$$\begin{array}{lllll} \text{CaOx} & + \ SO_4^{=} & \longrightarrow \text{CaSO}_4 & + \ \text{Ox}^{=} \\ \text{Solid} & \text{Solution} & \text{Interface} & \text{Solution} \\ \text{CaOx} & + \ \text{Ba}^{++} & \longrightarrow \text{BaOx} & + \ \text{Ca}^{++} \end{array}$$

An important conclusion which can be drawn from the occurrence of exchange adsorption is that the solubility of an ionic precipitate in an electrolyte solution is a function of the amount of solid present or, more precisely, of the amount of surface exposed by the solid in those cases in which cation or anion exchange takes place. Experimentally this was shown to be true. The solubility of calcium oxalate monohydrate was determined by shaking small and large quantities of precipitate with various solutions until equilibrium was attained; the saturated solutions were analyzed for oxalate or calcium by micro methods.

With small quantities of solid present, the normal solubilities were found ($[\text{Ca}^{++}] = [\text{Ox}^{=}]$ in saturated solution). Some data are given herewith.

$[\text{Ca}^{++}]$ AND $[\text{Ox}^{=}]$ IN SATURATED SOLUTIONS OF $\text{CaOx}\cdot H_2O$ AT 25°

Electrolyte	Concn., *M*	Normal solubility in millimoles per liter Ox	Ca	Solubility with 12 to 15 g. of CaOx per 250 cc. Ox	Ca
Water		0.067	0.067	0.067	0.067
$(NH_4)_2SO_4$	0.01	.112	.115	*.31*	.05
NH_4IO_3	.01	(.090)	.090	(.13)	.058
NaOH	.01	.126	(.126)	*.30*	(.052)
$BaCl_2$	.001	.078	(.078)	.03	(*.21*)

The saturated solutions of calcium oxalate contain an excess of oxalate ions in the experiments with alkali sulfates, iodates and sodium hydroxide, but an excess of calcium ions with barium and manganese chloride, the absolute values being a function of the amount of solid present.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

I. M. KOLTHOFF
E. B. SANDELL

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DIELECTRIC POLARIZATION IN SOLIDS

Sir:

In a study of the relation between dielectric properties and chemical constitution, in progress at Bell Laboratories for several years, some observations of interest in connection with recent communications on rotation of molecules or groups in crystalline solids [Hitchcock and Smyth, THIS JOURNAL, **55**, 1296 (1933)] deserve reporting. A transition in the solid state accompanied by a change of heat capacity and dielectric constant, ϵ, as predicted by Pauling for HCl has been observed for camphor, borneol and isoborneol.

d-Camphor shows a change of ϵ between −37 and −32° larger than that reported for HCl or H_2S. *d*-*l*-Camphor shows a change of the same magnitude between -70 and $-80°$. Borneol and isoborneol show changes of ϵ, though not as large as for camphor, between 70 and 80° and 25 and 45°, respectively. The curves of ϵ *vs.* T for camphor and isoborneol show a hysteresis effect at the transition point and the change for isoborneol is so spread out as to suggest the presence of impurities in the unpurified commercial materials used.

Some facts of interest about the change of dielectric properties at the transition point are the following. (1) The time of relaxation of the polarization to which the high value of ϵ above the transition point is due is less than 5×10^{-7} sec. (2) n_D^2 at 20° for camphor is approximately equal to ϵ below the transition point. (3) There is no dispersion of either ϵ' or ϵ'' over a wide range of temperatures, including the transition range, for frequencies to 10^5 cycles for borneol, isoborneol or *d*-camphor. (4) There is a distinct low frequency dispersion for *d-l*-camphor occurring just below the transition point and dependent on the purity of the material. (5) Preliminary data show that above the transition point ϵ does not decrease with increasing T sufficiently to cause the polarization to vary linearly with $1/T$. (6) Measurements on solutions of camphor in hexane over a range of temperatures including the transition range show that P_∞ *vs.* $1/T$ is linear for higher temperatures but departs from it at low.

The absence of dispersion in the transition range distinctly differentiates the polarization which is responsible for the high ϵ in these materials from that observed in many polar substances which form glasses on cooling. The temperature variation of ϵ of these solids indicates that the additional polarization present above the transition point is a different function of temperature than that for free orientation of dipoles. The temperature variation of polarization of the solutions may be interpreted either as a change of electric moment with temperature or as evidence of the existence of an atomic polarization or group rotation which depends upon temperature. Further study of the change of polarization of the solids with temperature is being made.

BELL TELEPHONE LABORATORIES
NEW YORK, N. Y.

S. O. MORGAN
W. A. YAGER
A. H. WHITE

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