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Electrochemical investigations on the decomposition of solid compounds by applying an electrical potential difference

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When an electrical potential difference E is applied by means of electron-conducting but otherwise inert electrodes to a solid compound with mixed ionic and electronic conductance, the compound is decomposed when the potential difference exceeds a critical value E^*. This process is analysed theoretically and experimentally for the decomposition of Ag_2S as a model sample. The critical electric potential difference E^* for the decomposition and the rate of decomposition are determined. Furthermore, the variation of the chemical potential of silver and the electrochemical potentials of silver ions and electrons within the sample are calculated and measured experimentally.

1. Introduction

When an electrical potential difference E is applied by means of electron-conducting but otherwise inert electrodes to a solid compound with mixed ionic and electronic conductance, the compound is decomposed when the potential difference exceeds a critical value E^*. When the solid is a metal–non-metal compound, the metal is deposited at one electrode, while the non-metal is set free at the other electrode; this will be discussed in detail below. The purpose of this investigation is to analyse this decomposition theoretically and experimentally for a model example. Apart from the critical electrical potential difference E^* for the decomposition, we shall calculate the variation of the chemical potential of the metal component, that of the electrochemical potential of the metal ions and that of the electrochemical potential of the electrons. The rate of decomposition will also be determined.

These investigations [6] are related to papers by Hebb [1], Wagner [2], Miyatani [3], Yokota [4] and Rapp [5], who have studied the polarization behaviour of solid mixed conducting compounds below the decomposition potential. The investigations reported here extend the range of the investigations to include the case of decomposition.

2. Theoretical considerations

As is shown schematically in Fig. 1, an electrical potential difference E is applied to a sample of Ag_2S by means of two electron-conducting probes, e.g. two platinum leads. The boundaries between the silver sulphide sample and the two platinum leads are denoted by the superscripts $'$ or $''$. The negative applied electrical potential difference multiplied by Faraday's constant is equal to the difference in electrochemical potential of the electrons in the two platinum leads:

$$\eta''_e - \eta'_e = -FE. \qquad (1)$$

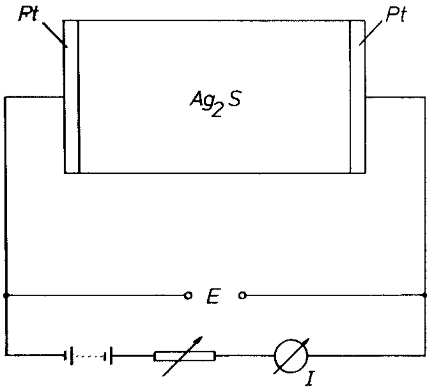

Fig. 1. Schematic diagram for applying an electrical potential difference to an Ag_2S sample with the help of Pt-electrodes.

When we assume that for the electrons equilibrium has been attained at the phase boundaries Pt/Ag_2S, Equation 1 is also valid for the electrochemical potentials of the electrons in Ag_2S at the two phase boundaries. Since the two platinum leads can only exchange electrons, only electrons can migrate in the silver sulphide in the stationary state as long as it is not decomposed. An ion current is prevented by the ion-blocking electrodes, since no silver ions can be delivered by them. Similar considerations apply for the investigations of Hebb [1] and Wagner [7], in which partial conductivities of solids were studied using electrodes which can only exchange certain types of particles, while they block the exchange of others. We shall see below that the fact that the silver ion current is hindered, which corresponds to the statement that the silver sulphide compound is not decomposed, is only valid for potential differences below a certain maximum value. Thus in this range we have

$$j_{Ag^+} = 0. \tag{2}$$

j_{Ag^+} is the particle current density of silver ions in equivalents per unit area and time. Since the ion current is equal to zero, the total electrical current I is equal to the electron current I_e. Thus for the electrical current

$$I = I_e. \tag{3}$$

The general relationship [8] between the particle current density of the silver ions and the gradient of the electrochemical potential of the silver ions in the solid is

$$j_{Ag^+} = -\frac{\sigma_{Ag^+}}{F^2}\,\mathrm{grad}\,\eta_{Ag^+} \tag{4}$$

where σ_{Ag^+} is the partial conductivity of the silver ions and F is Faraday's constant. Since the partial conductivity σ_{Ag^+} of the silver ions has a finite value [9], it follows from Equation 4, taking into account Equation 2, for the case where the compound is not decomposing so that the silver ion current is zero, that

