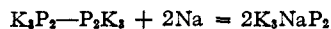senic,[15] and bismuth[15,16] have been investigated in some detail and all three elements behave in the expected fashion forming normal salts that react with an excess of the electronegative element to yield colored solutions of polyanionic substances. But phosphorus does not react with the alkali metals under these conditions to form normal salts; instead, polytype salts are formed immediately.

On the basis of evidence presented above, the empirical formulas for those phosphides prepared in liquid ammonia, which contain the highest ratio of metal to phosphorus, may be written as Li_2P, Na_2P and K_3P_2. It seems obvious, purely on the basis of valence theory, that these substances must be at least dimeric, i.e., Li_4P_2, Na_4P_2 and K_6P_4. Since all three phosphides are soluble in liquid ammonia (estimated as 0.1 to 0.3 g./100 cc.) these abnormal combining ratios cannot be attributed to lattice requirements of the solid phase. This indicates that the P–P bond in this type of compound possesses a considerable degree of stability in liquid ammonia solution and is not reduced by the "solvated" electron.[17]

Additional support of the dimeric formulas is given by the fact that the potassium compound may be reduced by sodium or lithium to form a phosphide having a total metal to phosphorus ratio of two to one. Likely the reduction takes place through the rupture of a P–P bond, according to the equation

(15) E. Zintl, J. Coubeau and W. Dullenkopf, Z. physik. Chem., 154A, 1 (1931); Brauer and Zintl, ibid., B37, 323 (1937); C. Hugot. Compt. rend., 129, 603 (1899).

(16) C. A. Kraus and H. F. Kurtz, THIS JOURNAL, 47, 43 (1925); G. W. Watt and T. E. Moore, ibid., 70, 1197 (1948).

(17) However, it will be shown in the next paper that phosphorus in the compound Na_4P_2 may be completely reduced to the trivalent state in the presence of ammonium bromide.

$$K_4P_2—P_2K_2 + 2Na = 2K_3NaP_2$$

But the existence of hexapotassium tetraphosphide, stable in the presence of excess potassium metal in liquid ammonia, is difficult to rationalize. We have here, it seems, examples where the size of the metal ion determines the extent of the reduction in liquid ammonia, and this must be related in some manner to the structure of the resulting compounds. The sodium compound is highly ionized and conducts the electric current with facility[18] and appears to dissociate into sodium ions and P_2^{-4} ions.

If the potassium compound were likewise completely ionic (it does conduct the electric current in solution) it would be difficult to account for the inability of potassium to effect as complete a reduction as sodium, since steric factors should then be largely inoperative. This suggests that at least part of the potassium in the compound may be bonded covalently; otherwise it would seem that the condition of the electron (the reducing agent) in liquid ammonia would have to be greatly influenced by the nature of the metal ion, which is contrary to experiment.

None of the chemical properties of the sodium compound, which have been investigated, are in contradiction with the dimeric formula; in fact, certain of the reactions of this substance tend to support this formulation, as will be made evident in the next paper of this series. Until evidence is presented to the contrary, it is proposed to use the dimeric formulas to represent these substances, namely, tetrasodium diphosphide, tetralithium diphosphide and hexapotassium tetraphosphide.

(18) J. M. Finn, Jr., unpublished observations. Experiments on the electrolysis of the sodium salt are now in progress.

The Low-frequency Dielectric Properties of Some Symmetrical Mixed Triglycerides in the Solid State[1a,1b]

BY ROBERT W. CROWE[2] AND CHARLES P. SMYTH

The dielectric properties at frequencies from 0.5 to 50 kilocycles have been investigated for a number of symmetrical mixed triglycerides in the solid state and correlated with existing X-ray diffraction and thermal data. The dielectric properties of the various solid forms of these compounds have also been compared with those of the recently investigated simple triglycerides. It was found that the dielectric properties and dispersion characteristics of the α-forms of 2-palmityldistearin, 2-oleyldipalmitin and 2-oleyldistearin were quite similar to those of tripalmitin and tristearin, for which it had been suggested that the dipole orientation was that of molecular segments rather than of the entire molecule, a process which could easily account for the observed distribution of relaxation rates. Although α-forms were found for 2-stearyldipalmitin and 2-lauryldistearin, they were not of sufficient stability to be isolated in the pure state. In all cases, only the α-form showed any indication of molecular freedom. The sharpness of the freezing point of the unusually stable α-form of 2-palmityldistearin indicated that, at least in this compound, the α-form was crystalline and not vitreous as had been reported. Like the simple triglycerides, the thermodynamically stable forms of these substances (usually β) showed slight variation of melting point with thermal history.

