

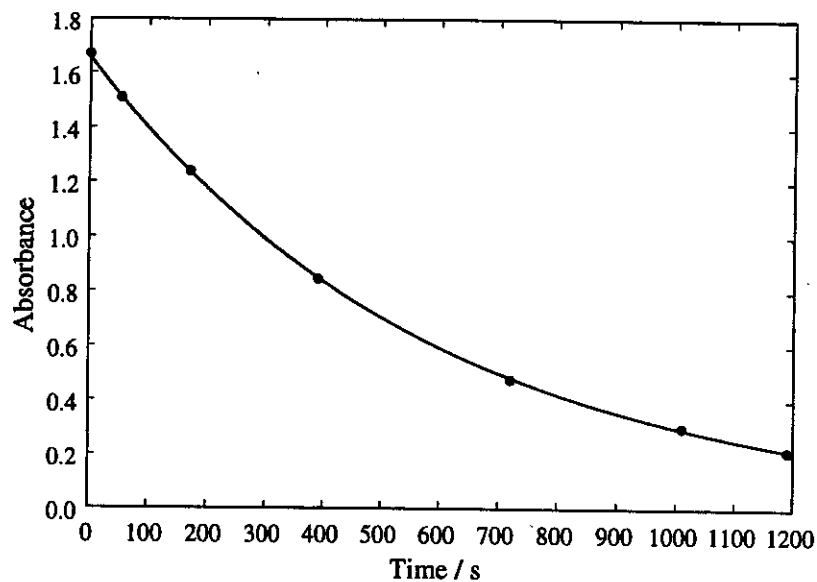
12.9

The progress of a reaction in the aqueous phase was monitored by the absorbance of a reactant at various times:

Time/s	0	54	171	390	720	1010	1190
Absorbance	1.67	1.51	1.24	0.847	0.478	0.301	0.216

Determine the order of the reaction and the rate constant.

The absorbance of a reactant is proportional to its concentration. The following plot shows absorbance as a function of time for the reactant.



According to the plot, the absorbance decreases from 1.4 to 0.70 as t goes from 100 s to 505 s. That is, the half-life is 405 s when the absorbance is 1.4. The absorbance decreases from 0.70 to 0.35, over the period t equals 505 s to 910 s. That is, the half-life is 405 s when the absorbance is 0.70. Since the half-life is independent of reactant concentration, this is a first order reaction.

Let $[C]$ and $[C]_0$ be the concentrations of the reactant at time t and at the beginning of the reaction respectively; and let A and A_0 be the absorbance of the reactant at time t and at the beginning of the reaction, respectively. Since this is a first-order reaction,

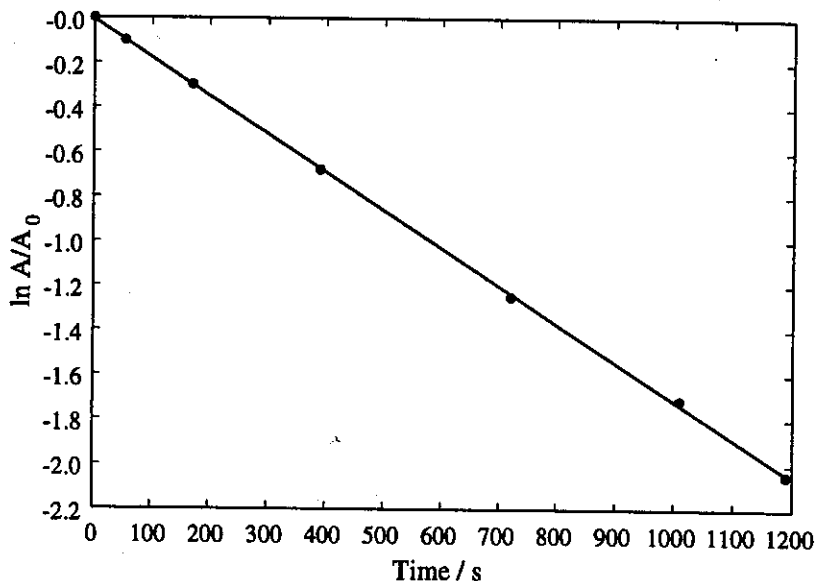
$$[C] = [C]_0 e^{-kt}$$

$$\ln \frac{[C]}{[C]_0} = \ln \frac{A}{A_0} = -kt$$

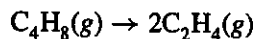
A plot of $\ln(A/A_0)$ vs t will give a straight line with a slope of $-k$.

Time/s	0	54	171	390	720	1010	1190
$\ln(A/A_0)$	0.0000	-0.1007	-0.2977	-0.6789	-1.251	-1.713	-2.045

The equation of the line is $y = -1.71 \times 10^{-3}x - 6.94 \times 10^{-3}$. Therefore, $k = 1.71 \times 10^{-3} \text{ s}^{-1}$.



