The total energy-difference between the water and its gases will be the same at a given temperature for all concentrations because of the constancy of the value of the product of pressure and volume for these gases, but the difference in free energy will depend upon the pressure and volume of the gases, for the greater the volume the less the free energy they contain. The electrical energy obtainable from these gases under ideal conditions is a measure of the free energy they contain. At great attenuations this would become very small, though the heat of reaction would be the same as before, conversely the decomposition of water into these attenuated gases requires the application of but little work.

The quantity factor of the electrical energy necessary to decompose the water is the constant of Faraday's law, but the intensity factor by which this must be multiplied to give the energy necessary, is the electromotive force of polarization. This, in accord with the Helmholtz-Nernst conceptions, is a function of the concentration of the active electrodes. This has been shown to be the case with cadmium and zinc amalgams, and it is natural to assume that it applies to the case of gas electrodes.

Dr. Bigelow's experiments really support this view. For example, the minimum current reached in his various cells when corrected for size and resistance of electrolyte is practically a constant whatever precautions were taken to previously remove gases from the electrolyte. In fact in the single case where he could have observed the actual production of gas at low pressure above the electrolyte he apparently did so, but attributed it to a leakage of air. It seems most probable that a low rate of electrolysis existed in each of the several experiments described, that this started without the introduction of dissolved gases and probably reached a condition of equilibrium in which the diffusion of one dissolved gas to the other electrode in both cases caused continual depolarization. In such a case there should also have been some gas pressure above the electrolyte and this while not demonstrated, was really indicated by the experiments. It would seem a radical step to adopt the theory of Dr. Bigelow that simple dissolved gases conduct the current and

the facts hardly warrant it. To build upon this theory the additional theoretical structure involving the mysterious corpuscles of Thomson would be still more dangerous. If all the phenomena of this particular subject seem on careful investigation to be in accord with our present theories it is simply fortunate. Such I believe is the case.

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THE OPTICAL ROTATING POWER OF CAMPHOR WHEN DISSOLVED IN CARBON DISULPHIDE, SULPHUR MONOCHLORIDE, PHOSPHORUS TRICHLORIDE, AND SULPHUR DIOXIDE

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The influence of different solvents on the optical rotating power of camphor has received careful study by several investigators. The effect of concentration on the specific rotation of camphor solutions has also been extensively studied, and a few observations have been made on the effect of temperature on the rotation. Landolt,¹ working at 20° C, determined the specific rotation of camphor at different concentrations in the following solvents: — Methyl alcohol, ethyl alcohol, benzene, acetic acid, ethyl acetate, monochlorethylacetate, and dimethylaniline. His results show that the specific rotation increases with the concentration in all of the solvents mentioned, and that the solvent exercises a marked influence on the rotation. The curves² representing the variation of the specific rotation with the concentration converge, and when extended, meet the axis on which the values for the specific rotation are plotted at points lying between 54 and 56. Hence by determining the specific rotation at several concentrations in different solvents, Landolt, by extrapolation, arrived at the value $+55.4 \pm 0.4$ for the specific rotation of pure camphor at 20°.

The optical rotating power of camphor was further investigated in Landolt's laboratory by H. Vogel.³ Solutions of camphor in the fatty acids, — formic, acetic, propionic, N-butyric, isovalerianic, and caprylic were studied. In general, Vogel's results confirm the regularities observed by Landolt, but additional relations appeared. In the first place, it was found that

¹ Liebig's Ann. 189, 333 (1877). See also Landolt. "Das Optische Drehungsvermögen," 2 Auflage, pp. 167-171.

² Landolt. "Drehungsvermögen," p. 169.

³ Inaug. Diss., Berlin, 1892. Landolt. "Drehungsvermögen," p. 176.

the specific rotation of solutions containing the same percent of camphor is least in formic acid, and increases with increase of molecular weight of the acids. Then it was found that isovalerianic and caprylic acids exert a singular influence on the rotation. First, the solution containing about 37 percent camphor has a minimum value for its specific rotation in these solvents, and secondly, solutions containing less than 15 percent camphor have a specific rotation considerably greater than the specific rotation of pure camphor, 55.4. Moreover, in these dilute solutions the specific rotation increases with the dilution.

Several other important investigations on the optical rotating power of camphor solutions are noted on p. 564 of Landolt's work — "*Das Optische Drehungsvermögen*" (2 Auflage). Rimbach¹ measured the rotation of camphor when dissolved in mixtures of benzene and ethyl acetate; and Förster² studied the effect of temperature on the specific rotation of camphor solutions in benzene. Hesse,³ in measuring the rotation of camphor dissolved in a solution of water and ethyl alcohol, containing 80 percent alcohol by volume, found that the specific rotation decreases with the concentration, — a result in contrast to the general behavior of camphor solutions in pure solvents.

