

GENERAL CHEMISTRY

Hydrolysis of salts. metal cations as Lewis acids. Soft and hard acids.

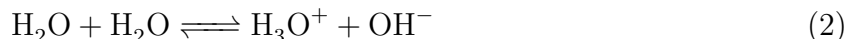
January 28, 2018

1 Hydrolysis of cupric, zinc and aluminium salts

Previously, we learned that the salts formed in a reaction between hydroxides that are strong bases and weak acids are not neutral, but basic in aqueous solution. As we already know, that happens because these salts dissociate upon the metal cation (Me^+) and an anion (Y^-) that is a conjugated base of some weak acid.



Being a conjugated base of a weak acid, Y^- converts a part of H^+ (actually, H_3O^+) into HY , so the balance between H_3O^+ and OH^- (described by the equation 2) shifts, and we observe an excess of OH^- , which means a solution becomes basic.

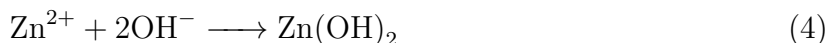


However, upon having a look at this equation, one can see a symmetry between H_3O^+ and OH^- , which means similar effect can be observed in a solution of a salt formed by a weak *base* and a strong acid. And it is intuitively clear that the solution is to be acidic in that case.

Is this hypothesis valid? Let's think. A typical example of a weak base is some low soluble hydroxide of a divalent metal, such as copper, iron or zinc, or a hydroxide of a trivalent metal like aluminium. They dissociate only very slightly, so the equilibrium in this reaction is shifted to the left side:



which means this reaction:



is fast, whereas the opposite process is slow.

What consequences does it have? Imagine we took zinc chloride ZnCl_2 and dissolved it in water. It immediately dissociates:



We already know that binding of chlorine ions to H^+ is a very slow and inefficient process (HCl is a strong acid, so its conjugated base, chloride ion, is a very weak base), which means the presence of chloride ions does not affect the equilibrium described by the equation 2. In contrast, Zn^{2+} avidly binds to OH^- , which means the presence of zinc cations in a solution leads to a decrease of a concentration of OH^- , so we observe an excess of H_3O^+ . That makes the solution of $ZnCl_2$ acidic.

The same effect can be observed in solutions of any salt between some strong acid (sulfuric, hydrochloric, perchloric, etc) and some metal whose hydroxides are weak bases or amphoteric (i.e. zinc, iron, copper, aluminium, scandium, chromium, etc. This list includes all transition metals and most metals from the main group III). Obviously, this effect is also called “hydrolysis of salts”.

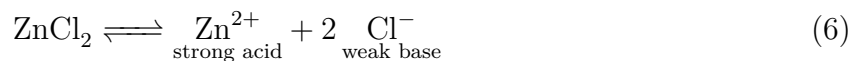
With this knowledge in mind, we can make a following general conclusion:

When a salt formed by a strong base and a weak acid dissolves in water, the solution becomes acidic. When a salt formed by a strong acid and a weak base dissolves in water, the solution becomes basic. The salts of a strong base and a strong acid make a neutral solution.

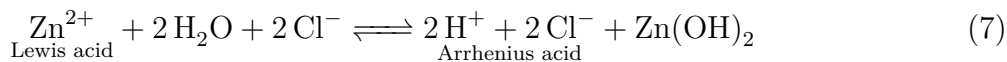
2 Metal cations as Lewis acids

If we take a look at the equation 4, we can easily see a commonality between this reaction and the reaction between a Bronsted acid (H_3O^+) and a base (e.g. OH^-). Indeed, zinc cation binds to a hydroxide ion, in other words, it behaved as an acid. Taking into account that Zn^{2+} has at least one empty orbital (because it lost two electrons) capable of accommodating an electron pair, which means it is a typical Lewis acid. Taking into account that it binds to OH^- pretty tightly (remember, $Zn(OH)_2$ is a weak base, because it does not dissociate well), Zn^{2+} is a comparatively strong Lewis acid.

That means, the whole process of hydrolysis of $ZnCl_2$ on aqueous solution can be described as follows. Initially, the salt dissociates upon a strong Lewis acid (Zn^{2+}) and a weak base:

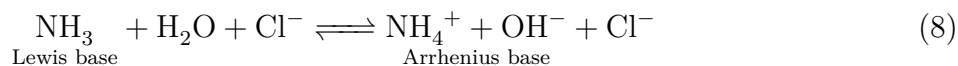


A Lewis acid interacts with water, takes away a hydroxyl and the remaining H^+ make a solution acidic.



The same process occurs with all other metal ions, which act as Lewis acids in aqueous solutions. The ions of alkiline and alkaline earth metals (the metals whose hydroxides are strong bases) are weak Lewis acids, whereas cations of all other metals are moderate to strong Lewis acids.

Just to maintain symmetry, let's draw the same style equation of hydrolysis of salts of a strong base and a weak acid (that we discussed on the previous lesson):



These two equations can be summarized as follows:

When some Lewis acid interacts with water, it produces an excess of H^+ (or H_3O^+ , which is the same). That means, any Lewis acid transforms into a classical Arrhenius acid in aqueous solution. Accordingly, an aqueous solution of any Lewis base contains an increased level of OH^- , which means Lewis bases transform into Arrhenius bases in aqueous solution.

