6. The value of ΔF at 25°, calculated from the heat of reaction and the entropy, is —33,600 cal.

7. The free energy of formation of $^1/_6(HF)_6$ is calculated to be —35,000 cal. at 25°, based upon the value —31,800 for monomolecular hydrogen fluoride.

Berkeley, California

[Contribution from the Havemeyer Chemical Laboratory, New York University]

THE MUTUAL SOLUBILITY OF LIQUIDS. III. THE MUTUAL SOLUBILITY OF PHENOL AND WATER. IV. THE MUTUAL SOLUBILITY OF NORMAL BUTYL ALCOHOL AND WATER

By Arthur E. Hill and William M. Malisoff[1]

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In an earlier publication[2] a new method was described for determining the mutual solubility of liquids by measuring the volumes of the two phases which result when the two components are put together in two different but known ratios by weight. If m represent the weight of one component taken for an experiment, a and b the volumes of the two phases resulting, x its concentration in g. per cc. in one phase and y its concentration in the second; and if the same symbols, written primed, be used for the second experiment, it follows that $ax + by = m$ and $a'x + b'y = m'$; from these simultaneous equations the concentrations x and y in g. per cc. can be calculated. If the weights of the second component, n and n', be now inserted in two similar equations, the concentration also of that component in each phase becomes known. By addition of the weights of the two components found in 1 cc. of each phase, the density of the phases also is found.

This method has recently been used by Kablukov and Malischeva[3] for measuring the mutual solubility of ether and water and of *iso*-amyl alcohol and water. The authors also include in their paper a general critique of the method, in which three principal points are raised; first, that the method does not require for accuracy such large volumes (100 to 400 cc.) as were used in our initial experiments;[2] second, that the apparent agreement between experimental results in a series of determinations depends upon the choice of the experiments taken for combination in the simultaneous equations; and third, that the inherent accuracy of the method is influenced largely by the relative weights (or volumes) of the com-

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[1] The material of this paper is part of a thesis presented by William M. Malisoff to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hill, This Journal, **45**, 1143 (1923).

[3] Kablukov and Malischeva, *ibid.*, **47**, 1553 (1925).

ponents taken for the experiments. With each of these statements we are in agreement; it seems to us, however, that only the third is of importance.

With respect to the use of smaller volumes, we have already[4] called attention to the surprising accuracy that can be obtained with the use of 100cc. graduated cylinders. In the present report, we have in every case carried out preliminary experiments with still smaller volumes, namely, something less than 50 cc. in each of the tubes, which were ordinary graduated eudiometers, and the results fell usually within a few tenths of one per cent. of those obtained with the special two-bulbed solubility bottles of 400cc. total capacity. The graduated eudiometers, or some similar device, are essential where the solubilities are wholly unknown, since the special bottles permit of only a few cubic centimeters of variation in the volumes of the two phases at equilibrium; they also permit the choice of optimum volumes, as will be shown later. The simple tubes are, however, awkward to tumble in a thermostat, and will give less reliable results where any tendency toward emulsification exists, as will be pointed out in the work on phenol and water. The special two-bulbed flasks of suitable volume ratio are preferable, in our estimation, wherever high accuracy is desired, which follows from the facts that the relative error in reading volumes becomes less as the total volumes increase and that the surface, which doubtless tends to hold small amounts of the wrong phase, also becomes relatively less as the volumes increase.

With regard to the choice of experiments for pairing in the simultaneous equations given above, it is obvious that the most probable result would be obtained by solving all existing combinations as pairs for a given temperature and weighting according to the method of least squares. Where conditions for the method are favorable, however, the differences between the various pairs of equations have been found to amount to but a few hundredths of one per cent.; it has not seemed advisable to us to try the more refined method of averaging.

