Chapter 12 Homework

2,6,7,13,17,22,23,31,35,36,43,53,55,58,70,75,79

2. Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

$$\Rightarrow -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

$$\Rightarrow -\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t}$$

neg for decomp.

6. Consider the following reaction in aqueous solution:

$$5Br^{-}(aq) + BrO_3^{-}(aq) + 6H^{+}(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

If the rate of disappearance of $Br^{-}(aq)$ at a particular moment during the reaction is 3.5×10^{-4} mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

$$\Rightarrow -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

$$\Rightarrow -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow -\frac{1}{5}(3.5 \times 10^{-4} \text{ mol } L^{-1} s^{-1}) = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[Br_2]}{\Delta t} = \frac{3}{5}(3.5 \times 10^{-4} \text{ mol } L^{-1} s^{-1})$$

$$\Rightarrow \frac{\Delta[Br_2]}{\Delta t} = 2.1 \times 10^{-4} \text{ mol } L^{-1} s^{-1}$$

As rate of disappearance of $Br^-(aq)$ is 3.5×10^{-4} mol L^{-1} s^{-1}, the rate of $Br_2(aq)$ appearance is 2.1×10^{-4} mol L^{-1} s^{-1}.

$$\underbrace{-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t}}_{\text{disappearance}} = \underbrace{+\frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}}_{\text{appearance}}$$

7. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Increase molarity & temp will increase reaction rate while increasing size will decrease reaction rate.

13. Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

a)

$$\text{rate} = k[A]^x$$

$$\Rightarrow [2]^x = 4$$

$$\Rightarrow x = 2$$

$$\Rightarrow \text{rate} = k[A]^2$$

second order

b)

$$\text{rate} = k[B]^x$$

$$\Rightarrow [3]^x = 3$$

$$\Rightarrow x = 1$$

$$\Rightarrow \text{rate}\ k[B]^1$$

first order

17. Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $NO + O_3 \longrightarrow NO_2 + O_2$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when $[NO] = 3.3 \times 10^{-6}$ M and $[O_3] = 5.9 \times 10^{-7}$ M?

rate = $k\,[NO]\,[O_3]$ $\quad\quad$ $k = 2.2 \times 10^7$

$\Rightarrow (2.2 \times 10^7)(3.3 \times 10^{-6}\,M)(5.9 \times 10^{-7}\,M)$

$\Rightarrow$ instantaneous rate $= 4.3 \times 10^{-5}$ M/s

22. Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate ($mol\ L^{-1}\ h^{-1}$)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

2x

stays same

Determine the rate law, the rate constant, and the overall order for this reaction.

rate law $= k[NH_3]^0 = k$

zero order

rate constant: $k = 1.5 \times 10^{6}$ mol $L^{-1} h^{-1}$

23. Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$$

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (M)	0.10 $\xrightarrow{\times 2}$	0.20	0.30
Rate (mol L^{-1} h^{-1})	8.0×10^{-10} $\xrightarrow{\times 4}$	3.2×10^{-9}	7.2×10^{-9}

rate = k [NOCl]

$\Rightarrow (2 NOCl)^x = 4$

$\Rightarrow x = 2$

rate law = $k[NOCl]^2$

2nd order

rate constant:

$\Rightarrow 8 \times 10^{-10}$ mol $L^{-1} h^{-1} = k[.1]^2$

$\Rightarrow k = \dfrac{8 \times 10^{-10} \text{ mol } L^{-1} h^{-1}}{[.1]^2}$

$\Rightarrow k = 8 \times 10^{-8} \dfrac{1}{Mh}$

$\dfrac{mol}{L \cdot h} \rightarrow \dfrac{M/h}{M^2} \rightarrow \dfrac{1}{Mh}$

31. The following data have been determined for the reaction:

$I^- + OCl^- \longrightarrow IO^- + Cl^-$

	1	2	3
$[I^-]_{\text{initial}}$ (M)	0.10	0.20	0.30
$[OCl^-]_{\text{initial}}$ (M)	0.050	0.050	$\xleftarrow{\times 5}$ 0.010
Rate ($mol\ L^{-1}\ s^{-1}$)	3.05×10^{-4}	6.20×10^{-4}	$\xleftarrow{\simeq \times 5}$ 1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

rate : $k[I^-]^x[OCl^-]^y$

$\Rightarrow \frac{r_1}{r_2} = \frac{\cancel{k}[.1]^x\cancel{[.5]^y}}{\cancel{k}[.2]^x\cancel{[.05]^y}}$

