The Theory of Photographic Sensitivity.

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SINCE 1920 our knowledge of the formation of the latent image has been greatly increased by investigations which divide themselves roughly into three chapters. The first notable advance was made by Svedberg during the years 1920-1922, and consisted in the proof that the latent image consists of small centres distributed on the silver halide grains of an exposed photographic plate, the distribution of the centres being entirely according to the law of chance. A grain is not developable unless it contains at least one such centre. The second step was to decide upon the origin of these development centres. Two theories were advanced. In one of these it was assumed that the light itself formed the centres, the grains themselves being supposed to be homogeneous. In the other, it was assumed that there exist in the grains, prior to exposure, nuclei which are not silver halide and which are formed during the manufacture of the emulsion, and that the action of light is to change their condition in such a way that they become centres at which development can start. The first theory was extensively investigated and modified by Silberstein and others in the Research Laboratories of the Eastman Kodak Company, whilst the second was developed by Toy in the laboratories of the British Photographic Research Association. Direct evidence in favour of the second theory was at length obtained by Clark in the latter-named laboratories.

The third advance has recently been concisely summarised by Sheppard (*Jour. Franklin Inst.*, 1925, 200, 51), and deals with the nature of the nuclei postulated in the second theory mentioned above. If the nuclei are light sensitive, and are essentially different from silver bromide, their spectral absorptions should determine the spectral sensitivity of the material, or, at any rate, powerfully affect it. The relative spectral sensitivity of plates before and after desensitising with chromic acid is found to be the same, however, and the distribution of sensitivity corresponds approximately with the absorption spectrum of gelatino-silver bromide (Sheppard, Wightmann, and Trivelli, *Jour. Franklin Inst.*, 1923, 196, 653). Moreover, the experimental relation between the quantity of the incident light energy and the photographic effect produced is just what is to be expected when allowance is made for the light absorption of the silver bromide, the agreement being all the better when the light absorbed is reckoned in quanta (Toy and Edgerton, *Phil. Mag.*, 1924, 48, 947).

As a result of the consideration of the above facts, the following theory of the nature of the nuclei has been arrived at. It is assumed that the action of light is to decompose the silver bromide into bromine and silver, and that the apparent sensitising action of a nucleus or "speck" is confined to increasing its size by accretion of photochemically reduced silver atoms until it is large enough to form a development centre. The mechanism by which this accretion is supposed to be brought about is, apparently, that light is absorbed all over the grain and that the energy of vibration of

the electrons in the atoms of the silver halide crystal is thereby increased; but, as a rule, the transfer of an electron from bromine to silver only occurs in the boundary layer at the surface of the specks. Thus energy flows from the surrounding crystal lattice to the specks where it is released as chemical work, the transfer from distant atoms occurring by radiationless collisions (vibrations) through neighbouring atoms until the edge of the speck is reached. It may be noted that Toy (*Phot. Jour.*, 1921, 61, 420) ascribed to Slade a somewhat similar idea as to the transference of energy within the crystal; at that time, however, the attempt was made to explain on this basis how development centres might be formed by light action without the aid of sensitising specks, the mechanism of the action being a kind of "surging" of energy within the crystal and the consequent formation of development centres where energy sufficient to bring about the necessary chemical decomposition is momentarily concentrated. The new theory may thus be considered to be an extension of Slade's original idea to that of the existence of sensitising specks.

According to Sheppard, the formation of the specks is due to casual adsorption and reaction with the silver bromide of a substance present in the gelatin. The theory given leads to the conclusion that once a speck is formed it tends to increase in size; further, not only will the average number of specks on large grains tend to be greater than on small ones in the same emulsion, but also the average size of speck will be greater. It further follows that the sensitising power of any speck is a function of its size. A large speck would not require so large an amount of chemical decomposition in its neighbourhood as would be required by a small speck in order to make a development centre. Svedberg had already touched on the idea that a certain minimum size of speck is necessary before it can act as a development centre, and Clark had deduced that it must be such that it contains somewhere about 300 atoms of silver.

The theory of the distribution of the specks is therefore in striking agreement with the conclusion arrived at by Toy in 1922 (*Phil. Mag.*, 1922, 44, 368) that there are two reasons why large grains are, on the average, more sensitive than small ones. First, there are more nuclei (specks) present in the larger grains, so that a single grain has a greater chance of having at least one; and secondly, the average sensitivity of the nuclei increases with the size of grain.

There is a third factor which may possibly assist in making large grains more sensitive than small ones. Specks on large grains have a greater volume of silver halide from which the absorbed energy necessary to produce the photographic effect may be drawn.

