[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE STATE UNIVERSITY OF IOWA]

SYSTEMS FORMED BY CERTAIN TETRAHALIDES

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RECEIVED MAY 2, 1929 PUBLISHED OCTOBER 5, 1929

Work in this Laboratory on solubilities in non-aqueous inorganic solvents has extended over several years and has included a large number of inorganic compounds. Such solvents as sulfur monochloride, liquid nitrogen tetroxide, thionyl chloride, liquid hydrogen fluoride and liquid sulfur dioxide have been investigated.[1] The work with anhydrous liquid sulfur dioxide has shown that in general the metal iodides and thiocyanates are soluble to a small degree, while the chlorides and bromides are less soluble. Bond and Beach[2] investigated the solubility of stannic chloride, stannic bromide, carbon tetrachloride and titanium tetrachloride in anhydrous liquid sulfur dioxide, and have found that these compounds form binary liquid systems at low temperatures with this solvent. They determined the nature of the systems formed by the first three of these compounds but their work with titanium tetrachloride was not completed. The present work had for its purpose the completion of the system formed by titanium tetrachloride and anhydrous liquid sulfur dioxide and the extension of the investigation to include the behavior of silicon tetrachloride and zirconium tetrachloride with this solvent.

The method employed was first used by Alexjew.[3] It consists in sealing a known quantity of solvent and solute in a small glass tube, rotating it in a bath with regulated variable temperature and noting the temperature at which the two phases become one. By doing this for a series of compositions the solubility curve may be constructed. This method offers the advantage that subsequent analyses of the saturated solutions are not necessary and the determinations are not confined to temperatures below the boiling point of sulfur dioxide. Inasmuch as solubility is practically independent of the pressure over a variation of a few atmospheres, this method is the most practical one for highly volatile solvents.

Experimental Part

The tetrachlorides of titanium, silicon and zirconium show a very great affinity for water. When exposed to moist air titanium and silicon tetrachlorides form dense white fumes, while zirconium tetrachloride gives off quantities of hydrogen chloride gas. This made it necessary to exclude as nearly as possible all moisture from the apparatus and to prevent the exposure of the compounds to the air. Another difficulty arose from the

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[1] Various unpublished theses, this Laboratory.

[2] Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

[3] Alexjew, *Wied. Ann.*, **28**, 395 (1886).

fact that titanium and silicon tetrachlorides are liquids and have considerable vapor pressures at room temperatures, which complicated transference of them to the various parts of the apparatus.

Because zirconium tetrachloride is a solid, and otherwise different from titanium and silicon tetrachlorides, it was necessary to use a different procedure for investigating it. The discussion of the experimental work with zirconium tetrachloride will, then, be taken up in the part devoted to the study of this compound.

Materials and Procedure.—The sulfur dioxide used was the ordinary laboratory grade contained in small iron cylinders. It was purified by passing it through a train of wash bottles containing concentrated sulfuric acid and through sodium bisulfite solution. The gas was dried by passing it through calcium chloride and phosphorus pentoxide, the system consisting of tubes about one inch in diameter with a total length of thirty feet. The dried gas was condensed in a spiral condenser cooled by an ice–salt mixture and received in a special Dewar flask. This flask was so constructed as to permit withdrawal of the liquid sulfur dioxide directly from the bottom through a small outlet tube. The flask was closed with a rubber stopper. This carried a mercury seal to which the condenser was connected, another mercury seal used for the glass rod which was ground into the outlet at the bottom as a glass stopper and a third tube to permit the sulfur dioxide gas to escape. In charging the specimen tubes with liquid sulfur dioxide the rod was slightly raised and the liquid allowed to flow directly into the tubes. The total weight of mixture used varied from 2.5 to 3 g. for each determination.

Procedure.—The apparatus and the procedure in filling the tubes were the same as those described by Bond and Beach.[2] This consisted in distilling the purified material as needed into a special receiving head and admitting it to the tubes by means of a rotating flask which permitted the transference in a dry atmosphere. The tubes were attached to the outlets of the filling flask by means of cleansed rubber tubing and were connected in such a way that the tetrachloride had no contact with the rubber. After the desired amount of the tetrachloride had been admitted to the tubes, they were cooled in a freezing-bath of ice and salt before detaching them. The cooling lowered the vapor pressure of the tetrachloride and thus reduced the chance for hydrolysis, and also made it possible to seal the tubes below the boiling point of the sulfur dioxide and at atmospheric pressure. This was necessary to prevent drawing moist air into the tube when it was subsequently cooled and opened to admit the liquid sulfur dioxide. Each tube with its contents, together with the part sealed off, was weighed and from this the weight of the tetrachloride was determined. The tube was then cooled to a temperature below the boiling point of sulfur dioxide, opened by breaking off the top of the stem and the liquid sulfur dioxide admitted from the special Dewar flask. It was then sealed off as close to the liquid as possible and the mixture together with all parts of the tube weighed again. This gave the weight of the sulfur dioxide and hence the composition of the mixture.