$$\mathrm{grad}\,\eta_{Ag^+} = 0. \tag{5}$$

Under these conditions the gradient of the electrochemical potential of the silver ions is zero. The electrochemical potential of the silver ions in silver sulphide is equal throughout the sample, and thus also in the vicinity of the two phase boundaries to the two platinum leads:

$$\eta''_{Ag^+} - \eta'_{Ag^+} = 0. \tag{6}$$

The electrochemical potentials of the electrons and the silver ions can be separated into a chemical and an electrical contribution. Thus

$$\eta_e = \mu_e - F\varphi \tag{7}$$

and

$$\eta_{Ag^+} = \mu_{Ag^+} + F\varphi. \tag{8}$$

It follows from Equations 7 and 8 that

$$\eta_e + \eta_{Ag^+} = \mu_e + \mu_{Ag^+} = \mu_{Ag} \tag{9}$$

i.e. the sum of the electrochemical potentials of the electrons and silver ions is equal to the chemical potential of the neutral silver. When we apply Equation 9 to the chemical potentials μ'_{Ag} and μ''_{Ag} of the silver in silver sulphide next to the two phase boundaries, to the platinum leads, and take the difference of these silver chemical potentials, we obtain the following equation:

$$\mu''_{Ag} - \mu'_{Ag} = (\eta''_e - \eta'_e) + (\eta''_{Ag^+} - \eta'_{Ag^+}). \tag{10}$$

Substitution of Equations 1 and 6 in Equation 10 leads to the expression

$$\mu''_{Ag} - \mu'_{Ag} = -FE. \tag{11}$$

Equation 11 states that, as long as no metal ions flow, the negative difference of the chemical potential of silver across the sample is equal to the applied electrical potential difference E multiplied by Faraday's constant F. However, the difference of the chemical potentials of the metal can, on thermodynamic grounds, only attain a maximum value. In this case the chemical potential of elementary silver, i.e. μ^0_{Ag}, is reached on one side and on the other a minimum value is reached which is determined by the fact that silver sulphide is in equilibrium with liquid or gaseous sulphur. The chemical potential of the silver which is reached when the silver sulphide is in equilibrium with liquid sulphur is denoted by μ^*_{Ag}; thus

$$\mu_{Ag}[Ag_2S/S_{(l)}] = \mu^*_{Ag}. \tag{12}$$

The chemical potential of the silver in Ag_2S in equilibrium with elementary silver is equal to μ^0_{Ag}, so that

$$\mu_{Ag}[Ag_2S/Ag_{(s)}] = \mu^0_{Ag}. \tag{13}$$

The maximum possible difference of the chemical potentials of the silver on thermodynamic grounds is denoted by $(\mu''_{Ag} - \mu'_{Ag})^*$; this difference is thus given by

$$(\mu''_{Ag} - \mu'_{Ag})^* = -(\mu^0_{Ag} - \mu^*_{Ag}) = -FE^*. \tag{14}$$

The corresponding electrical potential difference E is denoted by an asterisk. In principle this value could be exceeded; however, in this case the compound would be supersaturated with silver on the one side and with sulphur on the other, i.e. the compound would no longer be thermodynamically stable. We shall first neglect such supersaturation and assume that kinetic barriers to the formation of neighbour phases are not present.

The difference $\mu^0_{Ag} - \mu^*_{Ag}$, or E^*, is connected to the value of the Gibbs energy of formation $\Delta G^0_{Ag_2S}$ of Ag_2S from the elements [10]. The following relation is valid:

$$-\Delta G^0_{Ag_2S} = \mu^0_{Ag} - \mu^*_{Ag} = FE^*. \tag{15}$$

This equation states analogous relations to those which would apply for a galvanic cell with pure ionic conductance whose cell reaction is the formation of Ag_2S from the elements.

The relationship according to Equation 15 results from the application of blocking electrodes to the mixed ionic and electronic conductor Ag_2S.

