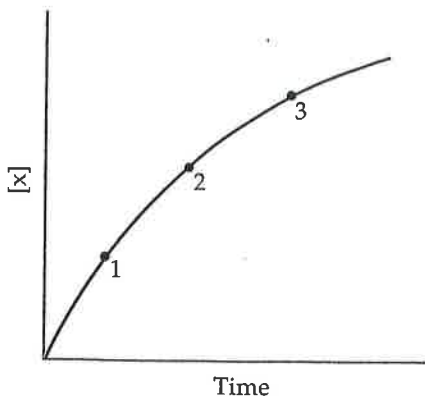


# Chapter 14

#2

14.2 Consider the following graph of the concentration of a substance over time. (a) Is X a reactant or product of the reaction? (b) Is the reaction speeding up, slowing down, or not changing its rate as time progresses? (c) Why is the average rate of the reaction different between points 1 and 2 than between points 2 and 3? [Section 14.2]



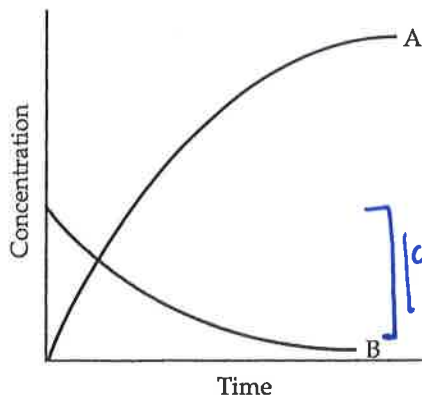
(a) X must be a product, since its concentration is increasing over time.

(b) the reaction is slowing down as time progresses (the rate of formation of X is decreasing); the slope is becoming less positive (the slope is the rate of formation of X;  $\frac{\Delta[X]}{\Delta t}$ )

(c) The rate is less between 2 and 3 than between 1 and 2 because points 2/3 are further along (more time has passed) than points 1/2. The rate of reaction is decreasing over time probably because reactant concentrations are decreasing as the reaction proceeds.

#3

14.3 You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:



Change in concentration of A, so A is increasing at twice the rate at which B is decreasing. stoichiometry must be  $\frac{2 \text{ moles A}}{1 \text{ mole B}}$ .

Which chemical equation is consistent with these data: (a)

$A \rightarrow B$ , (b)  $B \rightarrow A$ , (c)  $A \rightarrow 2B$ , (d)  $B \rightarrow 2A$  ← this one.

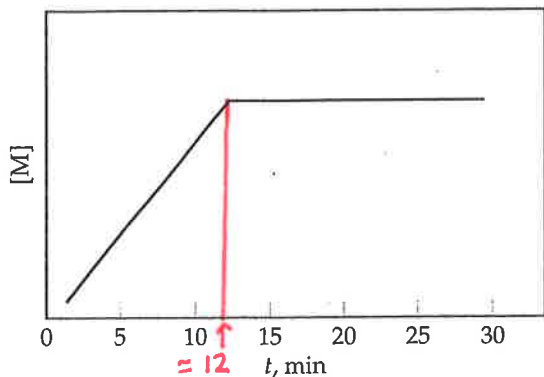
Explain your choice. [Section 14.2]

Since [A] is increasing and [B] is decreasing, A must be a product, and B must be a reactant. rxn (d) also gives the 2 to 1 stoichiometric ratio (2 moles A per 1 mole B) shown in the graph.

# Chapter 14

#4

14.4 You perform the reaction  $K + L \rightarrow M$ , monitor the production of M over time, and then plot this graph from your data:



(a) Is the reaction occurring at a constant rate from  $t = 0$  to  $t = 15$  min? Explain. (b) Is the reaction completed at  $t = 15$  min? Explain.

(b) yes, it is complete once about 12 minutes have passed.

(a) No. The rxn is occurring at a constant rate until about 12 minutes have passed, (the slope is constant so the rate is constant) but then the slope changes to zero at around 12 minutes, which means that the rxn has completed by then (rate drops to zero)

#5

14.5 You perform a series of experiments for the reaction  $A \rightarrow B + C$  and find that the rate law has the form  $\text{rate} = k[A]^x$ . Determine the value of  $x$  in each of the following cases: (a) There is no rate change when  $[A]_0$  is tripled. (b) The rate increases by a factor of 9 when  $[A]_0$  is tripled. (c) When  $[A]_0$  is doubled, the rate increases by a factor of 8. [Section 14.3]

$$r = k[A]^x$$

(a) if tripling  $[A]$  doesn't affect the rate,  $x = 0$  ("zeroth order")  
The rxn will occur at a constant rate, regardless of  $[A]$ .  
(of course if no A is present the rxn can't occur...)

(b) if tripling  $[A]$  causes the rate to increase by factor of 9,  $x = 2$   
("2nd order with respect to  $[A]$ ")

$$\frac{r_2}{r_1} = \frac{k[A]_2^x}{k[A]_1^x} \rightarrow \frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^x \rightarrow 9 = (3)^x \rightarrow \underline{x = 2}$$

(c) if doubling  $[A]$  causes the rate to increase by factor of 8,  
 $x = 3$ . (3rd order with respect to A)

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^x \rightarrow 8 = (2)^x \rightarrow \underline{x = 3}$$

17 (a) The reaction rate is the speed at which the rxn occurs. usually done in units of  $\frac{\Delta [ ]}{\Delta t}$ , for example  $\frac{M}{s}$ ,  $\frac{M}{\text{min}}$ ,  $\frac{M}{\text{hr}}$ , ...)

(b) Factors that affect rate of rxn (at least 3)

Temperature (rate increases as T increases)

Concentration of reactants (rate increases as conc'n increases)

presence of a catalyst (catalysts increase the rate of rxn)

presence of an inhibitor (inhibitors decrease the rate of rxn)

particle size (for solid phase reactants; decreasing particle size / increasing surface area increases the rate of rxn)

(c) Is rate of disappearance of reactants always same as rate of appearance of products? NO.

for example, in the reaction  $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

the rate of increase of  $[\text{N}_2\text{O}_4]$  is only half as large as the rate of decrease of  $[\text{NO}_2]$ .

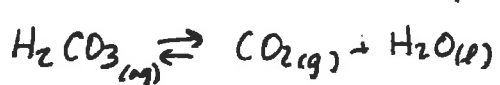
18 (a) In solution, the rate is usually expressed as change in concentration per "change in" time,

so the units would be  $\frac{\text{mole/L}}{s}$  or  $\frac{M}{s}$  or  $\frac{\text{mole}}{L \cdot s}$

or M/min, M/hr... but M/s is very common.

(b) Two every day experiences where Temperature affects rate of rxn.

Food spoils more quickly when it is at ~~high~~ warm temp than when at cold temp.



a warm soda fizzes more quickly when opened than a cold soda.



← the rate of this rxn is essentially zero at room temp, but if it is heated (say, with a flame from a match) the rxn rate increases.

alcohol + acid  $\rightarrow$  ester +  $\text{H}_2\text{O}$   
 we heated the reactants to increase rxn rate when we made esters

Yeast makes bread rise more quickly if heated (CO<sub>2</sub> is produced at a faster rate)

# Chapter 14



#21

14.21 The isomerization of methyl isonitrile ( $\text{CH}_3\text{NC}$ ) to acetonitrile ( $\text{CH}_3\text{CN}$ ) was studied in the gas phase at  $215^\circ\text{C}$ , and the following data were obtained:

Time (s)	$[\text{CH}_3\text{NC}]$ (M)
0	0.0165
2,000	0.0110
5,000	0.00591
8,000	0.00314
12,000	0.00137
15,000	0.00074

(a) Rate of formation of  $\text{CH}_3\text{CN}$  (M/s)

$2.8 \times 10^{-6}$   
 $1.7 \times 10^{-6}$   
 $9.23 \times 10^{-7}$   
 $4.43 \times 10^{-7}$   
 $2.10 \times 10^{-7}$

See work below. My rates were negative because I calculated the rate of change of the reactant  $\text{CH}_3\text{NC}$ . The rate of formation of product will be positive.

(a) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. (b) Calculate the average rate of reaction over the entire time of the data from  $t = 0$  to  $t = 15,000$  s. (c) Graph  $[\text{CH}_3\text{NC}]$  versus time and determine the instantaneous rates in M/s at  $t = 5000$  s and  $t = 8000$  s.

(a) From 0 s to 2000 s  $\text{rate} = \frac{\Delta[\text{CH}_3\text{NC}]}{\Delta t} = \frac{0.0110 \text{ M} - 0.0165 \text{ M}}{2000 \text{ s} - 0 \text{ s}} = -2.8 \times 10^{-6} \frac{\text{M}}{\text{s}}$

From 2000 s to 5000 s,  $r = \frac{(0.00591 \text{ M} - 0.0110 \text{ M})}{(5000 \text{ s} - 2000 \text{ s})} = -1.7 \times 10^{-6} \text{ M/s}$

From 5000 s to 8000 s  $r = \frac{(0.00314 \text{ M} - 0.00591 \text{ M})}{(8000 \text{ s} - 5000 \text{ s})} = -9.23 \times 10^{-7} \frac{\text{M}}{\text{s}}$

From 8000 s to 12000 s  $r = \frac{(0.00137 \text{ M} - 0.00314 \text{ M})}{12000 \text{ s} - 8000 \text{ s}} = -4.43 \times 10^{-7} \frac{\text{M}}{\text{s}}$

From 12000 s to 15000 s  $r = \frac{(0.00074 \text{ M} - 0.00137 \text{ M})}{(15000 \text{ s} - 12000 \text{ s})} = -2.1 \times 10^{-7} \frac{\text{M}}{\text{s}}$

(b)  $\frac{0.00074 \text{ M} - 0.0165 \text{ M}}{15000 \text{ s} - 0 \text{ s}} = -1.051 \times 10^{-6} \text{ M/s}$

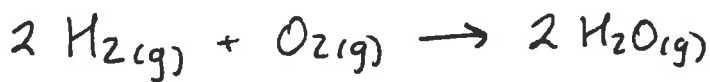
avg rate of rxn, or rate of formation of product, is  $+1.1 \times 10^{-6} \frac{\text{M}}{\text{s}}$  over the 15000 seconds.