This procedure in charging the specimen tubes provided for a minimum exposure to the air and the vaporization of the sulfur dioxide prevented to a very large degree the diffusion of water vapor into the tubes while sealing them. However, in case a trace of moisture got into the tube, its presence was shown by the ready formation of a cloudiness in the solution. Any tube showing such a condition was discarded. On account of the low temperature, and also due to the presence of sulfur dioxide gas in the tube, no measurable quantity of the tetrachloride was lost as vapor in that portion of the tube broken off.

Determination of Solution Temperatures.—The determination of the temperatures at which the mixtures of the various concentrations became completely miscible offered no particular difficulty for those which had solution points in the region of the binary liquid system. The solubility points in the solid–liquid region were more difficult to obtain on account of the increased viscosity of the liquids at the low temperatures and the slow rate at which the systems approached the saturation equilibrium. For those mixtures having solution temperatures above 0°, the determinations were carried out in a water-bath, the temperature of which was varied by adding small quantities of crushed ice. The temperature could be easily controlled in this manner, and any slight variation in it could be effected at will. For those mixtures having solution points at temperatures below 0° the bath consisted of acetone cooled with solid carbon dioxide and contained in a tall, unsilvered, wide-mouthed Dewar flask. The temperature in this bath could likewise easily be controlled by the rate of adding the carbon dioxide snow. As the presence of water and oil in the carbon dioxide made it undesirable for cooling at temperatures below about −50°, a eutectic mixture of acetone and chloroform (23% of chloroform by weight) cooled with liquid air was used instead. This latter bath remained clear and proved to be far more satisfactory for use at the lower temperatures.

In the determination of solution points the temperature was lowered until the solution showed a slight opalescence and then more slowly cooled to the point where it separated into two phases. At this point the cooling of the bath was stopped and the temperature was allowed to rise at the rate of about 1° per minute. The reading taken for the solution point in all cases was that at which the system just became homogeneous, while the temperature of the bath was slowly rising. With such a slow rate of temperature increase, together with rapid agitation of the specimen tubes, this change was sharp and the solution temperature could be read to within 0.1°.

In the region of the solid–liquid system, the solution was rapidly and sufficiently supercooled to produce crystallization while it was vigorously agitated. This gave fine crystals of nearly uniform size, which made the subsequent rate of solution quite uniform. The temperature of the bath was allowed to rise very slowly while the solid redissolved. Just before the last fragment of solid disappeared, the change of temperature was reversed by adding a small quantity of the cooling agent and the point at which there was any perceptible increase in the solid phase was noted. The temperature was again allowed to rise at the rate of 1 to 2° per hour until the last fragment of crystal became almost invisible, and the temperature change was again reversed slowly to the reappearance of crystals. A difference between the two temperatures of 1 to 2° for the first trials could be reduced in most cases to a difference of 0.3 to 0.4° for the last trials. The average from these latter readings was chosen as the solution temperature with a probable error of ±0.2°. In all of this work low-temperature pentane thermometers were used. These were checked against a low-temperature thermometer certified by the Bureau of Standards. In those cases where the stem could not be entirely submerged, a correction was applied and no large error could have resulted from this source.

Titanium Tetrachloride

Purification.—The starting material was an impure grade of titanium tetrachloride, colored red by ferric chloride, and containing vanadium chloride and possibly other chlorides. A product having a lemon-yellow color was easily obtained by fractional distillation. The yellow color was due to vanadium chloride, which has a boiling point very close to that of titanium tetrachloride, thus making further purification by fractionation undesirable on account of the great amount of time involved. V. Merz,[4] and also M. Billy,[5] have used sodium amalgam for purifying it, and O. F. von der Pfordten[6] distilled it from sodium to remove the vanadium chloride.

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[4] Merz, *J. prakt. Chem.*, [1] **99**, 157 (1866).

[5] Billy, *Ann. chim. phys.*, [9] **16**, 5 (1921).

[6] Von der Pfordten, *Ann.*, **234**, 257 (1886).

