

Chemical Kinetics

• The area of chemistry that concerns reaction rates.

Reaction Rates

• The questions posed in this chapter will be:

- How is the rate of a reaction measured?

- What conditions will affect the rate of a reaction?
- How do you express the relationship of rate to the variables affecting the rate?
- What happens on a molecular level during a chemical reaction?

Reaction Rate

•Change in concentration (conc) of a reactant or product per unit time.

Rate = $\frac{\operatorname{conc} \operatorname{of} A \operatorname{at} \operatorname{time} t_2 - \operatorname{conc} \operatorname{of} A \operatorname{at} \operatorname{time} t_1}{t_2 - t_1}$ $= \frac{\Delta [A]}{\Delta t}$

Definition of Reaction Rate

- The reaction rate is the increase in molar concentration of a product of a reaction per unit time.
 - It can also be expressed as the **decrease** in molar concentration of a **reactant** per unit time.

- 1. Rate of formation of product = Δ [product]/ Δ t This is the average rate over time
- 2. Rate of reaction of reactant = $-\Delta$ [Reactant]/ Δ t This is the average rate over time

Definition of Reaction Rates

• Consider the gas-phase decomposition of dintrogen pentoxide.

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

– If we denote molar concentrations using brackets, then the change in the molarity of O_2 would be represented as

$\Delta[O_2]$

where the symbol, Δ (capital Greek delta), means "the change in."

Definition of Reaction Rates

- Figure 14.5 shows the increase in concentration of O₂ during the decomposition of N₂O₅.
- Note that the **rate decreases** as the reaction proceeds.



TABLE 12.3Concentration/Tinthe Reaction $2N_2C$ $4NO_2(soln) + O_2(g)$	$O_5(soln) \rightarrow$	
[N ₂ O ₅] (mol/L)	Time (s)	
1.00	0	
0.88	200	
0.78	400	
0.69	600	
0.61	800	
0.54	1000	
0.48	1200	
0.43	1400	
0.38	1600	
0.34	1800	
0.30	2000	
		- 10



Definition of Reaction Rates

• Because the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be used to express the rate.

Rate of decomposition of $N_2O_5 = -\frac{\Delta[N_2O_5]}{\Lambda}$

• Note the negative sign. This results in a positive rate as reactant concentrations decrease.

Definition of Reaction Rates

• The rate of decomposition of N_2O_5 and the formation of O_2 are easily related.



• Since two moles of N_2O_5 decompose for each mole of O_2 formed, the rate of the decomposition of N_2O_5 is twice the rate of the formation of O_2 .



Factors Affecting Reaction Rates

- Concentration of reactants.
 - More often than not, the rate of a reaction increases when the concentration of a reactant is increased.
 - Increasing the population of reactants increases the likelihood of a successful collision.
 - In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.







Factors Affecting Reaction Rates

• Temperature at which a reaction occurs.

- Usually reactions speed up when the temperature increases.
- A good "rule of thumb" is that reactions approximately double in rate with a 10 °C rise in temperature.

Factors Affecting Reaction Rates

- Concentration of a catalyst.
 - A catalyst is a substance that increases the rate of a reaction <u>without being consumed</u> in the overall reaction.
 - The catalyst generally does not appear in the overall balanced chemical equation (although its presence may be indicated by writing its formula over the arrow). $2H_2O_{2(aq)} \xrightarrow{HBr(aq)} 2H_2O_{(l)} + O_{2(g)}$

Factors Affecting Reaction Rates

- Concentration of a catalyst.
 - Figure 14.2 shows the HBr catalyzed decomposition of H_2O_2 to H_2O and O_2 .

$2H_2O_{2(aq)} \xrightarrow{HBr(aq)} 2H_2O_{(1)} + O_{2(g)}$

- A catalyst speeds up reactions by reducing the "activation energy" needed for successful reaction.
- A catalyst may also provide an alternative mechanism, or pathway, that results in a faster rate.



Factors Affecting Reaction Rates

Effect of Surface Area of Solid or Catalyst (in case of solids) or Pressure (gases)

Increasing the surface area of a solid reactant or catalyst or the pressure of a gaseous reactant (without increasing the actual amount of the gas) usually increases the reaction rate.

