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The Application of Electrophysical Effects to the Study of the Thermal Decomposition of Solids

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A critical review is presented of work on the thermal decomposition of solid inorganic compounds, based on electrophysical phenomena (electrical conductivity, photoconductivity, contact phenomena, thermo-e.m.f., Hall voltage, and dielectric characteristics). It is shown that electrophysical methods offer an effective approach to the study of the thermal decomposition of solids. The need for further developments in the experimental procedures available, and for comprehensive analysis of the results, is stressed. 156 references.

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1. INTRODUCTION

Studies of the mechanism of chemical reactions in the solid phase have both theoretical and practical importance, because many of the reactions used in industrial practice involve solid compounds. Thermal decomposition reactions occur in the metallurgical industry, in the production of catalysts, in the synthesis of new semiconductor materials and phosphors, in the preparation of ferrites, and in the decomposition of explosives. The solution of the problems presented by the control of all these processes is tightly bound up with an understanding of their mechanisms and their kinetics.

Even as recently as 10 years ago, very little attention was paid to the physical aspects of thermal decomposition reactions, but there is no longer any doubt that a sound understanding of the correlation between the kinetics and the electrophysical characteristics of decomposition reactions involving solid inorganic compounds is essential to further progress. The predominant role of ionic and electronic crystal defects in determining decomposition mechanisms and various electrophysical properties has been convincingly demonstrated[1,2]. Electrical conductivity, photoconductivity, contact phenomena, thermo-e.m.f., Hall voltage, and dielectric effects are among the electrophysical phenomena which have been most widely studied. A systematic appraisal of the electrophysical methods of investigation of thermal decomposition reactions, and an analysis of the results, are now needed.

2. STUDIES OF THERMAL DECOMPOSITION BY MEASUREMENTS OF ELECTRICAL CONDUCTIVITY

McDonald and Sandison[3] tried to determine the form of the nuclei of the new phase produced during the thermal decomposition of silver oxalate by combining measurements of electrical conductivity with kinetic studies of the decomposition reaction. For the case of two-dimensional (planar) nuclei, a sudden increase in electrical conductivity was expected when the nuclei began to coalesce (10–25% decomposition). However, the jump in conductivity was observed experimentally at 60% decomposition. The authors concluded[3] that three-dimensional (spherical) nuclei are formed in this reaction. Bel'kevich and Osinovik[4] repeated this work, and arrived at the opposite conclusion. Coalescence of the silver nuclei was observed at 17–30% decomposition of the silver oxalate, suggesting the formation of two-dimensional nuclei. Thus, entirely different results were obtained in nominally similar experiments. One possible explanation is that detailed differences in technique were responsible for the discrepancy, including sample preparation before pressing (drying, ageing, grinding), during pressing (temperature, pressure, duration), choice of electrode material and method of deposition, and, lastly, strength and frequency of the electric field used in the measurement and duration of the electrical stress applied to the sample. No special mention of these experimental details is made in the published papers[3,4], and therefore it is difficult to comment meaningfully. McDonald and Sandison did not describe their measurements of electrical conductivity. Bel'kevich and Osinovik's only comment is that electrical conductivity was measured with pressed samples, using a constant applied d.c. voltage of 1.3 V. The present writer has made a special study[5] of the influence of a d.c. electric field of 80 V cm^{-1} on the electrical conductivity and on the decomposition kinetics of pressed samples of silver oxalate. The field was applied continuously, or intermittently. Bel'kevich and Osinovik[4] have shown that the rate of decomposition of the sample goes through a maximum at the instant when the flash is observed: we have used this observation in our measurements. In the absence of an electric field the sample flashed at 143 ± 4°; with a periodically applied field (5 s, at 10 min intervals) the flash took place at 130 ± 2°, and when the field was applied continuously the sample flashed at 122°. In all cases, the extent of decomposition at the moment of the flash was the same, and a sudden increase in conductivity was observed. Hence it was concluded that a steady electric field accelerates the thermal decomposition of the oxalate, but has no effect on the shape of the silver nuclei. Savel'ev and Greben'[6] placed silver oxalate between condenser plates with a field of 6–10 kV cm^{-1}, and they also observed an accelerated vacuum thermolysis of the oxalate. Similar effects were found with silver and barium azide. The influence of a constant magnetic field (1100 Oe) on the decomposition of these compounds was also examined: both types of field were found to accelerate the thermal decomposition of

barium azide, and to lower the rate of decomposition of silver oxalate. Since transverse electric and magnetic fields can influence only electronic processes, it follows that these processes must play an important role in the thermolysis of barium azide and silver oxalate. These facts give valuable insight into the development of methods for studying electronic processes, and also into the nature of the electronic steps in the thermal decomposition of solids. Sviridov and Branitskii[7] showed that silver oxalate is readily decomposed by grinding: 35% decomposition of the oxalate can be achieved by grinding the material for 20 min. During this treatment the colour of the material changes from white, through grey, to black. We have noted a colour change in silver oxalate during cold pressing. Thus, the grinding and pressing operations used in the prepatation of the samples can lead to the mechanochemical decomposition of the oxalate, with formation of a solid product (colloidal silver) which acts as a catalyst during the subsequent thermal decomposition[8]. But what is the shape of the growing silver nuclei during thermolysis of the oxalate? Assuming that the shape of the silver nuclei is unaffected by the partial decomposition during pressing of the samples and by other artefacts during sample preparation and measurement of the electrical conductivity, and taking into account Griffith's observation[9] of a layered structure in the silver nuclei, Bel'kevich and Osinovik's hypothesis seems the more credible.