(c) If we wanted to, we could plot  $[\text{CH}_3\text{NC}]$  vs time, and find the slope of the tangent lines at 5000 s and 8000 s.

The slopes of the tangent line (aka the first derivatives) at 5000 s and 8000 s would tell us the instantaneous rate of rxn at those times. The tangent lines would have negative slope; the reactant  $\text{CH}_3\text{NC}$  has a negative rate of formation.



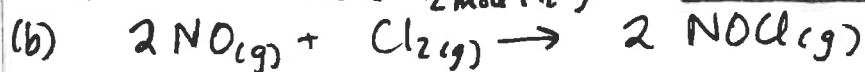
25



- (a) What is the rate of consumption of  $\text{O}_2$ , if  $\text{H}_2$  is burning at a rate of  $0.48 \text{ mole/s}$ . Also find rate of formation of  $\text{H}_2\text{O}(\text{g})$

$$\left( \frac{0.48 \text{ mole H}_2}{\text{s}} \right) \left( \frac{1 \text{ mole O}_2}{2 \text{ mole H}_2} \right) = \boxed{0.24 \text{ mole O}_2/\text{s}} \leftarrow \text{rate of disappearance}$$

$$\left( 0.48 \text{ mole H}_2/\text{s} \right) \left( \frac{2 \text{ mole H}_2\text{O}}{2 \text{ mole H}_2} \right) = \boxed{0.48 \text{ mole H}_2\text{O}/\text{s}} \leftarrow \text{rate of appearance.}$$



if  $\text{NO}$  is decreasing at  $56 \text{ torr/min}$ , what is the rate of change of the total pressure of the vessel?

$$\frac{\Delta[\text{NO}]}{\Delta t} = -56 \text{ torr/min}$$

$$\frac{\Delta[\text{Cl}_2]}{\Delta t} = \left( \frac{-56 \text{ torr NO}}{\text{min}} \right) \left( \frac{1 \text{ mole Cl}_2}{2 \text{ mole NO}} \right) = -28 \text{ torr/min}$$

$$\frac{\Delta[\text{NOCl}]}{\Delta t} = +56 \text{ torr/min} \quad \left( \begin{array}{l} 2 \text{ mole NOCl form for every} \\ 2 \text{ mole NO that react} \end{array} \right)$$

$$\begin{aligned} \text{Total pressure: rate of change} &= -56 \frac{\text{torr}}{\text{min}} + \frac{-28 \text{ torr}}{\text{min}} + 56 \text{ torr/min} \\ &= \boxed{-28 \text{ torr/minute}} \end{aligned}$$

# Chapter 14

#33

14.33 The iodide ion reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way:  $\text{OCl}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^-$ . This rapid reaction gives the following rate data:

$[\text{OCl}^-] \text{ (M)}$	$[\text{I}^-] \text{ (M)}$	Initial Rate (M/s)
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	$1.36 \times 10^{-4}$
$3.0 \times 10^{-3}$	$1.5 \times 10^{-3}$	$2.72 \times 10^{-4}$
$1.5 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.72 \times 10^{-4}$

$$r = k [\text{OCl}^-]^x [\text{I}^-]^y$$

(a) Write the rate law for this reaction. (b) Calculate the rate constant with proper units. (c) Calculate the rate when  $[\text{OCl}^-] = 2.0 \times 10^{-3} \text{ M}$  and  $[\text{I}^-] = 5.0 \times 10^{-4} \text{ M}$ .

(a) In trials 1 and 2,  $[\text{I}^-]$  is constant at  $.0015 \text{ M}$ .  $[\text{OCl}^-]$  doubles from  $.0015 \text{ M}$  to  $.0030 \text{ M}$ , which causes the rate of rxn to double from  $.000136 \text{ M/s}$  to  $.000272 \text{ M/s}$ . Doubling  $[\text{OCl}^-]$  makes the rate double, so rxn is first order wrt  $[\text{OCl}^-]$ , so  $x = 1$ .

In trials 1 and 3,  $[\text{OCl}^-]$  is constant at  $.0015 \text{ M}$ . Doubling  $[\text{I}^-]$  from  $.0015 \text{ M}$  to  $.0030 \text{ M}$  causes the rate to double from  $.000136 \text{ M/s}$  to  $.000272 \text{ M/s}$ , so the rxn is first order wrt  $[\text{I}^-]$ , so  $y = 1$ .

$$r = k [\text{OCl}^-]^1 [\text{I}^-]^1$$

(b) (I used trial 1)  $(1.36 \times 10^{-4} \frac{\text{M}}{\text{s}}) = k (.0015 \text{ M})^1 (.0015 \text{ M})^1$

$$k = \frac{1.36 \times 10^{-4} \frac{\text{M}}{\text{s}}}{(.0015 \text{ M})(.0015 \text{ M})} = 60.444 \rightarrow \begin{matrix} 60. \text{ M}^{-1} \text{ s}^{-1} \\ \text{or } 60. \text{ l/mol}\cdot\text{s} \end{matrix}$$

(c)  $r = (60.444 \text{ M}^{-1} \text{ s}^{-1})(2.0 \times 10^{-3} \text{ M})(5.0 \times 10^{-4} \text{ M}) = 6.0 \times 10^{-5} \frac{\text{M}}{\text{s}}$

14.36 The following data were collected for the rate of disappearance of NO in the reaction  $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ :

#36

Experiment	[NO] (M)	[O <sub>2</sub> ] (M)	Initial Rate (M/s)
1	0.0126	0.0125	$1.41 \times 10^{-2}$
2	0.0252	0.0125	$5.64 \times 10^{-2}$
3	0.0252	0.0250	$1.13 \times 10^{-1}$

(a) What is the rate law for the reaction? (b) What are the units of the rate constant? (c) What is the average value of the rate constant calculated from the three data sets? (d) What is the rate of disappearance of NO when [NO] = 0.0750 M and [O<sub>2</sub>] = 0.0100 M? (e) What is the rate of disappearance of O<sub>2</sub> at the concentrations given in part (d)?

(b) k has units of  $\text{M}^{-2}\text{s}^{-1}$  or  $\frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}$

(c)  $k = \frac{r}{[\text{NO}]^2 [\text{O}_2]}$

expt 1  $k = \frac{.0141 \text{ M/s}}{(.0126 \text{ M})^2 (.0125 \text{ M})} = 7105.06 \text{ M}^{-2}\text{s}^{-1}$

expt 2  $k = \frac{.0564 \text{ M/s}}{(.0252 \text{ M})^2 (.0125 \text{ M})} = 7105.06 \text{ M}^{-2}\text{s}^{-1}$

expt 3  $k = \frac{0.113 \text{ M/s}}{(.0252 \text{ M})^2 (.0250 \text{ M})} = 7117.66 \text{ M}^{-2}\text{s}^{-1}$

avg k =  $\frac{1}{3} (7105.06 + 7105.06 + 7117.66) \text{ M}^{-2}\text{s}^{-1} = 7109.26 \rightarrow 7110 \text{ M}^{-2}\text{s}^{-1}$  (c)

(d) rate of disappearance of NO (which is the rate reported in the chart): calculate when [NO] = 0.0750 M and [O<sub>2</sub>] = 0.0100 M

$r = (7109.26 \text{ M}^{-2}\text{s}^{-1})(.0750 \text{ M})^2 (.0100 \text{ M}) = 0.399896 \rightarrow 0.400 \text{ M/s}$  (d)  
(rate of disappearance of NO)

(e)  $\left(\frac{.399896 \text{ mole NO}}{\text{L} \cdot \text{s}}\right) \left(\frac{1 \text{ mole O}_2}{2 \text{ mole NO}}\right) = 0.200 \frac{\text{M}}{\text{s}}$  (e)

↑  
mole ratio  
from balanced equation

(a) in expts 1 and 2, [O<sub>2</sub>] is constant at 0.0125 M.

When [NO] doubles from 0.0126 M to 0.0252 M, the rate increases by a factor of 4, from 0.0141  $\frac{\text{M}}{\text{s}}$  to 0.0564  $\frac{\text{M}}{\text{s}}$ .  
 $(2)^x = 4$  so  $x = 2$ .

second order with respect to NO.

In expts 2 and 3, [NO] is constant at 0.0252 M. When [O<sub>2</sub>] doubles from 0.0125 to 0.0250, the rate also doubles, from 0.0564  $\frac{\text{M}}{\text{s}}$  to 0.113  $\frac{\text{M}}{\text{s}}$ .  
so the rxn is 1st order with respect to [O<sub>2</sub>].

$r = k [\text{NO}]^2 [\text{O}_2]$  (a)

\* approximately; it increases by a factor of 2.004.

# Chapter 14

[14.38] Consider the reaction of peroxydisulfate ion ( $S_2O_8^{2-}$ ) with iodide ion ( $I^-$ ) in aqueous solution:

#38



At a particular temperature the initial rate of disappearance of  $S_2O_8^{2-}$  varies with reactant concentrations in the following manner:

Experiment	$[S_2O_8^{2-}]$ (M)	$[I^-]$ (M)	Initial Rate (M/s)
1	0.018	0.036	$2.6 \times 10^{-6}$
2	0.027	0.036	$3.9 \times 10^{-6}$
3	0.036	0.054	$7.8 \times 10^{-6}$
4	0.050	0.072	$1.4 \times 10^{-5}$

← given in terms of  $S_2O_8^{2-}$

(a) Determine the rate law for the reaction and state the units of the rate constant. (b) What is the average value of the rate constant for the disappearance of  $S_2O_8^{2-}$  based on the four sets of data? (c) How is the rate of disappearance of  $S_2O_8^{2-}$  related to the rate of disappearance of  $I^-$ ? (d) What is the rate of disappearance of  $I^-$  when  $[S_2O_8^{2-}] = 0.025 M$  and  $[I^-] = 0.050 M$ ?

