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## **Demonstrations as a Tool for Ironing-Out Misconceptions: 2. Can a Strong Acid Be Displaced by a Weak One?**

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**Abstract:** It is generally believed that a stronger acid will displace a weaker one from its salts. This is often true, but there are examples where a weaker acid (e.g. H<sub>2</sub>S) will displace a much stronger one (e.g. HCl), providing practically insoluble precipitates are formed. A demonstration is offered to help students realize that there are important exceptions to the general rule. An explanation of the phenomenon is also given.

Key words: displacement reactions, acid strength, solubility, precipitates, misconceptions

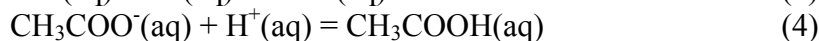
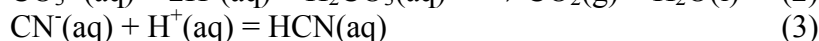
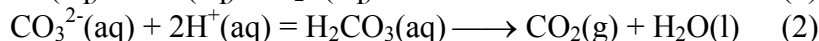
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### Introduction: the Misconception

“Strong acids displace weak ones from their salts.” It seems that many students adopt this general statement as an axiom. The results of an anonymous test of 2<sup>nd</sup> year Chemistry students showed that more than 60 % of them do believe that the above statement is true.

Indeed, it is true in many cases. The following equations represent only a few examples of reactions in systems composed of a mixture of a strong acid, designated as  $H^+(aq)$ , and a salt (i.e. water solution of a salt) of a weak acid:



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Usually an explanation that is offered goes like this: the above reactions are possible since (at least) one of the products is a weak electrolyte. In other words, one of the three criteria that govern the direction of chemical reactions (i.e. that the product be a gas, a precipitate or a weak electrolyte [1–2]), is met in all of the given examples.

The way equations 1–4 were written implies that all other ions in the solutions are spectator ions. Providing this is true, one easily comes to the assertion that strong acids displace weak ones. It is, one has to say, a useful rule of thumb in general chemistry. A consequence of this rule is that reactions are favored in the direction leading to a decrease in the number of ions in the system. This decrease in the number of ions is governed by the rather low values of the dissociation constant ( $K_a$ ) of the weak acid and the ionic product of water ( $K_w$ ).

No matter how useful this rule seems to be, one must say it is a rough rule and that there are exceptions to it. If the exceptions are overlooked, the rule may easily become a source of misconceptions. To put it straight, it is possible that **a strong acid be displaced by a weak one**. We shall demonstrate this by the following experiment.

### The Experiment

The experiment is, in essence, a reaction between water solutions of mercury(II) chloride and  $H_2S$ .

Solutions and equipment.  $H_2S(aq)$  is synthesized by bubbling  $H_2S$  gas through a microwash-bottle half-filled with distilled/deionized water (cf. Fig. 1).  $H_2S(g)$  is generated in the chemical reaction between solid  $FeS$  and hydrochloric acid (no high purity hydrochloric acid is needed). The solution, that is  $H_2S(aq)$ , may be stored for relatively long periods in a glass-stoppered bottle, preferably at low temperature (in a refrigerator). The important thing is that the contact with air has to be minimized, otherwise slow oxidation may turn all  $H_2S$  into elemental S and water. The concentration of the saturated water solution of  $H_2S$  is usually considered to be  $0.1 \text{ mol}\cdot\text{dm}^{-3}$ .

The solution of mercury(II) chloride is prepared by dissolving 0.25 g of  $HgCl_2$  in about  $20 \text{ cm}^3$  of deionized water (i.e. its concentration is roughly  $0.05 \text{ mol}\cdot\text{dm}^{-3}$ ).

The thymolblue solution is a 0.5 % solution of the indicator in ethanol. It has been chosen among many different indicators for it is a 3-color indicator. According to the literature data [3] in a strongly acidic medium the color changes from red ( $pH < 1.2$ ) to yellow ( $8 > pH > 2.8$ ), and in a weakly alkaline medium it changes from yellow to blue ( $pH > 9.6$ ).

One uses the above chemicals, a test-tube rack with test-tubes and a dropper.

