THE HEAT OF DISSOCIATION OF OXYGEN

Sir:

Mecke[1] and Henri[2] have noted two regions of predissociation in the absorption spectrum of NO_2, the first becoming prominent around 3700 Å., corresponding to dissociation into NO and O, and the second beginning at 2447 Å. with NO and O′ (excited O) as the products of dissociation. The value 3700 Å. (77,000 cal. per einstein) combined with the heat of reaction $NO_2 = NO + {}^1/_2O_2 - 13{,}000$ cal. yields them a heat of dissociation of oxygen of 128,000 cal. Kondvat'ev,[3] with the scheme

$$\begin{aligned} NO_2 &= NO + O' - 116{,}000 \\ O_2 &= O + O' - 162{,}000 \\ NO_2 &= NO + {}^1/_2O_2 - 13{,}000 \end{aligned}$$

obtains 118,000 cal. as the heat of dissociation.

I find that excess CO_2 does not lower the quantum yield in the photochemical decomposition of NO_2 into NO and O_2 by λ4047 Å., which thus indicates a non-collisional mechanism for this reaction. This is further proved by photochemical experiments at low pressures; the quantum yield shows no falling off down to 0.01 mm. It must be concluded that absorption of λ4047 will lead to dissociation into NO and O. Therefore the heat of dissociation of oxygen appears to be as low as 115,000 cal., in satisfactory agreement with the value 118,000 cal. found by Kondvat'ev. The implication of a quantum yield lower than unity, actually found with 4047, in the interpretation of diffuse spectra will be examined in the extended report now in preparation.

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Received June 30, 1930
Published August 5, 1930

CATALYSIS OF THE THERMAL DECOMPOSITION OF SILVER OXALATE BY SILVER SULFIDE

Sir:

It has been shown by one of us [S. E. Sheppard, "Colloid Symposium Monograph," **1925**, Vol. III, p. 76] that minute traces of silver sulfide formed on the silver halide grain of photographic emulsions have a powerful sensitizing effect for the formation of the latent photographic image. This sensitizing action is manifested in two ways. The more important is a general sensitizing for all wave lengths to which the silver halide is itself sensitive, or for which it has been optically sensitized by dyes.

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[1] Mecke, *Naturwissenschaften*, **51**, 996 (1929); *Z. physik. Chem.*, **7B**, 108 (1930).

[2] Henri, *Nature*, **125**, 202 (1930).

[3] Kondvat'ev, *Z. physik. Chem.*, **7B**, 70 (1930).

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Beside this, under certain circumstances, silver sulfide can act as an optical sensitizer for silver halide, like colloidal silver. The condition for the optical sensitizing appears to be a very high dispersity of the silver sulfide on and in the silver halide, and a relatively large amount of this highly dispersed silver sulfide. A number of hypotheses have been proposed to account for this sensitizing action, several of which have been discussed by one of the authors [*cf.* S. E. Sheppard, "Sixth Hurter and Driffield Memorial Lecture," *Phot. J.*, **68,** 397 (1928); also *Phot. J.*, **70,** 132 (1930)]. It has appeared to us that further light on the problem might be obtained by investigating the possible catalysis by silver sulfide of other reactions of silver salts. The thermal decomposition of silver oxalate

$$Ag_2C_2O_4 \longrightarrow 2Ag + 2CO_2$$

which has been studied by J. N. Macdonald and C. N. Hinshelwood [*J. Chem. Soc.*, **127,** 2764 (1925)] was tried first. Normally this reaction proceeds solely at the interface with silver nuclei, and shows a typical autocatalytic course. It was reported recently by A. F. Benton and L. Cunningham [paper read at the Physical and Inorganic Chemistry Section, American Chemical Society, April, 1930] that illumination by ultraviolet light produces silver nuclei which effectively catalyze the reaction.

