

The authors wish to acknowledge gratefully the interest and helpful suggestions kindly given by Dr. E. F. Farnau.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE MUTUAL SOLUBILITY OF LIQUIDS. I. THE MUTUAL SOLUBILITY OF ETHYL ETHER AND WATER. II. THE SOLUBILITY OF WATER IN BENZENE

BY ARTHUR E. HILL

Received February 8, 1923

An inspection of the literature shows that measurements of the mutual solubility of liquids are rather surprisingly few, in comparison with the numerous measurements of the solubility of solids in liquids. Such compilations as Landolt's "Tabellen" and Seidell's "Solubilities" contain in all but few pages of results on the liquid-liquid systems. The results themselves are in many instances founded on careful work; in others the results are only approximate, and frequently the temperature ranges are very limited. Lack of completeness and lack of certainty exist for some of the very common pairs of liquids, as for example chloroform and water, of which the composition of the chloroform phase is known at one temperature only, and ether and water, for which the observed values at 0° vary more than 20%. On account of these facts, work has been begun in this Laboratory with a view to extending the number of pairs investigated and to improving the accuracy of our present data when possible.

The solubility of liquids cannot ordinarily be determined by the simple and accurate technique which can be used for solids. No method of really general applicability has been devised. Probably the procedure which has been most often followed is that of Alexejew,¹ according to which weighed quantities of the 2 liquid components are sealed in a glass tube and heated to the temperature at which the 2 phases coalesce, or cooled until the single phase separates into 2 phases, the temperature being marked by the appearance or disappearance of a turbidity. In many cases the point of turbidity can be detected within 0.1° or less, making the method of high accuracy; in some others the tendency to form an emulsion is not present and the method loses in accuracy or fails completely. All in all, however, it appears to be the most generally reliable method which has been devised.

At the time of proposing this excellent method Alexejew, to whom we owe the first complete study of solubilities of liquids, thought well to introduce a general classification of methods. His own procedure, in which the composition of the systems studied was determined by weighing out the com-

¹ Alexejew, *Wied. Ann.*, 28, 305 (1886).

ponents, he called a synthetic method, and by a natural antithesis other methods were called analytic methods. This system of classification was adopted by Rothmund² and has become the only one widely used. It does not, however, appear to be the most logical system or the most helpful, and a better one ought to be adopted. An inspection of the problem from the standpoint of the phase rule suggests at once a simple and convenient classification. Two-component systems consisting of 2 liquid phases and vapor are univariant; that is, the fixing of one condition determines the system in all other conditions. If we fix the condition of temperature in such a system, the composition of the liquid phases as well as the pressure will be fixed at equilibrium; methods in which the work is done at a constant fixed temperature may, therefore, naturally be called *thermostatic* methods. Whether the composition of the resulting liquids be determined by analysis, as has occasionally been done, or by synthesis, as in Herz's inexact method³ of adding one liquid to the other up to the point of saturation, is a matter of secondary classification, and does not affect the essential thermostatic character of the method. If on the other hand a fixed composition is decided upon and the temperature varied until the liquid phase has just that composition, as in Alexejew's method, an essential difference has been adopted; for this class of methods the term *plethostatic*⁴ is suggested, (Greek $\pi\lambda\eta\theta\omicron\sigma$) signifying a fixed concentration. It is obvious that the plethostatic character of Alexejew's method remains unchanged whether the composition of the liquids be determined by synthesis as is usually done or whether the tubes be opened after the experiment and the composition found by analysis. A third class of methods, in which the experiments are conducted at constant pressure, is conceivable, and should be called *barostatic*; no such methods have been devised for 2-liquid systems, to my knowledge. It would appear that the classification of all methods for determining solubility as thermostatic, plethostatic and barostatic would have the virtue of directing attention to their essential differences instead of non-essentials.

In the experimental work here described, two new methods for the determination of the solubility of liquids have been devised, of which both are thermostatic in character.

I. The Mutual Solubility of Ethyl Ether and Water

For the study of ether and water a volumetric method was used which gave very consistent results and which is suitable for a large number

² Rothmund, *Z. physik. Chem.*, **26**, 443 (1898); "Löslichkeit und Löslichkeitbeeinflussung," Verlag J. A. Barth, Leipzig, 1907, p. 30.

