

A STUDY OF LATTICE DEFECTS IN IONIC CRYSTALS

A thesis presented for the Degree of
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by

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Abstract

The interactions between point defects of a uni-univalent ionic salt have been reviewed, as also have the phenomena of polarization and thermoelectric power in these salts.

The conductivity of pure KCl, and KCl doped with SrCl_2 up to 120×10^{-5} mole ratio, has been thoroughly investigated over the temperature range 700° to 800°C . This has enabled determination of the enthalpy and entropy of creation and migration of the Schottky defects and also the free energy of association, γ , of the divalent cation-cation vacancy complex. From this study it was found that a portion, c' , of the total concentration, c , of the added impurity did not contribute to the formation of cation vacancies. This is thought to be due to two factors. First, OH^- ions, which are always present in small amounts in KCl, will tend to complex with some of the Sr^{2+} . Second, SiO_2^{2-} ions, which may be introduced during the growing stage, will also tend to form complexes with the Sr^{2+} ions, thus decreasing the number of cation vacancies formed. It is not possible to distinguish between these two mechanisms with the data available.

The a.c. polarization of pure and doped KCl has been investigated and it has been concluded that the polarization capacity is due to the blocking of both negative and positive charge carriers at the boundary electrodes. It has been shown that the experimental results agree very well with the theoretical values of the capacity calculated from the theory for this type of blocking. The high

temperature polarization due to the application of a static d.c. field to the crystal has been investigated. This is again interpreted as the blocking of both ionic charge carriers; the residual current is electronic in nature.

Current-voltage curves, at various temperatures, have been obtained over a wide voltage range. Using this data, an attempt has been made to elucidate the nature of the electrode processes.

Thermoelectric power measurements have been completed over a wide temperature range, from which it has been possible to calculate the heats of transport of the migrating defect species. A new and more general theory of the heterogeneous thermoelectric power, has been developed.

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1. Introduction

1.1. The nature of lattice defects

Ionic crystals are composed of a well-defined geometrical array of ions which gives rise to the appropriate crystal lattice. When the Curies (1889) applied an electric field to a rock salt crystal, they were able to show that the crystal acted as a conductor of electricity. But the drift of ions through an ionic crystal is inconceivable if the crystal is perfect, for the transport of charge would only be possible if there were a direct exchange between cations and anions. In KCl and AgCl, for example, the energy which would have to be supplied to facilitate this exchange would be of the order of 15 eV, so that the probability of its ever occurring would be extremely small. Hence, Frenkel (1926) and Schottky (1935) postulated the idea of point defects. Frenkel supposed that, under the influence of thermal vibrations, some ions receive enough energy to leave their normal lattice positions and find new positions of low energy at the interstices in the lattice. Then, under the influence of an electric field, the interstitial ions move from one interstitial position to another. Positive interstitial ions in an electric field will jump more frequently in the direction of the field (i.e. towards the cathode) than against the field, so that an electric current flows.

Schottky envisaged a model in which both cation and anion vacancies exist, but no interstitial ions are present. This means in effect that a new layer of ions must be built up on the surface of the crystal so that it can accommodate the vacant sites. Whether

the disorder in any crystal is of Frenkel or Schottky type depends upon the relative magnitudes of the free energies of formation of the respective defects, as will be shown in section 1.2. As potassium chloride has been the subject of the present investigation, it is appropriate to point out now that potassium chloride contains Schottky defects. Further discussion will be limited to Schottky disorder and to cationic Frenkel disorder, since these predominate in the alkali and silver halides.

1.2. Statistical theory of point defects

Wagner and Schottky (1931) have developed a statistical theory of point defects which is applicable to ionic crystals. A thorough analysis of the problem was given by Allnatt and Jacobs (1961,b). Let M^+ , X^- denote lattice cations and anions and the subscripts +, - and i indicate cation vacancies, anion vacancies and interstitial ions respectively. The Gibbs' free energy of a real crystal relative to the infinitely dilute gaseous ions, $G(N_{M^+}, N_{X^-}, N_+, N_-, N_i)$ can then be written down and the chemical potentials of the individual species obtained by partial differentiation.

Further, the equilibrium condition for a closed system

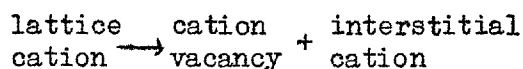
$$1.2.1. \quad (dG)_{T,P} = 0 ,$$

subject to the constraints of electroneutrality and stoichiometry yields the following relations between the chemical potentials:

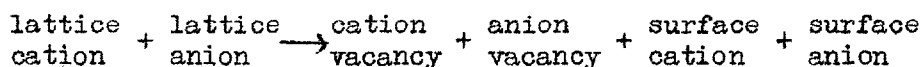
$$1.2.2. \quad \mu_{M^+} = \mu_+ + \mu_i$$

$$1.2.3. \quad 0 = \mu_+ + \mu_- .$$

It was pointed out by Allnatt and Jacobs (1961,b) that these relations are in accord with the quasi-chemical processes for the formation of Frenkel and Schottky defects, namely,



and



since the sum $\mu_{M^+} + \mu_{X^-}$ is clearly the same for surface and bulk ion pairs.

Howard and Lidiard (1957a) [and also Howard (1957), Lidiard (1957)] deduced an expression for the chemical potential of a cation in the crystal MX by equating it to the change in free energy when M^+ is taken from infinity to the interior of the crystal at constant temperature and pressure. This ion may be placed either in an interstitial site or in a cation vacancy. The change in free energy is thus equal to that resulting from the creation of an M^+ interstitial or the destruction of a cation vacancy. Therefore

$$1.2.4. \quad \mu_{M^+} = -\mu_+ = \mu_i.$$

Expressions for μ_+ and μ_i were obtained in the usual way from the equilibrium condition. The analogous expression to eqn.1.2.4 for anions is

$$\mu_{X^-} = -\mu_-$$

so that

$$1.2.5. \quad \mu_+ + \mu_- = -(\mu_{M^+} + \mu_{X^-}) = -g_{MX}$$

where g_{MX} is the Gibbs' free energy change on adding an ion pair to

the crystal. The Howard and Lidiard expressions (cf. also Haga, 1958, 1959) for the chemical potentials of vacancies differ essentially from those of Allnatt and Jacobs in having for the constant term g_+^{∞} , g_-^{∞} in place of g_+ , g_- where g_+ is the change in the Gibbs' free energy on taking a cation from a normal lattice site to the surface of the crystal and g_+^{∞} the corresponding change when the ion is removed to ∞ .

The discrepancies between the two treatments are however, more apparent than real. Howard and Lidiard's procedure corresponds to the choice of N_+^g , N_-^g , N_+ , N_- and N_i as independent variables, where N_+^g , N_-^g are, respectively, the number of cation and anion sites in the crystal. This alternative choice is available in view of the requirements:

$$\begin{aligned} N_+^g &= N_{M+} + N_+ \\ N_-^g &= N_{X-} + N_- \end{aligned}$$

Both equilibrium expression 1.2.3 and 1.2.5 yield, on substituting for the μ 's, the same relation between the numbers of defects, namely

$$1.2.6. \quad N_+ N_- = N^2 \exp(-g_s/kT)$$

$$\text{where } g_s = g_+ + g_- = g_+^{\infty} + g_-^{\infty} + g_{MX}$$

is the Gibbs' free energy change on forming a Schottky defect pair.

Similarly, for Frenkel defects, from 1.2.2 or 1.2.4, one has

$$1.2.7. \quad N_+ N_i = 2\eta N^2 \exp(-g_F/kT)$$

where

$$\varepsilon_F = \varepsilon_i + \varepsilon_+$$

and

$\eta (N_{M+} + N_{X-} + N_+ + N_-)$ is the total number of interstitial cation sites. For a f.c.c. lattice clearly $\eta = 1$. An economical notation introduced by Lidiard (1957) will now be adopted. This is to use the subscript 1 for cation vacancies and the subscript 2 to denote anion vacancies or interstitial cations. In addition the molar fraction of species r will be denoted by

$x_r = N_r/N$ since $N \gg N_r$. Equations 1.2.6 and 1.2.7 then become

$$1.2.8. \quad x_1 x_2 = \alpha \exp(-g/kT) = x_0^2 = K_1$$

where $\alpha = 1$ or 2 for Schottky or Frenkel disorder respectively and x_0 is the equilibrium number of defects (1 or 2) in the pure crystal.

1.3. Theory of ionic conductivity

The frequency of exchange between a vacancy and an adjacent ion, or alternatively the probability per unit time that an interstitial ion will have enough energy to pass over the energy barrier separating two equilibrium interstitial positions, is given by (Wert, 1950, Lidiard, 1957):

$$1.3.1. \quad w = \nu \exp(-\Delta g/kT).$$

In this expression Δg is the energy required to move the ion from its equilibrium position to the col of the energy barrier, at constant T and P , and ν is the frequency of vibration of the ion at its equilibrium position.

In the presence of a uniform field F along the x axis, the potential energy of an ion at a point x along this axis is

raised by $-eFx$. If a is the distance between two neighbouring equilibrium sites then the jump probability for motion in the direction of the field is

$$\begin{aligned}\Delta w &= \nu \exp \left[-(\Delta g - \tfrac{1}{2} eaF)/kT \right] - \nu \exp \left[-(\Delta g + \tfrac{1}{2} eaF)/kT \right] \\ &= \nu \sinh (eaF/2kT) .\end{aligned}$$

On using the approximation valid for low fields, this becomes

$$\Delta w = weaF/kT \quad (eaF \ll kT) .$$

The electric current density will thus be

$$j = nea\Delta w = ne^2 a^2 wF/kT .$$

Hence the specific conductance, σ , and mobility, u , are given by

$$\sigma = j/F = ne^2 a^2 w/kT = neu,$$

1.3.2.

$$u = a^2 ew/kT.$$

When there are more than one type of migrating species (e.g. cation vacancies and anion vacancies) the transport number t_s for the species s is defined by

$$t_s = \sigma_s / \sigma$$

where

$$\sigma = \sum_s \sigma_s = e \sum_s n_s u_s .$$

Extensive transport number measurements have been made by Tubant (1932). He showed that in the alkali halides, cation migration predominates except at very high temperatures. If the conduction is due to one type of carrier, then from equn. 1.3.1, 1.3.2 and 1.2.8,

$$1.3.3. \quad \sigma = \alpha N \exp(-g/2kT) \nu \exp(-\Delta g/kT) e^2 a^2 / kT$$

and hence

$$1.3.4. \quad \frac{\partial \log(\sigma T)}{\partial (1/T)} = - \frac{(\Delta h_1 + \frac{1}{2}h)}{k} = - \frac{E_1}{k}$$

where Δh_1 and h are, respectively, the enthalpy of activation for migration and the enthalpy of formation of the defect.

It is found experimentally that plots of $\log(\sigma T)$ against $1/T$ can usually be represented by two straight lines. For the high temperature part,

$$1.3.5. \quad \log(\sigma T) = \log A_1 - E_1/kT$$

and for the low temperature region,

$$1.3.6. \quad \log(\sigma T) = \log A_2 - E_2/kT.$$

The high temperature part is reproducible from crystal to crystal and corresponds to defects in thermodynamic equilibrium. The low-temperature line varies from crystal to crystal, depending upon the purity and history of the crystal. Koch and Wagner (1937) first suggested that electrical conduction in this region is due to defects generated by the presence of unavoidable impurities of a different valency to that of the ions of the host crystal. In this temperature region the number of defects depends therefore purely on the amount of impurity, which is constant in any one crystal, and so

$$1.3.7. \quad -k \partial \log(\sigma T) / \partial (1/T) = \Delta h_1 = E_2.$$

The study of ionic conductivity as a function of impurity content thus allows a direct determination of x_0 and u separately, although this is not possible from measurements of σ as a function of T alone. In the high temperature (or intrinsic) region, both

anion and cation vacancies may contribute to the conductance, so that

$$1.3.8. \quad \sigma = N_1 e u_1 + N_2 e u_2 = x_0 N e u_1 (1 + \phi)$$

where ϕ is the mobility ratio, u_2/u_1 . In the structure-sensitive (or low temperature) region

$$1.3.9. \quad \sigma = c N e u_1$$

where c denotes the number fraction of divalent impurity cations added to a 1:1 crystal. Thus, knowing c , u_1 may be found from equn. 1.3.9 and hence, if ϕ is known (or may be neglected) x_0 can be obtained from equn. 1.3.8. It will be shown later (section 3.1.) that ϕ may also be determined from the high-temperature conductance data.

1.4. Interaction between defects

Defects may be formed in crystals by the accidental presence or intentional addition of impurities. If every added impurity ion of the type M^{2+} is compensated for by the formation of a cation vacancy, then electroneutrality requires

$$1.4.1. \quad x_1 = c + x_2 .$$

Two extremes of this equation are possible. At high temperatures $x_0 \gg c$ for a pure crystal therefore

$$x_1 = x_2 = x_0 \quad (\text{intrinsic region})$$

while at low temperatures $c \gg x_0$,

$$x_1 = c \quad (\text{structure sensitive region}).$$

In the notation of section 1.2., for intrinsic defects

$$1.4.2. \quad x_1 x_2 = x_0^2 = K_1 .$$

Cation vacancies and bivalent metal impurities carry opposite

(virtual) charges and thus tend to combine to form neutral complexes consisting of a cation vacancy and an impurity ion on adjacent lattice sites. If all but the nearest neighbour interactions are neglected the equilibrium between complexes of number fraction x_k , impurity cations and free cation vacancies is given by

$$1.4.3. \quad \frac{x_k}{x_1(c - x_k)} = K_2 = z_k \exp(\zeta/kT)$$

where $-\zeta$ is the free energy of association and z_k the number of distinct orientations of the complex. In deducing equn. 1.4.3. the effect of possible coulombic interactions between unassociated defects was neglected. This effect was considered by Lidiard (1954). If f_n is the activity coefficient of species n , then equn. 1.4.2. and 1.4.3. become

$$1.4.4. \quad x_1 x_2 f_1 f_2 = K_1$$

$$1.4.5. \quad \frac{x_k}{x_1(c - x_1)} = K_2 f_1 f_j$$

where the subscript j refers to unassociated impurity ions. The expressions for the activity coefficients adopted by Lidiard are analogous to those in the Debye-Hückel theory of ionic interactions in solution:

$$\log f_1 = \log f_2 = \log f_j = \frac{-q^2}{2\epsilon kT} \frac{\kappa}{(1 + \kappa a)}$$

in which

$$\kappa = \frac{8\pi x_1 q^2}{v \epsilon kT},$$

q being the virtual charge (e.g. +1 for M^{++} impurity ions), v the

volume per ion pair and ϵ the permittivity. However, as a first approximation, the activity coefficients may be set equal to unity, so that only nearest-neighbour interactions are being considered. On eliminating x_k from equn. 1.4.2 and 1.4.3. and applying equn. 1.3.8, Stasiw and Teltow (1947) obtained

$$1.4.6. \quad \frac{c}{\sigma} = \frac{x_0}{\sigma_0} \frac{(y^2 - 1)(1 + \phi)(1 + x_0 K_2 y)}{y^2 + \phi}$$

where σ_0 is the conductance of the pure crystal, $y = x_1/x_0$ and $\phi = u_2/u_1$. At all but the highest temperatures in the alkali halides, $y^2 \gg 1 > \phi$ and equn. 1.4.6. reduces to

$$1.4.7. \quad \frac{c}{\sigma} = \frac{x_0}{\sigma_0} (1 + \phi) + \left\{ \frac{x_0}{\sigma_0} (1 + \phi) \right\}^2 K_2 \sigma.$$

In the absence of association, $K_2 = 0$, the c/σ isotherms are linear and parallel to the σ axis, as

$$1.4.8. \quad \frac{c}{\sigma} = \frac{x_0}{\sigma_0} (1 + \phi)$$

or

$$1.4.9. \quad c = x_0 \sigma / \sigma_0 t_1^0,$$

t_1^0 being the cation transport number in the pure crystal. It should be noted that c in equn. 1.4.7. is the concentration of added impurity that is effective in creating an equivalent number of cation vacancies and that this is not equal to the concentration of added impurity if precipitation occurs, or if the pure crystal already contains unavoidable impurity of amount c_0 . Thus the l.h.s. of equn. 1.4.9. should, in general, read $c + c_0$.

If association is not negligible, but $\phi \ll 1$, equn. 1.4.7.

becomes

$$1.4.10. \quad \frac{1}{\alpha_1} \left(\frac{c + c_0}{\sigma} \right) = 1 + \alpha_1 \sigma K_2$$

where $\alpha_1 = 1/Neu_1 = 2a^3/u_1 e$, a being the anion-cation nearest-neighbour distance. c_0 can be estimated graphically by extrapolation of the plot of σ against c to $\sigma = 0$, and the final plots of $(c + c_0)/\sigma$ against σ should then be linear of slope $\alpha_1^2 K_2$.

Lidiard (1957) has also allowed for the effect of coulombic interactions between non-nearest neighbours on the defect mobilities, when it appears that plots of $(c + c_0)/\alpha_1 \sigma$ against $\alpha_1 \sigma$ should show a recognizable curvature towards the σ axis at low values of σ , instead of being straight lines as in the Stasiw-Teltow theory.

The mobility u_s of a species s is related to its self diffusion coefficient D_s by the Nernst-Einstein relationship:

$$u_s/D_s = e_s/kT$$

$$\text{or} \quad \sigma_s/D_s = N_s e_s^2/kT$$

where N_s is the number of particles per unit volume. D_s is related to the tracer diffusion coefficient D_{Ts} by

$$D_{Ts} = f_s D_s$$

where f_s is the correlation factor which allows for the distinguishability of the tracer ions (see Bardeen and Herring, 1951) and depends on the jump mechanism and lattice geometry. Hence, for singly charged ions,

$$\frac{\sigma_s}{D_{Ts}} = \frac{1}{f_s} \frac{Ne^2}{kT} \quad .$$

Lidiard (1957) has reviewed this method of distinguishing the details of the jump mechanism. This approach is important for testing the association theory, as the complexes make no contribution to the electrical conductivity but do contribute to the diffusion of cation vacancies.

1.5. Previous experimental work

Among the earliest measurements of the conductivity of alkali halide single crystals are those performed by Phipps and Partridge (1929), Lehfeldt (1933) and Brennecke (1940). They were able to establish that the plot of the logarithm of the conductivity versus the reciprocal temperature consisted essentially of two linear regions in accordance with the equation

$$1.5.1. \quad \sigma = A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT)$$

where $E_1 \sim 2E_2$ and $A_2/A_1 \sim 10^{-5}$. Strictly, as shown by the theory presented in section 1.3., one should plot $\log(\sigma T)$ against $1/T$; in practice, plots of $\log \sigma$ against $1/T$ are also linear though the values of E_1 and E_2 may be slightly altered. Allnatt and Jacobs (1962,b) have made a thorough investigation of the $KCl + SrCl_2$ system and established the numerical values for the various parameters. Gründig (1960) investigated the structure-sensitive region of the conductance curve using zone-refined KCl and thus obtained what should be a reliable value for E_2 . Zone-refined KCl has also been

studied in the temperature range 2-450°C by Kanzaki, Kido and Ninomiya (1962). They obtained $E_2 = 0.7$ eV for the least ~~impure~~ pure part of the zone-refined crystal and 1.4 eV for the purest part. This high value is undoubtedly due to an extension of the intrinsic region to lower temperatures as the purity of the crystal increased, although Kanzaki et al. apparently failed to notice this complication. Values of the parameters A_1 , A_2 , E_1 and E_2 in equn. 1.5.1 obtained from conductivity measurements are presented in table 1. The values of these parameters have been further reviewed by Dreyfus and Nowick (1962).

Table 1

Experimental data for conductance of KCl crystals

	A_1	E_1 (kcal mole ⁻¹)	A_2	E_2 (kcal mole ⁻¹)
Phipps and Partridge (1929)	1×10^6	46.6	0.04	22.8
Lehfelddt (1933)	2×10^6	47.5		20.5
Brennecke (1940)		45.8		
Kelting and Witt (1949) (+CaCl ₂)				18.2
Kelting and Witt (1949) (+SrCl ₂)				19.8
Kelting and Witt (1949) (+BaCl ₂)				21.7
Wagner and Hantelmann (1950) (+SrCl ₂)				18.0
Gründig (1960)				18.4
Allnatt and Jacobs (1962b)	4.82×10^{-5}	44.9	4×10^{-4}	16.4
Kanzaki et al. (1962)				16.1

Witt (1953) measured the diffusion coefficient of the K^+ ion and found it to be 2.4 times that expected from the Nernst-Einstein equation. However, Aachner (1954) and Arnilear and Chemla (1951) have also studied cation diffusion in KCl and found the Nernst-Einstein relationship valid. Similarly, Mapother, Crookes and Maurer (1950), studying the self diffusion of Na^+ in NaCl and NaBr, found the Nernst-Einstein equation valid if allowance is made for anion diffusion. Thus it seems to be established that, with experimental error, for NaCl, NaBr and KCl at least, the Nernst-Einstein equation is valid.

Wagner and Hantelmann (1950), using pellets of KCl + $SrCl_2$ in the temperature range 600-725°C, calculated from their conductance data the number of Schottky defects assuming no association. The values of x_0 determined, were based on the transport number data of Tubant, Reinhold and Liebold (1931) which is not in agreement with the later work of Kerkoff (1951). In fact, the transport number data appear to be quite structure sensitive (see section 3.1.). Moreover, their values of x_0 must be suspect as Phipps and Partridge (1929) showed that the conductivity of pressed pellets differs from that for single crystals by being 4% higher at 700°C and 60% higher at 600°C.

The first quantitative test of the Stasiw-Teltow association theory was made by Etzel and Maurer (1950) on the NaCl + $CdCl_2$ system. The impurity had a maximum concentration of 68.5×10^{-5} mole fraction, the conductivity being studied between 250°C and 400°C.

Their conductivity isotherms were parabolic and fitted the equation (cf. equn. 1.4.7)

$$1.5.2. \quad c = L\sigma^2 + F$$

where L and F are constant. From the numerical values of L and F , K_2 and thus ζ , ($-\zeta$ is the free energy of association), were obtained. ζ was found to be 0.23 - 0.25 eV. Lidiard (1954) has re-analysed the isotherms of Etzel and Maurer using his coulombic-interactions theory and found $\zeta = 0.34$ eV.

The results for the $\text{NaCl} + \text{CaCl}_2$ system (Bean, 1952), have been analysed according to the Stasiw-Teltow theory. Conductivity isotherms were linear up to concentrations of $c = 250 \times 10^{-5}$. Bean thus concluded that $\zeta < 0.08$ eV, but his conductivity values were half those of $\text{NaCl} + \text{CdCl}_2$ at the same temperature and concentration, which apparently indicates a higher degree of association. The $\text{NaCl} + \text{CaCl}_2$ system was further studied by Thomson (1956) who found that the isotherms were in fact parabolic but with curvature opposite to that expected from the association theory. A further anomaly is that the mobility of cation vacancies found by Bean (1952) and Thomson (1956) was half of that found by Etzel and Maurer (1950).

Kelting and Witt (1949) determined the conductivity of $\text{KCl} + \text{SrCl}_2$, CaCl_2 or BaCl_2 as a function of concentration. Their plots of log conductivity against $1/T$ definitely appear curved, suggesting the presence of association, but unfortunately this data has not been analysed. The most curious feature of their work is the dependence of E_2 on the impurity ion present (table 1). Bassani

and Fumi (1954) have attributed this to a dependence of the interactions between the impurity ions and vacancies at close distances on the nature of the cation. The results of Allnatt and Jacobs (1962) on $\text{KCl} + \text{SrCl}_2$ apparently favoured non-nearest neighbour interactions though the authors considered that this feature of their conductivity isotherms might be an artefact, due to uncertainties in the values of c . A value of 0.3 ± 0.1 eV was deduced for γ , the wide limits being due to the curious and unexplained temperature-dependence found for γ . Gründig (1960), in his study of $\text{KCl} + \text{CaCl}_2$, also observed association effects and determined a binding energy of the complex of 0.52 ± 0.04 eV for $\text{KCl} + \text{CaCl}_2$ and 0.56 ± 0.04 eV for $\text{KBr} + \text{CaCl}_2$. Ninomiya (1960) has measured the d.c. conductivity and dielectric loss of quenched KCl crystals doped with CaCl_2 . He obtained evidence for higher aggregates than simple complexes from the decay of conductivity during annealing after quenching.

Despite all these investigations the evidence for the association theory is not very extensive. Principal support comes from the two systems $\text{NaCl} + \text{CdCl}_2$ (Etzel and Maurer, 1950) and $\text{AgBr} + \text{CdBr}_2$ (Teltow, 1949, Lidiard, 1957) while the evidence for non-nearest neighbour interactions is inconclusive. For the system $\text{NaCl} + \text{CdCl}_2$ the work of Bean and Thomson is conflicting, while for $\text{KCl} + \text{SrCl}_2$ the work of Allnatt and Jacobs (1962b) needs to be extended.

Since the impurity-vacancy complex is an electric dipole, with the vacancy end negative and the impurity end positive, its energy depends upon its orientation with respect to an applied electric

field. When an a.c. electric field is applied, the continual striving of the complexes to readjust their orientations to an equilibrium value consistent with the instantaneous applied field, produces an alternating current which lags in phase behind the field. This phenomenon is conveniently measured as a dielectric loss, which is expected to obey the Debye equations. The theory has been reviewed by Lidiard (1954, 1957).

If the frequency of dipole reorientation by direct exchange of the M^{2+} ion and the vacancy is w_2 , and that by the vacancy jumping from one nearest neighbour position to another is w_1 , the contribution to the loss factor should be

$$1.5.3. \quad (\tan \delta)_c = \frac{8\pi a^2 e^2 N_i p}{3 \epsilon kT} \frac{w \tau}{1 + w^2 \tau^2}$$

where $\tau = [2(w_1 + w_2)]^{-1}$ and p is the degree of association.

Dryden and Meakins (1957) found Debye absorption curves as predicted by equn. 1.5.3. The frequency of the absorption maximum, f_m , could be expressed by an Arrhenius equation

$$f_m = A \exp(-\Delta E/kT) .$$

Results for KCl were:-

	ΔE , eV
KCl + CaCl ₂	0.64
KCl + SrCl ₂	0.67
KCl + BaCl ₂	0.70

ΔE is the activation energy corresponding to either w_1 or w_2 , whichever is the smaller. Similar results have been found by

Haven (1953, 1954) for NaCl containing Cd^{2+} , Ca^{2+} and Mn^{2+} , by Teltow and Wilke (1954) for $\text{AgBr} + \text{CdBr}_2$ and by Dryden and Meakins (1957) for $\text{NaCl} + \text{CaCl}_2$.

As the doping level is increased a second absorption peak, wider than the Debye peak, becomes prominent. ΔE is nearly the same for both peaks in many alkali halide crystals (Dryden and Meakins, 1957). This second peak was ascribed to the precipitation of platelets found by Miyake and Suzuki (1954) by X-ray studies, when the concentration of CaCl_2 was greater than about 0.05 mole per cent. Such crystals often appear turbid to the eye.

Upon the application of a static d.c. field, the complex tends to become oriented in the direction of the field thereby producing a polarization current which decreases with time. Dreyfus (1961) studying $\text{NaCl} + \text{Ca}^{2+}$ or Mn^{2+} , found below 0°C a dominant 'fast polarization' in which the vacancy is in the nearest neighbour position (except for $\text{NaCl} + \text{Mg}^{2+}$). He also observed a 'very fast polarization' which was ascribed to next-nearest neighbour complexes, plus a 'slow polarization' due to vacancies jumping between more distant sites. The activation energies for the exchange of vacancies on nearest neighbour sites with Ca^{2+} and Mn^{2+} ions in a NaCl lattice were found to be 0.702 ± 0.010 eV and 0.680 ± 0.010 eV respectively.

The most direct study of impurity precipitation and complex formation has been by electron spin resonance studies of paramagnetic impurity ions such as Mn^{2+} . As the e.s.r. of paramagnetic ions is sensitive to their environment, the state around the paramagnetic

ions may be investigated by the structure of the resonance lines. Watkins (1959), studying $\text{NaCl} + \text{Mn}^{2+}$, observed several types of resonance spectrum with increasing temperature and classified the spectra according to their appearance. Spectrum 1 is a broad single line appearing before quenching, arising from Mn^{2+} ions in an aggregated state. Spectrum 2 consists of six lines appearing above 250°C . These arise from isolated Mn^{2+} ions free from any vacancy. Spectrum 3 is complex but was successfully analysed by Watkins and Walker (1956) and Morigaki, Fujimoto and Itoh (1958). It can be further divided into two types, designated 3(a) and 3(b); one of these comes from the Mn^{2+} ions with a positive ion vacancy at one of the nearest neighbour cation sites, and the other with a vacancy in the next-nearest neighbour cation site. Spectrum 3 was also observed for Mn^{2+} in KCl and LiCl single crystals by Watkins (1959) and Fukuda, Uchida and Yoshimura (1958, 1960). Besides these spectra Watkins observed spectrum 4, which had a lower intensity and larger splitting. This spectrum arises from Mn^{2+} associated with divalent anion impurities such as O^{2-} . From the relative intensities Watkins estimated the binding energies of the two sorts of complex corresponding to 3(a) and 3(b). These experiments showed that the binding energy for n.n.n and further separations may be strong enough for such pairs to be regarded as associated. The theoretical binding energies for nearest (E_1) and next-nearest neighbour pairs (E_2) are also comparable in order of magnitude (table 2).

Studies of e.s.r., dielectric loss and low temperature polarization effects thus give a more solid foundation to the association theories than do the rather inconclusive conductivity measurements.

Table 2

Association energy for complexes

System	E_1 eV	$E_1 - E_2$ eV	Reference
(1) Theoretical			
NaCl + CdCl ₂	0.38		Theoretical values from Bassani and Fumi (1954) and Tosi and Airoldi (1958).
NaCl + CaCl ₂	0.38		
NaCl + SrCl ₂	0.45	0.02	
KCl + SrCl ₂	0.39	-0.11	
KCl + CaCl ₂	0.32		
KCl + CdCl ₂	0.32		
(2) Experimental			
NaCl + CdCl ₂	0.23 to 0.25		Etzel and Maurer (1950)
NaCl + CdCl ₂	0.34		Lidiard (1954)
KCl + SrCl ₂	0.3		Camagini et al. (1954)
KCl + SrCl ₂	0.3 ⁺ 0.1		Allnatt and Jacobs (1962,b)
KCl + MnCl ₂	0.39		Watkins (1959)
KCl + CaCl ₂	0.52		Gründig (1960)
KBr + CaCl ₂	0.56		Gründig (1960)

1.6. Polarization effects

1.6.1. D.c. polarization

In their early experiments, the Curies (1889), upon applying a constant electric field to a rock salt crystal, observed that the current flowing through the crystal decayed with time. Jaffé and Röntgen (1913) were able to show that this current decay was due to a build-up of a 'polarization voltage' in opposition to the applied potential. They disconnected the crystal from the potential source and short-circuited it, whereupon a current flowed in the direction opposite to that in which it had passed through the crystal initially. Due to this current decay, two characteristic conductances of a crystal may be defined, σ_0 measured at $t = 0$ for zero polarization voltage, and σ_∞ , the steady state conductivity calculated from the steady state current i_∞ and applied voltage, V . We shall adopt the terminology of Parker (1954) for the d.c. polarization, whereby the current at time t is I , $I_p = I - I_\infty$ is the polarization current and $I_{op} = I_0 - I_\infty$ the initial polarization current.

V. Seelen (1924) and Gingold (1928) showed that charging and discharging currents were the same and that the current-time curves were similar. This suggested that the polarization is due to the blocking of the charge carriers at the electrodes building up a space-charge layer which tends to oppose the applied potential. The charging current-time curves were analysed by V. Seelen (1924) and Brennecke (1940) using the power law,

$$1.6.1.1. \quad I = at^{-n}$$

where n varied from 0.3 to 0.9. Brennecke (1940) studying KCl and KBr found n to be unity at room temperature and that it decreased with increasing temperature until the polarization completely disappeared at 200°C.

Parker and Schneider (1956), in their study of polarization effects in KCl, concluded that they were due to the blocking of vacancies at mosaic boundaries some 2000 Å apart. However, Okazaki and Suita (1951), investigating KCl + SrCl₂ in the same temperature range, attributed polarization to the blocking of vacancies at the surface of the crystal. As already noted (section 1.5) the polarization, observed by Dreyfus (1961) in doped crystals at low temperatures is due to the reorientation of complex pairs.

A fuller understanding of the polarization effects would be possible if the distribution of the field inside the crystal were known. Experiments to determine this are, however, quite difficult to devise and have not been performed apart from some early measurements by V. Seelen (1924).

1.6.2. Jaffé's polarization theory

Jaffé (1933) considered the movement of charged species under an applied electric field and formulated a theory based on the idea that at the boundaries of the medium (i.e. at the electrodes) certain ions can discharge whereas others cannot, thereby producing a space charge. This theory was later applied to semi-conductors (1952a), and to liquids by modifying the boundary conditions to allow for a finite rate of discharge (1952bc, 1953).

For the case of plane-parallel electrodes the differential equations for the actual concentrations of positive, p , and negative, n , charge carriers are:

$$\frac{\partial p}{\partial t} = -u_p \frac{\partial(pE)}{\partial x} + D_p \frac{\partial^2 p}{\partial x^2} + k_1(c_0^2 - pn)$$

1.6.2.1.

$$\frac{\partial n}{\partial t} = u_n \frac{\partial(nE)}{\partial x} + D_n \frac{\partial^2 n}{\partial x^2} + k_1(c_0^2 - pn)$$

$$\frac{\partial E}{\partial x} = \frac{4\pi e}{\epsilon} (p - n) .$$

The rate constants for formation and recombination of defects have been combined into the single constant k_1 (Friauf, 1954) by using the equilibrium condition and neglecting the small term $k_1 c_0^2 (c_0/N)$. c_0 is the concentration of either carrier (p or n) at equilibrium. The Einstein relationship $uD = e/kT$ is assumed valid for both species. For a static d.c. field the equations may be linearized by assuming (a) that the field is homogeneous, $E = E_0$, and (b) that the formation and recombination terms can be neglected. Equations 1.6.2.1 will then become linear and independent of each other and the current density of the positive charge carriers is given by (Jaffé, 1933)

$$1.6.2.2. \quad j_+ = e(u_p p E_0 - D_p \frac{\partial p}{\partial x}) .$$

One of the boundary conditions is always

$$\int_{-L}^L E dx = V$$

where the origin has been placed at the centre of the crystal of

length $2L$. Considering only the positive charge carriers, and dropping the subscript p , the other boundary conditions are

$$1.6.2.3. \quad j_+ = -e\mathfrak{L} [p(-L) - p^\infty] \quad , \text{ for } x = -L$$

$$1.6.2.4. \quad j_+ = e\mathfrak{L} [p(L) - p^\infty] \quad , \text{ for } x = +L$$

where p^∞ is the equilibrium value at the electrode in the absence of an applied field and $\mathfrak{L}$ is the rate constant for the discharge of positive carriers. It is convenient to introduce dimensionless parameters for the applied voltage V and for the discharge rate constant :

$$1.6.2.5. \quad v = (u/D)E_0 2L = (u/D)V = eV/kT$$

$$\rho = \mathfrak{L} 2L/D .$$

The solution to the linearized equations 1.6.2.1, subject to the above boundary conditions, is then (Jaffé and le May, 1953)

$$1.6.2.6. \quad p = p_\infty + \sum_{m=1}^{\infty} A_m \exp(-\lambda_m t) X_m$$

where p_∞ is the solution to the steady-state problem,

$$1.6.2.7. \quad X_m = \exp(vx/4L) \left[\cos(\mathfrak{v}_m x) + \left\{ (p + \frac{1}{2}v)/z_m \right\} \sin(\mathfrak{v}_m x) \right]$$

and

$$1.6.2.8. \quad z_m = \mathfrak{v}_m 2L \quad \text{are the roots of}$$

$$1.6.2.9. \quad \tan z = 2\rho z / \left[\left(\frac{1}{2}v \right)^2 + z^2 - \rho^2 \right] .$$

The values of λ_m are given by

$$1.6.2.10. \quad \lambda_m = (uE_0)^2 / 4D + D\mathfrak{v}_m^2 = (D/4L^2) \left[\left(\frac{1}{2}v \right)^2 + z_m^2 \right] .$$

Jaffé and le May have shown that (for the initial conditions $p = c_0$ right up to the electrodes) if

$$\exp\left(-\frac{1}{2}v\right) \ll 1$$

and $(\rho/v)^2 \ll 1$

then

$$1.6.2.11. \quad j_+ = \exp^{\frac{x}{2}} E_0 \left[\rho (\rho + v)^{-1} - 2 \left\{ c_0 - p^{\frac{x}{2}} v (\rho + v)^{-1} \right\} \times \sum_{m=1}^{\infty} \exp(-\lambda_m t) c_m \right]$$

where c_m is a complicated expression depending on v , ρ , z and m .

Clearly when $t = \infty$, the steady-state current is given by

$$1.6.2.12. \quad j_{+, \infty} = \exp^{\frac{x}{2}} E_0 \rho (\rho + v)^{-1}$$

in which expression $\rho = \infty$ corresponds to an open electrode and

$\rho = 0$ to a completely blocked one. The main feature of equn.1.6.2.11 is that the polarization current should be capable of being represented by a sum of exponential terms of the type $A \exp(-\alpha t)$.

Extensions to this theory of Jaffé have been made by Macdonald (1959) who has discussed the case of two blocking electrodes and one mobile charge carrier able to combine with the fixed, oppositely charged, carriers.

The Jaffé theory has been applied to the alkali halides by Parker and Schneider (1954, 1956) and also by Allnatt (1959). Parker and Schneider analysed their current-time curves for KCl in the temperature range 20-300°C by applying the equation

$$1.6.2.13 \quad I_p = A \exp(-\alpha t) + B \exp(-\beta t)$$

where the second exponential predominates for long times. They were thus able to compute values of α and β and found that:-

- (1) α and β both increase with V ;
- (2) σ_{op} and σ_{∞} depend only on temperature for a given crystal and can be represented by Arrhenius-type expressions

$$\sigma = \text{constant} \times \exp(-E/kT) ;$$

- (3) the results are independent of the electrode material.

The Jaffé theory was tested by comparing equn. 1.6.2.13 with the theoretical equation 1.6.2.11, as they concluded from their data that σ_{∞} represented a current flow by cation vacancies. Thus $\rho = 0$ for the positive charge carriers and ∞ for the negative charge carriers (cation vacancies). Then from equn. 1.6.2.11, if all terms above the second vanish,

$$1.6.2.14 \quad \frac{\alpha}{\beta} = \frac{(eV/\frac{1}{2}kT)^2 + 4\pi^2}{(eV/\frac{1}{2}kT)^2 + 1^2} \ll 4$$

Parker found $\alpha/\beta = 6.6$.

Secondly the voltage dependence of β was compared with the theory which predicts

$$1.6.2.15 \quad \beta = [(eV/\frac{1}{2}kT)^2 + \pi^2] D(2L)^{-2}.$$

However, β was proportional to V rather than V^2 . From equn. 1.6.2.15

Parker found

$$2L = 313,000 \text{ \AA} \text{ for NaCl; } 463,000 \text{ \AA} \text{ for KCl}$$

$$2L = 1,980 \text{ \AA} \text{ for NaCl; } 2,000 \text{ \AA} \text{ for KCl}$$

depending on whether he assumed surface conduction or the blocking of cation vacancies. They finally concluded that the blocking was

at mosaic boundaries, as the time to decay to a given fraction of I_0 showed a regular variation with thickness at constant applied potential, but not at constant field, which is inexplicable on the basis of surface conduction. Jaffé and le May (1953) have pointed out that $2L$ is to be regarded as the polarization layer thickness rather than the distance between the electrodes. Hence Parker's use of equn. 1.6.2.15 in estimating the distance between mosaic boundaries ($2000 \text{ \AA}$) is suspect. This, however, does not affect the other conclusions drawn.

Allnatt (1959) showed that there are two distinct regions of d.c. polarization, occurring above 350°C and below 170°C (the Parker polarization). The high temperature polarization had apparently not been observed before. This polarization, analysed in the manner of Parker (1954), was attributed to the blocking of cation vacancies at the electrodes.

1.6.3. A.c. polarization

When an a.c. field is applied to an ionic crystal the ions will move back and forth in phase with the field and thus contribute to the bulk conductivity. At the electrodes, however, if some of the ionic species are unable to discharge, they will constitute a space-charge which will produce a polarization capacity, the value of which should depend upon the frequency of the applied field. This a.c. space charge has been studied in ionic crystals by Friauf (1954) and Macdonald (1953). We shall consider the Friauf solution only, as Macdonald's solutions of the differential equations are essentially identical. Friauf linearized the differential equations 1.6.2.1 by

making two approximations. He assumed that (a) since the applied voltage may be expressed by

$$1.6.3.1. \quad V(t) = V_0 + V_1 \exp j\omega t ,$$

the dependent variables can be represented as

$$1.6.3.2. \quad p(x,t) = p_0(x) + p_1(x) \exp j\omega t ,$$

and that (b) the d.c. solution for zero applied field is

$$1.6.3.3. \quad p_0(x) = c_0 , \quad n_0(x) = c_0 \quad \text{and} \quad E_0(x) = 0 .$$

Using these assumptions, a set of linear, homogeneous equations is obtained from equn. 1.6.2.1,

$$j\omega p_1 = -u_p c_0 \frac{dE_1}{dx} + D_p \frac{d^2 p_1}{dx^2} - k_1 c_0 (p_1 + n_1)$$

$$1.6.3.4.$$

$$j\omega n_1 = u_n c_0 \frac{dE_1}{dx} + D_n \frac{d^2 n_1}{dx^2} - k_1 c_0 (p_1 + n_1)$$

$$\frac{dE_1}{dx} = \frac{4\pi e}{\epsilon} (p_1 - n_1) .$$

The general solutions (Friauf, 1954) are complex but these may be given in a compact form for various special cases. The values of the blocking parameters are conveniently given in parentheses

(ρ_p, ρ_n) . When both charge carriers are blocked at the electrodes, a condition referred to for brevity as $(0, 0)$, the boundary conditions are

$$1.6.3.5. \quad i_p(-L, t) = 0 \quad \text{and} \quad i_n(-L, t) = 0 .$$

With these boundary conditions (and also $\int_{-L}^L E dx = V$), it is found that

$$1.6.3.6. \quad C = c_0 / [1 + (\omega\tau)^2]$$

$$\text{and } -\Delta(1/R) = 1/\left[1 + (\omega\tau)^2\right] R_0$$

$$\text{where } R_0 = 2L/\left[e(u_p + u_n)c_0\right] = 2L/\sigma,$$

$$c_0 = \xi\alpha/4\pi\sqrt{2},$$

$$\tau = R_0 C_0 \quad \text{and} \quad \alpha^2 = 4\pi e^2 c_0 / \epsilon kT.$$

When the negative carriers are blocked, and positive carriers free,

i.e. $(\infty, 0)$, then

$$1.6.3.7. \quad -\Delta(1/R) = \omega C = \frac{eu_n c_0}{\sqrt{2}L^2} \left(\frac{D_p + D_n}{2D_p} \right)^{\frac{1}{2}} \left(\frac{D_n}{\omega} \right)^{\frac{1}{2}}$$

Analogous expressions for the impurity region, where only cation vacancies produced by impurity ions are present, have been derived by Ninomiya and Sonoike (1958). They are

$$-\Delta(1/R) = \omega C = \frac{\sigma^{3/2}}{2\sqrt{2}L^2} \left(\frac{kT}{Ne^2} \right)^{\frac{1}{2}} \times \frac{1}{\omega^{\frac{1}{2}}}.$$

The only detailed study of a.c. polarization in the alkali halides is that of Allnatt and Jacobs (1961) who applied the Friauf theory to their experimental results for KCl. From a comparison of the experimental dependence of capacity on frequency and temperature with the theoretical values, they concluded that positive carriers were blocked and the negative carriers free, i.e. $(0, \infty)$. The disturbing feature of their results was, however, that the observed capacity was 10^3 to 10^4 times greater than the calculated values. A similar discrepancy was observed in AgCl by Friauf (1954) who attributed it to the blocking of cation vacancies at internal boundaries. This explanation does not apply to the work of Allnatt and Jacobs (1961a), as they found that C varied as L^{-2} where, for blocking

at internal boundaries, C should depend on L^{-1} .

1.6.4. Metal-crystal interfaces

The charge distribution in a medium is governed by the boundary conditions and the conditions within the medium. In table 3 is presented a general classification of the typical possible charge distributions. A given physical situation corresponds to the combination of an entry in the left-hand column with one from the right-hand column. A thorough review of the literature based on this table has been made by Macdonald (1962). It is noteworthy that very little work has been done on the two-carrier, non-zero current, space charge problem with which we are concerned in connection with the steady state d.c. polarization currents.

