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Chemistry. — "*Ultramicroscopic investigation of very thin metal and saltfilms obtained by evaporation in high vacuum*". By Prof. W. REINDERS and L. HAMBURGER. (Communicated by Prof. J. BÖESFEN).

(Communicated in the meeting of October 28, 1916).

It is a well-known fact, that the blackening of incandescent lamps must be attributed to the slow sublimation of the material used for filament, which settles on the bulb as a very slight deposit, and becomes darker proportional to the time of incandescence.

Thin deposits on the bulb may be obtained in this manner, not only of carbon, tantalum and tungsten, but also of other metals such as silver and gold¹⁾ and — as one of us has described²⁾ — even of metal-compounds (NaCl , Na_2O , NaOH , Na_2WO_4 , etc.), when they are brought to a lower or higher rate of incandescence in the high vacuum of the incandescent lamp.

Whereas the films of carbon, tantalum and tungsten are black, those of silver and gold are coloured and the salts form an absolutely colourless, clear deposit, which is invisible to the eye, as long as it remains in the same condition.

We have subjected these films to an ultramicroscopic investigation, the results of which we shall communicate in the following pages.

Rock-salt. This deposit was obtained by heating in high vacuum (0.0003 to 0.0010 mm.) a tungsten filament, which had been fixed in an incandescent lamp in the usual manner and had been partially covered with solid NaCl . Before the connection with the air-pump had been broken by melting off, the lamp had been heated to 380°C . in order to exhaust the gases from the bulb.

As long as the vacuum is maintained, the salt-deposit is perfectly clear and colourless, so that it is imperceptible to the eye. When the lamp is opened, so that the moist air can enter, the deposit soon becomes opalescent and especially after the lapse of some time this phenomenon becomes more pronounced. When a bit of the bulb was brought under the ultramicroscope³⁾, as soon as possible

¹⁾ M. FARADAY. Phil. Trans. Roy. Soc. London **147**, 145 (1857).

G. T. BEILBY. Proc. Roy. Soc. London **72**, 226, (1903).

L. HOULLEVIGUE. Ann. chem. et phys. (8) **20**, 138 (1910).

²⁾ L. HAMBURGER. Chem. Weekbl. **13** (1916), 535.

³⁾ Cardioid condenser, Special object glass V of Zeiss, Compensation ocular 18, glycerine-immersion.

after the opening of the lamp, the deposit showed a network of small, radiant ultramicros. In course of time this network became distinctly coarser and after some hours separate particles could be discerned, while after a still longer period some of them clearly revealed the cubic form of rock-salt crystals. Hence a slow *crystallization* or *re-crystallization* of the rock-salt takes place.

This change caused by the addition of the moist air made it impossible to observe the layer of rock-salt in its initial state. In order to do this it should be shut off from the gasphase, both in the course of and after its formation, and after the opening of the balloon it should remain shut off as well.

Closure with oil, obtained by opening the balloon under oil, so that the latter entered instead of the air, proved unsuccessful. A better result was obtained by using Canada Balsam, which had been freed from dissolved gases by exposure to high vacuum under gentle heating, by which process the balsam got thickened. During this operation it had been present in a side-tube, which had been fused to the balloon. After the formation of the NaCl-film the Canada Balsam is made into a thin fluid by cautious heating and is spread out over the layer of salt, so that it was partly covered by the balsam. When the lamp was then opened, the layer of salt underneath the Canada-Balsam remained perfectly clear and transparent, whereas in the uncovered places it turned white.

In the ultramicroscope the layer covered with Canada Balsam was optically empty.

This became quite obvious when adjusting at the boundary-line Canada Balsam-air. Where the air had been allowed to operate the field was strongly lighted by the network of small ultramicros, where the Canada Balsam had protected, the field was dark. The two fields were separated by a very distinct line of demarcation.

So the rock-salt is deposited on the bulb as an optically homogeneous phase, crystals are altogether absent, the molecules are absolutely disordered, and we are dealing here with the amorphous, vitreous condition, that may be compared to the undercooled fluid.

