Physics. — *The Duration of Metastable States of Neon, Argon, and Helium.* By Prof. H. B. DORGELO and T. P. K. WASHINGTON. (Communicated by Dr. G. HOLST.)

(Communicated at the meeting of October 30, 1926).

1. *Introduction.*

In a former communication ¹) a few experiments have already been described in which the order of magnitude of the duration of the metastable $2s_5$- and $2s_3$-states of neon was measured.

The results of continued measurements concerning the dependence of this duration on the temperature, and also results of measurements of the duration of the metastable 2^3P_0- and 2^3P_2-states of mercury were communicated in the journal "Physica" ²).

As criterion of the presence of the metastable states of the atoms was used the absorption in consequence of these states of those lines that correspond with transitions, in which these metastable states are the final states. Measurements were made of the time that an absorption tube, after the interruption of the discharge through which the metastable states are excited, was still able to absorb the lines in question of another discharge tube.

In what follows we can now communicate the results of continued measurements on argon and helium. For neon we have also determined the dependence on the pressure of the duration of the s_5-state at different temperatures, which enabled us to discuss more fully the before-mentioned suppositions of JOFFÉ and FRANCK ³) concerning the process of the disappearance of the metastable s_5-states.

In order to be able to study better the course of the disappearance of the metastable states in the different gases and under different circumstances, the method used before was modified in so far that quantitatively the disappearance of the absorption could be measured in its dependence on the time. The curves thus obtained give an idea of the slow disappearance of the metastable state in the absorption tube.

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¹) H. B. DORGELO, These Proc. Vol. **27**. N⁰. 1, p. 7. Zs. f. Phys. **34**, 766, 1925.

²) H. B. DORGELO, Physica **5**, 429, 1925.

³) For mercury further investigations were made on this point by FRANCK and CARIO, Z. f. Phys. **37**, 619. 1926.

2. *The Method Used.*

In the investigations carried out now we have first used the method II described before [1], in which by the aid of two rectifiers one half period of a transformed alternating current was sent through an emission tube, the other half period through an absorption tube. The light of the emission tube was sent as a parallel beam through the absorption tube, and then by the aid of a second lens projected on a vacuum thermoelement of MOLL and BURGER [2], which was connected with a galvanometer.

At a definite frequency of the alternating current the value of the absorption in consequence of the metastable atomic states in the absorption tube, when the same half period of the alternating current was sent through both tubes (emission tube and absorption tube), was compared with the value of the absorption, when one half period was sent through the absorption tube and the other half period through the emission tube.

For the ideal case that the passage of the current through the absorption tube and through the emission tube takes place exactly in the middle of the half period(hence at the maximum tension during the half period), the absorption in the absorption tube is measured (with an alternating current of 50 periods) in the first case at the moment when the metastable states of the atoms are excited, and in the second case $^1/_{100}$ sec. after their excitation (with the use of an alternating current of 500 periods $^1/_{1000}$ sec. after the excitation etc.). By repetition of these measurements with other frequencies of the alternating current, the slow decrease of the absorption with the lapse of time may be followed.

In reality we have not to do with the above-mentioned ideal case of passage of the current through the tubes, but the current will continue for a pretty great part of the half period (if no particular precautions have been taken). This circumstance determines, of course, in a great degree the accuracy of the values of the duration found by this method. Oscillographic records of the current through the emission and absorption tubes really showed that, with the arrangement used (method II), the duration of the surrent gusts through the tubes was not small in relation to the duration of the half. period of the alternating current. (See Fig. 2a.)

We have then tried in various ways to render the time of the duration of the current gusts through the emission and absorption tubes as short as possible. We obtained the best results with the arrangement (to be denoted further as method III), which is represented diagrammatically in fig. 1, and which was used for the final measurements. The anode current of an emission lamp T_1 was sent through the emission tube E, that of an emission lamp T_2 through the absorption tube A. Two Philips triode-lamps Z. 4, anode tension 2000 V. were used.

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[1] Loc. cit. Physica **5**. 433. 1925.

[2] W. J. H. MOLL and H. C. BURGER, Phil. Mag. **50**, 618, 1925.

Alternating tension (of which the number of periods could be varied) was applied to the grating and in series with this a high negative continuous tension. By a suitable choice of the strength of the alternating tension and of the negative uniform tension it could be arranged that only during a short time of the half period during which the positive phase of the alternating tension was applied to the grating, the sum of the positive alternating tension and the negative tension of the battery was just sufficient to yield the desired anode current.

