

tested

demonstrations



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Acid-Base Reactions in the Gaseous State (An Illustrative Experiment)

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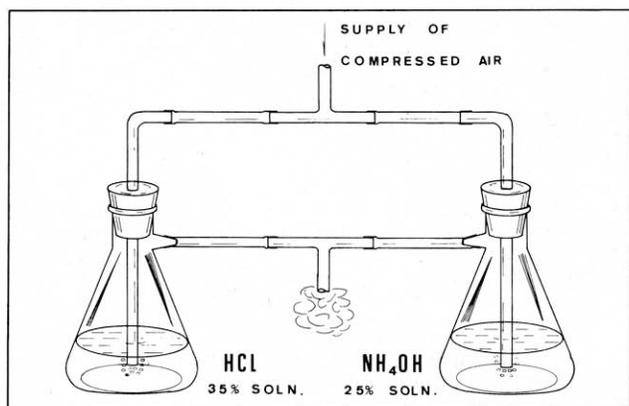
To demonstrate acid-base reactions in the gaseous state it is usual to bring together the openings of two flasks, one of them containing a solution of a volatile acid and the other a solution of a volatile base. The reaction can be observed in the area where the gases meet, the product of neutralization being visible like a solid in suspension. This method is limited by the rate of diffusion of the intermingling gases and also their concentrations.

A simple method to demonstrate this kind of reaction was successfully performed in our classes.

Two Pyrex, 500-ml, side-arm filtering flasks were used. One was filled with 100 ml of hydrogen chloride solution (35%) and the other with 100 ml of ammonium hydroxide solution (25%). Each flask was fitted with a rubber stopper having a right angle glass tube, the end of which was immersed in the solution. The glass tubes were connected together and to a supply of compressed air by means of rubber tubes and a "T" connector. The side tubes were also connected together by means of rubber tubes, "T" piece and vent pipe (see figure).

Demonstration

A reaction was visible when air was blown into the flasks. The reagents were pushed out of their solutions through the side tubes and together in the "T" piece. The reaction took place in the "T" piece and the product, ammonium chloride, was expelled through the vent pipe in the form of a strong white smoke.



Apparatus set-up for demonstrating gaseous state acid-base reactions.

Remarks

Other acids can also be used for this experiment, for example hydrogen nitrate.

This apparatus is also suitable for and was used by the Palaeontology lecturer of this Faculty in illustrating fossil formations (to obtain photographic contrasts, rock incrustations were coated with ammonium chloride blown over it).

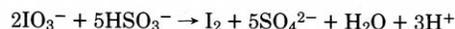
NOTE: To better illustrate the experiment, a few drops of acid-base indicators (such as methyl red and phenolphthalein) can be added to the solutions of the reagents.

The Landolt, "Old Nassau", and Variant Reactions

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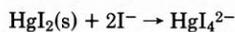
The "Old Nassau" reaction is a modification of the Landolt "clock" reaction of iodate, bisulfite, and starch. The Landolt reaction proceeds via the mechanism:



Steps (1) and (2) are slow in comparison to step (3). As long as bisulfite is present, then the rapidity of (3) prevents the accumulation of iodine and thus the blue-black starch iodine complex cannot form via step (4). Once the bisulfite is exhausted, however, iodine can no longer be reduced via step (3) and the starch-iodine complex suddenly appears. Note how the stoichiometry of the mixture in the Landolt and the "Old Nassau": (see Appendix) necessitates eventual iodine accumulation for 0.0175 M IO₃⁻ and requires 0.0525 M HSO₃⁻ for complete reduction to I⁻ but only 0.031 M HSO₃⁻ is available.

The "Old Nassau" reaction includes Hg²⁺ in the Landolt mixture so that as the iodine concentration increases by reactions (1), (2), and (3), orange HgI₂ abruptly precipitates when the solubility product of mercuric iodide is exceeded. Shortly after the mercuric iodide forms, the bisulfite is exhausted, iodine accumulates, and orange is masked by the blue-black iodine-starch complex. Hence, the clear, orange, blue-black color sequence.

In the Variant there is sufficient bisulfite, more than 3 × 0.0175 M, to reduce all the iodate to iodide. Again, as step (3) is much faster than (2), no I₂ can accumulate and the blue-black complex cannot form. Thus, as the reaction proceeds, the iodide concentration increases with mercuric iodide eventually precipitating as before. However, the iodide concentration continues to increase and the just-formed precipitate dissolves in a reaction reminiscent of amphotericism; mercuric ion forms a complex ion in excess iodide.



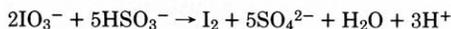
The Landolt reaction is well known to be acid catalyzed. The "Old Nassau" and Variant are, of course, also catalyzed by acid. Regular time variations for color changes versus acid concentration and temperature are found for all three reactions.

General References

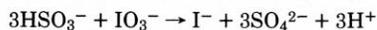
Sorum, C. H., Charlton, F. S., Neptune, J. A., and Edwards, J. O., *J. Amer. Chem. Soc.*, **74**, 219 (1952).
Church, John A., and Dreskin, Sanford A., *J. Phys. Chem.*, **72**, 1387 (1968).

Appendix

This can be seen by combining eqns. (1) and (2) yielding:



when the result is added to eqn. (3) one obtains:



The overall reaction in "excess" bisulfite.

The reactions-solution combinations quickly illustrating the three reactions.

Solutions:

3g/l $\text{HgCl}_2 = 0.011 M \text{Hg}^{2+}$

15 g/l $\text{KIO}_3 = 0.070 M \text{IO}_3^-$

13 g/l NaHSO_3 plus solubilized starch = $0.124 M \text{HSO}_3^-$

Procedures:

I: Landolt 30 ml KIO_3 + 30 ml NaHSO_3 + 60 ml H_2O

Color sequence: clear, blue-black

II: "Old Nassau": 30 ml HgCl_2 + 30 ml KIO_3 + 30 ml NaHSO_3 + 30 ml H_2O

Color sequence: clear, orange, blue-black

III: Variant: 30 ml HgCl_2 + 30 ml KIO_3 + 60 ml NaHSO_3

Color sequence: clear, orange, clear

NaHSO_3 in all cases is added last with continual swirling.

Reactant Concentrations:

Landolt $[\text{IO}_3^-] = \frac{1}{4} \times 0.0700 M = 0.0175 M$
 $[\text{HSO}_3^-] = \frac{1}{4} \times 0.124 M = 0.031 M$

"Old Nassau" $[\text{Hg}^{2+}] = \frac{1}{4} \times 0.011 M = 0.00275 M$
 $[\text{IO}_3^-] = \frac{1}{4} \times 0.0700 M = 0.0175 M$
 $[\text{HSO}_3^-] = \frac{1}{4} \times 0.124 M = 0.031 M$

Variant $[\text{Hg}^{2+}] = \frac{1}{4} \times 0.011 M = 0.00275 M$
 $[\text{IO}_3^-] = \frac{1}{4} \times 0.0700 M = 0.0175 M$
 $[\text{HSO}_3^-] = \frac{1}{2} \times 0.124 M = 0.062 M$