This condition is metastable and gradually passes into the crystallised, stable condition. Various circumstances may start or accelerate this conversion:

1. *Access of air.* Water vapour especially plays an active part here, very dry air has hardly any effect, breathing upon it makes the conversion take place very rapidly.

2. *A Rise of Temperature.*

3. *Increase of thickness of the layer by more prolonged sublimation.*

Silver. Instead of the tungsten filament a thin wire of very pure silver had been fixed in an incandescent lamp. The lamp had been carefully exhausted with the help of liquid air, during which process it had been heated to 380° C, and during a short time the wire itself was kept at a low dull-red heat by means of an electric current. Thus any impurities that might be found on the bulb and the wire were removed as well as possible. Hereupon the lamp was melted off. If now the filament was brought to a deep-red heat with the aid of the electric current a deposit soon appeared against the bulb. With a prolonged sublimation the colour of this deposit changed from an original pale yellow into orange-yellow, red, violet and finally into blue.

On opening the lamp we observed as a rule a deepening of the colour, i.e. a change of colour trending to yellow-red-blue. In some cases this change was quite pronounced and the colour became yellowish-red, almost blue, in other cases it was less marked and the yellow became only darker or more reddish-violet. The colours and particularly the order in which they occur during their formation and conversion are quite similar to those we observe with colloidal silver and photohaloids.¹⁾ Hence we cannot but think that likewise they all must be attributed to one and the same cause, viz. to the presence of small dispersed particles of the pure metal.

The ultramicroscopic investigation has quite corroborated this view.

We also find this similarity in the case of gold. As early as 1857 FARADAY²⁾ explicitly pointed this out in his classical experiments with extremely thin layers of gold and colloidal solution of gold. In both cases he accepted as an explanation that the colours were caused by small separate particles of the pure metal.

Ultramicroscopic examination. We once more observed a splinter of the balloon with the aid of the ultramicroscope (Cardioidcondenser).

The red and the blue deposits and in many cases the yellow ones as well were optically quite soluble. They proved to consist of a closely connected network of ultramicros, on the whole varying in colour, viz. blue, yellowish-brown, or green, the *principal* colour of which being complementary to the colour observed macroscopically; hence macroscopic: blue, ultramicroscopic: yellowishbrown; macrosc.:

¹⁾ W. REINDERS. Chem. Weekbl. 1910, 971 and 1001; Zeitschr. f. phys. Chem. 77, 213, 356.

²⁾ M. FARADAY. Bakerian Lecture, Phil. Trans. Roy. Soc. London, 147 (1857), 145.

red, ultramicro: green etc. With a very rare exception exhibiting Brownian motion, they all were immovable, therefore tied fast to the back-ground.

The apparent size of these ultramicros, hence their mutual distance was almost equal in the several compounds, there was at any rate no obvious connection between the variations in this apparent dimension and the macroscopically investigated colour of the deposit. So this proves that the *distance* between the particles is about equal, if, at any rate the thickness of the film is not such, that more layers are lying one above the other. But the intensity of the light of the particles varies; with the red and the blue films it is fairly strong; with the yellow films it is on the whole but slight.

Associating this with the theory of RAYLEIGH¹⁾ we draw the conclusion: *that the dimensions of the yellow ultramicros are smaller than those of the red and the blue ones.*

There is this essential difference between the coloured silver-film and the clear layer of salt that the latter is optically homogeneous, the former distinctly heterogeneous.

The question arose whether this heterogeneousness was already present in the silver deposit in its original form, or whether it proceeded from the effect of the air as is the case with rock-salt.

To obtain a solution to this question we again fused a side-tube with Canada Balsam to the silver-lamp as we had previously done with the salt-lamp. By gentle heating in high-vacuum the balsam was freed from the dissolved gases and when the deposit of silver had been formed it was carefully spread over it, so that part of it was covered by the Canada Balsam.

