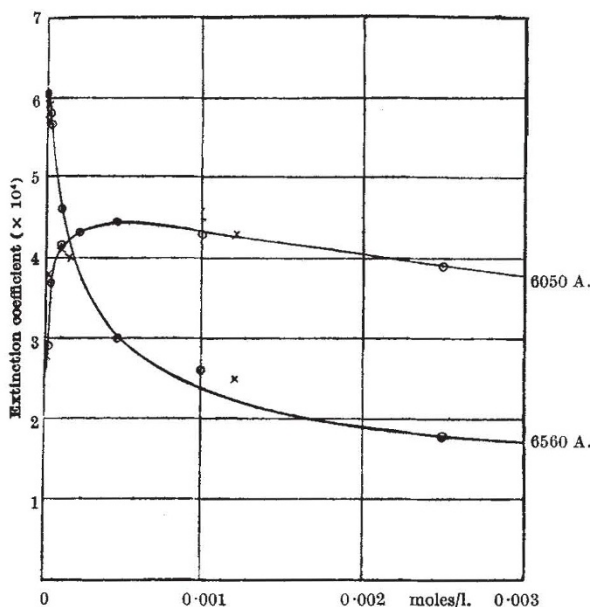


Aggregation of Dyes in Aqueous Solution

WE have recently been carrying out work on the aggregation of dyes in solution, and in particular have been interested in comparing the results obtained in a diffusion cell with those obtained by optical methods, since the latter involves no possibility of disturbing the state of dispersion. The optical method was that employed by Rabinovitch and Epstein¹, depending on the change in magnitude and wavelength of the absorption bands on aggregation.

Working with direct dyestuffs, the changes involved were found to be extremely small and the accuracy of measurements required was so high that a reliable estimate of particle-size could not be obtained. Accordingly, attention was turned to the basic dye, methylene blue, which has been shown by Rabinovitch and Epstein to alter very greatly in its absorption spectra with change in concentration, and, as a preliminary step, their work on this dye was repeated.

Rabinovitch and Epstein worked over the concentration range of 2×10^{-3} to 2×10^{-6} moles/litre, and found that on increasing the concentration, the intensity of the absorption band at 6560 Å. decreases while a new band appears at 6050 Å., increasing in intensity with increasing concentration. They ascribe these two bands to the monomeric and dimeric forms of methylene blue respectively, and by extrapolating the extinction coefficient at these two wave-lengths to infinite dilution and infinite concentration obtain values for the extinction coefficient of monomer and dimer respectively. These results are then used to determine the proportion of the two forms in any solution on the assumption that only monomer and dimer are present, and it is shown that the law of mass action is obeyed over the concentration range tested.



In our work the observed extinction coefficients were higher than those recorded by Rabinovitch and Epstein. The methylene blue used in this investigation was purified by repeated crystallization from alcohol and water and was of 97 per cent purity by titanous estimation and appeared homogeneous when subjected to chromatographic analysis. The concentration range was from 3.13×10^{-4} to 2.5×10^{-2} moles/litre, and it was found that the second absorption band (ascribed to dimer) does not merely increase in intensity with concentration, but also shifts continuously towards shorter wave-lengths. Thus, at 2.5×10^{-2} moles/litre the peak is at 6050 Å., and at 3.13×10^{-2} moles/litre it is at 5850 Å. Consequently, if the extinction coefficient at, say, 6050 Å. is plotted against concentration, the curve does not tend to a limiting value at infinite concentration, but passes through a maximum value, as shown in the accompanying graph. From this we conclude that a solution of methylene blue is not a simple mixture of monomer and dimer, but contains higher polymers, especially at high concentration. A similar conclusion may be drawn from the work of Lange and Herre², who found an activity coefficient of 0.48 for methylene blue by cryoscopic measurement, and it is further supported by the work of Shepperd and Geddes³, although these authors put forward an alternative explanation.

A detailed account of this work will be published elsewhere.

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¹ Rabinovitch and Epstein, *J. Amer. Chem. Soc.*, **63**, 69 (1941).

² Lange and Herre, *Z. phys. Chem.*, **181**, 329 (1937).

³ Shepperd and Geddes, *J. Amer. Chem. Soc.*, **66**, 2003 (1944).

