The $\Delta H_2$ values probably are uncertain to the extent of 2000 calories; the $\Delta H_3$ values are still more uncertain. If we assume that in the dissociation of the dimer and of the trimer to form the monomer two and three hydrogen bonds, respectively, must be broken, we may infer from the magnitude of the $\Delta H_2$ and $\Delta H_3$ values that the "strength" of a hydrogen bond in the vapor of propionic acid is about 9 ± 1 kcal.

## Summary

1. We have determined values of $pV$ for the vapor of propionic acid at 50, 55, 60 and 65° and at pressures ranging from 3 to 20 mm.

2. Under the conditions of the experiments the vapor is associated to a considerable degree. There are indications that not only the dimer but also higher polymers occur.

3. The equilibrium constants for the reactions $2A_1 = A_2$ and $3A_1 = A_3$ have been determined. From the calculated heats of association, we find the "strength" of a hydrogen bond in this case to be 9 ± 1 kcal.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Equilibrium Diagram of the System Carbon Tetrachloride–*t*-Butyl Chloride as Revealed by Dielectric Constant Measurements

BY W. P. CONNER AND C. P. SMYTH

It was thought to be of interest to investigate the effect of changing environment upon the rotation of molecules in a crystal. With this end in view, a continuous series of solid solutions was sought in which the molecules of at least one component would rotate. The rather symmetrically-shaped molecules of *t*-butyl chloride had been found to rotate over a considerable range of temperature in the crystal and their possession of a dipole moment made dielectric constant measurements a suitable method of observing the freedom of molecular rotation.[1] The similarity of molecular shape and size of the *t*-butyl chloride and carbon tetrachloride molecules and their isotropic lattices in the region just below the freezing point made it seem probable that these two substances would form a series of solid solutions. This was confirmed by the freezing point measurements of Mr. J. V. D. Hoffman, carried out in this Laboratory,[2] which showed that the two substances formed a continuous series of solid solutions from pure carbon tetrachloride on the one hand to pure *t*-butyl chloride on the other. The temperature–time cooling curves run in this investigation also showed the expected lowering of the rotational transition of each substance by the presence of the other. These curves represented a tentative step toward the establishment of an equilibrium diagram for the system, and showed the system to be suitable for the investigation of the effect of the presence of the carbon tetrachloride molecules upon the rotation of the *t*-butyl chloride molecules.

### Experimental Measurements

The carbon tetrachloride and *t*-butyl chloride were carefully purified in the usual way.[2] The dielectric constant measurements were made upon the mixtures with a capacity bridge coupled to a variable oscillator in the general fashion previously described.[1,3] The rate of change of temperature with time was normally less than 5° an hour. The dielectric constants and specific conductances of the mixtures were measured at frequencies of 50, 5 and 0.5 kilocycles, but, as the conductances in the solid state were of the order of $10^{-10}$ mhos, and as any anomalous dispersion was negligibly small, the conductances are not reproduced here and the dielectric constant data used are those obtained at 50 kc. In order to save space, the numerical values of the results are not reproduced, but the dielectric constants of the different mixtures are plotted against temperature in Fig. 1, the individual points being too numerous to indicate. Each curve in Fig. 1 is marked with the molar percentage of *t*-butyl chloride in the mixture which it represents, and the curves obtained with falling temperature are given in the upper half of the diagram marked (I). The curves for the same mixtures obtained with rising temperature are in the lower half marked (II). The temperatures of the breaks in the curves are plotted against composition in Fig. 2 to obtain an equilibrium diagram. A few points in Fig. 2 are obtained from curves which have been omitted from Fig. 1 to prevent overcrowding.

## Discussion of Results

In considering the behavior of the dielectric constants of these mixtures, it must be borne in

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

[2] Turkevich and Smyth, *ibid.*, 62, 2468 (1940).

[3] Smyth and Hitchcock, *ibid.*, 54, 4631 (1932); 55, 1830 (1933).