$\Rightarrow \frac{3.05\times10^{-4}}{6.2\times10^{-4}} = \left(\frac{.1}{.2}\right)^x$

$\Rightarrow \ln(.49) = x\ln\left(\frac{.1}{.2}\right)$

$\Rightarrow x = 1$

$[5OCl^-]^y = 5$

$\Rightarrow y = 1$

rate law : $k[I^-][OCl^-]$

rate constant:

$\Rightarrow 6.2\times10^{-4} = k(.2)(.05)$

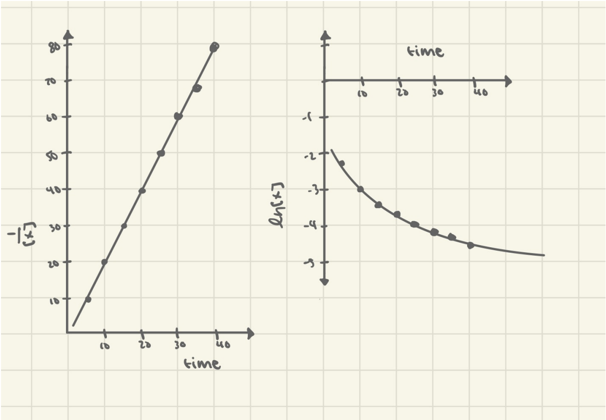
$\Rightarrow k = \frac{6.2\times10^{-4}}{.2 \cdot .05}$

$\Rightarrow k = 6.2\times10^{-2}\ L\ mol^{-1}\ s^{-1}$

35. From the given data, use a graphical method to determine the order and rate constant of the following reaction:

$2X \longrightarrow Y + Z$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
$[X]$ (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125
$\frac{1}{[x]}$	10.10	20.12	30.12	40.16	50	60.24	67	80
ln [x]	-2.3	-3	-3.4	-3.7	-3.9	-4.1	-4.2	-4.4



second order

rate law : $k[x]^2$

36. What is the half-life for the first-order decay of phosphorus-32? $\left({}^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-\right)$ The rate constant for the decay is 4.85×10^{-2} day^{-1}.

$$t_{1/2} = \frac{.693}{k} \qquad k = 4.85 \times 10^{-2}\, d^{-1}$$

$$t_{1/2} = \frac{.693}{4.85 \times 10^{-2}\, d^{-1}}$$

$$t_{1/2} = 14.3 \text{ days}$$

43. Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

$100\% \xrightarrow{6h} 50\%$

$100\% \xrightarrow{48h} \_\_\_\_\%$

$\ln[A] = -kt + \ln[A_0]$

$t_{1/2} = \frac{.693}{k}$

$\Rightarrow t_{1/2} = \frac{.693}{6}$

$\Rightarrow 6 = \frac{.693}{k}$

$\Rightarrow k = .1155\ h^{-1}$

$\ln[A] = -(.1155)(48) + \ln 1$

$\ln[A] = 5.544$

$e^{\ln[A]} = e^{.5.544}$

$A = 255.7$

53. Account for the relationship between the rate of a reaction and its activation energy.

Increasing the activation energy decreases the rate of reaction because once the activation energy is increased, the reaction will need more energy to occur.

55. How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

Increasing the temperature increased the rate of reaction because molecules move faster and collide more frequently during higher temperatures. When more collisions occur, more kinetic energy is created thus the likelihood of overcoming the activation barrier is higher.

