Exercise 12.4

Integrated Rate Laws & Reaction Half-Life

Name: ________________________

Date:________________ Per:________

The dependence of the rate of a chemical reaction on the concentration of the reactants is given by the **rate law** and takes the form:

$$\textbf{rate} = k\,[A]^m\,[B]^n\,[C]^p \ldots$$

where the exponents, m,n,p,…, may be zero, integers or fractions.

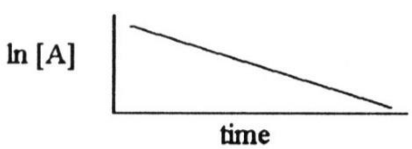
The sum of the exponents (a+b+c+…) is the **order** of the reaction. The expressions for the change in concentration with time are differential equations which, in some cases, can be integrated to give a different, but related, form of the rate equation. These are summarized below:

order	differential rate law	integrated rate law	½ life
zero	rate = k	$[A] = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$
first	rate = k[A]	$\ln [A] = -kt + \ln[A]_0$	$t_{1/2} = \ln 2/k$
second*	rate = $k[A]^2$	$1/[A] = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$
	* or rate = k[A][B] as long as $[A]_0 = [B]_0$ and they react in a 1:1 ratio		

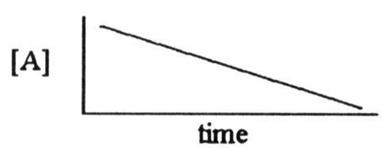
These are all **linear equations** of the form y = mx +b. Graphs of [A], ln[A] or 1/[A] (y) vs time (x) will give a **straight line** when the reactions are zero, 1st or 2nd order, respectively. There are no analytical solutions for other rate laws.

DIRECTIONS: Answer the following in the space provided.

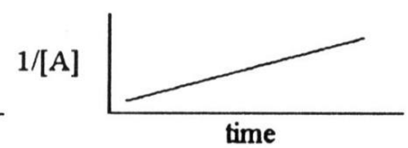
1. Label each of the following graphs with the order of the reactant A.



Order: ____________________

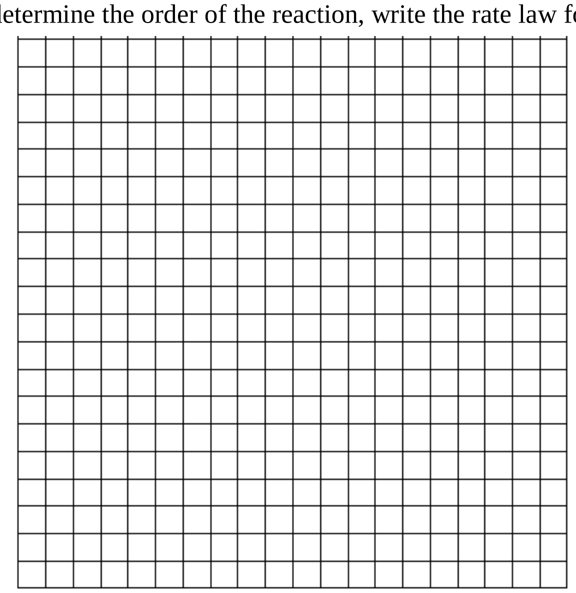


Order: ____________________



Order: ____________________

2. The reaction A → B + C is carried out at a particular temperature. The observed data is recorded at right. Graph the data to determine the order of the reaction, write the rate law for the reaction, and determine the value of k at this temperature.



