charge tube was in the two resonance lines, 2537 and 1849 Å., a simple calculation shows that 3–4% of its radiation must be of the shorter wave length in order to account for the results obtained. This is a plausible explanation for a photograph of the spectrum from the discharge tube showed the following lines below 2537 Å. were present: 2483, 2399, 2378, 2352, 2260, 2100, 2025, 1970, 1942 and 1849 Å. That the mercury line, 1849 Å., is present to an appreciable percentage in a low-pressure discharge tube also has been mentioned by Cline and Forbes,[7] who report about 2%, and by Rössler and Schönherr,[8] who report a maximum of 10% under certain conditions.

The quantum yield for the inactivation of pepsin may be calculated from the data of Gates.[2] From his data the quantum yields at wave lengths 2357, 2509, 2719 Å. are, respectively, 0.0014, 0.00034, 0.00045, and at 2930 Å. the quantum yield is very low, almost zero. These data indicate an increase in quantum yield with decreasing wave length. This is in agreement with the results of the present experiment.

A similarity in the reactions of both the urease and pepsin to ultraviolet radiation is worth mentioning. The loss of enzymatic activity seems to be more sensitive to effective radiant energy than a second observable change, indicated by increased molecular extinction coefficients in the absorbing region. A large amount of the enzymatic activity is actually destroyed before an appreciable change in absorption occurs.

The author wishes to thank Professors Fred M. Uber and Daniel Mazia for helpful suggestions in connection with this work.

Summary

1. The absorption spectrum of urease has been measured in a pyrophosphate buffer solution at *p*H 5.6. A maximum molecular extinction coefficient of 0.798×10^6 occurs around 2700 Å., assuming a molecular weight of 483,000, and a minimum occurs at about 2480 Å.

2. The quantum yield for urease inactivation has been determined for a number of wave lengths. From 3130 to 2537 Å. the quantum yield seems to be fairly constant with the value of about 0.0008 molecule/quantum; increasing at shorter wave lengths, it reaches a value of 0.00938 at 1860 Å.

3. The direct radiation from a low-pressure mercury discharge tube (Hanovia Sc-2537) was more efficient in inactivating urease than monochromatic radiation of 2537 Å.; this is shown to be due to radiation of wave length shorter than 2350 Å., probably the mercury line at 1849 Å.

RECEIVED JULY 3, 1940

(7) Cline and Forbes, THIS JOURNAL, **61**, 716 (1939).

(8) Rössler and Schönherr, *Z. tech. Physik*, **19**, 588 (1938).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Rotation and Polymorphism in the Methyl Chloromethanes

BY ANTHONY TURKEVICH AND CHARLES P. SMYTH

The almost spherical symmetry of the *t*-butyl chloride molecule and its low heat of fusion led to an investigation of the dielectric constants of the *t*-butyl halides[1] which showed rotational freedom in the solid for some distance below the melting points comparable to that in the liquid state. As rotation was made possible by the approximate similarity in size and shape of the halogen atoms and the methyl groups, it appeared highly probable that molecules containing not only one, but also two and three chlorines attached to the central carbon with methyl groups occupying the remaining positions possessed similar rotational freedom. Transitions have been found in the compound with four methyls around the central carbon, neopentane,[2] and in the compound with four chlorines, carbon tetrachloride,[3] which are to be interpreted as indicating the setting in of molecular rotation.[4] As the molecules of these two substances possess no dipole moments, they cannot be investigated by dielectric constant measurements, but the intermediate compounds have been studied by this method with the aim of enlarging our knowledge of the effect of molecular structure upon the rotational freedom of the molecule in the crystalline state.

The dielectric constant measurements were made with a capacity bridge coupled to a variable oscillator in the general fashion previously de-

(1) Baker and Smyth, THIS JOURNAL, **61**, 2798 (1939).

(2) Aston and Messerly, *ibid.*, **58**, 2354 (1936).

(3) Johnston and Long, *ibid.*, **56**, 31 (1934).

