though at low temperature this adjustment is relatively slow. The amount of adsorption of hydrochloric acid and of ferric chloride on the colloidal ferric hydroxide also is slight and in most respects negligible, although the slightly greater conversion in acidified solution indicates that some adsorption does take place.

3. The progress of the slow hydrolysis of ferric chloride and nitrate has also been followed by measurements of the color which develops in these solutions. The curves thus obtained have been found to parallel closely the corresponding curves obtained from the conductance measurements, indicating that a single colored substance, ferric hydroxide, is formed commensurately with the liberated hydrochloric acid responsible for the increase in conductance.

4. The potential of the silver–silver chloride electrode has been measured in dilute solutions of ferric chloride at intervals during the slow hydrolysis. In 1.3 millimolar solution a barely measurable while in a 0.3 millimolar solution no change in concentration of chloride ion is observed. This confirms the inferences from the conductance measurements as to a negligible adsorption of chloride on the colloidal ferric hydroxide in dilute solution.

CAMBRIDGE, MASS. RECEIVED JANUARY 12, 1938

# NOTES

## Rapid Exchange between Deutero-ammonia and Hydrazine

BY PAUL C. CROSS AND PHILIP A. LEIGHTON

Measurements of the photochemical decomposition of $ND_3$–$N_2H_4$ mixtures were undertaken recently in this Laboratory for the purpose of obtaining additional experimental data upon which to base a study of the mechanisms of the photodecompositions of ammonia, hydrazine, and ammonia–hydrazine mixtures.[1] Unfortunately, as far as the original intentions were concerned, the experiments showed that the exchange equilibrium was established by a rapid thermal exchange under all the experimental conditions employed, thus nullifying the value of the deuterium as an indicator.

Estimates of the rate of this exchange were obtained by the analysis, using a quartz fiber manometer, of the hydrogen–deuterium mixture from the thermal decomposition products of both the ammonia and the hydrazine of a mixture which had been separated by distillation at the temperature of an alcohol–carbon dioxide bath. The hydrogen and deuterium were separated from the nitrogen by diffusion through a palladium thimble under conditions which allowed the diffusion equilibrium to be established quickly, thus avoiding uncertainties due to diffusion-fractionation. The thermal decomposition was carried out on the heater of the palladium thimble. Contamination from previous samples was minimized by thorough outgassing of the compartments on both sides of the thimble with the latter at a temperature considerably higher than that used for the separation. The probable error of the analyses is of the order of 3 to 5%.

To quote a typical experiment, approximately 10 mm. of each $ND_3$ and $N_2H_4$ were mixed and in contact for about thirty seconds at 26.5° before the hydrazine was frozen down. The ammonia then analyzed 39% deutero-, and the hydrazine 45% deutero-. Mixtures from which the hydrazine was frozen down within a few seconds after mixing showed similar analyses. There was even evidence of an exchange between solid $N_2H_4$ and gaseous $ND_3$ at temperatures as low as −70°, as demonstrated by the following results: 10 mm. of $N_2H_4$ was frozen down and an equal amount of $ND_3$ introduced. A sample of ammonia taken at once analyzed 101% deutero-. After twenty-five minutes the ammonia analyzed 96% deutero-, and after six hours, 86%. The trend is unmistakable, and is definitely larger than the likely error in the analyses. At the conclusion of this run the hydrazine was evaporated with the remaining ammonia and immediately frozen down again, after which the ammonia analyzed 40% deutero-,

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(1) E. O. Wiig, THIS JOURNAL, **59**, 827 (1937); H. J. Welge and A. O. Beckman, *ibid.*, **58**, 2462 (1936); R. A. Ogg, Jr., P. A. Leighton and F. W. Bergstrom, *ibid.*, **56**, 318 (1934); E. O. Wiig and G. B. Kistiakowsky, *ibid.*, **54**, 1806 (1932); A. Farkas and P. Harteck, *Z. physik. Chem.*, **B25**, 257 (1934).

Although no experiments were performed to demonstrate the character of this exchange, the authors feel that it must certainly be heterogeneous, probably through a mechanism involving the simultaneous transfer of hydrogens in hydrogen bonds within groups of $N_2H_4$–$ND_3$ molecules. This explanation must not be too hastily accepted, however, because the absence of any pronounced super-conductivity of the hydrogen ion in hydrazine systems,[2] and the lack of tendency for ammonia and hydrazine to form mixed crystals[3] argue against such a mechanism. The effect of small amounts of water on the formation of mixed crystals[3] suggests that the observed exchange may have been due to water catalysis, although considerable care was taken to ensure the absence of water in the above experiments. Further experiments are desirable before more definite conclusions concerning the mechanism are attempted.

These observations were made during the course of a study of exchange reactions with deuterium which was supported by a grant from the Carnegie Institution of Washington.

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[2] P. Walden and H. Hilgert, *Z. physik. Chem.*, **A165**, 241 (1933).

[3] F. Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

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## Preparation of Barium Chlorite and Solubility of Silver Chlorite

BY W. V. SMITH, K. S. PITZER AND W. M. LATIMER

Our attention has been called to the omission of two references which might properly have been included in our paper on silver chlorite.[1]

Bruni and Levi[2] prepared pure barium chlorite and Levi[3] reported values for the solubility of silver chlorite, which are in close agreement with our value at 25°.

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[1] Smith, Pitzer and Latimer, THIS JOURNAL, **59**, 2640 (1937).

[2] Bruni and Levi, *Gazz. chim. ital.*, **45**, II, 169 (1915).

[3] Levi, *ibid.*, **53**, 525 (1923).

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# COMMUNICATIONS TO THE EDITOR

## BENTONITE AS AN ADSORBENT IN THE PURIFICATION OF INVERTASE[1]

*Sir:*

In the course of investigations on invertase we have developed, in the preparation of this enzyme, certain procedures which may be of value not only in connection with invertase but also in regard to other problems in biochemistry. Bentonite, a colloidal clay already well-known commercially, has been found to be an excellent adsorbent for invertase. Bentonite can be used, without preliminary treatment, in the undiluted autolysates from yeast. Both adsorption and elution can be carried out under conditions more favorable for the stability of invertase than those generally used with other clays. The optimal *p*H for adsorption is 4.1–4.3 while an acetate or phosphate solution of *p*H 5.3 or greater produces satisfactory elution. The amount of bentonite required for complete adsorption is relatively small and the five different samples of bentonite so far investigated have all proved excellent adsorbents for invertase, yielding preparations of similar time values.

Invertase solutions with time values of 0.20–0.27 minute as expressed in the customary units[2] have been obtained by dialysis following a single bentonite treatment of various types of autolysates from bakers' yeast. Similar solutions have been prepared from unenriched brewers' yeast by a slight modification involving fractional adsorption on bentonite with 10–20% adsorption and loss in the first fraction. From enriched brewers' yeast (*i. e.*, yeast which has been allowed to ferment a sucrose solution) preparations have been obtained with time values of 0.15–0.18 minute. The invertase solutions thus prepared do not lose activity during dialysis or subsequent storage over a period of several months in the refrigerator.

The following describes a typical procedure. A fractional autolysate of bakers' yeast was prepared by treating 430 g. of yeast (time value, 34.3) at 30° with 43 cc. of ether, adding 43 cc. of toluene,

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] C. Oppenheimer, "Die Fermente und ihre Wirkungen," fifth edition, 1928, Vol. III, pp. 770–774.