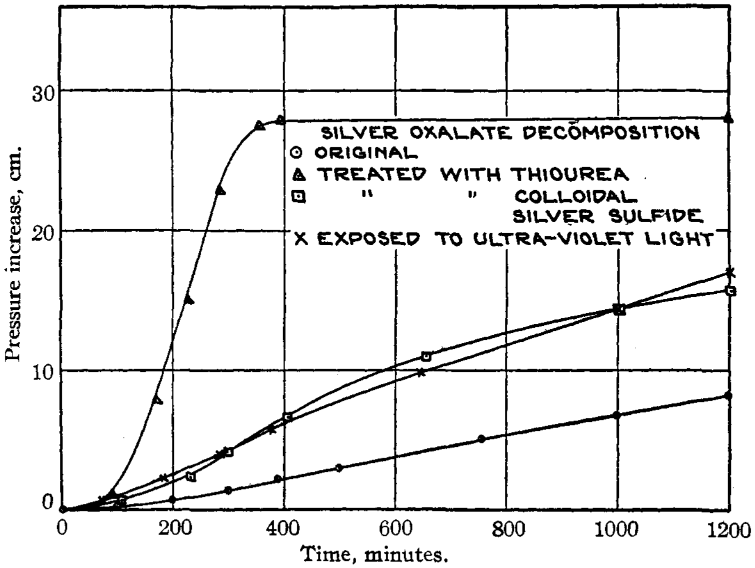

Fig. 1.

We have produced *silver sulfide nuclei* on silver oxalate by various methods and have found *silver sulfide* to be a very effective catalyst for the reaction, as shown by the graphs in Fig. 1.

A very marked diminution of the induction period is brought about. The extent of the catalysis evidently depends, in large degree, upon the dispersity of the silver sulfide. Although there is, in consequence of the decomposition, immediate accretion of silver to the silver sulfide nuclei, yet it appears evident that the latter are quite capable of replacing silver nuclei as catalytic phase.

According to the Ostwald–Langmuir conception of these heterogeneous reactions, the reaction should proceed only at the three-phase boundary line, gas:solid I:solid II. G. Adhikari and J. Felman [*Z. physik. Chem.*, **131,** 347 (1928)] have demonstrated actual "adlineation" in the case of the reaction

$$Hg + I_2 \longrightarrow \underset{\text{adsorption}}{Hg : I_2} \longrightarrow HgI_2$$

but they note that a physical theory which makes this result comprehensible is still lacking. The fact that silver sulfide can replace silver in the present reaction, as topochemically isomorphous, may give a clue to the mechanism, which will be discussed in a fuller report. Meanwhile, the replaceability of silver by silver sulfide in catalyzing the thermal decomposition of silver oxalate, where it can hardly act as an "acceptor" of carbon dioxide, makes less probable the "halogen acceptor" hypothesis proposed by K. C. D. Hickman [*Phot. J.*, **67,** 34 (1927)] for its photosensitizing effect with silver halides. Also it makes more doubtful the special photoelectrolytic theory of A. P. H. Trivelli [*J. Franklin Inst.*, **204,** 649 (1927); **205,** 111 (1928)]. The bearing of the present results on photosensitizing will be discussed in a fuller publication.

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RECEIVED JUNE 30, 1930
PUBLISHED AUGUST 5, 1930

ASSOCIATION POLYMERIZATION AND THE PROPERTIES OF ADIPIC ANHYDRIDE

Sir:

Faith in the existence of the once widely accepted hypothetical phenomenon, association polymerization, appears to have been revived (or strengthened) in the minds of some of its proponents by the discovery[1] of a spontaneously reversible relationship between a biosan (?) and a polysaccharide. No certain examples of this phenomenon have ever been adduced among materials of known structure, although its supposedly

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[1] Reilly and Donovan, *Sci. Proc. Roy. Dublin Soc.*, **19,** 409 (1930); Schlubach and Elsner, *Ber.*, **63,** 362 (1930); Vogel, *ibid.*, **62,** 2980 (1929); Pringsheim, Reilly and Donovan, *ibid.*, **62,** 2379 (1929). It now appears, however, that these observations may be capable of quite a different interpretation. See Berner, *ibid.*, **63,** 1356 (1930).