other disproportionation reactions occurring, *i.e.*, $4ReO_3 \rightarrow Re_2O_7 + Re_2O_5$, etc.

It will be observed that in spite of the high precision of these analytical data the value of the conversion factor $Re_2O_7/(C_6H_5)_4AsReO_4$ is low by about 0.2%. No satisfactory explanation for this discrepancy suggests itself.

If pure ReO_3 disproportionates according to the reaction

$$3ReO_3 \longrightarrow Re_2O_7 + ReO_2$$

the ratio of rhenium metal present at the end of the reaction as the (VII) oxide to that as the (IV) oxide should be exactly 2.000. Since the oxide used had a composition corresponding to $ReO_{2.96}$, the over-all equation should be

$$3ReO_{2.96} \longrightarrow 0.96\ Re_2O_7 + 1.08\ ReO_2$$

in which case the same ratio would be 1.777. The actual rhenium distribution between the two oxides was determined and the ratio (listed in column 6 of Table II) was calculated and found to be that expected. This indicates that not only does the disproportionation involve the four and seven valence states but that the rhenium oxide preparation $ReO_{2.96}$ very probably was contaminated with dioxide and not with any other phase.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Hydrates of Beryllium Sulfate

BY A. N. CAMPBELL, A. J. SUKAVA AND J. KOOP

The transition temperature for the change, $BeSO_4 \cdot 4H_2O \rightarrow BeSO_4 \cdot 2H_2O$ + solution, has been found to be 89.0°. Below this temperature the stable solid phase is the tetrahydrate, and above it the dihydrate. The normal boiling point of saturated aqueous beryllium sulfate solution is 108.2°, the equilibrium solid phase being the dihydrate. The existence of a monohydrate of beryllium sulfate has been disproved by X-ray diffraction studies. It is possible that a discontinuous series of solid solutions exists between the dihydrate and the anhydrous salt, with a miscibility gap lying between 19 and 11% water. The X-ray equipment was not sufficiently sensitive to decide this point, however, and it is also possible that the solid phases at the high temperature transition are simply dihydrate and anhydrous salt. This transition occurs at 270°, under an equilibrium pressure of 9.38 atm.

The literature concerning the hydrates of beryllium sulfate is summarily dealt with by Sidgwick,[1] and extensively by Gmelin.[2] Of the possible hydrates which have been claimed at various times, only the tetrahydrate, dihydrate and anhydrous forms can be said to be definitely proved to exist. A paper by Rohmer[3] has recently appeared in which the claim is made that the dihydrate has no stable existence and that the transition is from tetrahydrate to monohydrate. This claim we have disproved.

In order to complete (both verifying and correcting) available information, for the determination of lower hydrates and of their transition points, various equilibrium measurements were undertaken: solubilities in ternary systems with sulfuric acid and with alcohols, dilatometry, vapor pressure and X-ray examination.

I. Experimental Procedure

Preparation and Purification of Starting Material.—The tetrahydrate of beryllium sulfate was prepared from the carbonate (British Drug Houses "glucinum carbonate") by treating with excess sulfuric acid. The procedure of separation and purification was similar to that employed by Parsons[4] and by Krauss and Gerlach.[5] Analysis of the product always showed good agreement when the beryllium sulfate content was calculated from separate estimations of both sulfate and beryllium ion, and it indicated that the tetrahydrate was reasonably free from occluded sulfuric acid.

The dihydrate was prepared from the tetrahydrate by dehydration. The density of the dihydrate does not appear in the literature and, since we required it to calculate the expansion in the dilatometer accompanying the transformation of tetrahydrate to dihydrate, we determined it as 1.865 g. per ml. at 25°.

