

Although a fundamental relationship between the lyotropic series and some change or other in free energy might well be anticipated, it is not obvious (except perhaps for the halides) why the free energy of formation of ions from their constituent elements should show such a close apparent relationship, since complete disintegration of oxy-acids is not in question. The free energies of formation of the halide ions are proportional to their standard electrode potentials, so that for these an explanation of the lyotropic series may perhaps be sought in their relative readiness to engage in electron transfer.

It is suggested, therefore, that a more quantitative study of the series from the thermodynamic and electrode potential points of view at equal concentrations of hydrogen ions may well lead to results of great interest.

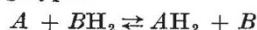
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<sup>1</sup> Cf. Loeb, J., "Proteins and the Theory of Colloidal Behavior" (New York, 1922), chapter v.

### A Photochemical Antagonism of Radiations

THE chemical action of light of different wavelengths on a thermal oxidation-reduction equilibrium of the following type :



may, under certain conditions, in the absence of oxygen, lead to displacements in opposite directions. Suppose that the hydrogen acceptors *A* and *B* have each an absorption band in different parts of the visible spectral region, *A* absorbing mainly the longer waves ( $\lambda \sim 700\text{--}500\text{ m}\mu$ ) and *B* the shorter ones ( $\lambda \sim 500\text{--}400\text{ m}\mu$ ). Then light of longer waves may drive the equilibrium to the right and that of the shorter waves to the left. A good example of such an equilibrium in a liquid system is constituted of the two oxidation reduction systems: methylene blue (*A*)—leucomethylene blue ( $AH_2$ ) and phenylhydrazine-sulphonate ( $BH_2$ )—benzenediazosulphonate (*B*) in diluted acid solutions<sup>1</sup>.

The following qualitative experiment shows the light-effects very well. A dark-equilibrium mixture of the reaction components in 0.01 molar hydrochloric acid, the concentrations of *B* and  $BH_2$  being about 0.01 molar and that of methylene blue about 0.0001 molar, is divided between two test tubes. The first tube stands in a tartrazine solution absorbing the radiation of shorter wave-lengths (blue, violet and near ultra-violet); the second in a saturated copper sulphate solution, chiefly absorbing in the red and yellow spectral region. Exposure to sunlight will give a more or less rapid bleaching of the dyestuff in the first tube, but an increased concentration of dyestuff in the second. A stationary state is reached, regulated by the light intensity and the thermal reactions, the velocity of which is increased with the temperature to about double for an increase of about ten degrees. The thermal reaction:  $A + BH_2 \rightarrow AH_2 + B$  also shows a very prominent dependence on the hydrogen ion concentration, increasing rapidly with the latter. On the reverse reaction,  $B + AH_2 \rightarrow BH_2 + A$ , the acidity has no such marked influence. After the cessation of illumination, the original equilibrium is restored by the thermal reactions.

On the other hand, the photo-active absorption of the two hydrogen donors,  $AH_2$  and  $BH_2$ , are

situated in the near ultra-violet ( $AH_2$ ) and in the middle ultra-violet ( $BH_2$ ). The spectra are characterized by a marked predissociation: both components are dissociated adiabatically by the absorbed radiation into an activated acceptor-molecule and gaseous hydrogen. In the presence of a suitable catalyst absorbing hydrogen, such as platinum black, the reverse recombination process goes on after completed illumination. The energies of dissociation may be preliminarily discussed on the basis of Franck's postulate from the equivalent energies of radiation on the absorption thresholds or maxima, and the calculated values are in an approximate agreement with the results obtained from electrometrical measurements (about 30 kcal./mol.).

According to J. Weiss<sup>2</sup>, the quenching of dyestuff fluorescence by ferrous ions and SH-compounds is connected with photo-reactions in which the light quantum is transferred from the excited dyestuff molecule to the quenching component (hydrogen donor) by a collision of the second kind. Thus the dyestuff, activated by the visible radiation, replaces a light quantum of higher frequency, splitting the hydrogen donor directly. The same mechanism may be valid here.

A complete investigation of the photo-reactions is going on, and will be published elsewhere.

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<sup>1</sup> Holst, G., *Z. phys. Chem.*, A, **169**, 1-19 (1934); **175**, 99-126 (1935).  
<sup>2</sup> Weiss, J., *NATURE*, **136**, 794 (1935). Weiss, J., and Fischgold, H., *NATURE*, **137**, 71 (1936); *Z. phys. Chem.*, B, **32**, 135 (1936).

### Gradients in Wool Growth

THE purpose of this letter is to suggest a possible fundamental and common interpretation of results derived by various investigators, including myself, from fleece analyses and from experiments concerned with the effects of diet and abnormal conditions on fleece and fibre characteristics. A recent paper by Swart<sup>1</sup> is one account of this kind of experimentation. Work of a different kind and concerning fibre-type arrays is described in a stimulating paper by Dr. Galpin<sup>2</sup>: it appears to be possible to link together results from such apparently different types of work.

Dr. Galpin states that in the New Zealand Romney lamb there is a main gradient in fibre-type arrays from britch to poll. Recent investigations of my own<sup>3,4</sup> point to a main gradient of a similar kind in mean fibre fineness: one fleece, for example, exhibited mean diameter at the shoulder region of  $31.4\mu$  and this gradually increased to  $33.3\mu$  at the britch.

Generally the finer parts of the fleece occur anterodorsally. Admitting general embryological evidence and results of studies on the fetal development of the sheep<sup>5</sup>, one must, I think, accept the idea of a physiological skin activity greater in the forward parts of the body than it is in the britch region. Assuming this, there is thus the apparent contradiction that where the activity is greater, the fibres are generally finer. This may be explained in the following way. The greater activity anteriorly is not expressed by the production of coarser fibres, but often by a greater number of fibres, that is, a fleece density which is greater anteriorly than posteriorly. General evidence for this view is supplied by analysis from three different breeds. In Suffolk, Cheviot, and Welsh Mountain fleeces examined, there appears to