SEMICONDUCTIVITY AND CATALYSIS

By PETER J. FENSHAM, M.SC., PH.D.
(DEPARTMENT OF CHEMISTRY, MELBOURNE UNIVERSITY)

Introduction

ONE of the main impetuses to the fundamental study of heterogeneous catalysis in the past decade has been the repeated suggestion that semiconductivity and catalytic activity are related phenomena. Not only have these two properties been qualitatively linked, but the hope has also been raised that one may be quantitatively predicted from the other. The purpose of this Review is to outline the main findings upon which these assertions have been based, and to examine critically the present state of the suggested relation.

It is largely through the developments in the theory of the solid state that these two phenomena have been considered as related. This theory has made possible models of the structures and properties of solids on the scale at which chemical reactions occur. Hitherto the main interest in heterogeneous catalysis had centred on the kinetics of the reactions rather than on their mechanisms ; now it is the catalyst itself and, in particular, its surface, which is the focus of attention. In considering the action of the catalyst and its surface, two particular factors have been explored and established as participatory. One is the geometrical factor on which Balandin [1] and Beeck [2] have made notable contributions. More recently the experiments of Gwathmey and his co-workers [3] and Sosnovsky [4] on chemisorption and catalysis on the various faces of single crystals have helped to define the rôle of this factor.

The second factor is the rôle of electrons in the catalytic process. As early as 1928 Roginskii and Schulz [5] hinted at this in explaining the catalytic decomposition of solids. Further development of this idea at this stage was hindered by the inadequacy of the atomic theory of solids. This electronic factor in reactions on semiconducting catalysts is the subject-matter of this Review.

It is now reasonably established that heterogeneous catalysis implies that one or other of the reacting species is adsorbed on the catalyst. Hence an understanding of adsorptive processes on solids has become a prerequisite to the elucidation of catalytic reactions. In a series of classical experiments Langmuir [6] showed that gas molecules could be adsorbed on solid surfaces,

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[1] Balandin, *Z. phys. Chem.*, 1929, **2**, *B*, 289 ; Trapnell, *Adv. Catalysis*, 1951, **3**, 1.

[2] Beeck, *Rev. Mod. Physics*, 1945, **17**, 61.

[3] Gwathmey *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 390 ; *J. Chim. phys.*, 1956, **53**, 667.

[4] Sosnovsky, *J. Chem. Phys.*, 1955, **23**, 1486.

[5] Roginskii and Schulz, *Z. phys. Chem.*, 1928, **138**, *A*, 21.

[6] Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2221 ; *Trans. Faraday Soc.*, 1922, **17**, 607.

and that the forces involved were similar in character to those which existed in the solid itself. These adsorptive forces were gradually differentiated into two types. When hydrogen had been adsorbed on zinc and chromium oxide catalysts at 100° c and above, Garner and Kingman [7] found that this adsorption was irreversible and that attempts to remove it by further heating resulted in the production of water vapour. For similar adsorptions on manganous oxide and MnO–Cr_2O_3, Taylor and Williamson [8] found that increase of temperature led to an increase in the amount of adsorption. Such experiments, involving what Taylor [9] called " activated adsorption ", clearly involved different forces from experiments where reversibility was maintained and in which no such high energy of activation was required.

In this way the distinction between physical adsorption and chemisorption was drawn. The forces in the former are van der Waals in character, non-specific, and involve energies of the order of a few kcal./mole, so that the adsorption occurs rapidly even at low temperatures. In chemisorption, however, the forces are specific and approximate more to electrostatic or covalent ones, with appropriately higher energies, giving rise to slower adsorption which is temperature-dependent like other activated processes.

In 1932 Lennard-Jones [10] gave these concepts a theoretical foundation when he showed that a gas molecule in adsorption on a solid may have to overcome a potential barrier. The early adsorption experiments also showed that the heat of adsorption of a gas on a solid varied with the extent of coverage.[11] This led Taylor [12] to postulate that solid surfaces are not homogeneous with respect to adsorption or catalysis, but that they contain, in fact, certain " active centres " for these processes. The " active centres " were thought of as specific points, edges, or positions on the surface, which were capable of adsorption and initiating reaction both energetically and geometrically.

The two concepts of " activated adsorption " and " active centres " have been very substantially modified in recent years but they have played most important parts in establishing the relation between semiconductivity and catalysis. " Activated adsorption " brought out the electronic factor which is common to both phenomena, while the " active centre " was peculiarly able to accommodate, in models of catalytic surfaces, many of the structural units that were appearing in the modern theory of solids.

Recently, the place of the electronic factor in chemisorption and catalysis has become firmly established, and Trapnell [13] has reviewed it for metallic catalysts. The contributions of Beeck,[2] Eley,[14] and Dowden and Reynolds [15]

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[7] Garner and Kingman, *Trans. Faraday Soc.*, 1931, **27**, 322.

[8] Taylor and Williamson, *J. Amer. Chem. Soc.*, 1931, **53**, 2168.

[9] Taylor, *ibid.*, p. 578.

[10] Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 333.

[11] Garner and Blench, *J.*, 1924, 1288.

[12] Taylor, *Proc. Roy. Soc.*, 1925, *A*, **108**, 105.

[13] Trapnell, *Quart. Reviews*, 1954, **8**, 404.

[14] Eley, *Discuss. Faraday Soc.*, 1950, **8**, 34.

[15] Dowden and Reynolds, *J.*, 1950, 242, 265.

have clarified much earlier work [16] on catalysis by metals and alloys. Stone has also reviewed catalytic processes in terms of the electronic factor, and he has included in his field the large group of semiconducting catalysts.[17] Such catalysts have been in use and under investigation for many years, especially the mixed-oxide catalysts of Hüttig and his co-workers,[18] who found that the catalytic activity could often be correlated roughly with various physical changes in the state of the catalyst such as the structure, colour, absorptive properties, and magnetic susceptibility. It is now clear that the electronic state of the solid was the dominant factor both in the physical changes in the catalyst and in its activity.

Semiconductivity and the theory of solids

The Band Approach.—Semiconductors are substances which exhibit electronic conductivity at high temperatures and whose conductivity tends towards zero as the temperature falls. For solid semiconductors the theory of the solid state which involves a model of a regular lattice of ions or atoms has been used extensively to explain the observed properties. Two theoretical approaches have been applied to semiconductors.[19] The first is analogous to the molecular-orbital method in molecular theory, and in it each electron is described by a wave function extending throughout the lattice. The outermost electrons are thus assumed to be free to move in the periodic field of the atomic cores and the other electrons. The second approach is analogous to the Heitler–London treatment of molecules, and the atoms or ions of the solid are treated as individual entities which interact with each other.

