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REVIEW

SOME PROBLEMS IN ELECTRON TRANSFER[*]

By

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Abstract

Charge transfer through disordered systems is considered first in terms of residual long range order; the long range forces involved are discussed. Charge transfer may occur *via* the thus resulting energy bands, by hopping over or by tunneling through a potential barrier or by an exciton-polaron mechanism. It is shown that at least in some cases it is the requirement for a sterically favourable orientation of an acceptor site which determines the rate of charge transfer.

The energetics of thermoelectric EMF's are reviewed and the entropy effects involved, as well as some other entropy effects relating to charge transfer, are discussed. Elements of relevant Solid State Theory are summarized together with a brief review of some aspects of charge transfer complex formation and their determination by conductivity titration.

The effects of molecular modifications such as introduction of double bonds and polymerization on charge transfer are discussed in the light of experiments on a series of dipyridilium model compounds. Since in these the carrier concentration appears to remain substantially constant even over extended ranges of temperature, it is proposed that charge transfer in these materials is determined by trapping.

Some applications of charge transfer complexes to electrochemical primary cells and to fuel cells are reported and the application of essentially solid state charge transfer ideas to problems of catalysis is discussed.

1. Introduction

We shall be concerned with electron transfer through systems devoid of the long-range order such as exhibited *e.g.* by single crystals of pure metals, or of covalent elemental semiconductors like Ge; thus we shall discuss electron transfer through systems possessing a degree of short-range order only. Purely ionic transfer as in aqueous solutions, intramolecular electron transfer, as well as types of electron transfer occurring in chemical reactions will be considered

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[*] This paper represents the contents of a course of seven lectures given by the writer to members and graduate students at the Institute.

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to be beyond the scope of these discussions. We shall thus confine ourselves to a non-ionic solid or liquid having a degree of short-range order only, as exemplified *e.g.* by a molecular crystal. We shall assume the flow of a measurable current through our system upon the application of a finite direct electric potential difference; in other words, we shall be concerned mainly, though not only with d.c. electrical conductance phenomena. Electron transport will be taken to include transport by means of electron vacancies, *i.e.* positive holes. Conductivity effects in alternating fields, and specially dielectric phenomena, will be treated only as far as relevant to the main problem of d. c. current flow.

We shall assume that all experiments to be discussed, unless stated expressly otherwise, refer to systems with electrically invisible contacts. An ohmic contact for n-type materials (majority carriers are electrons) may be realized if the work function of the contact metal is considerably below that of the system to be studied; for p-type material (majority carriers are positive electron vacancies, that is holes) the converse holds. While ohmicity is a necessary, though not a sufficient, condition for an electrically invisible contact and while electrodeless measurements may be done[1], we will assume that ohmic means electrically invisible.

We shall also be concerned with such contact effects as give rise to space charge accumulation and depletion layers and with space charge limited currents, as well as with surface effects of interest in electrode reactions.

These topics bear on a very wide range of subjects from solid rocket fuels to heterogeneous catalysis and from nerve synapses to energy conversion devices.

2. Order and Disorder[2]

While a degree of short-range order is caused by the mere presence of other molecules in the vicinity of a given molecule, one can estimate an upper limit to the extent of order required to produce appreciable band broadening and thus reduction of effective mass and increased mobility. Electrons are scattered strongly by random electric fields extending over distances which are much larger than a lattice vibrational wavelength[2] and by other inhomogeneities. We may thus consider the distance covered by a disturbance of the perfectly periodic crystal field within the period of a quarter lattice wavelength to represent such an upper limit.

A disturbance of the periodic crystal field, in which the electron moves, propagates as an electromagnetic waves with a velocity $c/\varepsilon^{1/2}$, where ε is the permittivity of the solid. Within a quarterwave period $h/4k\theta$ at the Debye frequency θ the wave covers a distance $l = hc/4\varepsilon^{1/2}k\theta$; which may be taken as the spatial extent of the system of long-range order. For values of the Debye temperature θ of 250°, $\varepsilon = 16$, h being PLANCK's constant, k BOLTZMANN's constant, and c the velocity of light in vacuo, a distance of 36,000 Å results. Thus, an orderly arrangement of the molecules extending over at least several thousand molecular distances would be needed to substantially raise the mobility of the carriers.

Following GUBANOV[3], short-range order, at least in one dimension, may be treated as a Markov chain. Thus, with GUBANOV, let us consider a perfectly periodic one-dimensional array of points, each representing one molecule; let the spacing be denoted by a. This represents a system having long-range, and indeed perfect order, though only in one dimension. Let this spacing now be disturbed so as to yield a new spacing $s \neq$ constant a, by adding a small random deviation δ so that

$$s = a(1+\delta). \tag{1}$$

GUBANOV assumes that the total length of the molecular chain remains fixed and constant. This means that δ may be either positive or negative, with equal probability; thus

$$\sum_0^\infty \delta \to 0. \tag{2}$$

However, a crystal lattice generally expands upon fusion, *i. e.*, upon the introduction of additional disorder, so that the total length of the chain, physically, does not remain fixed and constant. This also follows immediately if one considers the shape of the potential well of a molecule: the repulsive side of the well is far steeper than the attractive side. The probability for the lattice to contract so that δ becomes negative, will be vanishingly small compared to the probability for lattice expansion. Therefore, only positive values for δ may be admitted and the total length of the chain will increase upon introduction of the disorder parameter δ. δ will be proportional to a random number ε

$$0 \leqslant \varepsilon \leqslant 1 \tag{3}$$

$$\delta = \varepsilon r, \tag{4}$$

where r stands for the probability that any given random deviation does occur, given Eq. (3). We shall assume that this probability obeys a Poisson distribution and shall terminate its series expansion with the first term so that

$$r = ke^{-\varepsilon}, \tag{5}$$

where k is a normalizing factor given by the condition that

$$k\int_0^1 e^{-\varepsilon}d\varepsilon = 1\,. \tag{6}$$

Numerically, $k=1.575$ and we obtain for the deviation δ

$$\delta = 1.575\varepsilon \exp\{-\varepsilon\}\,. \tag{7}$$

The spacing thus is given by

$$s = a\Big[1 + 1.575\varepsilon \exp\{-\varepsilon\}\Big]. \tag{8}$$

It is seen that after a certain finite number of terms, n, the original spacing will reappear in that a molecule will be found at its proper lattice position. Thus, it is required to find the number(s) n so that

$$\sum_0^n \varepsilon_n e^{-\varepsilon_n} = I\,, \tag{9}$$

where I is a (positive) integer. However, we still have to take into account the uncertainty involved in the measurement of any physical quantity; we have to decide how accurate I may be determined, *i.e.*, what is its tolerance. The measurement of I in effect means the determination of a lattice spacing.

The Heisenberg uncertainty principle correlates the uncertainties in the momentum P and the position a by

$$\Delta p \Delta a \cong \hbar\,. \tag{10}$$

Since

$$dp = (2m)^{1/2}E^{-1/2}1/2dE \tag{11}$$

$$\therefore\quad \Delta a = 2\hbar E^{1/2}/(2m^{1/2})\,\Delta E\,, \tag{12}$$

where E is the energy and m the mass of the particle. This mass here is that of the molecule which has a position corresponding to the lattice spacing a with an uncertainty Δa. On a Debye model, and considering one-dimensional system

$$E = k\theta/2\,, \tag{13}$$

where θ is the Debye characteristic temperature. In the case of low mobilities scattering by acoustic modes should be dominant.[5] We may thus use for the uncertainty of E the condition[5]

$$\Delta E \geq h/\tau\,, \tag{14}$$

where τ is the relaxation time required for the molecule to adjust itself to the presence of the carrier, related to the velocity of sound in the solid, v, by

$$\tau \cong a/v\,. \tag{15}$$

Thus, we find that

$$(1/a)\,\Delta a = (k\theta)^{1/2}/2^{3/2}\pi v m_0^{1/2} M^{1/2}\,, \tag{16}$$

where m_0 is the mass of the hydrogen atom and M the molecular weight. Taking 10^5 cm./sec. for v as a fairly typical value for a solid, $\theta = 250°\mathrm{C}$ as a reasonable approximation for molecular solids, and $m_0 = 1.7 \times 10^{-24}$ g, Eq. (16) becomes

$$(1/a)\,\Delta a = 1.6/M^{1/2}\,\%\,. \tag{17}$$

Assume $M = 300$. $\Delta a/a$ then becomes about 0.1%.

We have obtained computer solutions for I for 4 different uncertainties, for 10,000 and for 50,000 molecules, corresponding to four different "cutoff" conditions : *i.e.*, conditions where the original lattice spacing was assumed to be restored within the limits of predetermined uncertainty. For computing purposes, we have used cutoff functions of e^{-2}, e^{-3}, e^{-5}, and e^{-7}, corresponding to positional uncertainties of 13.5, 5, 0.67, and 0.091%. The results are displayed in Table 1.

TABLE 1 Computation of residual long-range order.

Number of terms n	Probability for n; out of 10,000			
	Cutoff function e^{-2}	Cutoff function e^{-3}	Cutoff function e^{-5}	Cutoff function e^{-7}
4	7400	3250	400	49
8	790	1440	320	42
12	Not discernible	830	260	42
40		28	170	33
80		Not discernible	100	27
120			50	20

It is seen that the original lattice constant tends to reappear periodically, giving rise to a degree of residual long-range order. Moreover, the extent of residual long-range order increases as the cutoff is made sharper, *i.e.*, as the uncertainty of molecular position as expressed by Eqs. (16) and (17), is reduced.

Thus, in the case of an e^{-5} cutoff and using 10,000 cycles, *i.e.*, solving for 10,000 molecules, the original lattice spacing reappears after every fourth term ; this means that there is a certain probability that a molecule will be found, to the given uncertainty of e^{-5}, regularly and periodically at a distance of four times the original lattice spacing. This result is identical with that obtained for 50,000 molecules and for other values of cutoff. The extent of residual long-range order, as far as may be estimated from the computer solutions, goes to at least 135 a, thus corresponding to a periodicity over about 135 spacings each of 4 a, or something like a few 100 Å. However, the probability of regions of residual long-range order drops as the cutoff is made sharper.

While it is thus seen that the spatial extent of the order increases as the uncertainty of position diminishes, the probability of actually finding a molecule at any one given periodic "super-lattice" position drops rapidly as the cutoff is made sharper. In other words, the residual long-range order produced is not a permanent fixture but of a transient and temporary nature only. As the positional uncertainty is reduced so is the fraction of total time in which the residual order exists ; we have a system of islands of order in a disordered sea. Reduced uncertainty reduces the concentration of such islands, but increases their size.

However, it must be understood that these islands of order are by no means rare. Thus, as an example, the probability for 80 a with a e^{-5} cuttoff is about 1%, calculated from 10,000 molecules ; considering the number of molecules in a solid this means a great many ordered regions.

Since $\Delta a/a$ is proportional to $M^{-1/2}$ it is to be expected that, *ceteris paribus*, componuds of higher molecular weight should exhibit a greater spatial extent of long-range order than low molecular weight compounds. In particular, this should hold for polymers. It is of interest to note that several authors[6)] report that the carrier concentration as well as the catalytic activity of organic solids increase with increasing molecular weight.

The development of residual long-range order due to the accumulation of random disturbances, extending over relatively large region of the system, should persist upon fusion. The resulting energy bands, though again localized in space and time, thus should be much broader than those resulting from a state of short-range order only. Therefore, a band model should be applicable to such a system and remain valid across the melting point as well as in amorphous systems. It is well known[4)] that fusion of a solid, even of a metallic solid, causes only a relatively minor drop in the conductivity ; even compressed potassium vapour still exhibits at least a vestigial band structure and an electronic conductivity somewhat akin to that of the metal.

3. Conductivity

Being concerned with conductance phenomena, we shall use the conductivity equation first in the generalized, conventional, form

$$\sigma = \sum_i z_i e n_i \mu_i \,. \tag{18}$$

The conductivity will be denoted by σ, and considered due to i species of carriers each carrying z_i electronic charges e and present in the concentration n_i and having a mobility μ_i. The latter quantity, defined as velocity per unit field, will be measured in cm^2/V-sec. We shall then assume that nearly all the current is due to one species of carriers only, *viz.* the majority carriers, thus permitting us to drop the subscripts and the summation sign. The conductivity gives rise to a current I by virtue of

$$I = \sigma V \,, \tag{19}$$

V being the applied voltage; this is Ohm's Law. While the range of applicability of Ohm's Law is limited, the equation may still be used if deviations from Ohm's Law are assumed to be due to a voltage, or field, dependent conductivity.

There are three ways in which electric charge carriers may be transferred from one molecule to another: (1) by motion in an energy band, (2) by crossing over or (3) by tunneling through an intermolecular potential barrier. Considering disordered system, usually a highly faulted molecular crystal or an amorphous solid or liquid it is clear that there is no long-range order of the kind which gives rise to the familiar band structure of covalent crystals like germanium. Thus, if there is sufficient overlap of molecular wave functions to give rise to energy bands, these are likely to be quite narrow, corresponding to very high effective masses of the carriers. However, if the band width J_0 becomes very narrow, *i.e.* if $J_0 \ll kT$, then the energy states even at the top of the "band" will be occupied, with negative masses, and the concept of an effective mass will no longer be meaningful.[7] The conductivity should then become proportional to the inverse temperature[1]: $\sigma \propto \frac{J_0}{kT}$. This contradicts experiment because in nearly all cases the conductivity varies exponentially with inverse temperature.

A fundamental difficulty inherent in the hopping model concerns[8] the energy of activation ΔG:

$$\Delta G = \frac{A}{2}\left[\frac{C/A}{1+C/A}\right] = \frac{A}{2}\left[\frac{C}{A+C}\right], \tag{20}$$

where A is the energy required to move the lattice polarization around the initial site of the carrier, and C that around its final site, due to the shift of the carrier from one molecule to its neighbour. It is unlikely that C and A will be much different; thus $\Delta G \simeq A/4$ and for $\Delta G = 2\,\text{eV}$, A results as $8\,\text{eV}$ which is an altogether improbable value.

At the absolute zero of temperature, the hopping probability is zero; any charge transfer then must occur by tunneling. As the temperature is raised, the tunneling probability, which is virtually temperature independent, remains substantially constant while the hopping probability, being a thermally activated process, increases exponentially. Thus, a characteristic temperature T_c is reached at which both tunneling and hopping probabilities are equal and the number of carriers passing over the barrier, the hopping current, equals the tunneling current. CHRISTOV[9] gives equations for symmetrical as well as asymmetrical barriers corresponding to the ECKART[10], the parabolic, and an arbitrary potential energy function. This characteristic temperature, the CHRISTOV CHARACTERISTIC TEMPERATURE, T_c, is mainly determined by the rate of curvature atop the barrier and only to a very minor degree by its asymmetry and by its exact shape. For an arbitrary but smooth potential energy barrier having a curvature L_m at its top where the translational coordinate x has the value x_m, the characteristic temperature, T_c, for a carrier of mass m results as[9]

$$T_c \cong \frac{h\sqrt{L_m}}{2\pi k\sqrt{12m}}\,; \quad L_m = -\left[\frac{\partial^2 V}{\partial x^2}\right]_{x=x_m}, \tag{21}$$

h and k being PLANCK's and BOLTZMANN's constants, respectively.

While thus T_c is seen to depend critically on the shape of the barrier at its top, one may assume that the actual shape will fall somewhere in betweed two extremes: the rather steep ECKART barrier[10] and the rather flat parabolic barrier.

It is readily seen that even for a 20 Å wide barrier ($l = 10$ Å) 1 eV high, a characteristic temperature of about 4000°K results for a (symmetric) ECKART barrier, and of about 1300°K for a parabolic barrier, symmetric or asymmetric. Thus, at room temperature, nearly all the charge transfer must occur *via* tunneling processes. The problem then is how to reconcile the experimentally observed exponential temperature dependence of conductivity with a notoriously temperature insensitive mechanism such as tunneling.

Thus, ELEY[11], POHL[12], KEARNS[13], and others[4], envisage essentially a thermal excitation of the carrier to a higher, excited, energy level within the potential well of the "donor" molecule which has its resonating, vacant, counterpart in the neighbouring "acceptor" molecule. In fact, the mean activation energy of about 0.2 eV which has been experimentally found for materials having a resistivity to be expected from a simple tunneling model, would be a value which would correspond to a vibrationally excitable molecular energy level. It is of interest to note, that also the thermal activation energies of photoconductivity of most materials are in the vicinity of this value. Relatively low resistivity materials, having resistivities of the order of, say, 10^2 to 10^5 ohm-cm, may well owe their conductivities to such a mechanism.

For high resistivity materials, however, one must look for a different kind of thermally activated process.

We shall follow a suggestion by KEARNS[13)] who explains the anisotropic conductivity of certain TCNQ complexes by an electron transfer between adjacent neutral and ionized molecules. The actual transfer of the electron, though, he envisages to take place *via* a hopping process.

However, it may be more realistic to assume that the actual charge transfer from molecule to molecule is by tunneling.[14)] The rate determining precondition for tunneling, at least in the case of relatively large and complex molecules, then is a sterically favourable alignment between an "active donor site" on one molecule and an "active receptor site" on another, neighbouring molecule. Such alignment will occur by a process of hindered rotation[15)] involving the crossing of a rotational energy barrier and it is the activation energy involved in this process which appears as the thermal activation energy of the conductivity. The primary event is charge injection from the contacts resulting in the formation of a negative ion at the cathode and a positive ion at the hole injecting anode. Depending on the relative probability of an electron to move from the anion to a neighbouring neutral molecule, against the probability of electron-transfer from a neutral molecule to a positive ion, the material will exhibit n-type or p-type conduction. It should be emphasized that no translational motion of the ions is involved, only rotation which need not, and probably rarely does, involve more than a portion of the molecule, or ion.

The mechanism here envisaged is somewhat akin to that proposed by POHL[12)] and by POHL, REMBAUM and HENRY[16)] in order to explain the pressure dependence of the conductivity; these authors postulate[12)] "tunneling to depend upon an overlap reflected in an "effective 'area of contact', $a^{\#}$, for the activated state."

