

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons

By H. A. BENESI AND J. H. HILDEBRAND

Introduction

The various colors of iodine in different solvents have attracted the attention of investigators for over half a century. Beckmann¹ showed that the differences are not due to any change in the molecular weight of iodine and suggested solvation as the cause of brown color. Lachman² supported this explanation, pointing out that the solvents which give a violet color are saturated, those which give brown colors are unsaturated. He stated that small additions of alcohol to a solution of iodine in chloroform suffice to shift the color stepwise from violet to brown. Hildebrand and Glascock³ found that when iodine and an alcohol were both added to a "violet" solvent, bromoform or ethylene bromide, the molal lowering of the freezing point was considerably less than additive, indicating combination of iodine with alcohol. Furthermore, they investigated colorimetrically the equilibria of iodine with ethyl alcohol, ethyl acetate and nitrobenzene dissolved together in a "violet" solvent such as carbon tetrachloride, chloroform or carbon disulfide, and found in each case an equilibrium constant corresponding to a 1:1 compound. They calculated the heat of combination in one case. There followed a long series of investigations of the general problem, well summarized by Gmelin⁴ and in a recent review by Kleinberg and Davidson.⁵ But the original division of iodine solutions into two or more distinct color classes became untenable with the work of Waentig,⁶ Groh⁷ and Walker⁸ which showed that the position of the absorption bands of iodine solutions in the visible region moved gradually from violet to brown, the shift being only small in the case of benzene in which the color of iodine is a red-violet.

We have long been curious about the chemical basis for iodine solvates. It is not a question of dipole moment, as Walker⁸ concluded, for we have recently shown rather conclusively that the iodine solubility, which would be altered by solvation effects, bears little or no relation to the dipole moment of the solvent molecule.⁹ The alcohols are extraordinary dipoles, and their effect is readily understandable, but the case of benzene seemed

more puzzling, since it behaves as a normal non-polar liquid. The only plausible explanation appeared to be the one we stated some time ago in a brief "Communication to the Editor," as follows:

"A possible explanation for the presence of such a complex appears to lie in an acid-base interaction in the electron donor-acceptor sense such as we see in the union of I⁻, the base, with I₂, the acid, to form I₃⁻."¹⁰ Evidence of basic character in benzene is to be seen in its union with aluminum chloride,¹¹ sulfur dioxide¹² and trinitrobenzene.¹³ Additional evidence in support of this hypothesis is to be found in the recent work of Fairbrother¹⁴ who reports that iodine has an abnormally high dielectric polarization in the solvents dioxane, isobutylene, *p*-xylene and benzene. He concludes that the high polarization of iodine in these solutions is due to the presence of a solvent-I⁻ complex.

In order to obtain more definite evidence regarding this hypothesis, we first prepared solutions of iodine of equal concentration in carbon tetrachloride, benzene, toluene, xylene and mesitylene. Finding that the color shifted by visibly distinct steps from violet to brown, we decided to trace their complete absorption curves. We found, to our surprise, that the shifts in the visible portion of the spectrum are comparatively minor, but that in the ultraviolet region bands appear with extinction coefficients many times larger than those of the visible bands. We present below the complete absorption of such solutions between 270 and 700 m μ , followed by our interpretation of them.

Apparatus and Procedure.—The absorption curves were measured by means of a Cary Recording Quartz Spectrophotometer, Model 11, manufactured by the Applied Physics Corporation of Pasadena. Extinction measurements made with this instrument were reproducible to 1%. As a check on the absolute values of the extinction, one of the absorption curves for iodine in carbon tetrachloride was redetermined using an independently calibrated Beckman Quartz spectrophotometer, Model DU. The agreement between the two sets of values was within the experimental error of the Cary spectrophotometer.

Exploratory absorption measurements of the iodine solutions were made using quartz cells ranging from 1 mm. to 10 cm. in length. A matched pair of 2-cm. quartz cells was used for most of the subsequent measurements. The measurements were made by first filling the cells with solvent and obtaining a "blank" tracing over the desired spectral region. The solvent in one of the cells was then replaced by the iodine solution to be measured and a second tracing obtained over the same region. The absolute

(1) E. Beckmann, *Z. physik. Chem.*, **5**, 76 (1889).
 (2) A. Lachman, *This Journal*, **25**, 50 (1903).
 (3) J. H. Hildebrand and B. L. Glascock, *ibid.*, **31**, 26 (1909).
 (4) "Gmelin's Handbuch der anorganischen Chemie," R. J. Meyer, editor, System No. 8, pp. 111-129, eighth edition (Berlin, 1933).
 (5) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).
 (6) P. Waentig, *Z. physik. Chem.*, **65**, 513 (1909).
 (7) J. Groh, *Z. anorg. allgem. Chem.*, **162**, 287 (1927).
 (8) O. J. Walker, *Trans. Faraday Soc.*, **31**, 1432 (1935).
 (9) H. A. Benesi and J. H. Hildebrand, *This Journal*, **70**, 3978 (1948).