³ Herz, *Berl. Ber.*, **31**, 2669 (1898).

⁴ The use of the same root word, referring to concentration, might be of advantage in the general nomenclature of physical chemistry. We are familiar with isotherms and isobars; the use of the word isopleth would save us from the usual wordy circumlocution.

of pairs of liquids. It depends upon a simple application of the phase rule to the volumes obtained by mixing the 2 liquids in two different ratios by weight, in two separate experiments, at the same temperature. Let m and m' represent the weights of the first component used in the two experiments; let x represent its concentration in grams per cubic centimeter at equilibrium in the upper phase in both experiments, since by the phase rule the concentration at saturation cannot vary; and similarly let y represent its concentration in the lower phase in both experiments. If, now, the measured volumes of the upper phase are a and a' , and the volumes of the lower phase b and b' , it follows that $ax + by = m$, and $a'x + b'y = m'$.

Solving the equations for x and y will give the concentration of the first component in each phase, expressed in g. per cc. of solution. If the equations are again solved, substituting in place of m and m' the weights n and n' of the second component, its concentration in each phase becomes likewise known in the same units. By adding together the weight of each component present in 1 cc. of a given phase, the weight per cubic centimeter, or density, is obtained, and the percentage composition by weight thus follows. A single pair of experiments will, therefore, give the solubility in unit volume and in unit weight, and involves no assumptions as to changes of volume occurring; the accuracy of the work is dependent only upon the accuracy with which the volumes of the phases are read at equilibrium and of course upon the accuracy with which the quantities of the components taken were weighed. The apparatus used for securing accurate measurements of volume will be described below.

Aignan,⁵ and Aignan and Dugas⁶ have proposed a somewhat similar method for determining the solubility of liquids, but have stated their equations in terms of the volumes of the components taken; this has necessitated a complicated correction for the contraction of volume which occurs upon solution, and fails to give information as to the density of the solutions or their composition by weight. The three experiments carried out by them (ether and water at 12.5°, aniline and water at 11°, amyl alcohol and water at 13°) are in wide disagreement with the more reliable data in the literature, the errors being probably due to use of total volumes too small for accurate determination and to the uncertainties of the correction for contraction.

Volumetric methods have also been used by Rex⁷ who determined the solubility of several halogen derivatives of the hydrocarbons in water, and by Forbes and Coolidge,⁸ who measured the solubility of ether in water. In each of these determinations a graduated neck of a flask was used to measure the small excess of solute remaining undissolved from which the amount dissolved was computed.

Before discussing the high degree of accuracy which may be obtained by the new method with use of especially constructed apparatus, it should be pointed out that solubility measurements of rather surprising accuracy

⁵ Aignan, *Compt. rend.*, **124**, 1013 (1897).

⁶ Aignan and Dugas, *ibid.*, **129**, 643 (1899).

⁷ Rex, *Z. physik. Chem.*, **55**, 355 (1906).

⁸ Forbes and Coolidge, *THIS JOURNAL*, **41**, 154 (1919).

can be made within a few minutes and with apparatus at hand in every laboratory. Two ordinary 100cc. graduated cylinders may be shaken with the chosen weights of the 2 liquids at room temperature, and the saturation and subsidence of the liquids are usually complete within a few minutes. The reading of the volumes and the calculation can of course be done rapidly, and the results are usually within a few per cent. of those obtained by the most refined work. The introduction of this extremely simple and rapid experiment would do away with the estimated solubilities of liquids which are still published from time to time, and would require scarcely more time than the estimation.