A thorough search of the literature indicated that the current-voltage characteristics for the solid alkali halides had not been determined over a large voltage range. Császár (1958) investigated the current-voltage dependence in NaCl at 250°C using one plane and one point electrode and observed rectification effects (fig.1). It is apparent from fig.1 that the crystal containing F-centres shows more rectification than the pure NaCl. No theoretical explanation was offered. Ilschner (1958) using AgBr, AgCl and AgI was able to determine from the respective current-voltage curves the electronic contribution to the conductivity. According to Wagner (1956) the contributions of the conduction electrons and holes to the current density are:

$$i_- = (kT/2Le)\sigma_-^0 [1 - \exp(-eV/kT)]$$

1.6.4.1.

$$i_+ = (kT/2Le)\sigma_+^0 [\exp(eV/kT) - 1]$$

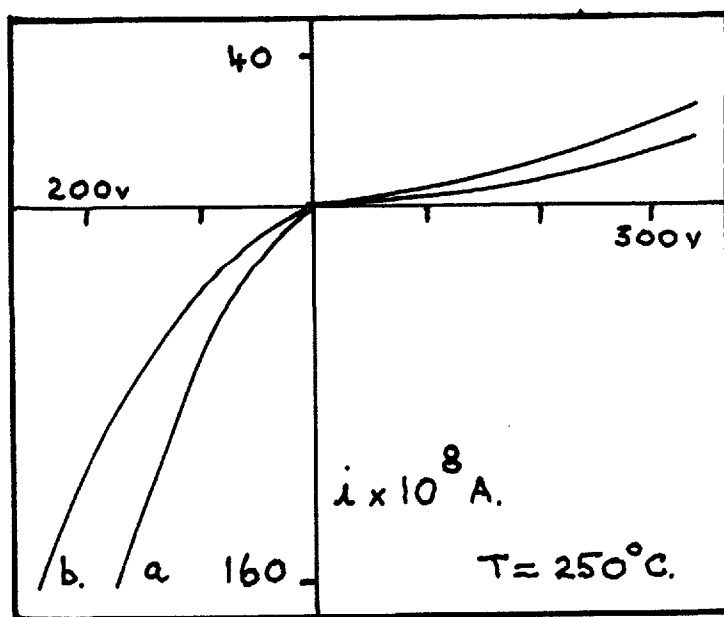
where σ_-^0 is the electronic conductivity of silver bromide in equilibrium with silver. It is apparent from equn. 1.6.4.1 that with increasing voltage V , the electronic part of the current tends to a saturation value $(kT/2Le)\sigma_-^0$ while the contribution from the holes increases exponentially with V . Ilschner's results for AgBr (see fig.2) show a saturation current from which he was able to find σ_-^0 . By this means it was established that AgBr exhibits electron conduction and AgI hole conduction. The results for AgCl were inconclusive.

The variations in potential energy at the interface between a metal and semiconductor are shown diagrammatically in fig.3a. At equilibrium the electrons in impurity centres nearest to the metal escape to the metal leaving a positive space charge in the semiconductor and producing an equal negative charge in the metal. This space charge depresses the conduction levels in the semiconductor as shown. There are now two possible ways in which an electron can cross the potential barrier: (a) electrons near the bottom of the conduction band may be able to penetrate the barrier by the quantum-mechanical tunnel effect, or (b), if the potential barrier is too wide for tunnelling to occur, the current flow must be due to thermally excited electrons which have enough energy to pass over the barrier.

Table 3Classification of charge distribution types

<u>Current conditions</u>	<u>Internal conditions</u>
I. Zero current	A. Mobile charges of one sign only.
II. Non-zero current; steady state	B. Mobile charges of one sign plus fixed recombination centres present.
(1) d.c.	(a) Zero recombination
(2) a.c.	(b) Non-zero recombination
III. Transients	C. Mobile charges of both signs present
1. Charging	1. Intrinsic
a) Zero final current	a) Zero recombination
b) Non-zero current	b) Non-zero recombination
2. Discharging	2. Extrinsic
a) One or both electrodes blocked	a) Zero recombination
b) Electrodes not or partly blocked	b) Non-zero recombination

FIG. 1



a. crystal containing F-centers.
b. pure NaCl.

FIG. 2

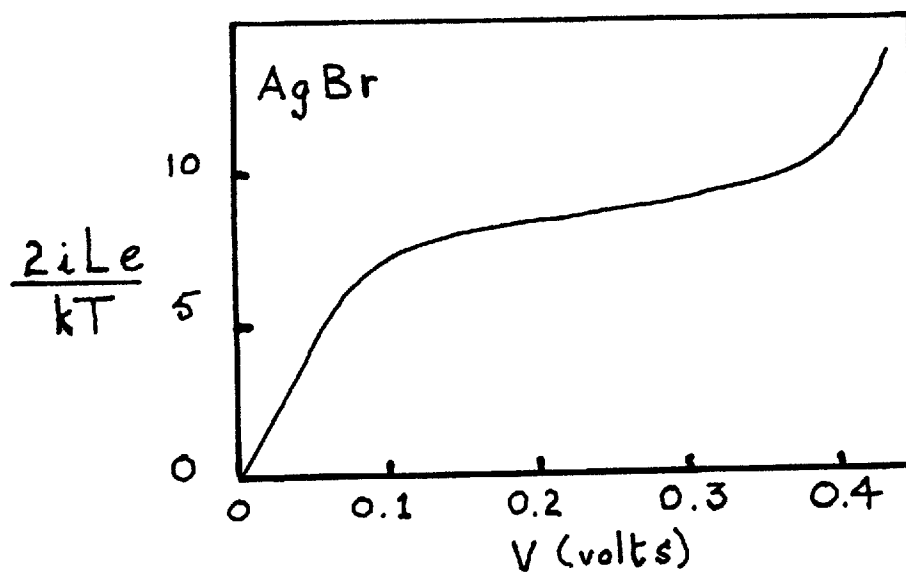
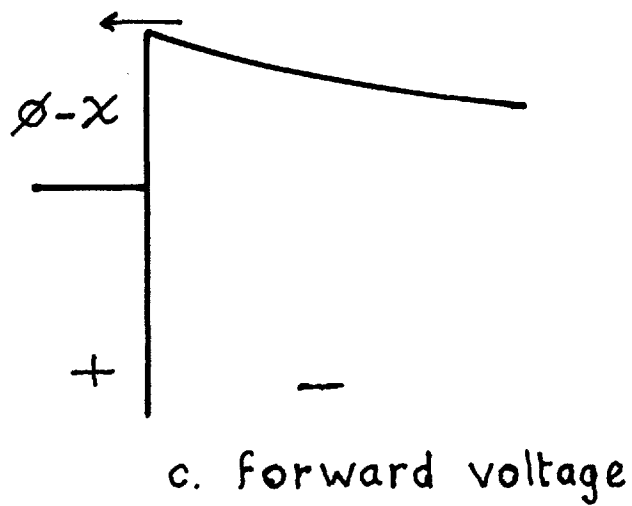
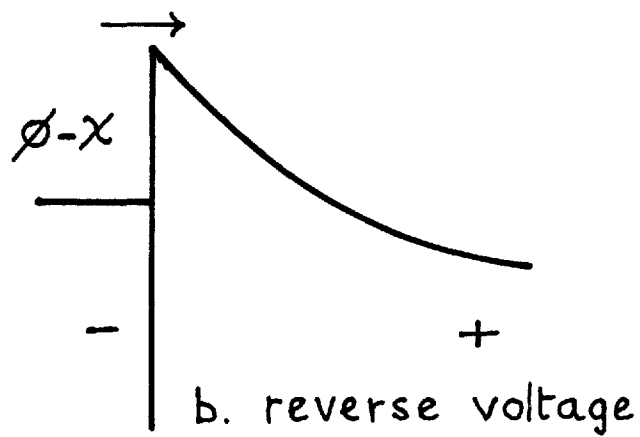
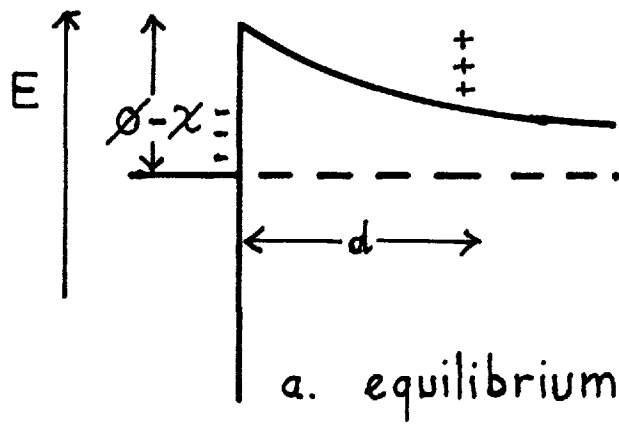


FIG. 3



It is found theoretically that, if tunnelling were to occur, rectification would be in the opposite direction to that observed experimentally. Thus the theory predicted a low resistance when the electrons flow from the metal to the semiconductor, for excess conductors, and in the opposite direction for a deficit conductor, e.g. Cu_2O . The direction of easy flow should, on this model, be from the metal to semiconductor as the number of electrons available is virtually ^{un}limited.

If tunnelling does not occur, in order to flow from the metal to the semiconductor, the electrons must receive thermal energy equivalent to $\phi - \chi$ (see fig.3). Therefore the layer of the semiconductor immediately in contact with the metal will contain a rather low density of electrons. Upon applying a field to pull electrons from the metal to the semiconductor (fig. 3b), there is no rapid rise in the current. But when a field is applied in the other direction (fig.3c), the magnitude of the potential barrier is decreased thus giving a rapid rise in the current density.

Mott and Gurney (1948) have discussed this model in detail. It leads to the prediction that, for fields such that

$$eV \gg kT,$$

the current density is

$$1.6.4.2. \quad j = e n_0 F [1 - \exp(eV/kT)]$$

where u is the electron mobility in the conduction band of the semiconductor and

$$1.6.4.3. \quad n_0 = 2 \left\{ \frac{2\pi mkT}{h^2} \right\}^{3/2} \exp \left\{ -(\phi - \chi)/kT \right\}$$

is the density of electrons in the conduction band at the metal-semiconductor interface (i.e. at $\chi = 0$). It must be emphasised that this treatment is only applicable to perfectly clean and plane surfaces. A comprehensive study of metal-semiconductor contacts of all types is given by Henisch (1957).

1.7. Thermoelectric power of ionic solids

When a temperature gradient is imposed across a crystal containing lattice defects there will be an increased defect concentration and increase in the jump frequency at the hot end, thus giving rise to a flow of defects. Since, in an ionic crystal there are at least two kinds of oppositely charged defects with different mobilities, the effect of the temperature gradient will be to cause a separation of charges. This separation is only incipient since the formation of a space charge immediately affects the flow of defects in such a way as to restore electroneutrality. The steady state is characterized by the existence of an electric field which is just sufficient to make the net electric current zero. The ratio of the difference in potential, ΔV , between the ends of a crystal to the temperature gradient, ΔT , is the homogeneous thermoelectric power, θ_{hom} , of that particular crystal at a specified mean temperature.

Although ionic crystals are favourable subjects for the study of thermal diffusion, very little work appears to have been done. Reinhold and his co-workers (1928, 1930, 1933a,b, 1937, 1938, 1939)

have measured the thermoelectric power and Soret effect of silver and cuprous salts, using electrodes with a cation common to the salt. The thermopower of lead and thallium salts was investigated by Thiele (1925) who also noted the existence of a potential difference across the crystal at room temperature in the absence of any temperature gradient. Modern work has been confined to KCl and the silver halides. Patrick and Lawson (1954) repeated the work of Reinhold and Blachny (1933) with the object of obtaining information about the heat of transport of the Ag^+ interstitials and vacancies in silver bromide in contact with silver electrodes. The measured power will be the sum of the homogeneous thermoelectric power and the heterogeneous power caused by the temperature-dependence of AgBr/Ag contact potential. They therefore subtracted from their total measured thermoelectric power the value of the heterogeneous power estimated by Reinhold and Blachny to be 140 microvolts/deg. This estimate was based on an earlier analysis by Wagner (1929), who assumed that

$$s_{M^+}^M = \int_0^T C_p(M) d \ln T$$

$$s_{M^+}^{MX} = \frac{1}{2} \int_0^T C_p(MX) d \ln T$$

Patrick and Lawson (1954) found that their results for pure AgBr could be analysed on the basis of the equation

$$1.7.1. \quad -e_{\text{hom}} = \frac{\phi(q_i + \frac{1}{2}h_F) - (q_v + \frac{1}{2}h_F)}{Te(\phi + 1)}$$

where ϕ is the mobility ratio, u_i/u_v , e the charge on the proton, h_F the heat of formation of a Frenkel defect pair and q_i , q_v are the heats of transport for interstitials and vacancies respectively. Using the Teltow (1949) values for ϕ and h_F , Patrick and Lawson found $q_i = 0.017$ eV for the heat of transport of interstitial Ag^+ ions and $q_v = -0.385$ eV for the cation vacancies. For AgBr doped with CdBr_2 the data was analysed using the equation

$$1.7.2. \quad -2Te \Theta_{\text{hom}} = (q_d + q_v)$$

where q_d is the heat of transport of the Cd^{2+} ion. In the doped crystals $T \Theta_{\text{hom}}$ was constant below 207°C , where the number of thermally produced defects is negligible.

Howard and Lidiard (1957a,b) considered theoretically the thermoelectric power of a crystal MX fitted with electrodes of metal M, as exemplified by AgBr and AgCl with Ag electrodes. They also considered the effect of doping with foreign ions, e.g. Cd^{2+} . In an isothermal system, the equation for the flux of defect r , with a virtual charge e_r , is

$$1.7.3. \quad J_r = D_r \left(-\frac{\partial n_r}{\partial x} + \frac{e_r n_r F}{kT} \right)$$

Irreversible thermodynamics shows that for an anisothermal system ($dT/dx \neq 0$) equn. 1.7.3 must be replaced by

$$1.7.4. \quad J_r = D_r \left(-\frac{\partial n_r}{\partial x} + \frac{e_r n_r F}{kT} - \frac{q_r n_r}{kT^2} \frac{\partial T}{\partial x} \right)$$

where q_r is the heat of transport of species r . For a system containing two types of intrinsic defects of charge $\pm e$, we have

$$1.7.5. \quad \begin{aligned} J_1 &= D_1 \left(-\frac{\partial n_1}{\partial x} - \frac{en_1 F}{kT} - \frac{q_1 n_1}{kT^2} \frac{\partial T}{\partial x} \right) \\ J_2 &= D_2 \left(-\frac{\partial n_2}{\partial x} + \frac{en_2 F}{kT} - \frac{q_2 n_2}{kT^2} \frac{\partial T}{\partial x} \right). \end{aligned}$$

Applying the electroneutrality and steady state conditions, $n_1 = n_2$; $e(J_2 - J_1) = 0$, the homogeneous thermoelectric power is found to be

$$1.7.6. \quad \Theta_{\text{hom}} = - \frac{\phi(q_2 + \frac{1}{2}h) - (q_1 + \frac{1}{2}h)}{Te(\phi + 1)}$$

which is essentially the same formula as that used by Patrick and Lawson for pure AgBr (see equn. 1.7.1).

In the impurity-controlled region (for doped AgBr) the flux of free cation vacancies is the same as that given by equn. 1.7.5 while that of impurity ions is equal to the flux of impurity-vacancy pairs,

$$1.7.7. \quad J_k = D_k \left(-\frac{\partial n_k}{\partial x} - \frac{q_k n_k}{kT^2} \frac{\partial T}{\partial x} \right)$$

where n_k is the number of complexes per unit volume and q_k the heat of transport of a complex. As n_k and n_1 are connected through the equation for the number of complexes,

$$1.4.3. \quad \frac{Nn_k}{n_1^2} = 12 \exp(\chi/kT),$$

a relation between $\partial n_k / \partial x$ and $\partial n_1 / \partial x$ can be established. The steady state conditions $J_k = 0$, $J_1 = 0$, together with this relation,

$$\frac{1}{n_k} \frac{\partial n_k}{\partial x} - \frac{\partial}{\partial x} \frac{n_1}{n_1} = - \frac{\chi}{kT^2} \frac{\partial T}{\partial x},$$

yield the expression

$$1.7.8 \quad \text{Te}\theta_{\text{hom}} = q_i - \frac{1}{2}q_k + \frac{1}{2}\chi.$$

$-\chi$ is the heat of association of the complex.

The difference between the thermoelectric power of pure AgBr and that of the doped crystals was also discussed by Howard and Lidiard. The heterogeneous contribution to the total power was first found by equating the electrochemical potentials of an M^+ ion in M and MX and differentiating with respect to T. On subtraction of the two expressions for the total power, they obtained

$$1.7.9. \quad \theta(y) - \theta(1) = \Delta\theta = \frac{(y^2 - 1)}{(y^2 + \phi)} \left(\frac{\phi Q}{eT(\phi + 1)} \right) - \frac{k}{e} \ln y$$

where y is the ratio of the concentration of vacancies in the doped crystal to that in the pure ($y = 1$) and $Q = q_i + q_v + h_r$. Additional data on the system AgBr + CdBr₂ have been obtained by Christy et al. (1959). Fitting their results to equn. 1.7.9, they evaluated $q_i + q_v$ as -0.57 eV at 175°C and -0.69 eV at 250°C. These numbers are not in agreement with those found by Patrick and Lawson. Christy (1961) also found, for the same system, that $Q = q_i + q_v + h_F$ is strongly temperature dependent; similar conclusions were drawn by Susuki et al. (1959). Objections may, however, be raised to this conclusion: (a) kinetic models do not suggest any physical basis for a temperature dependence of q_i and q_v ; (b) there may be uncertainties attached to the derivation of the formula for the heterogeneous part of the thermoelectric power.

Haga (1958, 1959) has also considered theoretically the system $\text{AgBr} + \text{CdBr}_2$ and has essentially reproduced the work of Howard and Lidiard. A comprehensive review of the work to date on AgBr has recently been prepared by Lawson (1962). Lawson has reconsidered the heterogeneous thermoelectric power by defining the electrode reactions as



1.7.10.



where Ag_M is a silver atom in the metal, Ag_S a normal lattice cation, and Ag_V^- a cation vacancy, the signs indicating the virtual charges. Let ΔG_i^0 and ΔG_V^0 be the free energy changes for the formation of one mole of Ag_i^+ and Ag_V^- , and $(\alpha + \Delta S_i^0)$ and $(\alpha - \Delta S_V^0)$ be the associated entropy changes. α may be considered as the difference in vibrational energy between a normal silver atom in the metal and in AgBr and may be estimated from the heat capacity difference of the two media. Lawson then shows that

$$1.7.11. \quad -\theta_{\text{het}} e = t_i (\partial \Delta G_i / \partial T) + t_V (\partial \Delta G_V / \partial T) + \Delta G_i (\partial t_i / \partial T) + \Delta G_V (\partial t_V / \partial T).$$

For pure AgBr it can be seen that θ_{het} is dependent on ΔG_i , ΔG_V and $\partial \phi / \partial T$ and is thus temperature dependent. For doped AgBr, assuming no association, eqn. 1.7.11 reduces to

$$1.7.12. \quad -e\theta_{\text{het}} = \alpha + \Delta S_V^0 - k \ln c$$

where c is the impurity concentration. Lawson believes that the temperature dependence of θ_{het} for pure but not doped AgBr, may account for the apparent temperature dependence of q_V found by

Christy. Again assuming no association, equn. 1.7.8 reduces to

$$1.7.13. \quad T\epsilon\theta_{\text{hom}} = q_v$$

so that (as θ_{het} is temperature independent (equn. 1.7.12) q_v may be found from the slope of θ against T . Using the data of Patrick and Lawson (1954), Lawson finds $q_v = -0.35$ eV by this procedure. As he remarks, however, it is rather mysterious that the thermopower data should apparently be fitted so well by assuming that there is no association between Cd^{2+} and cation vacancies.

In contrast to systems with a cation common to the electrode and the crystal, systems with no common ion show somewhat poorer reproducibility. Murin and Nikitinskaya (1955) found a detectable thermopower in NaCl above 500°C, but 'reproducible' results could only be obtained after prolonged heating. Despite the large experimental scatter, they evaluated θ as -0.9 mv/deg at 540° and 670°C for NaCl. For KCl, θ was found to be -1.2 mv/deg at 600°C, the experimental scatter being somewhat less. The most intriguing feature of their experiments was the observation of a potential difference in the absence of a temperature gradient, similar to effects observed by Thiele (1925). Curien and Mihailovic (1959), however, make no mention of this difficulty in their measurements of the thermoelectric power of lithium fluoride with silver electrodes in the temperature range 365 to 605°C.

A rigorous treatment of the homogeneous thermoelectric power of a crystal MX in contact with electrode material M' has been developed by Allnatt and Jacobs (1961b), in which the vacancies

are treated as separate thermodynamic species of zero charge and mass. To develop the theory expressions for the chemical potentials of the ions and defects are required and these were obtained as described in section 1.2.

As there is no common ion in the system under consideration, the only species common to both phases is the electron. It was further assumed that there are a number of electron traps present in the alkali halide and for simplicity, these were identified as F-centres arising from non-stoichiometry. Using a treatment based on irreversible thermodynamics, it was found that, for Schottky disorder,

$$1.7.14. \quad \Theta_{\text{hom}} = \left[(-Q_{M^+} + \frac{1}{2}h_s)t_+ - (-Q_{X^-} + \frac{1}{2}h_s)t_- \right] / eT$$

where Q_{M^+} , Q_{X^-} are the heats of transport of the cation and anion respectively, t_+ , t_- the respective transport numbers and h_s is the heat of formation of a Schottky defect. The heterogeneous thermopower was determined by equating the electrochemical potential of the electrons in the salt to those in the metal. Assuming the source of the electrons in the conduction band of the salt to be F-centres, Θ_{het} was found to be given by

$$1.7.15. \quad -e\Theta_{\text{het}} = \left[s_e^{M'} + (H_F - \frac{1}{2}h_s)/T + k \ln n_B \right]$$

Where n_B is the number of electrons per unit volume in the conduction band, $s_e^{M'}$ the (negligible) entropy of the electrons in the metal M' and H_F is the enthalpy change on taking an electron from an F-centre to the conduction band of the salt. Combining eqn. 1.7.14 and 1.7.15 gives the total power for a pure crystal, $\Theta(1)$:

$$1.7.16. \quad Te\theta(1) = \left[t_+(h_s - Q_{M+}) + t_-Q_{X-} - H_F - kT \ln n_B(1) \right],$$

In the doped crystal, if the electrons still distribute themselves between F-centres and the conduction band, equn. 1.7.15 remains unaltered and the total power is given by

$$1.7.17. \quad Te\theta(y) = \left[\frac{-y^2 Q_{M+} - \phi(-Q_{X-} + h_s)}{y^2 + 1} \right] - H_F + h_s - kT \ln n_B(y).$$

The difference between the thermoelectric power of a pure and a doped crystal is thus

$$1.7.18. \quad \Delta\theta = \theta(y) - \theta(1) = \left\{ \frac{y^2 - 1}{y^2 + 1} \right\} \frac{\phi(-Q_{M+} - Q_{X-} + h_s)}{(\phi + 1)eT} - (k/e) \ln \left\{ \frac{n_B(y)}{n_B(1)} \right\}.$$

Allnatt and Jacobs (1962a), have applied these equations to their experimental results for pure KCl and KCl doped with 107×10^{-5} mole ratio of $SrCl_2$, with platinum electrodes in the temperature range 560 to 695°C. Using temperature gradients up to 15 deg/cm a thermoelectric power of -1.85 ± 0.05 mv/deg was obtained. Although the graphs of potential difference against temperature gradient were good straight lines, there was some scatter when the values for the thermoelectric power were plotted against the temperature. A potential difference for zero temperature gradient was again observed and it was suggested that this potential difference may be due to plastic deformation of the crystal arising from the mild pressure applied to the electrodes. Fischbach and Nowick (1958) had

observed that plastic deformation of NaCl crystals produced a charge flow of 10^{-12} coulomb for 1 Kg cm^{-2} stress gradient. The heat of transport of the cation was found to be 0.99 eV and that of the anion 2.1 eV in the temperature range studied, with no temperature dependence. Calculations showed $n_B(y)$ to be of the order of 10^4 electrons/cm³ and $n_B(1)$ of the order of 10^6 electrons/cm³. Support for the theory was also shown by the correct temperature dependence of $n_B(y)$ and $n_B(1)$.

1.8. Heats of transport

An estimate of the value of heat of transport of an ion in a solid can be obtained by considering the processes by which an ion receives sufficient energy to move to a new equilibrium position. Wirtz (1943) considered the movement of an interstitial ion by the direct mechanism, and argued that each jump of the ion involved the co-operative movement of a number of ions. Firstly a certain amount of free energy Δg_1 must be given to the interstitial ion so as to move it in the direction of its final position. Secondly, energy Δg_2 must be given to the lattice ions situated between the initial and final positions to separate them sufficiently to allow the interstitial ion through. Finally, energy Δg_3 is required to produce a hole to accommodate the moving interstitial. The sum of these energies is the total activation energy Δg

$$1.8.1. \quad \Delta g = \Delta g_1 + \Delta g_2 + \Delta g_3 .$$

The important point behind Wirtz's kinetic argument is that the three energy terms are supplied at different temperatures. Thus,

if we consider a one-dimensional flow, and divide the lattice up perpendicular to the diffusion direction, we see that whereas Δg_1 may be supplied at temperature T , Δg_2 will be supplied at $T + \frac{1}{2}\delta T$ and Δg_3 at $T + \delta T$, where the ratio of δT to the jump distance is equal to the thermal gradient. Writing down the expression for the net flow of interstitials across the dividing plane by using an expanded form of equn. 1.3.1.,

$$1.8.2. \quad w = v \exp(-\Delta g_1/kT) \times \exp \left\{ -\Delta g_2/k(T + \frac{1}{2}\delta T) \right\} \times \exp -\Delta g_3/k(T + \delta T),$$

equn 1.7.5 is obtained where

$$1.8.3. \quad Q_i = \Delta h_1 - \Delta h_3 \quad (\text{interstitial mechanism}).$$

Δh_1 and Δh_3 are the enthalpy terms belonging to the free energies Δg_1 and Δg_3 . For vacancy motion, if Δg_1 is the energy supplied to the ion which jumps into the vacancy, then

$$1.8.4. \quad Q_{M^+} = \Delta h_1 - \Delta h_3 \quad (\text{vacancy mechanism}).$$

(Note that Q_{M^+} , which refers to the ion, has the opposite sign to Howard and Lidiard's q_1 or q_v). All the heats Δh_1 , Δh_2 and Δh_3 will be positive and thus the magnitudes of Q_i and Q_{M^+} must be less than the corresponding heats of activation, Δh . However, Wirtz's result is not substantiated by experimental evidence. The error seems to lie in a wrong interpretation of the heat of transport, which is defined as the energy which must be donated to the region of the origin of the flux of atoms in order to maintain it in an isothermal state. Le Claire (1954) assumed that the jump frequency and vacancy density depend only upon the local state of the lattice, particularly the temperature. By calculation of the

net flux of vacancies as the difference between the fluxes with and against the temperature gradient, he concluded that the heat of transport is just the activation energy for motion.

Allnatt and Rice (1960), by using a random-walk model, concluded that the heat of transport is exactly equal to the activation energy for motion and is always positive. The random-walk model implies that an atom forgets all about its origin before making another jump and also that the excess energy required to produce a jump is dissipated at the final site occupied by the atom. An alternative explanation of the heat of transport by Haga (1960) takes into account the variation of the vibrational frequency of the lattice ions due to the presence of defects.

1.9. Conclusion

From the foregoing summary of the literature it is apparent that more work is necessary on doped crystals to try and evaluate the relative importance of nearest neighbour and next-nearest neighbour interactions in the phenomenon of association. This was therefore made one of the objectives of the present research.

Other objectives were:-

- (a) to present a more detailed picture of the a.c. and d.c. polarization phenomena in the light of the Friauf and Jaffé theories;
- (b) to extend the thermoelectric power measurements of Allnatt (1962,a) over a wide temperature range; and
- (c) to investigate the current-voltage relationship with the object of gaining an insight into the electrode reactions in solid alkali halides.

2. Experimental

2.1. Preparation of single crystals

The two methods used were those of Kyropoulos (1926) and Stockbarger (1936).

2.1.1. The furnace

The same furnace was used for both techniques. The furnace core was a silica tube, 2.8 inches in outside diameter surrounded by firebricks (Morgan type F.F.). The windings were arranged in three sections. The two end sections, 3 inches long, were wound with 21 gauge 'Kanthal' A.1. wire at 10 turns per inch. The centre section of 10 inches consisted of 80 turns of the same wire. The three sections were connected in series and the current through each was controlled by a parallel resistor. The total voltage supplied to the windings was controlled by a 'Variac'. Temperature control was effected by an electronic controller of the type described by Roberts (1951), using a platinum resistance thermometer made from 1.5 metres of 0.01 cm diameter platinum wire wound into a single helix and inserted in a twin-bore pure alumina tube (0.6 cm external diameter, twin 2 mm bore) such that the helices were in opposite sense. The temperature was measured by means of a chromel-alumel thermocouple.

2.1.2. The Kyropoulos method

The Kyropoulos apparatus was similar to that described by Allnatt (1959). The water cooled chuck was made from a nickel tube $13\frac{1}{4}$ inches long and $\frac{1}{2}$ inch external diameter. A groove $\frac{3}{16}$ inch wide and $\frac{3}{16}$ inch deep in the bottom accommodated the seed crystal. A

piece of asbestos paper was placed between the crystal and chuck to prevent cracking due to thermal stresses. The crystal was held in position by means of a small screw. The chuck was guided by a small nickel guide held firmly about 2 inches above the furnace and entered the furnace through a block of syndano sheet.

The salt (50 g) was placed in a platinum crucible resting on firebrick slightly above the centre of the furnace. Before use the platinum crucible was cleaned by (1 + 1) hydrochloric acid, fused sodium carbonate, (1 + 1) hydrochloric acid, 2N hydrochloric acid and distilled water. The salt was melted over a period of 4 hours and allowed to come to thermal equilibrium at 820°C. The chuck was lowered into position with 80 ml of water flowing through it per minute. The seed was then lowered the final cm until it just touched the meniscus of the melt. Any crystal that formed immediately was melted off by raising the temperature. The temperature was then lowered slowly until a single crystal grew from the seed to about 3 mm from the side of the crucible, when the temperature was held steady and the new crystal pulled from the melt at a rate of 2 mm per hour. When about $\frac{3}{4}$ of the melt had crystallized the temperature was lowered sufficiently to freeze the remaining melt, after which the crystal was shaken back into the crucible. The temperature was lowered to 600°C and the crystal left to anneal for 12 hours. It was then cooled to room temperature over a period of 12 hours.

2.1.3. The Stockbarger method

The salt used was again of Analar quality. A quartz container 3.0 cm diameter and 8.0 cm long with a 2 cm long projection of 2 mm bore at the base, was just filled with 40 g of the salt. This was treated with a stream of hydrogen chloride + nitrogen for an hour at 100°, 200°, 300° and 500°C and evacuated to a pressure of 10^{-6} mm of Hg after each treatment. The container was then sealed off under vacuum.

The furnace was the same one as that used for the Kyropoulos method, with current passing through the middle and top sections only. The middle section was shunted by a 300 ohms resistance. With this arrangement a temperature gradient of 45° per inch was obtained.

The container was then supported in a silica tube and placed in the furnace such that the bottom of the basal projection was just above the centre of the furnace. The silica tube was attached to the drive from a gear box situated directly below the furnace. The temperature of the furnace was raised until it was steady at 770°C at the centre of the furnace. After about two hours the container was lowered through the furnace at a rate of 2 mm per hour until the top of the crystal was an inch below the centre of the furnace. The freshly grown crystal was then annealed for 12 hours at 700°C with the current flowing through all sections of the furnace. All the doped crystals were grown by this technique.

2.1.4. Additively coloured crystals

It was found by heating potassium chloride crystals obtained from different sources in a vapour of potassium that the commercially available Harshaw crystals colour more readily than those grown by either the Stockbarger or Kyropoulos techniques. All the crystals coloured were therefore those obtained from the Harshaw Chemical Company. Additive coloration was effected by heating the crystal in the presence of potassium vapour using a new technique described by van Doorn (1961).

- The apparatus, shown in fig.4, consisted of a nickel tube (length 25 cm, diameter 2 cm) open at one end. The open end was closed by a lid ground to fit exactly into the top of the tube. It was found that a little Apiezon grease was all that was necessary to make the seal gas tight. The nickel gauze container for the crystal was attached to the lid by nickel wire. The apparatus could be evacuated via a nickel tube attached to the lid. The crystal was placed in the container, a small piece of potassium added, and then the tube evacuated. The required pressure of dry nitrogen was then admitted, and the tube placed in a furnace, the temperature of which was steady at 700°C. After allowing 3 min for warming up, heating was continued for a further 10 min to allow equilibrium between the crystal and the potassium vapour to be established. Nitrogen was then admitted up to a pressure of one atmosphere, the tube opened and the crystal quenched in carbon tetrachloride.

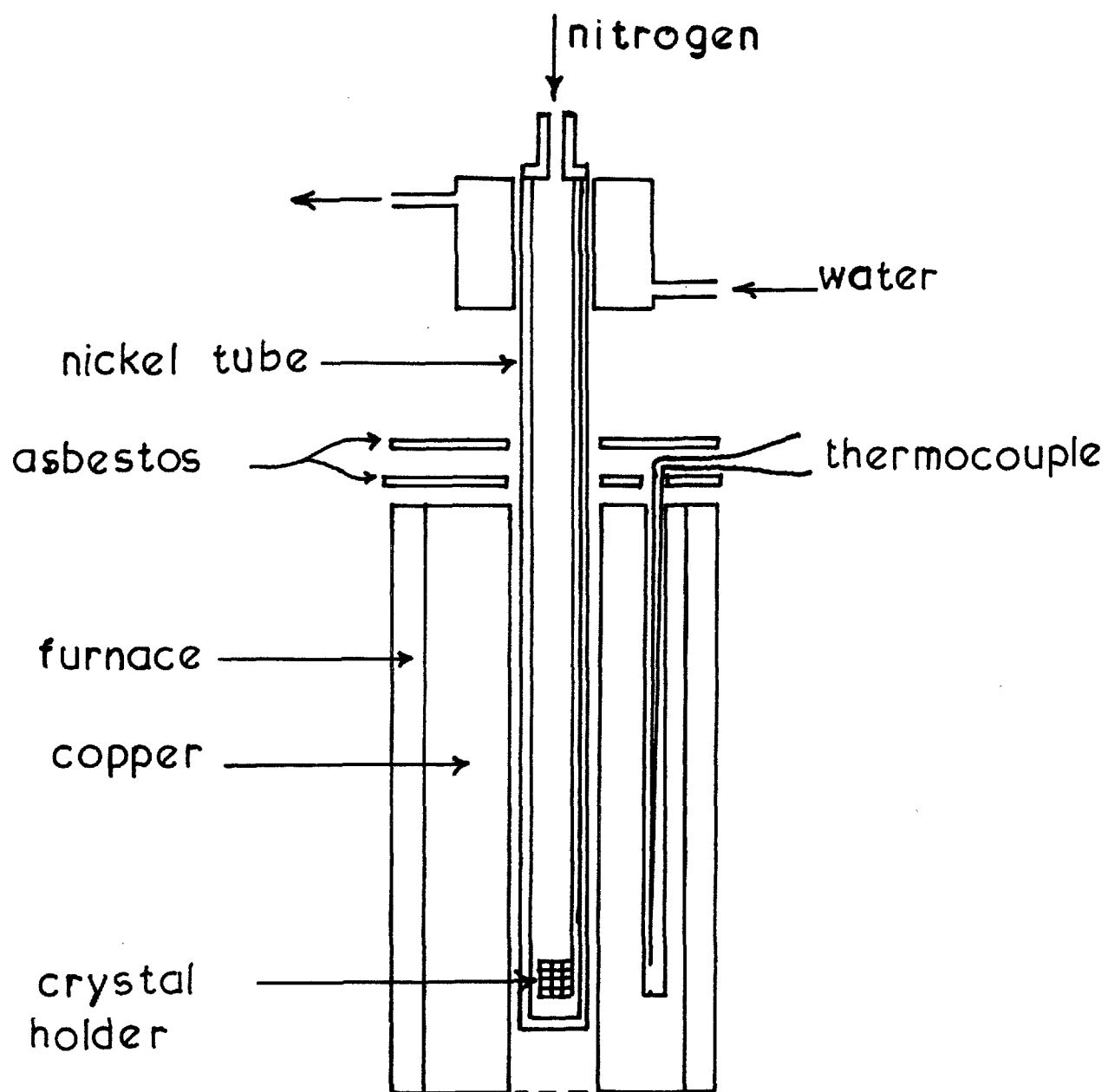
The principle of this apparatus is that of a circulation of vapour similar to that in a vapour diffusion pump. When the potassium metal is heated in the tube the vapour rises and finally condenses on the cool upper part of the tube. The liquid metal then runs down the walls until it vaporizes again so that a steady circulation of metal will be established. This circulation zone separates pure metal vapour in the lower part from nitrogen in the upper part. Due to the existing pressure equilibrium, the pressures of nitrogen and metal must be equal, thus giving a method of regulating the latter independently of the temperature. This apparatus has two advantages. First the pressure of the vapour is regulated directly and not by the temperature of the liquid metal as in other methods. Second, the lid is kept cool by the water cooling jacket, enabling the tube to be opened quickly and hence a rapid quenching of the crystal to be performed.

2.1.5. Preparation of specimens

Specimens were cleaved by means of a razor blade into regular parallelopipeds. The specimens used were 2 to 5 mm thick with faces 10 mm x 10 mm. The dimensions were measured with a micrometer screw gauge both before and after each experiment.

A few crystals had silver films deposited onto two faces by vacuum evaporating for one hour from a piece of silver wire attached to a chromel filament. A mica mask protected all but the upper face of the crystal from the vapour during deposition. The crystal lay (about 2 cm below the filament) at the bottom of the tube.

FIG. 4



2.2. Analysis of crystals

Conductance measurements were made on crystals containing 10×10^{-5} to 100×10^{-5} mole ratio of strontium chloride. Due to the concentration gradient in the doped crystals, it was essential to analyse the specimen rather than adjacent cleaves. Similarly the actual specimen used in the additively coloured crystals was analysed.

2.2.1. X-ray fluorescence analysis of the doped crystals

Crystal cleaves used in the conductivity measurements were ground to a powder in an agate mortar and analysed using a Phillips X-ray Diffractometer, type PW1051, using a sodium chloride analysing crystal. Standards of known strontium content, which had been prepared by Allnatt (1959), were used to establish the calibration graph shown in fig.5. The powdered sample was spread on the Mylar window, 2 x 2 cm square, to a depth of about 2 mm. The fluorescence of the strontium K_{α} line ($2\theta = 15.09^{\circ}$) was recorded for ten successive one-minute counts. The excitation was produced by a tungsten target tube run at 40 kV and 25 mA. A background count was recorded both before and after completion of the standardisation.

Similar measurements were made on the powdered crystals, and again the background counts established. After each 10 minute counting period a new Mylar window was fitted to reduce the possibility of contaminating successive crystals.

The mean of each set of ten counts for the standards were corrected for background counts and a calibration curve of mean

CALIBRATION OF X-RAY FLUORESCENCE

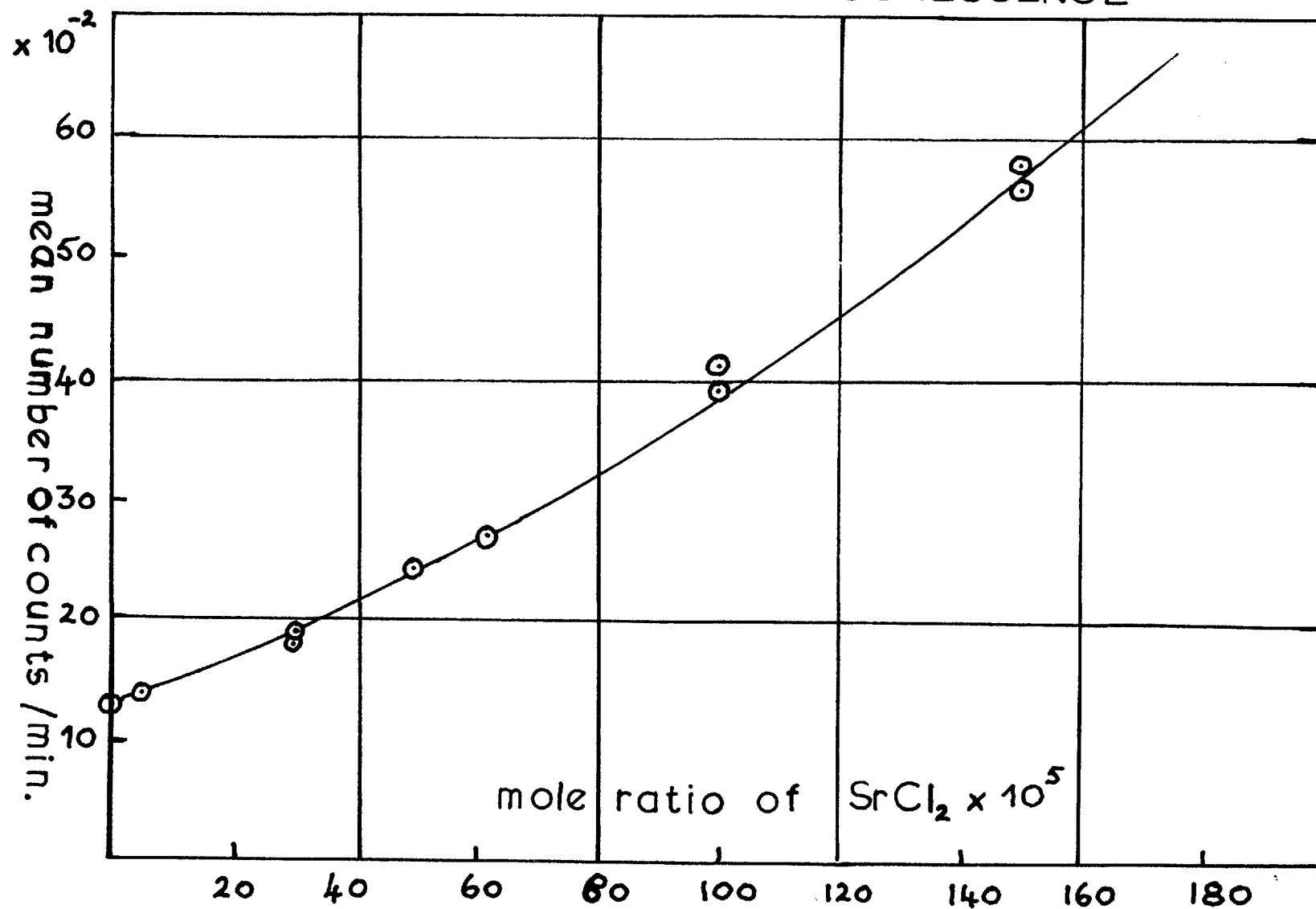


FIG. 5

counts per minute against concentration of strontium drawn. The strontium content of the unknowns was determined from this graph. Table 4 records the mean counts for the doped crystals used in conductivity measurements. The reproducibility of the mean counts was $\pm 3\%$ over the whole concentration range.

Table 4. Determination of Sr^{++} concentration in $\text{KCl} + \text{SrCl}_2$ mixed crystals

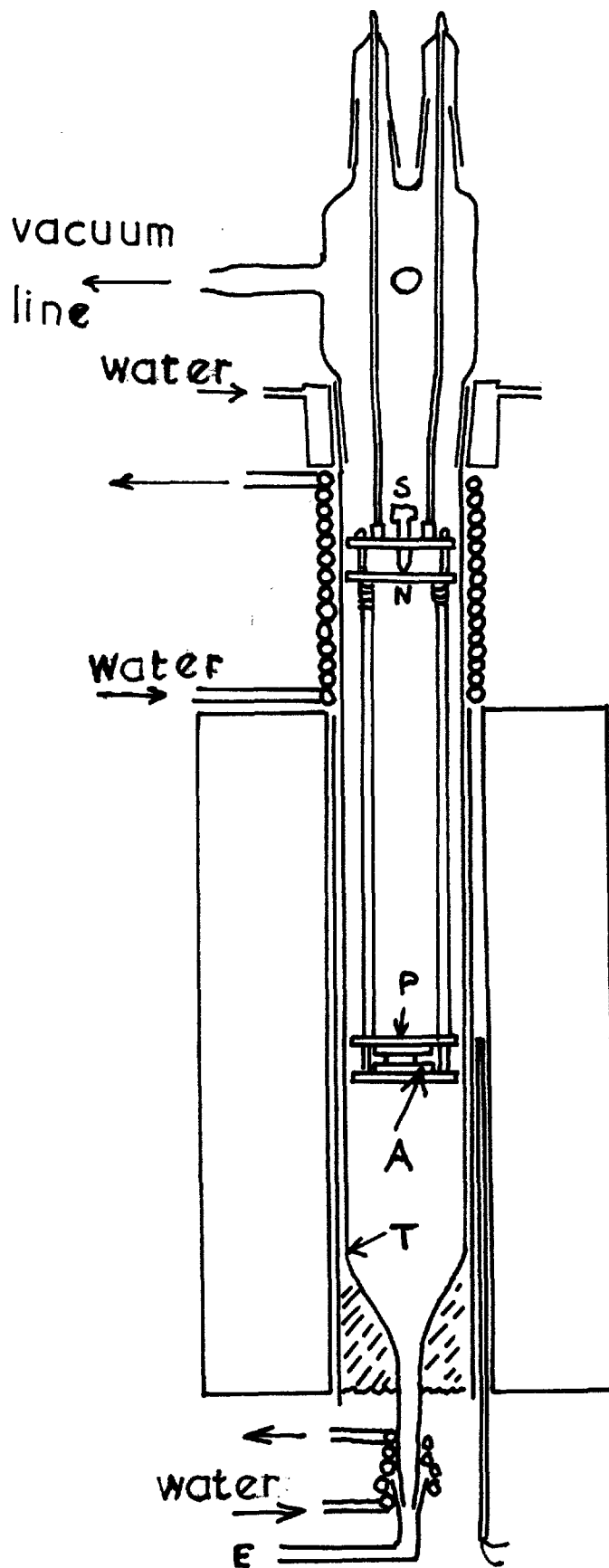
Crystal	Mean counts/min	Mole ratio of SrCl_2 in the crystal, $\times 10^{-5}$	Mole ratio in melt, $\times 10^{-5}$
Pure	1571	0	0
X1	1759	14.4	20
X2	2148	31.0	50
X3	2403	41.8	50
X4	4008	94.0	100
X5	4608	119.8	200

2.3. The conductivity cell

The crystal under investigation was mounted between circular (2 cm diam.) platinum electrodes with a platinum-13% platinum-rhodium thermocouple spot-welded to the centre of each electrode and insulated from it by a mica disc. Each electrode pressed against a recrystallized alumina disc with a radial groove to accommodate the thermocouple. The specific conductance of these discs is $10^{13} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 300°C and $10^9\text{--}10^{10} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 650°C .