A Light Reaction with Negative Temperature Coefficient

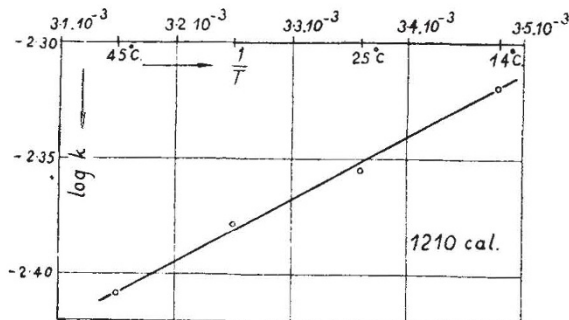
WE ascribe a negative temperature coefficient,

$$\frac{\partial k}{\partial T} < 0,$$

that is, the temperature quotient is less than one

$$Q_{10} = \frac{kT + 10}{kT} < 1,$$

to those chemical reactions the velocity of which decreases with increasing temperature. These reactions have seldom been observed, but some remarkable examples have been realized experimentally. The phenomenon can be explained by supposing a chemical equilibrium preceding the velocity-determining part of the reaction¹. With increasing temperature this equilibrium is displaced in such a manner that the concentration of one of the reacting components diminishes, and, consequently, the resulting reaction velocity decreases. It is evident that a negative temperature coefficient is more easily attained the more the equilibrium depends on the rise of temperature and the less the velocity-determining reaction depends on it. The velocity of light reactions is in general nearly independent of the temperature, the activation energy being provided—at least the greater part—by the light absorbed by the system. We believe that, in the field of photo-reactions, if reactions could be found for which the mechanism with a 'preceding equilibrium' and its dependence on the temperature is appropriate, then the negative temperature effect might be observed more frequently than it is.

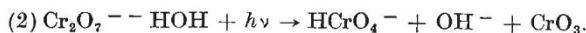
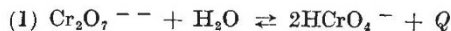


We have shown by kinetic investigations of the photo-oxidation of glycerol and ethyleneglycol with potassium dichromate that for these reactions, under special experimental conditions (concentration of dichromate and acidity of the solution), a decrease of reaction velocity with increasing temperature takes place. The initial velocity (v) of the reaction, with excess of glycerol, is proportional to the light energy which is absorbed by the dichromate, and we have the following velocity equation:

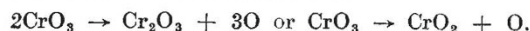
$$v = k.T_0(1 - e^{-icp}).$$

The values of the velocity constant k , obtained as mean of several measurements with different concentrations of dichromate, are plotted in the accompanying graph, in which the logarithms of the velocity constant are shown as a function of the reciprocal of the absolute temperature. It is evident that k diminishes with increasing temperature and the graph is, according to the theory, a straight line the inclination of which corresponds to an activation energy of 1210 cal.

It can be shown that in the reaction investigated the hydrolysis of dichromate ion represents the 'preceding equilibrium', and that the primary photochemical reaction consists of an electron transition—from one stationary state into another—inside the hydrated dichromate ion, which leads to the formation of the highly oxidizing CrO_3 . The reaction mechanism is as follows:



The CrO_3 formed in this manner oxidizes glycerol, or other oxidizable substance present, during which process chromium compounds in a lower oxidizing state are formed, as follows:



The heat of reaction (1) has not until now been directly measured, though Viktor La Mer and Chester L. Read² calculated it from measurements of the heat of neutralization of sodium dichromate with sodium hydroxide as $Q = -13,640$ cal./mol. They used an equilibrium constant for the above reaction (at 25°C.) quoted from S. M. Sherrill³, namely, $K_1 = [\text{HCrO}_4^-]^2 / [\text{Cr}_2\text{O}_7^{--}] = 0.019$, which seems to be too small. If we recalculate La Mer and Read's results with the constant $K_1 = 0.05$, found by R. H. Stokes, J. M. Wilson and R. A. Robinson⁴, a heat of reaction $Q = -1,186$ cal./mol. results, in good agreement with the activation energy determined from our kinetic measurements. This new calculation gives also a value for the heat of dissociation of hydrochromate ion (HCrO_4^-) of $-7,860$ cal., a value of the same order as that calculated from the temperature dependence of the dissociation constant ($-6,772$ cal.). La Mer and Read's value of the heat of dissociation using the 'old' constant is not only different but also of the opposite sign (+780 cal.).