tronenwechselwirkung nicht mehr zu verwenden. Durch Elektronenwechselwirkung werden demnach alle vier Übergänge verschieden beeinflußt, und darin liegt nach KUHN der Grund, warum die experimentellen Beträge die genannte Beziehung nicht genau erfüllen.

Vorliegende Arbeit hat also gezeigt, wie in der Chlorophyllchemie die theoretischen Voraussagen über thermische Schwingungsmöglichkeiten und Komplexbildung mit der Struktur und Veränderlichkeit der Spektren in Zusammenhang zu bringen sind, wenn man eine dementsprechend geeignete Zuordnung der berechneten Übergänge zu den experimentellen Übergängen vornimmt.

Electrical Effects observed with solid and Gaseous CO_2*

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I. In a recent work the author and others [1] have shown that when solid carbon-dioxide is formed by adiabatic expansion, a rather large charge separation can be observed. The dry-ice resulting from the process presents a negative charge "iced" in the bulk of the material. At first it was thought that this effect was similar to the COSTA RIBEIRO Effect [2] already observed with water, water solutions [3], and organic materials [4], but it was shown by the authors in the above mentioned paper that the effect is probably due to charge separation by friction in the nozzle through which the expansion takes place. This was further confirmed by the fact that by performing the solidification of the carbon-dioxide without the adiabatic expansion it was found that the material presented no such charges.

In the present work experimental results on the behavior of the charged solid and of the gas to which it vapourizes are described.

II. The measurement of the total charge of the solid was performed by putting it into a FARADAY-cage F (Fig. 1), connected with an electrometer-capacitor system. The electrometer E was a quartz-string WULF instrument in heterostatic mounting. The cage was put over the pan B of a highly damped sensitive balance, resting upon lucite insulators I. The whole assembly was protected by a metallic screen SC. Thus simultaneous measurements of charge and rate of phase-change were possible. The resulting gas could escape through a grid G in the base of F. Condenser C was used to measure the

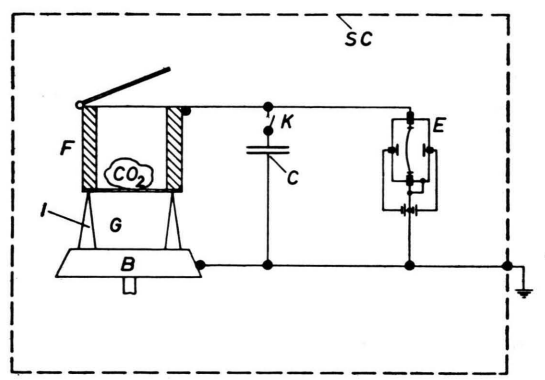

Fig. 1. Assembly for the measurement of the specific-charges of solid and gaseous phase. F-FARADAY-cage; I—Lucite insulators; B—balance pan; G—grid; C—air-condenser; E—WULF-electrometer: SC—general screen.

total initial charge of the solid, being out of circuit subsequently, when the smaller charges carried off by the gas were to be measured. We were thus able to measure the specific-charge (charge per unit mass) of the solid and of the gas. A typical result of such a measurement is shown in Fig. 2. Curves M I and M II show the variation of the mass of the solid with time and curves V I and V II are the cor-

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responding tension read off simultaneously in the electrometer. It is seen that the solid has a total negative charge which is gradually taken off by the gas as vapourization proceeds. The $V(t)$ curves follow the $m(t)$ curves and as soon as the mass is constant the total charge remains also constant.

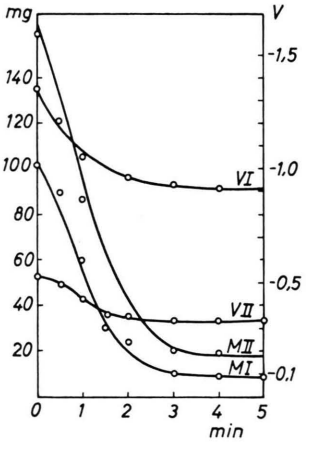

Fig. 2. M I and M II—mass variation of the solid with the time; V I and V II—corresponding tensions simultaneoulsy indicated by the electrometer.

From a certain portion of dry-ice obtained by the adiabatic expansion, several samples were taken and their charge measured as explained above. It was particularly observed that the specific charge of the solid lowered with the time of life of the sample. The gas correspondingly, carried off a smaller charge. This is shown in our results of Figs. 3 A and 3 B. These curves represent average results from 170 samples. For the calculation of the specific-charge of the gas the mass variation of the solid in a fixed interval of time was measured, and since this was small the fluctuations introduced in our results of Fig. 3 B were correspondingly larger. Nevertheless the ageing effect can be fairly recognized.

Although these experimental results were highly conclusive as respects the important fact that the gas carried away charges from the solid, we have performed another experiment in which the gas-charge was directly observed. This was simply done by pouring CO_2 gas (heavier than air) into a FARADAY-cage connected to the electrometer. Cotton was put inside the FARADAY-cage to act as a getter. The electrometer reading gradually rose indicating a total negative charge of the gas.