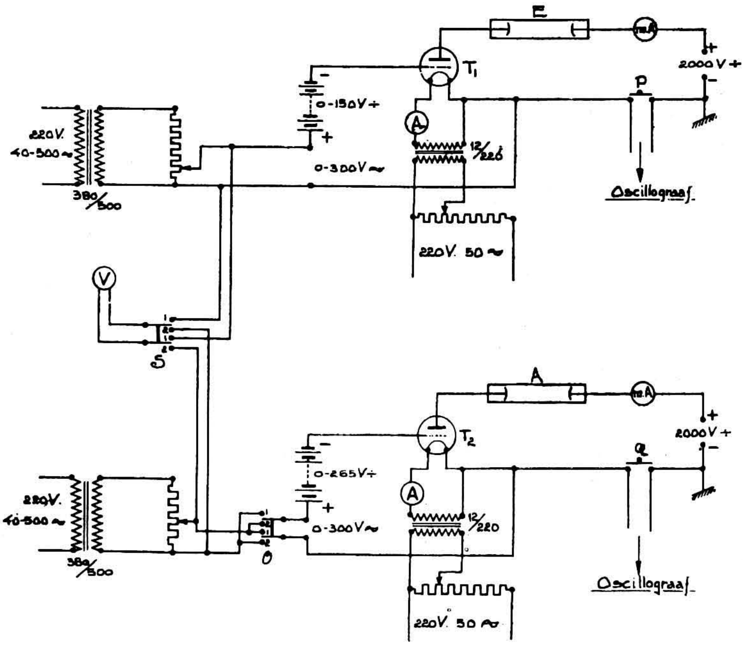

Fig. 1.

By cutting out the short-circuit switches *P* and *Q* the oscillograph could be placed in series with the discharge tubes.

By means of the commutator O it was possible to apply the same or else the opposite phases of the alternating tension to the two gratings.

Fig. 2 gives some reproductions of the oscillographic records of the current through the discharge tubes. In Fig. 2*a* the current-time curve through the emission tube is given at 20 mA, method II being used ; Fig. 2*b* with use of method III, and at the same mean intensity of the current. The great difference in duration of the current gusts and the great advantage of method III is very apparent.

Fig. 2*c* gives an oscillographic representation of the currents through absorption and emission tube with opposite phases of the alternating tension at the gratings.

For the case that opposite phases were applied to the gratings, we could measure from the oscillographical records of the current through the tubes, the length of the time interval between the end of the discharge through the absorption tube and the moment of maximum intensity of the current through the emission tube.

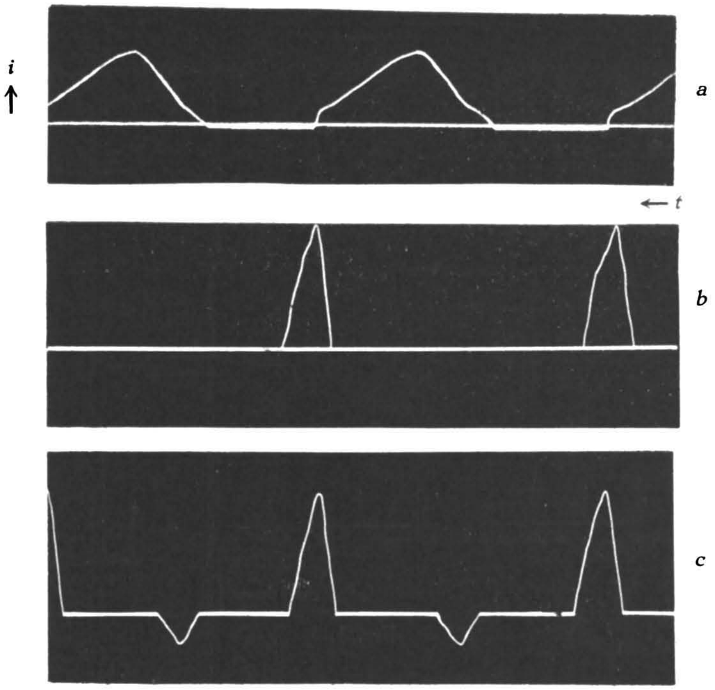

Fig. 2.