(10) H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 2832 (1948).
 (11) C. Friedel and J. Crafts, *Compt. rend.*, **85**, 74 (1877).
 (12) Mazzetti and De Carli, *Gazz. chim. ital.*, **58**, 36 (1928).
 (13) Hepp, *Ann.*, **215**, 376 (1882).
 (14) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

value of $\log I_0/I$ at any given wave length, could be obtained directly from the difference in height of the two tracings. The concentration of the iodine in the solutions studied was adjusted so that the maximum value of $\log I_0/I$ lay between 1 and 2.

In making up these solutions, a relatively concentrated solution was first prepared by weighing out 0.1 g. of iodine in a glass-stoppered, 25-ml. volumetric flask and making up to volume with the appropriate solvent. The final solution was then prepared by pipeting a portion of this concentrated solution of iodine into a separate volumetric flask and making up to volume. When a binary mixture of solvents was wanted, a mixture of liquids in the desired proportion was substituted for the pure solvent in the last step. The volumetric apparatus was calibrated in the usual way by weighing the volume of water needed to fill the apparatus to the mark. All solutions were freshly prepared directly before making absorption measurements. This was especially critical in cases where iodine gradually reacts with the solvent to form a permanent iodo compound.

Materials.—Reagent grade iodine by General Chemical Company was stored over phosphorus pentoxide in a desiccator and used without further treatment.

All of the liquids listed below were distilled through a 24-in. Vigreux column as the final step in purification. The first and last portions were discarded and the middle portion, boiling within a 0.2° -range, collected in a dry, glass-stoppered flask. In all cases, the boiling points were within 0.2° of the values given in Lange's "Handbook of Chemistry."

Because of the diverse reports in the literature⁵ concerning the color of solutions of iodine in benzene, special care was taken to obtain benzene of high purity. Thiophene-free benzene was fractionally crystallized three times, two thirds of the benzene being collected on a Buchner funnel at each stage. During the final crystallization the temperature of the mixture of solid and liquid benzene remained constant to 0.01° . The wet benzene that was collected from the crystallization procedure was dried by distillation and was kept over freshly prepared sodium wire in a glass-stoppered bottle. To see if the purification of benzene had any effect on the light absorption of its iodine solutions, two solutions of iodine were prepared using the starting material and the final product as solvents. The absorption curves of these solutions were identical within the experimental error of the measurements.

Trifluoromethylbenzene (benzotrifluoride), *o*-xylene, *p*-xylene, 1,3,5-trimethylbenzene (mesitylene), all by Eastman Kodak Co., and toluene were purified by the following procedure. Each liquid was shaken with three

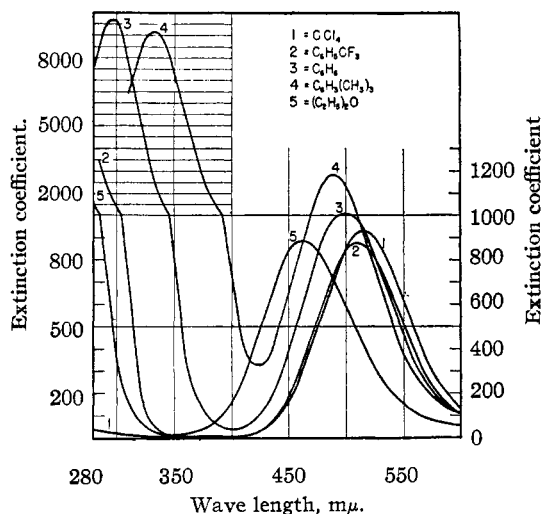


Fig. 1.—Absorption of iodine in various solvents.

portions of concd. sulfuric acid, rinsed with distilled water, then shaken with three portions of 10% sodium hydroxide solution, rinsed with water, and finally shaken with mercury. The product was dried over calcium chloride and distilled.