The first, or collective-electron, approach leads to a separation of the energy states of the free electrons into bands, which may overlap or be separated by gaps of forbidden energy. Wilson [20] applied this approach to semiconductors and described them as having a filled band of bound electrons at absolute zero, which is separated by an energy gap from a conduction band, empty at absolute zero, but able to accommodate electrons of suitable energy at other temperatures. Insulators appear as substances in which the energy gap between the filled band and the empty conduction band is so wide that, at normal temperatures, electrons have insufficient energy to bridge it.

Imperfections in the crystal lattice have the effect of introducing additional discrete levels in the gap between the filled and conduction bands. These imperfections may be due to any of a great variety of causes, some of which are discussed in more detail below, but the presence of impurity atoms in the lattice is a typical case which illustrates the general effect of these discrete energy levels on the conductivity. The impurity atom may have electrons associated with it which are available for excitation into the conduction band more easily than the electrons in the filled band.

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[16] Rienacker, *Z. Elektrochem.*, 1941, **47**, 805.

[17] Stone, " Chemistry of the Solid State ", Butterworths, London, 1955, chap. 15.

[18] Hüttig, *J. Chim. phys.*, 1939, **36**, 84.

[19] Mott, " Semiconducting Materials ", Butterworths, London, 1951, p. 1.

[20] Wilson, " Semiconductors and Metals ", Cambridge Univ. Press, 1939.

Alternatively, the impurity atom may give rise to empty energy levels to which electrons from the filled band can be excited more easily than they could be to the conduction band.

Types of Semiconductor.—We can now appreciate that the theory of semiconductivity distinguishes between three types of semiconductors, the energy levels of which are indicated schematically in Fig. 1. In these figures, the ordinate represents energy and the abscissa represents a dimension of distance through the crystal.

The first type (Fig. 1*a*) is called intrinsic semiconductivity, and examples of materials exhibiting it are germanium, lead sulphide, and silicon. Here the forbidden energy gap is of such a width that at various temperatures a reasonable number of electrons are excited across it. This excitation places an electron in the conduction band and leaves a vacancy in the filled band of electrons. Movement of the conduction electron, and of the electrons in the no-longer-filled band by means of the vacancy, can now both contribute to the conduction. The latter contribution is referred to as " positive hole " conduction and is equivalent, but of opposite sign, to the movement of an electron.

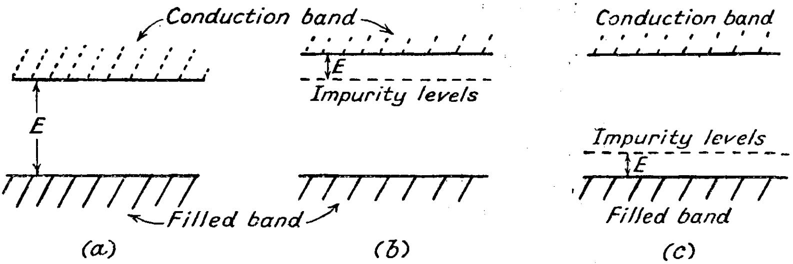

FIG. 1

Types of semiconductivity. (*a*) Intrinsic, (*b*) *n*-type extrinsic, (*c*) *p*-type extrinsic.

The other two types of semiconductor are both extrinsic, in that they depend for their conduction on the existence of energy levels arising from imperfections in the lattice. In *n*-type (normal or excess) conductors (Fig. 1*b*), the levels associated with the impurity are close to the conduction band into which electrons associated with the impurity atoms are excited or donated. Zinc oxide exhibits conduction of this type. In *p*-type (abnormal or deficit) conductors (Fig. 1*c*), the impurity levels are empty and close to the filled band, and electrons from it are excited into, or accepted by, these discrete impurity levels. This leaves positive holes in the filled band which give rise to the conduction. Cuprous oxide is a *p*-type conductor.

Fowler [21] has derived a relation for the variation of conductivity with absolute temperature (T) by using Fermi–Dirac statistics :

$$\sigma = A \exp(-E/2kT) \quad . \quad . \quad . \quad . \quad (1)$$

where E is the energy required to make the appropriate electron excitation in Fig. 1.

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[21] Fowler, " Statistical Mechanics ", Cambridge Univ. Press, 1936.

It will be clear from the above that for a particular substance at one temperature one type of conduction may predominate, but at other temperatures the other types may also contribute appreciably. The conductivity is then better represented by a sum of terms similar to that in equation (1). The electrical conductivity (σ) is thus a measure of the number of free electrons or positive holes in the semiconductor :

$$\sigma = e(n\mu_n + p\mu_p) \quad . \quad . \quad . \quad . \quad (2)$$

where e is the electronic charge, n and p are the number of free electrons and positive holes, and μ_n and μ_p are their respective mobilities.

Conductivity data are insufficient to give either n or p alone, but by also measuring another property of semiconductors, the Hall effect, these quantities can be isolated. This property was discovered in 1879. A conductor carrying a current has an electric field induced across it when it is placed in a magnetic field. The direction and magnitude of the induced field, $\mathbf{V}$, is given by the vector relation,

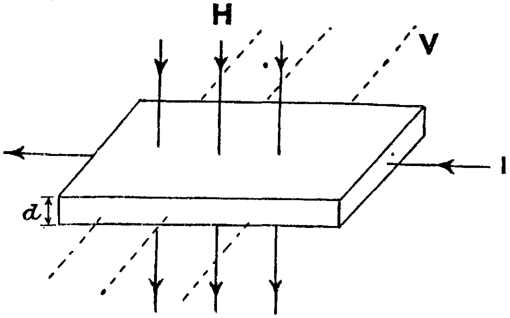

FIG. 2.
Hall-effect arrangement.

$$\mathbf{V} = R_{\mathrm{H}}\mathbf{I} \times \mathbf{H} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\mathbf{I}$ is the current per unit area, $\mathbf{H}$ is the magnetic field and R_{H} is the Hall constant.

The effect is usually measured by arranging a thin strip of the substance in such a way that the magnetic field is normal to the surface, and passing the current along it as in Fig. 2. Equation (3) becomes for this arrangement

$$V = R_{\mathrm{H}}IH/d \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For semiconductors use of the model outlined above gives the Hall constant [22] R_{H} as

$$R_{\mathrm{H}} = \pm \frac{\mu_{\mathrm{H}}}{c\sigma} = \frac{3\pi}{8\begin{pmatrix} - n \\ + p \end{pmatrix} ec} \quad . \quad . \quad . \quad . \quad (5)$$

where c is the velocity of light and μ_{H} is the Hall mobility.

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[22] Shockley, " Electrons and Holes in Semiconductors ", Van Nostrand, New York, 1950.

