

## **BROENSTED ACIDS AND BASES: THEY ARE NOT SUBSTANCES BUT MOLECULES OR IONS!**

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### **ABSTRACT**

For chemistry education we are discussing mainly two concepts of acids and bases: theories of Arrhenius and Broensted. For the first theory, dissociation into ions is generally discussed: acidic solutions contain  $\text{H}^+(\text{aq})$  ions, alkaline solutions contain  $\text{OH}^-(\text{aq})$  ions. This theory therefore deals with substances, which are referred to as acids and bases – it would be even better to take the logical names "acidic and alkaline solutions". If both solutions are mixed in equivalent quantities, the  $\text{H}^+(\text{aq})$  ions react with  $\text{OH}^-(\text{aq})$  ions to form  $\text{H}_2\text{O}$  molecules, while the other ions remain in solution (in exceptional cases an insoluble salt may precipitate: sulfuric acid solution reacts with barium chloride solution to solid white barium sulfate and water). The Broensted theory defines proton transfer: a molecule or an ion transfers a proton to another molecule or ion, two conjugated acid-base pairs are involved. Thus, Broensted acids and bases are no more substances, but individual types of particles. Due to the autoionization of  $\text{H}_2\text{O}$  molecules (not "autoionization of water"), the following equilibrium exists:



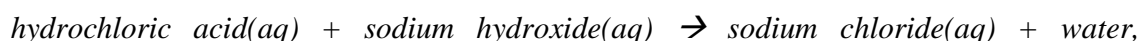
Through this protolysis it is more advantageous to argue rather with  $\text{H}_3\text{O}^+(\text{aq})$  ions than with  $\text{H}^+(\text{aq})$  ions. In this theory there are still ampholyte particles which react as acid or as base particles depending on the reaction partners:  $\text{H}_2\text{O}$  molecules,  $\text{NH}_3$  molecules,  $\text{HSO}_4^-$  ions – water, ammonia or sodium hydrogen sulfate cannot be regarded as ampholytes. The original publication of Broensted [1] from 1927 makes clear that acids and bases should be molecules or ions, but not substances. [AJCE 4(4), July 2014]

## MISCONCEPTIONS AMONG STUDENTS

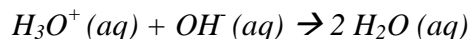
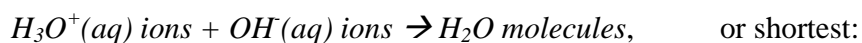
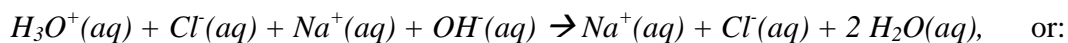
"Sulfuric acid releases 2 protons, phosphoric acid 3 protons", a candidate in the examination colloquium was sure with his assertion. When asked whether 1 mg or 1 mL of substance are meant, the candidate shakes his head and says after some time of meditation: "of course I mean the H<sub>2</sub>SO<sub>4</sub> molecule and the H<sub>3</sub>PO<sub>4</sub> molecule " – "so please say it next time this way", was my answer. We all know that there is a laboratory jargon among chemists, and chemists may maintain this jargon. But in chemistry didactics and chemistry education we must offer a successful learning of the scientific language: "the H<sub>2</sub>SO<sub>4</sub> molecule can emit two protons".

In a written exam students were asked to formulate basic facts according the topic "acids and bases" before considering a lesson plan according to this topic. Most of the students were not capable to write a free text without mistakes – they showed "school-made misconceptions" [2]. They mostly mixed the **levels of substances and particles**. For the reaction of mineral tablets with water they wrote "carbonate ions are reacting with citric acid" – rather than referring either to the level of substances with the reaction of calcium carbonate and citric acid, or to the level of small particles, with the reaction of carbonate ions and citric acid molecules. For neutralization they often quoted: „HCl(aq) + NaOH(aq) → Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq) + H<sub>2</sub>O(aq) – and mentally mixed substances and ions in one equation.

Consequently, they should either describe the substances:



or specify the ions of hydrochloric acid and sodium hydroxide in the equation:



If the ions in such a reaction equation are not formulated, but only empirical formulae such as  $HCl + NaOH \rightarrow NaCl + H_2O$  are given, then students very often think of "HCl molecules, NaOH molecules and NaCl molecules", and sometimes they describe those "molecules" with symbols like "H-Cl, Na-O-H or Na-Cl" [2].