12.10 Cyclobutane decomposes to ethylene according to the equation

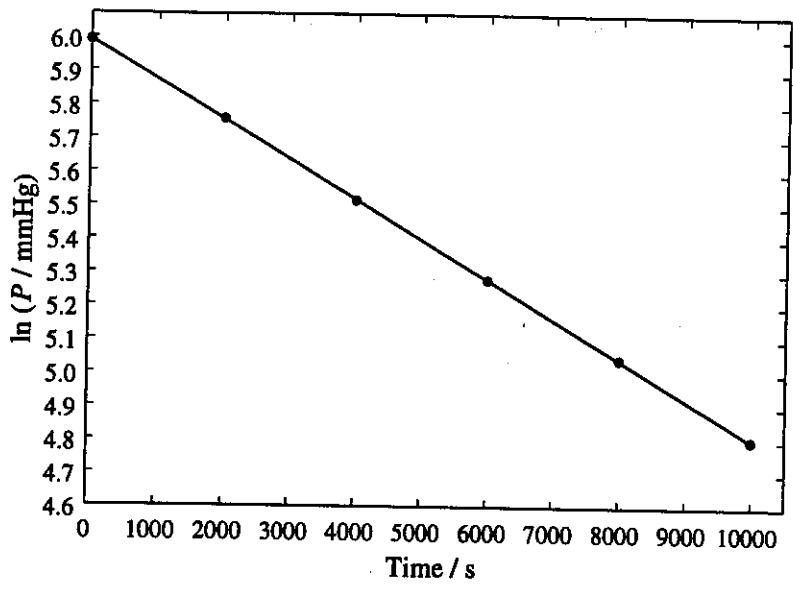


Determine the order of the reaction and the rate constant based on the following pressures, which were recorded when the reaction was carried out at 430°C in a constant-volume vessel:

Time/s	$P_{\text{C}_4\text{H}_8}$ /mmHg
0	400
2000	316
4000	248
6000	196
8000	155
10000	122

At constant temperature and volume, the pressure of cyclobutane is proportional to its concentration. A plot of $\ln P$ vs t shows a straight line with an equation of $y = -1.19 \times 10^{-4}x + 5.99$. Thus, the reaction is first order.

The slope of the line is $-k$. In other words, $k = 1.19 \times 10^{-4} \text{ s}^{-1}$.



12.11 What is the half-life of a compound if 75% of a given sample of the compound decomposes in 60 min? Assume first-order kinetics.

The rate constant is first calculated.

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$k = -\frac{1}{t} \ln \frac{[A]}{[A]_0} = -\frac{1}{60 \text{ min}} \ln (1 - 0.75) = 2.31 \times 10^{-2} \text{ min}^{-1}$$

The half-life is

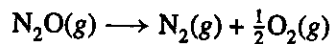
$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{2.31 \times 10^{-2} \text{ min}^{-1}} = 30 \text{ min}$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$t = \frac{1}{k} \left(\frac{1}{[A]} - \frac{1}{[A]_0} \right) = \frac{1}{0.54 \text{ M}^{-1} \text{ s}^{-1}} \left(\frac{1}{0.28 \text{ M}} - \frac{1}{0.62 \text{ M}} \right) = 3.6 \text{ s}$$

12.13 The decomposition of N_2O to N_2 and O_2 is a first-order reaction. At 730°C , the half-life of the reaction is 3.58×10^3 min. If the initial pressure of N_2O is 2.10 atm at 730°C , calculate the total gas pressure after one half-life. Assume that the volume remains constant.

The reaction is



After one half-life, the pressure of N_2O becomes 1.05 atm. Since an equal amount, 1.05 atm, of N_2O reacts, 1.05 atm of N_2 and $1.05 \text{ atm}/2 = 0.525 \text{ atm}$ of O_2 are produced. Therefore, the total gas pressure is

$$P = P_{\text{N}_2\text{O}} + P_{\text{N}_2} + P_{\text{O}_2} = 1.05 \text{ atm} + 1.05 \text{ atm} + 0.525 \text{ atm} = 2.63 \text{ atm}$$

12.17 If the first half-life of a zero-order reaction is 200 s, what will be the duration of the next half-life?

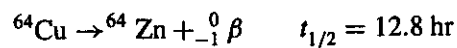
Since the first half-life is 200 s,

$$\frac{[\text{A}]_0}{2k} = 200 \text{ s}$$

The next half-life is

$$\frac{\frac{[\text{A}]_0}{2}}{2k} = \frac{[\text{A}]_0}{4k} = \frac{200 \text{ s}}{2} = 100 \text{ s}$$

12.18 Consider the following nuclear decay



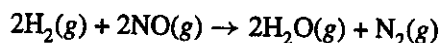
Starting with one mole of ${}^{64}\text{Cu}$, calculate the number of grams of ${}^{64}\text{Zn}$ formed after 25.6 hours.

Two half-lives would have elapsed after 25.6 hours. After the first half-life, $1/2$ mole of ${}^{64}\text{Cu}$ would remain. After the second half-life, $1/4$ mol of ${}^{64}\text{Cu}$ would remain. Thus, a total of $3/4$ mole of ${}^{64}\text{Cu}$ decays to form $3/4$ mole of ${}^{64}\text{Zn}$. The mass of ${}^{64}\text{Zn}$ produced is

$$m = \left(\frac{3}{4} \text{ mol}\right) (63.93 \text{ g mol}^{-1}) = 47.95 \text{ g}$$

12.22 The following data were collected for the reaction between hydrogen and nitric oxide at 700°C:

6



Experiment	$[\text{H}_2]/\text{M}$	$[\text{NO}]/\text{M}$	Initial rate/ $\text{M}\cdot\text{s}^{-1}$
1	0.010	0.025	2.4×10^{-6}
2	0.0050	0.025	1.2×10^{-6}
3	0.010	0.0125	0.60×10^{-6}

- (a) What is the rate law for the reaction? (b) Calculate the rate constant for the reaction.
(c) Suggest a plausible reaction mechanism that is consistent with the rate law. (*Hint:* Assume that the oxygen atom is the intermediate.) (d) More careful studies of the reaction show that the rate law over a wide range of concentrations of reactants should be

$$\text{rate} = \frac{k_1[\text{NO}]^2[\text{H}_2]}{1 + k_2[\text{H}_2]}$$

What happens to the rate law at very high and very low hydrogen concentrations?

(a) Comparing Experiment 1 and Experiment 2, the concentration of NO is constant and the concentration of H_2 has decreased by one-half. The initial rate has also decreased by one-half. Therefore, the initial rate is directly proportional to the concentration of H_2 . That is, the reaction is first order in H_2 .