In this work a special fractionation apparatus combining the essential features of the apparatus described by Peters and Baker[7] and improved by Loveless[8] was used. The fractionation column was about 30 inches long and surrounded by a silvered jacket which had been evacuated. The impure beginning material was fractionally distilled from this apparatus eight times. This was equivalent to a much larger number of fractionations from the ordinary type of column. It gave a lemon-yellow product which was allowed to stand over mercury for several days and was finally distilled from mercury. The yellow color still persisted and further purification was effected by repeated distillation from metallic sodium. The sodium was carefully freed from films of oil and other carbon compounds and cut into fine shavings. It was very essential to have the sodium as free as possible from these compounds, for whenever such were present it was observed that miniature explosions, producing sparks in the flask, took place when the temperature was raised to the boiling point of the titanium tetrachloride. The liquid was digested with the sodium at an elevated temperature for about one hour before each distillation. The number of such treatments for each portion taken varied somewhat, depending on the surface of the sodium exposed and the time of digestion. In most cases as many as six or eight distillations were sufficient, the last two or three being applied after the liquid had become colorless. This gave a colorless, highly refractive product. It boiled sharply at 136.1° (752 mm. pressure), and its freezing point was −24.4°. Other observers record the following boiling points: 136.0° by Stahler,[9] 136.5° (761 mm.) by Biltz and Meinecke,[10] and 136.0° by Bond and Beach.[2] The melting point recorded by Biltz and Meinecke was −23° and that recorded by Haase was −25°.[11]

Solution Points.—The specimen tubes were filled and the solution temperatures determined as already described. The results of these determinations of the solubility points for titanium tetrachloride in liquid

TABLE I

MISCIBILITY OF TITANIUM TETRACHLORIDE WITH SULFUR DIOXIDE

$TiCl_4$, %	Soln. point	M. p., °C.	$TiCl_4$, %	Soln. point	$TiCl_4$, %	Soln. point	M. p., °C.
100.00	..	−24.4	61.80	11.9	15.02	11.2	..
98.96	..	26.0	60.46	12.0	14.44	12.2	..
97.47	..	27.7	58.40	12.0	12.26	16.8	..
96.37	..	29.1	58.05	12.0	9.53	23.7	..
96.31	−42.2	28.9	56.23	11.9	8.23	27.9	..
94.95	33.7	30.1	52.82	11.8	7.05	31.4	−31.4
90.65	13.7	..	48.20	11.5	6.44	36.1	32.7
88.66	6.3	..	43.69	11.0	4.15	..	36.1
85.35	0.3	..	37.67	9.6	3.41	..	39.3
85.16	+ 0.1	..	33.87	8.3	2.86	..	46.5
82.43	4.0	..	30.47	6.5	2.01	..	54.2
79.35	6.8	..	26.17	3.5	1.64	..	57.8
73.26	10.2	..	23.56	1.5	0.96	..	66.8
68.08	11.5	..	21.09	−1.5	...	..	..
65.40	11.8	..	19.92	3.3	...	..	..

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[7] Peters and Baker, *Ind. Eng. Chem.*, **18**, 69 (1926).

[8] Loveless, *ibid.*, **18**, 826 (1926).

[9] Stahler, *Compt. rend. trav. chim.*, **37**, 4405 (1904).

[10] Biltz and Meinecke, *Z. anorg. Chem.*, **131**, 1 (1923).

[11] Haase, *Ber.*, **26**, 1053 (1893).

sulfur dioxide are contained in Table I and shown graphically in the diagram of Fig. 1. The separation of the solution into two liquid phases was sharp and the temperature at which the change took place was easily read. Opalescence near the critical solution point was slight and did not obscure the change at this temperature. In the region of the solid-liquid system the determination of the true solution points was more difficult on account of the slowness with which equilibrium developed. At concentrations below 7% and above 94.5% of titanium tetrachloride a metastable two-phase system was indicated, but it was possible to follow the binary liquid curve in this region only for a very short distance. These metastable points were obtained by slowly and carefully cooling the mixtures. In this way the solution separated into two distinct liquid phases without freezing. In every case the metastable liquid phases disappeared with rise in temperature at the same point at which the solid phase melted when frozen.

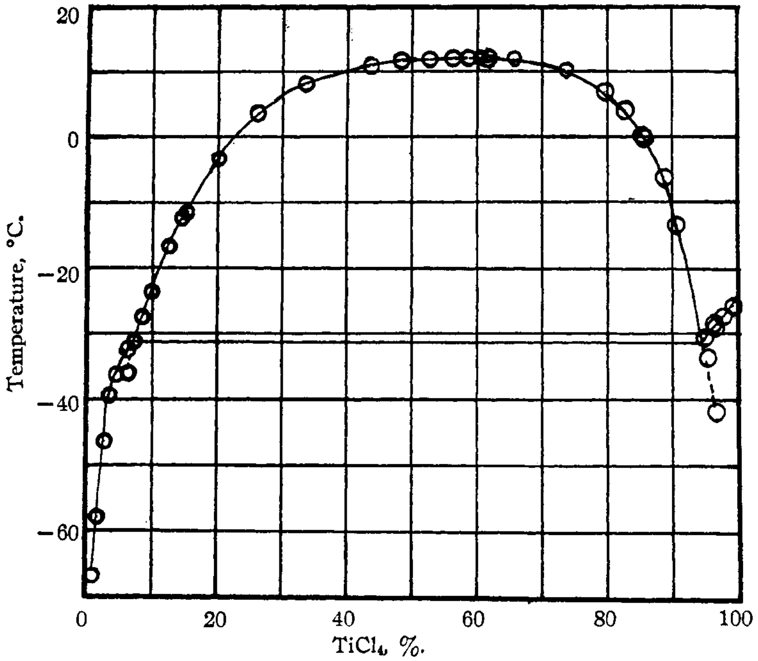

Fig. 1.—Miscibility of titanium tetrachloride with liquid sulfur dioxide.

