

Solutions to Chapter 13 Suggested Exercises  
Exercises taken from “Chemistry”, Raymond Chang, 8<sup>th</sup> edition, McGraw Hill.

**Problem #1:**

What is meant by the rate of a chemical reaction? What are the units of the rate of a reaction?

**Solution:**

It is important to keep the four “rate-thingys” clear. There is rate, rate law, integrated rate law and rate constant.

The rate is the central aspect of kinetics, it represents how quickly (or slowly) the reaction is occurring and is determined by the rate of change of the concentration of either the reactants or the products. As such, the units of the rate of the reaction are Molarity/sec (or Molarity/minute or Molarity/hour).

**Problem #2:**

Distinguish between average rate and instantaneous rate. Which of the two rates gives us an unambiguous measurement of reaction rate? Why?

**Solution:**

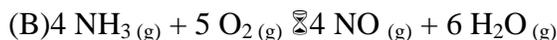
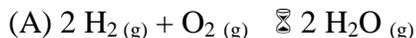
The average rate is just what it sounds like: the average of all the different rates of the reaction throughout the entire course of the reaction. The thing to remember about rate is that, except for 0 order reaction, it is NOT constant. The rate normally depends on the concentration of some or all of the reactants. As a result, as the reactants get used up, the rate changes.

The instantaneous rate is the rate of the reaction measured over a very short period of time (an “instant”), a time period so short that the concentration of the reactants can be considered to be unchanged during this period of time.

If you take all the rates at all the instants and average them, you will get the “average rate” during the entire reaction time.

**Problem #6:**

Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:



**Solution:**

The rate expression can be written in terms of any of the reactants or products and should be equivalent. In order to make them equivalent, the stoichiometry must be taken into account.

Looking at reaction (A), the rate expression can be written in terms of either the disappearance of H<sub>2</sub>, the disappearance of O<sub>2</sub>, or the appearance of H<sub>2</sub>O. The stoichiometry indicates the relative change in concentration. Based on the balanced equation, clearly you must use up 2 H<sub>2</sub> molecules for every O<sub>2</sub> molecule, this means the concentration of H<sub>2</sub> must be changing twice as fast. But the rate expression should be the same regardless of which species you choose, hence the use of the stoichiometry to adjust the different rate expressions.

You might also consider that the change in concentration of products is positive (+) because there is more being created as the reaction proceeds, while the change in concentration of reactants is negative (-) because there is less of those as the reaction proceeds.

When we write a rate expression, we need to cancel out these effects so that it is irrelevant which species I talk about.

$$\text{Rate of reaction A} = \frac{-1 \Delta[\text{H}_2]}{2 \Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1 \Delta[\text{H}_2\text{O}]}{2 \Delta t}$$

$$\text{Rate of reaction B} = \frac{-1 \Delta[\text{NH}_3]}{4 \Delta t} = \frac{-1 \Delta[\text{O}_2]}{5 \Delta t} = \frac{1 \Delta[\text{NO}]}{4 \Delta t} = \frac{1 \Delta[\text{H}_2\text{O}]}{6 \Delta t}$$

**Problem #17:**

Consider the reaction:



From the following data obtained at a certain temperature, determine the order of the reaction and calculate the rate constant:

<u>[A] (M)</u>	<u>[B] (M)</u>	<u>Rate (M/s)</u>
1.50	1.50	3.20x10 <sup>-1</sup>
1.50	2.50	3.20x10 <sup>-1</sup>
3.00	1.50	6.40x10 <sup>-1</sup>

**Solution:**

To determine the order of the reaction, we look at the relative rates of the different reaction mixtures. If you compare the first mixture to the second, we can compare the rates (take a ratio) and see how strongly the rate depends on the concentration.

