posal much material and many valuable suggestions. Their coöperation and interest have added to the pleasure of carrying out the work, and to the value of the results obtained.

Summary

Antimony trichloride, prepared from pure antimony and chlorine in a vacuum, was repeatedly distilled in a vacuum in an all-glass apparatus, dissolved in a solution of pure tartaric acid, and compared with pure silver. The mean of nine analyses gave 0.704864 $\pm$ 0.0000026 as the ratio of $SbCl_3$ to 3Ag, and 121.748 $\pm$ 0.00086 as the atomic weight of antimony.

ANN ARBOR, MICHIGAN

THE SOLUBILITY OF BENZOIC ACID IN BENZENE AND IN TOLUENE

BY JOHN CHIPMAN

The data on the solubility of benzoic acid in benzene quoted by Landolt, Börnstein and Roth[1] and by Seidell[2] are based on the work of Roloff.[3] The values of the logarithm of the mole fractions of solute calculated from these data plotted against the reciprocal of the absolute temperature do not form a smooth curve. The solubility at 25° is reported by several observers. Reduced to percentage by weight the data recorded are as follows: Seidell,[4] 10.9%, Marden and Dover,[5] 10.4%, von Euler and Lowenhamn,[6] 8.65%; Szyszkowski,[7] 10.85%. The only data available on the system, benzoic acid-toluene, are a single observation by Seidell[4] at 25° and a series of observations obtained in this Laboratory[8] which are not in as good agreement with the solubility in benzene as might be predicted from the close similarity in internal pressures of the two solvents. It has appeared worth while therefore to redetermine the solubilities over the entire temperature range.

Experimental Part

Materials.—Benzene was shaken repeatedly with sulfuric acid, then successively with water, dil. sodium hydroxide, water and saturated calcium chloride solution. It was then fractionally distilled over solid calcium chloride; about two-thirds of the liquid was

[1] Landolt, Börnstein and Roth, "Phys.-Chem. Tabellen," J. Springer, 1912, p. 523.

[2] Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., 1919, p. 135.

[3] Roloff, Z. physik. Chem., 17, 333 (1895).

[4] Seidell, U. S. Pub. Health Service Hyg. Lab. Bull., 67 (1910).

[5] Marden and Dover, THIS JOURNAL, 38, 1239 (1916).

[6] von Euler and Lowenhamn, Z. Elektrochem., 22, 199 (1916).

[7] Szyszkowski, Medd. Vetenskapsakad. Nobelinst., 3, No. 4, 1 (1915).

[8] Mortimer, THIS JOURNAL, 45, 633 (1923).

frozen out and this was distilled over metallic sodium. The first and last portions of each distillation were discarded. The product had a constant boiling point of 78.9° (733 mm.) and a freezing-point of 5.49°. Toluene was purified in the same way (omitting the freezing). The fraction used distilled at 109.4–109.45° (733 mm.). Benzoic acid was crystallized successively from 50% aqueous acetic acid, benzene, thrice from 30% aqueous alcohol, and twice from pure benzene. The melting point of the product determined in a small Dewar tube by the method of Washburn[9] was 121.7°. A short-stem thermometer which had been carefully compared with a Bureau of Standards certified thermometer was used for this determination.

Method.—Solubilities were determined in a 2.5 × 15cm. air-jacketed test-tube using short-stem thermometers graduated in 0.2°. The tube, together with thermometer, cork stopper and stirrer was weighed; benzoic acid was added and the whole again weighed. The total weight of the mixture was taken after the solution temperature had been determined, thus avoiding errors due to evaporation of the solvent. The mixture of benzoic acid and solvent was heated in a bath of water or glycerol until entirely homogeneous, cooled with rapid stirring to form a cloud of minute crystals, then warmed slowly (about 0.5° per minute) with constant stirring until the cloud of crystals disappeared. The temperature at which the solution became clear was taken as the solution temperature. No correction was made for solvent in the vapor space of the tube nor for the small amount of solute that adheres to the stirrer. These two errors tend to compensate each other. Stem corrections were applied where needed but these never exceeded 0.3°.

The solubilities in benzene at 25°, 21° and 12°, and in toluene at 0° were determined by titration. Glass-stoppered bottles containing mixtures of the components, both unsaturated and supersaturated, in contact with crystals were placed in a thermostat and allowed to reach equilibrium. The clear solution was siphoned off into glass-stoppered Erlenmeyer flasks and weighed. A measured slight excess of sodium hydroxide solution standardized against pure benzoic acid was added and the flask thoroughly shaken. The solvent was evaporated in a current of air freed from carbon dioxide and the end-point with phenolphthalein was reached by titration with standard acetic acid.

TABLE I

SOLUBILITY OF BENZOIC ACID IN BENZENE AND IN TOLUENE

(Interpolated)

T °C.	Weight per cent.		Mole fraction of solute	
	in benzene	in toluene	in benzene	in toluene
0.0	...	4.44	....	0.0339
4.3	5.1 (eutectic)	...	0.0332	....
10.0	6.1	5.6	.0399	0.0423
20.0	8.95	8.0	.0594	.0618
25.0	10.85	9.6	.0723	.0741
30.0	13.0	11.5	.0879	.0891
40.0	18.4	16.2	.1261	.1270
50.0	25.3	22.3	.1794	.1790
60.0	34.1	30.2	.249	.247
70.0	44.5	39.7	.337	.333
80.0	55.6	50.7	.444	.439
90.0	67.3	62.8	.568	.561
100.0	78.3	75.1	.698	.696
110.0	88.9	86.8	.835	.834
121.7	100.0	100.0	1.00	1.00

[9] Washburn, *Ind. Eng. Chem.*, **16**, 275 (1924).