It follows from the considerations given above that if the potential difference E is steadily increased starting from small values, when $E > E^*$ silver and sulphur can be set free at the boundaries to the platinum leads. The formation of the new phases of silver and sulphur determines the chemical potentials of the silver at the phase boundaries to the leads; thus for $E > E^*$ Equation 11 no longer applies. For this reason the preconditions which we have used for the derivation of Equation 11 can no longer all apply simultaneously. Equations 1 and 9 or 10 are, however, still valid since these equations contain generally valid thermodynamic statements. But Equation 2 and related Equations 5 and 6 can no longer be valid since an ion current must necessarily flow for the formation of the new phases. For the case

$$E > E^* \tag{16}$$

the following relationship must be valid

$$\mu''_{Ag} - \mu'_{Ag} = (\mu''_{Ag} - \mu'_{Ag})^* \tag{17}$$

i.e. the difference of the chemical potential of the silver has, when $E > E^*$, a constant value independent of the applied potential difference. Using Equation 10, which as a thermodynamic relationship is still valid, and Equation 1, it follows from Equation 17 that

$$\mu^0_{Ag} - \mu^*_{Ag} = FE - (\eta''_{Ag^+} - \eta'_{Ag^+}). \tag{18}$$

The substitution of Equation 14 into Equation 18 gives after rearrangement, the following expression:

$$\eta''_{Ag^+} - \eta'_{Ag^+} = (E - E^*)F \tag{19}$$

i.e. the difference of the electrochemical potential of the silver ions across the sample is equal to the difference of the applied electrical potential difference and the maximum possible electrical potential difference E^* which does not involve the decomposition of the compound multiplied by Faraday's constant. This potential difference must be considered as the driving force for the flux of silver ions according to Equation 4. According to Equations 19 and 4 silver ions are now transported through the sample, whereby elementary silver is formed on the one side and sulphur is set free from the compound on the other. When liquid sulphur is set free on this side, the chemical potential of the sulphur is fixed as well as that of the silver.

When sulphur evaporates from the silver sulphide sample, the derived equations are in general still valid. The chemical potentials of sulphur and of silver are, however, dependent on the rate of evaporation and thus on the rate of decomposition, so that they cannot be considered as constant.

Electrochemical techniques of measurement allow us to determine separately the electrochemical and chemical potential differences discussed in the above theoretical considerations. This will be shown in the following discussion in connection with experimental measurements.

Because of the ionic disorder in silver sulphide, the situation is particularly clear, thus making possible a further analysis of the variation of the electrochemical potential of the silver ions, the chemical potential of silver and the electrochemical potential of the electrons.

Because of the structural disorder, the partial conductivity σ_{Ag^+} of the silver ions in silver sulphide is constant, independent of deviations from the ideal stoichiometry or of variations of the chemical potential of silver in Ag_2S at a certain temperature. Furthermore the particle current density j_{Ag^+} of the silver ions is in the stationary state, of necessity constant throughout the sample. It thus follows from Equation 4 that the gradient of the electrochemical potential of the silver ions is also locally constant, i.e. the electrochemical potential η_{Ag^+} of the silver ions varies linearly across the length of the Ag_2S sample. The value of grad η_{Ag^+} is thus given by the following equation:

$$\operatorname{grad} \eta_{Ag^+} = (\eta''_{Ag^+} - \eta'_{Ag^+})/L \qquad (20)$$

where L is the length of the Ag_2S sample. Substitution of Equation 20 into Equation 4 leads to the expression

$$j_{Ag^+} = -\frac{\sigma_{Ag^+}}{F^2}\,\frac{\eta''_{Ag^+} - \eta'_{Ag^+}}{L} \qquad (21)$$

i.e. an expression for the magnitude of the silver ion particle current density. Using Equation 19, it follows that

$$j_{Ag^+} = -\frac{\sigma_{Ag^+}}{F}\,\frac{E - E^*}{L}\,. \qquad (22)$$

Equation 22, in the form of the particle current density of the silver ions, is a measure of the rate of decomposition of the Ag_2S sample as a function of the applied electrical potential difference E.

We shall proceed to discuss the variation of the electrical potential φ, the electrochemical potentials η_{Ag^+} and η_e of the silver ions and electrons and of the chemical potential μ_{Ag} of the silver in the Ag_2S sample. Because of the structural disorder of the silver ions in Ag_2S, the chemical potential μ_{Ag^+} of the silver ions in Ag_2S can be considered as constant [10]. Thus

$$\mu_{Ag^+} = \text{const.} \qquad (23)$$

It follows from Equation 8 that

$$\operatorname{grad} \eta_{Ag^+} = F \operatorname{grad} \varphi \qquad (24)$$

i.e. the electrical field strength grad φ is proportional to grad η_{Ag^+} and is thus also constant throughout the Ag_2S sample. Using Equation 19, the value of this quantity is as follows:

$$\operatorname{grad} \varphi = (E - E^*)/L. \qquad (25)$$

The electrical potential difference in the interior of the Ag_2S is thus $(E - E^*)$; this is true for applied electrical potential differences $E > E^*$. The contribution E^* of the applied electrical potential difference thus, of necessity, decreases at the phase boundaries Ag/Ag_2S or $Ag_2S/Pr, S(l)$.

