



Ch. 15 HW Club Probs.

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14.5

Analyze/Plan. Using the relationship $\text{rate} = k[A]^x$, determine the value of x that produces a rate law to match the described situation. *Solve.*

- (a) $x = 0$. The rate of reaction does not depend on $[A]_0$, so the reaction is zero-order in A.
- (b) $x = 2$. When $[A]_0$ increases by a factor of 3, rate increases by a factor of $(3)^2 = 9$.
- (c) $x = 3$. When $[A]_0$ increases by a factor of 2, rate increases by a factor of $(2)^3 = 8$.

14.11

- (a) The red pathway is slower, because it has the greater activation energy, E_a .
- (b) The reaction could occur by both catalyzed and uncatalyzed mechanisms. The initial reactants and final products would be the same, but the transition state and activation energy would be different.

14.12

- (a) $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$
 $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$
- (b) $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$
- (c) F is the intermediate, because it is produced and then consumed during the reaction.
- (d) $\text{rate} = k[\text{NO}_2][\text{F}_2]$

14.13

This is the profile of a two-step mechanism, $A \rightarrow B$ and $B \rightarrow C$. There is one intermediate, B. Because there are two energy maxima, there are two transition states. The $B \rightarrow C$ step is faster, because its activation energy is smaller. The reaction is exothermic because the energy of the products is lower than the energy of the reactants.

14.14

The most likely transition state shows the relative geometry of both reactants and products. It is reasonable to assume that multiple bonds, with greater total bond energy, remain intact at the expense of single bonds. In the black-and-white diagram below, open circles represent the red balls and closed circles represent the blue.

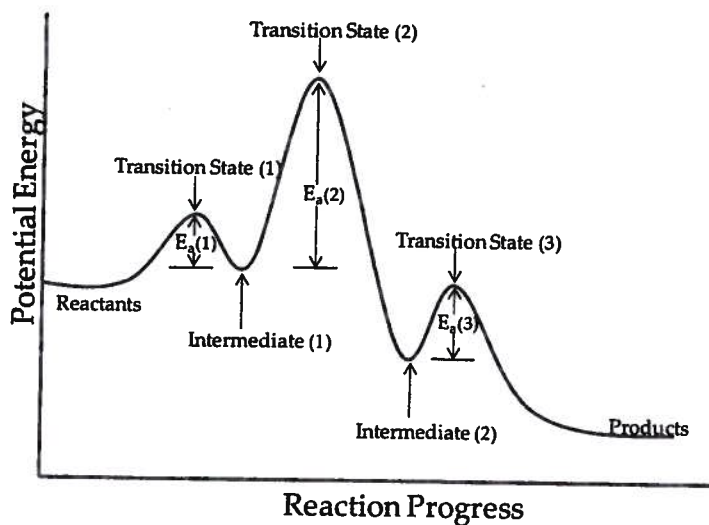


14.15

- (a) $A_2 + AB + AC \rightarrow BA_2 + A + AC$
 $BA_2 + A + AC \rightarrow A_2 + BA_2 + C$

 $\text{net: } AB + AC \rightarrow BA_2 + C$
- (b) A is the intermediate; it is produced and consumed.
- (c) A_2 is the catalyst; it is consumed and reproduced

14.16



The reaction is exothermic because the energy of products is lower than the energy of reactants. The two intermediates are formed at different rates because $E_a(1) \neq E_a(2)$. In order to have two intermediates, the mechanism must have at least three steps.

14.19 *Analyze/Plan.* Given mol A at a series of times in minutes, calculate mol B produced, molarity of A at each time, change in M of A at each 10 min interval, and ΔM A/s. For this reaction, mol B produced equals mol A consumed. M of A or [A] = mol A/0.100 L. The average rate of disappearance of A for each 10 minute interval is

$$-\frac{\Delta[A]}{s} = -\frac{[A]_1 - [A]_0}{10 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}}$$

Solve.