Measurement of the conductivity and the Hall constant of a semiconductor thus serves to give both the number of free electrons or positive holes, and the nature of the conduction, electronic or positive-hole.

It should be pointed out that despite the success of the band theory in explaining the properties of many semiconductors the approach breaks down for some substances of which nickel oxide is an example. This oxide has a cubic structure and on the band theory a crystal would have its 3*d* electrons split into two bands with four and six states per atom each. Ni^{2+} has eight 3*d* electrons which would mean that both these 3*d* bands could not be completely filled. On this model, then, NiO should be a metallic conductor whereas it is in fact an insulator when pure and a semiconductor when it contains impurities. In such cases where non-conductors have partially-filled bands, Mott [23] has suggested that a Heitler–London approach must be applied.

In intrinsic semiconductors, the effective values of n and p will depend on the temperature. However, in extrinsic semiconductors, though their actual effect on conductivity is again temperature-dependent, the potential values of n and p are determined by the history of the semiconductor and can vary immensely. For example, zinc oxide prepared in various ways had free-electron densities which ranged from 10^{15} cm.$^{-3}$ to 10^{19} cm.$^{-3}$.[24] The density of zinc atoms in zinc oxide is $\sim 5 \times 10^{22}$ cm.$^{-3}$ so that a very pure sample would have a concentration of lattice imperfections—say interstitial zinc atoms as donor impurities—as low as 1 in 10^7. Greenwood and Anderson [25] have very tentatively calculated densities for acceptor impurity centres and actual free positive holes in cuprous oxide. At room temperature their values are of the order of 10^{12} cm.$^{-3}$ and 10^{10} cm.$^{-3}$ respectively.

Lattice Imperfections.—The imperfections which can exist in crystal lattices can be classified as reversible or irreversible. Reversible imperfections exist in all crystals to minimise the total free energy at temperatures above absolute zero. They consist of Frenkel defects—interstitial units occurring in the lattice with or without vacant sites—or Schottky defects—vacant lattice sites. The particular type of reversible defect will depend on the respective energies of formation for the substance concerned. The theory of these reversible imperfections has been developed by Schottky [26] and Frenkel,[27] and recently reviewed, together with lattice imperfections of all types, by Stone.[28]

Irreversible imperfections, which also form discontinuities in the periodic lattice, depend however primarily on the history of the sample. They include flaws and strain-relieving Smekal cracks, as well as the surface of the crystal, and grain boundaries in polycrystalline material. Another type of irreversible imperfection which is becoming of increasing interest in solid chemistry is the dislocation. Dislocations involve the displacement from

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[23] Mott, *Proc. Phys. Soc.*, 1949, **62,** 416.

[24] Hahn, *J. Appl. Phys.*, 1951, **22,** 855; Scharowski, *Z. Physik*, 1953, **135,** 318.

[25] Greenwood and Anderson, *Proc. Roy. Soc.*, 1952, *A*, **215,** 353.

[26] Schottky, *Z. phys. Chem.*, 1930, **11,** *B*, 163.

[27] Frenkel, *Z. Physik*, 1926, **35,** 652.

[28] Stone, "Chemistry of the Solid State", Butterworths, London, 1955, chap. 2.

their normal position of some of the planes of the crystal lattice. There are two main types, edge and screw dislocations, and their general properties have been admirably discussed by Cottrell.[29] Dislocations are mobile through the crystal, and unlike other internal imperfections, their movement in the interior is reflected on the surface by a small mobile area of atoms where the dislocation emerges. This emergence at the surface has been used successfully by Frank [30] to explain crystal growth. Derry, Garner, and Gray [31] have also suggested that dislocation ends in the surface layers play an important part in removing vacancies during chemisorption, and so facilitating the incorporation of the adsorbed oxygen on *p*-type semiconducting oxides. Dislocations are able to act as sources and sinks of vacancies and interstitial ions by mechanisms suggested by Seitz.[32] The looping or curving of dislocations, or their mutual annihilation, may provide the thermal pulses that are required for the formation of these reversible imperfections. Mitchell and his co-workers [33] at Bristol have beautifully demonstrated some of these mechanisms with respect to photographic processes. While the theory of crystal growth would only require a few dislocations in each crystal, the dislocation densities that have been inferred for ordinary crystals are at least of the order of 10^8 cm. cm.$^{-3}$. Such densities of imperfections must be expected to affect the semiconductivity appreciably, although as yet only Read, Pearson, and Morin [34] have reported directly on this factor. They found that dislocation densities as low as 10^6 cm. cm.$^{-3}$ had a pronounced influence on the conductivity and the Hall effect in pure germanium.

As well as these irreversible imperfections of a physical nature others may arise from more chemical origins. These may be non-stoicheiometric compositions or the presence of actual foreign-ion impurities in interstitial or lattice positions. For these chemical imperfections appropriate rearrangements of charge occur to maintain overall electrical neutrality. Some examples of these imperfections are shown in Fig. 3 overleaf.

The surface of semiconductors. When attention is turned to the surface of a solid, as it must be when catalysis is considered, theory and existing knowledge are much less certain than has just been outlined for bulk properties. The electrical state of the bulk may be reflected in the surface layers as has usually been assumed in the past, but this is by no means necessary. At least it can be said that new possibilities must be considered through the very nature of the surface imperfection itself. For example, Tamm [35] showed that the discontinuity in a perfect lattice at its surface can give rise to energy levels in the forbidden gap. Electrons in these levels could then move freely on the surface, but not in the bulk. As yet there

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[29] Cottrell, " Progress in Metal Physics ", Butterworths, London, 1949, vol. 1.

[30] Frank, *Discuss. Faraday Soc.*, 1949, **5**, 49.

[31] Derry, Garner, and Gray, *J. Chim. phys.*, 1954, **51**, 670.

[32] Seitz, *Adv. Physics*, 1952, **1**, 91.

[33] Evans and Mitchell, " Report on Bristol Conference on Defects in Crystal Solids ", Physical Society, London, 1955.

[34] Read, Pearson, and Morin, *Phys. Rev.*, 1954, **93**, 666.

[35] Tamm, *Physikal. Z. Sovietunion*, 1932, **1**, 733.

has been no convincing evidence that these levels have a significant rôle in conductivity.