(4) Baker and Smyth, *ibid.*, **61**, 1695 (1939).

scribed,[1,5] and the substances were further examined down to liquid air temperatures with a polarizing microscope[1] and by means of temperature–time curves.

Preparation and Purification of Materials

2,2-Dichloropropane was prepared in the usual manner,[6,7] by allowing dry acetone to drip slowly, with cooling, on phosphorus pentachloride. The products were distilled off, washed carefully with salt water several times, then with sodium carbonate solution, and finally with saturated salt solution. The mixture was dried at −5° with fused calcium chloride and anhydrous sodium carbonate. It was then repeatedly fractionated and a fraction boiling at 69.3° within less than 0.1° was fractionally distilled under reduced pressure in a Vigreux column; f. p. −33.8 ± 0.1°. Timmermans and Delcourt[8] report a boiling point of 70.5°, and a freezing point of −34.4°. Van de Vloed[9] reports a freezing point of −34.6°.

Methyl Chloroform.—Eastman Kodak Company "practical" methyl chloroform was washed several times with concentrated sulfuric acid, sodium carbonate solution and water, dried over fused calcium chloride and finally repeatedly fractionated: b. p. 74.0, f. p −32.7°, $n^{20}\mathrm{D}$ 1.4379; "International Critical Tables" give b. p. 74.1°, $n^{20}\mathrm{D}$ 1.4349; Van de Vloed[9] has recently found a freezing point value −32.2°.

Experimental Results

The dielectric constants ϵ and specific conductances of the substances were measured at frequencies of 50, 5 and 0.5 kilocycles, but, as the conductances were all of the order of 10^{-10} mhos and as no anomalous dispersion was apparent, only the dielectric constant data at 50 kc. are given in Table I. The dielectric constant values are plotted against temperature in Figs. 1 and 2, in which hollow circles represent measurements made with decreasing temperature and half-filled circles values obtained with rising temperature.

TABLE I

DIELECTRIC CONSTANTS AT 50 KC.

t, °C.	ϵ	t, °C.	ϵ	t, °C.	ϵ
2,2-Dichloropropane, Cooling					
18.8	10.25	−34.2	14.11	−75.5	14.61
5.4	11.04	−39.6	14.18	−81.0	14.63
−6.4	11.80	−43.9	14.24	−87.0	13.49
−17.9	12.64	−49.0	14.32	−86.7	12.32
−27.8	13.38	−51.2	14.36	−86.4	4.80
−33.4	13.85	−53.7	14.42	−86.0	2.29
−38.4	14.25	−55.7	14.47	−86.3	2.28
−39.8	14.36	−59.0	14.51	−94.3	2.26
−34.1	14.28	−67.5	14.56	−106.0	2.23
Warming					
−90.8	2.26	−84.9	14.61	−34.0	14.21
−87.9	2.27	−84.4	14.72	−34.0	14.29
−86.3	2.28	−83.4	14.75	−33.9	14.31
−85.3	2.54	−79.5	14.71	−33.8	14.21
−85.1	3.07	−75.6	14.68	−33.7	14.00
−85.0	4.44	−64.7	14.51	−33.6	13.79
−85.0	8.57	−54.8	14.37	−33.2	13.73
−84.95	12.16	−39.9	14.27	−30.9	13.60
−84.95	14.37	−35.3	14.19	−29.4	13.47
−84.9	14.53	−34.1	14.13	−25.2	13.14
Methyl Chloroform, Cooling					
2.1	7.03	−38.1	8.82	−55.2	9.33
−9.9	7.44	−38.5	8.88	−48.9	5.20
−18.4	7.75	−39.0	8.89	−48.9	3.47
−19.0	7.76	−39.2	8.91	−48.9	3.10
−26.8	8.07	−39.9	8.92	−49.0	3.08
−29.8	8.19	−41.5	8.02	−50.6	2.88
−30.9	8.23	−41.7	9.01	−58.2	2.62
−32.3	8.28	−42.9	9.06	−59.1	2.61
−33.0	8.31	−43.9	9.12	−63.0	2.55
−33.5	8.33	−47.4	9.18	−68.3	2.50
−32.7	8.37	−48.7	9.15	−74.2	2.38
−33.2	8.53	−49.7	9.15	−88.7	2.33
−34.5	8.63	−51.4	9.19	−98.2	2.30
−34.8	8.65	−53.0	9.25	−123.2	2.26
−36.2	8.74	−54.0	9.30		
Cooling					
−32.4	8.28	−32.6	8.41	−33.1	8.54
−33.2	8.32	−32.9	8.50	−35.0	8.69
Warming					
−64.5	2.54	−48.5	8.99	−30.1	8.18
−53.9	2.74	−43.9	8.85	−25.7	8.01
−48.9	3.14	−41.1	8.68	−41.4	8.35
−48.7	3.28	−34.7	8.57	−40.3	8.30
−48.8	3.98	−33.7	8.51	−37.4	8.31
−46.8	5.73	−33.0	8.43	−34.0	8.46
−48.8	6.81	−32.7	8.39	−32.9	8.44
−48.8	7.84	−32.55	8.35	−32.1	8.31
−48.7	8.54	−32.1	8.26	−30.9	8.21
				−27.5	8.07