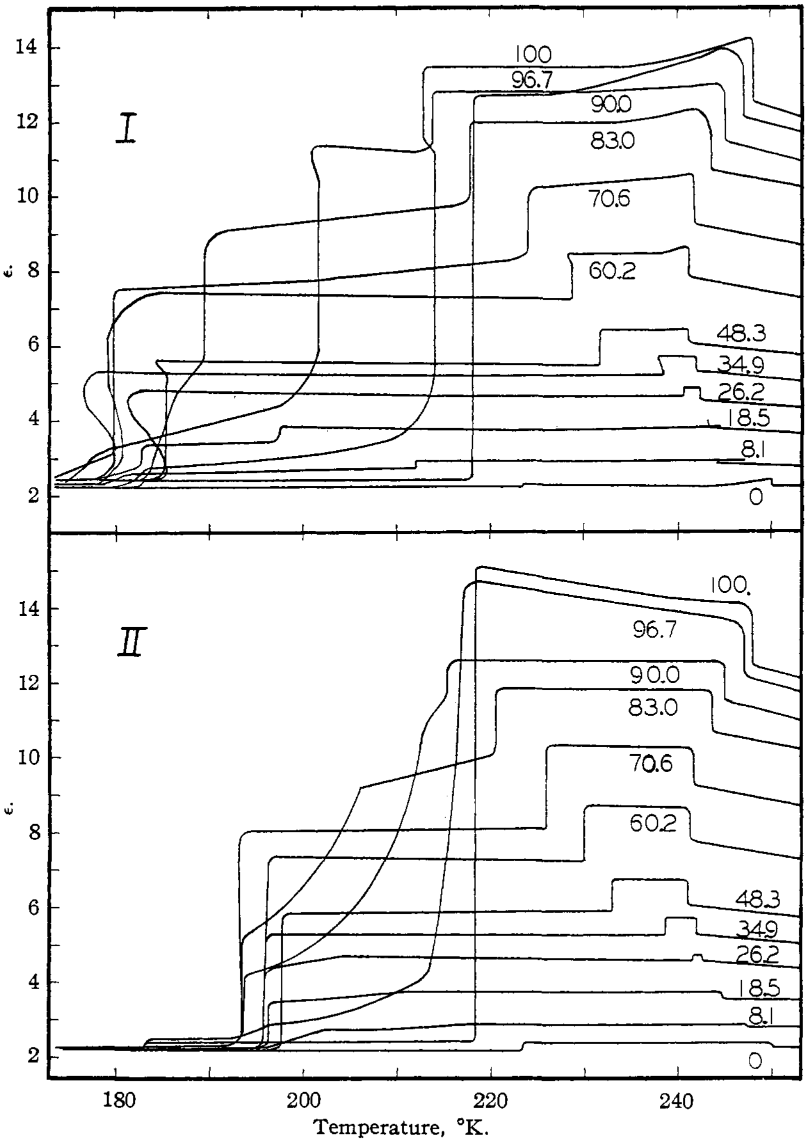

Fig. 1.—Dielectric constant–temperature curves of $CCl_4$-*t*-$C_4H_9Cl$ mixtures: I, with falling temperatures; II, with rising temperatures; molar % of *t*-$C_4H_9Cl$ indicated. The two uppermost curves in I intersect at the point at which they appear to be tangent, the 100% curve crossing both the 96.7 and 90.0% curves as shown, and the uppermost horizontal section belonging to the 96.7% curve.

mind that each of the two components possesses a single rotational transition point in the solid, the transition involving a greater change of entropy than that involved in fusion.[2] The dielectric constant–temperature curve for pure *t*-butyl chloride shows freedom of molecular rotation in the solid comparable to that in the liquid with correspondingly high dielectric constant because of dipole orientation between the transition temperature and the melting point. At the first transition temperature, on cooling, molecular rotation ceases abruptly, and, below this temperature, the low dielectric constant arises only from the induced polarization of the molecules. The slope of this section of the curve for the region of molecular rotation depends upon the internal field of the crystals. The rising temperature curves for pure *t*-butyl chloride and the 96.7% mixture show slopes but slightly less than those for the liquids. As the carbon tetrachloride molecule has no dipole moment, this substance has a low dielectric constant thoughout, arising only from induced polarization. A phase transition may here produce a small change in dielectric constant because of density change, which may accompany a slight change in intermolecular action. A second and previously unknown transition is evident in the curve for pure *t*-butyl chloride at 183°K. That no dipole rotation is involved in this transition is shown by the smallness of the change of the dielectric constant and by the fact that the dielectric constant between the two transition temperatures is very close to that of the non-polar carbon tetrachloride.