(a) In expts 1 and 2,  $[I^-]$  is constant at  $.036 M$ .

when  $[S_2O_8^{2-}]$  increases by a factor of 1.5 (from  $.018 M$  to  $.027 M$ ), the rxn rate also increases by a factor of 1.5, from  $2.6 \times 10^{-6} \frac{M}{s}$  to  $3.9 \times 10^{-6} \frac{M}{s}$ .

so the rxn is first order with respect to  $[S_2O_8^{2-}]$ ;  $x=1$  in  $r = k[S_2O_8^{2-}]^x [I^-]^y$

In expts 1 and 3, the rate increases from  $2.6 \times 10^{-6} M/s$  to  $7.8 \times 10^{-6} M/s$ , or by a factor of 3.  $[S_2O_8^{2-}]$  doubles, which in itself would cause the rate of rxn to double.  $\frac{3}{2} = 1.5$ , so the rate is increasing by a

factor of 1.5 due to the change in  $[I^-]$ .  $[I^-]$  changes by a factor of 1.5 (from  $.036 M$  to  $.054 M$ ), the same factor by which rate increased (due to  $I^-$  alone), so rxn is first order with respect to  $[I^-]$ ;  $y=1$

$$r = k [S_2O_8^{2-}]^1 [I^-]^1 \quad (a)$$

$$(b) \quad k = \frac{r}{[S_2O_8^{2-}] [I^-]}$$

$$k_1 = \frac{2.6 \times 10^{-6} M/s}{(.018 M)(.036 M)} = .0040123 M^{-1}s^{-1}$$

$$k_2 = \frac{3.9 \times 10^{-6} M/s}{(.027 M)(.036 M)} = .0040123 M^{-1}s^{-1}$$

$$k_3 = \frac{7.8 \times 10^{-6} M/s}{(.036 M)(.054 M)} = .0040123 M^{-1}s^{-1}$$

$$k_4 = \frac{1.4 \times 10^{-5} M/s}{(.050 M)(.072 M)} = .0038889 M^{-1}s^{-1}$$

$$\text{average } k = .0039814 \rightarrow .0040 M^{-1}s^{-1} \quad (b)$$

(c) the rate of disappearance of  $S_2O_8^{2-}$  is one third of the rate of disapp. of  $I^-$ , (or the rate of dis. of  $I^-$  is 3 times the rate of dis. of  $S_2O_8^{2-}$ ).

$$(d) \quad r = (.0039814 M^{-1}s^{-1})(.025 M)(.050 M) = 4.9768 \times 10^{-6} M/s$$

but this is for  $S_2O_8^{2-}$ , not  $I^-$

$$\left( \frac{4.9768 \times 10^{-6} M S_2O_8^{2-}}{s} \right) \left( \frac{3 I^-}{1 S_2O_8^{2-}} \right) = 1.5 \times 10^{-5} \frac{M}{s}$$

rate of disappearance of  $I^-$



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define  $[A]_0$ ,  $t_{1/2}$ ,  $[A]_t$ ,  $k$

$[A]_0$  = the starting concentration of reactant "A"  
(the concentration of A when zero time has passed)

$t_{1/2}$  = the half-life. the amount of time it takes for half of the A to react to form B; the amount of time it takes for concentration of A to decrease to one half its original amount.

$[A]_t$  = the concentration of A after  $t$  seconds have passed (or minutes, etc)

$k$  = the rate constant for the reaction, that relates the concentration of reactant to the rate of rxn, for example,  $r = k[A]^x$

(b) For a first order rxn, a plot of  $\ln[A]_t$  vs  $t$  will be linear.

(c) the rate constant  $k$  can be determined by finding the slope of the plot.  $k = -\text{slope.}$

40

(a) For a second order reaction, a plot of  $\left(\frac{1}{[A]}\right)$  vs time will be linear.

(b) the slope of this graph will be equal to  $k$ .  $k = \text{slope}$

(c) First order rxns have a constant half life (so long as temperature is constant).  $t_{1/2} = \frac{\ln 2}{k}$  ← the half life depends only on the rate constant, not on the starting concentration.

Second order rxns ~~do~~ do not have a constant half-life, in fact the half life is inversely proportional to the starting concentration

$$\frac{1}{[A]_0} = kt_{1/2} \quad t_{1/2} = \frac{1}{[A]_0 k}$$

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(a) at 600 K,  $t_{1/2} = 2.3 \times 10^5$  s. find  $k$ .

$$k t_{1/2} = \ln 2 \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2.3 \times 10^5 \text{ s}} = \boxed{3.0 \times 10^{-6} \text{ s}^{-1}} \text{ at 600 Kelvin}$$

(b) at 320°C (573 K)  
find  $t_{1/2}$  if  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{2.2 \times 10^{-5} \text{ s}^{-1}} = \boxed{3.2 \times 10^4 \text{ s}}$$

(Note: as Temp increased,  $k$  increased, and  $t_{1/2}$  decreased)



given: at 660 Kelvin,  $k = 4.5 \times 10^{-2} \text{ s}^{-1}$

$r = k[\text{SO}_2\text{Cl}_2]^1$   
 (we are told it is first order...  
 and you can tell this from  
 the units of  $k$  as well.)

(a) if we start w/  $P_{\text{SO}_2\text{Cl}_2}$  of 450 torr,  
 calculate  $P_{\text{SO}_2\text{Cl}_2}$  after 60 seconds.

Since it is first order,  $[\text{SO}_2\text{Cl}_2]_t = [\text{SO}_2\text{Cl}_2]_0 e^{-kt}$

Since the units cancel,  $\left(\frac{[\text{SO}_2\text{Cl}_2]_t}{[\text{SO}_2\text{Cl}_2]_0}\right) = e^{-kt}$   
 we don't have to use  
 molarities. we

could use molarity or moles or grams or pressure or # of atoms...

so we could say  $(P_{\text{SO}_2\text{Cl}_2})_t = (P_{\text{SO}_2\text{Cl}_2})_0 e^{-kt}$

$$P_{\text{SO}_2\text{Cl}_2} = (450 \text{ torr}) e^{-(4.5 \times 10^{-2} \text{ s}^{-1})(60 \text{ s})}$$

$$= (450 \text{ torr}) e^{-2.7} = (450 \text{ torr})(.0672) = 30.24$$

$$\boxed{P_{\text{SO}_2\text{Cl}_2} = 30 \text{ torr}}$$

(b) At what time will  $P_{\text{SO}_2\text{Cl}_2}$  decrease to  $\frac{1}{10}$ th its original value?

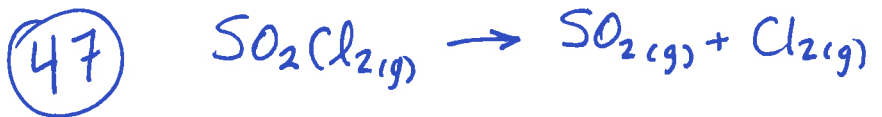
$$\frac{(P_{\text{SO}_2\text{Cl}_2})_t}{(P_{\text{SO}_2\text{Cl}_2})_0} = e^{-kt}$$

$$0.1 = \frac{1}{10} = e^{-kt}$$

$$\ln(0.1) = \ln(e^{-kt}) = -kt$$

$$t = \frac{\ln(0.1)}{-k} = \frac{-2.30258}{4.5 \times 10^{-2} \text{ s}^{-1}} = 51.17 \text{ seconds} \rightarrow \boxed{51 \text{ seconds}}$$

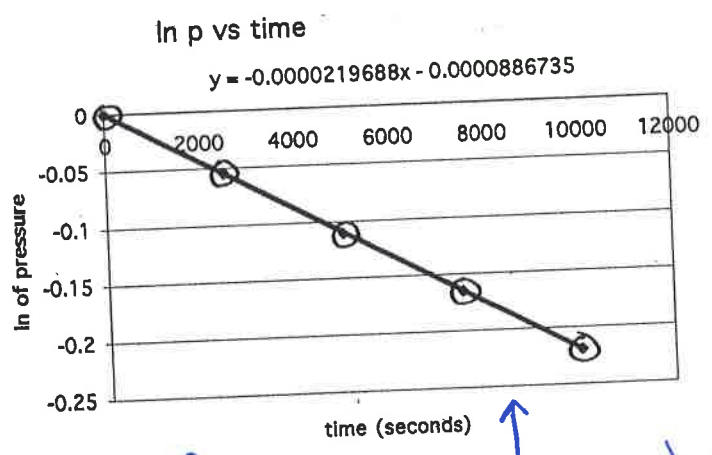
assuming the "one tenth"  
 had at least 2 SF.



(Given)	(Given)	(Calculated)	(Calculated)
Time (seconds)	Pressure $SO_2Cl_2$ (atm)	$\ln(P)$ (-)	$1/P$ (atm <sup>-1</sup> )
0	1.000	0	1
2500	0.947	-0.05445619	1.055966209
5000	0.895	-0.11093156	1.117318436
7500	0.848	-0.16487464	1.179245283
10000	0.803	-0.21940057	1.245330012

This rxn is first order. Use the data **given** to find the first order rate constant, k.

← I didn't actually need to do this since they tell us the rxn is first order...



Since the rxn is first order,  
 $[SO_2Cl_2]_t = [SO_2Cl_2]_0 e^{-kt}$   
 or  $(P_{SO_2Cl_2})_t = (P_{SO_2Cl_2})_0 e^{-kt}$

$\ln(P_{SO_2Cl_2})_t = -kt + \ln(P_{SO_2Cl_2})_0$

$\underbrace{\hspace{1.5cm}}_y = \underbrace{-k}_m t + \underbrace{\ln(P_{SO_2Cl_2})_0}_b$

so a graph of  $\ln P_{SO_2Cl_2}$  vs time should be linear, and the slope will be equal to  $-k$ .

