

*Citation:*

A. Smits & Wolff, L.K., On the repelling of ionisation of solutions of [NaOH,Na<sub>2</sub>CO<sub>3</sub>] and [NaHCO<sub>3</sub>] by addition of [NaCl], in:  
KNAW, Proceedings, 4, 1901-1902, Amsterdam, 1902, pp. 42-44

**Chemistry.** — Dr. A. SMITS and L. K. WOLFF: "*On the repelling of the ionisation of solutions of Na OH, Na<sub>2</sub> CO<sub>3</sub> and Na HCO<sub>3</sub> by addition of Na Cl.*" (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

In an article entitled: „Globulin als Alkali-eiweis-verbinding”<sup>1)</sup> STARKE has developed a theory based on some chemical phenomena noticed by him, which are so utterly in contradiction with the teachings of physical chemistry, that we found it very desirable to repeat his experiments and trace the cause of these singular results.

1. STARKE found, that, when he added 1 c.c. of a 0.15 percent solution of Na OH to 25 c.c. of a 15 per cent solution of Na Cl and the same amount to 25 c.c. of distilled water, mixtures were obtained of a different degree of alkalinity, the Na Cl solution having always the strongest alkaline reaction.

These experiments were repeated using instead of Na Cl, solutions of Na<sub>2</sub> CO<sub>3</sub> and Na HCO<sub>3</sub>; the result, however, was exactly the same.

From this, the conclusion was drawn that, contrary to theory, the alkaline reaction of a solution of Na OH perceptibly increases instead of decreasing on adding a salt with a homonymous ion.

Another phenomenon observed by STARKE appeared to confirm this.

2. He found namely that the solubility of globulin in a solution of Na OH is increased by addition of Na Cl. Addition of Na Cl, therefore, appeared to have the same effect as addition of more Na OH.

3. Another experiment which strengthened him in the conviction that theory utterly deserted us here was the following: Whilst convincing himself that Na Cl may be precipitated from its concentrated solutions by adding a strong solution of H Cl, he did not find it possible to cause a precipitation by adding a strong solution of Na OH.

4. On repeating the experiments (1) we found that on using water, which is not free from carbon dioxide, we noticed the same thing as observed by STARKE. Before proceeding further we may state that STARKE in his experiments always used red litmus paper to judge which solution was the most alkaline, whereas we have

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<sup>1)</sup> Zeitschr. f. Biologie B. XXII, S. 419 (1900).

used the colorimetric method with litmus and phenolphthalein as indicators.

As already stated, we got by a more accurate method the same surprising result as STARKE. When, however, we used instead of water containing carbon dioxide water, which was absolutely free from the same (obtained by passing air free from carbon dioxide for some hours through distilled water) we obtained just the *opposite* result and the Na OH solution always had a stronger alkaline reaction than the Na OH—Na Cl solution, which agrees with the theory which requires, that the ionisation of the Na OH solution be repelled by addition of Na Cl.

5. The explanation of the result obtained by STARKE is now as follows:

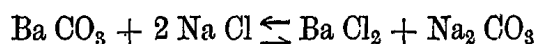
On dissolving Na Cl in distilled water a portion of the dissolved carbon dioxide is expelled, because the solubility of carbon dioxide in water is greater than its solubility in a solution of Na Cl. Distilled water has, therefore, a stronger acid reaction than a solution of *neutral* Na Cl<sup>1)</sup> in this same water and this stronger acid reaction of the water is so predominant that in STARKE's experiment it exceeded the decrease of the ionisation caused by addition of Na Cl and thus caused that perplexing result.

6. After obtaining the above result, we have tried to estimate the CO<sub>2</sub> in water and solution of salt colorimetrically by adding baryta water. Here we observed the peculiar phenomenon that, while the water became distinctly opalescent, this did not happen with the 15 percent solution of Na Cl. Another experiment where we started from 100 cc. of water containing CO<sub>2</sub> to which was added 100 cc. of a 15 percent solution of Na Cl and then baryta water gave the same result; no opalescence was observed and it was not until the solution had been diluted many times with water containing CO<sub>2</sub>, that barium hydroxide caused a turbidity. A colorimetric estimation was, therefore, not possible in this manner.

The explanation of this phenomenon must be found in the reversibility of the reaction

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<sup>1)</sup> It is plain that, if we want to find out the reaction of a salt, this should be dissolved in water absolutely free from carbon dioxide. We experienced the fact that Na Cl, which was thought to be neutral on account of its neutral reaction in distilled water showed a decided alkaline reaction when dissolved in water free from carbon dioxide.



which in our case, where a small quantity of Ba CO<sub>3</sub> could react with a very large excess of Na Cl, practically took place only from the left to the right.

7. Being thus obliged to abandon this method, we have taken another course.

A current of air free from carbon dioxide was first passed through a washbottle containing 300 cc. of distilled water and then through a little washbottle filled with baryta water; the current of air being thus again freed from carbon dioxide was passed through a washbottle containing 300 cc. of a 15-percent solution of Na Cl and then finally through a small washbottle containing baryta water. If now a piece of black paper was put underneath the bottles containing the baryta it was plainly noticed, that, after 5 minutes the first bottle contained already more Ba CO<sub>3</sub> than the second one, which difference was maintained even after passing the gas for several hours, thus freeing the water and the solution completely from carbon dioxide.

In this manner we had succeeded after all in demonstrating that the 15 percent solution of Na Cl contained less dissolved carbon dioxide than the distilled water from which it had been prepared. On dissolving Na Cl in water some of the CO<sub>2</sub> must, therefore, have been expelled.

8. As regards experiment 3 we may state that STARKE has made another mistake. Na Cl may be precipitated from a concentrated solution by addition of either H Cl or Na OH. The solution of the latter if used for this purpose should, however, be much more concentrated than the H Cl solution. There exists therefore, only a quantitative difference which may be explained by the difference in the degree of dissociation of equally concentrated solutions of H Cl and Na OH.

From the foregoing we see how, in this subtle question, STARKE has wandered from the right path through not sufficiently criticising his own results, and has arrived at totally wrong conclusions. His theory being based on erroneous principles must, therefore, be entirely rejected.

*Amsterdam, Chem. Lab. University, May 1901.*