Kinetics – Math Notes

In Thermodynamics, you determined whether a reaction will occur spontaneously, based on the relative states of reactants and products. Kinetics deals with the rate at which a reaction occurs between those states. The rate of chemical rxn is determined experimentally by measuring the rate at which a react disappears or a products appears.

Rate Law Using Initial Concentrations
(Including the Arrhenius constant, k, which takes into account the activation energy for the reaction and the temperature at which the reaction occurs.)

Here's a hypothetical:

Experiment	Initial concentration [A] Reactant (M)	Initial concentration [B] Reactant (M)	Initial concentration [C] Reactant (M)	Initial Rate of Formation of D [M/sec]
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.020	0.10	0.02
4	0.20	0.20	0.10	0.08

The rate law always takes the following form: Rate $= k[A]^x[B]^y[C]^z$

The greater the value of a reactant's exponent, the more a change in the concentration of that reactant will affect the rate of the reaction. The easiest way to find the exponents is to see what happens to the rate when the conc. Of an individual reactant is DOUBLED.

<u>Look at [A],</u>

From exp 3 and 4, [A] doubles while the other reactant concentrations remain constant. The rate quadruples from exp 3 to 4

$\qquad$ 0.02 M/sec to 0.08 M/sec

$(2)^x = 4$, so $x = 2$
$\quad$ Because the value of x is 2, then the reaction is said to be **second order** with respect to A.
Rate $= k[A]^2[B]^y[C]^z$

<u>Look at [B],</u>

From exp 1 to 3, [B] doubles while the other reactant concentration remain constant.

The rate doubles from exp 1 to 3, going from 0.01 M/sec to 0.02 M/sec.

$(2)^y = 2$, so $y = 1$
$\qquad$ Because the value of $y = 1$, the reaction is said to be **first order** with respect to B.
Rate $= k[A]^2[B][C]^z$
Look at [C],

From exp 1 to 2, [C] doubles while the other react concentrations remain constant.   The rate remains constant at 0.01 M. The rate change is $(2)^z = 1$, so $z = 0$.

Because the value of z=0, the reaction is **zero order** with respect to C.

Rate = k $[A]^2[B]$

Because the sum of the exponents is 3, the reaction is said to be a third order overall.

Once the rate law has been determined, the value of the rate constant can be calculated using any of the lines of data on the table. It is important to carry along units throughout all rate constant calculations.

Exp 3 can be used-----

$$k= \frac{Rate}{[A]^2[B]} = \frac{(0.02\ M/sec)}{(0.10\ M)^2\ (0.20\ M)} = 10\ \frac{M}{(M)^3\ (sec)} = 10\ M^{-2}\text{-}sec^{-1}$$

Rate Law Using Concentration and Time
2 Rate Laws:
Differential: Rate law; shows how the rate depends on concentration.
Integrated: Shows how concentration depends on time.

*The rate laws will be different depending on whether the reaction is 1st, 2nd, or zero order, but each rate law can be expressed as a GRAPH that relates the rate constant, the concentration of a reactant, and the elapsed time.

First Order Rate Law
The rate depends on the concentration of a single reactant raised to the 1st power.
$$Rate = k[A]$$

As the concentration of reactant A is depleted over time, the rate of reaction will decrease with a characteristic half-life. Nuclear Decay is a 1st order process.

Radioactive Decay: spontaneous; it is when nuclei lose energy.

- Nuclide - a unique atom that scientists use when discussing nuclear reactions.
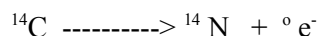- Isotope - A group of nuclides with the same atomic #.

Nuclear Decay Reactions:
alpha - "α" - Helium nuclei are emitted (^{4} He)

$$^{238}\ U\ \text{------>}\ ^{234}\ Th\ +\ ^4\ He$$
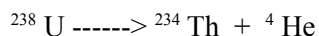
can be stopped by a sheet of paper, but deadly to skin cells
2.   beta - β Results in the release of an e^{-1}

$$^{14}C\ \text{---------->}\ ^{14}\ N\ +\ ^o\ e^-$$
can be stopped by Al foil and is smaller that alpha

3. gamma - "γ" - High energy radiation released as other nuclear transformations occur. (sun - it comes from the electromagnetic spectrum).

It passes easily through paper, wood, and foil. It can be stopped by concrete or lead.