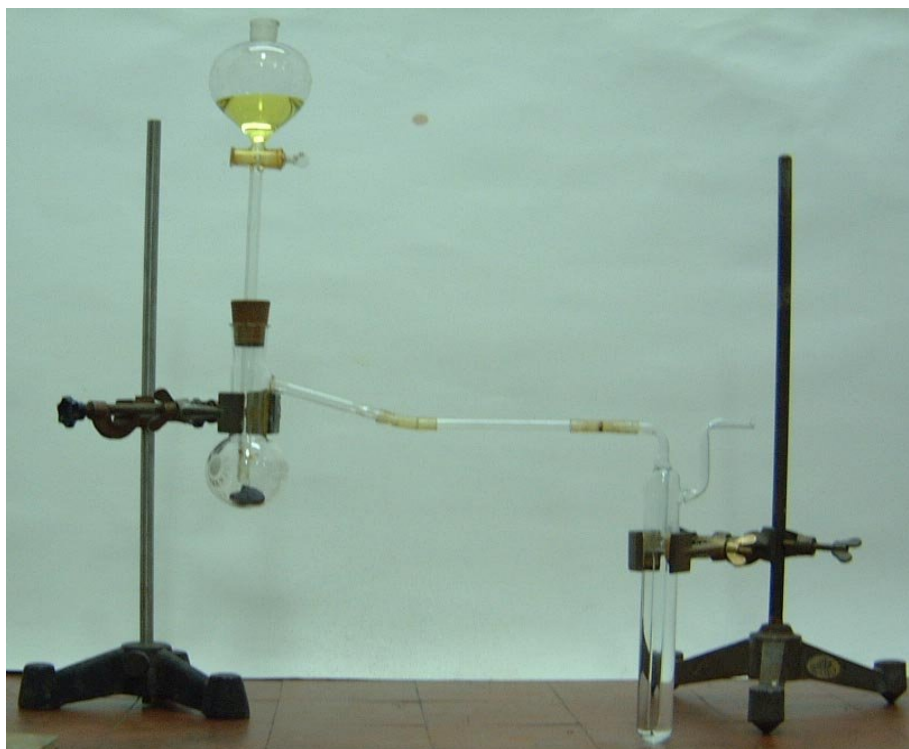


Figure 1

The demonstration. The instructor puts five test-tubes in a test-tube rack (cf. Fig. 2). The first one contains  $\text{HgCl}_2(\text{aq})$  solution. The second one is empty. The third one contains  $\text{H}_2\text{S}(\text{aq})$ . The fourth one is half-filled with distilled water and the last one contains a diluted ammonia solution. A few drops of the indicator (thymolblue) are added to all test-tubes.