The **Arrhenius theory** is often mentioned, but instead of relating it adequately to dissociation, it is often incorrectly connected with proton transfer– vice versa, when talking about the **Brønsted theory** of protolysis, students stay with the dissociation: "hydrochloric acid is dissociated into ions, strong acids dissociate completely in solution, acetic acid does not dissociate completely, weak acids are characterized by the ratio of dissociated and undissociated molecules". So the terms of both theories are mixed without understanding the historical genesis of those theories.

Also, the term "ampholyte" by Brønsted is often used incorrectly: "water is an ampholyte, it can react both as an acid and as a base" (instead of the  $H_2O$  molecule to be labeled as an ampholyte), the "autoionization of water" is noticed (not the autoionization of  $H_2O$  molecules), "the concentration of the water" is calculated as 55 mol / L (rather than the concentration of 55 mol  $H_2O$  molecules per liter). Also not applicable remarks such as "hydrochloric acid releases one proton, citric acid can deliver up to three protons" are very problematic: in hydrochloric acid, the  $H_3O^+(aq)$  ion can release one proton, in citric acid the  $H_3Cit$  molecule a maximum of three protons. Sulfuric acid is didactically difficult to communicate: in pure sulfuric acid,  $H_2SO_4$  molecules are the proton donors, in half-concentrated

acid, the  $\text{HSO}_4^-(\text{aq})$  ions and  $\text{H}_3\text{O}^+(\text{aq})$  ions, in diluted sulfuric acid only the  $\text{H}_3\text{O}^+(\text{aq})$  ions – as in any diluted solution of strong acids.

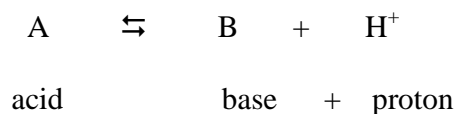
For **neutralization reactions**, students tend to write "acid and base are in equilibrium" – as if there was no reaction and equivalent amounts exist coevally. It is also stated that "salt formation" is a criterion for neutralization reactions – instead of  $\text{H}_2\text{O}$  molecules being formed. If students quote that the result of the standard neutralization reaction is " $\text{NaCl}(\text{aq}) + \text{H}_2\text{O}$ ", they mostly are thinking of NaCl molecules[2].

In the neutralization of acetic acid solution, the reaction of  $\text{H}_3\text{O}^+(\text{aq})$  ions is mostly foregrounded, while the reaction of acetic acid molecules (HAc) is being ignored. Since the degree of protolysis is about 1%, HAc molecules and ions exist in a ratio of 99 : 1 – so especially these molecules react by neutralization:  $\text{HAc}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq}) + \text{Ac}^-(\text{aq})$ .

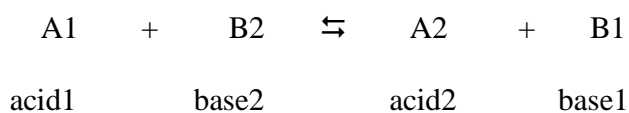
The **strength of acids** is often described with the pH value: "weak acids have a pH of 3 and higher" [2]. It should be seen that each solution of a strong acid can be diluted to the "pH of 3" and above: the protolysis equilibrium and the degree of protolysis are parameters for weak acids.

## HISTORICAL CONSIDERATIONS OF BROENSTED

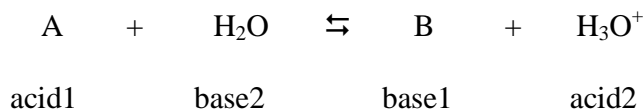
In his essay "On the theory of the acid-base function" [1] Broensted alluded already in the title to the function of acid and base molecules and left out the usual discussion of the properties of acidic and alkaline solutions. In particular, he identified the function through a central mental model:



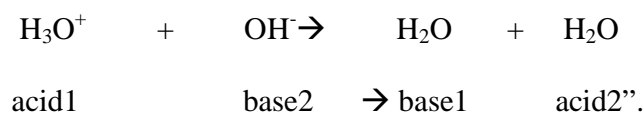
By donating a proton, the acid reacts to a base: "The A and B molecules are called corresponding acids and bases. By this definition, the OH<sup>-</sup> ion loses the special position of the bases: by losing a proton, any molecule A is transformed to a minus-charged base molecule". When HCl molecules react with NH<sub>3</sub> molecules, both molecules change into ions: NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>. Broensted also deals with "free H<sup>+</sup> ions" that do not exist in a solution. He therefore states: "an acid molecule A only releases a proton when the proton is simultaneously assimilated by a base molecule":