Comparing Experiment 1 and Experiment 3, the concentration of H_2 is constant and the concentration of NO has decreased by one-half. The initial rate has decreased by one-fourth. Therefore, the initial rate is proportional to the squared concentration of NO. That is, the reaction is second order in NO.

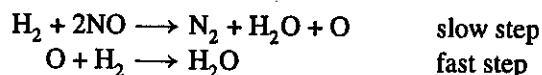
Therefore, the rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

(b) Using Experiment 1 to calculate the rate constant,

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{2.4 \times 10^{-6} \text{ M s}^{-1}}{(0.025 \text{ M})^2 (0.010 \text{ M})} = 0.38 \text{ M}^{-2} \text{ s}^{-1}$$

(c) The rate law suggests that the slow step in the reaction mechanism will probably involve one H_2 molecule and two NO molecules. Additionally, the hint suggests that the O atom is an intermediate. A plausible mechanism is



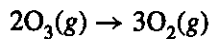
(d) At very high hydrogen concentrations, $k_2[\text{H}_2] \gg 1$. Therefore, the rate law becomes

$$\text{rate} = \frac{k_1[\text{NO}]^2[\text{H}_2]}{k_2[\text{H}_2]} = \frac{k_1}{k_2}[\text{NO}]^2$$

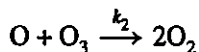
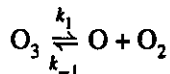
At very low hydrogen concentrations, $k_2[\text{H}_2] \ll 1$. Therefore, the rate law becomes

$$\text{rate} = k_1[\text{NO}]^2[\text{H}_2]$$

7
12.23 The rate law for the decomposition of ozone to molecular oxygen



is rate = $k \frac{[\text{O}_3]^2}{[\text{O}_2]}$. The mechanism proposed for this process is



Derive the rate law from these elementary steps. Clearly state the assumptions you use in the derivation. Explain why the rate decreases with increasing O_2 concentration.

The first step involves forward and reverse reactions that are much faster than the second step. The rates of the reaction in the first step are given by

$$\text{Forward rate} = k_1[\text{O}_3]$$

$$\text{Reverse rate} = k_{-1}[\text{O}][\text{O}_2]$$

Assume that these two processes rapidly reach a state of dynamic equilibrium in which the rates of the forward and reverse reactions are equal:

$$k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2]$$

Solving for $[\text{O}]$,

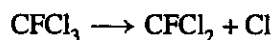
$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

The rate for the second step gives the rate of reaction,

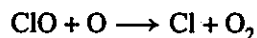
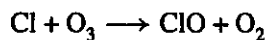
$$\text{Rate} = k_2[\text{O}][\text{O}_3] = k_2 \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} [\text{O}_3] = \frac{k_1 k_2}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

The rate law shows that higher concentrations of O_2 will decrease the reaction rate. This is due to the reverse reaction in the first step of the mechanism. If more O_2 molecules are present, they will serve to scavenge free O atoms and thus slow the disappearance of O_3 .

12.25 In recent years, ozone in the stratosphere has been depleted at an alarmingly fast rate by chlorofluorocarbons (CFCs). A CFC molecule such as CFCl_3 is first decomposed by UV radiation:

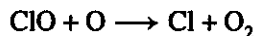
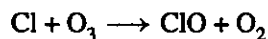


The chlorine radical then reacts with ozone as follows:

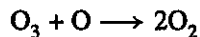


(a) Write the overall reaction for the last two steps. (b) What are the roles of Cl and ClO? (c) Why is the fluorine radical not important in this mechanism? (d) One suggestion for reducing the concentration of chlorine radicals is to add hydrocarbons such as ethane (C_2H_6) to the stratosphere. How will this approach work? (e) Draw potential energy versus reaction progress diagrams for the uncatalyzed and catalyzed (by Cl) destruction of ozone: $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$. Use the thermodynamic data in Appendix B to determine whether the reaction is exothermic or endothermic.

(a) The sum of the following reactions



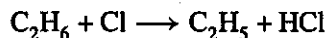
gives



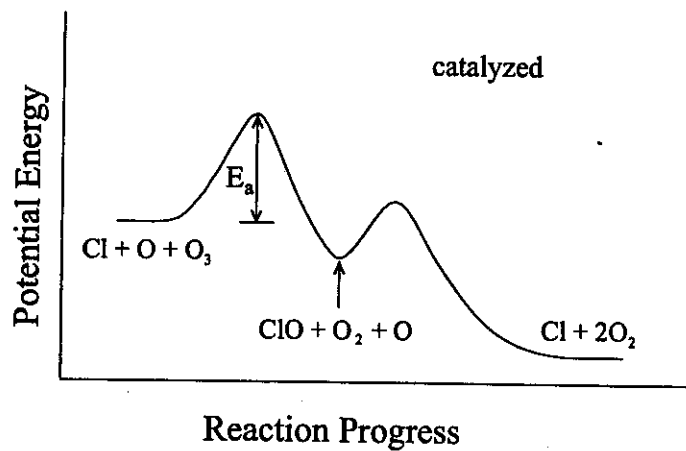
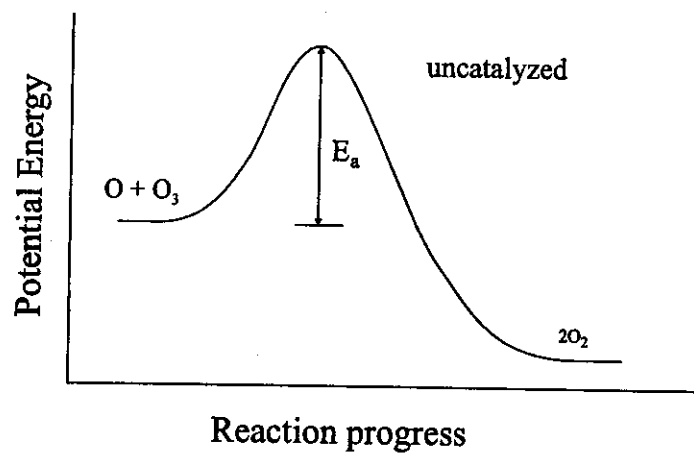
(b) Cl is a catalyst; ClO is an intermediate.