Garner and Heycock[10,11] monitored electrical conductivity in their study of the induction period attending the thermal decomposition of lithium aluminium hydride at 100°, and observed parallel changes in conductivity and in pressure of hydrogen evolved. The electrical conductivity increased by a factor of 2 (from 3×10^{-8} to 6×10^{-8} ohm^{-1}) in the first 35 min, reaching a maximum. After 45 min the conductivity had reverted to its original value, and after 160 min a minimum in conductivity was observed. After 500 min the conductivity rose sharply, as a result of the coalescence of the aluminium nuclei. The maximum and the minimum in electrical conductivity correspond roughly to points of inflection in the kinetic curves describing the thermolysis of the material. After the first point of inflection the rate of decomposition decreases by approximately 13%, and after the second point of inflection (corresponding to the conductivity minimum) the rate increases to a value 9% higher than the initial rate. Thus, a clear correlation exists between the rate of decomposition and the electrical conductivity of $LiAlH_4$. The authors showed that lithium aluminium hydride is a semiconductor, and suggested that its electrical conductivity at 100° is due to the presence of F'-centres. They further suggested that the formation and growth of aluminium nuclei proceeds by the association of F'-centres along dislocations and internal surfaces. The initial increase in conductivity is ascribed to an increase in the concentration of F'-centres (due to the desorption of hydrogen from the surface) and diffusion of the new F'-centres into the bulk, and the decrease in conductivity is identified with the association of F'-centres to give aluminium nuclei. This work provided one of the first unambiguous correlations between decomposition kinetics and changes in electrical conductivity.

Following the work of Garner and Heycock, Weidenthaler also reported a correlation[12,13] between conductivity and extent of decomposition as a result of his study of the thermolysis of silver oxide (in the form of pressed disks). The surface of the samples was found to be covered with a layer of Ag_2O_3, and the silver oxide behaved like an n-type semiconductor. Weidenthaler interpreted the proportionality between the extent of decomposition and the electrical conductivity of Ag_2O as evidence for the reaction

$$O^{2-} \rightarrow \square^{-} + 2\bar{e} + {}^1/_2O_2,$$

where $\square^-$ is an anion vacancy and $\bar{e}$ is a quasi-free electron.

However, other workers[14,15] found that silver oxide behaves like a typical p-type semiconductor. Garner and Reeves[16] measured the resistance of silver oxide samples undergoing thermolysis under "equilibrium" conditions (i.e. heated in an oxygen atmosphere), and observed a constant electrical conductivity and an activation energy (for the thermal decomposition of Ag_2O) approximately 6 times higher than Weidenthaler's value.

Torkar and coworkers[17,18] discussed the mechanism of thermal decomposition of silver azide in terms of their measurements of electrical conductivity. They observed a number of singularities in the temperature dependence of conductivity of silver azide samples heated at a uniform rate. The low-temperature electrical conductivity is ascribed to cation conduction by vacancies, and the high-temperature region (with a higher activation energy) to cation conduction by interstitials. In the high-temperature region sodium azide decomposes, and its electrical conductivity decreases because some of the interstitial ions are removed by the decomposition process. Further decomposition leads to an increase in conductivity, associated with the coalescence of the nuclei of the new phase. Under vacuum conditions the rise in conductivity is followed by full interlocking of the nuclei, and the electrical conductivity becomes independent of temperature over an appreciable temperature range. This stage is followed by flash decomposition. When the measurements are made in the air, the temperature coefficient of conductivity at first decreases, but eventually the activation energy adopts the same value as before the formation of nuclei, which is explained by the break-up of nuclei at the surface. These results were used to confirm the Mott mechanism of formation and growth of nuclei, involving alternate capture of electrons and interstitial cations. It would be interesting to devise an experiment to determine directly the nature of the current carriers. Conduction by vacancies can easily be distinguished from conduction by interstitials by the sign of the thermo-e.m.f., since these carriers stand in the same relationship as electrons and postive holes[19].

The writer has observed[20] anomalies in the temperature dependence of the electrical conductivity of silver sulphite, similar to the behaviour of silver azide. Above 156° the rate of thermal decomposition of silver sulphite begins to increase rapidly, and the electrical conductivity decreases and passes through a minimum. This effect is not observed[20,21] if the pressure used in the preparation of the samples is kept below 4 tonnes cm^{-2}, probably because conditions in low-density samples are not conducive to the development of ionic processes,[22] or because the partial mechanochemical decomposition of the sulphite does not take place at low pressures. The decrease in electrical conductivity was explained (as in the work of Torkar) by postulating association of interstitial cations, in keeping with currently held views on the mechanism of thermal decomposition of silver sulphite[23]. The sign of the thermo-e.m.f. confirms that interstitial cations are responsible for the fall in conductivity; the lack of dependence of the effect on the composition of the atmosphere leads to the same conclusion.

In ammonium perchlorate, heated in the temperature range 230–270°C, the rate of thermal decomposition[24] goes through a maximum (238°) and a minimum (251°). We find[25] that the thermal conductivity of the perchlorate (in contrast to that of silver sulphite) varies in the same sense as the rate of decomposition. This is evidently due to the generation of intrinsic current carriers during the decomposition of the perchlorate. Adopting Boldyrev's interpretation[26] of the initial stages of the thermolysis of ammonium perchlorate, and taking electrophysical data into account[25], it is easy to account for these anomalies. The native current carriers in ammonium perchlorate must be proton vacancies, since their concentration increases during decomposition of the perchlorate.

