to ascertain to what degree the above effects are manifested in the entropy or enthalpy terms. At lower confidence levels indications are that they both contribute. It should be further pointed out that other possible lines can be drawn (Fig. 2), but a consistent, reasonable explanation for the deviation of points from these lines is obtained only for the line drawn.

The similarity in the interaction of these amides with both iodine and phenol supports the above argument by demonstrating that the factors determining the basicity are inherent in the amide.

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Effects of High Pressure on Some Organic Semiconducting Polymers

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Certain organic polymers are shown to possess a very high piezo-resistive coefficient. Compared to metals which change up to two-fold in a given pressure range, these materials change by a factor of 100-fold or more. The results are explained in terms of the easily compressible intermolecular distances and energy barriers for electron transfer. A more quantitative theory in terms of an absolute reaction rate formalism is presented. Agreement in several respects with the theory by experiment is noted.

From what follows, it will be seen that certain organic polymers possess semiconducting properties which are quite pressure sensitive. The effects of high pressure on the conductivity of metals were studied intensely by Bridgman.[1] A majority of the metals examined showed an increase in conductivity as the pressure was increased, with the change in conductivity amounting to about two-fold as the external pressure attained some 100,000 atm. In these classic researches, samples of metal were imbedded in an insulating solid such that an approximately-uniform hydrostatic pressure was transmitted to the metal from an anvil arrangement.

The effects of hydrostatic pressure on the conductivity of germanium were studied by Paul and Brooks[2]; Paul and Pearson[3] studied effects on silicon. For pressures up to 30,000 atm., it was observed that the conductivity decreased as pressure increased.

Studies on the organic monomers have so far indicated that pressure has little effect upon the conductivity. Previous investigators have indicated the existence of a limiting pressure above which the electrical conductivity of organic materials does not change. Akamatsu and Inokuchi[4] found that the resistivity of iso-violanthrone powder decreases with pressure and then remains approximately constant above 80 atm. Eley, *et al.*,[5] reported that the effect of compression was to sharply lower the value of the activation energy for loose *versus* compacted powders of metal-free phthalocyanine by 50% and of iso-violanthrone by 25%. This change in energy of activation was attributed to packing effects upon the powders examined, an effect thought to be more marked in the needle-like crystals of phthalocyanine. It was concluded[6] on the basis of the above observations that pressurization serves only to remove macroscopic voids in the samples under investigation.

A study of the effect of pressure on the conductivity of an organic semiconducting polymer synthesized from 1-hydroxyanthraquinone and 1,8-naphthalic anhydride by condensation in the presence of $ZnCl_2$ at 306° by Pohl and Opp[7] showed that the conductivity increased quite reversibly, strongly and smoothly as pressure was increased up to about 60,000 atm.

The activation energy for the conduction process was also observed to change, falling as the pressure increased. Pohl and Engelhardt[8] noted a smooth change of conductivity with pressure on several similar polymers. In all cases, these organic polymers were observed to show an increase of conductivity with increase of temperature. It was conclusively demonstrated by Pohl and Engelhardt that conduction in these homogeneous polymers was electronic, and not ionic, as shown by the fact that (a) the conductivity did not change upon passage of many times more coulombs through the materials than was necessary to effect complete electrolysis of all atoms present and; (b) a rather large Hall effect could be measured. As a result of these preliminary studies, it was decided to examine more closely the effects of pressure on the electronic behavior of these polymers.

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(1) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **81**, 165 (1952).

(2) W. Paul and H. Brooks, *Phys. Rev.*, **94**, 1128 (1954).

(3) W. Paul and G. L. Pearson, *ibid.*, **98**, 1755 (1955).

(4) H. Akamatsu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

(5) D. D. Eley, G. D. Parfitt, M. J. Perry and D. H. Taysum, *Trans. Faraday Soc.*, **49**, 79 (1953); D. D. Eley and G. D. Parfitt, *ibid.*, **51**, 1929 (1955).

(6) G. P. Brown and S. Aftergut, "Semiconduction in Molecular Solids," Proc. Princeton Univ. Conf., ed. by Herbert A. Pohl, Ivy-Curtis Press, 1960, p. 37.