The investigations which led up to the point marked by the theories outlined above furnish no direct evidence of the chemical nature of the specks. Rapid advances were being made in various laboratories towards the solution of the problem, when a paper of Sheppard, from the Research Laboratories of the Eastman Kodak Company, appeared, in which it is

shown that silver sulphide is a substance which can act as a general sensitiser of the kind described. Sheppard (*Phot. Jour.*, 1925, 65, 380) directs attention to the well-known fact that some gelatins are photographically active, whilst others are relatively inert. Making use of the unrivalled facilities of such an organisation as that of the Eastman Kodak Company, which has its own gelatin manufactory, several thousand gallons of deliming liquor, which is formed in the manufacture of gelatin, and was found to be photographically active, were concentrated by appropriate treatment, active fractions being separated from time to time. Ultimately, after some years of investigation, the active substance was tracked down and identified as allyl isothiocyanate, or allyl mustard oil. In the course of manufacture of a photographic emulsion, this substance reacts with the silver halide grains to give the silver sulphide specks to which reference has been made above. It is estimated that photographically active gelatin contains only about 1 part per 1,000,000 to 1 part per 300,000 of the sensitising substance. Other sulphur compounds have been found to act in a similar manner, a necessary condition seeming to be that the sulphur must be doubly linked

to another atom, and not singly linked to two other atoms. The analogous compounds of selenium and tellurium act in a similar way.

The presence of a speck of silver sulphide in the silver halide crystal would result in a disorientation of the silver and halogen atoms at the common boundary, and consequently give rise to a region of instability in its neighbourhood, a view which is supported by the work of von Hevesey (*Z. physikal. Chemie*, 1922, 101, 337).

In all the work which has contributed to the achievement of the present position in regard to photographic sensitivity, it is remarkable how interwoven the ideas of various investigators have become. A mass of evidence from very different sources has now been accumulated in support of the theory that the high sensitivity of the modern photographic plate is due to the presence, before exposure, of minute traces or specks of some "impurity" on the surface of the silver halide grains in the emulsion. The work of Sheppard is a great step forward and opens up new avenues of research, but much work remains to be done before the problem of photographic sensitivity is finally solved.

Sino-Himalaya.¹

By F. KINGDON WARD.

THAT "Any Man's Land" where China, Tibet, and India meet has come into prominence amongst botanists in recent years by reason of the remarkable wealth of flora discovered there; and connected with the problems of plant distribution which arise is the no less interesting problem of geological structure and history. A brief description of the physiography of this region may serve to illustrate the nature of these problems.

We have as a starting-point the great Himalayan range and the mountainous area of western China. East of the 93rd meridian the Himalayan axis trends towards the north-east. It seems probable that this axis is prolonged across China, and that structurally it could be traced in that direction to the plains.

However, what the traveller, who is unable to follow the strike of the rocks composing a great mountain chain like the Himalaya, sees, is something rather different. He sees the Himalayan range ending abruptly at the gorge of the Tsangpo in the great peak of Namcha Barwa; and even if he recognises the peak of Gyala Peri, which forms with Namcha Barwa the gateway to the gorge, as being on the main Himalayan axis beyond the Tsangpo, he can follow it no farther, for the country is unexplored. From the Tsangpo gorge eastwards he perceives rather a wide breach in the Asiatic divide, beyond which in the complex skein of mountains which form a network over western China he is unable to pick up the dropped thread of the Himalayan axis, though the facts of both animal and plant distribution in eastern Asia point to its former, if not to its continued existence.

That this supposed breach in the Himalayan axis

does really exist seems clear enough; though whether at the eastern extremity or in the middle of the range is not so clear.

Rising on the plateau of Tibet are several great rivers whose sources are far apart and whose mouths ultimately open on different seas; but all of them, rolling down from the highlands, converge on one another, squeeze through a narrow gap flanked by lofty snow peaks, and separate again as they emerge from the mountains. In the west is the Brahmaputra (Tibetan Tsangpo), which, after rounding the great gable end of the Assam Himalaya, swings away to the west. In the extreme east is the Yangtze (Chinese Kin-sha), which, after squeezing through the breach, swings away to the east to cross China. Between them, but closer to the Yangtze than to the Brahmaputra, flow three other big rivers, the Mekong, Salween, and Taron (or eastern branch of the Irrawaddy).

The extreme breadth of this river gap is about 200 miles; but a much smaller distance—namely, 70 miles—will span the gap between the Yangtze and the Taron, including the gorges of the Mekong and Salween. That is to say, these four rivers, where they flow parallel to one another for a depth of about 100 miles, are confined to a strip only 70 miles wide. A further peculiarity about this strip is a pronounced tilt from east to west, whereby these rivers flow at successively lower and lower levels as we proceed westwards from the Yangtze to the Irrawaddy.

The reasons for this may be at least partly explicable on the theory of isostasy, the vast area of deposition towards the head of the Bay of Bengal being counterbalanced by a rise in the country to the east, which is essentially an area of denudation. Even the progressive lowering of the river beds might be due to a detailed isostatic equilibrium, being proportional to their

¹ Substance of two lectures delivered at the Royal Institution on April 3 and 30.