CHAPTER 4

COMPENSATION EFFECT IN SOME POLYENE SEMICONDUCTORS

4.1 Introduction

The electrical conductivity of conjugated π-electronic organic compounds follows the operational definition of a semiconductor

$$\sigma(T) = \sigma_0 \exp(-E/2kT) \tag{4.1}$$

where $\sigma(T)$ is the specific conductivity at any absolute temperature T, σ_0 is a pre-exponential factor, E the semiconduction activation energy and k is Boltzmann constant (E/2 is often written as E', however, we shall use the former throughout this chapter). Experimentally, E is obtained from the slope of the linear plot of log σ (T) [or log i (T)] versus $\frac{1}{T}$ and the extrapolated intercept of the line on the ordinate at $T^{-1} = 0$ yields the value of σ_0. Recently, the so called pre-exponential factor σ_0 has been the subject of much discussion[1-6] as experimental evidence accumulated shows that σ_0 contains exponential functions. Gutmann and Lyons[7] showed that a linear relationship of the form

$$\log \sigma_0 = \alpha E + \beta \tag{4.2}$$

holds good for one entire class of organic compounds. Here α and β are constants. Rosenberg et al[2] showed evidence that if E is varied by hydration or by complex formation relation (4.2) is valid for a single organic substance as well and they suggested an expression for the specific conductivity of the form

$$\sigma(T) = \sigma_0' \exp(E/2kT_0) \exp(-E/2kT) \tag{4.3}$$

where

$$\sigma_0 = \sigma_0' \exp(E/2kT_0) \tag{4.4}$$

Here the additional constant T_0 is called the characteristic temperature of the material. σ_0' and T_0 for the same compound remain invariant. The linear relationship between the logarithm of the pre-exponential factor and the activation energy is called the compensation effect. σ and E change in such a manner that their effect on σ_0 are mutually compensated. Johnston and Lyons[4] believe that the linear relationship between log σ_0 and E may originate solely from the calculation of these parameters and the compensation effect requires no physical interpretation. However, they have suggested that if σ_0 and E are physically related, one should get a linear relationship between log σ and E yielding the semiconductive parameters in agreement with the values obtained from other sources. Exner[8] also has pointed out that, in certain limited conditions, a compensation law may occur accidently, and he has provided a set of similar criteria for judging the validity of the rule.

From equation (4.3), for any particular temperature T_1, the specific conductivity is given by

$$\log \sigma(T_1) = \log \sigma_0' + \left[\frac{1}{T_0} - \frac{1}{T_1}\right] \frac{E}{2k} \tag{4.5}$$

Thus, the plot of log $\sigma(T_1)$ vs. E is expected to be linear with a slope $\left[\frac{1}{T_0} - \frac{1}{T_1}\right] \frac{1}{2k}$ and an intercept of log σ_0'. The value of σ_0' obtained from this plot should also show a good agreement with the values obtained from the log σ_0 vs. E and log σ vs. $\frac{1}{T}$ plots. In the experiment of Johnston and Lyons[4] in one component crystal of anthracene it has been observed by changing its purity and doping with tetracene that log σ_0 vs. E plots are linear. A very poor correlation between log σ and E was, however, observed[4]. Some recent theoretical work[9-11] suggest that in biological semiconductors the compensation effect arises due to the dark conduction process. In view of the scanty experimental work available on this effect, it was thought worthwhile to investigate the conduction process in more biological semiconductors. To test the validity of this compensation effect, E is generally varied by various ways[5,6,12] and log σ_0 is plotted against E.

In the previous chapter we have seen that the adsorption of various vapours changes the specific conductivity of the polyenes. Such change is generally associated with a change of the semiconduction activation energy. As for example, adsorption of moisture on dry proteins[13] and various vapours on β - carotene[14] increases the semiconduction current and decreases the activation energy. Epstein and Wildi[15] have reported that the removal of oxygen from polymeric copper phthalocyanine causes a sharp drop in the resistivity with a concomitant drop of the activation energy. In this chapter we present the results of our investigations on the effect of adsorption of various vapours on the semiconduction activation energy values of some polyenes. Using these changed activation energy values we further show the validity of the compensation rule in these cases. The results are in conformity with the idea that σ_0 and E are indeed physically related.

4.2 Experimental and Results :

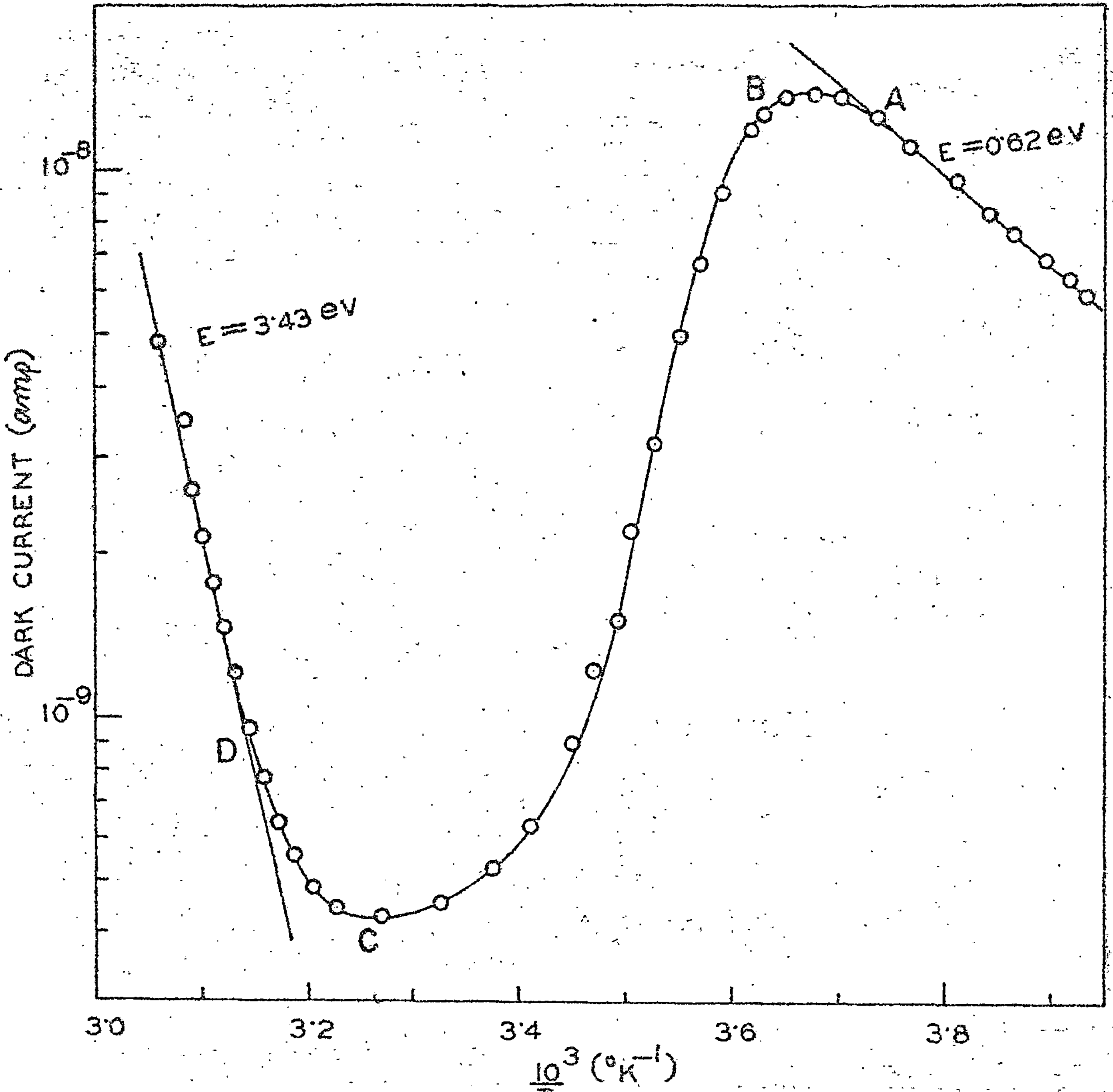
4.2.1 Effect of vapour adsorption on activation energy :

The semiconduction activation energy of crystalline powders of vitamin A alcohol, vitamin A acetate, β - apo - 8'- carotenal, astacene and methyl bixin was measured several times in dry nitrogen atmosphere and also in vacuum. All measurements gave consistent values. Almost same values were obtained in dry nitrogen and in vacuum. The observed values are 2.06, 3.50, 1.36, 1.30 and 1.32 eV (approx.) for the alcohol, acetate, β -apo-8'-carotenal, astacene and methyl bixin respectively. The adsorption of vapours changes the activation energy appreciably.

To determine the effect of adsorbed vapour on the semiconduction activation energy, the sample was allowed to adsorb the vapour at a fixed pressure and come to a steady state at a constant sample cell temperature in the chamber atmosphere containing the vapour in nitrogen. The pressure of the total gas mixture in the chamber was atmospheric and the partial pressure of the vapour was the saturation vapour pressure of the reagent liquid at the temperature at which it was kept. Both inlet and the outlet of the chamber was then sealed and the value of the saturation current was noted with time. The saturation current was found to be almost constant even after four hours indicating that the conduction in the system was mainly electronic[16,17]. The cell was then rapidly cooled to about - 40°C. The chamber was then flushed gently with dry nitrogen gas. The outlet of the chamber was kept open and the atmospheric pressure was maintained inside the chamber. The temperature was then slowly increased and the semiconduction current was measured with the increasing temperature of the sample cell. The result of one such typical experiment for ethyl acetate vapour adsorption on vitamin A acetate are shown in Fig. 4.1. For the region upto the point A, the current increases uniformly with temperature and the curve has a straight line portion. As the temperature increases further, there is gradual slowing down of the rate of current rise with temperature. At the point B, the current drops off, first slowly, then very fast until the point C is reached when the current gradually rises again. At the point D, the current rise becomes uniform and the curve is again a straight line. Evidently, the straight line portion in the low temperature region shows the semiconductive properties of vitamin A acetate powder with adsorbed ethyl acetate vapour and the slope of this line gives the activation energy (0.62 eV) of the system. At considerable higher temperatures, the adsorbed vapour starts desorbing and the rate of desorption increases with increasing temperature and the current begins to diminish. At the point C, the desorption is nearly complete and the current returns to the initial value before vapour adsorption. The straight line portion of the curve at the higher temperature region above the point C, gives the activation energy of vitamin A acetate powder in dry nitrogen atmosphere. The observed value (3.43 eV) is slightly lower possibly due to incomplete desorption of adsorbed vapours. Similar curves were also obtained with other vapours. Vitamin A alcohol shows similar behaviour on vapour adsorption. The effect of adsorption of ethyl acetate vapour on the activation energy of

FIG. 4.1 : Semiconductivity in an ethyl acetate adsorbed vitamin A acetate powder cell as a function of temperature.

Ambient vapour pressure 50 mm adsorbed at sample cell temperature 12.5°C.



10^{-8}
10^{-9}
DARK CURRENT (amp)
E = 3·43 eV
E = 0·62 eV
A
B
C
D
3·0
3·2
3·4
3·6
3·8
$\frac{10^3}{T}$ (°K^{-1})

FIG. 4.1

a vitamin A alcohol cell is shown in Fig. 4.2. In this case the straight line in the low temperature region gives the activation energy of 0.58 eV which is also less than the value observed in dry nitrogen. The activation energy (1.7 eV) obtained from the straight line at higher temperature region is slightly lower than the value at nitrogen atmosphere (2.06 eV). This is what we have seen in case of Vitamin A acetate also. Similar curves were obtained with toluene, benzene, n-heptane, ethanol and methanol vapours.

The effect of adsorption of ethyl acetate vapour on the activation energy of other polyene semiconductors is shown in Figs. 4.3 - 4.5 for β-apo-8'-carotenal, astacene and methyl bixin powders respectively. From the figures it is seen that in these cases also these plots give two portions of good straight lines — one in the low temperature and the other in the higher temperature region. The activation energy after adsorption of vapours in these polyenes are, however, appreciably higher than that in dry nitrogen atmosphere. The value of the activation energy obtained from the straight line at higher temperature region in all these plots agree satisfactorily to the value in nitrogen atmosphere though in case of methyl bixin (Fig. 4.5) this value is slightly higher possibly due to incomplete desorption.

In the previous chapter we have shown that the enhancement of conductivity depends on the chemical nature of the adsorbed vapours. We have studied the effect of different vapours on the activation energy of these polyene semiconductors and have measured the activation energy of each semiconductor after adsorbing different

FIG. 4.2 : Semiconductivity in an ethyl acetate adsorbed vitamin A alcohol powder cell as a function of temperature.

Ambient vapour pressure 50 mm adsorbed at sample cell temperature 12.5°C.

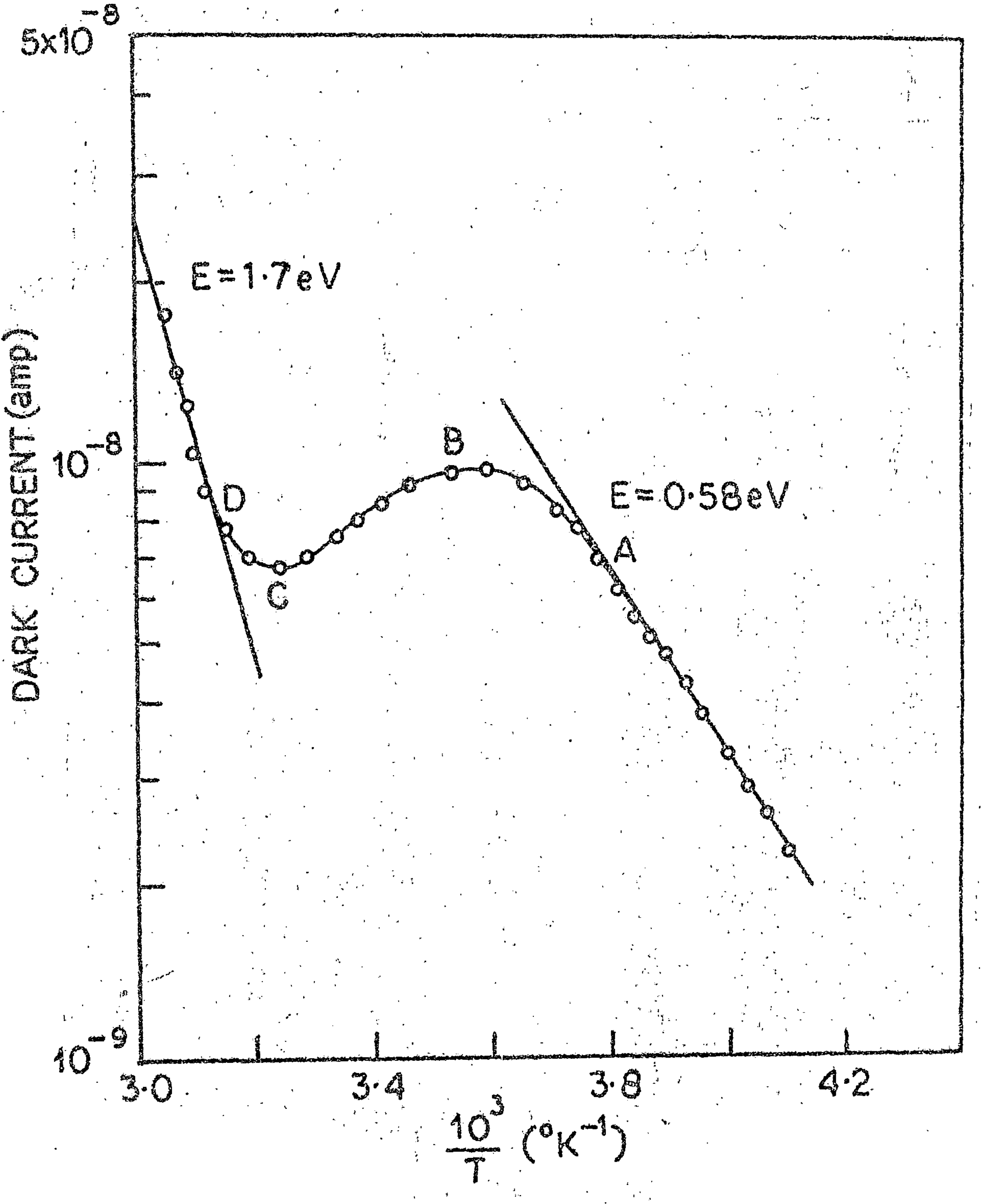

5x10^{-8}
10^{-8}
10^{-9}
DARK CURRENT (amp)
E=1·7eV
E=0·58eV
A
B
C
D
3·0
3·4
3·8
4·2
$\frac{10^3}{T}$ (°K^{-1})

FIG. 4·2

FIG. 4.8 : Semiconductivity in an ethyl acetate adsorbed β-apo-8'-carotenal powder cell as a function of temperature.
Ambient vapour pressure 40 mm adsorbed at sample cell temperature 18.5°C.