The supporting framework for the crystal and electrodes is shown in fig.6. Only the crystal, alumina discs A, quartz

FIG. 6



plates P and quartz tubing T were in the hot part of the furnace. The nickel head N never attained a temperature in excess of 500°C. The screw S used to clamp the crystal electrodes and alumina insulators was adjusted to finger tightness. The crystal holder was suspended by two nickel rods in a quartz tube which was fitted to the cell head by a B55 joint. Picien was used on this joint and proved very satisfactory as the tube above the furnace was cooled by a continuous flow of cold water. The thermocouple wires entered the cell through soda glass seals. Shielded coaxial leads were soldered to the platinum wires just above the seals in order to make the resistance measurements. When resistance measurements were made the two spare thermocouple leads could be lifted out of mercury cups close to the cell head and were allowed to hang freely in air thus giving maximum possible insulation.

The cell could be evacuated to 10^{-6} mm Hg on the vacuum line which consisted essentially of a vapour diffusion pump and a rotary oil pump. Nitrogen, purified by passing through a drying column of silica gel, over freshly reduced hot copper turnings to remove any oxygen, and then through two traps cooled in a methanol-cardice mixture to remove traces of water vapour, was passed in at D and out through a bubbler containing dinonyl phthalate at E (see fig.6). It has been reported by Barr et al. (1962) that sodium chloride crystals in contact with a nitrogen atmosphere at these high temperatures (700°C) undergo no chemical or mechanical change. Thus we are confident that the potassium chloride crystal was

similarly unaffected. A pressure of inert gas in the conductance cell was necessary to prevent evaporation of the crystal.

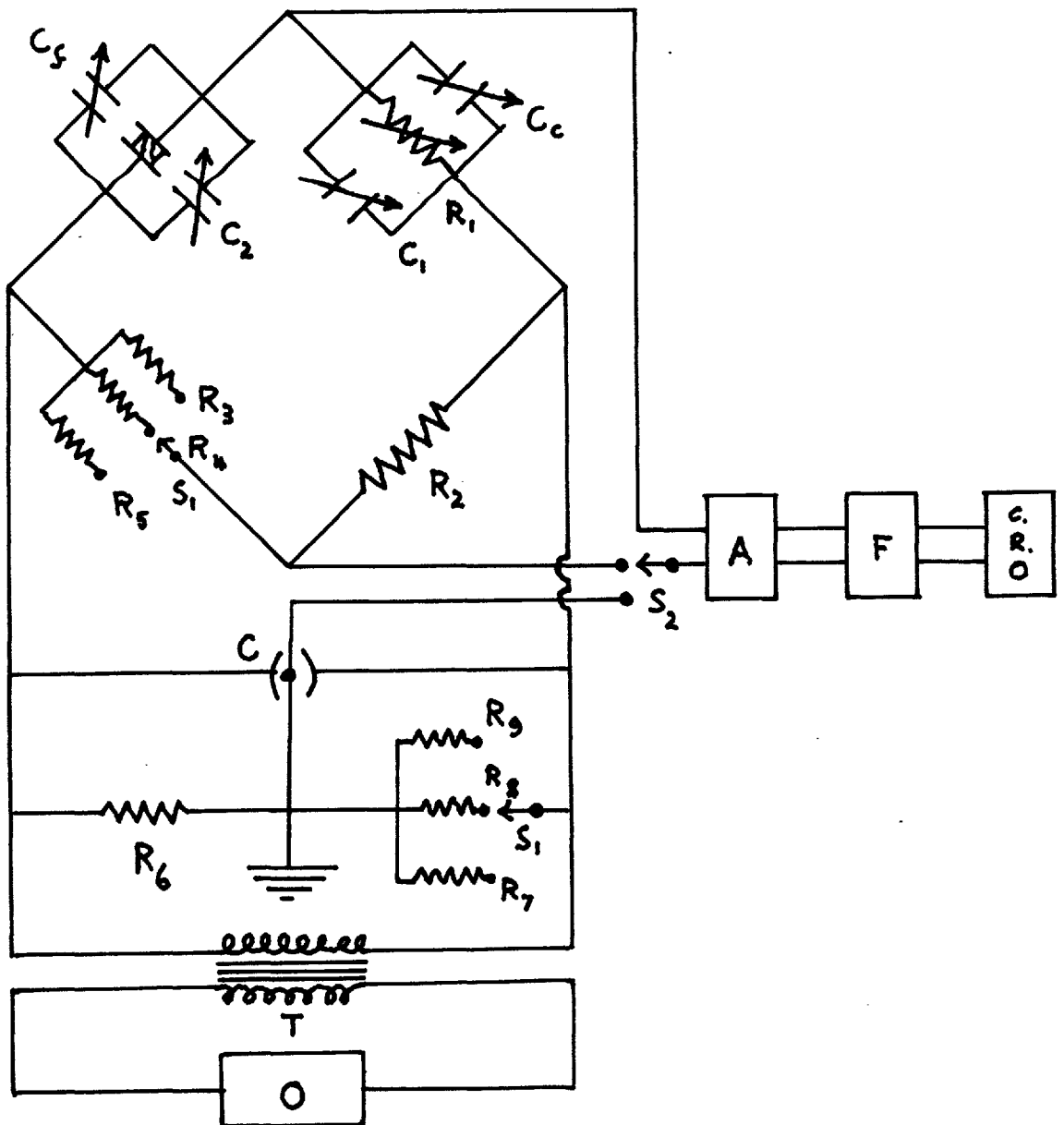
The furnace was wound in three sections, each of 10 cm long, on a silica tube 70 mm diameter. The resistance of the end sections was 18 ohms and that of the centre section, 14 ohms, all three being wound with 4 ohms per yd nichrome V wire. The three sections were connected in series and the current through each section was controlled by parallel resistors. The total current was controlled by a 'Variac' and the temperature regulated by the same type of controller as that described in section 2.1.

The outside of the furnace was covered with aluminium foil and the foil, the cooling coils and the nickel shield separating the furnace and cell were all earthed to eliminate 50 cycle 'pick-up' by the a.c. bridge.

2.4. The a.c. bridge

The bridge was used to measure resistances from 10^3 to 10^7 ohms with an accuracy of 0.1% and frequency dependent capacities over a range of 10^3 to 10^4 pF. The bridge used was a simple Wheatstone bridge incorporating a Wagner-earth to remove the effect of stray capacitances. The circuit and components are shown in fig.7. The input transformer T was used to minimise any asymmetry from the oscillator. The ratio arm resistors and Wagner-earth resistors were placed on perspex sheet in an earthed metal box. The switches S_1 and S_2 were ceramic base Yaxley switches mounted on the face of the box. The air condensers C_f and C_c are manufactured so that the

FIG. 7



Component values - fig.7

All resistances were precision Sullivan non-inductively wound.

R₁ Sullivan decade box (111, 111 ohms)

R₂ 1 K R₃ 100 K

R₄ 10 K R₅ 1 K

R₆ Pye decade box (11, 111 ohms)

R₇ 10 K R₈ 1 K

R₉ 100 ohms

S₁, S₂ Yaxley switches (ceramic base)

O Advance oscillator (J1)

A Amplifier

F Filter (parallel-T)

T Sullivan balanced and screened transformer

C_f Sullivan air condenser (C 859/S), 33 pF

C_c Sullivan air condenser (C 855/S), 300 pF

C₁ Sullivan decade condenser (C 2099) 1 F

C₂ Sullivan air condenser (C 500 D.) 1300 pF

casing is at the potential of the low potential (fixed vane) terminal. These terminals were connected to the ratio arms. The condensers stood on perspex and were mounted in a $\frac{1}{2}$ " thick perspex panel. Two additional capacity boxes C_1 and C_2 could be placed in parallel with either arm of the bridge. All connections were made with coaxial cable. The output of the bridge was connected to a C.R.O. via a parallel-T filter and a three-stage transistor amplifier.

In use the bridge was balanced by R_1 and C_1 and the Wagner-earth was then balanced against the arms containing the unknown. This procedure was repeated until switching to the Wagner-earth gave no difference in the output displayed on the oscilloscope.

The bridge was checked using standard resistors and capacitors. For resistances of 10^3 , 10^4 and 10^5 ohms the resistance was correct to 0.05% from 0.25 to 10 kc on the 1:1 and 1:10 ratios. From 10 to 50 kc, the accuracy was to 0.1% for 10^3 , 10^4 and 10^5 ohms on the 1:1 and 1:10 ratios. For higher resistances, on the 10:1 ratio the accuracy was 0.1% below 1 kc, but between 1 and 50 kc on the 100:1 ratio the accuracy decreased. For example, when a resistance of 10^7 ohms was measured at 10 kc on the 100:1 ratio, the value found was 10% low. In practice, however, the 100:1 ratio was never required other than for measurements at 1 kc. The voltages used for all resistance measurements were as follows: 100 mv below 10^4 ohms, 800 mv for resistances up to 10^6 ohms and 1200 mv for higher resistances.

As the length of unshielded wire in the cell was considerable, the measured capacity will not be the true crystal capacity. Moreover the bridge itself was not designed to yield absolute capacity values as only the incremental capacity of the condensers is known from the calibration supplied by the makers. However, it was found that the polarization capacity at 50 kc was negligible compared with that at lower frequencies (see fig.17), hence this value was always subtracted from the capacity measured at lower frequencies to give the polarization capacity.

Using standard capacitors, the measured capacity (at constant resistance) was found to be constant to 0.2 pF in the range 0.25 to 50 kc on the 1:1 ratio for the full range of C_c , except for resistances below 5×10^3 ohms for which the deviation is about 1 pF. On the 10:1 range, for resistances greater than 5×10^4 ohms the measured capacity is independent of frequency to 0.05 pF from 1 to 50 kc and to 0.1 pF from 0.25 to 1 kc. Subtraction of the 50 kc value is thus justified if the capacity to be analysed is greater than 10 pF.

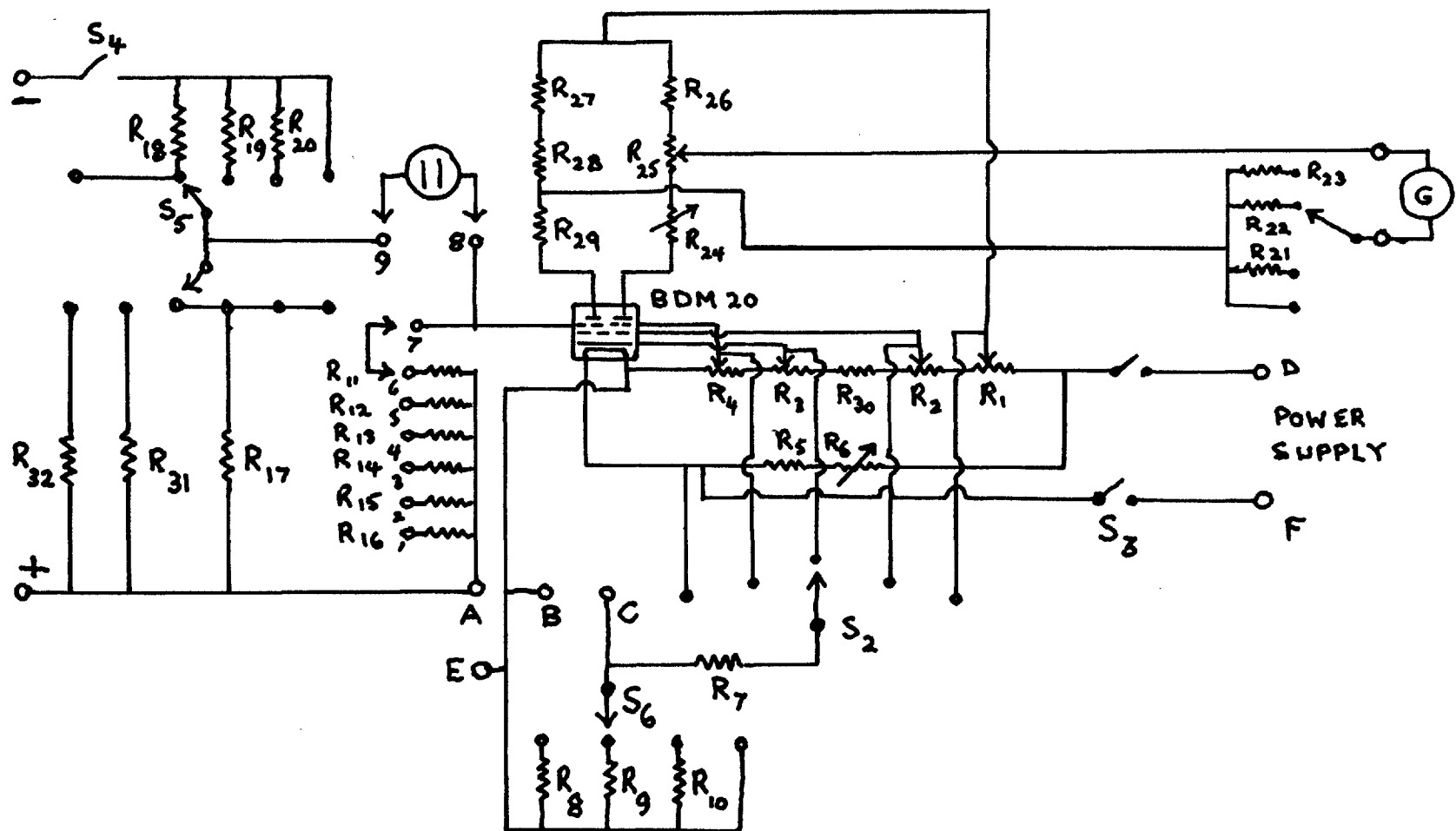
The accuracy attained was thus slightly greater than that of Allnatt (1959) with the same bridge, due probably to the introduction of the parallel-T filter giving a clearer signal from the amplifier and thus enabling a more precise determination of the null point to be made.

2.5. D.C. measurements

2.5.1. The d.c. amplifier

The amplifier used was based upon one developed by Jacobs (1953) and proved particularly suitable for studying the long polarization times encountered. The amplifier circuit is shown in fig.8. The Ferranti BDM 20 double electrometer valve and other components were housed in an airtight box containing silica gel to reduce the humidity. The valve was run at the recommended potentials so that the grid current was less than 10^{-15} amp. This type of valve was used due to the two halves being exceptionally well-matched. When checking the valve performance, the anode loads were equalized ($R_{27} = R_{26} = 50 \text{ K}$, $R_{28} = R_{25} = 1 \text{ K}$, $R_{24} = R_{29} = 2 \text{ K}$), and the galvanometer zeroed. The galvanometer deflection was measured as a function of heater voltage with equal anode currents. This process was repeated for various combinations of R_{29} and R_{24} and the family of curves obtained in a typical test are shown in fig.9. By choosing the right combination of R_{24} and R_{29} , the parabolic curve can be adjusted until it is as flat as possible with its latus rectum parallel to the heater voltage axis. Drift due to heater fluctuation will then be at a minimum. The only further adjustment needed was to the galvanometer-zero control, R_{25} , which required adjustment to neutralise a drift of about 2 mm per day in the galvanometer-zero. It was found necessary to check and adjust the grid, screen, anode and heater voltages of the BDM 20 about once every six months. Apart from this, very rarely was any other adjustment necessary. To

FIG.8



Component values - fig.8

R_1	50 ohms w.w. variable	R_2	25 ohms w.w. variable
R_3	25 ohms w.w. variable	R_4	10 ohms w.w. variable
R_5	750 ohms w.w.	R_6	25 ohms w.w. variable
R_7	1 M. H.S.	R_8	1 M. H.S.
R_9	250 K H.S.	R_{10}	100 K H.S.
$R_{11}-R_{16}$ 10^6 , 10^7 , 10^8 , 10^9 , 10^{10} , 10^{11} ohms Welwyn high stability			
R_{17}	6×10^4 ohms w.w.	R_{18}	10^7 ohms H.S.
R_{19}	2×10^6 ohms H.S.	R_{20}	2.5×10^5 ohms w.w.
R_{21}	10 M H.S.	R_{22}	1 M H.S.
R_{23}	100 K H.S.	R_{24}	5 K w.w. variable
R_{25}	1 K w.w. variable	R_{26}	50 K w.w.
R_{27}	50 K w.w.	R_{28}	500 ohms w.w.
R_{29}	w.w. (see text)	R_{30}	60 ohms w.w.
R_{31}	10^4 ohms w.w.	R_{32}	5×10^3 ohms w.w.
$S_1 - S_6$ Yaxley switches			
1 - 9 Pye plugs (polythene insulation)			
A, B, C, D, E. Belling terminals			
G Pye Scalamp galvanometer (1400 ohms)			

FIG. 9a

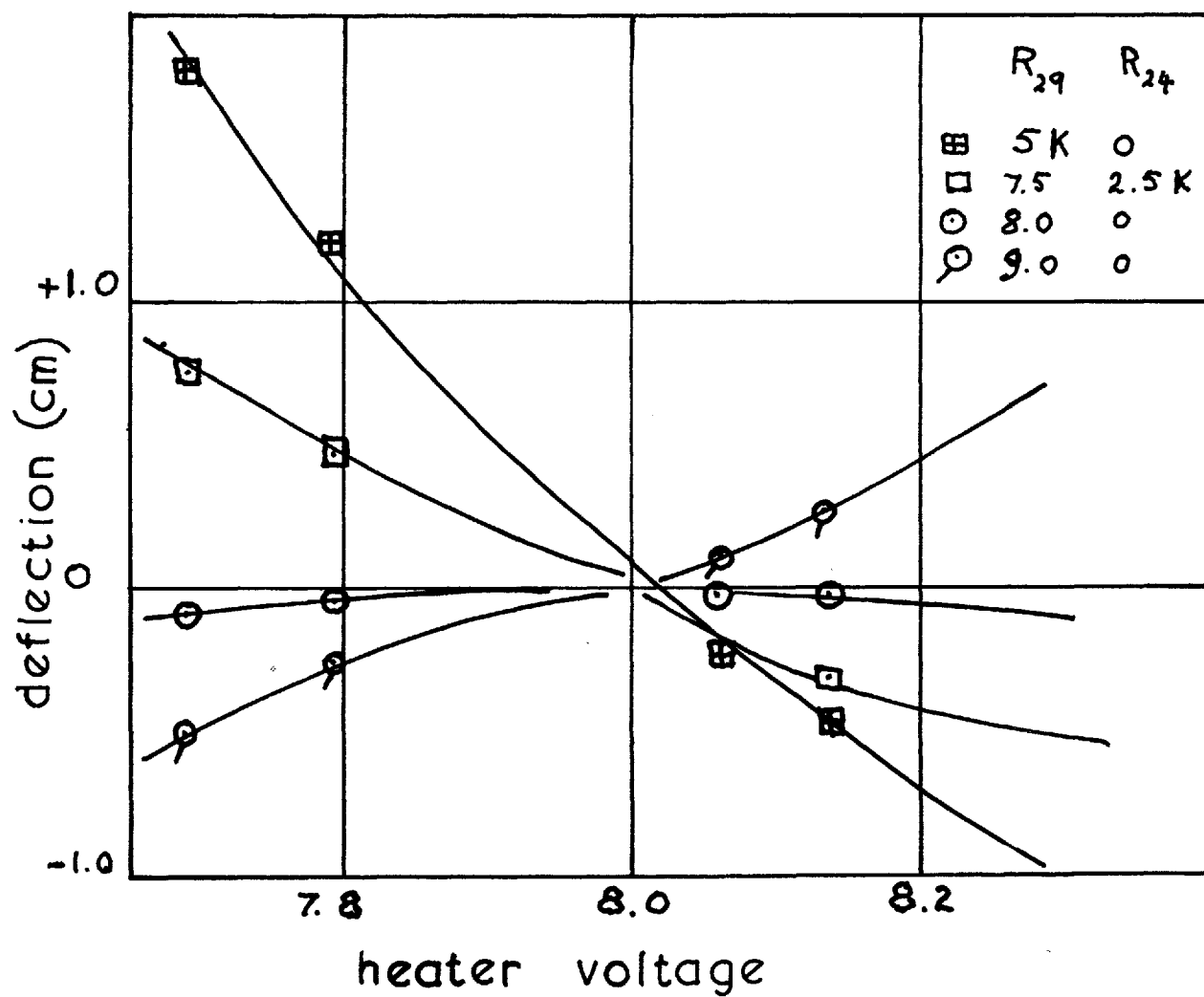
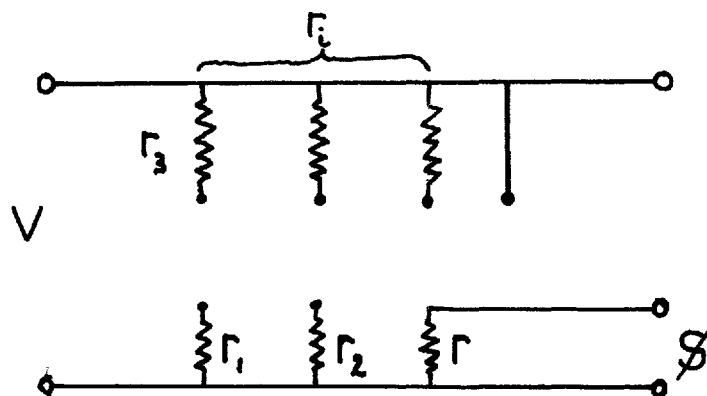


FIG. 9b



facilitate these adjustments, provision for connecting a vacuum tube voltmeter at BC was included in the circuit.

The amplifier was operated from a separately housed power supply unit such that the resistance chain DF of the amplifier was connected in series with the filaments of the amplifier section of the stabilizer across the output of the stabilizer, the correct filament current being obtained by setting a 1500 ohm wire wound series resistor. The output from this stabilizer across the terminals DF of the d.c. amplifier was 25 volts.

The voltage applied across the crystal was derived from a separate power pack supplying 230 volts d.c. constant to 0.1% over 2 hours. The circuit for this supply was based on that described by Solomon (1950). Four voltages (1.4, 7, 47 and 233 volts) could be applied through the potentiometer composed of the high stability resistors R_{17} to R_{20} , R_{31} and R_{32} . These were calibrated on the a.c. bridge with an accuracy of better than 0.1%. The method for resistance measurement was the following. With S_4 open and 8 and 9 shorted, the galvanometer was zeroed by R_{25} . S_4 was then closed, S_5 connected to R_{17} and a voltage $\mathcal{E}$ applied from a Tinsley potentiometer connected to AE so that no deflection was obtained on the galvanometer. The cell was connected across 8 and 9, the voltage selected by S_5 and the galvanometer rezeroed by a voltage u from the potentiometer. The resistance R is then given by

$$2.5.1.1 \quad R = R_g \frac{s - u}{u}$$

where $s = \mathcal{E} \times p$. p is a numerical factor calculated from the known

values of R_{17} - R_{20} , R_{31} and R_{32} . R_g is the appropriate value of the grid leak used. Since the sensitivity was 0.30 mv per mm and the scale could be read to ± 0.01 cm a sensitivity of 0.1 mv was attained. For resistances up to 10^{11} ohms using $s = 1.2$ volts the sensitivity was therefore 0.1%. This was maintained for resistances between 10^{11} and 10^{13} ohms by using higher applied voltages. When $(R + R_g)$ is less than or equal to 100 times greater than R_{17} , as will be so when $R_g = 10^6, 10^7$ ohms, then a shunting effect will occur. The resistance must then be calculated by successive approximations. The first approximation is found from equn. 2.5.1.1 and the second from

$$R = R_g \frac{s' - u}{u}$$

where $s' = a(1 + \frac{b}{R_g + R})^{-1}$, where a and b are constants calculated

from the known calibrations of the resistances when $p = 1$ (see appendix I).

The 10^6 and 10^7 ohms grid resistors were calibrated on the a.c. Wheatstone bridge against 0.1% Sullivan resistors with an accuracy of better than 0.1%. The 10^8 ohms grid leak was found in terms of the 10^7 ohms one by measuring an unknown high stability resistor (10^7 ohms) using both grid leads. A 10^{10} ohms high stability resistor was used to complete the internal calibration of the 10^8 to 10^{11} ohms grid leaks.

The value of p was calculated in the following way (see fig.9b). Let ϕ be the calibrating voltage, and S that used in the measurement where $S = p\phi$.

Then

$$V \frac{r}{r + r_3} = \phi$$

and

$$V \frac{r}{r_i + r_3} = S.$$

Therefore

$$\frac{S}{\phi} = \frac{r}{r_i + r} \cdot \frac{r_3 + r_i}{r} = p,$$

so that

$$p = \frac{r_3 + r}{r_i + r}$$

where $r_1 = R_{32}$, $r_2 = R_{31}$, $r = R_{17}$, $r_3 = R_{18}$ and $r_i = R_{18}$, R_{19} or R_{20} .

Both with regard to stability and sensitivity, the amplifier performed very well indeed. The one unexplained point about its operation was that the first calibration reading ϕ of the day was invariably slightly different to successive ones. Thus ϕ was always checked several times when the first measurement of the day was being made.

2.5.2. Measurement of low resistances and thermoelectric potentials

When making d.c. conductivity measurements at high temperatures, resistances of the order of 10^4 to 10^5 ohms were encountered. To limit the current passed, potentials of the order of 50 mv were supplied from a vernier potentiometer and the potential drop measured by a sensitive galvanometer. The circuit is shown in fig.10. All connecting wires were of shielded polythene-insulated cable. The cell was plugged in via polythene-insulated coaxial connectors mounted on a perspex block. The galvanometer sensitivity (6.504×10^{-9} amp/cm) and internal resistance (518 ohms) were determined

using a Sullivan resistance box (accurate to 0.02%) in place of the cell. Knowing the sensitivity and the applied voltage the resistance of the crystal could be calculated. The accuracy was about 5%.

Initially, the thermoelectric power was measured with this same circuit, by determining the e.m.f. required to balance that from the crystal, but at lower temperatures the crystal resistance became too great for accuracy to be maintained. In order to extend these measurements over as wide a temperature range as possible, the thermoelectric e.m.f. was fed directly into the d.c. amplifier and the current through R_g backed off with the Tinsley potentiometer. This procedure worked well above 550°C but below this temperature the impedance of the crystal became too high. Hence a secondary amplifier (fig.13) consisting of an ECC 83 double triode and a cathode follower was built. In this amplifier, the anode currents were equalized (using A) and drift from heater fluctuations checked by the same method as used for the electrometer. Any day-to-day adjustments of the galvanometer zero setting were made by adjusting R. The amplifier filaments were heated by connecting D.D.', in series with the filament of the stabilizer valves, to the stabilized H.T. which also constituted the anode supply. This second amplifier gave an additional gain of 30. It was then found that feeding the thermoelectric e.m.f. into the original amplifier and the resulting signal into the second amplifier enabled thermopower measurements to be made down to 100°C.

FIG. 10

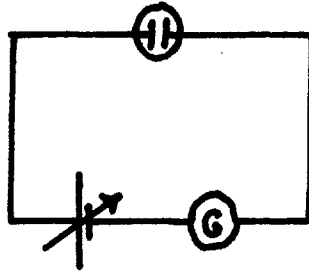


FIG. 11

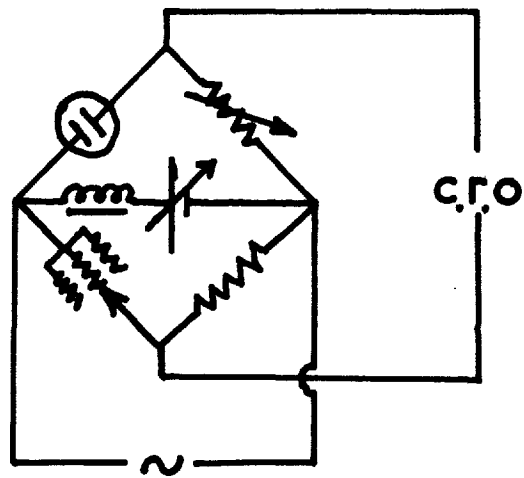
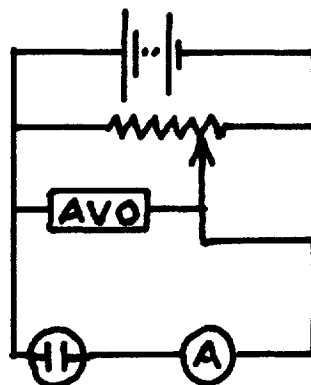


FIG. 12



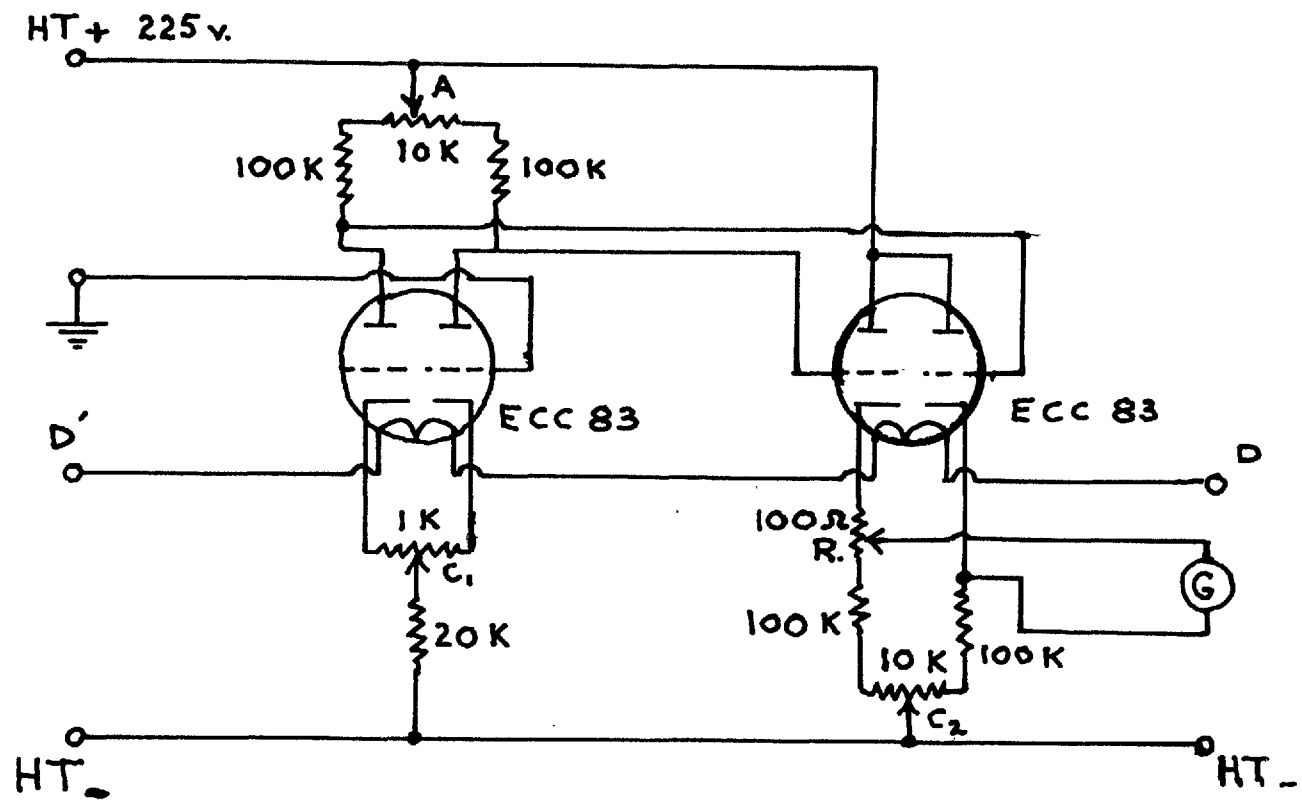


FIG. 13

2.5.3. Current-voltage and capacity-voltage measurements

When studying the current-voltage dependence the circuit shown in fig.10 was used. Outside the range of the potentiometer and galvanometer the voltage was supplied from 120 volt dry batteries and the current measured using a microammeter. The voltage supplied was measured with an Avometer, as shown in fig.12, that across the cell being found by correcting for the iR drop across the microammeter.

For measurements of the capacitance of the crystal under the influence of a d.c. field, the experimental arrangement shown in fig.11 was employed. Again the d.c. source was either a potentiometer or dry batteries as required.

2.6. Experimental procedure

Any deviations from the following general procedure are noted in the presentation of the results. The freshly cleaved and measured crystal was placed in the cell and the electrode assembly screwed to finger tightness. The cell was pumped down to 10^{-6} mm Hg and then a gentle stream of purified nitrogen was passed through it. The cell was heated to 600°C during 5 hours and the crystal left to anneal at this temperature overnight. The temperature was raised to $690^{\circ}\text{--}700^{\circ}\text{C}$ for two hours and a.c. conductance measurements commenced. The resistance was measured at 1 kc at 10° intervals and capacity-frequency measurements made at 20° - 25° intervals. For the 'pure' crystals the temperature was then raised to 680°C and d.c. measurements made using the potentiometer method.

Voltages used with the amplifier were 0.24 volts for $R_g = 10^6$ and 10^7 ohms and 1.4 volts for $R_g = 10^8 - 10^{10}$ ohms; 7, 43 and 233 volts were used for resistances greater than 5×10^{10} ohms which were measured with $R_g = 10^{10}$ ohms. The crystal was again measured at the end of a run when it was found that the geometric factor (length/area) was generally about 1% different from its initial value.

In several runs, thermopower measurements were made before the d.c. conductance measurements. For each point on the graph of e.m.f. against temperature gradient, the following measurements were made. The temperature of each electrode was measured alternately four times in rapid succession. Then the thermopower was measured four times and finally the electrode temperatures again recorded alternately four times in succession. The mean of each set of readings was taken for the appropriate point on the graph of e.m.f. against ΔT . Owing to the large series resistance R_g of the amplifier, the possibility of the crystal becoming polarized by its thermal e.m.f. was eliminated.

The current-voltage measurements were always the last set to be made on any one crystal due to the possibility of electrolysis occurring.

3. Results

3.1. A.c. conductance of pure KCl

Plots of $\log \sigma T$ against $1/T$ (where σ is the specific conductance and T the absolute temperature) can usually be represented by two straight lines corresponding to the intrinsic (high temperature) and structure sensitive (low temperature) regions. Thus

$$\sigma T = A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/dT)$$

where E_1 and E_2 are the appropriate activation energies for the intrinsic and structure sensitive conductance.

Using the a.c. bridge method, the highest resistance which could be measured was 10^8 ohms, which is just about the limit of the intrinsic region. Thus all a.c. conductance data refer essentially to the intrinsic region, and consequently

$$1.3.4. \quad k \partial \log(\sigma T) / \partial (1/T) = E_1 = \Delta h_1 + \frac{1}{2}h$$

if the conductance is purely cationic. The plot of $\log T$ against $10^3/T$ for the Kyropoulos crystal grown from recrystallized KCl is shown in fig.14. It is evident that there are distinct deviations from linearity at the higher temperatures. This departure from linearity is a result of the onset of anion conduction at these high temperatures. A straight line can be drawn through the points below 870°K , and the upward curvature at higher temperatures is then clearly apparent. The equation to the straight line was found and this was taken to represent the cationic contribution to the conductance. From this equation, and the actual points at the higher temperatures, values for the cationic transport number, t_1 , and the mobility ratio, ϕ , were determined. The

FIG.14
CONDUCTIVITY OF PURE KCl.

Kyropoulos KCl; run 20.

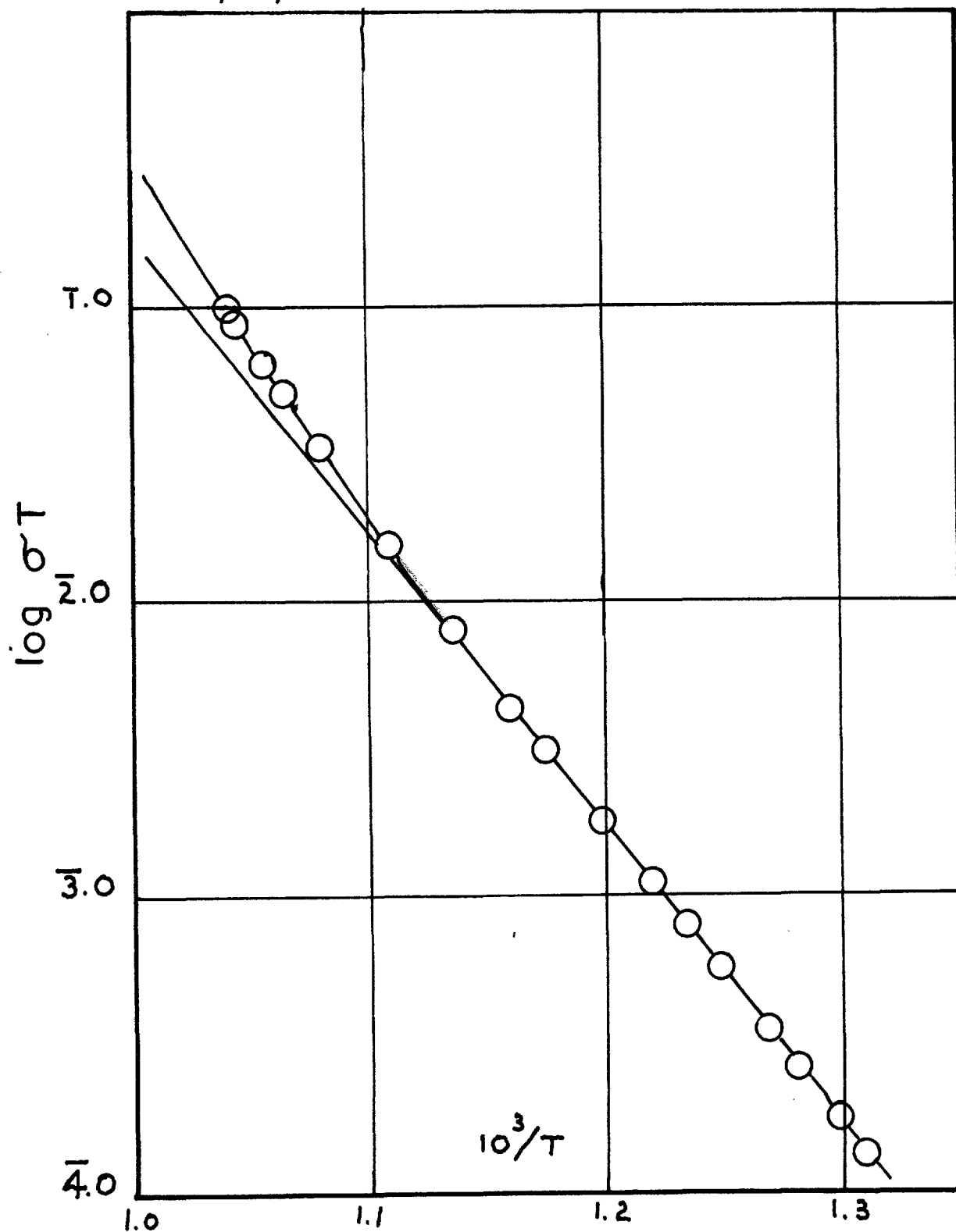
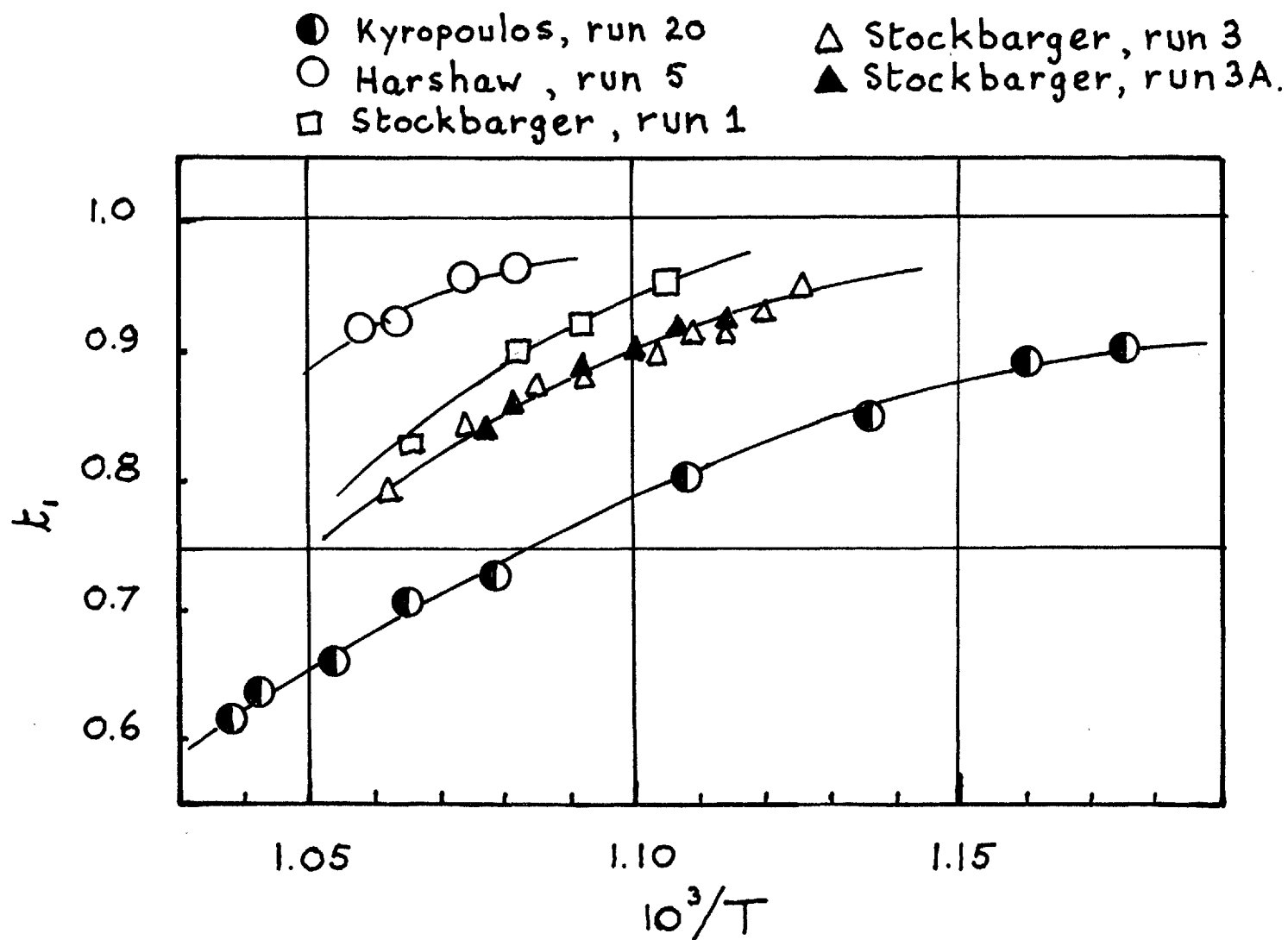


FIG.15

CATION
TRANSPORT NUMBERS



transport numbers so computed for a series of different pure KCl crystals are shown graphically in fig.15. Runs 3 and 3A refer to the same cleave of a Stockbarger crystal with a ten week anneal (during thermoelectric power measurements) between the two runs. Very good agreement is observed between the two sets of data, despite this long anneal. A curious feature of these curves is that the Stockbarger and Harshaw crystals show a far greater degree of cation conduction than the Kyropoulos crystals. This effect may be due to impurities (e.g. SiO_3^{2-} or other divalent anions). From t_1 , the mobility ratio $\phi = u_2/u_1$ can be calculated, if we assume that in the intrinsic region, $N_1 = N_2$. The specific conductance is

$$3.1.1. \quad \sigma = N_1 e u_1 + N_2 e u_2 ,$$

and thus $t_2/t_1 = (N_2/N_1)\phi$. From the theory presented in section (1.3), it is evident that

$$3.1.2. \quad \phi = \exp \left\{ (\Delta s_2 - \Delta s_1)/k \right\} \exp \left\{ -(\Delta h_2 - \Delta h_1)/kT \right\} ,$$

since

$$3.1.3. \quad u = 4a^2 e w / kT$$

and

$$1.3.1. \quad w = \lambda \exp(-\Delta g/kT) .$$

The factor 4 in equn. 3.1.3. arises because, in a f.c.c. lattice, there are four equivalent ions which can exchange places with a vacancy.

On plotting $\log \phi$ against $10^3/T$, straight lines are obtained in agreement with equn. 3.1.2., but the concordance between the heat and entropy terms for the different crystals is rather poor, as might have been anticipated from fig.15.

The activation energies and log A factors obtained by applying equn. 1.3.5, are given in table 5. The derived enthalpy and entropy data, obtained by employing equn. 1.3.4 and 3.1.2, are given in table 6.

Table 5

Platinum Electrodes

<u>Run</u>	<u>Source</u>	E_1 eV	$\log A_1$
1	Stockbarger	1.87	8.375
3A	Stockbarger	1.90	8.350
19	Kyropoulos	1.90	8.693
20	Kyropoulos (recrystallized)	1.91	8.771
5	Harshaw	1.76	7.836
10	Harshaw	1.76	7.816
3	Stockbarger	1.75	7.301
13	SO ₄ ²⁻ doped	1.74	7.550
14	SO ₄ ²⁻ doped	1.81	7.670

Rhodium Electrodes

2	Stockbarger	1.68	7.018
---	-------------	------	-------

Silver Electrodes

The intrinsic conductance comprises two linear regions.

		E_1' eV	E_1'' eV	Change Temp. °C
7	Harshaw	1.82	1.69	575
8	Harshaw	1.93	1.67	580
9	Harshaw	1.85	1.63	570

Table 6Conductance parameters for pure KCl

Run	Source	$\Delta h_1 + \frac{1}{2}h$ eV	$\Delta s_1 + \frac{1}{2}s$ 10^{-3} eV/deg	$\Delta h_2 - \Delta h_1$ eV	$\Delta s_2 - \Delta s_1$ 10^{-3} eV/deg
<u>Platinum Electrodes</u>					
1	Stockbarger	1.87	0.330	1.905	1.874
3A	Stockbarger	1.90	0.329	1.760	1.746
19	Kyropoulos	1.90	0.343	1.849	1.794
20	Kyropoulos (recrystallized)	1.91	0.346	1.103	1.10
5	Harshaw	1.76	0.309		
10	Harshaw	1.76	0.309		
3	Stockbarger	1.75	0.288		
13	SO ₄ ²⁻ doped	1.74	0.297	} no anion conductance	
14	SO ₄ ²⁻ doped	1.81	0.302		
<u>Rhodium Electrodes</u>					
2	Stockbarger	1.68	0.276		

3.2.. A.c. conductance of doped KCl

In fig.16 the conductance of five crystals doped with strontium chloride is compared with that of a pure crystal. All six crystals were grown from the same batch of KCl by the Stockbarger method. The experimental procedure was exactly the same for the doped crystals as for the pure. Thus the points were recorded with descending temperature. When put into the conductivity cell, several of the crystals were turbid, thus indicating a precipitated phase, but with the usual heat treatment it was found that the results were reproducible on thermal cycling. Hence we were confident that the Sr^{2+} went into solution under the heat treatment. Table 7 gives a selection of experimentally measured conductivities for the five crystals at the indicated temperatures.

