

# SCIENTIFIC SECTION

## SOLUBILITY DETERMINATIONS OF U. S. P. X CHEMICALS.\*

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The purpose of the following study was to determine accurately, when possible, the solubilities of those chemicals of the U. S. P. X, for which no definite solubility figures are given. In these cases the U. S. P. indicates the solubility by such terms as: "very soluble," "slightly soluble," etc. These expressions, however, indicate such a wide range in solubility as to make their usefulness rather limited.

In determining solubilities the procedure of Seidell (see *Hygienic Laboratory Bulletin* 67, 1910) was generally used. The solutions were prepared in thick-walled Pyrex test-tubes of about 50 cc. capacity. The tubes were tightly closed with rubber stoppers, or, if the nature of the solvent did not permit the use of rubber, cork stoppers were used, which had been previously paraffined. These tubes were attached to a rotating disc immersed in a constant-temperature water-bath and kept at the temperature desired for the solubility determination.<sup>1</sup>

Great care was taken to prevent volatilization of the solvent or absorption of moisture in drawing off the solutions for analysis.

Special apparatus was constructed for this purpose (see Fig. 1). A cylinder (*A*) wide enough to hold a 50-cc. weighing bottle (*B*) was closed with a two-hole rubber stopper. A glass tube was passed through one of the openings in the rubber stopper and connected by rubber tubing to a suction pump. Into the other hole was inserted a small ground-edge funnel (*C*). Another ground-edge funnel (*D*) of the same size was inverted over the first funnel, being connected by rubber tubing with a U-tube (*E*) of a bottle (*F*) through which air enters the apparatus when suction is applied. If the solution to be filtered contained glycerin, for instance, fused calcium chloride was placed in the U-tube to absorb the moisture of the influent air. If alcohol or water was the solvent, the air was saturated by passage through the proper solvent placed in the bottle (*F*).

In determining the exact quantity of solute present in the solutions, two or more methods of analysis, wherever possible, were employed as checks. Frequently a solution may be analyzed by merely evaporating the solvent and weighing the residue, while in other cases gravimetric or volumetric methods of analysis must be used. The character of the solvent used frequently necessitated modifications of the standard procedure of analysis as given in the U. S. P. and by other authorities.

Prior to their use in solubility determinations, the solutes and solvents were carefully analyzed to insure their being of U. S. P. X quality.

### PREPARATION OF THE SOLUTIONS.

In most cases the saturation point at the desired temperature was approached from two directions: one from room temperature and hereafter designated "under-

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<sup>1</sup> The constant-temperature bath and the agitation apparatus used in this work will be described in detail later on.

saturated" and the other, wherever the solute permitted heating without being decomposed, from a higher temperature than the one desired and hereafter designated "supersaturated." The solutions prepared by either method were kept at the desired temperature and continuously or frequently agitated for various lengths of time until equilibrium was attained.