However, the surface of a crystal also has possibilities for physical and chemical imperfections which are more varied than can exist in equilibrium in the bulk. Thus crystal surfaces are unlikely to maintain the regularity of the bulk lattice and they may contain steps and plateaux. Tolansky [36] has given much evidence of such irregularities on so-called " smooth " surfaces, and Rhodin [37] has discussed the difficulties of obtaining even metal single crystals that are atomically plane. Similarly, foreign atoms adsorbed on the surface, or occupying lattice positions in the surface layers, are possible when they could not be accommodated in the bulk without complete breakdown and recrystallisation of the lattice. All these imperfections may give rise to energy levels in the surface which enable the electrical character of the crystal surface to differ radically from that of the bulk. The existence of such surface levels was postulated by Bardeen [38] in an attempt to explain certain electrical properties of germanium. He suggested that a double or barrier layer occurs on the crystal surface which raises the surface energy levels above those in the bulk of the crystal.

FIG. 3. *Crystal imperfections of chemical origin.*

Zn^{2+}	O^{2-}	Zn^{2+}	O^{2-}
O^{2-}	Zn^{2+}	O^{2-}	Zn^{2+}
	Zn^{+}		
Zn^{2-}	O^{2-} e	Zn^{2+}	O^{2-}
O^{2-}	Zn^{2+}	O^{2-}	Zn^{2+}

(*a*) Excess of zinc in zinc oxide.

Cu^{+}	O^{2-}	Cu^{+}	O^{2-}	Cu^{+}	O^{2-}
	Cu^{+} ⊕		Cu^{+}		Cu^{+}
Cu^{+}	O^{2-}	□	O^{2-}	Cu^{+}	O^{2-}
	Cu^{+}		Cu^{+}		Cu^{+}

(*b*) Excess of oxygen in cuprous oxide.

Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}
O^{2-}	Li^{+}	O^{2-}	Ni^{2+}
Ni^{2+}	O^{2-}	Ni^{++} ⊕	O^{2-}
O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}

(*c*) Solution of Li^{+} in nickel oxide

e = quasi-free electron

⊕ = quasi-free positive hole
□ = cation vacancy

The effect of such a barrier layer in chemisorption has been discussed by Aigrain and Dugas,[39] Hauffe and Engell,[40] and Weiss.[41] It can be illustrated for the case of chemisorption of oxygen on a donor, or *n*-type, semiconductor. When the gas molecules are adsorbed, electrons are transferred from donor sites near the surface of the semiconductor, thus reducing the conductivity. As more gas is adsorbed, a negative charge is built up

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[36] Tolansky, *Proc. Roy. Soc.*, 1945, *A*, **184,** 51.
[37] Rhodin, *J. Amer. Chem. Soc.*, 1950, **72,** 5691.
[38] Bardeen, *Phys. Rev.*, 1947, **71,** 717.
[39] Aigrain and Dugas, *Z. Elektrochem.*, 1952, **56,** 363.
[40] Hauffe and Engell, *ibid.*, p. 366.
[41] Weiss, *J. Chem. Phys.*, 1953, **21,** 1531.

on the surface which is compensated by a positive charge extending some distance below the surface because of the low density of donor sites. This electric field across the space between the adsorbed layer and the lower surface levels raises the potential of the electron energy levels near the surface. This means that adsorption as it proceeds requires more and more energy for the required electron transfer, and the concentration of electrons in the boundary layer decreases. For a *p*-type semiconductor, when oxygen is adsorbed on its surface, the electrons are transferred from the full band of the semiconductor. The ready availability of such electrons in the immediate surface layers means that the space across which the induced field builds up is less, with an appropriately lower barrier to further adsorption. In this case the adsorption increases the concentration of positive holes in the double layer.

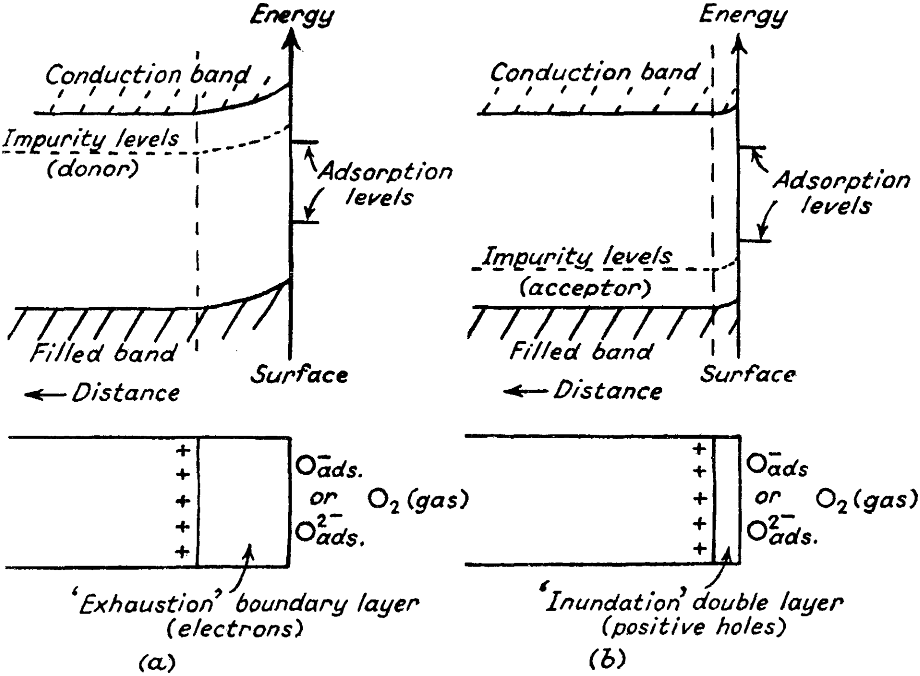

FIG. 4

Adsorption of oxygen on (*a*) *an* n-*type semiconductor and* (*b*) *a* p-*type semiconductor.*

Hauffe has called these two types of barrier layer " exhaustion " and " inundation " regions respectively.[42] The resulting energy levels are shown in Fig. 4. Conversely, adsorption on *n*- and *p*-type conductors can also occur in which inundation of electrons and depletion of positive holes follow respectively. For example, many authors have observed that the adsorption of oxygen on cuprous oxide increases the conductivity,[25] and

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[42] Hauffe, *Adv. Catalysis*, 1955, **7**, 213.

Brauer [43] has found that adsorption of water vapour decreased the conductivity.

The barrier layer predicts that adsorption reaches a point at which the potential barrier prevents further electron transfer and adsorption. In exhaustive adsorption this point will correspond with low surface coverages and the results for hydrogen on cuprous oxide [44] and oxygen on zinc oxide [45] bear this out. On the other hand, inundative adsorption should make possible much greater surface coverages; the adsorption of oxygen on cuprous oxide [46] and nickel oxide [47] and of hydrogen [48] and carbon monoxide [49] on zinc oxide have this character.