(7) H. A. Pohl and D. A. Opp, Abstracts of Papers Presented at Chicago, Ill., Sept. 1961, Amer. Chem. Soc., Div. Phys. Chem., pp. 32–33, *cf.* Opp, D. A., Master's Thesis, Princeton Univ., 1961.

(8) H. A. Pohl and E. H. Engelhardt, Papers Presented at the Chicago Meeting, Sept. 1961, Amer. Chem. Soc., Div. Polymer Chem., Vol. II, 150–160, 1961, *cf.* E. H. Engelhardt, Master's Thesis, Princeton Univ., 1961.

Table I

Electronic Characteristics of Some Semiconducting Polymers

Sample no.	Composition Hydrocarbon or substituted hydrocarbon portion	Acid portion[a]	Conductivity σ, mho/cm. at 25° and 4900 atm.	$\sigma_{\infty,0}$, mho/cm.	Spins/g. × 10^{-18}
36	Anthracene	PMA	2.21×10^{-7}	1.46×10^{-1}	..
46	Triphenylchloromethane	PMA	1.82×10^{-14}	1.61×10^{-5}	..
51	Terphenyl	PMA	1.3×10^{-7}	9.2×10^{-3}	..
71	Pyrene	PMA	3.88×10^{-5}	1.82×10^{-1}	.
107	1-Hydroxy-anthraquinone	1,8-Naphthalic anhydride	3.28×10^{-6}	6.7×10^{-2}	7

[a] PMA, pyromellitic dianhydride.

Experimental

The materials examined in this study had been synthesized earlier by Pohl and Engelhardt[8] in a manner closely similar to that described by Bornmann and Pohl.[9,10,11] The polymers (see Table I), before examination, were dried in a desiccator at room temperature for at least 200 hr. before use after being finely ground. Radio-isotope analysis showed them to contain less than 2 p.p.m. $ZnCl_2$. They were then placed between two tungsten-carbide Bridgman anvils of 6 mm. contact diameter. This small contact area afforded a maximum pressure of about 40,000 atm. in the hydraulic press used. The sample was surrounded by a Teflon gasket which prevented the material from being squeezed out at the start of the run. A thermocouple was in contact with one anvil. Two pieces of hardened steel backed up the anvils, a thin sheet of copper between the anvil and each steel back-up piece serving to more evenly distribute the pressure. The tungsten carbide pieces sat in pressure-fitted retaining rings (steel of 50 Rockwell C hardness). The whole assembly was placed in a steel retaining device with a thin sheet of Teflon lining the contact areas of anvil and retaining device. The retaining apparatus minimized improper alignment of the anvils which results in either or both anvils cracking as a result of side movement in a nerve-shattering slip-stick process. The anvil assembly was placed in a No. PA7 Preco hydraulic press and was thermally shielded by a thick glass-wool insulation and connected *via* shielded leads to a Model 610A Kiethley electrometer. The cell was heated by thermal conduction through two temperature-regulated platens on the Preco press. The highest pressure-and-temperature measurement was taken first to assure a relatively-constant thickness profile throughout the subsequent temperature and pressure examinations. This expectation was confirmed by the high reproducibility observed in the resistance pressure curves on repeated cycling. Measurements were most conveniently made of the resistance at constant temperature as the pressure was varied. The sample thickness was measured at the end of each run after removing the sample pellet from the cell.