The third point raised by Kablukov and by Malischeva—the choice of suitable relative weights of components—has been under investigation in this Laboratory for some time. The above named authors have offered no suggestion as to the best quantities to be taken. It is obvious that if two experiments were run with the components in the same ratio, the mathematical expressions would be identities and could not be solved; if the ratios were very close to each other, small errors in reading would lead to wide differences in the mathematical solution, and the same would be true if the quantity of one phase were made very small. It is possible, however, by mathematical analysis to deduce the optimum quantities of the components to be taken, so that errors in reading will affect the solution least. The following is a generalized solution of this problem.

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[4] Ref. 2, p. 1145.

Assuming for the sake of simplicity that in the two necessary solubility determinations the volumes of the two phases found in one vessel shall be exactly reversed in the second, let v equal the one volume found and kv the other. It is desired to find the value of k (the ratio of the two volumes) for optimum conditions, that is, conditions in which a small error in reading will make the minimum error in the solubilities determined. The two fundamental equations, previously given, now become

$$kvx + vy = m \qquad (1)$$

$$vx + kvy = m' \qquad (2)$$

whence

$$x = \frac{mk - m'}{v(k^2 - 1)} \qquad (3)$$

Differentiating

$$\frac{dx}{dk} = \frac{m(k^2 - 1) - 2\,k\,(mk - m')}{v(k^2 - 1)^2} \qquad (4)$$

Letting $dx/dk = 0$, for the optimum condition, we obtain $k = \infty$ and $v = \infty$, both of which are absurd in terms of an experiment, and also obtain the value

$$m(k^2 - 1) = 2\,k(mk - m') \qquad (5)$$

whence

$$k = \frac{m'}{m} \pm \sqrt{\left(\frac{m'}{m}\right)^2 - 1} \qquad (6)$$

The foregoing gives the optimum volume ratio k only in terms of the masses of one component taken (m and m'). In order to determine what these masses should be the following steps are necessary. Let p_1, p_2, p_3 and p_4 be the weights of the component in the four phases obtained; then

$$m = p_1 + p_2 \qquad (7)$$

$$m' = p_3 + p_4 \qquad (8)$$

and since the concentrations in the corresponding phases are equal

$$p_1/kv = p_3/v \qquad (9)$$

$$p_2/v = p_4/kv \qquad (10)$$

Now let ρ represent the distribution ratio by weight of the chosen component between the two phases at equilibrium; then

$$p_1/kv = p_2/\rho v \qquad (11)$$

$$p_3/v = p_4/\rho kv \qquad (12)$$

Substituting in Equation 6 the values for m'/m obtained from Equations 7, 8, 11, 12, we have

$$k = \rho \qquad (13)$$

whence it follows that the optimum volume ratio to be chosen (k) for a given component is the distribution ratio by weight of the component between the two phases. The optimum ratios for the two components will of course not be the same, but as it is generally true that the mutual solubilities are of the same order of magnitude, the ratios ordinarily will not vary widely. According to the demands of the case one may therefore choose some intermediate ratio as sufficiently good for both components, or may conduct separate pairs of experiments for each component.

III. The Mutual Solubility of Phenol and Water

The phenol used was Merck's "Recrystallized Phenol U. S. P.," purified by distillation with a 5-bulb still-head to remove water, the principal impurity and traces of organic materials. By using a slow distillation it was possible to obtain large fractions boiling within 0.1°. The criterion of purity used was a constant melting point obtained after refractionation, in a melting-point apparatus designed so as to exclude moisture; it consisted of a Beckmann freezing-point tube with mercury-sealed stirrer, with an air train through which aspirated air was passed successively over calcium chloride, sulfuric acid and phosphorus pentoxide. The melting points of the various samples used was 40.92 ± 0.01°, corrected (0.06°) for emergent stem of a standardized thermometer. This value is in excellent agreement with the careful determination of Leroux[5] (40.85°, uncorr.; 41.00°, corr.) and very close to that found by other careful workers. The only higher values we have found are Kremann's[6] (41.0°) and Burr and Gortner's[7] (42.6°); the latter figure is so much above any other authentic figure (1.6° difference) that we are inclined to believe it in error. The great majority of investigators have reported melting points between 40.5° and 40.8°; the slightly low values are probably due to traces of water, by which the melting point is lowered about 4° for 1% of water. Our samples were kept in Pyrex flasks tightly stoppered and with a tin-foil wrapping over the cork, the flasks being stored in a large desiccator over phosphorus pentoxide; their melting points were checked before each weighing. On account of the difficulty in transferring the solid phenol to the solubility flasks, standard solutions were made up synthetically containing from about 87 to 90% of phenol, which remained liquid at all laboratory temperatures.