Silicon Tetrachloride

A refined product which was colorless and appeared to be pure was taken for the starting material. It was allowed to stand over mercury for several days and finally distilled twice from mercury. It was then fractionally distilled four times, using the special fractionation apparatus already mentioned. The separation of the silicon compounds of higher order and boiling point was apparently complete by this process. The product was further distilled twice before using, the first and last portions being rejected each time. This gave a product of highest purity which boiled sharply at 56.8° (751-mm. pressure) and which had a freezing point of −69.7°. Other observers gave the following boiling points: 56.9° (760 mm.) by Becker and Meyer,[12] 56.8° (760 mm.) by Stock, Somiesky and Wintgen.[13] Latimer[14] recorded −70° for the melting point, and Stock, Somiesky, and Wintgen record −68.9°.

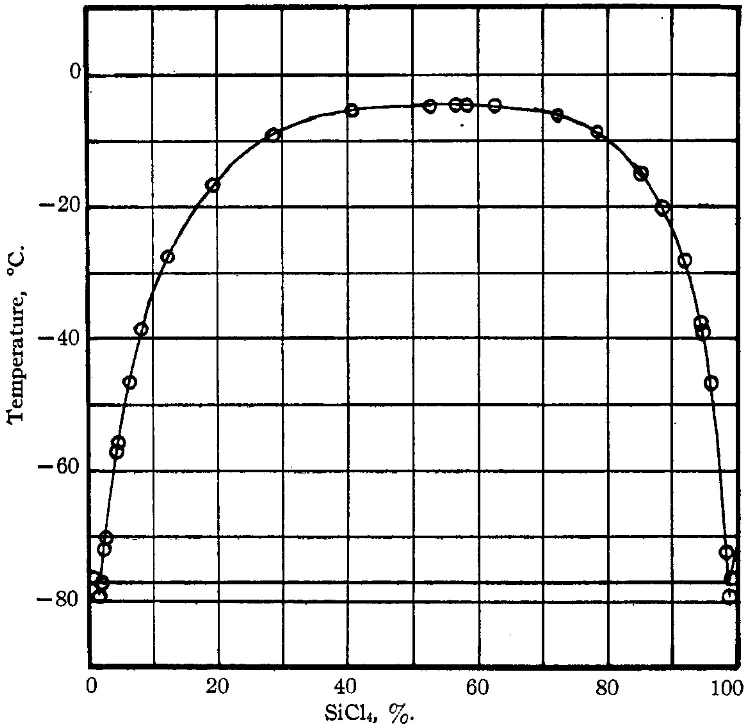

Fig. 2.—Miscibility of silicon tetrachloride with liquid sulfur dioxide.

The solution temperatures were determined in the same general way as for titanium tetrachloride. The results of these determinations are given in Table II and the accompanying diagram, Fig. 2. In the region of the binary liquid system the changes were sharp and without noticeable opalescence. In the region of the solid–liquid system the determinations were more difficult to make. The melting points were not sharp and the

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[12] Becker and Meyer, *Z. anorg. Chem.*, **43**, 251 (1905).

[13] Stock, Somiesky and Wintgen, *Ber.*, **50**, 1754 (1917).

[14] Latimer, This Journal, **44**, 90 (1922).

values given represent the average of several determinations for each mixture. The maximum error in these readings was not greater than 0.3°.

TABLE II

MISCIBILITY OF SILICON TETRACHLORIDE WITH SULFUR DIOXIDE

$SiCl_4$, %	Soln. point	M. p., °C.	$SiCl_4$, %	Soln. point	$SiCl_4$, %	Soln. point	M. p., °C.
100.00	..	−67.7	68.00	5.5	23.18	12.9	..
98.98	..	76.5	62.37	4.9	19.34	16.6	..
98.84	−77.0	79.2	60.72	4.8	15.40	22.0	..
98.70	72.4	..	58.28	4.8	12.37	27.5	..
96.03	46.9	..	56.71	4.8	10.27	32.4	..
94.66	38.6	..	54.05	4.8	8.35	38.4	..
94.37	37.5	..	52.55	4.9	6.33	46.6	..
91.90	28.2	..	46.87	5.0	4.69	55.7	..
88.46	20.1	..	45.29	5.1	4.36	57.0	..
85.19	15.0	..	40.85	5.4	2.83	70.2	..
83.12	12.8	..	37.44	6.1	2.58	72.1	..
78.19	8.8	..	33.32	7.0	1.97	79.1	−77.0
76.81	8.2	..	30.67	8.1	1.09	..	76.5
72.07	6.3	..	28.75	9.2	...	..	..

