Knowing the value of γ and the fraction of S_μ at different temperatures we may obtain a rough idea of the change of the specific heat with the temperature, from the above equation. We thus obtain the results plotted in Fig. 3, in which the abscissas represent centigrade temperature, and the ordinates actual specific heats. It will be seen that the specific heat changes very remarkably with the temperature, with a maximum value of 0.44 at about 160°.

It should be noted that all of these results refer to the specific heat of liquid sulfur in the presence of a suitable catalyzer. It is not therefore possible to compare them directly with the values obtained by other observers using sulfur of unknown character. We may refer to the value 0.234 between 119° and 147° obtained by Person,[1] the value 0.232 between 116° and 136° obtained by Classen[2] and several determinations by Dussy.[3]

Summary.

The total heat change is determined between rhombic sulfur at 23° and liquid sulfur (in a state of equilibrium) at the temperatures 100°, 140°, 184° and 390°. From the results obtained the following data are calculated in small calories per gram of sulfur. The heat of fusion at 100°, to form liquid sulfur in a state of equilibrium: from rhombic sulfur 14.9, from monoclinic sulfur 11.5. For the heat of fusion to form pure liquid S_λ: from rhombic sulfur 14.5, from monoclinic sulfur 11.1. For the heat of transformation in the liquid state from S_λ to S_μ, about 13. For the specific heat of pure liquid S_λ about $0.21 + 0.00016\ t$.

A diagram is given showing the approximate values of the specific heat of liquid sulfur, in the equilibrium state, over a range of temperature from 100° to 450°.

YTTRIUM POTASSIUM OXALATE.

By L. A. Pratt and C. James.

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The fact that the rare earth oxalates carry down the alkali oxalates is an interesting subject to those working on the rare earths.

In 1873, Cleve and Hoeglund,[4] in their articles on the compounds of yttrium and erbium, described two double salts of yttrium and potassium with oxalic acid, and assigned the following formulas (recalculated):

$$Yt_2(C_2O_4)_3.4K_2C_2O_4.12H_2O \text{ and } Yt_2(C_2O_4)_3.K_2C_2O_4.H_2O.$$

In 1906, Baxter and Griffen[5] studied the occlusion of ammonium

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[1] Person, *Ann. chim. phys.*, 21, 295 (1847).

[2] Classen, *Z. Instrumentenkunde*, 11, 301 (1891).

[3] Dussy, *Compt. rend.*, 123, 305 (1896).

[4] *Bull. soc. chim.*, 193–201, 289–297.

[5] THIS JOURNAL, 28, 1684.

oxalate by the oxalates of the rare earths, and in 1908, Baxter and Daudt[1] extended the work to sodium and potassium oxalates.

In 1907, von Welsbach[2] described a new method for the separation of the yttria earths based on the crystallization of the rare earth ammonium oxalates. He also worked with the sodium double salt and the potassium double salt. The former he found too insoluble and the latter too soluble for obtaining results by fractional crystallization.

Since no systematic study has ever been carried out on this subject, it has seemed to the authors that a careful investigation of the solubility of yttrium oxalate in potassium oxalate solutions and an examination of the accompanying solid phases would be of value.

The purification of the yttrium used for this research was accomplished by the crystallization of the bromates and the fusion of the nitrates, according to a paper by the authors.[3] The pure yttrium thus obtained was converted into the oxalate. A saturated solution of potassium oxalate was prepared from pure potassium oxalate.

Varying amounts of potassium oxalate and yttrium oxalate were added to sufficient water to make about 75 cc., placed in bottles of 100 cc. capacity and rotated in a thermostat at 25° for eight weeks, when equilibrium was proved to have been reached. The bottles were then allowed to stand in the thermostat until the solutions cleared. The settling of the solid phases required only a few hours.

Portions of the supernatant liquids were withdrawn and the yttrium and total C_2O_3 determined. The C_2O_3 was estimated by titration with standard potassium permanganate solution. The determination of the yttrium was somewhat more difficult, owing to the presence of potassium and oxalic acid. The oxalic acid was oxidized by boiling the solution with an excess of potassium bromate and nitric acid, and the yttrium was precipitated by ammonium hydroxide. The precipitate was carefully washed with hot water, containing a little ammonium hydroxide and ignited to the oxide. The liquid phases were all analyzed in this manner.