Zhuravlev and coworkers[27] studied the decomposition of silver oxalate, and observed a minimum and a maximum in electrical conductivity 60 and 120 min respectively after the crystals had been heated to the decomposition temperature. Conductivity was measured on crystals $2 \times 0.1 \times 0.1$ mm³ in dimensions by a contactless method. The fall in conductivity during the initial stages of decomposition was ascribed to the loss of weakly held interstitial cations, with formation of silver nuclei. A special study of the desorption of water molecules in relation to this effect showed that desorption of water does occur, but its contribution to the loss of electrical conductivity by a factor of 6 during the early stages of decomposition is far from predominant. The subsequent increase in conductivity is due to the accumulation of metallic product. Although the authors did not specifically attempt to investigate the mechanism of thermal decomposition, their experimental methods are undoubtedly interesting.

Young[22] studied the electrophysical properties of silver azide before and during decomposition, and concluded that the best method for studying the sintering of solids is to measure electrical conductivity with a d.c. applied potential, using powdered samples held between metallised glass plates. Detonation of the silver azide was observed in d.c. fields in excess of 250 V cm^{-1}. Young stresses the importance of the method of sample preparation and of the rate of heating and cooling in controlling the reproducibility of conductivity measurements. However, we cannot accept his conclusion that ionic conduction is more developed in the denser samples. Thus, Gladkovskii and Meiklyar[28] concluded from their electrical measurements that single crystals of silver bromide are electronic semiconductors, whereas polycrystalline samples show mainly ionic conductivity. Andrievskii and coworkers[29] observed faster diffusion of various ions (in isotopic form) in polycrystalline cuprous oxide than in single crystals of the same oxide. The conditions which favour the ionic or the electronic component of the conductivity are probably best discussed in the light of the structural and defect parameters of the samples.

It has been shown[30–36] that potassium permanganate and its solid decomposition products are electronic semiconductors, and the elementary mechanism of the thermolysis of this compound has been discussed[37]. The formation of potassium manganate (one of the decomposition products) in solid solution raises the conductivity of potassium permanganate in the structure-sensitive region and lowers the activation energy for conduction. Similar effects were observed in measurements of the conductivity of partly decomposed samples. It was concluded that the manganate formed by thermal decomposition of potassium permanganate is initially present in solid solution, in agreement with the report[38] that the crystal lattices of potassium manganate and permanganate are isomorphous, and with Glemser and Buthenuth's work on the decomposition of potassium permanganate in the beam of an electron microscope.[39] The writer has pointed out[36] that the β and γ modifications of manganese dioxide can be distinguished by the temperature dependence of their electrical conductivity, and hence that the manganese dioxide obtained as the end product of the thermal decomposition of potassium permanganate is not in the β modification. These results have shed new light on the differences of opinion[40–43] regarding the catalytic effect of manganese dioxide on the thermolysis of potassium permanganate: the discrepancies were due to failure to take account of the crystalline modification of the dioxide.

The method of homo-phase additives is widely used in studies of the influence of microdefects on the thermal decomposition of ionic salts. By artificially varying the concentration of a given kind of point defects in a crystal—usually Schottky or Frenkel' defects—the role of various defects in the thermal decomposition of the crystal can be clarified and suggested intermediate steps can be confirmed. Furthermore, the homo-phase additive method gives an indication of the presence of ions of different valency in the lattice of a solid electrolyte. Measurements of electrical conductivity are most commonly used for this purpose, since they offer a quick and simple test for substitutional solid solutions. When solid solutions are formed, the plot of electrical conductivity against concentration of additive has a characteristic V-shape[44–48]. The method enables the ionic defects which act as the main charge carriers to be identified (cations, anions, cation vacancies, anion vacancies), and it allows their concentration and mobility to be calculated by the Koch–Wagner method[49,50]. However, the homo-phase additive method has also a number of shortcomings. As a rule, only the change in concentration of ionic defects is considered, even though several other changes may occur in the crystal at the same time. The additive can affect the mobility of the ionic defects, the lattice parameters, and the concentration of electronic defects. High concentrations of additives can deform the crystal, thus perturbing the crystal field, and generating localised stresses in the crystal which can influence the electronic steps in the thermal decomposition reaction. Radically different conclusions can result if all the relevant factors are taken into consideration in the discussion of the effect of additives on the rate of a solid-phase reaction[47]: hence, it is important to give due weight to all such factors. The problem is by no means new. For example, lattice deformation and a change in the lattice parameters of silver oxalate were detected by X-ray diffraction[46] when bivalent lead ions were added in concentrations above 1 mol.%. Solov'eva and coworkers[51] stressed the need to allow for the effect of impurities on the mobility of ionic defects in studies of solid-state reactions. Brenet[52] observed that either the β or the γ modification of manganese dioxide can be obtained as the decomposition product of manganese nitrate by adding different homo-phase impurities, and that these modifications have different catalytic properties[53]. Lastly, a common weakness of many investigations by the method of additives is the lack of firm evidence on the amount of impurity which has entered the lattice. In this respect, the recent application of ESR by Boldyrev and coworkers[47,54] to the quantitative determination of impurity in the lattice is noteworthy.