In a way, it is also related to the "random walk" type of charge transfer proposed by RICE[17)]; the electron levels in a one-dimensional random lattice have been treated by FRISCH and LLOYD.[18)]

Given a carrier, charge transport thus depends (a) on a transport mechanism within a disordered, but rather narrow-range, molecular aggregate; (b) on getting the carrier into the energy band due to the residual long-range order, (c) on its drift mobility within that energy band, and (d) on its transition probability from one localized, temporary energy band into that of an adjacent one; that is on the carrier transition probability across a "barrier".

The conductivity and, more specially, the mobility, will depend on which of these processes, acting sequentially, is rate-determining in any particular measurement. The carrier generation process is likely to be an extrinsic one; the concentration of potentially free carriers is very much larger and about equal to the spin concentration; it is associated with additional energy levels within the energy gap.

Since molecules generally are not spherically symmetrical, their steric alignment or otherwise may give rise to a large discontinuity. It is suggested that the thermal activation energy measured in the case of highly resistive organics is largely determined by the probability that two molecules or molecular aggregates meet in a sterically favorable configuration. This is not a hopping model; it is envisaged that the carrier moves in a band which, however, in any one direction is a transient and not a permanent feature. The measured mobility then is a mean between the motion in the narrow band corresponding to the short-range order and the wide band temporarily appearing in the case of a sterically favorable alignment.

Energy bands arise from the periodicity of the potential, *i. e.* bands arise in the one electron approximation *if* the one electron functions have the same amplitude at equivalent positions in each unit cell. As KRAMERS has pointed out, such bands arise in any eigenvalue equation if the potential is periodic.[19)]

4. Mobility

The two quantities in the conductivity equation, *viz.* the mobility μ and the carrier concentration n, are difficult to separate and methods will be described which yield a second equation in order to do so.

The mobility μ will depend on certain details of the model employed. If the material is an intrinsic conductor, scattering of the charge carriers caused by impurities must be negligible, leaving only scattering by the lattice and by dislocations and other structural faults to limit μ. If lattice scattering alone limits μ, then the mobility should be proportional to $m^{*-5/2}T^{-3/2}$, where m^* is the effective mass of the carrier.

However, IOFFE[20)] and IOFFE and REGEL[21)] pointed out the serious contradictions encountered for very low values of μ. A carrier of effective mass m^* and a mobility μ has a mean free path L given[20], at ordinary temperatures, by the approximate relation

$$L \cong 10^{-8}\mu(m^*/m_0)^{1/2}, \tag{22}$$

where m_0 is the mass of the free electron. Values for L lie between 0.1 and 10^4 Å. Let us consider free electron or hole moving with thermal velocity at ordinary temperatures. Since its de Broglie wavelength λ_e is of the order of 70 Å, it appears that L becomes less than λ_e if the mobility drops below about 100 cm^2 volt^{-1} sec^{-1}. However, as an electron is "smeared out" over distances of the order of λ_e, a motion over a distance L less than λ_e becomes meaningless. Moreover values of μ are often less than 5 cm^2 volt^{-1} sec^{-1} so that the mean free path L, is then of the order of 0.1 to 1 Å, appreciably less than the lattice spacing. As IOFFE has emphasized, neither the concept of a mean free path nor that of a free electron mobility has any significance in such a case, because the electron wave is completely damped out within less than a single lattice spacing.

Thus, the mobility may have a meaning when intermolecular distances are of the order of several Ångstrom units. However, some means of charge transfer must exist to permit an electron or hole to migrate from one molecule to another. Whatever the nature of this process, it must be a very improbable event since the conductivities are so low. If such a transition is considered[20,21] as some kind of chemical reaction which possesses an activation energy barrier, the mobility can be written in the form of a rate equation:

$$\mu \propto \exp(-U/kT), \tag{23}$$

where U is the value of the activation evergy. It is assumed in Eq. (23) that thermal motion is the only energy possessed by the charge carrier, *i.e.*, that the applied field is small. The mobility would now be expected to increase exponentially with temperature rather than to decrease. Summarizing, one can say that a value of mobility above 1 cm^2/volt^{-1} sec^{-1}, decreasing with rising temperature, indicates that the carriers are free and limited in their free path by lattice collisions. In contradistinction, low values of μ, say below 1 cm^2/volt^{-1} sec^{-1}, and increasing with temperature are indicative of an activated mode of charge transfer across a potential barrier; this is often referred to as hopping. Hopping is also very likely where the mobility rises sharply upon fusion, since melting involves the loss of long-range order and, certainly, a lower state of order.

IOFFE's argument is a cogent one; thus it might be considered somewhat paradoxical that the band model yields data which agree with experiment in magnitude as well as in their temperature dependence.

However, the apparent contradiction might be resolved by rewriting the conductivity equation (18) in the differential form originally proposed by NERNST[22] and by PLANCK.[23]

$$i = \rho v - D(d\rho/dx) \tag{24}$$

This is sometimes stated in the form

$$d\rho/dt = D(d^2\rho/dx^2) - \rho/\tau\,. \tag{25}$$

In these equations ρ is the free charge density, the carriers having a drift velocity v, a diffusion coefficient D, and a relaxation time τ; x is a spatial coordinate. Thus it is seen that there are two contributions to the mobility; one arising from carrier diffusion, which is a thermally activated process, and one from its drift in the direction of the electric field. The latter process is activated by abstracting energy from the applied field; the contributions of this mode of carrier transport depend strongly on the microstructure of the electric field as seen by the carrier, and as expressed by the relaxation time. This quantity varies with the local permittivity of the region in the vicinity of the carrier. IOFFE's conclusions might therefore be affected by considering the variations in the local field[*]; moreover, the effective mass m^* also varies for a narrow band solid.

5. Energy Transfer and Electron Transfer

We shall confine our discussion to conductivity associated with charge transfer only; this is the conductivity which arises by virtue of Eq. (18). However, the requirement for a charge carrier, an electron for example, to enter the specimen at the cathode and to leave it at the anode, thus transporting charge through and across the specimen, does not necessarily involve the continuous presence of a free electron throughout the interelectrode space. Current will flow, and a conductivity will be measured, as long as a free electron enters at the cathode and leaves at the anode, or, conversely, a free hole enters at the anode and leaves at the cathode, regardless of any intermediary processes in the charge transfer across the specimen.

Pure charge transport, although certainly a sufficient condition for electric

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*) The behavior of excitons in an electric field was examined by BIERMAN[24]: The electric field gives rise to long range coupling, even when, in the absence of the field, coupling occurs only between nearest neighbors. The guiding of excitons by a field could be significant in the fields around a charged center.

conductivity, is not a necessary condition for it. Current flow involves the transport of electrical energy from cathode to anode, or *vice versa*, with the proviso that at the electrodes, free carriers must leave, and enter, the specimen. It is thus not at all necessary that the carriers remain free at all times during their migration from one electrode to the other; the essential step is the transport of electrical charge across the specimen, giving rise to a free carrier again at the exit electrode. Conductivity thus may arise by a carrier, an electron for example, entering at the cathode and then combining temporarily with an electron attachment center; *i.e.*, getting trapped. Accommodation of the electron in the attachment center causes the energy of the latter to rise, thus forming an excited state; this may well be electrically neutral.

The carrier has been rendered immobile and no longer exists in the form of a free carrier. In its place, a region of local excitation has been created which may or may not be charged. This surplus of energy may now migrate to other regions of the material; how far it will wander depends mainly on its stability, *i.e.*, on its lifetime. Eventually, the packet of extra energy may again cause the liberation of a charge carrier, say by ionization or by liberating a trapped carrier from its trap. The net effect is that a free carrier has reappeared in a different locality of the specimen, and thus charge has been effectively transported from one locality to the other. The important characteristic of this process is, however, that at no time does the free carrier migrate as such; what does migrate is merely an energy packet. Such mobile excited states are called excitons.25) They may transfer, for example, a free negative plus a trapped positive charge over large distances within a weakly bonded molecular crystal without requiring the transfer of electric charge from molecule to molecule. It suffices that energy is being transferred.

6. Self-Trapping

An electron-hole pair created by the absorption of energy need not necessarily be the combination of a free electron and a free hole. The positively charged hole tends to attract the negatively charged electron, and both may form an entity much akin to a hydrogen atom, the electron getting trapped in the field of the hole and forming an exciton, which is capable of migrating through the crystal lattice, since the excitation may pass from atom to atom. The exciton is electrically neutral and as such cannot carry current. However, once formed, its dissociation energy is comparatively low and it may dissociate into a free electron-hole pair. Thus, one component may get trapped at lattice imperfections, leaving the oppositely charged component, say the hole, free to conduct.

7. Polarons

Also, the interaction of electrons and phonons in some circumstances can lead to the electrons being trapped in self-induced potential wells. The entity which then moves through the crystal is not an electron by itself, but an electron accompanied by a localized vibration, a combination which is called a polaron.[25,26] The electron is accompanied by its own polarization field. Polaron theory has been developed chiefly for inorganic crystals[27] but has been applied qualitatively to molecular crystals *i.e.* by SIEBRAND.[28] The difference between ordinary band theory and polaron theory lies in the fact that in the ordinary theory the interaction of the electrons with vibrations of the nuclei is treated as a perturbation of the motion of the electrons in Bloch-type bands, whereas in the polaron theory bands of energy levels are formed only after the electron has interacted with a (local) nuclear vibration.

8. Excitons

The term exciton was introduced by FRENKEL[29], who considered[30] the transformation of light into heat in solids. He regarded a crystal as analogous to a molecule, so that upon the absorption of light the electronic excitation was not confined to a single atom but rather was spread over all the N atoms of the crystal. Because of interactions between the atoms, which were assumed to be fixed in position, there occur N states in the crystal which correspond to a single excited state of the individual atom. Each of these

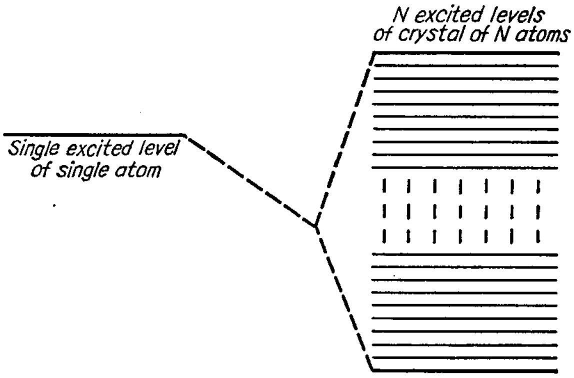

Fig. 1. Energy levels in a crystal of N atoms.

N states is described by an "excitation wave" which is somewhat similar to a sound wave describing heat motion in a similar crystal. Each wave is characterized by its wave vector $\boldsymbol{k}$ and by a characteristic energy. Schematically the situation is as depicted in Fig. 1. By superposing several excitation waves, excitation packets can be constructed to represent the motion of the excitation from one atom to another in the crystal.

FRENKEL$^{30)}$ established the selection rule for the absorption of light by crystals; it expresses the need to conserve momentum when the light quantum gives rise to an "excitation quantum". The excitation quantum has associated with it a momentum $\boldsymbol{p}$ equal to h/λ, where λ is the corresponding wavelength. The excitation wave vector $\boldsymbol{k}$ is thus proportional to $\boldsymbol{p}$: $2\pi\boldsymbol{k}=\boldsymbol{p}$. For instance, if $\lambda=6000$ Å, then $h/\lambda=\boldsymbol{q}\doteqdot 10^{-22}$ cgs units, where $\boldsymbol{q}$ is the magnitude of the momentum associated with the light. The selection rule can thus be stated in wave terms as: the wavelength (or momentum) of the light must equal that of the excitation wave. In a one-dimensional crystal, $\boldsymbol{p}=\boldsymbol{q}+j(h/a)$, where $j=0$, ± 1 and a is the lattice spacing.$^{29)}$ When $j=\pm 1$, momentum is transferred to the lattice as a whole. Since the greatest value of $\boldsymbol{p}$ occurs when the length of the excitation wave equals a, $|j|\ngtr 1$. There are consequently just three transitions allowed by the selection rule.

In a three-dimensional crystal there is a similar selection rule for each component of $\boldsymbol{p}$ and $\boldsymbol{q}$ along a crystal axis. Accordingly there are 3^3 lines allowed, provided that all directions of propagation of the incident light are considered. The selection rule for a given direction of propagation is given by

$$\boldsymbol{p}=\boldsymbol{q}+jh\boldsymbol{b}_i, \qquad i=1,2,3\,;\ j=0,\ \pm 1 \tag{26}$$

where the $\boldsymbol{b}_i$ are vectors of the reciprocal lattice; that is,

$$\boldsymbol{b}_i=\frac{\boldsymbol{a}_j\cdot\boldsymbol{a}_k}{\boldsymbol{a}_1(\boldsymbol{a}_2\cdot\boldsymbol{a}_3)}\,. \tag{27}$$

For visible or ultraviolet light, $\boldsymbol{q}\approx 0$; thus the rule becomes

$$\boldsymbol{p}=jh\boldsymbol{b}_i. \tag{28}$$

There is also the other selection rule requiring that the energy of the excitation equals that of the incident quantum of light. The two rules together restrict the number of transitions from the ground state of the crystal (a state of zero momentum) to that in which the frequency of the light equals $(W_k-W_0)/h$. If $j=0$ in Eq. (26), where W_0 is the energy of the ground state and W_k that of the excited state, the length of the excitation wave equals that of the incident light, which is very large compared with lattice spacings. Optical transitions from the ground state of the crystal to the N excited states shown in Fig. 1 are almost all forbidden. A sharp line is seen in the spectrum corresponding to the momentum selection rule $|\boldsymbol{p}| = h/\lambda_{\text{light}} \approx 0$.

The presence of lattice vibrations, which have momentum, increases the number of observable lines over that expected from the preceding considerations since now the momentum selection rule takes the form

$$\boldsymbol{p}_{\text{excitation wave}} \pm \boldsymbol{p}_{\text{lattice vibration}} = \boldsymbol{p}_{\text{light}} . \tag{29}$$

FRENKEL[29)] considered the absorption of light, or generally of energy, by crystalline dielectrics as either leading to an internal ionization or not. In the former case the resulting electron and positive hole are not localized but move throughout the crystal. In the latter case the excitation is mobile in the crystal, and FRENKEL pictured this as the motion of a quasiparticle which he termed an "exciton". Its motion is described with the aid of the excitation waves mentioned above, and its momentum is given by $\boldsymbol{k}$, where $\boldsymbol{k}$ is the wave vector. FRENKEL pointed out that the way in which Bloch's theory of energy bands had been applied rather indiscriminately to various types of solids resulted in the exclusion of non-conducting excited states of a crystal, that is, of those states which are characterized by moving excitons.

9. Types of Excitons

DAVYDOV's application[31)] of FRENKEL's[29,30)] exciton theory considered only excitons in which the electron and the hole were tightly bound, *i.e.*, in which both charges were essentially spread over only one molecule of the lattice. The exciton thus could be described in terms of neutral molecules. This "neutral"[32)] or "tightly bound" exciton represents one limiting case. The other limiting case is the "loosely bound" or "ionized" exciton in which the electron and hole are separated by a mean distance as large as or larger than the lattice spacing of the crystal. This is the type of exciton envisaged by WANNIER[33)] and by MOTT.[34)] The loosely bound exciton can be described by functions which include terms corresponding to positive and negative ions. The energies of loosely bound excitons, in which the electron moves around the hole in one or other of a series of bound states, resemble those observed in a hydrogen atom and converge toward a series limit at which the electron becomes independent of the hole. The exciton is then dissociated into separate ions. In addition to the relative motion of the electron and the hole, the exciton as a whole can diffuse in the crystal.

For the insulating crystals considered by MOTT and by WANNIER the series of exciton energy levels are placed just below the conduction band in which the ionization limit of the series lies. The energies of these exciton levels, E_n, referred to the ionization limit are given, for large radii of the exciton, by a modified Rydberg formula, $E_n = \mu e^4/(2\hbar^2 \varepsilon^2 n^2)$, where μ is the reduced mass, ε is the permittivity, and n is an integer. If ε is anisotropic, a more complicated formula must be used. In a free molecule both singlet and triplet states occur. In a singlet state there is no net electronic spin angular momentum, whereas in a triplet state there is a net positive electronic spin angular momentum and the molecule is paramagnetic. A triplet state lies lower in energy than the corresponding excited singlet state. Optical transitions between triplet states and a singlet ground state are multiplicity forbidden and therefore weak, while transitions between singlet states are often strong. Fluorescence, in which a molecule in an excited singlet state radiates energy and so returns to the ground state, can occur after a lifetime of the excited state of, typically, 10^{-8} sec. Phosphorescence, in which an excited triplet state is changed to the ground state by the emission of radiation, occurs after much longer periods of time. The half-life of a molecule in a triplet state can be, typically, 10^{-2} sec.

A localized exciton results from the energy absorbed by a molecule and transferred to a neighbor in a time which is long compared with the time necessary for the lattice to distort around the excitation. This moves through the crystal relatively slowly compared with the motion of a free exciton. The lifetime of a localized excitation depends[35)] on the temperature. AGRANOVICH[36)] distinguishes free excitons, deforming excitons and localized excitons, all of which correspond to a particular electronic state of a crystal. The relative stability of the various types of exciton is most clear at sufficiently low temperatures, but, when the temperature is raised enough, Agranovich prefers to speak of a single, averaged type of exciton, at least for the purposes of phenomenological theory.

The exciton, whichever type, will have a finite lifetime τ before it recombines; the mean distance ℓ covered by the exciton by means of its diffusion before recombination is called its DIFFUSION LENGTH and is given by $\ell = (D\tau)^{1/2}$ where D is the diffusion coefficient. Numerically, ℓ may have values of a few 100, to a few 1000, Å. Thus, exciton diffusion is capable of transporting energy over appreciable distances and, given a dissociation center, may result in the transport of charge over like distances.

