

TABLE III.—IN 100 PARTS PURE ASH (EXCLUDING Fe_2O_3 , Al_2O_3 , Mn_2O_4 AND SiO_2).

	Broom Sedge.	Wire Grass.	Blue Thistle.	Potato Weed.	Purslane.
Cl.....	7.48	11.77	4.76	4.47	4.43
SO_3	4.59	15.75	4.38	12.34	3.32
P_2O_5	7.79	7.75	5.46	23.08	5.40
K_2O	54.02	44.96	32.72	23.82	63.27
Na_2O	2.13	7.93	2.77	1.24	3.66
CaO.....	19.78	9.54	44.11	19.03	11.08
MgO.....	5.93	4.95	6.87	17.03	9.84
Deduct O replaced by Cl.....	-1.72	-2.65	-1.07	-1.01	-1.00
	100.00	100.00	100.00	100.00	100.00
	Sumach.	Sassafras.	Rag-weed.	Mullein.	Dock.
Cl.....	.85	.26	3.51	3.47	10.03
SO_3	8.43	11.89	8.31	7.78	8.73
P_2O_5	9.18	13.07	8.30	6.54	7.48
K_2O	46.90	36.37	32.59	53.30	55.60
Na_2O	2.19	6.66	.83	3.54	7.65
CaO.....	26.24	24.32	45.07	20.27	9.11
MgO.....	6.40	7.49	12.21	5.88	3.66
Deduct O replaced by Cl.....	-.19	-.06	-.82	-.78	-2.26
	100.00	100.00	100.00	100.00	100.00

UNIVERSITY OF VIRGINIA, Dec., 1879.

V.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

BY ALBERT B. PRESCOTT.

I. ALUMINATES OF POTASSIUM AND SODIUM IN SOLUTION.

The composition of certain solid aluminates of metals of the alkalis and alkaline earths, was well established long ago. Also, there are recorded observations of the action of water upon alkali aluminates, either effecting complete solution, or partial dissociation. Not finding statements of the proportions of potassium hydrate and sodium hydrate, necessary to dissolve precipitated aluminium hydrate, the writer instituted determinations of these data, in order to show the atomic ratio of K and Na, to Al, in the aluminate solutions, with different quantities of water, in the conditions of re-dissolved precipitate so common in chemical operations.*

*These operations for determination of potassium aluminate and sodium aluminate, were entrusted to the execution of Mr. J. N. Ayres.

Potassium Aluminate.

Two solutions of aluminium salt were used, one a decinormal solution of potassium aluminium sulphate, $K_2Al_2(SO_4)_4 \cdot 24aq.$; the other, one-third stronger, or tenth of $1\frac{1}{3}$ normal solution of the same salt—this being a nearly saturated solution. These aluminium salt solutions were treated respectively with normal and decinormal solutions of potassium hydrate, KOH , until the precipitate at first formed had just all dissolved. The determinations were made at $30^\circ C.$, then at 50° , and then at 70° ; and each determination was made by triplicate trial. The three trials, accepted for each determination, did not vary one from another by as much as two-tenths cubic centimeter. The trials at the different temperatures gave the same results. When the results were attained, that the aluminium precipitate had just dissolved under the continued addition of the potassium hydrate, it was found that the addition of the first drop of decinormal solution of sulphuric acid, in all trials, reproduced the precipitate. In most cases, the quantity of aluminium salt solution taken was 5 c.c. It was the single result, under all the conditions of dilution and temperature named, that 1 c.c. of a decinormal aluminium salt solution required 8 c.c. of decinormal potassium hydrate solution. (Thus, 5 c.c. of decinormal Al_2 solution took 40 c.c. decinormal K solution, and took 5 c.c. normal K solution, and 5 c.c. tenth of $1\frac{1}{3}$ normal Al_2 solution required 53.5 c.c. of decinormal K solution, and again 5.4 c.c. of normal K solution.) This gives the proportion of potassium to aluminium, in the soluble aluminate,

$K_2Al_2O_4$, or $Al_2 \left\{ \begin{array}{l} O \\ O \\ (OK)_2 \end{array} \right.$ And the equation is: $K_2Al_2(SO_4)_4 + 8KOH = K_2Al_2O_4 + 4K_2SO_4 + 4H_2O$. Calculation gives the following as the number of parts of water (*i. e.*, water solution of potassium sulphate) present for one part of the soluble potassium aluminate, in the several degrees of dilution:

