with definit acidic and basic properties, it is not at all strange that the heat of neutralization should vary considerably from solvent to solvent.

Summary.

1. Measurements of heats of reaction in non-aqueous solutions have been made and reported for the first time.
2. The amount of heat liberated for a given reaction in different solvents has been found to vary greatly from solvent to solvent.
3. These considerable differences cannot be explained as being due to any electrolytic dissociation of the acetate, nor are they due to differences in the heats of solution of the acetate in the different solvents.
4. The chemical nature of the solvents does not seem to give any clue as to the magnitude of the heat of neutralization in the cases investigated, nor of the magnitude or sign of the heat of solution of the resulting acetate.

It is proposed to continue this line of work, using such other reactions as may be found available.

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THE VAPOR PRESSURE OF HYDRATES, DETERMINED FROM THEIR EQUILIBRIA WITH AQUEOUS ALCOHOL.

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Received May 20, 1911.

The measurement of the small pressures of dissociation common to hydrated salts is a problem that presents many difficulties and has been the subject of numerous researches. The most general plan has been to place the salt in the Torricellian vacuum, and measure the depression of the mercury of the barometric column. On this plan were the methods of Debray,[1] Wiedemann,[2] Pareau,[3] Lescoeur,[4] and others, using various means for complete removal of the air from the barometric space. Lescoeur[4] also devised a method for measuring these pressures by getting the dew-point of the atmosphere which was in equilibrium with the salt in a closed space, and the vapor pressure of water at that dew-point gave the required pressure. Müller-Erzbach,[5] who has contributed a great deal of work on this subject, attacked the problem in two ways: One way, which he afterwards abandoned, was by comparing the losses of water from tubes containing water and the hydrate respectively, when placed for a time over concentrated sulfuric acid. This gave him the

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[1] *Compt. rend.*, 64, 603 (1867).

[2] *Pogg. Ann.*, *Jubeband*, 474 (1873).

[3] *Wied. Ann.*, I, 55 (1877).

[4] *Ann. chim phys.*, [6] 16, 378 (1889).

[5] *Ber.*, 14, 1093 (1881); *Z. physik. Chem.*, 2, 113 (1888).

relative rate of evaporation, which he took as equal to the relative pressure. His other plan was to find the dilution of sulfuric acid, over which the hydrate would neither gain nor lose weight. The vapor pressures of liquid and hydrate were therefore equal, and since that of the dilute acid had been measured by Regnault, the vapor pressure of the hydrate could be found from his tables. The most reliable data are probably those obtained by Frowein.[1] He arranged an apparatus in which the water vapor from the hydrates exerted a pressure on one side of a column of oil contained in a specially constructed U-tube, while sulfuric acid, contained in an expansion of the U-tube, kept the pressure of water vapor at zero on the other side. Means were devised for complete evacuation of the apparatus. Tammann[2] tried to measure these vapor pressures by passing dry air over the hydrates, and finding the weight of water taken up by a given volume of air. His results were not satisfactory. We have tried a similar plan, without success. The only other research on this subject that we have found, differing essentially from those already mentioned, was that of Linebarger.[3] He determined the equilibrium between hydrates and moist ether at the boiling temperature, then found the water content of the ether by a determination of its boiling point. A calculation of the partial pressure of the water vapor in the vapor from the ether solution gave him the vapor pressure of the hydrate. The theoretical basis of his work is the same as that upon which we have worked, and will now be discussed.

A pure hydrate may be in equilibrium at a given temperature with various pressures of water vapor, ranging between maximum and minimum limits. These limits are fixed as the vapor pressure of mixtures of the hydrate and the next higher hydrate of the salt (or its saturated solution) as a maximum, and the vapor pressure of mixtures of the hydrate and the next lower hydrate of the salt (or the anhydrous salt) as a minimum. This minimum pressure is the pressure usually meant in referring to the vapor pressure of a hydrate, and this meaning of the term will be understood in this paper. It follows from the above that a pure hydrate can be in equilibrium with various solutions of water and alcohol, whose aqueous pressures will lie between the maximum and minimum pressures of the hydrate itself. But a mixture of two hydrates can be in equilibrium with only one solution of water and alcohol, whose aqueous pressure must be equal to that of the mixture of hydrates.[4]

We have found the concentration of the alcohol-water solution in equilibrium at 25° with each of a number of hydrated salts, and have found the

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[1] *Z. physik. Chem.*, 1, 5, 362 (1887).

[2] *Wied. Ann.*, 33, 322 (1888).

[3] *Z. physik. Chem.*, 13, 500 (1894).

[4] Nernst, "Theoretische Chemie" (6 Aufl.), p. 661.

partial pressure of water in the vapor of this solution in each case. This partial pressure is equal to the vapor pressure of the hydrate.

EXPERIMENTAL WORK AND RESULTS.

(a) The Equilibrium between Hydrates and Aqueous Alcohol.

The salts used were obtained by recrystallizing the purest commercial salts available. Only those salts were chosen which were practically insoluble in alcohol. The crystals were filtered on a Büchner funnel, pressed between sheets of filter paper until free from excess water, and bottled. When a lower hydrate or the anhydrous salt was required, it was obtained by careful heating of the above material, until analysis showed the desired precentage of water, or a closed tube test showed no moisture whatever, as the case might be.

The sample of salt to be used for a determination was ground in a mortar and passed through a 100-mesh sieve—in some cases it was necessary to use a 200-mesh sieve—in order to get salt fine enough for a fairly rapid reaction. The first experiments were made without this precaution, using simply a mixture of powdered and crushed crystals, but the results were misleading. They could be explained only by assuming that the larger, solid crystals had resisted any change in water-content and equilibrium had not been reached. Water was determined in the sifted salt by ignition.

The alcohol was prepared by redistilling Kahlbaum's absolute alcohol with sodium, the first and last portions of the distillate being rejected. The resulting liquid was found by its specific gravity to be 99.8 per cent. alcohol.[1] From this absolute alcohol, mixtures were made of any desired composition, by adding distilled water from a buret to weighed amounts of alcohol. The exact composition of the mixture was then found from its specific gravity. Specific gravity determinations were made with an Ostwald pycnometer, holding approximately ten grams of water. This instrument was calibrated and used at 20°, and values for the specific gravities of alcohol-water solutions at that temperature were found by re-calculation from values given in Landolt and Börnstein's "Tabellen."