The curve in Fig. 1, I, for the 8.12% mixture shows a slight break at the freezing point due to increase of density on solidification, pronounced supercooling occurring. A second slight discontinuity appears at the temperature where the carbon tetrachloride molecules lose their freedom of rotation, this temperature being lowered by the presence of the *t*-butyl chloride. A somewhat greater drop occurs when the *t*-butyl chloride molecules lose their freedom of rotation so that the contribution of the orientation of their dipoles to the dielectric constant of the mixture disappears. The curve obtained for the mixture with rising temperature shows that, in spite of the low rates of warming and cooling, a considerable amount of hysteresis occurs at each of the two transition points. The lack of sharpness of the lower of the two transitions may be attributed, in part, at least, to some lack of thermal equilibrium arising from a less slow rate of temperature change than that employed in the rest of the investigation. The behavior at the freezing point gives no indication of any separation of the liquidus and solidus curves for the system at this composition. The curve for the mixture containing 18.52% of *t*-butyl chloride shows, as in all the mixtures and in pure *t*-butyl chloride, a freedom of rotation of the *t*-butyl chloride molecules in the solid, for some distance below the freezing point, of the same magnitude as in the liquid. The transition associated with rotation of the carbon tetrachloride molecules in the first mixture is further lowered in this mixture, as would be expected, and is found to reduce materially the freedom of rotation of the *t*-butyl chloride molecules, which disappears altogether at the second break as before. Again, hysteresis is apparent when the curves obtained with rising and with falling temperature are compared. A small, abrupt rise and fall of the dielectric constant, partially obscured by supercooling, occurs at the freezing point. This rise is slightly higher at 0.5 kc. than at 50 kc.

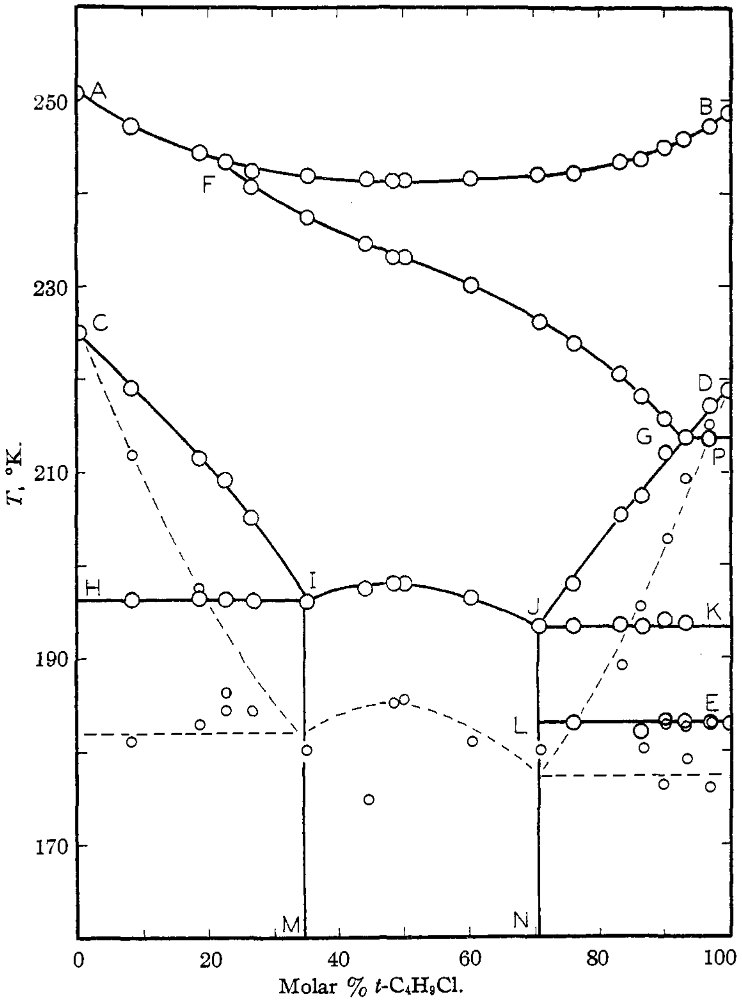

Fig. 2.—Equilibrium diagram of system, $CCl_4$–$t$-$C_4H_9Cl$: Small circles and dotted lines indicate discontinuities evident on cooling as a result of incomplete attainment of equilibrium.