When $E < E^*$, i.e. when the applied electrical potential difference is smaller than the decomposition potential E^* so that the Ag_2S sample does not decompose, it follows from Equations 5, 8 and 23

$$\operatorname{grad} \varphi = 0 \quad \text{for } E < E^* \qquad (26)$$

i.e. there is no electrical field in the interior of the Ag_2S sample. The electrons are thus moving only in a concentration gradient. If we now neglect the contribution of the electron defects, which is small in comparison to that of the quasi-free electrons, the following relationship applies for a linear geometry

$$j_e = -D_e \frac{dc_e}{dx} \qquad (27)$$

where c_e is the local concentration of the free electrons and D_e their diffusion coefficient, which we shall assume to be independent of c_e; this is certainly a good approximation. j_e is also locally constant, so that when $E < E^*$ there is a linear concentration gradient of the electrons. Using the following equation [11]

$$c_e = \frac{\pi(8m^*kT)^{3/2}}{2h^3} F_{1/2}\left(\frac{\mu_e - \mu_e^0}{RT}\right) \qquad (28)$$

the variation of the chemical potential μ_e of the electrons can now be calculated, when μ_e at one of the phase boundaries is known. In Equation 28 m^* is the effective mass of the electrons, h is the Planck constant, k the Boltzmann constant and $F_{1/2}[(\mu_e - \mu_e^0)/RT]$ denotes the Fermi–Dirac function which is tabulated for example by McDougall and Stoner [12]. The standard state μ_e^0 of the chemical potential of the electrons is here defined for $a_e = 1$ with $\lim a_e = c_e/N_c$ for $c_e \to 0$, where N_c is the effective state density of the electrons and a_e is the thermodynamic activity of the electrons.

Taking Equations 9 and 23 into account it is then possible to calculate the variation of the chemical potential μ_{Ag} of the silver along the axis of the Ag_2S sample. Since μ_{Ag^+} is constant, this variation is parallel to that of μ_e. However, as we shall see below, the chemical potential μ_{Ag} can be measured as a function of the position in the sample, so that the derived equations can be checked experimentally.

When $E > E^*$, so that the Ag_2S sample decomposes, the variation of the concentration c_e of the electrons is more complex, but can also be calculated. The electrons no longer move only in a concentration gradient, but in addition in an electrical field. The following general equation [8] applies for the flux j_e of the electrons:

$$j_e = -D_e \frac{dc_e}{dx} + c_e \frac{D_e F}{RT} \frac{d\varphi}{dx}. \qquad (29)$$

This equation is again formulated for the one-dimensional case, neglecting the small contribution due to electron defects, $d\varphi/dx$ is given by Equation 25. A closed solution is known for Equation 29, this is as follows:

$$c_e(x) = c_e(x = 0) \exp\left(\frac{F}{RT}\frac{d\varphi}{dx}x\right) + \frac{j_e RT}{D_e F \dfrac{d\varphi}{dx}}\left[1 - \exp\left(\frac{F}{RT}\frac{d\varphi}{dx}x\right)\right] \qquad (30)$$

as becomes clear on substitution.

Equation 30 is used to calculate the concentration c_e of the electrons as a function of x for the case of stationary decomposition; using Equation 28 the variation of the chemical potential μ_e of the electrons can also be calculated. Because of Equations 9 and 23, the variation of μ_e is again parallel to the variation of the chemical potential μ_{Ag} of silver. Thereby μ_{Ag} at the negative electrode is equal to μ^0_{Ag}, since the silver which is deposited here is in the standard state. The chemical potential μ_{Ag} of the silver can again be experimentally determined using suitable probes, as will be discussed in the following section. The latter considerations in the above theoretical discussion can thus also be checked experimentally.