Experiments with hydrates and aqueous alcohol were carried out as follows: A portion of several grams of the sifted salt, weighed to a decigram, was put into a small bottle with a ground glass stopper. The alcohol was added from a calibrated pipette, usually 25 cc. for each experiment. The stopper was then tightly inserted, and the bottle-neck immersed in melted paraffin for an instant, leaving a coating of paraffin which was an effective seal. The bottle was then fastened to one of the arms of the rotating axis in a thermostat tank, and shaken at 25° for at least two days. When it was judged that equilibrium had been reached as nearly as possible, the bottles were removed, wiped dry, and carefully

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[1] In Tables III, IV and V, this alcohol is tabulated as 100 per cent.

opened. The liquid was then immediately filtered through a dry quantitative filter into a dry bottle. For alcohol containing but little water, this was done under a bell-jar, to avoid either evaporation or absorption of atmospheric moisture. The specific gravity of the clear liquid was taken, which gave its composition within 0.1 per cent. The salt was removed from the filter, and a gram or so of it pressed dry between filter papers as rapidly as possible, until no more odor of alcohol could be detected. Water was then determined by ignition. It was found, however, that results too high in water were obtained in this way, because of the more rapid evaporation of the alcohol than of the water from the solution with which the salt had been mixed; this left some water which would be rapidly taken up by the salt, especially if it were one poor in water. Therefore when the quantity of salt exceeded two grams, and the alcohol changed less than two per cent., more accurate results on the composition of the residue could be obtained by calculation from the alcohol data and the original composition of the salt.

The charges of salt and aqueous alcohol put into the bottles in these equilibrium experiments were planned according to the known properties of the hydrate concerned. Preliminary trials were often necessary to determine approximately the dilution of alcohol in equilibrium with the salts. Owing to the slowness of reaction, if too great a change was necessary before the system could come to equilibrium, this could not be reached in a reasonable time; hence, for the final data, changes of only one or two per cent. in the alcohol composition were provided for. In the case of the salts commonly used as drying agents, it was usually safe to assume that the lowest hydrates could be treated with absolute alcohol and be expected to come into equilibrium within one per cent. Then, some of the anhydrous salt could be mixed with about 98 per cent. alcohol and be expected to produce approximately the same composition of alcohol by dehydration as that obtained from absolute alcohol by hydration. The higher hydrates offered a more difficult problem, and a number of trial charges were often necessary, a guess at the equilibrium being all that was available at the outset. A mixture of two hydrates would be added to a known dilution of alcohol, thus providing for a change in either direction—removal or addition of water, raising or lowering the concentration of alcohol. If the result showed the former, the next experiment employed a higher percentage of alcohol; if the latter, a lower percentage. In tabulating the results, most of these preliminary trials have not been given, since they would add nothing to an understanding of the results.

The slowness of reaction when equilibrium was nearly reached made it difficult to obtain this point exactly, but the final error involved is small. This is true because the partial pressure of water in the vapor

TABLE I.

Grams.	Salt used. Formula.	Alcohol used. Per cent.	Salt produced. Formula.	Alcohol at equilibrium. Per cent.	Solid phases at equilibrium.
5.0	K_2CO_3	98.2	$K_2CO_3.0.3H_2O$	99.20[2]	K_2CO_3 and $2K_2CO_3.3H_2O$
5.0	K_2CO_3	98.2	$K_2CO_3.0.3H_2O$	99.20	K_2CO_3 and $2K_2CO_3.3H_2O$
6.5	$K_2CO_3.1.5H_2O$	99.8	$K_2CO_3.1.2H_2O$	99.34	K_2CO_3 and $2K_2CO_3.3H_2O$
4.1	$K_2CO_3.1.5H_2O$	99.8	$K_2CO_3.1.3H_2O$	99.37	K_2CO_3 and $2K_2CO_3.3H_2O$
5.0	$K_2CO_3.1.4H_2O$	92.6	$K_2CO_3.1.5H_2O$	92.70	$2K_2CO_3.3H_2O$
1.8	K_2CO_3	90.2	$K_2CO_3.1.5H_2O$	91.30	$2K_2CO_3.3H_2O$
20.0	$Na_2SO_4.0.1H_2O$	50.7[1]	$Na_2SO_4.0.14H_2O$	52.7[2]	Na_2SO_4 and $Na_2SO_4.10H_2O$
30.0	$Na_2SO_4.0.2H_2O$	55.2[1]	$Na_2SO_4.0.15H_2O$	52.6	Na_2SO_4 and $Na_2SO_4.10H_2O$
10.0	$Na_2SO_4.10H_2O$	60.0	$Na_2SO_4.2.7H_2O$	53.5	Na_2SO_4 and $Na_2SO_4.10H_2O$
15.0	Na_2SO_4	50.7	$Na_2SO_4.1.8H_2O$	53.3	Na_2SO_4 and $Na_2SO_4.10H_2O$
15.0	$Na_2SO_4.10H_2O$	54.2[1]	$Na_2SO_4.9.4H_2O$	52.6	Na_2SO_4 and $Na_2SO_4.10H_2O$
2.5	CaO	98.0	$CaO.0.3H_2O$	99.37	CaO and $Ca(OH)_2$
2.5	CaO	98.0	$CaO.0.25H_2O$	99.13	CaO and $Ca(OH)_2$
6.0	$CaO.0.7H_2O$	99.8	$CaO.0.6H_2O$	99.50	CaO and $Ca(OH)_2$
6.0	$CaO.0.7H_2O$	99.8	$CaO.0.7H_2O$	99.8	CaO and $Ca(OH)_2$
10.0	$MgSO_4.0.7H_2O$	99.8[1]	$MgSO_4.0.6H_2O$	99.57	$MgSO_4$ and $MgSO_4.H_2O$
10.0	$MgSO_4.0.7H_2O$	99.8	$MgSO_4.0.6H_2O$	99.70	$MgSO_4$ and $MgSO_4.H_2O$
6.0	$MgSO_4$	98.0	$MgSO_4.0.4H_2O$	99.13	$MgSO_4$ and $MgSO_4.H_2O$
6.0	$MgSO_4$	98.0	$MgSO_4.0.4H_2O$	99.17	$MgSO_4$ and $MgSO_4.H_2O$
7.0	$MgSO_4.1.2H_2O$	91.8	$MgSO_4.2.2H_2O$	96.2	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$
7.0	$MgSO_4.3.6H_2O$	99.8	$MgSO_4.2.0H_2O$	98.1	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$
5.0	$MgSO_4.3.6H_2O$	96.2	$MgSO_4.3.6H_2O$	96.2	$MgSO_4.H_2O$ and $MgSO_4.4H_2O$

[1] Corrected for a small amount of dissolved salt, found by evaporating the liquid from the pycnometer.