The dielectric properties of the 1-mono-, 1,3-di- and simple triglycerides of palmitic and stearic

acids have recently been investigated in this Laboratory.[3] In these investigations, emphasis has been placed upon polymorphic behavior in the solid state, its dependence upon the previous history of the samples and on the presence or absence of molecular orientational freedom in the various crystalline phases. Like the simple tri-

(3) R. W. Crowe and C. P. Smyth, THIS JOURNAL, 72, 4427 (1950); ibid., 72, 5281 (1950).

glycerides,[4,5] a number of symmetrical mixed tri-saturated[6,7] and disaturated[8-12] triglycerides have been shown by X-ray diffraction and thermal data to exist in several polymorphic solid modifications. It, therefore, seemed of interest to investigate the dielectric properties of a number of these compounds in a similar manner to that employed in the previous investigations.[3]

In this investigation, the dielectric constants of 2-palmityldistearin, 2-stearyldipalmitin, 2-lauryldistearin, 2-oleyldipalmitin and 2-oleyldistearin of various thermal histories were measured over a wide temperature range at frequencies from 0.5 to 50 kilocycles.

Experimental Method and Results

Purified samples of the five glycerides investigated were kindly given to us by the Procter and Gamble Company of Ivorydale, Ohio. No attempt was made to purify them further. Before measurement, each sample was placed in a vacuum desiccator for eight hours to remove any occluded moisture. In Table I are listed the melting points of the substances in their most stable forms.

TABLE I

MELTING POINTS OF GLYCERIDES

	Melting point, °C.	
Glyceride	This research	Literature
2-Palmityldistearin	67.8	67.7,[7] 68[6]
2-Stearyldipalmitin	68.1	68.6,[7] 68[6]
2-Lauryldistearin	60.8	61.0[13]
2-Oleyldipalmitin	36.2	35.2,[8] 37.5,[12] 36.9,[14] 38.3[14]
2-Oleyldistearin	43.5	41.6,[8] 43.0,[10] 44.3,[9] 43.5[12]

The dielectric constant measurements were made with the impedance bridge previously described.[15] As in the investigation of the simple triglycerides,[3] measurements were made at 50, 5 and 0.5 kilocycles in regions of anomalous dispersion. In cases where no frequency dependence of the dielectric constant was observed, measurements were made only at 5 kilocycles. The average error in measurement of the dielectric constant was ±1% and the average rate of cooling and warming of the samples was about 0.2° per minute. Several runs were made with each sample to ensure satisfactory reproducibility. Obviously, the values obtained for the solid glycerides are not completely reproducible due to small differences in the manner in which the samples filled the measuring cell on solidification. Of greater significance are the shapes of the dielectric constant–temperature

(4) C. E. Clarkson and T. Malkin, J. Chem. Soc., 666 (1934); ibid., 985 (1948).

(5) E. S. Lutton, THIS JOURNAL, 67, 524 (1945).

(6) T. Malkin and M. L. Meara, J. Chem. Soc., 103 (1939).

(7) E. S. Lutton, F. L. Jackson and O. T. Quimby, THIS JOURNAL, 70, 2441 (1948).

(8) B. F. Daubert and T. H. Clarke, ibid., 66, 690 (1944).

(9) E. S. Lutton, ibid., 68, 676 (1946).

(10) L. J. Filer, S. S. Sidhu, B. F. Daubert and H. E. Longenecker, ibid., 68, 167 (1946).

(11) M. L. Meara, J. Chem. Soc., 22 (1945).

(12) T. Malkin and B. R. Wilson, ibid., 369 (1949).

(13) E. S. Lutton, private communication.