We can write the generic rate expression, but there are a few things we don't know: the rate constant and the orders of the reaction. But the unknowns will mostly cancel when we look at the ratio.

$$\text{Rate 1}^{\text{st}} \text{ mixture} = 3.2 \times 10^{-1} = k [\text{A}]^x [\text{B}]^y = k [1.50]^x [1.50]^y$$

$$\text{Rate 2}^{\text{nd}} \text{ mixture} = 3.2 \times 10^{-1} = k [A]^x [B]^y = k [1.50]^x [2.50]^y$$

We know look at the ratio:

$$\frac{\text{Rate 1}^{\text{st}} \text{ mixture}}{\text{Rate 2}^{\text{nd}} \text{ mixture}} = \frac{3.2 \times 10^{-1}}{3.2 \times 10^{-1}} = \frac{k [1.50]^x [1.50]^y}{k [1.50]^x [2.50]^y}$$

The k cancels (the rate constant should be constant!) And the first term will cancel no matter what "x" is. That is why we chose these two mixtures, they have the same concentration of everything except for a single reactant.

$$\frac{\text{Rate 1}^{\text{st}} \text{ mixture}}{\text{Rate 2}^{\text{nd}} \text{ mixture}} = 1 = \frac{k [1.50]^x [1.50]^y}{k [1.50]^x [2.50]^y} = \frac{[1.50]^y}{[2.50]^y}$$

$$1 = (1.50/2.50)^y$$

y must be equal to 0 (anything to the 0 power is 1), or you can solve the equation by taking the log of both sides

$$\log 1 = \log (1.50/2.50)^y = y \log (1.50/2.50)$$

- Recall that  $\log \#^{\text{power}} = \text{power} * \log \#$

Either way, y=0

We now need to determine x, so we look for a pair of reactions that have [B] constant but change [A]. That would be reaction mixtures 1 and 3. Again we look at the ratio:

$$\frac{\text{Rate 1}^{\text{st}} \text{ mixture}}{\text{Rate 3rd mixture}} = \frac{3.2 \times 10^{-1}}{6.4 \times 10^{-1}} = \frac{k [1.50]^x [1.50]^y}{k [3.00]^x [1.50]^y}$$

$$\frac{1}{2} = \frac{k [1.50]^x [1.50]^y}{k [3.00]^x [1.50]^y} = \frac{[1.50]^x}{[3.00]^x}$$

$$\frac{1}{2} = (1.50/3.00)^x = (1/2)^x$$

x must be equal to 1.

Now, we have the complete rate expression:

$$\text{Rate} = k [A]$$

We can now plug in measured values for [A] and the rate for each of the reaction mixtures and solve for k

$$0.320 = k [1.50]$$

$$k = 0.213 \text{ s}^{-1}$$

$$0.320 = k [1.50] \quad - \text{this is redundant because the reaction is 0 order in B}$$

$$k = 0.213 \text{ s}^{-1}$$

$$0.640 = k [3.00]$$

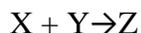
$$k = 0.213 \text{ s}^{-1}$$

All 3 calculated k values are exactly the same, this isn't always true. Sometimes, there will be a slight variation due to normal experimental variations. We take the average of all 3 values to get the correct one.

Rate =  $0.213 \text{ s}^{-1} [\text{A}]$  is the correct rate law

**Problem #18:**

Consider the reaction:



From the following data, obtained at 360 K, (a) determine the order of the reaction, and (b) determine the initial rate of disappearance of X when the concentration of X is 0.30 M and that of Y is 0.40 M.

Initial Rate of

<u>Disappearance of X (M/s)</u>	<u>[X] (M)</u>	<u>[Y] (M)</u>
0.053	0.10	0.50
0.127	0.20	0.30
1.02	0.40	0.60
0.254	0.20	0.60
0.509	0.40	0.30

**Solution:**

This problem gets solved just as problem 17. We select ratios of rates of different reaction mixtures that allow us to cancel either X or Y from the rate law.

If we compare the 3<sup>rd</sup> and 4<sup>th</sup> reaction mixtures, you'll note that [Y] is the same in both cases.

$$\frac{\text{Rate}_3}{\text{Rate}_4} = \frac{k [\text{X}]_3^a [\text{Y}]_3^b}{k [\text{X}]_4^a [\text{Y}]_4^b}$$

$$\frac{1.02 \text{ M/s}}{0.254 \text{ M/s}} = \frac{k [0.4]^a [0.6]^b}{k [0.2]^a [0.6]^b}$$

$$4.02 = \frac{[0.4]^a}{[0.2]^a} = (2)^a$$

$$a = 2$$

We then do the same thing for the 3<sup>rd</sup> and 5<sup>th</sup> reaction mixtures to get [X] to cancel.