[2] 30 cc. of alcohol.

TABLE I (*Continued*).

Grams.	Salt used. Formula.	Alcohol used. Per cent.	Salt produced. Formula.	Alcohol at equilibrium. Per cent.	Solid phases at equilibrium.
7.0	$MgSO_4.4.2H_2O$	91.6	$MgSO_4.4.05H_2O$	91.0	$MgSO_4.4H_2O$ and $MgSO_4.5H_2O$
4.0	$MgSO_4.4.2H_2O$	88.3	$MgSO_4.5.0H_2O$	90.2	$MgSO_4.4H_2O$ and $MgSO_4.5H_2O$
3.0	$MgSO_4.6.2H_2O$	90.6	$MgSO_4.5.9H_2O$	90.1	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
7.0	$MgSO_4.6.2H_2O$	91.8	$MgSO_4.5.5H_2O$	89.2	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
4.0	$MgSO_4.5.6H_2O$	88.3	$MgSO_4.5.9H_2O$	88.8	$MgSO_4.5H_2O$ and $MgSO_4.6H_2O$
7.5	$MgSO_4.7H_2O$	87.8	$MgSO_4.6.8H_2O$	87.3	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
7.5	$MgSO_4.6H_2O$	84.5	$MgSO_4.6.4H_2O$	85.9	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
8.0	$MgSO_4.6.9H_2O$	86.7	$MgSO_4.6.95H_2O$	86.9	$MgSO_4.6H_2O$ and $MgSO_4.7H_2O$
6.0	$ZnSO_4.H_2O$	99.8	$ZnSO_4.0.9H_2O$	99.5	$ZnSO_4$ and $ZnSO_4.H_2O$
5.0	$ZnSO_4.H_2O$	99.8	$ZnSO_4.0.8H_2O$	99.4	$ZnSO_4$ and $ZnSO_4.H_2O$
4.0	$ZnSO_4$	98.8	$ZnSO_4.0.3H_2O$	99.3	$ZnSO_4$ and $ZnSO_4.H_2O$
7.0	$ZnSO_4.1.2H_2O$	83.0	$ZnSO_4.1.2H_2O$	83.0	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
5.0	$ZnSO_4.H_2O$	81.8	$ZnSO_4.1.4H_2O$	82.5	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
5.1	$ZnSO_4.6.2H_2O$	84.1	$ZnSO_4.6.0H_2O$	83.8	$ZnSO_4.H_2O$ and $ZnSO_4.6H_2O$
9.0	$ZnSO_4.6.5H_2O$	80.8	$ZnSO_4.6.3H_2O$	80.3	$ZnSO_4.6H_2O$ and $ZnSO_4.7H_2O$
4.6	$ZnSO_4.6.2H_2O$	79.2	$ZnSO_4.6.3H_2O$	79.4	$ZnSO_4.6H_2O$ and $ZnSO_4.7H_2O$
6.7	$CuSO_4$	98.0[1]	$CuSO_4.0.5H_2O$	99.53	$CuSO_4$ and $CuSO_4.H_2O$
6.7	$CuSO_4$	98.0[1]	$CuSO_4.0.5H_2O$	99.37	$CuSO_4$ and $CuSO_4.H_2O$
3.5	$CuSO_4.H_2O$	99.8	$CuSO_4.0.8H_2O$	99.63	$CuSO_4$ and $CuSO_4.H_2O$
3.5	$CuSO_4.H_2O$	99.8	$CuSO_4.0.8H_2O$	99.60	$CuSO_4$ and $CuSO_4.H_2O$

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[1] 30 cc. alcohol.

8.0	$CuSO_4.2.5H_2O$	97.0	$CuSO_4.2.0H_2O$	96.6	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
4.0	$CuSO_4.H_2O$	95.0	$CuSO_4.1.7H_2O$	96.0	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
8.0	$CuSO_4.2.5H_2O$	97.1	$CuSO_4.2.4H_2O$	96.4	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
3.8	$CuSO_4.H_2O$	95.0	$CuSO_4.2.0H_2O$	96.2	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
5.0	$CuSO_4.H_2O$	95.1	$CuSO_4.1.7H_2O$	96.2	$CuSO_4.H_2O$ and $CuSO_4.3H_2O$
5.0	$CuSO_4.4\ H_2O$	99.8	$CuSO_4.2.7H_2O$	96.8	$CuSO_4.H_2O$ anc $CuSO_4.3H_2O$
5.0	$CuSO_4.4.0H_2O$	94.2	$CuSO_4.3.8H_2O$	93.7	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
4.9	$CuSO_4.H_2O$	87.2	$CuSO_4.4.2H_2O$	93.2	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
8.0	$CuSO_4.H_2O$	87.2	$CuSO_4.2.8H_2O$	93.3	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
2.0	$CuSO_4.1.8H_2O$	92.6	$CuSO_4.3.8H_2O$	93.6	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
5.0	$CuSO_4.2.8H_2O$	92.9	$CuSO_4.3.7H_2O$	93.5	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
2.0	$CuSO_4.5H_2O$	94.8	$CuSO_4.4.7H_2O$	94.1	$CuSO_4.3H_2O$ and $CuSO_4.5H_2O$
5.0	$BaCl_2.2H_2O$	99.0	$BaCl_2.1.4H_2O$	96.7	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
9.2	$BaCl_2.1.6H_2O$	93.5	$BaCl_2.1.8H_2O$	95.0	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
5.9	$BaCl_2.0.8H_2O$	95.0	$BaCl_2.1.8H_2O$	96.3	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
8.0	$BaCl_2.1.8H_2O$	96.0	$BaCl_2.1.9H_2O$	96.3	$BaCl_2.H_2O$ and $BaCl_2.2H_2O$
6.9	$BaCl_2.0.4H_2O$	98.0[1]	$BaCl_2.0.6H_2O$	98.4	$BaCl_2$ and $BaCl_2.H_2O$
5.0	$BaCl_2.0.4H_2O$	98.0[1]	$BaCl_2.0.5H_2O$	98.1	$BaCl_2$ and $BaCl_2.H_2O$
5.0	$Na_2HPO_4.10.2H_2O$	54.0	$Na_2HPO_4.11.0H_2O$	54.4	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
7.0	$Na_2HPO_4.8.9H_2O$	57.6	$Na_2HPO_4.7.9H_2O$	55.7	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
6.0	$Na_2HPO_4.7.1H_2O$	54.6	$Na_2HPO_4.7.0H_2O$	54.3	$Na_2HPO_4.7H_2O$ and $Na_2HPO_4.12H_2O$
7.0	Na_2HPO_4	76.0	$Na_2HPO_4.2.5H_2O$	83.2	$Na_2HPO_4.2H_2O$ and $Na_2HPO_4.7H_2O$
5.0	$Na_2HPO_4.6.5H_2O$	85.4	$Na_2HPO_4.5.5H_2O$	84.2	$Na_2HPO_4.2H_2O$ and $Na_2HPO_4.7H_2O$
4.0	$Na_2HPO_4.1.9H_2O$	90.2	$Na_2HPO_4.2.0H_2O$	90.3	Na_2HPO_4 and $Na_2HPO_4.2H_2O$
6.0	$Na_2HPO_4.2.0H_2O$	90.6	$Na_2HPO_4.1.9H_2O$	90.5	Na_2HPO_4 and $Na_2HPO_4.2H_2O$