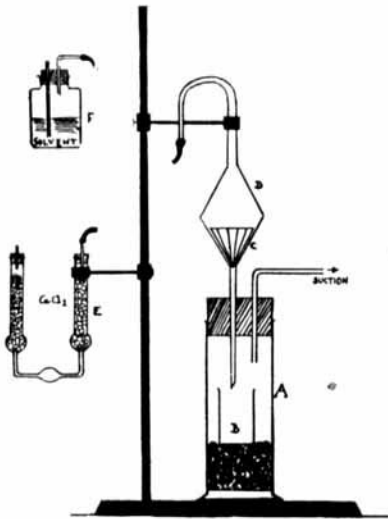


Fig 1

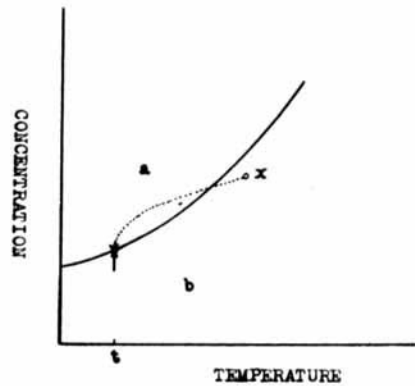


Fig 2

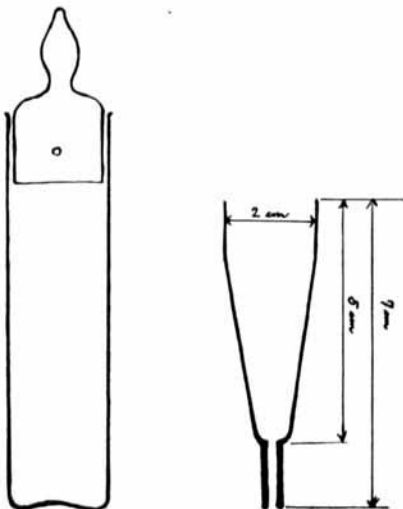


Fig 4

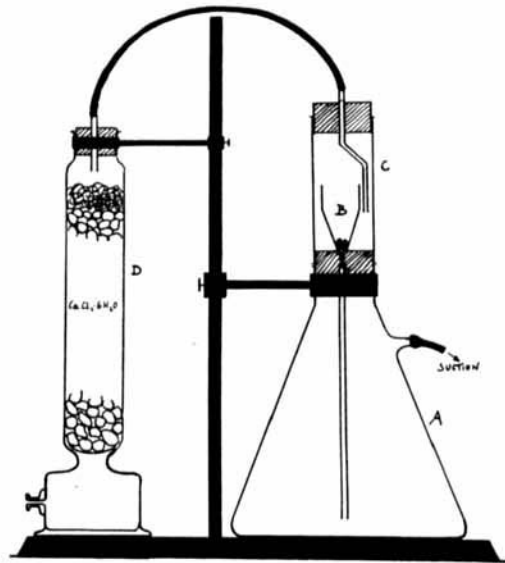


Fig 5

In preparing the solution from "undersaturation" the solute was quickly and finely powdered before being mixed with the solvent. In this mixture the smallest particles of the solute, having relatively the largest surface, will dissolve first while the larger particles remain, thereby lowering the solution tension of

the solute. Therefore, another small portion of finely powdered solute was added some time after the preparation of the solution when the solution was supposed to have reached a concentration close to the saturation point. In preparing the

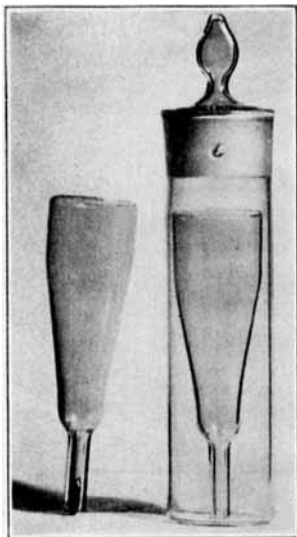


Fig. 3.

solution from "supersaturation," sufficient of the solute was used to leave a slight amount undissolved after heating. A distinct increase in the amount of the solute may be observed after keeping the solution at the desired temperature.

The solutions prepared by these two methods approach the point of saturation from two opposite directions, coming to equilibrium at the point of saturation for the desired temperature. This may be seen in the sketch on page 763 (Fig. 2) which shows a typical saturation curve.

The field below the curve, indicated by *b*, represents undersaturated solutions, which therefore will dissolve more of the solute until the saturation point is reached. Such is the case with the solutions prepared at room temperature. The field above the curve, indicated by *a*, is the region of supersaturated solutions. In preparing the solutions by heating solute and solvent, this solution may reach a point, represented by *x*. This solution is not necessarily saturated at the temperature represented by this point, but it contains more dissolved solute than a solution

which is saturated at the desired temperature, indicated by *t*. This solution is, therefore, supersaturated with respect to the desired temperature. On quickly cooling the heated solution the concentration may change, as indicated by the dotted line. Solute will separate until true equilibrium is attained. Whether or not equilibrium has been attained may be determined by analyzing portions of the solutions prepared by either method, over varying periods of time until concordant values of the concentration of the solution are obtained.

It is apparent that the correct saturation point is obtained when the solutions prepared by both methods yield upon analysis the same concentration values.

#### THE CALCULATION OF THE SOLUBILITY.

The U. S. P. X states the solubility as the number of cubic centimeters of solvent required to dissolve 1 Gm. of the solute. There is no simple relation existing between this statement and the experimental results. In the following paragraph is described the calculation of the solubility as based upon the results of analyses.