As is evident from fig.16 the conductivity lines show a small amount of curvature. At the higher temperatures where the curve is linear, the slope was measured. This activation energy, Δh_1 , is the activation energy for cation vacancy mobility and collected values found from both the a.c. data on the doped crystals and the d.c. data on the pure crystals are presented in table 8.

FIG.16

CONDUCTIVITY OF DOPED KCl

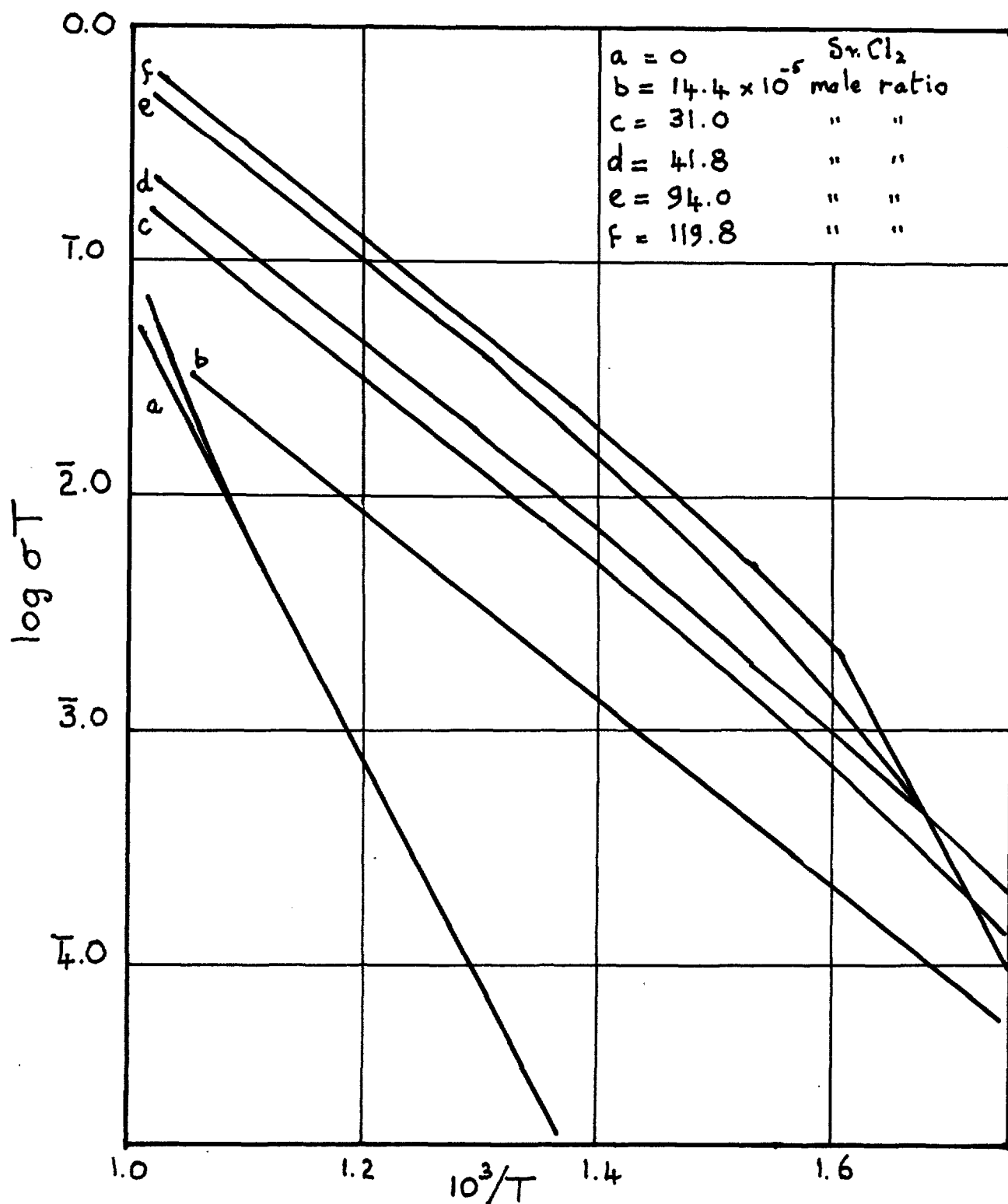


Table 7

Conductivity of pure and doped KCl, interpolated at the
given values of $10^3/T$

$\sigma \times 10^6, \text{ ohm}^{-1} \text{ cm}^{-1}$						
$10^3/T$	Pure KCl Run 3A	X 1	X 2	X 3	X 4	X 5
1.110	6.50	19.23	75.34	104.7	241.2	306.2
1.120	5.01	17.74	69.82	97.05	223.4	281.8
1.130	4.10	16.37	65.77	89.74	205.6	261.2
1.140	3.31	15.14	59.77	82.60	189.7	239.3
1.160	2.21	12.94	50.58	70.47	161.8	202.3
1.170	1.74	11.83	46.56	65.16	148.9	185.8
1.180	1.40	10.99	43.05	59.98	137.4	172.6
1.190	1.14	10.14	39.63	55.59	127.1	158.9
1.200	0.92	9.397	36.52	51.17	116.9	145.9
1.210	0.746	8.670	33.73	47.32	107.9	134.3
1.230	0.490	7.379	28.71	40.27	91.62	113.0
1.240	0.390	6.653	26.49	37.24	84.72	104.2
1.300	0.117	4.159	16.37	23.01	52.00	62.52
1.350	0.0389	2.773	10.72	14.96	33.88	41.11

Table 8

Numerical values of the activation energy Δh_1 for
cation vacancy mobility found from d.c. and a.c.
measurements

Crystal	Method	Δh_1 (eV)
Stockbarger, run 3	d.c.	0.793
Harshaw, run 5	d.c.	0.752
Stockbarger X 1	a.c.	0.764
X 2	a.c.	0.784
X 3	a.c.	0.772
X 4	a.c.	0.782
X 5	a.c.	0.863

3.3. A.c. polarization measurements

Measurements of capacity as a function of frequency were made simultaneously with the a.c. conductivity measurements recorded in section 3.1. A typical example of the variation of capacity with frequency is shown in fig.17. The capacity at 50 kc/s was taken as representing the residual capacity of the leads, etc. This value was subtracted from the measured capacities and the resultant capacity, C, taken as the polarization capacity; typical plots of $\log C$ versus $\log f$ are shown in fig.18. These plots were always good straight lines; their slopes (termed frequency slopes) are recorded in table 9(a,b).

Table 9bFrequency dependence of Sr^{2+} doped KCl

Run	mole ratio SrCl_2	Frequency slope at stated temperature in deg C					
11	119.8×10^{-5}	679°	659°	622°	569°	574°	545°c
		1.74	1.76	1.70	1.82	1.76	1.74
17	94.0×10^{-5}	681°					
		1.85					
16	41.8×10^{-5}	666°					
		1.88					
15	31.0×10^{-5}	677°					
		1.89					
12	14.4×10^{-5}	673°					
		1.80					

Mean frequency slope = 1.84

The plots of $\log C$ (measured at 300 c/s) versus $1/T$ were always linear within experimental error for pure KCl, a typical example being shown in fig.19. A truer representation in terms of the theory may be obtained by plotting $\log CT^{3/2}$ versus $1/T$, and again good straight lines were obtained. The slopes of these lines are given in table 10, together with the temperature range in which measurements were made.

For the impure crystals the frequency-dependence of capacity showed the same general behaviour as that for the pure crystals. However, the plots of $\log C$ versus $1/T$ showed a distinct curvature: this

shows up quite well in figs 20 and 21. Values of the capacity were reproducible for those crystals which had to be left overnight. In the most heavily doped crystal, X 5, the data was recorded in a single day thus decreasing the possibility of a capacity increase as found by Allnatt (1959) in his most heavily doped crystal.

A careful search for polarization resistance was made in all the crystals studied, but none was detected. However, in the most heavily doped crystal at 679°C there was a 10% decrease in the resistance over the frequency range 300 c/s to 3 kc/s. This was not a reproducible feature, and a probable explanation is that this decrease was not in fact polarization resistance, but was due to the non-equilibrium distribution of the Sr^{2+} in the crystal lattice.

Table 10Temperature dependence of capacity in pure KCl

Run	E(kcal/mole)	E(eV)	Temp. range, °C
1	83.7	3.63	693-615
2	82.0	3.57	667-607
3	76.3	3.31	669-625
5	73.2	3.18	683-617
19	73.2	3.18	678-615
20	70.5	3.12	690-587

Temperature dependence of $\log CT^{3/2}$ in pure KCl

Run	E(kcal/mole)	E(eV)	Temp. range, °C
1	85.6	3.71	693-615
2	85.09	3.69	667-607
3	79.09	3.43	669-625
5	74.95	3.25	683-617
19	74.95	3.25	678-615
20	74.0	3.21	690-587

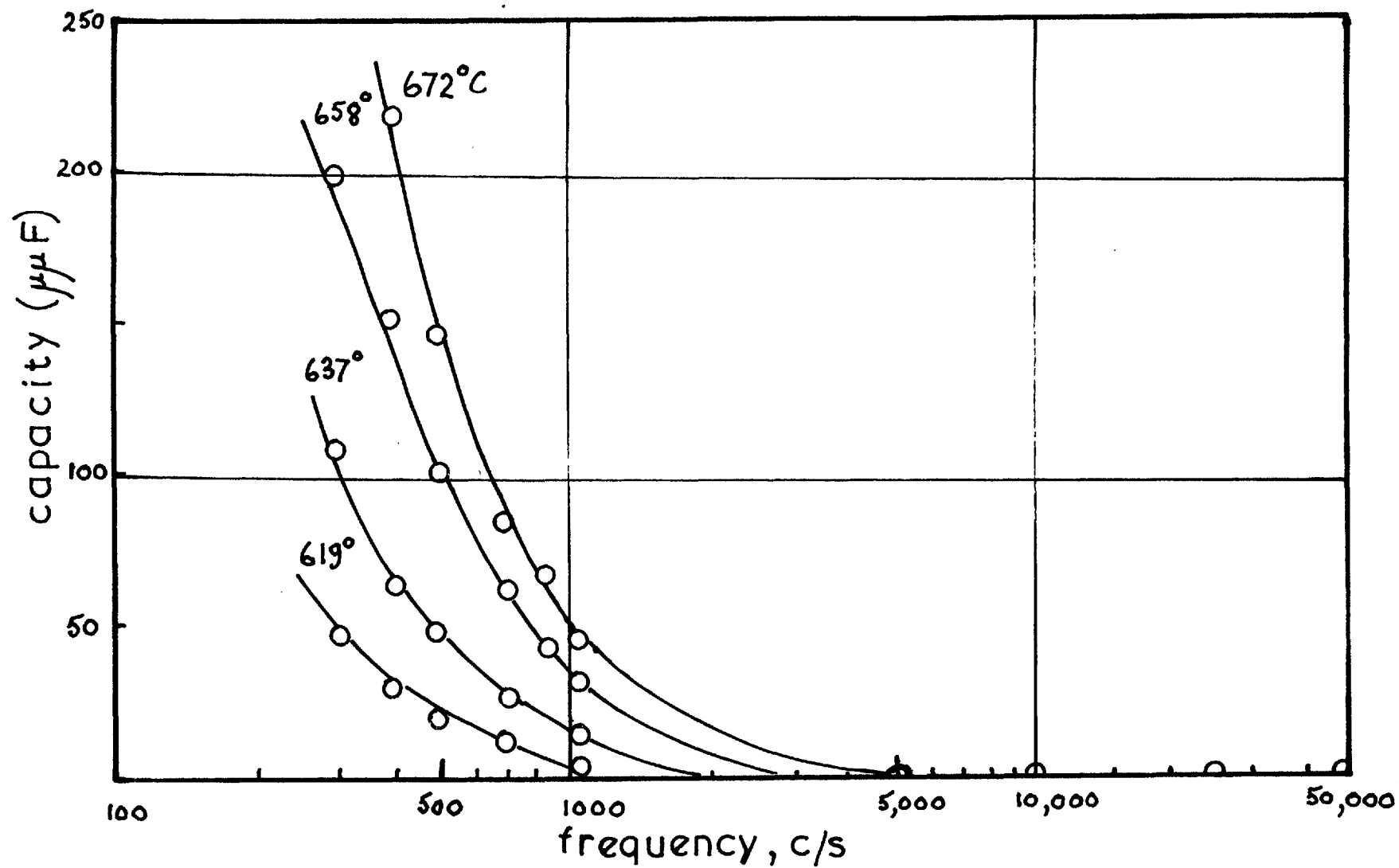


FIG. 17

FIG. 18

Stockbarger KCl, run 1

$A = 1.221 \text{ cm}^2$

$2L = 0.1761 \text{ cm}$

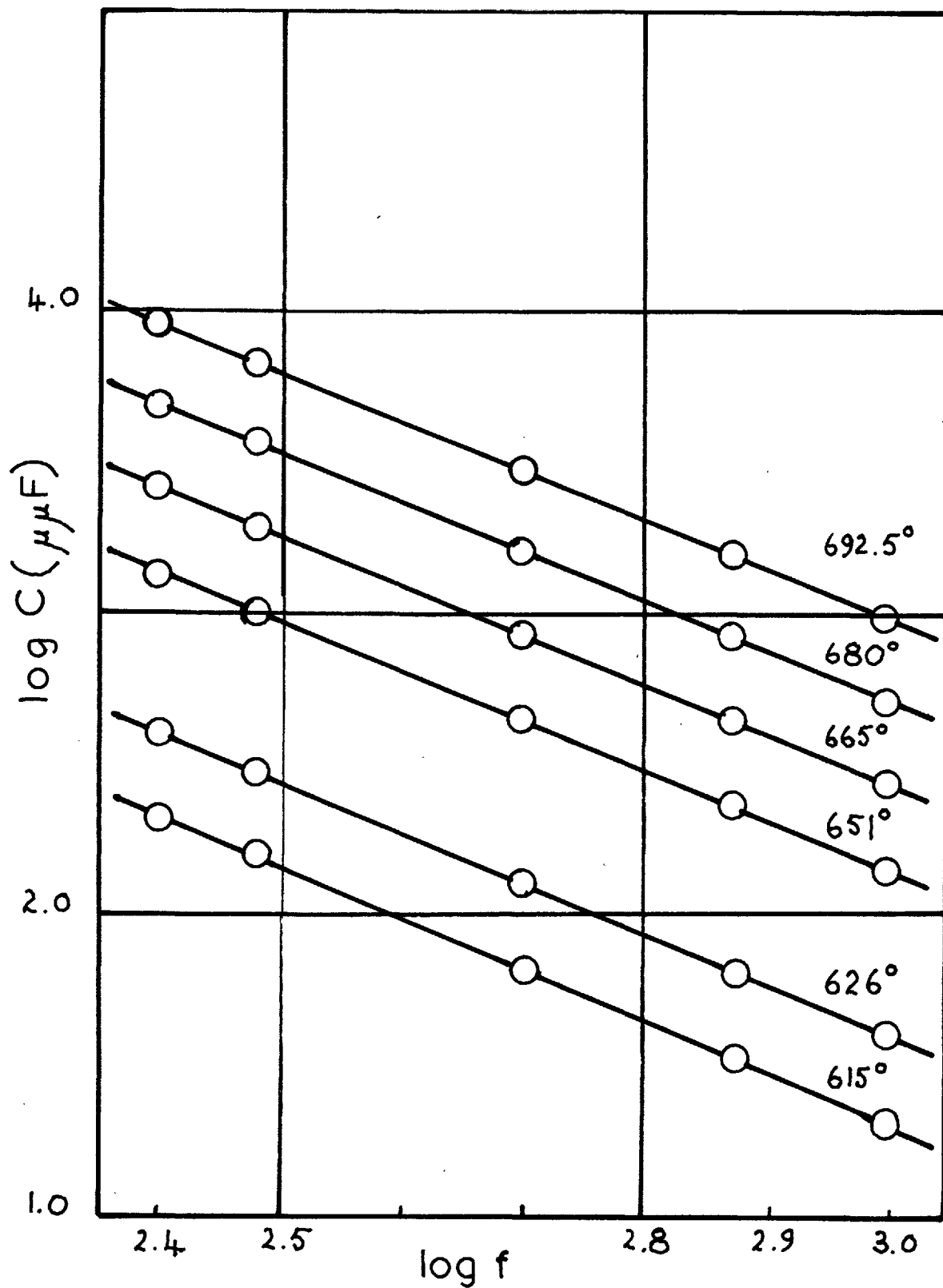


FIG. 19

CAPACITY OF KCl AT 300 c/s
run I

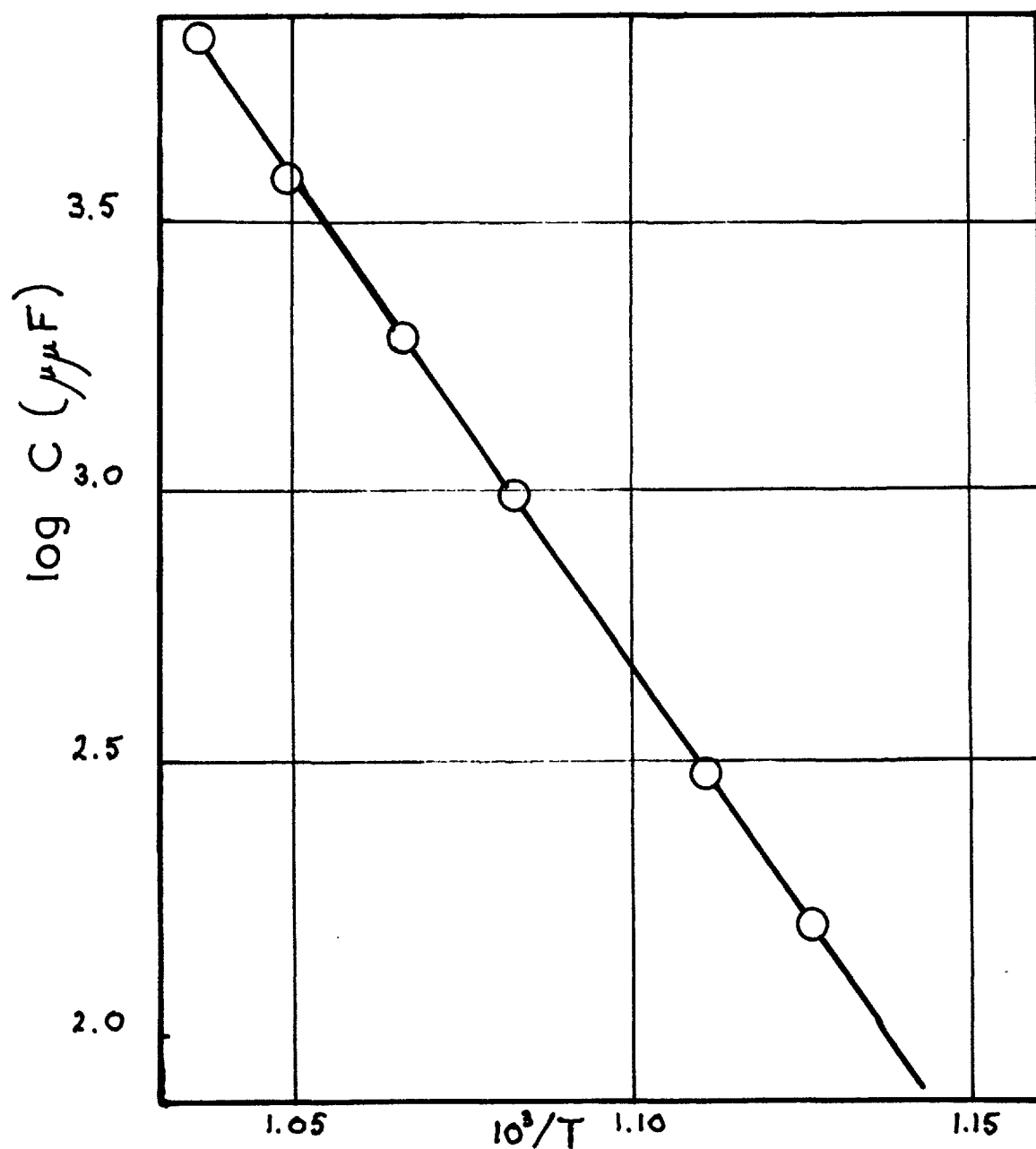


FIG. 20

CAPACITY OF CRYSTAL X 2

○ experimental
 ⊗ theoretical

at 300 c/s

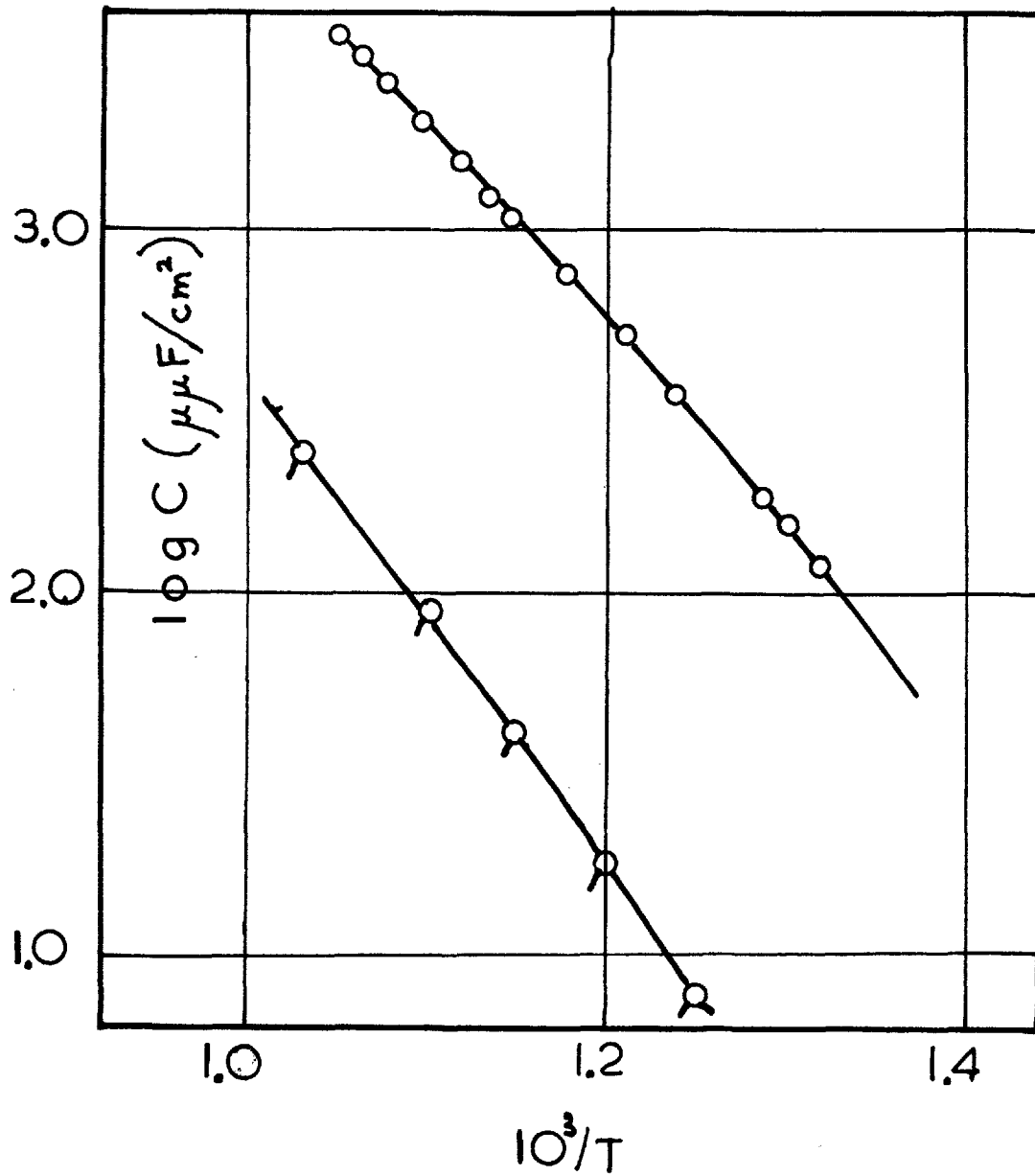
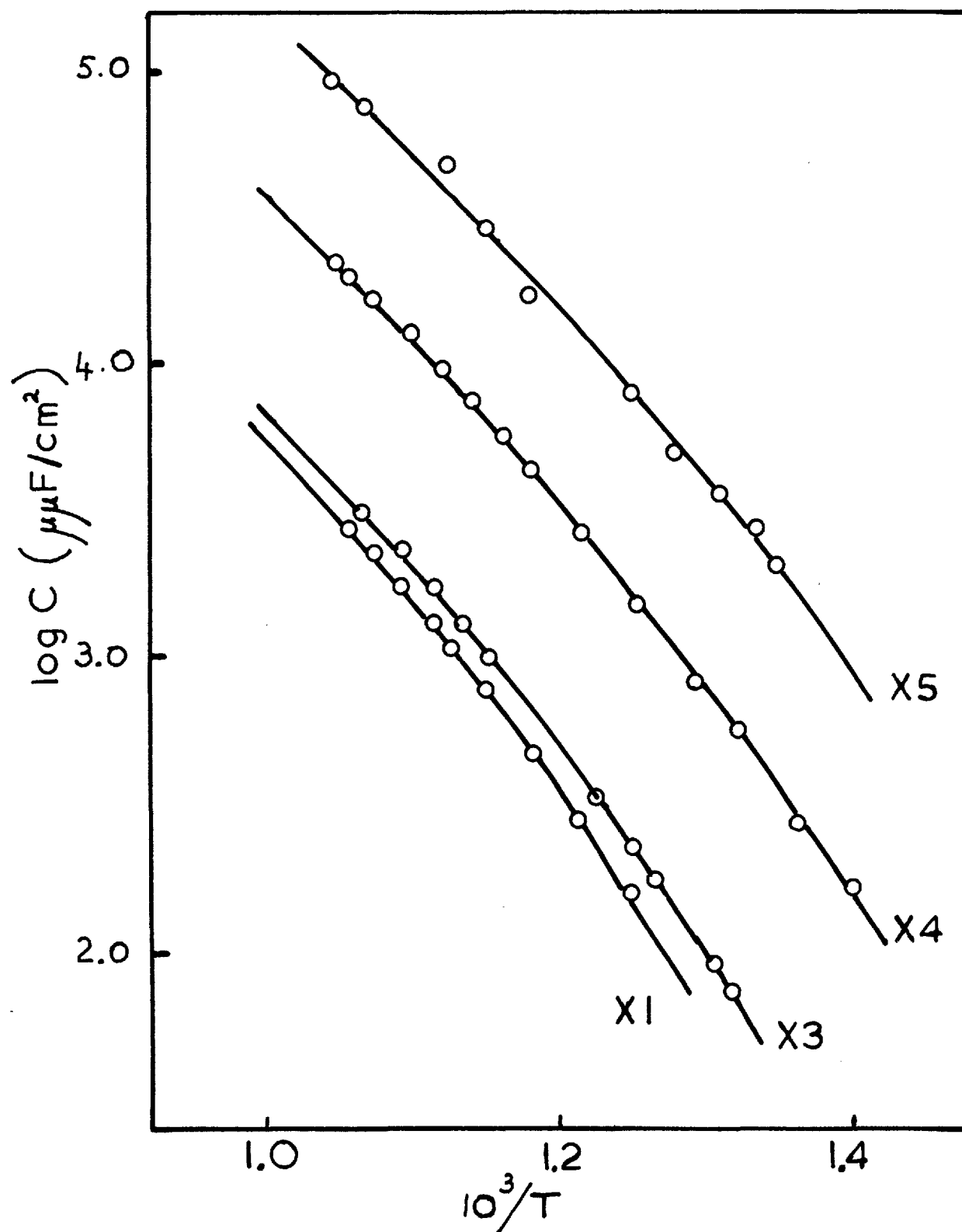


FIG. 21

all at 300 c/s



3.4. D.c. measurements

After the a.c. conductivity measurements in the pure KCl crystals, the temperature was raised to 660°C and d.c. measurements made. Fig.22 shows σ_{∞} as a function of temperature for run 3, together with the a.c. conductivity, σ_0 . Above 640°C the current assumed a steady-state value in about one minute, for an applied potential of 30 mV. σ_{∞} obeyed Ohm's law at 583°C using applied potentials up to 180 mV, and again at 570°C a further check showed that Ohm's law was obeyed (fig.23). The reproducibility of the current decay curves, fig.24, was quite poor at the higher temperatures due to the rapid decay but with the longer polarization times recorded at the lower temperatures, the reproducibility of the d.c. polarization curves improved. The crystal was always short-circuited between readings when a current flowed in the opposite direction. At temperatures above 500°C the charging and decay times were similar but below this temperature the decay time became much longer.

The charging curves down to 480°-500°C were plotted in the form $\log I_p$ versus t , where $I_p = I_t - I_{\infty}$ is the polarization current. Fig.25 shows a typical example from run 3 at 524°C. The theory of Jaffé (section 1.6.2) suggests that I_p should be represented by a sum of exponential terms. Writing

$$I_p = A \exp(-\alpha t) + B \exp(-\beta t),$$

if the second term on the right hand side dominates for large values of t , β and B may be found from the (linear) plot of $\log I_p$ versus t at long times by extrapolating this linear portion of the curve of

$\log I_p$ versus t , we can find $I_p - B \exp(-\beta t)$ for small values of t , where the first term dominates. Plots of $\log [I_p - B \exp(-\beta t)]$ versus t were accurately linear, and a typical example, for run 3 at 524°C is shown in fig.26. In table 11 are collected values of β and α/β down to 500°C. At the lower temperatures the current decay sometimes appeared to change in a step-wise fashion instead of showing the usual smooth exponential decrease and thus no values of β could be found below 480°C in the pure crystals.

Measurements of σ_∞ were continued down to 100°C and the complete conductance curve for run 3 is shown in fig.27. The high temperature polarization generally finished at $370 \pm 30^\circ\text{C}$, and a second polarization region was observed below 180°C. This polarization was not studied quantitatively, in view of the previous detailed study by Parker (1954). Measurements of σ_∞ at high temperatures were again made (run 3A) on Stockbarger cleaves from run 3, after a 10 week anneal, during which thermoelectric power measurements were made. There is a distinct difference in the two curves for σ_∞ , that after the anneal being markedly higher than σ_∞ before the anneal (fig.28). The two activation energies are also different.

Measurements were also made on the most heavily doped crystal after a.c. measurements had been made. The decay curves obtained were analysed in the same way as for the pure crystals, and values of β and α/β are collected in table 12. The plot of $\log \sigma_\infty$ versus $1/T$ for the doped crystal is given in fig.29.

FIG. 22

STEADY STATE AND INTRINSIC CONDUCTIVITY
OF PURE KCl, run 3.

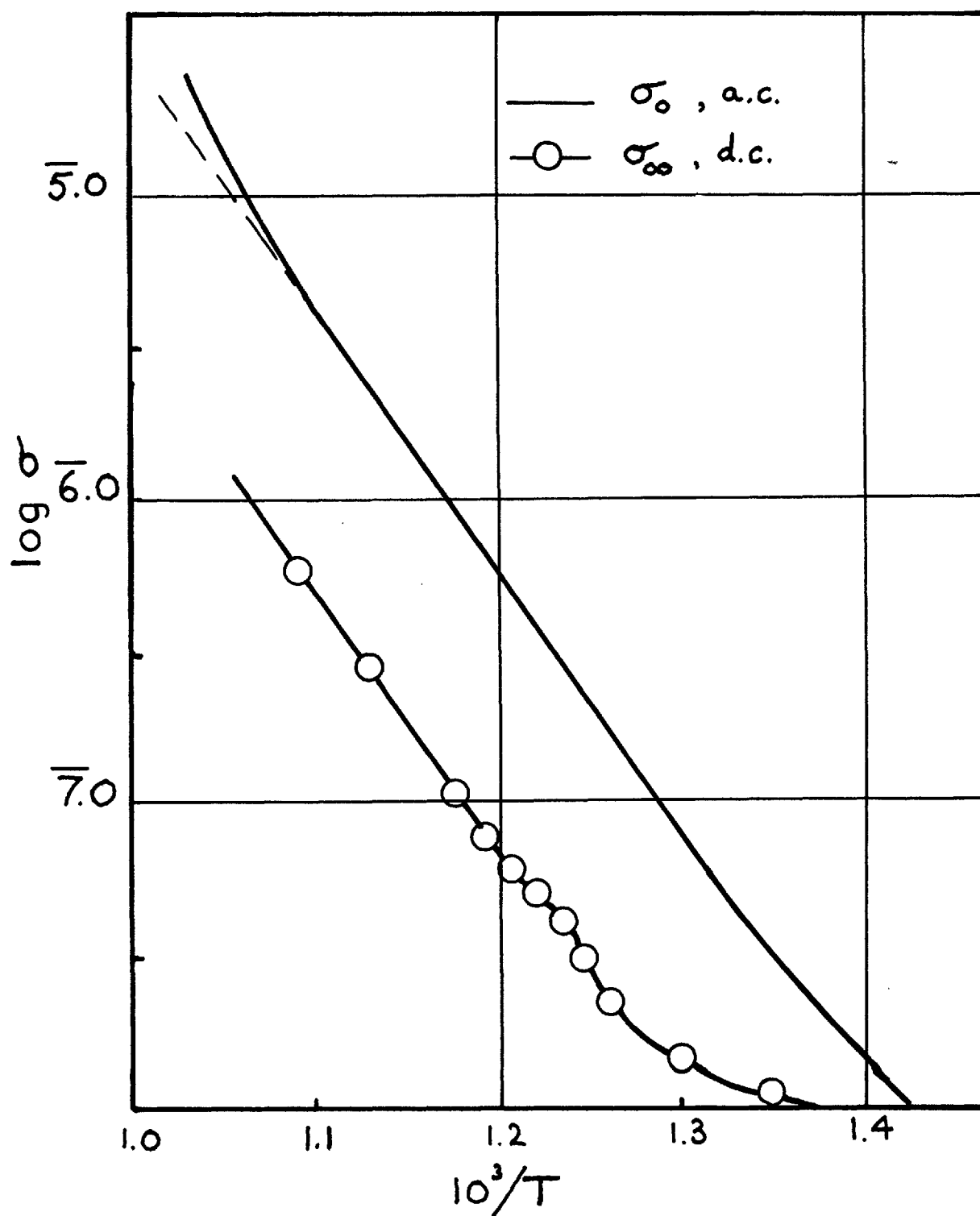


FIG. 23

OHM'S LAW CHECK

PURE KCl, run 3

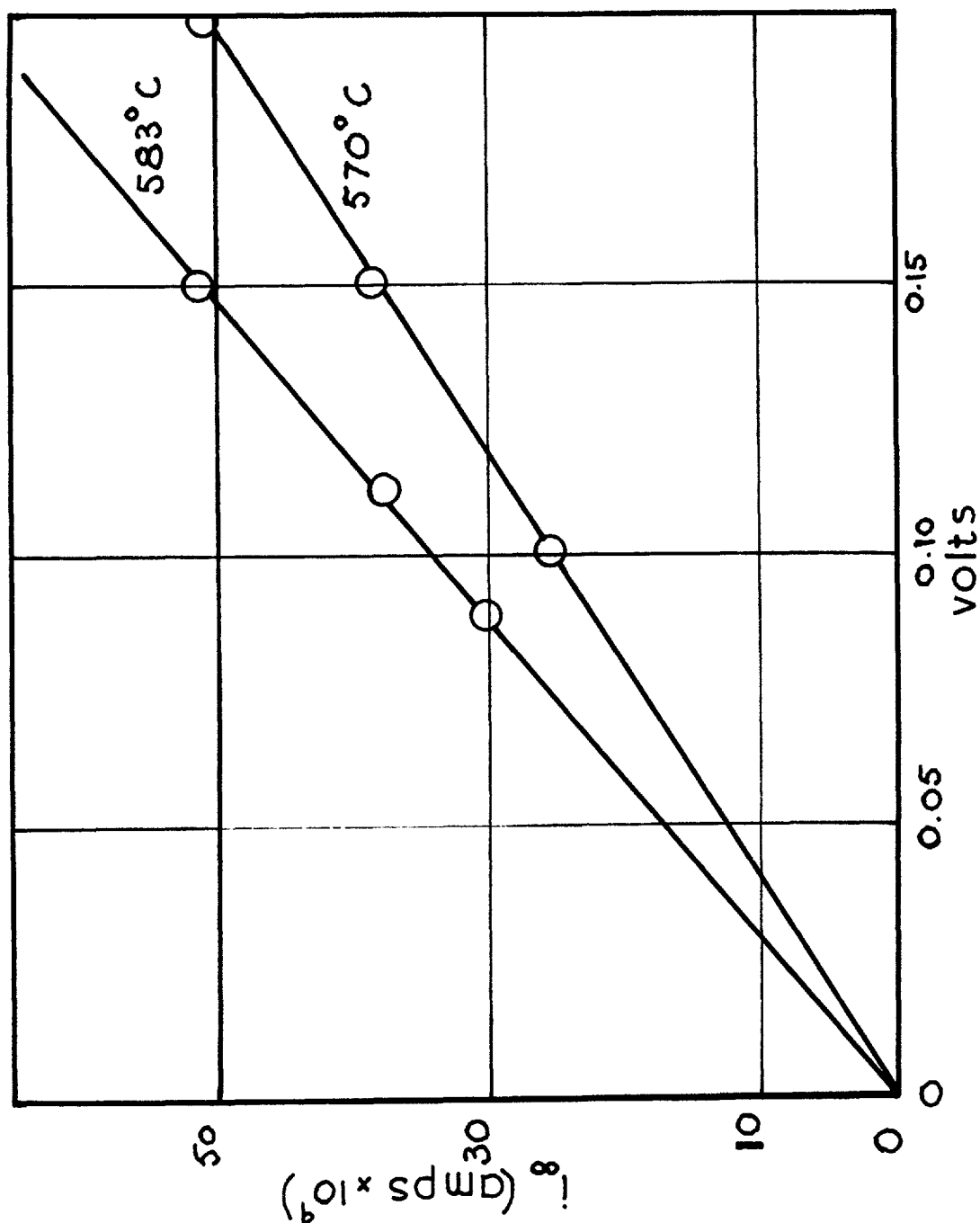


FIG. 24

POLARIZATION OF PURE KCl.