(note:  $\ln P$  is unitless, so the slope of this line will have units of (seconds)<sup>-1</sup> or s<sup>-1</sup>)

I calculated  $\ln P$  for each  $P_{SO_2Cl_2}$  given and did the graph. The line of best fit was

$y = -.000021969x - .0000886735$

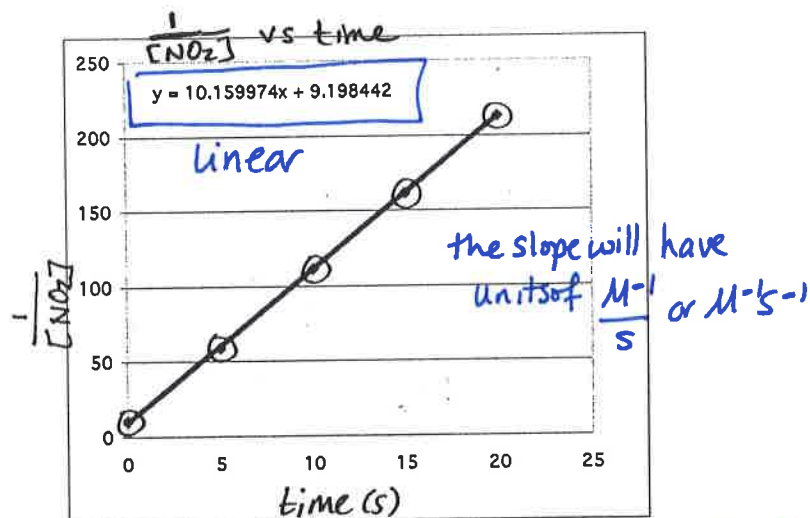
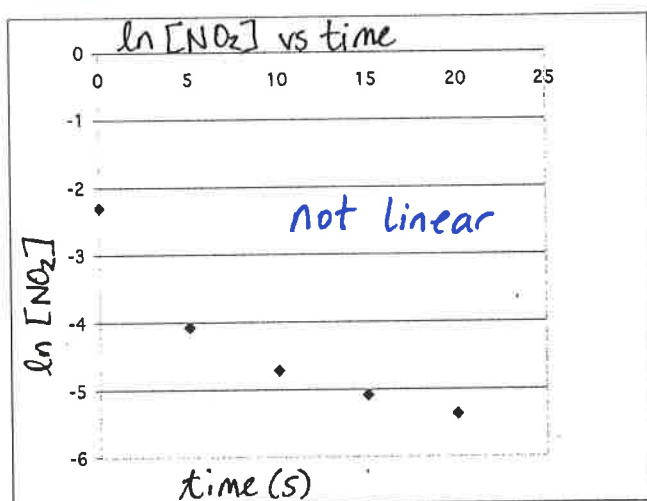
slope =  $-k = -.000021969$

$k = .0000220 \text{ s}^{-1}$



data given at 338°C

(Given) Time (seconds)	(Given) [NO <sub>2</sub> ] (mole/L)	(Calculated) ln[NO <sub>2</sub> ] (-)	(Calculated) 1/[NO <sub>2</sub> ] L/mole
0	0.1000	-2.30258509	10
5	0.0170	-4.07454193	58.82352941
10	0.0090	-4.7105307	111.1111111
15	0.0062	-5.08320599	161.2903226
20	0.0047	-5.36019277	212.7659574



(a) Since the plot of  $\frac{1}{[\text{NO}_2]}$  vs time is linear, the reaction is second order with respect to NO<sub>2</sub>.

(b) The rate constant = slope of  $\frac{1}{[\text{NO}_2]}$  vs time, or 10.159974

$$k = 10. \text{M}^{-1}\text{s}^{-1}$$

(c) find the initial rate of rxn if  $[\text{NO}_2]_0 = .200 \text{M}, .100 \text{M},$  and  $.050 \text{M}$

$$r = k [\text{NO}_2]^2 = (10.16 \text{M}^{-1}\text{s}^{-1}) (.200 \text{M})^2 = 0.406 \rightarrow 0.41 \text{M/s}$$

$$r = k (10.16 \text{M}^{-1}\text{s}^{-1}) (.100 \text{M})^2 = 0.1016 \text{M/s} \rightarrow 0.10 \text{M/s}$$

$$r = k (10.16 \text{M}^{-1}\text{s}^{-1}) (.050 \text{M})^2 = .0254 \text{M/s} \rightarrow 0.025 \text{M/s}$$

(d) calculate [NO<sub>2</sub>] after 30 seconds if  $[\text{NO}_2]_{\text{initial}} = 0.200 \text{M}$

$$[\text{NO}_2] = \frac{1}{\left(\frac{1}{[\text{NO}_2]_0} + kt\right)} = \frac{1}{\frac{1}{.200 \text{M}} + (10.16 \text{M}^{-1}\text{s}^{-1})(30.0 \text{s})}$$

$$[\text{NO}_2] = \frac{1}{5.00 \text{M}^{-1} + 304.8 \text{M}^{-1}} = 0.003228 \rightarrow 0.0032 \text{M}$$

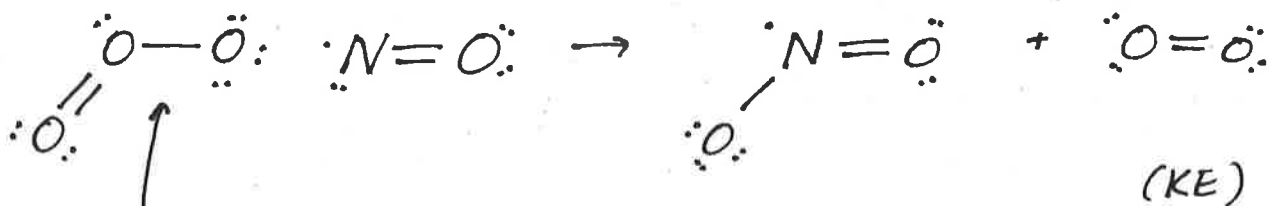
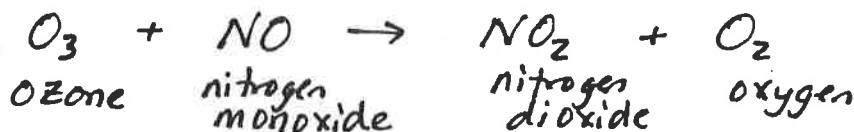
(e) **No**, this rxn is second order, so it does not have a constant half-life.



53) What factors determine whether a collision between two molecules will lead to a chemical rxn:

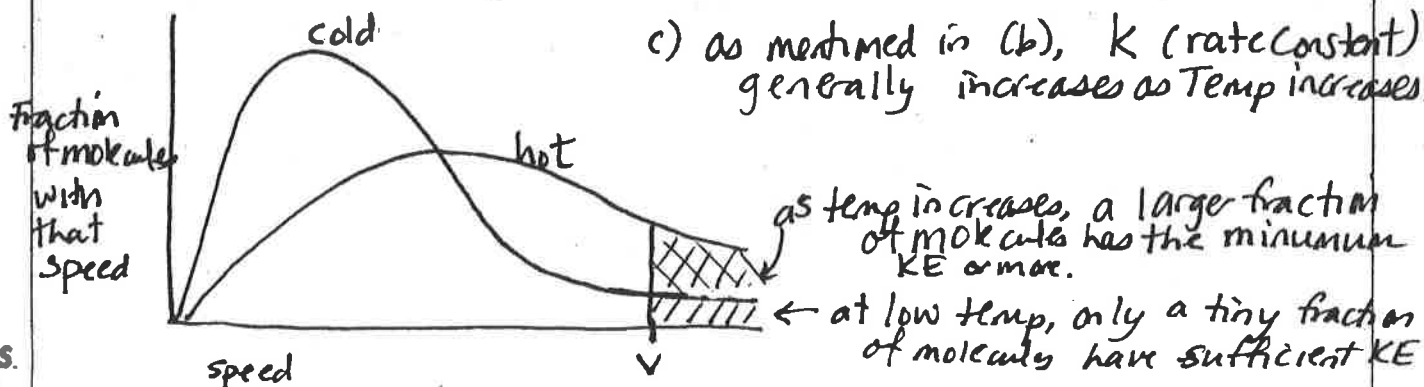
- (1) When the molecules collide, they must have enough kinetic energy to break bonds (breaking bonds requires energy!), or you could say they need enough kinetic energy to meet the activation energy requirement.
- (2) the molecules must be oriented so that the new bonds are able to form (the atoms that are going to form bonds must be near each other!)

For example, in this rxn, NO and O<sub>3</sub> collide:

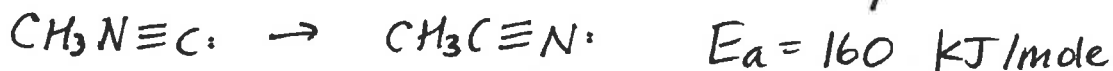


(KE)  
O<sub>3</sub> and NO must collide with enough kinetic energy to break the O-O bond (KE can be transformed to the Potential energy needed to break a bond) and the O from O<sub>3</sub> must collide with the N from NO, not the O from NO, so that the new N-O bond (in NO<sub>2</sub>) can form.

- b) Increasing temperature causes a rate constant (k) to increase because at higher temperature, a larger % of collisions will occur with sufficient energy to break bonds / meet the activation energy requirements for the rxn. avg kinetic energy is proportional to absolute temp, (higher temp corresponds to higher avg kinetic energy) but more importantly, the fraction of molecules with KE above  $K_{E_{min}}$  increases as the Boltzmann Distribution slides to the right.



