In a recent letter by Raistrick and Hobbs³ in which the structure of the hypophosphate ion was discussed, the space group and unit-cell dimensions of ammonium hypophosphate were reported. The figures are very similar to those given by Mooney for ammonium bicarbonate. The space group in each case is *Pccn*, and the unit-cell dimensions in the two cases are *a, b, c*: 7.26, 11.47, 9.38; and 7.29, 10.79, 8.76 Å., respectively.

It is interesting to speculate on the possible relationship between the structures of these two compounds. It seems very likely that $P_2O_6^{4-}$ ions could have an external shape and size nearly the same as the shape and size of a pair of neighbouring CO_3^{2-} ions on either side of a diad axis in ammonium bicarbonate, the configuration being governed in each case by the close packing of six oxygen atoms. If this were so, the similarity in cell sizes and space-group symmetry would make it a reasonable speculation that the two structures were in some respects closely related; possibly the oxygen atoms, the ammonium ion and hydrogen bonds occupy similar positions in the cell. This possibility, which would not be difficult to check by structure work, seems to fit in well with Raistrick's choice of structure for the hypophosphate ion.

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¹ Mooney, R. L., *Phys. Rev.*, **39**, 861 (1932).

² Zachariassen, W. H., *J. Chem. Phys.*, **1**, 634 (1933).

³ Raistrick, B., and Hobbs, E., *Nature*, **164**, 113 (1949).

Equivalence of Temperature and Frequency in Dielectric Measurements

ONE usual method of representing measurements of the complex dielectric constant is by a circular arc. Cole and Cole¹ pointed out that, if the dispersion and absorption of a dielectric could be represented by the empirical formula,

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \quad (1)$$

where ϵ^* , ϵ_0 and ϵ_∞ are the complex, static and infinite frequency dielectric constants respectively, τ_0 a generalized relaxation time and $\omega/2\pi$ the frequency of the applied electric field, then the dielectric constant - dielectric loss curve is the arc of a circle the centre of which is displaced below the real axis by an amount depending upon the constant α . If the dipoles in the dielectric are assumed to have a distribution of relaxation times, the distribution can be obtained from α .

This circular arc plot applies to the variation of the complex dielectric constant as a function of the frequency, which is not easy to determine experimentally. It is more usual to vary the temperature than the frequency, and to assume that changes in temperature are equivalent to changes in frequency. This equivalence follows from the theory of a dielectric model having a single relaxation time, but most dielectrics have a wide distribution of relaxation times. Even for these dielectrics, changes in the temperature are assumed to be equivalent to changes

in the frequency. An example of this is Sillars's² investigation of the dielectric properties of a dilute solution of long-chain esters in paraffin-wax. The dielectric loss - frequency curves were considerably broader than a Debye curve, yet temperature and frequency were related by the equation,

$$\log(1/f_0) = ST_0 + C, \quad (2)$$

where T_0 is the temperature at which the maximum occurs in the dielectric loss curve for a frequency f_0 , and S and C are constants.

If temperature and frequency can be interchanged, and if the behaviour of the dielectric is represented by equation (1), then a circular arc plot would also be obtained if the temperature instead of the frequency were the parameter.

Variation of the complex dielectric constant with temperature of a mixture of $C_6H_{13}.CO.C_{11}H_{23}$ and $C_{17}H_{35}$ from $-100^\circ C.$ to $-20^\circ C.$ at 50 kc/s.

This method of analysis was applied to the variation with temperature of the complex dielectric constant of a mixture of a ketone and a paraffin, and the result is shown in the accompanying graph. The mixture consisted of 28 per cent by weight of the ketone $C_6H_{13}.CO.C_{11}H_{23}$ and 72 per cent by weight of the paraffin $C_{17}H_{35}$. A maximum of 16-18 per cent of the ketone can be dissolved in the paraffin by quenching the mixture from the melt, the remainder of the ketone being precipitated as a separate phase which is dielectrically inert. The results shown in the graph are for the mixture in the super-saturated condition. Measurements were made with a Schering bridge at 50 c/s., 800 c/s. and 50 kc/s. over the temperature range $-100^\circ C.$ to $-20^\circ C.$ The same value of α , 0.64, was obtained at all three frequencies, and therefore only the results obtained at 50 kc/s. are shown.

A similar analysis of Powles's³ results for the transition in solid hydrogen bromide, a material which differs widely from that which I have used, also gave a circular arc diagram with temperature instead of frequency as the parameter. The value of α was 0.52 at 1 kc/s. as compared with 0.21 at $-196.2^\circ C.$ for the normal circular arc plot.

For both these substances, the locus of the dielectric constant in the complex plane is a circular arc with the centre of the arc considerably displaced below the real axis. This gives, therefore, experimental evidence for the equivalence of frequency and temperature for a dielectric with a wide distribution of relaxation times. No theoretical explanation for this equivalence in the presence of a wide distribution of relaxation times has yet been given.

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¹ Cole, K. S., and Cole, R. H., *J. Chem. Phys.*, **9**, 341 (1941).

² Sillars, R. W., *Proc. Roy. Soc., A*, **169**, 66 (1938).

³ Powles, J. G., *Nature*, **165**, 636 (1950).