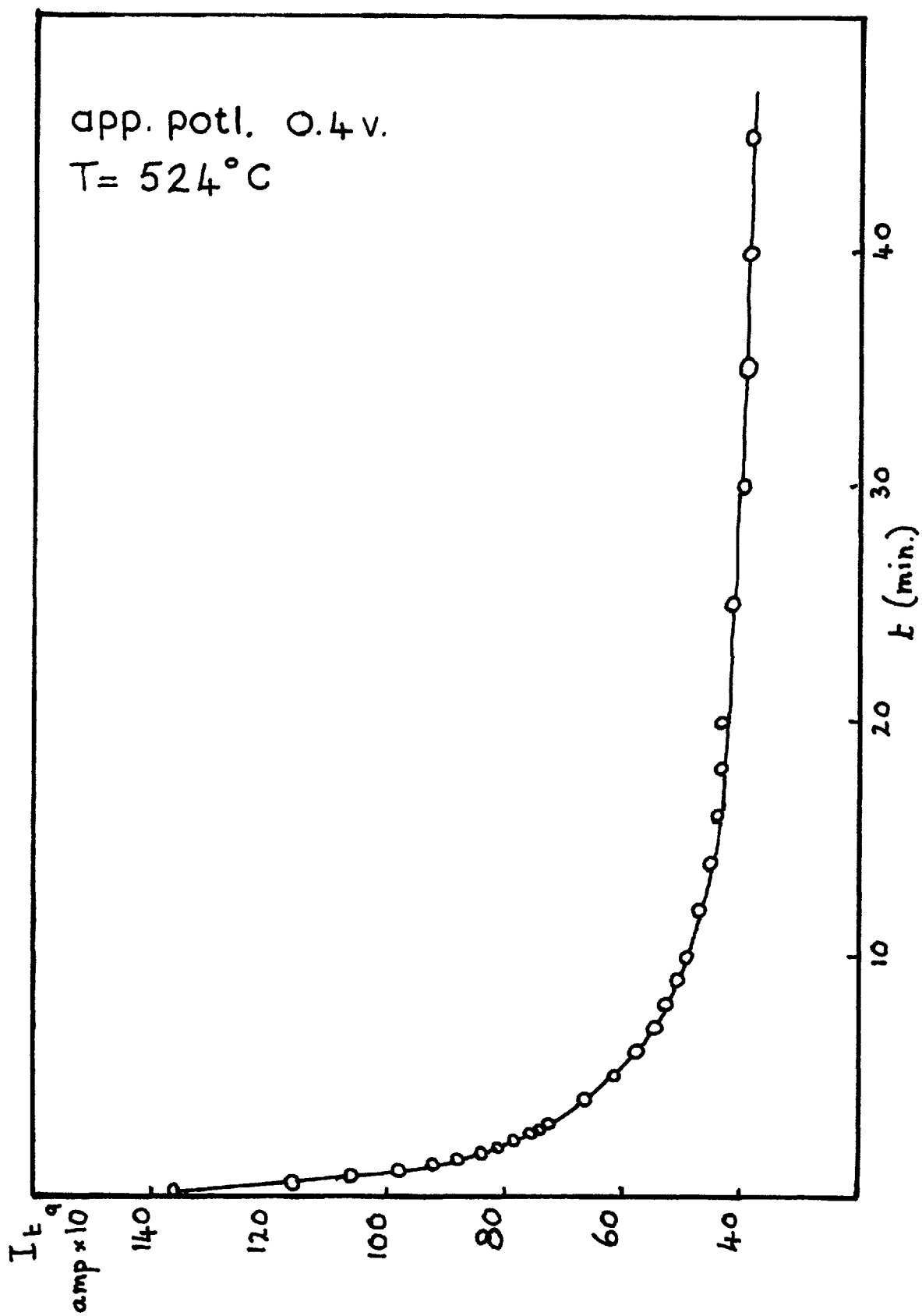


FIG. 25

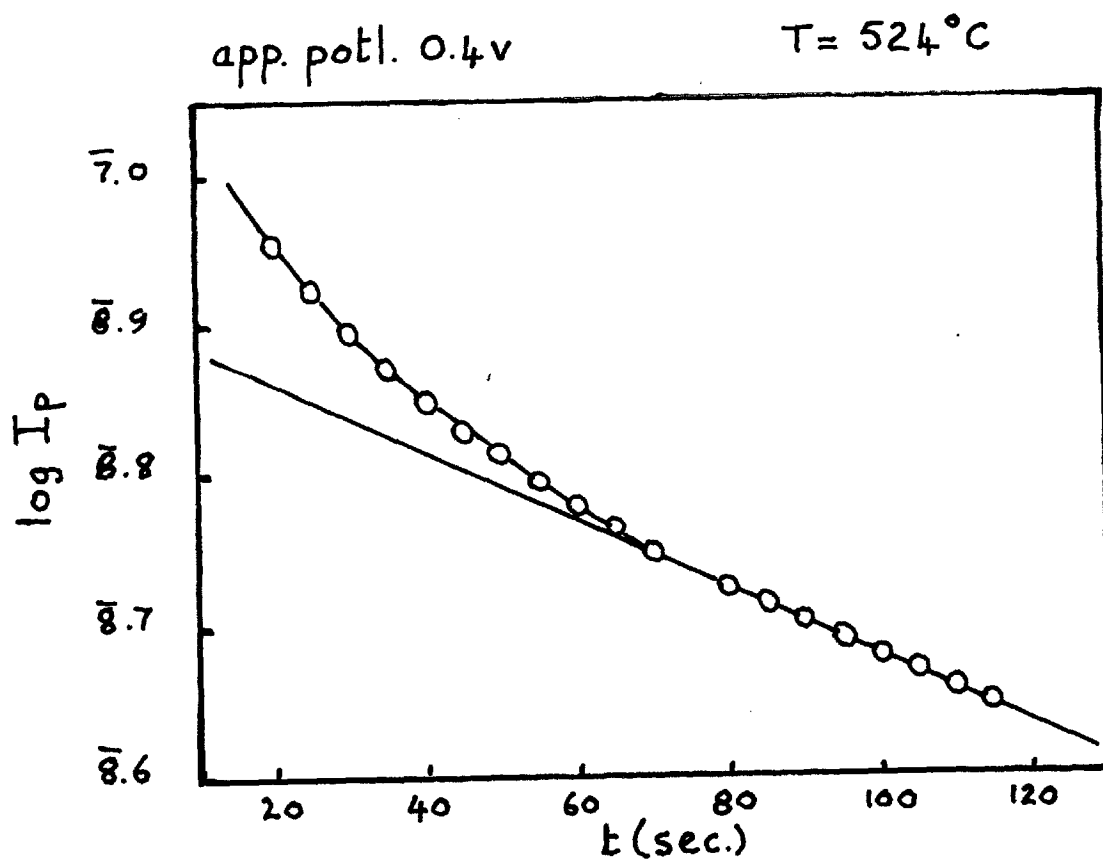


FIG. 26

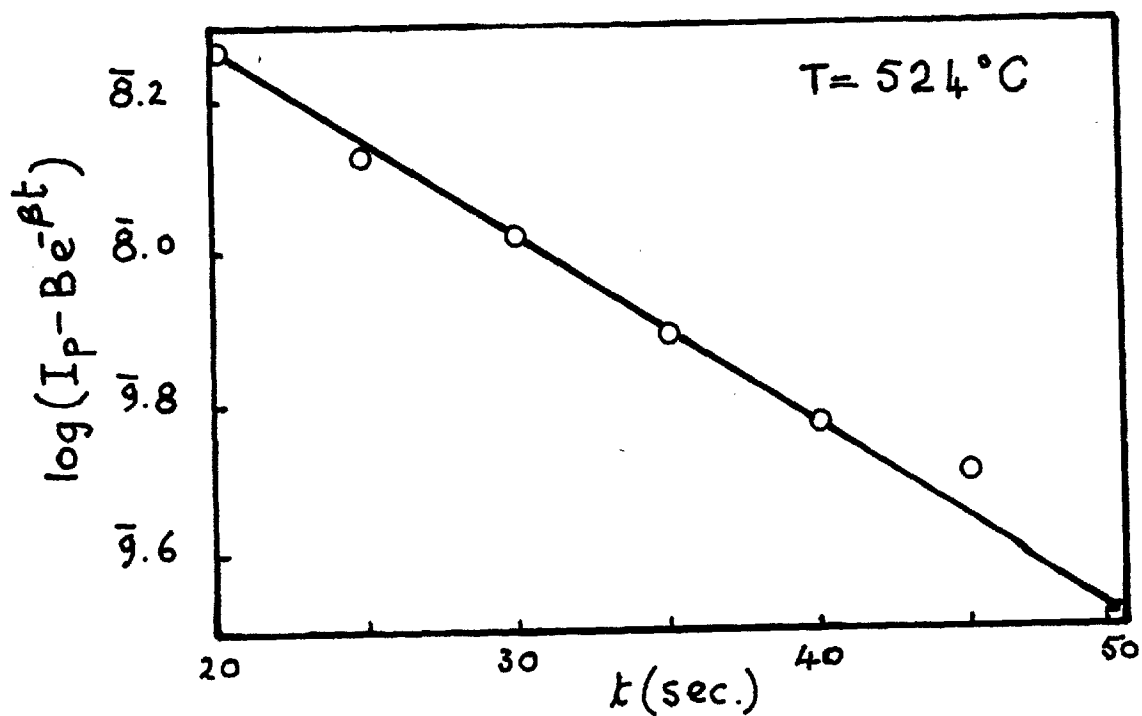


FIG. 27

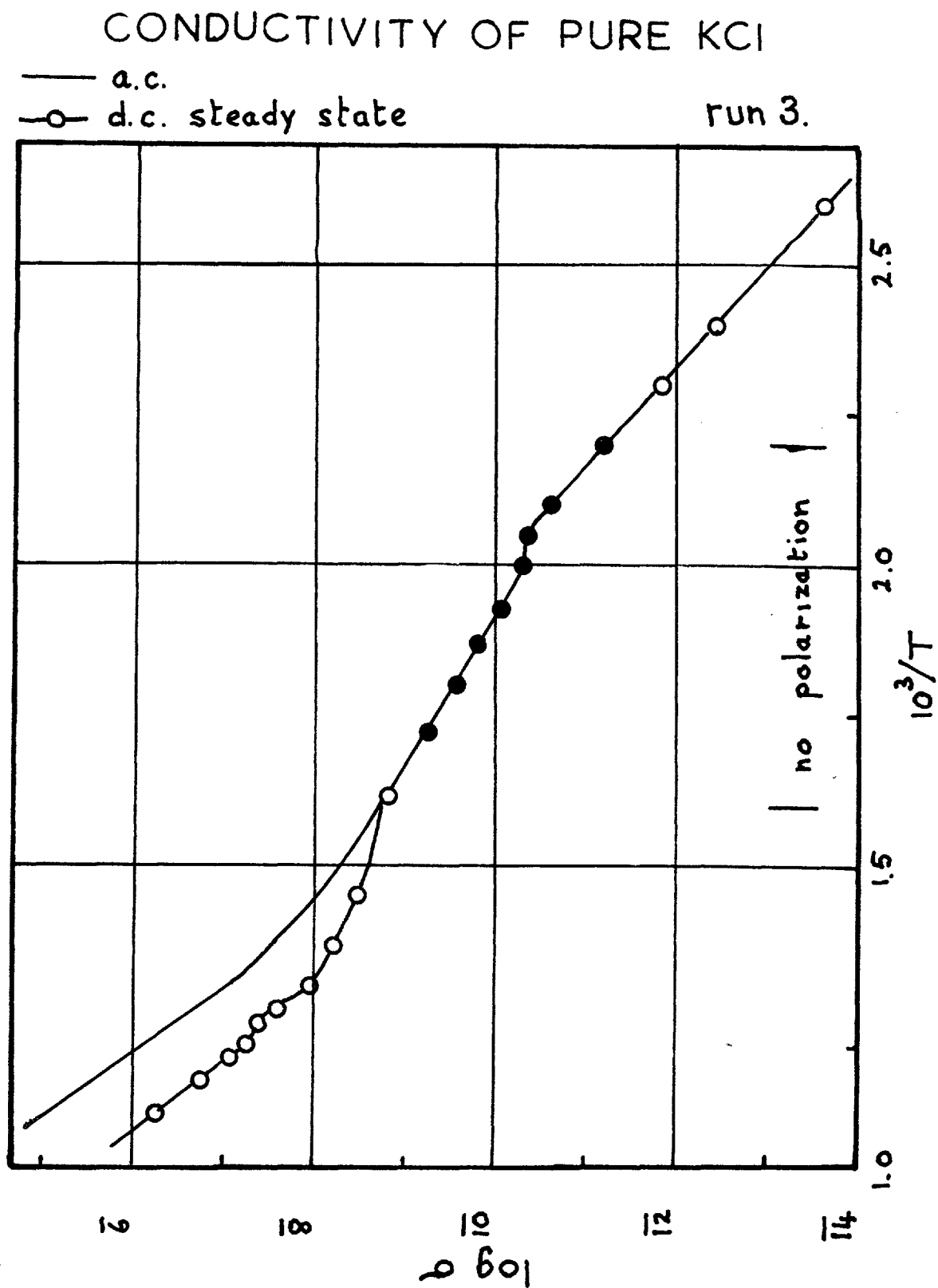


FIG. 28

STEADY STATE CONDUCTIVITY
PURE KCl

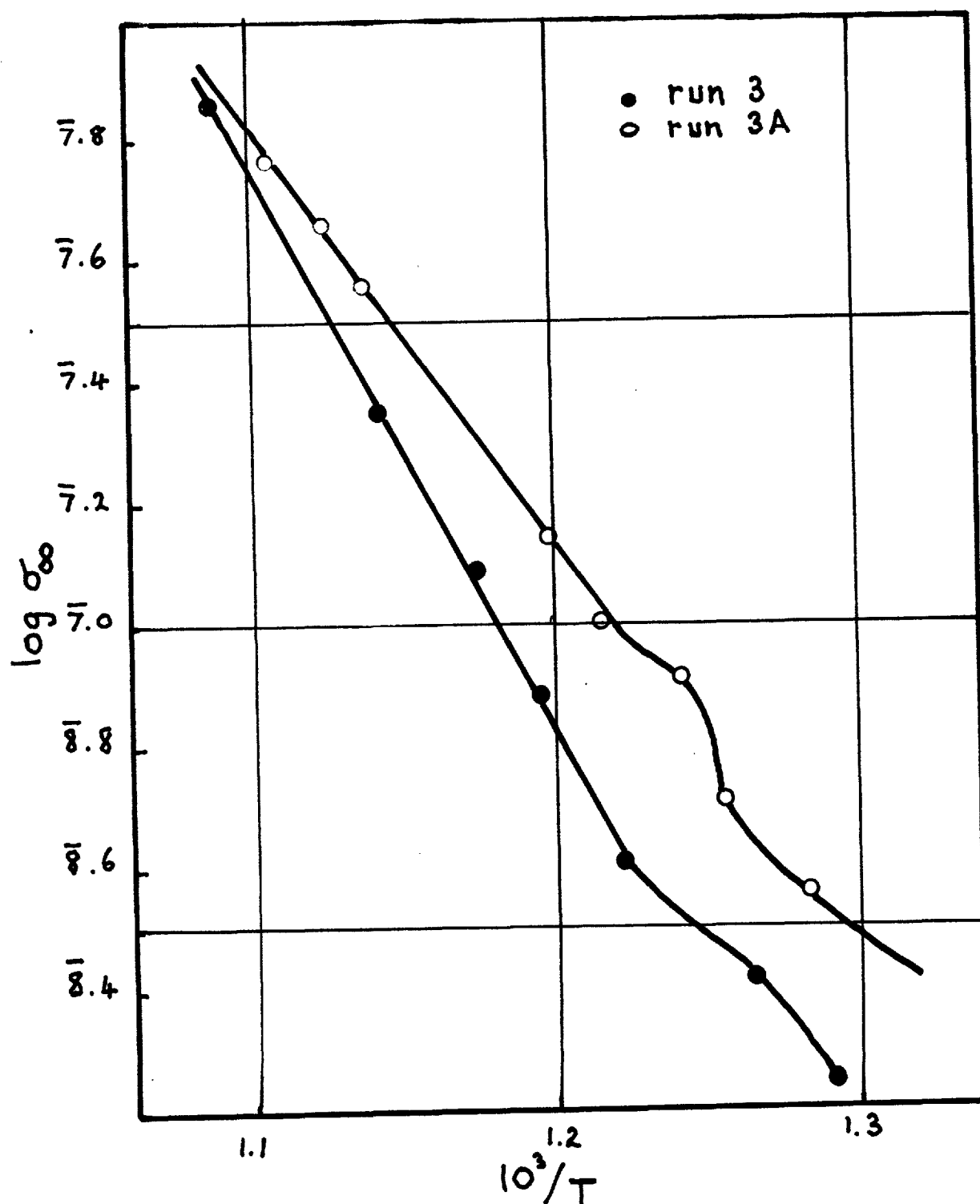


FIG. 29

STEADY STATE CONDUCTIVITY
OF $\text{KCl} + \text{SrCl}_2$, X5

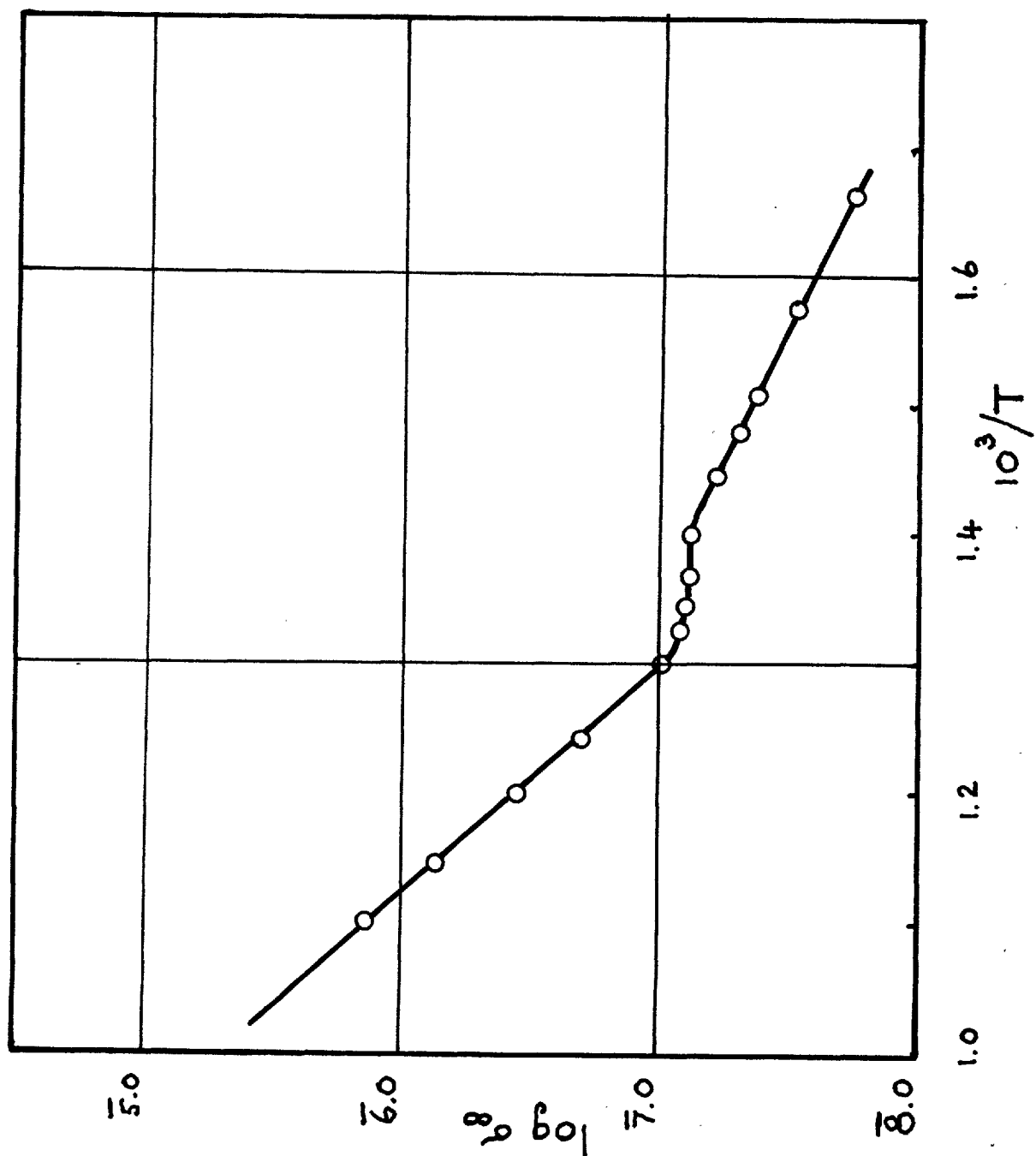


Table 11

Analysis of high temperature polarization in pure KCl

<u>Run 2</u>	$\beta \times 10^3,$ sec ⁻¹	α/β	Temp. °C	potl. diff. (volts)	
	4.08	7.03	617	0.04	A
	4.00	6.37	603	0.04	
⌘	2.50	-	587	0.03	
	3.50	4.97	565	0.10	
	3.20	8.59	534	0.30	B
	3.13	8.20	518	0.40	
	3.00	7.78	506	0.50	
	2.50	9.56	473	0.60	
	2.80	8.43	460	0.60	
	1.90	-	430	1.0	

⌘ Poor graph of $\log I_p$ versus t ; impossible to get $\log (I_p - Be^{-\beta t})$ versus t .

Between A and B the crystal was cooled to room temperature.

<u>Run 3</u>	5.14	5.06	647	0.03
	4.4	5.41	602	0.04
	4.52	5.98	579	0.05
	3.70	8.27	582	0.08
	5.03	7.67	583	0.10
	3.66	6.75	583	0.15
	3.54	5.85	583	0.18
	3.50	6.57	564	0.20
	2.60	7.15	545	0.40
	2.18	11.3	524	0.40
	2.40	16.68	519	0.50
	1.82	23.35	501	0.70
	1.48	16.9	477	0.80
	1.60	-	464	1.0
	3.68	6.68	570	0.25

Table 11 (continued)

	$\beta \times 10^3,$ sec^{-1}	α/β	Temp. °C	potl. diff. (volts)
<u>Run 3A</u>	5.3	9.1	631	0.04
	6.0	6.2	616	0.05
	5.5	6.4	606	0.06
	7.8	7.3	597	0.09
	5.7	6.7	583	0.08
	5.2	6.2	561	0.09
	4.6	5.4	550	0.10
	5.1	4.7	532	0.12
	4.0	6.4	523	0.15
	3.8	-	506	0.22
	2.3	-	487	0.35
 <u>Run 5</u>	34.0	5.1	688	0.01
	25.3	4.6	666	0.02
	14.5	5.3	641	0.025
	11.3	7.5	628	0.03
	14.3	5.4	609	0.035
	8.3	6.7	585	0.05
	7.7	7.3	579	0.06
	7.0	6.3	570	0.07
	5.0	7.2	552	0.09
	4.8	6.2	537	0.09

Table 12Analysis of high temperature polarization of the doped crystal,mole ratio $\text{SrCl}_2 = 119.8 \times 10^{-5}$

	$\beta \times 10^3,$ sec ⁻¹	α/β	Temp. ^o C	potl. diff. (volts)
<u>Run 11</u>	9.8	7.69	601	0.02
	7.04	7.77	562	0.03
	5.9	7.71	531	0.05
	4.4	9.3	495	0.07
	3.8	7.5	477	0.09
	3.8	7.9	477	0.10
	3.6	7.2	477	0.12
	3.5	8.28	477	0.15
	3.4	7.39	459	0.20
	2.8	6.6	440	0.30
	2.3	8.7	421	0.35
	1.8	9.4	399	0.35
	1.9	9.4	388	0.40
	1.6	8.7	361	0.45
	1.4	8.5	326	0.55

FIG. 30

DIAGRAMATIC CURRENT -
VOLTAGE CURVE, PURE KCl
 $T < 600^{\circ}\text{C}$

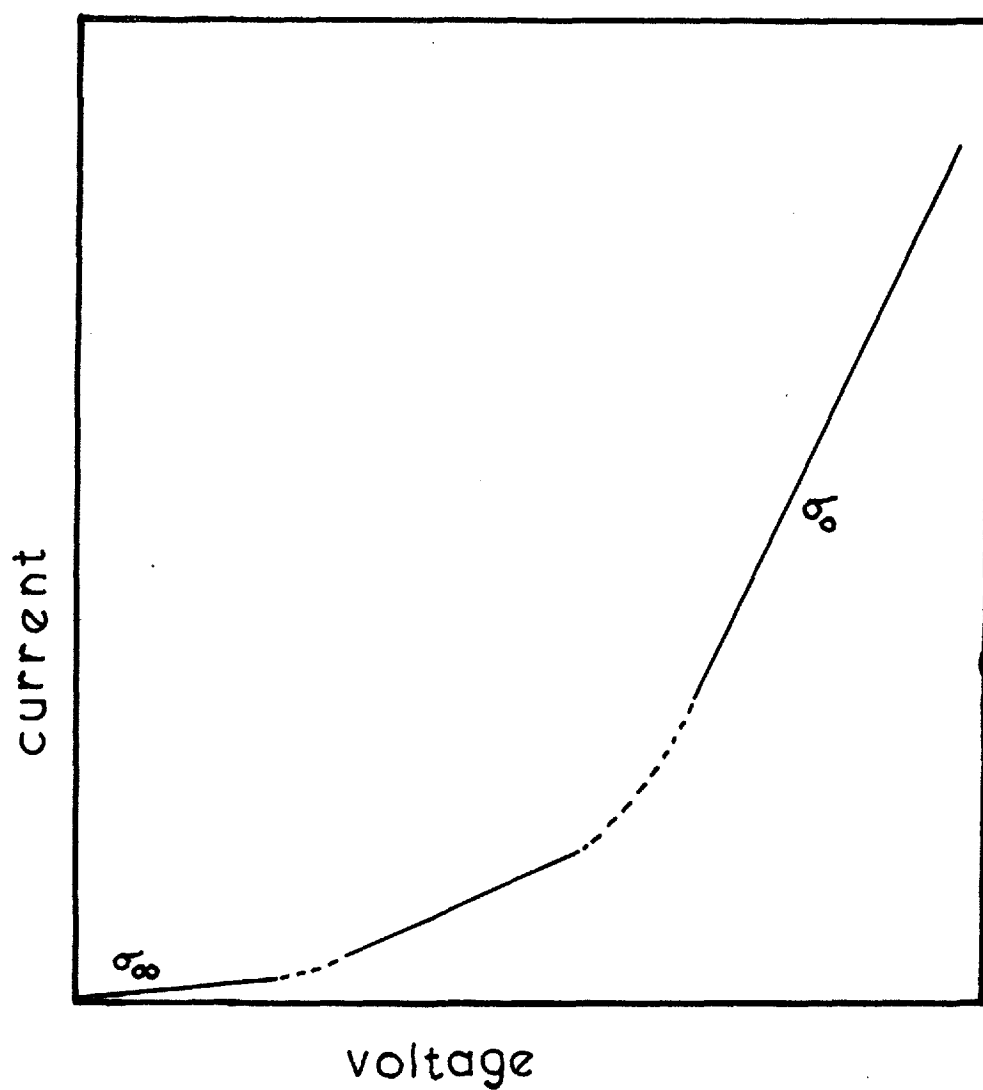
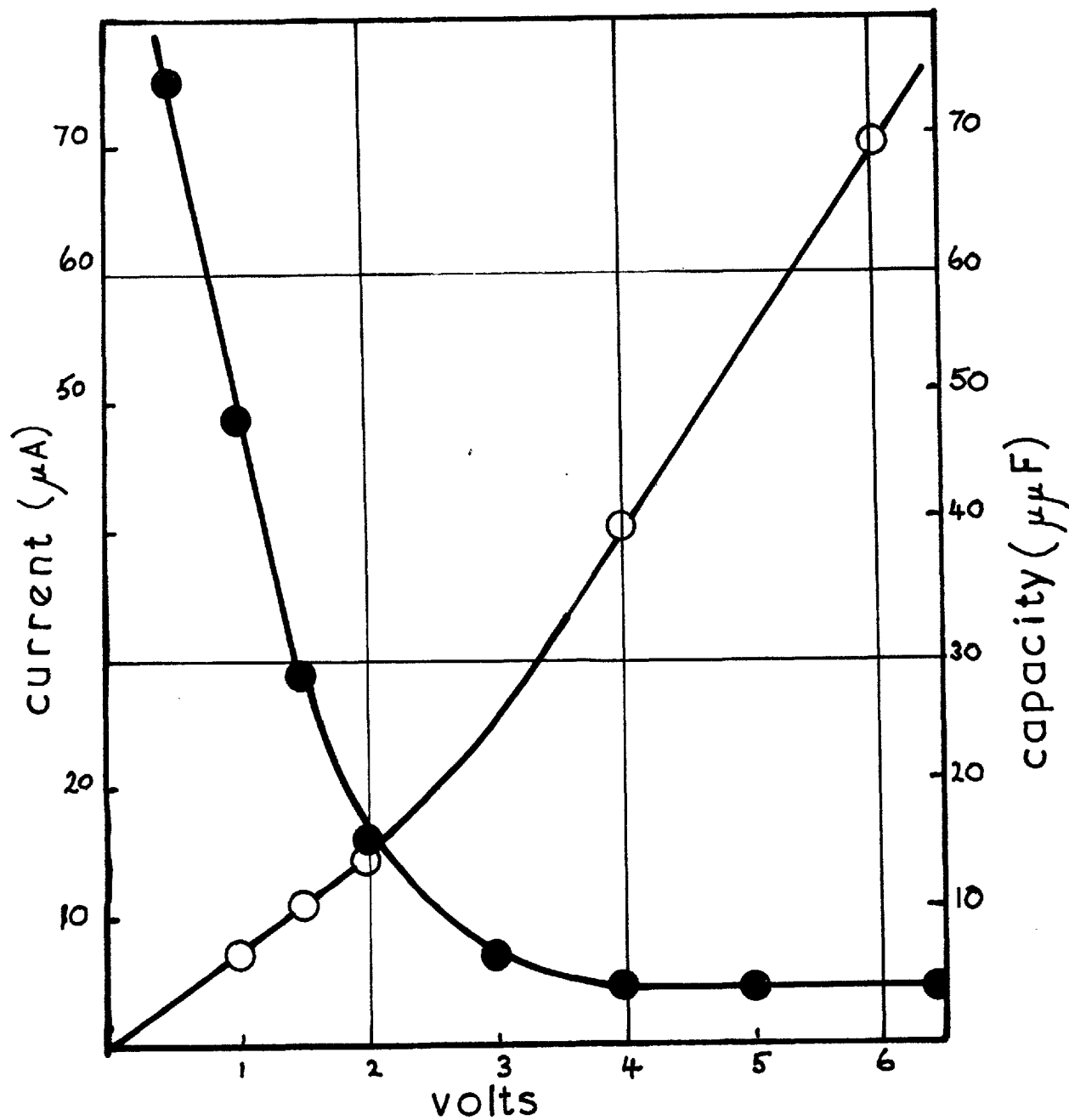


FIG. 31

CAPACITY-CURRENT-VOLTAGE

X 5

capacity at 300 c/s $T=660^{\circ}\text{C}$



3.5. Current-voltage dependence

The current-voltage characteristics were examined in run 5 for a pure Harshaw cleave of KCl. A diagramatic current-voltage curve is shown in fig.30. These curves exhibit three distinct regions. The linear region at low applied potentials obeys Ohm's law and the slope of this line corresponds to σ_{∞} . This then undergoes a smooth non-ohmic transition to a second linear region, where Ohm's law is again obeyed, which then changes over to the final linear region at higher field. The slope of this last linear region corresponds to σ_0 , or the a.c. conductivity. These measurements were repeated at 660°, 648°, 626°, 597°, 574° and 559°C and at all these temperatures they showed the same general behaviour, namely a transition from σ_{∞} to σ_0 as the voltage was increased. At 660° and 597°C the variation of the capacity at 300 c/s with the d.c. field was measured. The result is shown in fig.31.

Current-voltage curves for the doped crystals X 5 and X 4 were also determined. These curves were of the same general form as those observed for the pure crystal, again showing the transition from σ_{∞} to σ_0 with increasing voltage but without the intermediate linear region. At 602°C, with crystal X 5, the current produced from the applied voltage of 4.0 volts was initially 120 μ A. This rapidly increased until a steady value of 6000 μ A was reached after 10 minutes. The crystal was then short-circuited, but a period of 18 hours was required for the charge to decay.

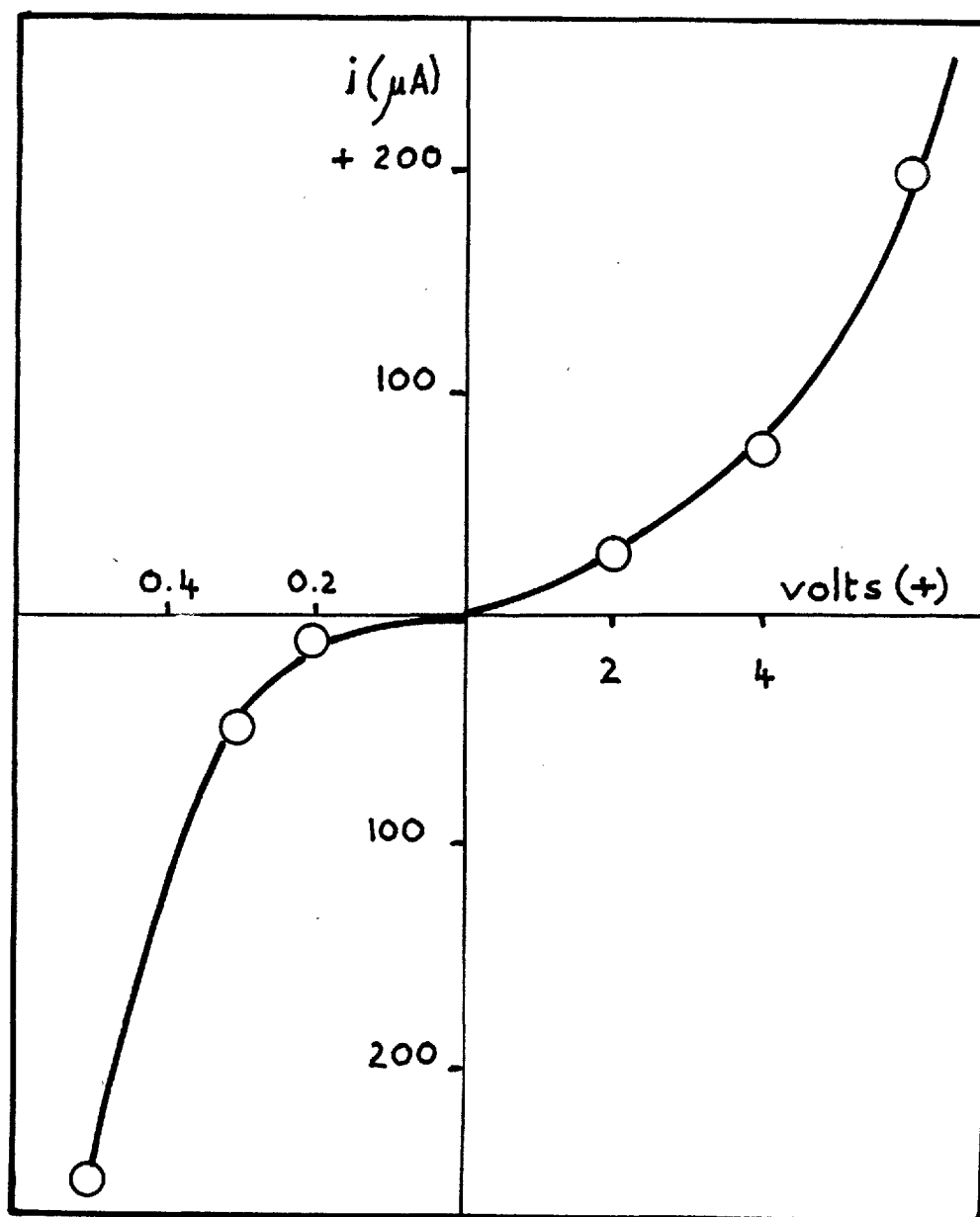
At 583°C a d.c. field was superimposed on a 300 c/s a.c. field and the variation of capacity with increasing d.c. field observed. At an applied potential of 8.0 V both the resistance and capacity of the crystal dropped to zero. Upon removing the d.c. field the resistance and capacity returned to their normal values after a period of 10-30 secs. The crystal was short-circuited for 30 minutes, and a potential difference of 6.0 V applied. Again both the resistance and capacity decreased to zero; but on switching the leads it was found that the resistance was higher than normal. After removing the crystal from the conductivity cell, a blue coloration near one face was clearly apparent while there was an overall yellow coloration.

This unusual behaviour was found again in crystal X 4, where at a temperature of 548°C with an applied d.c. voltage of 12 volts, i_0 increased rapidly from 800 μ A to 7000 μ A. On disconnecting the crystal, and connecting the positive terminal of an Avometer to the positive side of the crystal, the resistance was found to be very small (a few ohms). Switching the Avometer leads revealed again the presence of a high resistance (the order of $10^{10}\Omega$) in the opposite direction. After short-circuiting the crystal for 30-60 minutes, a potential of 48 volts was applied. This resulted in the same general behaviour. The field was then removed, and d.c. voltages applied in alternate directions, giving the current-voltage characteristics shown in fig.32.

CURRENT-VOLTAGE CURVE OF X4

The graph shows the relationship between current i (in μA) and voltage (in volts). The y-axis is labeled $i (\mu\text{A})$ and has markings at +200, 100, and 200. The x-axis is labeled volts (+) and has markings at 0.4, 0.2, 2, and 4. The curve is symmetric about the origin, indicating a non-linear relationship between current and voltage.

Volts (+)	Current i (μA)
0.4	200
0.2	100
0	0
2	100
4	200



3.6. Thermoelectric power measurements

Thermoelectric power measurements have been made on three cleaves of a Stockbarger-grown pure KCl crystal and on one cleave of the twice recrystallized Kyropoulos crystal. Platinum electrodes were used in all but run 2, when rhodium foil was used. In runs 1 and 2 thermopower measurements were the first measurements of any kind made on the crystal, and conductance measurements were only made after these had been completed. In these two runs the crystal was heated, over a period of five hours, to a temperature of 600°C and annealed overnight at this temperature. In run 1 with a temperature of 660°C and temperature gradient of 2°C an e.m.f. of 80 mV was found. After lowering the temperature to 600°C and annealing overnight and then raising the temperature to 650°C , an e.m.f. of 75 mV was found with a temperature gradient of 8°C . This e.m.f. decayed over a period of 3 hours to 11.3 mV which is the right order of magnitude for a thermoelectric e.m.f. After a further overnight anneal the e.m.f. was found to be constant at 11.00 mV for a gradient of 8°C corresponding to a thermoelectric power of 1.37 mV/deg. Thermopower measurements were then made, using the low resistance circuit, every 20° until this method proved impractical due to the high impedance of the crystal at the lower temperatures. Great care was always taken to avoid any polarisation effects. Thermal gradients of up to 20° per cm were used. Fig.33 shows a typical plot of potential difference against temperature gradient. The thermoelectric power of the crystal at a particular temperature is the slope of this

line. Values for run 1 are given in table 13. In all measurements the hot electrode was negative so that, on the convention adopted, θ is negative. Similarly in run 2, when rhodium electrodes were used, a large potential, which eventually decayed with time during annealing, was initially observed. By using the low resistance circuit, θ measurements down to 450°C were accomplished after which the conductance measurements were continued down to 80°C. Using the two amplifiers (run 2A) θ measurements were commenced again at 130°C and continued up to 190°C where, with a temperature gradient of 1°C, an e.m.f. of 368 mV was obtained. Over a period of 20 hours this only decayed to 247 mV. The temperature was then gradually raised to 600°C, checking the potential difference across the crystal at various intervals. The result is shown in fig.34. The crystal was then left to anneal overnight at 600°C, and it was then found to have a normal thermopower. Due to an electrical failure, the crystal was effectively quenched from 540°C to room temperature, but after reheating to this temperature the thermopower behaved normally.

In runs 3 and 20, a.c. conductance measurements were completed before thermopower measurements were made using the amplifier technique even at high temperatures. No spurious potentials were observed. All measurements were made with decreasing temperature, although several times when the temperature was cycled good reproducibility was obtained. The dependence of θ on reciprocal temperature for run 3 is shown in fig.35. The most striking features are the inverted 'lambda-point' in the region of 670°K and the rise in the value of θ at low

FIG. 33

PURE KCl, run 1

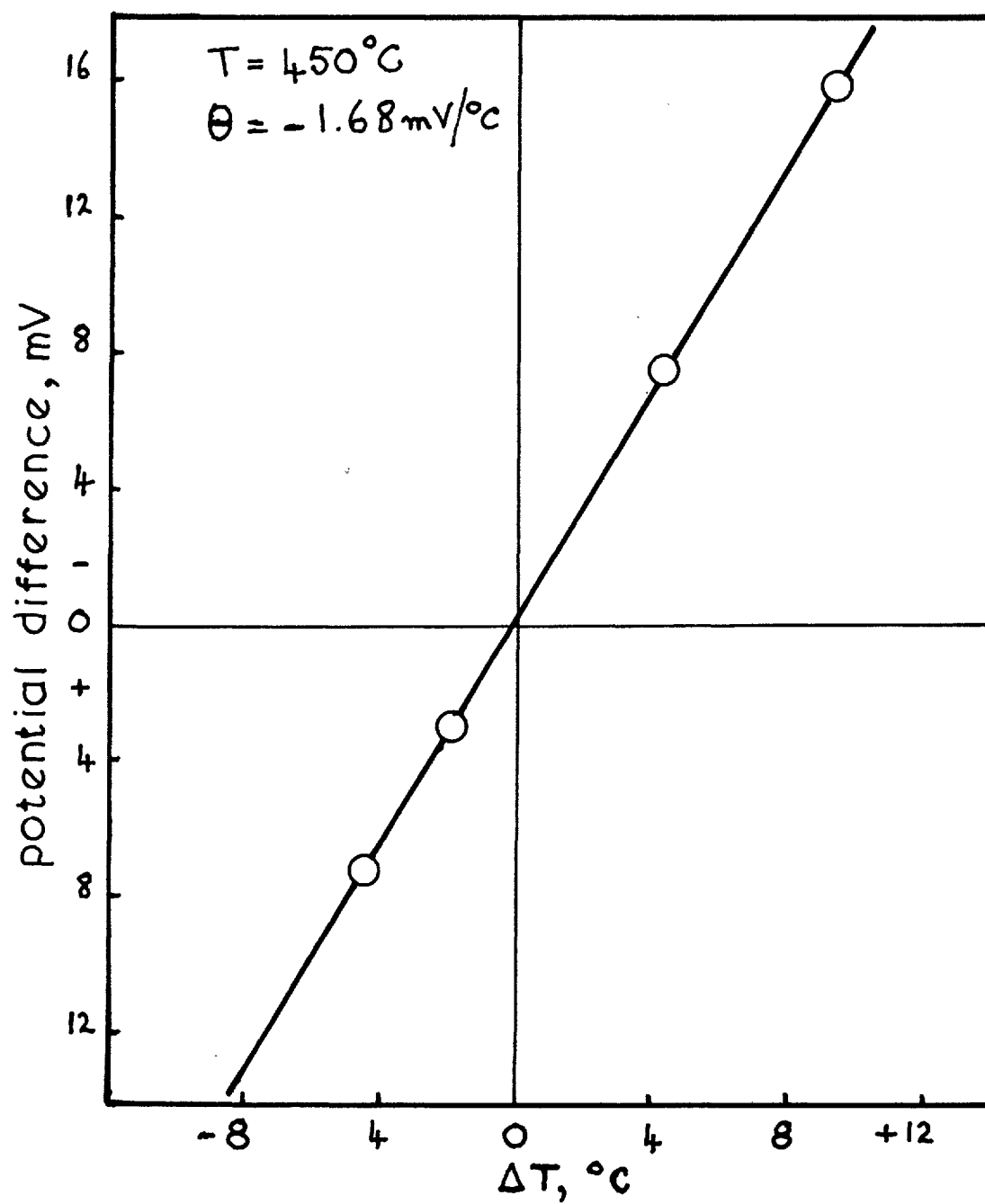


FIG. 34

DECAY OF POTENTIAL, ZERO ΔT

run, 2

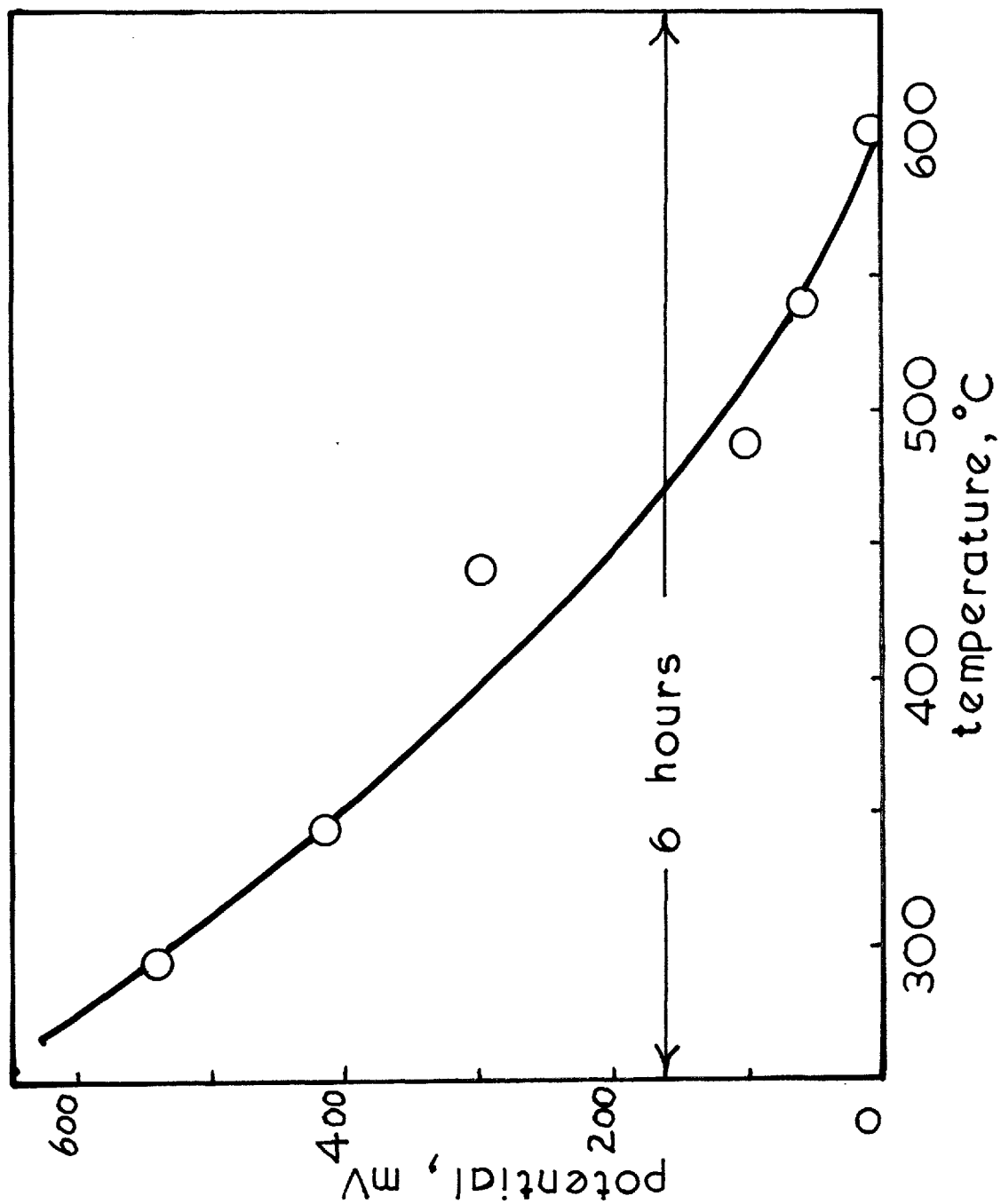


FIG. 35
THERMOELECTRIC POWER
OF PURE KCl, run 3

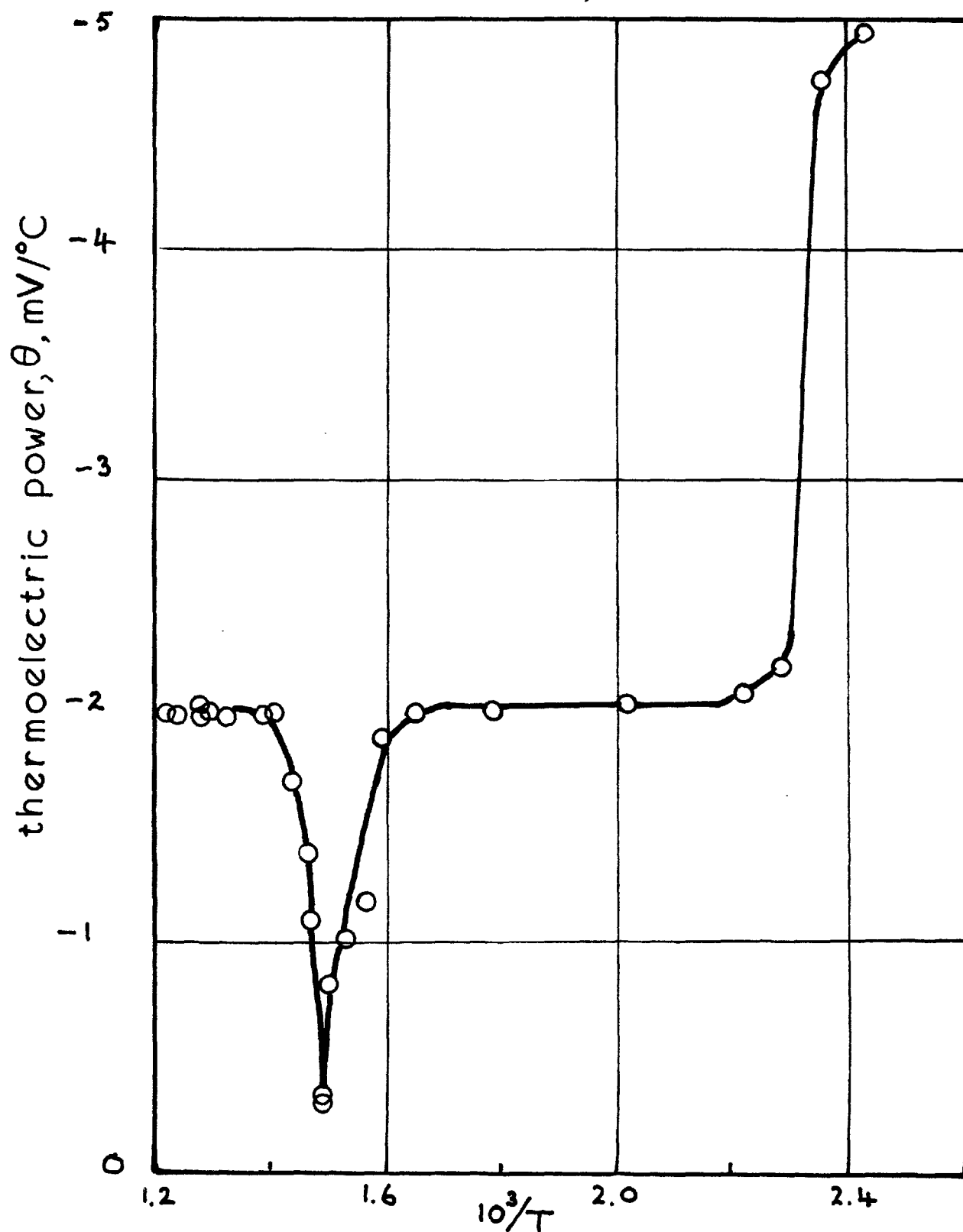


FIG. 36

THERMOPOWER OF Ag DOPED KCl.

run. 9

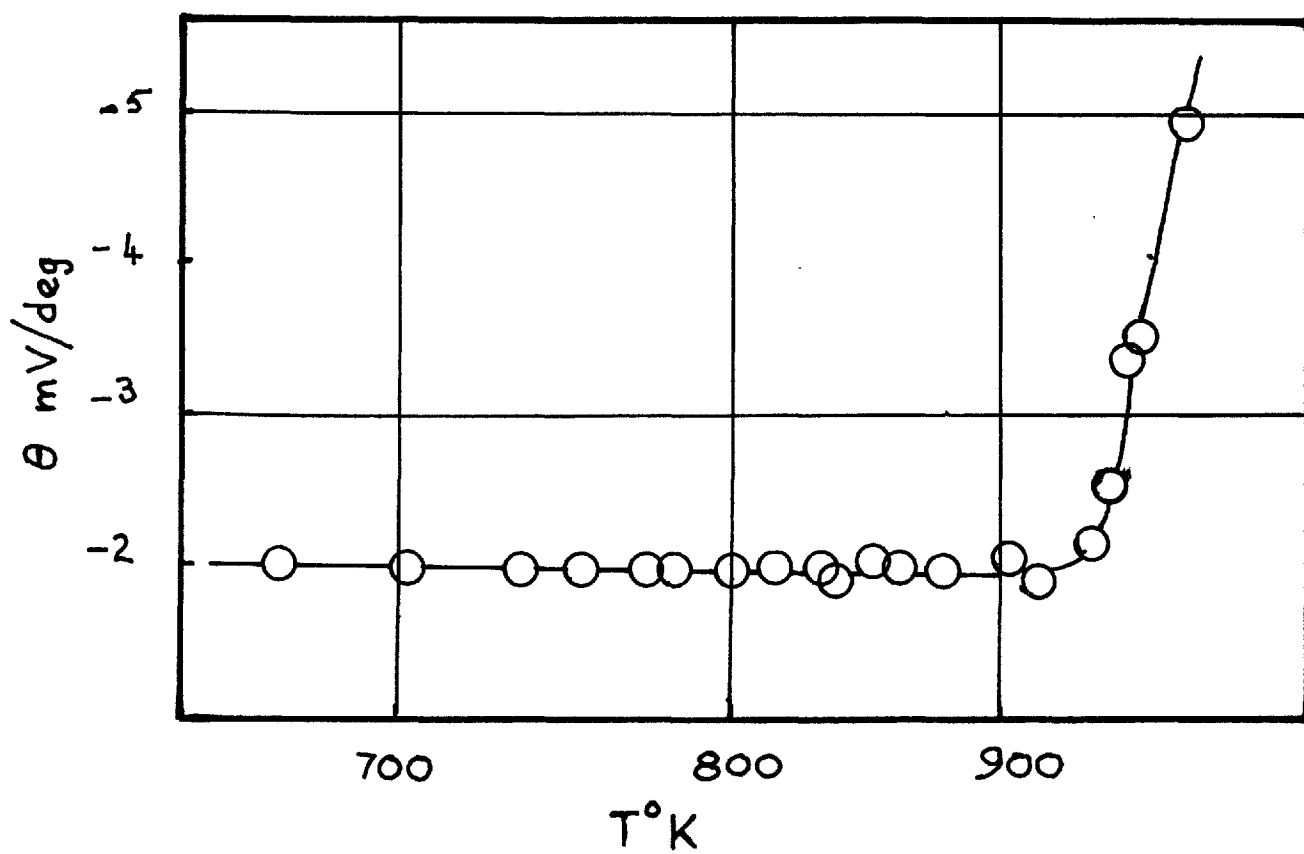
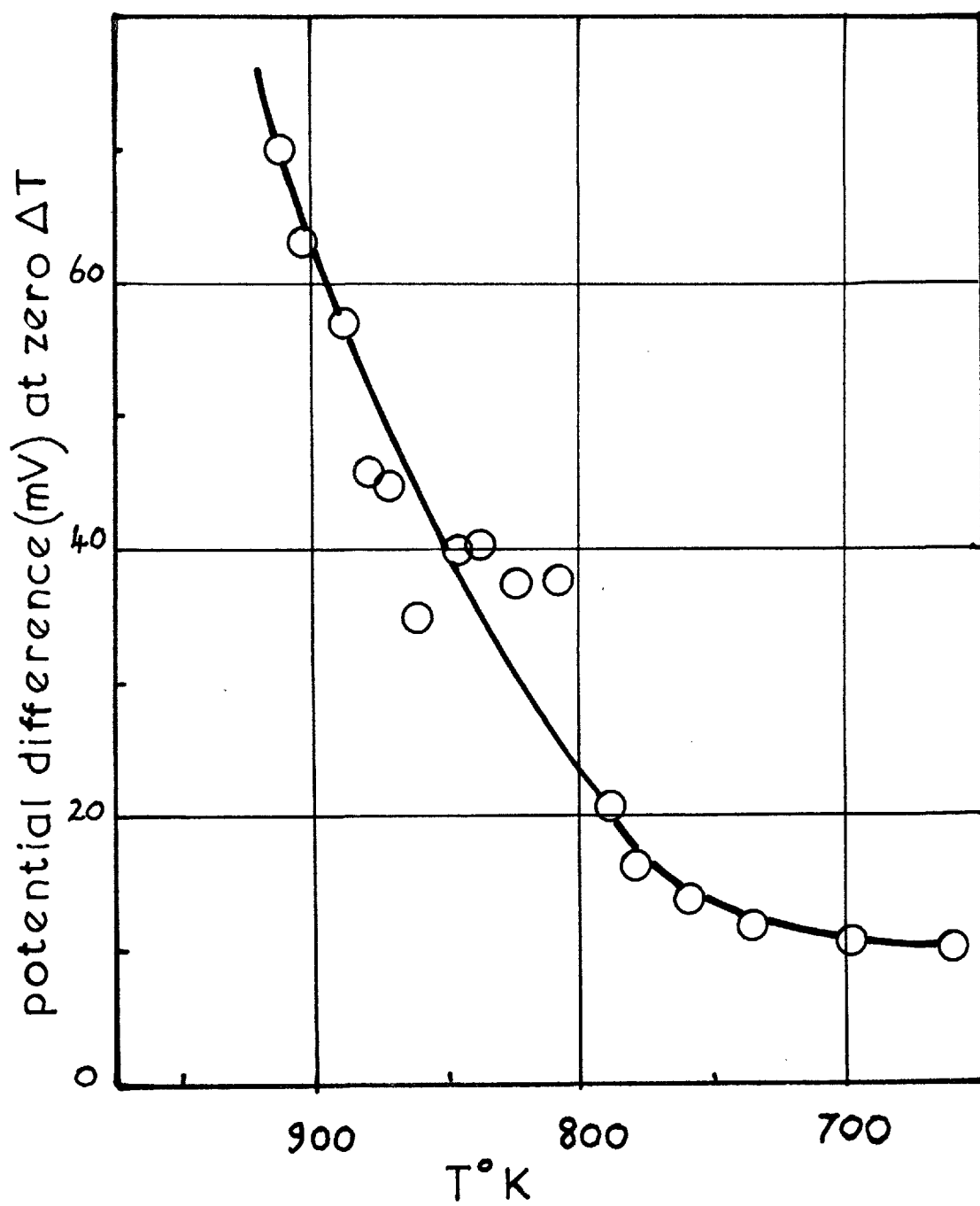


FIG. 37

Ag DOPED KCl, run 9

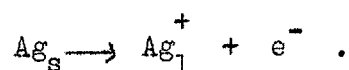


temperatures. The temperature dependence of Θ was similar for all the pure crystals.