On opening the lamp the colour of the deposit of silver that had been covered with Canada Balsam remained the same, whereas in the uncovered part a distinct change of colour set in.

In *ultramicroscopic investigation* it appeared that the part covered with Canada Balsam also consisted of a network of ultramicros. There was no marked difference between the apparent size of these ultramicros and those of that part that had been exposed to the air. A sharp demarcation line between the two fields, such as had been observed with the rocksalt and which here too, was macroscopically quite perceptible on account of the variation in colour, was looked for in vain. The two parts imperceptibly passed into each other: the network itself showed no difference and only in the total-colour of the ultramicroscopic field, which had more of brown in it

¹⁾ Phil. Mag. (4), 41, 107, 274, 447 (1871).

with the blue deposit, more of green with the red deposit, could any difference be observed.

The difference was quite obvious however, in a few isolated cases, with a lamp where the evaporation of the silver had been effected by a very slow process and where the deposit had assumed a pale yellow colour, which by the influence of the air passed into violet. The field that had not been covered with Canada Balsam produced the brilliantly lighted mosaic of connected ultramicros, while the protected field was optically hardly soluble, and but very faintly showed a similar network. The line of demarcation between the two fields was very marked.

With the deposit of silver too, access of air results in a coarsening of structure, as we noticed before in the case of rocksalt.

We have not been able to observe it utterly structureless, such as the layer of salt. Yet the possibility remains that the heating to 60° , necessary to equally spread the considerably thickened Canada Balsam, or even the mere contact with Canada Balsam is sufficient to prepare the passing into a more stable, granular condition and that the primarily formed greenish yellow deposit is structureless indeed, hence molecular-dispersed.

It further appears that with an increasing thickness of the layer, even without access of air, the discontinuity, the construction from separate particles becomes more obvious. In this respect too, there is analogy between the deposit of silver and that of salt.

The difference between the silver-film and the salt-film is a more gradual and a less essential one than seemed at first sight. In either case there arises primarily a thin layer of a great homogeneity, which, however, is unstable and shows a tendency to contract into separate particles. This tendency grows proportional to the increase of thickness and is also promoted by the presence of catalysers as vapour. With silver, however, the instability is much greater than with rocksalt; therefore we always find that with a very slight thickness deposits of silver are no longer homogeneous, but have separated into accumulations of small particles.

In connection with KNUDSEN's¹⁾ experiments on the influence of the temperature of condensation on the nature of the matter condensed, we also modified the temperature of the bulb during the entire time of the burning. From his experiments KNUDSEN draws the conclusion that when metal-vapour molecules strike against a bulb, the chance of their being reflected is extremely slight, if

¹⁾ Ann. d. Physik, (4) 50, 472 (1916).

only the temperature of that bulb is kept below a certain critical value, varying for each metal. For mercury he fixed this temperature at -135° , for silver he estimates it at 575° . Though the room temperature at which the glass was kept during our experiments, is far below this critical temperature of the silver, so that we may assume that the silver-molecules striking against the bulb do not reflect, yet it seems unacceptable, that they resume their position of rest immediately after the collision. The glass- and silver-molecules situated near the point of impact will be disturbed in their state of equilibrium and get into a state of motion; small separate particles of silver come into each other's sphere of attraction and find an opportunity of uniting into greater conglomerates. This motion will be so much the stronger and therefore the chance of the agglomeration of silver-molecules so much the greater, in proportion as the temperature of the bulb that is struck, is higher. By maintaining a low temperature of the bulb during the entire duration of the burning of the lamp, the possibility of acquiring an entirely structureless, amorphous deposit is heightened.

Hereupon some experiments were made in which the silver was sublimated, while the lamp had been cooled down to a temperature of liquid air, this temperature being maintained during the whole time of burning. The sublimate showed pretty nearly the same colours and succession of colours as those which arose in room temperature, any appreciable difference could not be observed. Thus a lowering of temperature to below 20° has no material effect on the nature of the film, when observed with the naked eye.