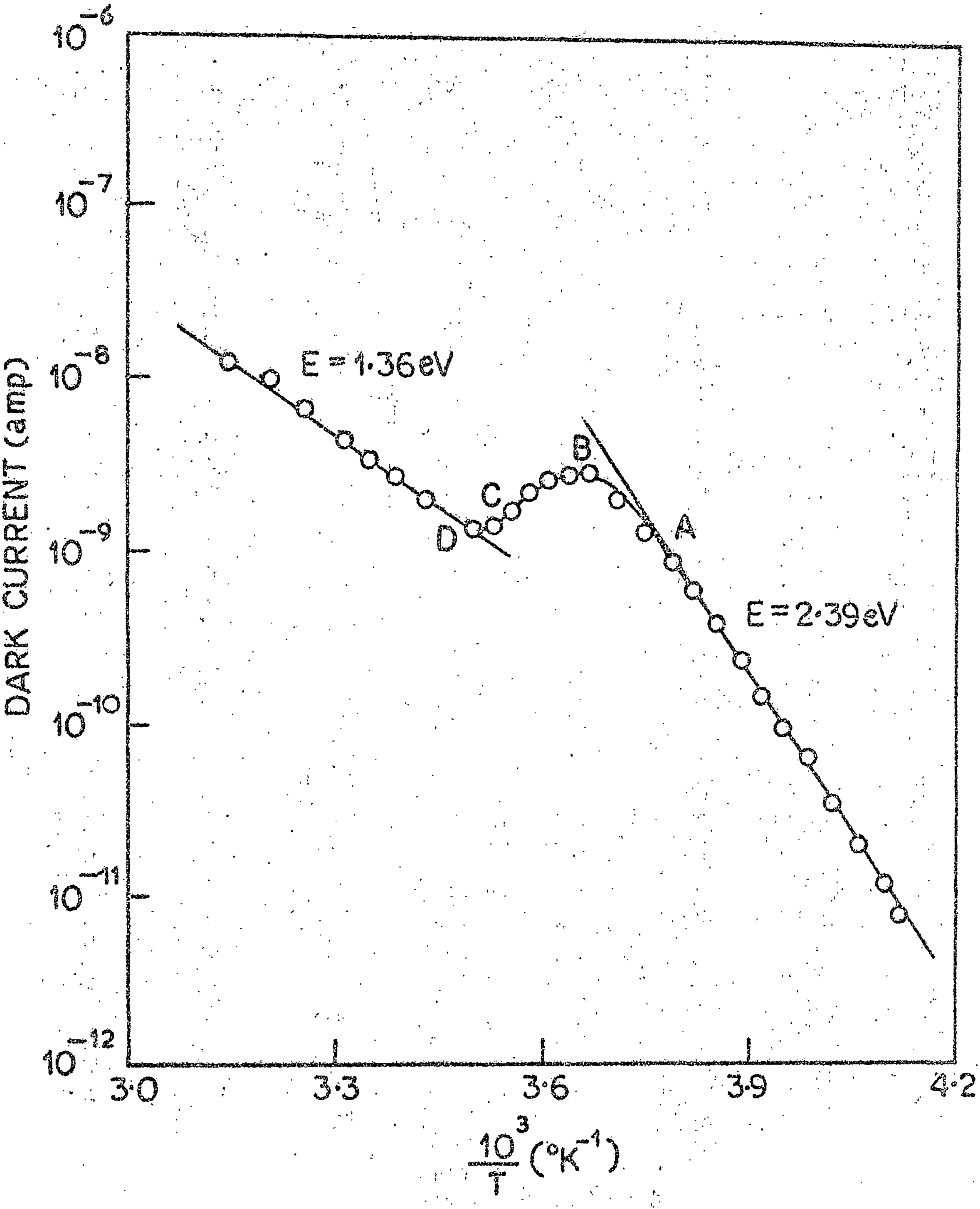
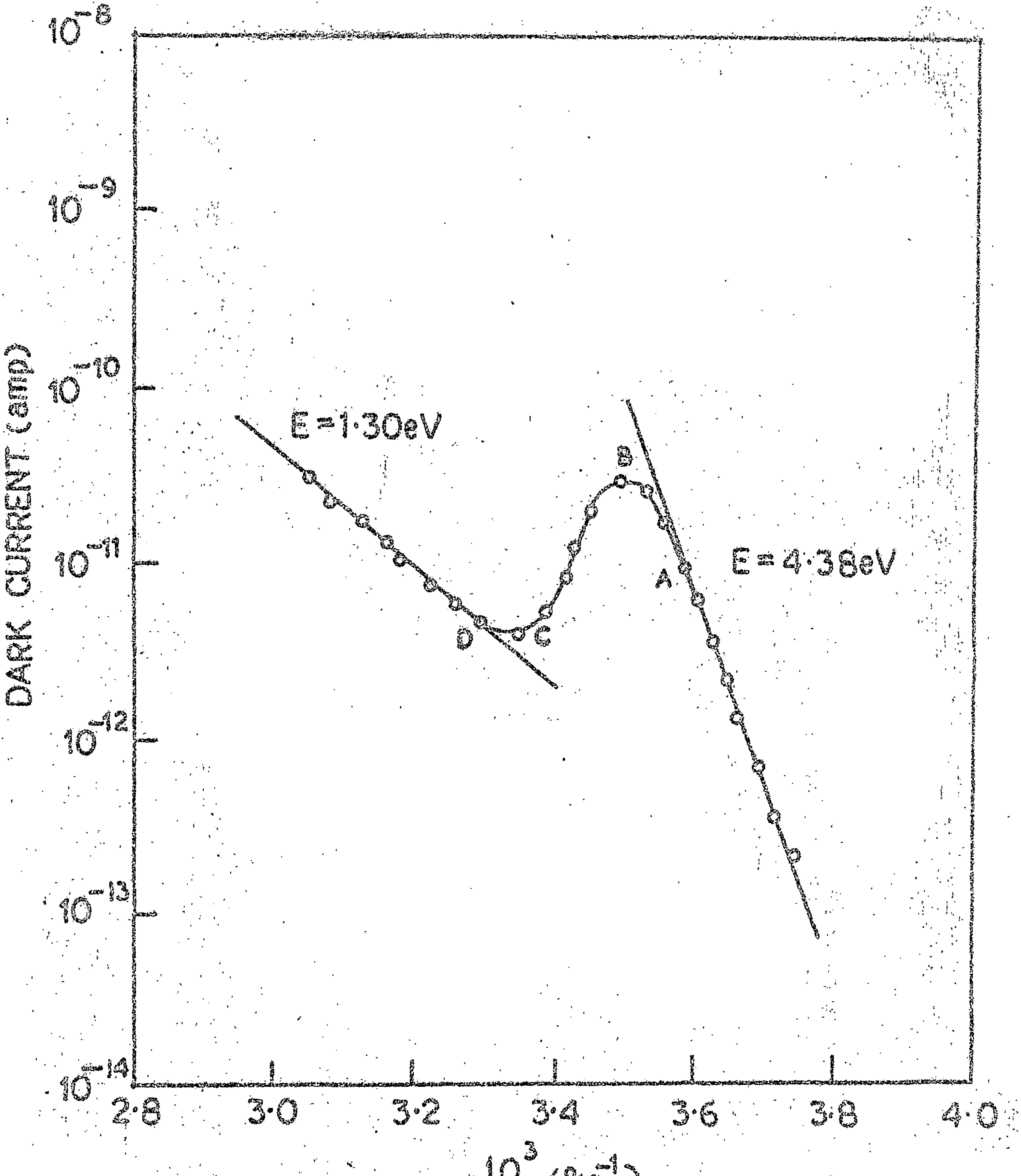

DARK CURRENT (amp)
10^-6
10^-7
10^-8
10^-9
10^-10
10^-11
10^-12
3·0
3·3
3·6
3·9
4·2
10^3/T (°K^-1)
E = 1·36eV
E = 2·39eV
A
B
C
D

FIG. 4·3

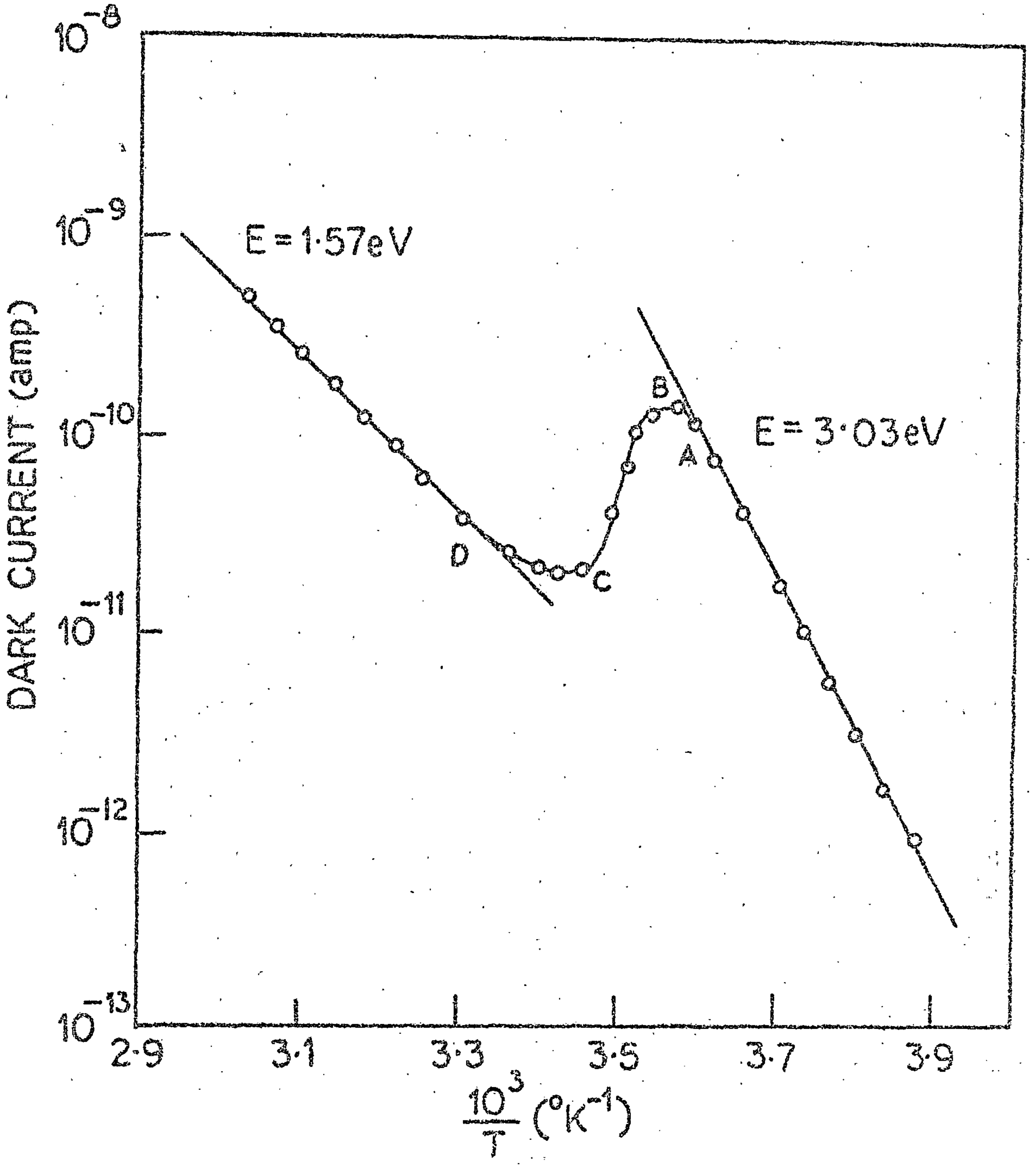
FIG. 4.4 : Semiconductivity in an ethyl acetate adsorbed astacene powder cell as a function of temperature. Ambient vapour pressure 45 mm adsorbed at sample cell temperature 18.5°C.



10^-8
10^-9
10^-10
10^-11
10^-12
10^-13
10^-14
DARK CURRENT (amp)
E = 1·30eV
E = 4·38eV
A
B
C
D
2·8
3·0
3·2
3·4
3·6
3·8
4·0
10^3/T (°K^-1)

FIG.4.4

FIG. 4.6 : Semiconductivity in an ethyl acetate adsorbed methyl bixin powder cell as a function of temperature. Ambient vapour pressure 65 mm adsorbed at sample cell temperature 18.6°C.



10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
DARK CURRENT (amp)
E = 1·57eV
E = 3·03eV
A
B
C
D
2·9
3·1
3·3
3·5
3·7
3·9
$\frac{10^3}{T}$ (°K^{-1})

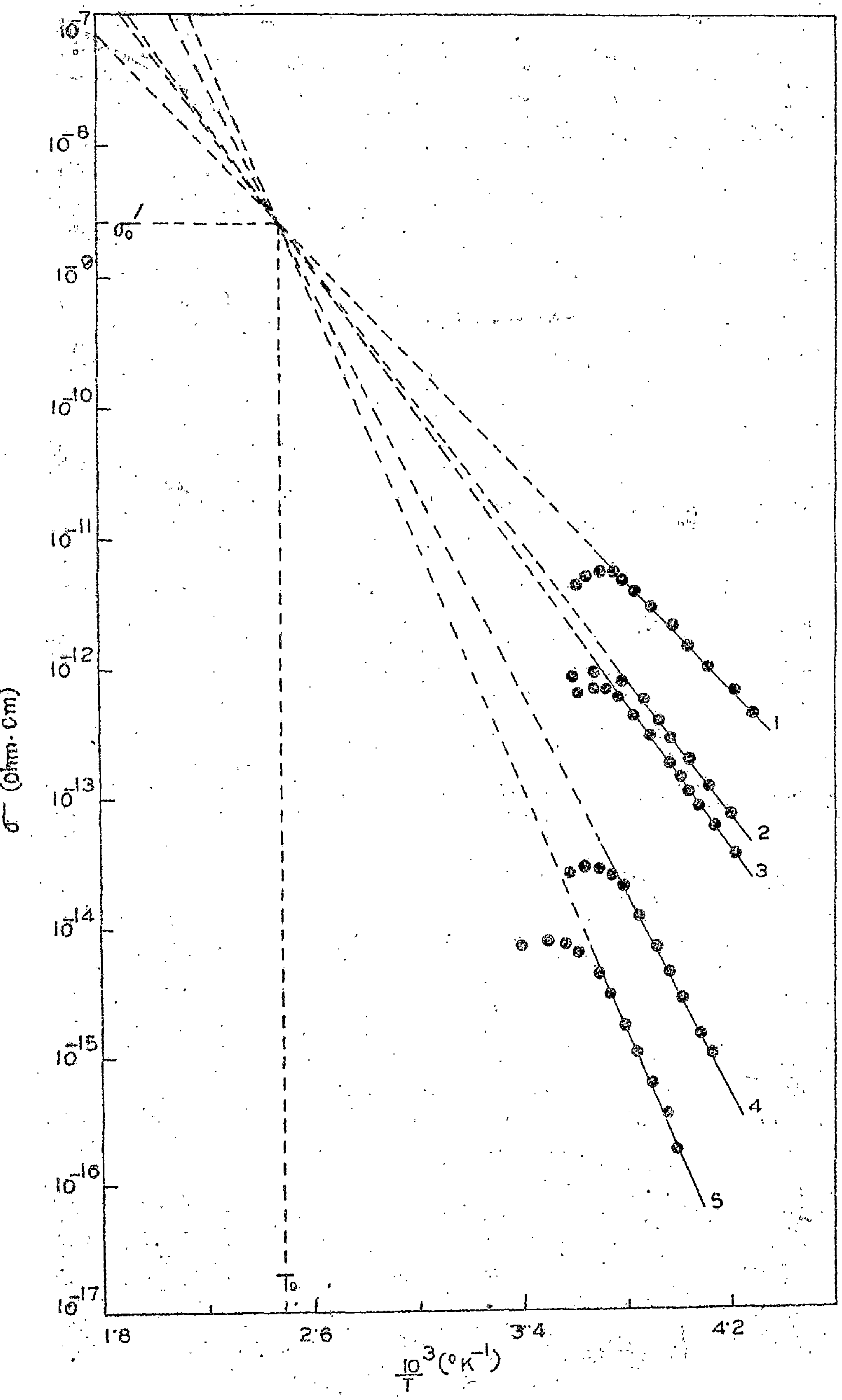
FIG. 4·5

vapours at a fixed partial pressure and maintaining the sample cell at a constant temperature. In Fig. 4.6, we show the straight line portion in the low temperature region for toluene, ethyl acetate, n-heptane, ethanol and methanol vapours adsorption in vitamin A alcohol. It is observed that with the adsorption of different vapours at the same pressure, the activation energy values are different for different vapurs. In Figs. 4.7 - 4.10 we show similar log σ vs. $\frac{1}{T}$ plots for Vitamin A acetate, β - apo - 8' - carotenal, astacene and methylbixin respectively. We see that the decrease [for Vitamin A alcohol and acetate in Figs. 4.6 and 4.7] and increase [for β - apo-8'-carotenal, astacene and methyl bixin in Figs. 4.8-4.10] in activation energy depends on the nature of the vapours.

