

computed from the experimental constants. In the case where two acid ions react per atom of metal this becomes: $kc_0'^2 = a + \eta$.

Only this equation seems to answer to the condition that k must be constant in the case of lactic acid; in the case of citric acid it could be described by the first one.

Table III gives the computed values of k for citric and lactic acids.

We now are able to establish the chemical formula of the first and of the second reaction product with great probability. The first product is $C_3H_5O \cdot COOH(COO)_2Sn$ and $(C_2H_5O \cdot COO)_2Sn$ respectively. The second one is a complex salt with one and two ions respectively for citric and for lactic acid.

Acknowledgment. The authors wish to thank Prof. Dr. L. S. ORNSTEIN for his keen interest in the investigation.

Physical Laboratory of the University of Utrecht.

Physics. — *Determination of the cross-section of metastable He atoms with the aid of their "photo-electric" effect.* By R. DORRESTEIN and J. A. SMIT. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of June 25, 1938.)

SUMMARY.

A method is described by which the cross-section of metastable He atoms for collisions with normal He atoms is determined by measuring the intensity decrease of a beam of metastable atoms in He of low pressure. The relative number of metastable atoms is measured with the help of the electrons they liberate from a metal surface.

§ 1. Introduction and discussion.

On performing measurements with the tube shown in fig. 1, filled with helium at low pressures (10^{-4} — 10^{-3} mm), we found, if the electrons in the main tube had sufficient energy, that the electrometer indicated a

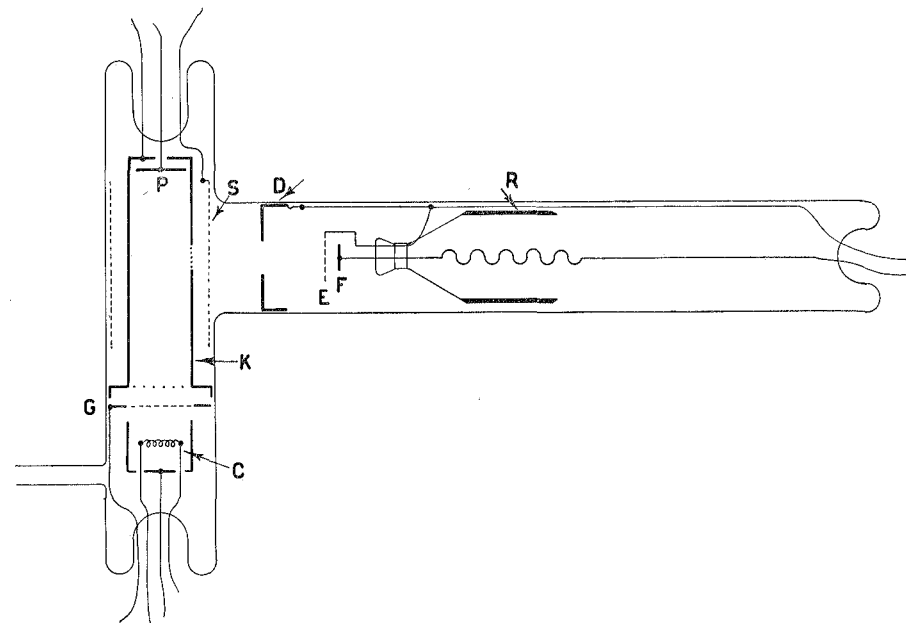


Fig. 1.

The electrons emitted from the oxide cathode C are accelerated by the grid G , reach their final velocity in the metal cylinder (cage) K and strike the plate P . The currents to K and P can be measured separately. The platinum plate F and grid E form a photo-electric cell which is mounted on a soft iron ring R and with the aid of an external magnet can be moved to any position in the side tube. The nickel diaphragm D is also movable. The current to the plate F can be measured with an electrometer.

positive current through the cell to the plate F which we could not explain as made by photons. As not only photons but also metastable atoms can liberate electrons from a metal surface¹), and in our experimental arrangement there are metastable atoms produced in the main tube, we believe that this cell current is caused by metastable atoms falling on the plate F . We shall now give the arguments in favour of this explanation.

A priori we have the following possible sources of the current in the cell:

- I. True photo-electric effect. The radiation responsible may be
 - a. helium resonance radiation,
 - b. other helium radiation,
 - c. radiation from other gases as impurities.
- II. Charged particles. These may be
 - a. primary electrons from the main tube,
 - b. secondary electrons,
 - c. positive ions from the main tube.
- III. Metastable atoms.

