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Determination of the solubilities of lithium, sodium, and potassium sulphates in absolute methyl and ethyl alcohols

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DETERMINATION OF THE SOLUBILITIES OF LITHIUM, SODIUM, AND POTASSIUM SULPHATES IN ABSOLUTE METHYL AND ETHYL ALCOHOLS.

by

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A

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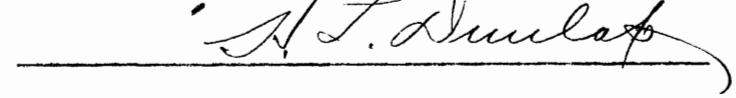
Approved by 

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In searching chemical literature for data on the solubilities of various inorganic salts in the different absolute alcohols, one finds very little, and that found is usually expressed in such terms as "very slightly soluble" or "almost insoluble". Some data on the chlorides of the alkali metals in absolute alcohols is available, but there is a wide divergence in results with different workers. Usually the data is given with some other point in view rather than that of being a careful determination of the solubilities. In such cases only the ordinary methods for preparing pure alcohols were used and this leaves appreciable quantities of water in the alcohols, which, of course, greatly affects the solubility of the salts.

No data whatsoever on the solubility of sodium, potassium or lithium sulphate in absolute ethyl or methyl alcohol was obtainable in the available literature. De Bruyn in 1900 (Seidell - Solubility of Organic and Inorganic Compounds) performed some experiments with sodium sulphate in aqueous ethyl alcohol at different temperatures and concentrations, but the concentrations, with one exception, did not run above 50% alcohol.

Gerardin, 1865, and Schiff, 1861, (Seudill - Solubilities of Organic and Inorganic Compounds), did some work with potassium sulphate in aqueous alcohol but mone with absolute alcohol. The available data on lithium sulphate in absolute alcohol was equally scarce.

It was thought by the author that there might be some relation between the solubility of a salt in the alcohols and the position of those alcohols in the series of monohydric alcohols; that is, that there should be a definite increase or decrease in the solubility of any particular salt in going from a higher to a lower alcohol ~~salt~~.

The object of this paper was to find the solubilities of some simple salts in as pure alcohol as could be prepared, and to find any relationships if possible.

Preparation of the salts and alcohols.

The c.p. salts were finely ground and heated for twelve hours at 130 degrees C. in an electric oven in order to dehydrate them thoroughly. Then while still hot they were put into bottles with air-tight ground-glass stoppers to keep for future use.

The alcohols were first dehydrated over lime, distilled, temperature range .4 degrees C.; redehydrated over anhydrous copper sulphate, distilled again; and then treated a third time over an amalgam of mercury - aluminum. This amalgam was prepared by heating aluminum and mercury together in a casserole covered with a watch

glass. Probably better results would be obtained if the two metals were heated in an atmosphere of carbon dioxide, but no definite information for its preparation was obtainable either in text books or chemical literature. The temperature range of distillation for the final treatment was .2 degrees. The boiling points used, figured to standard conditions were:

Methyl alcohol 65.9 - 66.1 Degrees C.

Ethyl alcohol 78.2 - 78.4 Degrees C.

Cohen gives 66 degrees C. as the boiling point of absolute methyl alcohol at ~~0 degrees C. and~~ 760 mm. pressure, while the boiling point used for absolute ethyl alcohol was that given by Brunel, Crenshaw and Tobin, in "The Purification and Some Physical Properties of Certain Aliphatic Alcohols" - Jr. Amer. Chem. Soc., March 1, 1921; i.e. - 78.32 degrees C.

Apparatus and Procedure

The alcohol distillation was carried out in a glass flask fitted with a cork stopper in which the thermometer could be fastened securely and completely suspended in the neck of the flask so that the mercury thread was surrounded completely by the vapors and no correction had to be made for it. The thermometers used were standard Gerhardt thermometers, graduated to read in tenths of a degree. The apparatus for the distillation consisted of a 36 inch condenser attached to the glass flask and the receiving vessel used was a glass flask fitted with a calcium chloride tube in order to prevent any moisture from the air

getting into the alcohols. The alcohols were placed in thoroughly dried ground-glass stoppered bottles during dehydration treatments and after the final distillation until used.

