

GENERAL CHEMISTRY

Lesson 15

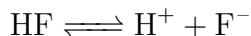
Chemical calculation using equilibrium constants

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During the last lesson we learned about equilibrium constants. Why this parameter is needed? The importance of this parameter is hard to overestimate: almost every chemist uses equilibrium constant values for making prediction of the outcome of various chemical reactions, for calculation of a position of chemical equilibrium in complex mixtures, and so on. These mixtures can be solutions of some acid or a base), or very complex reaction mixture (including protein mixtures in cell's interior). Equilibrium constants of the reaction of association of some protein and a drug usually serves as a characteristic of drug's efficiency. In industry, equilibrium constants are used to optimize large scale chemical processes. Today we will learn how to work with equilibrium constants, and how to use them to understand chemical processes better.

1 Equilibrium constant and position of chemical equilibrium.

Let's consider dissociation of some weak acid, for example, HF. It dissociates according to the equation:



and the equilibrium constant of this reaction is:

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

For HF, K_d equals to $6.64 \cdot 10^{-4}$, and, by definition, it is a property of HF molecules, so it does not depend on HF concentration. What does it tell us about the dissociation of HF? For example, since the acidic properties of any acid depend only on the concentration of hydrogen cations ($[\text{H}^+]$), can we calculate this concentration if we know the value of K_d ?

Yes, we can. To do that, we need to solve the above equation, which will give us $[\text{H}^+]$. Unfortunately, we cannot do that directly, because the equation contains more than one variable. This equation is possible to solve when the number of variable reduces to one. How can it be done?

By looking at the dissociation equation, and using a common sense, we conclude that $[H^+]$, $[F^-]$, and $[F]$ are not independent variables. Indeed, when one HF molecule dissociates, the amount of HF molecules decreases by 1, and the amount of H^+ , F^- increases by one. In other words, two of these variables can be expressed through the third one when the nominal concentration of hydrofluoric acid is C_{HF} , is known. As we already know, the nominal concentration is the concentration of the substance that was added to the reaction mixture. For example, if you prepare one liter of a solution that contains 20 grams of HF (i.e., one mole), the nominal concentration of HF (C_{HF}) is 1M. That does not tell us about exact value of $[H^+]$, $[F^-]$, and HF, but we know that

$$C_{HF} = [HF] + [F^-] ,$$

$$C_{HF} = [HF] + [H^+] ,$$

and

$$[F^-] = [H^+]$$

Now we can rewrite the equilibrium constant equation: replace $[F^-]$ with $[H^+]$ (because they are equal), and replace $[HF]$ with $C_{HF} - [H^+]$. We get:

$$K_d = \frac{[H^+][F^-]}{[HF]} = \frac{[H^+][H^+]}{C_{HF}-[H^+]} = \frac{[H^+]^2}{C_{HF}-[H^+]}$$

The equation we obtained is just a quadratic equation. If it is not clear, let's rewrite it:

$$K_d(C_{HF} - [H^+]) = [H^+]^2$$

and, finally,

$$[H^+]^2 + K_d[H^+] - K_dC_{HF} = 0$$

By solving this equation, we can find $[H^+]$, and, after that, calculation of other concentrations becomes straightforward (we do not need to do these calculations right now). What is even more important, we demonstrated that the ratio between the concentration of $[H^+]$ in the HF solution depends on two parameters: dissociation constant *and* a nominal concentration of HF. To understand this dependence better, let's calculate a fraction of dissociated HF molecules, $\alpha = [H^+]/C_{HF}$.

Using α all concentrations can be expressed as follows:

$$[H^+] = \alpha C_{HF}$$

$$[F^-] = \alpha C_{HF}$$

$$[HF] = (1 - \alpha)C_{HF}$$

If we do these replacements in the equilibrium constant equation we get this:

$$K_d = \frac{[H^+][F^-]}{[HF]} = \frac{\alpha C_{HF} \alpha C_{HF}}{(1-\alpha)C_{HF}} = \frac{\alpha^2 C_{HF}^2}{(1-\alpha)C_{HF}} = \frac{\alpha^2 C_{HF}}{(1-\alpha)}$$

Let's modify this equation in such a way that all parameters are in the left side, and α in the right side:

$$\frac{K_d}{C_{HF}} = \frac{\alpha^2}{(1-\alpha)}$$

What this equation tells us about? We will not do a complete analysis of this equation, let's consider just a situation when α is small (for example, in a case of some weak acid). In that case, $\alpha \ll 1$, so we assume the denominator is close to 1. That allows us to simplify the equation, which now looks like:

$$\frac{K_d}{C_{HF}} \approx \alpha^2$$

This equation tells us that that (i) the larger K_d , the greater α (which is obvious), and (ii) the lower a nominal concentration the greater dissociation, or, in other words, *in dilute solutions, electrolytes dissociate more easily than in concentrated ones*. This is a general conclusion, which works for all electrolytes.

