Chapter 13 Chemical Kinetics I

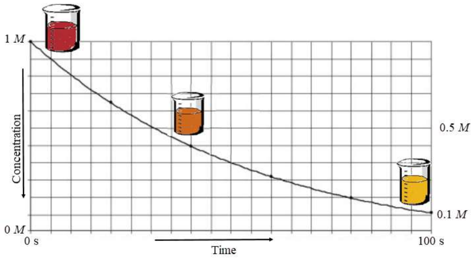
Chemistry by Chang and Goldsby

Chapter 13: Chemical Kinetics

13.1 The Rate of a Reaction.
13.2 The Rate Law

If a solution of a dye has a certain concentration, it is easy to visualize using a single image.

Kinetics deals with **changing** concentrations. Visualizing a change over time requires multiple images of concentration. The solution to the right changed from 1 M to 0.1 M over 100 seconds. However, the drop in concentration wasn't constant over the 100 seconds. The reaction rate changed with time. Instead of a straight line the concentration vs time is a curve. This unit deals with these changes over time,



13.1 The Rate of a Reaction.

Reactants decrease as products increase: A → B

Rate involves the change in concentration of **reactants per time**.

Products are ignored in reaction rate equations.

$$\text{rate} = -\frac{[\Delta \text{A}]}{\Delta t}$$

Chemical reaction rates are commonly expressed as the **decrease of molar concentration of reactants per second, M s^{-1}**. However, there are variations in rate that you should be on the lookout for.

Sometimes the time unit may be hours, days or even years instead of seconds.

Pressure can be used instead of molar concentration of gases.

If gas pressure is used instead of molar concentrations, dividing the atm pressure by RT will change the pressures into molar concentration. $M = P/RT$.
Conversely, you can change pressure readings into concentration by $P = M \times RT$.

For the reaction, A → B

Why do we track the change in reactants, *A*, rather than the products, *B*?

The concentration of the reactants in any reaction, except for zero order reactions, determines the rate of the reaction. The concentration of the products does not[1].

Why is there a negative sign in the rate equation? $\text{rate} = -\dfrac{[\Delta \text{A}]}{\Delta t}$

The rate of a reaction is based on how quickly concentrations of the reactants drop: ($[\text{A}]_2 - [\text{A}]_1$). The reactants are always used up, so the change in concentration or pressure of the reactants would always be negative. Constantly using a negative sign is a bother. Putting the negative sign in the rate equation makes the rate values positive.

When comparing rates of substance changes in a reaction, coefficients will allow you to convert rates of disappearance or formation of one substance with another.

The equations shown in the text are complex, but in the end, they are just stoichiometric ratios.
The bottom line is that the same factor label system used in stoichiometry works with rates.

For the reaction, $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$, the rate of production of $\mathbf{NO_2}$ is $4.0 \times 10^{-3}\ M\ s^{-1}$.

(a) Calculate the rate of appearance of $O_2(g)$.

$$2\ N_2O_5 \rightarrow \mathbf{4\ NO_2} + 1\ \mathbf{O_2}$$

$$4.0 \times 10^{-3}\, M\, s^{-1}\ \cancel{NO_2} \times \frac{1\, O_2}{4\ \cancel{NO_2}} = 1.0 \times 10^{-3}\, M\, s^{-1}\ O_2$$

(b) Calculate the rate of disappearance of $\mathbf{N_2O_5}$.

$$2\ \mathbf{N_2O_5} \rightarrow \mathbf{4\ NO_2} + 1\ O_2$$

$$4.0 \times 10^{-3}\, M\, s^{-1}\ NO_2 \times \frac{2\ N_2O_5}{4\ NO_2} = 2.0 \times 10^{-3}\, M\, s^{-1}\ N_2O_5$$

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[1] There is one exception to this rule. The products of a reversible reaction ⇄ can influence the reaction rate.

13.2 The Rate Law (speedometer equation):

Where the reaction is $a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$

$$\textbf{rate} = k\,[\mathrm{A}]^{x}[\mathrm{B}]^{y}$$

The coefficients of the balanced reaction (*a, b*) do not determine the superscripts (*x, y*) in the rate law.

This equation is also called the instantaneous rate law since the rate is for the instant the reactants are at a specific concentration. The Rate Law is the "speedometer" equation and will give you the rate (speed) of the reaction in *M*/s at specific concentrations of [A] and [B].

The superscripts in the equation x and y will usually be 0, 1, or 2 and k is the rate constant[2] which only varies with temperature. Most of this chapter is about the superscripts and the rate constant.

The order of the reaction

$$\textbf{rate} = k\,[\mathrm{A}]^{x}[\mathrm{B}]^{y}$$

The superscript values of x and y in the rate law expressions are the **orders of the reactants**.