The importance of boundary layers arising from chemisorption is immediately apparent for catalysis. The number of electrons available for a chemical reaction on the catalyst surface is determined by the potential in the boundary layer. In order, therefore, to understand one of the controlling factors in catalysis on semiconductors, it is necessary to have some means of observing boundary phenomena in the surface layers. The obvious property for this is the conductivity in the surface layers since this is directly related to the density of current carriers, which is in turn controlled by the barrier potential.

Measurement of the Surface Conductivity.—Examination of the literature on semiconductivity indicates that the distinction between bulk and surface conduction has not always been clearly drawn, nor are there simple techniques for their independent measurement. Much of the work on conduction has been done on compressed powders, and the difficulties in interpreting such measurements have recently been discussed by Gray.[50] Even under the best conditions the results are not easy to interpret, for it is often found that the conductivity varies with the frequency at which it is measured. One way of interpreting this variation is to identify the bulk conductivity with the high-frequency values, and to explain the lower conductivity at lower frequencies in terms of high intergranular contact resistances and surface effects.

With the notable exceptions of Verwey,[51] Miller,[52] and Morrison,[45] most authors have largely ignored such intergranular effects, and this makes many of the isolated studies of semiconductivity of doubtful value for correlation with chemisorption and catalytic data on the same substances.

In making use of these isolated data on semiconductivity, it must be remembered that the Hall effect is usually measured on single crystals or slabs of compressed powder. The Hall constant in such cases is an indication

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[43] Brauer, *Ann. Physik*, 1936, **25**, 609.

[44] Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, *A*, **197**, 294.

[45] Morrison, *Adv. Catalysis*, 1955, **7**, 259.

[46] Garner, Stone, and Tiley, *Proc. Roy. Soc.*, 1952, *A*, **211**, 472.

[47] Dell and Stone, *Trans. Faraday Soc.*, 1954, **50**, 501.

[48] Taylor and Liang, *J. Amer. Chem. Soc.*, 1947, **69**, 1306.

[49] Garner and Maggs, *Trans. Faraday Soc.*, 1936, **32**, 1744.

[50] Gray, "Chemistry of the Solid State", Butterworths, London, 1955.

[51] Verwey, "Semiconducting Materials", Butterworths, London, 1951, p. 151.

[52] Miller, *ibid.*, p. 172.

of the average number of current carriers, and in general reflects the properties of the bulk. That these electrical properties in the same sample can be dominated by different regions of the crystal has been strikingly demonstrated by Morrison.[45] He observed the Hall voltage and the conductivity of a sintered zinc oxide sample as a function of time at constant temperature. The result is shown in Fig. 5, and indicates that the Hall effect, reflecting the bulk properties, is largely insensitive to considerable changes which occurred in the conductivity presumably arising from surface phenomena.

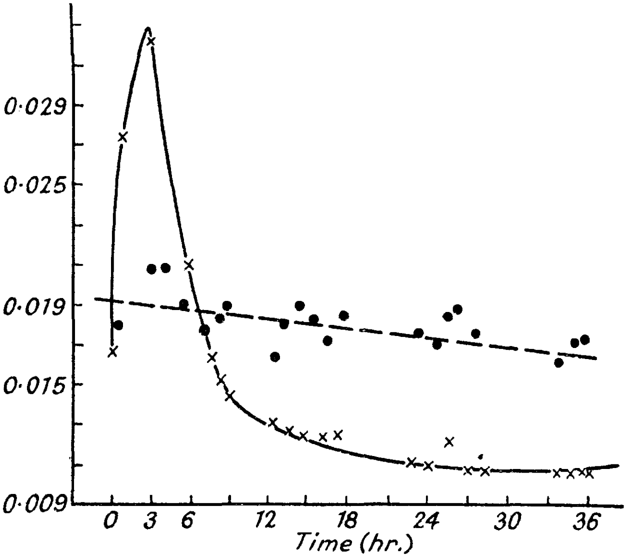

FIG. 5

Variation with time of the conductivity and Hall effect of zinc oxide at 100° (*from* 23°)

×, σ, Conductance (left-hand scale in arbitrary units)

●, KN = measure (left-hand scale) of number of carriers = $1/V_H$, where V_H is the Hall voltage in arbitrary units.

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Morrison has further calculated that particles with diameters of 10μ or less can be expected to exhibit conductivities which are largely indicative of the surface. Moreover, although sintered powders often consist of particles larger than this size, the fusion " necks " may well be of this order, so that at low frequencies the observed conductivities will again be surface dominated. For example, Bevan and Anderson [53] found that the effect of adsorbed oxygen on the conductivity of sintered zinc oxide was reversible down to temperatures as low as 500°. Since the melting point of zinc oxide is 2100°, bulk diffusion rates at 500° would be far too low to affect such reversible equilibrium in anything but the surface layers. Semiconducting films with their very small particle sizes, in general, are likewise found to be predominantly surface-controlled as far as conduction is concerned.[31, 50]

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[53] Bevan and Anderson, *Discuss. Faraday Soc.*, 1950, **8**, 238.

In this light it appears that conduction measurements can be used to produce precise information about boundary-layer conditions, but only when the physical conditions of the system are rigorously controlled.

Models of Adsorbing Surfaces.—Taylor's early model of an adsorbing surface consisted of static centres of varying energy content, some of which were particularly active in adsorption. Kwan [54] and others have found that this hypothesis is unnecessary for some adsorption data, and have suggested a heterogeneity induced by the adsorption itself rather than the inherent " active centres " to explain some of Taylor's experimental results. Nevertheless some adsorption results on semiconducting oxides do seem to require heterogeneous surfaces. The variation of the heat of adsorption on semiconductors may in part be explained by interaction between the adsorbed species or by differential energies of special adsorption sites. However, such explanations cannot deal with the whole range of surface coverages over which the heats vary.

A new approach to semiconducting surfaces was made by Volkenstein [55] and later by Boudart.[56] They both treated the surface as essentially dynamic in character. Volkenstein considers imperfections of all the types discussed above to be the adsorption centres. These then have mobility on the surface and can interact with each other, and their number is temperature-dependent. With such assumptions, he has shown that the amount of adsorption and the variation of the heat of adsorption can be predicted from the nature of the reversible and irreversible imperfections which are present.

Boudart treats the surface as a two-dimensional semiconductor with possible properties which differ markedly from the bulk conditions as has been discussed earlier. The energy levels are controlled by impurities and adsorbed species, thus presenting a surface model similar to the intermediate states in inter-oxide mixtures which Hüttig [18] has described. Such a surface has an induced heterogeneity in which all the sites are active for part of the time.

These dynamic models were indirectly the forerunners of the boundary-layer theory for adsorption systems which has been outlined above.

