

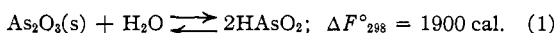
hydrochloric acid at 25°, the value of K_{11} is in the order of 10^{-21} at $m_{\text{HCl}} = 8$ and the corresponding $\Delta F^\circ_{298} = 27$ kcal.

This is in agreement, in magnitude, with the value calculated by Latimer²¹ from thermal data of Yost and Anderson²² and others for the reaction

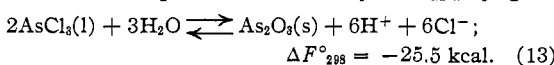
$$\text{AsCl}_3(\text{l}) + \text{H}_2\text{O} \longrightarrow \text{HAsO}_2 + 3\text{H}^+ + 3\text{Cl}^-;$$

$$\Delta F = -11.8 \text{ kcal.} \quad (12)$$

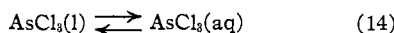
which may be converted to reaction (11) by the use of the relationship



on the assumption that $m_{\text{HAsO}_2} = a_{\text{HAsO}_2}$, giving



The data for ΔF of the reaction



are not available, hence the comparison of the values of ΔF for reactions represented by Equations (11) and (13) must be considered as comparison of magnitude only.

The Minimum Solubility.—The minimum in the solubility curve is lower than can be accounted for on the basis of the common ion effect. One explanation may be that it is due to salt effects, but the more probable one seems to be

(21) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 107.

(22) Yost and Anderson, *J. Chem. Phys.*, **2**, 624 (1934).

that it is due to a new molecular species possible (AsOCl) in the solution at that point. We have found it impossible to crystallize AsCl_3 or AsOCl from a solution of constant boiling hydrochloric acid-water mixture by slow evaporation even at low temperatures; apparently a sufficient amount of arsenic trichloride molecules is present and their vapor pressure is so nearly the same as that of the hydrochloric acid-water mixture that all of the arsenic escapes even at room temperature on slow evaporation.

Summary

The solubility of arsenious oxide has been determined in 0.1–6 *M* sodium hydroxide solutions and in 0.04–8.1 *M* hydrochloric acid solutions.

The arsenious oxide-sodium hydroxide data indicate that monobasic, mono-, di- and triarsenite ions are formed in alkaline solutions. The ionization constant of arsenious acid is 2.4×10^{-10} .

The arsenious oxide-hydrochloric acid data indicate that the minimum solubility occurs from $m_{\text{HCl}} = 3-4$ and that AsOCl may be the chief molecule in acid solution from $m_{\text{HCl}} = 3-6.5$. The value of the hydrolysis constant of arsenic trichloride is calculated from these data on the assumption that the solid phase is arsenious oxide.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Magneto-Optic Rotation: Carbon Disulfide and Benzene Solutions

BY CHARLES E. WARING,¹ HERBERT HYMAN AND SAMUEL STEINGISER

The purpose of this investigation was to begin the application and attempt to demonstrate the value of the magneto-optic method as an important tool in physico-chemical research. Eventually we hope to find a correlation between the magneto-optic rotations and structural effects both in pure substances and solutions. We also believe the method offers a possible new experimental approach for the investigation of reaction velocities. Further work in these directions is being continued by the authors.

Experimental

Materials and Apparatus.—The carbon disulfide used was the best available, 98–100% pure, redistilled twice

(1) Lalor Foundation Fellow. Address 1939–1940, Trinity College, Oxford Univ., Oxford, England.

through an efficient fractionating column, collecting the constant boiling middle portion. The final fraction was redistilled from over phosphorus pentoxide and the test using indicator Drierite showed no water. The observed boiling point was 46.3° (cor.), "I. C. T." value being 46.3°. The benzene was c. p. grade, redistilled twice, the second time from over phosphorus pentoxide. The water used was conductance water distilled from alkaline permanganate.

The solutions reported were prepared by direct weighing on a large balance using a counterpoise and correcting to vacuum. The weights were calibrated previously and the accuracy of the weighings was better than 1 mg. Due to the large volumes made up, the small surfaces exposed, and the short time of exposure during filling and emptying, it is believed no appreciable evaporation errors were introduced. The concentrations are given in weight and mole percentages calculated to the nearest hundredth of a per cent. and accurate to about that limit.

The apparatus built for this research is a modification of that described previously by Steingiser and Hyman.² It contains many improvements, such as increased magnetic field, a split field polarimeter and temperature control.

The coil was made by winding 3000 feet of number 12 gage double cotton coated copper wire on a hollow copper core, 5 cm. in diameter. Twenty layers were wound, four turns per cm. over a length of 50 cm. Two 25-cm. circular end plates were soldered onto the copper core and an outside copper cylinder fitted and cemented over the whole, forming a liquid tight compartment encasing the coil. This was filled with number two transformer oil to act as a cooling-bath. Cold water was passed continuously through a $1/4"$ (6-mm.) cooling coil of copper wound around the coil and in the oil.

