NOTES

Dissociation and the Color of Free Radicals.—M. Gomberg and F. W. Sullivan, Jr.,[1] have determined the depression in freezing point caused by dissolving diphenyl-β-naphthylmethyl in the three solvents, benzene, nitrobenzene and cyclohexane, at various concentrations and have paralleled these measurements with colorimetric examinations of the same solutions. They observed that the deviation from Beer's law exhibited by these solutions was not proportional to the dissociation as measured by cryoscopic methods and decided that the color could not be due to simple dissociation of tetraphenyldi-β-naphthylethane. They concluded[2] that "the observed facts can best be explained by the assumption that we are dealing here with an equilibrium between benzenoid and quinonoid tautomers of the triarylmethyl, and that an increase in the proportion of the quinonoid tautomer (upon dilution) is the cause of the increase of color."

This conclusion is incompatible with the evidence upon which it is based, for such an increase in the proportion of the quinonoid tautomer could not occur in a system obeying the law of ideal dilute solutions which was implicitly assumed in calculating the degree of dissociation. In such a system the mass action law has a rigid thermodynamic basis and for a simple tautomeric equilibrium between two molecular species

$$C/C' = K \qquad (1)$$

that is, the ratio of the equilibrium concentrations of the two tautomers is independent of the total concentration for an ideal solution. Gomberg and Sullivan necessarily assumed their solutions to be ideal in order to calculate the degree of dissociation from cryoscopic measurements. Therefore, if their calculations were valid, the tautomeric equilibrium constant could not vary upon dilution. Of course, this variation is possible in a real solution which need not behave ideally, but their calculations are not applicable to such a solution. Thus, the degree of dissociation, calculated from cryoscopic measurements by any known methods, *cannot possibly furnish any basis* for the conclusion that the equilibrium constant of a tautomeric process varies with dilution.

It is now pertinent to inquire what conclusions, if any, may be drawn from these measurements of Gomberg and Sullivan. The congruence of the cryoscopic data can be tested independently by calculating the equilibrium constant for a binary dissociation. This has been done by Walden,[3] who found that a satisfactory constant did not result. These cryoscopic measurements, therefore, do not give correct values for the dissociation of the ethane and, consequently, *they do not furnish a reliable basis for comparison with the colorimetric data.*

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[1] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810–1833 (1922).

[2] Ref. 1, p. 1832, lines 18–22.

[3] Walden, "Chemie der freien Radikale," Leipzig, **1924**, pp. 200, 294–297.

It is possible to test the colorimetric measurements, independently, to determine whether or not the dissociation and color are proportional, provided these measurements are sufficiently accurate. The law of mass action for a binary dissociation may be expressed.[4]

$$K = C\alpha^2/(1 - \alpha) \tag{2}$$

in which C is the molal concentration, α is the degree of dissociation and K is a constant. When the dissociation is proportional to the intensity of color (H)

$$\alpha = IH \tag{3}$$

and

$$K = CI^2H^2/(1 - IH) \tag{4}$$

The condition that K shall actually remain constant for two sets of experimental values, C_1, H_1 and C_2, H_2, is clearly

$$C_1I^2H_1^2/(1 - IH_1) = C_2I^2H_2^2/(1 - IH_2) \tag{5}$$

and the unique value of I which can satisfy this condition for any pair of measurements is given by

$$I = (C_1H_1^2 - C_2H_2^2)/(C_1H_1^2H_2 - C_2H_2^2H_1) \tag{6}$$

The values of $I \times 10^2$ have been calculated from the data of Gomberg and Sullivan[5] and appear in Table I, where the values given under H represent the intensity of color in mm. of standard solution and those under V are the volumes of the solutions employed. These investigators made up their solutions by dissolving 0.25 g. of the substance in 5 cc. of solvent and then diluting to 10 cc. and 25 cc., respectively. Since the value of I is related to the *ratio* of the concentrations and is independent of their absolute value, the simple numbers 1, 0.5 and 0.2 may be substituted for C_1 and C_2 in Equation 6. Accordingly, the absolute values of C are not recorded in the table.