(14) E. S. Lutton and F. L. Jackson, THIS JOURNAL, 72, 3254 (1950).

(15) C. P. Smyth and C. S. Hitchcock, ibid., 54, 4631 (1932); ibid., 55, 1830 (1933).

curves and the temperatures at which breaks and changes in slope of these curves appear. For the sake of brevity, the measured dielectric constant values are plotted completely in the graphs, but not tabulated.

Discussion of Results

Although there has been some disagreement as to the number of solid forms to be found for the simple triglycerides, it is generally realized that similar forms are possible for nearly all members of the series.[4,5] This similarity in polymorphic behavior from one member to the next is, as it should be, quite common in many series of long-chain compounds. If, however, one of the acid chains in the triglyceride molecule is made shorter or longer than the other two, the general shape or symmetry is altered and thus it would not be surprising to find somewhat different polymorphic behavior than in the simple triglycerides. Indeed, it has recently been reported by Lutton, Jackson and Quimby,[7] as a result of X-ray diffraction and thermal measurements, that the mixed triglycerides of palmitic and stearic acids are more striking in their individuality than in their similarity. They found that the α, or lowest melting form, of 2-palmityldistearin was unusually stable while the same form of 2-stearyldipalmitin was extremely unstable. They also found that, in contrast to the simple triglycerides,[5] which exist in three forms, α, β' and β, both of these compounds can exist in only one form other than α; β for 2-palmityldistearin and β' for 2-stearyldipalmitin. X-Ray and thermal investigations by Clarkson and Malkin[4] and by Malkin and Meara[6] have, on the other hand, led to the conclusion that both the simple triglycerides and symmetrical mixed triglycerides existed in four forms, vitreous, α, β' and β in order of increasing melting point. From an examination of melting points, it appears that Malkins' vitreous form corresponds to Lutton's α-form, and Malkin's α-form to Lutton's β'-form. Lutton has not reported melting points corresponding to Malkin's β'-form in any of the trisaturated glycerides, nor does he find a vitreous form.

The dielectric constants (5 kc.) of 2-palmityldistearin are plotted in Fig. 1 as functions of increasing and decreasing temperature. In the case of tripalmitin and tristearin,[3] the α-form was not sufficiently stable to allow cooling measurements to be made through its freezing point without transformation to the more stable β'- and β-forms. However, in this compound, complete α freezing could be observed dielectrically and is indicated by the sharp drop in the dielectric constant at 50.2°. Lutton, Jackson and Quimby[7] report 50.8° for this point. Once formed, the α-form was extremely stable until its melting point was approached on warming. However, instead of melting, it rapidly transformed to the more stable β-form, which melted at a higher temperature. The dielectric constant of the latter form is shown in the lower curve in Fig. 1, its value being close to the square of the refractive index. No intermediate melting form was observed from these measurements.
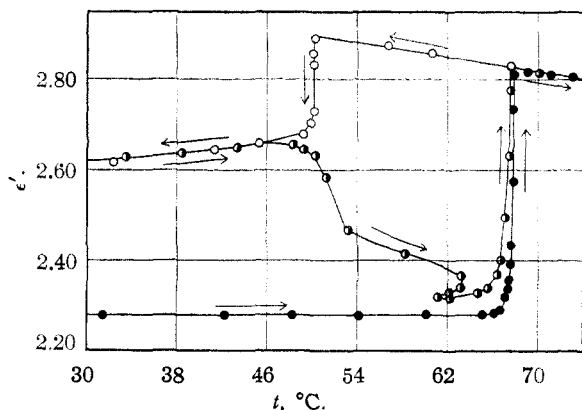
Fig. 1.—Temperature dependence of the dielectric constant of 2-palmityldistearin at 5 kc. Hollow circles are for cooling, half-filled circles for α-form on warming and filled circles for β-form on warming after tempering.