[1] 50 cc. alcohol.

of the alcohol solution changes, on the average, only 0.24 mm. for a change of one per cent. on the alcohol content. This change is not a linear function of the composition, but at most never exceeds 1.0 mm. for each difference of one per cent. in the molecular composition of the liquid. Hence, if the alcohol solution in equilibrium with the hydrate is located within one per cent., the value calculated for the vapor pressure of the hydrate will be fairly accurate—probably fully as accurate as most of the data on vapor pressures of hydrates found in the literature.

The results for the salts investigated are tabulated above. Formulas showing fractional molecular proportions of water are used for convenience in indicating composition. The quantity of alcohol in each charge is 25 cc., except where otherwise noted.

The results on potassium carbonate show that the hydrate $2K_2CO_3.3H_2O$ has a minimum vapor pressure equal to that of the water in 99.3 per cent. alcohol. That this hydrate is the one which forms from water solution at 25° was shown by recrystallizing some of the salt in a flask suspended in the thermostat, then analyzing some of the crystals. Before analysis, the crystals were freed from surplus water by standing over sulfuric acid—since this salt deliquesces in ordinary air. They were removed before any sign of efflorescence appeared, and ignited to determine water. A sample was boiled with tenth-normal hydrochloric acid, the excess of acid titrated with tenth-normal alkali, and K_2CO_3 calculated:

	Found.	Theory for $2K_2CO_3.3H_2O$.
H_2O	16.66	16.34
K_2CO_3	83.18	83.66
	99.84	100.00

This work is mentioned because there seems to be some uncertainty in the reference books as to the hydrate of this salt.

Sodium sulfate evidently has only one hydrate, the decahydrate, stable at 25°, and this has a vapor pressure measured by the aqueous pressure of 53.0 per cent. alcohol. This conclusion is sustained by the work of Schreinemakers[1] on solution equilibrium, who found a similar dilution of alcohol in equilibrium with the decahydrate.

It was difficult to reach equilibrium with lime, especially in attempts to hydrate absolute alcohol, using the hydroxide. The results are not contradictory, however, and show that lime is an excellent drying agent, producing approximately 99.5 per cent. alcohol.

Equilibrium was reached very slowly with magnesium sulfate. Several hydrates may be distinguished here. The same remarks apply to zinc sulfate. Copper sulfate was worked out rather carefully, because of the frequent use of this salt as a text-book illustration of the peculiari-

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[1] *Z. physik. Chem.*, 67, 551 (1909).

ties in vapor pressures of hydrates. The two hydrates of barium chloride have rather low vapor pressures. Sodium phosphate has an efflorescent hydrate, like that of sodium sulfate, and shows a corresponding equilibrium for the mixtures of the two higher hydrates, with 54.4 per cent. alcohol. This work demonstrates the existence of a dihydrate, about which there appears to be no certainty in the literature.

(b) The Composition of the Vapors from Aqueous Alcohol.

In order to find the pressure of water vapor in equilibrium with a given dilution of alcohol, it was necessary first to know the relative proportion of alcohol and water molecules in the vapor. This furnished by calculation a number representing the average molecular weight of the vapor, and this was later used in finding the total pressure. Then from the total pressure of a mixture, using as a factor the molecular per cent. of water in its vapor, the partial pressure of water vapor for the mixture could be calculated.

The means employed in determining the composition of these vapors consisted in analyzing them by combustion. Linebarger[1] has determined the composition of the vapors from mixed liquids, in which one component was an acid, or contained sulfur or a halogen, by a somewhat similar method. The general plan of the present work was to carry the vapors from the alcohol at 25° by means of a stream of pure, dry air, into a combustion furnace, the products of combustion and the original water of the vapor being collected and weighed in suitable apparatus, and the original constituents of the vapors determined by calculation from the analytical data.

The apparatus for this work was arranged as follows: Air under pressure, controlled by a valve so that the flow was about 50–60 cc. per minute, was led through a purifying apparatus. This comprised a wash-bottle containing a fifty per cent. solution of caustic potash, a tower filled with sticks of dry potash, and finally a wash-bottle containing concentrated sulfuric acid. From this apparatus the air passed into a Y-tube, the left-hand arm of which led through a series of two Geissler potash bulbs containing the aqueous alcohol, then into a second Y-tube inserted through a rubber stopper in the combustion tube of the furnace. A by-pass, closed by pinchcocks, connected the right-hand arms of the two Y-tubes. The combustion tube was filled with cupric oxide. Exit from this was through a series of three Geissler potash bulbs. The first contained concentrated sulfuric acid; the second, a fifty per cent. solution of caustic potash; the third, sulfuric acid like the first, to catch water vapor from the potash solution. This arrangement of absorption bulbs was adopted only after some preliminary work had shown that it was decidedly better than the arrangement commonly used in combustions.