(c) The C–F bond is stronger than the C–Cl bond. Thus, Cl is formed more easily than F.

(d) Ethane will remove the Cl atom:



(e)



The reaction is exothermic.

12.28 Over a range of about $\pm 3^\circ\text{C}$ from normal body temperature the metabolic rate, M_T , is given by $M_T = M_{37} (1.1)^{\Delta T}$, where M_{37} is the normal rate and ΔT is the change in T . Discuss this equation in terms of a possible molecular interpretation. [Source: "Eco-Chem," J. A. Campbell, *J. Chem. Educ.* **52**, 327 (1975).]

Converting to kelvin, and using the Arrhenius equation,

$$\ln \frac{M_T}{M_{37}} = -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{310 \text{ K}} \right)$$

Since the temperature range is so small, $f(T) = \frac{1}{T} - \frac{1}{310 \text{ K}}$ may be expanded in a Taylor series about $T_0 = 310 \text{ K}$. Keeping only the first non-zero term results in $f(T) \approx -\frac{\Delta T}{T_0^2}$, where $\Delta T = 310 \text{ K} - T$. Thus,

$$\ln \frac{M_T}{M_{37}} = \frac{E_a}{R} \frac{\Delta T}{T_0^2}$$

or

$$M_T = M_{37} e^{\frac{E_a}{RT_0^2} \Delta T} = M_{37} \left(e^{\frac{E_a}{RT_0^2}} \right)^{\Delta T} = M_{37} (\text{constant})^{\Delta T}$$

which is of the observed form, providing an implicit factor of 1 K^{-1} is incorporated into the argument of the exponential function and the ΔT is interpreted as a unitless number. Specifically, it must be true that

$$e^{\frac{E_a}{RT_0^2}} = 1.1$$

$$\frac{E_a}{RT_0^2} = \ln 1.1 = 0.0953$$

$$E_a = (1 \text{ K}^{-1}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K})^2 (0.0953) = 7.6 \times 10^4 \text{ J mol}^{-1}$$

This activation energy is consistent with a single rate determining step controlling the metabolic rate within this temperature range.

- 12.29 The rate of bacterial hydrolysis of fish muscle is twice as great at 2.2°C as at -1.1°C. Estimate a ΔE_a value for this reaction. Is there any relation to the problem of storing fish for food? [Source: "Eco-Chem," J. A. Campbell, *J. Chem. Educ.* 52, 390 (1975).]

Using the Arrhenius equation, with temperatures converted to the kelvin scale,

$$\ln \frac{k_{275.4}}{k_{272.1}} = -\frac{E_a}{R} \left(\frac{1}{275.4 \text{ K}} - \frac{1}{272.1 \text{ K}} \right)$$

$$\ln 2 = -\frac{E_a}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{275.4 \text{ K}} - \frac{1}{272.1 \text{ K}} \right)$$

$$E_a = 1.3 \times 10^5 \text{ J mol}^{-1}$$

(Note that there is a math error in the solution given in the reference that makes the answer there too large by a factor of 3.3².) Nevertheless, this is a relatively large E_a , and temperature will have a large effect on reaction rate. Thus, refrigeration is an essential, effective method of preserving fish and preventing spoilage. Note that the rate of bacterial hydrolysis at room temperature (298 K) is 74 times greater than the rate at 275.4 K.

- 12.30 The rate constants for the first-order decomposition of an organic compound in solution are measured at several temperatures:

k/s^{-1}	4.92×10^{-3}	0.0216	0.0950	0.326	1.15
$t/^\circ\text{C}$	5.0	15	25	35	45

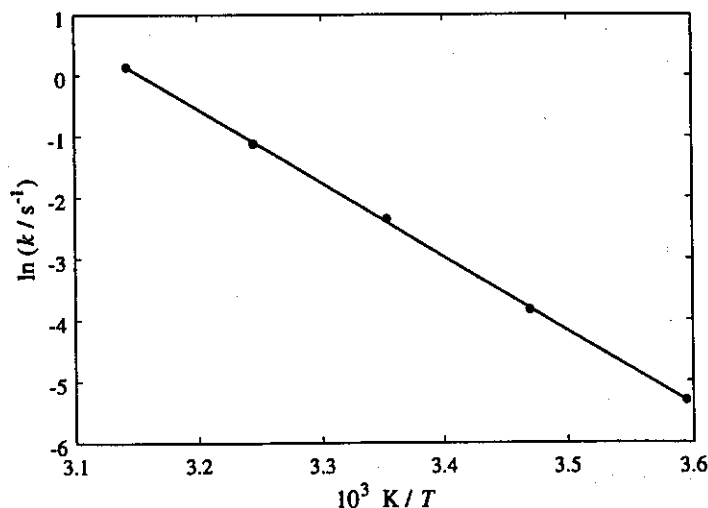
Determine graphically the pre-exponential factor and the energy of activation for the reaction.

