THE HEAT OF DISSOCIATION OF OXYGEN

Sir:

Mecke¹ and Henri² 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 $NO_2 = NO + \frac{1}{2}O_2 - 13,000$ cal. yields them a heat of dissociation of oxygen of 128,000 cal. Kondvat'ev,³ with the scheme

$$NO_2 = NO + O' - 116,000$$

 $O_2 = O + O' - 162,000$
 $NO_2 = NO + \frac{1}{2}O_2 - 13,000$

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 $\lambda 4047$ 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 $\lambda 4047$ 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.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA RECEIVED JUNE 30, 1930 PUBLISHED AUGUST 5, 1930 WARREN P. BAXTER4

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.

- ¹ Mecke, Naturwissenschaften, 51, 996 (1929); Z. physik. Chem., 7B, 108 (1930).
- ² Henri, Nature, 125, 202 (1930).
- ⁸ Kondvat'ev, Z. physik. Chem., 7B, 70 (1930).
- 4 National Research Fellow in Chemistry.