Ethylidene chloride (1,1-dichloroethane) by Eastman Kodak Company was purified by the method described previously.⁹

n-Heptane by California Chemical Company was very pure as evidenced by comparing its refractive index, density and boiling point with the recently compiled data on hydrocarbons.¹⁵ It was therefore used directly after a simple distillation.

Acetone was kindly donated to us by Mr. Loyd Frasher. It had been treated with potassium permanganate and potassium hydroxide and then distilled. Subsequently, it was kept in contact with potassium hydroxide in an evacuated system for two days, with shaking at frequent intervals, and then distilled at room temperature. The product was fractionally distilled in the normal manner.

Data and Discussion

Iodine in Aromatic Hydrocarbons.—The results of our absorption measurements of iodine in the aromatic hydrocarbon solvents are summarized in Table I. In Fig. 1 they are compared with the absorption curves of iodine in carbon tetrachloride and diethyl ether, which we chose to represent violet and brown solutions, respectively. The toluene and *o*- and *p*-xylene curves, which are omitted to prevent over-crowding Fig. 1, would have fallen stepwise between curves 3 and 4. The molar extinction coefficient, ϵ , plotted in Fig. 1 is calculated from the relation

$$\epsilon = (\log_{10} I_0/I)/ml \quad (1)$$

where $\log_{10} I_0/I$ is the extinction of a layer of solution l cm. deep containing m moles of iodine per

TABLE I

ABSORPTION OF IODINE IN AROMATIC HYDROCARBONS

Solvent	$[I_2] \times 10^4$, moles per liter	$\log I_0/I$	$\epsilon_{\max.}$	$\lambda_{\max.}$, m μ
Visible Region				
Benzotrifluoride	7.50	1.31	870	512
	8.70	1.84	1060	
Benzene	3.26 ^a	1.64	1010	500
	6.91	1.45	1050	
	16.48 ^b	1.68	1020	
<i>o</i> -Xylene	15.77 ^b	1.67	1060	497
<i>p</i> -Xylene	11.30	2.44	1080	495
Mesitylene	8.00	1.88	1170	490
	9.20	2.21	1200	
Ultraviolet Region				
Benzene	0.696	1.36	9800	297
	.163 ^a	0.79	9800	
	.326 ^a	1.58	9700	
Toluene	1.648 ^b	1.39	8400	306
<i>o</i> -Xylene	0.788 ^b	0.66	8400	319
<i>p</i> -Xylene	.904	1.34	7400	315
Mesitylene	.920	1.53	8300	333

^a Measured in 5-cm. absorption cell. ^b Measured in 1-cm. absorption cell. All other measurements made using 2-cm. absorption cell.

(15) "Selected Values of Properties of Hydrocarbons," Bureau of Standards Circular C461, Government Printing Office, Washington, 1947.

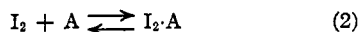
liter. The scale of the extinction coefficient has been compressed tenfold between 1000 and 10,000 in the range 280–400 $m\mu$. The values of the extinction coefficient and wave length at the absorption peaks are listed in columns 4 and 5 of Table I.

We call attention, first, to the peaks in the region, 280–400 $m\mu$. We have assumed that these intense absorption peaks are characteristic of an iodine–aromatic hydrocarbon complex since these bands do not appear in this region in the case of violet solutions of iodine, curve 1 in Fig. 1 being a typical example. Conclusive evidence for this assumption will be given below.

Second, the data in Table I show that the absorption peaks in the 400–700 $m\mu$ region are shifted stepwise from curve 3 toward curve 5 as methyl groups are substituted for the hydrogen atoms of benzene, making it a better electron donor. On the other hand, when a group like CF_3 —that reduces the electron density in the ring—is substituted, the shift is less than in the case of benzene, a result that was predicted from our hypothesis of acid–base interaction.

Third, the regular shifts in color, observed in the aromatic hydrocarbon solutions with increase in the number of substituted methyl groups, are due less to shifts in the main absorption band in the visible region than to the increasing overlapping of the ultraviolet bands into the violet end of the visible region. This explains why the color of mesitylene and ether solutions of iodine are almost identical even though their absorption peaks are in quite different positions in the visible region.

