NOTES

The Reaction of "Aluminon" with Hydroxides of Scandium, Gallium, Indium, Thallium and Germanium.—The reagent suggested by Hammett and Sottery[1] for the detection of aluminum has been applied by Middleton[2] to solutions of beryllium, zirconium, thorium and the rare earths. Middleton regretted that lack of a supply of scandium prevented his trying the behavior of that element towards the new reagent. The writers have been fortunate in having available sufficient scandium, gallium, indium and germanium to enable them to study the reactions of these elements with the Aluminon reagent.

Scandium produces a red lake, insoluble in ammonium hydroxide but readily soluble in ammonium carbonate. The gallium lake forms more slowly but, when once produced, more closely resembles that of aluminum, being insoluble in ammonium hydroxide and dissolving in a solution of ammonium carbonate only after standing for some time. Indium gives a red solution which is relatively stable in the presence of ammonium hydroxide, although no precipitate is produced. The red color of the solution is discharged by the addition of ammonium carbonate. In this respect it approaches the behavior of tervalent thallium whose lake forms with difficulty and is unstable both in ammonium hydroxide and in ammonium carbonate. Germanium forms no stable lake with Aluminon, in this respect resembling silicon, stannic tin and lead.

Solutions of germanium dioxide and of the chlorides of scandium, gallium, indium and thallic thallium were prepared, containing about 1 mg. of the element per cc. To 1 cc. of these solutions were added 5 cc. of N hydrochloric acid, 5 cc. of 3 N ammonium acetate and 5 cc. of 0.1% Aluminon solution. When, immediately after mixing, 3 cc. of 6 N ammonium hydroxide was added to the solution, scandium yielded a bright red precipitate similar to that obtained with aluminum. This precipitate became more dense on standing, finally settling, leaving a slightly turbid, pink solution above. In the solutions containing gallium and indium, however, no precipitates were produced, although a red color was imparted to the solutions which was not completely discharged by adding the alkali. Both the thallium and germanium solutions assumed the yellow color of the dye in alkali without the formation of visible precipitates.

When, however, the solutions were permitted to stand for ten minutes before the addition of the ammonium hydroxide, thus allowing time for the formation of the lake, the results obtained were much more conclusive. In the case of scandium, turbidity appeared before addition of the ammonium hydroxide, and the final precipitation with Aluminon seemed to be much more nearly complete. The precipitate was darker colored, coagu-

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[1] Hammett and Sottery, This Journal, **47**, 142 (1925).

[2] Middleton, *ibid.*, **48**, 2125 (1926).

lated and settled more readily, and left a clear, almost colorless solution. It dissolved completely when the solution was made normal in ammonium carbonate, the color changing from red to yellow. The acetate solution containing gallium became distinctly turbid on standing. The addition of ammonium hydroxide produced a red precipitate which settled quickly. Precipitation appeared to be incomplete, the supernatant liquid remaining distinctly red. The precipitate was only partially soluble in *N* ammonium carbonate solution. When the solution was made 2 *N* with this reagent and was allowed to stand for 10–15 minutes, the precipitate disappeared, but the red color still persisted throughout the solution. In the case of indium, no precipitate was produced at any time, but the solution remained bright red after the addition of ammonium hydroxide. This color was readily discharged when the solution was made normal in ammonium carbonate. With thallium and germanium no difference was observed. Lakes were not formed, and the addition of ammonium hydroxide destroyed the red color of the dye.

To compare the solubilities of the lakes with possible hydroxides or basic acetates, duplicate solutions were prepared as described in the third paragraph above, except that in one set 5 cc. of water was substituted for the 5 cc. of Aluminon reagent. The solutions were allowed to stand for 24 hours. A deep red scandium lake settled, leaving a clear, colorless, supernatant liquid. Gallium gave very similar results except that settling was not so complete, although the supernatant liquid was clear and colorless. The solutions containing indium, thallium and germanium were a clear, deep red with no evidence of turbidity. The solutions not containing the Aluminon reagent remained clear and colorless in every case.

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A Revision of Some Activities in Water-Alcohol Mixtures.—In a recent calculation of the properties of hydrogen chloride in water-alcohol mixtures,[1] there is an error in the computation of the average molecular weight of the solvent, w_1, and consequently in the derived values E_N, the electromotive force of solutions whose activities are one mole %, and γ_0, the corresponding activity coefficients. Corrected values of these quantities are given below.

The theoretical calculations also may be improved by utilizing the recent measurements by Dobson[2] of the partial vapor pressures of water-alcohol mixtures at 25°, which are much more accurate than the extrapolated values used in the previous computations, and which are represented

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[1] Scatchard, THIS JOURNAL, **47**, 2098 (1925).

[2] Dobson, *J. Chem. Soc.*, **127**, 2866 (1925).

closely by the simplified Margules equation:[3]

$$\log a_w = \log x_w + 0.9x_a^2 - 0.5x_a^3$$
$$\log a_a = \log x_a + 0.15x_w^2 + 0.5x_w^3$$

Values of —0.05915 log a_w computed from the first of these equations, and the values of E_N calculated for a substance which combines with one molecule of water to give ions of mean size 6.4 × 10^{-8} cm. are included in the table. The size is that which gives agreement with the measurements in water and in 50 mole per cent. of alcohol.

TABLE I

HYDROCHLORIC ACID IN WATER-ALCOHOL MIXTURES

Mole fraction of alcohol	w_1	E_N	γ_0	$-0.05915 \log a_w$	E_N (calcd.)
0.00	18.02	0.2528	1.00	0.0000	(0.2528)
.25	25.02	.2353	1.41	.0045	.2316
.50	32.03	.2128	2.18	.0082	.2127
.75	39.04	.1702	4.99	.0181	.1890
.85	41.84	.1422	8.88	.0285	.1724
.90	43.24	.1237	12.3	.0370	.1610
.95	44.64	.0967	20.9	.0543	.1408
.999	46.04	.0295	77.2	...	...

The revised values of E_N do not check as well as the earlier ones with the very simple assumptions, and do not preclude the combination of one molecule of hydrogen chloride with two molecules of water, but such a reaction seems to me improbable from the nature of the deviations as well as from evidence from other sources. No other conclusion in the previous paper is affected by this revision.

If the electromotive force of cells containing 0.1 *M* hydrochloric acid and sucrose[4] be computed with the ionic size mentioned above, the agreement with the experimental results is better than when the size 5 × 10^{-8} cm. is used. Because of uncertainty in the size and in other factors this improvement is not considered of great importance.

Recent measurements by Drucker and Schingnitz[5] of the electromotive force of lithium chloride cells in ethyl alcohol differ enormously from those of Pearce and Hart, used to compute the ionic size, *b*, of lithium chloride as 4.56 × 10^{-8} cm. The new measurements give 1.36 × 10^{-8} cm., which agrees much better with the effect of lithium chloride on the activity of non-electrolytes.

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[3] See Hildebrand, "Solubility," Chemical Catalog Co., Inc., **1924**, pp. 45–47.

[4] Scatchard, THIS JOURNAL, **48**, 2026 (1926).

[5] Drucker and Schingnitz, *Z. physik. Chem.*, **122**, 149 (1926).