Since

$$\ln k = \ln A - \frac{E_a}{RT}$$

A plot of $\ln k$ vs $1/T$ gives a slope of $-E_a/R$ and an intercept of $\ln A$. The following data are used for the plot:

$10^3 \text{ K}/T$	3.595	3.470	3.353	3.245	3.143
$\ln(k/s^{-1})$	-5.314	-3.835	-2.354	-1.121	0.140



The equation for the line that best fits these points is $y = -1.207 \times 10^4 x + 38.06$. Therefore,

$$E_a = -(-1.207 \times 10^4 \text{ K}^{-1})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 1.00 \times 10^5 \text{ J mol}^{-1}$$

- 12.33 The rate at which tree crickets chirp is 2.0×10^2 per minute at 27°C but only 39.6 per minute at 5°C . From these data, calculate the "activation energy" for the chirping process. (*Hint:* The ratio of rates is equal to the ratio of rate constants.) Find the chirping rate at 15°C .

First find the "activation energy" for the chirping process.

$$\ln \frac{k_2}{k_1} = \ln \frac{\text{Rate}_2}{\text{Rate}_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{2.0 \times 10^2 \text{ min}^{-1}}{39.6 \text{ min}^{-1}} = -\frac{E_a}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{300.2 \text{ K}} - \frac{1}{278.2 \text{ K}} \right)$$

$$E_a = 5.111 \times 10^4 \text{ J mol}^{-1} = 5.11 \times 10^4 \text{ J mol}^{-1}$$

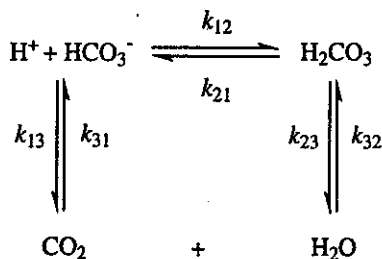
Now use one of the known rates and E_a to find the chirping rate at 15°C (288.2 K).

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{\text{Rate}_2}{39.6 \text{ min}^{-1}} = -\frac{5.111 \times 10^4 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{288.2 \text{ K}} - \frac{1}{278.2 \text{ K}} \right)$$

$$\text{Rate}_2 = 85.2 \text{ min}^{-1}$$

12.44 The equilibrium between dissolved CO_2 and carbonic acid can be represented by



Show that

$$-\frac{d[\text{CO}_2]}{dt} = (k_{31} + k_{32})[\text{CO}_2] - \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-]$$

where $K = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$.

From the equilibrium,

$$\frac{d[\text{CO}_2]}{dt} = k_{13}[\text{H}^+][\text{HCO}_3^-] - k_{31}[\text{CO}_2] + k_{23}[\text{H}_2\text{CO}_3] - k_{32}[\text{CO}_2]$$

Since H_2O is present in a great quantity, the effectively constant concentration, $[\text{H}_2\text{O}]$, is incorporated into the constants k_{31} and k_{32} . Rearranging the expression gives

$$\frac{d[\text{CO}_2]}{dt} = -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23}[\text{H}_2\text{CO}_3] \quad (12.44.1)$$

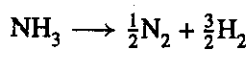
Since H^+ and HCO_3^- are in equilibrium with H_2CO_3 , let

$$\begin{aligned}
 K &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \\
 [\text{H}_2\text{CO}_3] &= \frac{[\text{H}^+][\text{HCO}_3^-]}{K} \quad (12.44.2)
 \end{aligned}$$

Substitute Eq. 12.44.2 into Eq. 12.44.1,

$$\begin{aligned}
 \frac{d[\text{CO}_2]}{dt} &= -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23} \frac{[\text{H}^+][\text{HCO}_3^-]}{K} \\
 &= -(k_{31} + k_{32})[\text{CO}_2] + \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-] \\
 -\frac{d[\text{CO}_2]}{dt} &= (k_{31} + k_{32})[\text{CO}_2] - \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-]
 \end{aligned}$$

12.48 At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows:



The kinetic data are expressed as the variation of the half-life with the initial pressure of NH₃:

<i>P</i> /torr	264	130	59	16
<i>t</i> _{1/2} /s	456	228	102	60

- (a) Determine the order of the reaction.
- (b) How does the order depend on the initial pressure?
- (c) How does the mechanism of the reaction vary with pressure?

(a) The half-life of a reaction and the initial concentration are related by

$$t_{1/2} = C \frac{1}{[A]_0^{n-1}}$$

where *C* is a constant. Taking the common logarithm of both sides of the equation,

$$\log t_{1/2} = \log C - (n - 1) \log [A]_0$$

Since pressure is proportional to concentration at constant temperature, the above equation can also be written as

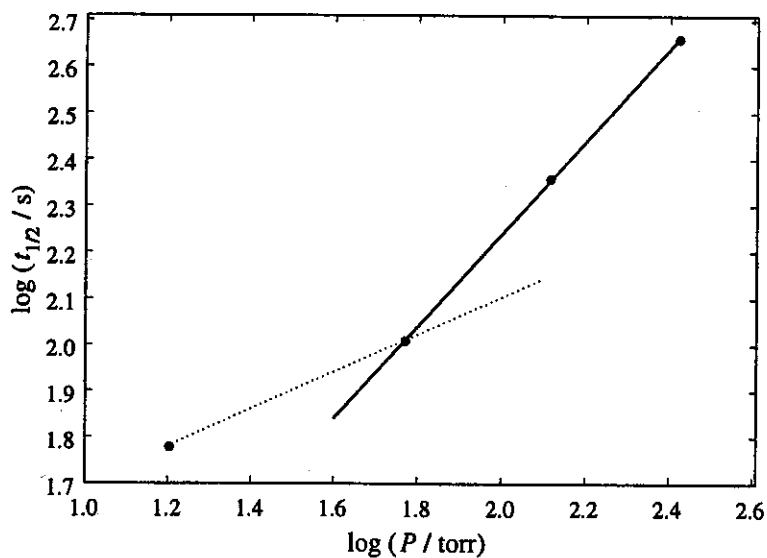
$$\log t_{1/2} = \log C' - (n - 1) \log P$$

A plot of log *t*_{1/2} vs log *P* gives a slope of *n* - 1. The data used for the plot are

log(<i>P</i> /torr)	2.422	2.114	1.77	1.20
log(<i>t</i> _{1/2} /s)	2.659	2.358	2.009	1.78

There are clearly two types of behavior exhibited in the graph. At pressures above 50 torr the graph appears to be a straight line, and fitting to these three points results in a best fit line with an equation of *y* = 1.00*x* + 0.24. Thus, 1 = -(*n* - 1), or *n* = 0, and the reaction is zero-order.