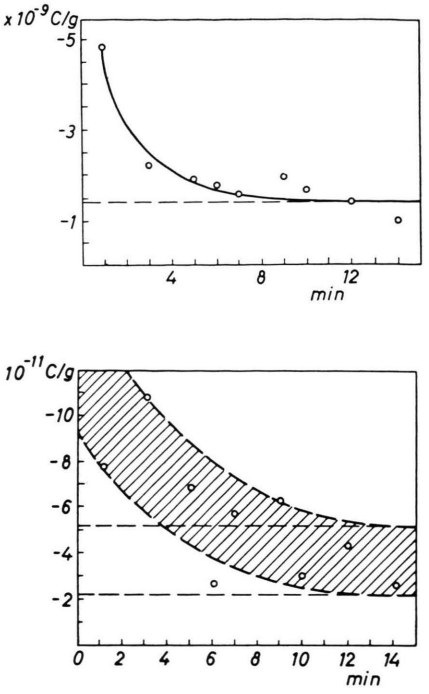

Fig. 3 A and 3 B. Specific-charge of the solid (3 A) and gas (3 B) for different "ages" of sample, showing decay effect. Results are averages over 170 samples.

The experimental findings described above can be thus summarized:

a) solid CO_2 obtained by adiabatic expansion presents electrical charges in the order of -10^{-9} C/g;

b) these charges suffer a decay-process from a maximum value of $-5 \cdot 10^{-9}$ C/g to a final value of -10^{-9} C/g in about 15 minutes;

c) the gas resulting from the vapourization of the charged solid is similarly charged and its specific charge amounts to about -10^{-10} C/g. The gas from a less charged solid has a corresponding lower specific-charge.

III. As regards the decay observed, we think that it is simply due to leakage of the charges from the interior of the solid to the surface, where neutralization is possible and surface conductance greater, owing to the inevitable water-film that exists at the surface of the material. It must be pointed out that dry-ice obtained from the adiabatic cooling presents itself as an aggregate of very small crystals.

Finally we would like to make some speculations about the above findings: untill now the little-known mechanism of rain-forming[5] by dry-ice is thought to depend primarily upon its temperature-lowering

[5] See R. C. SUTCLIFFE, Brit. J. Appl. Phys. **7**, 85 [1956] or F. H. LUDLAM, Nature, Lond. **177**, 320 [1956].

action. However from our results this does not seems to be the only hypothesis, for not only the solid is charged but so is the gas. This fact may give an important rôle to the gas, owing to its higher spreading-capacity. A rough calculation shows that if we suppose single-charged ions of the gas (the specific charge being in the order of -10^{-10} C/g) their number per cm^3 (taking the gas to be at NTP conditions) shall be about 10^7. Of course if it is intended to obtain the maximum possible number of nuclei, the dry-ice should be used at the moment of its formation, in view of the observed decay effect.

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Das Sperrverhalten von Siliciumgleichrichtern in feuchten Gasen

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Nach der entwickelten Theorie ist der Leckstrom in feuchten Gasen bei Siliciumgleichrichtern vom p s_p n-Typ im wesentlichen auf eine Ionenwanderung von chemisorbierten Wassermolekülen zurückzuführen. Die berechneten Gleichungen werden mit den experimentell erhaltenen Daten verglichen. Es lassen sich die Übergangswahrscheinlichkeit vom Zustand der physikalischen Adsorption in den der Chemisorption und andere Konstanten berechnen.

Adsorbierte Ammoniakmoleküle setzen die Übergangswahrscheinlichkeit vom Zustand der physikalischen Adsorption in den der Chemisorption von $W=0{,}055$ auf $W=0{,}995$ herauf. Ein Analogon zu diesem Effekt ist die Oberflächenverstärkung an chemischen Katalysatoren.

Es liegen bereits zahlreiche Arbeiten über den Einfluß von Feuchtigkeit und analog wirkenden Stoffen, wie z. B. Alkohol oder Azeton, auf Ge- bzw. Si-Oberflächen vor. Zusammenfassend werden sie z. B. in den Vorträgen von Brattain [1] oder Bardeen [2] und in den Arbeiten von Kingston [3] oder Harten und Schultz [4] dargestellt.

Es zeigte sich, daß der reine Channeleffekt des Wassers auf p-leitenden Halbleitern, der eine Vergrößerung der Fläche des p-n-Übergangs ergibt, nicht ausreicht, um die Sperrstromerhöhung in feuchten Gasen zu erklären. Die von Law und Meigs [5] vorgeschlagene Deutung durch eine elektrolytische Zersetzung der adsorbierten Wasserhaut konnten Eriksen, Statz und de Mars [6] durch Nachweis des Fehlens einer Wasserstoff- und Sauerstoffentwicklung widerlegen. Die genannten Autoren sind der Meinung, daß der äußere Leckstrom nicht durch eine Wanderung von Ionen hervorgerufen wird, sondern daß sich die adsorbierte Wasserhaut wie eine Art defektelektronenleitender Halbleiter verhält. Eine derartige Theorie gibt jedoch keine befriedigende Erklärung für die Sättigungserscheinung des Leckstromes. Ferner ist die von Statz und de Mars [7] gefundene Beweglichkeit der äußeren Ladungsträger viel zu gering für eine Defektelektronenleitung. Die Tatsache, daß der Leitungsmechanismus des Leckstromes eines Gleichrichters bei Abkühlung ohne Sprung durch den Gefrierpunkt der adsorbierten Substanz geht, spricht nicht gegen eine Art von Ionenwanderung. Die adsorbierte Schicht ist zu dünn (es liegt kein Niederschlag vor), um Kristallkeime von kritischer Größe entstehen zu lassen. Unterhalb des Erstarrungspunktes handelt es sich bei der adsorbierten Substanz vielmehr um eine Art unterkühlter Schmelze, und deren Viskosität und Diffusionskonstante gehen vollkommen stetig durch den Erstarrungspunkt [8].

Aus zahlreichen Arbeiten ist bekannt, daß das Wasser auf Ge- und Si-Oberflächen als positives Ion adsorbiert ist [1–4]. Eine Deutung der Erscheinungen

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