With Al_2 tenth of $1\frac{1}{3}$ normal, and K normal,	79 parts solution.
“ “ decinormal, “ “ “ “	91 “ “
“ “ tenth of $1\frac{1}{3}$ normal, “ decinor.	445 “ “
“ “ decinormal, “ “ “ “	456 “ “

Over fifty years ago the compound $K_2OAl_2O_3(K_2Al_2O_4)$ was obtained by saturating potassium hydrate solution with aluminium hydrate, evaporating to a small bulk, and removing all excess of alkali by alcohol.* Fremy obtained crystals of $K_2Al_2O_4 \cdot 2aq.$,

* Pogg. Annalen, 7, 723; Gmelin's Hand-book, 3, 320.

after fusing the alumina-saturated potash residue.* It was stated by Fremy that the di-potassium aluminate, $K_2Al_2O_4$, is decomposed by much water, precipitating aluminium hydrate, and leaving in solution an aluminate, probably $K_6Al_2O_6$. The symmetry of the compound last named, $Al_2(OK)_6$, may have had some influence in its frequent adoption, to represent the potassium hydrate solution of alumina. In nature, the form $R'Al_2O_4$ is represented by the spinels; and dibasic aluminates are formed by precipitating alkali aluminate solutions with barium or calcium hydrate solution, as is well known.

Sodium Aluminate.

Trials were made with decinormal and normal, solutions of sodium hydrate, corresponding in all particulars to the trials above-described for potassium aluminate. The results were not different in any particular. 1 c.c. of the decinormal aluminium solution, or its equivalent, gave a precipitate exactly dissolving on addition of 8 c.c. of decinormal sodium hydrate solution, or its equivalent. Therefore, the soluble sodium aluminate, in the stated conditions of dilution and

temperature, is a di-sodium di-aluminium tetroxide, $Al_2 \left\{ \begin{array}{l} O \\ O \\ (ONa)_2 \end{array} \right.$

The equation will be: $K_2Al_2(SO_4)_4 + 8 NaOH = Na_2Al_2O_4 + K_2SO_4 + 3Na_2SO_4 + 4H_2O$. The greatest dilution was 1 part of the soluble sodium aluminate in 546 parts of solution; the least dilution, 1 in about 95 parts solution.

Freymy did not obtain crystals of the sodium aluminate. Tissier† obtained four different combinations, $Na_2Al_2O_4$, $Na_3Al_4O_9$, $Na_4Al_2O_5$ and $Na_6Al_2O_6$ —all in some degree soluble in water, the last-named yielding sodium hydrate to alcohol. Schaffgotsch‡ found that one molecule of aluminium oxide, fused with sodium carbonate, expels rather more than one molecule of carbon dioxide.

II. ZINC OXIDE IN ALKALINE SOLUTIONS.

In 1834, Laux§ obtained crystallized potassium zinc oxide of the symmetric composition, $K_2O.ZnO$. The crystals were soluble in cold water; but boiling water caused precipitation of $K_2O(ZnO)_2$. Fremy|| obtained crystals of $K_2O(ZnO)_2$, these being decomposed by water.

* Ann. Chim. Phys. [3], 12, 362 (1846); Compt. Rend., 15, 1106.

† Compt. Rend., 48, 627; Jahresb. d. Chem., 1859, 143.

‡ Pogg. Annalen. 43, 117; Gmelin's Hand-book, 3, 320.

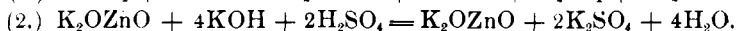
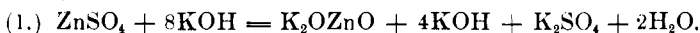
§ Ann. der Chem. und Pharm., 9, 165.

|| Compt. Rend., 15, 1106 (1846).

Ammonium zinc oxide was crystallized by Malaguti, as he reported,* with nearly the composition, $\text{NH}_3 \cdot \text{ZnO} \cdot 3\text{H}_2\text{O}$ [$\text{NH}_4\text{OH} \cdot \text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$; or $\text{Zn}(\text{OH})(\text{NH}_2) \cdot 3\text{H}_2\text{O}$]. Weyl, † by dissolving zinc in aqueous ammonia, in contact with iron, obtained the product, $(\text{NH}_3)_2\text{ZnO}$. This differs only by a molecule of water from zinc diamine, $(\text{NH}_2)_2\text{Zn}$. Neither the product of Malaguti, nor that of Weyl, appears to have been wholly soluble in water, without the help of ammonia.