4.2.2 Semiconduction activation energy as a function of the amount of vapour adsorbed :

To study the dependence of the activation energy change on the amount of a particular vapour adsorbed in a sample cell, measurements were done by repeated heating, partially desorbing and cooling cycles. A set of straight lines in the low temperature region for log σ vs. $\frac{1}{T}$ plots is shown in Figs. 4.11 and 4.12 for adsorption of different amounts of ethyl acetate vapour in Vitamin A alcohol and Vitamin A acetate respectively. The slopes of these lines depend on the amount of ethyl acetate adsorbed. It is seen that the value of activation energy increases in a regular monotonic fashion as more ethyl acetate vapour desorbs. The other vapours show a similar change in activation energy value with the amount of vapour adsorbed. The dependence of the

FIG. 4.6 : Semiconductivity in a vitamin A alcohol powder cell (steady state condition) with the adsorption of different vapours at the same pressure (40 mm) and at a sample cell temperature of 12.5°C. Solid lines represent the temperature region of measurements, broken lines are extrapolations. Each line refers to a specific vapour adsorbed state : (1), toluene ($E = 0.80$ eV); (2), ethyl acetate ($E = 1.06$ eV); (3), n-heptane ($E = 1.10$ eV); (4), ethanol ($E = 1.55$ eV); (5), methanol ($E = 1.82$ eV). (To avoid overlapping with (2) the line corresponding to benzene vapour ($E = 1.04$ eV) is not shown). The value of $T_0 \approx 408$°K; $\sigma_0' = 2.65 \times 10^{-9} (\Omega \cdot cm)^{-1}$



10^{-7}
10^{-8}
σ_0'
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
σ (ohm·cm)$^{-1}$
1
2
3
4
5
T_0
1·8
2·6
3·4
4·2
$\frac{10^3}{T}$ ($^\circ$K^{-1})

FIG. 4·6

FIG. 4.7 : Semiconductivity in a vitamin A acetate powder cell (steady state condition) with the adsorption of different vapours at the same pressure (40 mm) and at a sample cell temperature of 12.5°C. Solid lines represent the temperature region of measurements, broken lines are extrapolations. Each line refers to a specific vapour adsorbed state : (1), toluene ($E = 0.442$ eV); (2), benzene ($E = 0.821$ eV); (3), ethyl acetate ($E = 0.896$ eV); (4), n-heptane ($E = 1.310$ eV); (5), ethanol ($E = 1.570$ eV); (6), methanol ($E = 2.070$ eV). The value of $T_o \approx 335°K$; $\sigma_o' = 1.80 \times 10^{-10}$ $(\Omega \cdot cm)^{-1}$.

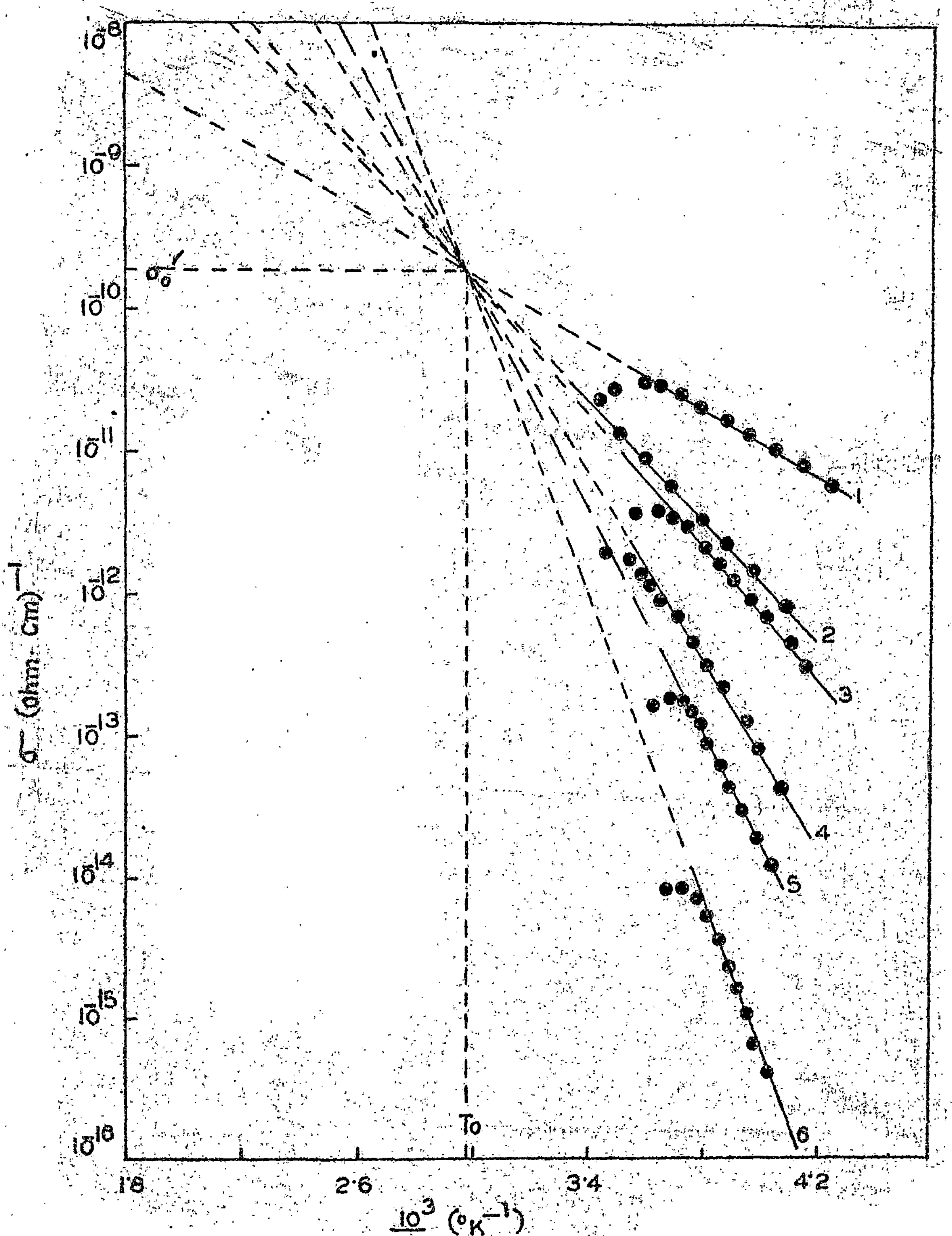
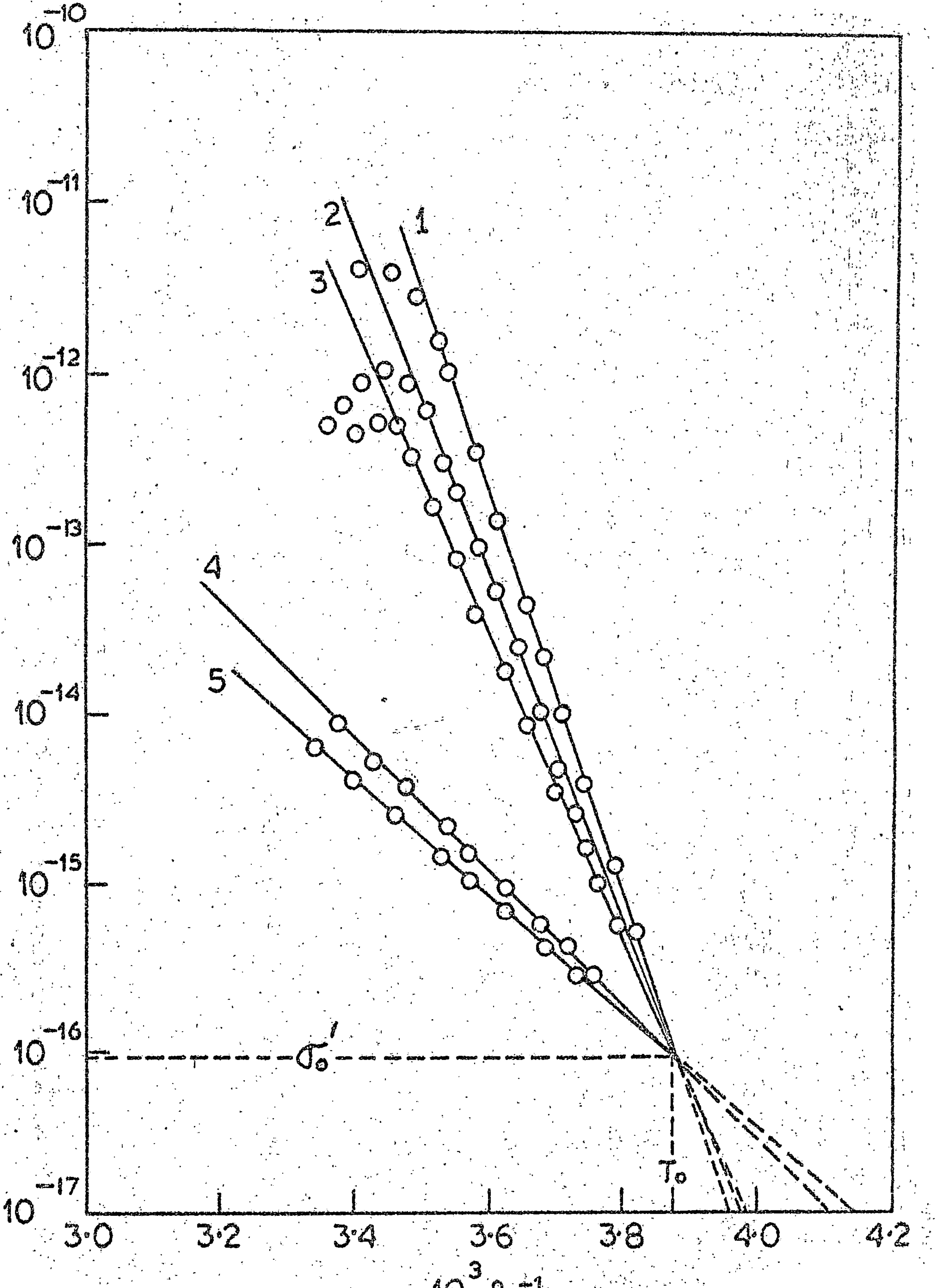

10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
σ_0'
σ (ohm- cm)$^{-1}$
T_0
1·8
2·6
3·4
4·2
$\frac{10^3}{T}$ (°K^{-1})
1
2
3
4
5
6

FIG. 4·7

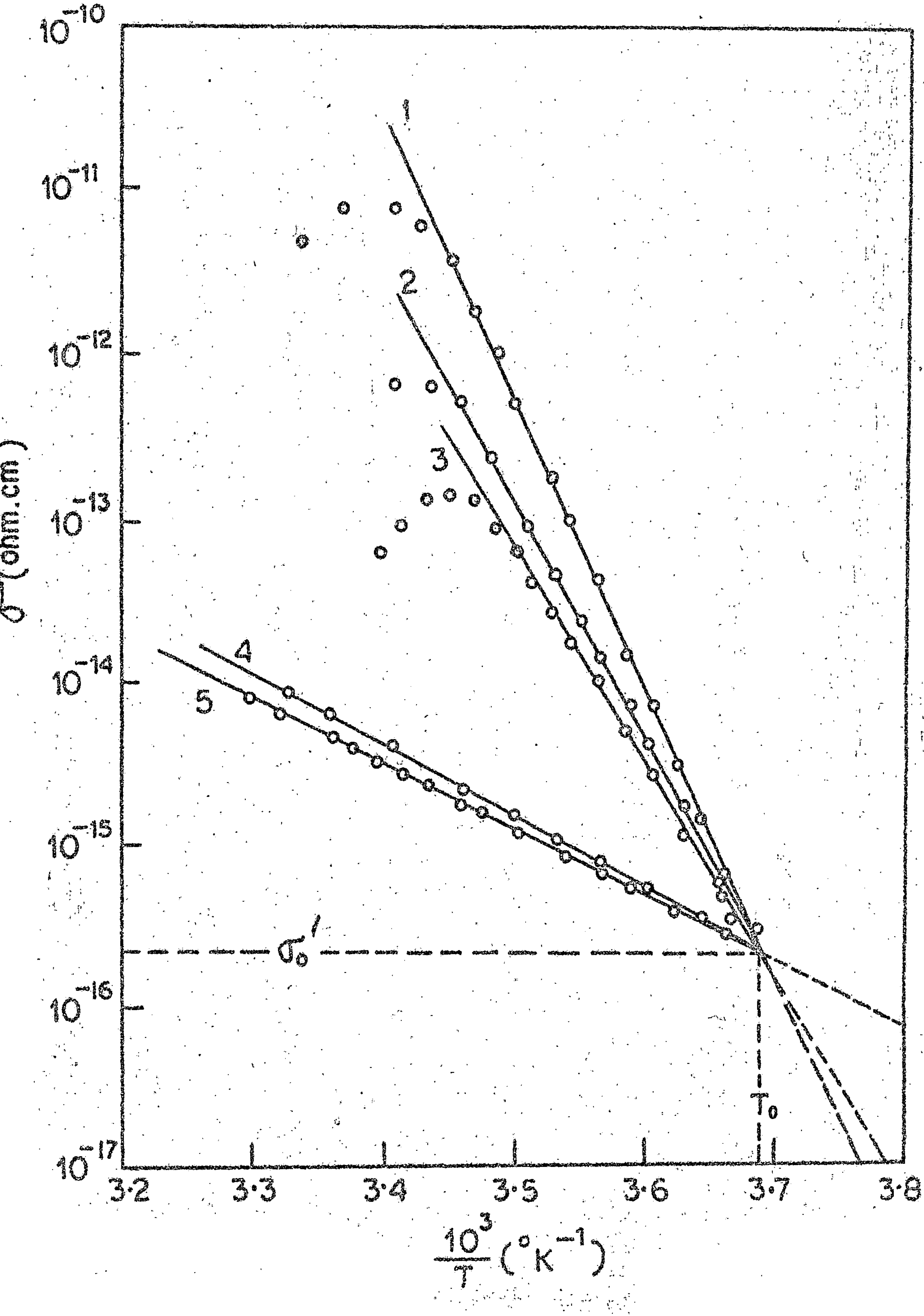
FIG.4.8 : Semiconductivity in a β-apo-8'-carotenal powder cell (steady state condition) with the adsorption of different vapours at the same pressure (42 mm) and at a sample cell temperature of 18.5°C). Solid lines represent the temperature region of measurements, broken lines are extrapolations. Each line refers to a specific vapour adsorbed state : (1), ethanol ($E = 4.80$eV); (2), methanol ($E = 3.94$ eV); (3), ethyl acetate ($E = 2.58$ eV); (4), toluene ($E = 1.57$ eV); (5), n-heptane ($E = 1.40$ eV). The value of $T_o \approx 258$°K; $\sigma_o' = 0.90 \times 10^{-16}$ $(\Omega \cdot cm)^{-1}$.