Zirconium Tetrachloride

Purification of Materials.—A quantity of purified zirconium oxychloride was taken as the starting material. It was recrystallized twenty times from hydrochloric acid and fractionally recrystallized six times from distilled water. A solution of this product gave no indication of iron with potassium thiocyanate. To remove silica it was evaporated to dryness on a steam-bath, redissolved and filtered. This was repeated and the product finally recrystallized from hydrochloric acid. This purified product was dried and strongly ignited to drive off excess hydrogen chloride and water. The product after ignition was chiefly the oxide, ZrO_2, which was used as the source material for zirconium tetrachloride.

The carbon tetrachloride was purified by allowing it to stand over calcium chloride and then over solid sodium hydroxide. It was washed with concentrated sulfuric acid and allowed to stand over phosphorus pentoxide, from which it was distilled and fractionated twice before using.

Preparation of Zirconium Tetrachloride.—The method of preparation of zirconium tetrachloride was that used by Venable and Bell.[15] This method consisted in passing a stream of dry chlorine saturated with carbon-tetrachloride vapor over zirconium dioxide heated to about 450°. The process was carried out in an apparatus essentially the same as that used by these workers. The reaction was quantitative and required only a few hours for the preparation of 10 to 15 g. There always appeared in the first product formed a small quantity of a light brown substance, presumably ferric chloride, which could be driven along before the zirconium tetrachloride by carefully controlling the temperature. To free the product from this substance, all carbon tetrachloride vapor was swept out of the apparatus with dry chlorine and the product resublimed back and forth in the apparatus several times. The zirconium tetrachloride crystallized in clear colorless needles some of which were an inch in length. This purified product was distributed among the several small bulbs and after all of the chlorine had been

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[15] Venable and Bell, THIS JOURNAL, **39,** 1598 (1917).

swept out with dry air they were sealed off. The product was analyzed for chlorine volumetrically by titrating the neutral solution with standard silver nitrate, using potassium chromate as the indicator. The results by this method showed a purity of 99.9% of $ZrCl_4$. It was analyzed for its zirconium content, using the method of Lundell and Knowles,[16] which consisted in precipitating the zirconium as the phosphate in a 20% sulfuric acid solution, igniting the precipitate to the pyrophosphate and weighing as such. Results by this method showed the equivalent of 99.8% of $ZrCl_4$.

Preliminary Test for Solubility and for a Binary System.—The fact that zirconium tetrachloride has a high affinity for water made it necessary to transfer it to the apparatus in a dry atmosphere. For this purpose a special air-tight transference box was prepared with a glass door in the top and one side consisting of a rubber diaphragm into which rubber gloves were fixed. The rubber diaphragm permitted a fairly free use of the hands in the manipulation. This box could be filled with dry air and all transferences of zirconium tetrachloride were made in it.

A mixture of zirconium tetrachloride and liquid sulfur dioxide was sealed in a small h-shaped glass tube. The saturated solution was decanted into the side arm and sealed off. This mixture was examined at temperatures up to the critical temperature of sulfur dioxide with no indication of a binary system being formed. Evaporation of the sulfur dioxide from the tube left an appreciable residue, which showed zirconium tetrachloride to be slightly soluble in liquid sulfur dioxide.

Determination of $ZrCl_4 \cdot SO_2$.—A boiling effect was observed when the sulfur dioxide and zirconium tetrachloride were mixed, which indicated liberation of heat and the probability of chemical reaction. Further investigation showed that a solvate was formed. To establish its composition, mixtures of zirconium tetrachloride and sulfur dioxide were prepared in h-tubes as before and the decanted solutions sealed off in the side tubes in the usual manner. These tubes were placed in a freezing mixture of ice and salt and a very small opening melted in the top. The open end of the tube was then connected to a T-tube through which a current of dry air was passed. The sulfur dioxide was allowed to evaporate very slowly and at temperatures never greater than $-10°$. The time required for this evaporation was about six hours. In this way the zirconium tetrachloride was allowed to separate out very slowly and any compound formed with the sulfur dioxide would involve all of the tetrachloride. When the sulfur dioxide had evaporated, the tube was alternately evacuated and filled with dry air, disconnected from the T-tube, closed with a rubber cap, wiped dry and immediately weighed It was connected to the T-tube again and immersed in boiling water for a few minutes to drive off the sulfur dioxide of solvation. The tube was allowed to cool with dry air passing over the opening, again evacuated and filled with dry air several times, removed, dried and weighed. The loss in weight represented the weight of sulfur dioxide held by the zirconium tetrachloride. The tube was opened and the residue washed out. The parts of the empty tube were washed, dried and weighed, and from this the weight of the zirconium tetrachloride was obtained. Several analyses were made which showed the residues to be only zirconium tetrachloride. The ratio of the molecular quantities of zirconium tetrachloride and sulfur dioxide calculated from these results corresponded to the formula $ZrCl_4 \cdot SO_2$. The results of these determinations are shown in Table III. This compound crystallized in water-clear plates which appeared to be quite stable at temperatures around 0° and below. It decomposed slowly at room temperature and rapidly at elevated temperatures, reverting to a white powder.