For accurate work it becomes necessary, of course, to devise apparatus in which the volumes can be measured accurately. Flasks similar to the sketch (Fig. 1) were made by the glass blower at a moderate price; the

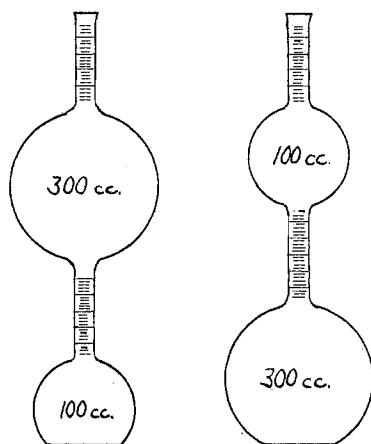


Fig. 1.—Solubility flasks.

volumes of the bulbs were 33 and 66 cc. for preliminary work and 100 and 300 cc. for the final measurements. The constrictions at which the levels were to be read were in the latter case of about 1 cm. diameter; they were graduated in 0.1 cc. divisions, as with ordinary burets, and were carefully calibrated.

Glass stoppers could not be ground sufficiently well to prevent leakage, but the use of selected cork stoppers proved entirely satisfactory, losses of vapor during an experiment being less than 5 mg., as established by weighings. In cases where the approximate solubilities are unknown, preliminary experiments with ordinary graduated cylinders will give results sufficiently accurate so that the quantities necessary to bring the surfaces of separation within the calibrations can be calculated.

With this apparatus the mutual solubility of ether and water was determined from the temperature of the quadruple point for ice, the 2 liquids and vapor, which was found to be at -3.83° , up to 30° , slightly under the boiling point of ether. The ethyl ether used was carefully purified by repeated washing with water, drying with calcium chloride and treatment with bright sodium wire to remove the alcohol. It was then distilled; 2 samples were used, each of which distilled wholly within a temperature range of 0.1° . The samples did not impart a yellow color to the sodium wire over which they were stored, which color Gomberg⁹ attributes to the presence of aldehydes. The density of the ether at 22.5° was 0.71066;

⁹ Gomberg, *THIS JOURNAL*, 45, 400 (1923).

the value obtained by interpolating from the results of Young¹⁰ by means of the equation, $\text{density} = 0.7362 - 0.001145t$, would be 0.71044. The experiments were conducted by rotating the flasks in a thermostat and calculating the solubilities by means of the equations, with the exception of the experiments at 0° and -3.83°, which were carried out by mechanically stirring the ether and water in a flask at the temperatures indicated, then siphoning suitable weights of the 2 phases into the measuring flasks, bringing the systems to equilibrium at 25°, and calculating from the previously determined solubilities at 25° the concentrations necessarily present at the lower temperatures. The results at 0° and -3.80° are, therefore, subject to an additional error through possible loss of vapor during the transfer.

TABLE I
MUTUAL SOLUBILITY OF ETHER AND WATER

Temp. ° C.	Ether phase				Water phase			
	Density	Water %	Av. density	Av. % water	Density	Ether %	Av. density	Av. % ether
30	0.70745	1.364	0.70763	1.409	0.98512	5.345	0.98505	5.340
	0.70782	1.454			0.98498	5.336		
25	0.71341	1.337	0.71309	1.338	0.98512	6.030	0.98508	6.027
	0.71293	1.352			0.98509	6.017		
	0.71294	1.326			0.98506	6.034		
20	0.71814	1.264	0.71835	1.264	0.98460	6.878	0.98478	6.896
	0.71855	1.264			0.98495	6.915		
	0.72397	1.228			0.98423	7.904		
15	0.72409	1.252	0.72404	1.240	0.98387	7.923	0.98405	7.913
	0.73001	1.164			0.98162	9.024		
10	0.72995	1.164	0.72998	1.164	0.98276	9.056	0.98219	9.040
	...	1.054			...	11.667		
0	...	1.102	...	1.078	...	11.670	...	11.668
	- 3.83	...	0.940	...	0.978	...	12.692	...
						12.812		

The temperature found for the quadruple point was -3.83°, in good agreement with that found by Nernst,¹¹ -3.853°. Using the constant 1.89 for the freezing-point depression of water, the quadruple point for the solution containing 12.75% of ether is calculated to be -3.729°, so that the actual depression is about 2.7% greater than that demanded by the freezing-point laws; the figures of Arrhenius¹² for unsaturated solutions, while somewhat irregular, vary from the ideal curve by about the same amount, but in the opposite direction.