All these statements show that Broensted is discussing molecules and ions – not substances. Supposing that a free proton does not exist in solution, the formulation of the hydronium ion, the H<sub>3</sub>O<sup>+</sup> ion, is as follows:



He furthermore states: "Whenever a proton is transferred from an electrically neutral molecule to another electrically neutral molecule, two ions of opposite charge arise". So if H<sub>2</sub>SO<sub>4</sub> molecules react with H<sub>2</sub>O molecules, three types of ions are created: H<sub>3</sub>O<sup>+</sup> ions, HSO<sub>4</sub><sup>-</sup> ions and SO<sub>4</sub><sup>2-</sup> ions. Concerning the neutralization reaction, Broensted showed a very modern view: "When hydrochloric acid (H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup>) and sodium hydroxide (Na<sup>+</sup> + OH<sup>-</sup>) are mixed in aqueous solution, the formation of the salt Na<sup>+</sup> + Cl<sup>-</sup> seems only a purely mechanical mixing process ..... the typical process of neutralization of strong acids and bases is thus not the salt formation. Instead, the actual acid-base reaction is:



Already in 1927, Broensted emphasized the formation of water molecules while many curricula today still argue with the "salt formation" by neutralization. Broensted also consistently described the molecules and ions as acid and base particles – with more progress than many chemistry teachers or lecturers nearly 100 years later.

### **POSSIBLE INTRODUCTION OF BROENSTED ACIDS AND BASES**

The famous "Chemical Triangle" (see figure 1) by Johnstone [3] shows the level of substances ("macro level"), separated from the level of the smallest particles and chemical structures ("sub-micro level"), finally goes to the level of symbols ("representational level"). Students work successfully if they observe firstly substances and phenomena on the macro level, then interpret those observations by looking at the involved particles and chemical structures on the sub-micro level and in the third step express those structures by symbols like formulas and equations on the representational level.

Johnstone [3] emphasized that the direct transition from the macro level to the representational level with all formulae and equations means learning by heart and only little understanding of chemistry results. Taking the sub-micro level into account with molecular models or sphere packing for crystal structures [4], chemical understanding is fostered because students can develop mental models from molecular models or from models of giant structures. Those mental models help a lot to write and reflect formulas or equations – they can be taken as shortened models of the participating atoms, ions or molecules.

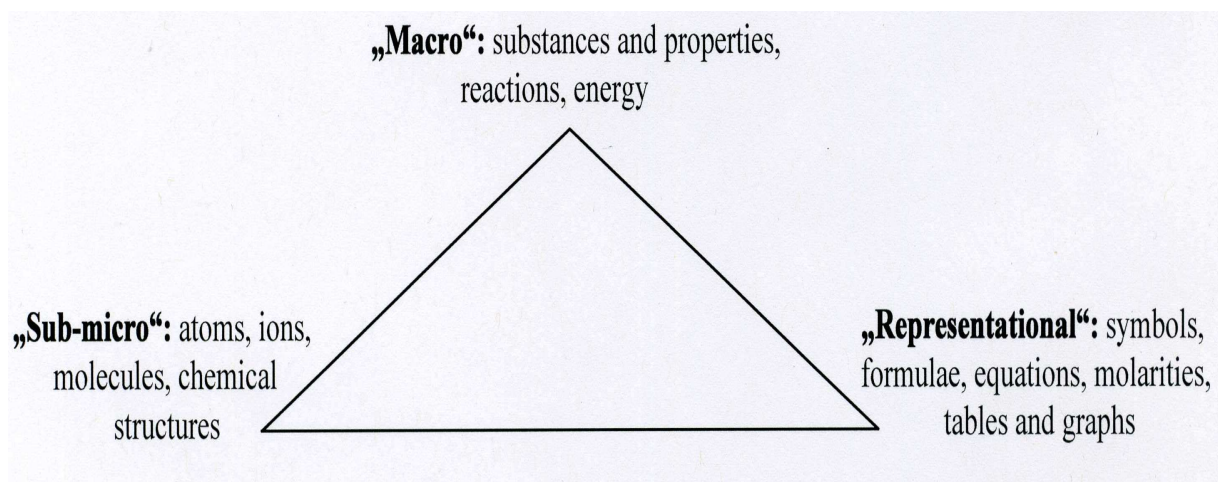


Fig. 1: "Chemical triangle" of Johnstone [3]

