nate bonds. Charcoal seems to be the most suitable catalyst for practical purposes.

In the presence of charcoal, aqueous ammonia displaces both chlorides from *cis*-$[\mathrm{Co\ en_2Cl_2}]^+$, giving preponderantly the *trans* product, $[\mathrm{Co\ en_2(NH_3)_2}]^{+++}$. In the absence of the catalyst, only one ammonia molecule enters the coördination sphere, and the product $[\mathrm{Co\ en_2(NH_3)Cl}]^{++}$ has the *cis* configuration, irrespective of whether the dichloro salt was *cis* or *trans*.

Triethylenediamine chromic chloride is readily prepared by the reaction of hydrated chromic chloride and hydrated ethylenediamine in the presence of charcoal.

In the presence of charcoal, sodium nitrite reacts with hexammine cobaltic ion and ammonium hydroxide reacts with cobaltinitrite to give trinitrotriammine cobalt, which thus seems to be the most stable member of the cobalt nitro ammine series.

Organic amines react with the dichlorodiethylenediamine cobaltic ion to give ions of the type $[\mathrm{Co\ en_2(RNH_2)Cl}]^{++}$ if no catalyst is present, but in the presence of charcoal, complete rearrangement to the extremely stable $[\mathrm{Co\ en_3}]^{+++}$ ion takes place.

The presence of charcoal during reactions of optically active cobalt ammines does not alter the sign of rotation of the products.

URBANA, ILLINOIS RECEIVED MAY 12, 1944

[CONTRIBUTION FROM THE BUREAU OF MINES, EASTERN EXPERIMENT STATION]

The System Aluminum Sulfate–Ethanol–Water at 30° and 80°[1]

BY EDWIN A. GEE[2]

Introduction

This investigation was undertaken to establish the 30 and 80° isotherms of the system aluminum sulfate–ethanol–water and to determine the various hydrates present at equilibrium.

A method for the preparation of iron-free aluminum sulfate using ethyl alcohol as a solvent was brought to the attention of the Bureau of Mines by Dr. P. S. Roller of the Bureau staff. In the pilot-plant development that followed, data on the system aluminum sulfate–ethanol–water were necessary to interpret certain phenomena that had been observed. Systems of the general type (inorganic salt–ethanol–water) have been previously investigated.

Experimental Methods

Solvent.—Ethanol–water mixtures were prepared from distilled water and purified ethyl alcohol. Commercial 95% alcohol was refluxed for several hours over lime and distilled; the distillate was redistilled to ensure complete separation from the lime. Density determinations were made to establish solution composition, pycnometers of 50-ml. capacity being used.

Aluminum Sulfate.—Baker analyzed aluminum sulfate was employed throughout.

Solubility Determinations.—Saturation was effected in 250-milliliter bottles which were rotated four to six days in two water-baths operated at 30 ± 0.01° and 80 ± 0.2°, respectively. When equilibrium was approached from undersaturation aluminum sulfate was added directly to the solvent. Approach from supersaturation was simulated by adding concentrated aqueous aluminum sulfate solution to the alcohol. After equilibrium was reached the mixtures were allowed to settle and were filtered through sintered glass of fine size.

Alcohol content was determined by distillation to dryness, the composition of the distillate being determined by density. This method yielded alcohol percentages accurate within 1 to 2% and this limited the over-all accuracy of the investigation. Aluminum sulfate solubility was determined by direct evaporation and ignition of the liquid sample or by precipitation with ammonia. Water was calculated by difference. The density of the equilibrium solutions was measured in 50-milliliter pycnometers.

Points near the plait point were determined by titrating two-phase liquid systems with water to homogeneous solutions.

Identification of Solid Phases.—Analysis of the solid phase was made by two methods. In the first, the crystals were separated from the mother liquor by filtration after which they were successively washed with absolute alcohol and anhydrous ether. The water of hydration was then determined by ignition. This method had a tendency to give low results in determination of the higher hydrates. This was probably due to the dehydration effect of the anhydrous alcohol and ether which were necessary to obtain a rapidly drying product. The second method is essentially an application of the work of Foote and Sholes in which the hydrates of inorganic salts in equilibrium with various alcohol mixtures are determined.[3] If a slightly soluble salt of known hydrate is placed in an alcohol-water mixture the specific gravity of the alcoholic solution will increase or decrease according to the release or absorption of water by the salt. If no change is noted the hydrate is in equilibrium with that alcoholic solution. Thus, by observing the change in specific gravity of the solvent the solid phase present at equilibrium with various alcoholic mixtures can be identified. This method necessitated the preparation of known hydrates which were prepared by precipitation of aluminum sulfate from alcohol-water mixtures. The various hydrates were dried over correspondingly lower hydrates. The final hydrate composition was determined by ignition.