It should be noted that the dielectric constant of the α-form of 2-palmityldistearin, although lower than that of the liquid, is sufficiently higher than that of the β-form to indicate a certain amount of dipole orientational freedom. Indeed, it is comparable in magnitude to that in the α-forms of tripalmitin and tristearin.[3] Its low temperature dispersion characteristics (Fig. 2) are nearly identical with those of the simple triglycerides, in which the orientation process was considered to be that of molecular segments instead of the molecules as a whole. The results obtained here are especially interesting in that they show the α solidification point to be extremely sharp as one would expect if the α-form were crystalline. As mentioned before, Malkin, et al.,[4,6] have repeatedly called this form a glass in the triglycerides. However, as pointed out recently by Lutton,[16] a solidification point as sharp as that observed here, indicates that we are not dealing with a glass, but with a structure of relatively high order.
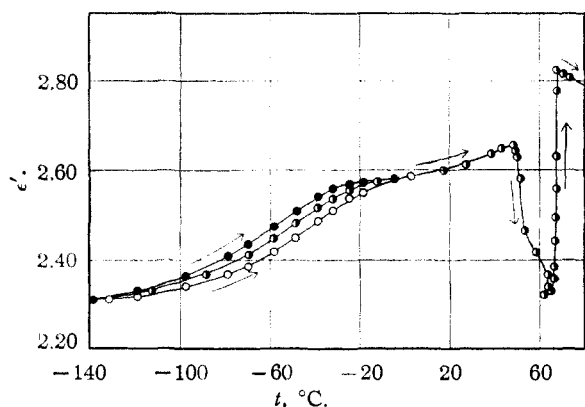

Fig. 2.—Variation of the dielectric constant of the α-form of 2-palmityldistearin with increasing temperature. Hollow circles are for measurements at 50 kc., half-filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

In Fig. 3 are plotted the dielectric constants of 2-stearyldipalmitin obtained from several warming

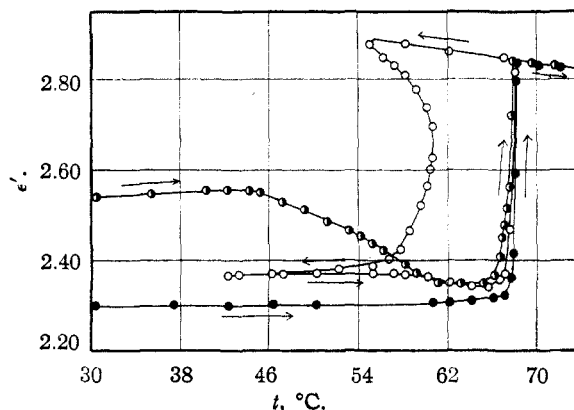(16) E. S. Lutton, J. Am. Oil Chem. Soc., 27, 276 (1950).

Fig. 3.—Temperature dependence of the dielectric constant of 2-stearyldipalmitin at 5 kc. Hollow circles are for cooling and warming immediately, half-filled circles for warming after rapid chilling of melt, and filled circles for thermodynamically stable β'-form after tempering.

and cooling runs. In contrast to 2-palmityldistearin, the α-form of this compound was so unstable that it could not be isolated in the pure state even by rapid chilling in the cell. Although it has been reported[7] that the β'-form is the thermodynamically stable form for this compound and that no β-form exists, it is interesting to note that, on slow cooling, the substance froze several degrees above the α melting point into a solid with a dielectric constant considerably higher than that of the stable form obtained by prolonged treatment just below its melting point. When this solid was warmed immediately, the dielectric constant remained essentially constant with increasing temperature up to about 60°. Between that temperature and the melting point a drop was observed, accompanied by considerable spontaneous warming of the sample. Although the results were not quantitatively reproducible, the same general behavior was always observed when the sample was treated in this manner. This phenomenon cannot be caused by transformation from α to β' because the α melting point is a good 15° below this region. Also, there is no break in the cooling curve at the α melting point. It has been found throughout this and previous investigations on the triglycerides, that variations in melting point occur for a single form, depending upon the time that the solids have been allowed to remain near their melting points. Since only two solid forms have been observed for 2-stearyldipalmitin, it may be that imperfections in chain alignment in the initially formed β' crystals are sufficient to account for the observed behavior, the gradual disappearance of these imperfections giving rise to the slight evolution of heat and change of melting point. As can be seen in Fig. 3, the results obtained by warming the slowly cooled sample show a melting point midway between that obtained by warming the rapidly chilled sample and that obtained for the β'-form which has been subjected to the tempering process at temperatures just below the melting point.