10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
σ (ohm.cm)$^{-1}$
1
2
3
4
5
σ_o'
T_o
3·0
3·2
3·4
3·6
3·8
4·0
4·2
$\frac{10^3}{T}$ ($^\circ$K^{-1})

FIG. 4·8

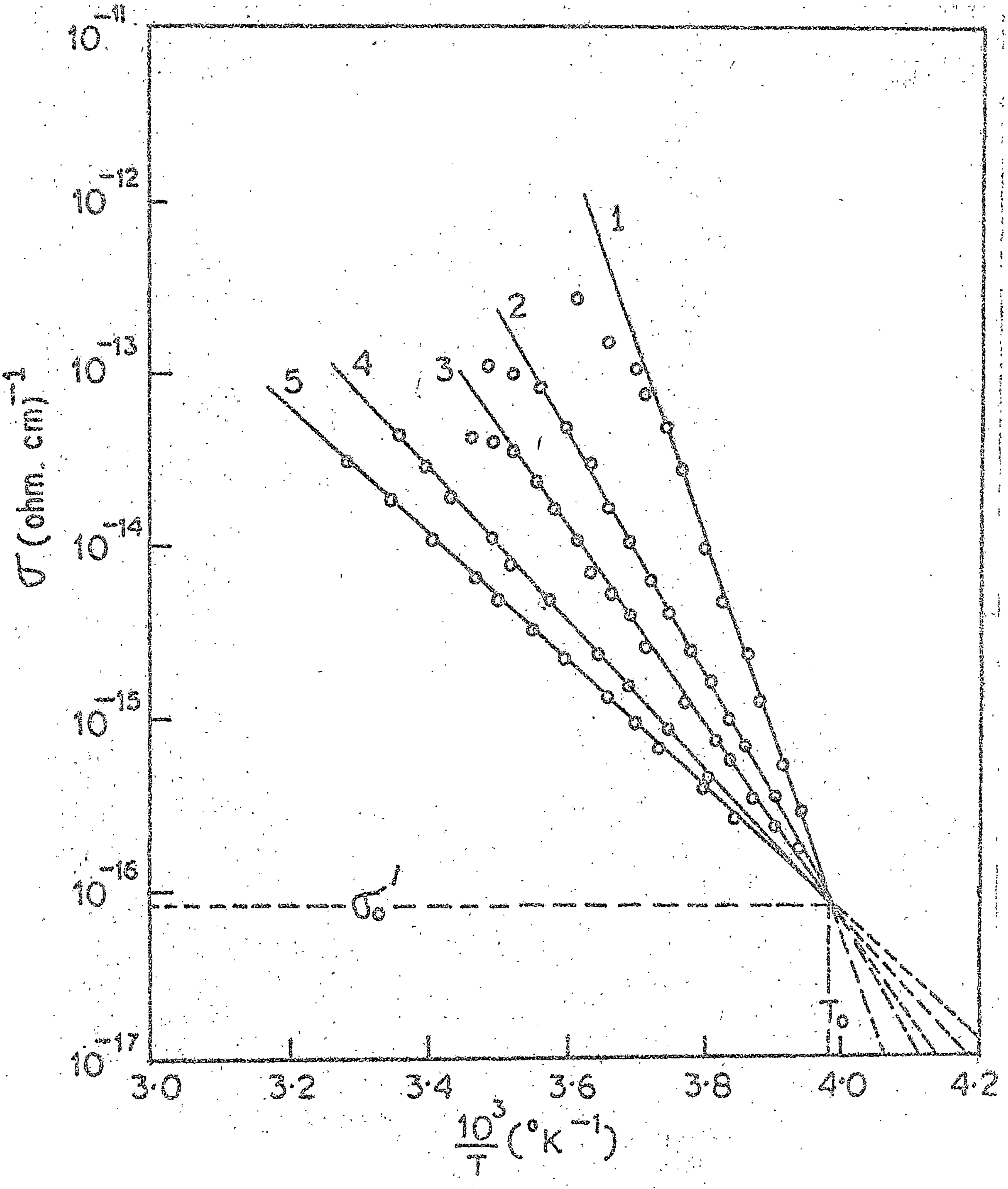
FIG. 4.9 : Semiconductivity in an astacene powder cell (steady state condition) with the adsorption of different vapours at the same pressure (50 mm) and at a sample cell temperature of 18.5°C. Solid lines represent the temperature region of measurements, broken lines are extrapolations. Each line refers to a specific vapour adsorbed state : (1), ethanol ($E = 7.14$ eV); (2), methanol ($E = 5.63$ eV); (3), ethyl acetate ($E = 6.26$ eV); (4), benzene ($E = 1.71$ eV); (5), toluene ($E = 1.67$ eV). The value of $T_0 \approx 272°K$; $\sigma'_0 = 2.15 \times 10^{-16}$ $(\Omega . \mathrm{cm})^{-1}$.



10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
$\sigma\,(\text{ohm.cm})^{-1}$
1
2
3
4
5
σ_0'
T_0
3·2
3·3
3·4
3·5
3·6
3·7
3·8
$\frac{10^3}{T}\,(°K^{-1})$

FIG. 4·9

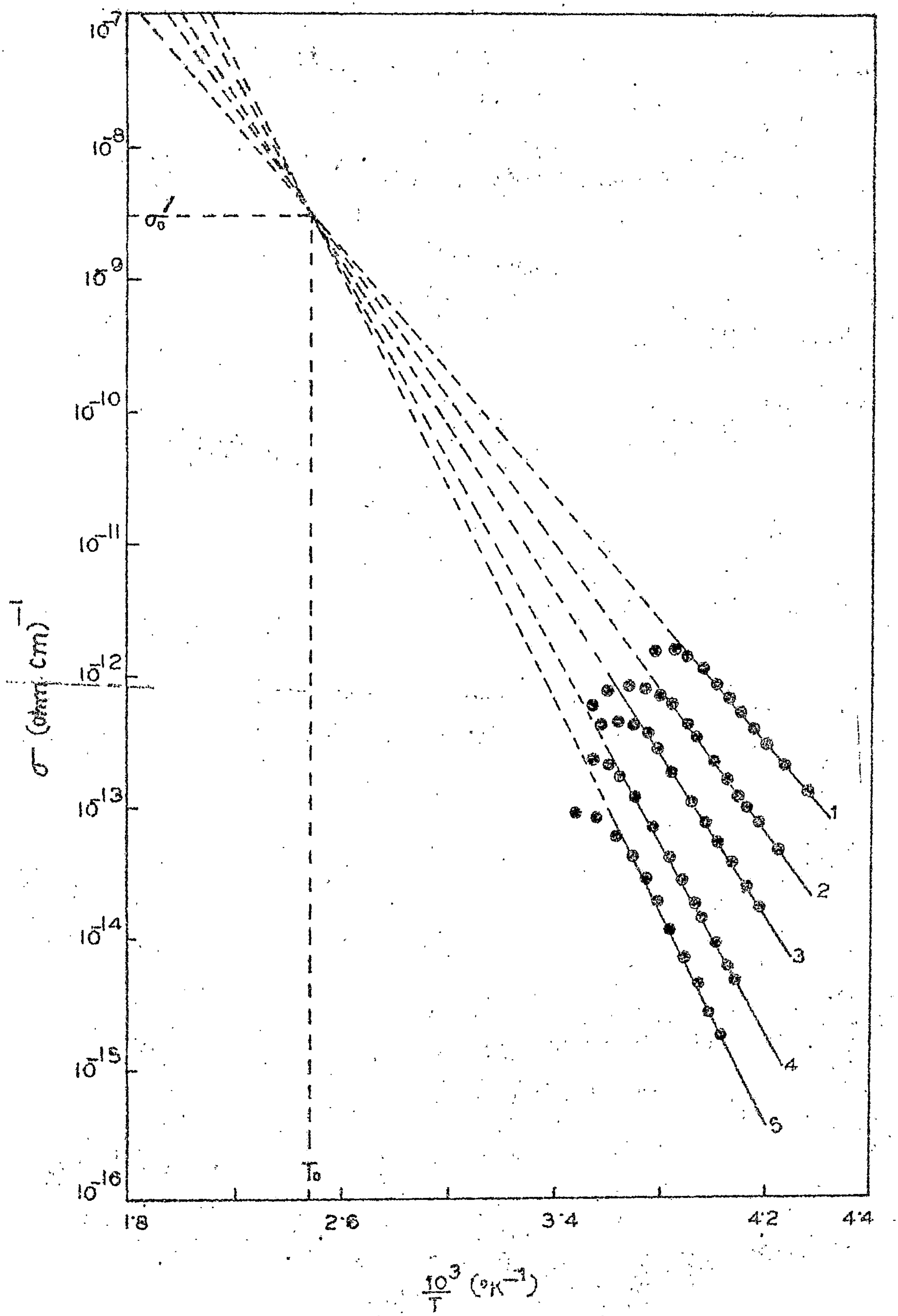
FIG. 4.10 : Semiconductivity in a methyl bixin powder cell (steady state condition) with the adsorption of different vapours at the same pressure (60 mm) and at sample cell-temperature of 18.5°C. Solid lines represent temperature region of measurements, broken lines are extrapolations. Each line refers to a specific vapour adsorbed state : (1), ethanol ($E = 4.43$ eV); (2), methanol ($E = 2.80$ eV); (3), ethyl acetate ($E = 2.28$ eV); (4), benzene ($E = 1.68$ eV); (5), toluene ($E = 1.44$ eV). The value of $T_0 \approx 251^{\circ}K$; $\sigma_0' = 0.85 \times 10^{-16}\ (\Omega . cm)^{-1}$.



10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
σ (ohm. cm)$^{-1}$
1
2
3
4
5
σ_0'
T_0
3·0
3·2
3·4
3·6
3·8
4·0
4·2
$\frac{10^3}{T}$ ($^\circ$K^{-1})

FIG. 4·10

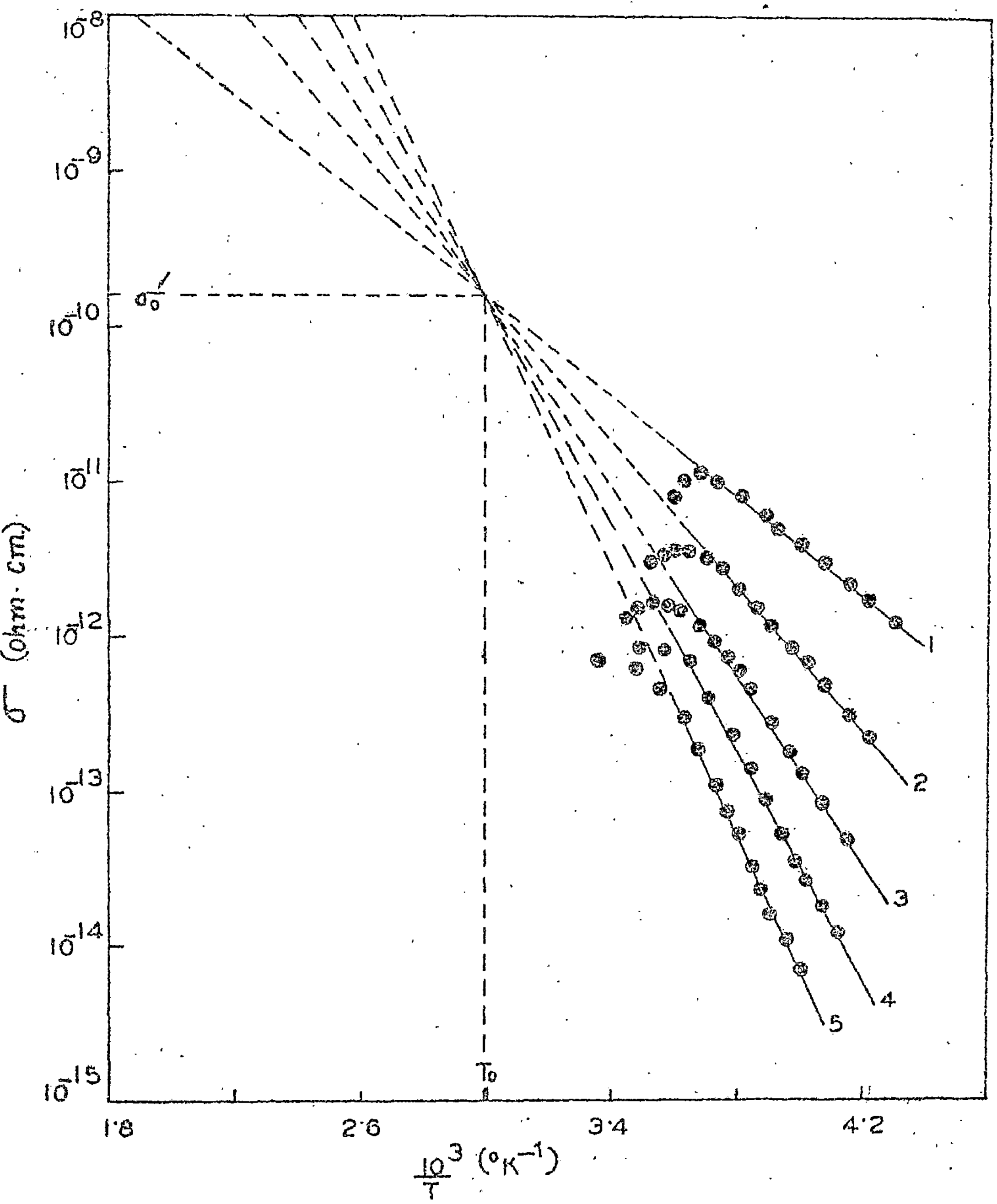
FIG. 4.11 : Semiconductivity data for vitamin A alcohol powder cell (steady state condition) with the adsorption of different amounts of ethyl acetate vapour. Solid lines represent the temperature region of measurements, broken lines are extrapolations. The lines (1) ⟶ (5) refer to the states with the decreasing amount of adsorbed vapour. The E values are (1) 0.94 eV; (2) 1.08 eV; (3) 1.19 eV; (4) 1.43 eV; (5) 1.62 eV. The value of $T_0 \approx 403^\circ K$; $\sigma_0' = 3.10 \times 10^{-9}\ (\Omega \cdot cm)^{-1}$.



10^{-7}
10^{-8}
σ_0
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
$\sigma\ (\text{ohm cm})^{-1}$
T_0
1·8
2·6
3·4
4·2
4·4
$\frac{10^3}{T}\ (°K^{-1})$
1
2
3
4
5

FIG. 4.11

FIG. 4.12 : Semiconductivity data for vitamin A acetate powder cell (steady state condition) with the adsorption of different amounts of ethyl acetate vapour. Solid lines represent the temperature region of measurements, broken lines are extrapolations. The lines (1) ⟶ (5) refer to the states with the decreasing amount of adsorbed vapour. The E values are (1) 0.63 eV; (2) 0.89 eV; (3) 1.16 eV; (4) 1.52 eV; (5) 1.80 eV. The value of $T_o \approx 334^oK$; $\sigma_o' = 1.65 \times 10^{-10}$ $(\Omega.cm)^{-1}$.



10^{-8}
10^{-9}
σ_0'
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
σ (ohm·cm)$^{-1}$
T_0
1
2
3
4
5
1·8
2·6
3·4
4·2
$\frac{10^3}{T}$ ($^\circ K^{-1}$)

FIG. 4·12

change in activation energy on the amount of vapour adsorbed in powder cells of β-apo-8'-carotenal, astacene and methyl bixin can be understood from the log σ vs. $\frac{1}{T}$ plots in Figs. 4.13 - 4.15 respectively. In case of methyl bixin the adsorbed vapour is ethanol and in the other two semiconductors ethyl acetate vapour has been used. However, in all these cases it has been observed that the slope of the straight lines in the low temperature region decreases with the decreasing amount of the adsorbed vapour. Thus, these results indicate that the value of the activation energy of these three semiconductors decreases in a regular monotonic fashion as more vapours desorbs from the sample. Similar change in activation energy with the amount of vapour adsorbed was also observed with other vapours.

4.2.3 The characteristic temperature for the polyene semiconductors

According to equation (4.1), the extrapolated intercept of the log σ vs. $\frac{1}{T}$ plot on the ordinate at $1/T = 0$ yields the value of σ_0. So from this equation (4.1), it is expected that the straight lines in the low temperature region in each of the log σ vs. $\frac{1}{T}$ plots should meet at a single point on the ordinate at $\frac{1}{T} = 0$ yielding a single value of σ_0 if the conductivity change is solely due to the change in activation energy E as in case of β-carotene[14]. But from the log σ vs. $\frac{1}{T}$ plots (Figs. 4.6 - 4.15) it is observed that no single value of σ_0 is obtained if either $T \to \infty$ or $E \to 0$. The extrapolated lines intercept the ordinate at a wide varieties of positions, but they all pass approximately through a single point at a temperature T_0, characteristics of the semiconductor. This is exactly what is expected

FIG. 4.13 : Semiconductivity data for β -apo-8'-carotenal powder cell (steady state condition) with the adsorption of different amounts of ethyl acetate vapour. Solid lines represent the temperature region of measurements, broken lines are extrapolations. The lines (1) ⟶ (5) refer to the states with the decreasing amount of adsorbed vapour. The E values are (1) 5.26 eV; (2) 3.90 eV; (3) 3.23 eV; (4) 2.19 eV; (5) 1.58 eV. The value of $T_o \approx 261\ ^oK$; $\sigma_o' = 170 \times 10^{-16}\ (\Omega \cdot cm)^{-1}$.