The technique required slight modification for application to this investigation. As several hydrates are present at the same temperature, there must be a transition point at which two hydrates will be in equilibrium with the same alcoholic solution. After the approximate location of this transition point had been ascertained, its position could be established by adding a mixture of the two hydrates involved and observing the change in composition.

Results and Discussion

The results of the investigation at 30 and 80° are recorded in Table I and Fig. 1 and in Table II

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Associate physical chemist, Bureau of Mines, Eastern Experiment Station, College Park, Md.

[3] H. W. Foote and S. R. Sholes, THIS JOURNAL, 33, 1309 (1911).

TABLE I

EQUILIBRIUM DATA FOR 30° ISOTHERM, 30°

Total composition, % A. S	Total composition, % EtOH	Composition of solution % A. S.	Composition of solution % EtOH	Density	Solid phase
2.8	97.1 (G)	0.1	99.8	0.781	$Al_2(SO_4)_3$
3.3	93.0	.1	96.0	0.790	$Al_2(SO_4)_3$
3.1	91.8 (R)	.1	95.1	.791	$Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 10H_2O$
1.0	91.2	.0	92.6	.800	$Al_2(SO_4)_3 \cdot 10H_2O$
1.8	88.6	.0	90.8	.804	$Al_2(SO_4)_3 \cdot 10H_2O$
2.7	80.5	.0	83.5	.824	$Al_2(SO_4)_3 \cdot 10H_2O$
1.0	76.0	.0	77.5	.841	$Al_2(SO_4)_3 \cdot 10H_2O$
3.5	66.8	.0	70.1	.861	$Al_2(SO_4)_3 \cdot 10H_2O$
2.4	66.6	.0	69.1	.863	$Al_2(SO_4)_3 \cdot 10H_2O$
1.6	66.0	.0	67.8	.867	$Al_2(SO_4)_3 \cdot 10H_2O$
5.2	60.8 (Q)	.0	66.4	.870	$Al_2(SO_4)_3 \cdot 10H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$
2.0	62.0	.0	64.0	.878	$Al_2(SO_4)_3 \cdot 16H_2O$
1.7	60.4	.1	62.4	.881	$Al_2(SO_4)_3 \cdot 16H_2O$
3.2	56.5	.2	59.4	.882	$Al_2(SO_4)_3 \cdot 16H_2O$
4.1	54.5	.2	58.8	.892	$Al_2(SO_4)_3 \cdot 16H_2O$
4.8	52.3	.3	56.8	.898	$Al_2(SO_4)_3 \cdot 16H_2O$
3.3	50.8	.4	53.5	.908	$Al_2(SO_4)_3 \cdot 16H_2O$
2.9	49.1	.7	51.8	.913	$Al_2(SO_4)_3 \cdot 16H_2O$
5.2	45.3	1.0	49.9	.919	$Al_2(SO_4)_3 \cdot 16H_2O$
6.0	41.8	1.4	46.0	.924	$Al_2(SO_4)_3 \cdot 16H_2O$
6.1	38.2	2.8	40.9	.935	$Al_2(SO_4)_3 \cdot 16H_2O$

Total composition, % A. S	Total composition, % EtOH	Double layer[a] Top % A. S.	Top % EtOH	Top Density	Bottom % A. S.	Bottom % EtOH	Bottom Density
13.2	24.7 (E and F)	3.8	38.1	0.947 (F)	11.4	26.1	1.038 (E)
10.2	27.7	6.9	33.0	0.957	15.3	20.0	0.990

Total composition, % A. S	Total composition, % EtOH	% A. S.	% EtOH	Density	Solid phase
13.2	24.7	19.5	15.5	1.162	$Al_2(SO_4)_3 \cdot 16H_2O$
24.2	11.4	20.3	13.0	1.186	$Al_2(SO_4)_3 \cdot 16H_2O$
24.2	7.3	22.5	8.1	1.223	$Al_2(SO_4)_3 \cdot 16H_2O$
27.2	2.0	26.6	2.0	1.293	$Al_2(SO_4)_3 \cdot 16H_2O$
28.7	0.0 (D)	27.7	0.0	1.302	$Al_2(SO_4)_3 \cdot 16H_2O$

[a] Aluminum sulfate hexadecahydrate is the solid phase throughout.

and Fig. 2, respectively. The table headings Total Composition, and Composition of Solution, refer to the composition of the initial over- or undersaturated mixture and to the final solution in equilibrium with solid phase, respectively.