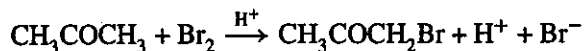
Although the data are limited, it is clear that there is a change in slope below 50 torr, indicating a change in reaction order. It does appear that the limiting slope as pressure approaches zero is itself zero. Thus, 0 = -(*n* - 1), or *n* = 1, and the limiting behavior is that of a first-order reaction.



(b) As discovered in part (a), the reaction is first order at low pressures and zero order at pressures above 50 torr.

(c) The mechanism is actually the same at all pressures considered. At low pressures, the fraction of the tungsten surface covered is proportional to the pressure of NH_3 , so the rate of decomposition will have a first order dependence on ammonia pressure. As discussed in Problem 12.16, however, at increased pressures, all the catalytic sites are occupied by, in this case, NH_3 molecules and the rate becomes independent of the ammonia pressure and zero order in NH_3 .

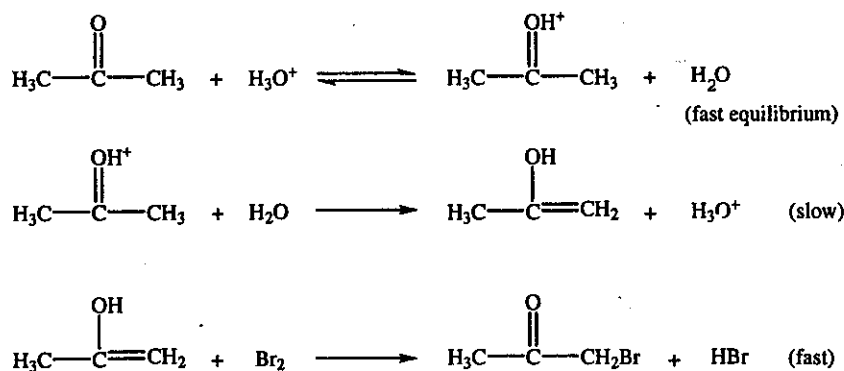
12.54 The bromination of acetone is acid-catalyzed:



The rate of disappearance of bromine was measured for several different concentrations of acetone, bromine, and H^+ ions at a certain temperature:

	$[\text{CH}_3\text{COCH}_3]/M$	$[\text{Br}_2]/M$	$[\text{H}^+]/M$	Rate of disappearance of $\text{Br}_2 / M \cdot s^{-1}$
(1)	0.30	0.050	0.050	5.7×10^{-5}
(2)	0.30	0.10	0.050	5.7×10^{-5}
(3)	0.30	0.050	0.1	1.2×10^{-4}
(4)	0.40	0.050	0.2	3.1×10^{-4}
(5)	0.40	0.050	0.050	7.6×10^{-5}

(a) What is the rate law for the reaction? (b) Determine the rate constant. (c) The following mechanism has been proposed for the reaction:



Show that the rate law deduced from the mechanism is consistent with that shown in (a).

(a) Comparing Experiment (1) and Experiment (5), the concentrations of Br_2 and H^+ are constant and the concentration of CH_3COCH_3 has increased 1.33 times. The rate has also increased 1.33 times. Therefore, the rate is directly proportional to the concentration of CH_3COCH_3 . That is, the reaction is first order in CH_3COCH_3 .

Comparing Experiment (1) and Experiment (2), the concentrations of CH_3COCH_3 and H^+ are constant and the concentration of Br_2 has increased 2.0 times but the rate has not changed. Therefore, the rate is independent of the concentration of Br_2 . That is, the reaction is zeroth order in Br_2 .

Comparing Experiment (1) and Experiment (3), the concentrations of CH_3COCH_3 and Br_2 are constant and the concentration of H^+ has increased 2.0 times. The rate has increased 2.1 times. Therefore, the rate is directly proportional to the concentration of H^+ . That is, the reaction is first order in H^+ .

Therefore, the rate law is

$$\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

(b) The rate constant can be calculated using data from any experiment. Using Exp. 1,

$$\text{Rate} = 5.7 \times 10^{-5} \text{ M s}^{-1} = k (0.30 \text{ M}) (0.050 \text{ M})$$

$$k = 3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

(c) Since step 2 is the slow step,

$$\text{Rate} = k_2 [\text{CH}_3\text{COHCH}_3^+] [\text{H}_2\text{O}] \quad (12.54.1)$$

The intermediate, $\text{CH}_3\text{COHCH}_3^+$ can be written in terms of the reactants using the first fast equilibrium step.