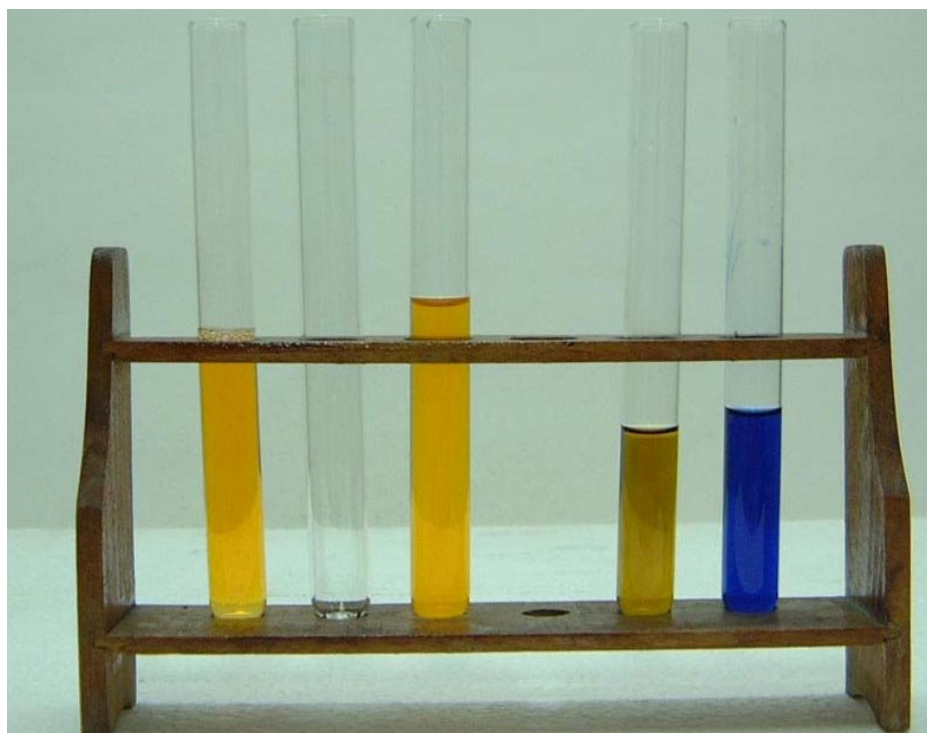


Figure 2

After the instructor explains the properties of thymolblue indicator, the students are asked to observe that the solutions of  $\text{H}_2\text{S}$  and  $\text{HgCl}_2$  are weakly acidic, that aqueous ammonia is of course basic, and that the color of distilled water is intermediate between the above two, but much closer to the color of  $\text{H}_2\text{S}(\text{aq})^{**}$ .

Once this is finished, the instructor pours off roughly half of the content of the test-tubes containing  $\text{H}_2\text{S}(\text{aq})$  and  $\text{HgCl}_2(\text{aq})$  into the empty test-tube. The solution immediately turns red! The students are again asked to witness that the medium is now strongly acidic. After a few minutes a dark precipitate settles down in the test-tube.

The instructor gives the necessary explanation for the unexpected phenomenon.

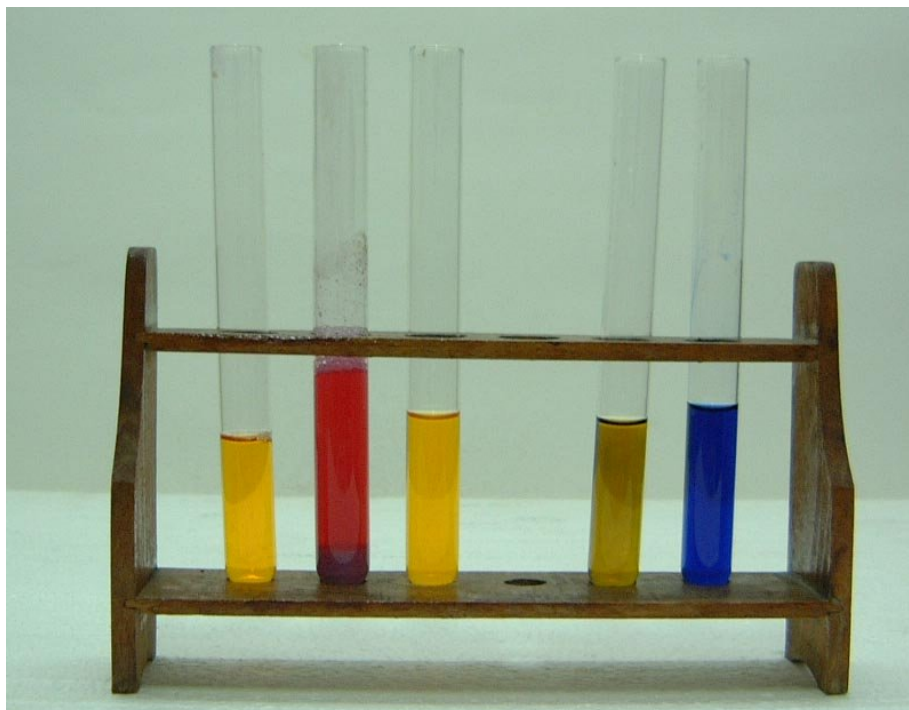


Figure 3

### Results and Discussion

It is known from literature data [4,5] that the number of ions in both  $\text{H}_2\text{S}(\text{aq})$  and  $\text{HgCl}_2(\text{aq})$  solutions is rather low, the values of the first dissociation constants being

$$K_1(\text{H}_2\text{S}) = \frac{c(\text{H}^+) \cdot c(\text{HS}^-)}{c(\text{H}_2\text{S})} \approx 6 \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3} \quad (5)$$

$$K_1(\text{HgCl}_2) = \frac{c(\text{HgCl}^+) \cdot c(\text{Cl}^-)}{c(\text{HgCl}_2)} \approx 3 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \quad (6)$$

The cumulative dissociation constants are much lower (by some 15 orders of magnitude in the case of  $\text{H}_2\text{S}$ ), i.e.