While the foregoing references are not exhaustive, still a further presentation of results would disclose no other solvents in which a systematic study of the rotation of camphor has been carried out. It appears then that the rotation of camphor has been studied in an extensive number of solvents. The list is however made up entirely of organic solvents.

Camphor, as is well known, dissolves readily and without undergoing decomposition in several inorganic solvents. The present investigation was undertaken with the view of studying the influence of some inorganic solvents on the optical rotation of camphor, and to determine the effect of concentration and, to some extent, the effect of temperature on rotation. Measurements were made in the following solvents, — Carbon disulphide,

¹ Zeit. phys. Chem. 9, 698 (1892).

² Ber. chem. Ges. Berlin, 23, 2981 (1890).

³ Liebig's Ann. 176, 119 (1875).

sulphur monochloride, phosphorus trichloride, and sulphur dioxide.

Apparatus and method

Polariscope. — A half-shadow instrument provided with a Lippich polarizer was used for the measurements. In form and construction it resembles the type of polariscope¹ figured and described by Landolt, l. c., p. 324. The large circular scale was divided into quarter degrees, and verniers permitted readings to be made to hundredths of a degree. The dimensions of the instruments were such as to permit the use of tubes 4 dm long.

Polariscope Tubes. — Three types of tubes were employed. The nature of the solvent and the temperature at which it was desired to make measurements determined the form of tube that was best suited for the measurements. All of the tubes used were made of glass, and were mounted and supplied with water jackets. The ordinary plain form of tube provided with cover glasses and screw caps was used for a few of the measurements at 20° C.

Since some of the solvents used are quite volatile the solutions were cooled before transferring them to the tubes. The rotation of some of these solutions was measured in a tube² provided with a short side-tube, which affords space for the subsequent expansion, and serves, moreover, for filling the tube and for holding a thermometer bulb in the solution above the line of sight. The tube was 40 cm long at 20° C, and was fitted with spring fastening caps, as recommended by Landolt. I am indebted to Prof. Kahlenberg for the loan of this tube.

In working with solutions of camphor in phosphorus trichloride, it was found that the spring fastening caps allowed the solution to creep out. A thin film soon formed on the outside of the cover glasses, which causes a blurring of the field. The phosphorus trichloride also injures the brass mountings. The rotation of the solutions in this solvent was measured in a form

¹ It was not supplied with the micrometer attachment described by Landolt.

² This form of tube is figured and described by Landolt, l. c., p. 396.

of tube with which cover glasses are not used. The ends of the tube were continuous with the body of the tube.

The tube was constructed from ordinary glass tubing of 1 cm internal diameter. It was made in three sections and these were finally fused together. For the end pieces tubes about 5 cm long were closed at one end, so as to have a flat bottom like a Nessler tube. By preparing a number of such tubes, several were obtained that had a bottom section of nearly uniform thickness. The outer and inner surfaces of the bottom were then ground down with fine emery and emery flour. The ground surfaces were polished with a mixture of stannic and lead oxide — the "putty powder" used by glass polishers. The inside grinding and polishing was done on a speed lathe. A rotating glass rod about 0.5 cm in diameter served for the grinding with emery, and a wooden rod was used for the polishing. No difficulty was experienced in obtaining excellent transparency, but a slight curvature of the inner surface could not be avoided. To the body of the tube two side tubes were fused at an angle as shown in Fig. 1. Finally the end sections and body were fused together.

Fig. 1

The accompanying figure is a cross-section drawing of the tube and its mountings. The tube was held in position in a metallic trough by means of the two pieces of rubber tubing R. To prevent the condensation of moisture on the ends of the tube when measurements at temperatures lower than the dew-point were in progress, the following accessories were fitted to each end of the trough, — a small tube T, for fused calcium chloride,

a cork washer C, to retard the conduction of cold, and a cover glass fastened to the cork with wax so as to form a small closed chamber A. The inside length of the tube was found by filling it with a solution of potassium permanganate and measuring the length of the liquid column with a cathetometer. The length was found to be 3.420 dm at 20° C.

The field obtained with the tube in position for observations, was not quite as clearly defined as with the ordinary form of tube operated with cover glasses; but a series of test readings — the tube containing phosphorus trichloride, — gave differences between successive readings that rarely exceeded those obtained with the ordinary form of tube when filled with water.

The tube served for all the measurements made with camphor solutions in phosphorus trichloride, and it was also used for some of the other solutions studied. The angle at which the side tubes were set greatly facilitated the cleaning and drying of the tube by permitting the easy introduction of rubber tubing.

