and tellurium dioxide, experiments were conducted with the view of ascertaining whether the brown salts could be obtained by direct union. To this end pure potassium tellurate was heated with tellurium dioxide in a platinum crucible. When the crucible was heated the mass was first converted into a yellow-brown mass which darkened on further application of heat in a manner quite similar to the reaction between tellurium dioxide and potassium nitrate. On treating the cold mass with hot water a yellow-brown powder resulted which acted towards reagents exactly like the substances formed with the nitrates. When, however, potassium tellurate is heated alone in a platinum crucible, it fuses clear and colorless, and elevation of the temperature sufficient to cause part or all of the active oxygen to be expelled causes no formation of intermediate colored products.

Conclusions.—The composition of the products which are produced by heating tellurium dioxide with the alkaline nitrates depends largely on the length of time of heating. The first action is the oxidation of a portion of the tellurium dioxide to potassium tellurate, whereupon the tellurate formed unites with large amounts of tellurium dioxide with the formation of brown, insoluble bodies. These substances then lose tellurium dioxide by continuing the heating with the excess of nitrate until finally a clear fusion results and the tellurium has been completely converted into tellurate.

The formation of these intermediate products proceeds in a similar manner when sodium nitrate is substituted for the potassium salt, and the resulting products are of the same order of composition and properties.

Fusion with the chlorates yields the same character of compounds.

Synthesis of the potassium compounds from pure tellurate and tellurium dioxide seems to confirm the view that the compounds are intermediate products consisting of potassium tellurate and tellurium dioxide.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE COLOR OF IODINE SOLUTIONS.

BY JOEL H. HILDEBRAND AND BEN LEON GLASCOCK.

Iodine gives, as is well-known, different colored solutions in different solvents. With one group of solvents the color is violet, and with another it is yellow, red or brown, according to the solvent and the concentration. The cause of this difference has been the subject of considerable investigation. The earliest assumption[1] was that the different colors were due to a difference in the molecular weight, the brown solutions containing more complex molecules, as I_4, while the violet solutions, like the vapor,

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[1] Loeb, *Z. physik. Chem.*, 2, 606 (1888).

contain I_2. The work of Beckmann and his co-workers,[1] however, has shown conclusively that the molecular weight in all solvents corresponds to the formula I_2. Beckmann expressed the opinion that in the brown solutions there was combination with the molecules of the solvent. In spite of this Krüss and Thiele[2] have assumed in the brown solutions molecules of $(I_2)_n$ which act as I_2 in molecular weight determinations. There is no evidence for this view, and it is at variance with the fact that the solvents giving brown solutions are non-associating solvents. Lachman[3] has investigated a large number of solvents and shown that saturated compounds, such as hydrocarbons, chlorides, bromides, etc., give violet solutions, while brown solutions result with those liquids having residual valencies, such as iodides, amides, and oxygen compounds—assuming quadrivalent oxygen. He also showed that but a few per cent. of alcohol is sufficient to turn violet solutions brown. Wiedemann[4] observed some years ago that the violet solution in carbon disulphide became brown if strongly cooled. While all the evidence, therefore, is in favor of combination of the iodine with the solvent as the source of the brown color, no real proof of this, or of the nature of the compound formed, has ever been offered.

In order to prove the existence of a compound, freezing-point measurements were resorted to. For brevity we will designate those solvents giving a violet solution "inactive," and those giving a brown solution, and in which we suspect combination, "active." If now we determine the freezing point of an inactive solvent containing a small amount of an active solvent, then add a small amount of iodine and observe the lowering produced, then, if this lowering is less than the normal, there must be at least partial combination of the iodine with the active solvent. If on the other hand we replace the active by a small amount of a second inactive solvent, then the addition of iodine should give the normal molecular lowering, since the iodine remains uncombined and exerts its full effect on the freezing point.

The inactive solvent chosen was bromoform, recrystallized by the aid of the centrifuge each time before use till it showed the true freezing point. This gave a pure violet solution with iodine. Its molecular lowering was determined to be 138. To a weighed amount of bromoform in the freezing point apparatus was added, in the successive experiments, small amounts of the various solvents given in the second column of Table I. The freezing point and the lowering produced by a small amount of iodine

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[1] *Z. physik. Chem.*, **5**, 76 (1890); **17**, 107 (1895); **58**, 543 (1907).

[2] *Z. anorg. Chem.*, **7**, 52 (1894).

[3] THIS JOURNAL, **25**, 50 (1903).

[4] *Wied. Ann.*, **41**, 299 (1890).

were observed, and the molecular lowering of the iodine calculated by the usual formula.