4. positron production - (antiparticle of the e^{-1}); A positron has the same mass as the e^{-1}, but opposite charge. When a low-energy positron collides with a low-energy electron, annihilation occurs, resulting in the production of two gamma ray photons

$^{22}Na \text{ -----}\rightarrow\ ^0e_{+1}\ +\ ^{22}Ne$
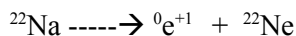
- When a positron collides with an e^{-1}, the matter is changed to radiation (photon).

5. <u>Electron Capture</u> - 1 of the inner-orbital electrons is captured by the nucleus.

$^{201}Hg\ +\ ^0e^{-1}\ \text{------}\rightarrow\ ^{201}Au\ +\ \gamma$
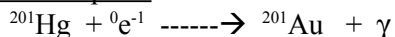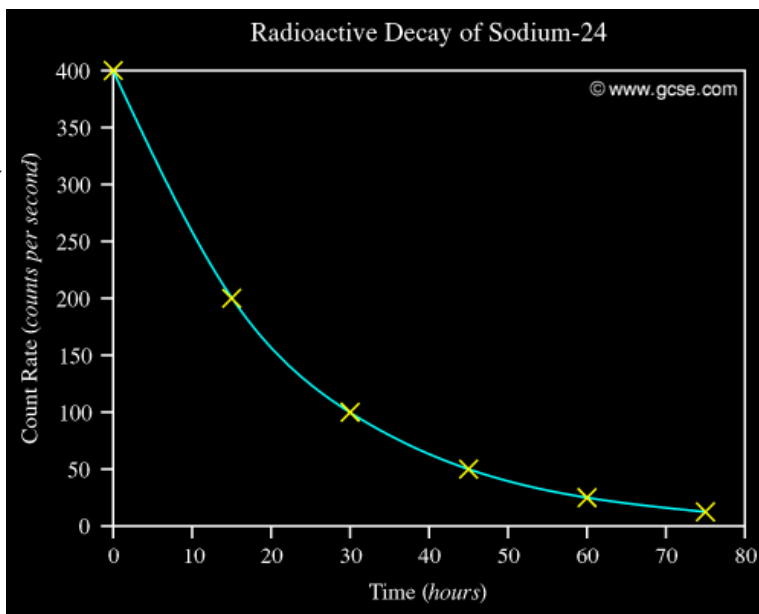
HALF-LIFE

Radioactive radioisotopes are naturally occurring in the air, soil, rocks, drink, and food. There are 350 radioisotopes with only 50 that are radioactive. Radioactivity refers to the particles which are emitted from nuclei as a result of nuclear instability. Because the nucleus experiences the <u>intense conflict</u> between the two strongest forces in nature, it should not be surprising that there are many nuclear isotopes which are unstable and emit some kind of radiation.

<u>1/2-life (t)</u> - Time required for 1/2 of the radioisotope atoms to emit radiation and decay to form new atoms.

*The long the 1/2 life, the more stable the isotope. (range: sec-years)

ex. age of rocks - compare the amounts of U-238 and Pb-206

ex: Thorium-234 has a 1/2 life of 25 days and through beta and gamma emission. It decays for 75 days. How much remains (initial mass = 50.0 g)

Radioactive Decay of Sodium-24
© www.gcse.com

# of 1/2 lives	Time (days)	Mass of Th-234
0	0	50.0g
1	25	25.0 g
2	50	12.5 g
3	75	6.25 g

After 3 half lives, there is 6.25 g of Th-234 left.

The rate law for a <u>1st order</u> reaction using natural logarithms:

$ln[A]_t - ln\ [A]_0\ = -kt$

$[A]_t$ - concentration of reactant A at time t   k – rate constant

$[A]_0$ - initial concentration of reactant A   t – time elapsed

If you are asked to give the half-life of a first order reaction, you can usually figure if out by looking at the graph or table given, but it's worth your while to know the equation that gives the half-life in terms of rate constant.

$T_{1/2}\ =\ \dfrac{ln\ 2}{k}\ =\ \dfrac{0.693}{k}$

[A] (M)	Time (min)
2.0	0
1.6	5
1.2	10

a. Find the value of k. (use the first two lines)

$\ln[A]_t - \ln[A]_0 = -kt$

$\ln(1.6) - \ln(2.0) = -k (5\text{min})$

$-0.22 = -(5 \text{ min}) k$

$k = 0.045 \text{ min}^{-1}$

b. Find [A] when 20 minutes have elapsed.