$$\frac{\text{Rate}_3}{\text{Rate}_5} = \frac{k [\text{X}]_3^a [\text{Y}]_3^b}{k [\text{X}]_5^a [\text{Y}]_5^b}$$

$$\frac{1.02 \text{ M/s}}{0.509 \text{ M/s}} = \frac{k [0.4]^a [0.6]^b}{k [0.4]^a [0.3]^b}$$

$$2 = \frac{[0.6]^b}{[0.3]^b} = (2)^b$$

$$b = 1$$

So, the rate law is:

$$\text{Rate} = k [\text{X}]^2 [\text{Y}]$$

To determine k, I plug in the rate and concentration data and then take the average of the 5 values.

$$\begin{aligned} \text{Rate}_1 &= k [\text{X}]^2 [\text{Y}] \\ 0.053 \text{ M/s} &= k (0.10 \text{ M})^2 (0.50 \text{ M}) \\ k &= 10.6 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate}_2 &= k [\text{X}]^2 [\text{Y}] \\ 0.127 \text{ M/s} &= k (0.20 \text{ M})^2 (0.30 \text{ M}) \\ k &= 10.6 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate}_3 &= k [\text{X}]^2 [\text{Y}] \\ 1.02 \text{ M/s} &= k (0.40 \text{ M})^2 (0.60 \text{ M}) \\ k &= 10.6 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate}_4 &= k [\text{X}]^2 [\text{Y}] \\ 0.254 \text{ M/s} &= k (0.20 \text{ M})^2 (0.60 \text{ M}) \\ k &= 10.6 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate}_5 &= k [\text{X}]^2 [\text{Y}] \\ 0.509 \text{ M/s} &= k (0.40 \text{ M})^2 (0.30 \text{ M}) \\ k &= 10.6 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

So, the rate law is:

$$\text{Rate} = 10.6 \text{ M}^{-2} \text{ s}^{-1} [\text{X}]^2 [\text{Y}]$$

To determine the initial rate of disappearance of X when the concentration of X is 0.30 M and that of Y is 0.40 M, we just plug in the values now that we have a rate law:

$$\begin{aligned}\text{Rate} &= 10.6 \text{ M}^2 \text{ s}^{-1} [0.30 \text{ M}]^2 [0.40 \text{ M}] \\ \text{Rate} &= 0.382 \text{ M/s}\end{aligned}$$

**Problem #20:**

Consider the reaction:



The rate of the reaction is  $1.6 \times 10^{-2} \text{ M/s}$  when the concentration of A is 0.35 M. Calculate the rate constant if the reaction is (a) first order in A and (b) second order in A.

**Solution:**

We simply write the rate law and solve for k, assuming the order in A given.

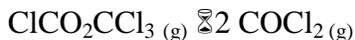
If the reaction is 1<sup>st</sup> order in A, then:

$$\begin{aligned}\text{Rate} &= k [A] \\ 1.6 \times 10^{-2} \text{ M/s} &= k (0.35 \text{ M}) \\ k &= 4.6 \times 10^{-2} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Rate} &= k [A]^2 \\ 1.6 \times 10^{-2} \text{ M/s} &= k (0.35 \text{ M})^2 \\ k &= 0.131 \text{ M}^{-1} \text{ s}^{-1}\end{aligned}$$

**Problem #22:**

The following gas-phase reaction was studied at 290 °C by observing the change in pressure as a function of time in a constant-volume vessel:



Determine the order of the reaction and the rate constant based on the following data:

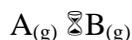
<u>Time (s)</u>	<u>P (mmHg)</u>
0	15.76
181	18.88
513	22.79
1164	27.08

**Solution:**

This problem is slightly different, we don't have a series of initial instantaneous rates measured for a number of different reaction mixtures. We have a single reaction mixture where the concentration of the species are monitored over a period of time.

This is also a little tricky in the sense that the progress of the reaction is being measured indirectly by measuring the total pressure. The only reason the pressure is changing is because this is a gas phase reaction with a change in the number of moles of gas between the reactants and products.