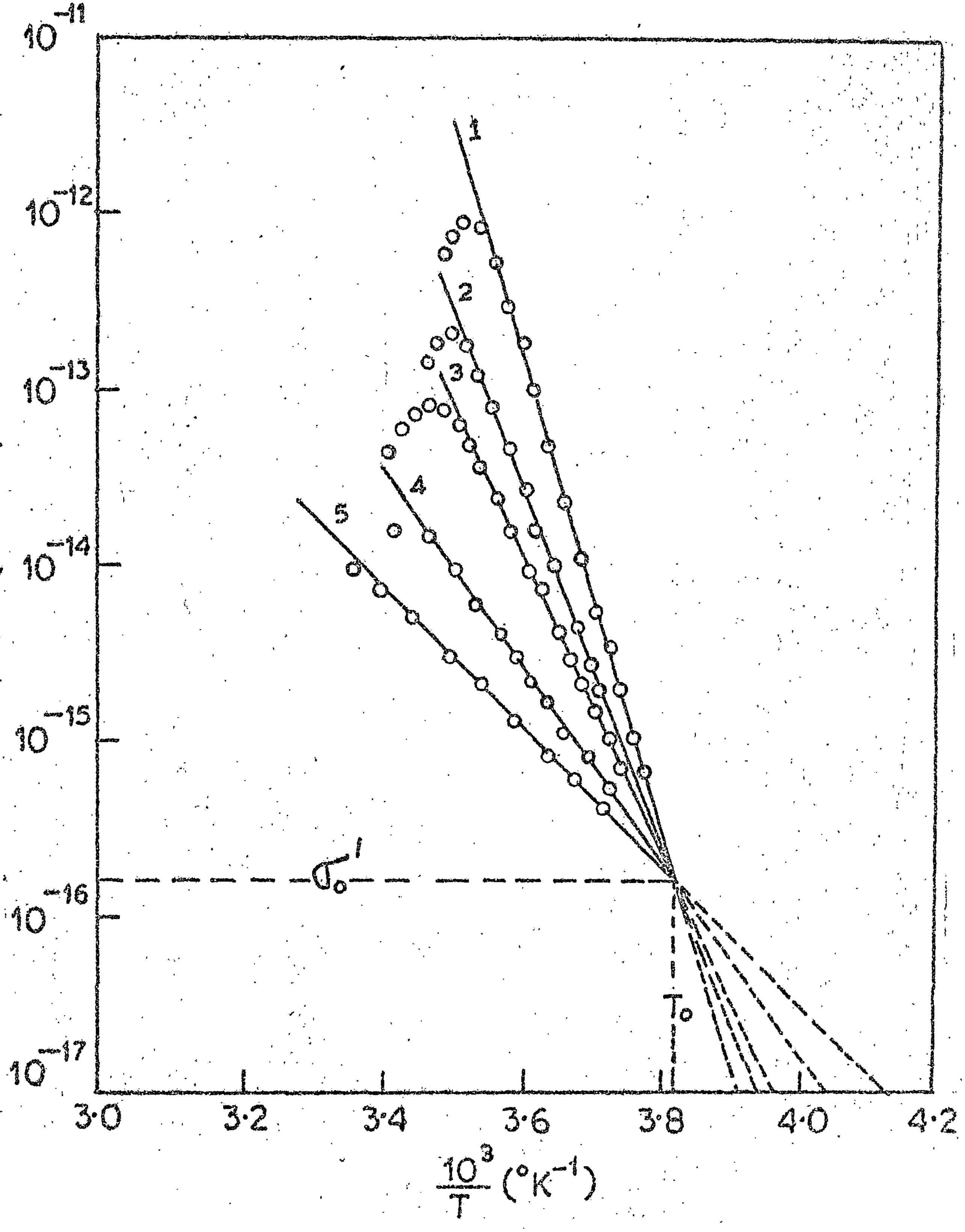
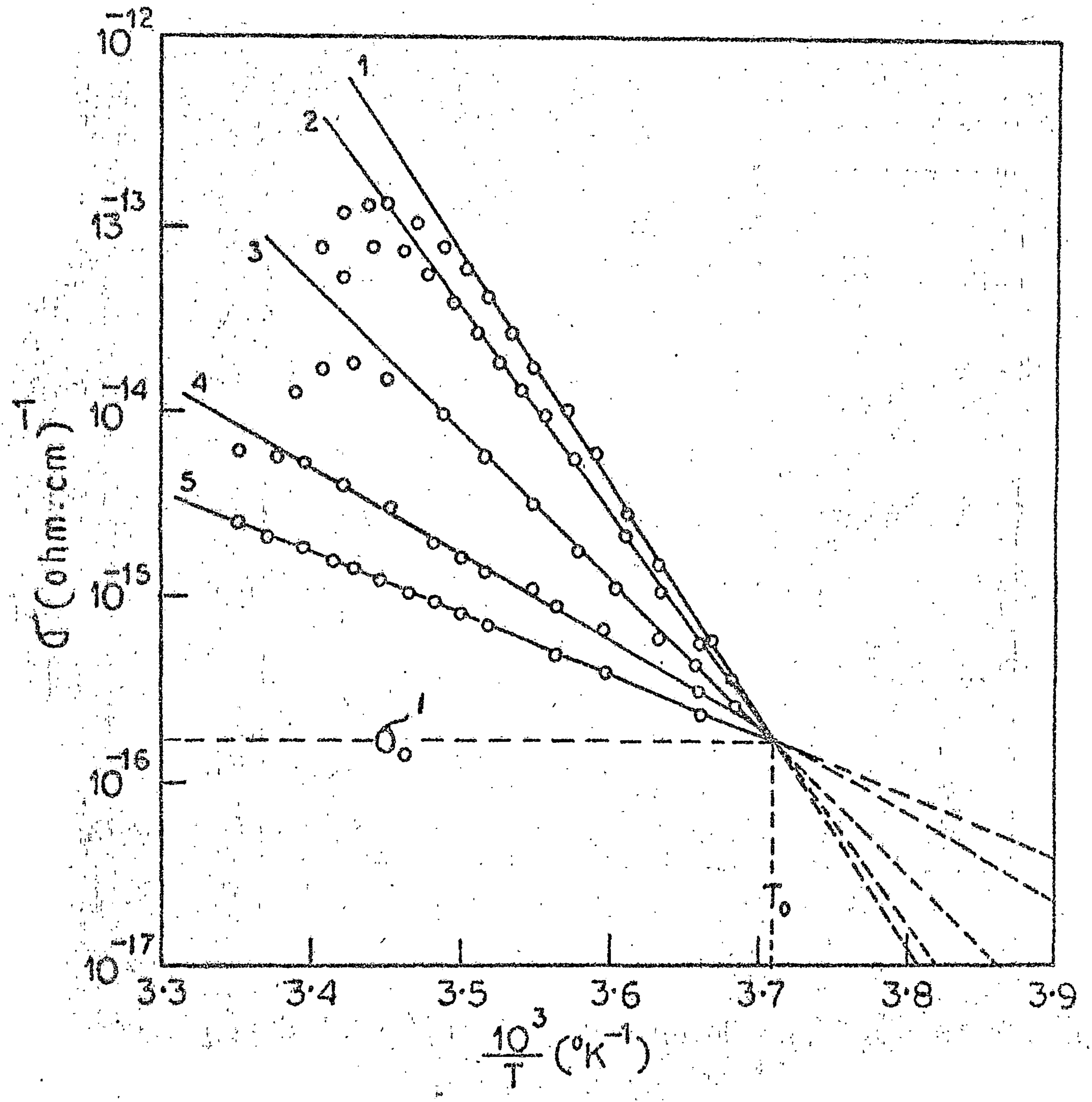

10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
$\sigma'(\mathrm{ohm.cm})^{-1}$
1
2
3
4
5
σ_o'
T_o
3·0
3·2
3·4
3·6
3·8
4·0
4·2
$\frac{10^3}{T}$ (°K^{-1})

FIG. 4·13

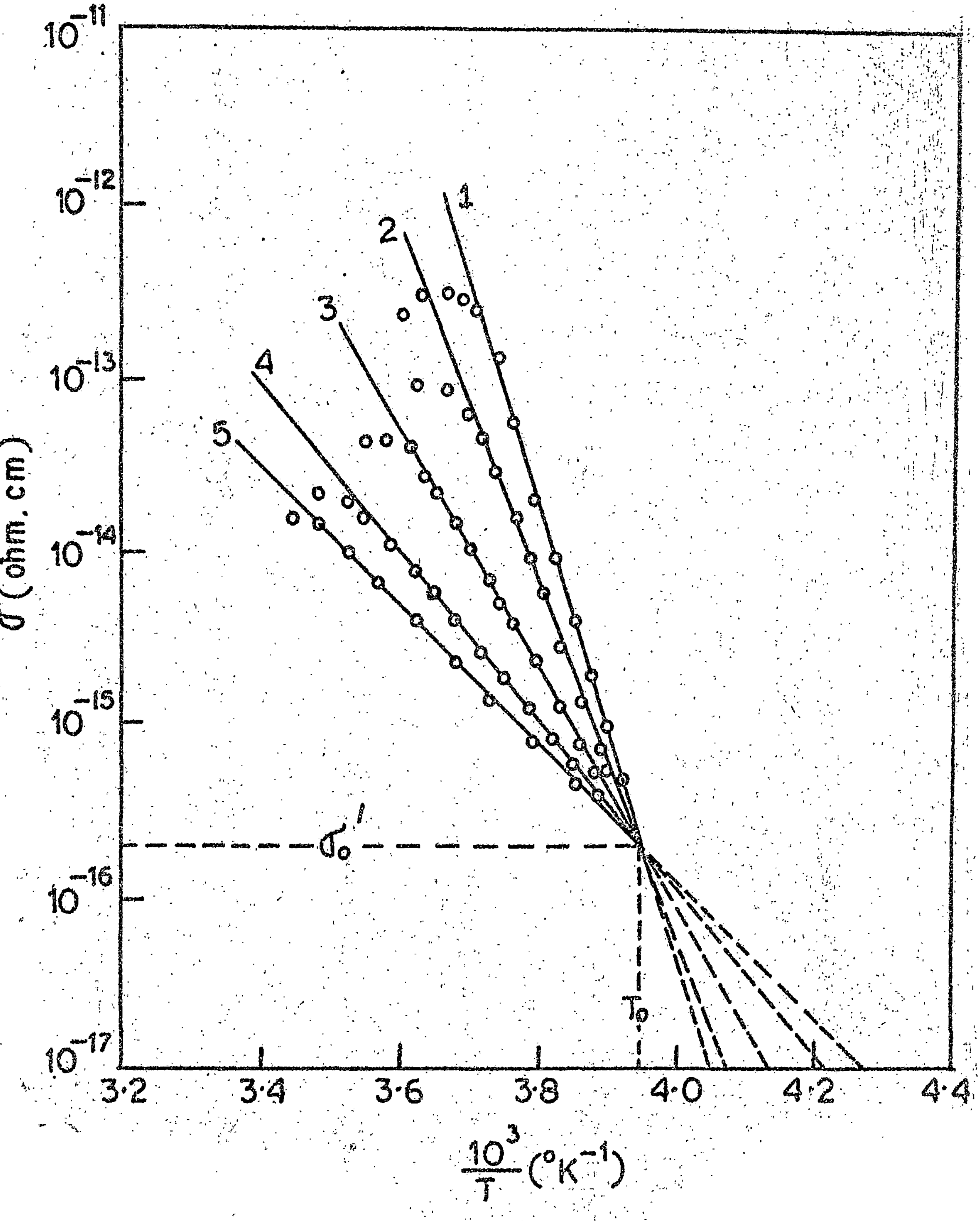
FIG. 4.14 : Semiconductivity data for astacene powder cell (steady state condition) with the adsorption of different amounts of ethyl acetate vapour. Solid lines represent the temperature region of measurements, broken lines are extrapolations. The lines (1) → (5) refer to the states with the decreasing amount of adsorbed vapour. The E values are (1) 4.93 eV; (2) 4.38 eV; (3) 3.13 eV; (4) 1.86 eV; (5) 1.31 eV. The value of $T_o \approx 270^oK$; $\sigma_o' = 1.80 \times 10^{-16} (\Omega . cm)^{-1}$.



10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
σ (ohm·cm)$^{-1}$
1
2
3
4
5
σ_0'
T_0
3·3
3·4
3·5
3·6
3·7
3·8
3·9
$\frac{10^3}{T}$ (°K^{-1})

FIG. 4·14

FIG. 4.15 : Semiconductivity data for methyl bixin powder cell (steady state condition) with the adsorption of different amounts of ethanol vapour. Solid lines represent the temperature region of measurements, broken lines are extrapolations. The lines (1) → (5) refer to the states with the decreasing amount of adsorbed vapour. The E values are (1) 4.98 eV; (2) 3.04 eV; (3) 2.82 eV; (4) 1.92 eV; (5) 1.61 eV. The value of $T_0 \approx 253^\circ K$; $\sigma_0' = 1.95 \times 10^{-16} (\Omega \cdot cm)^{-1}$.



10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
$\sigma\,(\text{ohm.cm})^{-1}$
1
2
3
4
5
σ_o'
T_o
3·2
3·4
3·6
3·8
4·0
4·2
4·4
$\frac{10^3}{T}\,(^\circ K^{-1})$

FIG. 4·15

from equation (4.3). At these characteristic temperatures (T_0), the value of $\sigma(T_0)$ gives the σ_0' values. The values of T_0's and σ_0''s obtained from different log σ vs. $\frac{1}{T}$ plots for the semiconductors studied are shown in table 4.1. From table 4.1 it is observed that the two sets of values of T_0's and σ_0''s are in good agreement.

The plots of log σ_0 vs. E are linear as expected from equation (4.4) [Since $\log \sigma_0 = E/2kT_0 + \log \sigma_0'$] and are shown in Figs. 4.16 - 4.19 for vitamin A (alcohol and acetate), β-apo-8'-carotenal, astacene and methyl bixin respectively. The values of T_0 and σ_0' can be obtained from the slopes and intercepts respectively of the log σ_0 vs. E plots. The values of T_0 and σ_0' obtained from the log σ_0 vs. E plots for different polyenes are shown in table 4.2. Thus the values of T_0 and σ_0' (tables 4.1 and 4.2) obtained from various log σ vs. $\frac{1}{T}$ and log σ_0 vs. E plots are consistent and show excellent agreement[18]. Using the values of T_0's and σ_0''s obtained from the log σ_0 vs. E plots we have calculated the expected σ_0 values and compare these with experimentally measured values. These are shown in the tables 4.3 - 4.12 for the various polyene semiconductors. The data presented in the tables 4.3 - 4.12 confirm the validity of equation (4.3) for the polyenes studied.

The plots of log $\sigma(T_1)$ against E are shown in Figs. 4.20-4.23 for vitamin A (alcohol and acetate), β-apo-8'-carotenal, astacene and methyl bixin respectively. In each case a good straight line is obtained as expected from equation (4.5). The value of the observed

Table - 4.1

The values of T_0's and σ_0''s obtained from different $\log \sigma$ vs. $\frac{1}{T}$ plots of some polyene semiconductors

Semiconductor	Value of T_0 (°K) obtained from the $\log \sigma$ vs. $\frac{1}{T}$ plots for		Value of σ_0' in $(\Omega \cdot cm)^{-1}$ obtained from the $\log \sigma$ vs. $\frac{1}{T}$ plots for	
	adsorption of different vapours	adsorption of different amounts of a particular vapour	adsorption of different vapours	adsorption of different amounts of a particular vapour
Vitamin A alcohol[1]	402	403	2.65×10^{-9}	3.10×10^{-9}
Vitamin A acetate[2]	336	334	1.80×10^{-10}	1.65×10^{-10}
β-apo-8'-carotenal[3]	258	261	0.90×10^{-16}	1.70×10^{-16}
Astacene[4]	272	270	2.15×10^{-16}	1.80×10^{-16}
Methyl bixin[5]	251	253	0.85×10^{-16}	1.95×10^{-16}

1. From Figs. 4.6 and 4.11; 2. From Figs. 4.7 and 4.12;
3. From Figs. 4.8 and 4.13; 4. From Figs. 4.9 and 4.14;
5. From Figs. 4.10 and 4.15.

FIG. 4.16 : Plots of the log σ_0 values against the activation energies (E) for vitamin A (alcohol and acetate). The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour. Slopes and σ_0' values are 14.45 eV^{-1} and 2.60 x 10^{-9} (Ω-cm)$^{-1}$ for vitamin A alcohol and 17.52 eV^{-1} and 1.50 x 10^{-10} (Ω-cm)$^{-1}$ for vitamin A acetate respectively. The right and left scales refer to vitamin A alcohol and vitamin A acetate respectively.

