General Chemistry
Lesson 14
Zero, first, second, and third order reaction kinetics. Chemical equilibrium.

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1 First order reactions

The dissociation of HCl depends on concentration of just a single reactant, HCl molecules, and, accordingly the kinetic equation is:

$\frac{d[HCl]}{dt} = -k \text{ [HCl]}$

where only one variable is present. This is the most typical kinetic equation, it is called *first order* kitenic equations, and reactions that can be described by this equation are called *first order* reactions. Why “first order”? We will learn that soon.

As a rule, first order reactions are the reactions where one reactant converts to something else, splits apart, etc. In other words, the reactions that can be described by equations:

$\text{A} \longrightarrow \text{B},$

or

$\text{A} \longrightarrow \text{B} + \text{C},$

are, as a rule, first order reactions. “First order” means that, no matter how much of the material A we have, one half of this amount converts for exactly the same period of time. This time period is called ***half-life***: if we have 1000 kg of some substance A, and this sibstance converts to something else as a result of some first order reaction, and 500 kg of this substance has reacted in 1 hr, then 250 kg of the remaining material will react in next 1 hr, and so on. Half-life is a parameter that describes a wide range of first order processes, not only chemical ones. For example, decay of radioactive isotopes is also characterized by their half-life.

The first order reactions can be defined in a more sophisticated way:

> ***First order reactions are the reactions where the rate of these processes depends on the concentration of the reactant to the first power.***

2 Second order reactions

Consider the neutralisation reaction beween NaOH and HCl. We know, that these two compounds dissociate upon dissolution in water, and that sodium and chloride ions do not participate in this reaction, so the short ionic equation of the reaction is:

$$H^+ + OH^- \longrightarrow H_2O,$$

Does the reaction rate depend on $[H^+]$? Yes. Does it depend on $[OH^-]$? Yes. Should both these variable be included in the reaction equation? Yes. That means, the equation will be:

$$\frac{d[H^+]}{dt} = -k\ [H^+][OH^-]$$

or

$$\frac{d[H_2O]}{dt} = k\ [H^+][OH^-]$$

(the latter equation describes not disappearance of hydrogen ions, but formation of water molecules, which is pretty much the same, because disappearance rate of hydrogen ions is equal to the formation rate of water molecules. Note, that the minus sign is absent in the second equation, because water concentration increases, not decreases in that reaction.)

As we can see, the equiation that describes this reaction includes two variables, which makes it different from a simple first order equation. To demonstrate that, let's look at even more simple equation, recombination of two hydrogen atoms into a hydrogen miolecule:

$$H + H \longrightarrow H_2,$$

The kinetic equation will be:

$$\frac{d[H_2]}{dt} = k\ [H][H] = k[H]^2$$

in other words, the rate of this reaction is proportional to the second power the concentrations of the reactant (hydrogen atoms). That means this kinetic equation is different from a first order kinetic equation. The kinetics of this type reaction is called *second order* kinetics.

If we compare this reaction with the reaction of association of H^+ and OH^-, we conclude the latter is alco a second order reaction, because the kinetic equation conatins a product of concentration of one reactant and anoter reactant, so the total power of concentrations is 2. That is not a surprize, because the probability of formation of a H_2 molecules from two isolated hydrogen atoms, and the probability of formation of H_2O from a hydrogen ion and a hydroxide ion depends on two factors: (i) a probability that two particles (two hydrohen atoms or H^+ and HO^-) meet each other, and (ii) a probability that a single collision between the two particles will lead to formation of a new molecule. As a result, the rate of a second order reaction depends on cocnentration much more significantly than the rate of a singleorder reaction: for example, a twofold decrease of concentration of the reagents A and B causes a four-fold decrease of the reaction rate (not twofold, as in the case of first order reactions).

Second order reactions are the reactions where the rate of these processes depends on the concentration of the reactants to the second power. If only one reactant is involved, the second order equation contains a factor [X^2], if two reactants are involved, it contains a product [X][Y].

Obviously, second order processes cannot be described by half-life.

3 Third order kinetics

This type reactions are very rare, and in these reactions, three particles *simultaneously* collide and from a new molecule (or molecules). From their name we can conclude that the rate of these processes depends on concentration of reactants to the third power. We leave these reactions beyond the scope.

4 Zero order reaction

When a zinc plate is immersed in aqueous HCl, the metal reacts, and a hydrogen gas and zinc chloride form. The rate of this reaction is described by a rate constant (which has the same physical meaning that rate constants from above equations) and on two variables: [H^+] and the area of zinc plate's surface (S), so the equation will be:

$\frac{d[\mathrm{H_2}]}{dt} = kS\ [\mathrm{H}^+$

At a first glance, this is a second order kinetics (because it depends on two variables), however, if we consider a realistic reaction conditions, a situation looks different. If you use a reasonably concentrated HCl and drop a zinc plate into it, and you will be measuring a rate of the H_2 gas formation, you will see hydrogen is forming with nearly constant rate. Why?