Preliminary solubility measurements were made in eudiometers, in order to determine the densities of the solutions with sufficient accuracy to permit the later use of the two-bulbed solubility flasks. In these preliminary experiments the accuracy obtained was not at all satisfactory; the tendency to emulsification, which makes even the later large-scale determinations of lessened accuracy, was here so pronounced as to cause the results to be in error as much as 1%. With the densities approximately determined, however, a number of solubility measurements were made using the special solubility flasks described in an earlier paper,[2] having the two bulbs of about 300 cc. and 100 cc. capacity. In the range of temperatures covered (20° to 35°) the optimum volume ratio for the phenol, calculated as given above, varies from 7.14 to 9.14, and the optimum volume ratio for the water from 2.68 to 3.16; the ratio used, 3.0, is very close to the optimum for water. The flasks were rotated very cautiously in order to reduce the amount of emulsification, and were allowed to stand for many hours in order to promote settling; further, it was found advisable to approach saturation from lower temperatures only, since cooling gave emulsions which did not clear for days. Despite these precautions, the results obtained, as shown in Lines 1 to 4 of Table I, lack the high precision of the data obtained by this method for ether and water and for the case of *n*-

[5] Leroux, *Compt. rend.*, **163**, 361 (1916); *J. pharm. chim.*, **20**, 88 (1919).

[6] Kremann, Odelga and Zawodsky, *Monatsh.*, **42**, 117 (1921).

[7] Burr and Gortner, THIS JOURNAL, **46**, 1240 (1924).

butyl alcohol and water given later in this paper; it is clear that the method is not at its best in this case.

In addition to the thermostatic determinations between 20° and 35°, experiments by the plethostatic method of Alexejeff[8] were carried out at higher temperatures up to the consolute point, 66°; for these higher temperatures it has been pointed out that our indirect volumetric method is not suited, because of the high pressures developed. In accordance with the usual practice, total weights of 2.5 to 4.0 g. of phenol (in the standard solution) and of water were weighed into small glass tubes, sealed and rocked in a well-stirred bath which was slowly heated or slowly cooled; the temperature of the disappearance or appearance of turbidity was noted The results are given in Lines 5 to 17 of Table I.

TABLE I

MUTUAL SOLUBILITY OF PHENOL AND WATER

		Phenol phase		Water phase	
No.	Temp., °C.	Weight % of phenol	Density	Weight % of phenol	Density
1	20	72.16	1.0541	8.36	1.0018
2	25	71.28	1.0469	8.66	1.0045
3	30	69.90	1.0429	9.22	1.0039
4	35	67.63	1.0405	9.91	0.9974
5	54.83	59.22	....	...	....
6	57.30	...	....	14.87	....
7	59.20	55.76	....	...	....
8	62.55	51.87	....	...	....
9	62.74	...	....	19.35	....
10	65.24	44.09	....	...	....
11	65.79	...	....	27.77	....
12	66.01	...	....	29.13	....
13	65.79	...	....	30.21	....
14	65.90	...	....	31.35	....
15	65.84	...	....	32.23	....
16	65.86	...	....	32.79	....
17	65.84	34.23	....	...	....