During the analyses of the solid phases it was discovered that this method introduced a slight error, due to the fact that it was impossible to free the precipitated yttrium hydroxide from all bromine. Therefore the per cent. of yttrium as determined in all the liquid phases must be a trifle too high. The error is so slight, however, that it makes no perceptible difference as plotted and, therefore, it was not considered necessary to repeat the analyses. In the case of the solid phases it was found imperative to apply a different method, since the error introduced

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[1] THIS JOURNAL, 30, 563.

[2] *Monatsh.*

[3] THIS JOURNAL, 32, 873.

was much greater than with the liquid phases. It was found by simply igniting a weighed sample of the solid in a tared platinum crucible, treating with water, and washing on a filter, that the potassium and C_2O_3 could be entirely separated, leaving only yttrium oxide. This method gave good results, when carefully tested with samples of known composition, and it was applied in the analyses of the solid phases.

The results of the analyses of the liquid phases are given in Table I and shown graphically in Fig. 1.

TABLE I.

No.	Sp. gr.	Per cent. $Yt_2(C_2O_4)_3$.	Per cent. $K_2C_2O_4$.	Grams $Yt_2(C_2O_4)_3$ per 100 grams H_2O.	Grams $K_2C_2O_4$. per 100 grams H_2O.
1	1.008	Trace	1.29	Trace	1.31
2	1.022	0.01	3.23	0.01	3.34
3	1.035	0.02	5.03	0.02	5.30
4	1.052	0.04	7.04	0.04	7.58
5	1.059	0.06	8.15	0.06	8.88
6	1.081	0.13	10.92	0.15	12.28
7	1.096	0.24	12.63	0.27	14.50
8	1.107	0.33	13.90	0.38	16.20
9	1.132	0.59	16.76	0.72	20.27
10	1.137	0.69	17.64	0.85	21.59
11	1.166	1.08	20.43	1.37	26.02
12	1.173	1.12	21.16	1.45	27.24
13	1.174	1.16	21.28	1.50	27.44
14	1.184	1.14	22.00	1.48	28.63
15	1.199	1.11	24.44	1.49	32.83
16	1.204	1.11	25.09	1.50	33.98
17	1.222	1.06	27.08	1.48	37.68
18	1.231	1.01	27.84	1.42	39.12
19	1.231	0.97	27.84	1.36	39.10
20	1.228	0.78	27.72	1.09	38.77
21	1.218	..	27.47	..	37.87

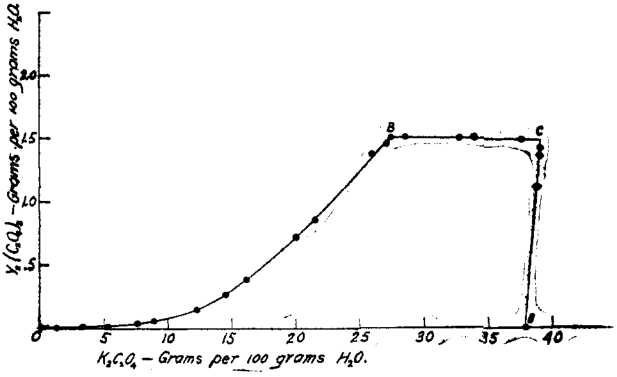

Fig- 1.

Bottles 18, 19 and 20 contained an excess of potassium oxalate. Bottle 21 contained pure potassium oxalate in excess, for the determination of the solubility.

In the analyses of the solid phases, the samples were withdrawn by means of a platinum spoon and pressed between filter paper in order to remove the adhering mother liquor as far as possible. The sample was then quickly transferred to a weighing bottle and thoroughly mixed. Two portions of this prepared sample were weighed out, and the C_2O_3 and Y_2O_3 determined as previously described.

The data obtained are shown in Table II and plotted in Fig. 2.

TABLE II.

