

Chapter 10

Chemical Kinetics

1. Distinguish between kinetic and thermodynamic regions of a reaction.

Concentrations change in the kinetic region, but they are constant at their equilibrium values in the thermodynamic region.

3. How does an increase in temperature affect the rate of reaction?

Increasing the temperature increases the rate of any reaction.

5. Why do reaction rates slow as the reaction proceeds?

As the reaction proceeds, the reactant concentrations drop, which causes the reactions to slow.

7. Distinguish between an average and instantaneous rates of reaction.

An average rate is a change in concentration divided by the time required to produce the change. An instantaneous rate is the rate at which the concentration is changing at any given instant.

9. Consider the following plot of $[\text{NO}_2]$ versus time.

a) What is the average rate of disappearance of NO_2 over the time of the experiment?

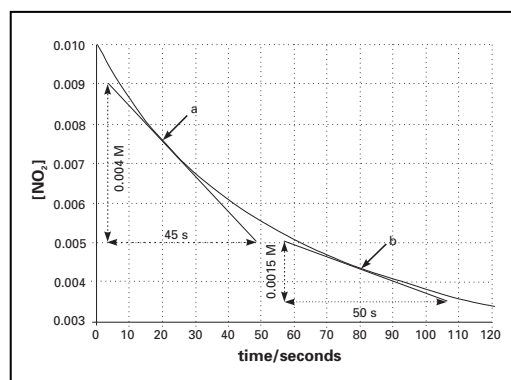
$$-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{(0.0100 \text{ M} - 0.0034 \text{ M})}{(0 \text{ s} - 120 \text{ s})} = 5.5 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$

To determine the instantaneous rates, determine the slopes of the tangent lines at the two times. The tangent lines are drawn in the above figure

b) Use the graphical methods presented in Section 10.1 to determine the rate of disappearance of NO_2

$$\text{at 20 seconds: } -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{(0.0090 \text{ M} - 0.0050 \text{ M})}{(3 \text{ s} - 48 \text{ s})} = 9 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$

$$\text{at 80 seconds: } -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{(0.0050 \text{ M} - 0.0035 \text{ M})}{(58 \text{ s} - 108 \text{ s})} = 3 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$



11. What is the rate of formation ($\text{M} \cdot \text{s}^{-1}$) of NOBr gas in a reaction in which 13.4 mmol of NOBr is produced in a 38.9 mL flask in 26.8 minutes?

$$\frac{\Delta[\text{NOBr}]}{\Delta t} = \frac{(13.4 \times 10^{-6} \text{ mol})/0.0389 \text{ L}}{26.8 \text{ min} \times \frac{60 \text{ s}}{\text{min}}} = 2.14 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}$$

13. What are the rates of appearance of NO_2 and O_2 when the rate of disappearance of N_2O_5 is $2.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$? $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

Define the rates of appearance of NO_2 and O_2 in terms of the rate of disappearance of N_2O_5 by using the coefficients from the equation.

$$\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \Rightarrow \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{4}{2} (2.0 \times 10^{-5}) = 4.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \Rightarrow \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} (2.0 \times 10^{-5}) = 1.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$

15. What is an exponential decay? What type of kinetics is characterized by an exponential decay?

A function, such as $y = e^{-ax}$, that decreases exponentially is an exponential decay. First order kinetics are characterized by an exponential decay.

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17. A reaction has the experimentally determined rate law: $\text{rate} = k[\text{A}][\text{B}]^2$.

a) What is the reaction order?

In a rate law, the sum of all the exponents in the rate law is called the *overall order* of the reaction.
overall order = $1+2 = 3$

b) What is the order with respect to A?

The exponent on each reactant exponent is referred to as the *reactant order*, in this case the order with respect to reactant A is 1.

c) What is the order with respect to B?

The concentration of B is squared in the rate law, so the reaction is second order with respect to B.

19. The reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ is second order in NO_2 . What is the second-order rate constant if the rate of formation of O_2 is $5.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$ when the concentration of NO_2 is 0.012 M ?