If we had a reaction like:



The pressure would be constant because there is no change in molar quantity of the gas (recall: pressure is proportional to moles of gas, it doesn't matter what the gas is).

With that understood, it is possible to calculate a rate based on the pressure change. Once you have the rate at a series of different times, you can determine the order by looking at the integrated rate laws.

1<sup>st</sup>, let's calculate the rate from the pressure.

$$PV = nRT$$

Now, the temperature, the gas constant "R", and the volume are all constant in this problem. So, in essence, we can rewrite the ideal gas law as:

$$P = (RT/V) n = K n$$

where "K" is a combination of all the other constants.

We have no way to calculate exactly what "n" is initially, we can only look at changes in "n":

$$\Delta P = K \Delta n$$

where  $\Delta n$  represents the increase in products since 1 mole of reactants yields 2 moles of product. Every time a mole of reactants turns to products, there is a net increase of 1 mole of total gases (2 new moles of product - 1 mole of reactant consumed).

<u>Time (s)</u>	<u>P (mmHg)</u>	<u>-<math>\Delta</math>Reactants</u>	<u><math>\Delta</math>Products</u>	<u>Net Reactants</u>
0	15.76	0 mmHg	0 mmHg	15.76 mmHg
181	18.88	3.12 mmHg	6.24 mmHg	12.64 mmHg
513	22.79	7.03 mmHg	14.06 mmHg	8.73 mmHg
1164	27.08	11.32 mmHg	22.64 mmHg	4.44 mmHg

You can use either the change in products or reactants as a measure of rate, it should end up being the same:

$$-\Delta[\text{reactants}]/\Delta\text{time} = \frac{1}{2} \Delta[\text{products}]/\Delta\text{time}$$

If you recall the integrated rate laws, they tell you what the rate should be at any point in time as a function of the concentration of the reactants:

1<sup>st</sup> order reaction (R=reactant)

$$\ln [R]_t = -kt + \ln[R]_0$$

2<sup>nd</sup> order reaction

$$1/[R]_t = kt + 1/[R]_0$$

We can solve this problem graphically or algebraically:

Graphically:

If we plot  $\ln[R]$  vs time, we should get a straight line with a slope of  $-k$  if it is 1<sup>st</sup> order, but a curved line if it is 2<sup>nd</sup> order.

If we plot  $1/[R]$  vs time, we should get a straight line with a slope of  $k$  if it is 2<sup>nd</sup> order, but a curved line if it is 1<sup>st</sup> order.

Algebraically:

If we calculate  $k$  for each of the times using the integrated rate law,  $k$  will only be constant if the order is correct. In other words:

If I calculate  $k$  at each of the times using

$$\ln [R]_t = -kt + \ln[R]_0$$

$k$  will be constant if and only if the reaction is 1<sup>st</sup> order. If it is 2<sup>nd</sup> order, I'll get all different values for  $k$ .