In the case of the solid reactant or catalyst there are more available reaction sites. In the case of the gas, the likelihood collisions resulting in reaction increases Figure 12.8: The decomposition reaction: $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

takes place on a platinum surface.



Types of Rate Laws

- Differential Rate Law: expresses how <u>rate</u> depends on <u>concentration</u>.
- Integrated Rate Law: expresses how concentration depends on time.

Dependence of Rate on Concentration

 $-2 \text{ NO}_2(g) \Rightarrow 2 \text{ NO}(g) + \text{ O}_2(g)$

- When the concentration of nitrogen dioxide is doubled, the reaction rate doubles.
- We need a mathematical expression to relate the rate of the reaction to the concentrations of the reactants.

Rate = - Δ [NO₂]/ Δ t = ?



		Concentration (mol/L)	
Time (±1 s)	NO ₂	NO	O ₂
0	0.0100	0	0
50	0.0079	0.0021	0.001
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0020
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.003
350	0.0034	0.0066	0.003
400	0.0031	0.0069	0.003



Decomposit	2 te (in mol/L · s) of ion of Nitrogen a Function of
$-\frac{\Delta[{\rm NO_2}]}{\Delta t}$	Time Period (s)
$\begin{array}{c} 4.2\times10^{-5}\\ 2.8\times10^{-5}\\ 2.0\times10^{-5}\\ 1.4\times10^{-5}\\ 1.0\times10^{-5} \end{array}$	$\begin{array}{rrrr} 0 & \rightarrow & 50 \\ 50 & \rightarrow & 100 \\ 100 & \rightarrow & 150 \\ 150 & \rightarrow & 200 \\ 200 & \rightarrow & 250 \end{array}$



Rate = $k[NO_2]^m$

- k = rate constant
- m = rate order

If rate doubles when [NO₂] is doubled, what is m?

Dependence of Rate on Concentration

- As a more general example, consider the reaction of substances A and B to give D and E. $aA+bB \xrightarrow{C} dD+eE$ C = catalyst- You could write the rate law in the form $Rate = k[A]^{m}[B]^{n}[C]^{p}$
 - The exponents m, n, and p are frequently, but not always, integers. <u>They must be determined</u> <u>experimentally</u> and cannot be obtained by simply looking at the balanced equation.

Dependence of Rate on Concentration

- Reaction Order
 - The reaction order with respect to a given reactant species equals the exponent of the concentration of that species in the rate law, as determined experimentally.
 - The overall order of the reaction equals the sum of the orders of the reacting species in the rate law.

Overall Reaction Order

•Sum of the order of each component in the rate law.

•rate = $k[H_2SeO_3][H^+]^2[I^-]^3$

•The overall reaction order is 1 + 2 + 3 = 6.

Dependence of Rate on Concentration

- Reaction Order
 - Consider the reaction of nitric oxide with hydrogen according to the following equation.

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

- The experimentally determined rate law is $Rate = k[NO]^2[H_2]$
- Thus, the reaction is second order in NO, first order in H₂, and third order overall.

Dependence of Rate on Concentration

- Reaction Order
 - Although reaction orders frequently have whole number values (particularly 1 and 2), they can be fractional.
 - Zero and negative orders are also possible.
 - The concentration of a reactant with a zero-order dependence has no effect on the rate of the reaction.

Dependence of Rate on Concentration

- Determining the Rate Law.
 - One method for determining the order of a reaction with respect to each reactant is the method of initial rates.
 - It involves running the experiment multiple times, each time varying the concentration of only one reactant and measuring its initial rate.
 - The resulting change in rate indicates the order with respect to that reactant.

Dependence of Rate on Concentration

- Determining the Rate Law.
 - If doubling the concentration of a reactant has a doubling effect on the rate, then one would deduce it was a first-order dependence.
 - If doubling the concentration had a quadrupling effect on the rate, one would deduce it was a second-order dependence.
 - A doubling of concentration that results in an eight-fold increase in the rate would be a thirdorder dependence.

Doubl	on Rate of ing the Initial ntration of	Rate = k[A] ⁿ
m	Rate Is Multiplied by:	
-1	$\frac{1}{2}$	
0	1	
1	2	
2		

A Problem to Consider • Iodide ion is oxidized in acidic solution to triiodide ion, I_3^- , by hydrogen peroxide. $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$ - A series of four experiments was run at different concentrations, and the initial rates of I_3^- formation

- From the following data, obtain the reaction orders
- with respect to H₂O₂, I⁻, and H⁺. – Calculate the numerical value of the rate constant.