As regards the accuracy of the figures, it will be seen that the agreement between duplicate experiments is excellent, the maximum difference be-

¹⁰ Young, Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1912, p. 151.

¹¹ Nernst, *Z. physik. Chem.*, 6, 29 (1890).

¹² Arrhenius, *ibid.*, 2, 495 (1888).

tween any pair being 0.09%, and the average deviation 0.04%; the relative deviation is, of course, higher in the case of the solubility of water in ether, in which the total concentration of water is only slightly over 1%. The errors in the method (excluding the experiments at 0° and -3.83°, in which transfers of liquid were made) can exist only in the following. (1) possible undersaturation, (2) incomplete separation of the phases (emulsification), (3) errors in weighing the separate components, (4) errors in reading the upper and lower meniscuses, (5) the retention of a thin layer of a phase on the glass surface of the bulb containing the other phase. Undersaturation and incomplete separation were eliminated by a half hour's rotation and a half hour's standing of the vessels; no change in the position of the meniscus could be detected upon repetition of the procedure. The weighings were made on a large and sensitive balance to the nearest 5 mg., with corrections for air displacement and are, therefore, not in error more than 1 part in 9000 for the smallest weights used (90 g. of ether). The meniscus could be read with the accuracy of the ordinary buret reading, about 0.02 cc., giving an error of 1 part in 5000 for the smallest volume, 100 cc. It is the retention of the wrong phase on the walls of the vessel which causes the principal error; such a retention undoubtedly occurs, and its magnitude cannot be ascertained, but careful inspections of the flasks indicate that the error is of very small amount.

As regards the curve for the solubility of water in ether, it will be seen that the solubility is small, of the order of 1%, and increases slowly with rise of temperature. The curve is substantially a straight line, and is quite accurately expressed by the equation, $S = 1.046 + 0.01183t$, where t is the temperature in degrees centigrade and S is the percentage solubility of water in the solution.

TABLE II
SOLUBILITY OF WATER IN ETHER

Temp. ° C.	Solubility found	Sol. calc. by equation	Absolute deviation	Relative deviation %
30	1.409	1.401	-.008	-.06
25	1.338	1.342	+.004	+0.2
20	1.264	1.283	+.019	+1.4
15	1.240	1.223	-.017	-1.4
10	1.164	1.164	±.000	+0.0
0	1.078	1.046	-.032	-3.0
- 3.83	0.978	1.001	+.023	+2.2
			Av. ±.015	±1.2

The results are in good agreement with the experiments of Klobbie,¹³ who determined the water present by evaporation of the solution through calcium chloride tubes designed to retain the water. His figures run

¹³ Klobbie, *Z. physik. Chem.*, 24, 615 (1897).

from 0.04% to 0.06% lower than those I obtained, and show a slightly greater irregularity. Klobbie carried the determinations up to 95° by means of Alexejew's plethostatic method, using "ponceau de xylydene" as indicator because of the failure of the pure components to show a detectable turbidity. Walker¹⁴ has numbers running from -20° to +30.3°, which give an almost horizontal curve between 0° and 30°; the water was determined by absorption from solution by anhydrous copper sulfate. The single result of Horiba¹⁵ at 25° is in good agreement with mine, and Linebarger's figure¹⁶ at the boiling point, 1.326%, falls nearly upon the curve. Bödtker¹⁷ also has a correct figure of 1.02% at "room temperature." Forbes and Coolidge⁸ have determined values at 15°, 20° and 25° by the method of evaporation used by Klobbie; the results are about 0.15% lower than Klobbie's. On the other hand, the results of Schuncke,¹⁸ 2.63% at 10° and 2.65% at 20°, are in wide disagreement with mine, being some 100% higher; the measurements were made by pouring water into ether to saturation and measuring the volumes poured. The results were transmitted by L. Meyer some 10 years after the completion of Schuncke's experiments, and it seems merely charitable to assume that an error was made in transcribing the notes. The single figure of Herz,³ 4.1% at 22°, was obtained by the same method as was Schuncke's, and is more than 200% higher than mine. It seems probable that the results of Schuncke and of Herz are unreliable, and that the true solubility of water in ether is shown by the results of Klobbie and myself within something less than 0.1%.