3. The principle of the electrochemical measurements

Fig. 2 shows schematically the experimental arrangement used. The central part is a silver sulphide sample about 5 cm long, 1·26 mm in diameter and somewhat thicker at the ends. Via two platinum leads Pt1 and Pt10, different electrical potential differences $E_{Pt1-Pt10}$ are applied to the ends with the aid of an external voltage source; when the stationary state has been reached, the electrical current I flowing through the sample is measured. Further equally spaced platinum probes Pt2, Pt3, etc., are fixed to the Ag_2S sample, and opposite to them are Ag/AgI probes. The first Ag/AgI probe Ag/AgI1 at the left-hand end was built larger. Different potential differences can be measured between these probes; these permit measurement of the variation of the following potentials in the Ag_2S sample:

(a) the electrochemical potential η_e of the electrons,

(b) the electrochemical potential η_{Ag^+} of the silver ions,

(c) the chemical potential μ_{Ag} of neutral silver.

The electrochemical potential η_e of the electrons between two sample sites can be obtained from the electrical potential difference $E_{Pt1-Pti}$ ($i =$ 2, 3, . . . 10). These probes lead to the formation of phase sequences of the type

$$Pt1/Ag_2S/Pti.$$

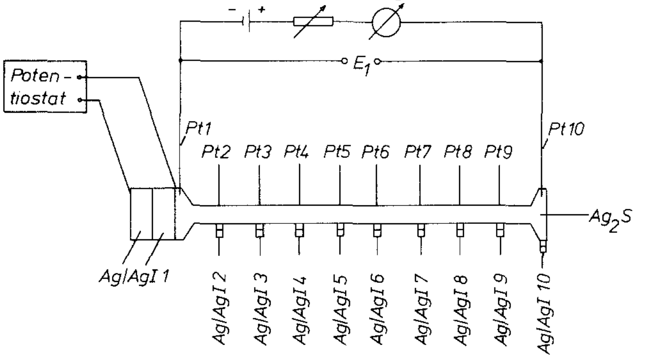

Fig. 2. Experimental arrangement with different Ag/AgI and Pt probes for measuring the variation of:
(a) the chemical potential of silver, (b) the electrochemical potential of silver ions, (c) the electrochemical potential of electrons along the Ag_2S sample during polarization or decomposition.

As has previously been discussed in detail, the following equation applies for these [8, 13]

$$FE_{\mathrm{Pt1-Pt}i} = F(\varphi_{\mathrm{Pt}i} - \varphi_{\mathrm{Pt1}}) = -[\eta_e(i) - \eta_e(1)] \quad (31)$$

i.e. the electrochemical potential difference $[\eta_e(i) - \eta_e(1)]$ of the electrons between the positions i and 1 is equal to the negative product of Faraday's constant and the electrical potential difference between the platinum contacts Pti and Pt1. Using only the Ag/AgI probes it is possible to measure the variation of the electrochemical potential η_{Ag^+} of the Ag$^+$ ions. The following equation applies [8, 13]

$$FE_{\mathrm{Ag/AgI1-Ag/AgI}i} = \eta_{\mathrm{Ag}^+}(i) - \eta_{\mathrm{Ag}^+}(1) \quad (32)$$

i.e. the electrochemical potential difference $[\eta_{\mathrm{Ag}^+}(i) - \eta_{\mathrm{Ag}^+}(1)]$ of the silver ion between the positions i and 1 is equal to the product of Faraday's constant and the electrical potential difference between the Ag/AgI probes at these positions.

Lastly, the local chemical potential μ_{Ag} of neutral silver can be measured between two corresponding probes Pti and Ag/AgIi. These probes form galvanic cells of the type

$$\mathrm{Ag/AgI/Ag_2S/Pt}.$$

The e.m.f. of these is a measure of the chemical potential μ_{Ag} of the silver in Ag_2S. The following relationship applies

$$-FE_{\mathrm{Ag/AgI}i\mathrm{-Pt}i} = \mu_{\mathrm{Ag}}(i) - \mu^0_{\mathrm{Ag}}. \quad (33)$$

The larger Ag/AgI1 probe at the left-hand end of the sample is in addition used to measure the rate of decomposition of the Ag_2S. When the applied electrical potential differences $E_{\mathrm{Pt1-Pt10}}$ are larger than E^*, the Ag_2S decomposes, so that silver would be set free at the left-hand end of the Ag_2S sample, were it not removed by the Ag/AgI1 probe and the corresponding Pt probe. This occurs as follows: a potential of about 1 mV is applied to the cell; although this potential is small, it is sufficient to remove the total amount of silver arriving. This is deposited at the Ag electrode of the Ag/AgI1 probe; the current I_{Ag^+} necessary for this is a measure of the rate of decomposition.