Thus, relatively few papers have been published on the rational application of electrical conductivity measurements to the study of thermal decomposition mechanisms in solids, but the results obtained so far offer conclusive

evidence that these measurements give valuable information when interpreted in the light of recent advances in solid-state physics. Thus, the further application, development, and refinement of these methods is to be welcomed.

3. USE OF PHOTOCONDUCTIVITY PHENOMENA

Maclaren and Rogers[55] observed photoconductivity in the region of the long-wave intrinsic absorption edge of undecomposed silver azide. With a partially decomposed sample the photoconductivity maximum is shifted towards longer waves, as a result of the photoeffect in the silver nuclei. The authors concluded, from the existence of photoconductivity at the decomposition temperatures of silver and lead azides, that the first decomposition step consists in the transfer of an electron to the conduction band, followed by trapping of the electron at an interstitial cation: the latter condition is favourable to the decomposition of the N_3 radical. These results suggest the possibility of applying photoconductivity measurements to the study of the nucleation of metals in azides, and to the interpretation of the autocatalytic effect of the solid decomposition product in azides. The catalytic effect of electron-acceptor impurities, predicted by this mechanism, was demonstrated by Mitchell.[56] Young's more careful measurements showed[22] that photoconductivity is absent in freshly prepared silver azide, and becomes significant only after partial decomposition of the material. This worker suggested that all the specimens used by Maclaren were partly decomposed by irradiation or by spontaneous ageing.

Forty and coworkers[57] studied nucleation in lead iodide undergoing thermal decomposition from the accompanying photoconductivity changes. The photoconductivity decreases as soon as lead nuclei appear: this effect is ascribed to the acceptor properties of the nuclei. The nucleation of lead in lead iodide is very fast at 180° because of the ready association of F-centres at this temperature, with trapping of free electrons. However, the nucleation of a new phase and loss of photoconductivity may result, also, from free electron trapping at interstitial cations. Dedman and Lewis[58] studied photoconductivity in lead azide with the aim of correlating the electrophysical properties and the decomposition kinetics of the compounds. Measurements of dark conductivity and photoconductivity in polycrystalline and single-crystal samples of lead azide gave different results. Heat treatment increased both the dark conductivity and the photoconductivity of the material, possibly as a result of incipient decomposition. The photocurrent was ascribed to exciton dissociation with formation of free electrons and positive holes. The dissociation energy of the excitons was calculated from the temperature dependence of the photoconductivity. The increased photoconduction in partially decomposed crystals was explained by postulating an increase in the mobility of the electrons.

Boldyrev and Skorik[59] studied the gamma- and photoconductivity of silver and barium azides under thermal decomposition conditions. In the decomposition of barium azide the electrical conductivity was significantly increased by irradiation with X-rays (using a dose rate of 110 rad min^{-1}). In the thermal decomposition of silver azide neither gamma- nor photoconduction was observed. The authors suggest that the decomposition of barium and silver azides proceeds through the formation of free electrons followed by electron capture at interstitial cations, and they conclude that the rate of thermal decomposition of the azides should be proportional to the concentration of free electrons as long as this concentrarion is smaller than the concentration of electron traps. It is suggested that this condition obtains in barium azide, since its rate of decomposition increases during irradiation with X-rays. The rate-limiting step in the thermal decomposition of barium azide is thought to be, on the basis of the above results, the transfer of an electron from an anion to the conduction band. In silver azide, on the other hand, the rate of thermolysis is unaffected by irradiation. It follows that the excitation of electrons to the conduction band is not rate-limiting in the decomposition of silver azide, in spite of statements to the contrary[49,55].

Zakharov and Savel'ev[23,49] concluded, from the absence of photoconductivity in pressed samples of silver sulphite and oxalate, that the thermal decomposition of these compounds involves the excitation of electrons from the valence band to exciton levels, and not to the conduction band. The absence of photoconductivity was used as an argument for classifying silver sulphite and oxalate among ionic conductors. Photoconductivity (like the Hall effect[60]) is one of the most accurate and unambiguous methods for the detection of electronic conduction in ionic compounds, but even when these effects are vanishingly small it cannot be argued that significant (or even predominant) electron or hole conduction must be absent[61]. This situation may arise through the dependence of the photoconductivity and the Hall e.m.f. on the mobility of the charge carriers: thus, the method is severely restricted by the limitations of the existing apparatus and experimental techniques for measuring these characteristics. It has been shown[62] that the Hall e.m.f. becomes very difficult to measure when the electron (or hole) mobility is lower than 0.04 $cm^2 V^{-1} s^{-1}$. Photoconductivity is difficult to measure[63] in semiconductors with a carrier lifetime below 10^{-4} s. Thus, arguments on the exciton mechanism of the initial stages of thermal decomposition of solids should be accepted with caution if they are based solely on the absence of photoconductivity or Hall effect.

4. APPLICATION OF ELECTROPHYSICAL PHENOMENA AT THE BOUNDARY BETWEEN TWO SOLIDS

Electronic effects[64-66] at the interface between two solids have been used with success[67-73] to discuss catalytic and autocatalytic mechanisms in the thermal decomposition of ionic salts. Because of differences in work function between the host material and impurities, the region of the crystals adjacent to the contact may become enriched or depleted in electrons. According to recent views[1,2,74], the thermal decomposition of ionic salts involves both electronic and ionic steps. Any change in concentration of the free electrons in the reaction zone can affect (directly or indirectly) the rate of thermal decomposition of the material[68,75]. Electrons near the contact always tend to pass into the medium with the higher work function. By suitable choice of dopants, this effect can be used to bring about a redistribution of the electron density near the surface in the desired sense. The effectiveness of catalytically active impurities is determined by the thickness of the depleted layer, which is proportional to the contact potential difference.