If I calculate  $k$  at each of the times using

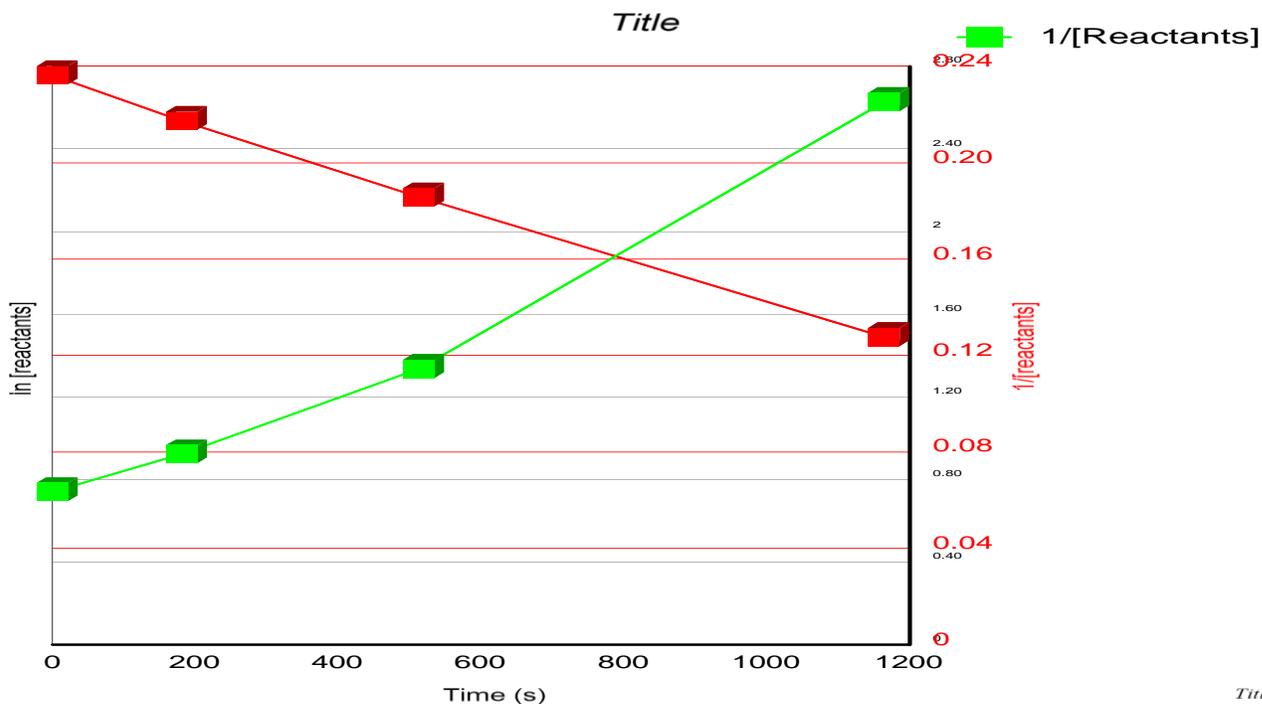
$$1/[R]_t = kt + 1/[R]_0$$

$k$  will be constant if and only if the reaction is 2<sup>nd</sup> order. If it is 1<sup>st</sup> order, I'll get all different values for  $k$ .

They are equivalent methods. The graph is usually easier, you can just plot it in Excel or by hand on graph paper.

The red line on the graph below is the 1<sup>st</sup> order curve ( $\ln [\text{Reactants}]$  vs time), the green line is the 2<sup>nd</sup> order curve ( $1/[\text{Reactants}]$  vs time). Clearly, the red line is straight while the green line is curved. This means the reaction must be first order.

# 1st order and 2nd order integrated rate law plots



Time (s)	Pressure (mm Hg)	delta	Reactants	Net reactants	ln (Net reactants)	1/Net reactants
0	15.76		0	15.76	2.757	0.0635
181	18.88		3.12	12.64	2.537	0.0791
513	22.79		7.03	8.73	2.167	0.1145
1164	27.08		11.32	4.44	1.491	0.2252

This is the data used to construct the graph. We could use this same data to construct the algebraic solution.

Once we have the order, we can calculate k from the best fit straight line (or algebraically).

Time (s)	Pressure (mm Hg)	delta	Reactants	Net reactants	ln (Net reactants)	$k = (\ln[R]_{\text{init}} - \ln[R]_{\text{at } t}) / \text{time}$
0	15.76		0	15.76	2.757	
181	18.88		3.12	12.64	2.537	0.00121883257298907
513	22.79		7.03	8.73	2.167	0.00115148092510375
1164	27.08		11.32	4.44	1.491	0.00108833394156838

If we plug the data into the 1<sup>st</sup> order rate law, we get 3 slightly different values for the data points (the 1<sup>st</sup> data point isn't defined because t=0 and there is no change in concentration). The correct answer would be the average of the 3 values:

$$k = 1.1 \times 10^{-3} \text{ s}^{-1}$$

**Problem #28:**

The thermal decomposition of phosphine (PH<sub>3</sub>) into phosphorus and molecular hydrogen is a first-order reaction:



The half-life of the reaction is 35.0 s at 680 °C. Calculate (a) the first-order rate constant for the reaction and (b) the time required for 95 percent of the phosphine to decompose.