Discussion of Results

On the cooling of the liquid, the dielectric constant of 2,2-dichloropropane increases (Fig. 1) in the usual manner until the freezing point is reached. If the sample is not stirred, the liquid can be made to supercool as much as 6.5° with the resulting dielectric behavior illustrated on a large scale in the inset in Fig. 1. Stirring, however, induces immediate crystallization, the dielectric constant changing abruptly by several tenths of a unit. Further cooling shows a continued steady increase in ϵ, but with a slope smaller than that in the liquid range. A thermal transition at −86°, preceded by supercooling of about 1°, is accompanied by a sharp drop in dielectric constant to a low value. Further cooling

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[5] Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[6] Friedel and Ladenburg, *Ann.*, **142**, 315 (1867).

[7] Henne and Renoll, THIS JOURNAL, **59**, 2434 (1937).

[8] Timmermans and Delcourt, *J. chim. phys.*, **31**, 85 (1934).

[9] Van de Vloed, *Bull. soc. chim. Belg.*, **48**, 229 (1939).

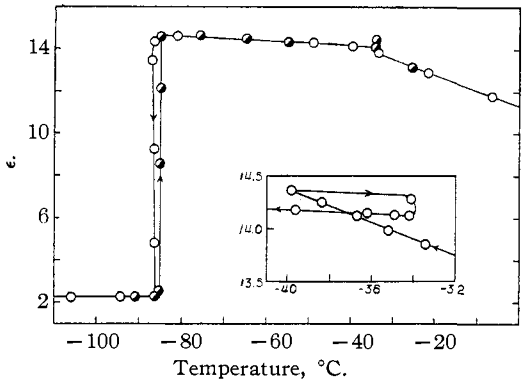

Fig. 1.—Temperature dependence of the dielectric constant of 2,2-dichloropropane (hollow circles represent points on cooling curve, half-filled circles, points on heating curve).

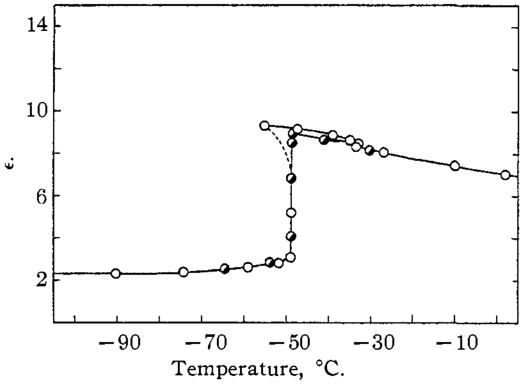

Fig. 2.—Temperature dependence of the dielectric constant of methyl chloroform (hollow circles represent points on cooling curve, half-filled circles, points on heating curve).

reveals no other dielectric or thermal anomalies. At no point is there any dispersion in the frequency range used.