The arguments for or against these explanations are:

I a. The values of the absorption coefficients for helium resonance radiation in helium do not seem to be known experimentally. However, there are theoretical calculations on these coefficients²). For the low resonance lines the absorption is so high, that no appreciable amount of this radiation reaches the cell, even when account is taken of re-emission. The wings of the lower lines, the higher m^1P-1^1S lines, and the forbidden resonance lines are less absorbed but will have very small intensity. This is in agreement with the fact that we found no absorption at all for the effect causing the cell current at a pressure of 10^{-4} mm; this absorption is present at 10^{-3} mm.

I b. The non-resonance helium lines can produce no effect in our photo-cell since their wave-lengths are all longer than the threshold wave-length for platinum. This is in agreement with the fact that we find no cell current if a quartzplate is placed across the side tube.

I c. Since our tube has been outgassed thoroughly and since before each series of measurements helium was renewed it seems very unlikely that there is appreciable radiation from impurities. In fact the cell current does not appear below an electron energy equal to the first excitation energy of helium (20 e.V.), which is much greater than the excitation potential of any impurity.

II a. To prevent electrons from the electron beam reaching the side tube we have surrounded the cage K by a gauze shield S which was maintained at a negative potential with respect to the cathode.

¹) H. W. WEBB: Phys. Rev. **24**, 113 (1924).
M. L. E. OLIPHANT: Proc. Roy. Soc. A **124**, 228 (1929).
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²) J. P. VINTI: Phys. Rev. **42**, 632 (1932).
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II b. To prevent secondary electrons, for instance from the gauze shield S , reaching the platinum plate F , either this was kept at a lower potential than the shield S , or the secondary electrons were bent away by a transversal electric rotatory field across the side tube. Besides they would give a current in the opposite direction to the current measured and hence could only decrease the apparent magnitude of our effect.

II c. During the experiments the accelerating potential was always kept below 24 volts (grid G and plate P being connected with the cage K), so that electrons in the main tube nowhere had an energy sufficient to make helium ions. Further the diaphragm D and the grid E were kept at a higher potential than the cage in order to avoid disturbances by ions of impurities. This is a necessary precaution because the current in the beam is some 10^9 times as large as that through the electrometer, and thus improbable processes in the electron beam can give relatively strong disturbances in the cell.

III. The following arguments favour the idea that our effect is caused by metastable atoms:

- a. As mentioned above, the effect begins just at the first excitation potential of helium.
- β. The velocity of the particles, responsible for the effect is approximately that of helium atoms at room temperature. See § 2.
- γ. The cross-section, calculated from the measurements, assuming this hypothesis, is roughly the same as the known cross-section for normal helium atoms. See § 3.

§ 2. Measurements with alternating potentials.

We have confirmed the above mentioned considerations by measuring the velocity of propagation of the active particles with the alternating tension method of WEBB³).

In this method a small alternating tension is put on the cage in addition to a direct tension equal to the excitation potential (20 V for He), the cell being activated by an alternating tension of the same frequency. During the positive half-period photons, metastable atoms, etc., are formed in the cage and can move in the direction of the cell. The cell current which is caused by them depends on the instant of their arrival, thus on the time t required by the particles to travel from the source K to the cell. The result is that the cell current shows a characteristic variation with frequency when the period is of the same order as t .

Our cell showed saturation at 5 volts and so we made the alternating potential across it several times larger. When the potential of the grid E is negative with respect to that of the plate F , the cell shows a rather large inverse current. We attribute this to electrons set free from the grid E and the surrounding ring by metastable atoms (inverse operation of cell). Because

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of this inverse effect we often found negative cell currents in our alternating tension measurements. The alternating potentials were furnished by a simple oscillator and measured with a triode voltmeter; the wave-form and phase-differences were controlled with the aid of a cathode ray oscilloscope. The frequency was found by comparison with a calibrated audio-frequency generator, the latter being used also directly as a source at the lower frequencies.

With a distance of 12 cm between electron beam and cell, we obtained the curves shown in fig. 2. The first minimum of curve I is at $5 \cdot 10^3 \text{ sec}^{-1}$.

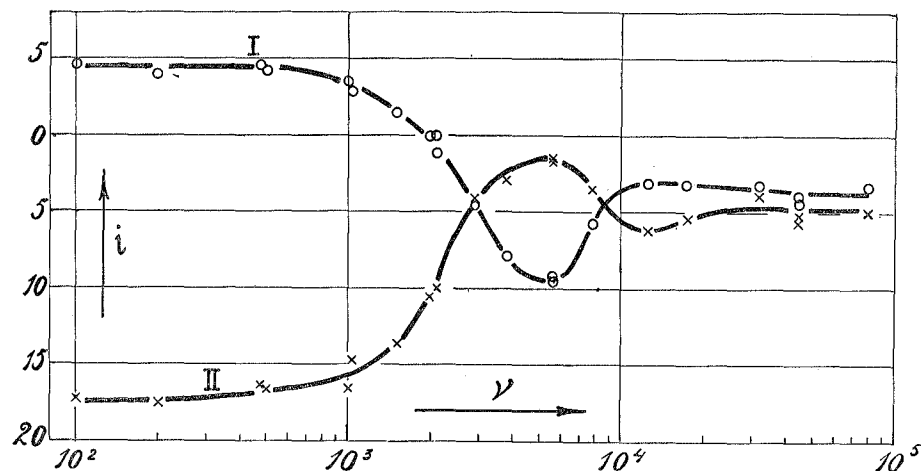


Fig. 2.