Although the α-form is very difficult to isolate in 2-stearyldipalmitin, rapid chilling did result in a

partial solidification into this form. That it was not free from another form with low dielectric constant is evidenced by the somewhat lower value of the dielectric constant than in the case of 2-palmityldistearin. The data recorded for this phase in Fig. 3 were obtained after several less successful attempts were made to isolate it. On warming, it began to transform to a more stable form at about 45°, which is just below the α melting point 46.5° reported by Lutton, et al.[7]

In the case of 2-lauryldistearin, the acid chain in the 2-position of the glycerol nucleus possesses six less carbon atoms than the other two. Thus, one might expect considerable departure in its polymorphic behavior from the simple triglycerides. This compound has been reported[13] to exist in four distinct crystalline forms. These are: α-2 (m.p. 34.6°), β'-2 (very fleeting), β'-4 (m.p. 54°) and β-3 (m.p. 61.0°). The number associated with the form symbols indicate double, triple or quadruple chain-length structures.[17] The absence of such a number indicates the common double chain-length structure. The data for this compound are shown in Fig. 4. Here again the α-form was extremely unstable near its melting point, making it difficult to form even by rapid chilling of the melt. This undoubtedly accounts for the relatively low value of the dielectric constant resulting from such treatment. On warming the rapidly chilled sample, small breaks were consistently observed at about 35° and 47°. The first undoubtedly corresponds to transformation of the small amount of α-form near its melting point to β'-2 or β'-4. Since the β'-2 has been reported to be very fleeting, it seems reasonable to assume that the higher break in the curve corresponds to transformation from β'-4 to β-3. When the sample was cooled slowly, no breaks were observed in the curve on subsequent warming. The intermediate melting form β'-4 was evidently too unstable to appear under these conditions.
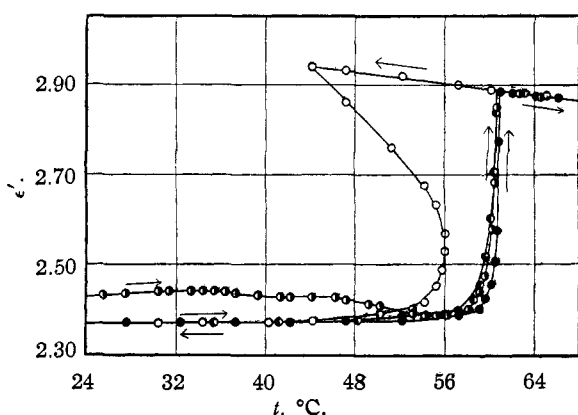

Fig. 4.—Temperature dependence of the dielectric constant of 2-lauryldistearin at 5 kc. O are for cooling, ◐ for warming after gradual cooling, ◑ for warming after chilling rapidly from melt, and ● for warming of stable β-3-form.

2-Oleyldipalmitin differs from 2-stearyldipalmitin in that one double bond exists in the center acid chain of the former. However, a comparison of

(17) E. S. Lutton, This Journal, 70, 248 (1948).

the stable melting points of the two compounds in Table I definitely suggests differences in crystal structure, and a recent X-ray and thermal study of this compound,[14] prepared synthetically and from natural sources, has definitely established the existence of four crystalline forms. These forms were designated as α-2 (m.p. 18°), sub β'-2 (m.p. 26.5°), β'-2 (m.p. 33.5°) and β-3 (m.p. 38.3°). The presence of the double bond evidently alters the zig-zag structure of the center chain to such an extent that the molecules cannot pack together in the same way as those of the saturated analog.