In the experiments, electrical potential differences $E_{\mathrm{Pt1-Pt10}}$ between 10 and 500 mV were applied; when the stationary state had been reached, the various potential differences, the current I_e and the current I_{Ag^+} were measured. When $E_{\mathrm{Pt1-Pt10}} < E^*$, I_{Ag^+} was always zero. Experimental results will be presented and discussed below.

4. Experimental

Silver was purchased from Degussa, Frankfurt, and sulphur was purified using Wartenberg's method [14]. The silver sulphide samples were grown in a unidimensional manner as described previously [9] in a thick-walled glass tube of length about 5 cm and internal diameter 1·26 mm. Radial holes were bored in this tube for the various probes, which were kept in contact with the sample by means of springs; in the case of the Ag/AgI probes, the AgI powder was pressed into the holes and placed in contact with silver rods. The experimental arrangement is shown schematically in Fig. 2. During the measurements it was located in a glass tube oven in a nitrogen atmosphere. The potentiostat and measuring instruments used were such as are usually employed for electrochemical measurements. It was possible to carry out measurements on the same sample over a period of several weeks; the results were reproducible using either the same sample or different ones.

5. Results and discussion

The studies were carried out using samples whose stoichiometry corresponded to a point approximately symmetrically situated between equilibrium of Ag_2S with silver and with sulphur. The results of a typical series of measurements at 473 K are shown in Figs. 3–7. The abscissa in Fig. 3 is the e.m.f. $E_{\mathrm{Pt1-Pt10}}$, i.e. the potential difference applied between the platinum probes at the ends of the sample. According to Equation 1 this, when multiplied by Faraday's constant, is identical to the negative difference of the electrochemical potentials of the electrons at the two ends of the sample. According to Equation 33, curves showing the potential difference $E_{\mathrm{Ag/AgI1-Pt1}}$ and $E_{\mathrm{Ag/AgI10-Pt10}}$ are a measure of the chemical potential of the silver at the left- or right-hand ends of the sample. When no external potential difference is applied between Pt1 and

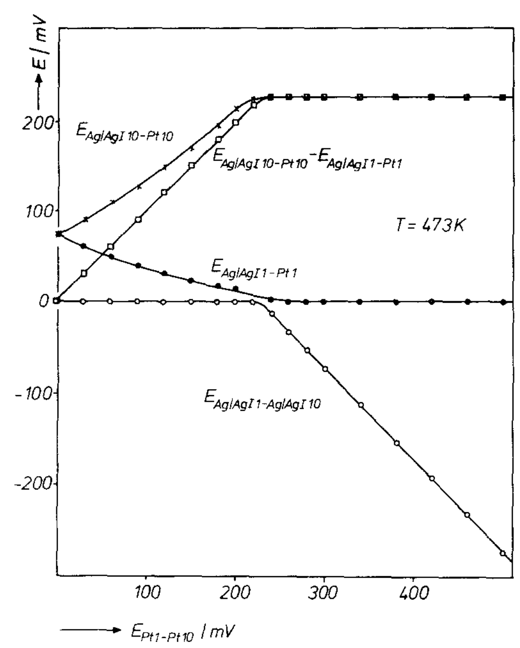

Fig. 3. Various potential differences at the ends of the Ag_2S sample as a function of the applied electrical potential difference between Pt1–Pt10 as explained in the text.

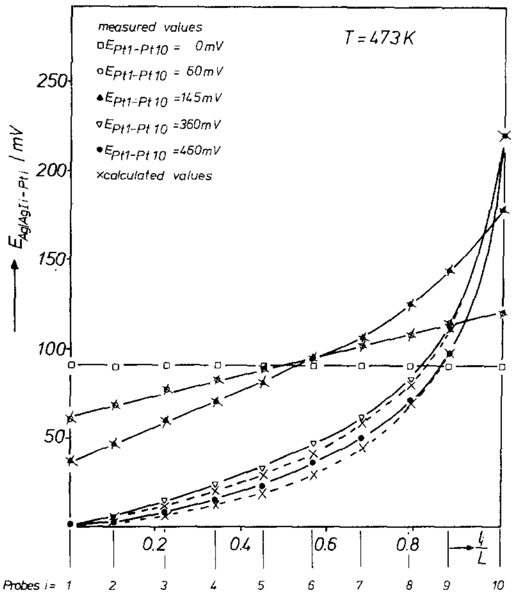

Fig. 5. Variation of the potential difference $E_{Ag/AgIi-Pti}$ along the Ag_2S sample for various applied potential differences.