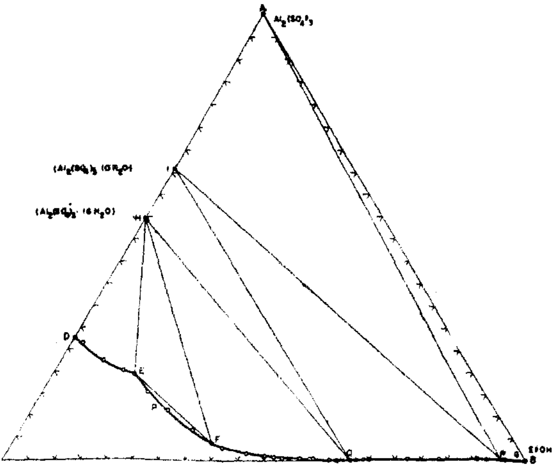

Fig. 1.—Phase diagram of the system $Al_2(SO_4)_3$–EtOH–H_2O at 30°.

In Fig. 1 the solubility of $Al_2(SO_4)_3 \cdot 16H_2O$ in alcohol–water solvents is represented by the curves DE and FQ, which are separated by the 2 liquid curve EPF, E and F being the isothermally invariant conjugate solutions in equilibrium with

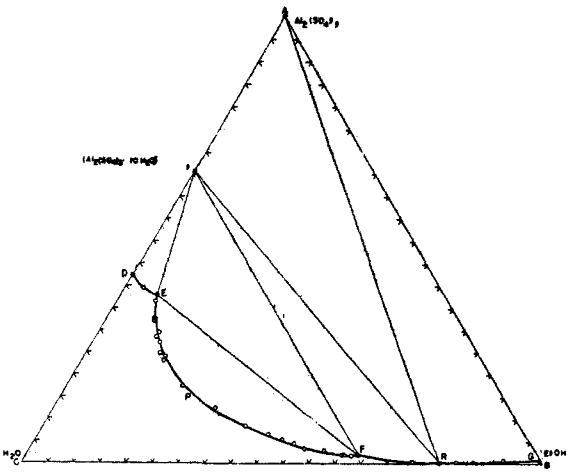

Fig. 2.—Phase diagram of the system $Al_2(SO_4)_3$–EtOH–H_2O at 80°.

TABLE II

EQUILIBRIUM DATA FOR 80° ISOTHERM, 80°

Total composition, %		Composition of solution					
A. S.	EtOH	% A. S.	% EtOH	Density	Solid phase		
3.0	96.8 (G)	0.9	98.9	0.745	$Al_2(SO_4)_3$		
2.0	90.9	.7	92.0	.759	$Al_2(SO_4)_3$		
2.4	84.3	.3	86.3	.776	$Al_2(SO_4)_3$		
2.5	81.0	.1	83.0	.783	$Al_2(SO_4)_3$		
3.1	77.5 (Q)	.0	80.0	.790	$Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 10H_2O$		
2.1	73.3	.1	74.9	.812			
		Double layer[a]					
		Top			Bottom		
		% A. S.	% EtOH	Density	% A. S.	% EtOH	Density
30.1	19.1 (E and F)	2.0	63.5	0.840 (F)	38.0	6.9	1.345 (E)
22.8	29.2	1.9	62.1	.848	36.4	7.2	1.320
15.3	38.9	2.0	60.8	.854	32.8	9.1	1.285
27.7	17.7	2.0	60.5	.856	32.9	9.0	1.280
21.1	26.9	3.0	56.5	.860	32.2	9.3	1.230
14.0	36.4	3.4	52.4	.871	29.4	11.5	1.210
25.7	16.4	4.5	50.0	.903	28.5	11.5	1.200
19.5	25.0	5.5	47.3	.912	27.2	12.8	1.152
13.0	33.7	6.6	44.0	.918	25.0	14.0	1.143
18.2	23.2	8.4	38.8	.964	23.2	15.5	1.132
					Solid phase		
24.0	15.3	24.0	15.3	1.131	$Al_2(SO_4)_3 \cdot 10H_2O$		
17.5	22.0	17.5	22.0	1.042	$Al_2(SO_4)_3 \cdot 10H_2O$		
12.3	31.0	12.3	31.0	0.990	$Al_2(SO_4)_3 \cdot 10H_2O$		
40.5	3.5	39.4	3.5	...	$Al_2(SO_4)_3 \cdot 10H_2O$		
43.5	0.0 (D)	42.2	0.0	...	$Al_2(SO_4)_3 \cdot 10H_2O$		

