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Kinetics

How often does this topic appear on the test?

In the Multiple-Choice section, this topic appears in about 3 out of 75 questions.

In the Free-Response section, you'll see this topic almost every year.

In thermodynamics, you determine whether a reaction will occur spontaneously, based on the relative states of the reactants and products. Kinetics deals with the rate at which a reaction occurs between those states. The rate of a chemical reaction is determined experimentally by measuring the initial rate at which a reactant disappears or a product appears. So reaction rates are generally measured in moles/time or M/time.

THE RATE LAW

The rate law for a reaction describes the dependence of the initial rate of a reaction on the concentrations of its reactants. It includes the Arrhenius constant, k, which takes into account the activation energy for the reaction and the temperature at which the reaction occurs. The rate of a reaction is described in terms of the rate of appearance of a product or the rate of disappearance of a reactant. The rate law for a reaction cannot be determined from a balanced equation; it must be determined from experimental data, which is presented on the test in table form.

Here's how it's done

The data below were collected for the following hypothetical reaction:

$$A + 2B + C \rightarrow D$$
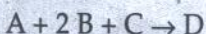
Experiment	Initial Concentration of Reactants (M)			Initial Rate of Formation of D (M/sec)
	[A]	[B]	[C]	
1	0.10	0.10	0.10	0.01
2	0.10	0.10	0.20	0.01
3	0.10	0.20	0.10	0.02
4	0.20	0.20	0.10	0.08

The rate law always takes the following form, using the concentrations of the reactants:

$$\text{Rate} = k[A]^x[B]^y[C]^z$$

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. To find the values for the exponents x, y, and z, we need to examine how changes in the individual reactants affect the rate. The easiest way to find the exponents is to see what happens to the rate when the concentration of an individual reactant is doubled.

Let's look at [A]

From experiment 3 to experiment 4, [A] doubles while the other reactant concentrations remain constant. For this reason, it is useful to use the rate values from these two experiments to calculate x (the order of the reaction with respect to reactant A).

As you can see from the table, the rate quadruples from experiment 3 to experiment 4, going from 0.02 M/sec to 0.08 M/sec.

We need to find a value for the exponent x that relates the doubling of the concentration to the quadrupling of the rate. The value of x can be calculated in this way:

$$(2)^x = 4, \text{ so } x = 2$$

Because the value of x is 2, the reaction is said to be second order with respect to A.

$$\text{Rate} = k[A]^2[B]^y[C]^z$$

Let's look at [B]

From experiment 1 to experiment 3, [B] doubles while the other reactant concentrations remain constant. For this reason it is useful to use the rate values from these two experiments to calculate y (the order of the reaction with respect to reactant B).

As you can see from the table, the rate doubles from experiment 1 to experiment 3, going from 0.01 M/sec to 0.02 M/sec.

We need to find a value for the exponent y that relates the doubling of the concentration to the doubling of the rate. The value of y can be calculated in this way:

$$(2)^y = 2, \text{ so } y = 1$$

Because the value of y is 1, the reaction is said to be first order with respect to B.

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

Let's look at [C]

From experiment 1 to experiment 2, [C] doubles while the other reactant concentrations remain constant.

The rate remains the same at 0.01 M.

The rate change is $(2)^z = 1$, so $z = 0$.

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

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

Because the sum of the exponents is 3, the reaction is said to be 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. The units of the rate constant are dependent on the order of the reaction, so it's important to carry along units throughout all rate constant calculations.

Let's use experiment 3:

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

You should note that we can tell from the coefficients in the original balanced equation that the rate of appearance of D is equal to the rate of disappearance of A and C because the coefficients of all three are the same. The coefficient of D is half as large as the coefficient of B, however, so the rate at which D appears is half the rate at which B disappears.

COLLISION THEORY

According to collision theory, chemical reactions occur because reactants are constantly moving around and colliding with each other.

When reactants collide with sufficient energy (**activation energy,** E_a), a reaction occurs. At any given time during a reaction, a certain fraction of the reactant molecules will collide with sufficient energy to cause a reaction between them.

Reaction rate increases with increasing concentration of reactants because if there are more reactant molecules moving around in a given volume, then more collisions will occur.

Reaction rate increases with increasing temperature because increasing temperature means that the molecules are moving faster, which means that the molecules have greater average kinetic energy. The higher the temperature, the greater the number of reactant molecules colliding with each other with enough energy (E_a) to cause a reaction.

It's also worth noting that the rate of a reaction will gradually decrease as the reaction progresses and the reactants are used up. If a reaction is first order overall, the concentration of the reactant will decrease exponentially as the reaction goes on. In fact, the reactant concentration will have a characteristic half-life, just like in nuclear decay. Another way of saying this is that the graph of a logarithm of the remaining reactant concentration will be a straight line.

When you graph change in concentration of reactants or products versus time, you can find the rate of the reaction at any point by looking at the slope of the graph.