Based on these fundamental findings, the chemical experiment may be the starting point. One way of experimental reflection of the important distinction between HCl molecules in hydrogen chloride gas and  $\text{H}_3\text{O}^+$  (aq) ions as acid particles in hydrochloric acid solution is provided by the classic experiment of the sulfuric acid – sodium chloride reaction: Pure sulfuric acid is added by a dropping funnel to solid sodium chloride in a gas developer and hydrogen chloride gas is stored in a syringe or cylinder. A glass bowl is prepared with tap water which is mixed with universal indicator – that way, the solution is colored green. Also a conductivity tester can be prepared. From the syringe, the colorless hydrogen chloride can be routed to the surface of the tap water: just when the color of the indicator changes to red the tester shows a big increase of electrical conductivity. In both reactions, several Broensted acids and bases are involved: they may be illustrated for better understanding on the submicro level with molecular models (see figure 2).

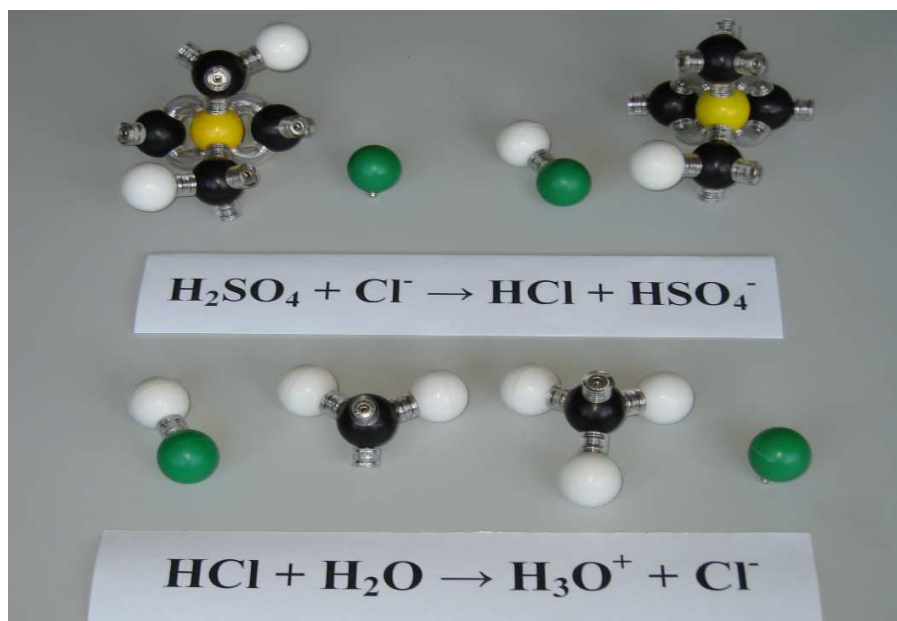


Fig.2 : Illustration of two acid-base reactions with molecular models [5]

After building and discussing those molecular models, the reaction equations can serve as a shortened representation of the models (see figure 2):

sulfuric acid(l) + sodium chloride(s)  $\rightarrow$  hydrogen chloride(g) + sodium hydrogensulfate(s)

$\text{H}_2\text{SO}_4$  molecule +  $\text{Cl}^-$  ion  $\rightarrow$  HCl molecule +  $\text{HSO}_4^-$  ion

acid1 base2  $\rightarrow$  acid2 base1

hydrogen chloride(g) + water(l)  $\rightarrow$  hydrochloric acid (aq)