The results of dielectric constant measurements on 2-oleyldipalmitin are shown graphically in Figs. 5 and 6. On slow cooling of the melt, the sample invariably solidified at about 24.5° (Fig. 5). On warming after such treatment, a relatively sharp rise in the dielectric constant appeared at about 26°, followed by a rather rapid drop accompanying a
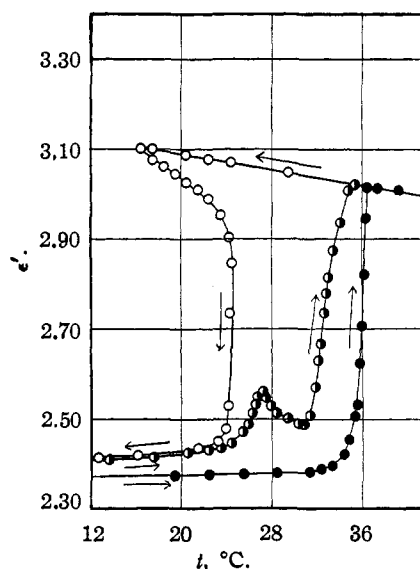

Fig. 5.—Temperature dependence of the dielectric constant of 2-oleyldipalmitin at 5 kc. Hollow circles are for cooling, half-filled circles for warming immediately after cooling, and filled circles for warming of stable β-3-form.
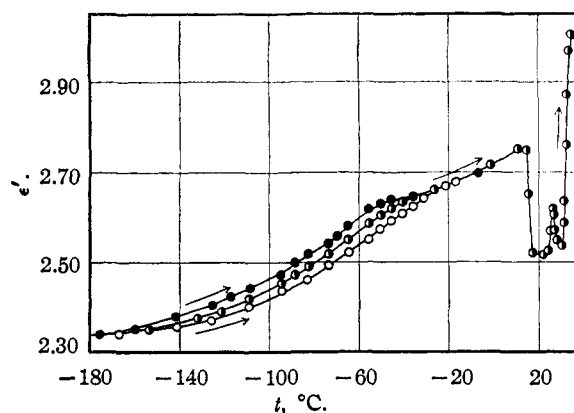

Fig. 6.—Variation of the dielectric constant of the α-form of 2-oleyldipalmitin with increasing temperature. Hollow circles are for measurements at 50 kc., half-filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

spontaneous increase in temperature. The sharp rise evidently corresponded to melting of the sub β'-2-form, since this is just slightly below the reported melting point of this form. However, before complete melting could be realized, the sample suddenly recrystallized into the β'-2-form, which accounts for the drop in dielectric constant and rise in temperature. On further warming, the sample melted at 33°, corresponding to the reported melting point 33.5° of the β'-2-form. By holding the temperature of the sample at about 32°, the β'-2-form was gradually transformed to the most stable β-3-form, complete transformation requiring about two days. The dielectric constant of this form is shown in the lower curve in Fig. 5. The melting point observed here for this form was 36.2°. The α-2-form was isolated by the usual technique of rapidly chilling the molten glyceride. As can be seen in Fig. 6, its dielectric properties are very similar to those of the α-forms of the simple triglycerides and 2-palmityldistearin.

2-Oleyldistearin, like 2-oleyldipalmitin, can be compared to its saturated analog, which in this case is tristearin. Here again the difference in

Fig. 7.—Temperature dependence of the dielectric constant of 2-oleyldistearin at 5 kc. O are for cooling, ◐ for warming after gradual cooling, ◑ for warming after chilling rapidly from melt, and ● for warming of stable β-3-form.

Fig. 8.—Variation of the dielectric constant of the α-form of 2-oleyldistearin with increasing temperature. Hollow circles are for measurements at 50 kc., half-filled circles for measurements at 5 kc., and filled circles for measurements at 0.5 kc.

melting points of the stable forms (73° for tristearin and 43.5° for 2-oleyldistearin) is considerable and suggests differences in crystal structure, which is indeed the case. Likewise, 2-oleyldipalmitin and 2-oleyldistearin differ in their polymorphic behavior to some extent. It has recently been shown[9,14] that 2-oleyldistearin exists in four solid forms: α-3 (m.p. 22.5°), β'-3 (m.p. 35°, from solvent only), sub β-3 (m.p. 37°) and β-3 (m.p. 44.3°). It should be noted that this is the first triglyceride investigated wherein the α, or rotator, phase possesses the triple chain-length structure.