In the determination of the solubility of the salts in the alcohols, 100 c.c. long-necked measuring flasks fitted with one-hole rubber stoppers to which calcium chloride tubes were attached, were used. The alcohol was placed in these flasks and an excess of the salt added; then the flasks were placed in a 225 liter De Khotinsky electrically heated thermostat whose temperature could be held constant within limits of .1 degree C. and allowed to stand for three hours or more. After standing for the time given, an electric stirring apparatus was attached to each bottle in succession and the contents stirred vigorously from 45 - 60 minutes. After stirring, the contents were allowed to settle for a minimum time of 4 - 5 hours, preferably over night; then 15 - 20 c.c. were carefully drawn off in a pipette which was kept at approximately the same temperature as the flasks, and put into weighing bottles with tightly fitting ground-glass stoppers, and the whole carefully weighed. These bottles had been carefully cleaned, dried in an electric oven, allowed to cool in a desiccator, and weighed. After weighing the bottles with the solution, they were placed in an electric oven and heated until all the alcohol was completely driven

off and the salt remaining in the bottle thoroughly dry, i.e. - heated to a constant weight - reweighed and the grams of salt in 100 grams ofsolution figured from the obtained weights. All samples were run in duplicate and the two samples were taken from each bottle. This gave four weights on each salt in each alcohol at each different temperature. If no fair check could be obtained from the four samples at any temperature, the contents ofthe bottles were stirred again, allowed to settle and resampled. This method was repeated until two results would check reasonably close, and usually three results that checked fairly well were obtained.

Different lengths of time for stirring and for allowing the contents to settle were tried, but 45 minutes were found to be sufficient for complete stirring to be obtained. The settling period, however, varied with the salt, sodium sulphate being completely settled in 3- 4 hours, while lithium sulphate had to stand over night. Potassium sulphate in methyl alcohol required almost as much time to settle as the lithium salt, but in ethyl alcohol it settled somewhat more rapidly.

RESULTS

Sodium sulphate in ethyl alcohol gave a descending curve with increased temperatures and the results

were fairly consistant throughout. Sodium sulphate evidently forms alcoholates with ethyl alcohol at the lower temperatures that break down with increasing temperatures. The break is complete at approximately 26 degrees C. This theory would account for the steadily decreasing solubility of the salt at higher temperatures. The other two salts in ethyl alcohol give broken curves but just reversed. Potassium sulphate becomes more soluble as the temperature increases up to approximately 35 degrees C., then its solubility decreases. Evidently the alcoholates formed at lower temperatures begin to break down rapidly at this point, becoming practically insoluble at temperatures above 55 degrees C. Just the reverse is true of lithium sulphate which gradually descends with increasing temperatures up to about 27 degrees C., then begins ascending. This would indicate that alcoholates are formed at temperatures above 25 - 27 degrees C. or higher. Only sodium and potassium were tested for solubility in methyl alcohol. Both curves are somewhat similar, descending with increased temperature to a point between 37 - 40 degrees C., then ascending. The chief difference is that potassium sulphate is more soluble in methyl alcohol than the sodium salt and consequently forms the steeper curve.

In the ethyl alcohol the potassium salt is more soluble than either of the other two, lithium being the least soluble and showing the least change in solubility with change in temperature.

A peculiarity of the solubilities is that the salts are more soluble in absolute ethyl alcohol than in absolute methyl alcohol. For any practical purpose, one can say that these salts are insoluble in absolute methyl or ethyl alcohols.

DATA SHEETS

Solubility of Sodium Sulphate in Ethyl Alcohol.