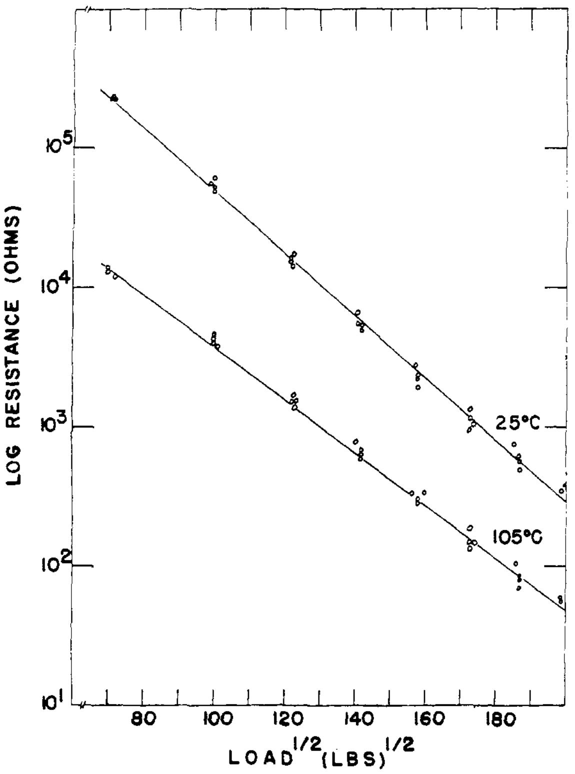

Fig. 1.—Observed resistance *versus* load for the PAQR polymer obtained from condensing anthracene with pyromellitic dianhydride. Sample no. 36.

Results

The resistance-load results obtained at various temperatures for the various polymeric semiconductors examined in this study are shown in Figs. 1–5. The data is plotted in terms of log resistance *versus* the square root of the load, as suggested by the theoretical discussions of the next section. A slight hysteresis noted was shown to arise largely in piston drag effects in the pressurizing apparatus.

Discussion

The materials which we are examining here are molecular solids of very high molecular weight.[10,11] The molecules are highly conjugated and possessed of many unpaired electrons, as evidenced by the high (e.s.r.) spin concentrations observed in this class of semiconductors. Sample 107, for example[7] exhibits a spin concentration of 7×10^{18} cm.$^{-3}$ at room temperature, with a peak half-width of 6 gauss. The general conductivity-spin density behavior of these condensation polymers of polyacene derivatives with acids (*i.e.*, the polyacene quinone radical or PAQR polymers) is described in further detail elsewhere.[7,8] So far, the spin concentrations observed in the PAQR polymers ranges from 5×10^{16} to 2×10^{20} cm.$^{-3}$. As noted earlier, they are electronic rather than ionic conductors. In general they are black or nearly black

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(9) J. A. Bornmann and H. A. Pohl, "Further Studies on Some Semiconducting Polymers," Princeton Univ. Plastics Laboratory Report *63A*, Sept. 1961, and *J. Electrochem. Soc.* (in press).

(10) H. A. Pohl, "Semiconduction in Polymers," Princeton Univ. Plastics Laboratory Tech. Report 61D, 1961; *cf.* "Semiconduction in Polymers," by H. A. Pohl, chapter in Vol. II, "Modern Aspects of the Vitreous State," ed. by J. D. Mackenzie, Butterworths (in press).

(11) H. A. Pohl, J. A. Bornmann and W. Itoh, "Semiconducting Polymers," Princeton Univ. Plastics Laboratory Tech. Report 60C, 1961, *cf. J. Electrochem. Soc.* (in press).

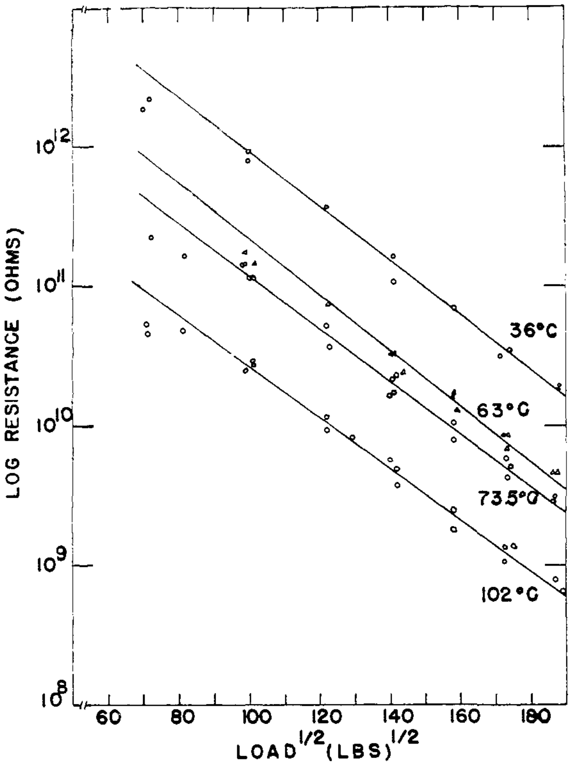

Fig. 2.—Observed resistance *versus* load for the PAQR polymer obtained from condensing triphenylchloromethane with pyromellitic dianhydride. Sample no. 46.