Examples of semiconducting catalysts

Some illustrative systems of various types in which the catalysis–conductivity relation has been explored will now be discussed in terms of the above theory and limitations.

Non-stoicheiometric Oxides.—(i) p-*Type cuprous oxide.* During several years Garner and his co-workers at Bristol have extensively studied cuprous oxide as an adsorbent and catalyst for the oxidation of carbon monoxide and the decomposition of nitrous oxide.[31, 44, 46, 47] Unfortunately, the conductivity measurements have all been made on films and the main

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[54] Kwan, *Adv. Catalysis*, 1954, **6**, 67.

[55] Volkenstein, *Zhur. fiz. Khim.*, 1949, **23**, 917 ; *Uspekhi fiz. Nauk*, 1953, **50**, 253.

[56] Boudart, *J. Amer. Chem. Soc.*, 1952, **74**, 1531.

adsorption studies on powdered samples. This difference in state of the catalyst in the various sets of measurements immediately introduces the uncertainties which have been outlined.

Adsorption of oxygen on oxidised copper films was found to increase the conductivity while carbon monoxide and hydrogen decreased it. If a mixture of carbon monoxide and oxygen was placed over the film, the conductivity indicated that the surface was saturated with carbon monoxide. When oxygen was adsorbed at room temperature on a cuprous oxide layer supported on powdered copper metal, it was found to be available for reaction with carbon monoxide. Carbon monoxide was itself adsorbed on the oxide surface and only some of it could be removed reversibly. On a surface previously exposed to oxygen, carbon monoxide was rapidly adsorbed and carbon dioxide was slowly liberated, followed by further adsorption of the monoxide. Mixtures of carbon monoxide and oxygen over the oxide powders gave rapid adsorption of the monoxide followed by slow oxidation, liberating carbon dioxide. Garner, Gray, and Stone [44] interpreted these results by assuming that oxygen adsorption involves electron transfer from the oxide leaving positive holes which increase the conductivity. Conversely, the carbon monoxide adsorption decreases the positive hole concentration reducing the conductivity.

Tiley [46] refined these adsorption observations when he found that oxide layers up to 150 Å thick on copper powder can adsorb more than a monolayer of oxygen at room temperature. This suggests that at this temperature the oxygen can penetrate into the lattice, and that in such oxide layers copper atoms from the bulk metal must be free to diffuse. Surface phenomena must therefore involve at least 20—30 lattice layers.

More detailed observations of the conductivity changes during the adsorption of oxygen on oxide films indicated that the rate-determining step is the dissociation of oxygen : [57, 31]

$$O_2 \rightleftharpoons 2O_{ads} \rightleftharpoons 2O^-{}_{ads} + 2\oplus$$

where $\oplus$ represents a positive hole. This reaction is then followed by the incorporation reaction,

$$O^-{}_{ads} \longrightarrow O^{2-} + \oplus$$

However, the difference between newly-adsorbed oxygen and lattice oxygen suggests that $O^-{}_{ads}$ ions are stable at room temperature, and magnetic-susceptibility measurements have lent tentative support to this suggestion.[58]

The nature of the adsorbed carbon monoxide became clearer when Tiley found that carbon dioxide did not adsorb on a clean oxide surface at room temperature but did so on an oxygenated surface in a way which depended on the time interval between the two adsorptions. The following reactions were postulated for these adsorptions :

$$\begin{aligned} CO_{gas} &\rightleftharpoons CO_{ads} + e \\ CO_{ads} + 2O^-{}_{ads} &\longrightarrow CO_{3\,ads} + 2e \\ CO_2 + O^-{}_{ads} &\longrightarrow CO_{3\,ads} + e \\ CO_{ads} + O_2 &\longrightarrow CO_{3\,ads} \end{aligned}$$

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[57] Gray and Savage, *Discuss. Faraday Soc.*, 1950, **8**, 250.

[58] Fensham, Ph.D. Thesis, Bristol University, 1952.

The oxidation reaction is then,

$$CO_{3\ \mathrm{ads}} + CO_{\mathrm{ads}} \longrightarrow 2CO_{2\ \mathrm{gas}}$$

These results indicate that at room temperature the course of this reaction over cuprous oxide depends on the *p*-type character of the catalyst, and they illustrate how conductivity measurements can be used to elucidate the reaction mechanism.

Turning to the kinetics of this reaction, Stone [17] considered the efficiency of various semiconducting catalysts. Despite the lack of uniformity in their physical and chemical state in the different experiments, he was able to generalise that *p*-type oxides are better than *n*-type oxides. In the *p*-type oxides, like cuprous oxide, the reaction can proceed without the diffusion of ions owing to the adsorption and subsequent reactivity of oxygen. However, on *n*-type oxides adsorption of carbon monoxide is readily achieved but the subsequent steps given above require diffusion of lattice oxygen. Hauffe, Glang, and Engell [59] have found that Stone's order of catalyst efficiency holds for the decomposition of nitrous oxide, but these generalisations remain qualitative and no quantitative statement is yet possible. Gray and Darby [60] have recently discussed the development of such a relation for the kinetics of adsorption of oxygen on oxide semiconductors.

(ii) n-*Type zinc oxide.* In 1938, Wagner and Hauffe [61] observed that the conductivity of zinc oxide was changed by the adsorption of hydrogen. Bevan and Anderson found that the activation energy of the conductivity of sintered zinc oxide powders varied with both temperature and ambient oxygen pressure.[53] This immediately suggested that the active energy levels were surface ones associated with adsorption and not Tamm levels or foreign-atom levels which would be independent of temperature. These authors also found that the conductivity was reversible at temperatures at which equilibrium between the bulk and the surface is most unlikely. These findings have been confirmed by Morrison and Miller ; [62] other authors have, on the contrary, found that at low temperatures the Hall and conductivity results on powdered zinc oxide were indicative of similar bulk mechanisms and independent of atmosphere.[63] Morrison suggests that during the preparation of the samples in the latter studies, adsorption on the surface greater than the low-temperature equilibrium values had already occurred. This would set up a barrier potential which would make the surface insensitive to further ambient pressures. Miller [52] has found that the mobilities in sintered zinc oxide at high frequencies agree with those observed in single crystals, supporting the analysis of the powder measurements given above. To explain these conductivity results Morrison has postulated a model of the zinc oxide surface in which surface levels involving both O^{2-} and O^{-} ions can exist. This model also explains various anomalous findings for hydrogen adsorption on zinc oxide, and the need for hydrogen activation of zinc

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[59] Hauffe, Glang, and Engell, *Z. phys. Chem.*, 1952, **201,** 223.

[60] Gray and Darby, *J. Phys. Chem.*, 1956, **60,** 201.