The voltmeter *V* served for the determination of the alternating tensions applied. This arrangement in combination with the before-mentioned thermo-electric-galvanometric method is very suitable for examining how the durations of the metastable states depend on the states in the absorption tube[1]).

Besides we could now also determine the order of magnitude of the duration of the 2*s*-state of helium. As in this case the absorption of the ultra-red line 10830 Å had to be used as criterion, photographic or visual observation was not possible.

3. *Results.*

Before mentioning the results obtained we refer to fig. 3, in which energy levels of helium, neon, argon and mercury are represented

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[1]) Instead of the thermo-electric galvanometric method we could of course use now, as before, a spectral apparatus, and measure the absorption of different lines separately.

As it was, however, our purpose in this investigation to inquire more closely into the circumstances that determine the duration of the metastable circumstances, the method used now takes much less time.

diagrammatically (in volt scale). The metastable energy-levels occurring with these elements are denoted in these figures by enclosing the notation (e.g. s_5 and s_3 for neon) of the levels in a square. For the sake of clearness the splitting up of the s-levels of neon and argon is represented slightly enlarged. Such a combination of different schemata of levels in one figure gives a lucid survey of certain processes, in which metastable atomic states play a part. Among other things it is, e.g. clear that an excited helium atom in the 2^1S—$(2S)$-state has sufficient energy to bring a neon atom into the $4s_2$-state through a collision of the second kind [1]), and can thus excite the line $1p$—$4s_2$.

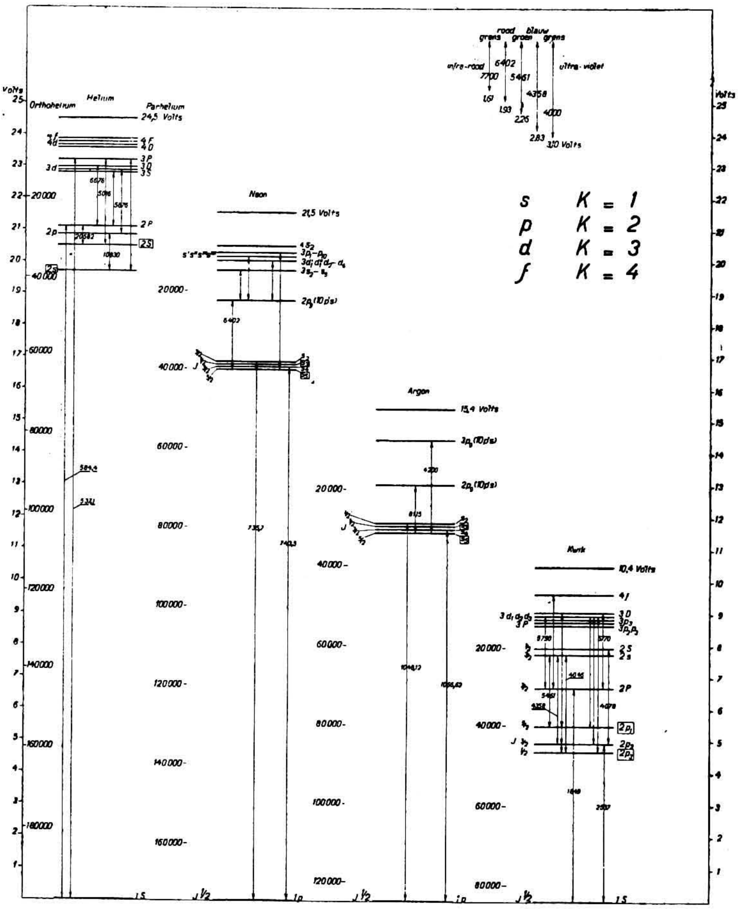

Fig. 3.

a. *Neon.*

The results for neon already mentioned in our previous communications were now extended by examining the disappearance of the metastable

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[1]) H. B. DORGELO and J. H. ABBINK, Physica 6, 153, 1926.

states of neon with the time elapsed and this at different pressures and temperatures.