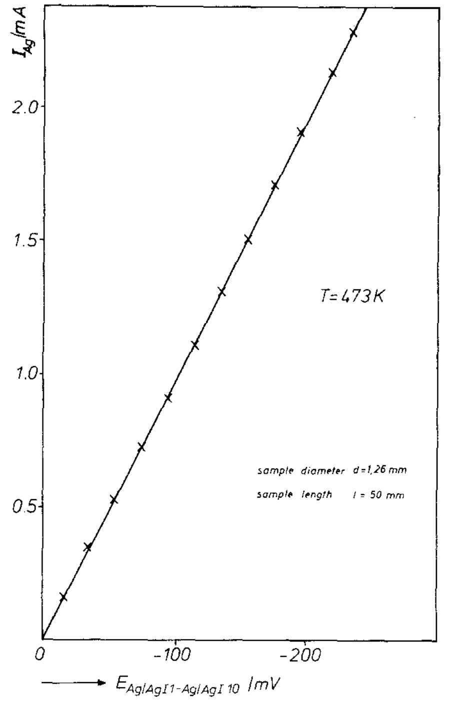

Fig. 4. Rate of decomposition measured as ionic partial current I_{Ag} as a function of $E_{Ag/AgI1-Ag/AgI10}$.

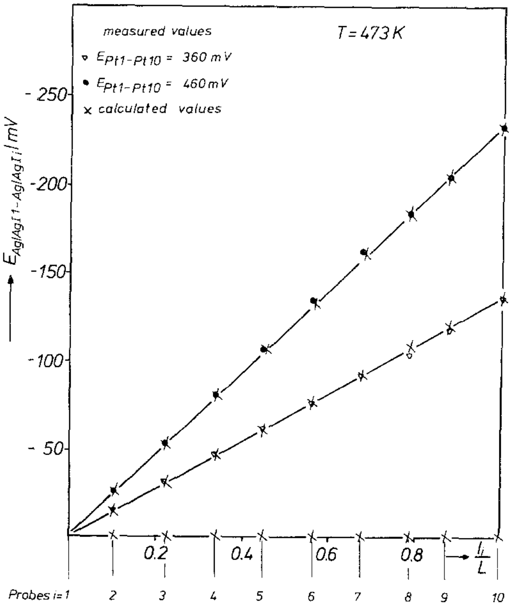

Fig. 6. Variation of the potential difference $E_{Ag/AgI1-Ag/AgIi}$ along the Ag_2S sample for various applied potential differences.

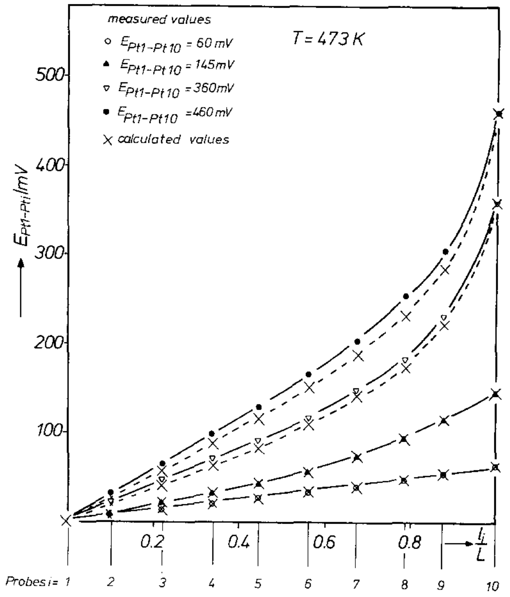

Fig. 7. Variation of the potential difference $E_{Pt1-Pti}$ along the Ag_2S sample for various applied electrical potential differences.