ν = frequency in sec^{-1} .

i = cell current (electron emission from the plate) in arbitrary units (about $4 \cdot 10^{-14} \text{ A}$).

In curve I there was no phase difference between the potentials of cage and cell, that means K and E were at the same time positive to resp. G and F . In curve II the phases were opposite, so K was positive when E was negative. The potentials were:

$$\begin{aligned} C - 20 \text{ V}, \quad G 0 \text{ V}, \quad K+P 0 \text{ V} + 3 V_{\text{eff}} \text{ alt. tens.} \\ S - 40 \text{ V}, \quad F 10 \text{ V} \text{ and } E+D 10 \text{ V} + 16 V_{\text{eff}} \text{ alt. tens.} \end{aligned}$$

The electron beam current was about $1.5 \cdot 10^{-4} \text{ A}$.

The distance of plate F from the electron beam was 12 cm (diaphragm D at 8 cm).

The gas pressure was $1.6 \cdot 10^{-3} \text{ mm}$.

Here the mean value of t for the active particles must be approximately equal to half the period, so to $1.0 \cdot 10^{-4} \text{ sec}$. Thus we find a mean velocity of $1.2 \cdot 10^5 \text{ cm/sec}$. The mean velocity of helium atoms at room temperature is $1.25 \cdot 10^5 \text{ cm/sec}$. This result cannot be understood if the effect is caused by photons or electrons, but is quite reasonable for metastable atoms.

§ 3. Measurements of Cross-section.

As our cell current at pressures of $10^{-4} - 10^{-3} \text{ mm}$ is apparently

caused by metastable atoms, we can determine the cross-section of these metastable atoms against collisions with normal helium atoms by "absorption" measurements.

Even if we consider only one kind of metastable helium atom, and assume that metastable atoms, after having collided, in no case reach the cell, the calculation is rather complicated because the metastable as well as the normal atoms have a Maxwellian velocity-distribution. If the cross-section is independent of the relative velocity, the mean free path for a particle with velocity v in a gas with temperature T is given by

$$\frac{1}{\lambda(v)} = NQF(B) \quad \text{with} \quad F(B) \equiv \left(1 + \frac{1}{2B} \right) \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{B}} e^{-y^2} dy + \left. \begin{aligned} &+ \frac{1}{\sqrt{\pi B}} e^{-B} \text{ and } B \equiv \frac{Mv^2}{2kT}. \end{aligned} \right\} \quad (1)$$

Here the cross-section $Q = \pi(r_m + r)^2$ where r_m is the radius of the particle and r that of the gas atom; N is the number of gas atoms per cm^3 , M their mass, k is BOLTZMANN'S constant.

With the aid of this $\lambda(v)$ we find for the intensity of a parallel beam of metastable atoms

$$I(s) = \frac{2}{\sqrt{\pi}} I(0) \int_0^{\infty} \sqrt{B} e^{-B - sNQF(B)} dB \quad \dots \quad (2)$$

where $I(0)$ is the intensity at the source and s is the distance from the source; this formula is valid for a Maxwellian velocity-distribution of the metastable atoms with the same temperature as the gas.

In our case this condition will be closely satisfied since the electrons can transfer only a small amount of kinetic energy to the helium atoms and since the heating of the cage by the cathode (and consequently that of the gas) is small⁴). The measured atom beam is not parallel, but limited by the cell plate F and the hole in the cage K , so we have to correct for its divergence by multiplying the cell current by s'^2 where s' is the distance between plate and hole. In the case of measurements with different gas pressures we have to take into account that the production of metastable atoms by a constant electron beam is proportional to the gas pressure, at least if the mean free path of the electrons is sufficiently large.