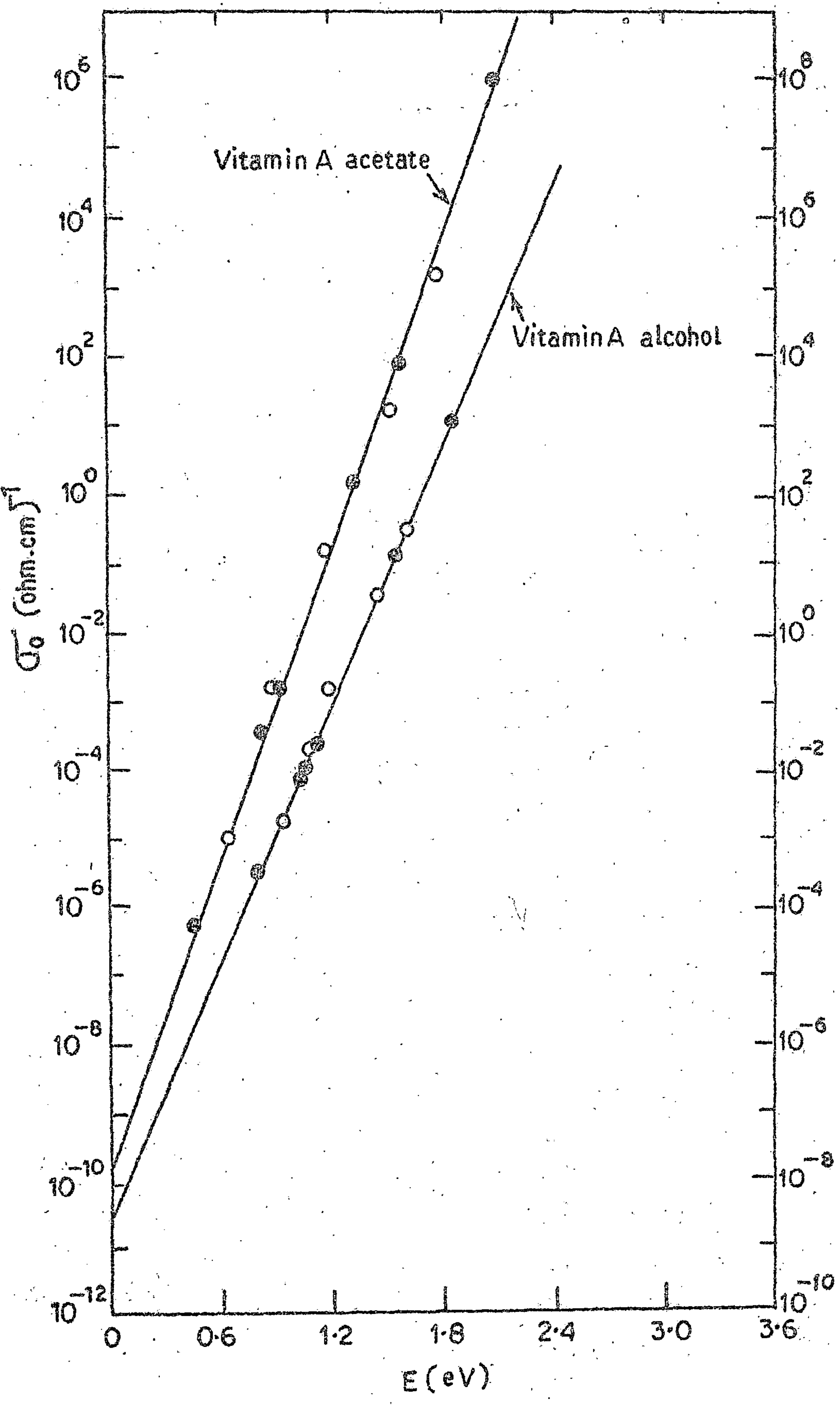
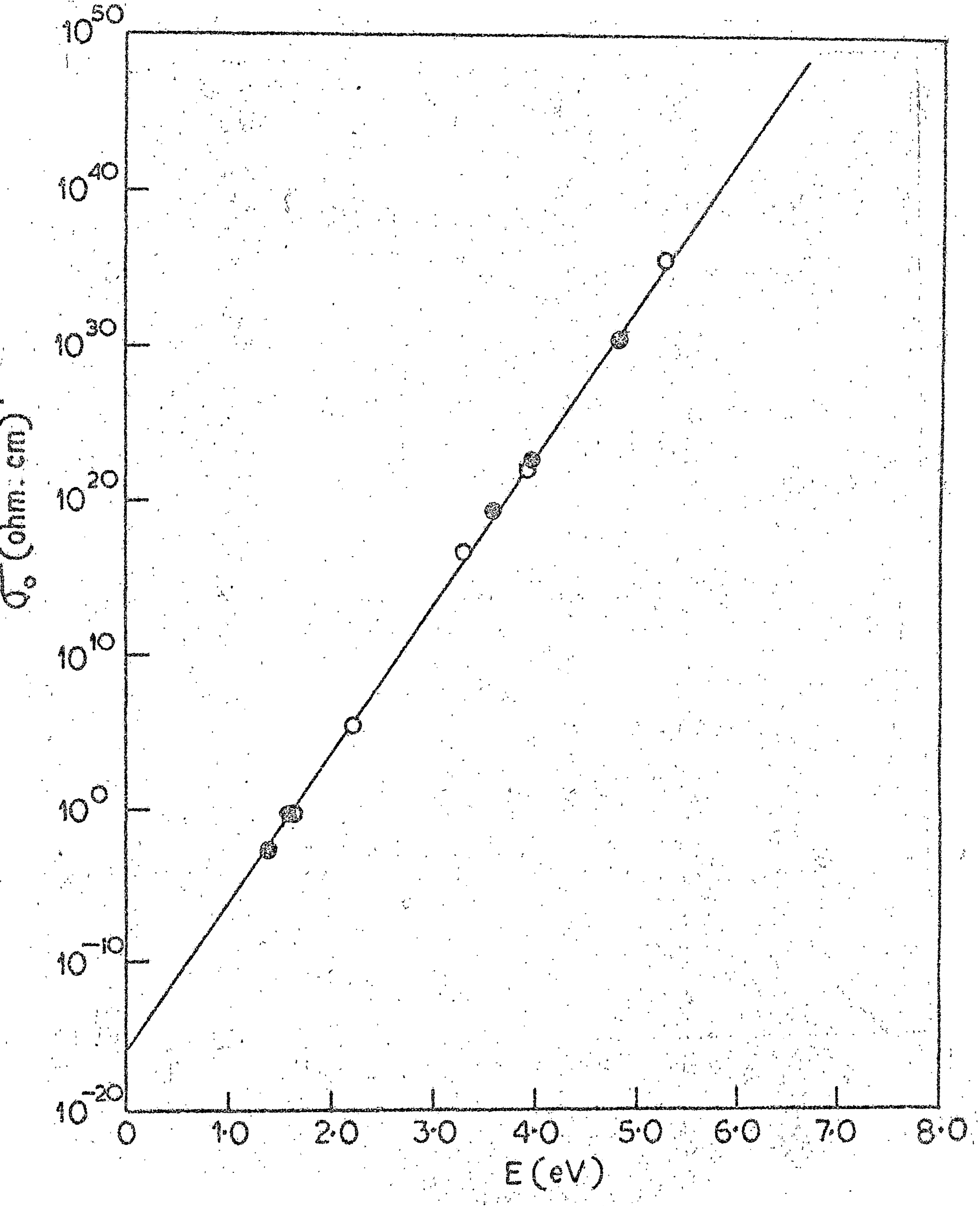

Vitamin A acetate
Vitamin A alcohol
σ_0 (ohm.cm)$^{-1}$
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^8
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
0
0·6
1·2
1·8
2·4
3·0
3·6
E (eV)

FIG. 4·16

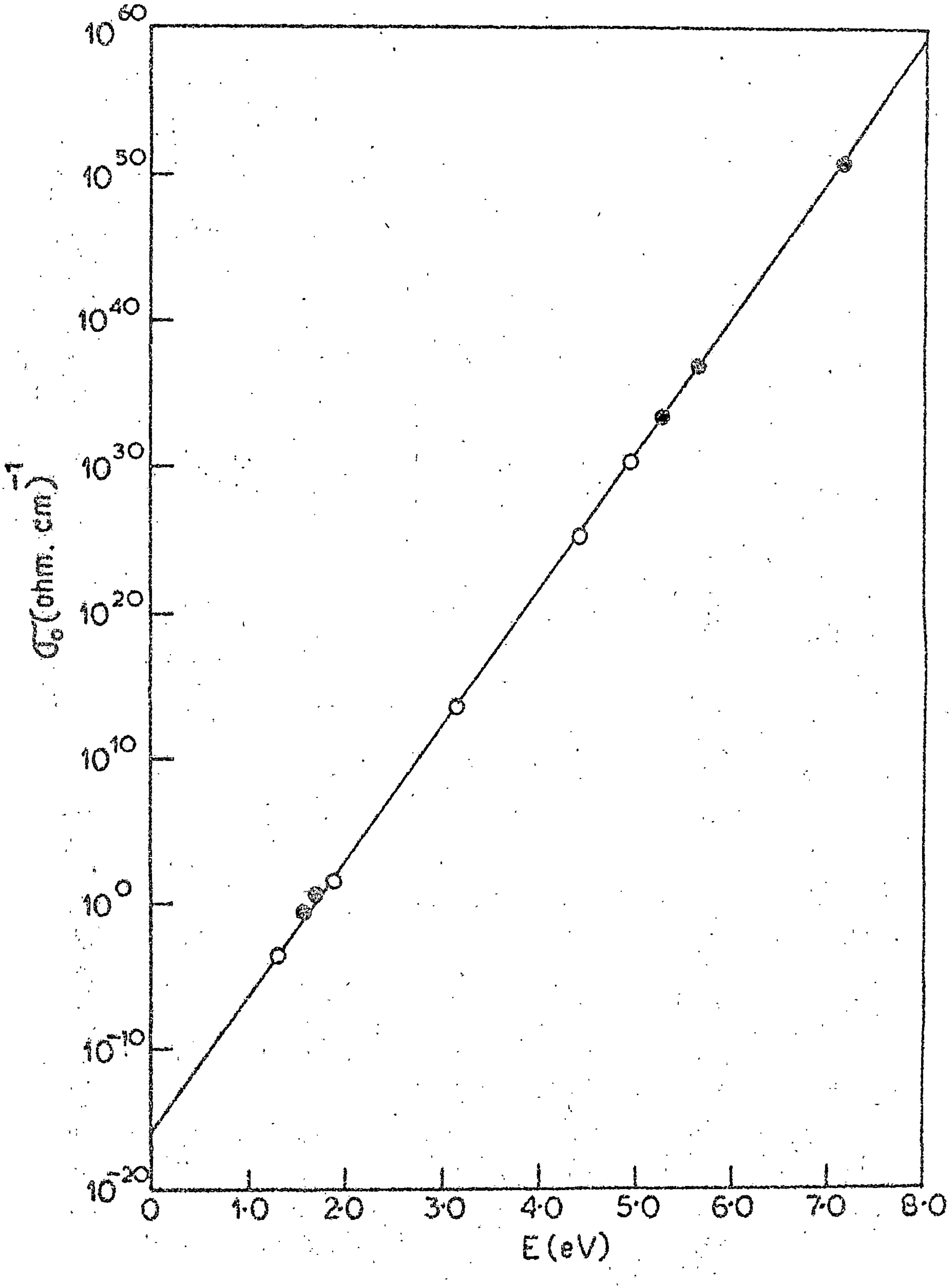
FIG. 4.17 : Plot of the log σ_0 values against the activation energies (E) for β-apo-8'-carotenal. The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour. The value of slope = 22.44 eV^{-1}; $\sigma_0' = 1.47 \times 10^{-16}\ (\Omega \cdot cm)^{-1}$.



10^{50}
10^{40}
10^{30}
10^{20}
10^{10}
10^{0}
10^{-10}
10^{-20}
$\sigma_o\ (\text{ohm}.\text{cm})^{-1}$
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
E (eV)

FIG. 4·17

FIG. 4.12 : Plot of log σ_0 values against the activation energies (E) for tetracene. The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour. The value of slope = 21.64 eV^{-1}; $\sigma_0' = 2.00 \times 10^{-16}$ $(\Omega \cdot cm)^{-1}$.



10^{60}
10^{50}
10^{40}
10^{30}
10^{20}
10^{10}
10^{0}
10^{-10}
10^{-20}
$\sigma_0 (\text{ohm. cm})^{-1}$
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
E (eV)

FIG. 4·18

FIG. 4.19 : Plot of log σ_0 values against the activation energies (E) for methyl bixin. The dark circles refer to different vapours and the open circles to different amounts of ethanol vapour. The value of slope = 23.31 eV^{-1}; $\sigma_0' = 1.58 \times 10^{-16} (\Omega \cdot cm)^{-1}$.

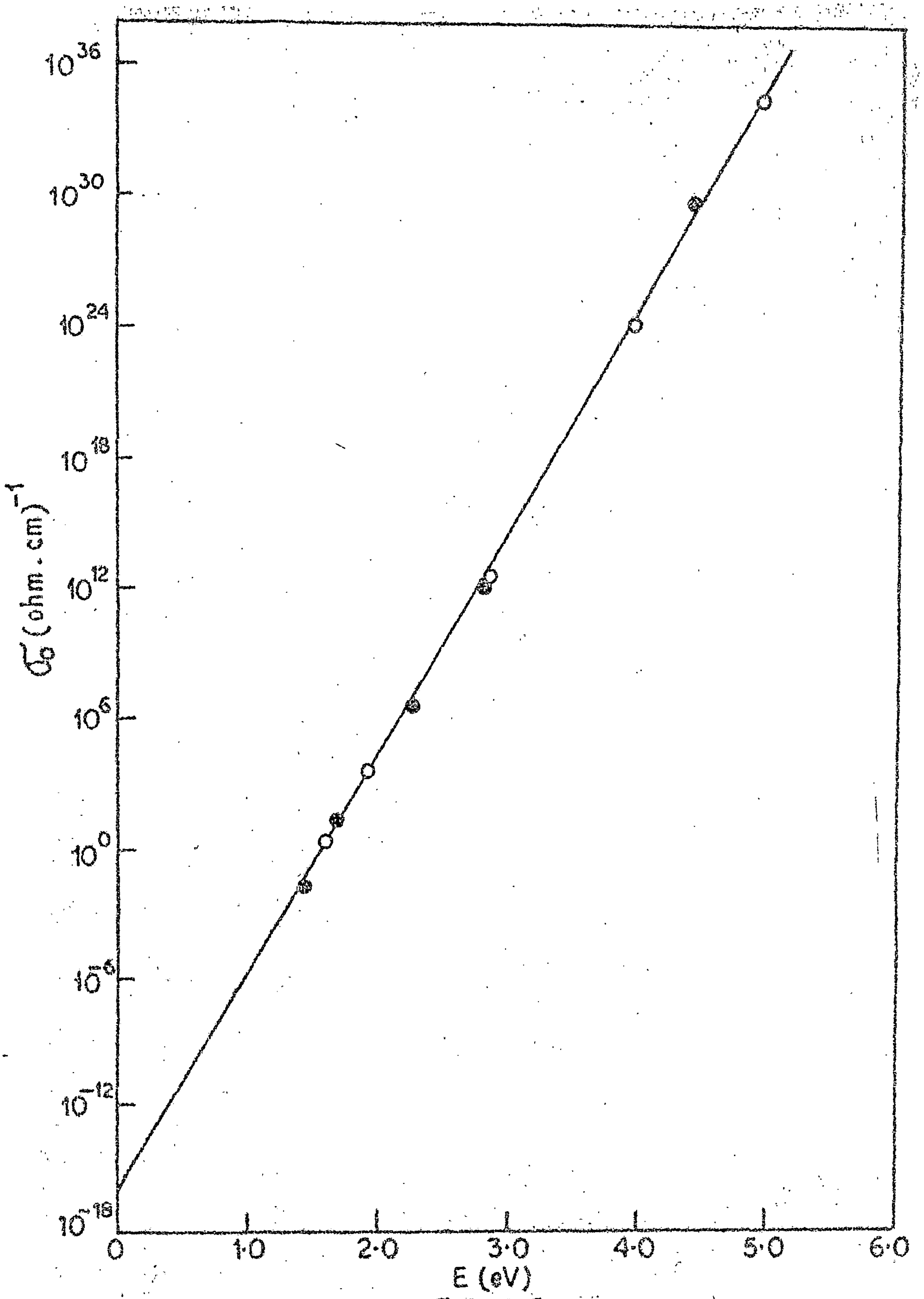

10^{36}
10^{30}
10^{24}
10^{18}
10^{12}
10^{6}
10^{0}
10^{-6}
10^{-12}
10^{-18}
σ_0 (ohm . cm)$^{-1}$
0
1·0
2·0
3·0
4·0
5·0
6·0
E (eV)

FIG. 4.19

Table - 4.2

Values of T_0 and σ_0' obtained from various $\log \sigma_0$ vs. T plots

Semiconductor	Value of T_0 ($^{\circ}$K)	Value of σ_0' in $(\Omega . \mathrm{cm})^{-1}$
Vitamin A alcohol[1]	404	2.80×10^{-9}
Vitamin A acetate[1]	333	1.50×10^{-10}
β-apo-8'-carotenal[2]	261	1.47×10^{-16}
Astacene[3]	270	2.00×10^{-16}
Methyl bixin[4]	251	1.68×10^{-16}

[1] From Fig. 4.16; [2] From Fig. 4.17;

[3] From Fig. 4.18; [4] From Fig. 4.19.

