Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

As the intensity of light of the apparatus used (ROWLAND's grating, then MICHELSON's echelon) has increased, so the percentage of ordinary light, possibly present, has decreased.

We must conclude, that the orbits of the equivalent electrons, in planes normal to the magnetic force, are with great approximation circles. Elliptic orbits, fortuitously distributed in planes normal to the field, need not be conjectured for the representation of the phenomena.

Rather closely connected with the subject of this paper, are the latest investigations of JEAN BECQUEREL [1]) and A. DUFOUR [2]). DUFOUR obtained various new results concerning the banded emission spectra of the alkaline-earth fluorides and chlorides radiating in a magnetic field and in some cases observed incomplete circular polarization. Several absorption bands of xenotime and tysonite according 'to J. BECQUEREL also exhibited incomplete circular polarization in a longitudinal magnetic field. He showed, however, lately [3]) that in the case of these crystals there is no real incomplete polarization, but that under the action of the magnetic field besides the principal components, others of slightly different wavelength, come into existence, which exhibit a polarization opposite to that of the principal lines.

Physics. — *"On photo- and electrochemical equilibria."* By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS.)

Already previously [4]) I pointed out that if a dark or thermo-chemical equilibrium is exposed to the action of light or electrical energy, and the system is *susceptible* to these forms of energy, a new equilibrium will be established, which deviates from the thermo-dynamic equilibrium, or in other words which is thermic metastable.

On that occasion the heterogeneous photochemical equilibria in the systems Ag_2Cl—Cl_2 and S—CS_2, and further the homogeneous photochemical equilibrium $2 SO_3 \rightleftarrows SO_2 + O_2$ and the homogeneous electrochemical equilibrium $3 O_2 \rightleftarrows 2 O_3$ were discussed, in which a photochemical dissociation equilibrium with HCl was predicted.

[1]) JEAN BECQUEREL C. R. T. 145, p. 413. 1907.

[2]) A. DUFOUR C. R. T. 146, p. 118 et p. 229. 1908. Journal de Physique Avril 1909.

[3]) JEAN BECQUEREL. These Proc. p. 146. June 1909. Contribution à la connaissance du phénomène de ZEEMAN dans les cristaux. See also supplement N°. 20. Leyden communications.

[4]) Inaugural Address. Amsterdam Dec. 9th 1907.

Recently this supposition was not only confirmed, but it has appeared to COEHN [1]) that even at the ordinary temperature this equilibrium is so clear and so easy to demonstrate that in future the dissociation of HCl-gas by light can be an experiment regularly made at university lectures.

Moreover of late some other equilibria have been studied in this direction, so that the number of photo- and electrochemical reactions begins greatly to increase.

Owing to the support of a few friends of science, also the Amsterdam laboratory has been able for some time to reconnoitre the new territory of photo- and electrochemical equilibria, and now it can already be stated that the search in this domain has not been in vain.

Before however proceeding to the results of the investigations, which were carried out in conjunction with Dr. ATEN, I will make some preliminary general remarks, from which it will appear, how in my opinion the photo- and electrochemical equilibria may be considered.

For this purpose I shall take the following example. Suppose a high column of an aqueous solution of some electrolyte; if we now lead a hot current of air through this solution, and that in so large a quantity per second that the loss of heat of the current of air during its passage through the solution is very small compared with its total amount of heat, the temperature of the air that leaves the solution will not be appreciably lower than the temperature of the air which enters the solution, and if we now disregard the influence of gravity, we may assume that the liquid column is a homogeneous system with everywhere the same temperature and the same concentration, so that we may apply the law of the active masses to such a system.

If we now expose the column of liquid to dark electrical dischargings or to light, and that in the direction of the longitudinal axis, we do the same thing as just now in so far that we send a current of energy through the column of liquid.

How this current of energy works, need not be discussed here; the result, however, must be that the potentials of the reacting substances are increased, which at constant temperature must exclusively be the consequence of an increase of the internal energy of the molecules.