**Solution:**

If the reaction is first order, it must follow the 1<sup>st</sup> order integrated rate law (see Problem 22 above):

$$\ln [\text{R}]_t = -kt + \ln [\text{R}]_0$$

The half-life of a reaction is how long it takes for the reaction to proceed halfway to completion or, in other words, how long it takes for half of the reactants to disappear:

$$[\text{R}]_t = \frac{1}{2} [\text{R}]_0$$

If we make that substitution into the integrated rate law:

$$\ln (\frac{1}{2} [\text{R}]_0) = -k (35.0 \text{ s}) + \ln [\text{R}]_0$$

Or, rearranging a little bit:

$$\ln (\frac{1}{2} [\text{R}]_0) - \ln [\text{R}]_0 = -k (35.0 \text{ s}) - \text{Recall } \ln A - \ln B = \ln (A/B)$$

$$\ln (\frac{1}{2} [\text{R}]_0 / [\text{R}]_0) = \ln (\frac{1}{2}) = -k (35.0 \text{ s})$$

$$k = - [\ln(\frac{1}{2})] / 35.0 \text{ s} = \mathbf{0.0198 \text{ s}^{-1}}$$

Once you have k, you can determine the exact progression of the reaction.

Part (b) asks how long it takes for 95% of the phosphine to decompose. In other words, how long does it take for  $[\text{R}]_t = 0.05[\text{R}]_0$  (95% gone, 5% left)

Well:

$$\ln ([\text{R}]_t) = -k (35.0 \text{ s}) + \ln [\text{R}]_0$$

$$\ln (0.05 [\text{R}]_0) = - (0.0198 \text{ s}^{-1}) (t) + \ln [\text{R}]_0$$

$$\ln (0.05[\text{R}]_0) - \ln[\text{R}]_0 = -0.0198 \text{ s}^{-1} t$$

$$\ln (0.05[\text{R}]_0 / [\text{R}]_0) = \ln 0.05 = -0.0198 \text{ s}^{-1} t$$

$$t = 151 \text{ s}$$

**Problem #37:**

Variation of the rate constant with temperature for the first-order reaction



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is given in the following table. Determine graphically the activation energy for the reaction.

<u>T (K)</u>	<u>k (s<sup>-1</sup>)</u>
298	1.74x10 <sup>-5</sup>
308	6.61x10 <sup>-5</sup>
318	2.51x10 <sup>-4</sup>
328	7.59x10 <sup>-4</sup>
338	2.40x10 <sup>-3</sup>

**Solution:**

The rate constant of a reaction changes with temperature. This change is determined, theoretically, by the Arrhenius equation:

$$\ln k = -E_a/RT + \ln A$$

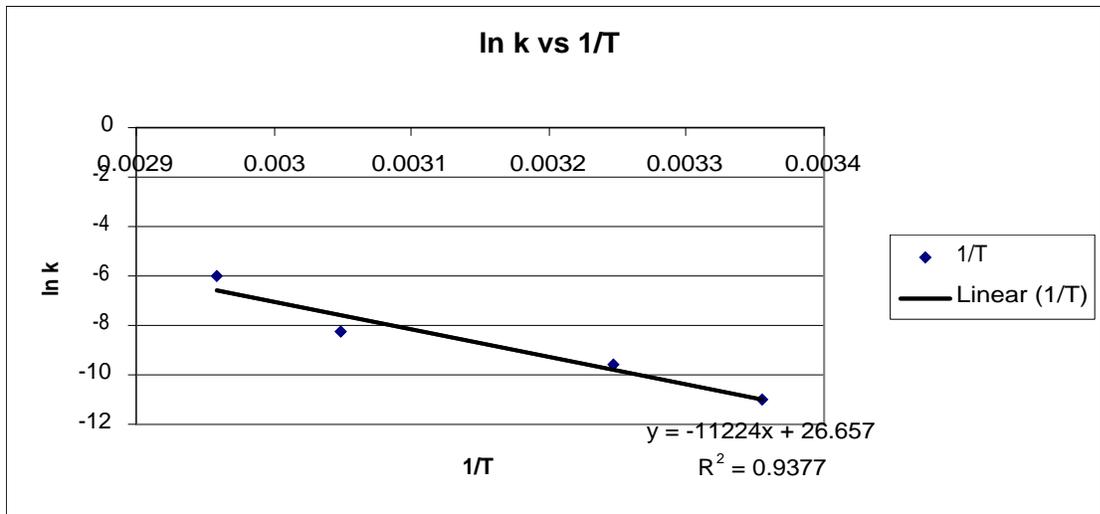
where k is the rate constant, E<sub>a</sub> is the activation energy of the reaction, R is the ideal gas constant (watch the UNITS!) and A is the Arrhenius factor.