Grams per 100 Grams Solvent			Temperature C. Degrees
.0355 .0367 .0359	Ave.	.0360	17
.01006 .01142 .01073	Ave.	.01073	25 Recheck here ran very low.
.0073 .0059 .0082	Ave.	.0072	30.5
.00617 .00690 .00698	Ave.	.00668	40.1
.00738 .00809	Ave.	.00773	47.2

Solubility of Sodium Sulphate in Methyl Alcohol.

.00992 .01260 .01600	Ave.	.012880	25.0
.00556 .00626 .00928	Ave.	.00703	31.2
.00445 .00385 .00464	Ave	.00431	36.9
.0223 .0267 .0143	Ave.	.0211	40.1

Solubility of Sodium Sulphate in Methyl Alcohol.

Grams per 100 Grams Solvent			Temperature C. Degrees
.0164 .0216 .0265	Ave.	.0215	47.2

Solubility of Potassium Sulphate in Ethyl Alcohol.

Grams per 100 Grams Solvent			Temperature C. Degrees
.0128 ,0163 .0154	Ave.	.0149	18.0
.0370 .0496 .0316	Ave.	.0356	25.0
.0568 .0540	Ave.	.0554	30.5
.0572 .0575 .0605	Ave.	.0584	40.1
.0355 .0300 .0317	Ave.	.0324	47.2

Solubility of Potassium Sulphate in Methyl Alcohol.

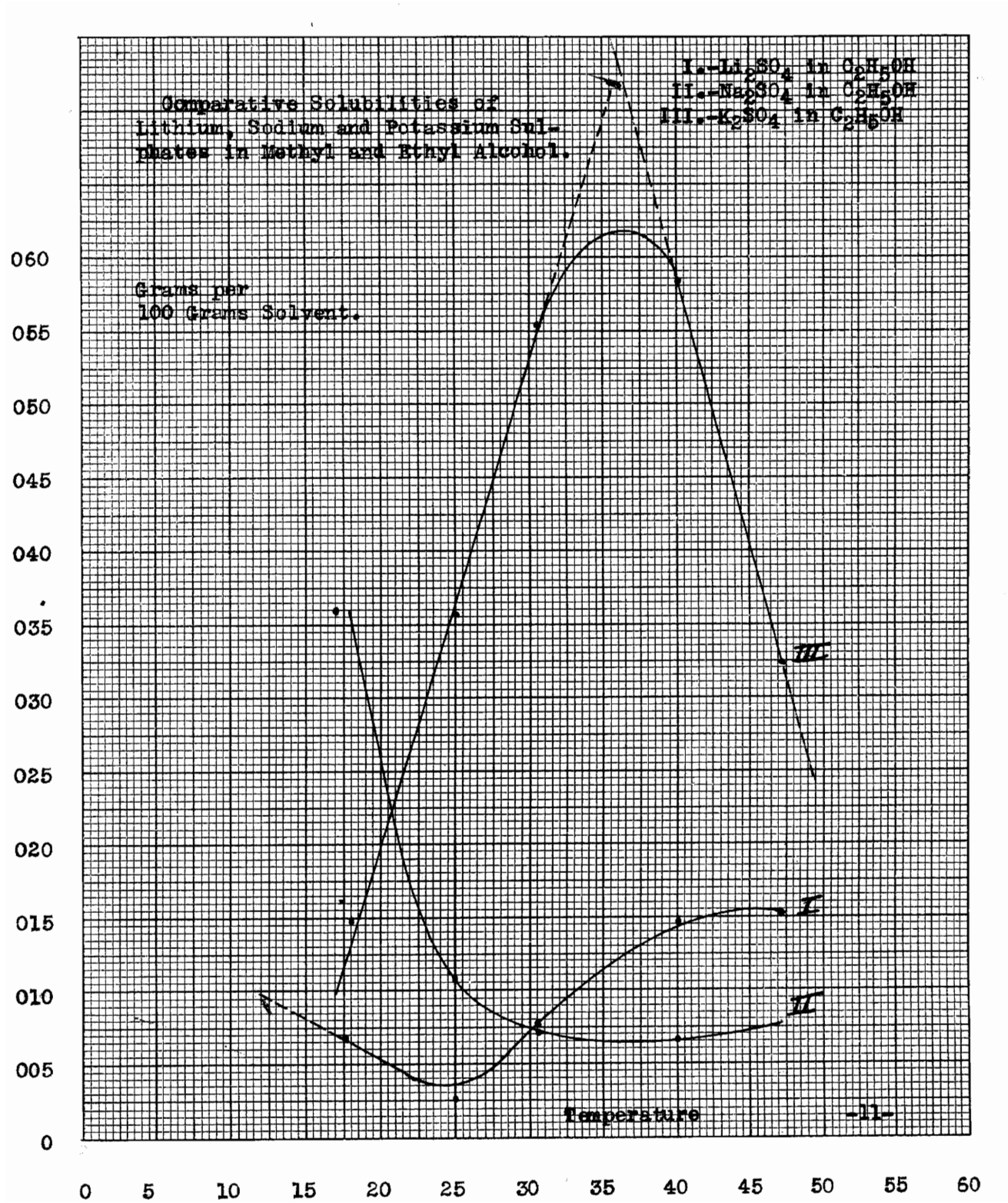
Grams per 100 Grams Solvent			Temperature C. Degrees
.0199 .0185 .0182	Ave.	.0189	25.
.01136 .01224 .01217	Ave.	.0119	31.5
.00807 .00769 .00742	Ave.	.007726	36.9