56



(a) what fraction of molecules have at least 160.0 kJ/mole at 500 K?

$$f = e^{-E_a/RT} = e^{\frac{-160.0 \text{ kJ/mole}}{(.008314 \frac{\text{kJ}}{\text{mol}\cdot\text{K}})(500.\text{K})}} = e^{-38.489}$$

$$f = 1.92 \times 10^{-17} !$$

at 500 K

(b) calculate at 520 K

$$f = \exp\left(\frac{-160.0 \text{ kJ/mole}}{.008314 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} \cdot 520.\text{K}}\right) = \exp(-37.009)$$

$$f = 8.46 \times 10^{-17} \text{ at } 520 \text{ K}$$

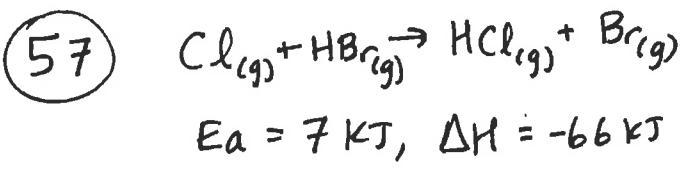
ratio of factors:

$$\frac{f_{520 \text{ K}}}{f_{500 \text{ K}}} = \frac{8.457 \times 10^{-17}}{1.924 \times 10^{-17}} = 4.39$$

So, the rate will be  $\approx 4.4$  times faster at 520 K than at 500 K, assuming the preexponential factor (A) in the Arrhenius equation is fairly constant over that temp range.

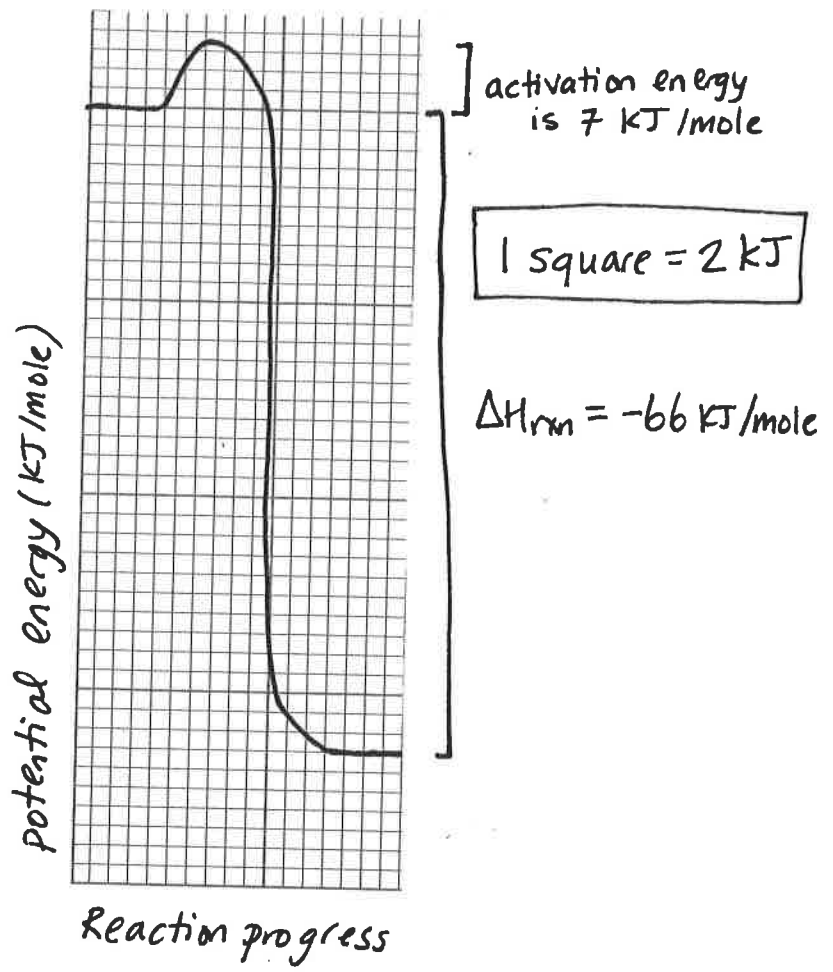
(A will probably increase by a couple percent over this range)

Chapter 14

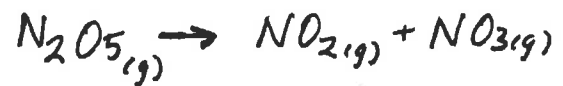
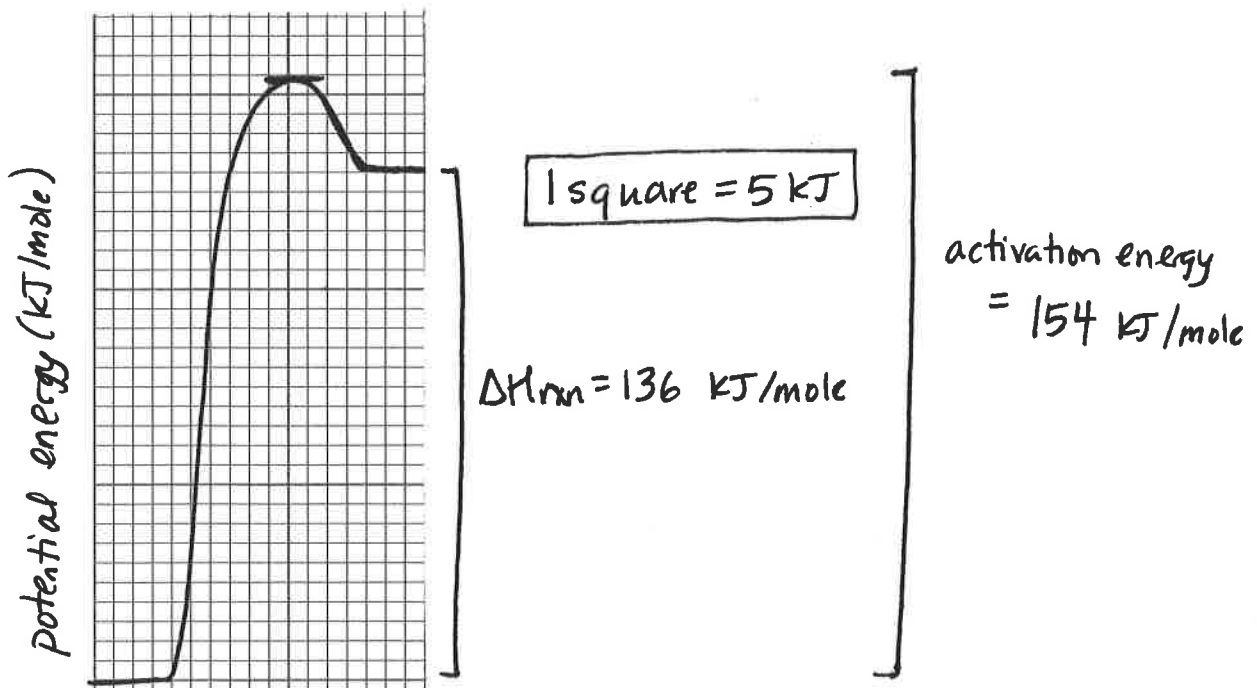


(a) Draw energy diagram!

(b) The  $E_a$  of the reverse rxn ( $HCl + Br \rightarrow HBr + Cl$ ) is  $66 \text{ kJ} + 7 \text{ kJ} = \boxed{73 \text{ kJ}}$



58



(b) the  $E_a$  of the reverse rxn is  $154 \text{ kJ} - 136 \text{ kJ} = \boxed{18 \text{ kJ}}$   
 ( $NO_2 + NO_3 \rightarrow N_2O_5$ )



59 True/False (correct if false)

- (a) If two rxns have similar collision factors, the one with the higher activation energy will be faster.

False. The one with higher activation energy would be slower (at a given temperature) since a smaller % of colliding molecules would have sufficient KE to meet the  $E_a$  requirements.

(KE = Kinetic energy.  $E_a$  = activation energy)

- (b) A reaction with a small rate constant must have a small frequency factor.

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

having a small frequency factor ("A") could be the cause of the low value for k,

but the low k could also be due to the  $E_a$  value being large, or the temperature being low (cold).

- (c) Increasing the rxn temperature increases the fraction of successful collisions between reactants.

True Dat!

61 (a)  $E_a = 45 \text{ kJ/mole}$ ,  $\Delta E = -25 \text{ kJ/mole}$

(b)  $E_a = 35 \text{ kJ/mole}$ ,  $\Delta E = -10 \text{ kJ/mole}$

(c)  $E_a = 55 \text{ kJ/mole}$ ,  $\Delta E = 10 \text{ kJ/mole}$

Q: assuming all collision factors are the same, which rxn is fastest, which is slowest?

Seems like we also need to assume temperature is the same? If so,

rxn (b) is the fastest since  $E_a$  is lowest (35 kJ)

rxn (c) is the slowest since  $E_a$  is highest (55 kJ)

63

- (a)  $k = 2.75 \times 10^{-2} \text{ s}^{-1}$  at  $20^\circ\text{C}$   
 $E_a = 75.5 \text{ kJ/mole}$   
 find  $k$  at  $60^\circ\text{C}$ !

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

$$2.75 \times 10^{-2} \text{ s}^{-1} = A e^{-\frac{75500 \text{ J/mole}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(293\text{K})}} = A e^{-30.993}$$

$$A = \frac{2.75 \times 10^{-2} \text{ s}^{-1}}{e^{-30.993}} = 7.9359 \times 10^{11} \text{ s}^{-1}$$

if we assume  $A$  is the same at  $60^\circ\text{C}$  as it is at  $20^\circ\text{C}$   
 (even though it is probably slightly higher at  $60^\circ\text{C}$ ...)

$$k = 7.9359 \times 10^{11} \text{ s}^{-1} e^{-\frac{75500}{(8.314)(333)}} = 1.138 \downarrow$$

$\uparrow$   
 333 Kelvin  
 $\checkmark 60^\circ\text{C}$

$k = 1.14 \text{ s}^{-1}$   
 at  $60^\circ\text{C}$

- (b) Another rxn has

$$k = 2.75 \times 10^{-2} \text{ s}^{-1}$$

but  $E_a = 125 \text{ kJ/mole}$

find  $k$  at  $60^\circ\text{C}$ .

In part (a) we solved for  $A$  and then plugged back in to the Arrhenius equation ( $k = A e^{-E_a/RT}$ ) with the new temperature.