Miscellaneous Accessories. — Sodium light was used for all the measurements except for the solutions in sulphur monochloride. Sodium chloride was volatilized in the flame of a simple form of Bunsen burner¹ adapted for polariscope work. The light was filtered in its passage through a crystal of potassium dichromate of about 1 mm thickness. In working with sulphur monochloride, the luminous gas flame was used as the source of light, as sodium light is absorbed by this solvent. A layer of sulphur monochloride 40 cm in thickness transmits a narrow band of light including the lithium line, but its region of greatest intensity is nearer the C line of the solar spectrum. Hence the specific rotations obtained for camphor in this solvent are expressed as $[\alpha]_C^t$.

In the preliminary experiments the densities of the solutions were determined by means of an Ostwald-Sprengel pycnometer of 10 cc capacity. But on account of the volatility of some of the solvents as well as the marked affinity that others have for moisture, it seemed desirable to determine the densities

¹ Landolt. 1. c. Fig. 62, p. 356.

by a method involving less manipulation. The densities given in the tabulated results below were determined by means of a "test-bottle" — a type of flask in general use for determining the percent of butter fat in milk. The capacity of the flask was 50 cc. It had a graduated stem of small bore 10 cm long with a capacity of 2 cc. Each scale division on the stem represented 0.02 cc, and by estimating tenths the volume readings may be expressed to three decimals. The flask was calibrated for the temperatures at which most of the density determinations were made, namely — 0° , 20° , 40° . The calibrations were made by weighing out different volumes of boiled distilled water in the flask. The weights thus obtained were converted into volume readings by multiplying them by the factors¹ representing the specific volume of water at the temperatures at which the scale readings were taken.

Method. — The solutions were prepared directly in the flask used for the density determinations. After weighing the flask with stopper, the camphor was introduced and another weighing made. The solvent was then added and a final weighing made. The flask was then placed in a bath at 20° , and the volume noted. From the data thus obtained the percentage strength of the solution and its density were calculated. Before transferring the solution to the observation tube, the densities desired at other temperatures were determined. When the solution in the tube had reached the desired temperature five settings were made, and the average taken for the reading.

The specific rotation, $[\alpha]_b^t$, was calculated from the usual formula, —

$$[\alpha]_b^t = \frac{\alpha_b^t \times 100}{l \times p \times d},$$

in which α_b^t represents the observed rotation at the temperature t° , l , the length of the tube in decimeters, p , the number of grams of camphor in 100 grams of solution, and d , the density of the solution at the temperature t° .

In connection with each solvent some determinations were

¹ Landolt and Börnstein. Tabellen, pp. 38, 39.

made to ascertain the effect of temperature on the rotation. For the measurements at 0° the trough was filled with melting ice, and lower temperatures were obtained by means of the usual freezing mixture of snow and salt. For 20° and higher temperatures, the trough was kept supplied with water maintained at the desired temperature in a small tank.

To test for birotation and to ascertain whether any of the solvents act chemically on camphor, a solution was prepared directly in the polariscope tube, and its rotation noted at intervals during twenty-four hours. A solution of camphor in phosphorus trichloride was kept for a week, but no change in rotation occurred. These preliminary tests showed that the solvents studied have no action on camphor. In the case of the phosphorus trichloride solutions the air apparently exerts a slight oxidizing action. A slight decrease in the rotation—less than 0.5 percent—was observed with a solution which had been kept for several days in a flask containing considerable air.

Reagents. — A sample of refined camphor was sublimed and the sublimate was used for most of the determinations. Its melting-point was 175.8° . The camphor used for the solutions in carbon bisulphide was from the same lot; but it was purified by crystallization from 50 percent alcohol. Its melting-point was 176.3° .

The phosphorus trichloride and carbon bisulphide were Kahlbaum's preparations. The sulphur monochloride was of Merck's manufacture. These solvents were redistilled and found to have very constant boiling-points.

Experimental results

The greater portion of the experimental results obtained is presented graphically in Fig. 2, to which Landolt's curve for benzene solutions has been added for comparison. The experimental data then follow in tabular form. The values given for the specific rotation of pure camphor were obtained for the most part, by extending the curves representing the effect of concentration on the specific rotation to the axis of ordinates.

Fig. 2

Solvent — Carbon Disulphide.— Its boiling-point was 45.3° under a pressure of 752 mm. Its density at 20° compared with

water at 4° was found to be 1.2633. The following results were obtained :

Percent of camphor	Density of solution	<i>l</i>	α_D^{20}	$[\alpha]_D^{20}$
3.5402	1.2487	4	7.87	+44.51
8.6954	1.2269	4	19.26	45.12
18.455	1.1910	4	40.69	46.26
24.119	1.1704	4	53.01	46.95
37.7975	1.1260	2	41.12	48.31
65.198	1.0461	2	70.31	51.54

The specific rotation of camphor at 20° when dissolved in carbon disulphide is expressed by the formula,

$$[\alpha]_D = 44.006 + 0.11402 C,$$

where *C* represents the number of grams of camphor in 100 grams of solution. The formula holds for values of *C* from 3 to 65. By assuming it to hold for *C* = 100, the specific rotation of pure camphor is found to be 55.41. The value obtained is the same as the one assigned to it by Landolt on the basis of his determinations.