TABLE I

DISSOCIATION AND THE COLOR OF DIPHENYL-β-NAPHTHYLMETHYL

	Nitrobenzene		Benzene		Cyclohexane	
V	H	$I \times 10^2$	H	$I \times 10^2$	H	$I \times 10^2$
5	13	2.5	11.5	0.6	10	0.5
10	17		16		14	
25	25	1.3	23	1.8	19	3.0

It is apparent from these values that Equation 3 is not established by the data. However, it is not disproved, either, for the values of H may obviously be in error by as much as 0.5 mm. By substituting 10.5 and 13.5 for the first two values of H in cyclohexane, for instance, the value 0.036 instead of 0.005 is obtained for I. Thus the large variations in the table are within the limits of accuracy of the colorimetric measurements.[6]

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[4] Nernst, "Theoretical Chemistry," 5th Eng. ed., London, **1923**, p. 589.

[5] Ref. 1, p. 1827.

[6] In fact, by choosing an optimum value of I from the table, much more satisfactory values of K are obtained than are furnished by the cryoscopic measurements.

It follows, therefore, that *these measurements are not sufficiently accurate to test thoroughly the relation between the color and dissociation.*

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The Confirmatory Test for Aluminum.—As a result of experiments carried out in this Laboratory last year, we were about to publish an account of a modified test for aluminum when a published account of practically the same test appeared.[1] Our procedure for carrying out the test was as follows. Pure asbestos fiber, one-half the size of a pea, was looped in a platinum wire, dipped into a solution of 0.05 N cobalt nitrate, ignited, then dipped into the solution of the aluminum hydroxide precipitate (dissolved in the least amount of nitric acid) and ignited.[2] We found that the test was easily sensitive to 0.2 mg. of aluminum, that the sodium salts did not interfere and that there was no danger of losing the test as with the fragile filter paper ash. This modified procedure is now being used successfully in our classes. Furthermore, we found that this procedure could be used for zinc, 0.5 mg. of the metal being detected with ease.

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A Method for Determining Vapor Densities at Room Temperatures.—A summary of various methods for determining vapor densities is given by Biltz,[1] Windisch[2] and Arndt.[3] A method differing somewhat from any of these was developed and tried out to some extent. It can be carried out at room temperature and the apparatus can easily be built from parts found in any chemical laboratory.

Two two-liter round-bottomed flasks are connected by an oil manometer made of glass tubing of 5-mm. inside diameter. Means for evacuating the flasks simultaneously is provided by two stopcocks joined by a

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[7] National Research Fellow.

[1] Pañganiban and Soliven, THIS JOURNAL, 50, 2427 (1928).

[2] A. A. Noyes, "Qualitative Chemical Analysis," p. 190.

[1] Biltz, "Practical Methods for Determining Molecular Weights," The Chemical Publishing Company, 1899.

[2] Windisch, "Bestimmung des Molekulargewichts," Julius Springer, Berlin, 1899.

[3] Kurt Arndt, "Handbuch der physikalisch-chemischen Technik," Ferdinandt Enke, Stuttgart, 1923.

glass tee and connected through a mercury manometer to a vacuum pump, which may be an ordinary aspirator. The liquid whose vapor density or molecular weight is to be determined is sealed up in an ordinary Victor Meyer vapor density bulb and hung in a loop formed by one end of a stiff copper wire coil wrapped around the sealed end of the oil manometer, projecting four inches into the flask. A small hole is blown in the manometer tubing just below the rubber stopper. The flasks are now evacuated to about one centimeter of mercury pressure and the stopcocks closed. The bulb containing the liquid is crushed against the manometer tubing by an angle bent at the end of the stem of the stopcock, which can be turned from outside. In a few minutes, when the liquid has evaporated and equilibrium conditions have been reached, the increase in pressure indicated by the manometer is observed. This amounts to about 29 centimeters of oil when 0.1 g. of ethyl alcohol is used.