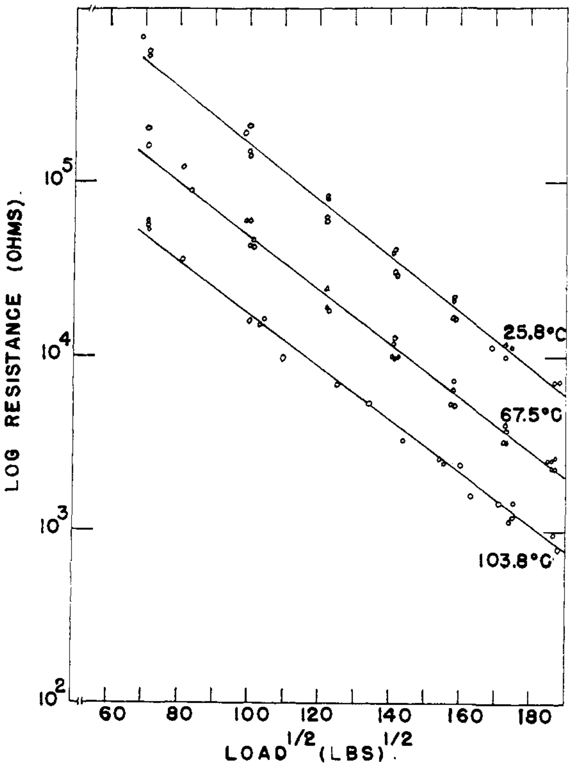

Fig. 3.—Observed resistance *versus* load for the PAQR polymer obtained from condensing terphenyl with pyromellitic dianhydride. Sample no. 51.

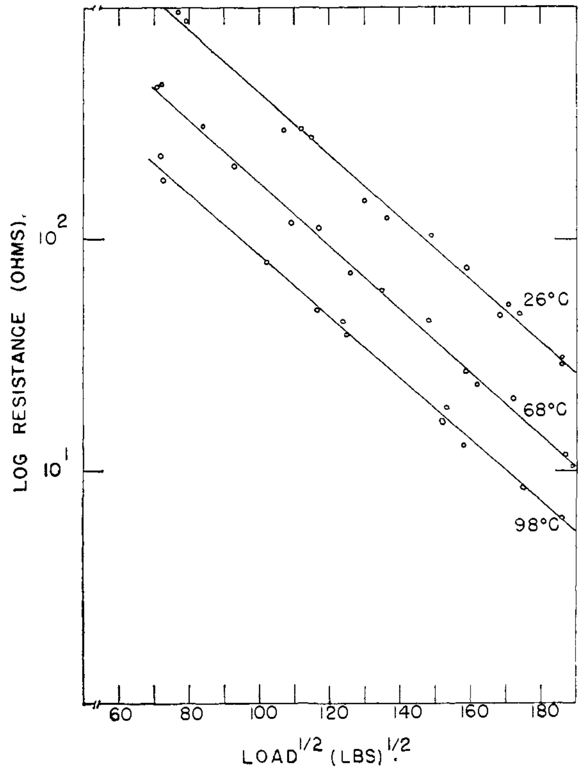

Fig. 4.—Observed resistance *versus* load for the PAQR polymer obtained from condensing pyrene with pyromellitic dianhydride. Sample no. 71.