10. Long Range Forces

Granted the existence of residual long-range order even in disordered systems, we look for the physical nature of the long-range forces which might thus be involved; a common form of long-range interaction is the attractive part of the van der Waals potential, varying with distance as R^{-6}. This may be thought to arise from a long-range interaction between transient, momentary dipoles which arise even in non-polar molecules because of random fluctuations in the local electronic density. However, such a disturbance cannot propagate instantaneously but only with the velocity of light in that medium; the thus resulting "retarded polarizations" and forces involved have been treated by CASIMIR and POLDER$^{37)}$, and by OVERBEEK$^{38)}$, and vary with distance as shown in Fig. 2.

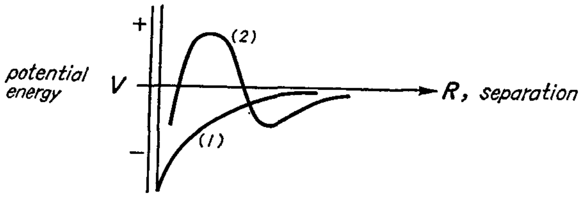

Fig. 2. Potential energy curves.

Curve (1) refers to the potential energy according to the classical van der Waals interaction, *i.e.* the London Dispersion, while curve (2) represents the total potential energy between two macroscopic spheres including the electrostatic interaction which is repulsive in this case; note the potential minimum.

The Casimir-Polder potential has a R^{-7} distance dependence; but it is active over large distances by means of a resonance effect. Quoting VERWEY and OVERBEEK, the London Forces being of an electrical nature need a certain time for their propagation. In the theory of London, this time is completely neglected as it uses the non-relativistic Schrödinger Equation. If we picture the London - van der Waals Forces as an attraction between the temporary dipole of one atom (or molecule, FG) and the dipole induced by it on the second atom (or molecule, FG) the finite velocity of propagation of electromagnetic actions causes the induced dipole to be retarded against the inducing one by a time equal to R/c. Here R is the distance and c the velocity of light in the medium. It is seen that one may expect a type of resonance effect when the time lag equals the dipole rotation time so that

$$R/c = 1/\omega\,; \quad R = c_0/\omega\varepsilon^{1/2} = \lambda/2\pi\,,$$

where ω is the angular frequency of dipole rotation; c_0 is the velocity of light in vacuo and ε the permittivity (dielectric constant) of the medium. λ is the wavelength corresponding to ω and c; the resulting absorption usually would be in the optical range. R therefore results as a few 1000 Å; a large distance indeed on an atomic or molecular scale. In view of the criterion for the existence of long-range order this interaction does indeed represent a (residual) long-range order.

The above assumes that both interacting molecules are in their ground state; if one of two otherwise identical molecules is in its first excited state, then the resonance interaction decays only with the inverse THIRD power of the separation and also depends on spin; it may become repulsive instead of attractive, though.

Given such a residual long-range order, does this give rise to an energy band structure? Is one then justified to apply the band model to systems devoid of long-range order? Here we refer to the work by McCUBBIN[39) and a review by MOORJANI and FELDMAN.[40) McCUBBIN points out that if N is the number of C bonds in a (reasonably large) molecule, then the $2N$ energy levels split into two groups, *viz.* bonding and antibonding orbitals. As N becomes very large, 2 energy BANDS result with a gap in between. In the ground state, the lower band is full and the upper band is empty. Thus the BASIC FEATURES OF THE BAND MODEL ARISE EVEN IN A SINGLE MOLECULE OF A LARGE PARAFFIN OR POLYMER, and *a fortiori* in the linear array of linear molecules considered. The band edges become imprecise, smeared out, and diffuse in the disordered system, the more so the greater the local disorder. To a certain extent, this is the effect of overlap of molecular wave functions, but McCUBBIN relates it to the state of order in the system. Qualitatively, GUBANOV and the Russian School come to a similar result.[4)

There appears to be some direct and strong evidence for the existence of long-range cooperative effects in disordered systems: DUWEZ and LIN working at Cal Tech, have shown that Fe-P-C alloys which have been rapidly cooled from the liquid (from above 1200 °C to room temperature in less than a millisecond), form glassy foils having a (supercooled) liquid structure and thus are completely amorphous. However they still are strongly ferromagnetic. The relatively small effect of fusion on the conductivity even of metals, and the near metallic behaviour observed is compressed potassium vapour, also point in the same direction.

Further support for the same reasoning comes from a consideration of electrochemical double layers: GRAHAME[41) has postulated that it is impossible to represent over a range of frequencies the impedance of the double layer by any finite combination of lumped circuit elements; for detailed analysis the reader is referred to a paper by TIEN CHAO-WU.[42) It appears that the double layer is equivalent to an ideally infinitely long transmission line; on a molecular scale this means a repeat distance of the order of molecular dimensions with the resulting order extending over several hundred such units. Thus, a double layer in a liquid involves a longe-range ordering interaction.

11. Activation Energy

The conductivity σ of most semiconducting systems as a function of temperature T just about invariably obeys an equation of the form

$$\sigma = \sigma_0 \exp(-E/kT), \tag{30}$$

where E is an activation energy usually derived from the slope of a log σ *vers.* $1/T$ plot. However, it may be readily shown that the above equation should be written in the form*)

$$\sigma = \sigma_0 \exp(-E^*/2kT) \tag{31}$$

for the following reason:

Consider the following Born-Haber Cycle:[4]

(a) remove an electron from a given molecule, or site, of the system to infinity,

(b) bring the electron back from infinity to an adjacent molecule or site in the system.

The enthalpy change involved in this transfer of a carrier from an electron donor to an acceptor may be written as the Lyons Equation:[44]

$$W = I_D - A_a - \Delta P,$$

where I_D is the ionization energy of the donor, A_a the electron affinity of the acceptor and ΔP stands for the change in polarization or, in the case of a liquid system, of the solvation energy. Note that the system as such remains electrically neutral; there is NO ADDITION of charge, we merely produce a cation + anion by transferring a charge. The entropy (change) associated with the formation of n cations is

$$S = k \ln N!/(N-n)!\, n!, \tag{32}$$

where N stands for the number of available molecules, or sites, to receive or donate, one electron. An exactly similar equation may be written for the anions. The TOTAL entropy thus is

$$S = 2k \ln N!/(N-n)!\, n! \tag{33}$$

At equilibrium, the free energy G is a minimum:

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*) Professor MATSUDA[43] remarked that this is a purely thermodynamic treatment and thus valid without regard to any model or any particular system employed. Professor MATSUDA's suggestion that thus this line of reasoning may be equally applicable for an electrochemical reaction and therefore might explain the transfer coefficient of 0.5 usually observed in such reactions, appears to be quite acceptable.

$$\partial G/\partial n = 0. \tag{34}$$

W is the work required to produce one pair of separated ions, or the net enthalpy (change):

$$G = nW - TS. \tag{35}$$

At equilibrium

$$\begin{aligned} &W - T\frac{\partial S}{\partial n} = 0 \\ &\frac{\partial S}{\partial n} = 2k \ln \frac{N-n}{n}, \qquad n \ll N \end{aligned} \tag{36}$$

$$\therefore \quad W = T\frac{\partial S}{\partial n} = 2kT \ln \frac{N-n}{n} \cong 2kT \ln \frac{N}{n} \tag{37}$$

$$\frac{n}{N} = e^{-W/2kT} \tag{38}$$

In this context, it might be apposite to consider the case where an electron is ADDED to an initially neutral system: For n electrons distributed over N molecules (sites), $n \ll N$, the number W of ways in which similar systems may be assembled, can be written[4)]

$$W = N!/(N-n)!\,n! \tag{39}$$

For the addition of 1 electron, the contribution to the free energy due to the entropy change is

$$-T\Delta S = -kT \ln N \qquad S = k \ln W \tag{40}$$

At 300°K this is about $-0.055 \log_{10} N$ eV. Thus, if we put one electron on any one of a few 1000 molecules (sites) which are otherwise identical (a region of about 40 Å or so in a solid or dense liquid), this amounts to about -0.2 eV. This is quite a large figure, and if such treatment is applicable to a double layer as it well may be following Professor MATSUDA's[43)] suggestions, a layer of about 10^{15} molecules, that is about a monolayer, should involve an entropy contribution to the free energy of about -0.8 eV which is quite a large amount of energy.

The entropy considerations here presented assuredly must have a bearing on problems in charge transfer catalysis. They arise from purely thermodynamical reasoning and thus do not depend on any model or special system. They do require for their applicability the presence of a certain degree of at least residual long-range order. It is hoped that the existence of such order has been demonstrated in the preceding argument.

12. Thermoelectric Effects[45)]

The Seebeck Coefficient α is defined in terms of the potential change across the sample, $\Delta\phi$:

$$\Delta\phi \equiv \alpha \Delta T\,. \tag{41}$$

Experimentally, $\Delta\phi$ as well as any change in the concentration n and/or the mobility of the carriers are due to the temperature gradient ΔT. The chemical potential μ or the Fermi-level of the carriers may be written

$$\mu = \mu_0 + kT \ln n\,. \tag{42}$$

We now introduce the electrochemical potential φ

$$\varphi \equiv \mu \pm e\phi = e\alpha\Delta T \tag{43}$$

e being the electronic charge.

But

$$\mu = \overline{E} - T\overline{S}, \tag{44}$$

where $\overline{E}$ and $\overline{S}$ are the partial molal internal energy, and entropy, respectively. Let $\Delta T \ll T$ allowing T to be taken as the sample average and assume that over the temperature interval considered, $\overline{E}$ as well as $\overline{S}$ are in zeroth approximation temperature independent:

$$\varphi = \overline{E} - T\overline{S} \pm e\phi \tag{45}$$

$$\Delta\varphi \rightarrow d\varphi \text{ as } \Delta T \rightarrow dT \tag{46}$$

$$d\varphi = e\alpha dT \tag{47}$$

$$\alpha = \frac{1}{e}\frac{d\varphi}{dT} \tag{48}$$

$$\frac{d\varphi}{dT} = \frac{d}{dT}\,[\overline{E} - T\overline{S} \pm e\phi] = -\overline{S} \tag{49}$$

$$\therefore \quad \alpha = -\overline{S}/e \tag{50}$$

Thus, the Seebeck Coefficient measures the entropy difference across the sample and can be interpreted as measuring the Entropy Flux across it: Let C be the geometric capacitance of the system exhibiting a permittivity (dielectric constant) of ε, and a resistivity of ρ ohm-cm giving rise to a resistance of R ohm and considered to be isotropic and homogeneous. Let the charge associated with the thermoelectric potential V be denoted by Q; e is the electronic charge; $S = -\alpha e$ as before

$$S = -eQ/C\Delta T, \text{ since } Q = CV \text{ and } V = \alpha\Delta T \tag{51}$$

$$F_s = \text{Entropy Flux} = \frac{dS}{dt} = \frac{-e}{C\Delta T} \cdot \frac{dQ}{dt} = \frac{-ie}{C\Delta T} \cdot \tag{52}$$

But the current

$$i = \frac{\alpha \Delta T}{R} \tag{53}$$

$$\therefore \quad F_s = -\frac{e\alpha}{RC} = \frac{-\alpha e}{\tau}, \tag{54}$$

where $\tau = RC =$ time constant of the system.

For a plane parallel geometry, $R = \rho \frac{l}{A}$ where $l =$ length and $C = \frac{A\varepsilon\varepsilon_0}{4\pi l}$, $A =$ area of the sample.

Thus:

$$RC = \tau = \frac{\rho\varepsilon\varepsilon_0}{4\pi} \qquad \varepsilon_0 = \text{permittivity of free space} \tag{55}$$

and

$$F_s = \frac{-4\pi\alpha e}{\rho\varepsilon\varepsilon_0}. \tag{56}$$

All Seebeck Coefficient values here given are ABSOLUTE Thermo-EMF'S relative to a hypothetical metal having zero thermo-electric power. However, the Seebeck values for these semiconductors are so much higher than those for metals that this assumption is practically justified.

The Seebeck Coefficient for metals is low because the electronic transport entropy of the electrons in a metal is so low. Difficulties arise in IONIC systems because the transport entropy of IONS in a metal is NOT low. Ionic Seebeck Coefficients are very complicated and little work has been done in that field.

The Seebeck and the Peltier Coefficients, Π for the latter, are related by the thermodynamic relation $\alpha = \Pi/T$.

The Peltier Coefficient is a measure of the position of the Fermi level, and thus of log n, as seen from Fig. 3.

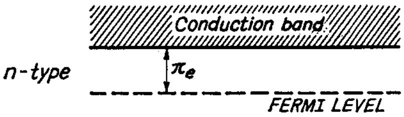

Fig. 3. Relation of Fermi level and Peltier coefficient Π.

According to a band model, the carrier concentration n increases exponentially with temperature,

$$n = N \exp(-E/2kT) \tag{57}$$

so that

$$\Pi \propto \text{FERMI-LEVEL} - L \cdot \propto \log n\,; \tag{58}$$

$$\therefore \quad \alpha T \propto T \text{ or } \alpha \cong \text{const}\,. \tag{59}$$

Thus, α should remain substantially constant and temperature independent; if anything it should slightly increase with temperature. The trend observed, however, is in the opposite direction.

We can write, for hole conduction

$$e\Pi = e\alpha T = \beta + kT \log_e N/n^+ \tag{60}$$

and for electron conduction

$$= -\alpha' - kT \log_e N/n^-\,, \tag{61}$$

where portions β and α' of the activation energy of the hole, or electron, are transported by the heat flux due to the temperature gradient. Writing for the Seebeck Coefficient therefore

$$\alpha = \frac{1}{e}\left[\frac{-\alpha'}{T} - k \log_e \frac{N}{n}\right] = \frac{1}{eT}\left[-\alpha - kT \log_e \frac{N}{n}\right]. \tag{62}$$

It is convenient to measure α' and β in units of kT so that $\alpha' = AkT$; $\beta = AkT$ as the case may be.

A of course must be a positive quantity, it is called the scattering parameter and depends on the scattering model envisaged. If there is very little carrier-phonon or lattice interaction, A is negligibly small; for scattering from ionized centers, $A = 2.5$ to 4 and for scattering from neutral centers, $A = 2$. We can write

$$\alpha = \frac{k}{e}\left[A + \frac{E}{2kT}\right]. \tag{63}$$

Here, E is the energy gap determining the carrier concentration n.

13. Space Charge Limited (SCL) Currents[4,46]

SCL currents are important because the injected currrent is independent of the mechanism of carrier generation and depends only on the transport and trapping of the carriers within the crystals.

Given ohmic contacts, the current-voltage relationship is linear at low fields but becomes nonohmic at higher values of the applied field. (a) At the higher current densities corresponding to higher values of field, there will be present between the electrodes a relatively large concentration of charge carriers in transit to the collector electrode. These carriers constitute a space charge, in exact analogy with the space charges encountered in vacuum diodes for example. (b) The other cause of nonlinearities in the current-voltage characteristic is found in the existence of traps. They may be due to a wide range of crystal defects, such as impurities, stacking faults, dislocations, and other lattice defects, which give rise to additional but highly localized energy levels within the energy gap. If the trapping center carries a net positive charge, it constitutes an electron trap and *vice versa.**) Such a trap gives rise to a localized energy level between the Fermi level and the bottom of the conduction band, as shown in Fig. 4. The traps may be deep or shallow. If the distance from the bottom of the trap, that is, from the trapping level shown on the right side of Fig. 4 to the bottom of the conduction band, is large compared to kT, we speak of deep traps, and *vice versa.* Thus trapping levels T_1 and T_2 would be shallow, and T_3 and T_4 would be deep. The main effect of shallow traps is the reduction of the mobility of the carriers, since thermal energy suffices to redissociate a carrier from such a trap. However, the reliberation of carriers from deep traps is a rare event; how rare depends entirely on the value of kT and on the depth of the trap.

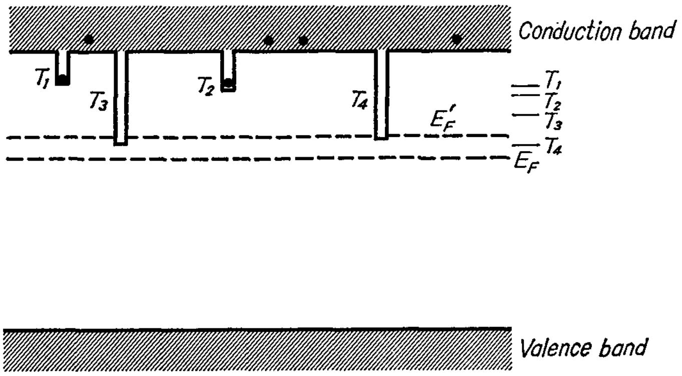

Fig. 4. Energy level diagram of a semiconductor with traps.