Contact phenomena were first invoked by Erofeev[67] to explain the mechanism of thermal decomposition. As the contact potential difference between an ionic compound

and the metal increases, the number of anions in the surface layer increases, and so does also the rate of thermal decomposition of the material. Using this approach, Erofeev postulated a proportionality between the rate of decomposition and the work function of the solid product of the reaction (for the case of solids with a common anion and cations of similar electronic structure). He quotes as an example the azides of barium, strontium, and calcium, in which the activation energy of thermal decomposition is found to be inversely proportional to the work function of the corresponding metals (which are also the decomposition products of the azides).

The realisation of the important role played by contact potential in thermal decomposition reactions has already produced useful results, but in many cases the available data are not sufficiently reliable. Thus, it is difficult to compare the electronic work functions of barium, strontium, and calcium[67] from results obtained under different conditions and by different methods because the scatter of the data is excessive. Fomenko[76], by averaging the results of 10–18 investigations, concludes that the work function of strontium is lower than that of barium. Thus, there is little justification for the statement that the rates of decomposition of barium, strontium, and calcium azides vary in the same sense as the work functions of the corresponding metals. Equally unjustified is the assumption that azides with different crystal lattices[77] and different physical properties[2,56] can have the same work function simply because they have a common anion and cations from the same group of the Periodic Table. To prove Erofeev's hypothesis we require a knowledge of the relative work functions of the contacting pairs of materials under the conditions which apply during the thermal decomposition of the azides: in particular, suitable allowance has to be made for the influence of a number of factors on the work function of metals and ionic crystals.

The method most commonly used to determine the thermodynamic work function is the vibrating condenser method[78–81], in which the key element is a vibrating metal plate whose work function is taken as standard. Allowance must be made for any change in the work function of the standard metal under the conditions used in the thermal decomposition of the experimental material. The electronic work function of metals usually decreases with increase of temperature[82,83] (if other complicating factors are excluded), and depends on the nature of any adsorbed gas[76,84,85]. The work function of compounds is even more sensitive to temperature[76,86,87], composition of the atmosphere[76,88–91], state of the surface, and intensity of illumination[92–94]. The electronic work function is a surface electronic characteristic of solids[95,96]. It is determined by the properties of a few monolayers of the material, since the surface of a crystal can be defined[97] as a layer of thickness equal to the mean free path of electrons, and therefore proportional[98] to the electron mobility and effective mass. Hence, the work function is affected by surface contamination (whether accidental of deliberate), and by the lapping and polishing treatments applied to the surface. If the decomposition product is a metal, we must allow also for the geometric factor[99,100] (an increase in work function with decreasing particle size). For example, Sviridov and Branitskii[8] found that the autocatalytic effect of silver nuclei in the thermolysis of silver oxalate disappears when the nuclei reach a certain critical size: one explanation of this effect could be the influence of the geometric factor.

Zakharov and Savel'ev[68,69] analysed published data on the effect of various oxides on the rate of thermolysis of potassium permanganate, ammonium perchlorate, and potassium chlorate, and noted a clear correlation between the catalytic effect of the oxides and their work function. Oxides with the highest work function had the strongest catalytic effect on the thermolysis of all three compounds. The thermal decomposition of silver oxalate was found[68] to be accelerated by additions of nickel oxide or cuprous oxide. On the other hand, zinc oxide or silver sulphide additions inhibit the decomposition of silver oxalate. In these experiments, too, the catalytic effect of the oxides was proportional to their work function, even when the work function values used in the calculation had been obtained under conditions far removed from those of the decomposition reaction. In a more recent paper[70], Zakharov and coworkers quote their own measurements of work function for silver azide and various additives under conditions close to those used in the thermal decomposition of silver azide. A more exact proportionality between the catalytic effect and the work function of the additives was observed, in spite of the failure to allow for oxygen evolution from the oxides at the decomposition temperature of the azide, and for the effect of the evolved oxygen on the work function of the standard gold electrode. A similar experiment is needed also to characterise the effect of the nitrogen (evolved from the silver azide) on the work function of the additives and of the standard. The experiment could take the form of a measurement of the contact potential difference between two gold plates under conditions leading to the decomposition of the appropriate substances.

Boldyrev and coworkers[71] confirmed the presence of electron-acceptor autocatalysis by manganese dioxide in potassium permanganate by measuring the work function of both materials at room temperature in an atmosphere of air, using the vibrating condenser method. The electronic work function of manganese dioxide was found to be 5.48 eV, that of potassium permanganate 4.76 eV. Hence, electron-acceptor catalysis is a possibility.