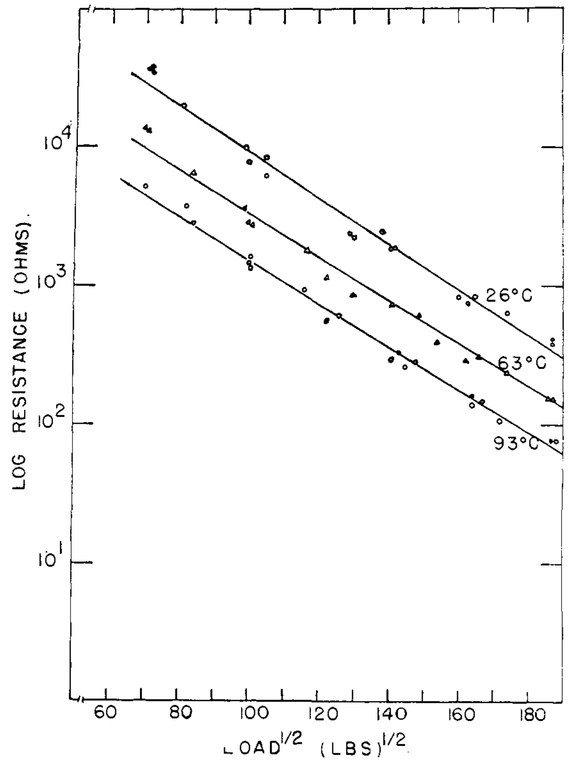

Fig. 5.—Observed resistance *versus* load for the PAQR polymer obtained from condensing 1-hydroxyanthraquinone with 1,8-naphthalic anhydride. Sample no. 107.

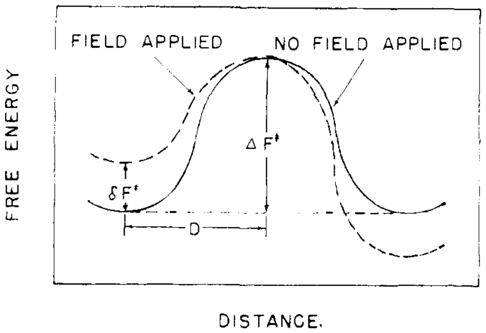

Fig. 6.—The free energy path for an electron in transfer between molecules.

materials, insoluble and infusible.[10,11] They are possessed of a slight degree of thermoplasticity which permits them to be compacted into non-porous briquettes. They are noticeably swellable by certain organic solvents such as acetone. X-ray diffraction indicates that they are partly amorphous, as is to be expected. On a molecular scale one would expect them to consist of highly conjugated chains, very entangled, and very cross-linked. Van der Waals distances of molecular approach between the molecular segments would be frequent. Pressure should bring about an increase of orbital overlap, especially between the electron-rich aromatic portions of the neighboring molecules. This increase of electron orbital overlap should be expected to increase the ease of intermolecular electron transfer, by decreasing the distance and energy barriers to diffusion and tunnelling and by increasing the chain-chain areas of contact, thereby increasing the probability (entropy factor) for electron transfer.

If this picture is correct and changes in the activation energy of electron charge transfer are due to orbital overlap changes, then as compression continues, the increasing repulsive forces should operate to reduce further changes in the size of the energy of activation.

The conductivity of a material may be defined as

$$\sigma = |e|n\mu \qquad (1)$$

where $|e|$ is the electronic charge
n is the number of carriers, and
μ is the mean mobility of the carriers.

For the case of an intrinsic semiconductor

$$n = n_0\exp(-E_g/2kT) \qquad (2)$$

In molecular solids, one may take the approach of the theory of absolute reaction rates in considering the mobility and drift velocity of the electronic carriers. In the transfer of any electron from one molecule to the next, the slow rate process is that of hopping between the molecular borders, whereas traverse of the molecule is rapid. The drift velocity along molecules of length L will then be

$$v = L \times k_0 \qquad (3)$$

where k_0 is the specific rate of hopping. In passing through the activated state of the hopping process, the unpaired electron must pass over a free energy barrier $\Delta F^\ddagger$ as indicated in Fig. 6.

The specific rate k in any direction is, as given by the theory of absolute reaction rates[12]

$$k_0 = K\left(\frac{kT}{h}\right)\exp(-\Delta F^\ddagger/kT)\ [\text{sec.}^{-1}] \qquad (4)$$

where k = Boltzmann's constant
h = Planck's constant
T = absolute temperature
$\Delta F^\ddagger$ = standard free energy for the activation process with datum reference the ground state of the unactivated state, in ev.
K = transmission coefficient, here assumed equal to unity.