[a] Aluminum sulfate decahydrate is the solid phase throughout.

the solid. The curve QR represents solutions in equilibrium with the deca-hydrate and RG solutions saturated with the anhydrous salt, Q and R being the isothermally invariant solutions saturated in each case with two solids, hexadeca- and deca-hydrate, and deca-hydrate and anhydrous salt, respectively.

In Fig. 2 the solubility of $Al_2(SO_4)_3 \cdot 10H_2O$ in alcohol water solvents is represented by the curves DE and FR, which are separated by the 2 liquid curve EPF corresponding to Fig. 1. The curve RG represents solutions in equilibrium with the anhydrous salt, R being the isothermally invariant solution saturated with deca-hydrate and anhydrous salt.

The data on the identification of the solid phases are given in Table III. The results are an average of at least five determinations.

TABLE III

IDENTIFICATION OF SOLID PHASE, MOLES H_2O, 30°

Direct ignition	Indirect density	Average	Probable formula
15.2 ± 0.3	16.4 ± 0.3	15.80	16.0
9.7 ± 0.2	10.9 ± 0.4	10.30	10.0
0.2 ± 0.1	0.0 ± 0.1	0.10	0.0
	Moles H_2O, 80°		
9.0 ± 0.5	10.1 ± 0.4	9.55	10.0
0.1 ± 0.1	0.2 ± 0.1	0.15	0.0

Difficulty was experienced in identification of the solid phases. As shown in Table III, considerable deviation occurred between the two methods. The direct separation of solid hydrates from equilibrium solutions was complicated by the presence of aqueous alcohol. The use of anhydrous alcohol and ether as a wash obviated this difficulty to a large degree as it permitted rapid drying of the solid. However, this procedure gave low results with the higher hydrates for the aforementioned reasons. The application of the method of Foote and Sholes was fairly simple at a room temperature but density determinations at the higher temperatures were difficult.

The method of wet residues was not applicable to this study because of insufficient precision of the alcohol determination at low concentrations. The literature gives numerous references for the hydrate in equilibrium with solution at room temperature. The majority of investigators give the octadeca-hydrate as the stable form. These data have been recently reviewed by N. O. Smith and a series of careful measurements made which establish the stable form as the heptadecahydrate at 25°.[4]

Inasmuch as the latter's work was at a lower temperature, the hexadecahydrate which coincides most closely with the experimental results was chosen as the most probable solid phase at 30°. As the investigation was of a preliminary nature, the possibility that other hydrates may exist within narrow fixed limits of alcohol strength must be admitted.

[4] N. O. Smith, THIS JOURNAL, 64, 41 (1942).

The data indicate two hydrates, the hexadeca and deca as well as anhydrous salt exist at 30°. One hydrate, the deca, and anhydrous salt were found to exist at 80°.

The precision of measurement was limited by the alcohol determination. As no special precautions were taken in these determinations the relative precision of the 30° isotherm is ±2%. At 80° difficulty was experienced in the sampling of solutions of high aluminum sulfate concentration. The relative precision of the 80° isotherm is thus limited to ±3%.

Summary

The 30 and 80° isotherms for the system aluminum sulfate–ethanol–water have been determined. Anhydrous salt, hexadecahydrate and decahydrate were found to be present at 30° and anhydrous salt and decahydrate at 80°.

COLLEGE PARK, MD. RECEIVED AUGUST 26, 1944

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polarographic Characteristics of Vanadium in its Various Oxidation States

BY JAMES J. LINGANE

The first polarographic study of vanadium compounds was carried out by Zeltzer,[1] who investigated the reduction of vanadium trichloride from acid solution, and the reduction of vanadate (+5 vanadium) from acid, strongly alkaline, and ammoniacal media. Unfortunately the vanadium trichloride solutions used by Zeltzer were more or less oxidized and not standardized, so that the polarograms that he obtained cannot be interpreted. Neither is it possible to deduce half-wave potential data for the reduction of vanadate, or to definitely assign oxidation states to the various waves of vanadate, from the incomplete polarograms given by Zeltzer.