In fig. 4 we have drawn as abscissae the values of t measured from the oscillographic records of the current-time curve which elapse on use of

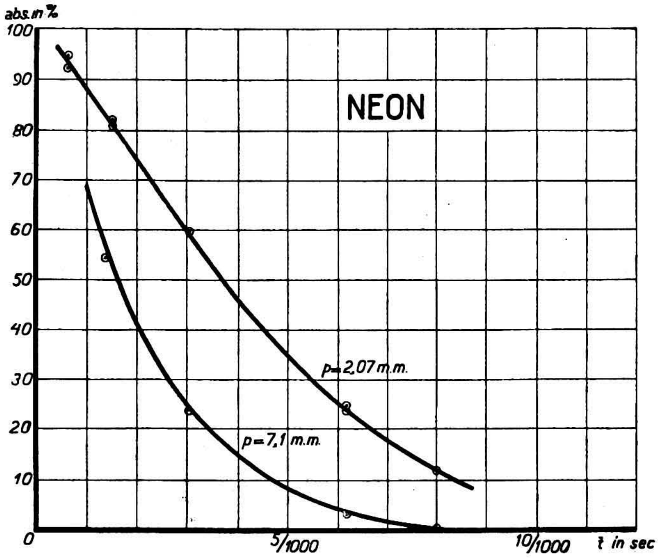

Fig. 4.

different frequencies between the end of the discharge through the absorption tube and the time of maximum intensity of the current through the emission tube ; as ordinates the ratio of the absorptions at the times *t* and those at the time $t = o$. Both curves refer to the same absorption tube (diameter 46 mm.), for the curve *A* the neon pressure was 2.07 mm., for the curve *B* 7.1 mm.

It is clearly seen that the absorption left after a definite time, hence also the duration of the metastable states, is smaller at a pressure of 7.1 mm. than at a pressure of 2.07 mm.

Fig. 5 (result of measurements in which the pressure in the absorption tube was varied with constant frequency of the alternating tension at the gratings of the triode lamps) gives a still better idea of this dependence on the pressure of the duration of the metastable states of neon. The curves represented in this figure were obtained in the following way. Each curve expresses the results of a series of measurements at definite frequency of the alternating tension at the grating of the triode lamps, but at different pressures of the neon in the absorption tube. At the different pressures the following values were determined :

1. the value *a* of the absorption when equal phases of the alternating tension were applied at the gratings of the two emission lamps.
2. the value *b* of the absorption when opposed phases were applied.

The ratio $\frac{b}{a}$ is drawn in fig. 5 as ordinate. The greater this ratio, i.e. the greater the absorption left after a half period ¹), the greater is the duration of the metastable states of the atoms.

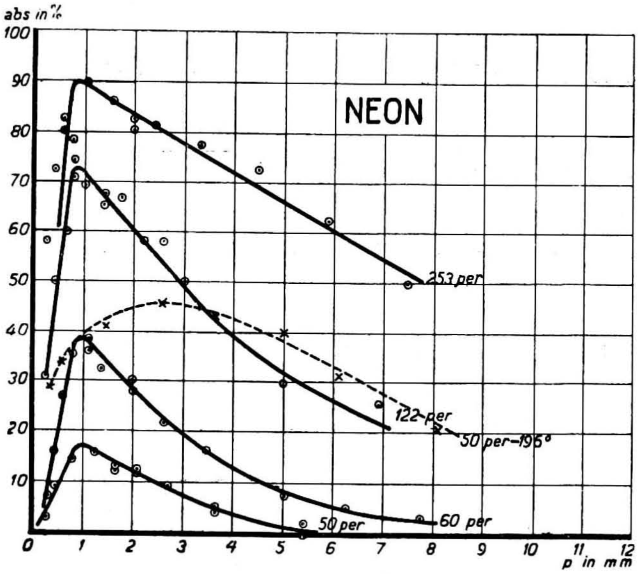

Fig. 5.

It is very clearly seen that *this duration* (passing from higher towards lower pressure) *first increases, reaches a maximum, and then again diminishes.*

At higher pressures (e.g. at 8 mm. pressure) the diffusion of the excited metastable conditions towards the wall plays as yet hardly any part. If, however, the number of collisions of the first kind of the metastable states with normal neon atoms is considered, in which sufficient energy can be transferred to bring a metastable neon atom from the s_5-state into the s_4-state, this number decreases at lower pressures and consequently the duration becomes greater. If the pressure becomes much smaller, the influence of the diffusion of the metastable states towards the wall will gradually begin to preponderate, so that with a given diameter of the tube a maximum of the duration will be found, while at still smaller pressures this duration must rapidly diminish.