99% of the time the orders of the reaction, will be the whole, positive numbers: 0, 1, or 2.
The order of the reaction with most likely be

0, zeroth order 1, first order 2, second order

The term "*overall order of reaction*" is the sum of exponents in the rate law.

The order of the reaction can be determined using two methods:

(1) experimental data
  (a) instantaneous rate (the rate a specific set of concentrations)
  (b) reaction concentration curves (next outline)

(2) examining the mechanism of the reaction (third outline)**.**

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[2] Note this is an italicized lower-case k. Do not confuse this with the upper case, nonitalicized K for kelvin.

The order of a reaction (exponent of [reactant] in the rate law) can be experimentally determined by a series of experiments. This method requires that you can see the relationship between the **change in concentration** in several trials and the **effect the change has on the rate**.

Experiments are run where rates of reactions and concentrations can simultaneously be determined. By examining the effect that the concentration changes have on the rate, it is possible to determine the order of each reactant. You just need to be clever with your math skills to determine x and y.

For example, in the reaction: $F_2 + ClO_2 \rightarrow 2\ FClO_2$

rate = $k\ [F_2]^x[ClO_2]^y$ the orders of the reaction, x and y are unknown.

Experiments are run where only one reactant concentration is altered and the rate of the reaction (speed) at each concentration is determined.

	Concentrations of reactants		Rate of Reaction
Experiment 1:	$[F_2] = 0.10\ M$	$[ClO_2] = 0.10\ M$	Initial Rate = $0.0012\ M\ s^{-1}$
Experiment 2:	$[F_2] = 0.20\ M$	$[ClO_2] = 0.10\ M$	Initial Rate = $0.0024\ M\ s^{-1}$

First find the order of the reaction with respect to $[F_2]$:
In experiments 1 and 2, the **$[F_2]$** doubled, **(×2)** while $[ClO_2]$ remained constant.
The rate of reaction also doubled, (×2).
Therefore, the $[F_2]$ is important in this reaction to the **first order, $[F_2]^1$.**

rate = $k\ [\mathbf{F_2}]^{\mathbf{1}}[ClO_2]^y$

Another experiment is run where only the concentration of chlorine dioxide is changed.

	Concentrations of reactants		Rate of Reaction
Experiment 1:	$[F_2] = 0.10\ M$	$[ClO_2] = 0.10\ M$	Initial Rate = $0.0012\ M\ s^{-1}$
Experiment 3:	$[F_2] = 0.10\ M$	$[ClO_2] = 0.40\ M$	Initial Rate = $0.0048\ M\ s^{-}$

In experiments 1 and 3, the **$[ClO_2]$**, quadrupled **(×4)** while the $[F_2]$ remained constant.
The reaction rate also quadrupled **(×4)**.
Therefore, the $[ClO_2]$ is important in this reaction to the **first order, $[ClO_2]^1$.**

rate= $k\ [F_2]^1[\mathbf{ClO_2}]^{\mathbf{1}}$

order of $[F_2]$ =1 order of $[ClO_2]$ 1 therefore the **overall order of rxn = 2**

If you have difficulty seeing the changes in the numbers, simplify the grid by dividing by the lowest value in each column. The patterns will be easier to spot.

Experiment	F_2 M	ClO_2 M	Rate $M\ s^{1-}$
1	0.10	0.10	0.0012
2	0.20	0.10	0.0024
3	0.10	0.40	0.0048

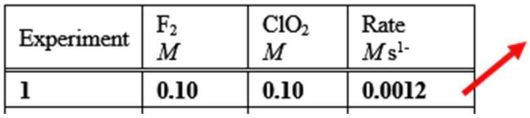
F_2 (simplified)	ClO_2 (simplified)	Rate (simplified)
1	1	1
2	1	2
1	4	4

All rate law problems given on the AP exams are simple enough to be solved using comparisons with the simplification method. Sometimes the patterns will have “tricks” to them, but you can be certain that the orders can be found by comparing the rate changes to the concentration changes. **So, look for the patterns.**

Once you have found the orders of the reactants and have the complete rate law expression (speedometer equation),

$$\text{rate} = k\,[F_2]^1[ClO_2]^1$$

The next step is to solve for the rate constant, *k*, for the reaction using any one of the experimental trials.
In this case of solving for *k*, the data from Experiment 1 was used, but any trial's data will work since the constant, *k*, is valid for all concentrations.