The results of Lines 1 to 4, done by the volumetric method and in duplicate (20° and 35°) are 2 to 3% divergent from the erratic results of Scarpa,[9] but agree with those of Rothmund,[10] the only other existing data at these temperatures, with an average deviation of 0.14% in the water phase and 0.23% in the phenol phase. As stated above, the emulsification of this system prevents a more accurate determination by our method, and it is to be regretted that the solubilities at these temperatures cannot yet be said to be known with satisfactory accuracy.

The experiments of Lines 5 to 17 were conducted by the method of Alexe-

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[8] Alexejeff, *Wied. Ann.*, **28**, 305 (1886).

[9] Scarpa, *J. chim. phys.*, **2**, 447 (1904).

[10] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

jeff in order to determine the consolute temperature and concentration and the shape of the curve in the consolute region, concerning each of which there has been considerable doubt. As collated in the International Critical Constants,[11] the consolute temperature has been given at temperatures from 65.3° to 70.7°. As shown in Fig. 1, our results give the consolute concentration as 34.0%, and the consolute temperature as 65.85 ± 0.15°. This falls close to the values of Scarpa[9] (65.8°C.), of Friedländer[11] (66.06°) and of Timmermans[12] (66.09°), who has revised his earlier value[11] of 65.3°, the only determination found lower in temperature than our own. We are inclined to account for the higher figures more frequently given as due to high pressures developed in the small tubes. It has been the usual practice in experimenting by Alexejeff's method to fill the tubes as full as possible, in order to avoid change in composition of the liquid phase through volatilization. Under this condition the expansion of the liquid at higher temperatures may completely fill the tube and lead to extraordinarily high pressures

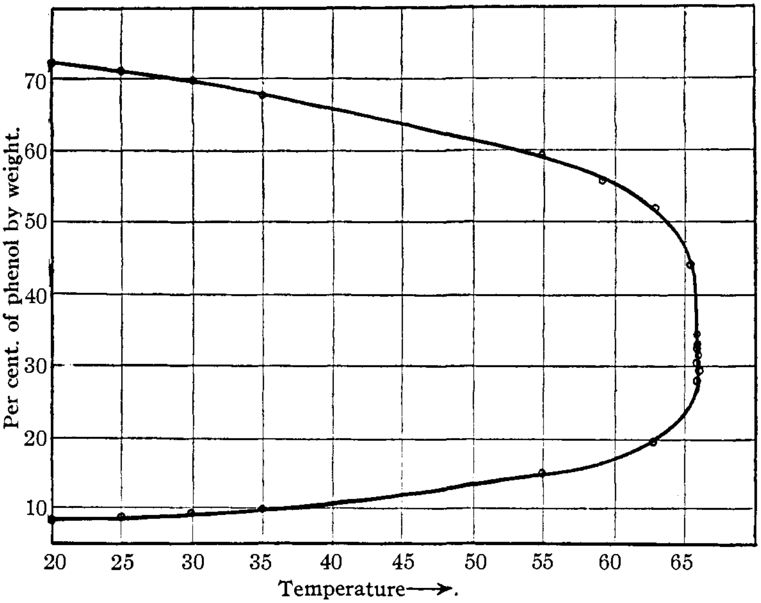

Fig. 1.—Solubility of phenol and water.

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[11] "International Critical Constants," Washington (in preparation). The references are as follows. Ref. 8. Ref. 10. Schreinemakers, *Z. physik. chem.*, **29**, 579 (1899). Friedländer, *ibid.*, **38**, 389 (1901). Ref. 9. Timmermans, *Z. physik. Chem.*, **58**, 184 (1907). Smits and Maarse, *Verslag. Akad. Wetenschappen Amsterdam*, **14**, 194 (1911). Dubrisay and Toquet, *Bull. soc. chim.*, **25**, 354 (1919). Rhodes and Markley, *J. Phys. Chem.*, **25**, 527 (1921). Leone and Angelesio, *Gazz. chim. ital.*, **52**, 63 (1923).