The Ternary System: Beryllium Sulfate–Sulfuric Acid–Water.—The determination of the transition temperature of beryllium sulfate tetrahydrate to the next lower hydrate was accomplished by us by an investigation of the ternary system beryllium sulfate–sulfuric acid–water. The compositions of the saturated solutions of beryllium sulfate in aqueous sulfuric acid of varying concentrations were determined at different temperatures, together with those of the equilibrium solid phases. Working at successively higher temperatures, an isotherm was finally obtained on which tetrahydrate did not occur as solid phase. The transition temperature was then interpolated. The intersection of the tie-lines indicated clearly that the next lower hydrate was the dihydrate.

This investigation was pushed to a concentration of sulfuric acid of 80 weight per cent. It could not be carried to a higher concentration of sulfuric acid, because the high viscosity of the solutions made it impossible to separate the solid phase from the liquid phase in a satisfactory manner.

The solubility isotherms were determined at 25, 50, 75, 85 and 95°, employing Schreinemakers' method of the "wet rest," for the determination of the composition of the equilibrium solid phase. The saturated solution was separated from the wet rest in a specially designed apparatus employing a fritted glass filter, and operating at the temperature of the thermostat. The sulfate ion was estimated by precipitation as barium sulfate. Despite the well known objections to this method, it was shown by analysis of pure material that the method is satisfactory in this case. For the estimation of beryllium a method suggested by Bleyer and Boshard[6] was employed. The beryllium ion was precipitated as the hydroxide with ammonia in the presence of ammonium chloride, filtered by ordinary methods, and ignited to the oxide.

The isothermally invariant solutions (tetrahydrate–dihydrate–solution) were obtained by addition of tetrahydrate to solution saturated with dihydrate; both solids were evident at the end, the tetrahydrate as long transparent crystals, the dihydrate finely divided and settling slowly.

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[1] Sidgwick, "The Elements and their Compounds," Vol. 1, Clarendon Press, New York, N. Y., 1950, p. 207.

[2] Gmelin, "Handbuch der anorganischen Chemie," 8 edit., No. 26, Beryllium, 1930, pp. 133–137.

[3] R. Rohmer, *Bull. soc. chim.* [5] **10**, 468 (1943).

[4] C. L. Parsons, THIS JOURNAL, **26**, 1433 (1904).

[5] F. Krauss and H. Gerlach, *Z. anorg. allgem. Chem.*, **140**, 61 (1924).

[6] B. Bleyer and K. Boshard, *Z. anal. Chem.*, **51**, 748 (1912).

Ternary Systems with Alcohols.—Since the isothermals with sulfuric acid failed to reveal the transition of dihydrate to a lower form, we passed to an investigation of the system beryllium sulfate–ethyl alcohol–water at 25°, and to that of the system beryllium sulfate–propyl alcohol–water at 90°. We advanced to high alcohol concentrations but in neither case was the dehydrating action sufficient to cause the dihydrate to dehydrate appreciably.

To determine the alcohol contents of the two phases, aliquot portions were distilled and the density of the distillate determined, after dilution to fixed volume. Standard alcohol tables were used to determine the ethyl alcohol content. Beryllium sulfate was determined both as sulfate and beryllium ion. In the ethyl alcohol system, formation of two liquid layers was not observed, but it may have escaped us, since the region 12 to 65% alcohol was not investigated. Practically speaking, ethyl alcohol has not sufficient dehydrating power to cause any transformation beyond the tetrahydrate–dihydrate transition.

The only literature values relating relative densities of aqueous propyl alcohol solutions to weight percentages refer to 15°.[7] Because of the practical difficulty of keeping a thermostat at 15°, a series of relative density determinations was made at 25° on accurately weighed propyl alcohol solutions, corresponding to weight percentages of zero to ten. The results were used by us to calculate the composition of propyl alcohol distillates, but the figures do not differ sufficiently from those for 15° to warrant publication.

An extensive miscibility gap was found in the propyl alcohol system, at 90°, and the limits of partial miscibility were determined. They are: propyl alcohol layer, 80.80% PrOH, 1.15% $BeSO_4$; aqueous layer, 1.30% PrOH, 42.00% $BeSO_4$.

