crystal studies are planned in an attempt to determine the positions of the halogens in $AlBrCl_2$.

TABLE I

POWDER PATTERN DATA AND INDICES FOR $AlBrCl_2$

d., Å. Experimental	Intensity	Indices
6.00	s	001
5.24	vf	020
3.05	vf	?
3.01	s	$002, (130)(20\bar{1})$
2.86_8	vs	$13\bar{1}, 200$
2.53_3	vs	$131, 20\bar{2}, (220)$
1.813	f	$202, 13\bar{3}(22\bar{3})(24\bar{2})$
1.752	s	$33\bar{1}, 060(241)$
1.714	f	222, 113
1.682	f	$061, 33\bar{2}, 330$
1.514	m	331, 062 +
1.443	f	$400, 13\bar{4}, 203, (42\bar{2})(024)$
1.142	f	$064, 333, 46\bar{2}, +$
1.113	f	$460, 40\bar{5}, 53\bar{3} +$
1.010	vf	$60\bar{2} +$
0.998_6	vf	0102 +
0.995_4	vf	+

The difference in the solubility limit of the chloride phase in the annealed mixtures and the exchange studies is of interest. We believe this to be associated with different solute species present in the two experiments. The reaction of HBr with aluminum chloride does not appear to form $AlBrCl_2$ directly at 24°; an aluminum bromide phase separates at 13.3% HCl concentration. The 2% solubility limit in the chloride phase shows that $AlBr_3$ (and closely similar species, *e.g.*, Al_2Br_5Cl) will not dissolve appreciably in $AlCl_3$. On the other hand, rearrangement of halogen atoms occurs readily at the temperatures used in forming and annealing the mixtures of $AlBr_3$ and $AlCl_3$; thus appreciable amounts of $AlBrCl_2$ can be produced which, on cooling, would be expected to form solid solution with $AlCl_3$. Hence, it is suggested that the bromide content of the saturated chloride phase of the annealed mixtures is largely present in the form of $AlBrCl_2$.

It is not believed that the equilibria obtained in and between the phases in the annealed samples are effectively frozen above room temperature. No significant variation in spacings could be observed in patterns taken from the same sample after several months. The small variations in distances observed for the saturated phases also indicate no appreciable difference in the equilibrium temperature for the various samples. The aluminum halides have vapor pressures between 10^{-2} and 10^{-4} mm. at room temperature which makes it unlikely that any phase could remain appreciably supersaturated over a long period of time.

The authors wish to express their appreciation to Professor E. C. Lingafelter and his group for their coöperation in the use of X-ray equipment.

SEATTLE, WASH.

[CONTRIBUTION FROM THE SIGNAL CORPS ENGINEERING LABORATORIES]

Electrical Conductivity of Ag_2HgI_4, Cu_2HgI_4 and their Eutectoid

BY LAWRENCE SUCHOW AND GEORGE R. POND

RECEIVED JUNE 8, 1953

The specific electrical conductivities of Ag_2HgI_4, Cu_2HgI_4 and their eutectoid (containing 43 mole % Cu_2HgI_4) have been determined as a function of temperature, and activation energies have been calculated. All the preparations exhibit sharp rises in conductivity at characteristic phase transition temperatures. The activation energies for the two phases of the eutectoid have been found not to be averages of the values for the parent compounds. Combined plots of specific conductivity *vs.* temperature upon heating and cooling appear in the form of hysteresis loops. In the case of the eutectoid, the loop indicates a lag of about 8° on returning to the low temperature phase.

Introduction.—The compound Ag_2HgI_4 has been shown by Ketelaar[1,2] to possess ionic conductivity of considerable magnitude, especially above a transition point at 50.7°, at which a sharp rise is observed. He also reported that Cu_2HgI_4 exhibited ionic conductivity, but with electronic conductivity superimposed upon it. However, he did not give data on the actual measurement of specific conductivity of Cu_2HgI_4. The purpose of the present work was to reinvestigate the specific conductivity of these two compounds as a function of temperature, and more especially, to make a similar investigation on the eutectoid of the two compounds containing 43 mole % Cu_2HgI_4, which was recently reported by this Laboratory.[3]