Note that the Arrhenius equation looks a lot like the equation for a straight line (y=mx+b) if you plot ln k vs 1/T the slope is -E<sub>a</sub>/R, the intercept is ln A.

$$y = m x + b$$
$$\ln k = -E_a/R (1/T) + \ln A$$

So, if I plot ln k vs 1/T, the slope will give me the activation energy!

T	k	ln k	1/T
298	1.74E-05	-10.959	0.003356
308	6.61E-05	-9.62434	0.003247
328	0.000251	-8.29006	0.003049
338	0.0024	-6.03229	0.002959



From the linear fit, the slope of the line is -11224 K

So,

$$-11224 \text{ K} = -E_a/R$$

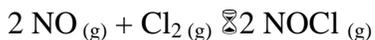
$R = 8.314 \text{ J/mol K}$  (Note that I use this not  $0.0821 \text{ L atm/mol K}$  because I want my answer for the activation energy to have UNITS of energy - Joules)

$$-11224 \text{ K} = -E_a/8.314 \text{ J/mol K}$$

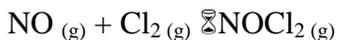
$$E_a = 93316 \text{ J/mol}$$

**Problem #51:**

The rate law for the reaction



is given by  $\text{rate} = k[\text{NO}][\text{Cl}_2]$ . (a) What is the order of the reaction? (b) A mechanism involving the following steps has been proposed for the reaction:



If this mechanism is correct, what does it imply about the relative rates of these two steps?

**Solution:**

(A) The order of the reaction is 1<sup>st</sup> order in NO, 1<sup>st</sup> order in Cl<sub>2</sub>, and 2<sup>nd</sup> order overall.

(B) You'll note that the first step in the proposed mechanism is 1<sup>st</sup> order in NO and 1<sup>st</sup> order in Cl<sub>2</sub>. Since this matches the overall order of the reaction, it implies that this is the SLOWEST step in the mechanism. The second step must be much much faster than the first step and, therefore, does not in any way limit the rate of the reaction or, in other words, contribute to the rate law.

**Problem #68:**

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



<u>Experiment</u>	<u>[H<sub>2</sub>]</u>	<u>[NO]</u>	<u>Initial Rate (M/s)</u>
1	0.010	0.025	2.4x10 <sup>-6</sup>
2	0.0050	0.025	1.2x10 <sup>-6</sup>
3	0.010	0.0125	0.60x10 <sup>-6</sup>

(a) Determine the order of the reaction. (b) Calculate the rate constant. (c) Suggest a plausible mechanism that is consistent with the rate law. (Hint: Assume that the oxygen atom is the intermediate.)

**Solution:**

As always, we determine the order by selecting suitable reaction mixtures and comparing the rate:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{1.2 \times 10^{-6}}{2.4 \times 10^{-6}} = \frac{k [\text{NO}]_2^a [\text{H}_2]_2^b}{k [\text{NO}]_1^a [\text{H}_2]_1^b} = \frac{k [0.025]^a [0.0050]^b}{k [0.025]^a [0.010]^b}$$

$$0.5 = (0.005)^b / (0.010)^b = 0.5^b$$

So, b = 1

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{0.60 \times 10^{-6}}{2.4 \times 10^{-6}} = \frac{k [\text{NO}]_3^a [\text{H}_2]_3^b}{k [\text{NO}]_1^a [\text{H}_2]_1^b} = \frac{k [0.0125]^a [0.010]^b}{k [0.025]^a [0.010]^b}$$

$$0.25 = (0.0125/0.025)^a = 0.5^a$$

So, a = 2

The rate law, then, becomes:

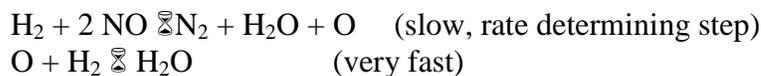
$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

$$2.4 \times 10^{-6} = k [0.025]^2 [0.010]$$

$$k = 0.384 \text{ M}^{-2} \text{ s}^{-1}$$

There are, of course, many plausible mechanisms that could be postulated when there are no restrictions other than the rate law to be considered. The suggestion that atomic oxygen is an intermediate narrows down the possibilities a little, but not down to only one.