The analysis yields two figures:

The weight in grams of solution used for analysis, which may be indicated by *x*, and the weight, also in grams, of solute, indicated by *y*, found to be present in *x* Gm. of the solution. The number of cubic centimeters of the solvent, indicated by *z*, required to dissolve 1 Gm. of solute will then be found by the following equation:

$$z = \frac{x - y}{y \cdot k}$$

where *k* is the density of the solvent at the temperature of the experiment. In this equation *z* is expressed in terms of two variables *x* and *y*, and of the density which is a constant at any par-

ticular temperature. If equal weights of the solution to be analyzed could always be taken, then  $x$  also would be a constant. In such a case  $y$  only will vary due to the analytical errors and consequently  $z$  also will vary. The ratio of variation of  $z$  with regard to  $y$  is expressed by the differential derivative of this equation, which is

$$\frac{dz}{dy} = \frac{-x}{y^2 \cdot k}$$

From this, it may be seen, that  $z$  varies inversely as the square of  $y$ . If  $y$  is small compared to  $x$ , as it is the case with slightly soluble substances,  $z$  will vary to a very large extent, even if the difference between  $y'$  and  $y''$ , which represent the results of the analyses of two equal portions of the same solution, is very small. Consequently great variations will appear in the results of a number of analyses of the same solution, if such results be expressed by the U. S. P. method.

This fact necessitated the use of another method of calculating the solubility. The postulate of such a method is that the variables in the equation should appear in a direct relationship of the first degree. In such an equation the differential derivative would be a constant, which means that the variations of the solubility values, calculated by this equation, would amount to a constant multiple of the difference between the results of the two analyses,  $y'$  and  $y''$ .

An equation which satisfies these requirements exists in the statement of the percentage (by weight) of solute present in solution. This solubility,  $w$ , is found by the equation

$$w = \frac{100 y}{x}$$

In this equation the ratio of variation of  $w$  with regard to  $y$  is independent of  $y$ , as may be seen from the differential derivative

$$\frac{dw}{dy} = \frac{100}{x} \text{ (} x \text{ being constant)}$$

Using this equation for the calculation of solubility, the variation in the results of duplicate analyses of a solution of a slightly soluble substance and of a solution of a very soluble substance will produce in both cases directly proportional variations in the expression of solubility by percentage,  $w$ .

The statement of solubility as the number of grams of solute present in 100 Gm. of the solution represents the actual experimental results expressed in percentage. This form of expression, being used quite extensively, appears in the tables reporting the results of the solubility determinations.

In the following papers the calculation of the solubility,  $Z$ , as stated in the U. S. P. X, is derived from all the values,  $w$ , of the saturated solutions, by taking the arithmetic mean,  $W$ , and substituting in the equation

$$Z = \frac{100 - W}{W \cdot k}$$

the symbol  $k$  denoting the density of the solvent at the experimental temperature.

#### THE SOLUBILITY OF MAGNESIUM SULPHATE HEPTAHYDRATE ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) IN WATER AND GLYCERIN AT 25° C.

The quantity of magnesium sulphate in solution was determined by three methods. 1. From "Residue." 2. From  $\text{SO}_4$  contents. 3. From Mg contents.

1. *Residue Method*.—A weighed quantity of the solution was evaporated to dryness and then the residue carefully ignited to constant weight. The final product was anhydrous magnesium sulphate.

2. *Sulphate Determination*.—The procedure used in the estimation of sulphate is a slightly modified form of the one originally introduced by H. L. Winkler (Budapest),<sup>1</sup> which consists in precipitating the  $\text{SO}_4^{2-}$  as  $\text{BaSO}_4$  under certain well-defined conditions. The method insures results of great accuracy.

The solution of the sulphate, either neutral or of known acidity, measuring about 100 cc. and containing an amount of  $\text{SO}_4$  yielding not more than 0.3 Gm. of  $\text{BaSO}_4$  is heated to boiling and from 5 to 10 cc. (but using equal amounts for duplicate analyses) of a 5 per cent barium chloride solution (5.0 Gm. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and water to make 100 cc.)<sup>2</sup> are added drop by drop. The solution is kept boiling for several minutes after precipitation and then allowed to stand over night. The precipitate is collected on a pledget of cotton placed in a "cup funnel" (see Fig. 3 and Fig. 4). The "cup funnel" containing the cotton must be previously dried at  $130^\circ$  for three hours.

