TABLE II

THE ACTIVITY COEFFICIENT OF SODIUM NITRATE IN DILUTE AQUEOUS SOLUTION AT 25°

c	0.0005	0.001	0.002	0.005	0.010	0.015	0.020
y^+	0.9746	0.9696	0.9508	0.9251	0.8933	0.8793	0.8643

unity is measured by the entire area under the graph. It is true that the selection of a value of the distance parameter, a, required for calculating the mobility term is arbitrary, but it should be observed that the variation of this mobility term with concentration is small and is not very sensitive to the value of a.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Electrical Conductivity of Ag_2HgI_4

BY THEODORE J. NEUBERT AND GEORGE M. NICHOLS

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The electrical conductivity of pressed samples of Ag_2HgI_4 has been studied as a function of temperature and time. A.c. measurements were made at a frequency of 1000 sec.$^{-1}$. Curves of steady state log σ *versus* T^{-1} data are similar to curves given by previous workers although there are differences which are described and discussed. The activation energy for the conduction process ($T < 20°$) in β-Ag_2HgI_4 was found to be 12 kcal. mole^{-1}. Transition temperature for temperatures increasing is *ca.* 52°. Measurements made with T-increasing and T-decreasing show a hysteresis the magnitude of which depends upon the rate of temperature change. Sample history and the time-schedule of measurement were found to be very important. Measurements as a function of time upon changing from one temperature to another indicate that in the region of the order-disorder transition (35-52°) resistance values relax more slowly than temperature can be changed. Analysis of the rate of this slow approach to a steady state indicates that both in the approach to order (T-decreasing) and in the approach to disorder (T-increasing) two nucleation steps are involved. The necessity for the two steps is also indicated in the steady state log σ *versus* T^{-1} curves by a secondary inflexion occurring at 48° for T-increasing and showing a constant hysteresis of 8°.

Silver tetraiodomercuroate (Ag_2HgI_4) is a thermochromic compound which exhibits an order-disorder transition[1] in the region of 52°. X-Ray diffraction,[2-6] specific heat,[7] electrical conductivity,[8,9] color transition[5] and dilatometric[10] studies have been reported. It is the purpose of this paper to report some extensions of the electrical conductivity data and to describe attempts to elucidate the approach of conductivity values to a steady state.

Although there are some variations in interpretation of the X-ray diffraction patterns, the order-disorder transition may be pictured (after Ketelaar) as follows. In both the low temperature β-modification (yellow) and the high temperature α-modification (red) iodine ions are cubic close-packed and silver and mercury ions occupy some of the tetrahedral holes. The β-modification has tetragonal symmetry; mercury ions situated at corners of a (cubic) unit cell and silver ions at the mid-points of the vertical faces. As the temperature is raised it becomes possible for silver and mercury ions to occupy each other's lattice sites and also the two extra lattice sites (the top and bottom face centers of the "unit cube") which are unoccupied at lower temperatures. Above 52° mercury ions and silver ions are completely disordered. The α-modification has, therefore, averaged face centered cubic symmetry.

Experimental

Preparation of Stock Material.—Ag_2HgI_4 was precipitated slowly, and with vigorous stirring, from 0.5 *m* $HgI_4^=$ solution by addition of the stoichiometric amount of 1 *m* Ag^+ solution. Reagent grade chemicals (KI, HgI_2 and $AgNO_3$) were used. The precipitated powder was washed (10-15 times) by decantation, filtered and dried *in vacuo* over P_2O_5. The preparation was carried out in diffuse light using brown bottles, but otherwise no extraordinary precautions were taken to avoid photochemical effects. Analysis showed the product to contain 1.009 times the theoretical amount of silver, the apparent loss of mercury iodide being presumably the result of too many decantations.