It should be noted that the values of ϵ_{\max} listed in the lower section of Table I are not true molar extinction coefficients, for they are based upon the concentration of iodine, not on the concentration of the complex responsible for the existence of ϵ_{\max} . Therefore, we know nothing thus far about the absolute or even the relative concentrations of the complexes giving these ultraviolet absorption bands. In order to obtain more information about the iodine complexes, we added small, known amounts of benzene and mesitylene to solutions of iodine in carbon tetrachloride. We again found the absorption peaks characteristic of the corresponding iodine complexes in the ultraviolet region, whose extinctions were directly proportional to the benzene and mesitylene concentrations. Noting that the extinction of the iodine complex in the case of pure benzene (see Table I) was directly proportional to the iodine concentration, we concluded that the following equilibrium existed.



where A denotes an aromatic hydrocarbon. In what follows we show how we obtained the quantitative information we sought by varying the aromatic hydrocarbon and iodine concentrations over a wide range in a neutral solvent.

The equilibrium constant, K , for the above reaction is defined by the equation

$$K = \frac{[c]}{([I_2] - [c])([A] - [c])} \quad (3)$$

where $[c]$ = molar concentration of the complex, $I_2 \cdot A$, $[I_2] - [c]$ = molar concentration of free iodine, and $[A] - [c]$ = mole fraction of free aromatic hydrocarbon, (c) in this term being expressed in terms of mole fraction. Since $[A] \gg (c)$ we replace $[A] - (c)$ with $[A]$. The units of $[c]$ and $[I_2] - [c]$ can be molarities because the concentrations of these two substances will always be small in the solutions studied. In our experiments the original concentrations of the aromatic hydrocarbon and the iodine are known. In order to determine K , however, we need to know more about $[c]$. We now assume that the intense absorption bands in the ultraviolet region are due only to the presence of the iodine complex and that the absorption of the free iodine is negligible in this region. The true molar extinction coefficient, ϵ_c , of the iodine complex at the wave length of maximum absorption will then be given by the equation

$$\epsilon_c = (\log I_0/I)/[c]l \quad (1')$$

Thanks to our choice of units, we can eliminate $[c]$ between equations (3) and (1)', rearrange the resulting equation, and obtain the relation

$$[I_2]l/\log I_0/I = (1/K\epsilon_c) 1/[A] + 1/\epsilon_c \quad (4)$$

which is now in the form, $y = mx + b$. We have made a tabular test of relation (4) in Table II for the iodine–benzene and iodine–mesitylene equilibria at room temperature (22°) in the neutral solvents, carbon tetrachloride and *n*-heptane. The term on the left side of equation 4 has been designated as y and is listed in the third column of Table II. The values of ϵ_c were calculated from the intercepts obtained when y is plotted against the reciprocal of the aromatic hydrocarbon concentration. A value of K was calculated for each set of experimental measurements.

According to the nomenclature listed under equation (3), K is related to the true thermodynamic equilibrium constant by a proportionality constant consisting of the ratio of the activity coefficients of the various species entering the equilibrium. Since the activity coefficient of each of these species is undoubtedly different in the two solvents it is not surprising that the K of a particular system changes as the solvent is changed. We were able to calculate the activity coefficients of the iodine and the aromatic hydrocarbons from their "solubility parameters" by means of the Van Laar–Hildebrand–Scatchard equation

$$\log \gamma_2 = \frac{v_2\phi_1^2(\delta_1 - \delta_2)^2}{2.303RT}$$

This type of calculation is described elsewhere.⁹ These values together with our equilibrium data allowed us to calculate the solubility parameter of the iodine complex, which was found to be approximately the arithmetical mean of the iodine and aromatic hydrocarbon solubility parameters. In order to determine how much the value of K devi-

TABLE II
I₂-BENZENE EQUILIBRIUM IN CARBON TETRACHLORIDE;
 $\epsilon_0 = 15,400$

[I ₂] × 10 ⁶ , moles per liter	[A], mol. fr.	(γ) × 10 ⁶ , cm.-moles per liter	K
3.26	1.000	10.29	1.73
6.96	0.924	10.58	1.73
10.42	.812	10.98	1.80
10.42	.619	12.59	1.74
17.40	.213	24.9	1.65
43.5	.0862	51.0	1.70
21.8	.0433	93.0	1.74
Av. = 1.72			

I₂-C₆H₆ Equilibrium in C₇H₁₆; $\epsilon_0 = 18,000$

3.26	1.000	10.29	1.18
43.5	0.1252	43.6	1.18
21.8	.0643	78.4	1.19
17.40	.292	22.6	1.13
241	.01312	398	1.08
1081	.00254	2000	1.10
Av. = 1.15			

I₂-C₆H₃(CH₃)₃ Equilibrium in CCl₄; $\epsilon_0 = 9300$

9.20	1.000	12.02	7.2
49.5	0.0281	62.9	7.3
1597	.0281	63.5	7.2
99.0	.01398	121.6	7.0
Av. = 7.2			