Not only the external, but also the internal energy of the molecules

---

[1]) Ber. 42, 3183 (1909).

increases with the temperature, and as we can say a priori, that the internal energy of the molecules will no doubt be the principal factor for a chemical reaction, this leads us already to expect, that when electrical energy and light-energy are absorbed, equilibria will be established at the ordinary temperature, which are also obtained with supply of heat-energy, but then at much higher temperature.

Now the examples to demonstrate this analogy, are pretty numerous.

REACTIONS.

Supply heat-energy	$3\,O_2 \rightleftarrows 2\,O_3$	$N_2 + O_2 \rightleftarrows 2\,NO$	$2\,H\,Cl \rightleftarrows H_2 + Cl_2$
„ electrical „	„	„	„ Smits Aten[1]
„ light „	„	„	„ Coehn[2]
Supply heat-energy	$8H_2S \rightleftarrows 8H_2 + S_8$	$Se_x + xH_2 \rightleftarrows xH_2Se$	$2\,HJ \rightleftarrows H_2 + J_2$
„ electrical „	„ (Smits Aten)	„ (Smits Aten)	„ (Smits Aten)
„ light „	„ „ „	„ „ „	„ „ „
Supply heat-energy	$P_4 + 6H_2 \rightleftarrows 4PH_3$	$As_4 + 6H_2 \rightleftarrows 4ASH_3$	$Sb_x + \frac{3}{2}xH_2 \rightleftarrows xSbH_3$
„ electrical „	„ (Smits Aten)	„ (Smits Aten)	„ (Smits Aten)
„ light „	„ „ „	„ „ „	„ „ „
Supply heat-energy	$2CO_2 \rightleftarrows 2CO + O_2$		
„ electrical „	„ (Smits Aten)		
„ light „	„ (Chapman)[3]		

Thus I might continue to show that really the photo- and electro-chemical equilibrium at the ordinary temperature corresponds with the thermic equilibrium of much higher temperature, and in connection with this it is easy to explain that photo- and electrothermic equilibria set in with great rapidity.

This is of importance particularly because we may consider this as a corroboration of our supposition that the most important factor for a chemical reaction is the internal energy of the molecules, which

---

[1] We will discuss the investigations, some results of which are communicated here, in a following paper.

[2] l. c.

[3] Chem. Soc. p. 942 (1907).