Thermopower measurements were also carried out on a strontium-doped crystal, containing 19.8×10^{-5} mole ratio of Sr^{2+} . The graphs of e.m.f. against temperature gradient were again accurately linear, but the graph of Θ against $1/T^\circ\text{K}$ showed no lambda-point (cf. fig.35) and the sudden increase in Θ occurred at a very much higher temperature, 750°K as compared with 450°K .

An attempt was made to measure the thermopower of an additively coloured Harshaw crystal, containing initially 1.8×10^{16} F-centres per cm^3 , at high temperatures. Unfortunately, the potassium evaporated from the crystal as shown by a deposit of potassium on the cool outlet tube from the cell. To overcome this difficulty, an attempt was made to measure Θ at low temperatures but the d.c. conductivity of the crystal was not constant (at a fixed temperature) due probably to the lack of equilibrium. This experiment was, therefore, reluctantly abandoned.

To introduce additional electrons into the crystal a film of silver was evaporated on to the two large faces of the crystal, which was then annealed at 700°C for 3 days, after which time the resistance was constant. The a.c. conductivity was then measured and from this it was inferred that the following reaction had taken place to some extent:



Thermopower measurements were then made and the graph of Θ against T is shown in fig.36. From the graphs of e.m.f. against ΔT it was observed that, for zero ΔT , there was a considerable e.m.f. which varied with temperature in the manner shown in fig.37.

A complete summary of measurements of Θ as a function of temperature is given in tables 13 to 18. The electrodes were platinum, unless otherwise stated.

Table 13

Run 1.

Pure Stockbarger KCl

$T^{\circ}K$	$-\Theta(mV/deg)$	$T^{\circ}K$	$-\Theta(mV/deg)$
933	1.66	803	1.26
908	1.60	797	1.50
878	1.68	778	1.48
848	1.60	773	1.61
823	1.56	768	1.65
803	1.40	733	1.64
803	1.40	723	1.68

Table 14

Run 2.

Pure Stockbarger KCl, rhodium electrodes

$T^{\circ}K$	$-\Theta(mV/deg)$	$T^{\circ}K$	$-\Theta(mV/deg)$
924	1.30	806	1.10
962	1.35	799	1.18
891	1.34	787	1.30
863	1.30	785	1.24
835	1.27	755	1.35
820	1.18	720	1.36
807	1.10		

Table 14Run 2A.Amplifier technique

$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$	$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$
903	1.37	795	1.34
885	1.33	784	1.35
865	1.36	733	1.35
841	1.32	679	1.34
837	1.35	593	1.36
832	0.825	461	1.95
823	0.96	450	2.36
820	1.18	435	4.50

Table 15Run 3.Pure Stockbarger KCl

$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$	$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$
400	5.25	810	1.90
422	4.75	830	1.90
436	2.20	832	1.94
706	2.04	844	1.92
726	2.22	864	1.94
760	2.02	865	1.92
779	2.07	897	1.92
789	1.82	899	1.96
792	1.83	909	1.84
805	1.89	931	1.46

Table 16Run 9.Ag film

	T°K	-θ(mV/deg)	T°K	-θ(mV/deg)
	924	3.8	810	2.0
	913	1.9	791	2.1
	904	2.1	782	2.0
⌘	888	5.8	759	2.0
	880	2.0	738	2.0
	870	2.0	701	2.0
	859	2.1	657	2.04
	847	1.9	937	3.4
	840	2.0	930	2.2
	825	2.05	947	3.6
			935	2.6
⌘	Result doubtful		959	5.0

Table 17Run 11.KCl + SrCl₂ (mole ratio 119.8 x 10⁻⁵)

	T°K	-θ(mV/deg)	T°K	-θ(mV/deg)
	930	1.36	804	1.38
	913	1.42	793	1.39
	897	1.41	766	1.46
	879	1.40	756	1.60
	863	1.41	730	2.60
	842	1.40	930	1.40
	813	1.39		

Table 18Run 20. Twice recrystallized Kyropoulos KCl

$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$	$T^{\circ}\text{K}$	$-\theta(\text{mV/deg})$
958	1.45	755	1.68
928	1.50	875	1.53
943	1.47	922	1.49
910	1.50	830	1.46
888	1.52	820	1.28
873	1.52	780	1.55
860	1.55	770	1.60
850	1.56	725	1.70
838	1.53	675	1.77
823	1.38	610	1.88
808	1.37	525	2.05
798	1.41	430	2.33
787	1.47	400	4.0

The data are recorded in the order in which measurements were taken.

4. Discussion

4.1. Properties of defects from a.c. conductance

The agreement between the conductivity slopes ($\pm 1\%$) for the pure crystals is, as would be expected, quite good. The disturbing feature however is that the Harshaw crystals and the run 3 Stockbarger crystal show a very much smaller slope (table 5). It is anticipated that this may be due to the unavoidable presence of impurities introduced into the Harshaw crystals during manufacture. The Stockbarger crystal of run 3 gave an activation energy of 1.75 eV, whereas the same crystal after an anneal of 10 weeks gave an activation energy of 1.90 eV, run 3A. This difference in slope, after the long anneal, is thought to be due to the precipitation of the original impurities thus leaving a relatively pure crystal. The mean value of 1.89 eV agrees quite well with the values obtained by Allnatt and Jacobs (1962,b) and Phipps and Partridge (1929).

In principle, there is a contribution to the curvature of the plots of $\log \sigma T$ against $1/T$ at high temperatures from the thermal expansion of the crystal. Assuming a crystal of thickness ℓ and cross sectional area a with equal sides d , then

$$4.1.1. \quad \sigma = \frac{1}{R} \cdot \frac{\ell}{a}$$

whence

$$4.1.2. \quad \frac{\partial \ln(1/R)}{\partial (1/T)} = \frac{\partial \ln \sigma}{\partial (1/T)} + \frac{\partial \ln(a/\ell)}{\partial (1/T)} .$$

If the coefficient of linear expansion is α , then

$$\ell = \ell_0 (1 + \alpha T)$$

$$d = d_0 (1 + \alpha T)$$

$$\text{and } d^2 \simeq d_0^2 (1 + 2\alpha T + \dots) .$$

As

$$4.1.3. \quad \ln(d^2/\ell) = \ln\left(\frac{1+2\alpha T}{1+\alpha T}\right) + \ln\left(\frac{d_0^2}{\ell_0}\right),$$

$$4.1.4. \quad \frac{\partial \ln(\ell/d^2)}{\partial (1/T)} \simeq -\alpha T^2,$$

and it is apparent that

$$4.1.5. \quad \frac{\partial \ln(1/R)}{\partial (1/T)} = \frac{\partial \ln \sigma}{\partial (1/T)} - \alpha T^2.$$

The second term supplies a contribution to the curvature as the temperature is raised, but this effect is negligible in comparison to the observed curvature which we attribute to the onset of anion conduction.

The disturbing feature about the calculated transport numbers is the wide discrepancy between the results for the Kyropoulos and Stockbarger crystals. A possible explanation is that the Stockbarger crystal was grown in a silica vessel and may thus be unintentionally doped with SiO_2^{2-} ions. If this is so, the SiO_2^{2-} ions may trap anion vacancies by electrostatic attraction in the usual way, or even by 'bridging' two anion sites, thus reducing the anionic contribution to the conduction.

A further interesting feature of the transport number data is that the limiting value of t_1 does not appear to be unity. This discrepancy is not due to experimental error as Kerkhoff (1951) has shown that a limiting value of 0.96 for t_1 may be raised to 0.99 (in the temperature range 430 - 590°C) in crystals doped with 20×10^{-5} mole ratio CaCl_2 . The conclusion to be drawn (Allnatt and Jacobs, 1962,b) is that there must be a small but finite electronic

contribution to the conductivity. As shown in section 3, there is general agreement between the transport number determinations for different crystals, but the absolute agreement is very poor.

From equations 1.4.2, 3.1.1 and 3.1.3, the cation conductance is given by

$$4.1.6. \quad \sigma_1 T = (4e^2 a^2 N \nu / k) \exp [(\Delta s_1 + \frac{1}{2} s)/k] \exp [-(\Delta h_1 + \frac{1}{2} h)/kT] .$$

Numerical values of these parameters are given in table 19. These were calculated from the slopes and intercepts of the linear portions of the plots of $\log \sigma_1 T$ against $1/T$, using the values

$$N = 1.615 \times 10^{22} \text{ cm}^{-3}$$

$$\text{and } \nu = 4.51 \times 10^{12} \text{ sec}^{-1} .$$

Table 19

Source (run)	$\Delta h_1 + \frac{1}{2} h$ eV	$\Delta s_1 + \frac{1}{2} s$ 10^{-5} eV/deg
Stockbarger (1)	1.87	0.330
Stockbarger (3A)	1.90	0.329
Kyropoulos (19)	1.90	0.343
Kyropoulos (20) 'recrystallised'	1.91	0.346
Harshaw (5)	1.76	0.309
Harshaw (10)	1.76	0.309
Stockbarger (3)	1.75	0.288
Stockbarger (13) (SO ₄ ²⁻ doped)	1.74	0.293
Stockbarger (14) (SO ₄ ²⁻ doped)	1.81	0.295

In an attempt to increase the anion conductivity, a crystal containing 200×10^{-5} mole ratio of K_2SO_4 was grown by the Stockbarger method. However, as is seen from fig.38 the intrinsic conductivity exhibits no curvature at all, thus indicating that the anion contribution has been suppressed rather than increased. This crystal, which was beautifully clear, showed the infra-red absorption peaks attributed by Coker et al. (1961) to the SO_4^{2-} ion dissolved in the KCl lattice (see fig.39). We thus concluded that SO_4^{2-} ions were present in the crystal. If the SO_4^{2-} ions had been substituted into the Cl^- sub lattice then for every SO_4^{2-} ion incorporated one extra anion vacancy would have been formed; this could not have been the case since the a.c. conductivity showed a suppressed anion contribution with a conductivity equal to that of the pure Harshaw crystals. We thus conclude that the SO_4^{2-} ion either 'bridges' two anion sites or binds the extra anion vacancy very tightly indeed. Since the anion contribution to the total conductivity of a pure crystal is in any case small, the overall conductivity of the SO_4^{2-} -doped crystals is comparable to that of a pure crystal. The structure-sensitive conductivity for this doped crystal was lower than that for the Harshaw crystals, as would be expected if the SO_4^{2-} 'pair' with the normal M^{++} impurity ions. A similar effect in the structure-sensitive region has been observed by Gruzensky and Scott (1961). They however observed a conductivity hysteresis, which was not found in the present work. It is possible that this effect was caused by their use of evaporated silver electrodes and also applied d.c. voltages between 1.6 and 930 V (see section 3.4).

FIG. 38

SO₄²⁻ DOPED KCl. run 14

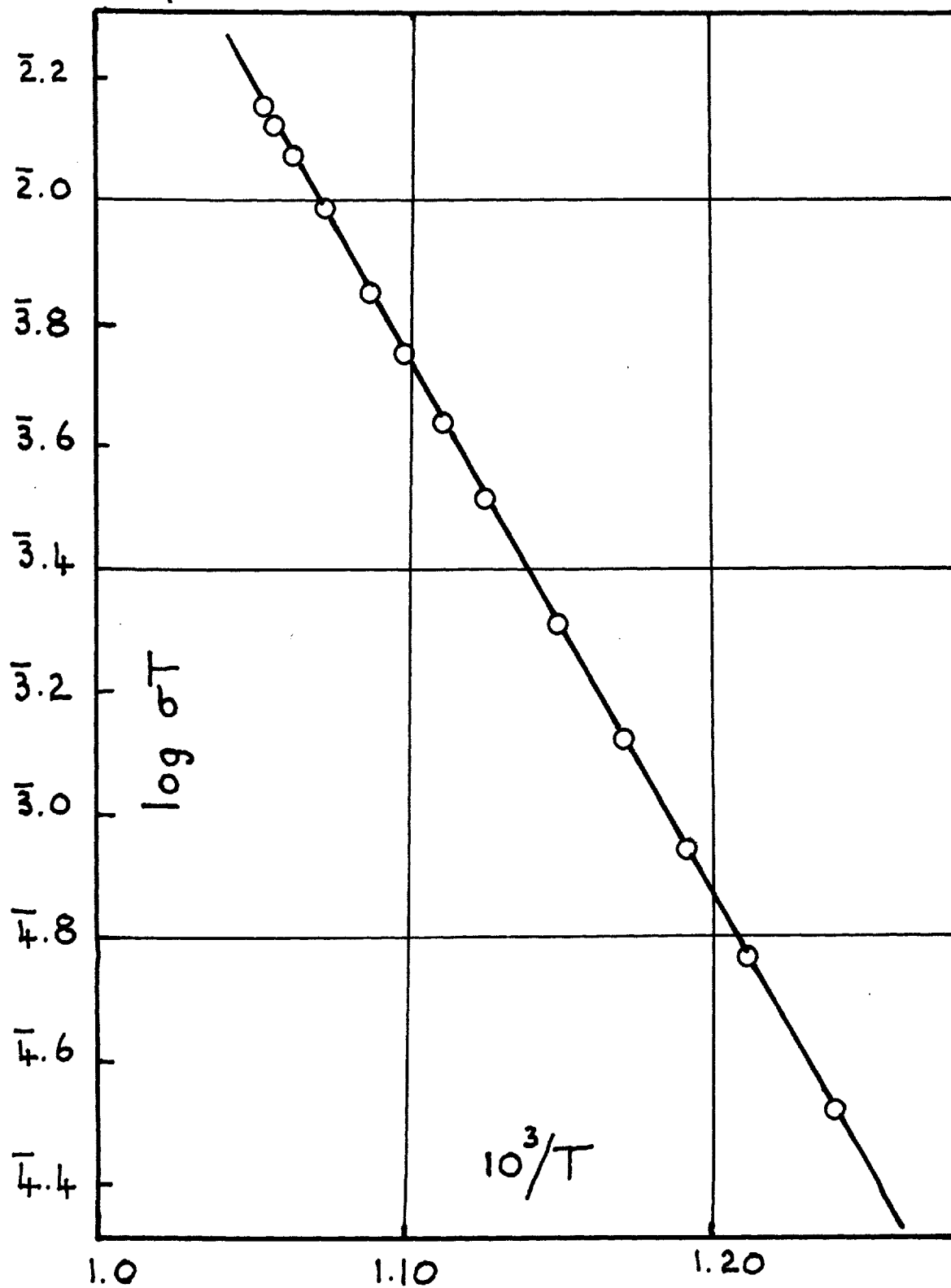
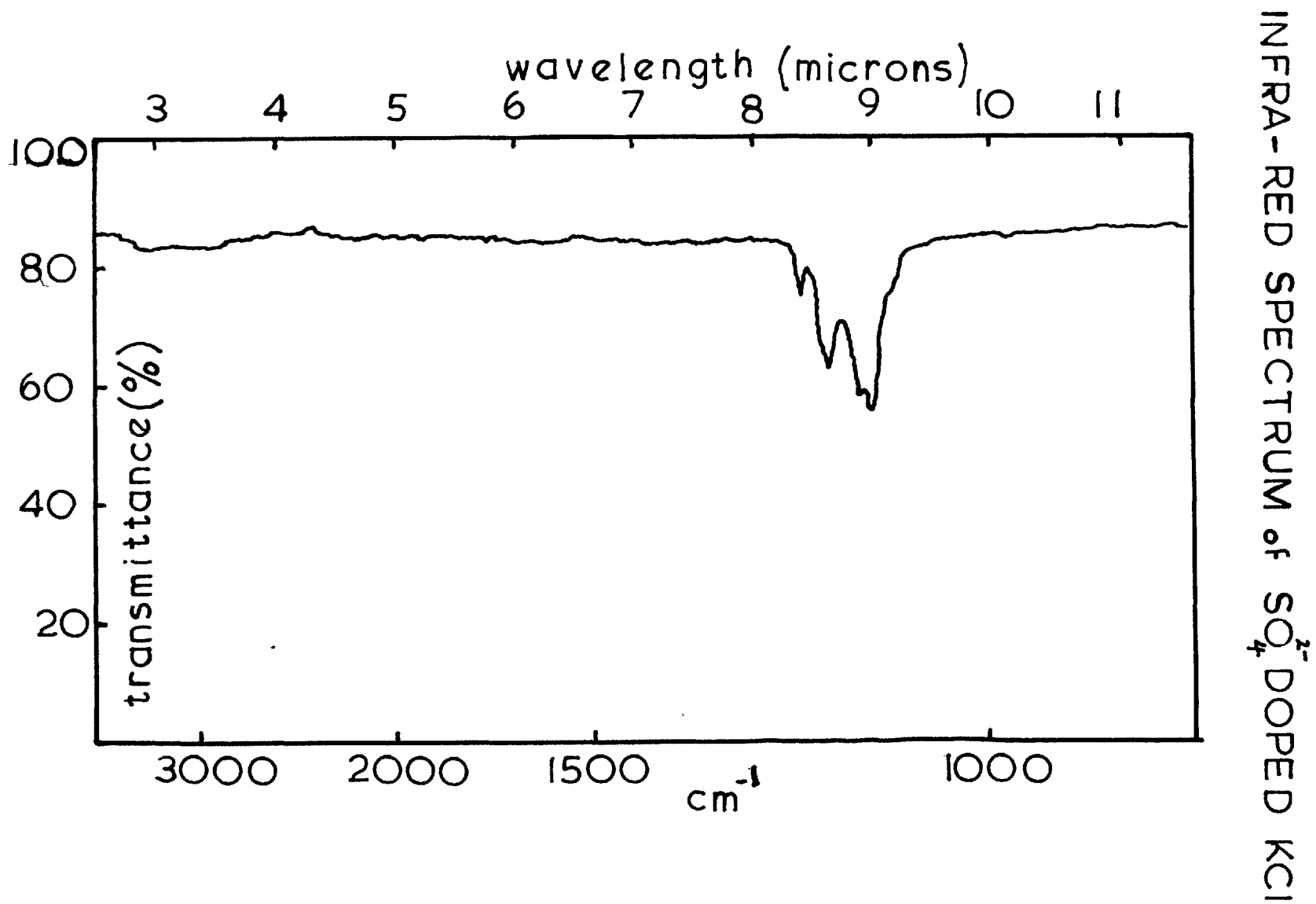


FIG. 39



The curvature of the $\log \sigma T$ versus $1/T$ plots for the Sr^{2+} doped crystals suggests that association effects are occurring. It is noticeable on the large-scale version of fig.16 that, at the highest temperatures, the curvature disappears indicating that association is no longer present. The conductivity-concentration isotherms for the five impure crystals should be smooth curves (slightly concave towards the concentration axis) if association is occurring but, as is evident from fig.40, these isotherms exhibit a 'kink' at the lowest impurity concentrations. We thus conclude that a portion c' of the added impurity concentration c does not produce the equivalent number of mobile cation vacancies. Hence the active concentration of strontium ions is $c - c'$. The calculated quantity c' (found, as indicated in fig.40, by the lateral displacement of the experimental points from the isotherms) is shown as a function of T^{-1} (c constant) and c (T constant) in figs.41 and 42 respectively. That part of the added Sr^{2+} which is effective in producing additional cation vacancies, $c - c'$, is also shown as a function of concentration and temperature in figs. 43 and 44 respectively. The significance of acknowledging the presence of a non-contributory c' is important in the application of the association theory, although the origin of c' is rather obscure. The one definite fact about c' is that it is related to unavoidable impurities present in the crystal. Etzel and Patterson (1958), have shown that any OH^- present in an alkali halide crystal will form complexes with some of the added Sr^{2+} ions. This effect would be expected to be small in the present situation as we went to great pains to remove any OH^- during the preparation of the

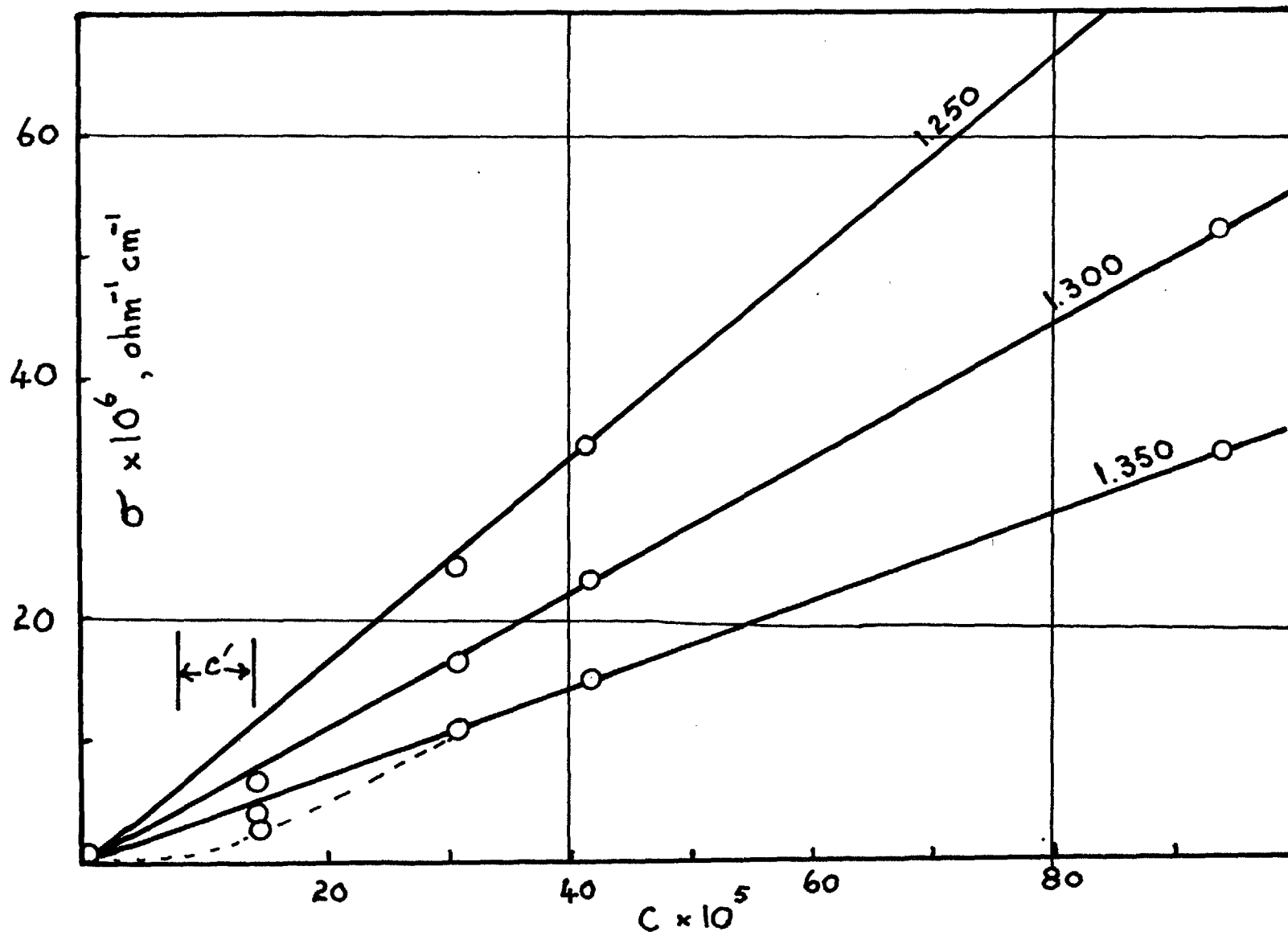


FIG.40

FIG. 41

INACTIVE CONCENTRATION, c' vs T^{-1}

ϕ 14.4×10^{-5} mole ratio
 analysed concs., $\circ$ 31.0 " " "
 $\bullet$ 41.8 " " "

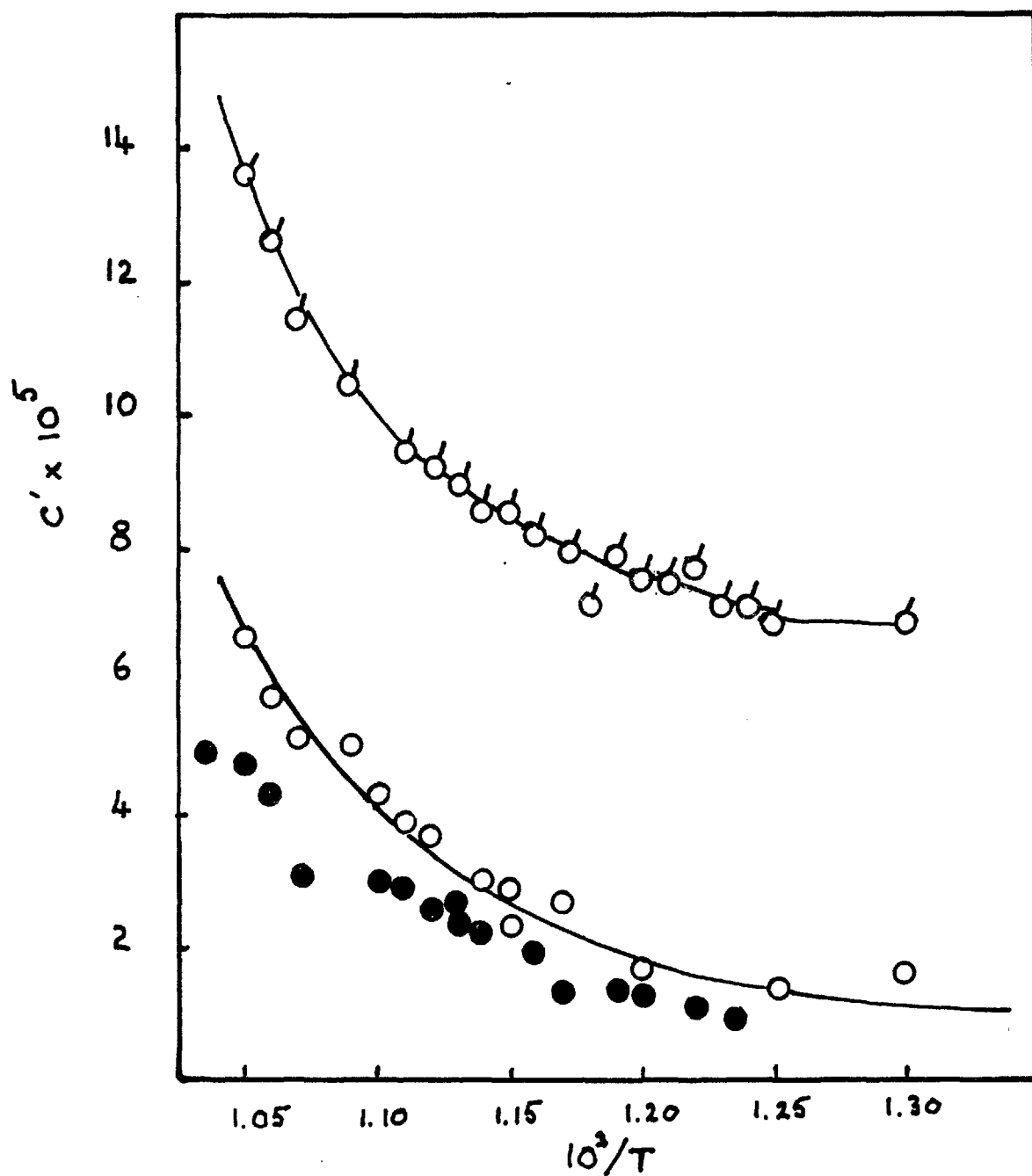


FIG.42
DEPENDENCE OF C' ON C

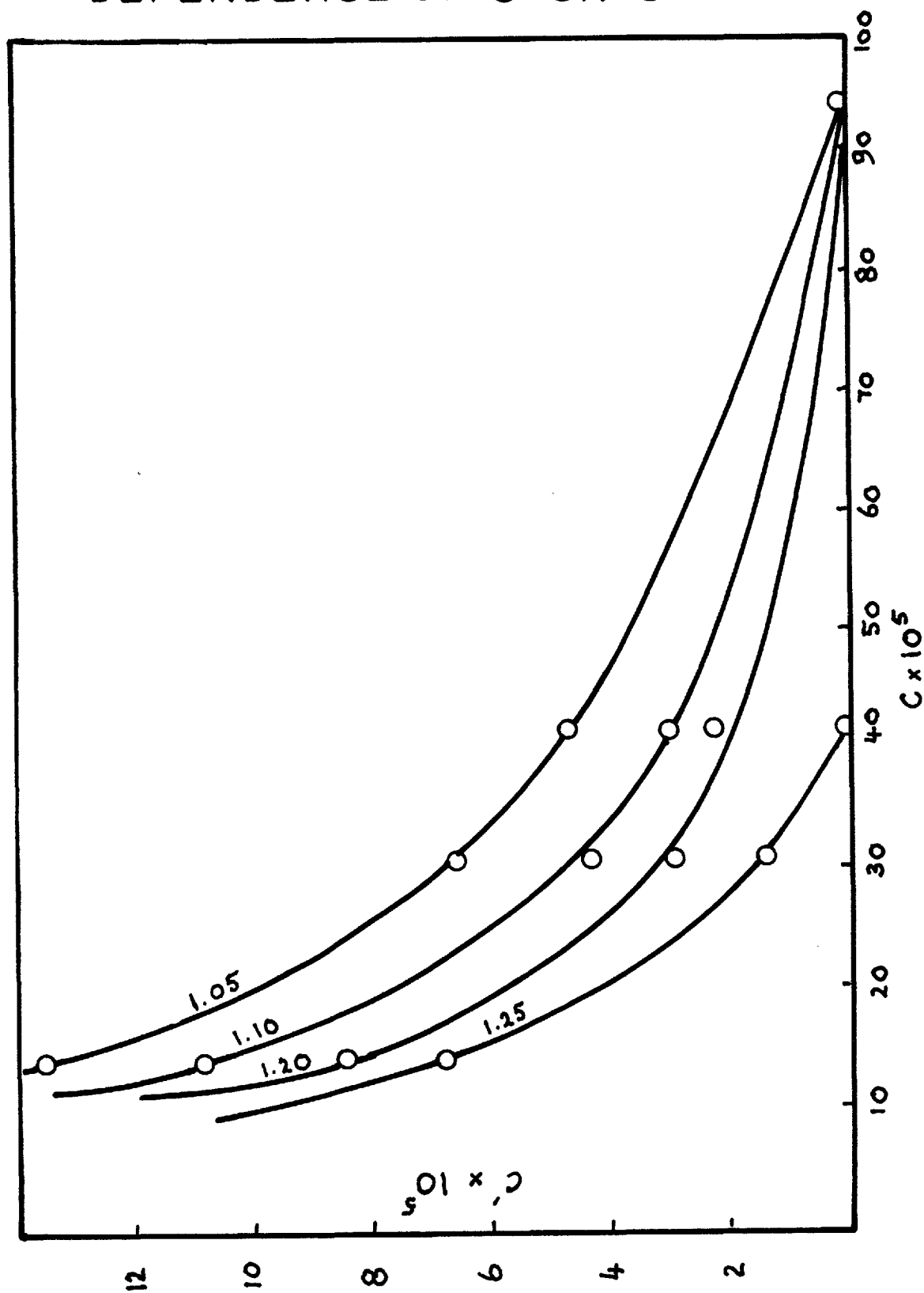


FIG. 43

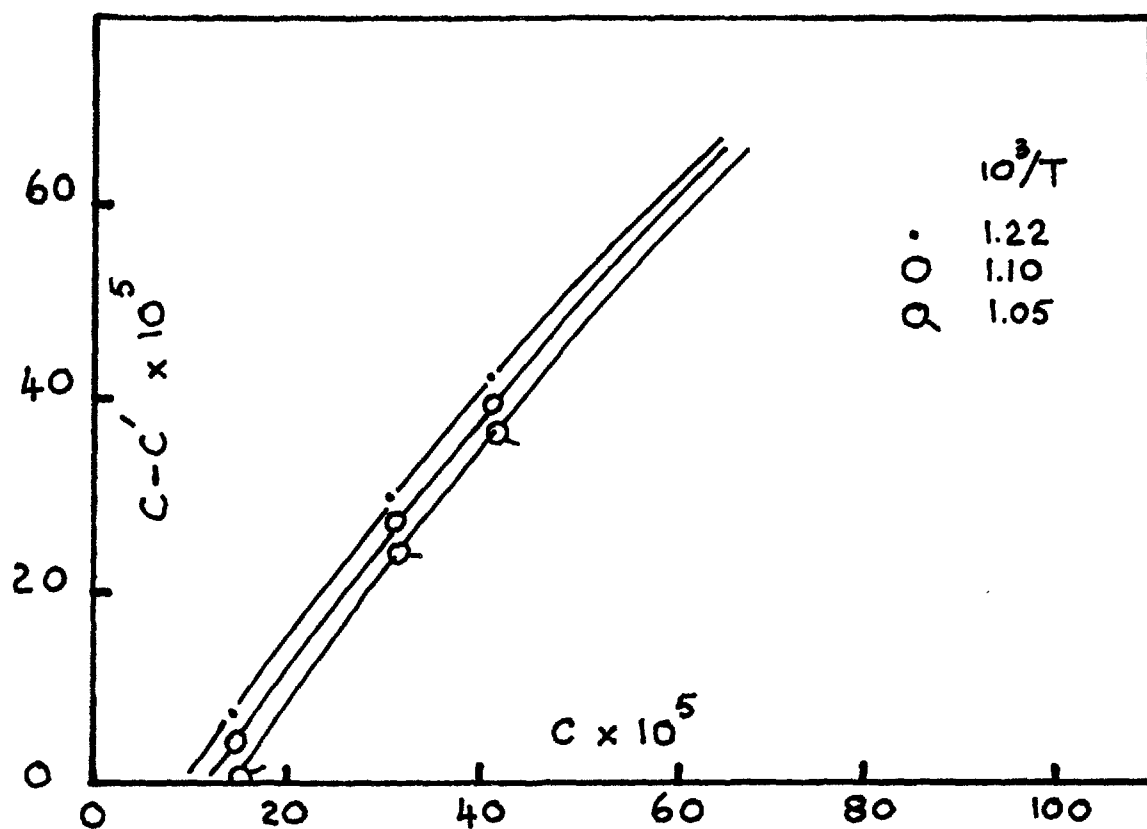
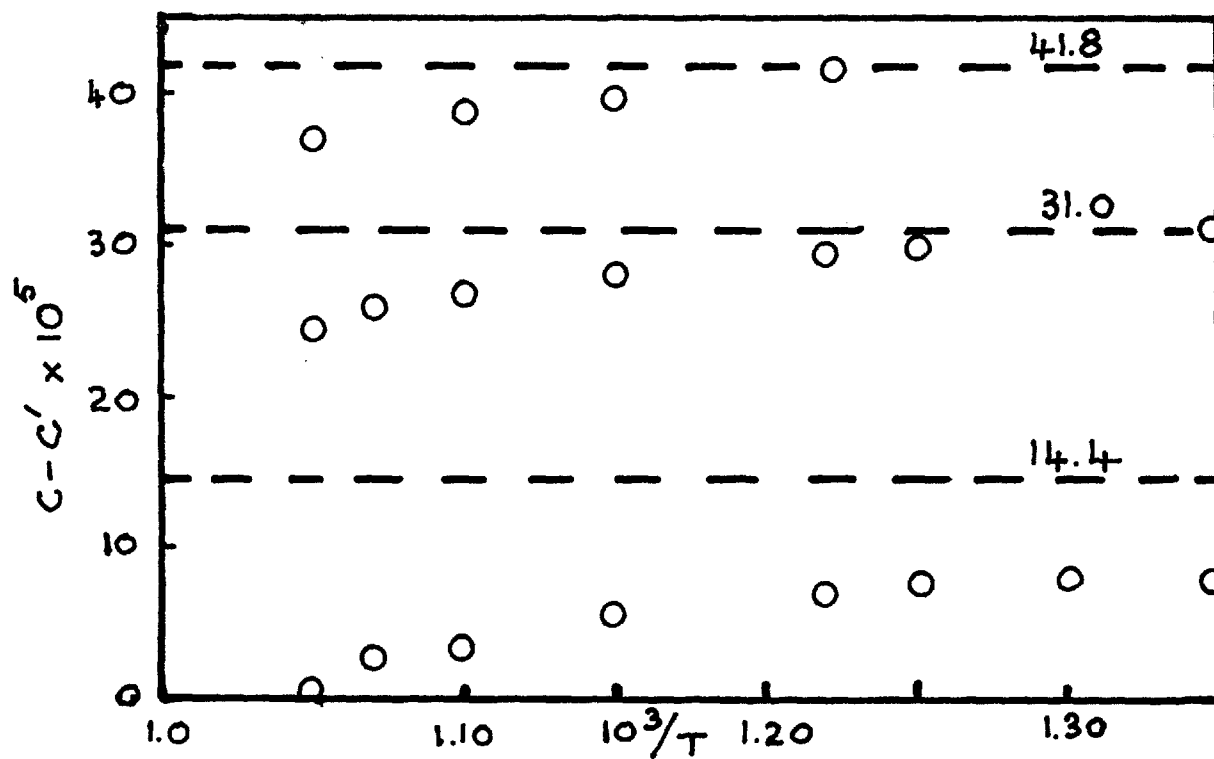


FIG. 44



crystals and no OH^- band was found at 204 μ in the u.v. spectrum. (All Harshaw crystals, for example, show a pronounced u.v. absorption band due to OH^- ions.) However, the u.v. spectra of the most heavily doped crystal, after being subjected to a very high d.c. field at a high temperature showed a very large absorption peak for OH^- at 204 μ . We are thus forced to conclude that some OH^- must have been initially present and then combined with the Sr^{2+} . The effect of the field was such as to regenerate the OH^- ions. Lütty (private communication) upon doping KCl crystals with KOH has also found evidence of an interaction between OH^- and Ca^{2+} impurities present by the strong suppression of the structure-sensitive conductance.

As the crystals were grown in silica vessels it is inevitable that some SiO_2^{2-} must have diffused into the melt with the consequent possibility of precipitating out some of the Sr^{2+} . This effect would be expected to be most apparent in the least heavily doped crystals, as was observed. It is not possible to decide between the two alternatives on the basis of the present results.

From the data in fig.16, using the Lidiard-Stasiw-Teltow association theory, it is possible to calculate (1) the fractional number x_0 of defects in the pure crystal, (2) the cation vacancy mobility u_1 , and (3) the free energy of association, $\mathcal{F}$.

First the values of the parameter $y(c,T) = x_1/x_0$ of equation 1.4.6, were calculated from the equation

$$4.1.7. \quad y = \frac{\sigma}{2\sigma_0} (1 + \phi) + \left\{ \frac{\sigma^2}{4\sigma_0^2} (1 + \phi)^2 - \phi \right\}^{\frac{1}{2}} \approx \frac{\sigma}{\sigma_0} (1 + \phi),$$

for $y \gg 1$ using values of the conductance interpolated from a large

scale graph of fig.16 and values of ϕ for the Stockbarger crystal (run 3A) interpolated from equation 3.1.1. using the data in table 6.

From equation 1.4.3., and as

$$x_1 - x_2 = c - x_k \quad \text{one finds that}$$

$$4.1.8. \quad c/(y - 1/y) = x_0(1 + K_2 x_0 y) .$$

At the lower concentrations $y < 10$, $1/y$ may not be neglected. Plots of $c - c'/(y - 1/y)$ against y are shown in fig.45. It is evident that, at the lower temperatures, these plots are linear. The intercept is x_0 and the slope $K_2 x_0^2$. By plotting $y - 1/y$ against c , it is possible to find the c' values, these values being more accurate than those found from the c versus σ^- curves (since the anion conductivity is now accounted for). Using these new, and more accurate $c - c'$ values it was found that all the plots of $c - c'/(y - 1/y)$ against y were straight lines. Table 20 presents the comparison between the two sets of $c - c'$ values. Thus the downward dip at the highest temperature in fig.45 is an artefact and not evidence for Debye-Hückel interactions.