HCl molecule +  $\text{H}_2\text{O}$  molecule  $\rightarrow$   $\text{H}_3\text{O}^+$ (aq) ion +  $\text{Cl}^-$ (aq) ion

acid1 base2  $\rightarrow$  acid2 base1

After identification of the involved molecules and ions as acid and base particles, special beaker models can help to understand separated ions in solutions (see figure 3): models of diluted hydrochloric acid, sodium hydroxide solution and sodium chloride solution are shown. It



should be noted that in hydrochloric acid, the  $\text{H}_3\text{O}^+$  (aq) ions are the acid particles, and in sodium hydroxide solution, the  $\text{OH}^-$  (aq) ions are the base particles. The (aq) symbol helps the learners to get the idea that the charge in hydrated ions is shielded and those ions can move freely in the solution – they are not linked to an ionic lattice like in solid sodium chloride. Other well-known reactions such as sodium hydroxide-water, ammonia-water and ammonia-hydrogen chloride may follow in order to acquire more experience with acid-base reactions. The last-mentioned reaction is particularly the acid-base reaction without involvement of water molecules:

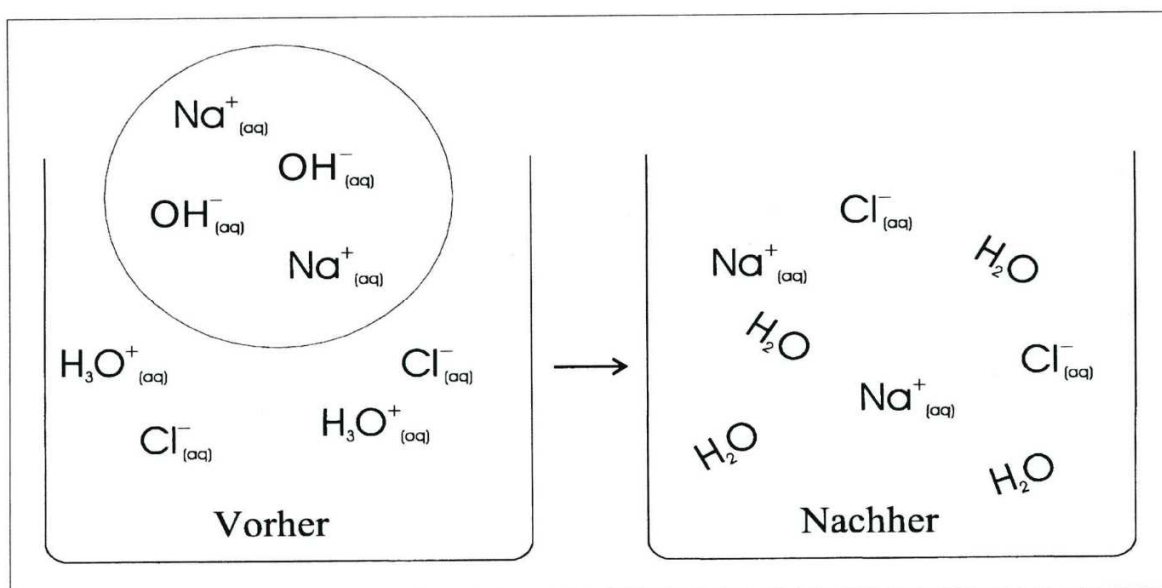
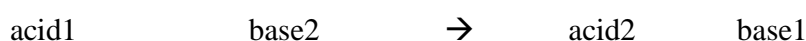
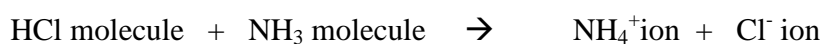


Fig. 3: Beaker model to visualize the neutralization of hydrochloric acid with sodium hydroxide solution [4]

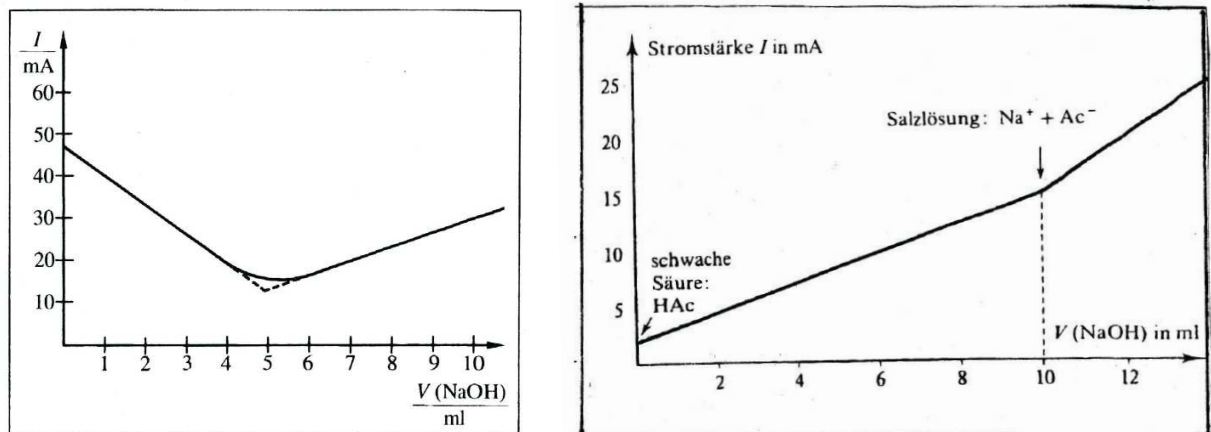
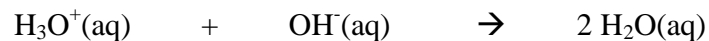
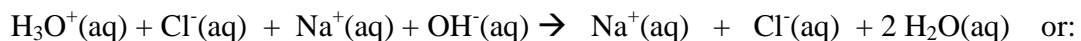