I₂-C₆H₂(CH₃)₃ Equilibrium in C₇H₁₆; $\epsilon_0 = 9900$

9.20	1.000	12.02	5.3
11.88	0.208	19.12	5.4
39.6	.0420	56.4	5.2
Av. = 5.3			

ates from the thermodynamic equilibrium constant we then calculated all of the activity coefficients entering into this type of equilibrium. We found that the activity coefficient of the complex is largely canceled by the product of the activity coefficients of the iodine and aromatic hydrocarbon, the degree of cancellation depending on the solvent used. Our values of K are therefore the same order of magnitude as the thermodynamic equilibrium constant.

The data listed in Table II have supplied us with the following important results. First, our measurements confirm the earlier evidence that the iodine complex consists of one molecule of iodine bound to one molecule of aromatic hydrocarbon. Second, the iodine-mesitylene complex is more stable than the iodine-benzene complex. More specifically, in a solution of iodine in pure benzene at room temperature, about 60 mole per cent. of the iodine is tied up as an iodine-benzene complex; in a mesitylene solution of iodine, 85 mole per cent. of the iodine is bound to mesitylene. These quantitative results place our hypothesis of acid-base interaction on a much firmer basis. Although our results show that in benzene and mesitylene solution most of the iodine is in the form of a complex, curves 3 and 4 of Fig. 1 differ

only slightly from curve 1; hence, we may conclude that in the visible region the iodine complex must have an absorption almost identical with that of free iodine, most of the additional absorption in the former case arising from the overlapping of the ultraviolet bands.

As an indirect test of our results, we have considered the abnormally high solubility of iodine in benzene, 4.82 mole per cent. at 25°, reported by Hildebrand and Jenks.¹⁶ The solubility calculated from their solubility parameters assuming no interaction is approximately 2.5 mole per cent. The ratio of these two values is in reasonable agreement with the ratio between total and unsolvated iodine calculated from the absorption measurements, as stated above.

Iodine in other Organic Solvents.—To make sure that the intense absorption bands appearing in solutions of iodine in aromatic hydrocarbons were characteristic of the aromatic hydrocarbons only, we measured absorption spectra of iodine in diethyl ether, acetone, *n*-heptane, carbon tetrachloride, carbon disulfide and 1,1-dichloroethane in the region from solvent absorption in the ultraviolet to 700 m μ . We found no absorption bands analogous to those of the iodine-aromatic hydrocarbon complexes in the region 270–400 m μ . Although the absorption spectra of most of these iodine solutions have already been measured, we are summarizing our results in Table III for comparison with the measurements of other investigations. All of the absorption curves are broad symmetrical peaks with a form similar to curve 1 in Fig. 1. Therefore, only the values of λ_{\max} and ϵ_{\max} for the absorption peaks are tabulated.

TABLE III

Solvent	This investigation		Other investigations	
	λ_{\max} , m μ	ϵ_{\max}	λ_{\max} , m μ	ϵ_{\max}
(C ₂ H ₅) ₂ O	462	880	456 ⁷	1030 ⁷
(CH ₃) ₂ CO	363	6100	460 ¹⁷	450 ¹⁷
C ₇ H ₁₆	520	910
CCl ₄	517	930	518 ⁸	900 ⁸
CS ₂	518	1120	518 ⁷	1170 ⁷
CH ₃ CHCl ₂	503	870

It is evident from Table III that the absorption spectrum of iodine in acetone is very unusual. The absorption peak appears in the ultraviolet region and the value of ϵ_{\max} is of a higher order of magnitude than those of the other solutions listed in Table III. The absence of an absorption peak in the visible region shows that the absorption is not of the type encountered in the case of the aromatic hydrocarbons. The large discrepancy between our values for λ_{\max} and ϵ_{\max} and those of Getman¹⁷ may possibly be attributed to the well known reaction of iodine with acetone to form the α -iodo-derivatives. Our acetone was purified very carefully and the absorption spectrum of the iodine solution remained unchanged for sev-

(16) J. H. Hildebrand and C. A. Jenks, *THIS JOURNAL*, **42**, 2180 (1920).

(17) F. H. Getman, *ibid.*, **50**, 2883 (1928).

eral hours. However, the value of ϵ_{\max} of iodine in unpurified acetone dropped rapidly, two-thirds of the iodine having reacted in fifteen minutes. We suggest, therefore, that Getman had not purified his acetone sufficiently to remove the impurity that catalyzes the reaction between iodine and acetone.