If however, the temperature is raised after the deposit has formed a change of colour sets in, in high vacuum as well. By heating to 260° for 20 minutes it passed back from reddish-violet to yellowish-brown, and yellowish-brown to a faint yellowish-green.

Ultramicroscopically this deposit showed larger particles, being better discernible by themselves. Several of them had loosened from the bulb and freely moved in the immersion-liquid.

FARADAY¹⁾ and BEILBY²⁾ also experimenting on the much thicker deposits of gold and silver which they had prepared by lamination of compact metal or precipitation by chemical process, both observed a retrogression of the tint and an agglomeration into larger particles as the effect of heating. When we remember that as a rule an enlargement of the particles is accompanied by a deepening of the

¹⁾ l. c. page 1.

²⁾ l. c. page 2.

tint (e.g. coagulation of gold sol) the connection between these two changes is not very clear, unless we take for granted that the total colour of the film is in the main that of a connected film, which both FARADAY and BEILBY have noticed between the larger conglomerations. Our own observations are not contrary to this statement. The conversion of colour quite makes the impression as if the film had become thinner. But we have not been able to ascertain a discrete and thinner film ¹⁾).

Gold. Similarly as with silver in this case too, thin deposits could be obtained, the colour of which first became pink, with prolonged sublimation blue and then green.

Here again access of the air of the room resulted in a deepening of colour.

When observed ultramicroscopically a mosaic of brownish-red, greenish or more bluish coloured ultramicros could again be discerned. The primary colour of this mosaic was complementary to the tint that was observed microscopically. So we see that on the whole this image bears a perfect resemblance to that of the deposit of silver.

Tungsten. The deposit of tungsten differs considerably from the silver-deposit.

Firstly it shows no colours, but immediately turns a muddy gray even with the thinnest layers.

Secondly these films, even the quite dark ones are ultramicroscopically utterly insoluble.

The investigation of the tungsten deposits which had been obtained by cathodic atomizing proves that the power of reflection of tungsten is in itself no impediment for the discrete particles being made perceptible, if only the latter are large enough (vide infra). So we must accept that the tungsten particles are much smaller than those of silver and gold. This admission is not a very improbable one. For in a normal temperature the vapour tension of tungsten is infinitely lower than that of gold or silver. Whereas a silverfilament glowing at a dull-red heat (600°) produces a distinct deposit on the bulb, even after half an hour, we require a heat of nearly 3000° ²⁾

¹⁾ J. C. M. GARNETT (Phil. Trans. Roy. Soc. London A. Pos. 237 1905)) tries to account for this change of colour by accepting that by heating the density of the layer decreases while consequently the volume of air, enclosed by the metal-particles increases. But such an assumption is not confirmed by any observation.

²⁾ With our tests we required for the formation of the tungsten deposit about 6 hours, for the silver deposit from 30 minutes to 2 hours.

to obtain a similar effect with tungsten. Therefore the difference between the temperature of evaporation and the temperature of condensation is for silver only 600° , for tungsten nearly 3000° . The "refrigeration" of the tungsten-vapour is thus exceedingly strong and therefore we may expect the state of agglutination of the tungsten-condensate on the bulb to differ but immaterially from that in the state of vapour. From the behaviour of tungsten towards nitrogen we deduce that the tungsten-vapour is mono-atomic¹⁾. From KNUDSEN's²⁾ measurements of the accommodation-coefficient I. LANGMUIR³⁾ too draws the conclusion that a reflection of the tungsten-atoms against a cold surface is highly improbable (c. f. besides p. 963). So we may expect that the tungstenatoms are immediately fixed by the bulb they collide against and will not find any opportunity for the formation of large conglomerations.

If the mere conglomeration of molecules is difficult, an arrangement as required by the crystallised state will surely not take place. Hence the state of the tungsten-deposit will agree with that of the rocksalt-deposit, with the amorphous-vitreous.