Measurements made while slowly heating the sample confirmed the general behavior outlined above. The dielectric constant stayed at about 2.3, with no dispersion, right up to the transition point, which occurred, thermally and dielectrically, at −85.0°. The dielectric constant rose sharply to the value of about 14.5 found for the high temperature solid form on cooling and thereafter followed the same curve as that obtained with falling temperature, the only exception being a slight anomalous rise at the melting point, which was, presumably, due to the presence of a small amount of impurity. The melting point was −33.7°, in agreement with the value obtained on cooling with stirring. During one of the cooling runs the sample was allowed to stand for about sixteen hours at −75°, that is, in the high temperature solid form. The dielectric constant was thereupon found to have diminished by about 0.3 unit. Such behavior in a solid with rotating molecules on prolonged annealing has been observed before in this Laboratory and probably is to be attributed to recrystallization.

The halts on the temperature–time curves on both cooling and heating runs indicated that the heat of transition was greater than the heat of fusion. This latter has been estimated from freezing point depressions[9] to be about 790 cal. per mole, which gives an entropy of fusion of 3.3 units. From the relative areas under the halts on the temperature–time curve at the freezing and transition points it may be estimated that the entropy of transition is more than 4 units and probably not far from 6. Observations with the polarizing microscope revealed that the high temperature form of 2,2-dichloropropane is isotropic. On cooling, the enantiotropic transition occurred very sharply to give anisotropic crystals.

The dielectric constant–temperature curve for methyl chloroform in Fig. 2 resembles that for the compound with two chlorines and two methyls on the central carbon, both showing only a slight change at the freezing point. In spite of all attempts to prevent it by slow cooling and stirring, the substance always supercooled one or two degrees as shown in Fig. 3. The temperature would then rise to −32.7°, but, due to the very low heat of fusion, would soon start dropping again. On further cooling the dielectric constant rose steadily until supercooling had occurred to a temperature about 7° below the transition point. Although this supercooling of about 7° always occurred, several attempts made to prevent the transition entirely by very rapid cooling did not succeed. From the low point reached in supercooling the

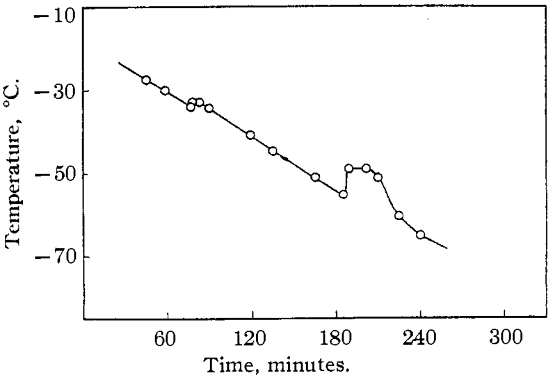

Fig. 3.—Temperature–time curve for methyl chloroform.

temperature rose to −48.9° where a definite flat occurred on the temperature–time curve as shown in Fig. 3, which consists of two separate cooling curves of identical slope placed adjacent to each other. At the same time the dielectric constant dropped abruptly from a value above 9 units to one of less than 3. Further cooling revealed no other unusual thermal or dielectric behavior, the dielectric constant decreasing gradually to a value of about 2.3, which arose entirely from induction.

The points obtained while heating the sample fall exactly on the curve obtained on cooling except in the high temperature solid form. Here the measurements with rising temperature are consistently slightly lower, as indicated in Fig. 2, and vary a few tenths among themselves, depending on the previous thermal history. The melting point is practically undetectable with the dielectric constant, the change of a few tenths taking place continuously. Van de Vloed[9] reports an entropy of fusion of 4.5 units. The temperature–time curves illustrated in Fig. 3 seem to indicate a very small heat of fusion, and a much larger transition heat. The lack of an appreciable flat at the freezing point and the poor melting point may indicate the presence of some impurity.