[61] Wagner and Hauffe, *Z. Elektrochem.*, 1938, **44,** 172.

[62] Morrison and Miller, *Univ. Penn. Tech. Report*, 1952, no. 6.

[63] Harrison, *Phys. Rev.*, 1954, **93,** 52 ; Fritsch, *Ann. Physik*, 1955, **22,** 375.

oxide catalysts for hydrogen–deuterium exchange. Residual O^- and O^{2-} ions on the surface from the preparation of the oxide are the main sites responsible for hydrogen adsorption, and hence two types of adsorption occur depending on the proportions of these sites, which in turn depend on the history of the sample. Hydrogen activation removes the residual oxygen ions from the surface, and a boundary layer inundated with electrons is restored which facilitates the electron transfer in the desorption of the H^+ and D^+ ions—the rate-determining step in the reaction. In support of this model, Voltz and Weller [64] found that the *p*-type conductor chromic oxide has maximum activity for hydrogen–deuterium exchange when it is in a reduced state with minimum conductivity and positive-hole density in the surface.

A qualitative generalisation can thus be made that *n*-type conductors are superior hydrogenation catalysts to *p*-type conductors; but again quantitative statements await detailed information about the nature of the surface. Some refinement of these generalisations has been attempted for semiconductors of the foreign-atom impurity type.

Controlled-valence Semiconductors.—The developments of the theory of impurity semiconductivity led to a method of producing semiconductors with controlled conductivity. In a series of careful studies Verwey and his co-workers [65] showed that the incorporation of foreign ions into a nickel oxide lattice altered the semiconductivity. They fired mixtures of nickel and lithium oxide in air at 1200° and then investigated the conductivities and compositions of the resulting oxides. Up to 10 atoms % of lithium, the mixtures appeared to be homogeneous with compositions $Li_\delta Ni_{1-2\delta}{}^{2+}Ni_\delta{}^{3+}O$. The conductivity increased by a factor of 10^5 as the lithium content was raised from 0 to 10 atoms %. Hauffe and Vierk [66] conversely found that the conductivity of nickel oxide was decreased by additions of chromic oxide.

The first use of these controlled-valence semiconductors to elucidate catalytic behaviour was by Wagner [67] in 1950. He showed that dissolution of gallium oxide in zinc oxide increased the conductivity, and simultaneously the converse decreasing effect of lithium oxide additions was demonstrated.[66] However, Wagner was unable to find any difference in the catalytic activity of pure or gallia-containing zinc oxide for the decomposition of nitrous oxide. This is not now surprising in view of the fact that *p*-type character has been found to be the operative feature for efficiency in this reaction, and the gallia merely increased the *n*-type conductivity of the zinc oxide.

A more fruitful investigation of this catalyst was that of Parravano and Molinari [68] who studied the hydrogen–deuterium exchange reaction which is catalysed by *n*-type oxides. They prepared their catalysts by firing them in air at 800° for three hours. For comparable surface areas the relative conversion rates at 160° were $ZnO + Li_2O < ZnO < ZnO + Al_2O_3 < ZnO + Ga_2O_3$;

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[64] Voltz and Weller, *J. Amer. Chem. Soc.*, 1953, **75**, 5227.

[65] Verwey *et al.*, *Chem. Weekblad*, 1948, **44**, 705; *Phillips Res. Report*, 1950, **5**, 173.

[66] Hauffe and Vierk, *Z. phys. Chem.*, 1950, **196**, 160.

[67] Wagner, *J. Chem. Phys.*, 1950, **18**, 6.

[68] Parravano and Molinari, *J. Amer. Chem. Soc.*, 1953, **75**, 5233.

this was exactly the order of the *n*-type conductivities. These findings showed a direct relation between reaction rate and electron density or activation energy of conduction. The correlation does indicate that donor-level electrons are involved in the exchange reaction, but uncertainty about the surface state of the catalysts prevents any further statement.

Similar series of experiments have been made on nickel oxide catalysts. Parravano [69] prepared a series of catalysts by firing the mixed oxides in air at 600° for three hours. Between 100° and 180° the activation energy for the oxidation of carbon monoxide was similar to that over pure nickel oxide. From 180° to 250°, however, the activation energies had the following values: $NiO + 0{\cdot}01$ mole % of $Cr_2O_3 < NiO + 1$ mole % of $NiCl_2 < NiO + 0{\cdot}01$ mole % of $Ag_2O < NiO + 0{\cdot}01$ mole % of Li_2O. Again the catalytic activity in the reaction appeared to correlate with the electronic state of the catalyst.

Shortly after this study, Schwab and Block [70] found quite opposite effects in the same system. Lithia-containing catalysts showed a lower activation energy than pure nickel oxide, which in turn was lower than the catalysts containing chromia. In this case the catalysts were fired at 850° for three hours, and the reaction was studied between 250° and 450°. Very recently a third set of conflicting results on this same system has been reported.[71]

Boudart and Parravano [72] have attempted to explain this discrepancy in terms of an inversion of the properties of nickel oxide, in which the foreign atoms first occupy actual thermal vacancies in the cation lattice and then, at a certain concentration, begin to expand the lattice by substituting for Ni^{2+} ions. The evidence for this seems to be doubtful and the physical changes could equally reflect the appearance of other phases in the crystal. Another explanation of the discrepancy between the above results suggests that in Parravano's case the catalysis was predominantly at surface discontinuities, while in Schwab and Block's experiments the electronic state leading to irreversible adsorption of carbon monoxide was dominant.[17] Thus, in the latter case the degree of *p*-type conductivity would be correlated with increased activity, as observed. Experiments on the effect of sintering temperature and ambient atmosphere on the preparation of these oxide solutions lend considerable support to such an explanation.[73] It is most unlikely that the overall concentration of the foreign atoms in an oxide fired at only 600° (m.p. of NiO is 2100°) is any indication of the concentration in the surface layers which are operative in the catalysis. At this temperature, solution by diffusion into the bulk would be very slow. This means that the concentration in the surface may be at least an order higher than has been assumed in the catalytic studies. The concentrations would certainly be different from those in Verwey's samples prepared as they were at temperatures where bulk diffusion occurs. With such surface conditions

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[69] Parravano, *J. Amer. Chem. Soc.*, 1953, **75**, 1448.

[70] Schwab and Block, *Z. phys. Chem. Frankfurt*, 1954, **1**, 42.

[71] Keier, Roginskii, and Sazonova, *Doklady Akad. Nauk S.S.S.R.*, 1956, **106**, 859.

[72] Parravano and Boudart, *Adv. Catalysis*, 1955, **7**, 47.