The Influence of the Diffusion and of the Collisions of the First Kind.

In fig. 6 the ordinates of the curve I represent for different pressures

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¹) As we already set forth at greater length under 2. in the description of the method used, the time interval between the end of the discharge through the absorption tube and the passage of the light of the emission tube through the absorption tube is actually shorter than a half period and may be derived from the obtained oscillograms of the currents through emission and absorption tube (see fig. 2).

in the absorption tube, the calculated percentage of the metastable neon atoms present at the time $t = 0$, which after the lapse of $1/250$ second would have been left, if the metastable atoms disappeared through diffusion to the wall; assuming in this that a metastable atom loses its energy on collision with the wall and that the metastable atoms are uniformly distributed over the tube at the time $t = 0$.

For the calculation of these curves use was made of the relation:

$$N_t = N_0 \, \Sigma \, 4 \, . \frac{1}{x_m^2} e^{-\frac{a^2 x_m^2 t}{d^2}}$$

in which N_0 = the number of metastable atoms in the tube at the time $t = 0$.
a^2 the diffusion constant,
x_m the roots of Bessel's function J_0,
and d the radius of the cylindrical absorption tube used.

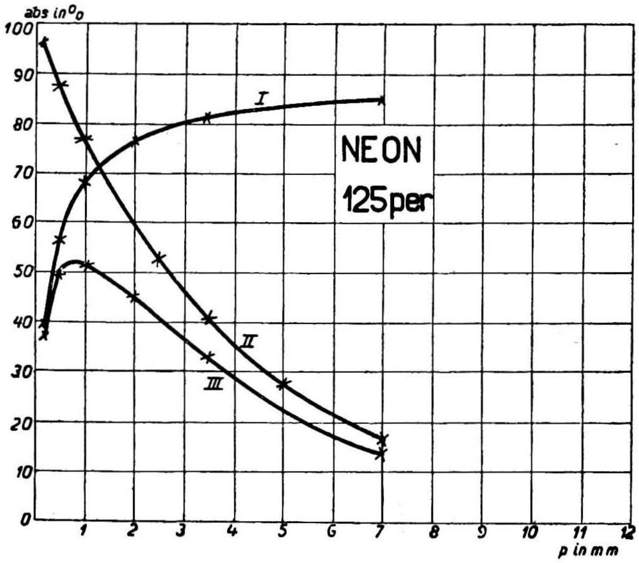

Fig. 6.

The ordinates of the curve II in this figure give the percentage that would have been left, if the metastable atoms disappeared exclusively by collisions of the first kind. The constant required for the calculation of this curve was derived from the experimentally derived curve of fig. 4 (valid for a pressure of 7.1 mm., at which pressure the diffusion does not play a part as yet within the time of $1/250$ second).

In order to obtain the result of the two processes (hence both of the diffusion towards the wall and of the collisions of the first kind), we have to multiply together the ordinates of the two curves. Curve III in fig. 6 represents the curve obtained in this way. We see that its shape is in perfect harmony with those of the curves of fig. 5 found experimentally.

That experimentally (for 122 per.) we found a higher maximum than the theoretical curve of fig. 6 indicates, is owing to the fact that the disappearance of the metastable atoms present at the time $t = o$ really proceeds more slowly, especially at the higher pressures, than is expressed by the curve I of fig. 6. As has been said, in the calculation of this curve it was assumed that the metastable atoms were distributed uniformly over the tube at the time $t = o$.

With the absorption tube used we see clearly, however, that the atoms are excited over the full breadth of the tube on a discharge of the latter only at very low pressures; as the pressure becomes higher, the discharge is more and more confined to the central part of the tube. In consequence of this the disappearance of the excited metastable atoms through diffusion towards the wall will take place less rapidly than is rendered by the curve I of fig. 6. The maximum of the resulting curves will also lie higher [1]).

In connexion with these results Dr. HOLST remarked that, at very low temperatures, at which, as already appeared from our earlier measurements [2]), the collisions of the first kind no longer play an important part, we ought to find that the diffusion would become predominant at higher pressures, and that therefore e.g. at the temperature of liquid nitrogen the maximum of the curves of fig. 5 ought to shift towards higher pressures.