Thermal Analysis.—It was found impossible to use thermal analysis to verify the temperature of the transition tetrahydrate $\rightleftarrows$ dihydrate, because of delayed transformation.

Refutation of Rohmer's Conclusions.—According to Rohmer,[3] the boiling point of the saturated solution of beryllium sulfate in water varies appreciably with time, the boiling point passing through three successive values, each of which corresponds to the presence of a different solid phase, namely, tetrahydrate, dihydrate and monohydrate, respectively. We investigated the boiling point of the saturated aqueous solution, using the apparatus of Scatchard, Raymond and Gilman,[8] which incorporates a Cottrell pump and entirely obviates superheating. The pressure inside the equilibrium still was maintained at exactly 760 mm. (at 0°) by means of a barostat. The normal boiling point was found to be 108.2°. The equilibrium solid phase was removed and identified by analysis and by X-ray powder photography as the dihydrate.

Dilatometry.—Amyl alcohol (fusel oil) was used as indicator liquid. These experiments were continued over many months. The procedure was to keep the dilatometer bulb, charged with a mixture of tetrahydrate and dihydrate, in a thermostat at all times and to raise or lower the temperature by only a few tenths of a degree every 24 hours. Repeated cycling increased the sensitivity of the method and finally reduced the hysteresis loop to a breadth of two or three degrees. In the final cycle, expansion on heating was observed at about 88.5° and contraction on cooling at about 86.5°. The volume change was quite considerable.

Vapor Pressure Measurements.—After we had shown that the first, or lowest temperature, transition was from tetrahydrate to dihydrate, it remained to find whether a monohydrate existed or whether the transition was directly from dihydrate to anhydrous form, and, in either case, whether solid solutions were formed. A product corresponding to the formula $BeSO_4 \cdot H_2O$ was prepared by careful dehydration of the dihydrate. If, as Rohmer contends, the dihydrate is always metastable with respect to the monohydrate, the latter will not rehydrate spontaneously when placed in contact with water vapor, at a temperature above that of the stable existence of the tetrahydrate. A weighed sample of the above product ($BeSO_4 \cdot H_2O$) was placed in a small open bottle, suspended in a stoppered flask. Sufficient tetrahydrate was placed in the bottom of the flask to produce, on transformation to dihydrate, the water necessary for the complete rehydration to dihydrate of the substance in the bottle. The flask was evacuated and kept at 100°, overnight. The material in the bottle was then found to have gained an amount of weight exactly corresponding to rehydration to the dihydrate. Therefore the original material did not consist of any substance more stable than the dihydrate itself, at 100°. An X-ray photograph of the final product showed nothing but the dihydrate pattern.

Visual observation, in a closed capillary, of the effect of heat on the dihydrate showed distinctly a transition to a lower hydrate (or a saturated solid solution of dihydrate in anhydrous salt) and saturated aqueous solution, at 268–270°. This was followed by an investigation of the vapor pressure of the system dihydrate + lower hydrate + water vapor, up to a temperature of 352°.

For pressures up to one atmosphere an all-glass system, including an ordinary closed (evacuated) mercury manometer, was used. Observations were carried out in duplicate, using samples of beryllium sulfate which had been carefully dehydrated to contain 19% of water. Previous investigation had indicated that such a preparation, whose composition lies between that of the dihydrate and the anhydrous salt, is heterogeneous. For vapor pressures above one atmosphere, we used a closed manometer, containing air. The apparatus was constructed entirely of capillary tubing to resist the high pressures produced. Vapor pressure readings were taken for both increasing and decreasing temperatures and the agreement throughout was very good. Measurements were carried up to 352° and a pressure of about 20 atmospheres.