Experimental Procedure.—The materials to be tested were prepared as by Suchow and Keck.[3] In order to measure specific conductivity as a function of temperature, the powders were pressed into pellets of 0.75 inch diameter and 0.05 to 0.1 inch thickness at a pressure of about 5 tons/in.^{2}. Such pellets were found to be of the same colors as the original powders. However, higher pressures (such as 12–20 tons/in.^{2}) were found to cause uneven darkening in the pellets and to lead to higher transition temperatures and higher conductivity values. The pellet's dimensions were determined accurately with a micrometer and its two flat surfaces were coated with graphite from an IBM Electrographic Pencil. It was then placed between two discs of platinum foil to which leads were attached. Adequate electrical contact between the platinum and the pellet was ensured by placing the pellet and the platinum foil discs between two Bakelite plates held tightly together by bolts insulated from the electrical system. This assembly was then placed inside a metal cylinder surrounded by an asbestos-wrapped metal jacket through which thermostated water could be passed in order to maintain the temperature at desired levels. The temperature in the vicinity of the pellet was controlled within ±0.2° and determined by means of an iron–constantan thermocouple connected to a Leeds and Northrup Potentiometer. The temperature was brought to each desired level and kept there for about ten minutes to ensure that equilibrium had been reached. Measure-

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[1] J. A. A. Ketelaar, *Z. physik. Chem.*, **B26**, 327 (1934).

[2] J. A. A. Ketelaar, *Trans. Faraday Soc.*, **34**, 874 (1938).

[3] L. Suchow and P. H. Keck, THIS JOURNAL, **75**, 518 (1953).

ment of resistance was then made, and specific conductivity was calculated therefrom. Determinations of conductivity were made over the range 10–85°. Most measurements were made with the General Radio Co. Impedance Bridge Type #650A, using a 1000-cycle signal from a Hewlett-Packard Oscillator #200A. However, for very high resistance values (those of Cu_2HgI_4 below the transition point), it was necessary to use the General Radio Co. Megohm Bridge Type #544-B, which impresses a d.c. voltage across the pellet. In this case, checks were made by reversing polarity. In all cases, whether a.c. or d.c. was used, the circuit was kept closed only as long as was required to obtain a reading, in order to minimize polarization or decomposition. Whenever desirable for controlling voltage or the level of resistance to be measured by the bridge, the pellet was placed in series or in parallel with known resistances.

Results and Discussion.—The curves for specific conductivity as a function of increasing temperature are plotted in Fig. 1, from which it may be seen that the conductivity values for the eutectoid are intermediate between those for the parent compounds, and that all exhibit sharp rises in conductivity at characteristic transition points after preliminary increases starting several degrees lower. The curves as plotted are not to be considered absolute, but rather average values, since somewhat varying results were obtained depending upon the history of the sample and of the pellet. The deviation was approximately ±0.1 log conductivity unit. Such factors as pressure and heat-treatment were especially found to affect the levels of the curves both above and below the transition points, although their slopes were affected but little. As indicated above, if the pressure employed was too high, discoloration was observed and there was a shift of the transition point as well as of the curves for the low temperature (β) and high temperature (α) forms.

The conductivity values found for Ag_2HgI_4 did not correspond as well as was hoped with those reported by Ketelaar,[1] who gave no details, however, concerning the preparation and treatment of his compound or his pellets. The transition points checked each other quite well though, and also checked the values found by observing color changes (see Table I). No evidence was observed for the change in slope of the conductivity curve of β-Ag_2HgI_4 at about 33°, as reported by Ketelaar. An increase in slope prior to the sharp transition was found instead to take place at about 40°.

TABLE I

TRANSITION TEMPERATURES (°C.)

Substance	Present work	From color change[3]	Ketelaar[1]
Ag_2HgI_4	50.0	50.7	50.7
Cu_2HgI_4	66.6	67	..
$Ag_{1.14}Cu_{0.86}HgI_4$	34.2	34	..

Ionic conductivity is usually governed by the equation

$$\sigma = \sigma_0 e^{-(Q/RT)}$$

where

σ = specific conductivity at an absolute temp., T
σ_0 = a constant
Q = activation energy
R = gas constant

Electronic semi-conduction usually follows this same law as well, so that when both types are present in the same material, the experimentally determined Q and σ_0 are weighted averages.