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[1] This Journal, 17, 615 (1895).

A preliminary set of experiments on combustion of alcohol vapors were carried out by Mr. H. H. Guest, of this laboratory, previous to the work here described. Many of the difficulties of the process were found out and provided against by him.

When a determination was to be made, the alcohol bulbs were filled with fresh alcohol of known specific gravity, and connected in place by means of short, thick pieces of rubber tubing, so arranged that the ends of the glass tubes in all cases came together. The bulbs were supported in a tank of water which was maintained at 25° and stirred. The furnace had previously been heated to redness, and the pieces of absorption apparatus attached. These had been separately weighed against a counterpoising bulb of the same form. The air was now turned on through the alcohol bulbs, and the combustion continued for about one hour. The amount of vapor that could be successfully burned was of course limited by the capacity for carbon dioxide of the potash in the absorption bulb. The rule was to stop when half the theoretical amount had been produced and absorbed, as could be judged from earlier experiments. The tubes leading from the air-purifying apparatus through the alcohol bulbs were now closed by screw pinchcocks, and the by-pass opened. By this means the furnace was swept clean of the products of combustion, a process for which fifteen minutes were allowed. The absorption bulbs were detached and weighed as usual, the gain of the first bulb representing water, that of the other two carbon dioxide. The weights of alcohol and water, respectively, in the vapor were found by calculation from the weights of carbon dioxide and water and their chemical relations to alcohol. The molecular per cent. of water in the vapor could then be calculated.

TABLE II.

Actual per cent. alcohol in liquid.	Molecular per cent. water in liquid.	Molecular per cent. water found in vapor.				Average of I–IV.
		I.	II.	III.	IV.	
96.35	8.66	5.85	6.11	4.44	5.73	5.53
95.60	10.53	8.48	.....	.....	.....	8.48
95.20	11.42	10.58	10.00	.....	.....	10.29
93.51	15.09	12.13	12.01	12.56	11.48	12.04
89.00	24.00	17.22	17.19	16.76	.....	17.06
84.17	32.58	23.24	22.78	22.22	.....	22.74
69.04	53.45	31.14	29.49	30.93	.....	30.52
53.77	68.79	36.36	36.99	36.91	.....	36.75
39.33	79.73	40.71	39.65	.....	.....	40.18
29.97	85.66	45.06	44.82	.....	.....	44.94
20.34	90.89	57.25	56.06	.....	.....	56.66
9.50	96.05	73.74	73.36	.....	.....	73.55

The greatest care was exercised in these analyses, and the results are considered as accurate as it is practicable to obtain by this method;

and we know of no other method which could be expected to give as satisfactory results. An error of one milligram in the weight of an absorption bulb produced in the case of some of the richer alcohol-water mixtures a difference of 0.5 per cent. in the molecular per cent. found, and it was hard to make the weights of carbon dioxide and water so large that this limit of accuracy was much exceeded. Even with the more dilute mixtures, an error of one milligram in weighing produced a difference of more than 0.2 per cent. in the final result. The preceding table gives the results of the combustions.

The above results are expressed graphically below, where the molecular per cent. of water in the liquid is plotted as abscissa, and the molecular per cent. of water in the vapor as ordinate, in a curve.

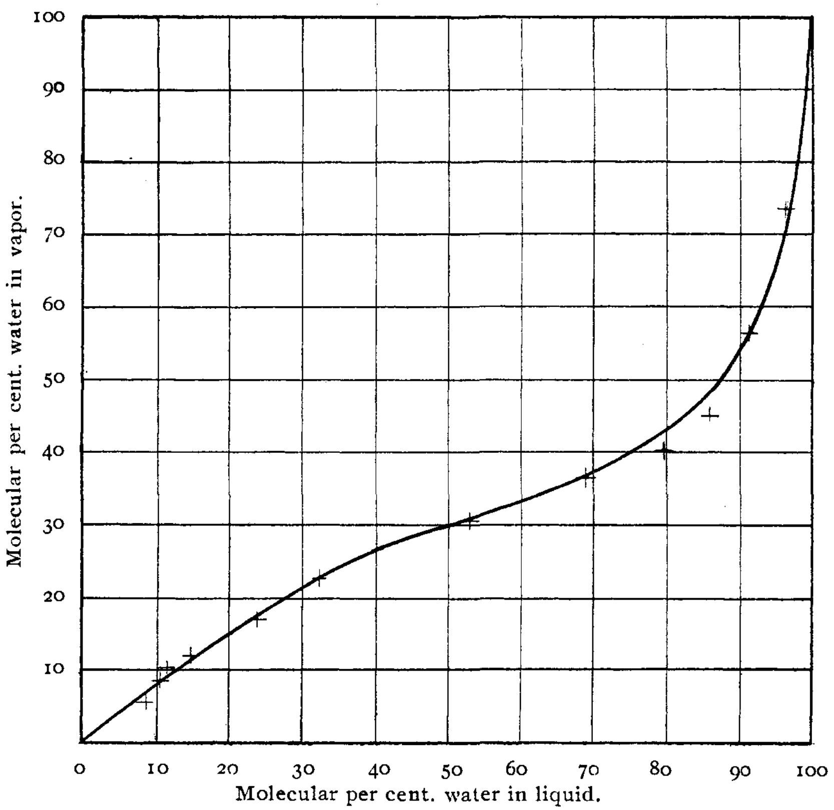

Fig. 1.

(c) The Vapor Pressures of Alcohol-Water Mixtures.

The method used to determin the total pressure of the vapors from aqueous alcohol depends on Dalton's law of partial pressures. It rests on the principle that if a given volume of air be saturated with a vapor, and if the weight of vapor, the molecular weight of the vaporized substance, and the corrected volume of air be known, the vapor pressure of the liquid from which the vapor was derived can be calculated. This principle was applied by Tammann[1] and Linebarger.[1]

The apparatus for the measurement in question was arranged as follows: The air was supplied and purified as in the preceding experiments, and the alcohol bulbs were similarly placed in a thermostat at 25.° No by-pass was necessary. The second alcohol bulb was connected directly with a wet gas meter, which had a drum capacity of 0.2 cu. ft., and read 0.001 cu. ft. on the dial. This meter had been proven at the laboratory of the New Haven Gas Co., and found accurate to 0.1 per cent. We are indebted to Dr. A. P. Beardsley for this assistance.