Table - 4.3

Semiconduction parameters for vitamin A alcohol on adsorption of various vapours according to equation (4.3)

Vapours adsorbed	Vitamin A alcohol $(2kT_0)^{-1} = 14.45\ \text{eV}^{-1}$ $\sigma_0' = 2.80 \times 10^{-9}\ (\Omega\cdot\text{cm})^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega\cdot\text{cm})^{-1}$	Measured* $\sigma_0\ (\Omega\cdot\text{cm})^{-1}$
Toluene	0.80	2.93×10^{-4}	4.10×10^{-4}
Benzene	1.04	9.41×10^{-3}	7.98×10^{-3}
Ethyl acetate	1.06	1.26×10^{-2}	1.15×10^{-2}
n-Heptane	1.10	2.24×10^{-2}	2.60×10^{-2}
Ethanol	1.55	1.49×10^{1}	1.30×10^{1}
Methanol	1.82	7.39×10^{2}	1.25×10^{3}

* From Fig. 4.6

Table - 4.4

Semiconduction parameters for vitamin A acetate on adsorption of various vapours according to equation (4.3)

Vapours adsorbed	Vitamin A acetate $(2kT_0)^{-1} = 17.52$ eV^{-1} $\sigma_0' = 1.50 \times 10^{-10}$ $(\Omega.\text{cm})^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega.\text{cm})^{-1}$	Measured* σ_0 $(\Omega.\text{cm})^{-1}$
Toluene	0.448	3.84×10^{-7}	6.1×10^{-7}
Benzene	0.821	2.65×10^{-4}	3.8×10^{-4}
Ethyl acetate	0.896	9.85×10^{-4}	1.7×10^{-3}
n-Heptane	1.310	1.39×10^{0}	1.2×10^{0}
Ethanol	1.570	1.32×10^{2}	7.0×10^{1}
Methanol	2.070	8.44×10^{5}	8.0×10^{5}

* From Fig. 4.7

Table - 4.5

Semiconduction parameters for β-apo-8'-carotenal on adsorption of various vapours according to equation (4.3)

Vapours adsorbed	β-apo-8'-carotenal $(2kT_0)^{-1} = 22.44$ eV^{-1} $\sigma_0' = 1.47 \times 10^{-16}$ $(\Omega \cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega \cdot cm)^{-1}$	Measured* σ_0 $(\Omega \cdot cm)^{-1}$
Ethanol	4.80	8.83×10^{30}	2.5×10^{30}
Methanol	3.94	3.67×10^{22}	7.0×10^{22}
Ethyl acetate	3.58	1.13×10^{19}	2.8×10^{19}
Toluene	1.57	2.93×10^{-1}	2.9×10^{-1}
n-Heptane	1.40	6.47×10^{-3}	2.4×10^{-3}

* From Fig. 4.8

Table - 4.6

Semiconduction parameters for astacene on adsorption of various vapours according to equation (4.3)

Vapours adsorbed	Astacene $(2kT_0)^{-1} = 21.64\ eV^{-1}$ $\sigma_0' = 2.00 \times 10^{-16}\ (\Omega.cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega.cm)^{-1}$	Measured* σ_0 $(\Omega.cm)^{-1}$
Ethanol	7.14	2.53×10^{51}	0.7×10^{51}
Methanol	5.63	1.63×10^{37}	1.4×10^{37}
Ethyl acetate	5.26	5.43×10^{33}	3.9×10^{33}
Benzene	1.71	2.35×10^{0}	4.5×10^{0}
Toluene	1.57	1.14×10^{-1}	3.2×10^{-1}

* From Fig. 4.9

Table - 4.7

Semiconduction parameters for methyl bixin on adsorption of various vapours according to equation (4.3)

Vapours adsorbed	Methyl bixin $(2kT_0)^{-1} = 23.31\ \mathrm{eV}^{-1}$ $\sigma_0' = 1.88 \times 10^{-16}\ (\Omega.\mathrm{cm})^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega.\mathrm{cm})^{-1}$	Measured* σ_0 $(\Omega.\mathrm{cm})^{-1}$
Ethanol	4.43	1.11×10^{29}	4.5×10^{29}
Methanol	2.80	3.50×10^{12}	1.2×10^{12}
Ethyl acetate	2.25	9.47×10^{6}	4.6×10^{6}
Benzene	1.68	1.60×10^{1}	2.8×10^{1}
Toluene	1.44	5.97×10^{-2}	4.0×10^{-2}

* From Fig. 4.10

Table - 4.8

Semiconduction parameters for vitamin A alcohol on adsorption of ethyl acetate vapour of different amounts according to equation (4.3)

Curve No. of Fig. 4.11	Vitamin A alcohol $(2kT_0)^{-1} = 14.45$ eV^{-1} $\sigma_0' = 2.80 \times 10^{-9}$ $(\Omega \cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega \cdot cm)^{-1}$	Measured* σ_0 $(\Omega \cdot cm)^{-1}$
1	0.94	2.22×10^{-3}	2.0×10^{-3}
2	1.08	1.68×10^{-2}	2.3×10^{-2}
3	1.19	8.22×10^{-2}	1.8×10^{-1}
4	1.43	2.64×10^{0}	3.5×10^{0}
5	1.62	4.11×10^{1}	3.0×10^{1}

Curve No. 1→5 corresponds to the decreasing amount of adsorbed ethyl acetate vapour.

* From Fig. 4.11

Table - 4.9

Semiconduction parameters for vitamin A acetate on adsorption of ethyl acetate vapour of different amounts according to equation (4.3)

Curve No. of Fig. 4.12	Vitamin A acetate $(2kT_0)^{-1} = 17.52\ eV^{-1}$ $\sigma_0' = 1.60 \times 10^{-10}\ (\Omega\cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega\cdot cm)^{-1}$	Measured* σ_0 $(\Omega\cdot cm)^{-1}$
1	0.63	9.32×10^{-6}	1.0×10^{-5}
2	0.89	8.87×10^{-4}	1.7×10^{-3}
3	1.16	1.00×10^{-1}	1.6×10^{-1}
4	1.52	5.51×10^{1}	1.5×10^{1}
5	1.80	7.43×10^{3}	1.2×10^{3}

Curve No. 1 → 5 corresponds to the decreasing amount of adsorbed ethyl acetate vapour.

* From Fig. 4.12

Table - 4.10

Semiconduction parameters for β-apo-8'-carotenal on adsorption of ethyl acetate vapour of different amounts according to equation (4.3)

Curve No. of Fig. 4.13	β-apo-8'-carotenal $(2kT_0)^{-1} = 22.44\ eV^{-1}$ $\sigma_0' = 1.47 \times 10^{-16}\ (\Omega \cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' \exp(E/2kT_0)$ $(\Omega \cdot cm)^{-1}$	Measured* σ_0 $(\Omega \cdot cm)^{-1}$
1	5.26	2.68×10^{35}	3.4×10^{35}
2	3.90	1.49×10^{22}	2.5×10^{22}
3	3.28	1.35×10^{16}	4.1×10^{16}
4	2.19	3.23×10^{5}	2.8×10^{5}
5	1.58	3.68×10^{-1}	5.1×10^{-1}

Curve No. 1 → 5 corresponds to the decreasing amount of adsorbed ethyl acetate vapour.

* From Fig. 4.13

Table - 4.11

Semiconduction parameters for astacene on adsorption of ethyl acetate vapour of different amounts according to equation (4.3)

Curve No. of Fig. 4.14	Astacene $(2kT_0)^{-1}$ = 21.64 eV^{-1} σ_0' = 2.00 x 10^{-16} $(\Omega\cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' exp(E/2kT_0)$ $(\Omega\cdot cm)^{-1}$	Measured* σ_0 $(\Omega\cdot cm)^{-1}$
1	4.93	4.30 x 10^{30}	2.1 x 10^{30}
2	4.38	2.91 x 10^{25}	2.7 x 10^{25}
3	3.13	5.21 x 10^{13}	3.4 x 10^{13}
4	1.86	6.04 x 10^{1}	2.7 x 10^{1}
5	1.31	4.10 x 10^{-4}	2.1 x 10^{-4}

Curve No. 1→ 5 corresponds to the decreasing amount of adsorbed ethyl acetate vapour.

* From Fig. 4.14

Table - 4.12

Semiconduction parameters for methyl bixin on adsorption of ethanol vapour of different amounts according to equation (4.3)

Curve No. of Fig. 4.15	Methyl bixin $(2kT_0)^{-1} = 23.31\ eV^{-1}$ $\sigma_0' = 1.58 \times 10^{-16}\ (\Omega\cdot cm)^{-1}$		
	E(eV)	Calculated $\sigma_0 = \sigma_0' exp(E/2kT_0)$ $(\Omega\cdot cm)^{-1}$	Measured* σ_0 $(\Omega\cdot cm)^{-1}$
1	4.98	4.10×10^{34}	2.1×10^{34}
2	3.94	1.22×10^{24}	1.5×10^{24}
3	2.82	5.68×10^{12}	3.0×10^{12}
4	1.92	4.32×10^{3}	4.6×10^{3}
5	1.61	3.14×10^{0}	2.3×10^{0}

Curve No. 1 → 5 corresponds to the decreasing amount of adsorbed ethanol vapour.

* From Fig. 4.15

FIG. 4.20 : Plots of log σ at a constant temperature ($1/T_1 = 3.30 \times 10^{-3}\ {}^{o}K^{-1}$) vs. E for vitamin A (alcohol and acetate). The left and right scales correspond to vitamin A alcohol and vitamin A acetate respectively. The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour. Slopes and σ_o' values are 7.70 eV^{-1} and 2.85×10^{-9} $(\Omega \cdot cm)^{-1}$ for vitamin A alcohol; 4.55 eV^{-1} and 1.60×10^{-10} $(\Omega \cdot cm)^{-1}$ for vitamin A acetate respectively.

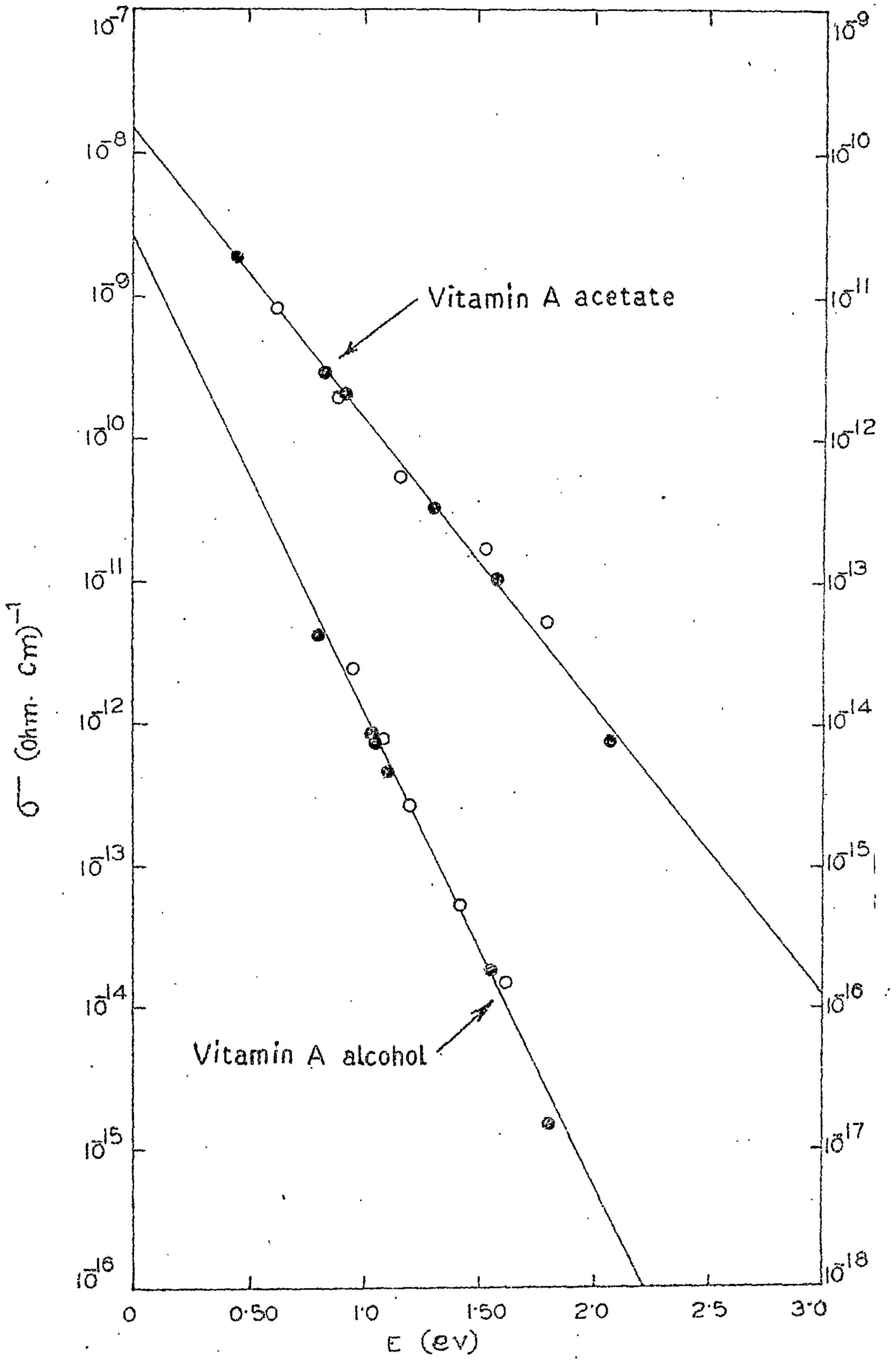

10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
10^{-18}
σ (ohm. cm)$^{-1}$
Vitamin A acetate
Vitamin A alcohol
0
0·50
1·0
1·50
2·0
2·5
3·0
E (ev)

FIG. 4·20

FIG. 4.21 : Plot of log σ at a constant temperature ($1/T_1 = 3.60 \times 10^{-3}\,°K^{-1}$) vs. E for β-apo-8'-carotenal. The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour.
The value of slope = 1.39 eV^{-1} ; $\sigma_0' = 1.25 \times 10^{-16} (\Omega \cdot cm)^{-1}$.