	A P	nsider		
	Initial Co	ncentrations	(mol/L)	
	H ₂ O ₂	I-	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶
Exp. 3	0.010	0.020	0.00050	2.30 x 10 ⁻⁶
Exp. 4	0.010	0.010	0.00100	1.15 x 10 ⁻⁶
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- Comparing Experiment 1 and Experiment 2, you see that when the H_2O_2 concentration doubles (with other concentrations constant), the rate doubles.
- This implies a first-order dependence with respect to H₂O₂.

A Problem to Consider

	Initial Concentrations (mol/L)			
	H ₂ O ₂	I-	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶
Exp. 3	0.010	0.020	0.00050	2.30 x 10 ⁻⁶
Exp. 4	0.010	0.010	0.00100	1.15 x 10-6

 Comparing Experiment 1 and Experiment 3, you see that when the I⁻ concentration doubles (with other concentrations constant), the rate doubles.

- This implies a first-order dependence with respect to I⁻.

A Problem to Consider

	Initial Co	ncentrations	(mol/L)	
	H_2O_2	I-	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶
Exp. 3	0.010	0.020	0.00050	2.30 x 10-6
Exp. 4	0.010	0.010	0.00100	1.15 x 10 ⁻⁶

- Comparing Experiment 1 and Experiment 4, you see that when the H⁺ concentration doubles (with other concentrations constant), the rate is unchanged.

- This implies a zero-order dependence with respect to H⁺.

A Problem to Consider

	Initial Co	ncentrations	(mol/L)	
	H ₂ O ₂	I-	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶
Exp. 3	0.010	0.020	0.00050	2.30 x 10-6
Exp. 4	0.010	0.010	0.00100	1.15 x 10 ⁻⁶

- Because $[H^+]^0 = 1$, the rate law is:

Rate = $k[H_2O_2][I^-]$

– The reaction orders with respect to $\mathrm{H_2O_2},$ I-, and H+, are 1, 1, and 0, respectively.

A Problem to Consider					
	Initial Co	ncentrations	s (mol/L)		
	H ₂ O ₂	I-	H^+	Initial Rate [mol/(L·s)]	
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶	
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶	
Exp. 3	0.010	0.020	0.00050	2.30 x 10 ⁻⁶	
Exp. 4	0.010	0.010	0.00100	1.15 x 10 ⁻⁶	
	7	1 1 4		4 41	

- You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain: $k = \frac{1.15 \times 10^{-6} s^{-1}}{0.010 \times 0.010 mol/L} = 1.2 \times 10^{-2} L/(mol \cdot s)$

A Problem to Consider

	Initial Concentrations (mol/L)			
	H_2O_2	ŀ	H^+	Initial Rate [mol/(L·s)]
Exp. 1	0.010	0.010	0.00050	1.15 x 10 ⁻⁶
Exp. 2	0.020	0.010	0.00050	2.30 x 10 ⁻⁶
Exp. 3	0.010	0.020	0.00050	2.30 x 10 ⁻⁶
Exp. 4	0.010	0.010	0.00100	1.15 x 10 ⁻⁶

- You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 you obtain:

 $1.15 \times 10^{-6} \frac{\text{mol}}{L \cdot s} = k \times 0.010 \frac{\text{mol}}{L} \times 0.010 \frac{\text{mol}}{L}$

TABLE 12.5 The Results from Four Experiments to Study the Reaction $BrO_3^{-}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_3(I) + 3H_2O(I)$					
Experiment	Initial Concentration of BrO ₃ ⁻ (mol/L)	Initial Concentration of Br (mol/L)	Initial Concentration of H ⁺ (mol/L)	Measured Initial Rate (mol/L · 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	-3.2×10^{-3}	

TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(I)$					
Experiment	Initial Concentration of NH ₄ +	Initial Concentration of NO ₂ -	Initial Rate (mol/L ⋅ s)		
1	0.100 M	0.0050 M	1.35×10^{-7}		
2	0.100 M	0.010 M	2.70×10^{-7}		
3	0.200 M	0.010 M	5.40×10^{-7}		

Change of Concentration with Time

- A rate law simply tells you how the rate of reaction changes as reactant concentrations change.
 - A more useful mathematical relationship would show how a reactant concentration changes over a period of time.