Determinations were made by passing the air at the rate of about five liters per hour, through the weighed alcohol bulbs and the meter, taking the temperature and dial-readings of the meter before and after each experiment, and re-weighing the bulbs to find the weight of vapor produced. In order to prevent condensation in the exposed outlet tubes of the bulbs, these tubes were warmed by means of a coil carrying a small electric current. The barometer reading completed the data.

The bulbs used for the alcohol in this and the preceding groups of determinations were regarded as very efficient for the purpose. Each one contained three separate small bulbs holding 4-5 grams of liquid apiece, so that the two bulbs were equivalent to six small bulbs of alcohol, and the air leaving the last one of these was pretty certainly saturated with the vapors. The second set lost in weight only about one-eightieth as much as the first set. Hence, in these experiments, and in the preceding series as well, the vapor finally leaving the bulbs must have been thoroughly in equilibrium with the alcohol-water mixture, and this liquid must have suffered little or no change in composition in the last section of the second bulb.

To avoid possible error from the accumulation of alcohol in the water in the gas meter, this was changed after every fifth determination at most. This prevented the percentage of alcohol from exceeding 0.5 per cent. in the meter liquid, and this was too dilute to affect the vapor pressure inside the meter appreciably.

Calculation of the vapor pressures required one more known value—the average molecular weight of the vapors themselves. This was found from the molecular composition given in Table II, by a simple calculation. The calculation of the vapor pressures was done by a formula similar to that given in Ostwald-Luther, "Physiko-Chemische Messungen," page 273. The air as registered by the meter is corrected in volume to standard conditions, $= v_0$. Given, that a gram-molecule of any gas

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[1] *Loc. cit.*

under standard conditions occupies 22.4 liters, then the volume that would be occupied by the mixed vapors without the air can be calculated, $= v_2$. The sum of these two corrected volumes is the volume that would be occupied by the air, saturated at 25° with the alcohol vapors, if it could be placed under standard conditions without losing the vapor. The volume of mixed vapors, divided by this sum, gives the partial pressure of the vapors, and this factor multiplied by 760 gives the pressure sought in millimeters of mercury $= p$, *i. e.*, if v is the volume in liters as read on the meter, p_1 the barometer reading, p_2 the vapor pressure of water at the meter temperature, $P = 760$. $T = 273$, t is the temperature of the meter, g is the weight of the vapors, and M their average molecular weight, then

$$\frac{v(p_1 - p_2)T}{760(T + t)} = v_0, \text{ and } \frac{22.4g}{M} = v_2, \text{ and } p = \frac{760 v_2}{v_0 + v_2}$$

In Table III are given the results of the measurements of total vapor pressures of alcohol-water mixtures:

TABLE III.

Per cent. alcohol used.	M.[1]	Liters of air.	Temp. of meter.	Barometer reading. mm.	Grams of vapor.	Vapor pressure. mm.	Average vapor pressure.
100.00	46.05	5.664	21.0	758	0.9032	60.04	.....
100.00	46.05	5.896	21.5	763	0.9159	59.26	.....
100.00	46.05	5.638	17.5	769	1.3702	59.85	59.72
96.35	44.49	5.664	14.5	749	0.8644	58.53	.....
96.35	44.49	5.692	20.5	764	0.8574	58.26	.....
96.35	44.49	5.664	19.0	765	0.8519	57.78	58.19
93.51	42.68	5.678	19.5	766	0.8233	58.11	.....
93.51	42.68	5.721	18.5	761	0.8329	58.42	58.26
89.00	41.26	5.664	18.5	759	0.7833	57.62	.....
89.00	41.26	5.678	19.0	758	0.7810	57.51	57.57
84.17	39.67	5.947	18.5	760	0.7813	56.89	.....
84.17	39.67	5.664	19.5	760	0.7391	56.79	56.84
69.04	37.50	5.664	21.0	762	0.6539	53.63	.....
69.04	37.50	5.664	21.5	763	0.6406	52.68	.....
69.04	37.50	5.664	20.5	764	0.6517	53.18	53.17
53.77	36.75	5.664	21.0	764	0.5880	49.38	.....
53.77	36.75	5.664	21.0	764	0.5886	49.43	49.40
39.33	34.79	5.664	20.0	765	0.5321	47.06	.....
39.33	34.79	5.664	20.5	775	0.5292	46.37	46.71
29.97	33.45	8.496	21.5	773	0.6868	42.14	.....
29.97	33.45	11.328	21.0	763	0.9174	42.76	42.45
20.34	30.17	8.538	21.0	762	0.5528	38.20	.....
20.34	30.17	11.328	21.0	752	0.7324	38.62	38.41
9.50	25.43	11.328	21.0	749	0.4877	30.96	.....
9.50	25.43	11.328	21.0	749	0.4814	30.58	30.77
water	18.02	16.992	21.0	766	0.4059	23.52	.....
water	18.02	12.631	19.0	765	0.2995	23.57	23.54