The rate of formation of O_2 is given: $\frac{\Delta[\text{O}_2]}{\Delta t} = 5.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$

The problem states that the reaction is "second order with respect to NO_2 ." Solve the rate law for the rate constant.

$$\frac{\Delta[\text{O}_2]}{\Delta t} = 5.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1} = k[\text{NO}_2]^2 = k(0.012)^2 \quad \rightarrow \quad k = \frac{5.0 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}}{(0.012)^2 \text{ M}^2} = 0.35 \text{ M}^{-1} \cdot \text{s}^{-1}$$

21. The following initial rate data were obtained for the reaction: $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$.

Experiment	$[\text{NO}]_0$	$[\text{H}_2]_0$	$(\Delta[\text{N}_2]/\Delta t)_0 \text{ M/s}$
I	0.326	0.118	0.0859
II	0.109	0.118	0.00954
III	0.326	0.0295	0.0215

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

Use Experiments I and II to obtain the order of NO. The concentration of H_2 can be ignored because it does

not change. $\frac{R_{\text{I}}}{R_{\text{II}}} = \frac{0.0859 \text{ M} \cdot \text{s}^{-1}}{0.00954 \text{ M} \cdot \text{s}^{-1}} = 9.00 = \left(\frac{0.326 \text{ M}}{0.109 \text{ M}}\right)^x = 3.00^x \Rightarrow x = 2$

The reaction is 2nd order in NO. Next, use Experiments I and III to obtain the order of H_2 . The concentration of NO

can be ignored because it does not change. $\frac{R_{\text{I}}}{R_{\text{III}}} = \frac{0.0859 \text{ M} \cdot \text{s}^{-1}}{0.0215 \text{ M} \cdot \text{s}^{-1}} = 4.00 = \left(\frac{0.118 \text{ M}}{0.0295 \text{ M}}\right)^y = 4.00^y \Rightarrow y = 1$

The reaction is 1st order in H_2 , so the rate law is $\text{Rate} = (\Delta[\text{N}_2]/\Delta t) = k[\text{NO}]^2[\text{H}_2]$

The rate is solved for k, and the results of experiment I are substituted into the equation to obtain the specific

rate constant. $k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{0.0859 \text{ M} \cdot \text{s}^{-1}}{(0.326 \text{ M})^2(0.118 \text{ M})} = 6.85 \text{ M}^{-2} \cdot \text{s}^{-1}$

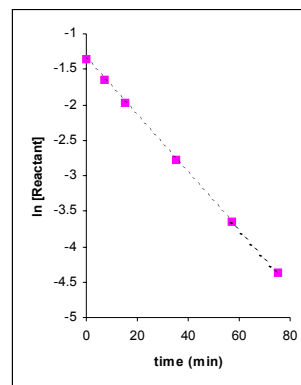
23. The kinetics of the conversion of cyclopropane to propene were studied at 500 °C by monitoring the concentration of cyclopropane versus time. The following data were obtained:

t	0	7.0	15.0	35.0	57.0	75.0	min
[Δ]	0.256	0.193	0.140	0.0626	0.0259	0.0126	M

Verify the first-order kinetics and determine the rate constant and half-life of the reaction at 500 °C.

Equation 10.4 indicates that a plot of $\ln [\Delta]$ versus time should be linear if the reaction is first order, so we first determine the values of $\ln[\Delta]$ and then plot the results

t (min)	[Δ]	ln [Δ]
0	0.256	-1.363
7	0.193	-1.645
15	0.140	-1.966
35	0.0626	-2.771
57	0.0259	-3.564
75	0.0126	-4.374

