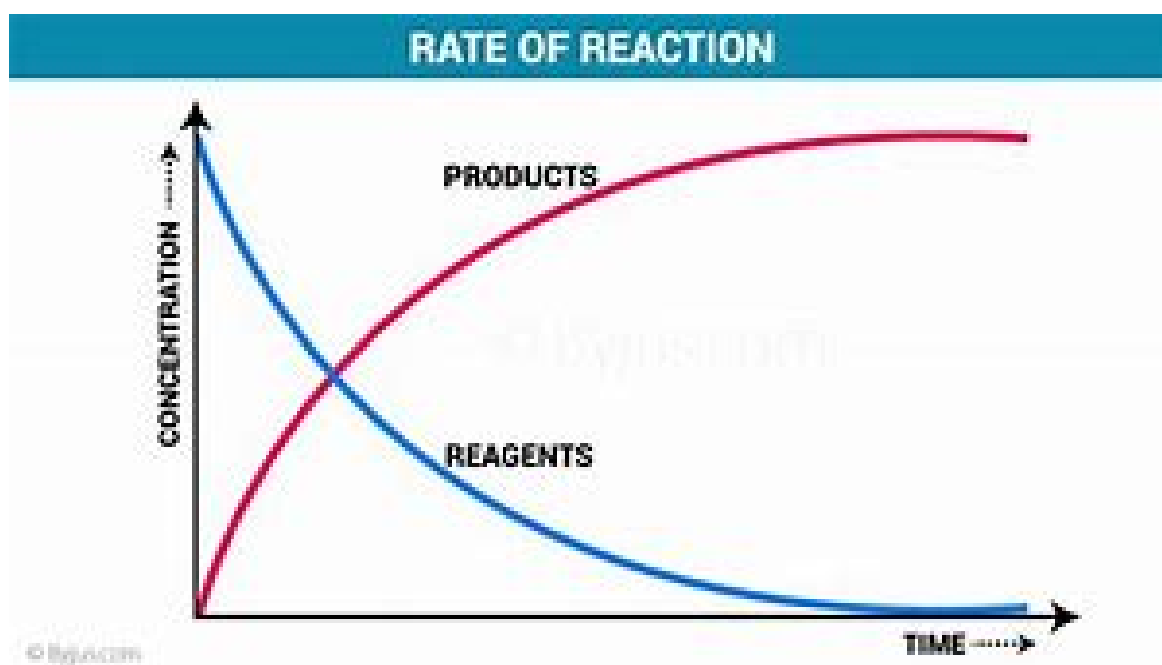# 12.1 - 12.2 Reaction Rates and Rate Laws

Chemical Kinetics

Chemical kinetics - the area of chemistry dealing with reaction rates - how fast or slow a reaction is.

We have learned about the spontaneity of a reaction, but some reactions, although spontaneous, will occur so slowly that it is impossible to see product formation.

As a reaction proceeds, and reactant quantities diminish, the reaction rate slows.

Reaction Rates

The instantaneous reaction rate is defined as a change in concentration of a reactant per change in time, and is shown thusly:

| $$Rate = \pm \dfrac{\Delta[A]}{\Delta t}$$	[A] = molar concentration of A t = time (often seconds)

Note 1: it is customary to report reaction rates as positive values. If a rate involves a reactant (where delta is negative,) add a negative sign in front of the expression.

Note 2: the delta symbol always indicates a final condition minus an initial one.

Note 3: [bracket] usage is chemistry's way of indicating "moles per liter."

Rate Example

Consider this decomposition reaction:

$$2\ NO_{2(g)} \longrightarrow 2\ NO_{(g)}\ +\ O_{2(g)}$$
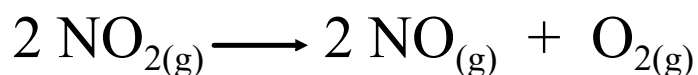
And the following data:

Time (s)	$[NO_2]$	$[NO]$	$[O_2]$
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Average Rate Examples

1. What is the average rate at which NO_2 changes between zero and 50 seconds?

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{0.0079M - 0.0100M}{50\,s} = 4.2\,E-5\,mol\,/\,L\bullet s$$

Between 50 and 100 seconds?

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{0.0065M - 0.0079M}{50\,s} = 2.8\,E-5\,mol\,/\,L\bullet s$$

Between 350 and 400 seconds?

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{0.0031M - 0.0034M}{50\,s} = 6.0\,E-6\,mol\,/\,L\bullet s$$

For the entire time?