X-Ray Powder Diffraction Experiments.—The X-ray photographs taken in this study were obtained from powder rollings of samples of beryllium sulfate whose water contents had been adjusted to the desired values by appropriate dehydration. In every case, except that of the tetrahydrate itself, the starting material was the dihydrate and the dehydration was accomplished by heating. To prepare samples of the anhydrous salt it was necessary to heat the dihydrate at 300° for several hours. The powder rollings were made as quickly as possible to minimize the possibility of rehydration and the rolled specimens were kept over concentrated sulfuric acid while drying. After drying for a day, the specimens were mounted in the cameras in the appropriate manner and exposed to copper Kα radiation for the required time. In accordance with standard procedure, the lines or arcs on each negative were "read" and tabulations of relative intensities and spacings made. No attempt was made to determine the unit cell dimensions of the dihydrated and anhydrous forms, since for this it is necessary to possess a knowledge of the crystal structure of the solid: such a crystallographic investigation is next to impossible with a microcrystalline, hygroscopic, nontransparent substance.

II. Experimental Results—Numerical Data

These are contained in a series of tables, with appropriate titles; in the case of the X-ray work, the characteristic powder lines for the tetrahydrate, dihydrate and anhydrous salt, with relative intensities, are given. Table I is illustrated by two graphs.

The solution data of Table I are given in the form of solubility isotherms in Fig. 1, the tie-lines being omitted to avoid confusion. Figure 2 represents the complete isotherm for 75°, the tie-lines being drawn in to show the nature of the solid phases.

III. Discussion of Results

The Tetrahydrate–Dihydrate Transition.—The transition point was estimated by dilatometry as 88° and by extrapolation of isothermally invariant solution compositions to zero content of sulfuric acid, as 89–90°.

The Transition from Dihydrate to Lower Hydrate. X-Ray Evidence.—A study of the patterns of the numerous X-ray photographs taken reveals

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[7] A. Doroshevskij and M. Rozhdestvenskii, *J. Russ. Phys.-Chem. Soc.* **41**, 1428 (1910).

[8] G. Scatchard, C. L. Raymond and H. H. Gilman, This Journal, **60**, 1275 (1938).

TABLE I

PARTIAL ISOTHERMS OF SYSTEM $BeSO_4$(A)-H_2SO_4(B)-H_2O(W)

Temp., °C.	Wt. % solution A	B	Wt. % wet residue A	B	Solid[a] phase
25	29.32	0.00	52.35	0.00	A·4 W
	12.64	23.88	51.68	3.99	A·4 W
	4.39	43.23	51.38	6.31	A·4 W
	3.10	51.42	37.37	20.17	A·4 W
	3.05	54.29	55.07	7.78	A·4 W + A·2 W
	3.08	54.27	51.32	12.41	A·4 W + A·2 W
	1.43	60.15	45.83	23.84	A·2 W
	1.28	62.08	42.62	27.01	A·2 W
	0.90	66.65	58.03	15.17	A·2 W
	0.64	74.65	49.18	26.80	A·2 W
	1.55	80.60	43.71	35.68	A·2 W
50	32.93	0.00	56.68	0.00	A·4 W
	21.02	16.01	52.01	3.23	A·4 W
	13.38	29.83	48.64	7.02	A·4 W
	9.45	39.67	53.07	5.15	A·4 W
	8.64	42.77	56.10	7.39	A·4 W + A·2 W
	8.91	42.75	49.64	13.19	A·4 W + A·2 W
	8.03	43.34	50.72	15.33	A·2 W
	4.89	49.98	52.37	15.91	A·2 W
	2.37	58.54	55.57	15.26	A·2 W
	1.54	64.49	45.81	25.88	A·2 W
	1.61	71.12	45.27	28.98	A·2 W
	2.71	78.03	43.35	34.69	A·2 W
75	37.98	0.00	...	...	A·4 W
	35.77	2.14	53.81	0.40	A·4 W
	26.45	16.14	57.30	0.98	A·4 W
	23.68	21.01	56.91	1.36	A·4 W
	23.52	21.90	58.70	4.01	A·4 W + A·2 W
	23.12	22.00	58.94	4.42	A·4 W + A·2 W
	23.64	21.68	54.03	7.65	A·4 W + A·2 W
	19.76	26.55	59.98	7.01	A·2 W
	14.61	34.02	55.98	10.51	A·2 W
	7.18	48.04	45.60	20.64	A·2 W
	4.14	56.03	45.49	23.19	A·2 W
	2.42	66.30	47.98	24.72	A·2 W
	3.40	69.29	44.40	29.40	A·2 W
	4.28	75.29	51.94	25.01	A·2 W
85	41.33	0.00	...	...	A·4 W
	36.42	4.14	57.56	0.48	A·4 W
	33.82	9.54	56.69	2.83	A·4 W + A·2 W
	33.63	9.00	68.34	0.89	A·4 W + A·2 W
	31.21	12.05	57.72	4.80	A·2 W
95	43.45	0.00	...	...	A·2 W
	41.80	1.20	65.84	0.43	A·2 W
	35.41	7.34	56.90	3.41	A·2 W
	26.86	17.50	57.25	6.50	A·2 W
	25.34	19.98	57.11	7.43	A·2 W
	23.10	22.85	53.36	9.52	A·2 W
	16.04	33.89	52.20	12.96	A·2 W
	9.16	46.40	44.39	20.98	A·2 W
	6.36	53.50	42.86	25.85	A·2 W
	4.65	61.24	42.50	28.21	A·2 W
	4.89	68.36	26.86	46.30	A·2 W
	6.04	70.95	38.80	37.35	A·2 W