Stirring of the oil-bath is accomplished by applying suction over the surface of the oil and then letting air bubble through the oil from the bottom.

The glass cell containing the solutions under investigation was made by E. Machlett & Sons, New York, of Pyrex glass with optically flat ends fused onto the body of the cell parallel to each other. The tube length is 40 cm., outside diameter 2.5 cm. It has a ground glass stoppered opening near one end for filling. Inside the copper core, a glass tube was sealed by means of two rubber stoppers in contact with the core. Water was circulated around the tube, thus cooling the upper copper tube and also providing an inner constant temperature air-bath into which the glass cell with the liquid could be placed. The temperature of the system was measured by means of a calibrated chromel-alumel thermocouple and a Brown millivoltmeter.

The D line of sodium was used as a light source for all experiments. The analyzer and polarizer were two Nicol prisms, the polarizer being a half-shadow Nicol giving a split field. The setting is made by adjusting to a uniform field. The scale is a large polarimeter scale reading, with the aid of a vernier and telescope, directly to 0.01° . The current is read on a 30-ampere ammeter, equipped with a mirror to eliminate parallax errors. The ammeter is read with the aid of a lens to 0.01 ampere and duplicated to about 0.05 ampere. The reading of the current is taken simultaneously with the setting to the uniform field.

Measurements.—The apparatus was calibrated using carbon disulfide and water and checked against benzene. The value of the Verdet constant at 15.0° for carbon disulfide was taken as 0.04240 Verdet unit. We are arbitrarily defining this standard as the value of the Verdet constant for carbon disulfide. The above value is within the limit of error of all previous determinations in terms of min./cm. oersted. This gives the constant of the apparatus as equal to 0.017659 Verdet unit/degree/ampere with an a. d. = 0.000042, A. D. = 0.000007, % Dev. = 0.04%. Using the best value of the Verdet constant of water as being 0.01308 min./cm. oersted at 15.0° , the constant of the apparatus becomes 0.01765 min./cm. oersted/degree/ampere, with an a. d. = 0.00009, A. D. = 0.00002, % Dev. = 0.11%. Using the value of the constant as 0.017659 Verdet unit/degree/ampere, the Verdet constant of benzene becomes 0.03027 Verdet unit with an a. d. = 0.00015, A. D. = 0.000025, % Dev. = 0.08% as against a previous best value of 0.0302 min./cm. oersted.

(2) Steingiser and Hyman, *THIS JOURNAL*, **60**, 2294 (1938).

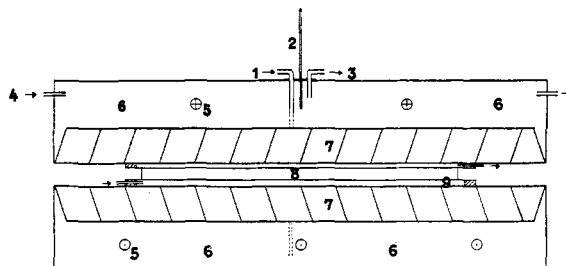


Fig. 1.—Section through tank containing coil: 1, air inlet; 2, thermometer; 3, connected to suction; 4, cold water inlet; 5, cooling coil; 6, oil-bath; 7, coil; 8, tube containing material under investigation; 9, inner jacket containing either cooled or thermostated water and a thermocouple junction connected to an outside indicator.

Each value of the constants is the result of at least sixteen independent readings with the current on. An equal number of readings were taken with the current flowing in both directions to eliminate zero setting errors. The percentage deviations are about 0.05 for most of the points investigated and in no case exceeded 0.11%. All Verdet constants are probably accurate on a relative basis (assuming that the Verdet constant of carbon disulfide is 0.04240) to at least 0.00005 unit. The "probable error" is considerably less. The absolute accuracy defined in terms of min./cm. oersted may be somewhat less, but it is not important.