Thus, as long as the concentration of traps is not very large, an increase in the applied field therefore in the concentration of carriers injected from an ohmic contact into the solid, will shift the equilibrium between occupied and unoccupied traps toward the former; at a certain value of field, all the traps are filled virtually all the time. Although the filled trap may be electrically neutral, it usually is not and thus the system of occupied traps constitutes a space charge within the solid. However, in contradistinction to the

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*) Although a net electric charge is a sufficient condition for a center to act as a trap, it is not a necessary condition. The essential feature is the existence of a localized region of lowered potential energy.

mobile space charge caused by the very presence of the carriers and giving rise to the V^2 voltage dependence described by a form of the Child-Langmuir law, the charge distribution arising from the filling of trapping levels is immobile and fixed in space.*)

We now consider these effects in somewhat greater detail.[47] The general shape of the current-voltage characteristic of an electrically neutral solid containing one single type of traps all of equal energy is shown in Fig. 5, in a log-log representation. At low voltages there is negligible injection of carriers from the contact and the current obeys Ohm's law, region A–B′ or A–B. In the absence of traps the current becomes space charge limited at a voltage corresponding to point B′, where the concentration of free carriers injected from the contact equals the concentration of majority carriers thermally generated. The Child-Langmuir law is then obeyed, and the current follows the line B′–D–E because the current I is given by

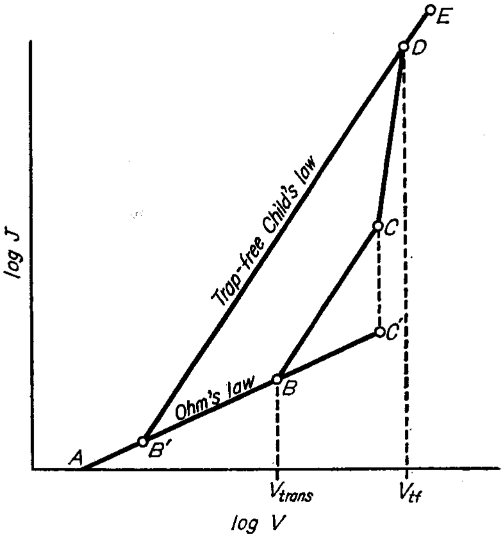

Fig. 5. Current *versus* voltage characteristics for solids containing traps; their filling causes space charges.

$$I \cong 10^{-13}\, V^2 \mu\varepsilon / d^3\,, \qquad \text{amp cm}^{-2} \tag{64}$$

where V is the applied voltage, μ the mobility of the carriers, d the inter-electrode distance, and ε the permittivity of the solid; a plane parallel geometry is assumed.

Following Rose[47], Eq. (64) may be derived: The solid between the two electrodes forms a plane parallel capacitor having a capacitance C cm^{-2};

$$C = \varepsilon/4\pi d \qquad \text{esu cm}^{-2} = 10^{-12}\varepsilon/4\pi d \text{ farad cm}^{-2}\,.$$

The voltage V is related to C and to the charge Q by

$$Q = CV\,.$$

The current, which here is space chage limited (SCL for short), in the steady state is given by

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*) refer to the footnote on page 120.

$$I = Q/\tau, \qquad (65)$$

where τ is the transit time of Q, that is, the time required for an element of the charge to pass from one electrode through the solid to the other contact. From the above

$$Q = (\varepsilon V/4\pi d) \times 10^{-12} \quad \text{coulomb}. \qquad (66)$$

The transit time can be expressed in terms of the field $E = V/d$ and of the carrier mobility μ:

$$\tau = d/E\mu = d^2/\mu V \qquad (67)$$

yielding for the SCL current I

$$I \cong 10^{-13} \mu V^2 \varepsilon/d^3 \quad \text{amp cm}^{-2}. \qquad (68)$$

In the trap-free solid, the current will thus be proportional to the square of the applied voltage and follow the line B'–D–E in Fig. 5. If only shallow traps are present, at any one instant, only a fraction of the carriers injected from the contact will be free; the remainder will be immobile within the traps. Since we are considering a steady state, an equilibrium distribution between carriers remaining free and those in traps is established, and we can write for the fraction θ of the total space charge which remains free:

$$\theta = (N_c/N_t) \exp(-E_t/kT), \qquad (69)$$

where N_c is the number of carriers injected into the conduction band per cubic centimeter of solid, that is, the concentration of free carriers; N_t represents the concentration of shallow trapping levels which are all assumed to have equal energy so that they are situated E_t eV below the bottom of the conduction band. Equation (69) can still be applied to describe the system, with the proviso that μ now represents an effective mobility defined as

$$\mu = \mu_0 \theta, \qquad (70)$$

where μ_0 stands for the free carrier mobility.

It is seen that the presence of traps causes the concentration of carriers in the conduction band to drop sharply. The current, however, still obeys the V^2 relation of the Child-Langmuir law.

The injection of carriers into the conduction band caused the Fermi level[*] to move upward from its equilibrium position indicated by E_F in Fig. 4. As long as the current remains low, that is, the concentration of carriers in

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[*] This discussion refers to a nonequilibrium, though steady state, regime. Thus the term "quasi-Fermi level" should be used rather than the term "Fermi level"; for the sake of brevity, however, the latter expression will be used here.

the conduction band remains low, this shift is negligible. However, it can no longer be neglected when the current becomes space charge limited, since nearly all the excess carriers injected now become trapped. The Fermi level thus moves upward by an energy of the order of kT.

This shift of the Fermi level yields another criterion for distinguishing between shallow traps and deep traps. Trapping levels which are situated between the bottom of the conduction band and the new position of the Fermi level are shallow, and those which are now below the Fermi level are deep traps. Referring again to Fig. 4, we see that T_3 and T_4 thus are deep traps, while T_1 and T_2 remain shallow. The V^2/d^3 relation (Eq. 64) holds as long as all traps are shallow in the definition above, even if they are deeper than kT.

Returning now to Fig. 5, we find that the current will become nonohmic above a certain transition voltage V_{trans}, point B, and the system at that point enters a space charge limited regime in which, however, the Fermi level is still substantially at its equilibrium, no-voltage position. The current then rises proportionally to a V^n relation. In that region the excess of free carriers injected from the electrode exceeds the concentration of majority carriers at equilibrium, n:

$$n_t \geq 2n\,. \tag{71}$$

The Fermi level commences to rise significantly as soon as point B is reached. The transition voltage V_{trans} is given by[47)]

$$V_{\mathrm{trans}} = end^2/2\varepsilon\varepsilon_0\,. \tag{72}$$

As the voltage is raised beyond point C, the Fermi level enters the region where deep trapping levels exist, and the ratio θ no longer remains constant but becomes a function of V.

Since now all the traps are filled, any more carriers injected from the electrode must go into the conduction band and the current commences to rise steeply and becomes proportional to V^n, $n>2$. This is the region C–D in Fig. 5. Point D corresponding to this transition defines another critical voltage, V_{tf}, given by

$$V_{tf} = ed^2 N_t/2\varepsilon\,, \tag{73}$$

where N_t stands for the total concentration of traps, or defect states. For applied voltages below V_{tf}, the excess charge injected above the equilibrium, no-voltage concentration of carriers is mainly held in the defect states, *i.e.* the traps. As soon as the voltage exceeds V_{tf}, the traps cease to play a major role because they are all filled and remain filled; the characteristic then again enters a region determined by the Child-Langmuir law since the solid is now virtually trap-free. This is now part *D–E* of the characteristic in Fig. 5. Actually, the break is not quite so sharp as indicated, and the V^2 relationship strictly holds only for voltages in excess of about $2V_{tf}$.

The space charge limited current density I in the region *D–E*, Fig. 5 is again given by

$$I \cong 10^{-13}\mu\varepsilon V^2/d^3 \quad \text{amp cm}^{-2}. \tag{74}$$

The concentration of traps, N_t is a highly important quantity; it can be obtained from an experimental determination of V_{tf}, from a current-voltage characteristic and using Eq. (73). It should be noted that the trap density, and its measurement from the current *versus* voltage characteristic, are independent of both the mobility and the effective mass of the carriers. Both quantities do enter into the expression for the current density, Eq. (74).

Within the space charge limited region *B–C*; Fig. 5, the current density is given by another form of the Child-Langmuir law:

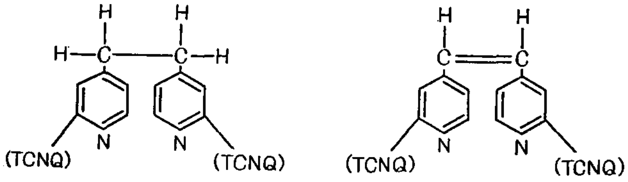
$$I_s \cong 10^{-13}(V^2\mu\varepsilon/d^3)\left[(N_c/N_t)\exp(-E_T/kT)\right] \quad \text{amp cm}^{-2}, \tag{75}$$

where, for a uniform trap distribution, E_T is the energy difference between the bottom of the conduction band and the defect level.

14. Change Transfer and Chemical Structure

A. Model compounds[48]

The method has been applied to a systematic study of the electrical properties of a series of monomeric and polymeric dipyridilium compounds, containing TCNQ (Tetracyano diquino methane).



D_S D_U

Fig. 6. Model compounds.

The following changes were introduced into the molecule one at a time: 1. the central single bond linking the two halves of the molecule were replaced by a double bond; 2. a second ionized TCNQ substituent was introduced in the position indicated; 3. additional, neutral, TCNQ was introduced in 1/2 molar and 1 molar concentrations; 4. the single bond as well as the double bond compounds were polymerized.

Subsequent to these changes, the electrical conductivities were measured in dependence on temperature and applied voltage, thus permitting the evaluation of the effective carrier concentration, the effective density of states, the thermal activation energy of the conduction process, and the mobility. For several compounds, a study was also made of Hall voltages and of the thermo-emf's over a range of temperatures.

B. Results and Discussion

It is seen from Table 2 that the equilibrium free carrier concentration n remains substantially constant, to the accuracy of the experiments, over temperature ranges from liquid nitrogen to room temperatures. The carrier concentration remains also substantially unaffected by steric modifications and by polymerization.

At the same time, the resistivities are seen to vary over six to nine orders of magnitude, giving rise to thermal activation energies E ranging from 0.1 to 0.21 eV.

In only two cases has it been possible to reach the trap filled region experimentally; the resulting trap concentrations are about identical for the monomer and its polymer; the values are relatively low. In these two cases, employing theoretical argument to be presented later, values for the effective masses of the carriers have been deduced and are listed in terms of the free electron mass m_0. Values for the Seebeck Coefficient, *viz.* the thermoelectric power, have been obtained; from these the scattering parameter A and the Fermi level E_F measured relative to the edge of the conduction band, have been calculated.

It is seen that (a) several A values are far in excess of the theoretical maximum of 4 and (b) there is a tendency for A to decrease with rising temperature.

Anomalous A values have been reported by several authors.[49] Remembering how the quantity A was introduced, it is seen that a large A value means a strong phonon interaction and a very low A value, a very weak lattice coupling. The excessively high A values thus may be interpreted as a very strong coupling of the carrier to the lattice, in other words the carrier is localized to a great extent.

Thus, it is seen that a) introduction of a double bond and/or b) polymerization move the Fermi level closer to the edge of the conduction band; c)

TABLE 2. Some electrical properties

Compound No.	ρ, Resistivity, Ωcm; at °C:					E	Seebeck coeff.	
	−190	−78	−11.5	+0.5	+20	eV	mV °C^{-1}	at °C
184-F	2×10^{12}	1.8×10^{8}	1.2×10^{7}	4.7×10^{5}	6.1×10^{4}	0.103	+0.62	15.5
174-F-1	6×10^{10}	1.7×10^{6}	—	1×10^{5}	1.2×10^{4}	0.143	+0.32±0.07	8—70
174-F-2	7.4×10^{10}	1.3×10^{6}	—	—	1.0×10^{4}	0.14	—	—
174-F-SC	$R=5\times10^{11}$	—	—	—	$R=4.6\times10^{5}$	0.149	—	—
204-1	2×10^{13}	3.1×10^{8}	—	2×10^{6}	3.5×10^{6}	0.121	+0.63±0.08	4.6—48.7
204-2	—	2.9×10^{8}	—	1.8×10^{6}	7×10^{5}	0.12	—	—
214-1	3×10^{15}	4×10^{9}	3.2×10^{7}	1.9×10^{7}	3.6×10^{6}	0.213	+0.80±0.06	35—78
214-2	—	—	—	1.5×10^{7}	4.5×10^{6}	0.2	+1.2 ±0.11	10—28
R-156	1.5×10^{13}	4×10^{8}	1.7×10^{7}	1.9×10^{6}	1.5×10^{6}	0.150	+0.24 +0.38 +0.72	67.1 10.3 4.9
R-155	2×10^{13}	4.4×10^{7}	—	1.0×10^{6}	6×10^{5}	0.15	+0.19±0.01	11—55

♯ 184-F	single bonded compound with ONE TCNQ substituted per molecule
♯ 174-F-1	same, double bond instead of single bond
♯ 174-F-2	repeat of ♯ 174-F-1, different sample
♯ 174-F-SC	small single crystal grown from ♯ 174-F
♯ 204-1	same as ♯ 174-F but with TWO TCNQ$^-$ per molecule

introduction of a second ionized center into the molecule moves the Fermi level away from the conduction band d) the Fermi level comes closer to the conduction band as the temperature increase. Note that Fermi level values here given refer to the edge of the conduction band and are NOT values relative to potential zero at infinity.

We also note, that shifts of the scattering parameter A parallel the movements of the Fermi level. There seems to be an unexplained correlation between A and E_F but A is more sensitive than E_F. However, we can say that a) and b) above tend to decouple the carrier from the lattice.

In the limit, if one could achieve a more complete decoupling, a possibility for producing an organic superconductor in a polymer, according to the theory of W. A. LITTLE[51)], might arise. This is so because superconductivity[50)] is bound up with the existence of COOPER PAIRS, in that a coupling between two electrons is produced thus: The movement of the first electron causes a slight shift of the positive metal ions (in a metal at very low temperature) towards its path. This means that the electron leaves behind a region of positive potential increment in the lattice, since the relaxation time of the ions, in view of their mass, is very much longer than the electron drift time.

of the model compounds, see Fig 6.

n; Carrier concentration, cm^{-3}, at °C:					N_t Trap concentration at -190°C, cm^{-3}	Scattering parameter A	Fermi-level eV to edge of conduction band	$\frac{m^*}{m_e}$
-190	-78	-11.5	$+0.5$	$+20$				
3×10^{12}	2×10^{12}	4.8×10^{11}	—	1.6×10^{12}	—	5.2	0.18	—
4.5×10^{11}	1.2×10^{10}	—	—	—	—	0.93	0.096	—
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
8.8×10^{10}	2.4×10^{11}	—	—	1.7×10^{11}	10^{13}	5.0	0.19	50
—	—	—	—	—	—	—	—	—
—	4.8×10^{11}	4.8×10^{11}	3.7×10^{11}	—	—	5.6, 35 to 78°C 9.8, 10 to 28°C	0.26 0.30	—
—	—	—	—	—	—	—	—	—
1.8×10^{10}	3×10^{10}	3.5×10^{10}	3.5×10^{10}	—	—	0.15, at 67.1°C 1.4, at 10.3°C 5.2, at 4.9°C	0.082 0.11 0.2	—
1.7×10^{10}	3×10^{10}	—	1.5×10^{10}	—	4×10^{12}	0	—	17

# 204-2	repeat of # 204-1, different sample
# 214-1	same as # 184-F but with TWO TCNQ per molecule
# 214-2	repeat of # 214-1; different sample
# R-156	Polymer of # 214
# R-155	Polymer of # 204

A second electron thus is attracted to the region previously occupied by the first and one may consider that the 2 electrons are coupled to each other in spite of their coulombic repulsion. At very low temperatures, where thermal motion of the lattice ions is negligible, superconductivity results. LITTLE[51] has proposed to produce the same effect in a polymer consisting of a conjugated backbone with polarizable side chains which are accurately spaced off the backbone; motion of an electron tends to produce an electrostatic polarization in the side chains which again would provide an attractive interaction with a following electron. While LITTLE[51], and MCCONNELL[52], have shown that such a superconductor could exist at temperatures much in excess of room temperatures, so far no such material has as yet been made.

If the coupling of the electrons to lattice were made so weak that thermal disturbances would have negligible effect, without, however, resulting in an entirely "free electron gas" independent of the crystal—which would be impossible—then a space charge cloud of polarons should be capable of an attactive interaction with another one in its vicinity, giving rise to what would be effectively a kind of Cooper Pairs.

We have drawn attention to the fact that the carrier concentration of the compounds studied, see Table 2, remains constant over wide temperature ranges while the resistivity, at the same time, varies by 6 to 9 orders of magnitude. It thus suggests itself that we are faced with a thermally activated mobility, *i.e.* with some form of a hopping mode of charge transfer. If we now calculate the mobilities required to satisfy the observed resistivities and carrier concentrations, then we find that values of the mobility result which are of the order of 1 to 100 cm^2 (V-sec)$^{-1}$ and higher. Such high mobilities, however, would require an energy band model and, in fact, would imply a fairly wide conduction band. Moreover, the relatively few direct measurements of the mobility in organic materials just about invariably yield very much lower values for the mobility.

The temptation arises to try to reconcile the apparent contradiction by introducing a temperature, and structure, dependent density of states N_0 in the classical band model equation[4] for the carrier concentration n,

$$n = N_0 \exp(-E/2kT) \tag{76}$$

$$N_0 = 2\left[\frac{2\pi m^* kT}{h^2}\right]^{3/2} \tag{77}$$

This means that the effective mass of the carrier depends strongly on temperature and structure, so as to maintain n constant, it means very narrow and likewise variable energy bands. Given the value for the effective number of states N^* in the conduction band, by calculating back from the conductivity and carrier concentration measured, we can derive the number of states from the equation[4]

$$N^* = [N_0 N_t]^{1/2}\,. \tag{78}$$

However, N_0 may also be calculated[4] as twice AVOGADRO's number times density/molecular weight, *i.e.* as about twice the molecular density, ASSUMING the effective mass of the carrier is that of a free electron. Since N_0 varies with m^* as $(m^*/m_0)^{3/2}$ we can now calculate the effective mass of the carriers which results as $m^* = 50$ for ♯204 and 17 for ♯R-155 which is the polymer of ♯204. Polymerization thus has reduced the effective mass of the carrier.

It is proposed that E as derived from resistance *vers.* tempearture plots is not related to the Fermi level or an energy gap, but represents a TRAP DEPTH. Since these materials all are compacted solid tablets, grain boundaries, impurities, and the like are expected to provide ample centers for trapping.