However, a number of criticisms must be levelled at this work, if only in order to highlight the complexity of the problem. The direction of electron transfer at the $KMnO_4$–MnO_2 boundary was determined from work function measurements made under conditions far from those which exist during the decomposition of potassium permanganate. Furthermore, the form of the manganese dioxide used in these experiments is not stated: the compound can exist in two stable modifications[101,102] as well as in an amorphous form. It is known[64–66] that the electronic work function of a semiconductor is equal to the sum of the work done against the electrical image forces and one-half of the width of the forbidden gap. Assuming that the work done against the electrical image forces remains the same for crystalline and amorphous forms of a compound as long as the short-range order is preserved[74,103–105], the work function difference between the two forms can be estimated from the difference in the forbidden gap. The γ modification of manganese dioxide has a greater activation energy for electrical conduction than the β modification.[53] Hence, we can expect the work function of γ-MnO_2 to be greater than that of β-MnO_2. When a compound is converted into the amorphous state the width of the forbidden gap usually increases because of the decrease in density[64,106]. For example, iodine (which is known to be a semiconductor[107]) has a work function of 2.8 eV in the monoclinic form and 6.8 eV in the amorphous state.[76] Hence, the most marked effects on the thermal decomposition of the original solid will be observed when the decomposition product (or the additive) is in the amorphous state if the catalysis is of the electron-

acceptor type. However, the production of manganese dioxide in an amorphous state during the thermolysis of potassium permanganate is highly unlikely[41].

In addition to the contact potential difference measured by the vibrating condenser method, the contact resistance can be used to compare the work functions of semiconductors, since it is associated[64-66] with the contact p.d. of the metal–semiconductor pair. The contact resistance is measured by the exponential portion of the current–voltage characteristic of the pair. By using different metal electrodes it is possible to evaluate[108] the work function of a semiconductor of a given conductivity type. The writer has used this method[73] to study the thermal decomposition of silver permanganate at 115°, catalysed by metal oxides. ZnO and ThO_2 were found to accelerate the thermolysis of silver permanganate, Co_3O_4 and NiO had no effect, and TiO_2 inhibited the process. No definite correlation was observed between the catalytic activity of the oxides and their published work functions. To explain the results, an electron exchange process between the additive and the undecomposed material through a layer of products was postulated. The current–voltage characteristics obtained at a number of temperatures for ZnO, $AgMnO_4$, and its solid decomposition product against platinum and gold electrodes were used to give a comparative assessment of the work functions of all these materials. The work function of zinc oxide was found to increase with temperature, whereas the work function of the decomposition products decreased and that of silver permanganate showed a barely significant increase. It was concluded from these results that under the conditions leading to decomposition of silver permanganate the electrons in the ZnO–product–$AgMnO_4$ system are transferred from the decomposition product towards both the zinc oxide and the silver permanganate. Mechanical admixture of the decomposition product or of its separate components (manganese dioxide and silver oxide) was found to inhibit the thermolysis of silver permanganate very markedly. Electron transfer from the decomposition product to the zinc oxide appears to minimise the inhibiting effect of the former and to accelerate the decomposition of the permanganate.

All the authors whose work has been discussed so far have considered only one effect at the contact: the transfer of electrons towards the material with the highest work function. This is by no means the only manifestation of contact phenomena at the solid–solid interface in catalysis and autocatalysis. Firstly, no account had been taken of the possible effect of the electric field at the contact. For the electrical conductivities and work functions of the materials most commonly investigated in solid-state chemistry, the voltage drop across the electron-deficient ("depletion") layer at the interface is of the order of 1 volt. Assuming a normal electron mobility and effective mass for ionic crystals, the thickness of the contact layer works out[98] to 10^{-4}–10^{-6} cm. Thus, the contact region of materials undergoing decomposition may experience electric fields of the order of 10^4–10^6 V cm^{-1}, i.e. field intensities sufficient to bring about decomposition. Furthermore, contact electric fields and electron transfer phenomena may occur not only at the contact between two different substances but also at the contact between crystals of the same material. The effect may arise from work function differences between different crystal faces: it has been observed in crystals of metals[76] (manganese, copper, silver, tungsten) and of semiconductors. The difference in work function between different faces in cadmium and lead sulphides[94] lies in the range 0.1 to 0.3 eV. Assuming an average depletion layer thickness of 10^{-5} cm, we obtain a contact surface field of the order of 10^4 V cm^{-1}. We cannot exclude the possibility that this effect may influence the rate of thermolysis of solids; the effect may also be responsible for the maximum observed in the plot of rate of thermolysis against degree of dispersion for a number of substances[109,110].

5. POTENTIAL APPLICATIONS OF THERMO-E.M.F. AND HALL VOLTAGE PHENOMENA

Although the well known thermo-e.m.f. phenomena can be measured simply[25,78,107,111] and without costly and cumbersome apparatus, it has not so far been used to any significant extent in studies of the mechanism of solid-state reactions. Even a cursory study of published work on the thermo-e.m.f. of ionic crystals reveals a number of questions of great importance to solid-state chemistry[1,2,74] and which could in principle be answered by measurements of thermo-e.m.f.

The existence of solid solutions in crystals can be recognised from anomalies in the differential thermo-e.m.f. isotherms[112-114]. Electron conduction in semiconductors can be distinguished from hole conduction by the sign of the thermo-e.m.f., even when alternative methods fail, as in polaron semiconductors[61,115,116] (oxides with partly filled 3*d* shells). In solid electrolytes, ionic conduction by interstitials can be distinguished from ionic conduction by vacancies according to the sign of the thermo-e.m.f. The differential thermo-e.m.f. (or thermoelectric power) in solid electrolytes can be used to calculate[44,117] the activation energy attending the formation and the motion of ionic defects. The concentration of current carriers in semiconductors of the band[118] and the polaron[119] types can be calculated from the thermo-e.m.f., and changes in carrier concentration due to various effects can be monitored.