Passing to the curve for the solubility of ether in water, which has its beginning at the quadruple point, -3.83°, it is odd to note that Tanret¹⁹ regards this as the transition point of a hydrate, $C_4H_{10}O \cdot 2H_2O$, without analytical figures to substantiate the statement, and that Jüttner,²⁰ while dismissing Tanret's improbable hypothesis, believes that the solid phase may be a cryohydrate, overlooking the fact that the cryohydric point must be on the other side of the diagram and at some temperature below the freezing point of pure ether.

The solubility of ether in water decreases with rise of temperature up to 30°. Klobbie¹³ believes that the solubility reaches a minimum and begins to rise again at temperatures above 100°, but has no figures to substantiate the hypothesis. My figures are expressed by the equation, $S = 11.642 - 0.28968t + 0.002639t^2$, where t is temperature in degrees centigrade and S is the percentage solubility.

¹⁴ Walker, *Z. physik. Chem.*, **5**, 196 (1890).

¹⁵ Horiba, *J. Tokio Chem. Soc.*, **31**, 944 (1910).

¹⁶ Linebarger, *Chem. News*, **70**, 52 (1894).

¹⁷ Bödtker, *Z. physik. Chem.*, **22**, 511 (1897).

¹⁸ Schuncke, *ibid.*, **14**, 331 (1894).

¹⁹ Tanret, *Bull. Soc. Chem.*, **30**, 505 (1878).

²⁰ Jüttner, *Z. physik. Chem.*, **38**, 56 (1901).

TABLE III
SOLUBILITY OF ETHER IN WATER

Temp. °C.	Solubility found %	Solubility calc. by equation	Absolute deviation %
30	5.340	5.327	-0.013
25	6.027	6.049	+0.022
20	6.896	6.904	+0.008
15	7.913	7.891	-0.022
10	9.040	9.009	-0.031
0	11.668	11.642	-0.026
- 3.83	12.752	12.790	+0.038

Av. ± 0.023

There are several previous determinations for this curve.²¹ At 25° they are in reasonable agreement, ranging from 5.62% to 6.25%; but at 0° the divergence amounts to 2.13%, ranging from 11.08% to 13.4%, a variation of over 20%. My figures agree most nearly with those of Schuncke;

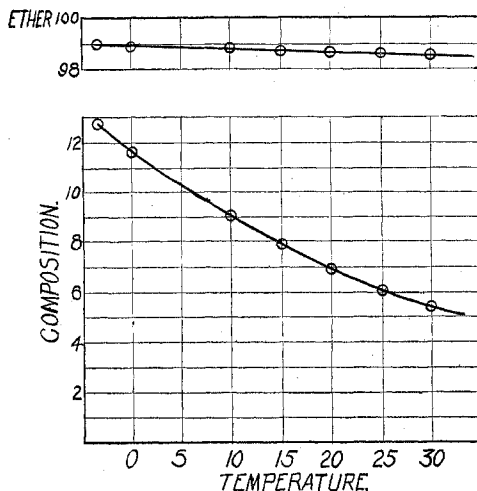


Fig. 2.—Mutual solubility of ether and water.

and in the temperature range 13° to 21°, where Schuncke's work was checked by the careful measurements of Tolloczko,²² the difference is between 0.1% and 0.2%. Forbes and Coolidge's⁸ results at 15° to 25° agree with mine within 0.1% or less. Klobbie's curve, for which the figures were obtained by evaporation and retention of the water by calcium chloride, shows an irregular shape below 10° which casts suspicion upon its accuracy. The results of Osaka, obtained by measuring the refraction of ether-water solutions, are about 2% higher than Schuncke's figures or my own at lower temperatures.

There seems to be no basis upon which the absolute accuracy of these various results may be determined. The method of volumes which I have used would seem, however, to have less probability of systematic error than Schuncke's method of pouring from open vessels, or Klobbie's method of evaporating in the presence of quantities of ether large enough to affect the partial pressures; since the only error in the volumetric method great

²¹ Ref. 13, p. 613. Ref. 15. Osaka, *J. Tokyo Chem. Soc.*, 31, 236 (1910). Thorne, *J. Chem. Soc.*, 119, 262 (1921). Ref. 18. Ref. 8.