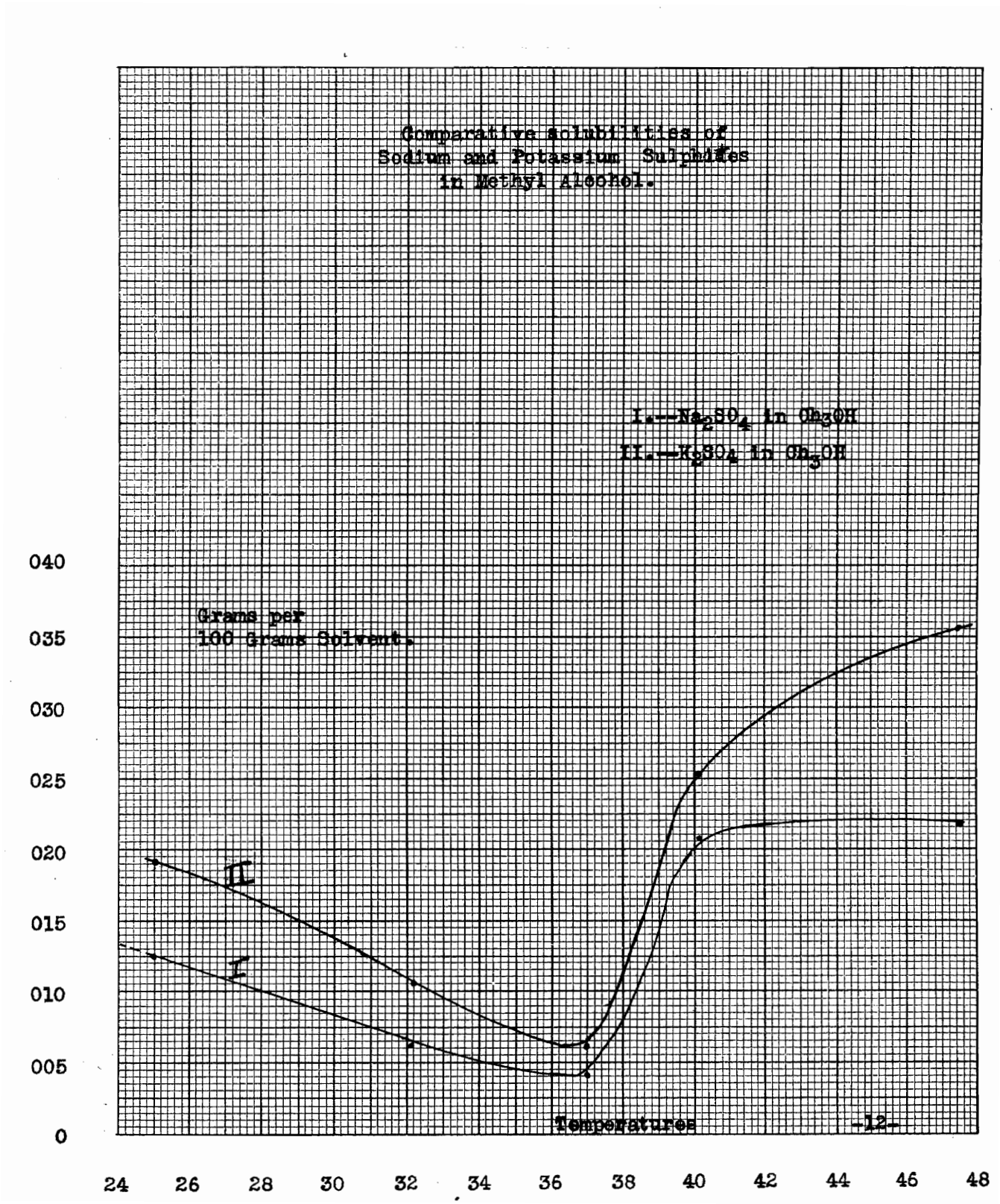
Solubility of Potassium Sulphate in Methyl Alcohol.