With the help of formula (2) we have to calculate the cross-section Q from the experimental intensity curves as functions of distance or pressure. As a preliminary result we have found:

$$\begin{aligned} Q &= 21 \cdot 10^{-16} \text{ cm}^2 \text{ from measurements at constant pressure } (9 \cdot 10^{-4} \text{ mm}); \\ Q &= 18 \cdot 10^{-16} \text{ cm}^2 \text{ from measurements at constant distance } (s = 12 \text{ cm}); \end{aligned}$$

⁴) For this purpose it is important to have sufficient distance between cathode and cage, which necessitates the use of the grid G .

the electron energy was 23 e.V. (According to JEANS⁵⁾ the cross-section for normal He atoms is $15 \cdot 10^{-16}$ cm²). The excitation functions of helium⁶⁾ suggest that at our small electron velocity mainly the 2³S metastable state is formed, whereas at greater velocities chiefly the 2¹S state will be formed.

Since the mean free path is smaller for small velocities (cf. eq. (1)), the mean velocity of the metastable atoms in the beam continually increases as the beam traverses the gas. This may be a source of error in our experiment if the efficiency of the cell depends appreciably on the velocity with which the metastable atoms strike the metal surface. It must be possible to find this by accurate analysis of the shape of the experimental curves, if the disturbance by scattered atoms is not too large. However, it seems likely to us that this effect is unimportant for thermal velocities.

In combination with absolute measurements of the production of metastable atoms (method see⁷⁾) our measurements can also yield the probability of liberation of an electron from a metal surface by a metastable atom. A preliminary estimation gives that this probability is rather more than less than 10 %.

⁵⁾ J. H. JEANS: The Dynamical Theory of Gases (1925).

⁶⁾ O. THIEME: Zs. f. Phys. 78, 412 (1932).

J. H. LEES: Proc. Roy. Soc. A 137, 173 (1932).

⁷⁾ J. M. W. MILATZ and L. S. ORNSTEIN: Physica 2, 355 (1935).

J. M. W. MILATZ: Dissertatie, Utrecht (1937).

H. MAIER-LEIBNITZ: Zs. f. Phys. 95, 499 (1935).

Physics. — *A theory of plastic stability and its application to thin plates of structural steel.* *) By P. P. BIJLAARD. (Communicated by Prof. J. M. BURGERS).

(Communicated at the meeting of June 25, 1938.)

In our preceding communication we assumed that at any given moment the deformation of a body and the then existing state of stress determine each other reciprocally. In order to compare this mode of deformation for our case with other possible modes of deformation we represent the deformation deviators T_0 and the stress deviators Γ_0 by representative vectors in a nine-dimensional space, the components being equal to the nine components of the deviators, in the same way in which HOHENEMSER and PRAGER¹⁾ represented the results of their tests with steel tubes. We suppose a body to be charged until the yield stress by a pure compressional stress σ_x , already causing plastic deformations $\sigma_v/E_p = e\sigma_v/E$. We assume another deformation to be superposed on this first deformation, by keeping the strain ε_y constant with further deformation by σ_x , whilst the strain in Z direction is not impeded.

This case occurred with the originally locally bent strip with which we dealt in footnote 11 and equation (8) of our preceding communication, and — be it with somewhat more complicated conditions — also with the locally weakened plates we considered before.²⁾ It was assumed in those two cases, however, that e was equal to 0. It is to be observed in addition that the relation obtained for the above case between the finite quantities $\Delta\sigma_x$, $\Delta\sigma_y$ on the one hand, and $\Delta\varepsilon_x$ on the other, will result with infinitely small deformations in the relation which is expressed more generally — i. e. with $tg\varphi > 0$ — in (21)³⁾ by the equations $\sigma'_x = EA\varepsilon'_x$ and $\sigma'_y = EC\varepsilon'_x$.

As in our case the X , Y and Z axes are principal axes of the state of stress, the deviators may be represented by representative vectors lying in the three-dimensional spaces $(\sigma_x - \sigma)$, $(\sigma_y - \sigma)$, $(\sigma_z - \sigma)$ and $(\varepsilon_x - \varepsilon)$, $(\varepsilon_y - \varepsilon)$ and $(\varepsilon_z - \varepsilon)$ respectively.⁴⁾ The line which depicts the gradual development of the deformation — further on called deformation course — as the result of the addition of the representative vectors of the deviator, in fig. 1 is projected on the plane traversing the axes $\varepsilon_x - \varepsilon$ and $\varepsilon_z - \varepsilon$.

*) Sequel to: "A theory of plastic buckling with its application to geophysics". Proc. Kon. Ned. Akad. v. Wet., Vol. 41, No. 5, 468 (1938).

¹⁾ HOHENEMSER and PRAGER, Zeitschrift f. angew. Math. u. Mech., No. 1 (1932).

²⁾ BIJLAARD, De Ingenieur, No. 23 (1933).

³⁾ Numbers of equations below (42) refer to our preceding communication.

⁴⁾ σ and ε represent the average principal stress and the average strain, and so $\sigma_x - \sigma$, $\sigma_y - \sigma$, etc. are the deviator components.