The thickness of this layer is extrememely slight. A bulb of 120 c.m³. covered with 0.12 m.gr. tungsten was already decidedly grey-coloured. If we fix the specific weight of tungsten at 20, then the thickness of that layer is calculated $0.5 \mu\mu$. But layers of a fourfold thickness were quite insoluble (optically) as well.⁴⁾

Deposits of metal obtained by means of Cathodic Atomizing.

By cathodic atomizing as well, very thin deposits of metal may

¹⁾ I. LANGMUIR. Journ. Amer. Chem. Soc. **35**, 931 (1913).

²⁾ Ann. d. Physik, **34**, 593 (1911).

³⁾ Phys. Review 1913², 332. C. f. also, Ibid 1916² 149.

⁴⁾ This difference in dimension of the particles of silver and tungsten is also manifested in the conductivity of thin films of metal, on which S. WEBER and E. OOSTERHUIS have just now published very careful measurements. (Proc. of the the Koninkl. Akad. v. Wetensch. Amsterdam **25** (1916), 606).

For the appearance of a perceptible conductivity it will be necessary that the separate particles coalesce or that their distance has fallen at any rate below a certain minimum value. With a forming layer of metal this condition will be satisfied so much the sooner (i.e. with a lesser average thickness) the smaller the dispersed particles are. W. and O. discovered that the conductivity of tungsten becomes perceptible with a thickness of $0.5 \mu\mu$ and that it shows a marked increase at $2.5 \mu\mu$; for silver these figures were respectively 65 and $25 \mu\mu$.

be obtained on the bulb¹⁾. We have prepared such deposits so that we could compare them with the deposits obtained by evaporation.

As a cathode we used a loop-shaped or spiral-shaped curved wire of the metal to be atomized, which was connected *inside* the glass with the platinum feeding-wires. It had been placed in a pear-shaped balloon, the latter being united by a narrow tube to the space of the anode, in which the platinum-anode was. The latter had been entirely fused into a quartz-tube, with the exception of the extreme point of some mm' surface. The atomizing took place under a pressure of $\frac{1}{16}$ mm. mercury, in a dry, oxygenless, current of hydrogen, which ran from the space of the cathode to the space of the anode to wash away any gases that might come from the anode.

Silver. The development of heat during the atomizing was such that the filament partially melted. As the vapour-tension of silver is rather high at the melting-point, part of the silver will evaporate in the cathode-vacuum and sublimate against the bulb. The deposit thus obtained will therefore be formed partly by atomizing, but partly by sublimation as well.

The colour of the deposit was blue, violet, red or yellow, proportional to the shorter or longer distance from the bulb to the cathode.

Ultramicroscopically it again showed in the first place a mosaic of very small ultramicros, of equal dimensions, and perfectly similar to the deposit obtained by evaporation. By the side of these ultramicros, however, or strictly speaking in the background were much larger particles of about $1\ \mu$ diameter and separated from each other by a distance of 6—12 μ .

As with the experiments on the sublimation deposit, here too part of the layer had been covered with Canada Balsam, which being softened by careful heating, had been extended over the film, when still in the vacuum. By this process the twofold nature of the particles of silver clearly came to light. Whereas the Canada Balsam had no effect on the mosaic of the underground, the coarser particles above were loosened by the balsam and had accumulated on the rim of the drop. The line of demarcation of the Canada Balsam which otherwise would be imperceptible was now very clearly marked by this line of radiant larger particles.

¹⁾ M. FARADAY, l.c. pag. 1.

L. HOULLEVIGUE, Ann. chim. et phys. (8) 20, 138 (190): 21, 197 (1911).

H. FRITZE, Ann. der Physik. (4) 47, 763 (1915).

B. POGANY, Ann. d. Physik. (4) 49, 481 (1916).

A. RIEDE, Ann. d. Physik. (4) 45, 881 (1914).

Evidently the silver of the underground is due to evaporation and the larger particles proceeded from atomizing.