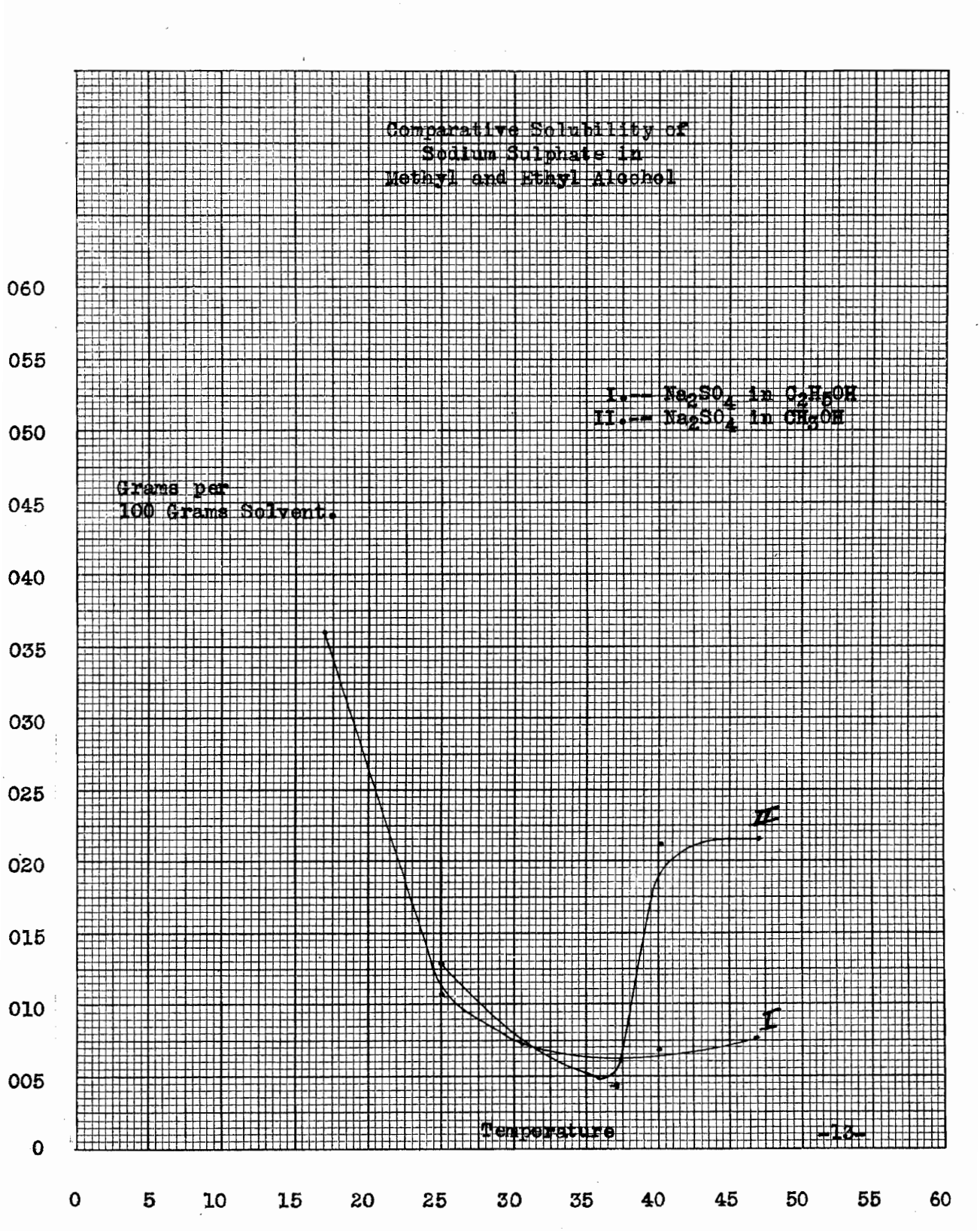
Grams per 100 Grams Solvent			Temperature C. Degrees
.0247 .0256 .0269	Ave.	.0257	40.1
.0366 .0326 .0368	Ave.	.0353	47.2