It is of interst to note that even in compacted tablets of other organic materials, as well as of CdS, similar trap densities were obtained by several workers.[4]

15. Charge Transfer Complexes[4)]

A. Introduction*)

Consider a molecule which has a relatively low ionization potential I_D and thus tends to be electron donating (a donor), and another one which has a large electron affinity E_a and thus tends to be an electron acceptor. The energy required to transfer an electron from donor to acceptor is given by a Lyons Equation[44)]

$$E = I_D - E_a - e^2/\varepsilon r - I_x - P, \tag{79}$$

where the third term represents the coulombic interaction, I_x the resonance energy and P the polarization energy; in solution, the solvation energy S replaces P. In the limit, if charge transfer is complete, a MOLIONIC LATTICE[53)] results. However, there is no definite evidence so far for the existence of molionic lattices. In a way, the ionic lattices formed by ionic salts like NaCl are extreme cases of charge transfer in that the electron has been completely transferred from the donor, Na, to the acceptor, Cl. The molionic lattice would be the molecular-ion-counterpart.

In practice, the electron is only partially transferred, meaning that it spends part of its time on the donor and part of time on the acceptor, or in their vicinity. Thus depending on the degree of transfer, we can distinguish strong and weak complexes formed as the result of such transfer. Which type will form depends on the relative values of the terms entering into the Lyons Equation; in particular, the two last terms are affected by charge transfer complexing. From another point of view, we can distinguish π-complexes if mainly π-electron orbitals are involved, and σ-complexes if the bonds involved are sp^3 bonds. The former involve but little resonance energy and the resulting electrical conductivity is highly anisotropic because of the tendency of donors and acceptors to assume stacks like pack of cards, see Fig. 7.

σ-complexes are stabilized by a great deal of resonance energy; they exhibit, generally, less anisotropic conduction than the π-complexes. The drop in resistivity due to charge transfer complex formation is quite large; thus

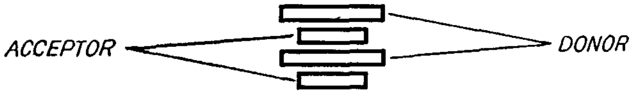


Fig. 7. Sacking of donor and acceptor molecules in columnar (lamellar) complexes.

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*) For the original work of MULLIKEN, see Ref. 70).

e.g. the dipyridilium compounds discussed have room temperature resistivities of the order of 100000 ohm-cm and higher; complexing with neutral, interstitial, TCNQ (tetracyanodiquinomethane, a powerful electron acceptor) lowers the resistivity to a few ohm-cm, thus by 5 orders of magnitude. Likewise, phenothiazine[54)] has a resistivity of about 10^{13} ohm-cm and iodine about 10^{10} ohm-cm: the resulting complex[54)] first studied by MATSUNAGA[55)] has a resistivity of a few ohm-cm's only, thus drop of at least 10 orders of magnitude.

The wave function for the formation of a charge transfer complex[4)] from a neutral donor and a neutral acceptor may be written thus:

$$\psi_{DA}(D_1 A) = a\psi_0(DA) + b\psi_1(D^+A^-) \qquad (80)$$

If $a \gg b$; in the limit $a \rightarrow 1$ the complex is weak; the ground state is given by a non-bonding wave function. If $a \ll b$ the complex is strong; the ground state is ionic and only these complexes exhibit good electric conductivity. For the excited state, we may write;

$$\psi_{EXC}(D_1 A) = a^* \psi_1(D^+A^-) - b^* \psi_0(DA) \qquad (81)$$

Here, it is seen that even for weakly interacting complexes where $a \gg b$, the excited state is ionic. There is yet another, transitory, type of charge transfer complex, *i.e.* CONTACT CHARGE TRANSFER COMPLEXES, in which transfer takes place only momentarily upon contact and while in contact; the complex itself is unstable. These are very weak complexes which we shall not discuss in any detail.

B. Steric Effects[4)]

Probably no other type of organic semiconductor is more effected by steric changes than is a charge transfer complex.

Structurally, we can distinguish two types; homogeneous solids and those which have a pronounced layered structure, that is, systems in which donor and acceptor molecules are each contained in parallel planes which are then alternately superimposed.

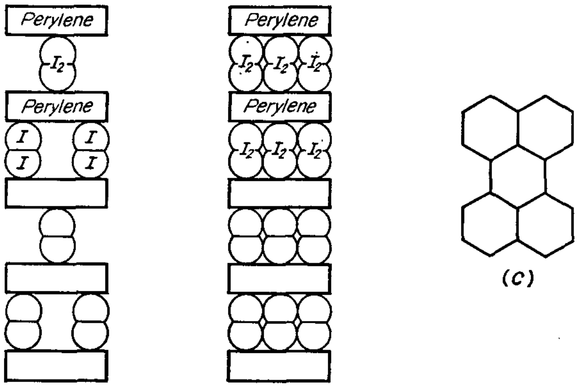
Although quite generally charge transfer complexes exhibit closer packing than do molecular crystals, this is particularly true of complexes resulting in the formation of a linear, columnar arrangement of stacked donor and acceptor units. In these complexes, we have, in effect, formation of ion-radical stacks; electron transfer takes place at the highest filled level according to the scheme

$$D^+A^-D^+A^- \rightarrow D^+ADA^- \rightarrow D^+AD^+A^{2-}\,. \qquad (82)$$

This electron transfer is supposed to occur at least partially by tunneling; the resulting complexes are σ-bonded, and mainly of the lamellar type. A strong charge transfer interaction between adjacent donors and acceptors require a steric arrangement in which the dipole moment is aligned along the symmetry axis. Thus, KOBINATA and NAGAKURA[56], measuring the dipole moments of the charge-transfer complexes between iodine and several aliphatic amines, found that the dipole moments greatly increase with the increment in the amine concentrations. This can be explained by considering that the contribution of the charge-transfer configuration in the ground states of these complexes increases with the increment in the dielectric constant of the environment, amounting to 35–41% for some amine-iodine complexes. It is of interest, in this context, to note that the enthalpy change upon complexing has been found[57] to be proportional to $\Delta\mu/r$ where $\Delta\mu$ is the change in the dipole moment upon complexing and r the separation between bonding centers in the donor and acceptor molecules, respectively.

In some complexes the columns consist neither of stacks of single donor and acceptor molecules in an alternating sequence nor of separated stacks of either donor or acceptor, but rather of subcolumns, each of several molecules of each species, arranged in an alternating order. Charge transfer then occurs between a particular donor molecule and the greatest possible number of nearest neighbors.

Other charge transfer complexes are amorphous and rather like a solid solution ; for example, the violanthrene-iodine complex yields an X-ray diffraction pattern indicating an amorphous structure consisting of a homogeneous distribution of iodine molecules in a host matrix of donor molecules : log (conductivity) is linearly related to the mole ratio, as one would expect from a solution.



(a) Perylene-$1.5I_2$ (b) Perylene-$3I_2$

Fig. 8. Structure of perylene-iodine complexes. The structure of perylene is given in (c). After UCHIDA and AKAMATU.[59]

The arrangement in iodine-aromatic hydrocarbon complexes is generally more ordered: the iodine molecule is said to sit above the benzene molecule with its center in the 6-fold axis of symmetry of the benzene ring. FUKUI[59] couludes that the axis of the iodine molecule is aligned parallel to the symmetry axis, and thus perpendicular to the plane of the ring system. Crystallographic studies by UCHIDA and AKAMATU[59] are in agreement with the model proposed by FUKUI. The resulting structure is shown in Fig. 8.

These complexes involve a weak charge transfer, that is, having a relatively high value of $I_c - A_c$. They thus show a high resistivity, but factors other than $I_c - A_c$ must be considered. The greatest conductivity occurs when molecules of the donors (or acceptors) are not separated from one another within any one chain by molecules of the other species. Such an arrangement has been realized, for the example, in the TCNQ complexes.

A 1 : 1 ratio of donor to acceptor is not as favorable to a high conductivity as, for example, a 1 : 2 ratio, in the case of n-type materials. Thus quinolinium$^+$(TCNQ)$^-$ has a conductivity of 10^{-4} ohm^{-1} cm^{-1}, while for quinolinium$^+$(TCNQ)$_2^-$ the value is 10^2 ohm^{-1} cm^{-1}. Conductivities of 10^{-1} ohm^{-1} cm^{-1} were found in some metallocene and quinone complexes by MATSUNAGA.[58] Here the ratio of donor to acceptor was also 1 : 2.

C. Energetics. Stoichiometry :[4]

We have to distinguish between strongly interacting systems in which the ground state already has at least partially ionic character, and weakly interacting complexes in which only the excited state is ionized.

It appears that those charge transfer complexes which are strongly interacting, that is, those in which the ground state already is ionic, have very low resistivities, while the weaker interactions lead to room temperature resistivities which are very much higher, but still lower than those of ordinary molecular crystals.

For conduction to take place, it is first necessary to ionize a molecule and then to remove the electron until its coulombic energy has become negligibly small (compared to kT, the thermal energy). For a solid, this energy E_0 is given by

$$E_0 = I_D - I_A - e^2/\varepsilon r - I_x - P, \tag{83}$$

where I_D is the ionization potential, I_A the electron affinity, and the next term represents the coulombic interaction. I_x represents the resonance energy and P the polarization energy. For a charge transfer complex, this expression must be modified to include charge transfer interaction which will affect primarily I_x and P. Thus an increased polarizability will increase P and therefore reduce E_0.

The reasoning above is supported by the experiments of UCHIDA and AKAMATU[59] on violanthrene-iodine complexes. Addition of small amounts of iodine causes the resistivity to drop monotonically until a mole ratio of 1 : 2.2 is reached where an intermolecular "pseudo-compound" forms. Further addition of iodine then causes the resistivity to rise again.

Both the conductivity and the energy E are quite tolerant of relatively large changes in relative composition of the homogeneous complexes, but they are critically dependent on composition in the lamellar complexes. The resistivities of the violanthrene-iodine complex, which is homogeneous, changes only from 24 to 127 ohm cm, with a minimum of 18 ohm cm, if the mole ratio is varied between 1 : 1.31 and 1 : 3.17; the energy E likewise changes only between 0.18 and 0.25 eV, with a minimum of 0.14 eV at the resistivity minimum. In contrast, the potassium-isoviolanthrene complexes, which are layered, exhibit a change in E from 0.060 to 0.166 eV, and in resistivity from 27 to 100 ohm-cm if the mole ratio is altered only from 4.35 to 4.05.

D. Anisotropy[4]

A low resistivity 1 : 1 columnar complex is formed only if the interaction is sufficiently strong, that is, if there is considerable but not complete charge transfer. This requirement again involves a π-electron overlap along the columns of donors or acceptors thus formed with their axes perpendicular to the planes containing the ring systems. The resulting interaction should then cause a great deal of anisotropy, the direction of highest conductivity being parallel to the columns and perpendicular to the planes of the rings.

Complexes of chloranil with the donors 1, 6-diaminopyrene or 1, 5-diaminonaphthalene, *e.g.* show quite pronounced anisotropies, but their resistivities are so high that they indicate rather weak interaction.

The anisotropy of the charge transfer interaction is more pronounced in π-complexes, where there is relatively little resonance energy in their formation. The inherently more stable σ-complexes, involving sp^3-type bonds, are stabilized by hyperconjugation and, although still anisotropic, should be less so than π-complexes.

The interchelation of a metal atom, as *e.g.* in the metal phthalocyanines, causes the activation energy as well as the resistivity to drop. It has been shown by MCCONNELL *et al.*[60] that this is due to charge transfer now taking place primarily *via* the central metal atoms. This causes again a great deal of anisotropy: thus some metal-organic square planar complexes exhibit a conduction anisotropy of the order of 1000. An example for this are[61] crystals of square planar d^8 complexes of the Group VIII metals, believed to a new class of polymers which are based on a metal-metal bonded skeleton. In these crystals, the planar molecules are stacked in columns, with the metal atoms aligned along the columnar axis. The bulk conductivity parallel to the metal-metal axis is about three powers of ten larger than that in the perpendicular direction. The fact that the crystal axis along which the metal atoms are aligned is also the axis of maximum conductivity is strong evidence for associating the electrical transport with polymeric metal bonding.61) In these complexes, while monomeric in solution, the short metal-metal distances and the dichroism exhibited by single crystals suggest a polymeric metal interaction in the solid state.62)

It is of interest to note that also these authors61) find it difficult to reconcile their experimental results with any one particular model; assuming a density of states of the order of $10^{19}\,\mathrm{cm}^{-3}$ yields a mobility limit of $0.1\,\mathrm{cm}^2/\mathrm{V\text{-}sec}$ and thus far too low for a band model to be applicable. However, they also find that the conductivity activation energies are isotropic, which would argue against a hopping model.

E. Spectra63,70)

The stronger charge transfer complexes, at least, are characterized by spectra—often in the infrared—which are significantly different from the superimposed spectra of the components. The bands are usually broad and have little fine structure, and the absorption edge shifts toward longer wavelengths.

Ultraviolet absorption spectroscopy of charge transfer complexes, meets with difficulties since charge transfer bands are often masked by absorption due to the component molecules or to presumed chemical reaction.

The infrared spectrum of a charge transfer complex resembles very closely the superimposed spectra of its components if the complex is loose or transient, *e.g.*, a contact charge transfer complex. When the complex is strongly bonded, with specific relative orientations of donor and acceptor, stabilized in the ground state by the dative structure D^+-A^-, the infrared spectrum may be altered markedly.64)

However, infrared spectral differences may also be caused by solid-solid transitions or by phase changes: for instance it is well known that a multiple set of absorption bands of a solid sample may, on liquefaction of the sample, coalesce into one band.65)

Polarized single-crystal spectroscopic studies, which may permit the simultaneous examination of charge-transfer and "molecular" transitions and to resolve and distinguish between these transitions through their differing polarizations, hold the potential of providing important information in regard to this problem.66)

A charge transfer peak in the spectra of solutions of a donor and an acceptor occurs at a position E_{CT} given approximately by

$$h\nu_{CT} = E_{CT} = (I_G)_D - (A_G)_A - \phi\,, \tag{84}$$

where $(I_G)_D$ is the ionization energy of the donor molecule, $(A_G)_A$ is the affinity of the acceptor molecule, and ϕ is a term which includes the coulombic energy of the charge transfer state.

The $h\nu_{CT}$ values in the solid state are often[67)] smaller than those in solution, indicating that the CT absorption probably produces a neighboring ion pair rather than a delocalized electron. As such, the CT energy is much higher than the E_g values determined from the electrical conduction. This holds true even if the E_g values are compared to the energies of the optical-absorption edges instead of the corresponding absorption maxima. Such observations have been made[68)] for other CT complexes. Apparently, in the solid complexes of TB, there are other low-lying levels contributiug to the electrical conduction. It is, however, interesting that the charge-transfer energy varies linearly with the E_g.[67)]

16. Conductance Titrations of Charge Transfer Complexes[69)]

Figure 9 shows[71)] the resistivity of perylene-bromine complexes as a function of bromine content; the curve appears to be like that resulting from titration of a strong acid with a weak base, or *vice versa.* Similar results have been obtained with aromatic diamine-iodine complexes.

The effect has been utilized for the determination of the stoichiometry of charge transfer complexes in solution by means of conductivity titratious.[69)]

The probability of charge transfer in solution increases with increasing permittivity (ε) of the medium. If (ε) is sufficiently high, the resulting complex may dissociate into ions giving rise to appreciable ionic conductivity;

$$\left.\begin{array}{l} D + A \rightleftharpoons DA \\ DA \rightleftharpoons D^+ + A^- \end{array}\right\} \tag{85}$$

The formation of charge transfer complexes thus can be followed by measuring changes in the electrical conductivity of a solution of, say, the donor in an inert solvent of sufficiently high permittivity, consequent upon additions of a solution of the acceptor in the same solvent, or *vice versa.* In effect, this amounts to a conductimetric titration; the donor may be titrated with the acceptor or *vice versa.*

The dielectric solvents concerned are usually of relatively low conducti-

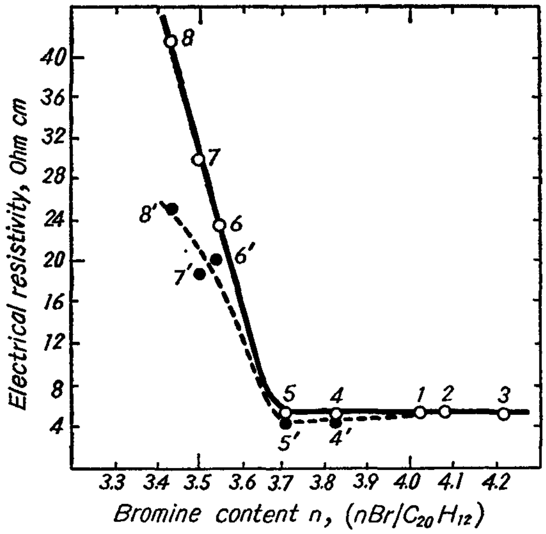


Fig. 9. Electrical resistivity of perylene-bromine complexes as a function of bromine content. The numbers refer to freshly prepared samples (1, 2 and 3) and to samples which had been permitted to lose progressively some of the bound bromine (points 4, 5, 6, 7 and 8). The primed numbers refer to samples which had the lost bromine restored by exposure to bromine vapor. After AKAMATU *et al.*[71]

vity, *e.g.* acetonitrile, acetone, benzene or dimethylsulphoxide (DMSO). While their conductivity appears to be mainly ionic, the charge carriers are probably generated by a mechanism involving the population of localized excited states, and their subsequent migration under the influence of the applied electric field.

Let C_D and C_A stand for the concentration of the solutes D and A respectively. Concentrations will be used instead of activities, and the conductivity of the solvent, or medium, itself will be neglected.

In a titration, where the volume changes upon additon of titrant, donor and acceptor are supplied to the system in concentrations C_D^0 and C_A^0 respectively, so that

$$\left.\begin{aligned} C_D^0 &= D_0 C_0^D/(A_0+D_0) \\ C_A^0 &= A_0 C_0^A/(A_0+D_0) \end{aligned}\right\}, \qquad (86)$$

where D_0 and A_0 refer to the volumes of stock solutions of D and A, with concentrations C_0^D and C_0^A respectively, which have been supplied to the system, *e.g.* from a burette.

In the absence of interaction, $C_D=C_D^0$ and $C_A=C_A^0$. Since the conductivities are additive, it follows that σ, in the absence of interaction, should be linearly related to the concentration of titrant.