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{0.0031M - 0.0100M}{400\,s} = 1.7\,E-5\,mol\,/\,L\bullet s$$

Average Rate Examples

2. What is the average rate at which NO changes between zero and 50 seconds?

$$Rate = \frac{\Delta[NO]}{\Delta t} = \frac{0.0021M - 0M}{50s} = 4.2E - 5\,mol\,/\,L \bullet s$$

Between 50 and 100 seconds?

$$Rate = \frac{\Delta[NO]}{\Delta t} = \frac{0.0035M - 0.0021M}{50s} = 2.8E - 5\,mol\,/\,L \bullet s$$

Between 350 and 400 seconds?

$$Rate = \frac{\Delta[NO]}{\Delta t} = \frac{0.0069M - 0.0066M}{50s} = 6.0E - 6\,mol\,/\,L \bullet s$$

For the entire time?

$$Rate = \frac{\Delta[NO]}{\Delta t} = \frac{0.0069M - 0M}{400s} = 1.7E - 5\,mol\,/\,L \bullet s$$

Average Rate Examples

3. What is the average rate at which O_2 changes between zero and 50 seconds?

$$Rate = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0011M - 0M}{50\,s} = 2.2\,E-5\,mol\,/\,L\bullet s$$

Between 50 and 100 seconds?

$$Rate = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0018M - 0.0011M}{50\,s} = 1.4\,E-5\,mol\,/\,L\bullet s$$

Between 350 and 400 seconds?

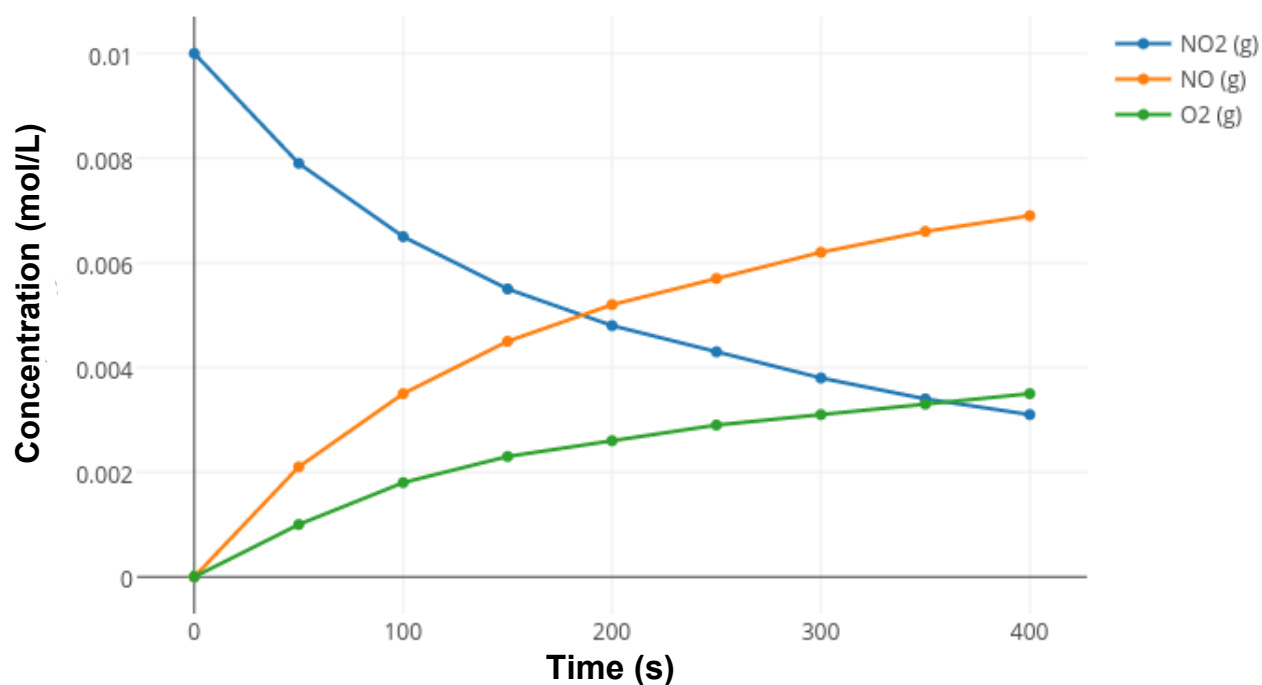$$Rate = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0035M - 0.0033M}{50\,s} = 4.0\,E-6\,mol\,/\,L\bullet s$$

For the entire time?

$$Rate = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0035M - 0M}{400\,s} = 8.8\,E-6\,mol\,/\,L\bullet s$$