We don't have to explicitly solve for  $A$  to do the problem though... here is another way to do it:

$$k_1 = A_1 e^{-E_a/RT_1} \leftarrow k \text{ at Temp 1}$$

$$k_2 = A_2 e^{-E_a/RT_2} \leftarrow k \text{ at Temp 2}$$

$$\frac{k_2}{k_1} = \frac{A_2 e^{-E_a/RT_2}}{A_1 e^{-E_a/RT_1}} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{\frac{-E_a}{RT_2} + \frac{E_a}{RT_1}}$$

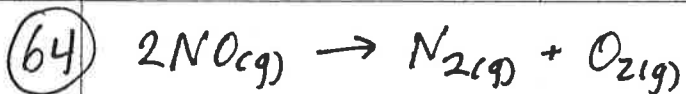
$\uparrow$  assume  $A_2 = A_1$ , so they cancel

$$\frac{k_2}{k_1} = e^{\left(-\frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)} = e^{\frac{-125000 \text{ J}}{8.314 \frac{\text{J}}{\text{K}}}} \left(\frac{1}{333 \text{ K}} - \frac{1}{293}\right)$$

$$\frac{k_2}{k_1} = e^{6.1638} = 475.2 \quad k_2 = 475.2 \cdot k_1 = 475.2 (2.75 \times 10^{-2} \text{ s}^{-1})$$

$$k_2 = 13.069 \rightarrow \boxed{13.1 \text{ s}^{-1}} \text{ at } 60^\circ\text{C}$$

- (c) We assumed  $A$  was independent of temperature.



↑ a pollutant produced  
at high temperature in your car engine!

Hopefully most of the NO will turn back into  $\text{N}_2$  and  $\text{O}_2$   
in your car's catalytic converter!

$$r = k[\text{NO}]^2$$

$$k = .0796 \text{ M}^{-1}\text{s}^{-1} \text{ at } 737^\circ\text{C}$$

$$k = .0815 \text{ M}^{-1}\text{s}^{-1} \text{ at } 947^\circ\text{C}$$

} calculate  
 $E_a$  for the rxn.

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

$$\frac{k_2}{k_1} = \frac{A_2 e^{-E_a/RT_2}}{A_1 e^{-E_a/RT_1}} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

↖ if we assume  $A_2 = A_1$ , these will cancel.  
 $A$  is only weakly temp-dependent..

$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

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

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

$$E_a = \frac{-8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \ln \left( \frac{.0815}{.0796} \right)}{\left( \frac{1}{1220 \text{ Kelvin}} - \frac{1}{1010 \text{ Kelvin}} \right)} = 1150.7 \text{ J/mole}\cdot\text{K}$$

↓  
1.15 kJ/mole

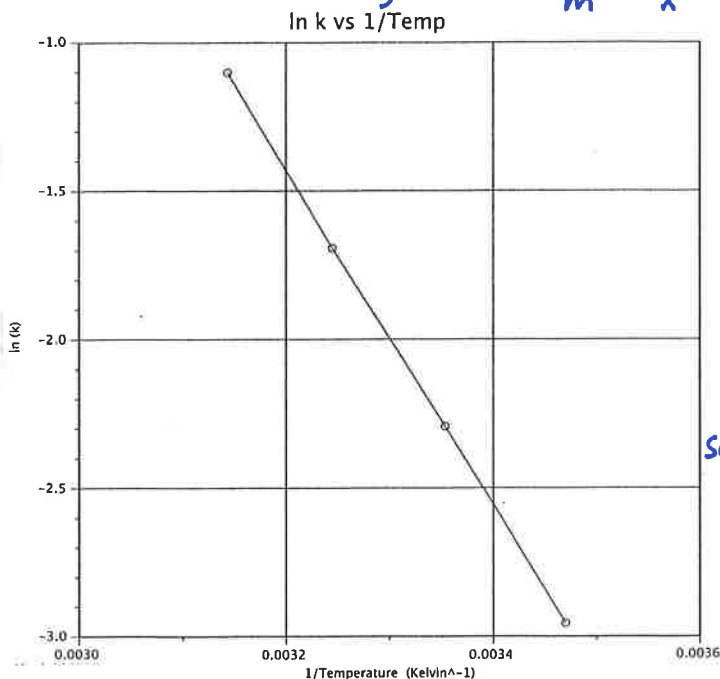
65 Calculate  $E_a$  using the info given.

(Given) Temperature (Celsius)	(Given) k (rate constant) L/(mole-s)	(Calculated) Temperature Kelvin	(Calculated) 1/Temperature Kelvin <sup>-1</sup>	(Calculated) ln of k (-)
15	0.0521	288.15	0.003470415	-2.95459033
25	0.101	298.15	0.003354016	-2.29263476
35	0.184	308.15	0.003245173	-1.69281952
45	0.332	318.15	0.003143171	-1.10262031

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

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$

$\underbrace{\hspace{1.5cm}}_y \quad \underbrace{\hspace{1.5cm}}_m \quad \underbrace{\hspace{1.5cm}}_x \quad \underbrace{\hspace{1.5cm}}_b$



accto Logger Pro,  
this would have a  
line of best fit with the  
equation

$$y = -5644x + 16.63$$

$$\text{so } \ln k = -5644\left(\frac{1}{T}\right) + 16.63$$

The slope of  $\ln k$  vs  $1/\text{Temp}$  is  $-E_a/R$

$$\frac{-E_a}{R} = -5644 \text{ K} \quad E_a = 5644R = 5644 \text{ K} \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)$$

$\uparrow$   
ln k is unitless, so the  
slope has units of  $\frac{1}{(1/\text{K})} = \text{Kelvin}$

$$E_a = 46924 \text{ J/mole}$$

$$E_a = 46.9 \text{ kJ/mole}$$

#66

Use the given info to calculate  $E_a$  and  $A$ .

Chapter 14

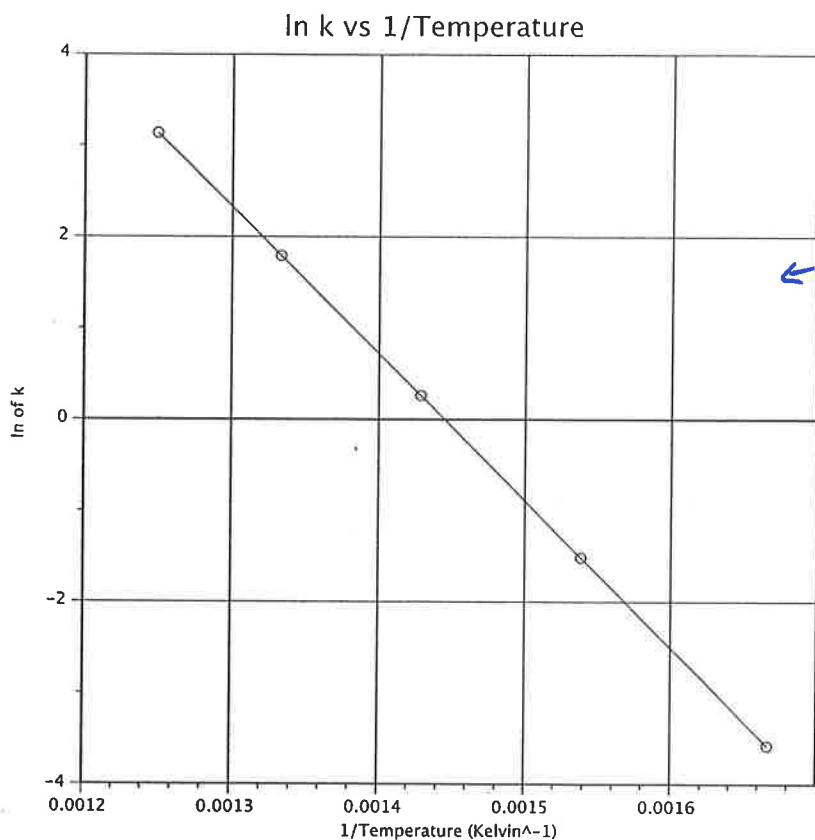
(Given) Temperature (Kelvin)	(Given) k (rate constant) L/(mole-s)	(Calculated) 1/Temperature Kelvin <sup>-1</sup>	(Calculated) ln of k (-)
600	0.028	0.001666667	-3.575550769
650	0.22	0.001538462	-1.514127733
700	1.3	0.001428571	0.262364264
750	6.0	0.001333333	1.791759469
800	23	0.00125	3.135494216

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

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

$$\ln k = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

$$\begin{matrix} \checkmark & \checkmark & \checkmark & \checkmark \\ y & m & x & b \end{matrix}$$



line of best fit has the equation

$$y = -16110x + 23.27$$

$$\text{slope} = -16110 \text{ Kelvin}$$

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

$$-\frac{E_a}{R} = -16110 \text{ K}$$

$$E_a = (16110 \text{ K})(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})$$

$$E_a = 133939 \text{ J/mole}$$

$$\rightarrow 133.939 \text{ kJ/mole}$$

$$E_a = 130 \text{ kJ/mole}$$

$$y\text{-intercept} = \ln A = 23.27$$

$$A = e^{23.27} = 1.277 \times 10^{10}$$

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

↑

$k$  and  $A$  must have the same units.  $k$  was given in L/mol·s

$$A = 1.3 \times 10^{10} \text{ L/mol}\cdot\text{s} \quad \text{or} \quad \text{M}^{-1}\text{s}^{-1}$$

69 Definitions, etc

(a) an elementary reaction (also known as an elementary step) is a chemical reaction which involves a collision between all reactants shown (the reaction occurs via a collision between any and all molecules/ions shown on the reactant side of the equation) one or more elementary steps/reactions will make up the mechanism of the reaction.

For example,  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$  is an elementary reaction because this rxn occurs when NO and  $\text{O}_3$  molecules collide.

but  $2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}$  is not an elementary reaction because it doesn't occur in a single collision between 27 molecules (2+25). It occurs in several smaller steps, each involving fewer molecules (2, or maybe 3) in any one collision.

(b) a "unimolecular" elementary rxn vs a "bimolecular" elementary rxn:

a unimolecular elementary reaction has only one ion or molecule on the reactant side; it does not require a collision. A bimolecular elementary rxn has two molecules or ions on the left side, so the reaction occurs when these two ions/molecules collide with each other.