Consider now charge transfer to occur, resulting first in the formation of a complex DA followed by its dissociation into ions D^+ and A^-, and thus giving rise to excess conductivity besides any due to the solvent and to the stock solutions themselves. Let the concentration of the complex DA be given by C_{DA}, and the concentrations of D^+ and A^- by C_{D^+} and C_{A^-} respectively.

We can write the following equations for the equilibrium state of the system:

(a) Complex formation: $D+A\rightleftharpoons DA$

$$\frac{C_{DA}}{C_D C_A}=K_1=f(\varepsilon,\ T\cdots) \tag{87}$$

(b) Complex dissociation: $DA\rightleftharpoons D^+ + A^-$

$$\frac{C_{D^+}C_{A^-}}{C_{DA}}=K_2=f'(\varepsilon,\ T\cdots) \tag{88}$$

(c) Direct transfer and recombination: $D^+ + A^- \rightleftharpoons D+A$

$$\frac{C_D C_A}{C_{D^+}C_{A^-}}=K_3=f''(\varepsilon,\ T\cdots) \tag{89}$$

The solution must be electrically neutral, so that

$$C_D^+=C_A^-=n\,. \tag{90}$$

This yields eventually:[69]

$$\left[C_D^0-(n+K_2/n^2)\right]\left[C_A^0-(n+n^2/K_2)\right]=n^2K_3=n^2(K_1K_2)^{-1}\,. \tag{91}$$

The conductivity σ, which is proportional to n, thus follows a complicated, fourth power relation to added donor or acceptor. However, it is readily seen that n, and thus σ, is a maximum if $C_D^0=C_A^0$, as in the case of a 1 : 1 complex. Equating dn/dC_D^0 to zero yields

$$-C_A^0+n+n^2/K_2=0\,. \tag{92}$$

Since $n+n^2/K_2=C_D^0-C_D$, a σ peak will appear if

$$C_D^0-C_D=C_A^0 \tag{93}$$

or in terms of the titrating solutions:

$$\left.\begin{aligned} D_0 C_0^D &= A_0 C_0^A \\ D_0/A_0 &= C_0^D/C_0^A \end{aligned}\right\} \tag{94}$$

The stoichiometry of the complex may thus be deduced from the titration volumes at the endpoint, *i.e.* the conductivity peak, and from the known concentrations of the stock solutions.

The analysis assumes both donor and acceptor to be univalent, resulting in a 1 : 1 complex. The same treatment also applies to the case of a bivalent donor. The endpoint of the titration *viz.* the conductivity peak, will then occur at a 2 : 1 stoichiometric ratio instead of at a 1 : 1 ratio.

The value of the conductivity peak above a baseline connecting the conductivities of pure donor and acceptor solutions is a measure of the excess conductivity caused by the formation and subsequent dissociation of the complex ; see Fig. 10.

We define a molar conductivity coefficient σ_M

$$\sigma_M \equiv \frac{1}{dM} \frac{\sigma_p - \sigma_0}{\sigma_0}, \tag{95}$$

where M is the molar concentration of the titrant, either donor or acceptor, at the conductivity peak where $\sigma = \sigma_p$. σ_0 is the linearly interpolated conductivity background, read off a baseline joining the conductivities of pure donor and pure acceptor solutions as shown below. The complex may not be fully dissociated ; the dissociation constant has to be allowed for, since the carrier

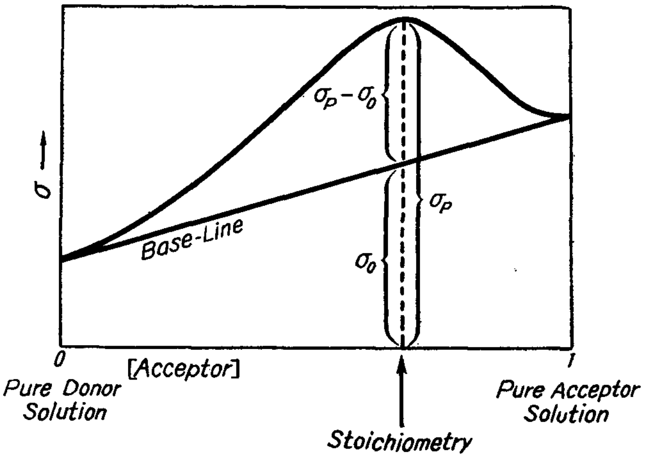


Fig. 10. Idealized conductivity titration curve superimposed upon a baseline. [The latter results in the absence of an interaction]. This figure illustrates the molar conductivity coefficient defined in Eq. (95).

TABLE 3. Results of conductivity titrations of charge transfer complex solutions.

Donor	Acceptor	Solvent	Apparent stoichiometry	σ_M
Anthracene	Chloranil	Methanol	1 : 1	1200
do	I_2	Acetonitrile	1 : 3	2200
Benzene	Chloranil	CCl_4	1 : 1	150
do	do	Methanol	1 : 1	390
do	I_2	Acetonitrile	1 : 2	480
Naphthalene	I_2	do	1 : 1	240
Phenothiazine	Chloranil	do	1 : 1	280
do	I_2	do	1 : 2	2100
Phthalocyanine (metal free)	I_2	Dimethylsulphoxide	1 : 2	870
Tetracene	I_2	Acetonitrile	1 : 3	1540
Pyridine	I_2	do	1 : 1	350

concentration is proportional not to the concentration M of the reagents, but rather to αM, where α is the dissociation constant of the complex.

Since this relation was derived on the assumption that direct recombination is negligible, and dissociation nearly complete, it appears that, generally, this is the case at least to a first approximation.

Values of σ_M for a number of complexes are listed in table 3, together with the stoichiometries as determined from the position of σ_p. The dissociation constant α has been assumed to be unity.

Charge transfer complexes may also be prepared by combining cationic and anionic dyes, as shown by KUSABAYASHI *et al.*[72]

17. Complexes Involving Excited States[4,73]

In some cases charge transfer complexes only form upon supply of additional energy by, *e.g.* irradiation ; a case of practical importance is the complex produced between chlorpromazine, a powerful donor, and melanin, a good acceptor, under the influence of ultraviolet irradiation.[74] Melanin is a polymer, its structural details are unknown. Natural melanin, as obtained *e.g.* from Japanese squid, contains a protein moiety which plays a so far unknown role in the process. Melanin is at least partially soluble in DMSO though leaving an insoluble residue which might be the protein component. While a certain amount of complexing appears to take place between chlorpromazine and melanin even in the dark, as evidenced by an increase in the conductivity ; ultraviolet light causes an appreciable rise in the conductivity.

Moreover, the ESR signal due to the melanin alone—which is a stable free radical yielding a large signal—dropped to about one half upon combination with chlorpromazine solution and to below one fourth of the original value upon ultraviolet irradiation. Thus, the concentration of free spins has dropped upon complexing as to be expected.

Ultraviolet irradiation, in general, will cause an increase in conductivity of most organic compounds, by promoting free radical formation and shifting the equilibrium in that direction. Thus irradiation of both the solutions of chlorpromazine and melanin in triethanolamine resulted in increased conductivity. However, the increase in conductivity due to the photoelectric generation of excess carriers in the individual solutions of chlorpromazine and melanin, does not account for the further increment noted upon combination of two pre-irradiated components, nor for the final increase on re-irradiation of the mixture. The phenomenon was accordingly attributed to formation of a charge-transfer complex. Complexes formed under UV irradiation showed appreciable green fluorescence extending mainly over the 4100 to 4800 Å region, indicating reversible complex formation. The complex decomposes within minutes of the cessation of irradiation and the fluorescence decays simultaneously.

UV spectroscopic studies of the chlorpromazine melanin system in DMSO74) bear out the existence of a charge-transfer complex: a new band appears attributed to a charge-transfer reaction, at approximately 290 mμ.

18. Pressure Effects75)

The resistivity of charge transfer complexes drops approximately exponentially with increasing pressure, as predicted by MULLIKEN76) on the basis of the rapid increase of charge transfer forces as the overlap of the wave functions increases. However, there is a certain amount of evidence that the conductivity tends to level off and becomes pressure independent at about 200 kilobars or higher.

The activation energy behaves likewise; OKAMOTO, SHAH, and MATSUNAGA75) find that for tetrathiotetracene-halogen complexes it approaches zero at about 35 kilobars. ANDERSON, WOOD, LIVINGSTON and EYRING77), however, find that E attains a nonzero minimum at the stoichiometric mole ratio. The sign of the majority carrier, as evaluated from the Seebeck coefficient, tends to reverse at high pressure.

Of course, it must be understood that sufficient pressure, in the limit, causes the electronic system to become degenerate in any compound: even water at extremely high pressure exhibits metallic conductivity. The phthalocyanines become metallic conductors at pressures of a few 100 kilobars.[78]

19. Primary Cells Based on Charge Transfer Complexes

Various types of solid electrolyte cell have been previously reported.[79] Most of them are unable to discharge more than a few μA at room temperature. This is due to the poor conductivity of the electrolytes used, even the best being between 10^{-5} and $10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperature; that is, the internal resistances of the cells are about 10^4 times as large as that of the conventional dry cell. We have devised[80] solid-state electrochemical cells, using a variety of metals as anodes and electronically conducting charge-transfer complexes as cathodes. The product of the electrochemical reaction, the electrolyte, is formed in situ. The energy-producing electrochemical reaction is the formation of the corresponding metal salt.

A number of metals were tested, under standardized conditions, using a compacted pellet of pure iodine as the electrolyte and Pt, graphite, or Au as the counter electrode. Pt, graphite and Au form good inert contacts to iodine. Results are summarized in Table 4.

TABLE 4 Variation of the open-circuit voltage with the heat of formation of the metal iodide for cells of the type, metal/I_2/Pt, C, or Au.

Metal 1	Open-circuit voltage, E	Metal 2	Heat of formation of the metal iodide, kcal-mole^{-1}
Ba	2.25	Au	−144
Ca	2.20	Pt	−127
Mg	1.85	Pt	− 86
Al	0.82	Pt	− 75
Ag	0.66	Pt or C	− 15
Sn	0.23	Pt	
Fe	0.006	Pt	− 30
Pt	0	Pt	0

The voltages are in agreement with the heat of formation of the iodides. This quantity is listed in Table 4 rather than the free energy of formation because of lack of data on the latter.

The heat of formation of MgI_2 predicts a reversible, open-circuit potential of 1.85 V against an inert electrode.

From the Gibbs-Helmholtz equation we may write

$$E=\frac{\Delta H}{zF}+T\frac{dE}{dT}, \tag{96}$$

where ΔH is the enthalpy change, *viz.*, -86 kcal/mole, z the number of electrons involved in the reaction, F the Faraday, E the open-circuit voltage, and T the absolute temperature.

Since the open-circuit voltages of a given metal are virtually the same with pure iodine and with iodine complexes as with the electrolyte, it appears that the energy-producing reaction is the formation of the metal iodide from the elements. The electrochemical information available (see later) is the following: number of electrons involved in the over-all reaction, $z=2$; stoichiometric number, $\gamma=2$; Tafel coefficient, $\beta=0.018$; exchange current density, $i_0=9.4$ μa/cm^2. This assumes that the affinity factor δ of the rate-determining step has a value very close to unity; the affinity factor is defined as the number of electrons involved in one single rate-determining event.

Several reaction mechanisms may be devised to agree with these requirements. Thus, *e.g.*, the following mechanism is compatible with $z=2$ and $\gamma=2$

$$\begin{array}{l} 2[\mathrm{Mg}+\mathrm{I}^- \rightarrow \mathrm{MgI}+\mathrm{e}^-] \\ \underline{\quad 2\mathrm{MgI} \rightleftharpoons \mathrm{MgI}_2+\mathrm{Mg} \quad} \\ \mathrm{Mg}+2\mathrm{I}^- \rightarrow \mathrm{MgI}_2+2\mathrm{e}^- \end{array} \tag{97}$$

The first step is the rate-determining one, while the second step involves a reaction at or near equilibrium. There must be, linked with the above reaction scheme, a further reaction as a source of I^- ions; this could well be

$$\mathrm{I}_2+2\mathrm{e}^- \rightleftharpoons 2\mathrm{I}^- . \tag{98}$$

The open-circuit voltage of solid state cells being determined by thermodynamics, its overall performance, that is its power capabilities, are wholly dependent on the current which the cell is capable of delivering.

For the MgI_2 reaction described, $z=2$. If one retains the first term only and neglects the entropy contribution, one obtains the Helmholtz-Thomson equation which yields $E=1.85$ V. Direct measurement of dE/dT showed that it is negligible in the vicinity of room temperature. At temperatures above 45°C a value of about -5×10^{-4} V/deg was obtained. Since ΔH is negative, the voltage tends to drop with increasing temperature.

Current *vers.* voltage plots for several temperatures are shown in Fig. 11.

The Tafel equation is obeyed at current densities in excess of a few 100 μa/cm^2. At low current densities and correspondingly low values of overvoltage, the current obeys

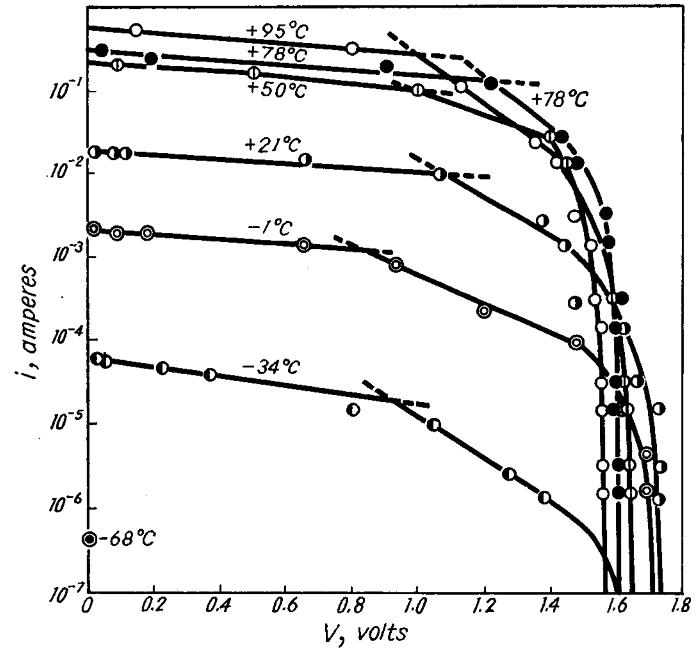


Fig. 11. Temperature dependence of the current-voltage characteristics for the system.

Mg	Poly-2-vinylpyridine	40% by wt	C
	Iodine	50% by wt	
	Graphite	10% by wt	

$$i = \frac{i_0 \eta F}{RT}, \tag{99}$$

where i is the current corresponding to an overvoltage η, and i_0 is the exchange current ; R, T, and F have the usual meaning. From the slope, a dynamic resistance of 2300 ohms/cm^2 electrode area for a freshly prepared Mg/I$_2$—C complex/Pt cell is obtained, valid up to about 156 μa/cm^2. This resistance corresponds to an exchange current density of 9.4×10^{-6} amp/cm^2. At higher current densities and thus higher overvoltages, a Tafel slope of -0.714 results ; the exchange current density then follows by extrapolation as 58.3 μa/cm^2 which is not too different from the value obtained for the low current region.

The stoichiometric number γ of the rate-determining step represents the number of times this reaction has to occur for the over-all reaction to advance by one DeDonder unit.[81] A value for γ may be obtained from

$$\gamma=\left|\frac{Fi_0}{RT}\left(\frac{\partial\eta}{\partial i}\right)_{\eta\to 0}\right|. \tag{100}$$

This yields $\gamma=2.12$, *i.e.*, practically 2, meaning that the rate-determining step must occur twice in order for the over-all reaction to be advanced by one unit. It is also assumed that there is no change in the rate-determining mechanism between the reversible region and the region of activation control.

From the slope of the current-voltage curve, a value for the Tafel coefficient $\beta_a=0.018$, valid for the region of activation control, is obtained for the freshly prepared Mg/I_2–C/Pt system. For this region, we may write

$$I=I_0(e^{\alpha_a F\eta/RT}-e^{-\alpha_c F\eta/RT}), \tag{101}$$

where the first term refers to the forward and the second term to the reverse reaction. The transfer coefficients α_a for the forward and α_c for the reverse reaction must add up to unity: $\alpha_a+\alpha_c=1$. We may also write

$$\left.\begin{aligned}\beta_a+\beta_c&=(\alpha_a+\alpha_c)\frac{2\delta}{\gamma}\\ \alpha_a&=\beta_a/(\beta_a+\beta_c)\end{aligned}\right\}. \tag{102}$$

For the linear, low overvoltage region, we may approximate

$$I\simeq I_0\frac{(\beta_a+\beta_c)F\eta}{RT}. \tag{103}$$

Since $\delta\simeq 1$, it follows that $\beta_a+\beta_c=1$, so that

$$\left.\begin{aligned}\beta_c&=0.982\\ \alpha_a=\beta_a&=0.018\\ \alpha_c=\beta_c&=0.982\end{aligned}\right\} \tag{104}$$

The great disparity in the values of the transfer coefficients, and thus of the forward and reverse reaction rates, indicates that the system lacks microscopic reversibility.[82] In irreversible thermodynamics

$$\gamma\tilde{A}^0=\delta\tilde{A}. \tag{105}$$

Here, $\tilde{A}^0$ stands for the electrochemical affinity of the rate-determining step and $\tilde{A}$ for the total electrochemical affinity of the over-all reaction, given by

$$\tilde{A}=zF\eta. \tag{106}$$

The electrochemical affinity of the rate-determining step thus follows as

$$\begin{aligned}\tilde{A}^0=zF\eta\delta/\gamma&=6.9\times 10^4\ \text{volt-coul/mole}\\ &=16.5\ \text{kcal/mole}\end{aligned} \tag{107}$$

for the same cell operating under matched load conditions, $\eta = 750\,\text{mV}$.