Pt10, the chemical potential of the silver μ_{Ag} is constant throughout the whole sample and is thus also identical at the left- and right-hand ends of the sample. It corresponds to the chemical potential in the starting sample and corresponds in this experiment to an e.m.f. of about 80 mV. When the applied electrical potential difference is increased, the chemical potentials of the silver μ_{Ag} at the left- and right-hand ends of the sample change. The potential differences were chosen so that the probe Pt1 was always negative with respect to Pt10. At the left-hand end of the sample the value μ_{Ag} approaches the value μ^0_{Ag}, i.e. equilibrium of Ag_2S with silver, while at the right-hand end of the sample μ_{Ag} approaches the value for Ag_2S in equilibrium with sulphur. The difference between the potentials $(E_{Ag/AgI10-Pt10} - E_{Ag/AgI1-Pt1})$, which is a measure of the difference of the chemical potentials across the sample, is in the range below $E = 228$ mV in which the sample does not decompose, equal (according to Equation 11) to the applied potential difference $E_{Pt1-Pt10}$. In this range the curve is thus a straight line with a slope of 45°. Above 228 mV, decomposition was observed in the sample. This value corresponds to that calculated from Equation 15 [15]. When $E_{Pt1-Pt10}$ is greater than 228 mV, the values $E_{Ag/AgI1-Pt1}$ and $E_{Ag/AgI10-Pt10}$ remain constant. This means that Ag_2S is always in equilibrium with silver at the left-hand end and in equilibrium with sulphur at the right-hand end. The electrical potential difference $E_{Ag/AgI1-Ag/AgI10}$, which according to Equation 32 is a measure of the difference of the electrochemical potentials η_{Ag^+} of the silver ions across the silver sulphide sample, is (as can be seen from Fig. 3) equal to zero when no decomposition occurs. This corresponds to the behaviour expected from Equation 6. When decomposition occurs, the e.m.f. is linearly dependent on the applied potential difference $E_{Pt1-Pt10}$; this corresponds to the behaviour expected from Equations 18 and 19. The rate of decomposition can be calculated using Equations 32 and 21.

The current, which is a measure of the rate of the decomposition, is shown in Fig. 4. (This experiment belongs to a sample of length 5 cm and of diameter 1·26 mm.)

Using the dimensions of the sample and the partial conductivity of the Ag^+ ions which is $3{\cdot}60\,\Omega^{-1}\,cm^{-1}$ at 473 K, the agreement between the experimental and calculated values is extremely good within the limits of precision of the measurements. Fig. 5 shows the variation of the potential difference $E_{Ag/AgIi-Pti}$ for various applied potential differences $E_{Pt1-Pt10}$ for the various probes. These potential differences are a measure of the chemical potential of the silver μ_{Ag} along the axis of the sample. The measured values agree sufficiently with the calculated ones, particularly when it is remembered that approximations were made in the calculations, the influence of the electron defects being neglected.

In Fig. 6 the potential difference $E_{Ag/AgI1-Ag/AgIi}$ across the sample is plotted for various applied potential differences $E_{Pt1-Pt10}$. According to Equation 32 these differences are a measure of the variation of the electrochemical potential of the silver ions η_{Ag^+} along the axis of the silver sulphide sample; as is expected from Equation 20 the variation is linear. For applied potential differences smaller than 228 mV, the quantities $E_{Ag/AgI1-Ag/AgIi}$ were, as expected from Equations 6 and 32, always zero.

Finally, Fig. 7 shows the potential difference $E_{Pt1-Pti}$ along the sample for the same experiments. This difference is a measure of the electrochemical potential η_e of the electrons and was, in agreement with Equations 18, 32 and 33, the sum of the electrical potential differences $E_{\mathrm{Ag/AgI1-Ag/AgI}i}$ and $E_{\mathrm{Ag/AgI}i-\mathrm{Pt}i}$.

In summary, we can say that, by means of electrical potential differences of suitable combinations of probes, it is possible to measure variations in

(a) the chemical potential of the silver μ_{Ag},

(b) the electrochemical potential of the silver ions η_{Ag^+},

(c) the electrochemical potential of electrons η_{e}

across a silver sulphide sample when an electrical potential difference is applied to it by means of two platinum probes. This is true not only for the range in which the $\mathrm{Ag_2S}$ sample does not decompose, but also for that in which decomposition is observed. The values of the decomposition potential difference, the rate of decomposition and the variations of the various chemical and electrochemical potentials are either completely in agreement with theoretical calculations or are in agreement within the limits of the approximations made. This shows the internal consistancy of the investigations carried out.

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