(c) A reaction mechanism is the sequence of elementary steps

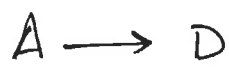
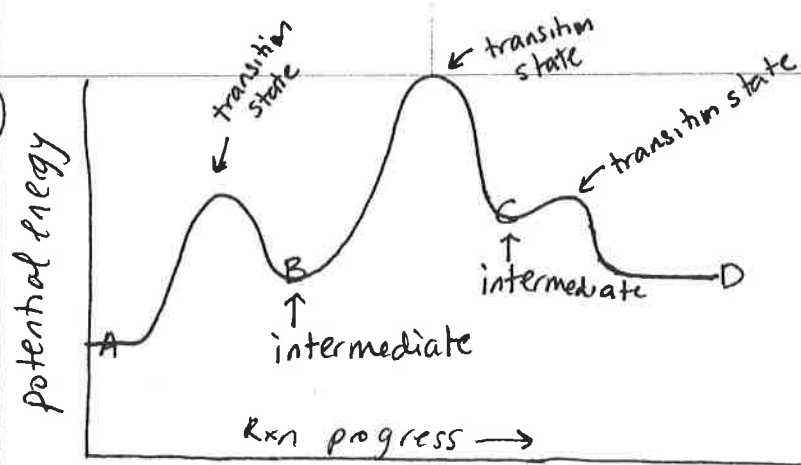
that add up to the overall reaction. The mechanism shows the step or steps that must occur as reactants become products, including any catalysts or intermediates. Each elementary step shows the collisions that must occur as reactants form products.

↑  
for that particular sequence; some rxns have more than one possible mechanism and there won't always be one really "dominant" one.

70 b) termolecular elementary rxns are very rare because three molecules/ions must collide simultaneously for the rxn to occur.

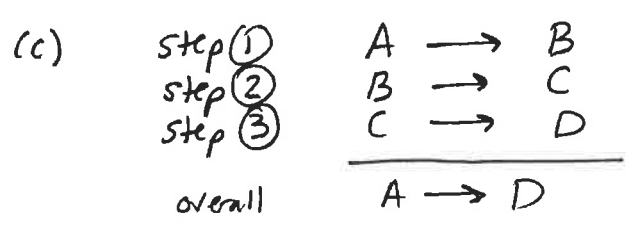
three molecule collisions occur much less frequently than two molecule collisions.

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(a) There are two intermediates in the rxn sequence:  
B and C.

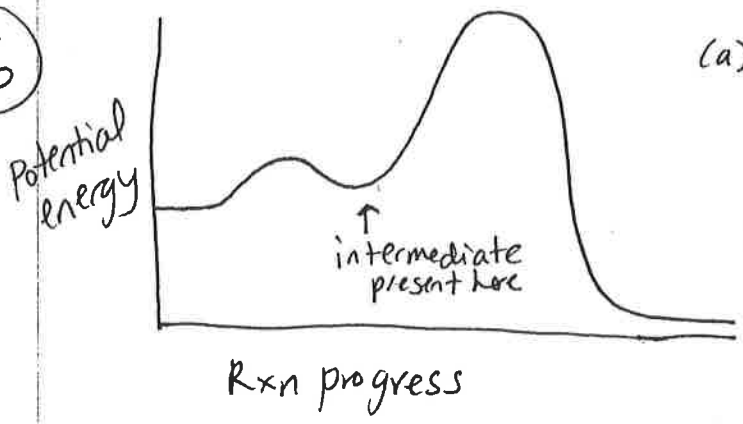
(b) There are three "transition states."  
The top of each peak represents a transition state; so there is one for each step of the reaction.



step 3 is the fastest, since it has the lowest activation energy (assuming the "A" values are similar in  $k = Ae^{-E_a/RT}$ )

(d) The overall rxn is endothermic.  
Acc to the graph, D has more Potential energy than A; D is higher on the graph.

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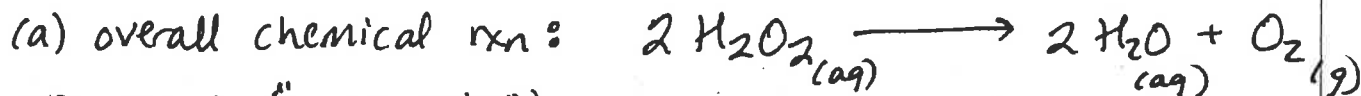
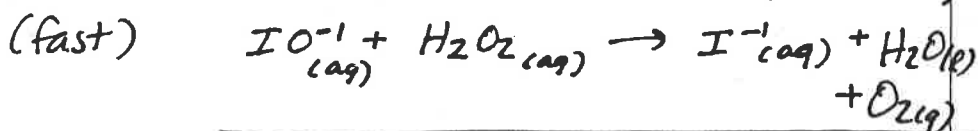
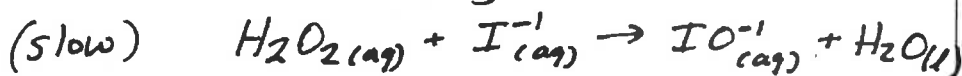
(a) The graph shows two activation energy peaks, so it must have two elementary steps.

(b) There is one intermediate (assuming only one is produced in step 1)

(c) step 2 is probably rate limiting. It has the higher activation energy, so it probably has the lower rate of rxn (assuming the A values are similar in the Arrhenius equation!)

(d) The rxn is exothermic overall.

78 Decomposition of  $\text{H}_2\text{O}_2$ , when catalyzed by iodide ion!



(b)  $\text{IO}^-$  ("hypoiodite") is the intermediate.

(c) Assuming the first step is rate determining (since it is the slow step)

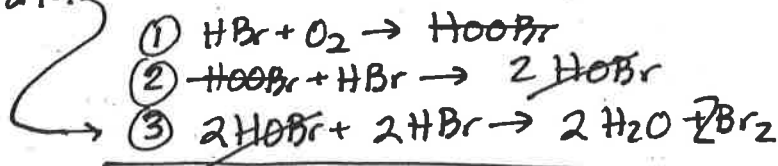
$$r = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

80  $4 \text{HBr} + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{Br}_2$   $r = k [\text{HBr}]^1 [\text{O}_2]^1$  (given)

proposed Mechanism:

- ①  $\text{HBr} + \text{O}_2 \rightarrow \text{HOBr}$
- ②  $\text{HOBr} + \text{HBr} \rightarrow 2 \text{H}_2\text{O}$
- ③  $\text{HOBr} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2$

(a) it does add up to the overall rxn, but you have to double step 3 to make it work.



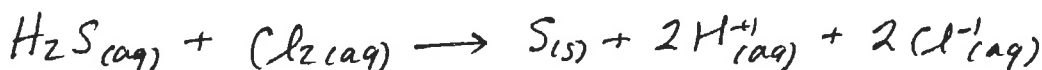
(b) Since the rate law (acc to experiment) is  $r = k [\text{HBr}]^1 [\text{O}_2]^1$ , it would make sense that step ① is the rate determining step; it does involve a collision of one HBr and one O<sub>2</sub>, which would cause a first order dependence on  $[\text{HBr}]$  and  $[\text{O}_2]$

(c) The intermediates are HOBr and HOBr

(d) No. inability to detect HOBr or HOBr among the products does not disprove the mechanism; these are intermediates so they react away as products form. If step 2 and 3 are very "fast" relative to step 1, the HOBr and HOBr will not be able to significantly accumulate; they will react soon after forming.



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H<sub>2</sub>S removal from wastewater(H<sub>2</sub>S is poisonous and smells like rotten eggs)

given:  $r = k[\text{H}_2\text{S}][\text{Cl}_2]$

$$k = 3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \text{ at } 28^\circ\text{C}$$

Find rate of Cl<sup>-</sup> formationfor the disappearance of H<sub>2</sub>S.

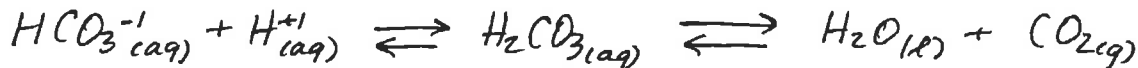
if  $[\text{H}_2\text{S}] = 2.0 \times 10^{-4} \text{ M}$

$[\text{Cl}_2] = 0.025 \text{ M}$

$$r = k[\text{H}_2\text{S}][\text{Cl}_2] = (3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})(2.0 \times 10^{-4} \text{ M})(0.025 \text{ M}) = 1.75 \times 10^{-7} \text{ M/s}$$

$$\left( \frac{1.75 \times 10^{-7} \text{ mole H}_2\text{S}}{\text{L} \cdot \text{s}} \right) \left( \frac{2 \text{ mole Cl}^-}{1 \text{ mole H}_2\text{S}} \right) = \boxed{3.5 \times 10^{-7} \text{ M/s rate of formation of Cl}^-}$$

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EQUILIBRIUM lies to the right (toward CO<sub>2</sub> and H<sub>2</sub>O), but the rxn does not occur very quickly without a catalyst.

Carbonic anhydrase catalyzes the rxn so that we can remove CO<sub>2</sub> from our blood (and "exhale" it). Otherwise CO<sub>2</sub> would accumulate, since we produce it in cellular respiration.

The enzyme catalyzes the dehydration (release to air) of 10<sup>7</sup> CO<sub>2</sub> molecules per second. Identify the enzyme, substrate, and turnover number.

Carbonic anhydrase is the enzyme (an enzyme is a protein that functions as a catalyst)

H<sub>2</sub>CO<sub>3</sub> is the substrate. The substrate is the reactant

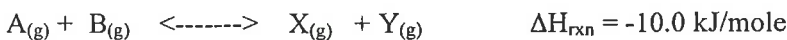
in the rxn catalyzed by the enzyme, and is the substance that will fit into the "active site" of the enzyme.