When collecting the precipitate the supernatant liquid is first decanted through the cotton pledget in the funnel and the clear filtrate discarded. The precipitate is then mixed with distilled water and the mixture poured into the funnel so that the pledget of cotton will be completely covered with  $\text{BaSO}_4$ . If the filtrate is not clear it is refiltered. If directions are carefully followed the filtrate will be clear from the first. The precipitate is dried for two hours at  $130^\circ \text{C}$ . The "cup funnel" is then taken out of the drying oven, placed in a weighing bottle of proper size, allowed to cool for fifteen minutes then placed in the balance case and finally weighed after standing for fifteen more minutes. A desiccator is not used during cooling. Here, as in all other determinations in which the "cup funnel" is used, the lid of the weighing bottle which holds the funnel is grooved to permit the access of air.<sup>3</sup>

Before using the "cup funnel" for the collection of the precipitate, the funnel stem is lengthened by attaching a piece of glass tubing to provide the advantage of a long stem funnel.

In applying this method to the determination of sulphates in solutions resulting from solubility determinations, the "cup funnel" is attached to a suction flask, the use of which materially diminished the time required for filtration (for arrangement of this apparatus see description and figure given in "The determination of Magnesium," described further on).

Winkler found that the precipitate obtained from a very acid solution contains barium hydrosulphate which gives low results. He established a table of correction factors for the precipitates obtained from solutions of varying acidity. This table shows that the weight of precipitate obtained from a neutral solution requires no correction, if the precipitate is ignited. It also shows that if the sulphate is precipitated from a solution containing 2.25 cc. of tenth-normal  $\text{HCl}$  per 100 cc. (0.00225 normal) and the precipitate collected and dried according to Winkler's procedure ("cup funnel" method), the results so obtained require no correction.<sup>4</sup>

<sup>1</sup> *Zeitschrift für angewandte Chemie*, **30**, **I**, 251-252, 259-260, 301-303 (1917). Winkler and his coöperators investigated the composition and amount of precipitate obtained from neutral solutions and solutions of varying degrees of acidity and also from solutions containing other salts beside the sulphate.

<sup>2</sup> Five cc. of a 10 per cent solution of  $\text{BaCl}_2$  are originally recommended by Winkler. A weaker solution, however, has been preferable in this work as it dealt in many cases with small amounts of  $\text{SO}_4^{2-}$ ; an excess of  $\text{SO}_4^{2-}$  as compared to  $\text{Ba}^{++}$  was found to be essential in order to obtain a crystalline precipitate.

<sup>3</sup> In this work a weighing bottle was used which had a single perforation through the upper part of the bottle and the lid (see Fig. 4).

<sup>4</sup> The following analyses performed by this method yielded slightly higher results.

In some cases the sulphate was determined according to the commonly used procedure which consists of igniting the precipitate. The precipitate was obtained from a neutral solution requiring no correction after ignition.

3. *Magnesium Determination.*—In determining the magnesium content of magnesium sulphate or its solutions the method of Winkler (Budapest),<sup>1</sup> slightly modified, was used. The magnesium is precipitated as magnesium-ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) under conditions yielding a crystalline precipitate which may be easily collected on cotton, dried over  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (having the same vapor pressure as  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) and weighed. The original procedure is as follows:

A quantity of the salt corresponding to not more than 0.05 Gm. of magnesium, and 3 Gm. of ammonium chloride is dissolved in 100 cc. of water in a beaker and heated to boiling. The solution is then removed from the source of heat and mixed with 10 cc. of a 10 per cent ammonia water and 10 cc. of a 10 per cent solution of secondary sodium phosphate (10 Gm. of  $\text{Na}_2\text{HPO}_4 \cdot 10\text{H}_2\text{O}$  and water to make 100 cc.), the latter being added in a thin stream from a burette, while agitating.

The precipitate is at first amorphous but upon standing about fifteen minutes begins to assume a crystalline form. The conversion into the crystalline form is completed in from two to three hours if the directions have been carefully followed. The precipitate is allowed to stand in the beaker for twenty-four hours at a temperature of from  $16^\circ$  to  $18^\circ$  C. After this time the crystalline precipitate is collected on a pledget of cotton placed in a "cup funnel."<sup>2</sup> In collecting the precipitate the supernatant liquid is first decanted through the cotton pledget in the "cup funnel" and subsequently the precipitate remaining in the beaker is mixed with 1 per cent ammonia water and the whole transferred to the funnel. If the directions for the precipitation of the magnesium have been followed rigidly, the filtrate will be clear from the first. About 50 cc. of 1 per cent ammonia water are used for washing the beaker and precipitate. Finally the precipitate is washed with two 10-cc. portions of recently distilled methyl alcohol, the first portion being used to wash the precipitate, while gently stirred with a glass rod, and the second to wash back into the funnel the particles clinging to the rod. The funnel and contents are then dried over  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  for twenty-four hours at a temperature of from  $20^\circ$  to  $25^\circ$  C. and finally weighed in a weighing bottle of proper size after standing for ten minutes in the balance case. From this result is calculated the amount of magnesium salt present in the analyzed solution. Prior to the collection of the precipitate the funnel and the cotton pledget are washed with diluted ammonia water and subsequently with recently distilled methyl alcohol, the alcohol removed by drawing air through the funnel by means of suction and the funnel and cotton then dried for twenty-four hours over  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and then weighed as already mentioned.