At approximately the same concentration as that at which the upper of the two solid phase transitions disappears, the slight, abrupt rise and fall of dielectric constant at the freezing point noted in the 18.52% mixture begins to separate with increasing concentration of the *t*-butyl chloride, so that the drop acquires the appearance of a transition point, being sharp and not gradual as it would, probably, be in the region between a liquidus and a solidus curve. If the liquidus and solidus were practically coincident in the first two mixtures studied, but began to separate in this region of concentration, the area between the sharp rise and fall of the dielectric constant might correspond to a region of coexistence of a liquid and a solid phase. This region of coexistence of a liquid and a solid phase should, however, disappear in the region of approximately equimolecular concentration, where the liquidus curve AB in Fig. 2 shows a minimum at which point the solidus and liquidus curves must be tangent to one another. Instead of disappearing as the mixtures approach and pass through the concentration corresponding to the minimum of the liquidus curve, the area between the rise and fall increases in height and in width, indicating that the fall is a transition involving some loss in the rotational freedom of the *t*-butyl chloride molecules. Indeed, the drop increases with increasing *t*-butyl chloride content until, in pure *t*-butyl chloride, it corresponds to the entire disappearance of rotational freedom of the molecules.

The curves for all the mixtures from the 34.9% through the 70.6% mixture show only these two transitions, the lower one, at which rotation of the *t*-butyl chloride molecules ceases, being subject to extensive hysteresis, which makes its reproducibility much less than that of the upper one. In the 83.0% mixture, the great drop in dielectric constant showing the final disappearance of the rotational freedom of the *t*-butyl chloride molecules is broken into two parts, the reason for which will be evident in the discussion of Fig. 2. The change of rotational freedom associated with these lower breaks is small in the 93.86% mixture, not shown in Fig. 1, and even smaller in the 96.7% mixture.

The plotting of the temperatures of the dielectric constant discontinuities against the compositions of the mixtures in Fig. 2 establishes an, at least, partial phase diagram for the binary system. The clearly established liquidus curve AB agrees satisfactorily with that previously found by freezing point measurements, and the close agreement between the apparent freezing and melting points shown by the dielectric constant curves indicates that the liquidus and solidus curves are practically coincident, an indication which receives further support from the flatness of the halts on the temperature–time cooling curves previously determined.[2] The curves, CI and DG, descending from the rotational transitions, C and D, of the two pure components check those previously established by means of temperature–time curves.[2] The dielectric constant curves fail to show any discontinuity in the region between temperatures 211 and 235°K. and concentrations 20 and 40% *t*-butyl chloride, where a dotted line was formerly drawn to close the gap in the curves left by the absence of discontinuities in the temperature–time curves in the region between part of the curve GF and part of the curve CI. The discontinuities in the dielectric constant curves corresponding to the upper part of FG evidently involve energy changes so small as to have escaped attention in the temperature–time curves. This is borne out by the fact that the transitional halt in the temperature–time curve for the 38.19% mixture was so short as to show small heat evolution and strong supercooling, which apparently lowered it some degrees below the curve established by the dielectric constants.

Above 220°K. the halts on the dielectric constant–temperature curves obtained with falling temperature agree closely with those on the curves obtained with rising temperature. Below 220°, the halts obtained with falling temperature tend to occur well below those obtained with rising temperature, indicating a lack of equilibrium which is not surprising at such low temperatures, in spite of the slow rate of the temperature change used in the measurements. As the halts obtained at these low temperatures for different mixtures with falling temperature were much less consistent with one another than those obtained with rising temperatures, the latter were taken to correspond more nearly to equilibrium conditions and represented in Fig. 2 by the same large circles which had been used for the points above 220° where equilibrium conditions evidently prevailed. The falling temperature halts where, apparently, equilibrium did not prevail are represented in Fig. 2 by small circles which are connected as far as possible by dotted lines of the same general form as the curves given by the rising temperature halts. The lack of equilibrium shown by the irregularity of points at the lowest temperatures obviously renders these dotted curves of much less significance than the solid curves, which seem to give a consistent representation of all the points obtained with rising temperature.