The dotted curve of fig. 5 gives the results of measurements with an alternating tension of 50 periods, the absorption tube having been cooled with liquid nitrogen. We see that the maximum of this curve lies at greater pressure. We further see here that at —196° C. the curve for 50 periods lies much higher than the traced curve for 50 periods, which is valid for room-temperature, i.e. the number of metastable states that are still left in the tube after $^1/_{100}$ sec., is much greater at —196° C. than at room-temperature. This too, is in harmony with the conception of the destruction of the metastable states by collisions of the first kind with the other neon atoms in the normal state.

b. Argon.

From the investigations of K. W. MEISSNER [3]) on the absorption of argon lines by excited argon-atoms and his analysis of the red argon spectrum and also by the investigations of the red argon spectrum

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[1]) (As we have to do with the diffusion of excited atoms, hence with particles with greater diameter than the normal atoms, the diffusion constant will be smaller than that for normal atoms. In our calculation of the curve I of fig. 6 we have, somewhat arbitrarily, assumed a diffusion constant four times smaller than the gas-kinetic one for normal atoms).

[2]) Loc. cit. Physica **5**. 434. 1925.

[3]) K. W. MEISSNER, Phys. Zs. **26**, 686, 1925; Z. f. Phys. **37**, 238, 1926; Id. **39**, 172. 1926.

in the extreme ultra-violet by LYMAN and SAUNDERS[1]), HERTZ[2]) and DORGELO and ABBINK[3]), a close analogy has been established between the neon and the argon spectrum. Also argon has two metastable states (indicated in fig. 2 as the $2s_5$- and the $2s_2$-states of argon), which clearly appears from the fact that with argon there are also only two resonance lines λ 1048 and λ 1066 in the extreme ultra-violet. The transitions from the $2s_3$- and $2s_5$-states to the fundamental state do not take place.

In fig. 7 we give a reproduction of some photographs, which very clearly show the absorption by the excited metastable argon-atoms.

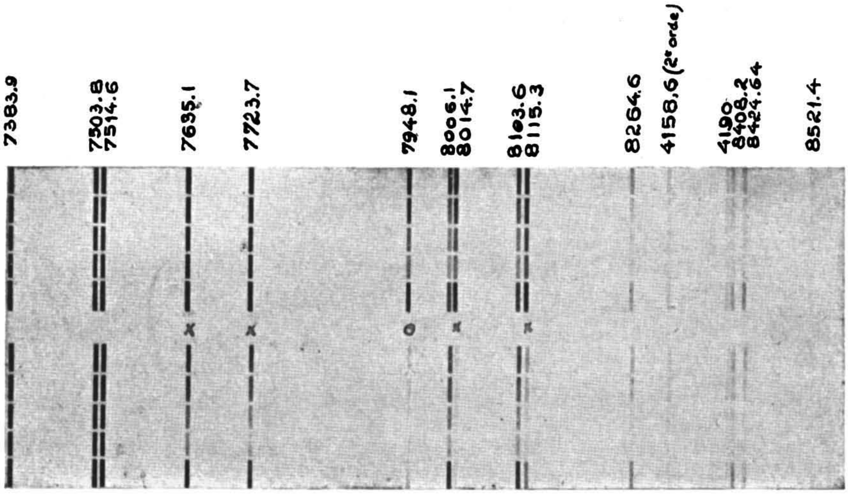

Fig. 7.

Spectrum I gives the reproduction of a photograph[4]) of part of the argon spectrum in the ultra-violet of an argon column, again without absorption of the light of this column by excited metastable states of argon, spectrum II with *absorption*. The great absorption of the lines marked with crosses (combinations with the $2s_5$-state of argon) and with a circle (combination with the $2s_3$-state of argon) is very apparent.

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[1]) TH. LYMAN and F. A. SAUNDERS, Nature **116**, 358, 1925.

[2]) G. HERTZ and J. H. ABBINK, Naturwiss. **14**, 648, 1926.

[3]) H. B. DORGELO and J. H. ABBINK, Naturwiss. **14**, 755, 1926.

[4]) These photos were taken with plates which had been sensitized with dycianine, the stigmatic arrangement of the grating of our physical laboratory being used. The stepwise weakening of the spectrum lines was obtained by the aid of a quartz-platinum gradual weakener placed before the slit. We wish to draw attention to the efficiency of these step-by-step weakeners also in this part of the ultra red region of the spectrum examined by us. In the reproduced lines λ 8264 (1st order) and λ 4158,6 (2nd order) it is clearly seen that the weakening action of the different parts of the weakener is pretty well the same for both wave-lengths. Combining these results with earlier measurements in the ultra-violet, we may now say that these quartz-platinum weakeners are very efficient in a wave-length region of from 9000 Å to 2200 Å.