In the presence of an externally imposed electric field, there will be a preferential drift of the carriers. In a potential gradient ϕ, the free energy of activation at an angle θ to the direction of the external field is

$$\Delta F^\ddagger = \Delta F_0^\ddagger - \delta F^\ddagger \qquad (5)$$

where

$$\delta F^\ddagger = \phi\cdot d\cdot\cos\theta$$

The drift velocity v in the direction of the field is then

$$v = L\cdot k_0 = L\cdot\frac{kT}{h}\cdot\cos\theta\cdot\exp(-\Delta F^\ddagger/kT)\exp(g\cos\theta) \qquad (6)$$

where d is the hop half-length (Fig. 6), and

$$g = \frac{\phi d}{kT}$$

The mean drift velocity $\bar{v}$ is

$$\bar{v} = \frac{\int_0^{4\pi} v\,d\omega}{\int_0^{4\pi} d\omega} = \frac{\int_0^{\pi} 2\pi v\sin\theta\,d\theta}{\int_0^{\pi} 2\pi\sin\theta\,d\theta} \qquad (7)$$

where ω is the solid angle.

Since the applied fields are small, we may set $\exp(g\cos\theta) = 1 + g\cos\theta$. Making this substitution and carrying out the indicated integrations gives

$$\bar{v} = L\cdot\frac{kT}{h}\cdot\frac{g}{3}\ [\text{cm./sec.}] \qquad (8)$$

As

$$\mu = \bar{v}/\phi \qquad (9)$$

$$\mu = \frac{Ld}{3h}\exp(-\Delta F_0^\ddagger/kT) \qquad (10)$$

$$\mu = \frac{Ld}{3h}\exp\left(\frac{\Delta S^\ddagger}{k}\right)\exp(-\Delta H^\ddagger/kT) \qquad (11)$$

In the activated state for electron transfer between the molecules, the unpaired electron may be considered as roughly equivalent (quantum mechanically) to a particle in a box comprised of the "overlapped" segments of the two molecules.

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[12] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

This approximation allows evaluation of the entropy term as a ratio of translational partition functions:

$$\exp(\Delta S\ddagger/k) = \frac{f\ddagger}{f} = \frac{(2\pi mkT)a\ddagger/h^2}{(2\pi mkT)^{3/2}\ V/h^3} = \frac{h}{(2\pi mkT)^{1/2}} \cdot \frac{a\ddagger}{V} \quad (12)$$

where $f\ddagger$ and f are the partition functions of the activated and precursor systems, m is the effective mass of the electron, $a\ddagger$ is the "area of contact" of the two molecules and V is the volume of the originating molecule.

In an *ab initio* analysis one should attempt to calculate changes in molecule–molecule interaction by rigorous quantum-mechanical methods. However, one may skirt this difficult task by using the area-of-contact analogue. The change in "area of contact" $a\ddagger$ with pressure P can be expected to be direct. As compression is continued, the increasing repulsive forces should operate to reduce further changes in area of contact. *i.e.*, as $a\ddagger$ is increased, the accumulated changes in $a\ddagger$, representable by $a\ddagger - a_0\ddagger$, will act to oppose further changes. Instead of using combinations of shielded potential functions such as modified Slater functions, for example, to describe the effects on overlap, we shall here use the following simple approximation

$$da\ddagger = \frac{gdP}{2(a\ddagger - a_0\ddagger + c'')} \quad (13)$$

where g is a constant of proportionality, and c'' is a small constant describing the initial "softness" of the molecular contact at zero external pressure. The factor 2 is included here for later convenience. It can be seen that the constructed function 13 has the desired features. It forms a simplified postulate of the change of contact area with pressure.

Integration gives

$$\int_{a_0\ddagger}^{a\ddagger} (a\ddagger - a_0\ddagger + c'')da\ddagger = \frac{g}{2}\int_0^P dP \text{ or} \quad (14)$$

$$a\ddagger = a_0\ddagger - c'' + \sqrt{(c'')^2 + gP} \quad (15)$$

For modest pressure ranges one may expect

$$gP \gg (c'')^2 \quad (16)$$

Hence

$$\Delta a\ddagger = a\ddagger - a_0\ddagger \cong g^{1/2}P^{1/2} \quad (17)$$

Letting $g = (a\ddagger\, b''/k)^2$ for later convenience

$$\Delta a\ddagger = a\ddagger - a_0\ddagger \cong \frac{a_0\ddagger b''}{k}\, P^{1/2} \quad (18)$$