The reduction of vanadate at the dropping electrode from acidic, strongly alkaline, and ammoniacal media has since been studied by Stackelberg, *et al.*,[2] Thanheiser and Willems,[3] Voriskova,[4] and Page and Robinson,[5] but, since these authors were completely preoccupied with the development of empirical methods for determining vanadium in various materials, very little fundamental information can be gleaned from their papers. Indeed, their conclusions in several respects are bewildering. For example, Stackelberg, *et al.*,[2] concluded that vanadate ion is reduced to the +3 state from ammoniacal medium, whereas Zeltzer[1] had concluded that reduction proceeds to the +2 state. In the text of his paper Voriskova[4] assumes reduction to the +2 state, but in an accompanying table he presents an equation showing reduction to the +3 state. Furthermore, although the polarograms of vanadic acid in dilute hydrochloric acid presented by Zeltzer[1] clearly show a double wave, those published by Stackelberg, *et al.*, display only a single wave, and Thanheiser and Willems[3] state that they observed only a single wave from slightly acid solutions (*p*H 2 to 6) of +5 vanadium at about −0.9 v. *vs.* the S.C.E.

These latter conclusions are surprising and difficult to reconcile with the fact that +5 vanadium in acid medium is a rather strong oxidant, easily reduced to the +4 state, and with the additional facts that the standard potentials of the $V^{+5} \rightarrow V^{+4}$ and $V^{+4} \rightarrow V^{+3}$ couples in acid medium differ by nearly 0.7 v., and those of the $V^{+4} \rightarrow V^{+3}$ and $V^{+3} \rightarrow V^{+2}$ couples in acid medium are about 0.6 v. apart, so that conditions are very favorable for stepwise reduction.

These contradictory conclusions, and the lack of any information at all on the polarographic behavior of vanadium in its lower oxidation states, prompted the present investigation.

Experimental

Ammonium metavanadate, purified by recrystallization, served as the source of +5 vanadium. An 0.08 *M* stock solution was prepared in 1 *N* sulfuric acid and standardized by the sulfurous acid–permanganate procedure.[6]

A stock solution of vanadyl sulfate in 0.5 *N* sulfuric acid was prepared by reducing a 250-cc. portion of the stock ammonium metavandate solution with sulfur dioxide gas. The excess sulfur dioxide was expelled by boiling the solution, while a stream of purified nitrogen was swept through it, until the effluent gas ceased to reduce permanganate ion. The solution was cooled and diluted to exactly 500 cc. The concentration of +4 vanadium in this solution, determined by permanganate titration, checked the value expected from the concentration of the ammonium vanadate solution used in its preparation, and the solution remained unchanged over a period of six weeks in contact with air.

A stock solution of vanadic sulfate, 0.01 *M* in respect to V^{+++}, was prepared in 0.1 *N* sulfuric acid from a sample of pure $V_2(SO_4)_3 \cdot 10H_2O$ which was kindly furnished by Professor Grinnell Jones. The preparation and analysis of this salt have been described by Jones and Colvin.[7] Since vanadic ion is rather easily air-oxidized, care was taken to prepare and store the solution in an atmosphere of purified nitrogen. The concentration of +3 vanadium in this solution determined by permanganimetric titration was 0.3% larger than the value computed from the weight of

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[1] S. Zeltzer, *Coll. Czechoslov. Chem. Commun.*, **4**, 319 (1932).

[2] M. v. Stackelberg, P. Klinger, W. Koch and E. Krath, *Forschungsberichte Tech. Mitt. Krupp. Essen*, **2**, 59 (1939).

[3] G. Thanheiser and J. Willems, *Arch. Eisenhüttenw.*, **13**, 73 (1939).

[4] M. Voriskova, *Coll. Czechoslov. Chem. Commun.*, **11**, 588 (1939).

[5] J. E. Page and F. A. Robinson, *Analyst*, **68**, 269 (1943).

[6] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 359.

[7] G. Jones and J. H. Colvin, THIS JOURNAL, **66**, 1563, 1573 (1944).