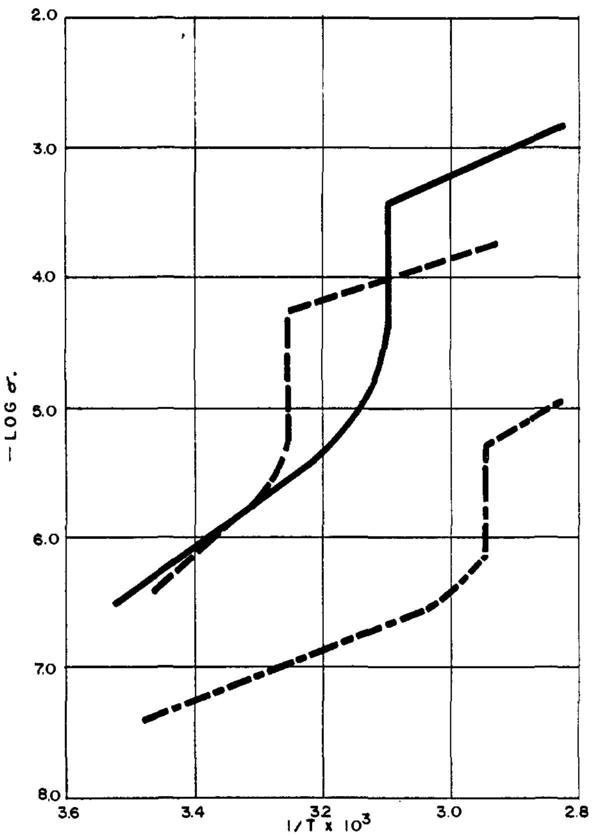

Fig. 1.—Specific conductivity as a function of temperature: —, Ag_2HgI_4; — - — - —-, Cu_2HgI_4, — — — — —, eutectoid (43 mole % Cu_2HgI_4).

Ketelaar has stated[2] that for the β-phase of Ag_2HgI_4, Q is the sum of the activation energy (A) found in the α-phase, and one-half the increase in potential energy (V) of the crystal upon moving one mole of metal ions from ordered into disordered positions. Ketelaar then determined V by assuming that σ_0 was the same for the β- and α-phases. Table II is a listing of the values reported by Ketelaar, as compared with those found in the present investigation. It will be seen that if it is assumed, as Ketelaar did, that $\sigma_{0\alpha} = \sigma_{0\beta}$, the determined values are within 25% of his, but that if $\sigma_{0\beta}$ is found independently (from the straight line portion of the curve), the values are considerably different.

TABLE II

CONDUCTIVITY OF Ag_2HgI_4

	Present work	Ketelaar[1,3]
A(cal./g. atom)	10,200	8600
σ_0 from α-phase curve (ohm^{-1} cm.$^{-1}$)	7.5×10^3	4×10^2
σ_0 from β-phase curve (ohm^{-1} cm.$^{-1}$)	1.4×10^6	.....
V in cal./g. atom at transition temp.,		
(a) assuming $\sigma_{0\beta} = \sigma_{0\alpha}$	4000	5660
(b) using $\sigma_{0\beta}$ from β-phase curve	10,800	.....
V in cal./g. atom at temperatures along straight line portion of β-phase curve,		
(a) assuming $\sigma_{0\beta} = \sigma_{0\alpha}$	6300	7400
(b) using $\sigma_{0\beta}$ from β-phase curve	12,500	.....

The conductivity plot for Cu_2HgI_4 shows a sharp rise at the transition temperature which indicates an increase in ionic conductivity at that point. However, the slope of the β-phase curve is lower than that of the α. Since this indicates a lower Q for the β-phase than for the α-phase, the data do not fit directly into the Ketelaar scheme. It may be that the lower Q is due to the presence of electronic conductivity which would contribute a higher percentage of the current to the β-phase than to the α. A knowledge of the percentage electronic conductivity would be required to solve for Ketelaar's V. Electronic current carriers might be expected to be of less importance in the eutectoid with its highly mobile silver ions and, therefore, the β-phase Q is again higher than that for the α-phase. The values found for Q and σ_0 in all preparations are given in Table III. The Q-values for the eutectoid are not averages, but are instead outside the ranges bounded by the values for the parent compounds (resulting in a minimum for α and a maximum for β).