Experiment	F_2 M	ClO_2 M	Rate $M\,s^{1-}$
1	**0.10**	**0.10**	**0.0012**

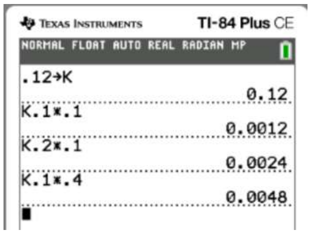
$$0.0012\ M\,s^{-1} = k\,[0.10\ M]^1[0.10\ M]^1$$

$$k = \frac{0.0012\ M\ s^{-1}}{[0.10\ M]^1[0.10\ M]^1} = 0.12\ M^{-1}s^{-1}$$

$\boldsymbol{k = 0.12\ M^{-1}\,s^{-1}}$
rate = $(0.12\ M^{-1}\,s^{-1})\,[F_2]^1\,[ClO_2]^1$

With the rate law expression and the rate constant, *k*, you can find the rate of a reaction at any instant for any set of concentrations.

Experiment	F_2	ClO_2	rate = $k\,[F_2]\,[ClO_2]$		Rate
1	0.10 M	0.10 M	$(0.12\ M^{-1}\,s^{-1}) \times 0.10\ M \times 0.10\ M$	=	0.0012 $M\,s^{1-}$
2	0.20 M	0.10 M	$(0.12\ M^{-1}\,s^{-1}) \times 0.20\ M \times 0.10\ M$	=	0.0024 $M\,s^{1-}$
3	0.10 M	0.40 M	$(0.12\ M^{-1}\,s^{-1}) \times 0.10\ M \times 0.40\ M$	=	0.0048 $M\,s^{1-}$



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.12→K
                    0.12
K.1*.1
                  0.0012
K.2*.1
                  0.0024
K.1*.4
                  0.0048
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Units:

The units of a rate are always $M\ s^{-1}$ or pressure s^{-1}.
The unit for the rate constant, *k*, is dependent on the rate law equation's overall order.

The rate law equation multiplication of the rate constant with the concentrations must always produce a rate with the correct speed unit, $M\,s^{-1}$.

There is often an FRQ question on the reaction order constant on the AP Exam. One point is given for the calculated value of the rate constant, and **one point is given for the correct unit for the rate constant**!

Rate Law Equation	overall order, *n* $n = x + y$ where **rate = $k[A]^x[B]^y$**	**rate constant, *k*, unit** $\boldsymbol{M^{(1-n)}\,s^{-1}}$	Unit calculation of the **rate of the reaction must always produce $M\,s^{-1}$**
rate = $k\,[A]^0$	zeroth order $n = 0$	$M^{(1-0)}\,s^{-1} = \boldsymbol{M\,s^{-1}}$	rate = $(M\,s^{-1})\,[M]^0 = M\,s^{-1}$
rate = $k\,[A]^0\,[B]^1$	first order $n = 1$	$M^{(1-1)}\,s^{-1} = s^{-1}$	rate = $(s^{-1})\,[M]^1 = M\,s^{-1}$
rate = $k\,[A]^1\,[B]^1$	second order $n = 2$	$M^{(1-2)}\,s^{-1} = \boldsymbol{M^{-1}\,s^{-1}}$	rate = $(M^{-1}\,s^{-1})\,[M]\,[M] = M\,s^{-1}$
rate = $k\,[A]^2\,[B]^1$	third order $n = 3$	$M^{(1-3)}\,s^{-1} = \boldsymbol{M^{-2}\,s^{-1}}$	rate = $(M^{-2}\,s^{-1})\,[M]^2\,[M] = M\,s^{-1}$

[3]The reaction $2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O$ is found experimentally to be second-order in [NO] and first-order in $[H_2]$.

(a) The rate law for this reaction is: rate = *k*___________________
(b) The overall order for this reaction is: __________
(c) What are the units for the rate constant *k* ? ________________

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[3] (a) rate = $k\,[NO]^2\,[H_2]$; (b) third order overall; (c) $M^{-2}\,s^{-1}$

Work on this problem to test your skills in determining reaction orders from experimental data.

Chlorine Dioxide is a reddish-yellow gas that is soluble in water and produces chlorate and chlorite ions. In basic solution, it reacts according to the following equation:

$$2\ ClO_2 + 2\ OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

The rate law for this reaction will be: rate = $k\,[ClO_2]^x\,[OH^-]^y$
To determine the order of reaction for each reactant, the initial rates of the reaction were measured at various initial concentrations as recorded in the table below. Determine the rate law order and rate law constant for the reaction from these data.

Experiment	$[ClO_2]$	$[OH^-]$	Initial Rate ($M\ s^{-1}$)
1	0.060	0.030	2.48×10^{-2}
2	0.020	0.030	2.76×10^{-3}
3	0.020	0.090	8.78×10^{-3}

Change all the rates to the same power of ten, so that you can correctly compare them.

Experiment	$[ClO_2]$	$[OH^-]$	Initial Rate ($M\ s^{-1}$)
1	0.060	0.030	2.48×10^{-2} changed to 24.8×10^{-3}
2	0.020	0.030	2.76×10^{-3}
3	0.020	0.090	8.78×10^{-3}

Simplify the table by dividing the values by the lowest rate to see the relationships.