Preparation of Samples.—Samples for conductivity measurement were formed by pressing at room temperature in an evacuable stainless steel die. The piston was one inch in diameter and ram pressures were 20-40 thousand pounds. Measured densities were 5.8-6.0 g. cm.$^{-3}$, depending upon the pressing force and upon whether or not the die was evacuated during pressing. Carefully pressed samples were a uniform yellow-orange color and were semi-translucent, *e.g.*, ordinary typewriting could be read through specimens 1 mm. thick. Before making measurements, new samples were cycled to above and below the transition temperature two or three times in order to relieve strains and improve their homogeneity.

Some measurements were made on cast samples. These were prepared by heating Ag_2HgI_4 powder in glass tubes enclosed in an iron bomb to *ca.* 450°. No specific data for cast specimens will be reported because their stoichiometry was somewhat altered from Ag_2HgI_4 by the casting operation. The results were, in general, very similar to those obtained with pressed specimens.

Conductivity Measurements.—Sample resistances were determined using an essentially symmetrical conductance-capacitance impedance bridge with a Wagner grounding arm. The bridge was constructed in this Laboratory to measure the equivalent parallel resistance (R_p) and equivalent parallel capacitance (C_p) over the wide range of values exhibited by Ag_2HgI_4 in the temperature region −35° to 90°. Although the accessible frequency range was 5 to 300,000 sec.$^{-1}$, only work at 1000 sec.$^{-1}$ is discussed in this paper. Bridge balances at 1000 sec.$^{-1}$ usually could be made to a precision of 0.1% in R_p.

Electrode System.—Samples were introduced into the bridge circuit *via* a three electrode (guarded) cell intended to

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[2] J. A. A. Ketelaar, *Z. Krist.*, **80**, 190 (1931); **87**, 436 (1934).

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[4] C. E. Olsen and P. M. Harris, *Phys. Rev.*, **86**, 651 (1952).

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

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[7] J. A. A. Ketelaar, *Z. physik. Chem.*, **B30**, 53 (1935).

[8] J. A. A. Ketelaar, *ibid.*, **B26**, 327 (1934).

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[10] D. G. Thomas, L. A. K. Stavely and A. F. Cullis, *J. Chem. Soc.*, 1727 (1952).

eliminate spurious lead capacitances and to minimize sample edge effects and surface effects.[11] Aquadag, colloidal graphite, electrodes applied directly to the sample surface made contact to the more massive artificial graphite electrodes of the cell proper which were held against the sample by springs. The entire assembly was enclosed in a watertight brass housing which was integrated with the shielding of the impedance bridge. As is conventional, specific resistance (or conductance) was calculated from R_p using as the effective sample diameter the average of the outer diameter of the measuring electrode and the inner diameter of the guard ring.

Temperature Control.—The brass housing containing the sample in its mounting was immersed in a thermostated bath (water and ethylene glycol) which regulated to ±0.05° over the range −40 to 90°. Temperatures could be set at predetermined values or varied linearly at various rates, *e.g.*, 5° per day. Sample temperature was determined by appropriately positioned thermocouples and by a mercury in glass thermometer in the thermostat bath. All were checked against a platinum resistance thermometer.

Experimental Results

Figures 1, 2 and 4 (upper portion) show the results of a.c. resistance measurements for three typical samples. Figure 1 gives log σ *versus* T^{-1} for sample P-8, 2.5 cm. in diam. × 0.49 cm. thick, pressed at 40,000 pounds ram pressure. Temperatures were varied automatically at a rate of 5° per day, beginning at 19.8° warming to 66.7° and cooling to 11.1°. The conductivity is relatively low ($\sigma = 10^{-6}$ ohm^{-1} cm.$^{-1}$) at room temperature. As temperatures are raised it increases more rapidly than exponentially and changes very rapidly in the region just below the transition temperature, 52°. Above 52° the conductivity is high ($\sigma > 10^{-3}$ ohm^{-1} cm.$^{-1}$) and changes approximately linearly in T^{-1}. As temperatures are decreased the high temperature behavior persists to nearly 49° beyond which point σ decreases quite suddenly by a factor of 20 in about 1°. The T-decreasing curve then exhibits a "small bump" near 40°. A small bump is also discernible in the T-increasing curve near 48°. Below 35° conductivities for temperatures increasing and decreasing are practically identical.