Change of Concentration with Time

- A rate law simply tells you how the rate of reaction changes as reactant concentrations change.
 - Using calculus we can transform a rate law into a mathematical relationship between concentration and time.
 - This provides a **graphical method** for determining rate laws.

Concentration-Time Equations

- · First-Order Rate Law
 - You could write the rate law in the form

Rate =
$$-\frac{\Delta[A]}{\Delta t} = k[A]$$

Concentration-Time Equations

- First-Order Rate Law
 - Using calculus, you get the following equation.

$$\ln \frac{[A]_t}{[A]_o} = -kt$$

- Here $[\mathbf{A}]_t$ is the concentration of reactant A at time t, and $[\mathbf{A}]_0$ is the initial concentration.
- The ratio $[A]_t/[A]_o$ is the fraction of A remaining at time t.

TABLE 12.3Concentration/Time Data for the Reaction $2N_2O_5(soln) \rightarrow$ $4NO_2(soln) + O_2(g)$ (at 45°C)		
[N ₂ O ₅] (mol/L)	Time (s)	
1.00	0	
0.88	200	
0.78	400	
0.69	600	
0.61	800	
0.54	1000	
0.48	1200	
0.43	1400	
0.38	1600	
0.34	1800	
0.30	2000	





A Problem to Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s⁻¹. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, what is the concentration of N_2O_5 after 825 seconds?
- The first-order time-concentration equation for this reaction would be:

$\ln \frac{[N_2O_5]_t}{[N_2O_5]_0} = -kt$

A Problem to Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s⁻¹. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, what is the concentration of N_2O_5 after 825 seconds?
- Substituting the given information we obtain:

 $\ln \frac{[N_2O_5]_t}{1.65 \times 10^{-2} \text{ mol}/\text{L}} = -(4.80 \times 10^{-4} \text{ s}^{-1}) \times (825 \text{ s})$

A Problem to Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s⁻¹. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, what is the concentration of N_2O_5 after 825 seconds?
- Substituting the given information we obtain:

$$\ln \frac{[N_2 O_5]_t}{1.65 \times 10^{-2} \, mol \, / L} = -0.396$$

A Problem to Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x $10^{-4}s^{-1}$. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, what is the concentration of N_2O_5 after 825 seconds?
- Taking the inverse natural log of both sides we obtain:

$$\frac{[N_2O_5]_t}{1.65 \times 10^{-2} \text{ mol}/\text{L}} = e^{-0.396} = 0.673$$

A Problem to Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s⁻¹. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, what is the concentration of N_2O_5 after 825 seconds?
- Solving for [N₂O₅] at 825 s we obtain:

 $[N_2O_5] = (1.65 \times 10^{-2} \text{ mol} / \text{L}) \times (0.673) = 0.0111 \text{ mol} / \text{L}$







Concentration-Time Equations

- Second-Order Rate Law
 - You could write the rate law in the form

Rate =
$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

Concentration-Time Equations

- Second-Order Rate Law
 - Using calculus, you get the following equation.

$$\frac{1}{[\mathbf{A}]_{t}} = \mathbf{k}t + \frac{1}{[\mathbf{A}]_{t}}$$

- Here $[A]_t$ is the concentration of reactant A at time t, and $[A]_0$ is the initial concentration.









A Summary

- 1. Simplification: Conditions are set such that only forward reaction is important.
- 2. Two types: differential rate law integrated rate law
- 3. Which type? Depends on the type of data collected differential and integrated forms can be interconverted.

A Summary

(continued)

- 4. Most common: method of initial rates.
- 5. Concentration v. time: used to determine integrated rate law, often graphically.
- 6. For several reactants: choose conditions under which only one reactant varies significantly (pseudo first-order conditions).

	Order		
	Zero	First	Second
tate Law:	Rate $= k$	Rate = $k[A]$	Rate = $k[A]^2$
ntegrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[\mathbf{A}] = -\mathbf{k}t + \ln[\mathbf{A}]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_t}$
lot Needed to Give a Straight Line:	[A] versus t	In[A] versus t	$\frac{1}{[A]}$ versus t
lelationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
lalf-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$