The rise in the dielectric constant as the transition temperature was approached from the low temperature side although small was very reproducible, both heating and cooling runs agreeing very closely. The effect must be considered real and is probably ascribable to an increased librational freedom of the molecules as the temperature is raised. A critical amplitude in these librations is finally reached at which point the orientational effect of neighboring molecules vanishes, and the true transition takes place. Similar effects have been observed before in dielectric studies of phase transitions. They are especially large in the case of the long chain compounds.[10] Excessive rises in the specific heats of solids just below phase transitions have also been attributed to librational effects.[11] The polarizing microscope shows the high temperature form of the solid methyl chloroform to be isotropic and to change in the transition to an anisotropic low temperature form.

These results indicate that the almost spherical molecules of methyl chloroform and 2,2-dichloropropane possess rotational freedom in their high temperature solid forms. Comparative density determinations are not available, but qualitative observations indicate that the densities of liquid and solid near the melting point are very nearly equal. Thus, when all dissolved gases are removed, the liquids set to perfectly transparent solids. Any large density change on freezing would be expected to lead to voids and cracks which would give the solid an opaque appearance. Similar observations have been noted[12] about other solids with rotating molecules. Since there is but little change in dielectric constant on freezing, we can conclude that the rotational freedom in the solid is practically the same as in the liquid state of these compounds.

As previous work[4] has shown that molecular rotation in the solid leads to an abnormally high melting point and short liquid interval, it is interesting to compare the melting points, boiling points and liquid intervals $\Delta T^{\circ}_{\text{liq.}}$ for these substituted methanes with those of their isomers, whose molecules presumably do not rotate in the solid state. The data given in Table II are taken from "International Critical Tables" unless otherwise indicated.

TABLE II

MELTING POINTS, BOILING POINTS AND LIQUID INTERVALS OF ISOMERIC SUBSTANCES

Compound	M. p., °K.	B. p., °K.	$\Delta T^{\circ}_{\text{liq.}}$
n-Pentane	143.5	309.3	165.8
Isopentane	113.6	301.2	187.6
Neopentane	256.6	282.6	26.0
n-Butyl chloride	150.0	351.0	201.0
i-Butyl chloride	141.9	341.4	199.5
t-Butyl chloride	248.5	323.7	75.2
1,3-Dichloropropane[13]	173.7	393.6	219.9
2,2-Dichloropropane	239.4	343.7	104.3
1,1,2-Trichloroethane	236.5	386.7	150.7
1,1,1-Trichloroethane (methyl chloroform)	240.5	347.3	106.8

Neopentane has a much higher melting point and shorter liquid interval than *n*-pentane or isopentane and the same is true of *t*-butyl chloride as compared to its two isomers for which data are given, and of 2,2-dichloropropane and the non-rotating 1,3-dichloropropane. The differences are so small in the case of the two trichloroethanes as to suggest some rotational freedom in the 1,1,2-trichloroethane, since the molecules of methyl chloroform undoubtedly possess rotational freedom in the solid.

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(10) Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

(11) Eucken, *Z. Elektrochem.*, **45**, 126 (1939).

(12) White and Bishop, THIS JOURNAL, **62**, 8 (1940).

(13) Serwy, *Bull. soc. chim. Belg.*, **42**, 483 (1933).

Table III summarizes for the five methyl chloromethanes the transition points, t. p., the melting points, m. p., the boiling points, b. p., the entropies of transition, ΔS_t, as far as known, the entropies of fusion, ΔS_f, and the dipole moments, μ. The crystals of all five substances are isotropic and, therefore, cubic, above their transition points and, with the possible exception of neopentane for which no result has been obtained below the transition point, anisotropic below.