Solvent — *Sulphur Monochloride* (S₂Cl₂). — The boiling-point of the sample used for the measurements was 136.9° under a pressure of 756 mm. Its density at 20° = 1.6768. A 4 dcm tube was used for the measurements. Solutions of greater strength are readily prepared, but a uniform field could not be obtained with the stronger solutions. An attempt to measure the rotation with lithium light proved but a partial success. The results here given were obtained by using the luminous gas flame.

Percent of camphor	Density of solution	α_C^{20}	$[\alpha]_C^{20}$
3.4362	1.6345	8.38	+37.30
9.8907	1.5620	24.29	39.31
20.1721	1.4562	49.85	42.43

The temperature coefficient of these solutions is positive.

Solvent—Sulphur Dioxide.—According to Schulze¹ sulphur dioxide is absorbed quantitatively by camphor at 0°. The gas is also readily absorbed at room temperatures. The first liquid solution prepared contained 76 percent camphor, but a solution containing 85 percent camphor is still liquid at room temperatures.

Three solutions were prepared and their rotation measured. The sulphur dioxide, prepared by the action of concentrated sulphuric acid on copper turnings, was passed into a weighed quantity of camphor contained in the flask used for the density determinations. The resulting solution was weighed and its volume noted at 20°. From these data the concentration and density were calculated. By cooling and continuing the flow of gas for a time after the camphor has dissolved solutions containing a relatively small percent of camphor may be prepared. The measurements were not extended to more dilute solutions owing to a considerable loss of solvent incurred when the solutions were transferred to the tube. The following results were obtained :

Percent of camphor	Density of solution	<i>l</i>	α_D^{20}	$[\alpha]_D^{20}$
64.515	1.0924	4.0	113.63	+40.31
76.595	1.0449	4.0	145.44	45.24
79.492	1.0345	4.0	153.55	46.77
79.492	1.0345	3.42	131.58	46.78

By extrapolating these results the value 55.64 is obtained for the specific rotation of pure camphor at 20°.

To ascertain the effect of temperature on the rotation a qualitative test was made with a solution containing approximately 77 percent camphor. The following readings were obtained in a tube 3.42 dcm long :

$$\begin{aligned}\text{At } 20^\circ \alpha &= 127.24^\circ \\ 0^\circ \alpha &= 125.12^\circ \\ -12^\circ \alpha &= 123.60^\circ\end{aligned}$$

¹ Jour. prakt. Chem. [2] 23, 351 (1881).

Solvent — Phosphorus Trichloride.— The boiling-point of the solvent used was 75.8° under a pressure of 750 mm. The following densities of the pure solvent were determined:

Temperature	50°	20°	0°	-15°
Density	1.5232	1.5794	1.6146	1.6655

All but one of the measurements were made with the tube figured, $l = 3.42$ dcm. The following results were obtained:

Percent of camphor	Density of solution	t	α_D^t	$[\alpha]_D^t$
1.0468	1.5714	20	2.63	+46.81
1.1887	1.5678	"	2.99	46.80
3.0745	1.5519	"	7.69	47.13
"	1.5865	0	7.52	45.08
5.5447	1.5274	20	13.82	47.71
5.1442	1.5255	25	12.83	47.80
"	1.5680	0	12.53	45.42
6.7257	1.5190	20	16.77	48.00
"	1.4825	40	17.06	50.08
"	1.5538	0	16.43	45.97
10.028 ¹	1.4878	20	28.91	48.44
18.296	1.4199	"	43.86	49.37
"	1.3870	40	44.68	51.47
"	1.4498	0	43.07	47.48
26.1346	1.3601	20	61.05	50.22
"	1.3311	40	62.24	52.28
"	1.3888	0	59.70	48.09
"	1.4031	-10	58.90	46.96
42.075	1.2516	20	92.66	51.43
"	1.2304	40	94.40	53.31
"	1.2753	0	91.14	49.65
"	1.2865	-10	90.49	48.87
59.114	1.1716	0	119.78	50.65
"	1.1510	20	121.58	52.29
"	1.1281	40	123.88	54.19
"	1.1165 ²	50	125.00	55.38
"	1.1048 ²	60	125.95	56.39
"	1.0943	70	126.46	57.16
"	1.0816 ²	80	127.12	58.13
"	1.0709	90	127.11	58.71
"	1.1510	20	121.62	52.31

¹ $l = 4$ dcm.

² The density was determined by interpolation.