Forward rate of step 1 = Reverse rate of step 1

$$k_1 [\text{CH}_3\text{COCH}_3] [\text{H}_3\text{O}^+] = k_{-1} [\text{CH}_3\text{COHCH}_3^+] [\text{H}_2\text{O}]$$

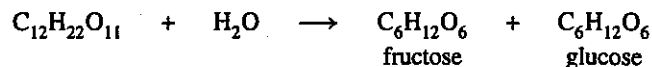
$$[\text{CH}_3\text{COHCH}_3^+] [\text{H}_2\text{O}] = \frac{k_1}{k_{-1}} [\text{CH}_3\text{COCH}_3] [\text{H}_3\text{O}^+] \quad (12.54.2)$$

Substituting Eq. 12.54.2 into Eq. 12.54.1, the rate law becomes

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{CH}_3\text{COCH}_3] [\text{H}_3\text{O}^+] = \frac{k_2 k_1}{k_{-1}} [\text{CH}_3\text{COCH}_3] [\text{H}^+]$$

which has the same form as that shown in (a).

12.58 Sucrose ($C_{12}H_{22}O_{11}$), commonly called table sugar, undergoes hydrolysis (reaction with water) to produce fructose ($C_6H_{12}O_6$) and glucose ($C_6H_{12}O_6$):



This reaction has particular significance in the candy industry. First, fructose is sweeter than sucrose. Second, a mixture of fructose and glucose, called *invert* sugar, does not crystallize, so candy made with this combination is chewier and not brittle as crystalline sucrose is. Sucrose is dextrorotatory (+) whereas the mixture of glucose and fructose resulting from inversion is levorotatory (-). Thus, a decrease in the concentration of sucrose will be accompanied by a proportional decrease in the optical rotation. (a) From the following kinetic data, show that the reaction is first order and determine the rate constant.

time/min	0	7.20	18.0	27.0	∞
optical rotation (α)	+24.08°	+21.40°	+17.73°	+15.01°	-10.73°

(b) Explain why the rate law does not include $[H_2O]$ even though water is a reactant.

(a) The total change in rotation (from $t = 0$ to $t = \infty$), given by $(\alpha_0 - \alpha_\infty)$, will be proportional to the decrease in concentration of sucrose by that time. Therefore, the concentration of sucrose remaining at time t will be proportional to

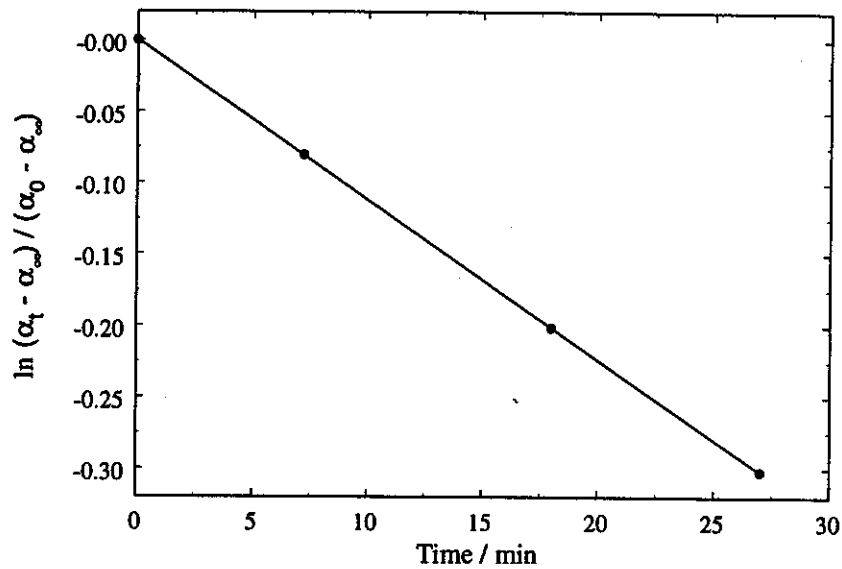
$$(\alpha_0 - \alpha_\infty) - (\alpha_0 - \alpha_t) = \alpha_t - \alpha_\infty$$

If the reaction is first order, then

$$\ln \frac{[\text{sucrose}]}{[\text{sucrose}]_0} = \ln \frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty} = -kt$$

A plot of $[\ln(\alpha_t - \alpha_\infty) / (\alpha_0 - \alpha_\infty)]$ vs t should give a straight line with a slope of $-k$. The plot uses the following data:

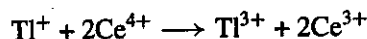
time/min	0	7.20	18.0	27.0
$\ln(\alpha_t - \alpha_\infty) / (\alpha_0 - \alpha_\infty)$	0	-8.0115×10^{-2}	-0.20141	-0.30186



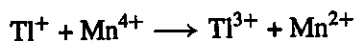
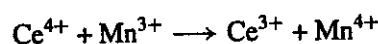
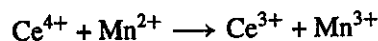
The plot indeed results in a line described by $y = -1.112 \times 10^{-2}x + 1.5 \times 10^{-4}$. Therefore, the rate constant is $1.11 \times 10^{-2} \text{ min}^{-1}$.

(b) The rate law does not include $[\text{H}_2\text{O}]$ because water is present in very high concentration (ca. 55.5 M) and this is a pseudo first-order reaction.

12.59 Thallium(I) is oxidized by cerium(IV) in solution as follows:



The elementary steps, in the presence of Mn(II), are



(a) Identify the catalyst, intermediates, and the rate-determining step if the rate law is rate = $k[\text{Ce}^{4+}][\text{Mn}^{2+}]$. (b) Explain why the reaction is slow without the catalyst. (c) Classify the type of catalysis (homogeneous or heterogeneous).

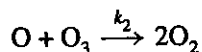
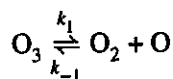
(a) The catalyst is Mn^{2+} . It participates in the reaction but is regenerated at the end. The intermediates are Mn^{3+} and Mn^{4+} .

The first step is the rate-determining step because the rate depends on the concentrations of the reactants for that step.