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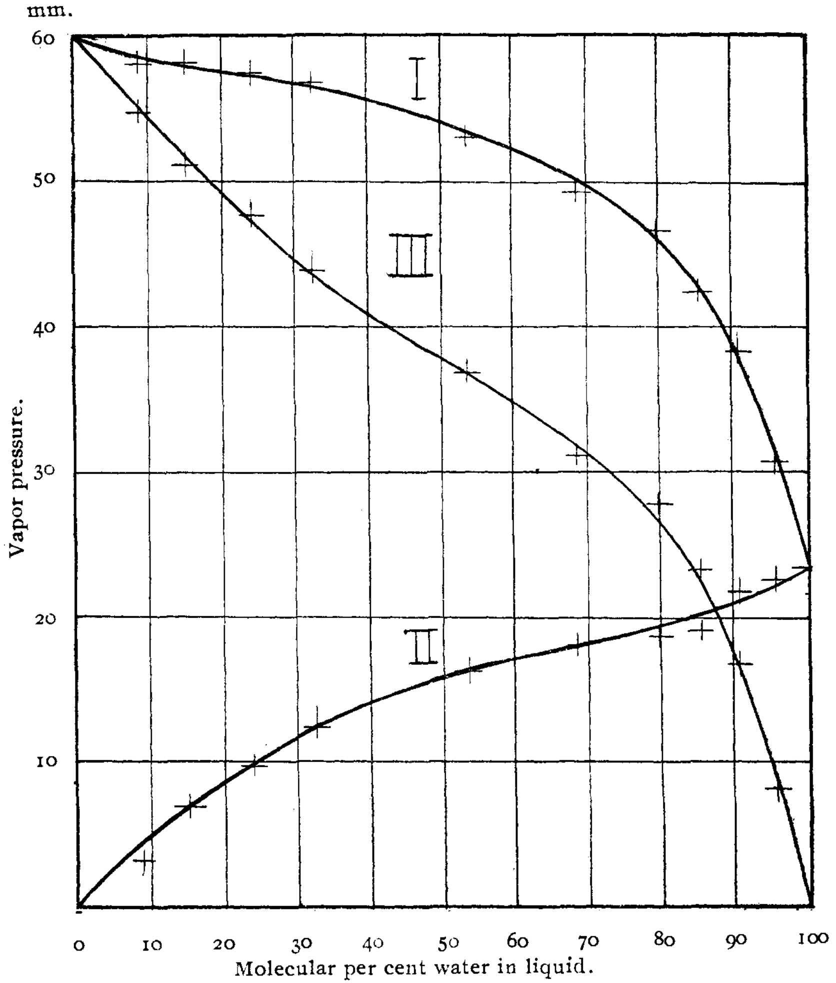
[1] The average molecular weight of the vapor.

A set of values furnishing an interesting comparison with the results above were obtained by means of the formula of Doroszewsky and Polansky.[1] They determined the boiling points of various alcohol-water mixtures at pressures of 700, 760, and 800 mm., and found from their results that the absolute temperatures of the boiling points were proportional to the pressures. From this relation they obtained a formula for calculating the vapor pressure of a given mixture: if t_1 is the given temperature, t the boiling point of the given mixture at 760 mm., and x the



I. Total vapor pressure of alcohol—water mixtures.
II. Partial vapor pressure of water.
III. Partial vapor pressure of alcohol.

Fig. 2.

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[1] *Z. physik. Chem.*, 73, 192 (1910).

boiling point of pure alcohol at the pressure required, $\frac{t + 273}{t_1 + 273} = \frac{78.3 + 273}{x + 273}$. The vapor pressure of pure alcohol at x is the pressure required. Using the boiling points of various dilutions of alcohol at 760 mm., given by Noyes and Warfel[1] and the vapor pressures of pure alcohol at certain temperatures given by Landolt and Börnstein,[2] we have calculated by this means vapor pressures for alcohol-water mixtures for which data are given in Table III, and these are arranged below for comparison:

TABLE IV.

Per cent. alcohol.	t.	Calculated vapor pressure.	Measured vapor pressure.
100.00	78.300	59.03	59.73
96.35	78.178	59.55	58.19
93.51	78.211	59.48	58.26
89.00	78.385	58.97	57.57
84.17	78.70	58.06	56.84
69.04	80.04	54.44	53.17
53.77	81.88	49.72	49.40
39.33	83.20	46.64	46.71
29.97	84.70	43.31	42.45
20.34	87.10	38.54	38.41
9.50	92.15	30.25	30.77

The agreement is good, considering the variety of data used and the fact that the formula can be regarded only as an approximation, for temperatures considerably removed from those at which it was derived.

In the next table, the results of the last two series of experiments are given, together with the partial pressures of water and alcohol derived from them:

TABLE V.

Liquid.		Vapor.			
Per cent. alcohol by weight.	Molecular per cent. water.	Molecular per cent. water.	Total Pressure. Mm.	Partial pressure, water.	Partial pressure, alcohol.
100.00	0.00	0.00	59.72	0.00	59.72
96.35	8.83	5.53	58.19	3.21	54.98
93.51	15.07	12.04	58.26	7.01	51.25
89.00	24.00	17.06	57.57	9.79	47.78
84.17	32.47	22.74	56.84	12.92	43.92
69.04	53.42	30.52	53.17	16.23	36.94
53.77	68.72	36.75	49.40	18.15	31.25
39.33	79.95	40.18	46.71	18.77	27.94
29.97	85.65	44.94	42.45	19.07	23.38
20.34	90.91	56.66	38.41	21.76	16.65
9.50	96.05	73.55	30.77	22.63	8.14
0.00	100.00	100.00	23.54	23.54	0.00

The values in the last three columns above are plotted as ordinates of

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[1] THIS JOURNAL, 23, 463 (1901).

[2] "Tabellen" (3 Aufl.), p. 136.

the curves on page 1322, with the values in the second column as abscissas. The forms of these curves show that the addition of a small amount of alcohol to water, or to a very dilute alcohol, causes a disproportionately large increase in vapor pressure. On the other hand, the addition of water to the higher concentrations of alcohol causes no great change in vapor pressure. At the ends of the curves, there are differences between the observed and smoothed-out valves, because of the difficulty in getting accurate results with mixtures high in either constituent.

Summary and Comparison of Results.

Taking from Curve II the values corresponding to the alcohol-water mixtures found to be in equilibrium with various hydrates, we have the vapor pressures of the latter. In the next table are incorporated the pressures so measured for the salts investigated, and, for the purpose of comparison, values determined by others. In this table, the formula representing a mixture of hydrates is placed in the first column; in the second column is the per cent. of alcohol in the mixture in equilibrium with the mixture of hydrates; in the third, the molecular per cent. of water in this liquid; and in the fourth, the calculated vapor pressure of the hydrate in millimeters of mercury. The last four columns contain the results of other measurements on hydrates. They are in most cases obtained for 25° by interpolation from the published figures. Our results are uniformly lower than Frowein's, but his values would be expected to have a positive error, if any, because of possible failure to remove all air from his apparatus. The same would be true of the work of Les-