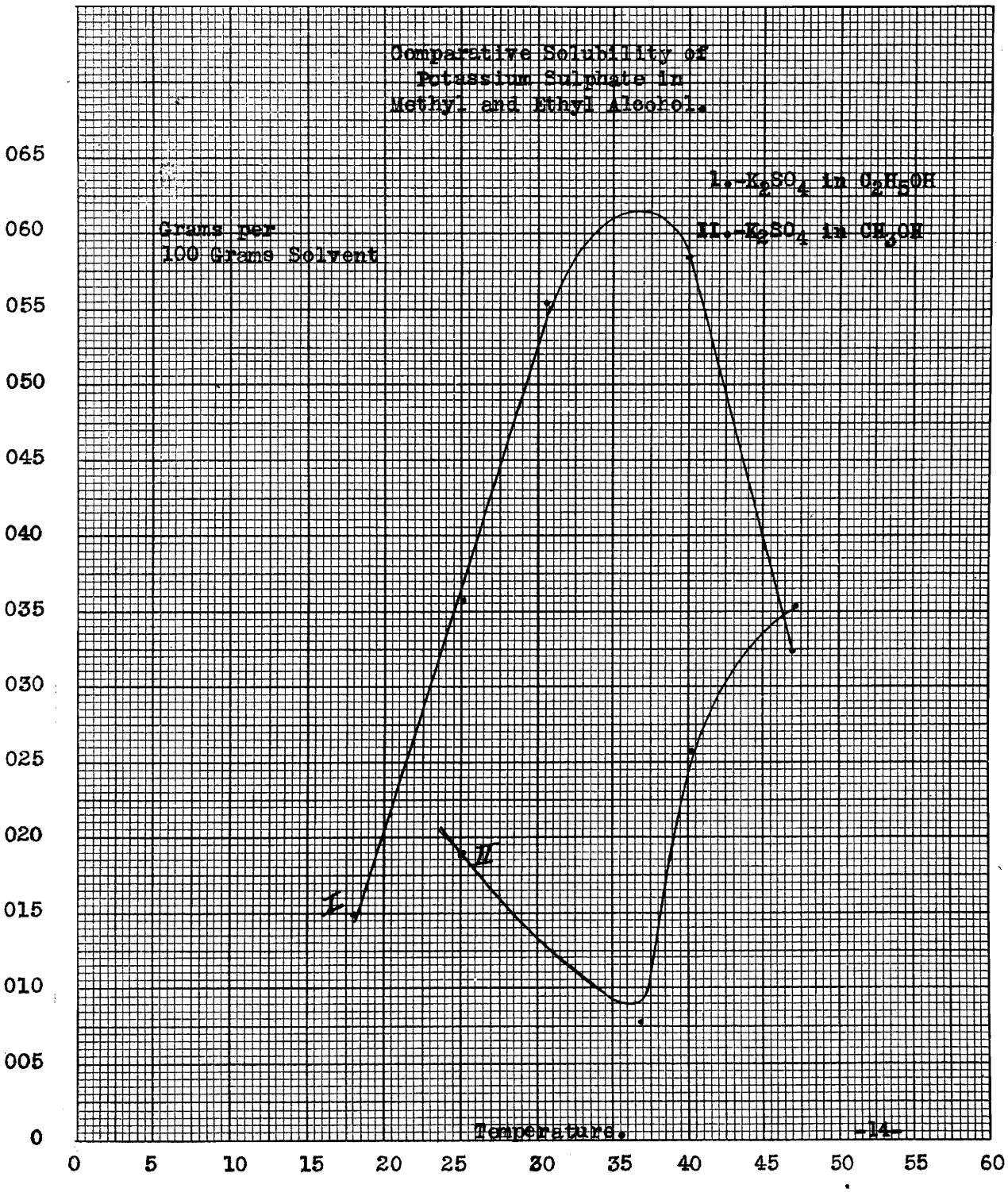
Solubility of Lithium Sulphate in Ethyl Alcohol.