[12] Timmermans, *J. chim. phys.*, **20**, 491 (1923).

which the small tubes are able to withstand without bursting. As an example of this, a tube so filled by us as to leave no free space upon heating gave a consolute temperature of 66.79°, nearly a degree above what we believe to be the true temperature; since Timmermans[12] has found the change of consolute temperature to be 0.00456° for 1 kg. pressure per sq. cm., it is clear that changes of one or two degrees could result only from enormous pressures, yet we are of the opinion that many determinations suffer from an error due to this cause. We have left a volume of about 0.5 cc. in each of our experiments in order to avoid this source of error, and believe that our value is nearly correct; Rothmund's value[11] of 68.4° is most frequently quoted in the literature, and is surely in error to the amount of over 2°.

With respect to the shape of the solubility curve in the consolute region, it appears to be parallel to the solubility axis, within the error of experimentation, between about 28% phenol and 36% phenol. Friedländer's values[11] show the same blunt end to the curve; no others of the investigators give sufficient points in this region to permit an accurate plot. The diameter gives the consolute concentration as 34% phenol.

IV. The Mutual Solubility of *n*-Butyl Alcohol and Water

Although *n*-butyl alcohol has now been on the market for some years as a solvent, we have not been able to find measurements of its mutual solubility with water in the periodical literature save in one determination at 25° noted later.

Our material was obtained from the Eastman Kodak Company, and was first refluxed with lime and then treated with small amounts of sodium to remove water, with which it forms an azeotropic solution boiling at 92°. The dried material was then repeatedly fractionated with a 5-bulb still-head, until a fraction was obtained boiling *wholly* within 0.1°, namely, at 117.70° to 117.80° corrected; this temperature is in close agreement with the figures of Reilley and Ralph[13] (117.6°), Kahlbaum and Arndt[14] (117.6°), and of Brunel, Crenshaw and Tobin.[15] The value of Lieben and Rossi,[16] 117.1° at 740 mm. pressure, becomes nearly 117.8° when corrected to 760 mm.

Measurements by our volumetric method were made at intervals of 5° or 10° between 5° and 80°, using volumes of 50 cc. in eudiometers; those from 5° to 40° were used as guides for later determinations in the large flasks of 400 cc. capacity. It was found that the determinations with the smaller volumes varied irregularly from those with the larger volumes by amounts from 0.03 to 0.28%, the average being 0.12%. We are prepared to say, therefore, in partial agreement with the views of Kablukov and Malischeva, that in suitable cases a volume of 50 cc. will give results not

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[13] Reilley and Ralph, *Sci. Proc., Roy. Dublin Soc.*, **15**, 597 (1919).

[14] Kahlbaum and Arndt, *Z. physik. Chem.*, **26**, 577 (1898).

[15] Brunel, Crenshaw and Tobin, THIS JOURNAL, **43**, 561 (1921).

[16] Lieben and Rossi, *Ann.*, **158**, 137 (1871).

further than 0.3% from those obtained by the more tedious but more accurate use of large volumes.

The complete values for the solubility of this pair are given in Table II. The results of Lines 1 to 8 are by the volumetric method, using total volumes of 400 cc. and a ratio[17] of 3:1; those of lines 9 to 12 are by the same method, using volumes of 50 cc. and a volume ratio of about 3:1; those of Lines 13 to 23 are by the Alexejeff plethostatic method.