Just as with argon, this absorption by the metastable states could be used to determine the duration of these states in argon. For this purpose we used method III described in this paper.

It appeared at once that the duration of the metastable argon atom states depended in a great degree on the impurities present in the tube. In particular the addition of hydrogen appeared to exert a strongly destructive influence on the metastable states of argon [1]).

It was, therefore, of great importance to purify the argon as much as possible. We have applied several methods of purification to make the argon, which had been obtained by distillation of solid argon, still purer if possible. Among other methods the following were tried: purification by means of Na, or Mg, spluttering of Ca and Wa and circulation over heated CuO; further addition of small traces of O_2 during the discharge, in which the water vapour, if any had formed, was condensed with liquid air, and the excess of O_2 was removed by evaporation of Wo. The result of all these methods of purification was that at low pressure it was quite possible (especially by purification by means of Wo-vapour) to get the argon so pure that in a discharge through the tube only the argon lines appeared. At pressures of 1 cm. and higher the colour of the discharge of the column (current density about 1 mA/cm^2.) was always grey. If, however, at these high pressures the current density was increased, this grey discharge disappeared, and the line spectrum of argon reappeared.

Spectrographic records of the quartz spectrograph of this grey argon discharge [2]) gave a continuous spectrum, which extended over the entire spectral region of the quartz spectrograph.

This grey "argon" discharge had already been observed before in this laboratory by Dr. PENNING, in his attempts at purifying the argon required for his measurements of the anode-heating. PENNING also, always obtained the grey column discharge at higher pressures, however carefully the gas had been purified.

We have, so far, not been able to ascertain whether this continuous spectrum, which appears at higher pressures of the argon in a column discharge, really belongs to argon, or whether it might, possibly, be due to very small traces of residual hydrogen. Different experiments on this point (which are still in progress) render it probable that the latter is really the case.

With regard to our results of the measurements of the duration for the metastable states of the argon atom, we may state that we had already been able to detect a perceptible absorption by the metastable states of

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[1]) Very probably the Lyman bands of H_2 are excited by collisions of the second kind of the metastable states of the argon atom with H_2 molecules (Cf. E. E. WITMER, Proc. Nat. Acad. Amer. **12**, 238, 1926).

[2]) This column discharge was excited in a tube provided with a quartz window, which had been fused to glass. Hence the whole tube could be pumped at temperature (± 350°). Besides, spluttered Mg was present in the tube.

the argon atom by means of method I (with rotating disc) 1) about $^1/_{75}$ sec. 2) after interruption of the current by the absorption tube.

In fig. 8 is found a curve obtained by method III, representing the value of the remaining absorption in its dependence on the time (argon pressure

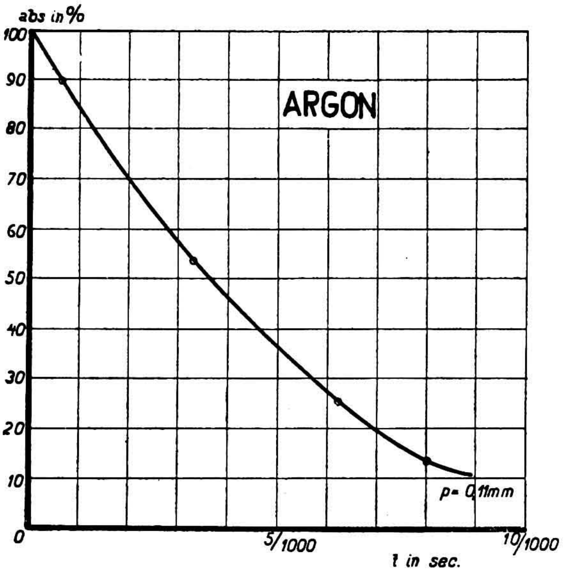

Fig. 8.

in absorption tube 0.11 mm.; inner diameter 46 mm.; abscissae and ordinates of fig. 7 analogous to those of fig. 4 for neon).