The diagram below is often used to show that increasing temperature increases the fraction of reactant molecules above the activation energy.
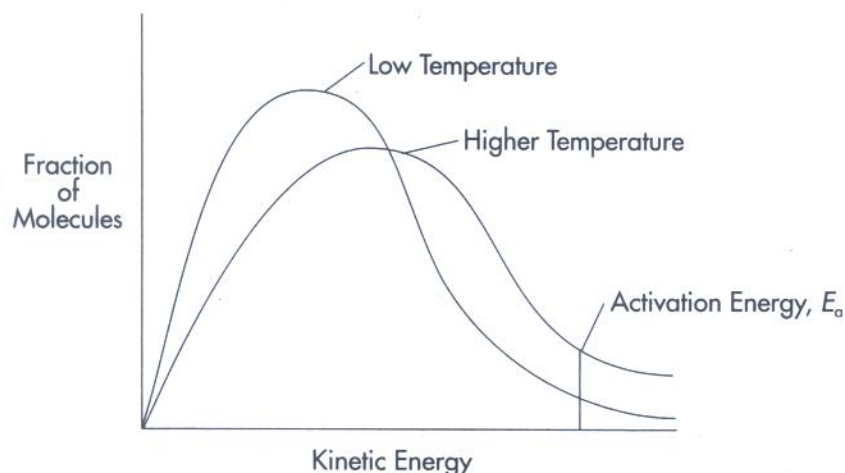
REACTION MECHANISMS

Many chemical reactions are not one-step processes. Rather, 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 one or two reactants at a time.

For instance, the following hypothetical reaction:

$$2\,A + 2\,B \rightarrow C + D \qquad\qquad\qquad Rate = k[A]^2[B]$$

could take place by the following three-step mechanism:

    I. $A + A \rightleftharpoons X$ (fast)

    II. $X + B \rightarrow C + Y$ (slow)

    III. $Y + B \rightarrow D$ (fast)

Species X and Y are called **intermediates** because they appear in the mechanism, but they cancel out of the balanced equation. The steps of a reaction mechanism must add up to equal the balanced equation, with all intermediates cancelling out.

Let's show that the mechanism above is consistent with the balanced equation by adding up all the steps.

    I. $A + A \rightleftharpoons X$

    II. $X + B \rightarrow C + Y$

    III. $Y + B \rightarrow D$

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

Cancel species that appear on both sides.

$$2\,A + 2\,B \rightarrow C + D$$
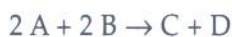
By adding up all the steps, we get the balanced equation for the overall reaction, so this mechanism is consistent with the balanced equation.

As in any process where many steps are involved, the speed of the whole process can't go faster than the speed of the slowest step in the process, so the slowest step of a reaction is the **rate-determining step.** Because the slowest step is the most important step in determining the rate of a reaction, the slowest step and the steps leading up to it are used to see if the mechanism is consistent with the rate law for the overall reaction.

Let's look at the reaction and the three-step mechanism again:

$$2\,A + 2\,B \rightarrow C + D \qquad\qquad\qquad \text{Rate} = k[A]^2[B]$$

The reaction above takes place by the following three-step mechanism:

I. $A + A \rightleftharpoons X$ (fast)

II. $X + B \rightarrow C + Y$ (slow)

III. $Y + B \rightarrow D$ (fast)

Let's show that the reaction mechanism is consistent with the rate law (Rate = $k[A]^2[B]$).
The slowest step is the rate-determining step, so we should start with the rate law for step II:

$$\text{Rate} = k_2[X][B]$$

But X is an intermediate, which means that it can't appear in the overall rate law. To eliminate X from the rate law, we need to look at the equilibrium reaction in step I. We can assume that the reaction in step I comes to equilibrium quickly. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction, so we get:

$$k_f[A][A] = k_r[X]$$

Now we can solve for [X].

$$[X] = \frac{k_f}{k_r}[A]^2$$

Once we have solved our equilibrium rate expression for [X] in terms of [A], we can substitute for [X] in our step II rate law:

$$\text{Rate} = k_2\frac{k_f}{k_r}[A]^2[B] = k[A]^2[B]$$

Now we have a rate law that contains only reactants from the overall equation and that's consistent with the experimentally derived rate law that we were given. You can always eliminate intermediates from the rate-determining step by this process.

CATALYSTS

A catalyst increases the rate of a chemical reaction without being consumed in the process; catalysts do not appear in the balanced equation. In some cases, a catalyst is a necessary part of a reaction because in its absence, the reaction would proceed at too slow a rate to be at all useful.

A catalyst increases the rate of a chemical reaction by providing an alternate reaction pathway with a lower activation energy.

KINETICS AND EQUILIBRIUM

There is a relationship between the rate constants for the forward and reverse directions of a particular reaction and the equilibrium constant for that reaction.

$$K_{eq} = \frac{k_f}{k_r}$$

K_{eq} = the equilibrium constant

k_f = the rate constant for the forward reaction

k_r = the rate constant for the reverse reaction