TABLE II

MUTUAL SOLUBILITY OF *n*-BUTYL ALCOHOL AND WATER

		Alcohol phase		Water phase	
No.	Temp., °C.	Wt. % of alcohol	Density	Wt. % of alcohol	Density
1	5	80.38	0.8598	9.55	0.9883
2	10	80.33	.8567	8.91	.9877
3	15	80.14	.8533	8.21	.9881
4	20	79.93	.8484	7.81	.9873
5	25	79.73	.8450	7.35	.9865
6	30	79.38	.8424	7.08	.9851
7	35	78.94	.8397	6.83	.9835
8	40	78.59	.8345	6.60	.9841
9	50	77.58	.8307	6.46	.9799
10	60	76.38	.8253	6.52	.9766
11	70	74.79	.8200	6.73	.9721
12	80	73.53	.8159	6.89	.9675
13	92.0	69.24	....	...	....
14	97.9	...	....	8.74	....
15	106.1	63.88	....	...	....
16	114.5	...	....	12.73	....
17	116.9	...	....	13.46	....
18	122.3	49.85	....	...	....
19	123.3	...	....	19.73	....
20	124.33	42.02	....	...	....
21	124.83	...	....	27.26	....
22	125.10	...	....	32.82	....
23	125.15	32.82	....	30.44	....

We have found only a single determination to bring into comparison with the above figures, namely, that of Reilley and Ralph;[18] at 20° they found the *n*-butyl alcohol content of the two phases to be 79.93% and 7.90%, the former value being identical with ours and the latter 0.09% higher. Linnemann[18] gives rough figures at 15° and 22° expressed in volumes; these are of the same general order of magnitude as ours, but cannot be recalculated to the same units.

The values of Table II are plotted in Fig. 2 as Curve I. The two-liquid system begins at the quadruple point, which we determined as —2.95°,

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[17] The optimum ratios, calculated as given above, are 8.4 to 11.9 for the butyl alcohol, and 4.1 to 4.36 for the water.

[18] Linnemann, *Ann.*, **161**, 191 (1872).

and ends at 125.15°; the consolute solutions have, at this point, a concentration of 32.5% of *n*-butyl alcohol, as found by extrapolating the diameter of the curve. The curve shows a minimum at about 55°; a maximum was not found.

In the same diagram are plotted the solubility curves of the two isomers, *iso*butyl alcohol and *sec.*-butyl alcohol; the *tert.*-butyl alcohol is soluble in water in all proportions. The two curves are averaged curves prepared for "International Critical Constants:" that for *iso*butyl alcohol is based upon the work of Alexejeff[8] and of Verschaffelt,[19] that for *sec.*-butyl alcohol upon the work of Alexejeff,[8] Timmermans,[20] and Dolgolenko.[21] The curve for the normal alcohol falls in the main between the other two curves, but crosses that for *iso*butyl alcohol at about 70° on the side of the water-rich phase. The estimate of Orton and Jones[22] that the consolute point for the normal alcohol would be found above 150°, some 20° above that of the *iso*butyl alcohol, is found to be in error by 25°.

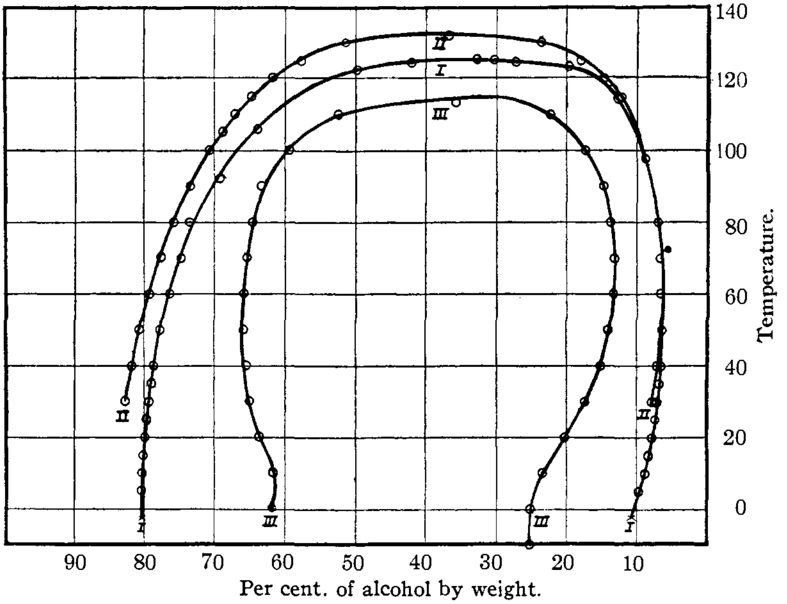

Fig. 2.—Solubility of butyl alcohols and water. Curve I, *n*-butyl alcohol. Curve II, *iso*butyl alcohol. Curve III, *sec.*-butyl alcohol.