Table I gives the values of the Verdet constants of solutions of benzene and carbon disulfide at different concentrations. Table II gives the partial Verdet constants for both components as determined from the graph of concentration against Verdet constant, Fig. 2 by the method of intercepts at the various concentrations.³ The accuracy is naturally much less than that of the measured quantities, but is of the order of 0.0001 Verdet unit for most of the points. The

TABLE I

Concentration Wt. %	C ₆ H ₆ Mole %	\bar{M}	d^{25}_D	V_{15}°	$V = \frac{V}{MV/D}$
0.000	0.00	76.12	1.2705	0.04240	2.5400
2.256	2.20	76.16	1.262	.04230	2.557
4.192	4.10	76.20	1.253	.04198	2.553
7.025	6.86	76.25	1.238	.04126	2.542
11.15	10.90	76.33	1.212	.03957	2.492
41.54	40.93	76.91	1.081	.03556	2.530
53.22	52.60	77.14	1.037	.03441	2.559
81.79	81.41	77.70	0.932	.03153	2.624
94.92	94.80	77.95	.897	.03059	2.661
100.00	100.00	78.05	.8841	.03027	2.6722

TABLE II

Mole % C ₆ H ₆	Partial Verdet constants CS ₂	Partial Verdet constants C ₆ H ₆ × 10 ³
0.00	42.40	40.5
10.00	43.4	8.0
20.00	40.8	27.7
40.00	39.8	29.4
60.00	39.7	29.5
80.00	38.1	30.1
100.00	36.4	30.27

(3) Lewis and Randall, "Thermodynamics," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 38.

densities given in Table I are interpolated from the values in the "I. C. T." and the last column gives a number proportional to the actual rotation per molecule, the molecular Verdet constant which we designate V . The significance of this value will be taken up in the next section. \bar{M} is the average molecular weight of the solutions.

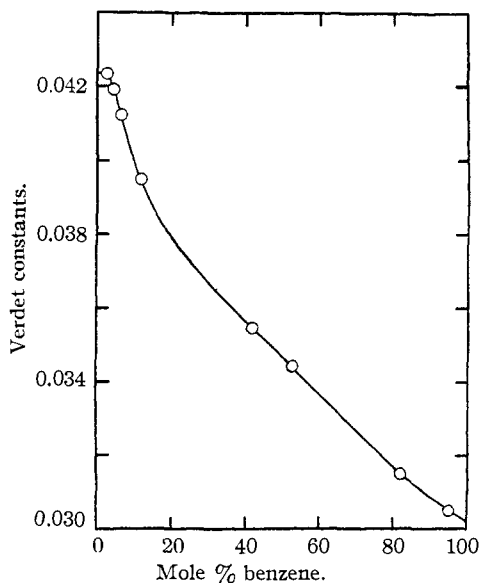


Fig. 2.

Discussion

For correlation and comparison of data, the Verdet constants were reduced to a value that is a function of the actual rotation produced by one molecular group (*e. g.*, the carbon disulfide unit). This is done by multiplying the rotation in Verdet units by the molecular weight and dividing by the density. If we assume that the intramolecular structure does not change very much with small changes in temperature, this value should be nearly independent of temperature, another advantage of using it.

In choosing the system for investigation, it was ascertained in advance that the density data over the entire range were available. The values are given in the "I. C. T." for 19.8° and it is relatively simple to convert the measurements to 15.0°. While the measurements are reported in the literature to 0.00001 g./cc. and in the "I. C. T." to 0.0001 g./cc., the points do not lie on a smooth line to that accuracy. After graphical interpolation, an accuracy of ± 0.001 is probably about all that can be expected. Unfortunately, however, since an insufficient number of measurements had been made on dilute solutions, the shape of the density curve is not very certain in

that region. As a result the exact shape of the molecular rotation curve is not very definite either.

TABLE III

Solution	Mole %	\bar{M}	D	V	V
(1) CS ₂ -Acetic Acid					
12.076	14.84	73.75	1.226	0.03312	1.992
50.354	56.26	67.06	1.125	.02239	1.334
61.284	66.18	65.44	1.105	.01942	1.149
77.605	81.81	63.22	1.078	.01535	0.901
100.00	100.00	60.03	1.0554	.01035	0.5887
(2) CS ₂ -Isobutyric Acid					
20.336	18.08	78.28	1.181	0.03258	2.160
45.276	41.70	80.78	1.093	.02414	1.780
49.112	45.48	81.20	1.079	.02312	1.740
100.00	100.00	88.06	0.956	.01135	1.046
(3) CS ₂ -Isovaleric Acid					
32.725	26.62	83.04	1.145	0.02828	2.053
46.203	39.03	86.25	1.076	.02411	1.933
50.099	42.81	87.24	1.065	.02317	1.895
63.543	56.51	90.82	1.026	.01973	1.749
100.00	100.00	102.08	0.936	.01208	1.320
(4) CS ₂ -Isobutyl Alcohol					
15.803	16.16	75.79	1.165	0.03402	2.218
50.080	50.76	75.08	0.980	.02275	1.741
75.360	75.91	74.57	.878	.01695	1.442
100.00	100.00	74.08	.807	.01267	1.159

Some previous work on carbon disulfide solutions had been done by Schwers in 1912.⁴ His data were taken in their final form from the "I. C. T." Correcting all of his values (density