(b) Without the catalyst, the reaction would be a termolecular one involving 3 cations (Tl^+ and two Ce^{4+}). The reaction would be slow.

(c) The catalyst is a homogeneous catalyst because it has the same phase (aqueous) as the reactants.

12.60 Under certain conditions the gas-phase decomposition of ozone is found to be second order in O_3 and inhibited by molecular oxygen. Apply the steady-state approximation to the following mechanism to show that the rate law is consistent with the experimental observations:



State any assumption made in the derivation.

The rate of decomposition of O_3 is

$$\begin{aligned} -\frac{d[\text{O}_3]}{dt} &= k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}][\text{O}_3] \\ &= k_1[\text{O}_3] + (k_2[\text{O}_3] - k_{-1}[\text{O}_2])[\text{O}] \end{aligned} \quad (12.60.1)$$

Apply the steady state approximation to O:

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}][\text{O}_3] = 0 \\ [\text{O}] &= \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \end{aligned} \quad (12.60.2)$$

Substitute Eq. 12.60.2 into Eq. 12.60.1:

$$\begin{aligned} -\frac{d[\text{O}_3]}{dt} &= k_1[\text{O}_3] + (k_2[\text{O}_3] - k_{-1}[\text{O}_2]) \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \\ &= \frac{k_1 k_{-1}[\text{O}_3][\text{O}_2] + k_1 k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} + \frac{k_1 k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} - \frac{k_1 k_{-1}[\text{O}_3][\text{O}_2]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \\ &= \frac{2k_1 k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \end{aligned} \quad (12.60.3)$$

If the rate of the second step is assumed to be much slower than the rate of the reverse reaction for the first step, then

$$k_2[\text{O}][\text{O}_3] \ll k_{-1}[\text{O}_2][\text{O}]$$

$$k_2[\text{O}_3] \ll k_{-1}[\text{O}_2]$$

Equation 12.60.3 becomes

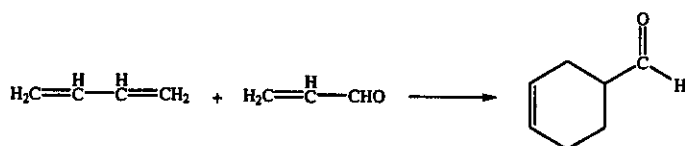
$$-\frac{d[\text{O}_3]}{dt} = \frac{2k_1 k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2]}$$

Since the rate for the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ is $-\frac{1}{2} \frac{d[\text{O}_3]}{dt}$, the rate law predicted by this mechanism is

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{k_1 k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2]}$$

which is consistent with experimental observations.

12.61 The rate constants for the reaction



have been measured at several temperatures:

$10^3 k/M^{-1} \cdot s^{-1}$	0.138	1.63	7.2	36.8	81
$t/^\circ\text{C}$	155.3	208.3	246.5	295.8	330.8

Calculate the values of the pre-exponential factor, E_a , ΔS^\ddagger , and ΔH^\ddagger for the reaction. Use 516 K as the mean temperature for your calculation. [Data taken from G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.* **58**, 123 (1936).]

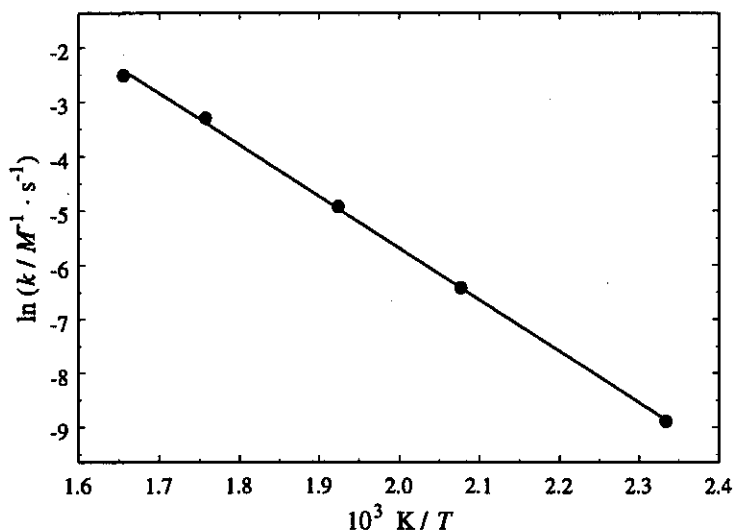
Since

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

A plot of $\ln k$ vs $1/T$ gives a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$.

$10^3 K/T$	2.3337	2.0768	1.9242	1.7575	1.6556
$\ln(k/M^{-1} \cdot s^{-1})$	-8.8883	-6.4192	-4.934	-3.3023	-2.513



The best fit line has a formula of $y = -9499x + 13.31$. Therefore,

$$E_a = -(-9499 \text{ K}) (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) = 7.897 \times 10^4 \text{ J mol}^{-1} = 7.90 \times 10^4 \text{ J mol}^{-1}$$

$$A = e^{13.31} = 6.032 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} = 6.03 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

For this gas-phase, bimolecular reaction, (see Equation 12.43)

$$A = e^2 \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R}$$

$$\Delta S^{\ddagger} = R \left(\ln \frac{hA}{k_B T} - 2 \right)$$

$$= (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \left[\ln \frac{(1 \text{ M}) (6.626 \times 10^{-34} \text{ Js}) (6.032 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ JK}^{-1}) (516 \text{ K})} - 2 \right]$$

$$= -155 \text{ JK}^{-1} \text{ mol}^{-1}$$

and

$$\Delta H^{\ddagger} = E_a - 2RT$$

$$= 7.897 \times 10^4 \text{ J mol}^{-1} - 2 (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (516 \text{ K})$$

$$= 7.04 \times 10^4 \text{ J mol}^{-1}$$