Equation 12 may be rewritten as

$$\exp\left(\frac{\Delta S\ddagger - \Delta S_0\ddagger}{k}\right) = \frac{a_0\ddagger + \Delta a\ddagger}{a\ddagger} = 1 + \frac{\Delta a\ddagger}{a_0\ddagger} \quad (19)$$

$$\frac{\Delta S\ddagger}{k} - \frac{\Delta S_0\ddagger}{k} = \ln\left(1 + \frac{\Delta a_0\ddagger}{a_0\ddagger}\right) \cong \frac{\Delta a\ddagger}{a_0\ddagger} \quad (20)$$

for small changes in $a\ddagger$, hence

$$\frac{\Delta S\ddagger}{k} \cong \frac{\Delta S_0\ddagger}{k} + \frac{b''}{k}\, P^{1/2} \quad (21)$$

In an analogous manner, we may also expect the heat of activation for electron mobility $\Delta H\ddagger$ and the activation energy for carrier formation E to vary with external pressure P

$$dE = \frac{-b^2dP}{2(E_0 - E + c)} \quad (22)$$

which on integration becomes

$$E = E_0 + c - (c^2 + b^2P)^{1/2} \quad (23)$$

For modest pressure ranges one may expect $b^2P >> c^2$, hence

$$E_0 = E \cong bP^{1/2} \quad (24)$$

Similarly for $\Delta H\ddagger$, giving

$$\Delta H\ddagger = \Delta H_0\ddagger + c' - [(c')^2 + (b')^2P]^{1/2} \quad (25)$$

and for $(b')^2P >> (c')^2$

$$\Delta H_0\ddagger - \Delta H\ddagger \cong b'P^{1/2} \quad (26)$$

In a well behaved, non-degenerate, intrinsic semiconductor, the population of carriers, n, obeys the exponential relation

$$n = n_0 \exp(-E/kT) \quad (27)$$

(For certain semiconductors, $E = Eg/2$ where Eg is the forbidden energy gap.)

Combining equations 1, 10 and 27, we have

$$\sigma = |e|n_0 \frac{Ld}{3h} \exp\left(\frac{\Delta S\ddagger}{k}\right) \exp\left[-\frac{(\Delta H\ddagger + E)}{kT}\right] \quad (28)$$

Inserting the approximations of equations 21, 24 and 26, we obtain, on letting $b_0 = b' + b$

$$\sigma \cong |e|n_0 \frac{Ld}{3h} \cdot \exp\left(\frac{\Delta S_0\ddagger T - \Delta H_0\ddagger - E_0}{kT}\right) \exp \frac{P^{1/2}}{kT}(b''T + b_0) \quad (29)$$

Setting σ_0, the conductivity at zero external pressure as

$$\sigma_0 = |e|n_0 \frac{Ld}{3h} \exp\left(\frac{\Delta S_0\ddagger T - \Delta H_0\ddagger - E}{kT}\right) \quad (30)$$

we obtain

$$\ln(\sigma/\sigma_0) = P^{1/2}\left(\frac{b_0}{kT} + \frac{b''}{k}\right) \quad (31)$$

Evaluation of the constants b_0, b'' using $E_a = \Delta H\ddagger + E$, and equations 28 and 31 can be done by examining the conductivity *versus* temperature relationship at constant pressure

$$\ln(\sigma/\sigma_\infty) = -E/kT \quad (32)$$

where σ_∞ is the "conductivity" at pressure P and at extrapolated infinite temperature.