Evaluation of the Data

Fig. 1 shows the method used in interpolating the data. The common logarithm of the mole fraction is plotted against the reciprocal of the absolute temperature as suggested by Hildebrand[10] and a smooth, nearly straight, line is drawn through the points. The two supplementary curves A and B are of great assistance where many points are to be located and are especially useful in interpolation. Curve A[10a] is a graph of centigrade temperature plotted against the reciprocal of the corresponding absolute temperature. Curve B shows the weight-per cent. plotted against
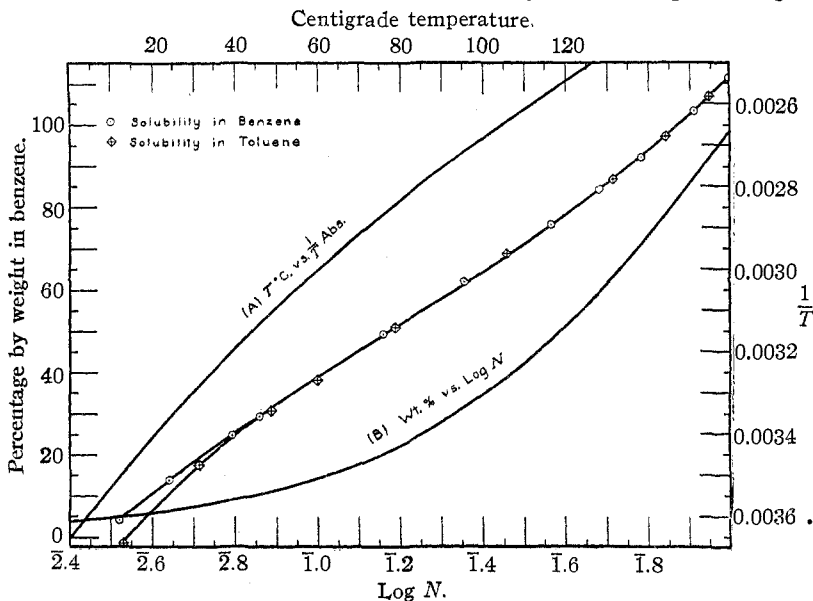

Fig. 1.—Solubility of benzoic acid in benzene and toluene.

the logarithm of the mole fraction in benzene. The corresponding curve for log N vs. weight-per cent. in toluene is omitted from the figure. With the assistance of these curves the solubility in weight-per cent. may be read at any temperature without the tedious calculation that would otherwise be necessary. The points shown in the figure are representative of a large number of observations obtained. It will be observed that above 30° the solubilities in the two solvents expressed as mole fraction of solute are practically identical. Table I gives the solubility at round temperatures obtained from large scale curves similar to Fig. 1, the two systems being plotted independently.

The heat of solution of benzoic acid in benzene or toluene can be readily calculated from the slope of the curve by the expression:[11] $S = \dfrac{d \log N}{d\,(1/T)}$

[10] Hildebrand, THIS JOURNAL, **42**, 2180 (1920).

[10a] For this and other suggestions the author is indebted to Dr. F. S. Mortimer.

[11] Mortimer, THIS JOURNAL, **44**, 1418 (1922).

$= \dfrac{-L}{4.58}.$ The values of L calculated from this expression are, in calories per mole: near the melting point, in benzene 4770, in toluene 4630; from 25° to 80°, in benzene 6900, in toluene 6760; and as an average for both systems over the entire range, 6360. The marked discrepancy between these values might be thought to indicate a transition point in the vicinity of 95°, and attempts were made to detect this point by cooling curves. No transition point was observed. Moreover the solubility data in both solvents indicate a gradual rather than an abrupt change in the slope of the curve.

Summary

The solubility of benzoic acid in benzene and in toluene has been determined. These solubilities, expressed as mole fractions are practically identical above 30°.

A labor-saving device for evaluating solubility data has been described.

The latent heats of solution of benzoic acid in the two solvents have been calculated.

BLOOMINGTON, ILLINOIS

THE IODIMETRIC DETERMINATION OF VANADIUM

BY ARTHUR E. STOPPEL, CHARLES F. SIDENER AND PAUL H. M.-P. BRINTON

Several investigators have attempted the iodimetric determination of vanadium, by titrating with sodium thiosulfate the iodine liberated by pentavalent vanadium in acid solution. A comprehensive review of the literature of this method has been given by Ditz and Bardach.[1] The conditions under which the different investigators worked varied considerably, as did also their results. In some instances nearly correct results could be obtained by basing the calculation on a reduction to the vanadyl state, while in others the assumption of a reduction to the trivalent stage was necessary for even approximately correct results.

Other investigators[2] have claimed that under proper conditions the reduction goes definitely to the vanadyl stage, but there is lack of agreement as to what these proper conditions are.

The statement of Ditz and Bardach that vanadic acid passes by reduction with hydriodic acid directly from the pentavalent to the trivalent state without formation of any vanadyl compound as an intermediate

[1] Ditz and Bardach, Z. anorg. Chem., 93, 97 (1915).

[2] Rosenheim, Dissertation, Berlin, 1888. Browning, Am. J. Sci., [4] 2, 185 (1896). Warynski and Mdivani, Mon. Sci., 22, 11, 527 (1898). Perkins, Am. J. Sci., [4] 29, 540 (1910).