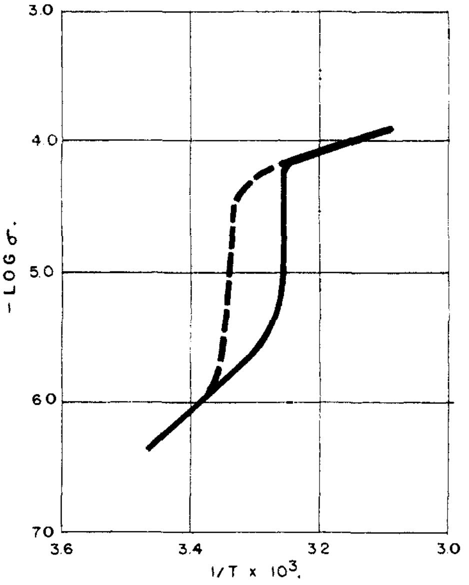

Fig. 2.—Hysteresis loop found for eutectoid: ---, increasing temperature; — — — —, decreasing temperature.

TABLE III

CONDUCTIVITY DATA

Substance	σ_0 (ohm $^{-1}$ cm. $^{-1}$)	Q (kcal./g. atom)
β-Ag_2HgI_4	1.4×10^6	16.4
α-Ag_2HgI_4	7.5×10^3	10.2
β-Cu_2HgI_4	2.2×10^{-1}	8.9
α-Cu_2HgI_4	3.3×10^3	13.7
β-$Ag_{1.14}Cu_{0.86}HgI_4$	4.2×10^{19}	19.7
α-$Ag_{1.14}Cu_{0.86}HgI_4$	9.1	7.4

The compounds and the eutectoid exhibit a temperature lag in the transition point on cooling. Figure 2 is a plot of the data obtained in a typical run with the eutectoid in which conductivity values were obtained both upon increasing and decreasing the temperature. The result is a hysteresis loop which indicates a temperature lag of about 8° on cooling. This checks observations of the color change in the free powder, but is considerably less than the lag previously reported[3] where the powder was bound in a silicone lacquer and observed for color change. It therefore appears that the lacquer serves to insulate grains against each other and thus minimize spread of nuclei. The more gradual change in conductivity on cooling as compared with the sharp change on heating corresponds to the visual observations in the previous paper.[3]

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, BARRETT DIVISION, ALLIED CHEMICAL AND DYE CORPORATION]

Calorimetric Determination of the Freezing Point of Phthalic Anhydride

BY A. C. WERNER AND S. V. R. MASTRANGELO[1]

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The triple point of pure phthalic anhydride, determined in an adiabatic calorimeter, was 131.10°. Sources of error in previous determinations are analyzed. The effect of pressure on the melting temperature, independent of the effect of dissolved air, was 0.033° per atmosphere. The difference between the freezing point and the triple point was 0.012°. The effect of phthalic acid, benzoic acid, maleic acid, fumaric acid, maleic anhydride, 1,4-naphthoquinone and phthalimide, singly, in pairs and altogether, on the freezing point of phthalic anhydride has been determined for the first time. Normal behavior was encountered on all systems but the pair benzoic acid and phthalic acid. When this pair is present, deviation from ideal behavior occurs due to solid solution formation.

Introduction

Several values have been reported for the freezing point of pure phthalic anhydride. Monroe[2] has reported 130.84°; Debeau,[3] 130.95°; and Burriel-Marti,[4] 131.60°.

Monroe's method did not permit calculation of the freezing point of 100 mole per cent. material. Debeau employed the method of Glasgow, Streiff and Rossini,[5] which usually permits such a calculation to be made. However, we have found that this method does not give consistent values of the freezing point of pure phthalic anhydride, presumably because its crystallization rate is such that equilibrium is not maintained at all times. It was necessary, therefore, to determine first the triple point of pure phthalic anhydride by data obtained in an adiabatic calorimeter on a specially purified sample, and then to add to this figure the difference

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(1) To whom inquiries may be directed.

(2) K. P. Monroe, *Ind. Eng. Chem.*, **11**, 1116 (1919).

(3) D. E. Debeau, THIS JOURNAL, **68**, 2725 (1946).

(4) F. Burriel-Marti, *Bull. soc. chim.*, **39**, 590 (1930).

(5) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).