The dielectric constants of 2-oleyldistearin are plotted in Figs. 7 and 8. On slow cooling (Fig. 7), the sample solidified at about 35°. Below this temperature, the dielectric constant continued to decrease slowly with decreasing temperature. On warming immediately, the data were reasonably reproducible up to the melting point at 36.6°. This undoubtedly corresponds to the sub β-3 melting point. When this form was held near 36° for several days, it transformed completely to the stable β-3-form, which possessed a somewhat lower dielectric constant and melted at 43.5°. The α-3-form of this compound was at least partially isolated in the usual manner by chilling the melt. Its dielectric properties are shown in Fig. 8 and in part in Fig. 7. Although they are quite similar to those of 2-oleyldipalmitin, the low temperature dispersion is somewhat less pronounced. This difference is not surprising in view of the fact that the triple chain-length structure persists in 2-oleyldistearin. As the α-3 freezing point was approached on warming, this form rapidly transformed to the sub β-3-form which melted almost completely near 37°. However, the gradual downward trend of the dielectric constant between 30° and 35° was probably caused by partial transformation of the sub β-3-form to the β-3-form. In any event, the dielectric constant began decreasing again for several degrees above the sub β-3 melting point, due to recrystallization into the β-3-form (Fig. 7).

It has been found that the thermodynamically stable forms of all of the trisaturated triglycerides (usually β) show variations in melting point, depending upon the time that the samples were tempered just below their melting points. It may be that Malkin has confused the existence of a fourth form for these compounds with this variation in melting point. The reason for this variation is not known, but it may be due to changes in perfection of chain alignment in the crystals.

It has been observed that the α phase of the triglycerides has a dielectric constant lower than that of the liquid, but high enough to show orientational freedom in the solid. Its low temperature dispersion characteristics show a large distribution of relaxation times for the orientation process, such as might be expected of segment orientation, the only orientation possible in the case of these molecules. The sharp freezing point observed for the α-form of 2-palmityldistearin (Fig. 1) supports the views of Lutton[16] that this form in all triglycerides is crystalline and not vitreous as Malkin[4,6] contends.
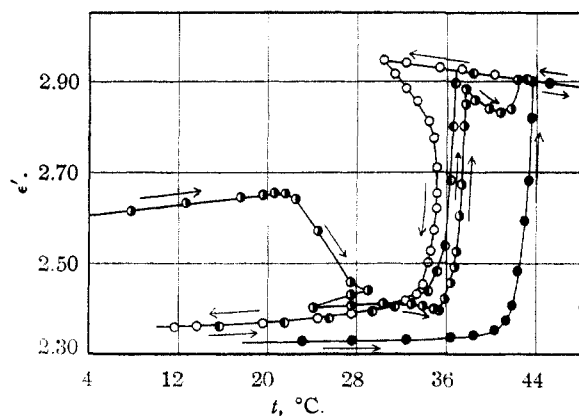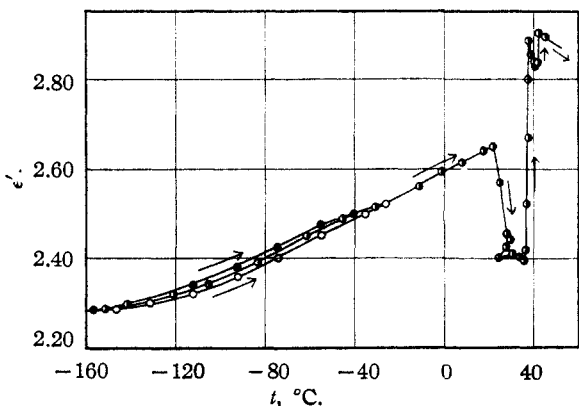
As a rule, the intermediate melting forms of the triglycerides, when isolatable, possess somewhat higher dielectric constants than the highest melting forms, at least near their melting points. Instead of being nearly constant with temperature, their dielectric constants rise gradually with increasing temperature (Figs. 5 and 7). The same behavior was observed for a number of n-alkyl brom-ides[18] which were found to exist in two solid modifications. Since metastable forms might be expected to consist of more loosely packed structures than stable forms, the gradual rise in dielectric constant could well be the result of the gradual increase in orientational freedom as the melting point is approached.

(18) R. W. Crowe and C. P. Smyth, THIS JOURNAL, 72, 1098 (1950).