The thermo-e.m.f. has one important "drawback" in comparison with the Hall effect, the photo-e.m.f., and photoconductivity. The former can be induced by charge carriers of any kind, whereas the latter three effects are specific to electronic and positive hole process. However, the ionic thermo-e.m.f. becomes significant only at high temperatures (most commonly, in the region of intrinsic ionic conduction), because ionic mobilities are extremely low. Under these conditions the concentration of ions involved in the conduction process, and their mobility, become high enough to support a significant thermoelectric current. However, with mixed (electronic–ionic) conductors, or when the conduction type is unknown, the characteristics of both ions and electrons can be calculated by combining the measurements of thermo-e.m.f. with other methods of measuring the kinetic parameters of charge carriers (Hall voltage, transport numbers, photo-e.m.f., and photoconductivity). Very little has been published[44,117,120] on the ionic thermo-e.m.f.: the phenomenon is much less well documented than the electron (or hole) thermo-e.m.f. But even among the few available results, some are difficult to accept (particularly those relating to thermionic currents). For example, the report by Reingold[120] of an ionic thermo-e.m.f. in silver sulphide, selenide, and telluride is unconvincing since these compounds are known to be electronic semiconductors[19,61,121,122]. However, in spite of the rare occurrence of ionic thermo-e.m.f.s, the contribution of ions to the total thermo-e.m.f. should always be treated as a possibility.

There is little published information on the thermo-e.m.f. (or other electrophysical properties) of the complex systems of interest in studies of solid-state reactions. The early work of Lashof[123] on the electrophysical properties of lead chromate is noteworthy. In spite of the low conductivity of lead chromate (of the order of 10^{-9} ohm^{-1}cm^{-1} at 100°), measurements of transport numbers and of thermo-e.m.f. showed that the compound is an electronic semiconductor. Lashof was among the first to point out the importance of colloidal metal particles (formed by thermal or photochemical decomposition) in the development of electronic conduction in ionic salts. The Hall effect of lead chromate could not be measured because of the high resistance of the samples. The sign of the thermo-e.m.f. was taken as evidence that the conductivity is by electrons (and not by holes). Good agreement was obtained between the measured thermo-e.m.f. and the value calculated from the free electron model: this was quoted as additional evidence that $PbCrO_4$ is an n-type semiconductor. Lashof's work is interesting for the methods used, but it failed to characterise satisfactorily the mechanism of electronic conduction, since the author[123] ignored the possibility of electron transfer between chromium ions of different valencies, which is frequently found in systems of this type[124-127] and accounts for most of their electronic conduction.

The writer[20] has used the thermo-e.m.f. to demonstrate cation transport through interstitials of the silver sulphite lattice, and hence to confirm the growth of nuclei by the Mott mechanism. The sign of the thermo-e.m.f. was one of the arguments[25] in favour of a proton conduction mechanism through vacancies in the cation sublattice of ammonium perchlorate, in agreement with the onset of thermal decomposition[26]. Measurements of thermo-e.m.f. have been used[31,36,73] to confirm the n-type conduction of univalent metal permanganates, in which photoconductivity and Hall effect could not be measured.

Young[2,22] applied the thermo-e.m.f. phenomenon in his studies of electronic and ionic processes in pure and in partially decomposed silver azide. By combining these measurements with optical spectra, Hall e.m.f., electrical conductivity, and photoconductivity studies he concluded that undecomposed silver azide is a cation conductor, whereas the same compound partly decomposed by heating or illumination is an electronic conductor. He suggested that the optimum conditions for electronic conduction occur in powdered samples, and the optimum conditions for ionic conduction occur in monolithic samples. Colloidal silver particles, formed during irradiation or heating, are responsible for the electronic conduction of these samples.

Young[22] quotes his measurements of thermo-e.m.f. in support of these conclusions. The differential thermo-e.m.f. of partially decomposed (up to 180°) silver azide remains negative but decreases in absolute value. Beyond this temperature the coefficient changes sign, reaching a maximum at 185°, and at 187° it falls almost vertically, changes sign, and goes through a sharp peak at 190°. At 192–193° the thermo-e.m.f. of the azide decreases very rapidly, changes sign, and returns to the previous maximum value. The final value remains unchanged on cooling the sample. This complicated and unusual variation of thermo-e.m.f. with temperature is consistent with the conclusions reached by Young from his measurements of the other electrophysical properties of the material. The first change of sign of the thermo-e.m.f. is due to sintering of the particles, and "displacement" of electronic conduction by cationic conduction. The anomalies in the region of the transition at 190° are explained by alternate enhancement and interaction of electronic and cationic conduction as a result of the collapse and re-growth of crystals during heat treatment. According to both electrical conductivity and thermo-e.m.f. measurements, this transition in silver azide is irreversible. However, the temperature difference used by Young (2–3°) may have been too low[118] to give reliable values of the differential thermo-e.m.f.: a temperature difference of the order of 10° across the sample is preferred[128,129] for the measurement of differential thermo-e.m.f.