Equations calculated from the data of Fig. 1 are: (a) presuming linearity above 52°, $\sigma = 0.364 \exp(-1827/T)$ and (b) presuming linearity between 22 and 35°, $\sigma = 9.9 \times 10^4 \exp(-7505/T)$. These relations are of only secondary interest because of the irreproducibility of σ values for the α-modification and because careful examination of Fig. 1 indicates that log σ is not strictly linear in T^{-1} in the region below 40°.

Figure 2 shows the results of measurements on Sample P-12 in which emphasis was placed on the conductivity of the β-modification below room temperature. Sample P-12 was 2.5 cm. in diam. × 0.08 cm. thick and was pressed *in vacuo* with a ram pressure of 40,000 pounds. The points shown in Fig. 2 were made after a waiting period of 12–24 hr. at each temperature and were taken with temperatures both increasing and decreasing. The two distinct sets of data were observed a year apart. Below 10° the dependence of log σ on T^{-1} is very nearly linear and is well represented by the equation: $\sigma = 5.86 \times 10^2 \exp(6045/T)$, *i.e.*, the activation energy for the conduction process in β-Ag_2HgI_4 is 12 kcal. mole^{-1}.

Electrical conductivity data are reproducible from sample to sample to within a tenth of a log unit in the region below the transition provided: (a) samples have been cycled two or three times to temperatures >52° and (b) the time schedule of temperature change is suitably slow. As a result of cycling pretreatment the conductivity of a newly pressed sample in the β-modification is decreased by a factor of *ca.* 2 in the first excursion to high temperature and decreased by lesser factors in subsequent excursions. The effect of cycling on the conductivity of the α-modification is variable; there seem to be no systematic trends. The high temperature portions of curves differ in diverse ways even for successive runs on a single sample. Cycling does not affect the steep portion of the T-increasing curve (near 52°) to any great extent but the point of intersection with the α-modification line does vary as the latter moves about. Thus transition temperatures are slightly higher than usual if α-modification conductivities are higher than usual and *vice versa.* Transition temperatures for T-increasing were always close to 52°. No dependence of transition temperature on pressing pressures was noticed.

The main hysteresis observed with temperatures decreasing depends primarily upon the rate of temperature change, but some dependence upon cycling has not been excluded. For rates of a few degrees per day the hysteresis is *ca.* 3°; for rates of a few hundred degrees per day it can be 7°. It is apparently impossible, however, to quench Ag_2HgI_4 in the disordered state. Thus Ag_2HgI_4 powder in the red α-modification turns to the yellow of the β-modification immediately upon being poured into liquid nitrogen.

The small bump which is observed in the data for all samples exhibits a constant hysteresis of 8° provided the temperature has exceeded 52°. It occurs in T-increasing curves at 48° and in T-decreasing curves at 40° and is rate independent at least up to 300° per day. If, however, temperatures are not permitted to exceed 50° no hysteresis is observed; T-increasing and T-decreasing curves are practically identical, each exhibiting a "small bump" at 48°.

When the time schedule and direction of temperature traverse were found to be so important a preliminary investigation of the kinetics of approach of Ag_2HgI_4 to order (and disorder) was begun. Kinetics experiments are complicated by: (a) irreversible changes in the specimen, *e.g.*, recrystallization and grain growth, (b) the time required for balancing the impedance bridge and (c) the thermal inertia of the electrode and sample system which is necessarily electrically insulated from the thermostatting baths. Large changes in temperature (*e.g.*, 25°) could be effected with a half-time of *ca.* 8 min. only by overcompensating the temperature of the sample holder (but not the sample!) in an auxiliary bath of ice or boiling water prior to insertion of the sample system into the final thermostat. Examination of kinetics data from several runs performed in this manner indicated that for final temperatures not in the region 35–50°, log σ changed with the half-time of the temperature change, *i.e.*, 8 min. When final temperatures were within the region 35–

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[11] R. M. Fuoss, THIS JOURNAL, **59**, 1703 (1937).