Acknowledgment.—We wish to express our appreciation to the Office of Naval Research for financial support of this research, and to the American Chemical Society for the post-doctoral fellowship held by the junior author during part of the period spent upon this research.

Summary

The absorption spectra of iodine in trifluoromethylbenzene, benzene, toluene, *o*- and *p*-xylene and mesitylene have been measured in the region 270–700 $m\mu$. In the visible region, the absorption peaks of these solutions showed moderate shifts toward shorter wave lengths in the order listed

above. With the exception of iodine in trifluoromethylbenzene, each of the aromatic hydrocarbon solutions had an intense absorption band in the ultraviolet region which we have shown to be characteristic of a complex containing one iodine and one aromatic hydrocarbon molecule.

The equilibrium between iodine and the aromatic hydrocarbons has been investigated in the neutral solvents, carbon tetrachloride and *n*-heptane, and the results show that the iodine-mesitylene complex is more stable than the iodine-benzene complex. These findings are strong evidence for an acid-base interaction between iodine and aromatic hydrocarbons.

Absorption measurements have also been made of iodine in carbon tetrachloride, carbon disulfide, *n*-heptane, ethyl ether, acetone and 1,1-dichloroethane. No absorption bands analogous to those of the aromatic hydrocarbon solutions were found in the region 270–400 $m\mu$.

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Effect of Sodium Iodide on the Phase Separation in the System Sodium-Ammonia

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Kraus¹ has shown that solutions of sodium in liquid ammonia separate into two liquid phases which have an upper critical temperature of -41.6° .² Similar behavior is observed in lithium and potassium solutions.³ In a report prepared for the Office of Naval Research Ogg suggests⁴ that the separation of these alkali metal-liquid ammonia solutions into two liquid phases that are both *dilute* solutions of metal in ammonia indicates an origin for the phase separation different from that of other liquid phase separations, such as that in the system water-phenol, where one of the conjugate solutions is rich in one component and the other, rich in the other component. The present investigation was undertaken to determine the effect of a dissolved salt, sodium iodide, on the phase separation in the system sodium-ammonia and to determine the distribution of sodium iodide between the two phases. Sodium iodide was selected since it is sensibly inert with respect to the two components of the system and has an appreciable solubility even in the concentrated solutions.

The temperature of phase separation for the system sodium-ammonia in the presence of sodium iodide was investigated by the method of Kraus and Lucasse,² in which the resistance of a given solution of sodium in ammonia was deter-

mined as a function of decreasing temperature. The discontinuity in the slope of the resistance-temperature curve corresponds to the temperature at which phase separation occurs.

Experimental Procedure

The conductance cell is shown in Fig. 1. M indicates a thin-walled capillary of 1.5 mm. inner diameter across which the resistance is measured by means of tungsten electrodes in mercury-filled wells K and L. In order to check the apparatus and the possibility that the substitution of tungsten electrodes for platinum electrodes may have an effect on the temperature of phase separation, solutions were also prepared without any sodium iodide. The observed temperatures of phase separation were in excellent agreement with the results reported by Kraus and Lucasse.

The solutions were prepared by introducing into arm H 0.50 ml. of an aqueous solution of sodium iodide (containing 0.52 millimole per ml. of solution) from a graduated 1-ml. pipet. With stopcocks G closed and F open, the solution was rinsed down into the cell with a few ml. of distilled water. H was sealed and the water pumped off by gradual evacuation of the cell through A. The sodium iodide deposited in the capillary was degassed for twenty-four hours at a pressure of 5×10^{-6} mm. and a temperature of about 80° . Ammonia, stored over sodium in B, was allowed to diffuse through the cell while H was opened and a section of glass tubing containing approximately the desired weight of sodium was introduced. H was resealed and the cell re-evacuated and degassed for another twenty-four hours. Heat was subsequently supplied from a spiral heater around H to just melt the sodium which flows through constriction J into the cell. (Experiments in which sodium was actually distilled into the cell from a horizontal arm H without constriction J proved to be rather lengthy and did not affect the reproducibility of the final results.) J was heated with the tip of an oxygen flame and H pulled off. Copper wires were introduced

(1) C. A. Kraus, *THIS JOURNAL*, **29**, 1565 (1907)

(2) C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

(3) D. Loeffler, M. J. Sienko and R. A. Ogg, Jr., unpublished.

(4) R. A. Ogg, Jr., mimeographed report dated at Stanford University on April 11, 1947.