The turnover number is 10<sup>7</sup> molecules per second,

or 10<sup>7</sup> s<sup>-1</sup>, since 10<sup>7</sup> CO<sub>2</sub> molecules are produced,

or really, since 10<sup>7</sup> H<sub>2</sub>CO<sub>3</sub> molecules react per second.

Problem "R"



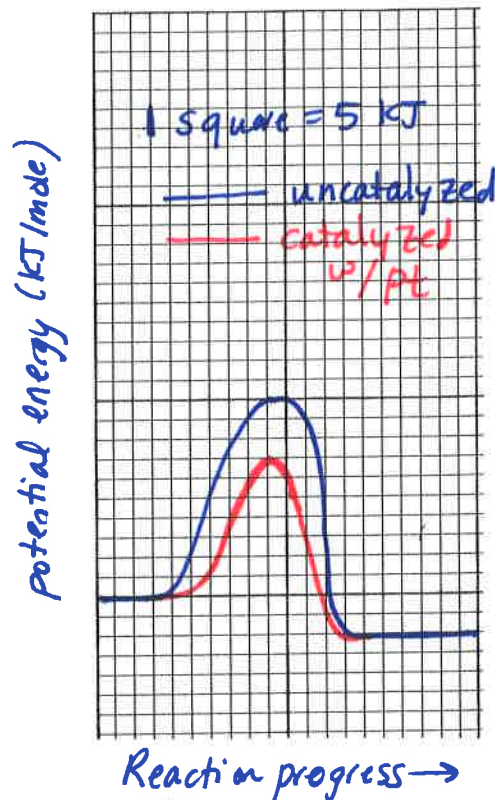
In the above reversible reaction, the forward reaction involves a collision of an "A" with a "B", and the reverse reaction involves a collision of an "X" with a "Y". (Both the forward and reverse reactions occur in a single elementary step).

Therefore, the forward reaction has the rate law,  $r_{fwd} = k_{fwd} [A]^1 [B]^1$   
and the reverse reaction has the rate law,  $r_{rev} = k_{rev} [X]^1 [Y]^1$

In the forward direction, the Arrhenius parameters for the rate constant are as follows:  $A = 1.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$   $E_a = 50.0 \text{ kJ/mole}$

In the reverse direction, the Arrhenius parameters for the rate constant are as follows:  $A = 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$   $E_a = 60.0 \text{ kJ/mole}$

1a. Use the  $\Delta H_{rxn}$  and  $E_a$  of the forward reaction to sketch the energy profile for this reaction on the graph. Use a scale of 1 square = 5 kJ



b. What is the value of  $\Delta H_{rxn}$  for the reverse reaction? +10.0 kJ

c. What is the value of  $E_a$  for the reverse reaction? 60.0 kJ  
(fill this in on the blank above, also.)

2. a. Use the Arrhenius parameters (A and  $E_a$ ) to calculate the rate constant for the forward reaction at 20. °C.

$$k_f = A_f e^{\left(\frac{-E_{af}}{RT}\right)} = 1.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1} e^{\frac{-50000 \text{ J/mole}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(293 \text{ K})}}$$

$$= 1.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1} e^{-20.525} = 0.0185251$$

$$k_f = 0.0185 \text{ M}^{-1}\text{s}^{-1} \text{ at } 20^\circ\text{C}$$

b. Use the Arrhenius parameters (A and  $E_a$ ) to calculate the rate constant for the reverse reaction at 20. °C.

$$k_{rev} = A_{rev} e^{\frac{-E_{a(rev)}}{RT}} = 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \exp\left(\frac{-60000 \text{ J/mole}}{(8.314 \text{ J/mol}\cdot\text{K})(293 \text{ K})}\right)$$

$$= 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \exp(-24.6305)$$

$$= .00034966 \rightarrow k_{reverse} = .000350 \text{ M}^{-1}\text{s}^{-1} @ 20^\circ\text{C}$$

c. Write an expression for  $K_c$ , in terms of the appropriate concentrations.

$$K_c = \frac{[X_{(g)}][Y_{(g)}]}{[A_{(g)}][B_{(g)}]}$$

d. Use your rate constants for the forward and reverse reactions to calculate  $K_c$  at 20. °C

$$K_{eq} = \frac{k(\text{forward})}{k(\text{reverse})} = \frac{.0185251}{.00034966} = 52.9799 \rightarrow K_c = 53.0 @ 20^\circ\text{C}$$

e. Does equilibrium lie "to the left" or "to the right" at 20°C?  $K_c > 1$  so eqm lies to the right  
(products are favored / it is "spontaneous")

"Problem R" cont'd

4. Now we will raise the temperature from 20°C to 40°C!!!!

We will assume that A and Ea remain constant as the temp changes.

a. Use the Arrhenius parameters (A and Ea) to calculate the rate constant for the forward reaction at 40. °C.

$$k_{\text{forward}} = Ae^{-E_a/RT} = 1.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \exp\left(\frac{-50000 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(313 \text{ K})}\right)$$

$$k_{\text{forward}} = .068762 \rightarrow \boxed{0.0688 \text{ M}^{-1}\text{s}^{-1} \text{ at } 40^\circ\text{C}}$$

b. Use the Arrhenius parameters (A and Ea) to calculate the rate constant for the reverse reaction at 40. °C.

$$k_{\text{rev}} = Ae^{-E_a/RT} = 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \exp\left(\frac{-60000 \text{ J/mole}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(313 \text{ K})}\right)$$

$$k_{\text{rev}} = .00168717 \text{ M}^{-1}\text{s}^{-1} \rightarrow \boxed{0.00169 \text{ M}^{-1}\text{s}^{-1} \text{ at } 40^\circ\text{C}}$$

c. Use the rate constants to calculate Keq at 40. °C.

$$K_{\text{eq}} = \frac{k_f}{k_r} = \frac{.068762}{.00168717} = 40.756 \rightarrow \boxed{40.8 = K_{\text{eq}} \text{ at } 40^\circ\text{C}}$$

d. How did increasing temperature affect the value of the forward rate constant (and, therefore, the forward rate of reaction)? (did r(forward) and k(forward) increase or decrease?) r and k increase as T increases  
(.0688 M<sup>-1</sup>s<sup>-1</sup> > .0185 M<sup>-1</sup>s<sup>-1</sup>)

e. How did increasing temperature affect the value of the reverse rate constant (and, therefore, the rate of the reverse reaction)? r and k increase as T increases  
(.00169 > .000350)

f. How did increasing temperature affect the value for Keq? Keq decreases as T increases

g. Does the effect on Keq seem consistent with the fact that the reaction is exothermic? Explain. (40.8 < 53.0)

yes. For exothermic rxns, Keq decreases as temperature increases, because the reverse rate <sup>constant</sup> increases by a larger factor than the forward rate constant increases.

h. A (the "frequency factor") is actually slightly temperature dependent, though we assumed it is not.

As temp increases, does A increase or decrease? (which one?) it increases

Explain (on a molecular level) why A increases/decreases as T increases.

as temperature increases, molecular speed increases, so the reactants collide more frequently.

i. The main effect on the rate as T increases is due to the e<sup>-Ea/RT</sup> part of the Arrhenius equation. With this in mind, explain how/why increasing temperature increases the rate of reaction.

the e<sup>-Ea/RT</sup> part of the equation represents the fraction of molecules with kinetic energy greater than or equal to the Ea. As temp increases, -Ea/RT becomes "less negative", so e<sup>-Ea/RT</sup> increases, meaning that a larger fraction of collisions will occur with sufficient energy to break bonds/meet the activation energy requirements.

problem "R" cont'd

5. Now we will go back to 20. °C, but we will add a platinum catalyst, which changes the activation energy for the forward reaction from 50 kJ/mole to 35 kJ/mole!

$60. - 15 = 45 \text{ kJ/mole}$

a. Show the energy diagram for the catalyzed rxn. (use the same graph that you used for the uncatalyzed rxn)

b. What is the activation energy for the reverse reaction, when catalyzed with Platinum? **45 kJ/mole**

c. Use the A and the new  $E_a$  to calculate the rate constant for the forward reaction, when catalyzed, at 20. °C.

$$k = A e^{-E_a/RT} = 1.52 \times 10^7 \text{ M}^{-1}\text{s}^{-1} e^{\left(\frac{35000}{8.314 \cdot 293}\right)}$$

$$= 1.52 \times 10^7 e^{-14.3678} = 8.7495$$

**$k_f = 8.7 \text{ M}^{-1}\text{s}^{-1}$  catalyzed at 20°C**

d. Use the A and the new  $E_a$  to calculate the rate constant for the reverse reaction, when catalyzed, at 20. °C.

$$k = A e^{-E_a/RT} = 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1} e^{\frac{-45000}{(8.314)(293)}}$$

$$= 1.74 \times 10^7 \text{ M}^{-1}\text{s}^{-1} e^{-18.4729} = 0.165148$$

**$k_r = 0.17 \text{ M}^{-1}\text{s}^{-1}$  catalyzed at 20°C**

e. Use the rate constants to calculate  $K_{eq}$  at 20. °C, in the presence of a catalyst.

$$K_{eq} = \frac{k_f}{k_r} = \frac{8.7495}{0.165148} = 52.9798 \rightarrow \text{53} = K_{eq} \text{ at } 20^\circ\text{C} \text{ catalyzed}$$

- d. How did adding a catalyst affect the value of the forward rate constant?  $k_{fwd}$  **increased** (8.7 > 0.185)
- e. How did adding a catalyst affect the value of the reverse rate constant?  $k_{rev}$  **increased** (0.17 > 0.00035)
- f. How did adding a catalyst affect the value for  $K_{eq}$ ?  $K_{eq}$  **did not change!!!**  
(the forward and reverse rates both increased by factor of 473!)
- g. Explain, on a molecular level, how/why a catalyst increases/decreases the rate of reaction.

Since the catalyst lowers the required activation energy, a higher fraction of collisions will involve enough kinetic energy to break bonds/ meet the activation energy requirements.

$f = e^{-E_a/RT}$  ] as  $E_a$  decreases,  $e^{-E_a/RT}$  increases

↑  
fraction of molecules with  $KE \geq E_a$