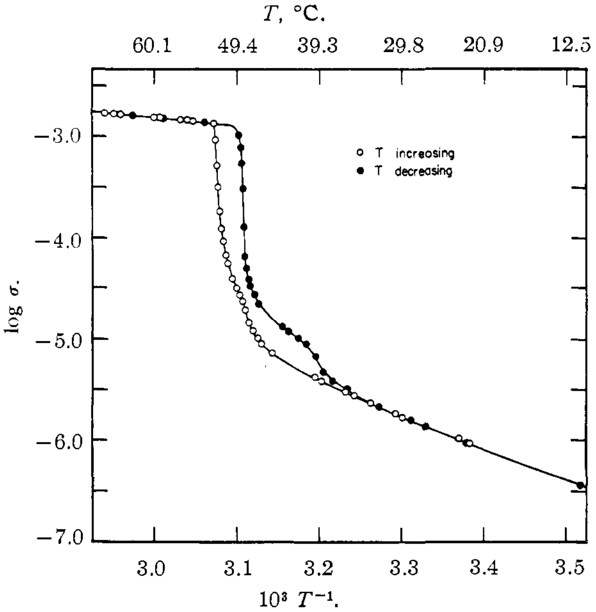

Fig. 1.—Electrical conductivity (σ in ohm^{-1} $cm.^{-1}$) of pressed Ag_2HgI_4 sample P-8 as a function of temperature. Temperatures were varied continuously at a rate of 5° per day.

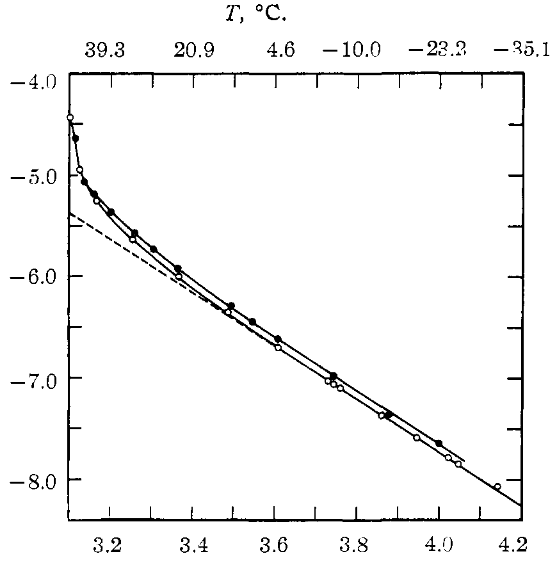

Fig. 2.—Electrical conductivity (σ in ohm^{-1} $cm.^{-1}$) of pressed Ag_2HgI_4 sample P-12 as a function of temperature. Solid points and open points represent sets of data taken one year apart.

50°, log σ changed with half-times in some instances very much longer than 8 min., and measurable rates of change were still observable after one week. Changes in the disordering direction always took place more rapidly than changes in the ordering direction. Superimposed on all measurements was a small continual drift of values due to irreversible changes in the specimen.

Only in the region 35–52° did the approach of log σ to its final value appear to take place more slowly than temperatures could be changed. A more systematic investigation of that region was therefore undertaken in which less emphasis was placed upon rapidity of temperature change. The material used was sample P-7, 2.5 cm. in diam. × 0.21 cm. thick, pressed at 25,000 pounds ram pressure. It had an effective diameter of 1.85 cm. Temperature changes were effected with a half-time of 20 ± 4 min. using the heaters or the refrigerator of the thermostat without removing the sample from the thermostat. An attempt was made to choose temperatures which would space curves evenly in log R_p in the range 35–53°. Temperatures were raised stepwise from 2.0° to 79.9° and then lowered stepwise to 9.9°. The sample was held at each temperature for 12 hr. and as many measurements as possible were made throughout the 12 hr. period. Figure 3 shows log R_p *versus* time for the T-increasing part of the run. In order to illustrate the rate at which log R_p is changing, the portion between 260 and 540 min. has been removed (at the expense of only 7 points). The various curves are seen to be flat after *ca.* 80 min. except for temperatures near 48° and near 51.5°. Similar effects are evident near 48° and 40° in the companion graph (not shown) for temperatures decreasing.