	Liquid.		Solid.	
No.	Per cent. $Y_2(C_2O_3)_4$.	Per cent. $K_2C_2O_4$.	Per cent. $Y_2(C_2O_4)_3$.	Per cent. $K_2C_2O_4$.
1	trace	1.29	48.84	15.79
2	0.01	3.34	45.98	15.44
5	0.06	8.15	46.17	17.64
8	0.33	13.90	44.10	18.75
10	0.69	17.64	45.09	19.49
11	1.08	20.43	42.28	17.88
14	1.14	22.00	29.93	46.56
16	1.11	25.09	31.11	48.01
17	1.06	27.08	31.45	49.14

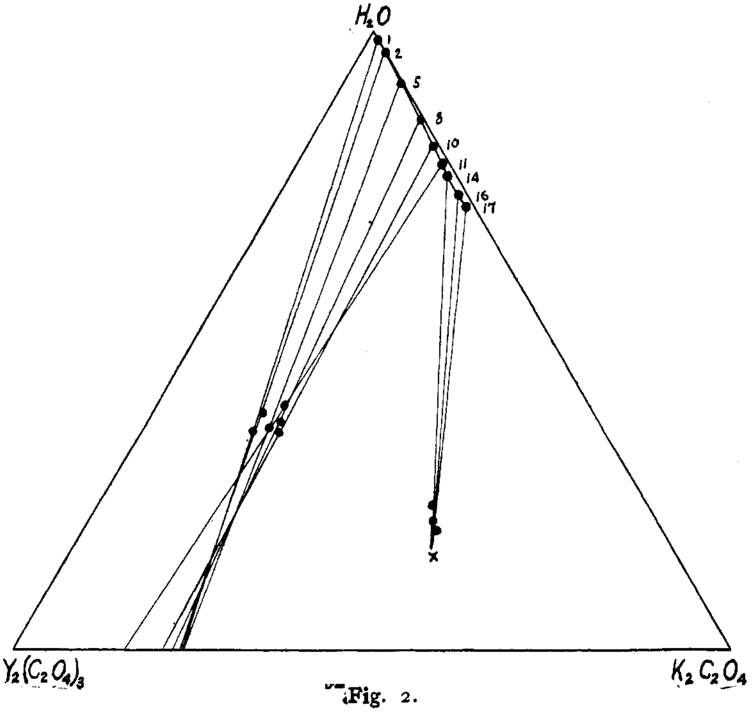

Fig. 2.

The solubility curve (Fig. 1) shows three distinct parts: AB, BC and CD. In the study of the solid phases along AB (Fig. 1), by means of the triangular diagram (Fig. 2) it is apparent that only solid solutions exist. It is very interesting to note that yttrium oxalate has the power to withdraw a comparatively large amount of potassium oxalate from dilute solutions.

From B to C (Fig. 1) the solid portions were very crystallin, settled readily and had the appearance of a distinct compound. Lines joining points representing liquid and corresponding solid phases along this portion of the curve intersect at the common point X (Fig. 2), corresponding to a definit double oxalate of yttrium and potassium, represented by the formula $Y_2(C_2O_4)_3.4K_2C_2O_4.12H_2O$.

Another interesting fact, shown by the branch CD (Fig. 1), is the increased solubility of potassium oxalate in the presence of yttrium oxalate.

A small quantity of the double oxalate of yttrium and potassium was prepared by dissolving yttrium oxalate in a hot, fairly concentrated solution of potassium oxalate. Upon cooling, the compound crystallized out slowly. The mother liquor was poured off and an attempt was made to free the crystals from the adhering solution. Since the compound is rapidly decomposed by water, it was necessary to find some other solvent to remove the mother liquor. The first method tried was by the use of a solution of ammonium acetate, followed by alcohol to remove the ammonium acetate. This caused only a slight decomposition of the compound. The second method employed glycerol as the washing reagent and this was followed by alcohol to remove the glycerol. By this procedure the amount of decomposition was less than by the first method.

The analyses of the material prepared in this manner are given below:

Calculated	$Y_2(C_2O_4)_3$—33.40,	$K_2C_2O_4$—50.24,	H_2O—16.36.
Found	$Y_2(C_2O_4)_3$—33.25,	$K_2C_2O_4$—49.65,	H_2O (diff.) 17.10.
Found	$Y_2(C_2O_4)_3$—33.24,	$K_2C_2O_4$—49.63,	H_2O (diff.) 17.13.

Summary.

1. The foregoing work shows the existence of only one double oxalate of yttrium and potassium at 25°, possessing the following formula: $Y_2(C_2O_4)_3.4K_2C_2O_4.12H_2O$.

Cleve and Hoeglund mentioned this double salt.[1]

2. This compound can exist in contact with an aqueous solution of potassium oxalate of concentration greater than 27.5 grams of the oxalate to 100 grams of water.

3. The oxalate $Y_2(C_2O_4)_3.K_2C_2O_4.H_2O$, described by Cleve and Hoeglund, does not exist at 25°.

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[1] *Loc. cit.*