TABLE III

PROPERTIES OF METHYL CHLOROMETHANES

Substance	T. p., °K.	M. p., °K.	B. p., °K.	ΔS_t	ΔS_f	μ ($\times 10^{18}$)
$C(CH_3)_4$[2]	140.0	253.1	282.6	4.39	3.03	0
$C(CH_3)_3Cl$[1]	219.3	248.5	323.7	>3	2.0	2.14[14]
$C(CH_3)_2Cl_2$	188.1	239.4	343.7	>4	3.3[9]	2.18[15]
$C(CH_3)Cl_3$	224.3	240.5	347.3	>5	4.5[9]	1.57[16]
CCl_4[3]	225.3	250.3	349.8	4.79	2.30	0

The entropies of transition are very roughly estimated for the three intermediate compounds, but there is no doubt that they, as well as those for neopentane and carbon tetrachloride, are larger than the entropies of fusion, which are of the magnitude calculated for a substance with molecules rotating in the crystal.[17] When a methyl group of neopentane is replaced by a chlorine to give a large dipole moment to the molecule, a large increase in boiling point occurs and a slight decrease in melting point. Successive replacements of methyl by chlorine give smaller and smaller boiling point increases, while the slightly affected melting point decreases through a minimum and returns in carbon tetrachloride almost to the melting point of neopentane. No such regularity is apparent in the transition temperatures. The large rise from neopentane to *t*-butyl chloride is due to some extent, at least, to the rise in the potential barrier to rotation caused by the field of the dipole of the *t*-butyl chloride molecule. In the cases of the hydrogen halides[5] and the *t*-butyl halides,[1] increase in the size of the halogen atom lowers the temperature at which the molecules acquire rotational freedom in the crystal. The irregularities in the transition temperatures of the methyl chloromethanes is reminiscent of the fact that the melting points of an homologous series are less regular in their variation than the boiling points because of differences in molecular packing in the lattices. In the anisotropic crystals in which these compounds exist below their transition points, differences in the packing of the molecules can easily account for the irregular variation of the transition temperatures. Once the molecules are rotating, however, their spherical symmetry gives rise to a cubic lattice,[18] which breaks down at very similar temperatures for the similar molecules. Rotational transitions have much in common with the melting points of solids in which the molecules cannot rotate and the high temperature solid forms in which molecular rotation can occur differ little in some ways from the liquid state.

The rotational freedom of these methyl chloromethane molecules in the crystal is due to their symmetrical form, which is approximately that of a tetrahedron with its corners so rounded that it can turn easily from one position to another in the lattice much as if it were a sphere. When one of the methyl groups of *t*-butyl chloride is changed to an ethyl to give *t*-amyl chloride, the protrusion of the ethyl group seems to cause sufficient interlocking of the molecules in the lattice to prevent rotation. This absence of rotation is established by the sharp drop of the dielectric constant of *t*-amyl chloride on solidification to a low value which arises from induction. The experimental data on this substance will be presented in another connection in a subsequent paper.

As it was thought that the similarity in molecular shape and size would cause mixtures of these methyl chloromethanes to form solid solutions, which would be of interest for dielectric studies, a preliminary examination with the polarizing microscope was made[1] upon a 50% by volume mixture of *t*-butyl chloride and carbon tetrachloride. The evidence of solid solution formation thus obtained made it seem desirable to carry out a thermal investigation of the system *t*-butyl chloride–carbon tetrachloride. The measurements described below were made by Mr. Joseph V. D. Hoffman. The freezing point diagrams obtained by Van de Vloed[9] with 2,2-dichloropropane as one component and *t*-butyl chloride, methyl chloroform or carbon tetrachloride as the other component justified the expectation of solid solution formation.

The freezing points and transition points were measured with an apparatus like one which has been described previously,[19] except that the glass tube surrounding the inner

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(14) Smyth and Dornte, THIS JOURNAL, **53**, 545 (1931).

(15) Gross, *Physik. Z.*, **32**, 587 (1931).

(16) Sutton, *Proc. Royal Soc.* (London), **A133**, 668 (1931).

(17) Hirschfelder, Stevenson and Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

(18) Smyth, *Chem. Rev.*, **19**, 329 (1936).