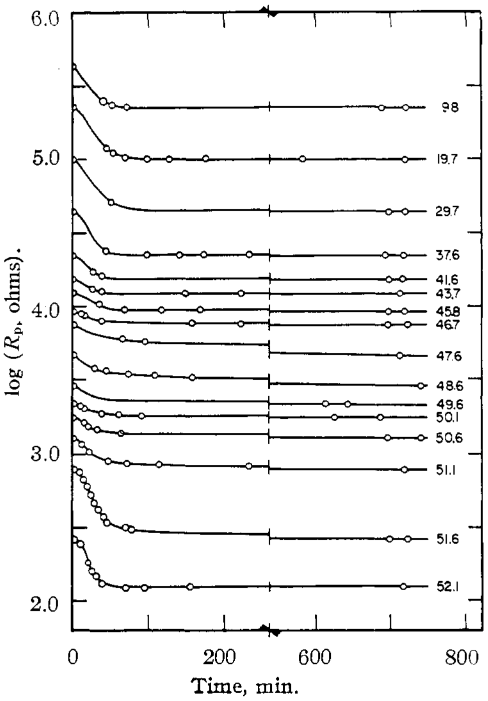

Fig. 3.—Electrical resistance (R_p in ohms) of pressed Ag_2HgI_4 sample P-7 as a function of time at various temperatures. Temperatures were increased in steps. The half-time for temperature change was *ca.* 20 ± 4 min.

Although the amount by which log R_p is changing can be gauged by the miss-match of curves on either side of the index strokes in Fig. 3, a more appropriate perspective is gained by including a measure of the total change in log R_p. To this end a quantity F, the fractional logarithmic change, is defined as

$$F = \{\log (R_{700})_f - \log (R_{100}\}_f / \{|\log (R_{700})_i - \log (R_{700})_f|\} \quad (1)$$

Here $(R_{700})_i$ is the value of R_p after 700 minutes at the initial (previous) temperature, while $(R_{100})_f$ and $(R_{700})_f$ are the values of R_p after 100 and 700 minutes, respectively, at the final temperature. The absolute value is taken in the denominator so that F will be positive for increasing order (T-decreasing) and negative for decreasing order (T-increasing). Figure 4 shows both log $(R_{700})_f$ *versus* T (upper portion) and F *versus* T (lower portion). Points on the F-curves were calculated from values interpolated from large, carefully drawn graphs similar to Fig. 3. Although the imprecision of points is large, the trends in the F values are clear. There are very definite peaks with sharp leading edges at 47.5 and 51.5° for T-increasing and at 49.5 and 40.5° for T-decreasing. Note that large F values mean that log R_p relaxes slowly and has not reached a steady state in, *e.g.*, 6 hr. In most of the region surveyed (2–80°), F values are small indicating that changes in log R_p took place as rapidly as temperatures could be changed. The fact that F is positive rather than zero above 52° is attributed to continuing drift of log R_p values due to recrystallization. That something of the sort has occurred is indicated by miss-matching of the extremes of the log R_p *versus* T curves in Fig. 4.

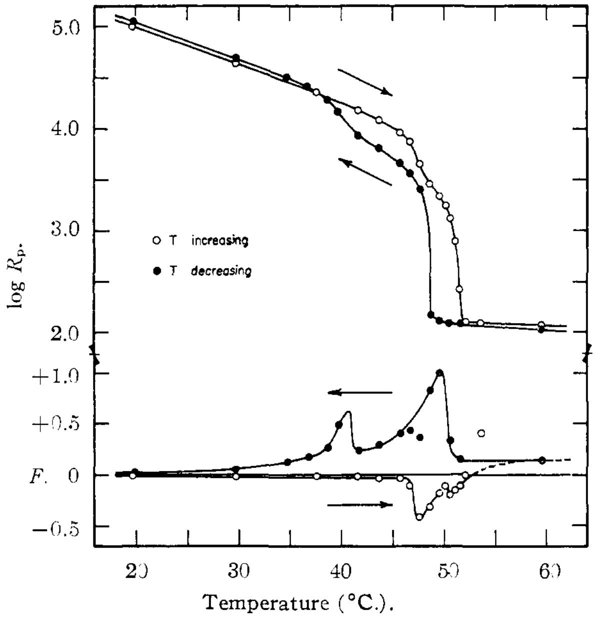

Fig. 4.—Behavior of pressed Ag_2HgI_4 sample P-7 as a function of time and temperature; see text for details.