In applying this method for the analysis of solutions resulting from solubility determinations of magnesium salts, the procedure is slightly modified, in so far as the drying of the precipitate is concerned. Air, entering through a tower filled<sup>3</sup>

<sup>1</sup> *Zeitschrift für angewandte Chemie*, 31, I, 211-212 (1918).

<sup>2</sup> See Figs. 3 and 4 and for description under: "Sulphate Determination."

<sup>3</sup> This device was used by Winkler later on, as told to one of the authors Dr. Schulek, a former assistant of Winkler.

with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , is drawn through the funnel and contents until they become of a constant weight. This treatment materially shortens the time of drying. The drying requires but one or two hours as compared with twenty-four hours in the original procedure.

The apparatus used for filtering and drying the  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is illustrated in the sketch on page 763 (Fig. 5).

*A* is a suction flask attached to the pump. The flask is stoppered with a rubber stopper having a single perforation to hold the "cup funnel" *B*, the stem of which slides into a tube of slightly larger diameter, which nearly reaches to the bottom of the suction flask. The arrangement thus far described is used in the actual filtration. After the precipitation is collected, the cylinder *C* is slipped over the funnel. This cylinder is closed at the other end by a rubber stopper which is perforated to allow the entrance of a glass tube, so bent that the incoming air will not be blown directly on the precipitate. The other end of the glass tube is connected, by rubber tubing, with the tower *D*, which is filled with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The suction pump is then turned on and the precipitate is dried to a constant weight.

#### TEST AND ANALYSIS OF THE MAGNESIUM SULPHATE USED FOR THE EXPERIMENTS.

The magnesium sulphate used in the solubility determinations met the U. S. P. X requirements for purity and yielded the following quantitative results:

TABLE I.—RESULTS OF THE QUANTITATIVE ANALYSIS OF THE MAGNESIUM SULPHATE HEPTAHYDRATE USED FOR THE SOLUBILITY DETERMINATIONS.

Method of analysis.	Gm. of magnesium sulphate taken.	Gm. of . . . . . obtained.	Equal to Gm. of magnesium sulphate.	Per cent magnesium sulphate.
"Residue method"	0.5652	0.2851 residue	0.2851	50.44
	0.5276	0.2661 residue	0.2661	50.43
"Sulphate method"				
BaSO <sub>4</sub> precipitated from neutral solution and ignited	0.25974 <sup>1</sup>	0.2543 BaSO <sub>4</sub>	0.1311	50.49
	0.25974	0.2548 BaSO <sub>4</sub>	0.1314	50.59
	0.25974	0.2561 BaSO <sub>4</sub>	0.1321	50.84
"Sulphate method" (Winkler)	0.25974	0.2559 BaSO <sub>4</sub>	0.1320	50.80
	0.25974	0.2559 BaSO <sub>4</sub>	0.1320	50.80
	0.25974	0.2560 BaSO <sub>4</sub>	0.1320	50.82
"Sulphate method" (Winkler-Schulek) <sup>2</sup>	0.2874	0.2836 BaSO <sub>4</sub>	0.1463	50.89
	0.2160	0.2131 BaSO <sub>4</sub>	0.1099	50.88
"Magnesium method" (Winkler)	0.25974	0.2684 $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	0.1316	50.67
	0.25974	0.2682 $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	0.1315	50.63

<sup>1</sup> Ten-cc. portions of a solution of 2.5974 Gm. of magnesium sulphate in 100 cc. were taken for these analyses.

<sup>2</sup> This is a slightly modified form of Winkler's original method. *Zeitschrift für angewandte Chemie*, 33, I, 59-60, 159-160, 162-163 (1920).

Magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) contains theoretically 48.84 per cent of  $\text{MgSO}_4$ . The salt under examination was slightly effloresced.