²² Tolloczko, *Z. physik. Chem.*, 20, 404 (1896).

enough to affect the figures sensibly is that of retention of the wrong phase on the glass walls, it is believed that the figures obtained are correct within a few tenths of 1%. The results are shown graphically in Fig. 2.

II. The Solubility of Water in Benzene

The solubility of water in benzene was determined by a new thermostatic method which can be used for a number of cases of water with organic liquids, though of far less general applicability than the volumetric method given above. It depends upon the very unusual solubility relations of silver perchlorate. This compound, which can be prepared with no great difficulty, has been found²³ to have the highest solubility in water of any inorganic salt; the saturated solution at 25° contains 84.5% of the perchlorate, or 2371 g. per liter. It possesses a marked solubility, but usually of a much lower order, in various organic solvents also,²⁴ including benzene, toluene, aniline, ether, ethyl alcohol, acetone and nitrobenzene. In many of these its solubility is greatly increased by the presence of traces of water; this marked increase makes possible a simple and moderately accurate method for determining the amount of water present. The method consists in making a standard or reference curve, at a standard temperature, for the solubility of the salt in the organic liquid containing varying known amounts of water; the presence of the salt greatly increases the solubility of water in the liquid, so that the curve can be extended very far beyond the solubility limit of water in the pure solvent. In order to determine the solubility of water in the organic liquid at various temperatures, it is necessary only to saturate the liquid with water at the desired temperature, and then use the saturated solution as solvent for silver perchlorate at the temperature of the standard curve; from the solubility of the silver salt found, the percentage of water in the solvent becomes known.

The samples of benzene used were purified by recrystallization until, after drying over calcium chloride and finally over bright sodium wire, they showed a melting point of 5.4° or higher. They were treated several times with fresh sodium wire in order to remove the water completely.

The standard curve for the water-benzene system was obtained by weighing small quantities of water, from 5 to 50 mg., into carefully dried tubes, adding about 20 g. of benzene, also carefully weighed, and then a sufficient amount of pure dry silver perchlorate (also weighed) to saturate the solutions. The tubes, after careful sealing, were agitated in a thermostat at 25°, opened, and about 10 cc. of the saturated solution was pipetted into glass-stoppered flasks and weighed; the content of silver perchlorate was then determined, after addition of water, by titration with ammonium thiocyanate by the Volhard method, thus giving the percentage of silver perchlorate in the saturated solution. It happens, however, that the solid

²³ Hill, *THIS JOURNAL*, (a) **43**, 254 (1921); (b) **44**, 1163 (1922).

²⁴ Gomberg, *Ber.*, **40**, 1867 (1905); *Ann.*, **370**, 160 (1909). Ref. 23.

phase present is the compound,²⁵ $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$, for which reason a correction for the benzene in the solid phase was necessary in each case before the residual benzene concentration of the solution became known. This correction having been made, the results were plotted on coördinate paper with the percentage of silver perchlorate in the solution as ordinate and the percentage of water in the solvent as abscissa. The points fall with a little irregularity upon a straight line, expressed by the equation, $S = 4.981 + 23.95 w$, where w is the percentage of water in the solvent and S that of silver perchlorate in the solution. The curve has its upper end at about $w = 0.21$, above which concentration a second liquid phase separates.^{23b} The slight irregularity of the results is of course due to the difficulty in controlling the extremely small quantities of water present and in preventing the absorption of small amounts of water from the air during the transfers of liquid. The silver perchlorate was kept continuously in an electric oven at 100° during the experiments, on account of its extremely deliquescent character. Table IV contains the observed and calculated results, which are also shown graphically in Fig. 3. The average deviation of the observed results from the straight line curve is 0.79%, and the maximum deviation 1.3%.