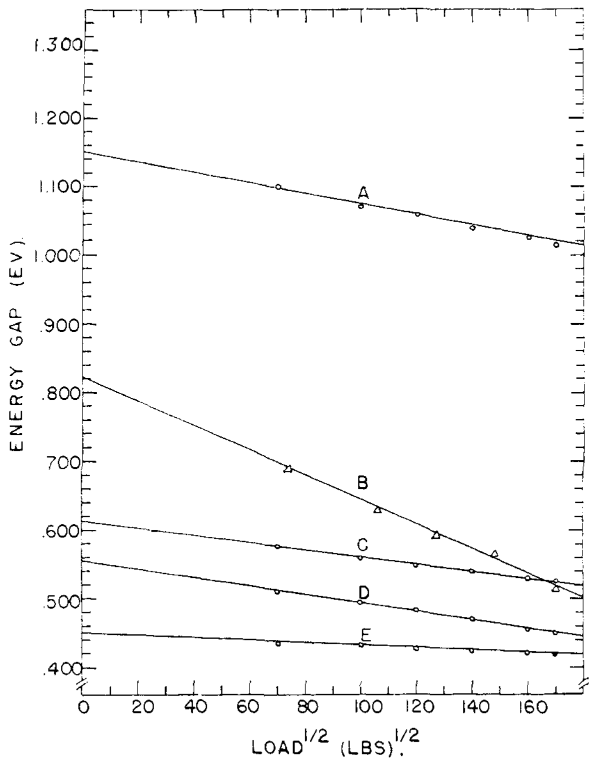

Fig. 7.—The variations of E, the 'forbidden energy gap' parameter, expressed as electron volts, *versus* external pressure. The highest pressures shown correspond to about 40,000 atmospheres.

This gives, experimentally

$$\begin{aligned} E_a &= \Delta H^{\ddagger} + E \\ &= \Delta H_0^{\ddagger} + E_0 - b_0P^{1/2} = E_{a,o} - b_0P^{1/2} \quad (33) \end{aligned}$$

On examination of the variation of the conductivity with pressure (eq. 31) and use of the value of b_0 obtained above, one can evaluate b'', the entropy coefficient from the observed slope of the conductivity-pressure curve.

$$\ln(\sigma/\sigma_0) = P^{1/2}\left(\frac{b_0}{kT} + \frac{b''}{k}\right) = \frac{b^*}{k}P^{1/2} \quad (34)$$

As may be seen from inspection of the data of Figs. 1–5, plots of log conductivity versus the square root of the applied load are linear over the pressure range investigated, supporting the simple arguments given above. Furthermore, as required by the theory, plots, shown in Fig. 7 of the variation of activation energy E_a *versus* the square root of the applied load are also quite linear over the range investigated.

Pertinent values for the specific conductivity are shown with one datum for spin concentration in Table I. For the several polymeric semiconductors examined, values of the derived parameters $E_{a,o}$, the activation energy at nil pressure, b_0, the $\Delta E^{\ddagger}$–pressure term, and b'', the entropy–pressure term are shown in Table II. The observed constancy of the b'' values for each polymer at different temperatures independently supports the interpretations given here.

TABLE II

PRESSURE–CONDUCTIVITY PARAMETERS FOR VARIOUS SEMICONDUCTING POLYMERS

Polymer sample no.	b'' × 10^6, eV./(atm.)$^{1/2}$ (°K.) ($\Delta S^{\ddagger}$ term)	b^* × 10^6, eV./(atm.)$^{1/2}$ (°K.)	b_0 × 10^3, eV./(atm.)$^{1/2}$ ($\Delta E^{\ddagger}$ term)	$E_{a,o}$(eV.)	T, °C.
36	1.05	4.17	0.935	0.410	25
36	1.14	3.61	.935	.410	105
46	2.38	3.66	.395	.576	36
46	2.57	3.75	.395	.576	63
46	2.40	3.54	.395	.576	73.5
46	2.40	3.45	.395	.576	102
51	2.11	2.98	.260	.306	25.8
51	2.11	2.87	.260	.306	67.5
51	2.12	2.81	.260	.306	103.8
71	2.23	2.52	.086	.225	26.5
71	2.24	2.49	.086	.225	68
71	2.23	2.46	.086	.225	98
107	2.04	3.05	.300	.277	25
107	1.96	2.85	.300	.277	63
107	2.06	2.88	.300	.277	93

There is a trend for b_0, the activation energy–pressure parameter to be large for large $E_{a,o}$. This is as would be expected, since if the orbital overlap integrals are small, their rate of change with pressure should also be large.

It will be noted, in conclusion, that the changes in conductivity of the PAQR polymers with pressure are quite large compared to those observed in the metals. The metals change by a factor of about two, the polymers by a factor of about 100 or more in the same pressure range. Extension of the examinations to still higher pressures should result in the observation of very low activation energies. This is presently under study.

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