#### SOLUBILITY OF MAGNESIUM SULPHATE HEPTAHYDRATE IN WATER AT 25° C.

Four separate solutions were prepared for the solubility determination of magnesium sulphate in water. Experiments I and III were prepared at room temperature, thereafter reaching the saturation point from undersaturation; Experi-

ments II and IV were prepared by boiling solute and solvent in the way described in the introduction. The solutions of Experiments I and II were analyzed by the residue method and the solutions of Experiments III and IV by Winkler's methods for sulphate and magnesium. The results conform closely.

TABLE II.—RESULTS OF THE SOLUBILITY DETERMINATION OF MAGNESIUM SULPHATE HEPTAHYDRATE ( $MgSO_4 \cdot 7H_2O$ ) IN WATER AT 25° C.

Stated as Percentage of Solute in Solution.

Experiments.	Method of analysis.	Time of preparing solution, days.				
		1.	3.	7.	12.	14.
I		...	54.67	...	...	...
Prepared by undersaturation method	"Residue" method	...	54.83	...	...	...
II						
Prepared by supersaturation method	"Residue" method	...	54.76	...	...	...
III						
Prepared by undersaturation method	"Sulphate" method (Winkler)	...	...	...	54.44	...
	"Magnesium" method (Winkler)	...	...	...	54.45	...
	"Sulphate" method (Winkler)	...	...	...	54.43	...
	"Magnesium" method (Winkler)	...	...	...	54.37	...
IV						
Prepared by supersaturation method	"Sulphate" method (Winkler)	55.53	...	54.42	...	54.45
	"Magnesium" method (Winkler)	...	...	...	...	54.43
	"Sulphate" method (Winkler)	...	...	54.41	...	54.38
	"Magnesium" method (Winkler)	...	...	...	...	54.39

The average of all the results stated in this table is 54.57.

*Conclusion.*—54.57 Gm. of  $MgSO_4 \cdot 7H_2O$  are present in 100 Gm. of an aqueous solution, saturated at 25°C.

*Therefore:* One gram of  $MgSO_4 \cdot 7H_2O$  is soluble in 0.835 cc. (= 0.833 Gm.) of water at 25° C. (Density of water 25°/4° = 0.9970.)

This result is not in accordance with the statement of the U. S. P. X which states: One Gm. of Magnesium Sulphate is soluble in 1.3 cc. of water at 25° C.

Other statements:

Seidell, "Solubilities of Inorganic and Organic Substances," 1907:

38.5 Gm. of  $MgSO_4$  per 100 Gm. of water at 25° C., which is equal to

56.92 Gm. of  $MgSO_4 \cdot 7H_2O$  in 100 Gm. of solution.

"Handbook of Chemistry and Physics" (13th edition):

26.2 Gm. of  $MgSO_4$  in 100 Gm. of solution at 20° C.

29.0 Gm. of  $MgSO_4$  in 100 Gm. of solution at 30° C.

Interpolated solubility value for 25° C.:

27.6 Gm. of  $MgSO_4$  or

56.51 Gm. of  $MgSO_4 \cdot 7H_2O$  in 100 Gm. of solution.

"Chemiker Kalender," 1929 (vol. II, 329):

26.8 Gm. of  $MgSO_4$  or

54.88 Gm. of  $MgSO_4 \cdot 7H_2O$  in 100 Gm. of solution at 25° C.

SOLUBILITY OF MAGNESIUM SULPHATE HEPTAHYDRATE IN GLYCERIN AT 25° C.

The magnesium sulphate used in this determination was taken from the same specimen as in the determination of the water solubility. The glycerin



used in this determination conformed with the requirements of the U. S. P. X. The specific gravity was found to be  $1.250 \frac{25^\circ}{25^\circ}$  which is equivalent to a density of  $1.246 \frac{25^\circ}{4^\circ}$ .

The solution in Experiment I was prepared by the undersaturation method finely powdered magnesium sulphate being used. This mixture was shaken by hand, the mechanical agitation apparatus not having been constructed at this time. The solution was analyzed gravimetrically, the sulphate being determined as  $\text{BaSO}_4$ . Analysis of the solution after a period of 24 days showed a slight increase (see Table III) of the concentration as compared with the solution analyzed 11 days after its preparation. The slight increase is probably due to the fact that the solution was shaken by hand and thereby did not become completely saturated. To determine the saturation point other experiments were made. In Experiments II and III a mechanical agitation device was applied. The solution in Experiment II was prepared at room temperature and the solution in Experiment III was heated and then cooled to  $25^\circ \text{C}$ . while being agitated. The solutions were analyzed by Winkler's methods for the determination of sulphate and magnesium (already described).