TABLE IV
REFERENCE CURVE: SOLUBILITY OF SILVER PERCHLORATE IN WATER-BENZENE SOLUTIONS AT 25°

Water in solvent %	AgClO_4 in solution (found) %	AgClO_4 calc. by equation %	Water in solvent %	AgClO_4 in solution (found) %	AgClO_4 calc. by equation %
0.0000	5.000	4.981	0.1407	8.277	8.351
0.0384	5.958	5.900	0.1648	9.010	8.928
0.0547	6.182	6.267	0.1810	9.400	9.316
0.0798	6.841	6.892	0.1868	9.382	9.455
0.1110	7.708	7.639	0.2070	9.910	9.938

In order to determine the solubility of water in benzene, purified and carefully dried benzene was mechanically stirred with water at the various temperatures and, after saturation was obtained, was transferred to small cylinders, treated with weighed amounts of silver perchlorate and the solubility of the salt in the mixed solvent determined at 25° . After correction for the amount of benzene present in the solid phase the original water content of the saturated benzene solution could be determined from the reference curve. For temperatures higher than 50° dry benzene was added before agitating with silver perchlorate at 25° in order to prevent the formation of the second liquid phase which appears when the water content is about 0.21%; the weighed benzene added was taken into account in the calculation.

The determinations were carried on at temperatures ranging from 5.4° , the temperature of the quadruple point for water and benzene, up to 69.5° ,

²⁵ Ref. 23b, p. 1166.

which is the boiling point of the 2-liquid system, as calculated from the partial pressures of water and benzene. Considerable difficulty was en-

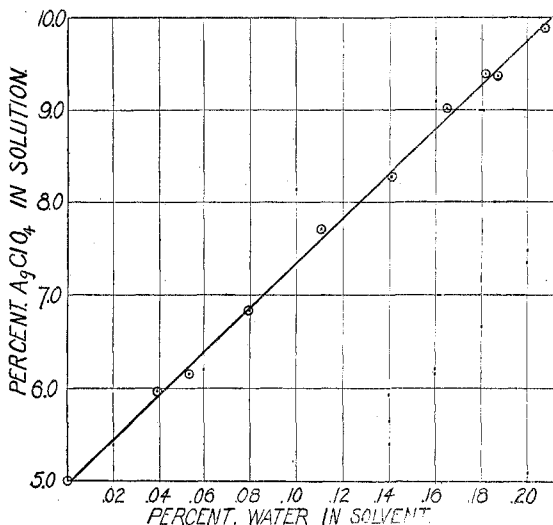


Fig. 3.—Reference curve: solubility of $AgClO_4$ in benzene-water solution at 25°.

countered in the effort to secure saturation of the benzene with water at this temperature; the irregularities in ebullition from this system are under investigation, and will be reported upon later.

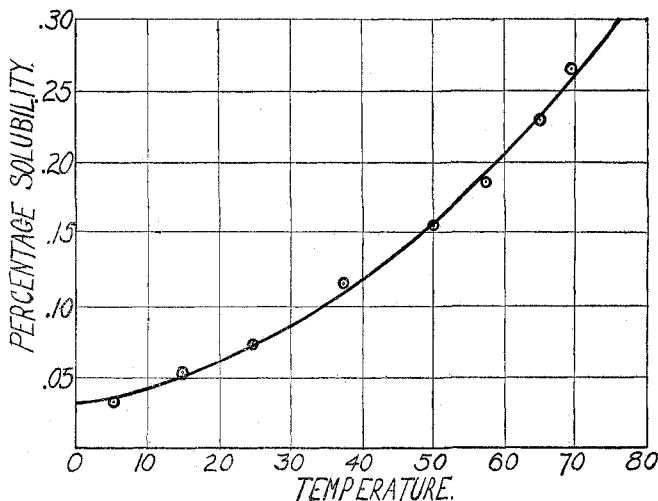


Fig. 4.—Solubility of water in benzene.

The results on the solubility are given in Table V and shown graphically in Fig. 4; they may be expressed by the equation $S = 0.03294 + 0.0006449t$

+ 0.00003728 t^2 , where S is the percentage of water in the benzene solution at saturation and t the temperature in degrees centigrade. The observed figures fall away from this curve by moderate amounts, owing to the difficulty in avoiding the absorption of water from the air during transfers of material as well as to possible errors in saturation of the benzene with water.