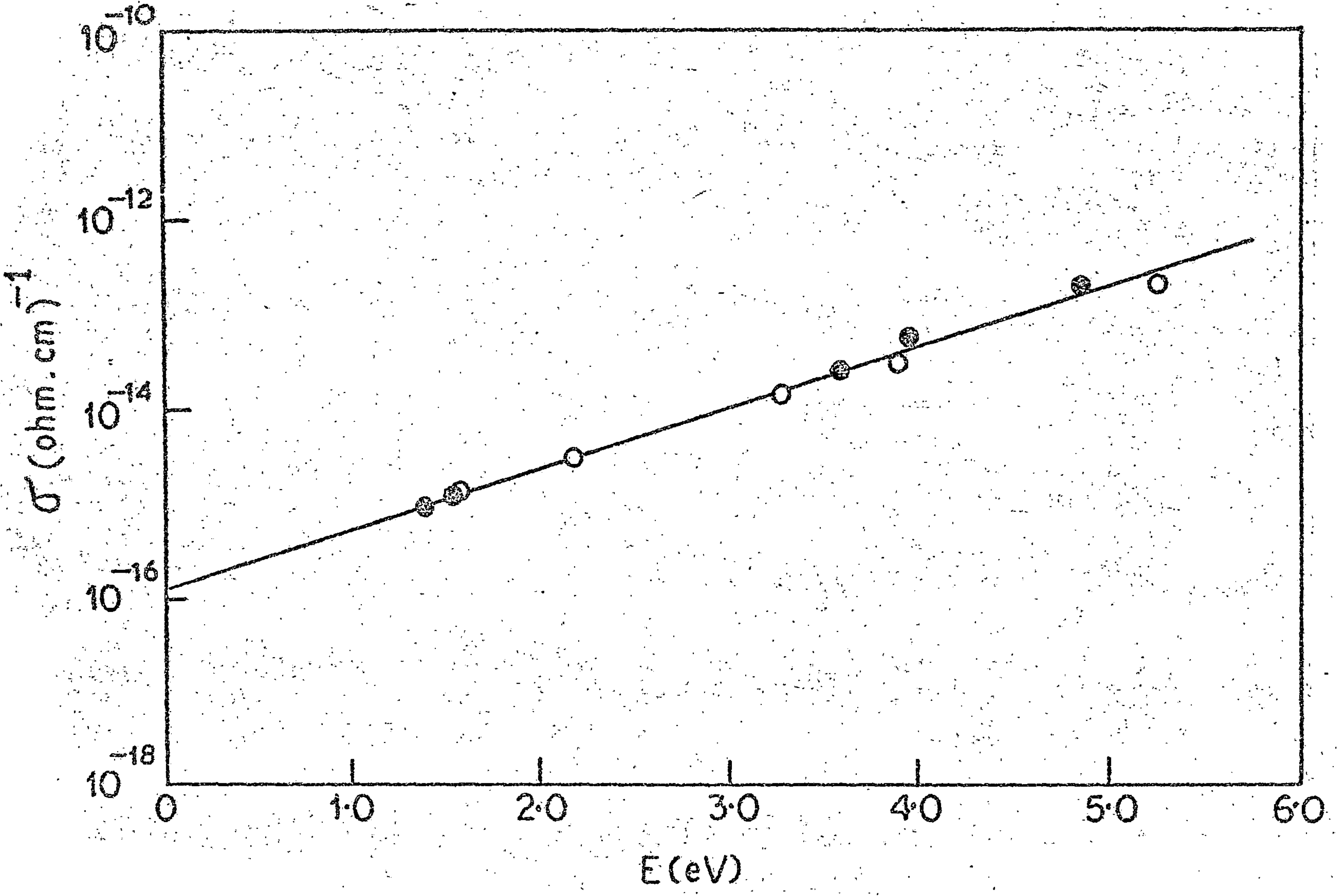
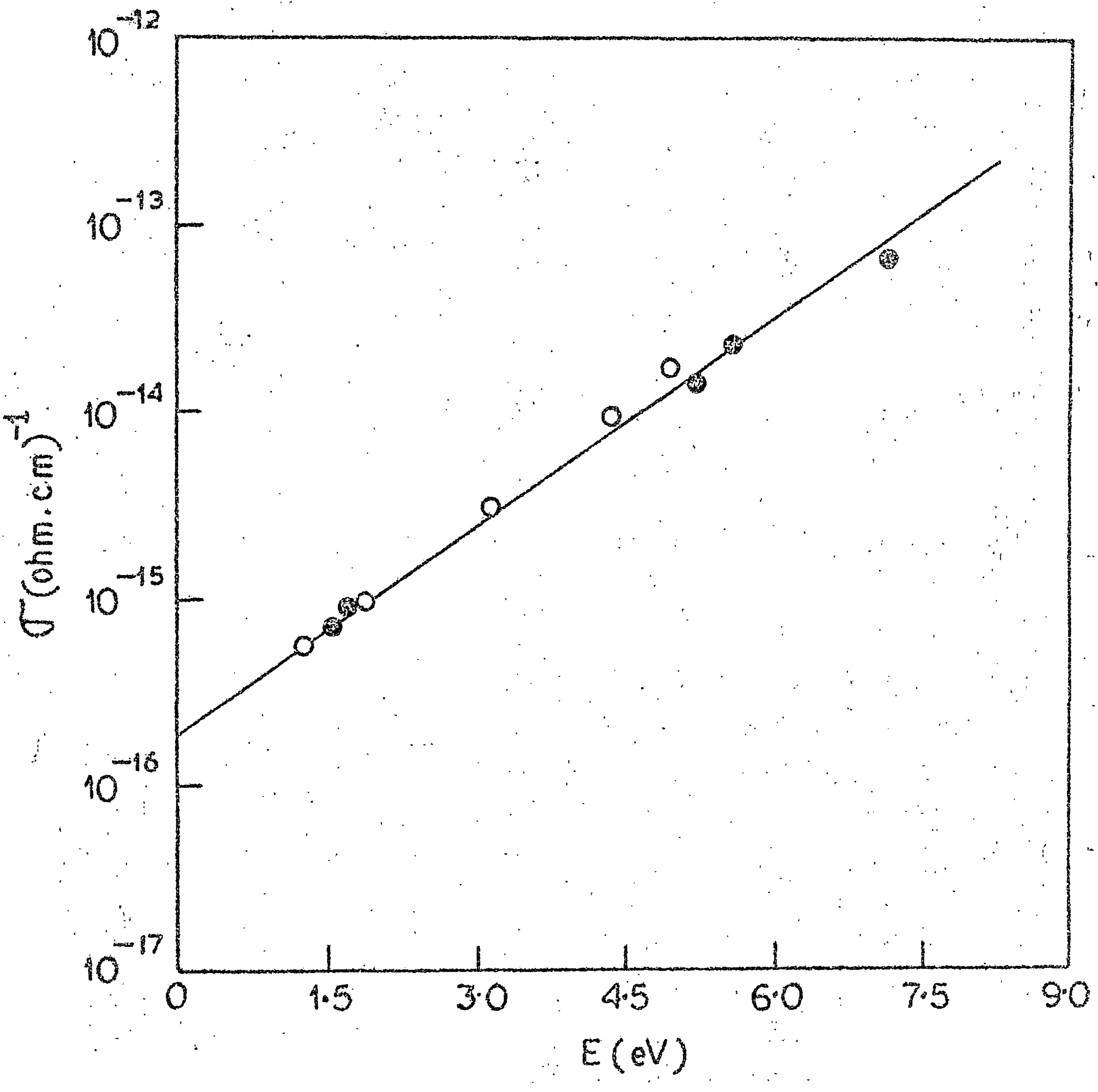


FIG. 4·21

FIG. 4.22 : Plot of log σ at a constant temperature ($\frac{1}{T_1} = 3.65 \times 10^{-3}\ {}^{o}K^{-1}$) vs. E for estacene. The dark circles refer to different vapours and the open circles to different amounts of ethyl acetate vapour. The value of slope = 0.86 eV^{-1}; $\sigma_0' = 1.80 \times 10^{-16}\ (\Omega \cdot cm)^{-1}$.



10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
$\sigma\,(\mathrm{ohm.cm})^{-1}$
0
1·5
3·0
4·5
6·0
7·5
9·0
E (eV)

FIG. 4·22

FIG. 4.23 : Plot of log σ at a constant temperature ($\frac{1}{T_1}$ = 3.70 x 10^{-3} $^{\circ}K^{-1}$) vs. E for methyl bixin. The dark circles refer to different vapours and open circles to different amounts of ethanol vapour. The value of slope = 1.60 eV^{-1} ; σ_0' = 1.00 x 10^{-26} $(\Omega \cdot cm)^{-1}$.

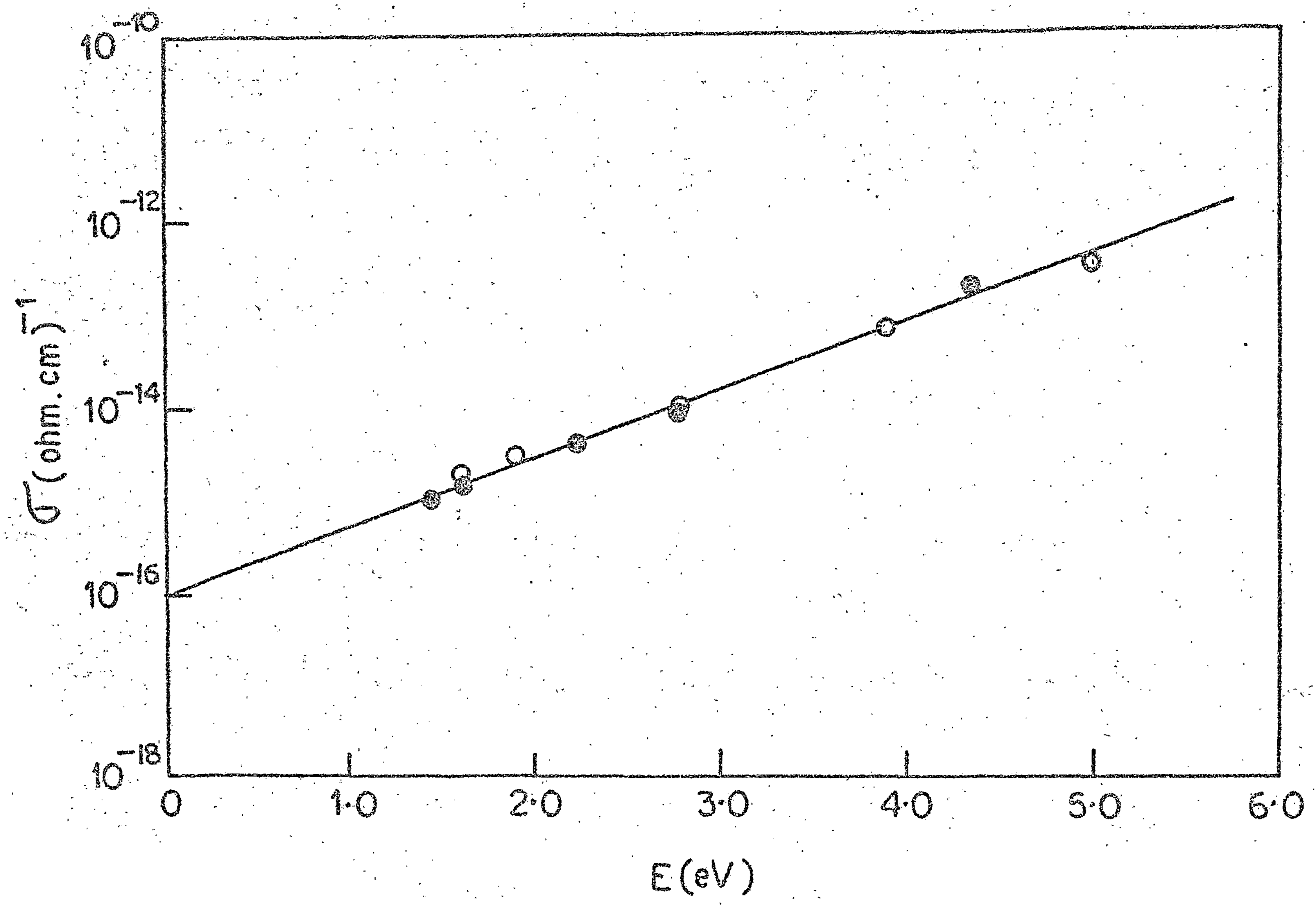


FIG. 4·23

slope of the line for each polyene is shown in table 4.13 for comparison with the value of the slope expected from the equation (4.6). The value of σ_0' obtained from each log σ vs. E plot is also shown in this table to compare this value with the values obtained from the log σ vs. $\frac{1}{T}$ and log σ_0 vs. E plots. From the table 4.13 it is seen that the observed slopes from log σ vs. E plots are in excellent agreement with the slopes expected from equation (4.6). Also the σ_0' values obtained from log σ vs. E plots agree satisfactorily with the values obtained from the log σ_0 vs. E and log σ vs. $\frac{1}{T}$ plots. Thus the high correlation between the relevant parameters in the semiconductors under study on adsorption of various vapours indicates that compensation rule is valid in these semiconductors and that σ_0 and E are indeed physically related.[18,19]

4.3 Discussion

There are number of theses about the mechanism of conduction in organic semiconductors leading to compensation effect. The carrier injection model of Green[20] produces the type of activation energy dependence of the pre-exponential factor as observed experimentally but it does not provide any physical basis for the interpretation of T_0.

Kemeny and Rosenberg[21] observed compensation law in tunneling of small polaron through molecular barrier from thermally activated energy levels of molecules. Their model predicts that $T_0 = \frac{\theta}{2}$ (where θ is the Debye-Temperature) and that at $T > T_0$, small polaron tunneling is not possible and compensation effect is not expected to be observed. Out of the five semiconductors studied, in case of three (β-apo-8'-

Table - 4.13

Expected (Eqn. 4.6) and observed slopes and observed σ_0' from the log σ vs. E plots for the polyene semiconductors

Semiconductor	Expected slope (eV^{-1})	Observed slope (eV^{-1})	Observed σ_0' $(\Omega \cdot cm)^{-1}$
Vitamin A alcohol[1]	7.73	7.70	2.25×10^{-9}
Vitamin A acetate[1]	4.66	4.65	1.60×10^{-10}
β-apo-8'-carotenal[2]	1.41	1.39	1.25×10^{-16}
Astacene[3]	0.91	0.86	1.80×10^{-16}
Methyl bixin[4]	1.70	1.69	1.00×10^{-16}

1. From Fig. 4.20 ; 2. From Fig. 4.21 ;
3. From Fig. 4.22 ; 4. From Fig. 4.23 .

carotenal, astacene and methyl bixin) the semiconductive behaviour of the compounds has been studied at $T > T_o$. The experimental results show that the compensation rule is also valid in these cases. Further, Debye- temperature for these semiconductors are not known. It has been reported[22] that the Debye-temperature for a series of crystals of large aromatic molecules lies in the range 100-130°K. It seems that the T_o values measured are far too high to justify the polaron tunneling model.

Because of widespread occurrence[23] of the compensation effect (besides semiconduction process, it is observed in chemical reactions, catalytic process, thermal denaturation of macromolecules, thermal killing of unicelluler organisms etc), Kemeny and Mahanti[11] have proposed a theory of electronic charge transport as involved in kinetic processes (also applicable to equilibrium processes) from the absolute rate theory equation[24,25] within two special models. The first one (quadratic polarons) involves the coupling of electrons with a set of oscillators, whereas the second one (magnetic polarons) involves the coupling of electrons with a set of spins. Both the models show that the activation entropy is proportional to the activation energy thus providing a compensation effect. The use of N number of oscillators or of spins to bring about the compensation effect seems to appear reasonable in view of the fact that the variable amount of adsorbed dielectric (vapour) screen off the interaction of a charge with a more distant parent molecules; N depending on the number of such molecules with which the charge effectively interacts. But in quadratic polaron model, the characteristic temperature T_o is always negative in contradiction to our observation. The spin polaron model gives a positive T_0 but predicts no activation energy at very high temperatures. At a temperature around T_0, the process is activated and the activation energy becomes function of temperature i.e.

$$E(T) = E(0)\left[1 + \alpha \frac{T}{T_0}\right] \tag{4.6}$$

Here E(0) is the activation energy at low temperature and α is a function of temperature;

$$\alpha = \frac{1}{\log 2} \cdot \log\left[1 + \exp\left\{(-2\log 2)\frac{T_0}{T}\right\}\right] \tag{4.7}$$

Though our experiments were done in a limited range of temperature, the excellent linear plots in Figs. 4.6 - 4.15 do not suggest such temperature dependence.

Other theoretical attempts[9,10] to derive the compensation rule were restricted to the temperature dependence of the number of activated carriers in a model consisting of two electronic levels associated with each molecular site, the electronic states being coupled to a set of N oscillators associated with each molecular site. A change in the electronic state (due to vapour adsorption) gives rise to an activation entropy because of a change in vibrational frequencies. If one assumes the semiconduction equation as

$$\sigma(T) = \sigma_0' \exp\left(\frac{S}{k}\right) \exp\left(-\frac{E}{2kT}\right) \tag{4.8}$$

then the variation in both the electronic energy gap (E) and the activation entropy (S) can account for compensation effect if the changes in those parameters are given by

$$E = E_0 + n E_1 \qquad S = S_0 + n S_1 \tag{4.9}$$

where n is a definite number for each system and E_0, E_1, S_0 and S_1 are same for all the systems. In this case the characteristic temperature is given by $T_0 = E_1 / 2S_1$

Unfortunately due to the fact that the nature of the activated complex (due to vapour adsorption) is not precisely known, the activation entropy S (hence S_1) is a relatively obscure quantity and any quantitative estimate of T_0 is not possible.

The experimental results presented in this chapter show that the enhancement of conductivity is associated with a change in activation energy of the semiconductors on vapour adsorption. This change in activation energy depends on the chemical nature and also on the amounts of vapours adsorbed. In case of vitamin A alcohol and acetate the conductivity increases with the decrease of activation energy whereas in β-apo-8'-carotenal, astacene and methyl bixin the activation energy increases with the increase of conductivity. This behaviour, however, is quite understandable from the conductivity expression (4.3). If $T_0 > T$; where T is any temperature in the working temperature range, then ($\frac{1}{T_0} - \frac{1}{T}$) becomes negative and the increase in σ at a particular temperature T is suggested with the decrease in the value of E. Thus for a semiconductor having the characteristic temperature (T_0) at a higher value than the working temperatures, enhancement of its conductivity is expected with the decrease of its activation energy. This is what we have observed in case of vitamin A alcohol and acetate. Again, if $T_o < T$, then $\left(\frac{1}{T_0} - \frac{1}{T}\right)$ becomes a positive quantity and so increase in σ at a temperature T is associated with an increase in activation energy. Thus a semiconductor having the characteristic temperature (T_o) at a lower value than the working temperatures should show an enhancement of its conductivity with the increase of its activation energy. We have observed such behaviour in case of β-apo-8'-carotenal, astacene and methyl bixin. Now it is clear from our experiment that the characteristic temperature (T_o) of a semiconductor plays an important role in the dark conduction process.

The characteristic temperature (T_o), however, has been thought to be a molecular property[2]. Our results also show distinct T_o values (tables 4.1 and 4.2) for each of the polyenes. It is, however, not understood why T_o has a high value for vitamin A and also for β - carotene[2] whereas for β-apo-8'-carotenal, astacene and methyl bixin T_o is small though all these molecules belong to the long chain conjugated polyene group with alternating single and double bonds. Also the number of double bonds of the second group of polyenes lie in between vitamin A and β-carotene suggesting that this parameter is not related to T_o. Possibly it is the end group of the polyenes with which T_o is somehow related. It is to be of interest to note that the two groups of the polyenes investigated are distinct in that the molecules of the second group, β-apo-8'-carotenal, astacene and methyl bixin, have a $>C=O$ group which is conjugated with the polyene chain whereas the $>C=O$ group in vitamin A acetate is not conjugated with the main carbon chain and vitamin A alcohol has no carbonyl end group (shown in Part - I, Chapter 2, page - 33). Thus it seems that the presence of the conjugated carbonyl end group, in the second group of the polyenes studied is somehow related to the low value of T_o.

4.4 Conclusion

Our experimental results indicate that the compensation rule is valid for the polyene semiconductors studied and the activation energy (E) is physically related with σ_o. The distinct variation in the observed values of T_o of these semiconductors suggests the possibility of dependence of T_o on the molecular property of the semiconducting material. The characteristic temperature (T_o) of an organic semiconductor plays an important role in the dark conduction process.

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