Solubility of Zirconium Tetrachloride.—There being no existing methods for the determination of solubilities in highly volatile solvents which do not require the application of corrections that are more or less uncertain, a direct method was developed

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[16] Lundell and Knowles, THIS JOURNAL, **41**, 1801 (1919).

TABLE III

DETERMINATION OF $ZrCl_4 \cdot SO_2$

$ZrCl_4$, g.	SO_2, g.	Moles of $ZrCl_4$	Moles of SO_2
0.1243	0.0339	0.000533	0.000530
.1883	.0519	.000808	.000811
.1242	.0338	.000532	.000528
.0914	.0212	.000392	.000331
.1416	.0386	.000608	.000603
.2058	.0559	.000883	.000874

which is an adaptation from one previously used in this Laboratory.[17] A bomb made of monel metal was used (Fig. 3). The walls of this bomb are 1.5 mm. thick, the outside diameter of the main part is 2 cm. and the total length about 18 cm. Its weight assembled is about 210 g. It consists of two separate chambers, B and C, which are held together by the hexagonal nut H when assembled. In the lower part of B there is a needle valve arrangement which consists of the needle G, held in position by the collar F into which it screws. The needle is seated against the shoulder L, as shown, closing the outlet J. From the bottom of chamber B there is a narrow projection D 0.5 cm. long through which is a small opening to the needle-valve compartment. In order to withstand the pressure developed and at the same time to permit the manipulation of the needle, the needle valve was packed by winding rubber threads on the stem of the needle to fit into the space K. These threads when wound on G were held in place by two small washers which are not shown. The rubber was tested for the action of the solvent and of the solution on it by sealing pieces in both the solvent and in the solution, letting stand overnight, opening and examining the rubber for any change in weight or strength. No effect could be detected. Tests made to ascertain the effect of solvent or of solution on the metal of the bomb showed that if moisture was rigorously excluded no action took place.

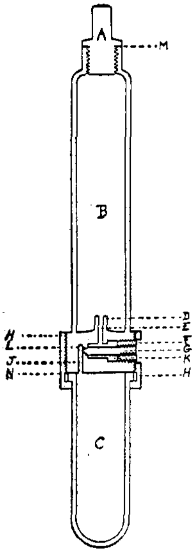

Fig. 3.

Determination of Solubility.—The needle G was seated by grinding with 600-mesh carborundum against the shoulder L (Fig. 3). Into the opening in D was inserted a small bit of cotton to serve as a filter, and the parts were assembled as shown, using gaskets of lead foil at M and N.

The chambers B and C were washed and thoroughly dried by alternately evacuating and filling with dry air. The needle G was closed tight to shut off chamber C, and a quantity of zirconium tetrachloride transferred to B. The bomb was cooled and the liquid sulfur dioxide admitted in the usual way. The mixture was agitated in a constant temperature bath for twelve to fourteen hours. At the end of this time agitation was stopped and the bomb allowed to stand in a slightly inclined position for about an hour to permit the residue to settle to one side of D. A portion of the saturated solution in B was collected in C by loosening the needle G, and allowing it to filter into the valve chamber and to flow into C. The needle was very slightly loosened at first to prevent supercooling of the solution in the valve chamber, and any zirconium tetrachloride precipitated by the evaporation of the sulfur dioxide was deposited beyond the valve seat and subsequently swept into C by the liquid which followed.

When the sample had been thus collected, the needle was again tightened and the

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[17] Stowe, Doctor's "Thesis," this Laboratory, 1927.

bomb removed from the bath. In this way a sample of the saturated solution was collected from beneath the surface of the liquid in B. The vapor in C is therefore a part of the sample and no correction for its presence is necessary. Throughout this process the bomb was kept in a stoppered glass jacket tube to protect it from contact with the bath liquid. In the manipulation of the needle valve the bomb was raised from the bath for only a few seconds at a time.

The excess sulfur dioxide was allowed to vaporize from B, which was then washed out with absolute alcohol and dried with ether. The bomb containing the sample was weighed. The needle G was slightly loosened and the sulfur dioxide in C allowed to vaporize in a desiccator having a current of dry air flowing through it. After the sulfur dioxide had evaporated, the bomb was alternately evacuated and filled with dry air to remove all sulfur dioxide gas from C, and was weighed to ascertain the amount of sulfur dioxide.