[73] Fensham, *J. Amer. Chem. Soc.*, 1954, **76**, 969.

two phases probably exist, or at least a homogeneous lattice is most unlikely. Much further work on the formation of semiconductors of the controlled-valence type is necessary before the catalytic activity of the surface can be considered directly in terms of its known and reproducible electrical state.

Germanium.—Although germanium was listed earlier as exhibiting intrinsic semiconductivity, it also displays all the impurity effects which have been discussed for oxides. For example, if an element of valency other than four is substituted into the lattice, the foreign atoms can operate as electron donors or electron acceptors.[22] Hence, boron impurities produce *p*-type conduction and arsenic impurities lead to *n*-type behaviour.

Physical imperfections, such as dislocations [34] and lattice vacancies, have also been shown to influence the conductivity. Morrison [74] and Bardeen and Brattain [75] found that the electrical properties of germanium were sensitive to the ambient atmosphere. Oxygen was found to produce acceptor levels on the surface [76] and Morrison actually observed a *p*-type surface on an *n*-type conductor during his adsorption experiments. Because of its importance in transistor electronics, germanium has been very extensively studied as a semiconductor, and more quantitative information is available about its behaviour than for any other semiconductor.

In order to make use of these data in exploring the catalytic behaviour of semiconductors, a series of experiments have recently been undertaken by Taylor and his co-workers at Princeton.[77] The decomposition of germanium hydride was found to be heterogeneous over a germanium surface, produced by previous thermal decomposition of the hydride, and the mechanism is known to involve the following reaction,

$$GeH_4 \longrightarrow GeH_{3\,\mathrm{ads}} + H_{\mathrm{ads}}$$

As yet these experiments have not been completed and, in particular, no simultaneous measurements of conductivity and reaction rate have been made. Nevertheless, Tamaru has been able to show that the presence of traces of arsine in the system accelerates the decomposition rate. This result can be explained if arsenic atoms from the arsine enter the germanium lattice, producing donor levels with available electrons which increase the desorption of the H^+_{ads}, the rate-determining step in the decomposition. Evaporated germanium films are invariably *p*-type conducting owing to their high concentrations of vacancies and other lattice imperfections which seem to be inevitable in such situations of high thermal non-equilibrium. Becker and Lark-Horovitz [78] found that films produced by thermal decomposition at 600° were more crystalline than evaporated films, although at room temperature all were still *p*-type. However, they did induce *n*-type conduction in such films by additions of arsenic, antimony, and bismuth. The films in the catalytic experiments described above were slowly produced

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[74] Morrison, *J. Phys. Chem.*, 1953, **57**, 860.

[75] Bardeen and Brattain, *Bell System Technol. J.*, 1953, **32**, 1.

[76] Clarke, *Phys. Rev.*, 1953, **91**, 756.

[77] Fensham, Tamaru, Boudart, and Taylor, *J. Phys. Chem.*, 1955, **59**, 806 ; Tamaru, Boudart, and Taylor, *ibid.*, p. 801.

[78] Becker and Lark-Horovitz, *Proc. Natl. Electronics Conf.*, 1952, **8**, 506.

at temperatures below 300° under conditions of thermal equilibrium, and it would be of great interest to know more of their electrical properties.

If indeed it is possible to control the electronic state of such films in the way that is possible for single crystals of germanium, then further experiments on the above lines give promise of greatly increasing our knowledge of the conductivity–catalysis relationship.

Mixed Oxides.—A final class of semiconductors which have been investigated in terms of the general relation are Hüttig's classical mixed oxide systems. In these the catalysts cover the whole range of compositions of the component oxides, and not only low concentrations of one in the bulk of the other. It is to be expected, therefore, that all the complexities of a multiphase system which existed in Hüttig's work make the interpretation of the basic electronic mechanisms in these catalytic reactions difficult.

Garner, Dowden, and de la Banda [79] studied the activity of a complete series of ZnO–Cr_2O_3 catalysts for the decomposition of *iso*propyl alcohol. Catalysts rich in zinc oxide were found to catalyse dehydrogenation to acetone, whereas those rich in chromia favoured dehydration to propene. The conductivity of the catalysts was not followed during these reactions, but separate measurements showed that the activation energy of their semiconduction (in hydrogen) increased parallel with the increase in the proportion of dehydration to dehydrogenation. These authors tentatively suggest that the rate-controlling step in the dehydrogenation is favoured by the electron-donor properties of the ZnO-rich catalysts. It is clear that in such a system, the results cannot justify any more definite statement about the general relation.

The importance of measuring conductivity and catalytic activity simultaneously in such systems has been shown by Weisz, Prater, and Rittenhouse.[80] They found that chromia–alumina catalysts changed from *p*-type to *n*-type conduction during the catalysis of the dehydrogenation of *cyclo*hexane and butane.

Organic semiconductors

A quite different class of semiconductors is the, as yet, small group of organic compounds. In 1941 Szent-Györgi [81] suggested that some biochemical mechanisms may be better approached by considering that protein molecules and extended systems of proteins have common energy bands similar to those which appear in the collective-electron approach to crystalline solids. He postulated this model to account for the transfer of energy and electrons during oxidations and fermentations catalysed by insoluble enzymes bound to insoluble proteins. The observed semiconductivity of some protein films provided meagre evidence for such a model.

[79] Garner, Dowden, and de la Banda, *Anales real Soc. Españ. Fís. Quím.*, 1954, **50**, *B*, 35.

[80] Weisz, Prater, and Rittenhouse, *J. Chem. Phys.*, 1953, **21**, 2236.

[81] Szent-Györgi, *Nature*, 1941, **148**, 157; 1946, **157**, 875.

In 1948 Eley [82] and Vartanyan [83] revived interest in these ideas when they showed independently that phthalocyanines—structurally related to the porphyrins—were semiconductors. Since then Eley [84] and Inokuchi [85] and their co-workers have found semiconductivity in a number of other organic compounds, including some protein molecules. Eley has also recently detected impurity semiconduction in phthalocyanines. The conductivity in many of these cases is found to be associated with the π electrons of the aromatic nuclei.

Most of these studies have used only direct-current techniques and contact resistances have been a confusing factor. The relation between biochemical catalysis and semiconductivity remains unexplored, but this field holds great possibilities for many more refined experiments of the type which have already proved successful in inorganic catalysis.

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[82] Eley, *Nature*, 1948, **162,** 819.

[83] Vartanyan, *Zhur. fiz. Khim.*, 1948, **22,** 769.

[84] Eley *et al.*, *Trans. Faraday Soc.*, 1953, **49,** 79; 1955, **51,** 1529.

[85] Inokuchi *et al.*, *J. Chem. Phys.*, 1950, **18,** 810; *J. Chem. Soc. Japan*, 1951, **24,** 222.