DANÉ, *et al.*[83] have studied the iodine-iodide redox couple using a Pt electrode in 0.5 M H_2SO_4. They find that the electrode reactions are

$$\left.\begin{array}{l} I^- \rightleftharpoons I_{ADS} + e^- \\ I_{ADS} + I^- \rightleftharpoons I_2 + e^- \\ I_2 + I^- \rightleftharpoons I_3^- \end{array}\right\} \qquad (108)$$

where the second step is rate-determining, giving an exchange current density of 400 ma cm^{-2}, the activation energy being 15 kcal mole^{-1}. This value is close to that obtained for the electrochemical affinity of the cell reactions considered; thus it may well be that a similar adsorption step is involved. However, the reaction mechanism proposed before is supported by the quantitative recovery of the reaction product.[84]

A cell using a 1 : 2 phenothiazine : iodine complex was continuously discharged in ambient atmosphere and at room temperature over a period of nine months into a constant 31.6 ohm load. Integration of the area under the current *vs.* time curve showed that 219 coulombs had been delivered. The cell was then dismantled and analyzed for MgI_2. The recovery was 190 mg of $MgNH_4PO_4$ corresponding to the passage of 282 coulombs. Thus, the difference of 66 coulombs must have been consumed in a side reaction. This reaction is most likely an internal corrosion process at the Mg anode.

The above data, therefore, support the reaction mechanism which was based on the formation of MgI_2. Under matched load conditions a current density of about 500 μa/cm^2 is obtained using a Mg anode and an I_2-C complex as a cathode. A reaction rate of 2.5×10^{-9} moles-cm^{-2} results. This may be inserted into the equation

$$\nu = d\xi/dt = \left[\tau \frac{kT}{h} \exp\left(\frac{-\Delta G^{\#}}{RT}\right)\right]\left[C_s(1-\theta)\right],$$

where τ is a transmission coefficient, $\Delta\bar{G}_0^{\#}$ the electrochemical standard free energy of activation, C_s the concentration of the reactant at the Mg-electrolyte interface, and $(1-\theta)$ gives the specific fractional area available for the discharge of additional molecules at the surface. θ represents the fraction of the surface area covered with reaction product (MgI_2) at the given current. Generally, $\tau \simeq 1$. Direct measurement of the current at 20° and 135°C showed an increase by a factor of 300; thus, $\Delta\bar{G}_0^{\#}$ = about 12.4 kcal/mole. At 300°K, the quantity in the square brackets, representing an effective surface concentration, results as 4×10^{-13} moles/cm^{-2} $= 2.4 \times 10^{11}$ molecules of I_2 per cm^2 area. Since a monolayer of I_2 contains about 5.2×10^{14} molecules cm^{-2}, this shows a coverage of about 4.6×10^{-4} of the total electrode area; $(1-\theta)=4.6 \times 10^{-4}$. Thus only a minute fraction of the total electrode area is available for further internal discharge; most of the area is covered with the MgI_2 produced by the reaction.

Under reversible conditions, about 1/7th of a monolayer participates in the electrochemical reaction if the exchange current value of 1.4×10^{-5} amp/cm^2, valid for a freshly prepared cell, is used. At higher current densities the effective electrode area shrinks rapidly until the previously calculated fraction of about 4.6×10^{-4} of the total electrode area is reached; "polarization" thus is due to the cumulative poisoning of the electrode surface by the accumulation of reaction product.

A series of discharge tests was performed using an electromechanical oscillator as the load. A typical oscillogram is shown in Fig. 12. This oscillator draws a current pulse of 200–300 μa of 6–8 msec duration at a repetition frequency of 6 sec^{-1}; its impedance is partly inductive, causing the transient waveshape of the sharp spikes. This discharge test was carried out at room temperature in (uncontrolled) laboratory atmosphere. The cell, with initial open circuit voltage 1.62 V and short-circuit current 3.4 ma, operated in a room atmosphere with the oscillator load for 480 hr. At this point, the open-circuit voltage had dropped to 0.5 V. Upon exposure without load to a high humidity atmosphere for 24 hr, the open-circuit voltage recovered completely. Continuing the test under load in the high humidity environment, 550 hr were required for the voltage to drop to 0.5 V. The difference ΔV between open-circuit and loaded voltage remained fairly constant, even though the open-circuit voltage itself dropped. Total operating time was 1032 hr

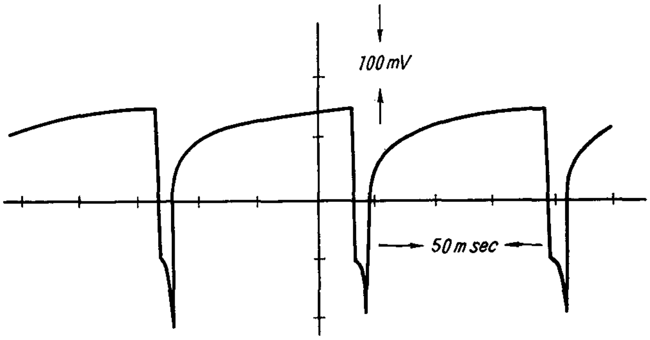


Fig. 12. Pulsed oscillogram depicting the time dependence of the terminal voltage for the cell. Mg |phenothiazine: iodine 1:2| Pt.

Current was drawn for 6 to 8 msec at a repetition frequency of 6 per sec causing the terminal voltage drop illustrated.

(43 days) of which 552 hr occurred in a humid atmosphere.

In an uncontrolled laboratory atmosphere, ΔV increased significantly with time.

In a controlled, humid atmosphere, the wave forms remained constant and showed no variation with time, *i.e.*, there was no difference in the shape nor in the amplitude of the voltage pulses as measured by connecting an oscilloscope across the cell throughout the duration of the test.

The difference ΔV between the terminal voltage under a load R_L, and the voltage V' to which the cell recovers just before the start of the following pulse, thus remains constant, though the recovery voltage itself decreases approximately linearly during the test.

It can be shown that[84] for $\Delta V \neq f(\text{time})$, it is necessary that the dynamic internal resistance $\dfrac{\partial V}{\partial I} = \text{const} \neq f(t)$ AND that it matches the load resistance. The second condition, of course, was at least approximately imposed on the system in these tests by the nature of the experiment.

We note that $(\partial V/\partial I)$ remains constant in the humid environment though not in the uncontrolled laboratory atmosphere. Since the dynamic internal resistance is the sum of a constant ohmic series resistance plus a polarization and diffusion resistance term, it follows that the diffusion resistance is held constant in the presence of a vapor of high permittivity liquid, but not in its absence. Hence the admission of solvent, although not necessarily water, vapor tends to assist the diffusion processes, causing a substantially constant and improved rate of diffusion of I^- ions into the reaction site. The decay involves the shift of the entire polarization curve to lower voltage values, parallel to itself, without a change in its slopes.

Further experiments aimed at determining the influence of gases and vapors on the performance of these cells showed[84] that the complete removal of all solvent and water vapors reduces the short-circuit current by 2 to 3 orders of magnitude below the value recorded in ambient laboratory atmosphere. Likewise, the introduction of benzene or CCl_4 vapor into the otherwise dry and solvent free system causes no increase in the short-circuit current density. However, dry vapors of acetone, methylalcohol, or acetonitrile cause the current density to rise to values of up to several 100 ma/cm^2, higher by about an order of magnitude than the best current densities obtainable in an uncontrolled room atmosphere. Water vapor has a similar effect. It appears that the presence of vapors of liquids of high permittivity improves the performance of these cells while vapors of low permittivity liquids do not affect the short-circuit current densities available as compared to those under vacuum or dry conditions.

The beneficial effect of high permitivity solvent vapors must be due to their permeation into the anode-electrolyte interface: (i) corrosion of the electrode surface starts at the edges and thence penetrates inwards; (ii) assembly of a complete cell under high pressure in a hydraulic press yields cells with characteristics essentially those of cells maintained in a completely solvent free enironment; (iii) insertion of a semipermeable membrane, say a thin sheet of cellulose or of polypropylene-acrylic acid graft copolymer, between the Mg anode and the solid, tends to raise the value of the short-circuit current considerably; the open-circuit voltage likewise is brought even closer to its thermodynamical value of 1.85 V. Insertion of such a separator anywhere else but directly into the anode-solid interface causes both open circuit voltage and short circuit current to decrease. It appears that the separator acts as a wick assisting the penetration of solvent vapor into the interface. Cells assembled with the separator extruding beyond the electrode and then wetted with acetonitrile produced current densities of the order of hundreds of ma cm^{-2}, significantly in excess of the performance of untreated cells; (iv) the constancy of the dynamic resistance in the presence of vapors, discussed above, indicates that such vapors are effective in assisting processes within the reaction zone near the anode.

At higher current densities, where the current becomes diffusion controlled, the introduction of vapor involves an improved diffusion rate. At least in part, this is due to the increased diffusion gradient caused by the increase in reaction rate. However, it may well be that a liquid layer at the interface as such substantially assists in the diffusion processes.

Electrolysis experiments have shown85) that the phenothiazine/iodine complex exhibits mainly electronic conductivity, plus a relatively small component of ionic conductivity. The role of the complex is to provide a low resistivity reservoir of iodine. The improvement which its employment offers is considerable, since pure zone-refined iodine has a resistivity of the order of 10^9 ohm-cm, while iodine complexes have resistivities of a few ohm-cm, 4 ohm-cm being a typical figure at room temperature.85) The theoretically attainable current is thus increased by 9 orders of magnitude if the current is limited by the ohmic series resistance of the iodine reservoir.

The 1:2 phenothiazine/iodine complex remains soft and pliable if loss of iodine is avoided. It is quite stable and may be formed by extrusion.85)

Magnesium anodes are the subject of a competing parasitic corrosion reaction with elemental iodine even in the absence of current flow:

When iodine is present in solution at a Mg surface, a chemical as well as an electrochemical reaction are possible:

(a) $2\,Mg + 2\,I_2 \rightarrow 2\,MgI_2$ Chemical

(b) $2\,I^- + Mg^{++} \rightarrow MgI_2$. Electrochemical

In the absence of any reaction at all, an equilibrium will be established

(c) $6\,I^- \rightleftharpoons 2\,I_3^- \rightleftharpoons 3\,I_2$.

The chemical reaction causes this to shift in the direction of $I^- \rightarrow I_2$.

The reaction product is MgI_2 which poisons the Mg surface. Thus, this type of cell requires the presence of water or of an organic solvent to dissolve away the MgI_2 layer. Such parasitic reactions are minimal with silver anodes which do not require the presence of liquids. Cells using an Ag anode have been prepared85) from dry components in a dry box, and sealed before removing the cell for testing. While it is not impossible that traces of water were still present in the cell, extended drawing of current from these cells over periods of weeks showed a drop in current from an initial 3 ma/cm^2 to an apparently stable value in the region of 0.5 ma/cm^2. The penalty for avoiding the parasitic corrosion reaction on Mg by using silver is a severe drop in cell voltage, *viz.* from 1.8 to 0.63 V.

20. Other Solid State Primary Cells

For comparison, we may note that *e.g.* TAKAHASHI and YAMAMOTO86) have developed a $Ag/Ag_3SI/I_2$ cell:

In the cell, silver amalgam/Ag_3SI/I_2-acetylene black, the voltage dropped by only 100 mV after 3 hr at a steady current discharge of 1000 μa/cm^2. The internal resistance of the cell did not change during the discharge, probably because the cell reaction product, AgI, dissolves in Ag_3SI. The electrical conduction of Ag_3SI was almost entirely ionic; the ionic conductivity was about $1 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at room temperature. Unless limited by internal cell resistance, the maximum current is determined by diffusion. Thus, the small size of the silver ion moving through a very open crystal lattice should result in a favourable diffusion regime.

The best solid state cells at present available are those developed by OWENS and coworkers87) at Atomics International. They use an alkali double salt such as $RbAg_4I_5$ as the electrolyte; the Ag^+ ion is the mobile and active species. It moves essentially like a liquid in a very open crystal lattice consisting of I^- and say, Rb^+ ions. While the reaction product *viz.* AgI, accumulates in the cathode region causing appreciable cathodic polarization, this may be counteracted by incorporating a depolarizer consisting of RbI_3–C–$RbAg_4I_5$.

These cells yield current densities of the order of 1 Amp cm^{-2}; the main difficulty is associated with the fact that the very open crystallographic conformation of the double salt is thermodynamically stable only above 27°C. However, it may be quenched in to remain stable for a reasonable length of time by suitable heat treatment. Other cells[79)], including those commercially available, operate at current densities of only a few microamperes cm^{-2}.

In a solid system, it is to be expected that diffusion limitation sets in at lower overvoltages already than in a corresponding liquid system: indeed, the exchange current density I_0 obtained for the solid iodinous system is of the order of 10^{-5} amp-cm^{-2}, while VETTER[88)] reports values of the order of 10^{-2} to 10^{-3} amp-cm^{-2} for a liquid iodine/iodide redox system. Even higher values, *viz.* 400 ma/cm^{-2} were more recently reported by DANÉ and coworkers.[83)]

21. Some Systems Using Liquid Organic Electrolytes

Conventional electrochemical cells were assembled[85)] consisting of a Mg anode, Pt cathode, and the following solvents as electrolytes, first without and then with added (dissolved) iodine; the concentration to the latter was 0.025 M or saturated in case of low solubility: Formamide, Acetonitrile, Water, Acetamide, Dimethylacetamide, Glycol, Glycerol, Methanol, Ethanol, Acetone, Pyridine, Aniline, Chloroform, Benzene, Furan, Carbontetrachloride.

None of the iodine-free solvents by themselves gave any measureable currents into a 1 ohm load, with the exception of formamide which delivered 0.3 mA cm^{-2} anode area. Open-circuit voltages, however, were obtained even with the pure solvents, except methanol, ranging from 0.4 V in pyridine to 1.6–1.7 V in formamide, acetamide and acetone; acetonitrile gave 1.2 V.

The added 0.025 N (or saturation) I_2 yielded measureable currrents into a 1 ohm load with formamide, acetonitrile, acetamide, methanol, ethanol, acetone, pyridine, chloroform and furan, the last two yielding only 10^{-8} A-cm^{-2} (furan) and 2×10^{-6} A-cm^{-2} respectively. The highest currents were obtained with methanol, acetone and acetonitrile, *viz.* about 7 mA cm^{-2}, the others being about 1 mA cm^{-2}.

The open-circuit voltages were 2–2.2 V for all solvents containing 0.025 N iodine (or saturation), acetamide with 2.2 V being the highest. Glycerol (1.6 V), glycol (zero), nitrobenzene (1 V), pyridine (1.1 V), aniline (1 V), chloroform (1.8 V), benzene (1.0 V) and furan (1.5 V) being exceptions.

The coulombic efficiency was 53% for formamide where 77 coul. were delivered into a 1 ohm load for 144 coul. equivalent of Mg having been consumed; acetonitrile gave 50% and acetone 35%. Acetamide showed 65% efficiency. However, it was noted that small flakes of metal tended to drop off the anode so that these figures, at this juncture, present lower limits only.

The actual efficiency in all cases thus is higher.

22. A Multi-Shot Reserve Cell

The absence of gas evolution in *e.g.* the Mg |iodine in acetonitrile| carbon system suggested its use as a multishot reserve cell. Such a device[85], using a saturated solution, may be hermetically sealed and consists of 2 compartments separated by a septum, one containing the electrodes and the other the electrolyte. Application of excess pressure by means of *e.g.* a bellows causes the septum to break admitting the electrolyte into the electrode compartment. The ensuing electrochemical reaction may be stopped at any time by inverting the device; the electrolyte then drains back out of the electrode compartment. Discharge continues until all the Mg or I_2 is consumed. Typical performance data are: open-circuit voltage 2.25 V, current density into a matched load about 10 mA cm^{-1} at 1.1 V terminal voltage; consumption about 20 mg of Mg per hour, coulombic efficiency 23%.

23. Aqueous Magnesium-Iodine Cells

Observing the large increases in power output due to the presence of water vapor in the phenothiazine iodine Mg cells, a cell was made using a magnesium anode, carbon cathode, and an equeous solution of iodine as the electrolyte, adding potassium iodide in order to increase the solubility of iodine and cell conductivity. High current densities were found at 1.5 V cell potential, the cathode redox reaction $I_2 \rightleftharpoons 2I^-$ being limiting. This limiting current was found to increase with I_2 concentration, see Fig. 12. However, the magnesium anode again suffers severe corrosion due to the I_2 and hydrogen corrosion reactions, the former dominating. From Fig. 12 it is seen that above 0.8 M I_2 concentration, the corrosion rate becomes excessive.