2 Titration curve

Sometimes, the concentration of the dissociation products may be different. That may happen, for example, when we add some strong acid or a strong base the solution of the acid HX (or its salt). As an example of a weak acid we can use phenolphthaleine. This compound is an acid with a very small K_d (around 10^{-9}). This compound possesses one interesting property: a neutral molecule (it has a very complex structure, so let's denote it as PhH) is colourless, but its anion (Ph^-) has a very intense pink colour. That allows us to monitor dissociation of phenolphthalein just by looking at the colour of the solution. From the previous section, we know that the dissociation of an acid can be facilitated by dilution, so the *relative* amount of (Ph^-) will increase upon dilution. However, what about an *absolute* amount? Do any methods exist that allow us to shift dissociation equilibrium?

To answer this question, let's consider a situation of some acid (let's continue using phenolphthaleine as an example) where a concentration of $[\text{H}^+]$ is artificially changed by adding some strong acid or base. This case is different from the situation described above, because the concentration of hydrogen cations $[\text{H}^+]$ and ionized acid (we will denote it X) are not equal any more. However, $[\text{HX}]$ is still equal to $C_{HX} - [\text{X}^-]$ (for the reason described in the previous section). That means the basic equation:

$$K_d = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

can be rewritten as:

$$K_d = \frac{[\text{H}^+][\text{X}^-]}{C_{HX} - [\text{X}^-]}$$

By regrouping this equation, we obtain the following:

$$K_d(C_{HX} - [\text{X}^-]) = [\text{H}^+][\text{X}^-]$$

and

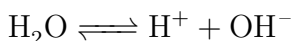
$$[X^-] = \frac{K_d C_{HX}}{K_d + [H^+]}$$

(I skipped some steps during this transformation. Do it by yourself at home.)

This curve has interesting properties. Firstly, when $[H^+]$ is very big, the denominator is big, which means the concentration of dissociated acid $[X^-]$ is small. When $[H^+]$ is very small, $[X^-] = C_{HX}$, which means almost all HX molecules are dissociated. However, when $[H^+] = K_d$, $[X^-] = C_{HX}/2$. In other words, at this concentration of hydrogen ions exactly one half of all HX molecules is dissociated.

3 pH

Water dissociates into a proton¹ and a hydroxide ion OH^- .



Water dissociation constant

$$K_d = \frac{[H^+][OH^-]}{[H_2O]}$$

is very small ($2 \cdot 10^{-16}$), which means $[H_2O]$ is much bigger than $[H^+][OH^-]$. That means we can assume $[H_2O]$ equals to the concentration of water in water, i.e. $1000/18 = 55.56$ M. In other words the denominator in this equation is a constant. That is why it is convenient to speak about **ionic product of water**, or K_w , which is equal to the water dissociation constant times 55.56 M. It is easy to calculate that K_w is 10^{-14} .

The fact that $[H^+][OH^-] = 10^{-14}$ means that in the presence of an acid concentration of hydrogen ions goes up, whereas the concentration of hydroxide ions goes down, and when a base is added to water, the situation is opposite. In other words, $[H^+]$ (or $[OH^-]$) can serve as a single measure of acidity/basicity of the media. In 1 M solution of some strong acid, $[OH^-]$ is approximately 1M, whereas $[H^+]$ is 10^{-14} . In 1M NaOH, $[OH^-]$ is 1M, and $[H^+]$ is 10^{-14} . In neutral media, when there is neither an acid nor base in the solution, $[H^+] = [OH^-] = 10^{-7}$.

Since $[H^+]$ changes so significantly, the exact concentration value is less important than its order. That is why it is more convenient to use not the concentration itself, but its negative decimal logarithm. This index is called pH:

$$pH = -\lg[H^+]$$

pH is a measure of acidity or basicity of aqueous media. It usually varies from 1 to 14. Neutral media has pH = 7.

pH can be high (when the media is basic), or low (when the media is acidic). However, pH itself can NEVER be acidic or basic, because a number has no taste. It is INCORRECT and ILLITERATE to say “acidic pH”, or “basic pH” (although many teachers do that).

¹Actually, on the hydronium (oxonium) ion H_3O^+ , but, for simplicity, chemists assume H^+ is formed.

Homework

1. Try to make by yourself all transformations that we did to obtain the titration curve equation. Try to understand the logic behind that.
2. 0.1 M of some acid HX has $\text{pH}=3$ calculate dissociation constant of this acid.
3. K_d of the acid XY equals to 0.004. At which pH the concentration of $[\text{Y}^-]$ and HY will be equal to 0.05M?

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