One possibility is:



This is probably the simplest you could suggest. It has a single, rate determining step with an atomic oxygen intermediate. There are other possible answers.

### **Problem #73:**

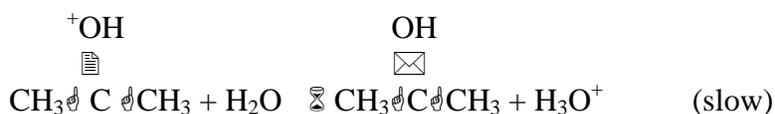
The bromination of acetone is acid-catalyzed:



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

	$[\text{CH}_3\text{COCH}_3]$	$[\text{Br}_2]$	$[\text{H}^+]$	Rate of Disappearance of $\text{Br}_2$ (M/s)
(1)	0.30	0.050	0.050	$5.7 \times 10^{-5}$
(2)	0.30	0.10	0.050	$5.7 \times 10^{-5}$
(3)	0.30	0.050	0.10	$1.2 \times 10^{-4}$
(4)	0.40	0.050	0.20	$3.1 \times 10^{-4}$
(5)	0.40	0.050	0.050	$7.6 \times 10^{-5}$

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





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

**Solution:**

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{5.7 \times 10^{-5}}{5.7 \times 10^{-5}} = \frac{k [\text{CH}_3\text{COCH}_3]_2^a [\text{Br}_2]_2^b [\text{H}^+]_2^c}{k [\text{CH}_3\text{COCH}_3]_1^a [\text{Br}_2]_1^b [\text{H}^+]_1^c} = \frac{k[0.030]^a [0.10]^b [0.050]^c}{k[0.030]^a [0.050]^b [0.050]^c}$$

$$1.0 = (0.10)^b / (0.050)^b = 0.5^b$$

So,  $b = 0$ .

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{1.2 \times 10^{-4}}{5.7 \times 10^{-5}} = \frac{k [\text{CH}_3\text{COCH}_3]_3^a [\text{Br}_2]_3^b [\text{H}^+]_3^c}{k [\text{CH}_3\text{COCH}_3]_1^a [\text{Br}_2]_1^b [\text{H}^+]_1^c} = \frac{k[0.030]^a [0.050]^b [0.100]^c}{k[0.030]^a [0.050]^b [0.050]^c}$$

$$2.11 = (0.10/0.050)^c$$

Therefore,  $c = 1$

$$\frac{\text{Rate}_5}{\text{Rate}_1} = \frac{7.6 \times 10^{-4}}{5.7 \times 10^{-5}} = \frac{k [\text{CH}_3\text{COCH}_3]_5^a [\text{Br}_2]_5^b [\text{H}^+]_5^c}{k [\text{CH}_3\text{COCH}_3]_1^a [\text{Br}_2]_1^b [\text{H}^+]_1^c} = \frac{k[0.040]^a [0.050]^b [0.050]^c}{k[0.030]^a [0.050]^b [0.050]^c}$$

$$1.33 = (0.04/0.03)^a$$

$a=1$

That makes the overall rate law:

$$\begin{aligned} \text{Rate} &= k [\text{CH}_3\text{COCH}_3] [\text{H}^+] \\ 7.6 \times 10^{-4} &= k (0.040) (0.05) \\ k &= 0.38 \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

To rationalize the mechanism in terms of the rate law is a little tricky in this case. The actual rate determining step depends on two reactive intermediates rather than any of the actual reactants. BUT, you can't write a rate law in terms of reactive intermediates. The very fast equilibrium in the first step that creates the intermediates contains both of the relevant reactants to 1<sup>st</sup> order. Hence, the overall rate law is 1<sup>st</sup> order in the acetone and the H+.