Grams per 100 Grams Solvent			Temperature C. Degrees
.00665 .00658 .00683	Ave.	.00678	17.5
.00706			
.00441 .00540 .00560	Ave.	.00514	25.0
.00848 .00753 .00703	Ave.	.00768	30.5
.0183 .0112	Ave.	.0147	40.1
.0147 .0156	Ave.	.0153	47.2


Comparative Solubilities of Lithium, Sodium and Potassium Sulphates in Methyl and Ethyl Alcohol.
I.-Li_2SO_4 in C_2H_5OH
II.-Na_2SO_4 in C_2H_5OH
III.-K_2SO_4 in C_2H_5OH
Grams per 100 Grams Solvent.
060
055
050
045
040
035
030
025
020
015
010
005
0
0 5 10 15 20 25 30 35 40 45 50 55 60
Temperature
-11-
III
I
II


Comparative solubilities of
Sodium and Potassium Sulphites
in Methyl Alcohol.
I.—Na_2SO_4 in CH_3OH
II.—K_2SO_4 in CH_3OH
Grams per
100 Grams Solvent.
040
035
030
025
020
015
010
005
0
II
I
24
26
28
30
32
34
36
38
40
42
44
46
48
Temperatures


Comparative Solubility of
Sodium Sulphate in
Methyl and Ethyl Alcohol
I.-- Na_2SO_4 in C_2H_5OH
II.-- Na_2SO_4 in CH_3OH
Grams per
100 Grams Solvent.
060
055
050
045
040
035
030
025
020
015
010
005
0
II
I
Temperature
-13-
0
5
10
15
20
25
30
35
40
45
50
55
60


Comparative Solubility of
Potassium Sulphate in
Methyl and Ethyl Alcohol.
I.-K_2SO_4 in C_2H_5OH
II.-K_2SO_4 in CH_3OH
Grams per
100 Grams Solvent
065
060
055
050
045
040
035
030
025
020
015
010
005
0
0
5
10
15
20
25
30
35
40
45
50
55
60
Temperature.
I
II