P. ZEEMAN. "The degree of completeness of the circular polarisation of magnetically divided lines."

- 5 -
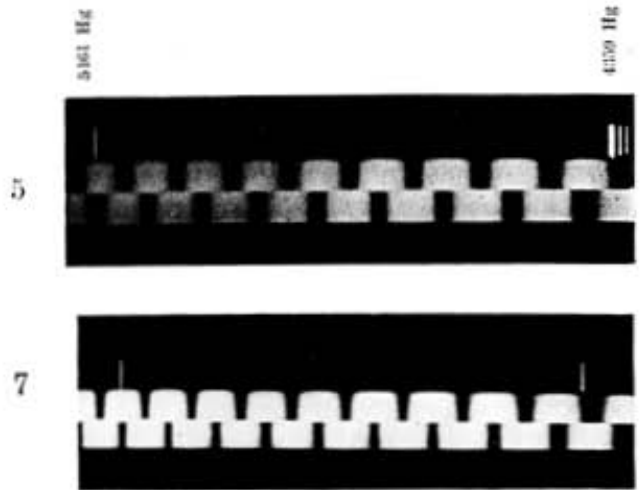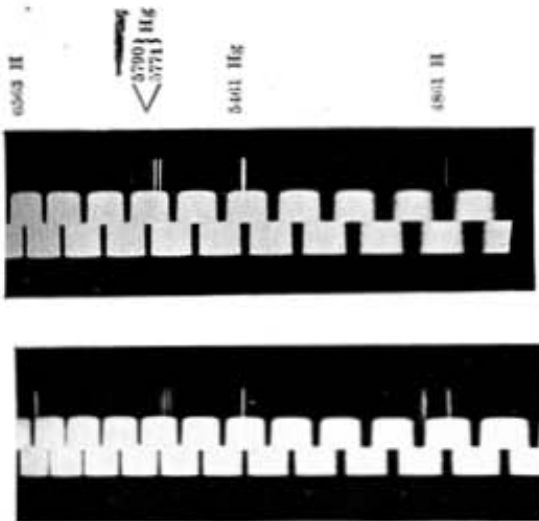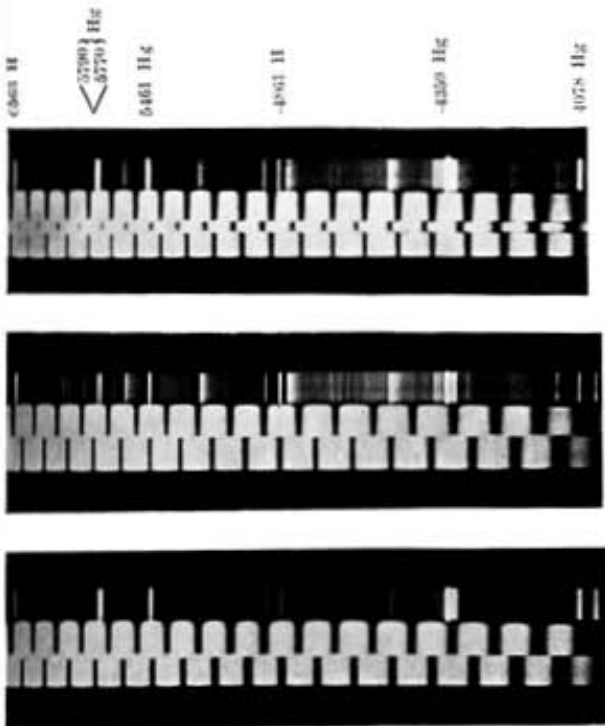
was to be expected, as it is not the molecules, but the atoms or the particles composing the atoms which react chemically.

It is now the question, when may the law of the active masses be applied to a system which is exposed to light energy or electrical energy? The answer to this question is, in my opinion, as follows:

When the quantity of transmitted energy is so great that during the passage of the current of energy no decrease of the energy which is active here, is to be observed, though energy is absorbed by the system, then the system is to be considered as in all respects homogeneous just as in the case mentioned just now of the current of heat-energy, and the law of active masses must be of application.

If, however, the current of energy is less intense, the decrease of energy will be clearly to be demonstrated, the state will differ from layer to layer, and so the system will be non-homogeneous.

So in this case the law of active masses will not be applicable.

It is clear that when the current of energy is too feeble, the equilibrium will be susceptible to a change of the intensity of the current of energy, and so that it is possible to decide in a simple way whether a system at a certain moment may be considered as a homogeneous system or not.

Here we must observe that it must be borne in mind that all kinds of complications may appear; thus it appears among others from DAVIES' investigations [1] that some component or other may exert influence on the current of energy, which e. g. may give rise to peculiar light phenomena in the case of dark electrical dischargings. It is not surprising that in such a case it seems that the law of active masses does not hold, for the current of energy has been subjected to a change, and what the investigation has revealed is simply this that a change in the properties of the current of energy is of great influence on the situation of the equilibrium.

Since light energy and electrical energy are of a much more complicated nature than heat energy, phenomena may occur in this new domain which were never met with in the thermic region.

In conclusion we may point out that when equilibria are studied at such high temperatures that the vessel in which the system is placed, has become a source of light, we shall get a final state which represents a photo-chemical equilibrium at this high temperature; in a few cases this circumstance will have to be reckoned with.

Amsterdam, October 1909.   *Anorg. Chemical Laboratory*
                                     of the University.

---

[1] Zeitschr. f. physik. Chem. 64, 657 (1908)

(November 25, 1909).