Summary

1. It is shown that for solubility determinations by the indirect volumetric method, the optimum volume ratio for determining a given com-

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[19] Verschaffelt, *Rec. trav. chim.*, **42**, 683 (1923).

[20] Timmermans, *Thesis*, Brussels, **1911**; *Z. physik. Chem.*, **58**, 129 (1907).

[21] Dolgolenko, *Z. physik. Chem.*, **62**, 499 (1908).

[22] Orton and Jones, *J. Chem. Soc.*, **115**, 1194 (1919).

ponent is the ratio of its distribution by weight between the two phases.

2. The mutual solubility of phenol (m. p., 40.92° ± 0.01) and water has been redetermined between 20° and the consolute temperature; this has been found to be 65.85° ± 0.15° and the consolute concentration is 34% of phenol.

3. The mutual solubility of normal butyl alcohol (b. p., 117.7–117.8°) has been determined between the temperature of the quadruple point, —2.95°, and the consolute temperature, 125.15°; the consolute concentration is 32.5% of *n*-butyl alcohol.

New York, N. Y.

[Contribution from the Chemical Section, Physical Chemical Unit, Pittsburgh Experiment Station, Bureau of Mines, United States Department of Commerce]

THE SOLUBILITY OF CALCIUM SULFATE AT BOILER-WATER TEMPERATURES[1,2]

By R. E. Hall,[3] J. A. Robb[4] and C. E. Coleman[5]

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The solubility of gypsum has received much attention, and the values are well established. The solubility of those phases of calcium sulfate that may exist at the temperatures of boiler waters has long needed direct determination to substantiate the data of the literature.

The Solid Phase in Equilibrium with the Solution

A number of investigators[6] have described different forms of anhydrous calcium sulfate; van't Hoff and co-workers,[7] however, recognized but two forms, and showed the transition temperatures between them and gypsum to be 66° for gypsum-natural anhydrite, and 89° for gypsum-soluble anhydrite. They assert that gypsum and natural anhydrite are the only forms of calcium sulfate that are stable in the presence of solution, and the

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[1] Published with the approval of the Director, U. S. Bureau of Mines.

[2] This work was done in part in the coöperative investigation of boiler-water conditioning by the Bureau of Mines and the Hagan Corporation of Pittsburgh, Pa., and in part as a fellowship problem of the coöperative arrangement between the Bureau of Mines and the Carnegie Institute of Technology.

[3] Physical Chemist, Pittsburgh Station, U. S. Bureau of Mines.

[4] Carnegie Institute Fellow.

[5] Chemist, Hagan Corporation.

[6] Shenstone and Cundall, *J. Chem. Soc.*, **53**, 544 (1888). Lacroix, *Compt. rend.*, **126**, 360, 553 (1898); *Bull. soc. franç. mineral.*, **21**, 39 (1898). Davis, *J. Soc. Chem. Ind.*, **26**, 727 (1907). Rohland, *Z. anorg. allgem. Chem.*, **65**, 105 (1910). De Forcrand, *Bull. soc. chim.*, **35**, 781 (1906). Potilitzin, *Chem. Zentr.*, **1894**, II, 515, 609; **1895**, II, 1066. Cloez, *Bull. soc. chim.*, [3] **29**, 169 (1903). Zunino, *Gazz. chim. ital.*, **30**, I, 333 (1900).

[7] Van't Hoff and co-workers, *Z. physik. Chem.*, **45**, 257 (1903).