Theoretical Calculation of the Stability of Solid and Gaseous Alkali and Alkaline Earth Oxides[2]

BY LEO BREWER AND DONALD F. MASTICK[3]

A theoretical method is described for calculation of stabilities of gaseous alkali oxides and solid and gaseous alkaline earth suboxides. Results of the theory are compared with existing experimental data. Calculations indicate that at 1000°K. all the gaseous alkali oxides except Li_2O are unstable with respect to dissociation, and that the alkaline earth suboxides are unstable toward disproportionation in both gaseous and solid states. The method is not applicable to divalent gaseous oxides such as the alkaline earth oxides because of the high attractive forces between the doubly charged ions.

The oxides of the elements in the first two columns of the Periodic Table were chosen as the subject of this treatment primarily because of their apparent ionic bonding and, secondly, since the information in the literature concerning the stability of the gaseous species studied herein is very limited it is considered that these calculations will be a practical addition to the existing thermochemical data of gaseous oxides.

In the following, ionic models are assumed for the solid and gaseous states; on this basis calculations of stability are made which are compared with experimental values for the stability of the specific molecule or one of the same coulombic nature.

Two empirical expressions[4] for dealing with the mutual repulsive potential existent between ions were investigated, namely, the Born expression

$$V_r = b/r^n \qquad (1)$$

and the Born and Mayer exponential expression

$$V_r = ae^{-r/\rho} \qquad (2)$$

Here, b and n are constants and r is the distance between the ion, ρ is taken in Eq. (2) as 0.345×10^{-8} if a is determined as a function of the valences, the number of valence electrons and the ionic radii of the two ions. While the potential of the type given in Eq. (2) leads to a more satisfactory value of the repulsion and has the further merit of having some theoretical foundation, it was found that Eq. (1) was not only convenient to apply but also was of sufficient accuracy in view of the fact that in many cases the radii of ions in the solid and gaseous state were necessarily estimated. The

latter uncertainty was indeed of such a nature to allow the combination of secondary forces such as those arising from polarization, distortion and slight covalency to be neglected. Actually, this treatment deals with the coulombic force and the apparent repulsive force between ions, the latter function being of such nature to give agreement between theoretical and experimental heats of formation.

The expressions given by Pauling[5] for the calculation of interionic forces and crystal energy are adopted. The mutual potential energy of two ions is written as

$$V_{ij} = \frac{z_i z_j e^2}{r_{ij}} + \frac{b_{ij} e^2}{r_{ij}^n} \qquad (3)$$

and the total potential energy of an ionic crystal by incorporation of the appropriate geometrical factor A is given as

$$V = -\frac{A e^2 z^2}{R} + \frac{B e^2}{R^n} \qquad (4)$$

In Eq. (3) z_i and z_j refer to the algebraic value of the valence of the ions, b is an appropriate constant and r_{ij} the distance between the ions. In Eq. (4) z is the largest common factor of the valences of the ions, A is the Madelung constant and R is a crystal dimension appropriate to the value of A used. It is convenient to eliminate the repulsive constant B from Eq. (4) by allowing $dV/dR = 0$ at $R = R_0$, the equilibrium distance. Thus, by substitution in Eq. (4), one obtains for the crystal energy

$$U_0 = \frac{N A e^2 z^2}{R_0}\left(1 - \frac{1}{n}\right) \qquad (5)$$

The values for the repulsive exponent n are given by Pauling for crystals of mixed ion type:

Ion type	n	Ion type	n
He	5	Kr, Ag^+	10
Ne	7	Xe, Au^+	12
Ar, Cu^+	9		

(1) This document is based in part on work performed under Contract No. W-7405-eng-48B for the Atomic Energy Commission.

(2) Abstracted in part from the thesis submitted by Donald F. Mastick in partial satisfaction of the requirements for the degree of Doctor of Philosophy in chemistry at the University of California. Presented before the Inorganic and Physical Division of the American Chemical Society at the 116th National Meeting at Atlantic City, N. J., September, 1949.

(3) Atomic Energy Commission Fellow in chemistry, 1948-1949.

(4) F. Seitz, "The Modern Theory of Solids," Chapter II, McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(5) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, Chapter X.