Upon plotting the logarithm of the calculated values of x_0 (obtained from equation 4.1.8 and the plots of $c - c'/(y - 1/y)$ versus y) against T^{-1} , a good straight line was obtained. The equation to this line was found to be

$$4.1.9. \quad \log x_0 = 1.753 - (5.78 \times 10^3)/T .$$

As $x_0^2 = \exp(-g/kT)$, the enthalpy and vibrational entropy changes on forming a Schottky defect pair may be found: these are $h = 2.29$ eV and $s = 0.696 \times 10^{-3}$ eV/deg.

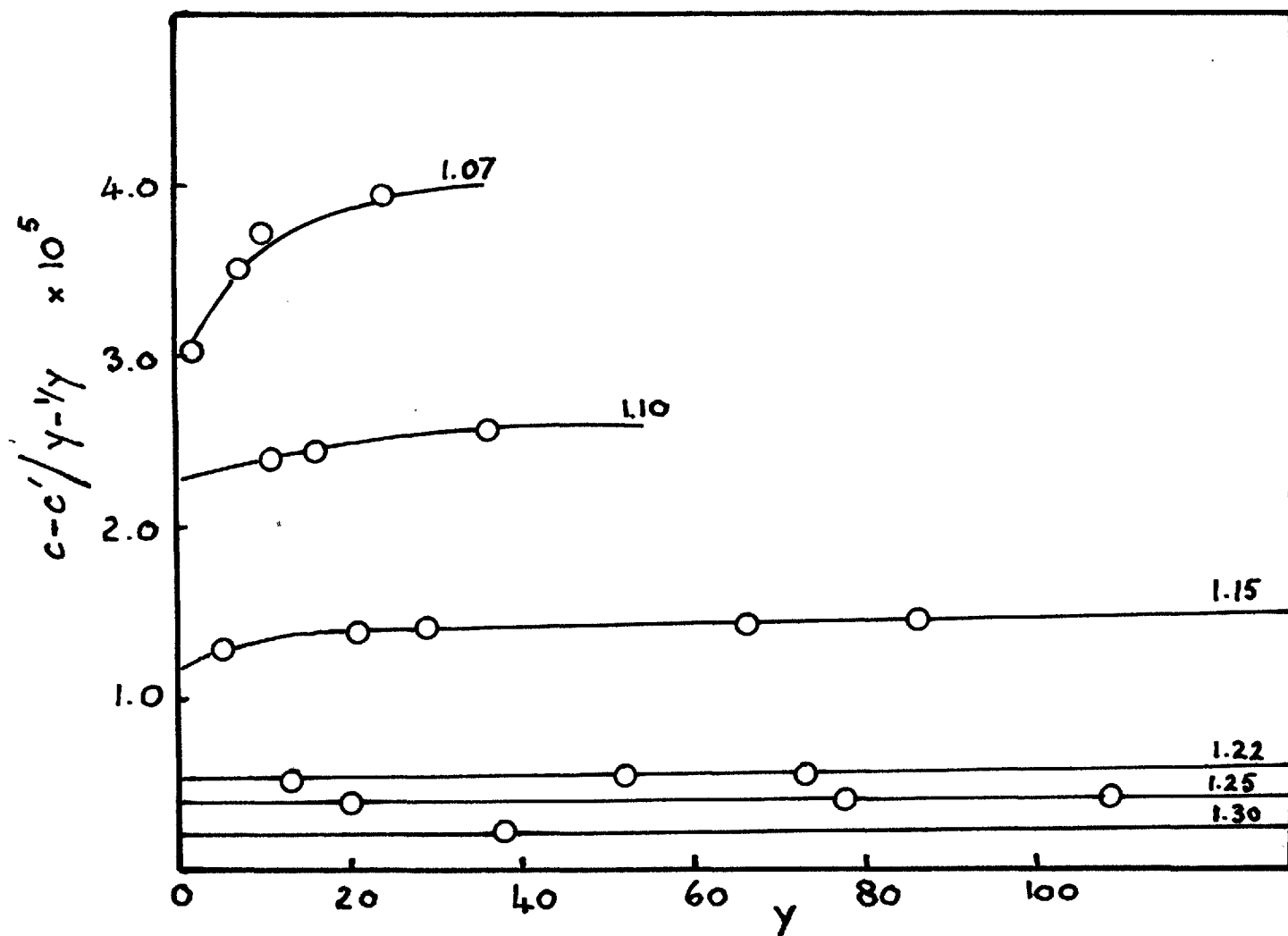


FIG. 45

As the vibrational entropy change on forming a pair of vacancies is

$$4.1.10 \quad s = 2zk \ln(\nu/\nu'),$$

we find $(\nu/\nu') = 1.959$. Thus the vibrational frequency of an ion next to a vacancy, in the direction of the vacancy, is nearly halved.

These values agree very well with those found by Allnatt and Jacobs (1962,b) and the predicted value of 2 for (ν/ν') by Mott and Gurney (1948) although Etzel and Maurer (1950) found $(\nu/\nu') = 1.32$ for sodium chloride. These are the only values presently available.

Table 20

Comparison of $c - c'$ values obtained by the two different methods

$10^3/T^{\circ}K$	Crystals	<u>A. From $y - 1/y$ versus c</u>			<u>B. From σ versus c</u>		
		X 1	X 2	X 3	X 1	X 2	X 3
1.10		6.0	29.0	40.5	3.5	26.7	38.7
1.12		6.5	29.3	41.0	5.2	27.3	39.2
1.14		6.8	29.5	41.0	5.9	28.0	39.5
1.16		7.5	29.3	40.8	6.3	29.1	40.9
1.18		7.3	29.4	41.0	7.3	28.3	40.0
1.20		7.6	29.2	41.0	7.0	28.4	40.5
1.22		7.5	29.3	41.0	6.7	29.4	41.0
1.24		7.5	29.3	41.8	7.4	29.4	40.7

For crystal X 4, c' is negligible at all temperatures.

From equation 3.1.0 it follows that

$$4.1.11 \quad \sigma = Neu_1 x_0 (y + \phi/y) .$$

Using the calculated values of y , ϕ and x_0 , u_1 can be calculated and $\log(u_1 T)$ plotted against T^{-1} . This gave a good straight line of equation

$$4.1.12 \quad \log(u_1 T) = 3.275 - (3.90 \times 10^3)/T .$$

Using equations 3.1.2 and 3.1.3 we find that $\Delta h_1 = 0.774$ eV and $\Delta s_1 = 0.131 \times 10^{-3}$ eV/deg. Using the values, found for a Stockbarger cleave (3A), of $\Delta h_2 - \Delta h_1$ and $\Delta s_2 - \Delta s_1$, we find that $\Delta h_2 = 2.5$ eV and $\Delta s_2 = 1.88 \times 10^{-3}$ eV/deg.

For crystals X 1 to X 3, when $y^2 \gg 1$, equation 4.1.8 can be approximated to

$$4.1.13 \quad c - c'/x_1 = 1 + K_2 x_1 .$$

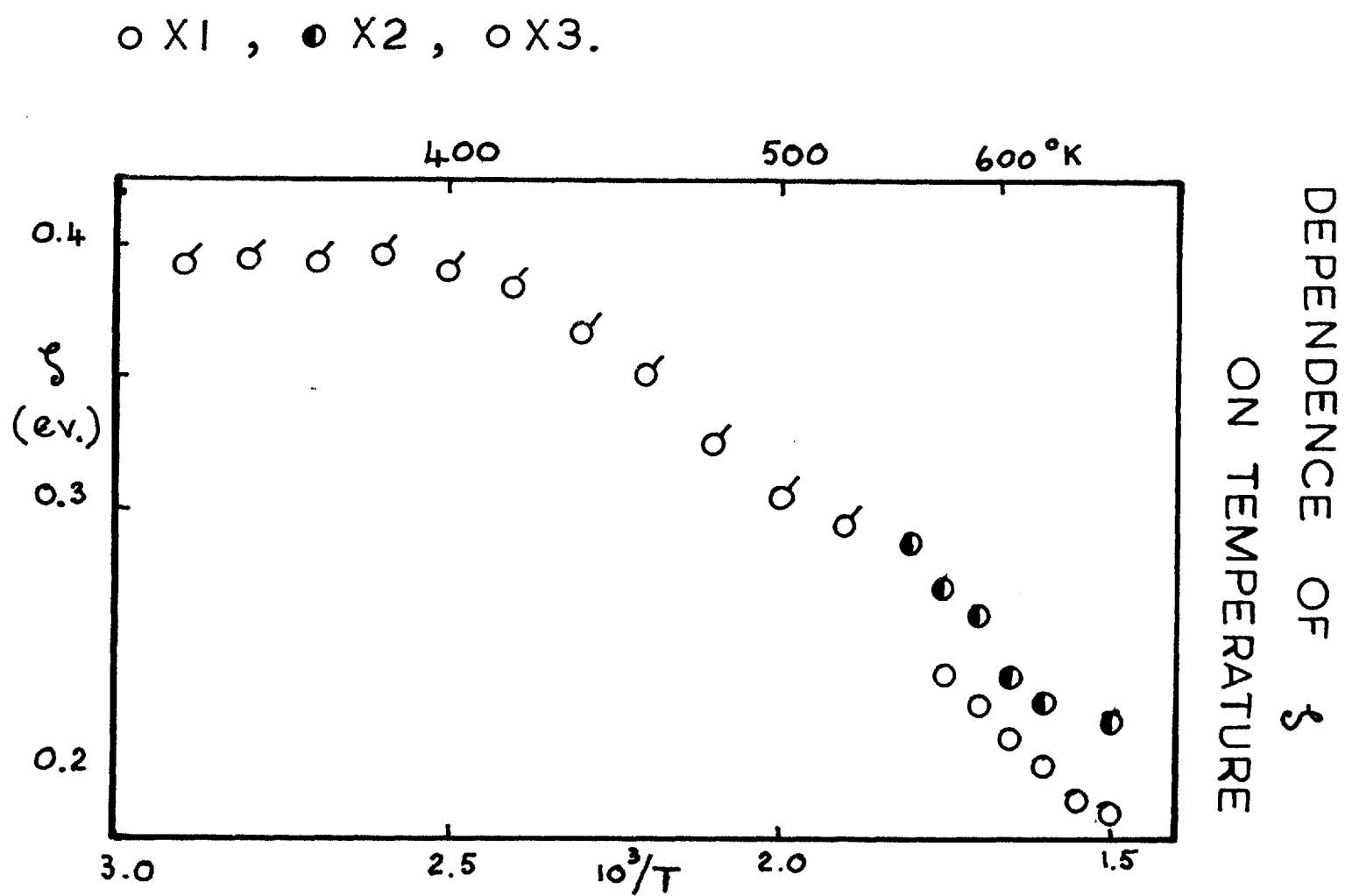
Using known values of $c - c'$ and values of x_1 calculated from σ/Neu_1 , values of K_2 were found as a function of temperature. Since

$$4.1.14 \quad K_2 = z_k \exp(-\mathcal{G}/kT)$$

with $z_k = 12$, values of $\mathcal{G}$, the free energy change of the association of the Sr^{2+} cation vacancy complex may be calculated. The computed values of $\mathcal{G}$ are shown in fig.46 as a function of temperature. From fig.46 it is apparent that association does not occur above 650°K.

To check on this mysterious temperature-dependence for $\mathcal{G}$, the conductivity line for crystal X 4 was calculated assuming association even to the highest temperatures, i.e., using a constant value of 0.395 eV for $\mathcal{G}$. This line was curved over the whole temperature range, whereas the observed conductivity lines exhibit a linear region at the highest temperatures. Values of $\mathcal{G}$ for X 4 and X 5 could not be calculated

FIG. 46



due to the early onset of the precipitation of Sr^{2+} . The numerical values of the parameters, h , s , Δh_1 , Δh_2 , Δs_1 and Δs_2 are presented in table 21, together with values found by other workers. The self-consistency of the data is quite good: $\Delta h_1 + \frac{1}{2}h$ from table 5 gives 1.90 eV in excellent agreement with the data from table 21. Similarly the $\Delta s_1 + \frac{1}{2}s$ values are in good agreement. The numerical parameters for the 'recrystallised' Kyropoulos crystal should be the most accurate since this is the purest crystal studied. All the calculated h and Δh_1 values are acceptable. The activation energy Δh_2 for anion diffusion for the Stockbarger crystal seems too high. The value for the 'recrystallised' Kyropoulos crystal agrees quite well with the value determined by Ewles and Jain (1957) by diffusion studies in quenched crystals (1.89 eV). Mizuno and Miyamoto (1961) studying the diffusion of F-centres in KCl found $\Delta h_2 = 2.0 \pm 0.1$ eV. Guccione et al. (1959) have shown theoretically that the difference in Δh_1 and Δh_2 is basically a consequence of the difference in ionic radii (K^+ 1.33, Cl^- 1.81 Å). It thus appears that the high value of Δh_2 found for the Stockbarger crystals may be due to the higher impurity content. The only other values available of s and Δs_1 are those of Allnatt and Jacobs (1962,b) and Phipps and Partridge (1929). Agreement between the present values and those of the former investigators is quite good.

The curious temperature dependence of γ seems inexplicable since the vibrational entropy contribution should be negligible. This form of this dependence has been observed by Allnatt and Jacobs. We can nevertheless evaluate γ as 0.3 ± 0.1 eV for temperatures less than 600°K, association being absent at higher temperatures.

Table 21Numerical values of conductance parameters for KCl

Source	how obtained	h (eV)	Δh_1 (eV)	Δh_2 (eV)	s (10^{-3} eV/deg)	Δs_1 (10^{-3} eV/deg)	Δs_2 (10^{-3} eV/deg)
This work	Stockbarger crystals	2.29	0.774	2.51	0.696	0.131	1.88
	Kyropoulos	2.28	0.77	1.87	0.43	0.131	0.97
Allnatt and Jacobs (1962,b)	Stockbarger	2.30	0.75	2.45	0.69	0.114	1.75
	Kyropoulos			1.77			1.10
Kelting and Witt (1949)	conductance	2.40					
Wagner and Hantelmann (1950)	conductance (pellets)	2.08					
Tosi and Fumi (1958)	theoretical	2.20					
Gründig (1960)	conductance (KCl + CaCl ₂)		0.77				
Aschner (1954)	conductance + diffusion		0.68				

4.2. Polarization studies

The a.c. polarization, manifested as a frequency dependent capacity, was observed and recorded at the same time as the a.c. conductivity data. The calculated polarization capacities have been analysed using the Friauf (1954) theory. The notation (o, o) is used to describe the situation when both electrodes are blocking, (o, ∞) for positive carriers blocked and negative ones free, and (∞ , o) for positive carriers free and negative carriers blocked. Friauf (1954) has shown that

$$4.2.1. \quad C = \frac{C_0}{1 + (\omega\tau)^2}$$

for the (o, o) case, where

$$\tau = R_0 C_0, R_0 = 2L/\sigma \text{ and } C_0 = e \left(\frac{\epsilon x_0}{8\pi kT} \right)^{\frac{1}{2}} = M(x_0/T)^{\frac{1}{2}}$$

where M is a numerical factor equal to 0.1557 for KCl (assuming that the permittivity ϵ does not vary with temperature), and x_0 is the number fraction of Schottky defects present in the system. Since $\omega\tau \gg 1$, equn. 4.2.1. reduces to

$$4.2.2. \quad C = \frac{\sigma^{-2}}{\omega^2 (2L)^2 M (x_0/T)^{\frac{1}{2}}}$$

For the (∞ , o) case, Allnatt and Jacobs (1961,a) showed that

$$4.2.3. \quad \omega C = \frac{\sigma^{\frac{3}{2}}}{\sqrt{2} L^2} \times \frac{t_n^{\frac{3}{2}}}{(2t_p)^{\frac{1}{2}}} \left(\frac{kT}{Ne^2} \right)^{\frac{1}{2}} \times \frac{1}{\omega^{\frac{1}{2}}}$$

where the t's are the respective transport numbers of the charge carriers, (positive = p, negative = n). From equations 4.2.2. and 4.2.3. it is apparent that the frequency slopes (i.e. the slopes of

plots of $\log C$ against $-\log \omega$) should be 2.0 and 1.5 respectively. From table 9 we observe that the mean frequency slope is 1.62, which is indicative of $(\infty, 0)$ or $(0, \infty)$ blocking although this is by no means definite. A truer test of the frequency-dependence obtained by plotting ωC against $1/\omega$ and $1/\omega^{\frac{1}{2}}$: for the $(0, 0)$ case the former should be a straight line and for $(\infty, 0)$ the latter. Using the available data it is found that $\omega C \propto 1/\omega$ rather than $1/\omega^{\frac{1}{2}}$, thus indicating that both charge carriers are blocked. Typical graphs to test the frequency dependence are shown in fig.47. The theoretical slopes expected for the plots of ωC against $1/\omega$, calculated from equn. 4.2.2. are compared with the experimental values in table 22. These calculated values, based on the $(0, 0)$ model, are in excellent agreement with the experimental slopes, the discrepancy being about 1.5 - 3.

Both models predict $C \propto (2L)^{-2}$ and this is well borne out by the experimental results, as shown in fig.49. The theoretical line for the $(0, 0)$ case has been included and the absolute agreement may again seem to be good. If the capacity is calculated assuming $(\infty, 0)$, it is found to be a factor of 10^3 smaller than the measured capacity. The two lines drawn in fig.49 have a slope of -2, as predicted by the theory.

The Friauf theory also predicts that the slope of the graph of $\log CT^{\frac{3}{2}}$ against $1/T$ should be $\frac{3}{2}h + 2\Delta h_1$ for pure KCl. Using the values of h and Δh_1 obtained from the conductivity data, this predicted slope is 3.2 eV. Experimentally determined values are given in table 10 and the calculated intercepts, assuming $(0, 0)$, are compared with the experimental intercepts in table 23. The data for the recrystallised

Kyropoulos crystal is represented in fig.50. Again, good agreement between theory and experiment is observed (see tables 10 and 23).

Table 22

Slopes of ωC versus $1/\omega$ for pure KCl

Run	Crystal type	Calculated	Observed
5	Harshaw	8.71×10^{-4}	1.50×10^{-3}
20	Recrystallized Kyropoulos	8.71×10^{-3}	1.13×10^{-3}
19	Analar Kyropoulos (Harshaw seed)	1.39×10^{-4}	3.43×10^{-4}
15	SO_4^{--} doped	2.67×10^{-3}	7.6×10^{-4}

Table 23

Intercepts for $\log CT^{3/2}$ versus $1/T$

Run	Crystal type	Calculated	Observed
1	Stockbarger	13.03	15.70
2	Stockbarger (Rh electrodes)	9.89	11.46
3	Stockbarger	12.32	13.61
5	Harshaw	10.27	13.25
19	Analar KCl, Kyropoulos	11.32	12.31
20	Recrystallized KCl, Kyropoulos	11.83	11.78
15	SO_4^{--} doped	9.44	13.93

The experimental data for the pure crystals definitely shows that both electrodes are blocking, i.e. (o, o) in the Friauf

FIG. 47a

PURE KCl, run 20, $T = 963^\circ\text{K}$

$2L = 0.351\text{cm}$

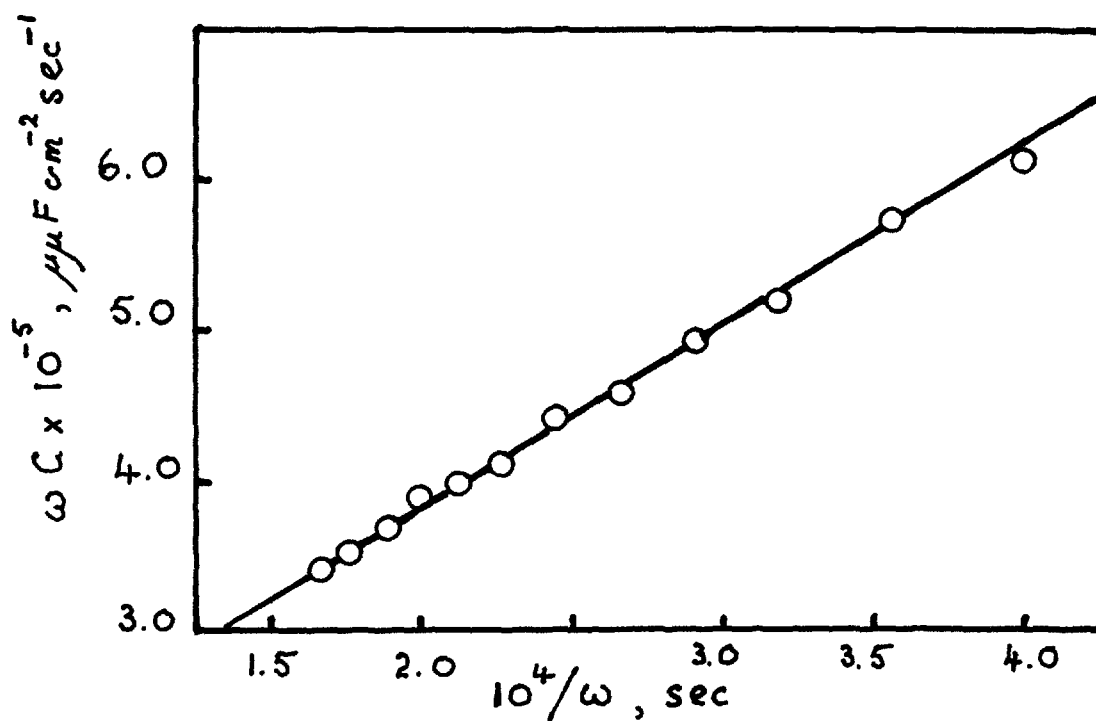


FIG. 47b

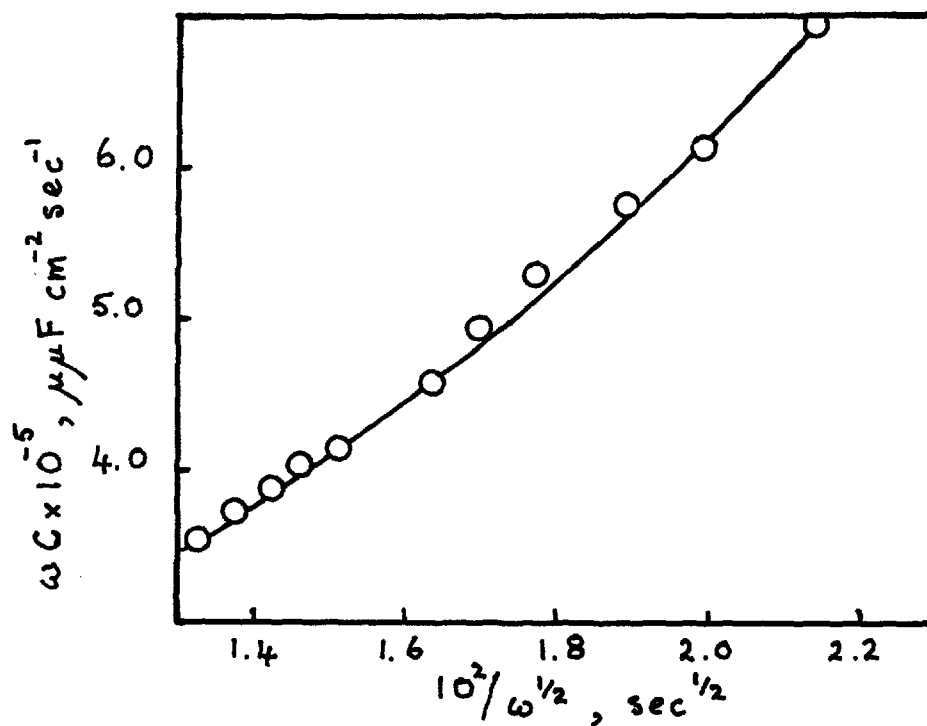


FIG.48a

DOPED KCl, X3 , $T=933^{\circ}\text{K}$
 $2L=0.565\text{cm}$

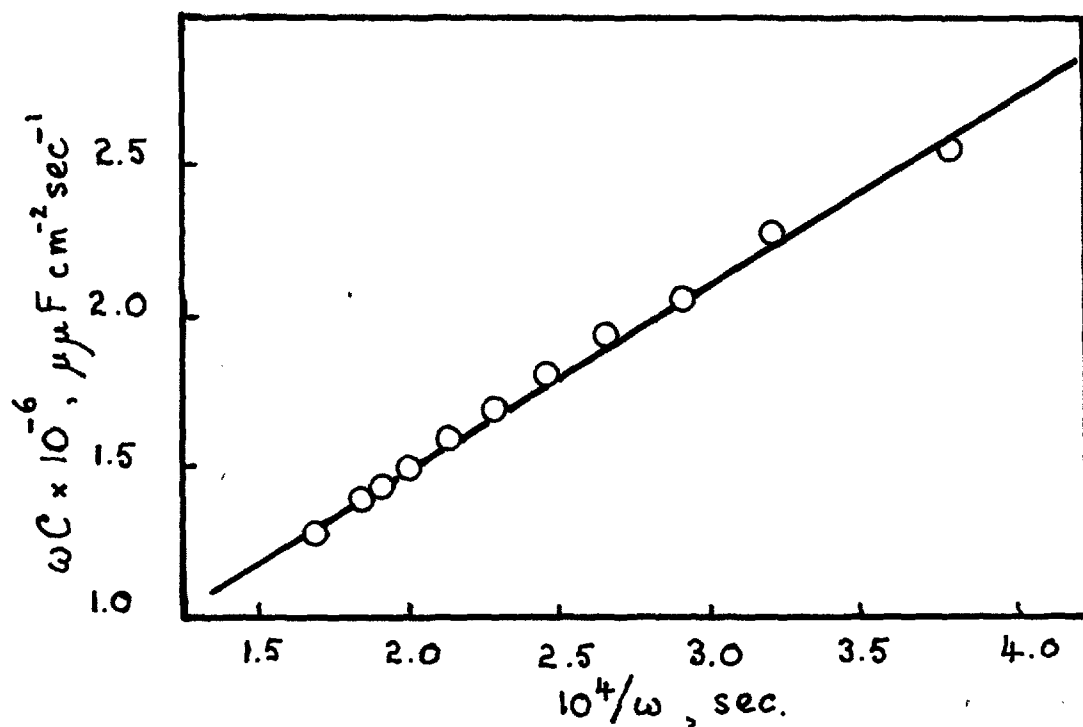


FIG.48b

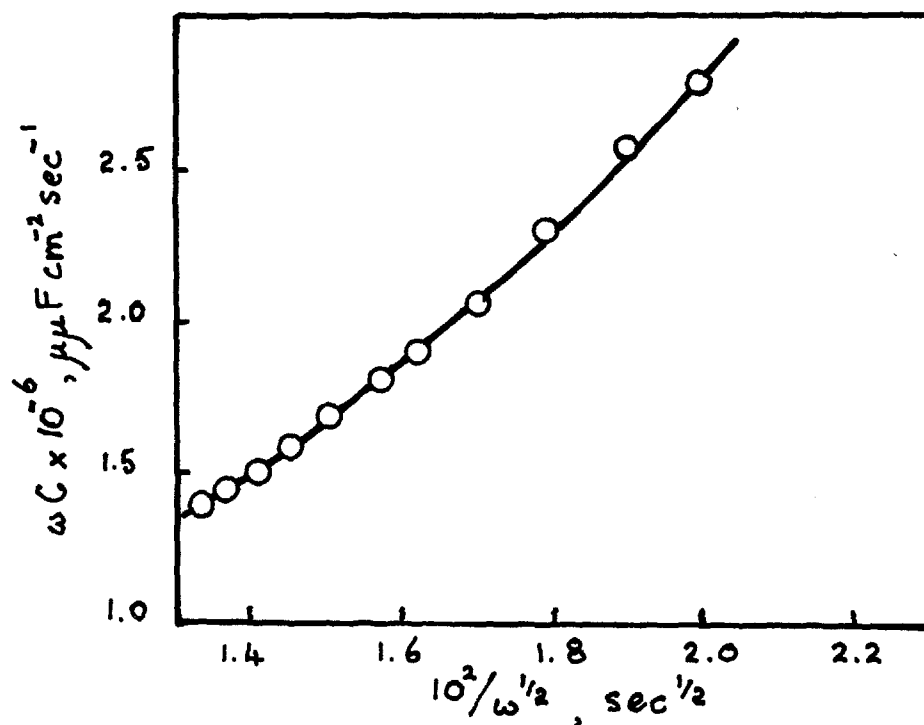


FIG.49

run numbers,

● 2

○ 5

▽ 14, SO_4^{2-} DOPED

○ 3

● 19

---- THEORETICAL C FOR (0,0)

○ 3A

● 20

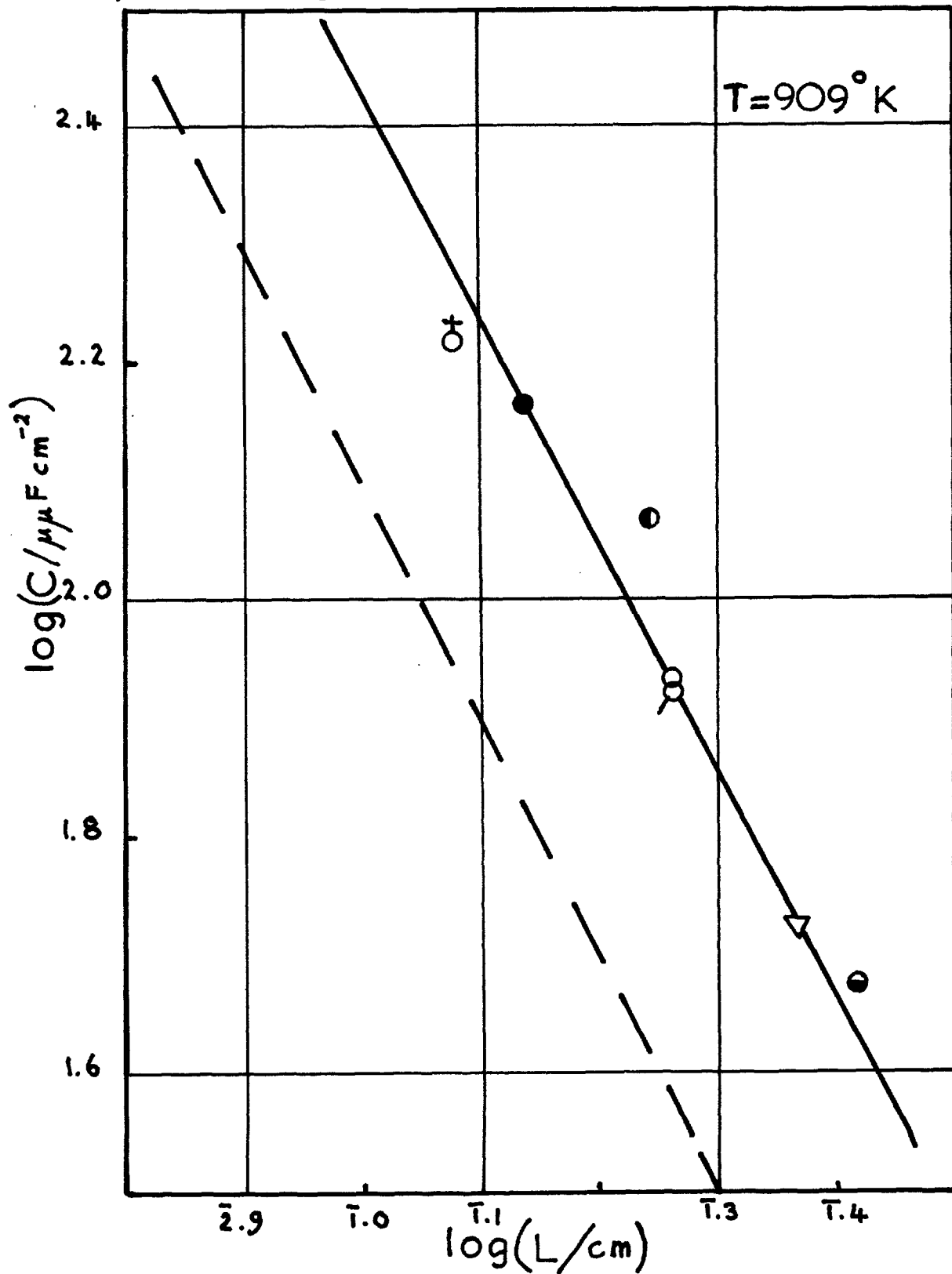
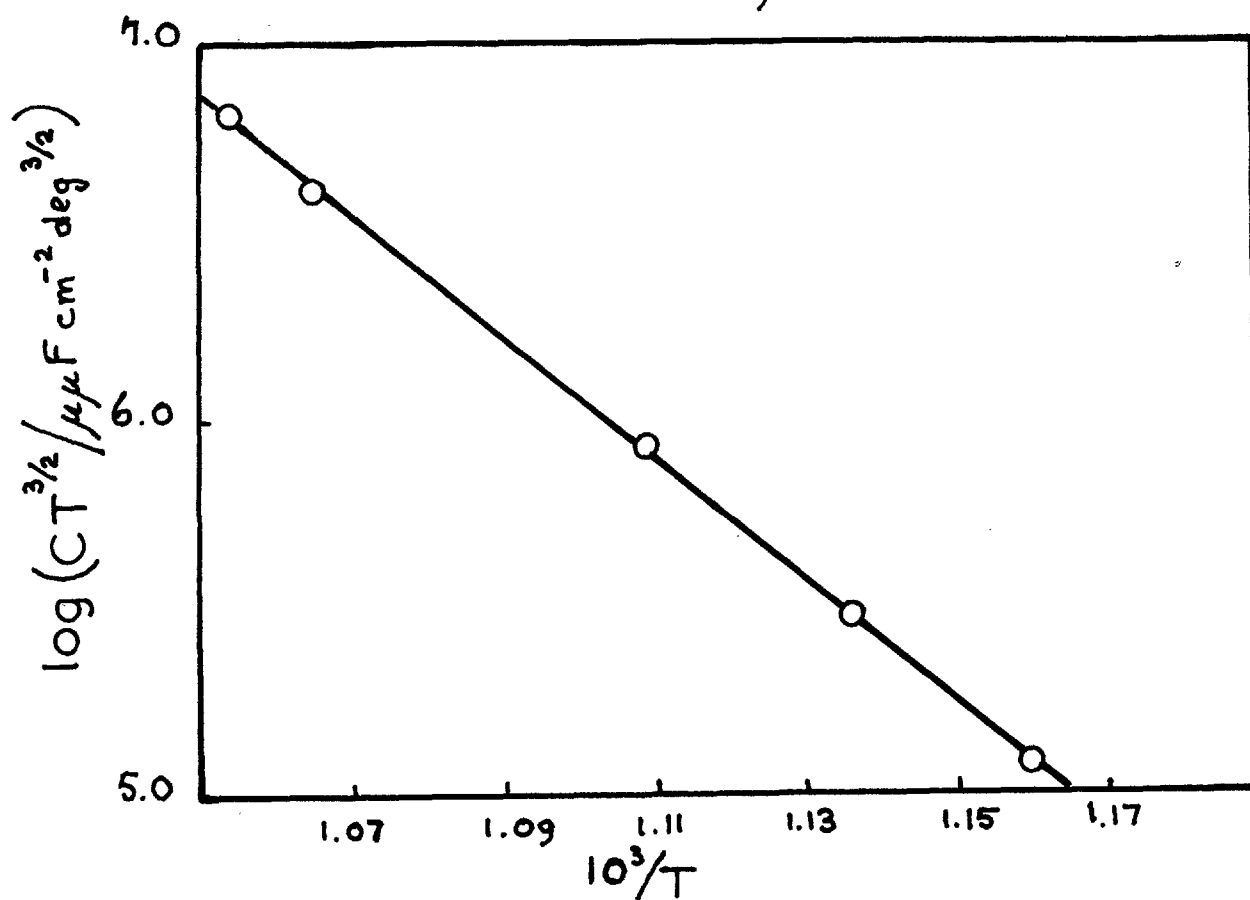


FIG. 50

TEMPERATURE DEPENDENCE
OF CAPACITY

PURE KCl, run 20



notation. The principal objection to the possibilities of one carrier being discharged, i.e. $(0, \infty)$ or $(\infty, 0)$, is that on using the theoretical equations (e.g. 4.2.3) to calculate the capacity, C is found to be a factor of 10^3 smaller than the experimental capacity, whereas the calculated capacity for $(0, 0)$ is only a factor of 1.5 - 3 too small. Also the plots of ωC versus $1/\omega^{\frac{1}{2}}$ were always slightly curved whereas those of ωC versus $1/\omega$ were found to be linear (figs. 47, 48). The direct plots of ωC versus ω^{-n} are of course more reliable than the logarithmic plots used previously.

For the impurity region where only cation vacancies produced by immobile divalent cation impurities are present, Ninomiya and Sonoike (1958) deduced that

$$4.2.4. \quad \omega C = \frac{\sigma^{\frac{3}{2}}}{2\sqrt{2}I^2} \left(\frac{kT}{N_0^2} \right)^{\frac{1}{2}} \times \frac{1}{\omega^{\frac{1}{2}}} .$$

Thus ωC should be proportional to $1/\omega^{\frac{1}{2}}$. This, however, is not borne out by experiment (fig.48) which shows $\omega C \propto 1/\omega$ as for pure crystals. Similar graphs were obtained at all temperatures at which a.c. measurements could be made. We thus conclude that the Ninomiya and Sonoike model is incorrect. There is nothing in the Friauf theory to preclude its application to doped crystals provided x_0 is replaced by x_1 where x_1 is the number fraction of cation vacancies present at a temperature T . The frequency dependence of C certainly favours equn. 4.2.2. rather than equn. 4.2.4.

Using the Ninomiya and Sonoike equation (4.2.4), the slopes of the calculated curves of $\log C$ as a function of T agree quite well

with experiment (cf. Allnatt and Jacobs, 1961,a) but the magnitude of the capacity is 10^3 to 10^4 too small. The experimental curves are compared with those calculated from the Friauf formula (equn. 4.2.2, with x_1 replacing x_0) in fig.20 and 21. The discrepancy between experiment and theory is roughly a factor of 30, which, though less satisfactory than the agreement for pure crystals, is still a good deal better than that found using equn. 4.2.4.

For the impure crystals the plot of $\log C$ versus $\log \sigma$, (fig.51), is a straight line of slope 1.30 compared with the expected 1.50. The values of the capacity C at 636°C and 300 c/s were corrected to the values appropriate to a crystal of thickness 4 mm using the square law which has been verified experimentally (fig.49). The theoretical line in fig.51 has been calculated from equn. 4.2.2, again with the substitution of x_1 for x_0 for the doped crystals.

Further evidence for the (o, o) model is that a plot of $\log C$ against $\log x_1$ gives an accurate straight line of slope 1.26 (theory 1.5). Thus we find

$$\begin{aligned} C &\propto \omega^{-2} \\ 4.2.5. \quad &\propto (2L)^{-2} \\ &\propto x_1^{3/2} \end{aligned}$$

and we are therefore justified in using the adapted Friauf equation. The Ninomiya and Sonoike equation (4.2.4) gives calculated capacities which are far too small, as does the (∞ , o) equation (4.2.3).

The Stockbarger crystal doped with 200×10^{-5} mole ratio of K_2SO_4 showed a polarization capacity comparable to that of the pure crystals (fig.49). At first sight this might appear illogical, since

we might have expected a large increase in the number of anion vacancies and hence a proportional increase in the capacity. However, the conductivity of this crystal showed a conductivity comparable to the pure crystal in the intrinsic region, indicating that the anion vacancies are not mobile. The capacity should therefore also be comparable to that of the pure crystals. The plot of $\log CT^{3/2}$ versus reciprocal temperature gives a slope of 3.59 eV which is in fair agreement with the calculated slope (3.2 eV). This larger slope is responsible for the large discrepancy in the intercepts (table 23).

4.3. D.o. steady-state conductivity and d.c. polarization

The steady-state conductivity, calculated from the current-time plots, for two pure crystals is shown in fig.52. The surprising feature of these plots is the variation of the magnitude of the conductivity and the respective activation energies, given in table 24. The similarity of the magnitude of the conductance of the Sr^{2+} doped crystal to that of the pure crystals is most interesting. In the temperature range being covered the pure crystals are in the intrinsic region, and the doped crystal will contain a far greater number of cation defects than these pure crystals, as shown by a.c. conductance measurements. Hence if this steady-state conductivity were connected with the number of cation vacancies, as is σ_0 , the conductivity of the doped crystal would be several orders of magnitude greater than that of the pure crystals; it may also be assumed that anion migration is negligible. We are thus led to believe that the conduction processes in all these crystals must be due to some species of comparable magnitude in each crystal, namely the electron. The origin of these 'conduction'

FIG. 51

capacity values for $2L=0.4\text{cm.}$

$$10^3/T = 1.10$$

○ experimental

Q theoretical.

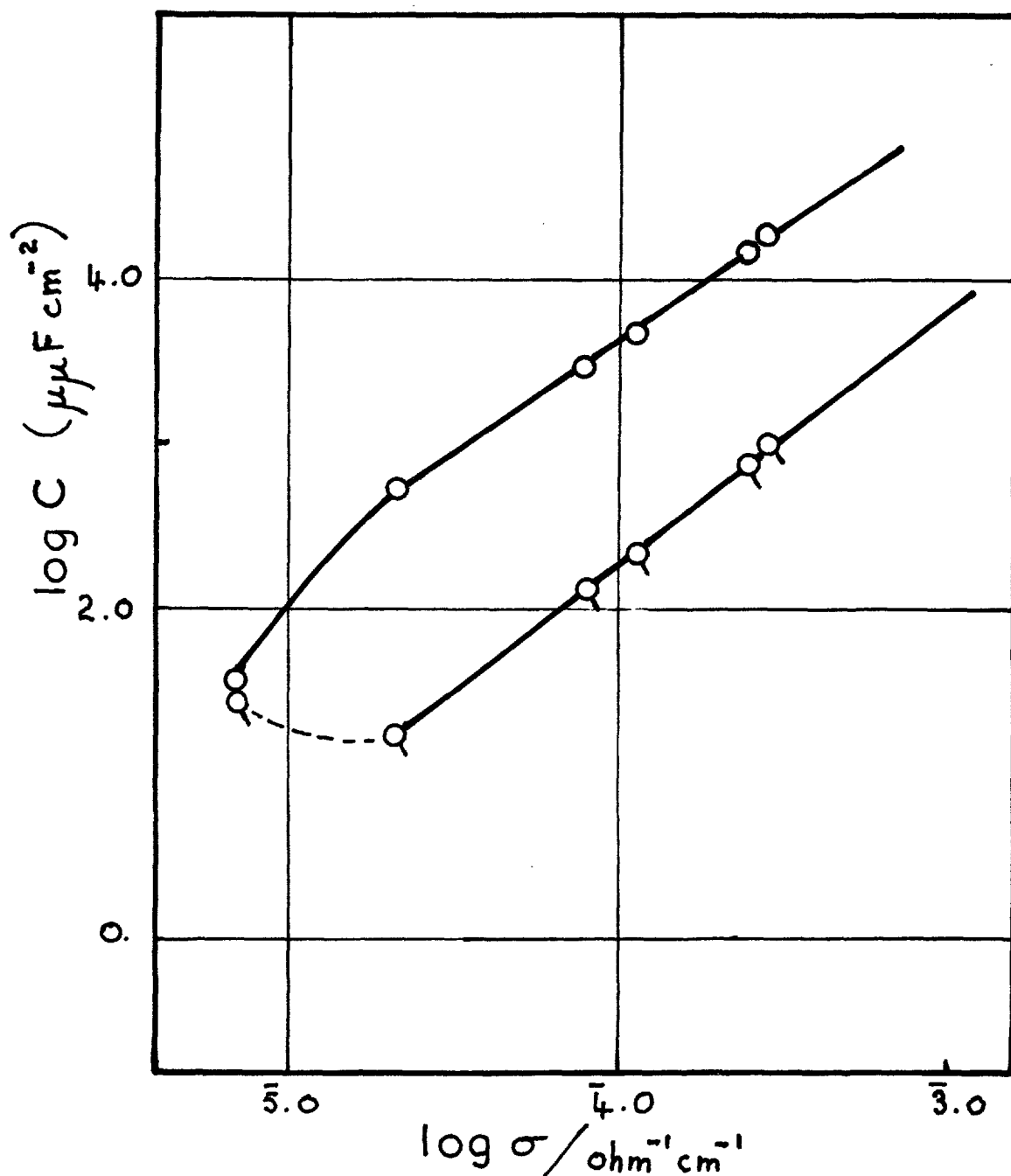
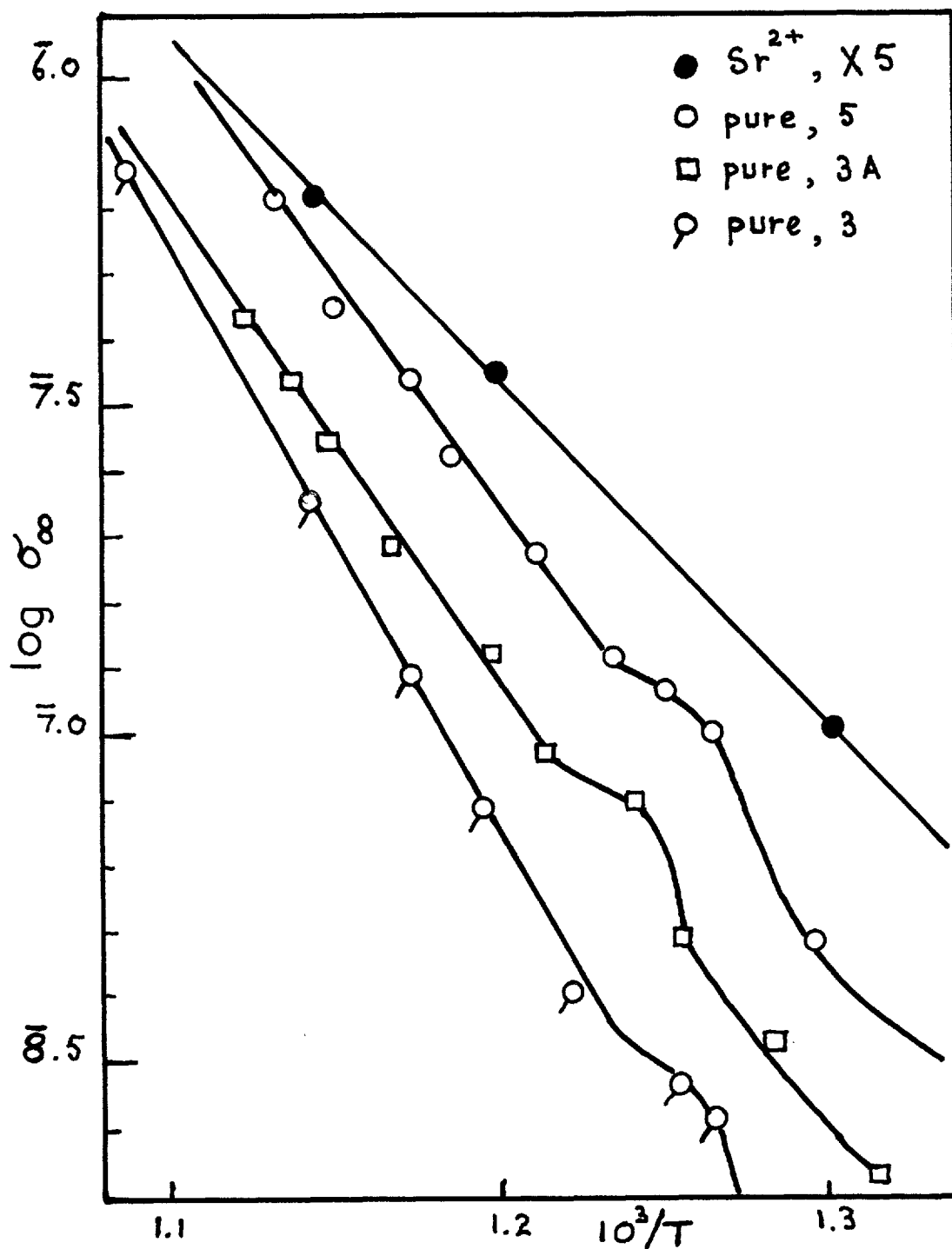


FIG. 52

STEADY STATE CONDUCTIVITY
pure and doped KCl



electrons cannot be precisely defined, although they must be produced from donor states of energy just below the conduction band. It is thus not surprising that the conductivity of KCl from different sources is so different since we would expect the number and depth of the donor states (themselves due to random impurities) to vary considerably from crystal to crystal. This is apparent for run 3 where after a long anneal (8 weeks) run 3A exhibits a higher conductivity of lower activation energy. The long anneal thus removes, possibly by precipitation, some of the electron traps or supplies, by solution, additional donor states. The identification of the steady-state conduction with electronic conduction is in agreement with conclusions drawn from the a.c. polarization studies, namely that both of the ionic charge carriers are completely blocked at the electrodes (in low fields). The number of electrons per cm^3 in the conduction band has been calculated to the nearest order of magnitude over the temperature range utilised and the results are given in table 25. Unfortunately no values for the mobility of electrons in the alkali halides at these temperatures are available, although Radfield (1954) found from Hall effect measurements that the mobility of electrons in an additively coloured KCl crystal at $90 \pm 10^\circ\text{K}$ was $100 \pm 50 \text{ cm}^2/\text{volt sec}$. The mobility will decrease with increasing temperature and the values have therefore been calculated on the basis of $u_e = 1 \text{ cm}^2/\text{volt sec}$. The numbers in the table are thus strictly $n_e \times u_e / \text{cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$.