Just as for neon, we have also made measurements at different pressures of the argon in the absorption tube. We found a maximum duration of the metastable states of the atom with the given diameter 3) of the tube at about 0.1 mm. pressure.

Repeated measurements yielded the same result.

Summarizing the results obtained for argon, we get the following:

1. With thoroughly purified gas durations of the metastable states are found which are still greater than those that are measured for neon.
2. The durations of the metastable states in argon are influenced by added impurities (especially hydrogen) in a much greater degree than they are in neon.

c. *Helium.*

As is shown in fig. 3, there appear in helium two metastable excited states (2*s*- and 2*S*-states). The metastability of these states was proved by

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1) Zs. f. Phys. **34**, 766, 1925; Physica **5**, 431, 1925.

2) Communication at the XXIVth Flemish Physical and Medical congress, held at Ghent on April, 11th 1926. Compare Wis- en Natuurk. Tijdschrift (organ of the Flemish Physical and Medical Congress) III volume, p. 65, 1926.

3) The curves of fig. 5 of Neon had been obtained with a tube of the same bore.

PASCHEN's well-known researches [1]) on the absorption by excited helium atoms.

In order to determine the duration of the 2s-state by our method, the course of the absorption with time of the line 10830 A in the ultra-red should be followed. This line was filtered out in the way indicated by PASCHEN by the aid of a water filter in combination with a Wratten-filter for ultra-red. As by our method III (triode lamp with 2000 V. anode tension) we could not get passage of the current in the helium tubes used, we give in fig. 9 curve I obtained by method II.

The helium pressure in the absorption tube used (diameter 32 mm.) was 5 mm. [2]). Curve II represents the theoretically calculated curve, which indicates the disappearance of the metastable states with course of the time through diffusion towards the wall. In this it was assumed that every atom in the metastable state loses its energy on collision with the wall; further as diffusion constant that calculated from the gas-kinetic data was assumed. As we have to do here with the diffusion of excited atom states, which have greater diameter than the atoms in the normal state, the curve will, in reality, have to be somewhat higher. In consequence of the drawbacks already mentioned, which belong to method II, curve I will have to lie slightly lower. From results concerning the disappearance of the

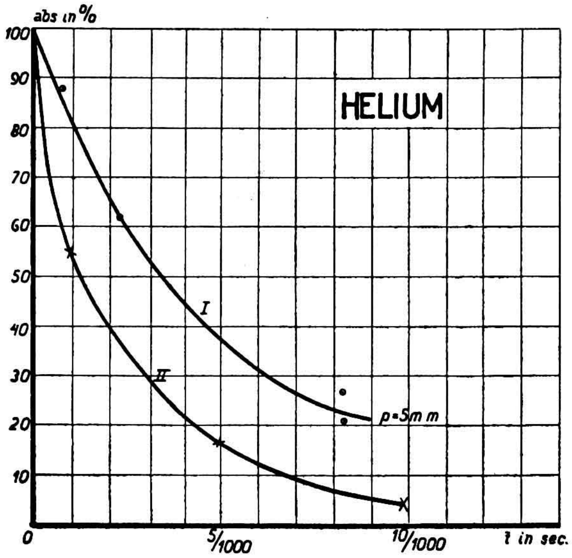

Fig. 9.

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[1]) F. PASCHEN, Ann. d. Phys. **45**, 625, 1914.

[2]) The helium used was obtained according to HERTZ's diffusion method from a Ne-He mixture. In the column discharge exclusively He-lines appeared and no Ne-lines were any longer to be seen.

metastable state found for the $2s$-state, we are, therefore, justified in concluding that the disappearance of the metastable $2s$-states of He after interruption of the current through the absorption tube is entirely determined by the diffusion to the wall. On account of the great difference of energy in helium between the metastable $2s$-state and the next higher energy-condition it is not possible that the metastable $2s$-states are brought to a higher state of energy by collisions of the first kind with normal helium atoms.

Attempts to determine the duration of the $2s$-states have so far yielded no result. For this it was required to filter out only the line 20852 A from the radiation of the emission tube. According to PASCHEN biotite may be used for this purpose. It appeared to us, however, that the biotite kindly put at our disposal by Prof. RUTTEN of Utrecht, could not be used for this purpose.

N.V. PHILIPS *Gloeilampenfabrieken.*

Eindhoven, Oct. 13, 1925.