[a] Determined graphically by tie-lines.

TABLE II

SYSTEM: $BeSO_4$-EtOH-H_2O AT 25.00°

Solution % $BeSO_4$	% EtOH	Wet residue % $BeSO_4$	% EtOH	Nature of solid phase
20.51	12.14	47.05	4.23	A·4 W
2.10	64.81	49.50	11.87	A·4 W
0.31	89.50	41.03	27.88	A·4 W + A·2 W
0.50	89.00	38.04	37.11	A·4 W + A·2 W
0.29	89.20	42.70	29.95	A·4 W + A·2 W
1.01	97.43	49.85	31.70	A·2 W
1.05	98.95	48.10	36.27	A·2 W

only two unique diffraction patterns, namely, those of the dihydrate and of the anhydrous salt (apart, of course, from that of the tetrahydrate). The data of the three patterns are given in Table III. There is no positive evidence from the X-ray patterns made in a camera of small diameter for the formation of a discontinuous series of solid solutions by these two chemical individuals which would be accompanied by a shift in the positions of diffraction lines of the pure components.

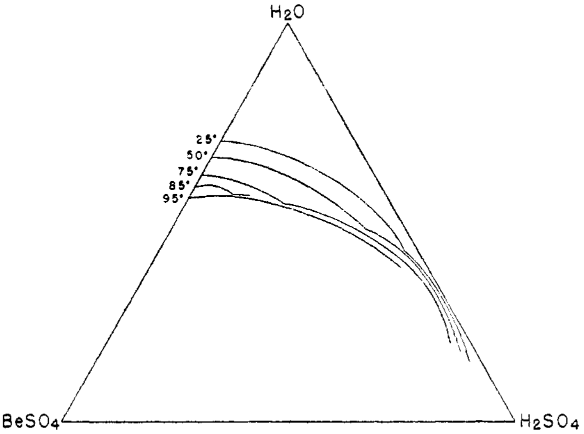

Fig. 1.—The isotherms at 25, 50, 75, 85 and 95°.