A cell using this concentration of I_2 with 60 mℓ of 4 M KI supporting electrolyte gave an initial current of 1.25 A, or 135 ma/cm^2 cathode geometric area (hereafter given as C. G. A.) at a cell potential of 1.3 V, falling over 1 hour to 0.85 A at 0.9 V. The cell resistance was initially 0.6 ohms, rising to 1.15 ohms at the end of the experiment. The decrease in cell conductivity due to the erosion of the anode accounts for the major part of the decrease in output, the decrease in the I_2 concentration playing a minor role. A faradaic efficiency with respect to magnesium of 25% was found. This was increased to 43% by pre-annealing the magnesium at 600°C in a hydrogen atmosphere; the annealing increased the grain size, which served to diminish the disinteg-

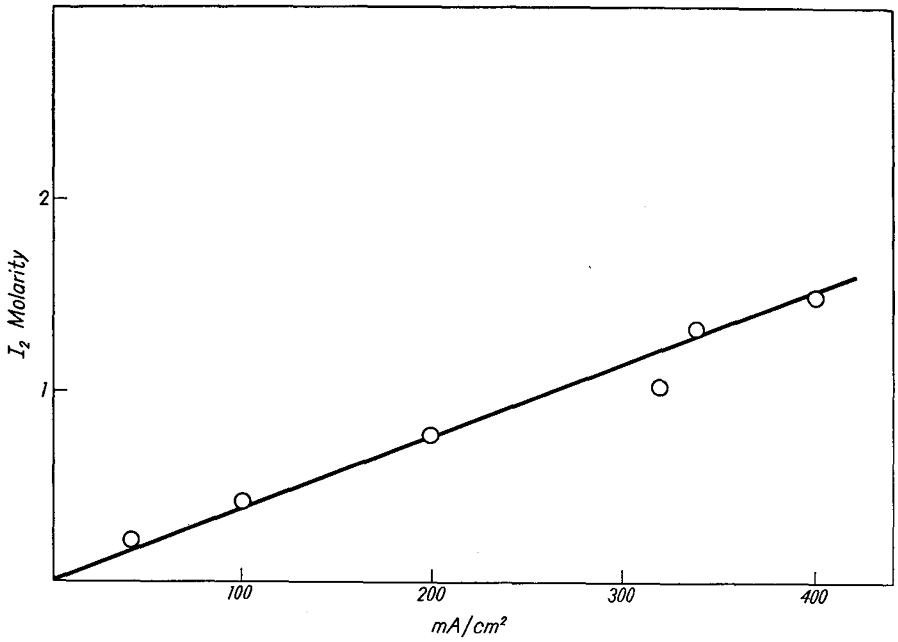


Fig. 13. Cathode diffusion limiting current *vs* I_2 concentration. C = C electrodes driven cell, 4 M KI supporting electrolyte.

ration of the anode surface under the rigors of high current densities. The hydrogen anodically evolved was collected in the latter experiment, and proved to account for only 20% of the magnesium, the rest going to I_2 corrosion. Various anionic membranes were tried to provide a barrier to restrict the I_2 to the cathode. In all cases, the barrier was leapt with comparative ease by the I_2.

Another approach to the problem was that of creating a diffusion gradient between the cathode and anode by admitting the iodine as a liquid *via* a porous cathode, the ratio of current density to flow rate being such that little or no iodine would enter the bulk electrolyte before being oxidized to iodide ions. This approach gave the required result.

The electrolyte remained free of any yellow iodine discoloration stains, its color being clear at low current densities, and an opaque grey at high current densities due to the precipitation of the reaction products. The cell proved to be completely functional, responding to small changes in hydrostatic pressure over the iodine cavity in the cathode with changes in cathode overvoltage and current flow. It was not possible to reduce the cathode overvoltage

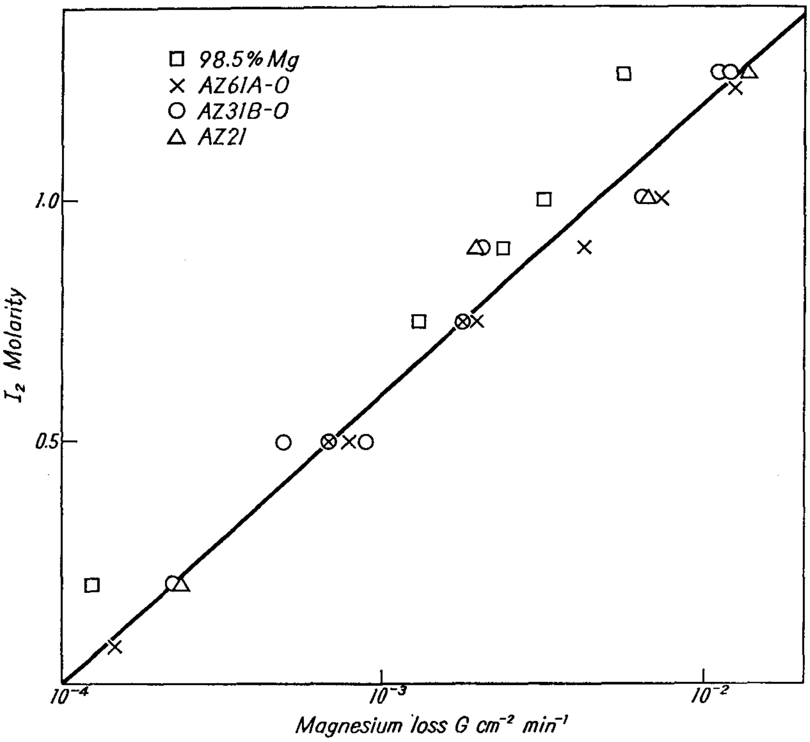


Fig. 14. Relative resistance to I_2 corrosion of Mg alloys. 4 M KI aqueous I_2 solution.

below 200 to 300 mV without iodine entering the cell. Interrupting the current flow momentarily whilst operating close to optimum conditions caused iodine immediately to appear in the cell. The pressure over the iodine cavity had to be adjusted to reoptimize the cathode performance when changes in external load were made, the operation of the cavity pressure being analogeous to the throttle control in the carburetor of a gasoline engine. The response time, however, was too slow in this case to provide a complete analogy. The faradaic efficiency with respect to the total weight of the alloyed magnesium was 80%, and approached 100% with respect to iodine within the accuracy of the experiment. The cell was run for over 17 hours; the first six hours at a current density of 110 ma/cm^2 C. G. A., followed by an overnight discharge for ten hours of 55 ma/cm^2 C. G. A., the change being affected by lowering the pressure over the cathode cavity and increasing the external load to raise the cell voltage (the output was lowered to conserve the Mg anode). The experiment was discontinued after a further two hours' operation the next day.

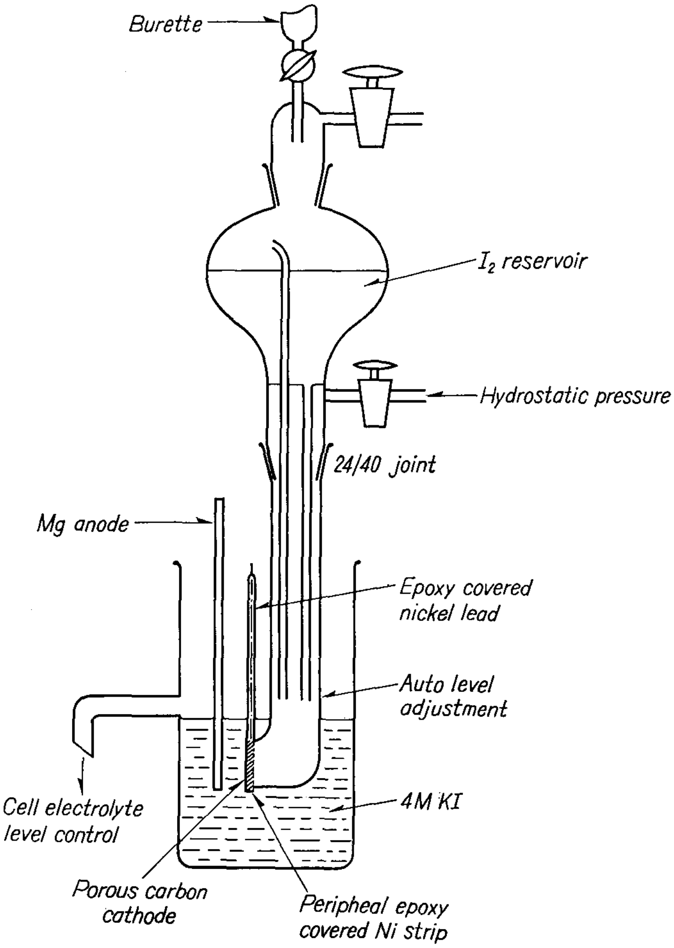


Fig. 15. Design of a diffusion gradient controlled Mg | I_2 in KI aqu. | C cell.

24. A Liquid Electrolyte Reserve-Type Cell

A reserve type of cell giving current densities of several 100 mA cm^{-2} has been made[85)] by using a Mg anode and an iodine/iodide redox couple, with a carbon electrode, as the cathode, the electrolyte being a highly concentrated solution of elemental iodide in an aqueous potassium iodide solution. Several such cells have been built delivering useful currents of say 250 mA cm^{-2} at 1.5 V terminal voltage into a load resistance of 4 ohm for at least 30 min. A great deal of hydrogen is being evolved and the device might also be useful as a hydrogen generator in conjunction with a conventional fuel cell supplying at the same time significant amounts of electric power in addition to the H_2. In effect Mg would be burned with iodine.

In a typical experiment, 11800 Coul. total were delivered as weight loss of the Mg anode; of this 5080 Coul. appeared as useful current in the external load and 3000 Coul. were available as hydrogen gas.

It appears that heat treatment of the Mg anodes substantially improves the performance; about 200 mV higher voltages and less corrosion were obtained with a Mg–Hg alloy.

These devices are the subject of a patent application. The behavior of the liquid systems is illustrated in Fig. 16 which shows the electrode potential of a Mg anode and of a C cathode *versus* a C reference electrode; the electrolyte was an aqueous solution of 2 N KI saturated with I_2. The KI acted as a supporting electrolyte; the AC cell resistance measured at 1000 cps was 10 ohm. While gas evolution (H_2 discharge) took place, it is seen that nearly all the polarization occurs at the cathode, the Mg anode remains just about unpolarized.

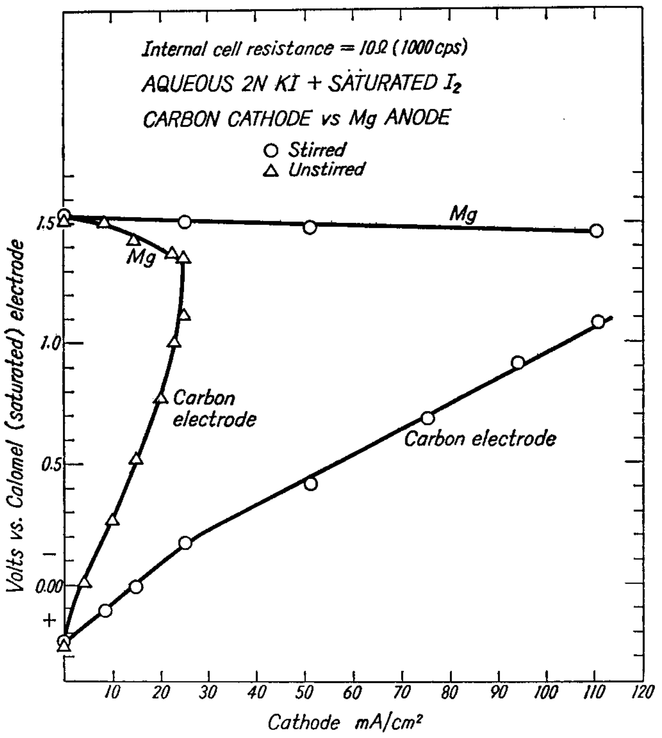


Fig. 16. Electrode potentials of a cell Mg | 2 N KI sat. with I_2 | C.

25. Comparisons with Commercially Available Cells

Commercially available reserve batteries operate, typically, in single shot operation at 40 mA cm^{-2} for 1 hour; the aqueous iodine solution cell here reported betters this by a factor of about 4 as to current density.

Its lifetime is limited only by the supply of Mg and I_2. The cell which liberated copious amounts of hydrogen, cannot be sealed. However, its storage life should be unlimited.

The reserve cell described before using acetonitrile as the solvent, operates without any gas evolution and thus may be hermetically sealed. Its current density however is well below that commercially available. Again, its storage life should be unlimited.

The current densities employed in torpedo drive batteries are, of course, very much higher; running near boiling point they yield about 3 Amp cm^{-2} though only for about 15 minutes.

26. An Oxygen Electrode

A high current of over 100 ma/cm^2 C. G. A. was noted[85)] to be available prior to admitting the iodine. This has been shown to be due to the air in the pores of the cathode. Simply bubbling oxygen through the pores enabled a current density of 40 ma/cm^2 C. G. A. at a cell potential of 0.5 V to be drawn. Unless the cathode material used is very effective in oxygen reduction, a possible explanation might be the initial oxidation of I^- ions, the resulting iodine oparating in the normal cathode redox reaction. If the latter is the case, the use of present knowledge of porous electrodes will substantially increase this performance, and this cathode may be used with a number of anode reactions (*i. e.* H_2, Mg, Al, *etc.*).

The iodide electrolyte causes the water corrosion reaction on magnesium virtually to cease. The cell may be left at open-circuit for days without any visible sign of corrosion taking place. Upon closing the circuit, the Mg immediately depassivates.

27. Application to Fuel Cells

Another application of the high current densities obtainable from the Mg/iodine-iodide electrode described before, concerns a thermally regenerable fuel cell, consisting of a magnesium anode and a porous cathode of an inert material, *e. g.* carbon, immersed, while working, in a concentrated solution of potassium iodide, which on one side of the porous electrode contains dissolved iodine at high concentrations. The iodine diffusing through the cathode is completely consumed by reduction to iodide, and thus no iodine diffuses to the anode and corrosion of magnesium by iodine is prevented. The anode reaction is magnesium dissolution. Current-producing consumption of magnesium is above 80% of its total consumption, the remaining balance being used up by corrosion with hydrogen evolution (in aqueous solution). The hydrogen evolved can be utilized in an additional hydrogen-oxygen fuel-cell, or burned to provide a heat source.

Typical useful current densities (per 1 cm^2 of the cathode area) are of the order of $\sim 150\,\text{mA/cm}^2$ at a terminal voltage of ~ 1.1 V operating at a load resistance of ~ 5 ohms. The open-circuit voltage in the aqueous electrolyte is 1.8 V.

The cell reaction product, magnesium iodide, may be recovered and thermally dissociated[89)] to yield back the original reactants, iodine and magnesium. This occurs[89)] at 90% efficiency at a temperature of about 400°C.

28. Adsorption and Catalysis

The electrode reaction itself frequently appears to be activation-controlled, that is, the reaction rate is determined by a relatively high potential barrier between the electrode and a charge carrier adsorbed on it. This is essentially the same problem as that which we have here discussed, namely, a charge transfer problem. Solution of one may well throw light on the other. This has become more than a mere possibility in view of the work of GARNETT and co-workers[90)], who have shown that π-complexes, involving an electron transfer, play a decisive role in the catalysis of chemisorbed organic compounds on the surface of a transition metal catalyst.

Some work along these lines has been reported by INOUE, HAYASHI, and IMOTO[91)], who studied the photo-oxidation of isopropylalcohol to acetone with oxygen under irradiation. They find that p-type organic materials, especially heterocyclic aromatic compounds, are catalytically active, while n-type materials are not. The effect is ascribed to the migration of a hole, transferring positive charge to the compound being oxidized.

GERISCHER[92)] has employed suspensions of Raney nickel as catalysts in fuel cell experiments with very promising results. The current densities obtained compare favorably with those at highly activated electrodes and are far lass critically dependent on surface structure.

Both metal-free and Cu-phthalocyanines were found[93)] to be active catalysts for hydrogen reactions in general agreement with the π-complex hypothesis advanced by GARNETT.

Many inorganic as well as organic semiconductors are catalytically active[94)] in various processes of an oxidation-reduction type. In some cases, this catalytic activity is intrinsic to the organic semiconductor, and not due to inorganic impurities, In the case of polymer semiconductors, it is likely that the catalytic activity is realized by the organic macromolecule and not by metal ions included in them, nor by dissolved or adsorbed molecules.

In catalyzed reactions[94)], besides simple model reactions, we find some reactions which have practical significance *e.g.* oxidation of cumol, of toluol and the polymerization of styrol.

In the case of processes which involve oxidation-reduction and acid-base reactions, the properties of the products obtained on organic semiconductors are analogous to those obtained on inorganic semiconductors and metals. The kinetic laws are also similar. In some cases, organic semiconductors show high selectivity in accelerating the reaction in one direction only among several possible catalytic processes.

The presence of transition metal ions in semiconductors[95)] affects greatly their catalytic properties. Some systems may even exhibit the activity of alkali metals. Thus, the tungsten bronzes have been shown to be highly active electrocatalysts[96)] : they represent a means to employ the alkali metals as catalysts which otherwise would be too reactive chemically for that purpose. Some conjugated organic semiconductors have been reported by ROGINSKI and CAKHAROV[94)] also to approach the activity of alkali metals.

However, the presence and identity of an interchelated metal atom such as in the metal phthalocyanines raises only one of several questions which are involved in determining the catalytic activity ; thus the crystal habit and other details of crystal structure are of crucial importance. Electrocatalysis and electroadsorption studies[97)], generally, have shown how critically are these effects dependent on what could be termed the semiconducting properties of the system, in particular of the interfaces involved. It appears that the presence of electronic or hole conductivity is essential for the realization of the catalytic activity of semiconductors in many reactions. This is explained by the important role of local and of long range transitions of electrons in oxidation-reduction catalysis. The presence or absence of any correlation between the catalytic activity and the collective electronic properties may also be connected with the nature of the chemisorption bond which should not necessarily cause the transfer of electrons. This bond may be donor-acceptor, π-bond with ions of transition metals of chelate compounds, and the bond in which unpaired electrons are involved. The latter might account for the correlation between the concentration of paramagnetic centers and the catalytic activity.

The some times predominant effects caused by the presence of deep as well as shallow traps should permit yet another approach to chemisorption and related catalytic problems[98]: it should be possible to employ an electrode consisting of a very thin layer of a compound exhibiting the desired trapping and surface state energy levels, though such layer might exhibit but a poor bulk conductivity; if it is thin enough it might provide a set of advantageously placed intermediate energy levels and still be capable of passing a reasonable current. Thus, it has been reported[99] that methylenblue addition favourably affects the performance of fuel cells.

Finally, the action of many biochemically important enzymes appears to involve the oxidation of one reactant at one acceptor site of the enzyme-coenzyme system, coupled to the simultaneous reduction of another reactant at a distant donor site on the same system, both being coupled by charge transfer through the intervening protein moiety[100]. In many cases it seems to be the rate of this charge transport which determines the reaction kinetics.

29. Epitome

We hope to have shown that questions of charge transfer are of importance in a very wide variety of processes. What can be learned from the elucidation of one type of charge transfer necessarily must shed light also on other related processes. In particular, we suggest that the study of charge transfer through relatively simple, monomeric as well as polymeric, model compounds should be a valuable avenue towards clarification of many problems involving charge transfer.

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