The usual form of freezing-point apparatus was used, provided with a magnetic stirrer to avoid evaporation of the volatile liquids employed.

TABLE I.

Weight $CHBr_3$.	Solvent added.	Weight.	Weight iodine.	Molecular lowering.
20.80	$C_2H_4Br_2$	0.960	0.2370	138
36.45	CS_2	0.442	0.0885	137
19.12	$C_6H_5CHCl_2$	0.471	0.1692	140
20.99	CCl_4	0.457	0.0654	137
19.21	C_2H_5OH	0.117	0.0570	110
20.13	$C_6H_5CH_2OH$	0.478	0.0691	114
19.55	$C_6H_5NO_2$	0.444	0.1242	132

It will be seen from Table I that iodine in the presence of the first four, inactive, solvents gives the normal lowering, within the limits of experimental error. In the presence of the last three or active solvents, however, the molecular lowering is decidedly less, showing a partial combination.

Similar measurements with ethylene bromide as solvent are given in Table II. The normal molecular lowering here is 120. This we see is obtained in the presence of the first two inactive solvents, while the last two, being active, show combination.

TABLE II.

Weight. $C_2H_4Br_2$.	Solvent added.	Weight.	Weight iodine.	Molecular lowering.
14.93	$CHCl_3$	...	0.1146	119
15.76	$C_6H_5CHCl_2$	...	0.1228	121
15.05	C_2H_5OH	0.309	0.3310	71
17.15	$C_6H_5NO_2$	0.442	0.1480	110

The question next arises, what is the compound formed? We have the equilibrium

$$n(\text{solvent}) + I_2 \rightleftarrows (\text{solvent})_n.I_2.$$

Since the molecular weight of iodine is the same in both violet and brown solutions, the brown compound must have the formula assigned above, the only doubtful point in the equation being the value of n. If we denote the concentration of the solvent by C_1, that of the iodine by C_2, and that of the compound by C, then according to the mass law

$$KC = C_1^n C_2,$$

in which n is likely 1 or 2. In order to determine n we may vary C, C_1, and C_2 and find which value for n gives a constant value to K.

The equilibria between iodine and various active solvents were determined in the inactive media carbon disulphide, carbon tetrachloride and chloroform. Taking the equilibrium between alcohol and iodine in carbon tetrachloride as an example, if one adds to a violet solution of known concentration successive portions of alcohol, the color gradually becomes brown. Now we know the total iodine concentration; that of the alcohol can be determined from the weight of the portions added, so that if we can determine the amount either of the brown compound or of the violet free iodine, then we will know C, C_1, and C_2. This was done colorimetrically. The violet solution transmits blue light almost completely, while the brown solution asborbs most strongly in the blue. A mercury vapor lamp, which gives strong blue lines, was used as the source of light. A filter of ammoniacal copper sulphate and one of alkali blue cut off all the red and green light from the box containing the colorimeter. By this arrangement the amount of brown absorbing compound could be determined in the presence of the non-absorbing violet, by comparing the intensity of the blue light transmitted by the mixture with that transmitted by a standard brown solution. The difference between this brown compound and the total iodine present gave the violet free iodine. A correction was made for the small amount of blue light absorbed by the violet solution.

The results for the various equilibria investigated are shown in Table III. The temperature of the laboratory was about 25°.

The constancy of the values in the last column for each series shows that the general equation for the equilibria between iodine, one of the active solvents, alcohol, ethyl acetate[1] or nitrobenzene and the brown compound formed in each case must be written in the form $KC = C_1C_2$, that is, the formula of the brown compound is (solvent) I_2. With acetic acid, which exists in solution as double molecules, the equilibrium must be written $KC = C_2\sqrt{C_1}$, which is confirmed by experiment.

The constant obtained with nitrobenzene, 0.19, being smaller than that with alcohol, 1.23, confirms the results given above by the freezing-point method, which show greater combination with the alcohol than with nitrobenzene. Since we now know the formula of the brown compound formed, equilibrium constants could be calculated from the above freezing-point measurements. However, the colorimeter is many times more sensitive to iodine than the freezing point, so that calculations based on the latter would have comparatively little value.

In order to calculate the heat of association of the brown compound $CH_3COOC_2H_5.I_2$, measurements of K were made at two different temperatures. At 12° it was found that $K_1 = 0.75$, while at 28° $K = 0.57$. Using these values in the van't Hoff equation

$$\ln K_1/K_2 = Q/R(1/T_1 - 1/T_2), \text{ where}$$

$R = 2$ cal. and T_1 and T_2 are the absolute temperatures, we find that Q, the heat of association, is 3060 cal. per gram molecule.