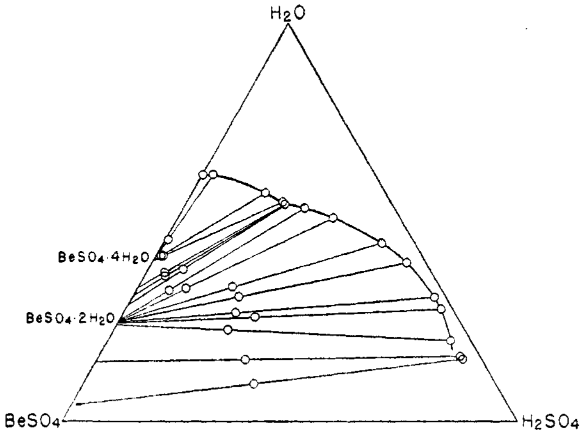

Fig. 2.—The isotherm at 75°, showing the tie-lines.

With decreasing water content of powder samples the dihydrate pattern persists, until a water content of approximately 19% is reached. On further dehydration the X-ray patterns become suddenly more complex. All the lines of the dihydrate pattern can still be recognized readily but there are a considerable number of additional lines which coincide exactly with the lines of the anhydrous pattern. The pattern complexity persists down to a water content of approximately 11%. On further dehydration the lines corresponding to the dihydrate pattern disappear entirely and the an-

TABLE III

X-RAY POWDER DIFFRACTION DATA

The symbols in this table have their usual significance, *viz.*, *I* intensity and *d* lattice spacings

I	*d*	*I*	*d*
X-Ray powder diffraction pattern for $BeSO_4 \cdot 4H_2O$			
5	5.719	1	1.485
2	5.325	5	1.455
10	3.897	4	1.411
5	3.392	0.5	1.368
5	3.194	0.5	1.349
2	2.819	4	1.326
8	2.515	0.5	1.297
1	2.416	2	1.263
0.5	2.213	0.5	1.231
5	2.165	1	1.218
2	1.996	4	1.176
1	1.939	0.5	1.142
5	1.879	0.5	1.127
4	1.836	4	1.107
4	1.772	0.5	1.086
2	1.697	0.5	1.069
4	1.599	0.5	1.048
0.5	1.540	0.5	1.030
X-Ray powder diffraction pattern for $BeSO_4 \cdot 2H_2O$			
8	4.887	1	1.883
4	3.975	1	1.854
10	3.594	2	1.773
2	3.392	0.5	1.705
6	2.841	1	1.656
2	2.614	0.5	1.601
2	2.535	0.5	1.554
3	2.398	1	1.508
5	2.185	1	1.449
0.5	2.056	0.5	1.398
0.5	1.996	0.5	1.359
5	1.936	1	1.327
X-Ray powder diffraction pattern for $BeSO_4$			
7	5.325	2	2.107
0.5	4.427	0.5	1.984
10	3.889	1	1.879
7	3.552	2	1.773
0.5	3.366	0.5	1.720
1	3.200	2	1.601
0.5	3.029	1	1.488
2	2.832	2	1.469
2	2.629	1	1.404
2	2.522	0.5	1.352
7	2.355	0.5	1.324
3	2.195		

hydrous pattern characterizes all powder photographs of samples of lower water content. If, however, solid solution really exists there should be a gradual displacement of lines in the pattern with increasing beryllium sulfate content and this we have not observed. This may be due to the imperfection of our camera, or it may simply be that there is no solid solution, but we fail to detect heterogeneity when it really exists.

There was no indication of any unique monohydrate pattern. A number of X-ray photographs was taken of samples of beryllium sulfate whose water contents corresponded to that of the monohydrate. A comparison of these photographs with those of pure dihydrate and anhydrous forms indicated clearly that the monohydrate pattern is in actual fact a composite of the patterns of dihydrate and anhydrous forms. The possibility of the existence of the monohydrate as a chemical individual is thus eliminated.