Simplified by dividing by the lowest number in each column			
Experiment	C	OH^-	Rate
1	3	1	≈ 9
2	1	1	1
3	1	3	≈ 3

The data from experiments may not be exact, so you may have to do a little rounding as in the rate for Experiment 1 and 3.

To determine the order of $[ClO_2]^x$

Experiments 1 and 2 changed $[ClO_2]$ by 1/3 while $[OH^-]$ remained unchanged and the rate changed by 1/9 or $(1/3)^2$. Therefore, concentration of the ClO_2 affects the rate as a second order reactant, $[ClO_2]^{\mathbf{2}}$.

To determine the order of $[OH^-]^y$

Experiments 2 and 3 changed $[OH^-]$ by ×3 while $[ClO_2]$ remained unchanged and the rate changed by ×3. Therefore, the concentration of the OH^- is first order, $[OH^-]^1$.

[4] (a) rate law expression: rate = ____________________
(b) substituting data from any of the experiments: k = ____________________
(c) The overall order for this reaction is: __________

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[4] (a) rate = $k[ClO_2]^2[OH^-]$; (b) 230 $M^{-2}\ s^{-1}$; (c) 3rd order overall
Answer for (b) must include the units! The answer is automatically wrong if units are not included.

There is a mathematical formula that can be used to solve for the exponents of instantaneous rate law problems. However, it is cumbersome. This algebraic method will not be needed on any AP Chemistry question. I've only included this method because some students like to see a mathematically based solution.

You can skip this explanation if you like.

Since *x* and *y* are superscripts, logarithms can be used to solve for *x* and *y*.
The order of the reaction, *m*, for a substance whose concentration is changed from $[A_1]$ to $[A_2]$, while no other concentration is being altered, is the **log of the ratio of two rates**, **divided by the log of the ratio of two concentrations**.

$$\text{The order of the reaction with respect to } A: \quad m = \frac{log\left(\dfrac{\text{rate at }[A_1]}{\text{rate at }[A_2]}\right)}{log\left(\dfrac{[A_1]}{[A_2]}\right)}$$

$$2\ ClO_2 + 2\ OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

To determine the order of reaction for each reactant, the initial rates of the reaction were measured at various initial concentrations as recorded in the table below. Determine the rate law order and rate law constant for the reaction from these data.

Experiment	$[ClO_2]$	$[OH^-]$	Initial Rate (M s^{-1})
1	0.060	0.030	2.48×10^{-2}
2	0.020	0.030	2.76×10^{-3}
3	0.020	0.090	8.78×10^{-3}

ClO_2 order using Experiment 1 and 2
since $[OH^-]$ is unchanged.

$$\text{rate} = k\,\boldsymbol{[ClO_2]}^x[OH^-]^y$$

$$x = \frac{\log\left(\frac{0.0248 M s^{-1}}{0.00276\ M s^{-1}}\right)}{\log\left(\frac{0.060\ M}{0.020\ M}\right)} = \frac{\log(8.98)}{\log(3.0)} = 2$$

$x = 2$

OH^- order using Experiment 1 and 3
Since ClO_2 is unchanged

$$\text{rate} = k\,[ClO_2]^x\boldsymbol{[OH^-]}^y$$

$$y = \frac{\log\left(\frac{0.00276 M s^{-1}}{0.00878 M s^{-1}}\right)}{\log\left(\frac{0.030\ M}{0.090\ M}\right)} = \frac{\log(0.314)}{\log(0.333)} = 1$$

$y = 1$

The rate law for this reaction will be: rate = $k\,[ClO_2]^2\,[OH^-]^1$

You may need to round your answer to the nearest whole number, but this equation always works and would be a valid method of solution for an FRQ question asking for the order of a reaction based on instantaneous rates.

Now see if you can find the rate law in this problem that was used on an AP Exam Free Response question.

The following data were obtained at 25°C for the reaction that converts a halogenated alkane into an alcohol.

$$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$$

Determine the rate law equation and rate law constant for the reaction from these data.

$[C_2H_5Br]$ (M)	$[OH^-]$ (M)	Initial Rate ($M\ s^{-1}$)
0.150	0.200	4.8×10^{-5}
0.300	0.200	9.6×10^{-5}
0.450	0.200	1.44×10^{-4}
0.300	0.600	2.88×10^{-4}

Answer for (c) must include the units!

[5] (a) The Rate Law for this reaction is: rate = ___________________
(b) The overall order for this reaction is: __________
(c) The rate constant for this reaction is: k = _____________

If you cannot solve this last problem, go to the video link for this example problem.

https://app.screencast.com/rc2AfNC9rTn9v

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[5] (a) rate = $k[C_2H_5Br][OH^-]$; (b) 2nd order overall; (c) 0.0016 $M^{-1}\ s^{-1}$