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[1] This was purified the same day it was used.

TABLE III.

Equilibrium.	C_1.	C_2 (violet).	C (brown).	C/C_1C_2.
$C_2H_5OH + I_2 \rightleftarrows C_2H_5OH.I_2$ in CCl_4	0.877	0.00113	0.00149	1.32
	0.595	0.00153	0.00114	1.25
	0.527	0.00164	0.00104	1.26
	0.383	0.00188	0.00083	1.15
	0.194	0.00221	0.00052	1.21
	0.130	0.00236	0.00039	1.27
			Mean,	1.23
Same in CS_2	0.611	0.00134	0.00099	1.21
	0.398	0.00157	0.00079	1.26
	0.300	0.00171	0.00067	1.30
			Mean,	1.26
$CH_3COOC_2H_5 + I_2 \rightleftarrows CH_3COOC_2H_5.I_2$ in CS_2	1.82	0.00086	0.00091	0.58
	1.06	0.00149	0.00069	0.46
	0.69	0.00169	0.00056	0.48
			Mean,	0.51
Same in CCl_4	1.44	0.00131	0.00107	0.57
	1.01	0.00172	0.00078	0.45
	0.71	0.00196	0.00062	0.45
			Mean,	0.49
Same in $CHCl_3$	2.45	0.00166	0.00214	0.53
	1.51	0.00248	0.00178	0.47
	0.82	0.00311	0.00150	0.59
			Mean.	0.53
$C_6H_5NO_2 + I_2 \rightleftarrows C_6H_5NO_2.I_2$ in CCl_4	2.74	0.00129	0.00070	0.20
	1.59	0.00178	0.00054	0.19
	1.12	0.00204	0.00041	0.18
			Mean,	0.19
				$C/C_2\sqrt{C_1}$.
$\frac{1}{2}(CH_3COOH)_2 + I_2 \rightleftarrows CH_3COOH.I_2$ in CS_2.	6.20	0.00083	0.00072	0.35
	7.90	0.00064	0.00069	0.38
	8.55	0.00060	0.00064	0.37
			Mean,	0.37

Summary.

1. It is proven that the brown color of certain iodine solutions is due to a combination of iodine with the solvent.

2. The equilibrium constants for several solvents were determined and it was found that the brown compound formed consists, in all the cases investigated, of one molecule of iodine with one molecule of solvent.

3. The heat of combination of iodine and ethyl acetate is calculated to be 3060 cal.

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

ON A PHENOMENON OBSERVED IN THE ACTION OF HYDROCHLORIC ACID ON VERY DILUTE ALKALI AMALGAMS.

BY GEORGE MCPHAIL SMITH.

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In the action of solutions on the amalgams of the alkali metals, especially during the decomposition of the latter with hydrochloric acid, preparatory to their analysis, the writer has often observed that, just before the evolution of hydrogen slows up, a characteristic cloud of minute gas bubbles is suddenly liberated from the surface of the amalgam, and that at the same time the amalgam suddenly shrinks together.

A series of electromotive measurements, which was published in a previous paper,[1] was preceded by two other series of experiments, which were considered less suitable for publication in that connection. The first of these throws light on the phenomenon referred to, and is the subject of the present paper.

The apparatus employed consisted of a vertically disposed glass tube, A, 11.8 cm. in length, with an internal diameter of 1.28 cm., which was held in position by a clamp. A small glass tube, B, carrying a short, platinized platinum wire, and partially filled with mercury, was inserted in the mouth of the larger tube, where it was held by means of a cork. The arrangement will be understood at a glance from Fig. 1. The voltmeter used was a Weston standard direct-reading instrument, with a range of 5 volts, divided into 150 equal parts.

The amalgams employed contained very close to 1 mg. atomic weight of amalgamated metal in 100 grams, and, unless otherwise stated, the hydrochloric acid was 0.1 normal.

Before starting the series, 2 cc. of mercury were run into the tube from a burette, and then 9 cc. of 0.1 normal hydrochloric acid, also from a burette, were added. A mark was made on the tube at the line of demarcation between the mercury and the solution, and also a line at the upper meniscus of the solution. In the subsequent experiments the same volumes of amalgam and solution were always used, the marks serving as guides. The circuit was closed in every case by inserting the cork bearing the platinum electrode, immediately after the addition of the hydrochloric acid.

With the combination Hg/N/10HCl/Pt, no perceptible deflection of the needle was observed on closing the circuit.

In the case of the alkali amalgams, there was at first a fairly uniform

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[1] *Z. anorg. Chem.*, **58**, 381 (1908).