Fig. 4: Conductivity curves by neutralizing 0.1-M hydrochloric acid and 0.1-M acetic acid [6]

**Neutralization.** After the experiment of mixing hydrochloric acid and sodium hydroxide solution and observing the exothermic reaction an initial beaker model is drawn (see figure 3) – before the reaction of  $\text{H}_3\text{O}^+(\text{aq})$  ions and  $\text{OH}^-(\text{aq})$  ions is formulated. On the macro level, the following reaction equation may be quoted in words:

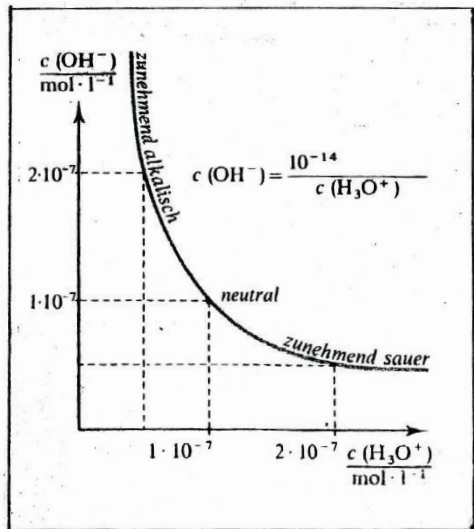
hydrochloric acid (aq) + sodium hydroxide (aq)  $\rightarrow$  sodium chloride (aq) + water.

After that, the beaker model should be developed on the submicro level (see figure 3) and finally, after identifying the involved smallest particles, the equations are created on the third level:

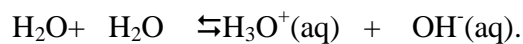


In particular it should be emphasized that for interpreting the neutralization reaction and the observed decrease of electric conductivity (see figure 4) not the number of ions gets smaller – but the  $\text{H}_3\text{O}^+(\text{aq})$  ions are replaced by  $\text{Na}^+(\text{aq})$  ions. In Figure 3 the beaker model shows four ions before the neutralization and four ions after the reaction: the conductivity tester indicates the

good conductivity of  $\text{H}_3\text{O}^+(\text{aq})$  ions before the neutralization and the decreasing conductivity during neutralization due to the appearing  $\text{Na}^+(\text{aq})$  ions.



**pH values.** To convey the idea of the pH, the ionic product must be comprehended. We first compare the autoionization of  $\text{H}_2\text{O}$  molecules by this equilibrium:



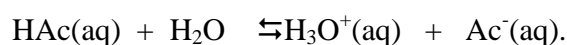
Now we come to the fact that both ion concentrations depend on each other. Experts measured some concentrations at the temperature of 25 °C, the result is the familiar hyperbola (see figure 5):

$$c(\text{H}_3\text{O}^+) \times c(\text{OH}^-) = 10^{-14}.$$

Fig. 5: Correlation of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentrations [6]

As the equilibrium is valid for all aqueous solutions, the definition of the pH can be derived either from the concentration of  $\text{H}_3\text{O}^+(\text{aq})$  ions or of  $\text{OH}^-(\text{aq})$  ions. The pH is determined by the concentration of  $\text{H}_3\text{O}^+(\text{aq})$  ions – taking the logarithmic function: if the concentration is  $c(\text{H}_3\text{O}^+(\text{aq})) = 10^{-2} \text{ mol/L}$ , the pH is defined as 2.