I have obtained some determinations ‡ of the quantities of potassium hydrate, sodium hydrate and ammonium hydrate, respectively required to re-dissolve their precipitates in solution of zinc salt, in certain conditions of dilution and temperature. It was found that, in all conditions, some excess of the alkali needed to dissolve the precipitate, could be neutralized by an acid before the precipitate re-appeared.

At 17°C ., each c.c. of a normal solution of zinc sulphate, required 8 c.c. of a normal solution of *potassium hydrate*, to re-dissolve the precipitate at first formed. (In four trials, the numbers were, of c.c., 8.0, 8.1, 8.0 and 8.0.) In taking up the excess of alkali, with semi-normal solution of sulphuric acid (each c.c. equivalent to a c.c. of the normal solution of potassium hydrate), it was found that 4 c.c. could be added before causing a precipitate. So that 4 c.c. of the KOH solution were required to retain in solution the zinc from 1 c.c. of the ZnSO_4 solution. The titrations with alkali and acid, then, sustain the following equations:



The solution with excess of alkali (not titrated back with sulphuric acid) was precipitated on adding about twelve times its volume of water. A decinormal solution of zinc sulphate required, for each 10 c.c., an average of 12.6 c.c. of normal solution of potassium hydrate, to re-dissolve the precipitate; or about fifty per cent. more, by reason of the dilution of the zinc solution from normal to decinormal. Decinormal solution of potassium hydrate would not re-dissolve the precipitate which it produced in normal solution of the zinc salt, however much was added. A solution of 16.5 grms potassium hydrate to the liter ($\frac{16.5}{56.1}$ normal) was the weakest solution that would at all re-dissolve a precipitate in the normal zinc solution. A stronger solution of potassium hydrate, 121.121 grms to the liter, was tried,

* Compt. Rend., 62, 413 (1866).

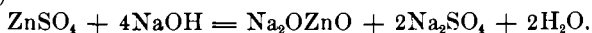
† Jahresb. d. Chem., 1864, 165; Pogg. Ann., 123, 353.

‡ These estimations were made by Mr. F. S. Wilson, under my direction.

and 3.8 c.c. of this, equivalent to 8.2 c.c. of normal solution, were required to dissolve the precipitate from 1 c.c. normal solution of zinc sulphate. So it appears that dilution, as far as the "normal" standard, does not lessen the solubility of the precipitate in aqueous alkali; beyond the strength of the normal solution, dilution rapidly diminishes the solubility.

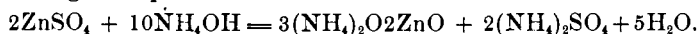
The above trials were all made at 16° to 17° C. In trials at 50° C., about three times as much of the potassium hydrate solution was required to dissolve the precipitate, as at 17°, and this was true with both normal and decinormal zinc solutions. It is well known that boiling precipitates zinc from its alkali hydrate solutions.

The *sodium hydrate* solution was prepared from metallic sodium and adjusted to normal strength. Of this normal solution, at 17° C., 7 c.c. were needed to dissolve the precipitate made with 1 c.c. zinc sulphate normal solution. Then 3 c.c. of half-normal sulphuric acid solution were added, before a precipitate resulted. Subtracting the sodium hydrate neutralized by the acid, short of re-precipitation, we have this equation (corresponding to the result with potassium hydrate):



The solution bears dilution with 10.5 times its volume of water before precipitation, the trial being at 17° C. At 50° C., each c.c. of the normal solution of zinc sulphate took 18 c.c., and each 10 c.c. of the decinormal zinc solution took 27.6 c.c. of the decinormal sodium solution, to re-dissolve the precipitate. It appears, then, that solution, under different conditions, requires somewhat less proportional excess of sodium hydrate than of potassium hydrate.