TABLE III.—RESULTS OF THE SOLUBILITY DETERMINATION OF MAGNESIUM SULPHATE HEPTAHYDRATE ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) IN GLYCERIN AT  $25^\circ \text{C}$ .

Experiments.	Method of analysis.	Time of preparing solution, days.			
		7.	11.	17.	24.
I					
Prepared by undersaturation method	$\text{BaSO}_4$ precipitated from slightly acid solution and ignited	...	35.61	...	36.02
		...	34.97	...	36.37
II	"Sulphate" method	42.99	...	...	...
Prepared by undersaturation method	(Winkler)	42.75	...	...	...
	"Magnesium" method	42.80	...	...	...
	(Winkler)	42.78	...	...	...
III	"Sulphate" method	42.82	...	42.40	...
Prepared by supersaturation method	(Winkler)	42.82	...	42.40	...
				42.33	
	"Magnesium" method	42.03	...	42.25	...
	(Winkler)	42.56	...	42.29	...

The average of the results of the saturated solutions, from Experiment II (7 day time interval) and Experiment III (7 and 17 day time interval) is 42.56.

*Conclusion.*—42.56 Gm. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  are present in 100 Gm. of a glycerin solution, saturated at  $25^\circ \text{C}$ .

*Therefore:* One Gm. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is soluble in 1.08 cc. of glycerin (= 1.35 Gm.) at  $25^\circ \text{C}$ . (density of glycerin at  $25^\circ = 1.246$ ).

This result is in accordance with the statement of the U. S. P. X which states:

One gram of Magnesium Sulphate is soluble in about 1.1 cc. of glycerin at  $25^\circ \text{C}$ .

However, from theoretic consideration, there should be no true equilibrium between  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and glycerin, as the system consists of four phases:  $\text{MgSO}_4$ ,  $\text{H}_2\text{O}$ , glycerin and water vapor. A variation in the excess of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  should accordingly cause variation in the solubility, for the water of crystallization is

partially absorbed by the glycerin, acting as a diluent. But contrary to theory the results of the Experiments II and III, of which the latter actually contained much larger an excess of solute, conformed closely. This would show that the tension of  $MgSO_4 \cdot 7H_2O$  to retain its water of crystallization is greater than the tension of glycerin to absorb water.

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### SOME ANALYTICAL ASPECTS OF COD LIVER OIL.\*

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The important place which cod liver oil has attained in the prevention or treatment of certain deficiency diseases is now uncontested.

Little is to be found in the literature, however, on some of the lesser known properties of this oil and a study of a few of these properties brought out some interesting facts which form the basis of this paper.

All results listed below were obtained on good medicinal grade cod liver oil, from which the "Stearin" had been removed.

#### SPECIFIC GRAVITY AND VISCOSITY, IODINE AND SAPONIFICATION VALUES.

A preliminary examination of an average sample of Newfoundland cod liver oil gave the following results:

Specific gravity at $\frac{25^\circ \text{C.}}{25}$	0.9221
Hanus Iodine Value	157.2
Viscosity at $100^\circ \text{F.}$ (Saybolt Universal Viscosimeter)	160 sec.
Saponification Value	186.1

#### UNSAPONIFIABLE MATTER.

The method used for the determination of the unsaponifiable residue was the official one given in the "Methods of Analysis of the A.O.A.C.," 1925 edition and gave for per cent of unsaponifiable matter: 0.88.

During this test care must be exercised to prevent oxidation after evaporation of the alcohol, especially since a double saponification is nearly always advisable if accurate results are desired. In this respect, the U. S. P. method is not believed to yield sufficiently exact figures and should be amended to include resaponification of the residue obtained after hydrolysis of the oil.

#### ACETYL VALUE.

The acetyl value, defined as the number of mg. of potassium hydroxide required for the neutralization of the acetic acid obtained on saponifying 1 Gm. of the acetylated fat, was determined next, the filtration method described by Lewkowitsch (1) being used.

The figures obtained were: Apparent acetyl value: 11.1; true acetyl value: 8.7.

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\* Scientific Section, A. Ph. A., Portland meeting, 1928.