TABLE IV

VAPOR PRESSURE MEASUREMENTS

Temperature (T, °K.)	Vapor pressure (P, mm.)	Temperature (T, °K.)	Vapor pressure (P, mm.)	Temperature (T, °K.)	Vapor pressure (P, mm.)
324	1.3	457	684	545	7447
337	3.1	467	955	553	7889
351	6.8	483	1556	563	8979
368	17.1	492	1968	573	9530
381	33.5	497	2296	578	10100
395	64.9	508	3034	585	10870
408	112	513	3451	593	11860
420	182	521	4345	603	12420
437	344	528	5082	611	13300
440	383	535	5932	622	14520
449	510	540	6918	625	14860
453	577	543	7295		

Vapor Pressure Data and Visual Evidence.—When the results of the vapor pressure measurements are plotted in the form log p *versus* $1/T$, two straight lines are obtained intersecting at the transition temperature, 270°. At 270° liquid solution makes its appearance and the system becomes invariant under an observed pressure of 7130 mm. or 9.38 atm. After the temperature rises above 270°, the single solid phase is either anhydrous salt or a homogeneous solid solution of decreasing water content. The phase change at 270° involving the disappearance of pure dihydrate or dihydrate solid solution and the appearance of liquid solution is borne out in a striking manner by the visual experiment in which a slightly dehydrated sample of beryllium sulfate dihydrate was heated in a sealed tube.

The linearity of the two portions of the log p *versus* $1/T$ plot permits of calculations of the enthalpy changes involved in the corresponding phase reactions. The phase reaction for the plot below 270° is

$$\alpha(s) = \beta(s) + H_2O(g) \qquad (1)$$

where α and β are either pure dihydrate and anhydrous salt, respectively, or the corresponding solid solutions. Applying the integrated form of the Clausius–Clapeyron equation to this portion of the plot, the enthalpy change is found to be 13630 cal., that is

$$\Delta H_1 = -13630 \text{ cal.}$$

The phase reaction for the linear portion of the plot above 270° is

$$\text{solution (1)} = \beta(s) + H_2O(g) \qquad (2)$$

where solution (1) refers to an aqueous solution saturated with respect to the anhydrous salt or solid solution. The calculated enthalpy change for this reaction is found to be 6160 cal., that is, $\Delta H_2 = -6160$ cal. The phase reaction at the transition point and the enthalpy change involved are obtained as

$$\alpha(s) = \text{solution(1)} + \beta(s) \qquad \Delta H_3 = -7470 \text{ cal.}$$

The net reaction at the transition point is thus seen to be a transformation of the solid dihydrate to a saturated aqueous solution of the anhydrous salt and anhydrous salt or from saturated solid solution of the dihydrate form to aqueous solution and saturated solid solution of the anhydrous form.

WINNIPEG, CANADA RECEIVED OCTOBER 16, 1950

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY, KNOLLS ATOMIC POWER LABORATORY]

The Polarography of Ruthenium(IV) in Perchloric Acid Solutions

BY L. W. NIEDRACH AND A. D. TEVEBAUGH

This work was undertaken to determine the stability of the lower valence states of ruthenium in non-complexing solutions. Well-developed polarograms were obtained for ruthenium(IV) which is reduced in three steps to ruthenium(II). The data indicate that the first two waves correspond to the reduction of two different hydrolysis species of ruthenium(IV) to ruthenium(III). On the third wave ruthenium(III) is reduced to ruthenium(II). The formal potentials for two ruthenium couples have been estimated.

Although there is a rather extensive literature on ruthenium, most of the published work is devoted to studies of the chloride and ammine complexes and to discussions of properties of solid compounds. Few quantitative data exist relative to the chemistry of non-complexed ruthenium in acid solutions, and in particular, very little work has been reported on the polarographic behavior of ruthenium. Herasymenko and Slendyk, although observing no reduction of ruthenium at the dropping mercury electrode, did report a catalytic effect on the discharge of hydrogen.[1] Later, Willis, using chloride complexes of ruthenium(III) and ruthenium(IV), was unable to obtain reduction at the dropping mercury electrode from acid or buffered solutions.[2] More recently Silverman, confining his attention to alkaline solutions, reported the first polarographic reductions of ruthenium(VI) and ruthenium(VII), both of which are unstable in acid solutions.[3]