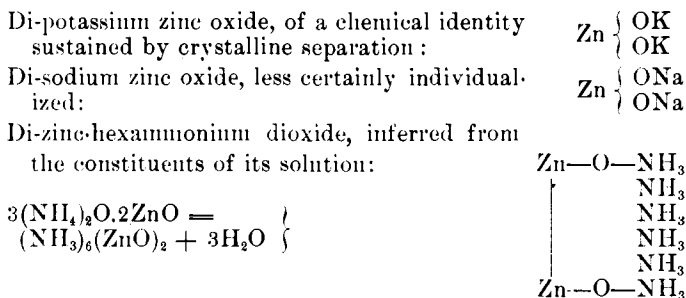
The normal solution of *ammonium hydrate* was adjusted in the burette, which was kept corked as much as possible. After the work, the solution was again tested, and found not to have lost strength to an appreciable extent. Each c.c. of the normal solution of zinc sulphate took 6.6 c.c. of the normal solution of ammonia. (In four trials the results were, c.c., 6.6, 6.5, 6.6, 6.6.) Of the seminormal solution of sulphuric acid, 1.6 c.c. were added, in reaching the point of precipitation. So 5 c.c. of the ammonia solution remained united with the zinc oxide and sulphuric acid of 1 c.c. of the zinc solution, indicating the equation:



The solution can be diluted with nine times its volume of water before precipitation. 10 c.c. of decinormal solution of zinc sulphate required an average of 10 c.c. of normal ammonia solution to re-

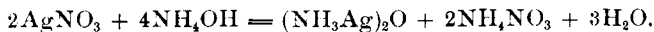
dissolve the precipitate. At 50° C., no more of the ammonia was required to re-dissolve the precipitate than at 17° C., a marked difference from the results with the fixed alkalis. It will be observed, a much smaller proportional excess of ammonium hydrate, than of potassium or sodium hydrate, is required to dissolve the precipitate.

We have, then, apparently, the following alkali-zinc oxides, intact in water solutions not too dilute:



III. SILVER-AMMONIUM OXIDE IN SOLUTION.

The proportion of ammonium hydrate required to dissolve the precipitate it first forms in silver nitrate solution, at various degrees of dilution and temperature, was carefully determined.* The results show that pretty nearly two molecules of ammonium hydrate are, in every case, required for one molecule of silver nitrate, in attaining solution of the precipitate. Conditions of dilution and temperatures do not materially influence the result. The variations in results were greater than those found with corresponding determinations for fixed alkalis, possibly owing to vaporization of ammonia, in spite of precautions. The detailed results are given below, as well as the particulars of the work. It is impossible to say how much influence is exercised by the ammonium nitrate, in dissolving the silver oxide. If this influence be disregarded, the action of the ammonia is represented by the following equation:



The hypothesis of silver-ammonium oxide, $\left. \begin{matrix} \text{NH}_3\text{Ag} \\ \text{NH}_3\text{Ag} \end{matrix} \right\} \text{O}$, is adopted as more in accord with known compounds, than the silver and ammonium oxide, NH_4AgO , or silver-ammonium hydrate, NH_3AgOH .

The solutions of silver nitrate used were the normal and decinormal. The ammonia solutions were of indefinite strength, one

* All of these determinations were carried out, with much care and discrimination, by Mr. D. E. Osborne.

near normal, and one near decinormal, and their exact strength was found after each trial, or set of trials, by titrating with solutions of oxalic acid, normal and decinormal. The burette was kept closed as far as possible, by rubber tube and pinch at the top. Five beakers were set, each with 1 c.c. of the normal solution of silver nitrate, and one beaker for titration with normal solution of oxalic acid. In the first estimation, there were required to dissolve the silver precipitate, respectively, 1.6, 1.7, 1.5, 1.6, c.c. of the nearly normal solution of ammonia, and 5 c.c. of the ammonia solution required 6.5 c.c. of normal solution of oxalic acid. Then,

$$5.0 : 6.5 : : 1.6 \text{ (average of five) } : x = 2.08.$$

In like manner, other estimations were made, mostly starting with 2 c.c. silver solution, giving results as follows:

1st	5 trials,	1 c.c. normal Ag sol.	requires	2.08 c.c. normal NH ₃ sol.			
2nd	5 "	1 c.c. "	"	1.95 c.c. "	"	"	"
3rd	5 "	1 c.c. "	"	1.90 c.c. "	"	"	"
4th	5 "	1 c.c. "	"	1.95 c.c. "	"	"	"
5th	5 "	1 c.c. decinormal "	"	2.23 c.c. decinormal "			
6th	5 "	1 c.c. "	"	2.24 c.c. "	"	"	"

The 1st set of trials were made at 30° C.; the 2nd, at 23° C.; the 3rd, at 24° C.; the 4th, at 23° C.; the 5th, at 30° C.; the 6th, not noted.

The silver-ammonium solutions were not precipitated by normal or decinormal solution of nitric acid, at any point of its addition; and were not precipitated by decinormal solution of sulphuric acid until the neutral reaction was reached.