Time (min)	Mol A	(a) Mol B	[A]	$\Delta[A]$	(b) Rate $-(\Delta[A]/s)$
0	0.065	0.000	0.65		
10	0.051	0.014	0.51	-0.14	2.3×10^{-4}
20	0.042	0.023	0.42	-0.09	2×10^{-4}
30	0.036	0.029	0.36	-0.06	1×10^{-4}
40	0.031	0.034	0.31	-0.05	0.8×10^{-4}

(c)
$$\frac{\Delta M_B}{\Delta t} = \frac{(0.029 - 0.014) \text{ mol}/0.100 \text{ L}}{(30 - 10) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 1.25 \times 10^{-4} = 1.3 \times 10^{-4} \text{ M/s}$$

14.25 *Analyze/Plan.* Use Equation [14.4] to relate the rate of disappearance of reactants to the rate of appearance of products. Use this relationship to calculate desired quantities. *Solve.*

(a) $\Delta[H_2O]/2\Delta t = -\Delta[H_2]/2\Delta t = -\Delta[O_2]/\Delta t$

H_2 is burning, $-\Delta[H_2]/\Delta t = 0.48 \text{ mol/s}$

O_2 is consumed, $-\Delta[O_2]/\Delta t = -\Delta[H_2]/2\Delta t = 0.48 \text{ mol/s}/2 = 0.24 \text{ mol/s}$

H_2O is produced, $+\Delta[H_2O]/\Delta t = -\Delta[H_2]/\Delta t = 0.48 \text{ mol/s}$

(b) The change in total pressure is the sum of the changes of each partial pressure. NO and Cl_2 are disappearing and NOCl is appearing.

$-\Delta P_{NO}/\Delta t = -56 \text{ torr/min}$

$-\Delta P_{Cl_2}/\Delta t = \Delta P_{NO}/2\Delta t = -28 \text{ torr/min}$

$+\Delta P_{NOCl}/\Delta t = -\Delta P_{NO}/\Delta t = +56 \text{ torr/min}$

$\Delta P_T/\Delta t = -56 \text{ torr/min} - 28 \text{ torr/min} + 56 \text{ torr/min} = -28 \text{ torr/min}$

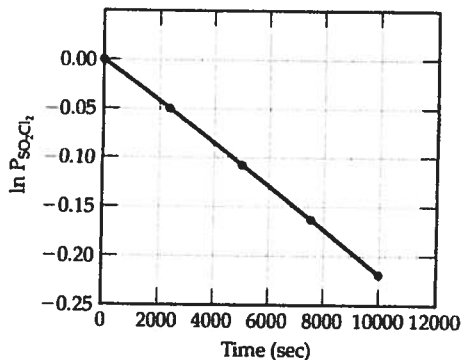
(c) Use the reaction stoichiometry and Equation [14.4] to relate the designated rates. $\Delta[NOBr]/2\Delta t = -\Delta[Br_2]/\Delta t$; the rate of disappearance of Br_2 is half the rate of appearance of NOBr.

(d) Note that the data are given in terms of appearance of NOBr.

$$\frac{-\Delta[Br_2]}{\Delta t} = \frac{k[NO]^2[Br_2]}{2} = \frac{1.2 \times 10^4}{2 \text{ M}^2 \text{ s}} \times (0.075 \text{ M})^2 \times (0.250 \text{ M}) = 8.4 \text{ M/s}$$

14.47 *Analyze/Plan.* Given reaction order, various values for t and P_t , find the rate constant for the reaction at this temperature. For a first-order reaction, a graph of $\ln P$ vs t is linear with as slope of $-k$. *Solve.*