$\ln[A]_t - \ln[A]_0 = -kt$

$\ln[A]_t - \ln(2.0) = -(0.045 \text{ min}^{-1})(20 \text{ min})$

$\ln[A]_t = -0.21$ $[A]_t = e^{-0.21} = 0.81 \text{ M}$

c. The half-life would be: $T_{1/2}$ = $\dfrac{0.693}{k}$ = $\dfrac{0.693}{0.045 \text{ min}^{-1}}$ =   15.4 minutes

Second Order Rate Law –p. 575

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

The rate law for a second-order reaction uses the inverses of the concentrations.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

The use of inverses in the rate law creates a linear graph comparing concentration and time.

Zero-Order Rate Law

The rate doesn't depend on the concentrations of reactants at all, so the rate of a zero-order reaction will always be the same at a given temperature.

$\text{Rate} = k$

Great summary on p. 578 of textbook!

COLLISION THEORY

Chemical reactions occur because reactants are constantly moving around colliding with one another.

The Boltzmann distribution is often used to show that increasing temperature increases the fraction of reactant molecules above the activation energy.

The Rate Constant and Temperature

The rate constant will increase when the temperature increases. Using natural logarithms, the equation is given by Arrhenius as:
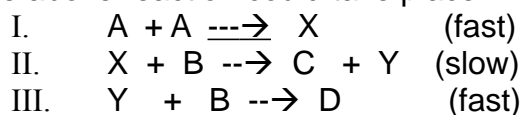
$$\ln k = \frac{E_A}{R} \left(\frac{1}{T}\right) + \ln A$$
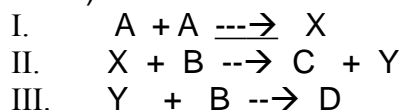
Reaction Mechanisms
Not all chemical reactions are one-step processes. The balanced equation is the SUM of a series of simple steps. Three molecules will not collide simultaneously very often, so steps of a reaction mechanism involve only 1 or 2 reactants at a time.

$2A + 2B \rightarrow C + D$ rate $=k[A]^2[B]$

The above reaction could take place in 3 steps:

I.	$A + A \dashrightarrow X$	(fast)
II.	$X + B \dashrightarrow C + Y$	(slow)
III.	$Y + B \dashrightarrow D$	(fast)

Species x & y --- intermediates   (they appear in the "mechanism", but cancel in the balanced equation)

I.	$A + A \dashrightarrow X$
II.	$X + B \dashrightarrow C + Y$
III.	$Y + B \dashrightarrow D$

$A + A + X + B + Y + B \dashrightarrow X + C + Y + D$

Adding up and canceling out…give you: $2A + 2B \rightarrow C + D$

Example Kinetics Problem:

The reation between HBr and O_2 is believed to occur in 3 steps:

$HBr + O_2 \rightarrow HOOBr$
$HOOBr + HBr \rightarrow 2HOBr$
$HOBr + HBr \rightarrow H_2O + Br_2$
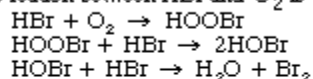
a) Write a balanced equation for the overall reaction
b) Identify the intermediates .
c) From the mechanism, the rate $= k[HBr][O_2]$. Which is the rate - determining step?
d) Why does increasing temperature increase k?

Kinetic Qualitative Solution
a) Multiply step 3 by "2" so the HOBr's will cancel
    After adding and cancelling you will get..

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$
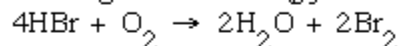
b) HOOBr and HOBr are the intermediates because they are
    formed in one step but used up in another
c) rate for step 1: rate $= k[HBr][O_2]$

$$2: \text{rate} = k[HOOBr][HBr] = k[HBr]^2[O_2]$$

$$3: \text{rate} = k[HOBr][HBr] = k[HBr]^4[O_2]$$

    step 1 is the slow step because its rate agrees with the observed rate
d) Increasing the temperature gives more molecules the needed
     activation energy so more molecules will react.
    Using Arrhenius' equation, increasing T makes the exponent
     less negative therefore increasing k.