				Values found by			
Salt.	Per cent. alcohol.	Molecular per cent. water.	Vapor pressure.	Frowein.	Lescoeur.	Pareau.	Müller-Erzbach.
$CuSO_4.3–5H_2O$	93.6	14.9	7.0	7.3	8.5	7.9	7.3
$CuSO_4.1–3H_2O$	96.5	8.7	4.7	....	....	...	4.6
$CuSO_3.0–1H_2O$	99.5	1.3	0.8	....	....	...	0.5
$Na_2SO_4.0–10H_2O$	53.0	69.4	18.2	....	19.0	...	17.6
$K_2CO_3.0–1.5H_2O$	99.3	1.7	1.1	....	1.5	...	....
$CaO.0–1H_2O$	99.5	1.3	0.8	....	....	...	....
$ZnSO_4.6–7H_2O$	79.9	39.1	13.6	14.6	14.0	...	12.9
$ZnSO_4.1–6H_2O$	83.0	34.4	12.8	13.2	....	...	11.7
$ZnSO_4.0–1H_2O$	99.4	1.5	1.0	....	....	...	0.5
$MgSO_4.6–7H_2O$	87.1	27.0	11.5	11.6	11.7	...	....
$MgSO_4.5–6H_2O$	89.0	23.9	9.8	....	....	...	....
$MgSO_4.4–5H_2O$	90.6	20.8	8.8	....	....	...	....
$MgSO_4.1–4H_2O$	96.2	9.0	4.9	....	....	...	....
$MgSO_4.0–1H_2O$	99.4	1.5	1.0	....	....	...	....
$BaCl_2.1–2H_2O$	96.3	8.9	4.8	5.2	....	2.9	4.7
$BaCl_2.0–1H_2O$	98.4	4.0	2.5	....	....	...	2.4
$Na_2HPO_4.7–12H_2O$	54.4	68.2	18.0	18.6	18.0	...	17.6
$Na_2HPO_4.2–7H_2O$	83.7	33.2	12.4	....	....	...	13.6
$Na_2HPO_4.0–2H_2O$	90.4	20.4	8.9	....	....	...	1.4

coeur. Pareau must have been working with the lower hydrate of barium chloride, for which he finds the vapor pressure 2.9. Müller-Erzbach's results for vapor pressures are obtained by using his values for relative pressure at about 18° as factors with the vapor pressure of water at 25°, since, according to him, there is not much change in the relative pressure for a few degrees difference in temperature.

Application of Vapor Pressures in the Choice of Salts as Drying Agents.

It was one of the earliest chemical operations to free a liquid from water by using a salt. Lescoeur[1] says that Raymond Lully, in the XIIth Century, found that potassium carbonate would remove most of the water from alcohol. It is, of course, a very common practice to-day, in organic chemistry, to use salts that form hydrates for drying liquids. Only one research, however, and that a recent one, has been found which aims at studying the efficiency of the various salts used. In this, Siebenrock[2] shows that calcium chloride and potassium carbonate produce ether nearest free from water, while the much used sodium sulfate is really a poor drier; magnesium sulfate (forming the heptahydrate) is better.

In the present work, the percentage of alcohol found in equilibrium with the various salts shows directly their drying efficiency. It has been feasible to work this out for salts having only a small solubility in alcohol, and the chlorides of calcium and strontium have been omitted because of their solubility and the fact that they form alcoholates.

Two cases of liquids to be freed from water may be distinguished in this connection: one, of a liquid which dissolves water, either to a considerable extent or in all proportions; the other, of a liquid in which water is not appreciably miscible, but is present as an emulsion. When an anhydrous salt is added to a liquid of the first sort, containing water, equilibrium is established finally between the vapor pressure of the hydrate that forms and the partial pressure of water vapor from the mixed liquids in which it is. The salt chosen must have therefore a hydrate of low vapor pressure, and at the same time of high percentage of water. Calcium chloride answers these conditions well for liquids in which it is insoluble. Copper sulfate is excellent, but its lowest hydrate contains only about ten per cent. of water; potassium carbonate is in the same class, having about sixteen per cent. of water in its lowest hydrate; while the sulfates of magnesium and zinc, used in quantities such that only their monohydrates can form with the amount of water present, are very good driers. It is clear that sodium sulfate would be worthless here. For instance, water-alcohol mixtures are only dehydrated by it to the extent of 53.0 per cent. alcohol, as shown above.

Oils that do not mix with water appreciably offer a different, simpler

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[1] *Ann. chim. phys.*, [7] 9, 540 (1896).

[2] *Monats. für Chem.*, **30**, 759 (1909).

problem in their drying. In emulsions of these, water must be present as an independent liquid, and have nearly its own vapor pressure. Obviously, no salt can form a stable hydrate having a vapor pressure greater than that of its saturated solution, and this is less than the vapor pressure of pure water. Therefore, a salt shaken in such an emulsion will continue to take up water until it is entirely converted into the highest hydrate it can form at the temperature of the experiment, or until all the water is removed from the oil. The choice of the salt to be used would depend simply on its cheapness and the percentage of water when hydrated. Sodium sulfate answers both these requirements, and seems well adapted to drying this class of liquids.

SHEFFIELD CHEMICAL LABORATORY OF YALE UNIV.,
NEW HAVEN, CONN., May, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW HAMPSHIRE COLLEGE.]

A NEW METHOD FOR THE SEPARATION OF CERIUM.

BY C. JAMES AND L. A. PRATT.

Received June 3, 1911.

Cerium differs from the other elements of the rare earths, in that it forms a series of more highly oxidized compounds. It is a well known fact that many of these ceric compounds very readily undergo hydrolysis, and this property has been made use of for the separation of the element. Cerium material obtained by those methods, which give a precipitate of hydrated ceric oxide, is usually less pure than that obtained from operations giving basic salts. Hitherto, the great disadvantage of precipitating cerium as basic ceric nitrate has been that only a portion of the cerium could be thrown out of solution. The authors have found that potassium bromate is capable of oxidizing cerous nitrate in a faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths.

When a solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble (saccharoid limestone), the cerium is entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. The cerium obtained in this manner is free from other rare earths, if the operation has been carefully conducted.

In working on a large scale with concentrated solutions, it is advisable to use a slight excess of bromate, and to stop the action while a little (about 1 per cent.) cerium remains in the liquid. Under these conditions, a cerium product is obtained which, after washing with a 5 per cent. ammonium nitrate solution, gives a pale straw colored oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.