The 'kink' in the conductivity curve is of no great significance as it coincides with an increase in the voltage required to

produce a measurable current. This increase in voltage, as seen from section 3.4, produces deviations from Ohm's law due to the onset of ionic plus electronic conduction and hence gives an apparent enhancement in the conductivity.

The two regions for the Sr^{2+} -doped crystal (fig.29) suggests that there are two donor states of different energy participating in the conduction process. This behaviour is typical of an impurity doped semiconductor in which traps of two different energy levels are acting, and where the temperature-independent conductivity corresponds to a saturation region due to the number of electrons in the conduction band being equal to the number of (fully ionized) donor states.

From the Jaffé theory of d.c. polarization we saw that the current-time curves could be analysed by

$$4.3.1. \quad I_p = A \exp(-\alpha t) + B \exp(-\beta t)$$

where β is given by

$$4.3.2. \quad \beta = \left\{ \left(\frac{eV}{2kT} \right)^2 + \pi^2 \right\} D(2L)^{-2}.$$

Thus as V tends to zero, $\beta = \pi^2 D (2L)^{-2}$. We should thus expect β to be proportional to V^2 , but in fact β is independent^{den} of V (fig.53), and similarly for α . For the pure crystals studied β is approximately proportional to $(2L)^{-1}$ and not $(2L)^{-2}$ as expected from the Jaffé theory. This result is shown in fig.54. Upon plotting $\log \beta$ against T^{-1} (fig.55), we observe two distinct sets of straight lines depending upon the thermal history of the crystal. For the crystals studied immediately after a.c. measurements, we observe an activation energy of 0.59 eV whereas the crystal studied after a long anneal (run 3A)

FIG. 53

VOLTAGE DEPENDENCE OF β .
 $\times$ (3) 582°C , Δ (3) 570°C , $\circ$ (2) 557°C

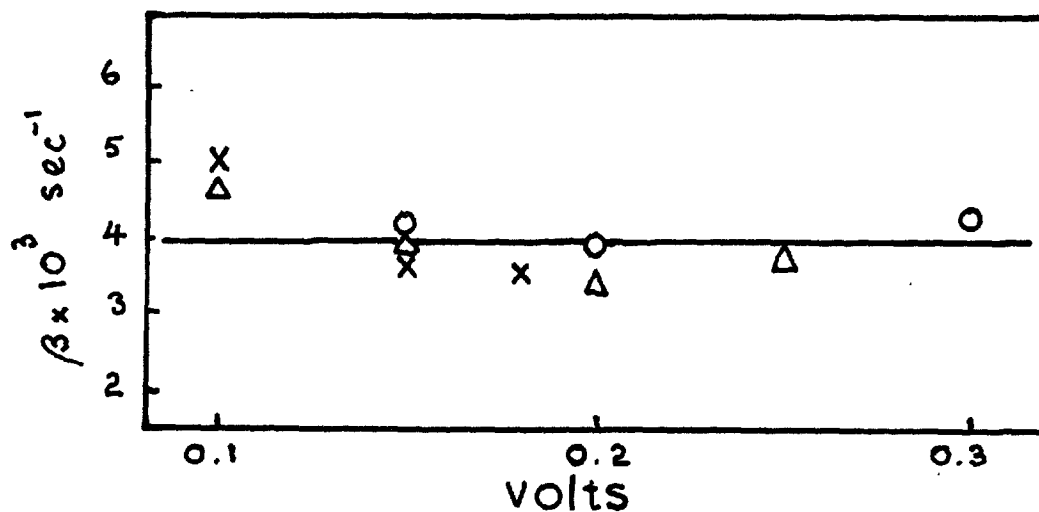
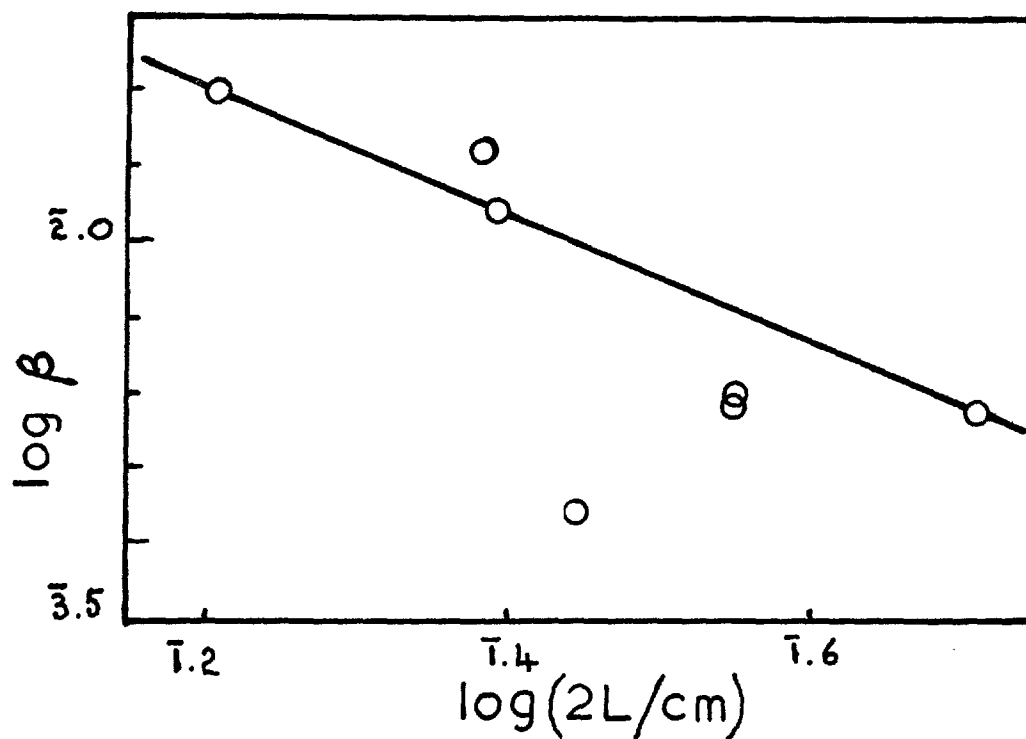


FIG. 54



$T = 636^{\circ}\text{C}$, slope = 0.9

FIG. 55

DEPENDENCE OF $\text{LOG } \beta$ ON T^{-1}

AFTER ANNEAL ; BEFORE ANNEAL

◇ 3A ○ 3

□ 2 (RH. ELECTRODES). ○ 5

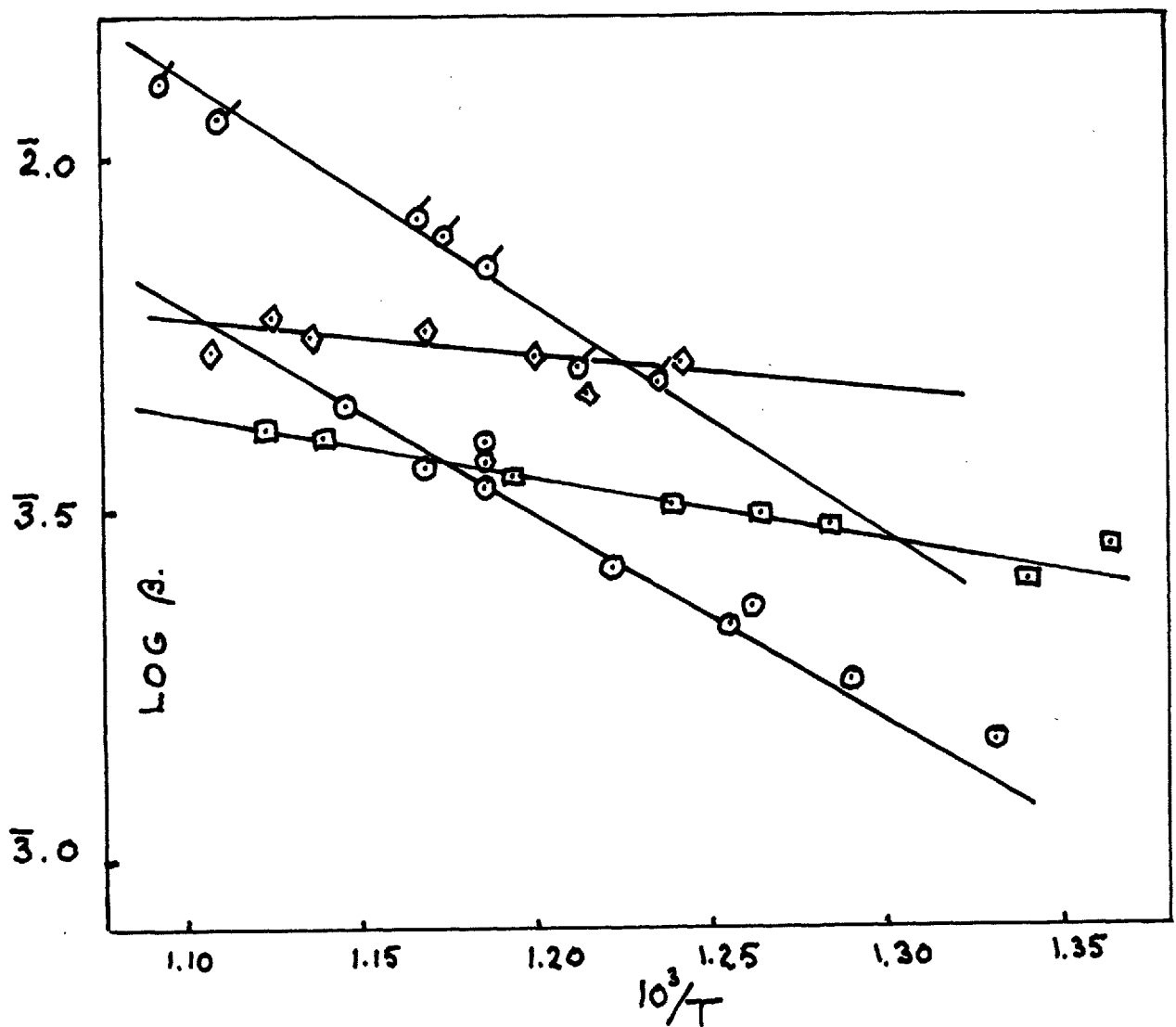


Table 24Activation energies for the steady-state conductivity of KCl

Crystal (run)	E(eV)	Temp. range ($10^3/T$)
Stockbarger (2) Rhodium electrodes	1.63	1.100 - 1.200
Stockbarger (3)	1.74	1.100 - 1.200
Stockbarger (3A)	1.41	1.100 - 1.200
Harshaw (5)	1.39	1.100 - 1.220
Doped 119×10^{-5} mole ratio SrCl_2 (11)	{ 1.05 0.46	1.100 - 1.130
		1.400 - 1.700

Table 25Calculated values for the number of electrons in the conduction band per cm^3 if the mobility of the electron = $1 \text{ cm}^2/\text{volt sec}$

$10^3/T$	1.10	1.15	1.20
Run			
3	10^{13}	10^{12}	10^{12}
3A	10^{13}	10^{12}	10^{12}
5	10^{13}	10^{13}	10^{12}
2	10^{13}	10^{12}	10^{12}
Sr^{2+} doped (11)	10^{13}	10^{13}	10^{13}

These values are to the nearest power of 10.

shows an activation energy of 0.09 eV. A similar conclusion was reached by Allnatt (1959). Since, for small voltages, β should be directly proportional to the diffusion coefficient of the species,

this implies that we have two different activation energies of diffusion dependent on thermal history. This is in accord with the change in the activation energy for the steady-state conductivity on annealing (run 3 and 3A) although the magnitude of the energies involved is rather different.

The numerous inconsistencies found by the use of the Jaffé theory lead us to conclude that this theory must be inapplicable to the system under investigation despite its initial success in predicting a sum of exponential terms for I_p . This may be a result of the numerous assumptions made. For this theory to be strictly applicable, the electric field should be homogeneous throughout the medium; this however is extremely unlikely and has in fact been shown by Kahn (1962) to be false. The Jaffé theory was constructed with the idea of ionic polarization leading to a residual ionic current, whereas in the present situation we do have the build-up of an ionic space charge but the final steady-state current is largely electronic. As we are not able to distinguish between ionic and electronic steady-state currents, the justification for this statement stems from (a) the similarity in the order of magnitude of σ_{∞} in pure and Sr^{++} -doped crystals, and (b) from the agreement between the measured capacities and those calculated on the assumption that both ionic carriers are completely blocked at the electrodes, (o, o). This inevitably means that the electrode reactions must be an important feature of the conductance process. They must clearly involve the taking of an electron from the Fermi level of the metal

electrode into the crystal at one electrode (the cathode) and vice versa at the anode. Since the valence band of potassium chloride is 9.4 eV below the conduction band, an enormous amount of thermal energy would be required to remove an electron from the valence band to the conduction band. We are thus forced to the conclusion that there must be donor states present whose ionization energy is small enough to allow thermal excitation of the electrons into the conduction band. The identity of these donor states is uncertain, although if the crystal were slightly non-stoichiometric the excess electrons could be trapped by anion vacancies to form F-centres of energy ~ 2.0 eV below the conduction band. Since, from the a.c. conductivity data, we know that there are always a certain number of divalent impurity ions present, there exists also the possibility of the presence of z-centres, particularly in the doped crystals. The relevant optical absorption band is the z_2 -band which is thought to be due to a Sr^{2+} ion plus an electron and a vacancy pair at temperatures above $1100^\circ C$. These bands have been investigated by Chiarotti et al. (1954) and shown to replace the z_1 -band which is due to an electron trapped at a Sr^{2+} ion in KCl. Thus if these centres are present they could act as donor states. Unfortunately, no theory of electrode reactions between platinum and potassium chloride has yet been given.

4.4. Current-voltage characteristics

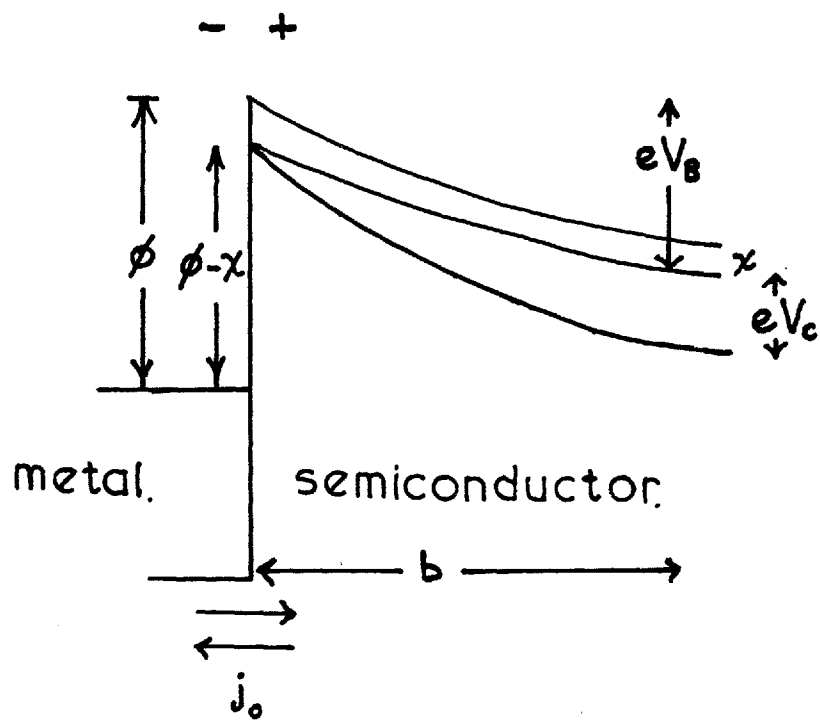
As is readily seen from the diagrammatic representation of the current-voltage curves (fig.30), the combination of the various conduction processes is extremely complex. It is thought that the

electrode-salt reaction is a dominant feature.

When an external voltage V is applied to a two-electrode system, a current flows and the total voltage is shared between the two contact resistances and the bulk resistance of the salt, hereafter regarded as a n-type semiconductor. That part of the voltage which appears across the barrier, the barrier voltage, will be denoted by V_B ; eV_B corresponds to the energy difference between the bottom of the conduction band at $x = 0$ (the interface) and at $x \gg b$ which denotes the end of the barrier. Neglecting corrections due to the image potential, the difference between the work function ϕ of the metal and the electron affinity χ of the crystal, $\phi - \chi$, can be regarded as constant. The distortion of the barrier under the applied voltage is shown in fig.56. eV_0 is the amount by which the conduction levels are lowered at the cathode when the field is applied. The Fermi level of the metal is taken as the reference level. With this convention, the height of the barrier as seen from the semiconductor side increases when the applied voltage is positive and diminishes when it is negative.

In the absence of an electrical field the electrons in the metal are in dynamic equilibrium with those in the semiconductor. The two horizontal arrows symbolizing the rates at which the barrier is crossed are therefore drawn of equal size. When the semiconductor is made positive with respect to the metal, the probability of an electron transition from the metal to the semiconductor is still governed by the factor $\exp(-(\phi - \chi)/kT)$. On the other hand, the

FIG. 56



probability of an electron transition into the metal from the conduction band is proportional to $\exp(-e(V_C + V_B)/kT)$. The equilibrium is thus lost and a current flows. The current from crystal to metal is now

$$j = j_0 \exp(-eV_C/kT);$$

that from the metal electrode to the crystal is still j_0 , so that the net current into the crystal is

$$4.4.1 \quad j = j_0 \left\{ 1 - \exp(-eV_C/kT) \right\}.$$

If the field can be considered uniform, $V_C = bF$.

Similarly, at the anode, the conduction levels are raised by an amount eV_A as the semiconductor is negative with respect to the metal. Thus the electron current from semiconductor to metal is

$$j = j_0 \exp(eV_A/kT)$$

and the net current (in the same direction) is

$$4.4.2. \quad \begin{aligned} j &= j_0 \left\{ \exp(eV_A/kT) - 1 \right\} \\ &\simeq j_0 \exp(eV_A/kT). \end{aligned}$$

A steady current in the external circuit will only be observed when a particular carrier becomes unblocked at both electrodes. Thus it should be possible to decide at which electrode the carriers become unblocked last, from the applicability of either equn. 4.4.1 or 4.4.2. V_C and V_A are unknown but they may be replaced by the applied voltage, V .

In analysing the data with the use of equations 4.4.1 and 4.4.2, the current j was obtained by subtracting from the actual measured values, the electronic component of the current at that applied voltage. This latter current, j_e , was found by an extrapola-

tion of the initial linear part of the $i(V)$ curve. It was found that the second curved portion of the $i(V)$ curve could be fitted by equn. 4.4.1, and the curved section immediately following the σ_{∞} line could be fitted to equn. 4.4.2. Qualitatively, the entire current-voltage curve for the pure KCl can thus be split up into five regions with increasing applied voltage as the controlling factor. (1) At low voltages both ionic charge carriers are blocked and the residual current is electronic in nature. (2) This is succeeded by a voltage-region in which the cations gradually become discharged. (3) In the next (ohmic) region, anions are blocked and the current is limited by the number and mobility of the cations giving a conductivity $\sigma' = j_0 F$. (4) In the next curved region, discharge of anions commences. (5) Finally, both carriers are unblocked and the conductance becomes equal to σ_0 . On this basis we were able to calculate the barrier thickness, b , for the two Harshaw crystals used in runs 5 and 10. The values of these parameters are presented in table 26. The quantity σ_1 should represent the cationic contribution to the conductivity of KCl; when $\log \sigma_1$ is plotted against T^{-1} , an activation energy of 1.86 eV was obtained. This is in good agreement with the analysis of the a.c. conductivity, from which we find that $(\Delta h_1 + \frac{1}{2}h) = 1.9$ eV. However, it was found that $\sigma_1 \simeq \frac{1}{2} \sigma_0$, which indicates that the cationic transport number should be approximately 0.5. This value is in poor agreement with the a.c. results since we have shown in section 3.1. that $t_1 \sim 0.9$. It must therefore be concluded that the present theory is rather oversimplified and involves too many

Table 26

Values of barrier thickness, calculated from
equations 4.4.1 and 4.4.2

Run 5	T°C	anode b(cm)	cathode b'(cm)
	575	2.37×10^{-4}	4.07×10^{-4}
	636	3.29×10^{-3}	4.78×10^{-3}
	653	4.41×10^{-2}	-
Run 10			
	559	9.42×10^{-4}	1.47×10^{-3}
	574	9.58×10^{-4}	1.98×10^{-3}
	597	1.10×10^{-3}	5.78×10^{-3}
	626	2.27×10^{-3}	-
	648	1.02×10^{-2}	-

Table 27

Run 10	T°C	b(cm)
	559	6.77×10^{-4}
	574	8.26×10^{-4}
	597	8.88×10^{-4}
	626	1.96×10^{-3}
	648	8.02×10^{-3}

approximations to be a complete solution to the problem of these
current-voltage curves.

In all the above calculations for b , we have always subtracted the extrapolated electronic current. However, we have no proof that with increasing voltage the electronic current increases linearly. The other extreme would be to calculate values of b neglecting the electronic contribution. This new set of values is presented in table 27. The difference between the two sets is not very great, so it appears that inclusion or omission of j_e does not affect the calculations too drastically. Unfortunately, we are left with quite a clear qualitative picture of the phenomenon but the quantitative interpretation is so far very uncertain.

Fig.31, which shows the effect of an increasing d.c. applied voltage upon the capacity of the crystal, is in agreement with the above qualitative picture. As this graph indicates, at high voltages the ionic space charges are negligible, in agreement with the interpretation of the current-voltage curves.

The current-voltage curves measured for the two doped crystals X 4 and X 5 can be broken up into three regions. (1) The first of these corresponds, as in the pure crystal, to all ionic species blocked at the electrodes. (2) Since very few anion vacancies are present, the only curved region is due to the discharge of the cations. (3) The final linear region corresponds to σ_0 , for at these fields the cations are completely free and their rate of discharge $\geq$ their rate of arrival at the electrode. The curved portions (2) were fitted to equn. 4.4.2 giving values of b' presented in table 28.

Table 28Calculated values of b' for the doped crystals

Run 11, Crystal X 5

$T^{\circ}\text{C}$	$b'(\text{cm})$
550	1.62×10^{-5}
583	3.28×10^{-4}
602	1.68×10^{-4}

Run 17, Crystal X 4

$T^{\circ}\text{C}$	$b'(\text{cm})$
570	1.71×10^{-3}
590	1.97×10^{-3}
603	1.44×10^{-3}

Until the precise electronic contribution is known it seems impossible to get a full understanding of the current-voltage curves. The distribution of the field within the crystal must also be known, since if the voltage falls mainly over the blocking region the field to be used in equations 4.4.1 and 4.4.2 must be $\sim 10^5$ volts/cm instead of the $\sim 10^2$ volts/cm used.

Unfortunately, no quantitative work has been done on this problem although Császár (1958) has observed rectifying effects, similar to those reported in the present work, in sodium chlorido.

4.5. Thermoelectric power

In section 1.7 it was shown that Allnatt and Jacobs (1961,b) have derived an expression for the thermoelectric power of an alkali halide crystal in contact with metal electrodes containing no cation in common with the salt. The heterogeneous thermoelectric power was found by equating the chemical potential of the electron in the two phases, assuming that the dominant source of electrons in the salt was the F-centre. Henceforth this theory will be referred to as the F-centre theory. For the impure crystals it was also assumed that the F-centres were the main source of electrons, although the presence of other traps was suspected. Hence they established that the thermoelectric power of an impure crystal can be expressed by

$$4.5.1. \quad \text{Te}\theta(y) = \left[\frac{-y^2 Q_{M^+} - \lambda(-Q_{X^-} - h_s)}{y^2 + \lambda} \right] - (H_F - h_s) - kT \ln n_B(y).$$

Q_{M^+} and Q_{X^-} are the heats of transport of the cation M^+ and anion X^- , λ is the ratio* of the mobility of the anion and cation vacancies, $y = n_+/n_0 = n_0/n_-$ where n_+ is the number of cation vacancies per unit volume in the crystal, n_- the number of anion vacancies and n_0 the value of $n_+ = n_-$ in the pure crystal at the same temperature. $n_B(y)$ is the number of electrons per unit volume in the conduction band and H_F is the enthalpy change on taking an electron from an F-centre to the conduction band at constant temperature and pressure. h_s is the enthalpy of formation of a Schottky defect pair.

* In this section λ is used to denote the mobility ratio so that the symbol ϕ can be reserved for the electric potential.

Since $y \gg 1$, for the impure crystal, we have

$$4.5.2. \quad -Te\theta(y) = Q_{M+} + H_F - h_s + kT \ln n_B(y).$$

Assuming that Q_{M+} is independent of T it can then be shown from equn.

4.5.2 that

$$4.5.3. \quad \frac{3kT - Te\theta(y) - T \partial [-Te\theta(y)] / \partial T}{\partial T} = Q_{M+}.$$

The mean value of $\partial [Te\theta(y)] / \partial T$ found from the plot of $Te\theta(y)$ against T by the method of least mean squares, was 1.12×10^{-3} eV/deg over the temperature range 780°K to 930°K. Q_{M+} was then calculated from equn. 4.5.3 for each temperature. The results varied from 0.38 to 0.32 eV giving a mean of 0.36 eV with no obvious temperature-dependence.

Using this value of Q_{M+} and the expression for $Te\theta(1)$, Q_{X-} was then calculated from the results for two Stockbarger crystals and the Kyropoulos crystal used in run 20. The mean value of Q_{X-} was found to be 2.3 eV with no significant temperature dependence.

As a check on the theory we have calculated $n_B(y)$ and $n_B(1)$. It was found that $n_B(y)$ was of the order of 10^6 electrons/cm³ and $n_B(1)$ varied from crystal to crystal over the range 10^7 to 10^9 electrons/cm³. These results are of a reasonable order of magnitude.

A further check on the theory may be made by examining the temperature dependence of n_B , as

$$\frac{\partial \ln n_B(y)}{\partial (1/T)} = (h_s - H_F)/k$$

4.5.4. and

$$\frac{\partial \ln n_B(1)}{\partial (1/T)} = (\frac{1}{2}h_s - H_F)/k.$$

The graph of $\ln n_B(y)$ against T^{-1} is a very good straight line of the correct slope. In the graph of $\ln n_B(1)$ against T^{-1} the points lie on straight lines although the slope is approximately half the theoretical one given by equn. 4.5.4. However, this calculation involves t_+ , t_- and Q_{X-} , hence the accuracy of the values of the final quantity, $n_B(1)$ might be expected to be rather poor.

As a check on the sensitivity of the equations, two additional arbitrary values of $\frac{\partial}{\partial T} [-Te\theta(y)]$ were used to calculate Q_{M+} and $n_B(y)$. As is evident from table 28, variations in $\frac{\partial}{\partial T} [-Te\theta(y)]$ can produce a marked change in Q_{M+} and $n_B(y)$. On a physical basis (e.g. the theory of Wirtz) we would expect Q_{M+} to be approximately 0.7 eV in KCl and we can see from table 28 that the relevant value of $\frac{\partial}{\partial T} [-Te\theta(y)]$ is quite reasonable. However, putting $n_B(y) = 10^{13} \text{ cm}^{-3}$ as found from d.c. conductivity data (assuming $u_e = 1 \text{ cm}^2/\text{volt sec}$), we find $Q_{M+} = -1.5 \text{ eV}$ which is impossible. A knowledge of the mobility of the electron would help to clarify this situation.

A disappointing feature of the calculated quantities lies in the agreement with the only other existing data, that of Allnatt and Jacobs (1962,a). They found a mean value of 0.99 eV for Q_{M+} and 2.0 eV for Q_{X-} . It appears that the value Q_{M+} cannot be fixed too precisely at present and the rather wide limits quoted on a value of $0.7 \pm 0.3 \text{ eV}$ are probably realistic. It was suspected that these wide limits might have been due to the extremely limited interpretation of the origin of the electrons in the salt in the original theory. With this in mind, a general approach has been adopted by considering the salt to be a

rather poor n-type semiconductor. As with the F-centre theory there will be a heterogeneous thermoelectric power at the electrode interface due to the temperature-dependence of the contact potential. At equilibrium

$$4.5.5. \quad \bar{\mu}_e^{M'} = \bar{\mu}_e^{MX}$$

where the $\bar{\mu}$'s are the electro-chemical potentials of the electrons in the two phases, electrode (M') and crystal (MX). The contact potential $\bar{\Phi}$ is then given by

$$4.5.6. \quad e\bar{\Phi} = -\mu_e^{MX} + \mu_e^{M'} = e(\phi^{M'} - \phi^{MX})$$

where e is the charge on the proton. Hence

$$4.5.7. \quad \frac{e\partial\bar{\Phi}}{\partial T} = e\theta_{het} = s_e^{MX} - s_e^{M'}$$

where s is the entropy of the electron in the respective phases.

The term $s_e^{M'}$ is small and may be neglected. For a non-degenerate semiconductor, Fowler and Guggenheim (1939), have shown that

$$4.5.8. \quad \mu_e^{MX} = kT \ln \lambda_e = kT \ln n/N_c$$

where n is the electron concentration in the conduction band and

$$N_c = \left\{ \frac{2(2\pi m_e kT)}{h^2} \right\}^{3/2},$$

m_e being the effective mass of the electron in the conduction band.

As pointed out by Rosenberg (1960), this expression for μ_e is valid only when

$$\frac{n}{N_c} < 0.1.$$

$$\text{As } N_c = 2.53 \times 10^{19} \left(\frac{T}{300} \right)^{3/2} \left(\frac{m_e}{m} \right)^{3/2} \text{ cm}^{-3},$$

m being the free-electron mass, and $10^{-2} < \frac{m_e}{m} < 10$, N_c lies between about 8×10^{16} and 4×10^{21} in the temperature range 600 - 900°K. For the electron concentrations expected in the alkali halides (at most 10^{12} cm^{-3} , from the d.c. conductivity data) the formula

$$\mu_e^{MX} = kT \ln \frac{n}{N_c}$$

is thus exact. At very high electron concentrations ($> \sim 0.1 N_c$) it would be necessary to allow for the degeneracy of the electron gas (Rosenberg, 1960). Thus

$$4.5.8.1 \quad \mu_e^{MX} = kT \ln \frac{n}{N_c} - \chi_0$$

if our usual convention that the energy zero corresponds to an electron at rest outside the crystal is adopted. On differentiating equn.

4.5.8.1 with respect to temperature, we have

$$4.5.9. \quad s_e^{MX} = -k \ln \frac{n}{N_c} - \frac{E_0}{2T} + \frac{3k}{2}$$

since

$$n = \left\{ \frac{N_c N_D}{2} \right\}^{1/2} \exp(-E_D/2kT)$$

for a single set of donor states, N_D in number, located at an energy $-E_D$ below the bottom of the conduction band provided

$$N_D \gg N_c e^{-E_D/kT}.$$

We know $E_D \sim 3-4 \text{ eV}$, from the d.c. conductivity results; therefore, $\exp(-E_D/kT) \sim 10^{-20}$ at 1000°K. Only if E_D is as small as 2 eV will the approximation be in jeopardy and then only if N_D is as small as 10^{12} cm^{-3} . More likely, N_D will be about 10^{16} or 10^{17} cm^{-3} . Thus from equn. 4.5.7,

$$4.5.10. \quad -Te\theta_{het} = +kT \ln \frac{n}{N_c} + \frac{E_D}{2} - \frac{3kT}{2}$$

$$\text{and} \quad T \left[\frac{\partial}{\partial T} (-Te\theta_{het}) \right] = kT \ln \frac{n}{N_c} + \frac{E_D}{2} - \frac{3kT}{2}$$

so that

$$4.5.11. \quad -Te\theta_{het} - T \left[\frac{\partial}{\partial T} (-Te\theta_{het}) \right] = 0.$$

The form of this result is unaltered by doping with M^{2+} , although N_D , E_D may be changed. From the Allnatt and Jacobs (1961,b) theory we have for the homogeneous contribution to the thermopower

$$-Te\theta_{hom}(1) = (Q_{M^+} - \frac{1}{2}h_s)t_+ - (Q_{X^-} - \frac{1}{2}h_s)t_-$$

$$4.5.12. \quad -Te\theta_{hom}(y) = Q_{M^+} - kT^2 (\partial \log n_+ / \partial T).$$

In this theory association of defects to form complexes was neglected.

To include association effects, we write

$$4.5.13. \quad N_+ = cN(1-p); \quad \log n_+ = \log c + \log(1-p),$$

where p is the degree of association and χ the enthalpy of association of a complex. Therefore

$$\frac{\partial \log n_+}{\partial T} = \frac{\partial \log(1-p)}{\partial T} = \frac{1}{kT^2} \frac{\chi p}{1+p}$$

and hence, from equn. 4.5.12,

$$4.5.14. \quad -Te\theta_{hom}(y) = Q_{M^+} - \frac{\chi p}{1+p}$$

and

$$T \left[\frac{\partial}{\partial T} \{-Te\theta_{hom}(y)\} \right] = T \frac{\partial Q_{M^+}}{\partial T} + \frac{\chi^2}{kT^2} \cdot \frac{p(1-p)}{(1+p)^2}.$$

The total thermoelectric power will therefore be given by the sum

of equn. 4.5.10 and 4.5.14,

$$4.5.15. \quad -Te\theta(y) = Q_{M^+} - \frac{\chi p}{1+p} + kT \ln \frac{n}{N_c} + \frac{1}{2}E_D - \frac{3}{2}kT$$

$$= Q_{M^+} + kT \ln \frac{n}{N_c} + \frac{1}{2}E_D - \frac{3}{2}kT$$

if association effects are small as was shown to be the case by the a.c. conductivity measurements. If they are not negligible, the term $-\chi p/(1+p)$ must be added to the r.h.s. Therefore, in the region where association is small,

$$4.5.16. \quad -Te\theta(y) - T \left[\frac{\partial}{\partial T} \left\{ -Te\theta(y) \right\} \right] = Q_{M^+} - T \frac{\partial Q_{M^+}}{\partial T}.$$

In other words, since the temperature dependence of θ_{het} is zero, the temperature dependence of $\theta(y)$ is due solely to that of Q_{M^+} , apart from possible corrections due to association. Since experimentally $\theta(y)$ is practically constant, Q_{M^+} must be independent of temperature, as anticipated, and

$$4.5.17. \quad Q_{M^+} = -Te\theta(y) - T \left[\frac{\partial}{\partial T} \left\{ -Te\theta(y) \right\} \right], \quad p \ll 1$$

$$y^2 \gg 1.$$

This result is essentially the same as that obtained by the F-centre theory. The total thermoelectric power of the pure crystal is (from equn. 4.5.10 and 4.5.2) given by

$$4.5.18. \quad -Te\theta(1) = t_+ Q_{M^+} - t_- Q_{X^-} - \frac{1}{2}h_s(t_+ - t_-) + kT \ln \frac{n(1)}{N_c}$$

$$+ \frac{1}{2}E_D - \frac{3}{2}kT,$$

from which it can be shown that

$$4.5.19. \quad Q_{X^-} = \frac{(h_s - Q_{M^+}) \left[(t_+ t_- / kT) (\Delta h_- - \Delta h_+) + t_+ \right] - \frac{1}{2}h_s - Te\theta(1) + T \frac{\partial [Te\theta(1)]}{\partial T}}{(t_+ t_- / kT) (\Delta h_- - \Delta h_+) - t_-}$$

which is the same as that found from the F-centre theory. Hence using this semiconductor theory with the experimental data the calculated values of Q_{M^+} and Q_{X^-} are the same as those found earlier. However, using the values of $\frac{\partial}{\partial T} [-Te\theta(y)]$ we have calculated values of $n_B(y)$ and found them to be impossibly high. If $n_B(y)$ is allowed to have a reasonable value, 10^{13} cm^{-3} , the calculated value of Q_{M^+} is then 1.8 eV and that of $\frac{\partial}{\partial T} [-Te\theta(y)]$ $3.0 \times 10^{-3} \text{ eV/deg}$. Both these values are unacceptably high and we are forced to conclude that this theory is not the correct solution to the present problem. (see table 29). We can summarize the applicability of the semiconductor theory by remarking that whatever value is chosen for $\frac{\partial}{\partial T} [-Te\theta(y)]$ we do not obtain reasonable values of $n_B(y)$. On the basis of the values of n_B obtained and their temperature-dependence, the F-centre theory must therefore be preferred.

Table 29

Summary of the applicability of the F-centre theory and the semiconductor theory of the heterogeneous thermoelectric power

	$\frac{\partial}{\partial T} [-Te\theta(y)]$ eV/deg	Q_{M^+} eV	order of magnitude for $n_B(y)$ in cm^{-3} (semiconductor)	(F-centre)
Least mean squares	$1.12 \times 10^{-3} \times$	+0.35	10^{20}	10^6
	1.38×10^{-3}	+0.13	10^{22}	10^7
	0.80×10^{-3}	+0.62	10^{18}	10^4
	$\sim 2.9 \times 10^{-3}$	-1.5	10^{35}	$10^{13} \times$
	$\sim 3.0 \times 10^{-3}$	+1.8	$10^{13} \times$	10^{-2}

$\times$ Experimental data: n_B from the d.c. conductivity curves, assuming $u_e = 1 \text{ cm}^2/\text{volt sec}$.

The plot of θ against T^{-1} , of which fig.35 is a typical example, shows two remarkable features. The very sharp increase in θ at $T^{-1} = 2.2 \times 10^{-3}$ is very reproducible and it is believed that it is due to the precipitation of impurities. The temperature at which this occurs is the same as that at which precipitation is detected by conductivity measurements. This is very well exhibited in the crystal doped with 119.8×10^{-5} mole ratio of SrCl_2 . All crystals studied showed a large potential difference across them, immediately after raising the temperature to 500°C . After raising the temperature to 600°C and annealing for 12 hours this potential decreased to the normal thermopower. This behaviour has also been noted by Allnatt and Jacobs (1962,a) and interpreted tentatively as being due to the annealing out of dislocations.

The very pronounced 'lambda' point has not been observed before. This feature was observed in all the pure crystals, but was absent in the doped crystal. It has so far not proved possible to find an acceptable explanation for this effect, although it is thought that it may be connected with a decrease in the number of electrons over this temperature range. Weiss (1962), in the course of thermopower measurements on $\alpha\text{-AgI}$ has observed a 'lambda' point at 280°C . He has proposed that the Ag^+ and I^- ions exchange lattice positions thereby producing the appropriate entropy changes. The minimum of the 'lambda' point he attributes to a complete dissociation of the silver lattice. This idea would not be applicable to KCl because the energy required for a cation and anion to interchange

lattice positions would be considerable.

From the thermopower measurements on the crystal with evaporated Ag electrodes it is apparent that the electron concentration has not been increased much. However, the high values of θ at the highest temperatures may be due to excitation of electrons from deep traps.

Appendix 1

Voltage selection system

For the calibration voltage it is apparent from fig.57 that

$$\frac{s}{S} = \frac{r_1 R_g}{r_1 + R_g} \bigg/ r_2 + \frac{R_g r_1}{r_1 + R_g} = \frac{r_1 R_g}{r_1 r_2 + R_g (r_1 + r_2)} .$$

When taking the voltage for conductivity measurements, we have (fig.58):

$$\begin{aligned} \frac{ps}{S} &= \frac{r_1 (R + R_g)}{r_1 + R + R_g} \bigg/ r_2' + \frac{r_1 (R + R_g)}{r_1 + r_2 + R_g} \\ &= \frac{r_1 (R + R_g)}{r_1 r_2' + (r_1 + r_2') (R + R_g)} \end{aligned}$$

and

$$\frac{u}{ps} = \frac{R_g}{R + R_g} ,$$

therefore

$$\frac{u}{S} = \frac{r_1 R_g}{r_1 r_2' + (r_1 + r_2') (R + R_g)} .$$

Finally

$$\frac{s}{u} = \frac{r_1 r_2' + (r_1 + r_2') (R + R_g)}{r_1 r_2 + R_g (r_1 + r_2)} .$$

When $R, R_g \gg r_1, r_2, r_2'$

$$\frac{s}{u} \approx \frac{R + R_g}{R_g} \cdot \frac{r_1 + r_2'}{r_1 + r_2} = \frac{R + R_g}{R_g} \quad \text{if } r_2 = r_2' .$$

If $r_2 \neq r_2'$, $\frac{ps}{S} = \frac{r_1}{r_1 + r_2'}$

and $\frac{s}{S} = \frac{r_1}{r_1 + r_2} .$

Therefore $\frac{ps}{s} = \frac{r_1 + r_2}{r_1 + r_2}, = p,$

and $\frac{ps}{u} = \frac{R + R_g}{R_g},$ giving $R_g = \frac{uR}{ps - u}.$

$r_2 = r_2'$ corresponds to the case $p = 1$. Thus, if R_g (the grid lead) is known,

$$R = \frac{sr_1 r_2 + sR_g(r_1 + r_2) - ur_1 r_2' - uR_g(r_1 + r_2)}{u(r_1 + r_2')}$$

which gives

$$R_g = \frac{\left[\frac{(u - s)(r_1 r_2)}{r_1 + r_2} \right] + uR}{ps - u}.$$

When $r_1 r_2 \ll R_g$

$$R_g = \frac{uR}{ps - u} = \frac{uR}{s - u}.$$

FIG. 57

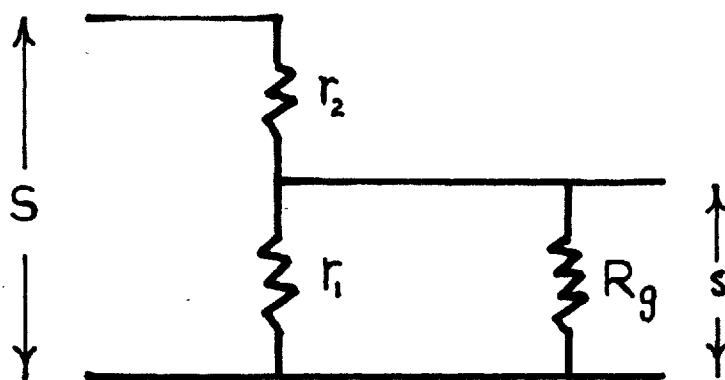
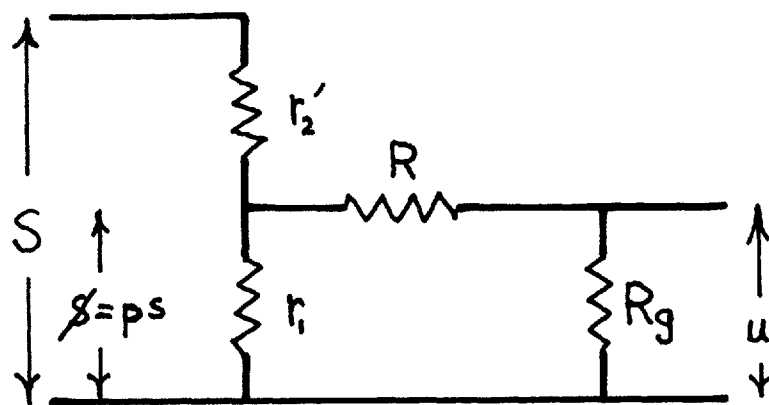


FIG. 58



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