The bomb was disconnected and the residue in C washed out and analyzed for zirconium according to the method of Lundell and Knowles[16] already mentioned. From the previous weights and the result of the analysis of the residue, the composition of the solution was calculated. The solubility was found to be a straight-line function of the temperature; the results of determinations from 0 to 20° are given in Table IV.

TABLE IV

SOLUBILITY OF ZIRCONIUM TETRACHLORIDE

	0°		10°		20°	
Sulfur dioxide, g.	5.3286	5.2905	5.8132	6.4758	5.8122	4.1985
$ZrCl_4$, g.	0.2742	0.2667	0.4247	0.4815	0.5649	0.4011
Mole fraction $ZrCl_4$	0.0139	0.0137	0.0198	0.0200	0.0260	0.0257

Discussion

The miscibility of liquids is closely connected with the polarity of their molecules. The dielectric constant gives direct evidence of polarity inasmuch as it indicates the intensity of the electrical moment in the molecule due to electron displacement. The value of this constant for titanium tetrachloride is 2.73,[18] that for silicon tetrachloride is 2.4,[19] and that for sulfur dioxide 16.2.[20] These values show titanium and silicon tetrachlorides to be alike in polarity. The greater value for sulfur dioxide could account for the partial miscibility of the tetrachlorides with it at low temperatures. Comparing the polarities of these substances on the basis of the Ramsey and Shields constant, the value of which for silicon tetrachloride is 2.20, and that given by Stowe[21] for sulfur dioxide is 2.134, we find like polarities for sulfur dioxide and silicon tetrachloride. Sufficient data were not available for calculating this value for titanium tetrachloride. To compare the polarities of these compounds further, the entropy of vaporization was calculated by applying Hildebrand's modification of Trouton's rule[22] to the value of vapor pressure at various temperatures

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[18] Matthews, *J. Phys. Chem.*, **9**, 641 (1905).

[19] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, **1924**, p. 89.

[20] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924**, p. 593.

[21] Stowe, THIS JOURNAL, **51**, 410 (1929).

[22] Hildebrand, *ibid.*, **37**, 970 (1915).

as given in the "International Critical Tables" for sulfur dioxide, and to those given by Wintgen[23] for silicon tetrachloride. This gave for sulfur dioxide the value 25.6, and for silicon tetrachloride 27.9. Hildebrand has shown the value of this constant to be 27.4 for non-polar substances in general. The values for these compounds are in sufficient agreement with that for non-polar substances in general to indicate again their non-polarity.

Hildebrand[24] has shown that the relative internal pressures of various solvents may be estimated from the solubility data of a common solute by plotting the common logarithm of the mole fraction of the solute against the reciprocal of the absolute temperature and comparing these with a like curve for the ideal solution of the solute. The displacement of these curves from that of the ideal is a measure of their internal pressure differences, and from such a plot it is possible to arrange the solvents in a relative internal pressure series. A plot of the solubilities of liquid sulfur dioxide as the solute in the various tetrahalides as solvents was made in order to compare the relative internal pressure of these compounds. The ideal solubility curve for liquid sulfur dioxide was constructed on the basis of its heat of vaporization and boiling point. The boiling point was taken as $-10°$ and the value of ΔH was that given in the Landolt and Börnstein "Tabellen" as 6157 cal. per mole. These curves are shown in Fig. 4, where the curves for carbon and stannic tetrachlorides and stannic bromide are plotted for comparison from the data given by Bond and Beach.[2] Now Stowe[21] has calculated the internal pressure of sulfur dioxide from the relation $\gamma/V^{1/3}$ to be 6.33 at 20°, where γ is the surface tension

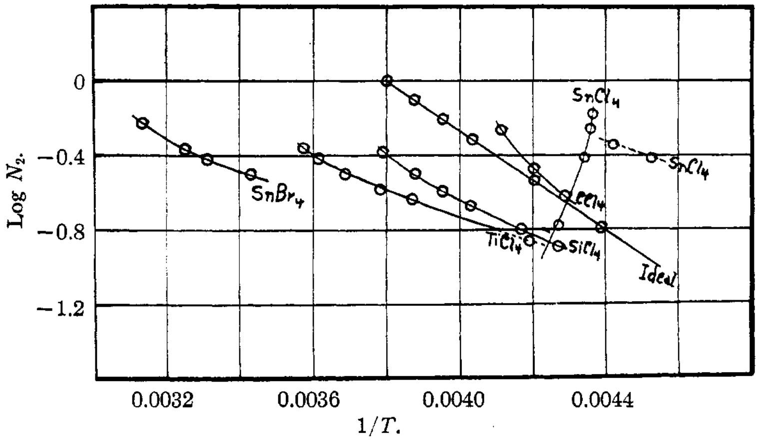

Fig. 4.—Solubility relations of sulfur dioxide.