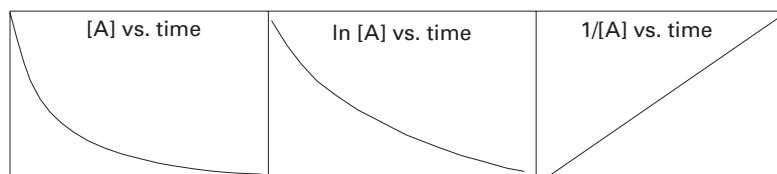


The resulting plot is a straight line, so the reaction is first order. The first order rate constant is obtained from the slope of the line, which can be obtained from the slope of the best-fit line shown in the figure. Alternatively, it can be determined from two points. For example, for the change between 0 to 7 minutes, we obtain

$$\text{slope} = \frac{\Delta \ln[\text{cyclopropane}]}{\Delta t} = \frac{-1.645 - (-1.363)}{7 \text{ min} - 0} = -0.040 \text{ min}^{-1}$$

The first order rate constant is simply the negative of the slope or $k = 0.040 \text{ min}^{-1}$. The half-life of the conversion is determined with Equation 10.6: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.040 \text{ min}^{-1}} = 17 \text{ min}$

25. The kinetics of the reaction $2A \rightarrow C$ was studied by monitoring the concentration of A as a function of time. The following graphs were constructed from the data:



- a) What is the rate law for the reaction?

The $1/[A]$ vs. t plot is linear, so this reaction is second order.

- b) Given the following concentrations, determine the specific rate constant for the reaction at the temperature of the experiment.

t	0	2.000	5.000	s
[A]	0.2600	0.0892	0.0450	M

The coefficient of A is 2, so the slope of the $1/[A]$ vs. t plot is $2k$.

$$2k = \text{slope} = \frac{\Delta(1/A)}{\Delta t} = \frac{\frac{1}{0.0450} \text{ M}^{-1} - \frac{1}{0.2600} \text{ M}^{-1}}{5.000 \text{ s} - 0 \text{ s}} = 3.68 \text{ M}^{-1} \cdot \text{s}^{-1}; k = \frac{3.68 \text{ M}^{-1} \cdot \text{s}^{-1}}{2} = 1.84 \text{ M}^{-1} \cdot \text{s}^{-1}$$

27. Explain how the rate of a reaction would change if the hydronium ion concentration were doubled if the reaction is

- a) First order in H^{1+}

Rate = $k [\text{H}^{1+}]^1$, the rate is proportional to $[\text{H}^{1+}]$, therefore rate would double.

- b) Second order in H^{1+}

Rate = $k [\text{H}^{1+}]^2$, the rate is proportional to the square of $[\text{H}^{1+}]$, therefore the rate quadruples.

Chemical Kinetics

29. Living organisms maintain a constant level of carbon-14, but upon death of the organism, the carbon-14 decays with first-order kinetics with a half-life of 5730 years. The decay is the basis of carbon dating. The carbon-14 level in a piece of charcoal at an archeological dig was found to be 62% of the constant level maintained by living organisms. Approximate the age of the charcoal.

$$\text{The rate constant is } k = \frac{\ln(2)}{5730} = \frac{0.693}{5730} = 1.21 \times 10^{-4} \text{ years}^{-1}$$

Calculate the age of the charcoal using this rate constant. The amount of ^{14}C remaining is 62% that of the original, so the $[\text{C}^{14}]_0/[\text{C}^{14}]$ ratio is $1/0.62 = 1.61$.

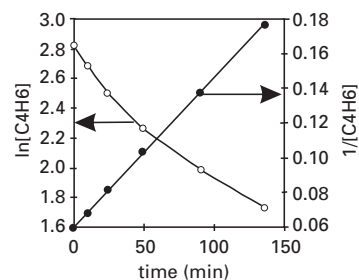
$$1.21 \times 10^{-4} \text{ years}^{-1} = \frac{\ln(1.61)}{t}, \text{ so } t = \frac{\ln(1.61)}{1.21 \times 10^{-4} \text{ years}^{-1}} = 3.95 \times 10^3 \text{ years}$$

31. The gas phase dimerization of butadiene (see below) was monitored at 326°C . Determine the order of the reaction and the rate constant at 326°C .