58. The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2C_2H_4$ is $6.1 \times 10^{-8}\ s^{-1}$, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

$k = Ae^{-Ea/RT}$

$k = 6.1 \times 10^{-8}$

$T = 325 + 273.15 = 328.15K$

$Ea = 261000 J$

$A = ?$

$\Rightarrow 6.1 \times 10^{-8} = A \cdot e^{-261000/8.314 \cdot 328.15}$

$\Rightarrow 6.1 \times 10^{-8} = A(1.61 \times 10^{-23})$

$\Rightarrow A = \dfrac{6.1 \times 10^{-8}}{1.61 \times 10^{-23}}$

$\Rightarrow A = 3.79 \times 10^{15}\ 1/s$

70. What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow$ products? For $3A \longrightarrow$ products?

$A + 2B \rightarrow$ products rate: $k[A][B]^2$

$3A \rightarrow$ products rate: $k[A]^3$

75. The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$Cl_2(g) \rightleftharpoons 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)

$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)

$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

(a) Write the overall reaction.

(b) Identify all intermediates.

(c) Write the rate law for each elementary reaction.

(d) Write the overall rate law expression.

r = rate

c) $r_1: \; k_1[Cl_2] = k_{-1}[Cl]^2$

$r_2: \; k_2[CO][Cl]$

$r_3: \; k_3[COCl][Cl]$

a) $Cl_2 + CO + \cancel{Cl} + \cancel{COCl} + \cancel{Cl}$

$\rightarrow \cancel{2Cl} + \cancel{COCl} + COCl_2$

$Cl_2 + CO \rightarrow COCl_2$

b) intermediates are Cl & COCl

d) $r_2: \; k_2[CO][Cl]$

$\Rightarrow k_1[Cl_2] = k_{-1}[Cl]^2$

$\Rightarrow [Cl]^2 = \frac{k_1 [Cl_2]}{k_{-1}}$

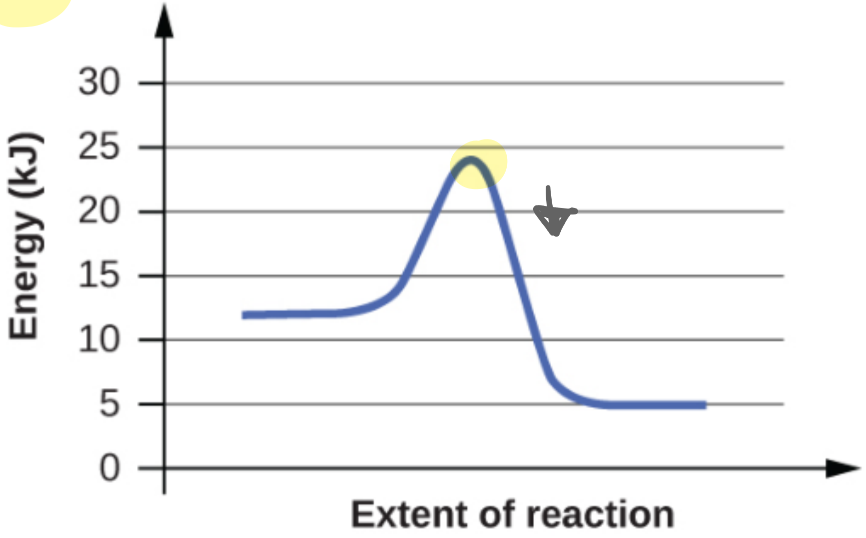
$\Rightarrow [Cl^2] = \left(\frac{k_1 [Cl_2]}{k_{-1}}\right)^{1/2}$