During the course of our work several other investigators were studying the electrochemistry of the lower oxidation states of ruthenium in acid solutions. Turk[4] observed stepwise reduction of ruthenium(IV) at graphite and at platinum electrodes from perchloric, nitric, hydrochloric and sulfuric acid solutions, but a complete discussion of the data has not yet been published. Alkire[5] also obtained reproducible polarograms from nitric acid and acetate-buffered solutions of ruthenium(IV) using the dropping mercury electrode; the reduction waves observed were interpreted as being due to stepwise reduction to ruthenium(III) and then to ruthenium(II). Related experiments on the electrochemistry of ruthenium in perchloric acid solutions have been conducted by Wehner and Hindman.[6] From coulometric titration data they established upper and lower limits for the potential of the ruthenium(IV)–ruthenium(III) couple at 0°.

The present paper describes the polarographic behavior of ruthenium in a non-complexing medium. We have interpreted the observed stepwise reduction of ruthenium(IV) and estimated the formal potentials for the ruthenium(IV)–ruthenium(III) and the ruthenium(III)–ruthenium(II) couples.

Experimental

Preparation of Materials.—A stock solution of ruthenium(IV) in 1.0 *M* perchloric acid was prepared from ruthenium chloride by the following procedure. Chloride was first removed by repeated evaporation of a phosphoric acid solution. Potassium permanganate was then added to the hot solution and the ruthenium was oxidized to the tetroxide which was swept from the solution and collected in cold 1 *M* perchloric acid. The tetroxide was reduced to ruthenium(IV) with hydrogen peroxide, and the excess peroxide was destroyed by boiling the solution. Filtration of the solution through a fine, sintered-glass filter showed that no appreciable amount of insoluble ruthenium dioxide was formed during the preparation. In addition, dialysis of a portion of the filtered solution through a cellophane membrane indicated the absence of colloidal ruthenium.

The stock solution was analyzed for total ruthenium by a colorimetric method similar to that employed by Wehner and Hindman[6] in which the ruthenium is oxidized to the tetroxide and the optical density is measured at 385 mμ. Oxidation was accomplished at room temperature with about 200 mg. of periodic acid in 25 ml. of 1 *M* perchloric acid solution, and density values were measured on a Beckman model DU spectrophotometer. The calibration curves used for these determinations were obtained by using a ruthenium solution that had been standardized gravimetrically by hydrogen reduction of the ruthenium to the metal.[7] The over-all precision of the spectrophotometric measurements indicates that the stock solution in perchloric acid was 0.00554 *M* in ruthenium within an uncertainty of somewhat less than 1%.

The absorption spectrum of the reddish-brown stock solution in the range 400 to 700 mμ was in good agreement with that reported by Wehner and Hindman[6] for ruthenium(IV) in perchloric acid solution. But as a further check on the valence state, potentiometric titrations with chromous sulfate were performed in 6 *M* hydrochloric acid solutions.[8] The concentration of ruthenium obtained by this method was 0.00558 *M* which, on the basis of the original work, is considered accurate to within 1%. Because of the good agreement between the two standardization methods, the concentration of ruthenium(IV) in the stock solution was taken as the average, 0.00556 *M*.

The stock solution was also tested for the presence of chloride with silver nitrate. Interference from ruthenium(IV), because of its tendency to form stable chloride complexes, was eliminated by oxidation to the tetroxide with persulfate in the presence of silver ion as catalyst.[9] The

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[6] P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950).

[7] R. Gilchrist, *J. Research Natl. Bur. Standards*, **12**, 283 (1934).

[8] E. Zintl and P. Zaimis, *Ber.*, **60**, 842 (1927). These authors claim that the reaction involves reduction of ruthenium(III) to ruthenium(II), but W. R. Crowell and D. M. Yost, THIS JOURNAL, **50**, 374 (1928) have pointed out that the reaction involves reduction of ruthenium(IV) to ruthenium(III), and that in the original work an error was made in the valence state assigned to the starting material.

[9] P. Wehner, private communication.