3 Soft and hard acids and bases

Thinking logically, we must conclude that every salt is just a combination of some Lewis acid and some Lewis base. For example, sodium chloride is composed of a sodium ion, which is a weak Lewis acid, and a chloride ion, which is a weak Lewis base. It is not a surprise that this salt dissociates in water solution easily. If we continue to speculate, we may come to a conclusion that a salt composed of a strong Lewis acid and a strong Lewis base would not dissociate. Indeed, silver sulfide may be a good demonstration of that principle: a silver ion is a reasonably strong Lewis acid, whereas a sulfide ion S^{2-} is a strong Lewis base. Silver sulfide is a very insoluble solid, and that fully supports our conclusion: salts do not go into a solution in a form of neutral molecules, they either dissolve as separate ions, or, when ions bind each other tightly, do not dissolve at all. Low solubility of silver sulfide means that silver and sulfide ions form a very tight connection via a dative bond formation, and their interaction is much stronger than the interaction of each of them with water molecules. And, again, that fully correlates with the fact that Ag^+ is a strong Lewis acid and S^{2-} is a Lewis base.

However, this picture becomes more complicated when we consider other examples. Thus, the iodide ion seems to be a very weak base, because, as we know, HI is an extremely strong acid, whereas F^- is known to be a strong base. However, silver iodide is a very insoluble solid, whereas silver fluoride has a reasonable solubility. These two facts (as well as many other examples) do not fit our theory.

In attempts to explain this, as well as many other inconsistencies in the Lewis acid-base theory, American chemist Ralph G. Pearson proposed the theory that can be summarized as follows:

Acids and bases can be soft or hard. Hard acids prefer to make a dative bond with hard bases, whereas soft acids make a strong bond with soft bases

This theory is called Hard and Soft Acids and Bases theory, or **HSAB theory**.

On the Pearson scale, H^+ is a hard acid, and OH^- and F^- are hard bases. Ag^+ is a soft acid, and, accordingly, I^- is a soft base.

This allows us to explain the above facts as follows:

1. HI is a strong acid (it dissociates easily) because H^+ (a hard acid) makes a weak bond with I^- (a soft acid).
2. AgF is composed of Ag^+ (a soft acid) and F^- (a hard base), so these ions do not bind tightly, which makes AgF soluble in water.
3. AgI is composed of Ag^+ (a soft acid) and I^- (a soft base), so these ions *do* bind tightly, which makes AgI extremely insoluble in water.
4. The only thing that remains unclear is why HF, which is a combination of a hard acid and a hard base, dissociates in aqueous solution. The answer is simple: *water is also a hard acid and base*. That means, although hydrogen and fluorine are connected with a strong bond, the interactions between water and HF are strong enough to break a part of HF molecules onto H^+ and OH^- in aqueous solution. That is why HF solution is acidic.

3.1 What does softness and hardness mean

These two terms are not arbitrary: soft bases and acids are really soft, which means they are big and polarizable (soft) species. All heavy metal ions are soft acids, and large anions are soft bases.

Accordingly, small and compact particles, such as a hydrogen cation or boron trifluoride, alkaline metal ions, alkaline earth cations (Mg^{2+} , Ca^{2+}) are hard acids, and F^- , OH^- are hard bases. Negative oxygen atoms in such ions as sulfate, nitrate, phosphate etc, are also hard bases.

The structural factors responsible for softness and hardness will be discussed during the next class.

3.2 HSAB theory and a solubility chart

Now we are ready to explain a secret of the solubility chart. We need to take just one additional factor into account: double and triple charged hard acids and bases interact stronger with each other than with water: thus, whereas calcium nitrate (a combination of a hard acid and a hard base) is soluble in water, calcium carbonate (a combination of a hard Ca^{2+} and hard CO_3^{2-}) is not. The explanation is as follows: both calcium and carbonate ions are double charged, which means attraction between them is four times stronger than, e.g., attraction between Na^+ and F^- . As a result, water molecules are incapable of breaking bonds between them, and calcium carbonate is insoluble in water.

The rules explaining the solubility chart are as follows:

1. Compounds formed by soft cations and soft anions are insoluble in water. Examples: HgS, AgBr
2. Compounds formed by hard acid (cation) and soft base (anion) or soft base and hard acid are soluble. Examples: sodium iodide (NaI), silver nitrate ($AgNO_3$)

3. Compounds formed by a hard acid and hard base are soluble if at least one of them is single charged, otherwise they are insoluble. Examples of soluble compounds: Na_2SO_4 , $\text{Ca}(\text{NO}_3)_2$. Examples of insoluble compounds: CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$.

From these rules, we can conclude that *all* nitrates, perchlorates, and similar salts are always soluble, and all salts of alkaline metals are soluble too¹.

Homework

1. Predict which salts shown below are basic, neutral or acidic in aqueous solution:
 Na_2SO_4 , K_2SiO_3 , NaI , Na_2S , CaCl_2 , FeCl_3 , CoSO_4 , CsCl , NH_4Br , NiCl_2 .
2. Look at the solubility chart (available on Internet or from previous year's homework) and decide which cations and anions listed there are hard or soft acids or bases.

If you have any questions, feel free to ask.

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¹There are some exceptions, but they are extremely rare. Thus, few lithium salts are insoluble.