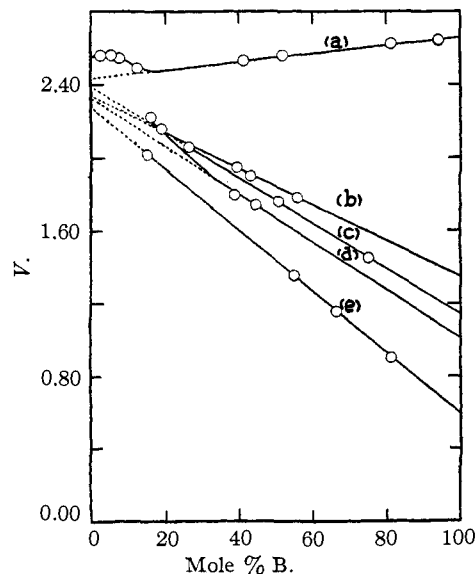


Fig. 3.— V for systems AB where A is carbon disulfide and B is (a) benzene, (b) isovaleric acid, (c) isobutyl alcohol, (d) isobutyric acid and (e) acetic acid.

(4) Schwers, *Proc. Chem. Soc.*, **28**, 294 (1912).

and magneto-optic rotation), which were made at temperatures from 13–17°, to 15°, they are tabulated in Table III. The curves for V against concentration are given in Fig. 3, where that for carbon disulfide–benzene is plotted for comparison.

Inasmuch as the molecular rotation of benzene is slightly larger than that for carbon disulfide, while that of the other substances is smaller, the curves are not strictly analogous. They have, however, certain features in common. Over the region from about 15% component B to pure B, the points lie on a smooth curve which for all the substances (except isobutyl alcohol) is practically a straight line within the experimental error. The alcohol curve is straight also in the middle region.

But, for every curve, if these straight lines are produced to the A axis, they do not meet it at the value for pure carbon disulfide. While the lines do not meet exactly at a point, they cross at values nearer to each other than to the true value. The value for isobutyl alcohol is also slightly higher than a line extrapolated in the other direction. Schwers made no measurements in the dilute region and, as we have pointed out, our density measurements make the exact shape of the curve

uncertain. But we can state definitely that the magneto-optic rotation of carbon disulfide is greater per molecular group in the pure state or dilute solution than it is in the concentrated solutions.

As a first hypothesis, it is possible that the carbon disulfide has an intermolecular structure which in itself produces an additional rotation in dilute solution. Therefore its molecular rotation is higher than that which would be expected on a simpler basis. This structure is disturbed by the presence of the B component producing a distortion of the curve in dilute solutions. If this is true, it may be possible to obtain some information as to the intermolecular structure of various substances both in the pure state and in solutions.

Summary

The Verdet constants of different solutions of carbon disulfide and benzene were determined together with the partial Verdet constants. A correlation is shown with similar data in the literature. The possibility of the determination of intermolecular structure from Verdet constants is suggested.

BROOKLYN, NEW YORK

RECEIVED JUNE 30, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD AND SYRACUSE UNIVERSITIES]

Reactions of Nitriles and Related Compounds with Sulfur in the Presence of Amines; Synthesis of Quaternary Ammonium Thiocyanates¹

BY C. R. McCROSKY, F. W. BERGSTROM AND G. WAITKINS²

The cyanide, cyanate, thiocyanate, and selenocyanate groups in many inorganic compounds often simulate the behavior of the halogens in the common inorganic halides and for this reason have been called halogenoids. Analogies between organic halides and organic compounds containing halogenoid groups do not appear to have been stressed; however, it has been shown that methyl thiocyanate reacts with trimethylamine at ordinary temperatures to form tetramethylammonium thiocyanate,^{3,4} just as aliphatic halides produce quaternary ammonium halides when they combine with tertiary amines. Reactions of this

type between nitriles and tertiary amines have never been demonstrated but such reactions would not be expected to take place at ordinary temperatures because of the greater bond energy of the C–C linkage as compared to the C–S and C–halogen bondings. It was therefore of interest to see whether nitriles would undergo quaternary salt formation at elevated temperature and determine whether this reaction was influenced by removing the ionizable cyanide as produced either as an iron cyanide complex or as thiocyanate.

Experiments showed that tetramethylammonium cyanide, on being heated at 200° with methyl alcohol as a solvent in a sealed tube, decomposed to form trimethylamine and acetonitrile. The reverse of this reaction could not be demonstrated by the formation of the quaternary cyanide when

(1) Constructed from a thesis submitted by G. Waitkins to the Faculty of the Graduate School of Syracuse University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address, Battelle Memorial Institute, Columbus, O.

(3) Walden, *Z. Elektrochem.*, **27**, 36 (1921).

(4) Lecher and Heydweiller, *Ann.*, **445**, 77 (1925).