4. Graphical Example

Consider the following graph:
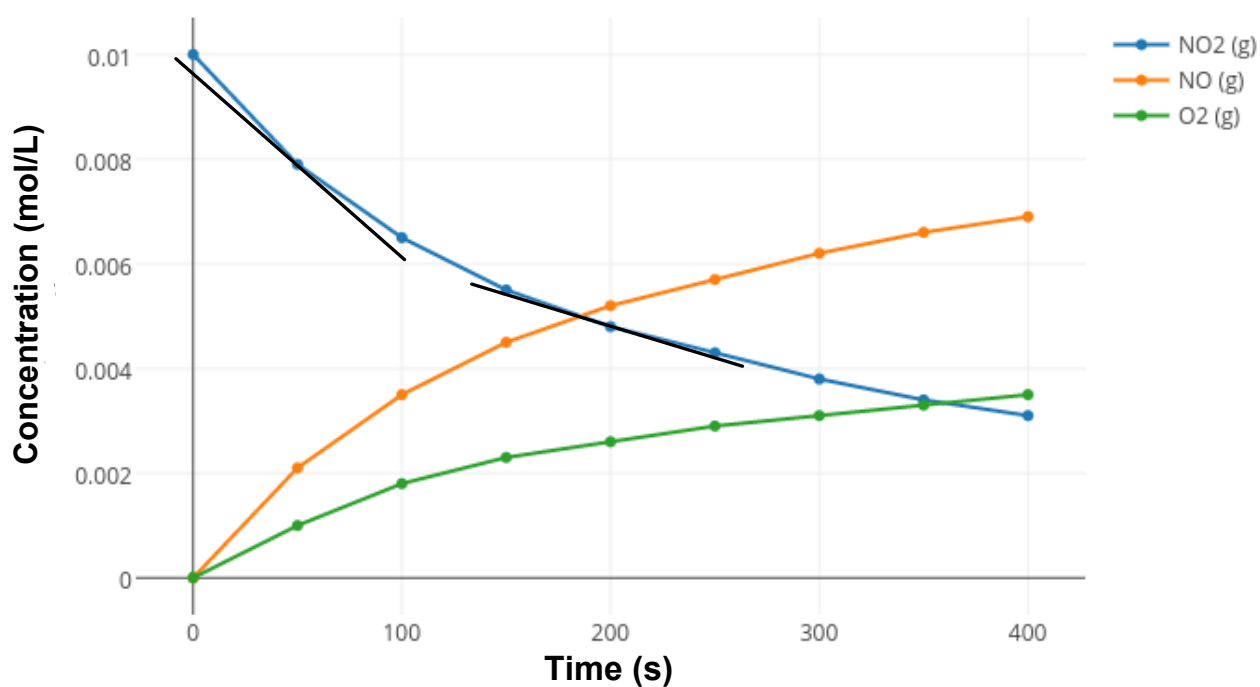
Analysis of Decomposition of Nitrogen Dioxide

Determine the slope of the NO_2 curve at $t = 50$ s and $t = 200$ s.

4. Graphical Example

Determine the slope of the NO_2 curve at t = 50 s and t = 200 s.

Analysis of Decomposition of Nitrogen Dioxide

Summarizing Related Rates

In the example, as NO_2 diminishes, NO and O_2 increase proportionally to the reaction coefficients.

Verbally:

Consumption Rate NO_2 = Production Rate NO = 2(Production Rate O_2)

Mathematically:

$$-\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t} = 2\left(\frac{\Delta[O_2]}{\Delta t}\right)$$

Equilibrium Effects

At this point, we will assume that reactions proceed in a forward direction only.

After reactions proceed far enough, though, and concentrations of products get sufficiently high, the reverse reaction starts occurring more frequently as the reaction moves into a state of equilibrium.

We will study <u>equilibrium</u> later - the point at which the rate of the forward reaction equals the rate of the reverse reaction.

Therefore, for now we will consider reactions soon after reactants are mixed (or activated).

Introduction to Rate Laws

If we choose conditions where the reverse reaction can be neglected, the reaction rate depends only on the concentration of reactants.

For the decomposition of NO_2, a <u>Rate Law</u> is:

$$Rate = k[NO_2]^n$$

Interpretation:

k = the <u>rate constant</u>: an experimentally determined number specific to a particular reaction.

n = the <u>order</u> of a reactant. This can be zero, a fraction, or an integer. Also experimentally derived.

Rate Law Notes

A. Products don't appear in the rate laws because the reaction rate is studied under conditions where the reverse reaction does not contribute to the overall rate.

B. The value of the exponent must be determined experimentally - it can't be determined from the balanced reaction.

In any reaction rate expression, it is important to clearly define which species are being defined.

Types of Rate Laws

So far we have looked at rates in terms of concentration: concentration drives the rate Because a change of concentration per short time gives the slope of a tangent line to the reaction curve, this type is technically called the <u>differential rate law</u>.

A second kind is an <u>integrated rate law</u>, and it expresses how concentrations depend on time: concentrations diminish as time goes by.

The type of rate law use depends on which data is easiest to obtain.

Homework

Preview 12.3

12.1-.2 Problems in your Booklet
Due: Next Class