TABLE V
SOLUBILITY OF WATER IN BENZENE

Temp. ° C.	Water found %	Av.	Water calc. by equation %	Water found (Groschuff) %
3.0	0.035	0.030
5.4	0.034	0.034	0.037	...
15.0	0.054	0.054	0.051	...
	0.054			
23.0	0.063	0.061
25.0	0.074	0.073	0.072	...
	0.072			
37.5	0.118	0.115	0.109	...
	0.113			
40.0	0.118	0.114
50.0	0.151	0.156	0.158	...
	0.160			
55.0	0.181	0.184
57.5	0.182	0.185	0.193	...
	0.188			
65.0	0.228	0.230	0.232	...
	0.238			
	0.224			
66.0	0.238	0.255
69.5	0.265	0.265	0.258	...
77.0	0.304	0.337

In the fifth column of the above table are given the results obtained by Groschuff,²⁶ which he obtained by use of Alexejew's plethostatic method. The results agree quite closely with my own, being slightly lower at temperatures below 50° and slightly higher for the remainder of the curve up to 77°. From this agreement of results by the two different methods it may be concluded that the true figures are close to those given in Table IV. Three other investigations have been made. Herz³ has a single result, 0.25% at 22°, which is apparently about 300% too high; all his other data based upon his method of direct additions are also highly erratic. Hantzsch²⁷ has a determination, 0.013% at 25°, obtained by the action of metallic sodium upon the saturated solution, the water being calculated from the volume of hydrogen evolved; it appears to be as much too low as Herz's figures is too high. Clifford²⁸ also has determinations running

²⁶ Groschuff, *Z. Elektrochem.*, 17, 348 (1911).

²⁷ Hantzsch, *Z. physik. Chem.*, 30, 295 (1899).

²⁸ Clifford, *J. Ind. Eng. Chem.*, 13, 630 (1921).

from 21° to 55°; the water was found by selective absorption, the mixed vapors from the saturated solution being passed over calcium chloride and the absorbed water found by weighing. The results obtained are about $\frac{1}{3}$ lower than those of Groschuff and myself; the presumption is that the absorption of water was not complete.

For the composition of the other phase (benzene in water) a reliable method has not yet been devised. The existing figures are few. Hantzsch²⁷ has a value of 0.113% for the solubility of benzene in water, determined by fractional distillation of the saturated solution. Herz⁸ gives the figure 0.08% at 22°, obtained by direct measurement of benzene dissolved. I have calculated^{23b} from the freezing-point depression of water saturated with benzene that the solubility at 0° is about 0.15%. Moore and Roaf²⁹ have found the same value, 0.15%, for 15°. No great reliance can be placed upon any one of these figures, and a truly reliable method is greatly to be desired.

Summary

1. It is proposed that all methods for determining solubility be classified on the basis of the phase rule, as *thermostatic*, *plethostatic* or *barostatic*.

2. A volumetric method, thermostatic in character, is proposed for the determination of the mutual solubility of liquids.

3. The mutual solubility of ethyl ether and water has been determined by the volumetric method between the temperature of the quadruple point (−3.83°) and 30°, slightly below the boiling point.

4. A method is proposed for determining the solubility of water in a limited list of organic liquids by means of silver perchlorate.

5. The solubility of water in benzene has been determined by this method from the temperature of the quadruple point (5.4°) to the boiling point (69.5°).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF GALLIUM

BY THEODORE W. RICHARDS AND WILLIAM M. CRAIG

Received February 10, 1923

The atomic weight of gallium has received less attention than almost any other atomic weight, largely because of the scarcity of this element. Until very recently our knowledge of the subject was confined chiefly to the work of the discoverer, Lecoq de Boisbaudran, who determined the atomic weight in two ways.¹ By igniting gallium ammonium alum he obtained the value 70.1; and by converting the metal into the oxide

²⁹ Moore and Roaf, *Proc. Roy Soc.*, **77B**, 96 (1905).

¹ Lecoq de Boisbaudran, *Compt. rend.*, **86**, 941 (1878).