Time (min)	[A]	ln[A]	1/[A]
0.00	2.000		
2.00	1.107		
4.00	0.612		
6.00	0.338		
8.00	0.187		
10.00	0.103		

Rate Law: _________________

k: _______________

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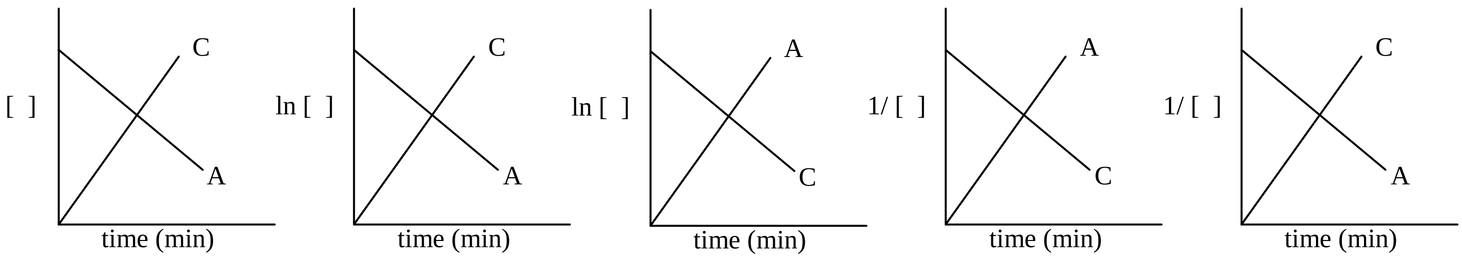
3. The reaction A → B is second order in [A] and the rate constant is 0.039 $M^{-1}s^{-1}$. If the concentration of A was 0.30 *M* at 23 s, calculate the initial concentration of A.

4. The reaction A → B + C is first order in A. When $[A]_0$ = 0.10 M, the reaction is 20% complete in 40.0 minutes.
   a. Calculate the rate constant, k, for this reaction, with the correct units.

   b. Which of the following plots best describes the changes in concentration of A and C? ______________________

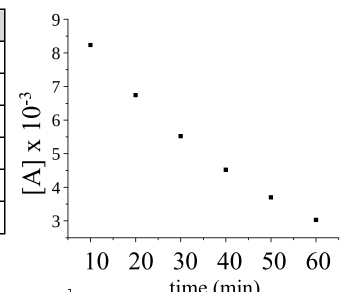


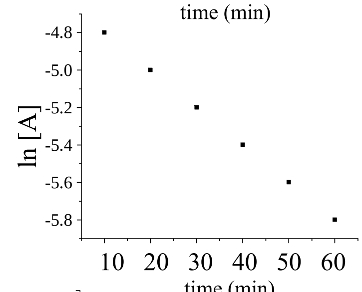
5. For the reaction 2A → 2B + C, the following data were collected. The data is graphed by [A], ln[A], and 1/[A].
   a. Determine the rate law using the graphed data:

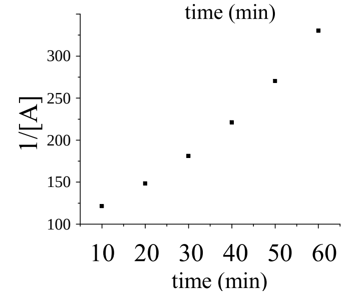
      _________________________.

   b. Calculate k for this reaction using the appropriate integrated rate law for the reactant order:

[A]	t (min)
8.23×10^{-3}	10
6.74×10^{-3}	20
5.52×10^{-3}	30
4.52×10^{-3}	40
3.70×10^{-3}	50
3.03×10^{-3}	60







   c. Calculate the half-life for this reaction:

   d. Calculate $[A]_0$

   e. Calculate [A] after 70 minutes

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6. The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1}. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3.
   a. What is the concentration of the insecticide on June 1 of the following year?