(19) Huettig and Smyth, THIS JOURNAL, **57**, 1523 (1935).

tube containing the melt was encased in a short length of iron pipe to make the temperature more uniform. Cooling was ordinarily effected by adding dry-ice to the surrounding alcohol-bath in a Dewar tube. The solution containing 17.83 molecular % of *t*-butyl chloride was cooled by placing the tube in the metal block ordinarily used for the dielectric cell and blowing liquid air into the block.[5]

The materials used were purified in the usual way. Carbon tetrachloride from Merck and Company was dried over previously fused potassium hydroxide and twice fractionated; b. p. 76.7°; f. p. −22.7°; n^{20}_D 1.45946. *t*-Butyl chloride from the Eastman Kodak Company was washed with ice water, dried over previously fused calcium chloride and fractionally distilled; b. p. 50.5°; f. p. −25.4°; n^{20}_D 1.38786.

The relative lengths of the halts obtained on the temperature–time curves for the pure substances were consistent with the data in Table III, the heats of transition being larger than the heats of fusion. For the mixtures, the halts at the transition were, naturally, less sharp, showing also a tendency toward supercooling. In the mixture containing 25.33 molecular % of *t*-butyl chloride, the halt at the transition could not be detected although repeated attempts were made to find it. In Table IV are listed the molecular percentage of *t*-butyl chloride in each mixture and the transition point, t. p., and freezing point, f. p., of the mixture. The freezing and transition points are plotted against composition in Fig. 4, a dotted line connecting the transition points for the 17.83 and 38.19% mixtures, since the transition point for the intervening mixture could not be detected, presumably because of the steepness of the curve in this region.

TABLE IV

TRANSITION AND FREEZING POINTS OF *t*-BUTYL CHLORIDE–CARBON TETRACHLORIDE MIXTURES

Mol. % $(CH_3)_3CCl$	T. p., °K.	F. p., °K.
0.00	225.1	250.4
5.84	214.8	248.5
10.31	208.4	246.7
17.83	195.7	245.2
25.33	...	243.5
38.19	231.0	242.3
49.71	231.1	241.7
63.68	227.8	241.5
74.65	223.4	242.2
87.05	215.3	244.1
93.83	211.9	245.9
97.91	216.4	247.0
100.00	218.8	247.7

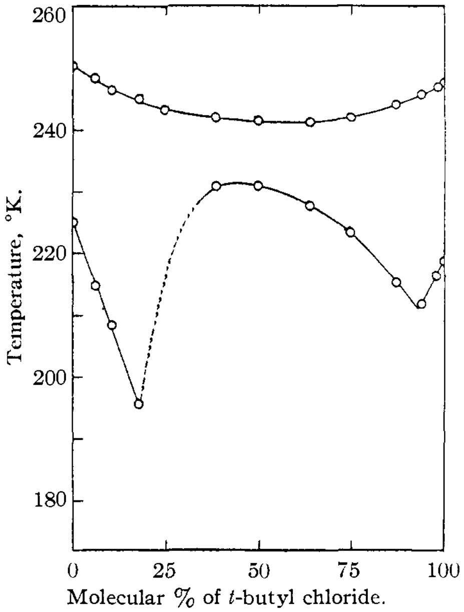

Fig. 4.—*t*-Butyl chloride–carbon tetrachloride system.

Although the solidus curve was not obtained, the freezing point curve in Fig. 4 shows clearly that the two substances form a continuous series of solid solutions as was expected. Examination with the polarizing microscope indicated that the solids were isotropic near their melting points and were apparently anisotropic at low temperatures. The flat maximum in the transition point curve occurs not far from the composition of an equimolecular mixture, which might lead to speculation as to the formation of a one-to-one intermolecular compound. However, quite aside from the fact that there appears to be no mechanism available for binding a *t*-butyl chloride molecule to one of carbon tetrachloride, it seems better to regard the solution at the maximum merely as one in which the molecules can pack together most efficiently to give a particularly stable lattice. Any departure in either direction from the composition of this mixture lowers the transition point, while addition of either component to the other enables molecular rotation to set in at a lower temperature, resulting in the occurrence of two eutectoid points in the curve. It is natural to suppose that, in the region between the freezing point and the transition point curves, the molecules possess rotational freedom comparable to that which they possess above the freezing point curve. This supposition will be investigated later by dielectric constant measurements.

The writers wish to express their thanks to Mr. Joseph V. D. Hoffman for the freezing and transition point measurements reported in Table IV and Fig. 4.