The Hall e.m.f. is a reliable method[60,61,64] for separating the electronic component of the conductivity and at the same time determining the concentration of the charge carriers. The method can be used to monitor changes in the concentration of free electrons and holes during various types of treatment of solids (including decomposition). However, the sensitivity of existing apparatus is inadequate to identify the mechanism of solid-state reactions in the majority of solid inorganic compounds. So far, the Hall effect has been used to study electronic processes in solids having a resistivity not greater than 10^8 ohm[130-132]. A more promising method of studying reactions in solids is the photo-Hall effect[133-136], in which the Hall e.m.f. is generated by light-induced electrons, since many of the compounds used in research on solid-state reactions are ionic conductors[1,2]. For example, in silver azide the Hall e.m.f. appears only after partial decomposition[22], showing that the undecomposed azide is an ionic conductor and confirming Young's hypothesis on the donor properties of colloidal silver particles.

6. USE OF DIELECTRIC CHARACTERISTICS

The dielectric constant and the tangent of the dielectric loss angle are the most important electrophysical characteristics of a material. The variation of these characteristics with temperature, frequency, atmosphere composition, illumination, and pre-treatment (heating, irradiation, grinding, etc.) gives valuable information[64,137-143] on the mechanism of thermal decomposition of solids. The variation of ϵ and $\tan\delta$ with frequency reflects changes in physicochemical properties such as mobility and concentration of charge carriers, decomposition of neutral associations of ionic defects, effective mass of electrons and holes, and phase transitions[144-146], which may accompany the thermal decomposition of ionic salts. The rate of thermal decomposition usually changes rapidly at temperatures close to the modification transition[20,21,24,25], and so does also the electrical conductivity. Measurements of ϵ and $\tan\delta$ can be expected to give additional information on changes affecting electronic and ionic processes in the temperature region of the modification transition.

Very little has been published on the application of ϵ and $\tan\delta$ measurements specifically to the study of reaction mechanisms in the solid state. This is due, at least in part, to the experimental difficulties and to the difficulty of interpreting the results. In addition to the detection of modification transitions, two applications of ϵ and $\tan\delta$ in solid-state chemistry should be mentioned. They are the detection of solid solution formation from dielectric characteristics[45,46,147] and the calculation of the activation energy of thermally excited electrons[2,55-58] from the dielectric constant and the optical excitation energy of the electrons to the conduction band. The well known Mott formula[148] is used in the latter calculation. Having determined the width of the forbidden gap, and converted the optical

excitation energy into the thermal excitation energy by the Mott formula, this latter value is compared with the experimentally observed activation energy of the thermolysis reaction. Close agreement between theory and experiment is taken as evidence that electronic excitation is the rate-limiting step of the thermolysis reaction. However, Mott's formula is known to be only an approximation in calculations of this type.[75] A number of experimental findings are inconsistent with Mott's formula[61,107,148-152]. Alkali-metal halides with *F*-centres, barium and zinc oxides, and zinc and cadmium sulphides are semiconductors for which the activation energy differs very substantially from the expected value. Alkali halide crystals become semiconductors when colour centres are induced in them. By analogy with Sikorskii's results[153] for sodium chloride, the influence of *F*-centre polarisation on the static dielectric constant can be ignored. Thus, energy calculations by Mott's formula can be misleading.

Suzuki and Kotera[154] studied the kinetics of the anatase–rutile phase transformation by a dielectric method. The ϵ values of these modifications of titanium dioxide differ by a factor of 3.5. Hence, the presence of a new phase could be detected by the dielectric method even at concentrations below 10%. The method is particularly attractive, since the variation of ϵ with the concentration of the new phase is almost linear.

Ellis and Hall[155] used the dielectric method to monitor changes in the defect structure of sodium azide during thermal decomposition. The decomposition kinetics were studied, in parallel with ϵ and $\tan\delta$, from the pressure changes in the vacuum system. No change of ϵ was noted during the early stages of decomposition, but both ϵ and $\tan\delta$ showed a sharp maximum near the point of inflection in the decomposition curve. With further decomposition, the low-frequency values of ϵ and $\tan\delta$ continued to increase, whereas the high-frequency values did not change significantly. The authors ascribe these changes in the dielectric characteristics to the lattice defects produced during decomposition, rather than to the decomposition products. Since the predominant ionic defects in sodium azide are believed to be of the Schottky type, defect pairs consisting of an *F*-centre and an anion vacancy are likely to be formed during thermolysis. The *F*-centres may be formed by the reaction

$$2N_3^- \rightarrow 3N_2 + 2\bar{e} .$$

Zhuravlev[156] made a detailed study of the dielectric properties of silver oxalate and silver nitrite before and during thermolysis. The dielectric properties before decomposition had to be studied in order to establish the nature of the dielectric losses and of the polarisation. It was concluded that electrical polarisation in these compounds consists mainly of electronic, ionic, and migrational polarisation, and these processes were invoked in the discussion of the decomposition mechanism. A sharp decrease in $\tan\delta$ and in electrical conductivity was noted[156] during the early stages of the thermal decomposition of silver oxalate and nitrite. It was shown that the reaction kinetics during this period can be followed from the changes in $\tan\delta$, and that the rate of disappearance of defect ions (with formation of a metallic phase) can be assessed in the same way. The dielectric constant does not change at first, but after some time it begins to rise very rapidly, suggesting the coalescence of fine silver nuclei into coarser structures. The overall conclusion was that the decomposition kinetics of compounds of this type can be studied by using changes in dielectric properties to monitor the amount of metallic phase produced.

Thus, a comprehensive and objective study of electrophysical properties is a powerful means of characterising the electronic and the ionic steps in the thermal decomposition of solids.

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