t	0	10.1	24.5	49.5	90.1	135.7	min
$[\text{C}_4\text{H}_6]$	16.79	14.64	12.26	9.67	7.29	5.67	mM

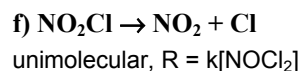
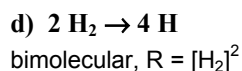
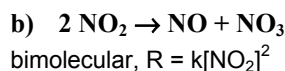
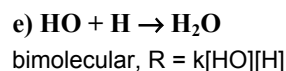
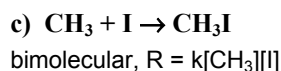
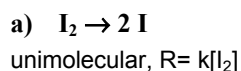
Tabulate $\ln [\text{C}_4\text{H}_6]$ and $1/[\text{C}_4\text{H}_6]$ and plot them both against $t(\text{min})$. If $\ln[\text{C}_4\text{H}_6]$ is linear with respect to time, the reaction is first order. If $1/[\text{C}_4\text{H}_6]$ is linear with respect to time, the reaction is second order.

t (min)	0	10.1	24.5	49.5	90.1	135.7
$[\text{C}_4\text{H}_6]$	16.79	14.64	12.26	9.67	7.29	5.67
$\ln [\text{C}_4\text{H}_6]$	2.821	2.684	2.506	2.269	1.987	1.735
$1/[\text{C}_4\text{H}_6]$	0.0596	0.0683	0.0816	0.1034	0.1372	0.1764

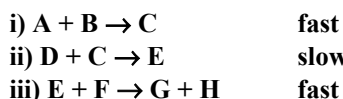


$1/[\text{C}_4\text{H}_6]$ is linear with respect to time. Thus, the reaction is 2^{nd} order in C_4H_6 . The rate constant is equal to the slope of the line, which is $8.6 \times 10^{-4} \text{ mM}^{-1}\cdot\text{min}^{-1}$ or $0.86 \text{ M}^{-1}\cdot\text{min}^{-1}$.

33. Each of the following is an elementary reaction. Indicate the molecularity and write the rate law for each.



35. Consider the following three-step mechanism:

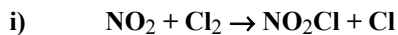


- a) What is the molecularity of each step? All steps are bimolecular
b) Identify any intermediate(s). C and E are intermediates
c) What is the overall reaction? $\text{A} + \text{B} + \text{D} + \text{F} \rightarrow \text{G} + \text{H}$
d) What is the rate law?

The rate law of the RDS is $\text{Rate} = k_2[\text{D}][\text{C}]$. C is an intermediate and cannot appear in the rate law, so we use the equilibrium established in Step I to determine its concentration in terms of [A] and [B].

$K_1 = [\text{C}]/[\text{A}][\text{B}]$, so $[\text{C}] = K_1[\text{A}][\text{B}]$, which is substituted into the RDS rate law to yield the rate law for the reaction: $\text{Rate} = k[\text{A}][\text{B}][\text{D}]$.

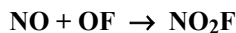
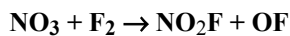
37. Consider the following two-step mechanism:



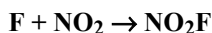
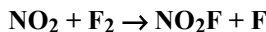
- a) Write the overall reaction. Add the two reactions together: $2 \text{NO}_2 + \text{Cl}_2 \rightarrow 2 \text{NO}_2\text{Cl}$
- b) What is the intermediate? The Cl atoms cancelled in the sum, so Cl is the intermediate.
- c) The first step is the rate-determining step. What is the rate law? $R = k[\text{NO}_2][\text{Cl}_2]$

39. Consider the two mechanisms shown below. The rate law for the reaction is $\text{Rate} = k[\text{NO}_2]^2$.

Mechanism I



Mechanism II



a) Which mechanism is NOT acceptable. Explain.