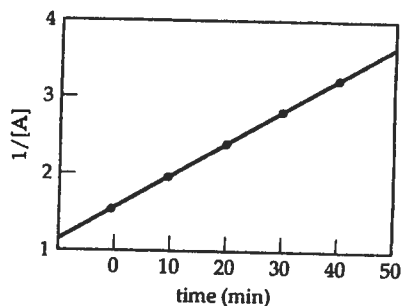
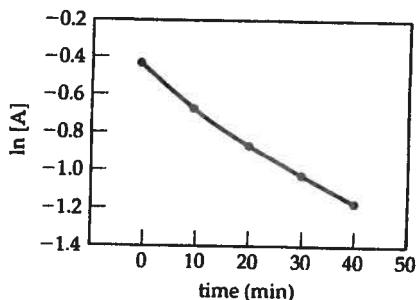
$t(s)$	$P_{SO_2Cl_2}$	$\ln P_{SO_2Cl_2}$
0	1.000	0
2500	0.947	-0.0545
5000	0.895	-0.111
7500	0.848	-0.165
10000	0.803	-0.219



Graph $\ln P_{SO_2Cl_2}$ vs. time. (Pressure is a satisfactory unit for a gas, since the concentration in moles/liter is proportional to P .) The graph is linear with slope $-2.19 \times 10^{-5} s^{-1}$ as shown on the figure. The rate constant $k = -\text{slope} = 2.19 \times 10^{-5} s^{-1}$.

14.49 *Analyze/Plan.* Given: mol A, t . Change mol to M at various times. Make both first- and second-order plots to see which is linear. *Solve.*

(a)	time(min)	mol A	[A] (M)	$\ln[A]$	1/mol A
	0	0.065	0.65	-0.43	1.5
	10	0.051	0.51	-0.67	2.0
	20	0.042	0.42	-0.87	2.4
	30	0.036	0.36	-1.02	2.8
	40	0.031	0.31	-1.17	3.2



The plot of $1/[A]$ vs time is linear, so the reaction is second-order in $[A]$.

(b) For a second-order reaction, a plot of $1/[A]$ vs. t is linear with slope k .

$$k = \text{slope} = (3.2 - 2.0) M^{-1} / 30 \text{ min} = 0.040 M^{-1} \text{ min}^{-1}$$

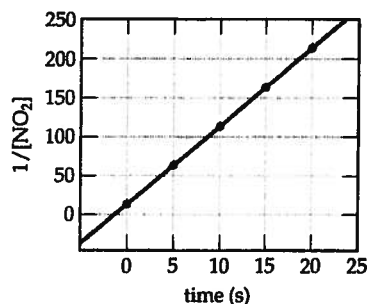
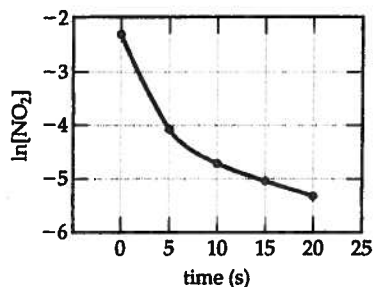
(The best fit to the line yields slope = $0.042 M^{-1} \text{ min}^{-1}$.)

(c) $t_{1/2} = 1/k[A]_0 = 1/(0.040 M^{-1} \text{ min}^{-1})(0.65 M) = 38.46 = 38 \text{ min}$

(Using the "best-fit" slope, $t_{1/2} = 37 \text{ min}$.)

14.51 *Analyze/Plan.* Follow the logic in Solution 14.49. Make both first and second order plots to see which is linear. *Solve.*

(a)	time(s)	[NO ₂](M)	ln[NO ₂]	1/[NO ₂]
	0.0	0.100	-2.303	10.0
	5.0	0.017	-4.08	59
	10.0	0.0090	-4.71	110
	15.0	0.0062	-5.08	160
	20.0	0.0047	-5.36	210



The plot of $1/[NO_2]$ vs time is linear, so the reaction is second order in NO_2 .

(b) The slope of the line is $(210 - 59) M^{-1} / 15.0 s = 10.07 = 10 M^{-1}s^{-1} = k$. (The slope of the best-fit line is $10.02 = 10 M^{-1}s^{-1}$.)

