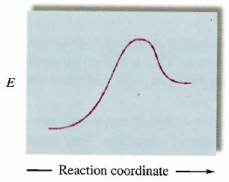
Temperature Dependence of Rate Constants and the Collision Model

25. For the following reaction profile, indicate

a) the positions of reactants and products.

b) the activation energy.

c) ΔE for the reaction.



26. Draw a rough sketch of the energy profile for each of the following cases:

a) ΔE = +10 kJ/mol, E_a = 25 kJ/mol

b) ΔE = -10 kJ/mol, E_a = 50 kJ/mol

c) ΔE = -50 kJ/mol, E_a = 50 kJ/mol

27. The activation energy for the reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

is 125 kJ/mol, and ΔE for the reaction is -216 kJ/mol. What is the activation energy for the reverse reaction [$NO_{(g)} + CO_{2(g)} \rightarrow NO_{2(g)} + CO_{(g)}$]?