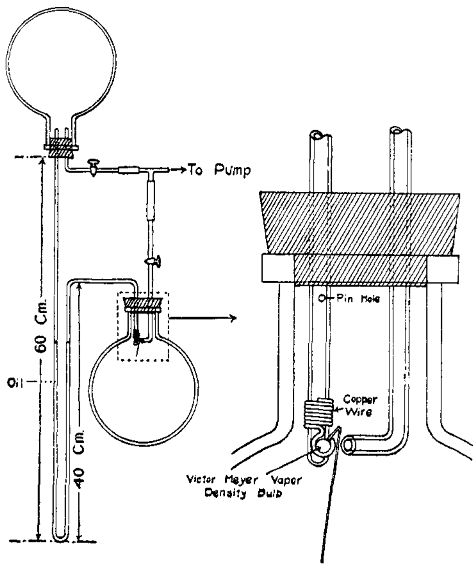

Fig. 1.

The temperature can be determined by a thermometer hung inside or near the flask. The volume of the flask, which must be determined, is made more uniform for different determinations by grinding a shoulder on a rubber stopper that is much too large at first. All the quantities in the familiar gas equation, $PV = WRT/M$, are known except M, which can be calculated.

The error in the pressure reading due to the decrease in volume in the upper flask and increase in the lower flask totals on the average 0.2 mm. of oil and may be neglected. The main precaution to be observed is not to warm the flask with the hands.

The approximate minimum vapor pressure which the substance exerts at room temperature should be 4 cm. of mercury or more. For substances of lower vapor pressure or small molecular weight, a small sample, a larger flask or higher temperatures would be required.

Of the data thus far obtained may be mentioned those taken by Trepp[4] for benzene, 79.7, 79.38, 81.0, 79.13, 79.64, 80.19, 79.42 and 80.23 and for ethyl alcohol 45.34, 44.30, 45.86, 45.99, 45.53, 45.48, 45.29 and 45.34.

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These determinations were made at 23–26°. The benzene was of high purity. The average value obtained for the sample of alcohol corresponded closely to that obtained for it by the Victor Meyer method.

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DOUBLE SALTS OF ANILINE HYDROHALIDES WITH METAL HALIDES

BY GORDON D. BYRKIT AND WILLIAM M. DEHN

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Aniline reacts in a great variety of ways with metallic salts to form molecular compounds, to yield oxidized and halogenated derivatives and to substitute amino or nuclear hydrogen by metal or metal–halide groups.[1] The object of this study is to review and extend the knowledge of molecular compounds of the types $n\text{An}\cdot n\text{HX}\cdot\text{MX}_n$, wherein An is aniline, X is halogen and M is metal. These and their hydrated forms are assembled in the following table. The asterisk indicates new compounds herewith contributed. The symbol of the metal is followed by its valence only where it is other than of the "ic" salt. The types of salts are arranged in the order of increasing complexity with respect to aniline hydrohalide. It will be noted that anhydrous salts are only numbered, while hydrated salts are lettered and correspondingly numbered. There are nine degrees of complexity of anhydrous salts and eight of hydrated salts, making seventeen types of complexity with respect to both aniline hydrohalide and water. In the absence of molecular weight determinations, the simplest formulas are used in the table. There is no evidence that these salts are not polymerized. For example, $\text{AnHCl}\cdot\text{HgCl}_2$ may be $(\text{AnHCl}\cdot\text{HgCl}_2)_8$.

Many of the compounds indicated by the blanks of the table were sought but could not be prepared. The known compounds, therefore, because they are most easily formed, roughly represent comparative capacities of the different metals to unite with aniline hydrohalide, their limits of capacity to enter into such union and the relative affinities of the three halogens.

As is shown in its greater number of types and its ability to form the *octo-aniline* compound, it is concluded that mercury has the greatest

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[1] See especially Whitmore's "Organic Compounds of Mercury," Chemical Catalog Company, New York, **1921**, p. 205.