It has already been pointed out that the curve AB represents practically coincident liquidus and solidus curves. In analogous fashion, the curve IJ presumably represents two conjugate curves which cannot be distinguished from each other. They should be tangent to one another at the flat maximum, which presumably corresponds to an equimolecular lattice of slightly greater stability than those represented by the rest of IJ. These two conjugate curves do not intersect precisely at I and at J but, actually, meet the tie-lines HI and KJ at points so close to I and J as to be experimentally indistinguishable from one another. Similarly, instead of the single point of intersection G, conjugate curves, indistinguishable from the lower part of FG, intersect PG at two points too close to G to be distinguished from it experimentally. The lines IM and JN are drawn merely as approximate indications of the boundaries of different phase areas.

It would appear that, as pure carbon tetrachloride separates out of solid solution along the line CI, its molecular rotation ceases, while rotation of the *t*-butyl chloride molecules, if not all molecular rotation, ceases in the solid solution of composition M at the constant temperature represented by HI. As would be expected, the curves in Fig. 1 show a continuous variation of the dielectric constant in the region between CI and HI. IJ gives the temperatures at which molecular rotation ceases in the solid solutions of composition between M and N, and GJ and KJ are analogous to CI and HI, respectively. The line HIJK thus gives the temperatures below which there is no evidence of molecular rotation in the mixtures. The horizontal line LE represents the low temperature, non-rotational transformation of the pure *t*-butyl chloride in equilibrium with the solid solution of composition N.

As an equilibrium diagram, Fig. 2 is incomplete in the region of the line FG, which corresponds to an increasing loss of energy and of freedom of molecular rotation during the first part of the course from F toward G. Examination with the polarizing microscope showed that the solid solutions represented by the area under AF were isotropic down to CI, at which line they changed to anisotropic as molecular rotation ceased. The solid solutions represented by the area under FB and above FGD were also found to be isotropic, but lowering of the temperature below the line FGD resulted in the appearance of a certain amount of anisotropy, the amount of anisotropy becoming greater with increasing content of *t*-butyl chloride, just as the drop in dielectric constant becomes greater. A further increase in the anisotropy of the solid solutions was observed when the temperature was lowered below the line IJG.

It is evident that, as previously observed for pure substances, complete freedom of molecular rotation gives an isotropic lattice to the solid solutions and that, when molecular rotation ceases, the lattice becomes anisotropic. The previously undiscovered low temperature transition of *t*-butyl chloride makes this compound resemble *t*-butyl bromide in possessing two transitions, although it is the lower of the two transitions thus far discovered for the latter compound which causes molecular rotation to cease, instead of the upper transition as in the case of the chloride. Although these dielectric constant measurements have not given us all the details of the complete equilibrium diagram for the system carbon tetrachloride–*t*-butyl chloride, it is evident that they have yielded much more information than was obtainable by the ordinary thermal method of investigation. It is interesting to note that the dielectric constant measurements give accurate evidence of the two transitions in which dipole rotation is not involved as well as of changes in which it is involved.

The writers wish to express their gratitude to Professor Donald P. Smith for his advice on the interpretation of these results.

## Summary

The dielectric constants of a continuous series of solid solutions of carbon tetrachloride and *t*-butyl chloride have been measured over a wide range of temperature at frequencies of 0.5, 5 and 50 kc. in order to study the effect of the presence of the carbon tetrachloride upon the rotation of the *t*-butyl chloride molecules. The temperature of the rotational transition of each component is lowered by the presence of the other component. The dielectric constant data are used to construct an equilibrium diagram for the system more complete than could be obtained by thermal methods of investigation.

Examination of the solid solutions with a polarizing microscope showed that their lattices were isotropic as long as the molecules possessed freedom of rotation comparable to that in the liquid. The cessation of molecular rotation caused the lattices to become anisotropic.

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