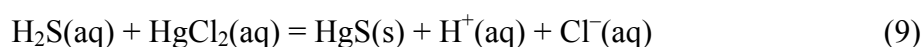
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\*\* Since thymolblue retains the yellow color in a wide range of pH values (from 2 to 8, as mentioned above), we used 'universal' indicator paper to further check the acidity of solutions. It appeared that the pH value of  $\text{H}_2\text{S}(\text{aq})$  is about 3.5, that of  $\text{HgCl}_2(\text{aq})$  about 5.5 and that of distilled water about 7.

$$K(\text{H}_2\text{S}) = K_1(\text{H}_2\text{S}) \cdot K_2(\text{H}_2\text{S}) = \frac{c(\text{H}^+)^2 \cdot c(\text{S}^{2-})}{c(\text{H}_2\text{S})} \approx 6 \cdot 10^{-22} \text{ mol}^2 \cdot \text{dm}^{-6} \quad (7)$$

$$K(\text{HgCl}_2) = K_1(\text{HgCl}_2) \cdot K_2(\text{HgCl}_2) = \frac{c(\text{Hg}^{2+}) \cdot c(\text{Cl}^-)^2}{c(\text{HgCl}_2)} \approx 4 \cdot 10^{-13} \text{ mol}^2 \cdot \text{dm}^{-6} \quad (8)$$

However, the solubility product of HgS is so very low ( $K_{\text{SP}} \approx 10^{-54} \text{ mol}^2 \cdot \text{dm}^{-6}$ ), that the molar solubility of HgS is of the order of magnitude of  $10^{-27} \text{ mol} \cdot \text{dm}^{-3}$ ! Since the concentration of sulfide ions in a solution with  $c(\text{H}_2\text{S}) \approx 0.1 \text{ mol} \cdot \text{dm}^{-3}$  is of the order of magnitude of  $10^{-14} \text{ mol} \cdot \text{dm}^{-3}$ , and that of  $\text{Hg}^{2+}$  ions may be estimated as being of the order of magnitude of  $10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ , the immediate formation of HgS is more than justified. In that case, the solution is  $\text{H}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  enriched, the net effect being displacement of HCl by  $\text{H}_2\text{S}$ , i.e.:



thus increasing the pH value by several units, as shown by the color change of the thymolblue indicator.

*‘Weak acid displaced the strong one from the water solution of its salt’.* The phenomenon is perhaps not really expected, but is definitely possible.

### Conclusion

It is obvious that there are cases where the weak acid displaces the strong one from the solution of its salt. The latter phenomenon is possible in all cases where a practically insoluble salt of the weak acid can be formed (or at least, a salt that emits several orders of magnitude less anions of the weak acid, than is ‘allowed’ by its dissociations constant  $K_a$ ). Displacement of the strong acid occurs then as the only way of keeping the concentration of the weak acid anions low enough, as dictated by the solubility product ( $K_{\text{SP}}$ ) of the ‘practically insoluble salt’.

### Safety Tips

**All mercury compounds are extremely toxic.** Wear gloves when working with mercury and its compounds. If a solution containing mercury compounds is swallowed (or even sipped), call for a physician immediately. The waste should be disposed of according to safety regulations. An alternative could be to saturate the waste with  $\text{Na}_2\text{S}(\text{aq})$  and to dispose of it down the drain.

**$\text{H}_2\text{S}$  is a very toxic gas – avoid inhalation.** It is recommended to work in a hood (even when using water solutions). Dispose of the water solutions down the drain with large quantities of water.

### Advice for Instructors

The success of the demonstration is complete, providing the students possess the required background knowledge. Thus, students should be able to make a clear-cut distinction between strong and weak acids (the former being completely, and the latter only partly dissociated in water). Further, they should be familiar with the types of reactions that go one-way only (left to right), that is reactions in which a precipitate is formed, a gas is evolved or a weakly dissociated entity is formed. Finally, they should be familiar with the definitions (and corresponding mathematical equations) of a

dissociation constant and a solubility product.

It is important to mention that, despite the knowledge of the above, it is to be expected that many students will be astonished by the fact that a weak acid is capable of displacing the strong one from the water solution of its salt. The experiment thus appears as a kind of ‘experiment of surprise’, where the result of the experiment is in sharp disagreement with the (intuitive) expectations. In this way (giving results that are markedly different from expectations) these experiments are really effective in resolving misconceptions. They teach that simple reasoning, based on some elementary chemical knowledge, is not necessarily correct.

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