(c) From the results above, the rate law is: $rate = k[NO_2]^2 = 10 M^{-1}s^{-1}[NO_2]^2$
Using the rate law, calculate the rate at each of the given initial concentrations.

$$Rate @ 0.200 M = 10 M^{-1}s^{-1}[NO_2]^2 = 10 M^{-1}s^{-1}[0.200 M]^2 = 0.400 M/s$$

$$Rate @ 0.100 M = 10 M^{-1}s^{-1}[NO_2]^2 = 10 M^{-1}s^{-1}[0.100 M]^2 = 0.100 M/s$$

$$Rate @ 0.050 M = 10 M^{-1}s^{-1}[NO_2]^2 = 10 M^{-1}s^{-1}[0.050 M]^2 = 0.025 M/s$$

14.55 *Analyze/Plan.* Given the temperature and energy, use Equation [14.18] to calculate the fraction of Ar atoms that have at least this energy. *Solve.*

$$f = e^{-E_a/RT} \quad E_a = 10.0 \text{ kJ/mol} = 1.00 \times 10^4 \text{ J/mol}; \quad T = 400 \text{ K} (127^\circ\text{C})$$

$$-E_a/RT = -\frac{1.00 \times 10^4 \text{ J/mol}}{400 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{8.314 \text{ J}} = -3.0070 = -3.01$$

$$f = e^{-3.0070} = 4.9 \times 10^{-2}$$

At 400 K, approximately 1 out of 20 molecules has this kinetic energy.

14.67 *Analyze/Plan.* Given E_a , find the ratio of rates for a reaction at two temperatures. Assuming initial concentrations are the same at the two temperatures, the ratio of rates will be the ratio of rate constants, k_1/k_2 . Use Equation [14.21] to calculate this ratio. *Solve.*

$$T_1 = 50^\circ\text{C} + 273 = 323 \text{ K}; T_2 = 0^\circ\text{C} + 273 = 273 \text{ K}$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = \frac{65.7 \text{ kJ/mol}}{8.314 \text{ J/mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \left[\frac{1}{273} - \frac{1}{323} \right]$$

$$\ln(k_1/k_2) = 7.902 \times 10^3 (5.670 \times 10^{-4}) = 4.481 = 4.5; k_1/k_2 = 88.3 = 9 \times 10^1$$

The reaction will occur 90 times faster at 50°C , assuming equal initial concentrations and Arrhenius kinetics.

14.79 *Analyze.* Given data on concentration of a reactant vs time, determine whether the proposed reaction mechanism is consistent with the data. *Plan.* Based on the graph, decide the order of reaction with respect to $[\text{NO}]$. Write the two possible rate laws, depending on which step is rate-determining. Decide if one of the rate laws, and thus the mechanism, is consistent with the rate data. *Solve.*

The graph of $1/[\text{NO}]$ vs time is linear with positive slope, indicating that the reaction is second order in $[\text{NO}]$. The rate law will include $[\text{NO}]^2$. We have no information about reaction order with respect to $[\text{Cl}_2]$.

If the first step is slow, the observed rate law is the rate law for this step: $\text{rate} = k[\text{NO}][\text{Cl}_2]$. Since the observed rate law is second-order in $[\text{NO}]$, the second step must be slow relative to the first step. Follow the logic in Sample Exercise 14.15 for determining the rate law of a mechanism with a fast initial step.

From the rate-determining second step, $\text{rate} = k[\text{NOCl}_2][\text{NO}]$.

Assuming the first step is a fast equilibrium, $k_1 [\text{NO}][\text{Cl}_2] = k_{-1} [\text{NOCl}_2]$.

Solving for $[\text{NOCl}_2]$ in terms of $[\text{NO}][\text{Cl}_2]$, $[\text{NOCl}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Cl}_2]$

$$\text{rate} = \frac{k_2 k_1}{k_{-1}} [\text{NO}][\text{Cl}_2][\text{NO}] = [\text{NO}]^2 [\text{Cl}_2]$$

This rate law is second order in $[\text{NO}]$. It is consistent with the observed data.

[The graph of $1/[\text{NO}]$ vs time is linear with positive slope, indicating that the reaction is second order in $[\text{NO}]$. The rate law obtained by assuming the second step is rate determining is: $\text{rate} = [\text{NO}]^2 [\text{Cl}_2]$. The two step mechanism is consistent with the data.]