Discussion

The electrical conductivity of pressed samples of Ag_2HgI_4 in the β-modification decreases upon cycling to $T > 52°$. There is also a slow but continual and monotonic downward drift in σ for samples standing at $T < 52°$. It is difficult to ascribe such behavior to anything other than growth of crystallites and increasing perfection of crystallites. Further a cursory examination of β-modification conductivities as a function of pressing pressures and pressing time indicates that σ-values are greater the higher the pressure and the longer the time samples are held at top pressure. This is most simply understood in terms of decreasing size of "good crystal" regions.

The annealing and pressing behavior, together with a study of the dielectric properties,[12] suggest the following reasonable description of the state of pressed specimens of Ag_2HgI_4 in the β-modification. The bulk of the specimen consists of relatively large "grains" of good quality ordered crystal, having specific conductivity σ_G. Individual grains contact one another *via* "point contacts" of poorly organized boundary material having specific conductivity σ_B. Where grains are not in contact there are non-conducting "voids." Contact material, because of its high state of disorganization, and therefore low degree of order, is presumed to have a high conductivity. Thus for $T < 52°$, $\sigma_B > \sigma_G$. Transformation of disordered material into ordered material by grain growth during annealing together with a concomitant decrease in the number of contacts causes specimen conductivity to decrease. Conversely higher pressures or longer pressing time lead to increased conductivity because grains are sheared and broken and the relative amount of disorganized material is increased.

The analysis of the dielectric behavior over a wide range of frequencies[12] permits the conclusion that the value of R_p measured at 1000 sec.$^{-1}$ is a good measure of the resistance of grains. Therefore, the sample conductivities calculated from R_p and specimen dimensions are proportional to σ_G, the specific conductivity of the grains of crystalline Ag_2HgI_4. Accepting these conclusions the data can be examined.

We first emphasize that only the dielectric behavior of the β-modification has been investigated. That of the α-modification is much more complicated and has not been studied extensively. Accordingly we have nothing to conclude about the conductivity of α-Ag_2HgI_4 or its activation energy. Our results agree neither with those of Ketelaar[8] nor with those of Suchow and Pond.[9] On the other hand, since sample conductivity is proportional to σ_G for crystalline β-Ag_2HgI_4, our results in the region of the β-modification may be important.

An activation energy of 12 kcal. mole^{-1} was found for the conduction process in the β-modification below 20°. The value was reproducible from sample to sample and is to be contrasted with 15 kcal. reported by Suchow and Pond[9] and *ca.* 8 kcal. calculated from d.c. conductivity data reported by Ketelaar.[8] Suchow and Pond worked at 1000 sec.$^{-1}$ and their log σ *vs.* T^{-1} graph has approximately the same shape as our Fig. 1 in the region 25–45°, but their curve is shown as linear between 12 and 35°. Our results, however, indicate that log σ becomes linear in T^{-1}, if at all, only below 12°. The best straight line drawn through points between 22–35° in Fig. 1 has a slope of 15 kcal., a value relatively close to that of Suchow and Pond.