Consequently evaporation produced a much finer deposit than atomizing.

The results which H. FRITZE¹⁾ obtained with cathode-atomizing of silver agree with this statement. For he explicitly states that the colour of his deposits was never yellow, though he devoted much attention to the exhausting and the removing of vapour of water and other gases absorbed by the bulb. As a rule the deposit was blue, with a decrease of thickness it became red, while finally with still thinner layers, no distinct colour can be identified, it results in "jede Andeutung einer ausgeprägten Farbtönung zu verlieren".

Such a vague, non-characteristic colour as indicated by FRITZE may also be found in the film proceeding from the effect of air on our thin greenish-yellow silver-deposits. It is, as we have seen, distinctly heterogeneous and much coarser of granule than the greenish-yellow layer formed by slow sublimation.

Tungsten. Again the colour of the film was black, like that obtained by evaporation. It appeared ultramicroscopically that by rapid atomizing very coarse particles were formed (2 to 5 μ diameter); by slow atomizing small particles arose, radiant without colour and — also with an extremely thin black deposit — so numerous that they filled the whole field. So here again it appears that coarser particles are obtained by cathode atomizing than by evaporation²⁾.

S U M M A R Y.

1. The clear, colourless condensate of rock-salt that settles on the bulb during evaporation in high vacuum is, also under ultramicroscopic investigation, optically homogeneous and must be considered as a salt in the amorphous-vitreous state.

2. The opalizing, which this deposit undergoes, by the influence of moist air, originates in the formation of separate crystals, whose growth could be followed ultramicroscopically.

¹⁾ Ann. der Physik (4) **47**, 763 (1915).

²⁾ Of course, the coarseness of the particles in cathode-atomizing depends on the temperature the material attains during the process. When the temperature is high coarser particles are torn off than when the cathode-atomizing is conducted in such a manner (e.g. by repeated rests) that the temperature of the material remains lower.

3. During evaporation in vacuum silver develops a deposit against the bulb. With increasing thickness the colour of this deposit passes through greenish-yellow, orange, red, violet and blue.

4. The red, the violet and the blue films are distinctly heterogeneous. They consist of a network of very small ultramicros. The yellow deposit shows a hardly perceptible heterogeneousness and approaches in structure the amorphous-vitreous state.

5. The deposits are not proof against the influence of moist air. The colour changes in the direction yellow \rightarrow red \rightarrow blue and the structure becomes coarser. Heating likewise causes a coarsening of structure.

6. Gold forms — in a similar way as silver — coloured deposits, which are ultramicroscopically heterogeneous.

7. Tungsten forms a black deposit, ultramicroscopically it is not soluble.

8. Deposits obtained by cathode-atomizing consist as a rule of coarser particles than the evaporation-deposits.

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Physics. — *“The virtual displacements of the electro-magnetic and of the gravitational field in applications of HAMILTON’s variation principle”*, By Dr. A. D. FOKKER. (Communicated by Prof. LORENTZ).

(Communicated in the meeting of January 27, 1917.)

In some papers on EINSTEIN’s theory of gravitation Prof. LORENTZ¹⁾ recently applied HAMILTON’s principle to the deduction of the principal equations of this theory from one single variation law. Starting from an invariant equation he was able to reach conclusions which again were represented by invariant equations. It was however not necessary to keep the equations invariant during the whole deduction. On the contrary, an artifice, consisting in the choice of a specially defined virtual displacement (without taking into consideration the conditions of invariancy), proved very useful.

Now it is possible to let the invariancy exist continually during

¹⁾ H. A. LORENTZ, *On HAMILTON’s principle in EINSTEIN’S theory of gravitation*, *Proceedings*, Kon. Ak. v. Wet. Amsterdam, XIX, p. 751. *Over EINSTEIN’S theorie der zwaartekracht*, I, II, III, *Verslagen*, Kon. Ak. v. Wet. XXIV, p. 1389, 1759, XXV, p. 468.