Summary

The dielectric constants and specific conductances of 2,2-dichloropropane and methyl chloroform have been measured over a wide range of temperature at frequencies of 0.5, 5 and 50 kilocycles. Temperature–time curves have been run with falling and rising temperature and the substances have been observed over a wide range of temperature with a polarizing microscope. These as well as the other three substances with methyls or chlorines attached to a central carbon solidify to cubic crystals in which the molecules have much the same freedom of rotation as in the liquid state. With decreasing temperature, the isotropic form undergoes a sharp transition to an anisotropic form in which the molecules have lost their rotational freedom.

Temperature–time curves show that *t*-butyl chloride and carbon tetrachloride form a complete series of solid solutions. When the temperature of the rotational transition which occurs throughout these solid solutions is plotted against composition, the curve obtained shows two eutectoids with a maximum at the composition of the most stable solid solution.

PRINCETON, NEW JERSEY RECEIVED JUNE 29, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 776]

The Rate of Exchange of Elementary Radiosulfur with Sulfur Monochloride

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Introduction

The reactions between sulfur or sulfur monochloride and chlorine have been the subject of investigation since 1782. The mechanisms that have been suggested for the reactions usually involve intermediates having the general formula S_mCl_n, or even ions,[1] but of these compounds only S_2Cl_2, SCl_2, and SCl_4 have been isolated, the evidence for the existence of such substances as S_3Cl_4, S_4Cl_2, S_2Cl, S_3Cl_2, and chloride or sulfur chloride ions being of an indirect nature. In the interpretations of the results of both equilibrium and kinetic studies of the sulfur chlorides, the existence of one or more of the compounds not capable of isolation, in slow or rapid equilibrium with sulfur, frequently is assumed, but has never been proved directly. The use of radiosulfur makes it possible for the first time to establish the existence of such equilibria.

In this paper are described the results of experiments made on the slow rate of interchange of radiosulfur in solutions of sulfur dissolved in sulfur monochloride. The experiments show that exchange of dissolved sulfur with the combined sulfur does take place at a measurable rate, and some light is thrown on the mechanism of the reaction, but further investigation will be necessary to establish the steps in other reactions of the sulfur–chlorine system.

Preparation of Materials and Experimental Procedures

Materials.—The radiosulfur was obtained from iron sulfide which had been bombarded with 8 MEV deuterons in the cyclotron at the University of California Radiation Laboratory. To remove radioactive contaminants completely, the irradiated sulfide was treated with acid, the resulting hydrogen sulfide was passed into an acid solution of cupric ion, and the precipitate of cupric sulfide was filtered and washed. Continued digestion of the cupric sulfide with concentrated nitric acid converted it into sulfate and this was precipitated as barium sulfate. The barium sulfate was completely reduced at 900° to barium sulfide with hydrogen. Addition of hydrochloric acid to the barium sulfide produced hydrogen sulfide which was oxidized to elementary sulfur by passing through a solution of triiodide ion. Finally, the elementary sulfur was converted into a form completely soluble in carbon disulfide by heating in an autoclave.[2]

The sulfur monochloride was prepared by causing accurately weighed, equivalent amounts of pure dry liquid chlorine and purified sulfur to react at 100° for one hour in the sealed evacuated tube B of Fig. 1. The sulfur monochloride was completely distilled, after breaking the tip at C with the glass-enclosed magnetic hammer M, at room temperature into the evacuated tube F which contained a weighed amount (usually 6 mg.) of radiosulfur. The operations of preparation and distillation without losses were facilitated by using liquid air-baths. After sealing the reaction vessel at D and E, it was brought to the temperature at which the exchange was to be measured.

Rate Measurements.—The first experiments made showed the rate of exchange of the dissolved radiosulfur with the sulfur in the monochloride to be extremely slow at

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[1] See, for example, Spong, *J. Chem. Soc.*, 1283 (1934).

[2] Cooley, Yost and McMillan, THIS JOURNAL, **61**, 2970 (1939).