**Weak acids.** If we examine the pH values of 0.1-molar hydrochloric acid and 0.1-molar acetic acid solution, we obtain the values 1 and 3: the concentrations of  $\text{H}_3\text{O}^+(\text{aq})$  ions differ by a factor of 100. Looking at the conductivity in the neutralization of both solutions with sodium hydroxide solution, the results are completely different graphs (see figure 4). These observations can only be explained by the fact that the acetic acid solution shows equilibrium between molecules and ions which lies strongly on the side of the molecules:



To illustrate the existence of molecules and ions in solutions of weak acids, beaker models are again used (see figure 6).

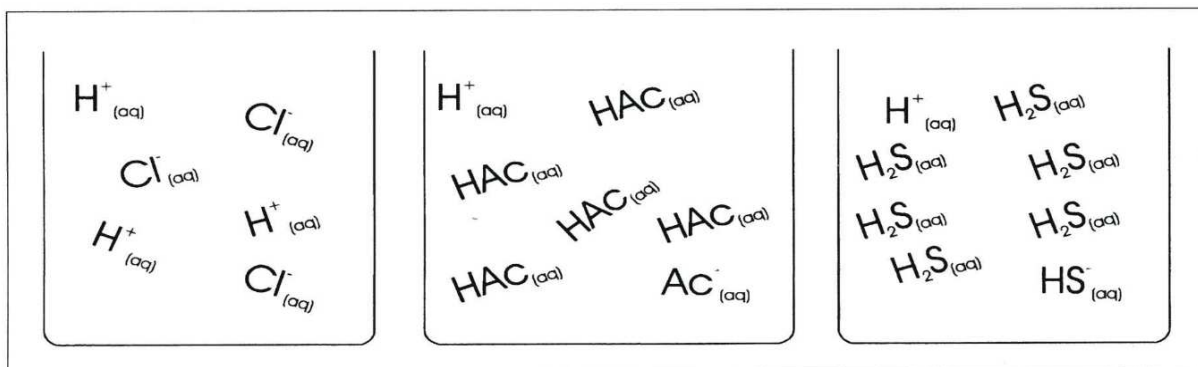


Fig. 6: Beaker models of strong hydrochloric acid and two solutions of weak acids [4]

In the discussion of the beaker models it must be clarified that with a degree of protolysis of about 1% for diluted acetic acid solution, the model must show 99 HAC molecules before one  $H_3O^+_{(aq)}$  ion and one  $Ac^-_{(aq)}$  ion is symbolized. For the model of the hydrogen sulfide solution, the number of 999  $H_2S$  molecules per one  $H_3O^+_{(aq)}$  ion and one  $HS^-_{(aq)}$  ion should be symbolized: this way, the degree of protolysis of 0.1% is illustrated. The beaker models thus serve to clear the concept of protolysis degree and equilibrium for learners, to prepare the very difficult concept of equilibrium constants like  $pK_S$  and  $pK_B$  constants, and to develop a scientific mental model.

## CONCLUSIONS

One likes to quote the advantages of Broensted's acid-base theory – but mixes the argumentation with ideas of Arrhenius' theory: protolysis and degree of protolysis (Broensted) with dissociation and degree of dissociation (Arrhenius), one speaks of substances as acids and

bases instead of the involved molecules or ions (“sulfuric acid gives two protons, water is an ampholyte”), or takes the "salt formation" as a criterion for neutralization.

Broensted with his famous fundamental equation  $A \rightleftharpoons B + H^+$  gave the symbols A and B always the meaning of molecules or ions – and thus the theory got the important sense. So for teaching and instruction it makes sense to designate molecules and ions, which act in reactions as proton donors or acceptors, which can act as ampholytes and which are defined as conjugated acid-base pairs.

If the teacher helps to look at the particles which are reacting by emitting or taking protons, and if the teachers works with molecular models and beaker models, the learners will develop scientific mental models, will better understand formulas and equations, and will better understand chemistry!

The same basics are valid for the understanding of redox reactions: teachers have to look to atoms, ions or molecules which donate electrons, and to atoms, ions or molecules which accept electrons [7]. Also from suitable concrete models [7], students will create their mental models and will not blame chemistry as a very difficult subject!

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