To understand this, we have to keep in mind that HCl is usually present at huge excess, which means [H^+] does not change appreciably, so we can consider it as a constant parameter. Next, dissolution of zinc does not lead to significant change of the surface area. In other words, both [H^+] and S are constant parameters in this equation, so it has no variables at all, so we can write:

$\frac{d[\mathrm{H_2}]}{dt} = const$

For consistency, this equation is called a *zero order* equation, because a zero power of any variable equals to 1 (i.e. it is a constant). Zero order kinetics is frequantly observed when some solid material reacts with a liquid, or a liquid reacts with some gas. Enzymatic reaction, and catalytic reactions in general are frequently zero order reactions.

5 Reversible reactions

Many polar compounds dissociate when they dissolve in water. Let's take hydrogen fluoride as an example. It dissociates onto a hydrogen cation and a fluoride anion:

$$\mathrm{HF} \longrightarrow \mathrm{H^+} + \mathrm{F^-}$$

The rate of this reaction is described by the following equation[1]:

$$\frac{d[\mathrm{HF}]}{dt} = -k_d[\mathrm{HF}]$$

In this equation, k_d is a rate constant of hydrogen fluoride dissociation.

Obviously, during the reaction, the HF concentration decreases, whereas the concentration of H^+ and F^- increases. Will that lead to a complete disappearance of HF molecules? Actually, no.

5.1 Direct and reverse reactions

When a hydrogen cation and a fluoride anion meat each other, they can *associate*.

$$\mathrm{H^+} + \mathrm{F^-} \longrightarrow \mathrm{HF}$$

This reaction is the outcome that is opposite to the dissociation reaction. Accordingly, this association can be considered an *reverse* reaction, and the dissociation reaction is a *direct* reaction [2].

The kinetic equation of this reaction is[3] :

$$\frac{d[\mathrm{H^+}]}{dt} = -k_a[\mathrm{H^+}][\mathrm{F^-}]$$

In this equation, k_a is the association rate constant. Therefore, in a HF solution, HF molecules, H^+, and F^- are present simultaneously, so both dissociation and association takes place, which can be described using the following equation:

$$\mathrm{HF} \rightleftharpoons \mathrm{H^+} + \mathrm{F^-}$$

Reactions that can go in both directions (the reactions where both the direct and reverse processes are possible) are called *reversible reactions.* Overwhelming majority of chemical reactions are reversible.

In our case, dissociation of HF and association of H^+ and F^- occur simultaneously, which means that to calculate the actual rate of [HF] change we need to combine both equations, so we get:

$$\frac{d[\mathrm{HF}]}{dt} = -k_d[\mathrm{HF}] + k_a[\mathrm{H^+}][\mathrm{F^-}]$$

Now we are ready to discuss a very important subject, a chemical equilibrium concept.

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[1] A minus sign in this equation means the concentration decreases.

[2] Actually, which reaction is a direct reaction and which is an reverse reaction depends on a context. Each of these two reactions can be considered as a direct or reverse.

[3] Either $[H^+]$ or $[F^-]$ can be used in this equation, because the rate of their disappearance is the same

5.2 Dynamic equilibrium

When direct and reverse reaction are possible, which is faster? Consider the HF solution as an example. If upon dilution with water HF has been standing long enough (for our purpose, several minutes), it is supposed to come to equilibrium. Does it mean the dissociation and association processes has stopped? No. Although the concentrations of HF, H^+, and F^- do not change any more, both dissociation and association processes still continue, although their rates are equal. The system is at equilibrium, however, this is a special type of equilibrium called *dynamic equilibrium.*

When a systen came to a dynamic equilibrium, concentrations of reactants do not change any more, so the previous kinetic equation can be rewritten as follows:

$$\frac{d[\mathrm{HF}]}{dt} = -k_d[\mathrm{HF}] + k_a[\mathrm{H}^+][\mathrm{F}^-] = 0$$

or

$$-k_d[\mathrm{HF}] + k_a[\mathrm{H}^+][\mathrm{F}^-] = 0$$

or

$$k_d[\mathrm{HF}] = k_a[\mathrm{H}^+][\mathrm{F}^-]$$

From this equation, we can see that some simple relationship exists between rate constants of a direct and reverse reactions (k_d and k_a) and equilibrium concentrations of reactants. To understand what this relationship is, let's regroup this equations to move all concentration independent factors to the left and all concentrations to the right side:

$$\frac{k_d}{k_a} = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]}$$

The fraction in the left part contains two constants, the rate constant of the direct and reverse reactions. What does this constant mean? As we know, k_d and k_a describe the property of *reaction* and are concentration independent. Accordingly, we can conclude the fraction we obtained is a characteristic of the *equilibrium* between HF and the free ions that form during its dissociation. This new constant is called *dissociation constant*, and it is usually denoted as a capital K[4].

Homework

1. Dissociation constant of HF is about $7 \cdot 10^{-4}$. Calculate $[\mathrm{H}^+]$ in 1 M, 0.1 M, 10 mM, and 1 mM solutions of HF. Calculate the ratio between $[\mathrm{H}^+]$ and [HF] in each of these solution. Which conclusion can be drawn from that?
2. Google dissociation constants of ten common acids (choose any acid you want) and arrange them according to their strength.

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[4] As a rule, small letter are used for rate constants, and capital letter for equilibrium constants.

3. In 100 millimolar solution of some acid HX, $[H^+]$ and $[X^-]$ are equal to 90 mM. Find a dissociation constant of HX.

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