   b. How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

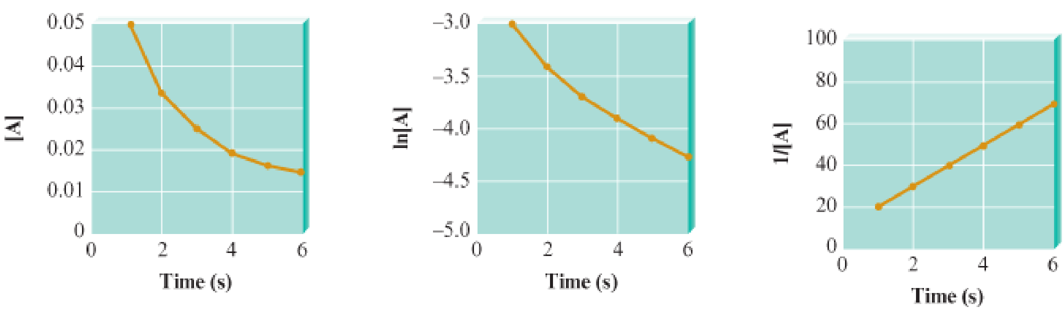
7. The reaction, $2NO_2 \rightarrow 2NO + O_2$ follows second-order kinetics. At 300°C, [NO_2] drops from 0.0100 M to 0.00650 M in 100.0 s. The rate constant for the reaction is __________ $M^{-1}s^{-1}$.

8. For the reaction A → product, the first two half-times are 10 minutes and 20 minutes respectively. At the beginning of the reaction, [A] was 0.10M.

   a. What is the rate law for this reaction?

   b. What is the [A] at t = 80 min?

9. Experimental data for the reaction A → 2B + C have been plotted in the following three different ways (with concentration units in mol/L):



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

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10. The rate of the reaction depends only on the concentrations of nitrogen dioxide below 225°C. At a temperature below 225°C the following data were collected:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Time (s)	$[NO_2]$ (mol/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

a. Determine the rate law

b. Determine the integrated rate law

c. Determine the value of the rate constant. Calculate $[NO_2]$ as 2.70 x 10^4s after the start of the reaction.

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

Assuming that $Rate = -\frac{\Delta[H_2O_2]}{\Delta t}$

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

a. Determine the rate law

b. Determine the integrated rate law

c. Determine the value of the rate constant.

d. Calculate $[H_2O_2]$ at 4000. s after the start of the reaction.

12. *The reaction* A → B *is first order in* [A]. *Consider the following data.*

a. Determine the value of the rate constant.

Time (s)	[A] (mol/L)
0	1.60
10.0	0.40
20.0	0.10

b. Determine the half-life of this reaction.

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13. 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 (s)	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 gas, we can express the rate law for a gaseous reaction in terms of partial pressures.

Using the above data to calculate the following: (all in terms of pressure units in atm and time in seconds)

a. the rate law

b. the integrated rate law

c. the value of the rate constant

d. Predict the pressure of C_2H_5OH after 900.s from the start of the 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.*

14. The decomposition of dimethyl ether, $(CH_3)_2O$ at 510º C is a first-order process with a rate constant of 6.8×10^{-4} s^{-1}.

$$(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?

15. The half-life for ^{40}K is 1.3×10^9 years. What percent of the original remains after 3.9×10^9 years? Radioactive decay is a first order process.

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16. The dimerization of butadiene was studied at 500 K, and the following data were obtained:

$$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$$

Time (s)	$[C_4H_6]$ (mol/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 = $-\frac{\Delta[C_4H_6]}{\Delta t}$, 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.)

17. Determine the form of the integrated rate law and the rate law for the decomposition of benzenediazonium chloride:

$$C_6H_5N_2Cl(aq) \rightarrow C_6H_5Cl(l) + N_2(g)$$

from the following data, which were collected at 50°C and 1 atm (the total solution volume was 40.0 mL).

Time (s)	N_2 Evolved (mL)
6	19.3
9	26.0
14	36.0
22	45.0
30	50.4
∞	58.3

18. A compound decomposes by a first-order process. If 25.0% of the compound decomposes in 60.0 minutes, determine the half-life of the compound.

19. The reaction below is first order in $[H_2O_2]$:

$$2H_2O_2\ (l) \rightarrow 2H_2O\ (l) + O_2\ (g)$$

A solution originally at 0.600 M H_2O_2 is found to be 0.075 M after 54 min. Find the half-life of this reaction.