$\Rightarrow k_2[CO]\left[\left(\frac{k_1 [Cl_2]}{k_{-1}}\right)^{1/2}\right]$

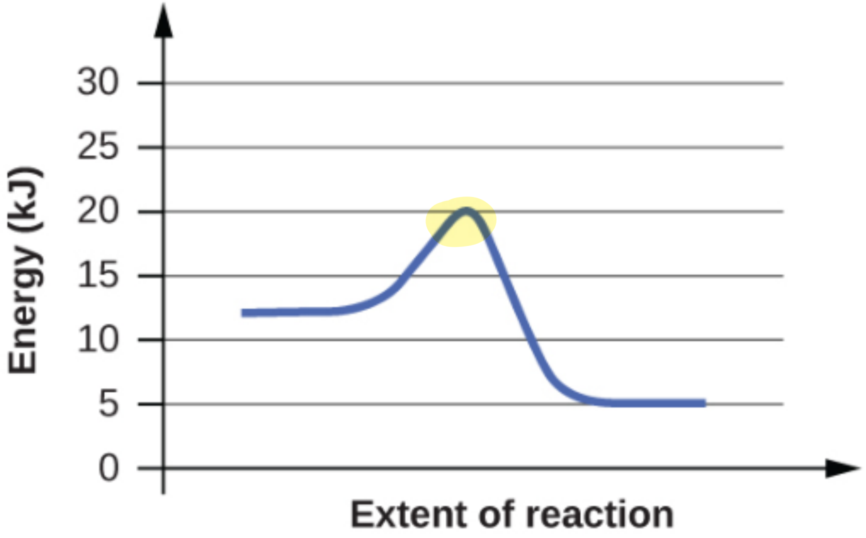
$\Rightarrow k[CO][Cl_2]^{1/2}$

79. For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

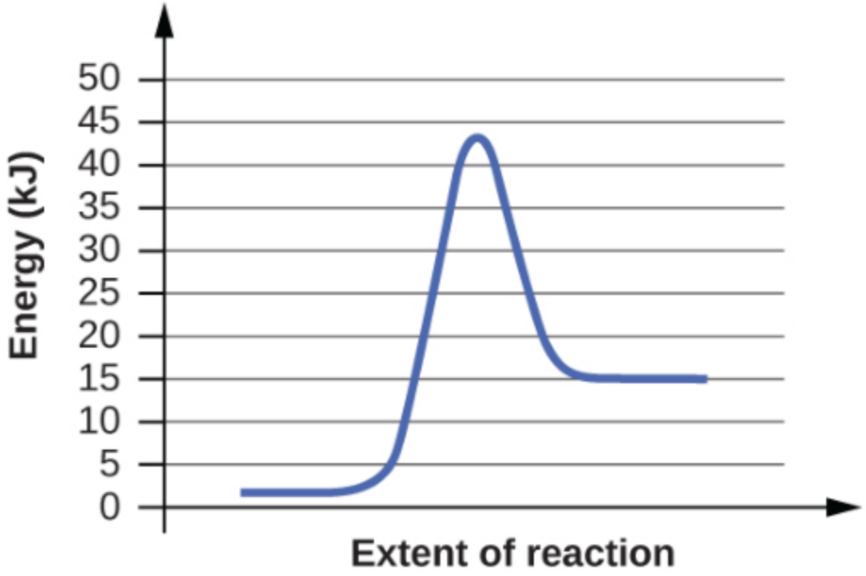


(a)

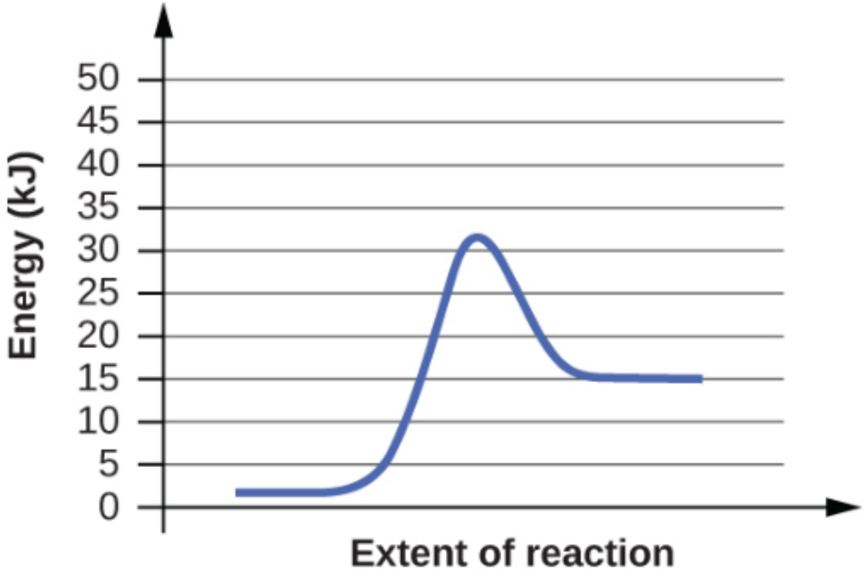


(b)

(b)



(a)



(b)