The kinetics data represent only a beginning to a rather complicated problem. They nonetheless indicate the extreme importance of paying careful

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[12] G. M. Nichols and T. J. Neubert, "Dielectric Behavior of Pressed Samples of β-Ag_2HgI_4," to be submitted to *J. Chem. Phys.*

attention to such details as sample history and time-schedule of measurements when working with pressed specimens. Thus our results provide a point of departure for future work with Ag_2HgI_4 and in particular indicate quite clearly that, both in the approach to order and the approach to disorder, two nucleation steps are involved, *cf.* Fig. 4 (lower part). This conclusion is supported by the fact that a small bump is observed in conductivity curves both for T-increasing and T-decreasing. The bump is real; it occurs in all samples, both pressed and cast. That it has not been noted in previous conductivity studies is indicative of measurements made too rapidly.

The two transitions implied by the two nucleations may be designated (for T-increasing) as $\beta \rightarrow \beta'$ and $\beta' \rightarrow \alpha$. We suggest that in the $\beta \rightarrow \beta'$ transition Ag-ions become disordered occupying at random $^2/_3$ of the face center positions of the unit cube and in the $\beta' \rightarrow \alpha$ transitions Ag and Hg-ions become further disordered occupying at random $^3/_4$ of the corners plus face centers of the unit cube. This picture, however, leads to some difficulty in interpretation of the relative sizes of the conductivity changes. It is usually said, following Ketelaar,[1] that the large increase in conductivity near 52° is the result of one mole of lattice vacancies becoming available to the conduction process. Thus since transference number measurements for the α-modification[8] show that Hg-ions account for only 6% of the current, one would expect the $\beta \rightarrow \beta'$ transition to exhibit the largest conductivity effect. An alternative assignment would let the $\beta \rightarrow \beta'$ transition involve mixing of Ag and Hg-ions, and the $\beta' \rightarrow \alpha$ transition the extension of the disorder to the normally unoccupied top and bottom face centers of the unit cube. X-Ray diffraction and transference experiments would be fruitful in deciding between these possibilities provided suitable single crystals can be prepared and adequate attention is paid to details of sample history.

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CHICAGO 16, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Effect of Adsorbed Films on Kinetics of Electrode Reactions[1]

BY H. A. LAITINEN AND W. J. SUBCASKY

RECEIVED NOVEMBER 11, 1957

The transfer coefficient and electron transfer rate constant for a totally irreversible electrode reaction can be measured by determining the dependence between the current and potential at the foot of the polarographic wave. This method was used to study the effect of the adsorption of such surface active agents as *n*-octyl alcohol, β-naphthol and camphor upon the reduction of nickel(II) ions in sodium perchlorate medium, iodate ions in basic and acidic media, the reduction of the chloro complexes of tin(IV) and tin(II), the reduction of the ammonia and some amine complexes of copper(II), and the reduction and oxidation of the ammonia complexes of copper(I). The effect of high concentrations of sodium perchlorate upon the reduction of nickel(II) also was studied.

During recent years, many observations have been made on adsorption and its effect upon electrochemical reactions. No attempt will be made here to survey the field,[2] but mention should be made of the extensive work of Loshkarev and Kryukova[3] on the effect of organic compounds on electrode systems, the observations of Meites and Meites[4] on the effects of gelatin upon the characteristics of polarographic waves, the work of Berzins and Delahay[5] on the kinetics of adsorption, and that of Strassner and Delahay[6] on the effect of gelatin upon the kinetics of irreversible electrode reactions.

Two quantities, the transfer coefficient and the electron transfer rate constant, are usually used to describe the kinetics of electrode reactions. These two quantities can be determined by polarographic methods,[7-10] by chronopotentiometry,[11] by a.c. impedance measurements[12] or by determining the relationship between current and electrode potential.[13] The latter method is particularly simple for totally irreversible electrode reactions under conditions such that the rates of mass transfer are very large in comparison to the rate of electron transfer.

This condition is readily fulfilled by measuring the current at the foot of a polarographic wave.[9] By increasing the concentration to a relatively high value (*ca.* 0.01 *M*), the currents at the lower 10 to 15% of the polarographic wave are increased to readily measured magnitudes. If the rate of the

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[1] This work was supported by grants G-750 and G-2420 of the National Science Foundation, and a fellowship donated by the U. S. Rubber Co.

[2] For references, see W. J. Subcasky, Ph.D. thesis, University of Illinois, 1957.

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