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[23] Wintgen, *Ber.*, **52**, 724 (1919).

[24] Hildebrand, ref. 19, p. 113.

and V the molal volume, and has placed liquid sulfur dioxide between chloroform and benzene in the Hildebrand solubility series.[25] Mortimer[26] pointed out that the ratio of the slope of the experimental curve to that of the ideal for any solute is a measure of the relative internal pressure of the solute and solvent. Applying this method to the curves for titanium and silicon tetrachlorides as solvents we find values which indicate titanium tetrachloride not only to belong above sulfur dioxide but also above silicon tetrachloride in the Hildebrand series. In view of this relation we would expect the miscibility of sulfur dioxide to be less in titanium tetrachloride than in silicon tetrachloride for a given temperature. The experimental results are in accord with this view.

In general this investigation has shown that the systems formed by liquid sulfur dioxide with titanium and silicon tetrachlorides accord with the principles of the various factors usually considered in the problem of solubility. The results of these measurements agree in a satisfactory way with the physical properties of the compounds, such as melting points, boiling points and dielectric constants. The critical mixing temperatures are in harmony with the various melting points and the relative positions of the elements in the periodic arrangement.

The solubility of zirconium tetrachloride in liquid sulfur dioxide was examined in the region of temperature where the compound $ZrCl_4 \cdot SO_2$ is fairly stable. The noticeable heat effect, also the formation of a solvate, when zirconium tetrachloride is mixed with sulfur dioxide would indicate a large negative deviation from Raoult's law. No data are available from which its polarity and internal pressure may be measured according to the criteria usually applied. On the basis of theory we would expect it to have an internal pressure close to that of liquid sulfur dioxide and would also expect that its apparent higher polarity would be largely induced as a result of polar bonds within the molecule. This is in accord with the general increase of basic properties of the elements from the top toward the bottom of the periodic groups. In general the solubility relations of zirconium tetrachloride in liquid sulfur dioxide are in accord with the principles governing solubility where there is a large difference of polarity.

Summary

1. The solubility relations of titanium and silicon tetrachlorides with liquid sulfur dioxide have been determined over the entire range of compositions.

2. The solubility relations are in accord with theory as to polarity, internal pressure, melting points, etc.

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[25] Hildebrand, ref. 19, p. 111.

[26] Mortimer, THIS JOURNAL, **45**, 633 (1923).

3. A direct method for the determination of solubilities in highly volatile solvents has been utilized.
4. The solubility of zirconium tetrachloride in liquid-sulfur dioxide from 0 to 20° has been determined and the solvate $ZrCl_4 \cdot SO_2$ has been established.

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THE REACTIONS OF ETHYLENE, HYDROGEN AND THE SATURATED HYDROCARBONS UNDER THE INFLUENCE OF EXCITED MERCURY[1]

BY HUGH S. TAYLOR AND DOUGLAS G. HILL[2]

RECEIVED MAY 4, 1929 PUBLISHED OCTOBER 5, 1929

The photosensitized combination of hydrogen and ethylene has been the subject of a number of investigations.[3] The results have been in such disagreement that it seemed worth while to reopen the subject in the hope of discovering the mechanism of what would *a priori* be considered one of the simplest of hydrocarbon reactions. This hoped-for simplicity has not been found, and no final statement as to mechanism may be ventured, but it is believed that the facts to be presented afford an empirical explanation of the variations previously found. It may also be possible, we believe, to correlate them with experiments in which the same gases, although activated by other means, react to give very similar products. We may cite, for example, the reactions of ethylene[4] in the presence of hydrogen under the influence of alpha particles. Correlation should also be possible with other reactions due to hydrogen atoms, which Franck and Cario[5] have shown are produced under the experimental conditions employed.

Experimental Details

Apparatus.—The apparatus used in these studies consisted of a quartz reaction vessel which surrounded the arc concentrically, thus securing as great an intensity of illumination as possible, together with a constant-volume manometer to follow the pressure changes. A gas buret and a storage reservoir were also attached through

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[1] This paper is based upon a thesis submitted by Douglas G. Hill to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Albert Plaut Fellow in Chemistry.

[3] (a) Berthelot and Gaudechon, *Compt. rend.*, **150,** 1169 (1910); (b) Taylor and Marshall, *J. Phys. Chem.*, **29,** 1140 (1925); (c) Olson and Meyers, THIS JOURNAL, **48,** 389 (1926); (d) **49,** 3131 (1927); (e) Taylor and Bates, *ibid.*, **49,** 2483 (1927).

[4] Lind, Bardwell and Perry, *ibid.*, **48,** 1556 (1926).

[5] Franck and Cario, *Z. Physik,* **11,** 162 (1922).