Mechanism II is not acceptable. The rate law derived from it would be first order in F_2 because F_2 reacts in the first step, but the observed rate law is zero order in F_2 .

b) What is the rate-determining step?

The rate is derived from the rate-determining step, which is the first step. Any step beyond the first step would involve F_2 in the rate law.

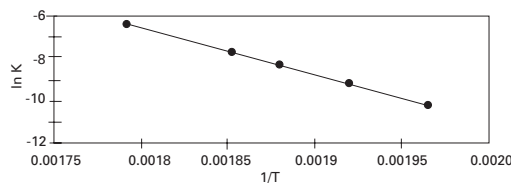
41. What is an Arrhenius plot? How is it used?

An Arrhenius plot is a plot of the rate constant against $1/T$. The result is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$, where A is called the preexponential. An Arrhenius plot can be used to determine activation energies or rate constants at different temperatures.

43. The following rate constant data were obtained for the isomerization reaction shown below. What is the activation energy for the isomerization?

t ($^{\circ}\text{C}$)	236	248	259	267	285
k	0.376	1.08	2.44	4.61	16.6

$\times 10^4 \text{ s}^{-1}$



A plot $\ln k$ vs. $1/T$ (shown to the right) has a slope of $-2.18 \times 10^4 \text{ K}$. The activation energy for the isomerization is then determined from Equation 10.9.

$$E_a = -R \times \text{slope}$$

$$= -(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(-2.18 \times 10^4 \text{ K})$$

$$= 182 \text{ kJ/mol}$$

45. The rate constant for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is $4.3 \times 10^{-7} \text{ M}^{-1}\cdot\text{s}^{-1}$ at 500 K and 6.3×10^{-2} at 700 K. What is the activation energy for the reaction and what is the rate constant at 600 K?

Use Equation 10.11

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \ln \frac{6.3 \times 10^{-2}}{4.3 \times 10^{-7}}}{\frac{1}{500 \text{ K}} - \frac{1}{700 \text{ K}}} = 1.73 \times 10^5 \text{ J/mol} = 173 \text{ kJ/mol}$$

Using Equation 10.10 and the above activation energy to find the rate constant at 600 K:

$$\ln \left[\frac{k_2}{4.3 \times 10^{-7}} \right] = \frac{1.73 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \times \left[\frac{1}{500} - \frac{1}{600} \right] = 6.94$$

$$\frac{k_2}{4.3 \times 10^{-7}} = e^{6.94} = 1.0 \times 10^3$$

$$k = (4.3 \times 10^{-7})(1.0 \times 10^3) = 4.3 \times 10^{-4} \text{ M}^{-1}\cdot\text{s}^{-1}$$

Chemical Kinetics

47. Distinguish between a homogeneous catalyst and a heterogeneous catalyst.

A homogeneous catalyst is in the same phase as the reactants, while a heterogeneous catalyst is in a different phase than the reactants. Heterogeneous catalysts are often solids that increase the rate of a gas or liquid phase reaction. For example the catalytic converter in an automobile is a mixture of Pt, Pd, and Rh that completes the combustion of CO and unspent hydrocarbons in automobile exhaust.

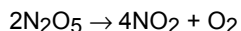
49. What distinguishes a transition state from an intermediate?

A transition state is species that the reaction passes through. Transition states cannot be observed because they lie at the maxima of the energy curve for the reaction. An intermediate is a species produced in one step of the reaction mechanism, then consumed in a later step. Intermediates lie in minima in the reaction energy curve, so they can often be observed or even isolated if they lie in a deep well.

51. Consider the following three-step mechanism:



- a) What is the overall reaction? Note: the first elementary reaction must be multiplied by two to obtain the correct stoichiometry, but it is still unimolecular.



- b) What are the intermediates? NO_3 and NO are intermediates

- c) What is the rate law? $R = k_2[\text{NO}_2][\text{NO}_3] = K_1k_2[\text{N}_2\text{O}_5] = k[\text{N}_2\text{O}_5]$