(2) It can be used with low-boiling compounds such as ethyl bromide. (3) Metals in the residue may be very easily determined. (4) The accuracy is greater than in Robertson's method, as shown by a comparison of analyses. (5) The use of oxygen and platinized asbestos is never necessary. (6) There is no danger of the reaction becoming too violent or of the projection of particles onto the walls of the flask. (7) The time required is less, particularly because it has been found since publication of the last paper by Willard and Thompson,[3] that the apparatus described by them for the micro determination of halogens can also be used for samples as large as 0.1–0.2 g. This results in a saving of time as well as of space required for the apparatus. For samples of 0.01–0.02 g. an apparatus about half the size of this, or only 28 cm. high, works perfectly.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

J. J. THOMPSON
U. O. OAKDALE

RECEIVED JULY 17, 1930
PUBLISHED AUGUST 5, 1930

COMMUNICATIONS TO THE EDITOR

THE HEAT OF FORMATION OF MOLECULAR OXYGEN

Sir:

In a recent communication Copeland[1] has reported a value for the heat of formation of molecular oxygen of 165,000 cal. We have been engaged in a similar determination by an experimental method which differs only in minor details from the method used by Copeland. The results of our first determinations were in substantial agreement with those reported by Copeland, the average of a number of runs being about 160,000 cal. When we checked the method for possible errors we discovered that we were getting spurious heat effects in the calorimeter. When we took precautions to eliminate these heat effects we obtained as the average of a number of fairly consistent runs 131,000 cal. We do not find any evidence that metastable atoms reach the calorimeter.

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. RODEBUSH
S. M. TROXEL

RECEIVED JUNE 27, 1930
PUBLISHED AUGUST 5, 1930

---

[3] Willard and Thompson, THIS JOURNAL, **52,** 1893 (1930).

[1] Copeland, *ibid.*, **52,** 2581 (1930).

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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
WARREN P. BAXTER[4]

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.

---

[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).

[4] National Research Fellow in Chemistry.

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.

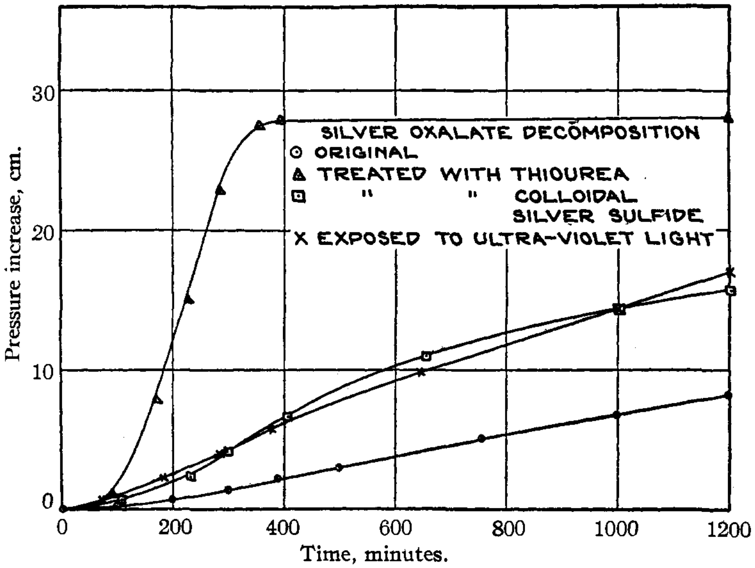

Fig. 1.

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.

RESEARCH LABORATORY
EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

S. E. SHEPPARD
W. VANSELOW

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

[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).

diagnostic features are clearly presented by certain six-membered cyclic esters.[2]

Adipic anhydride, recently studied by Dr. Julian W. Hill in this Laboratory, has already been described[3] as a solid melting at 97°, but the published evidence concerning its molecular weight is equivocal. It has now been found that adipic anhydride as prepared by the usual methods is polymeric. Its melting point varies considerably with accidental details of its preparation. It cannot be distilled as such, but on being heated in vacuo it is partially depolymerized, and the resulting (7-ring) monomer can be distilled. The latter is a colorless liquid that freezes at about 20°. It reverts spontaneously to the polymeric form. The reversion is catalyzed by traces of water: when it is poured into a not especially dried glass vessel, a scum of the polymer is formed at the walls within a few minutes.

The monomer and the polymer are sharply differentiated by their chemical behaviors. Both react practically instantaneously with aniline at room temperature; but the former yields only adipic acid monoanilide, whereas the latter yields a mixture of adipic acid, adipic acid monoanilide and adipic acid dianilide. The formation of dianilide (in 25% of the theoretical amount) constitutes a direct and decisive demonstration of the presence in the polymer of a series of adipyl residues united in a linear fashion by anhydride linkages

$$\mathrm{CO{-}(CH_2)_4{-}CO{-}O{-}CO{-}(CH_2)_4{-}CO{-}O{-}CO(CH_2)_4{-}CO{-}O{-}etc.}$$

Thus the existence of a very high degree of mobility in the relationship between a monomer and its polymer does not preclude the intervention of real primary valence forces in the process or the presence of a definite macro-molecular chemical structure in the polymer, even though the monomer may not be unsaturated in the usual sense.

A more detailed report of the study of adipic anhydrides will be submitted at an early date.

Experimental Station
E.-I. du Pont de Nemours and Company
Wilmington, Delaware

Wallace H. Carothers

Received July 2, 1930
Published August 5, 1930

THE PHOTOCHEMICAL OXYGEN-CARBON MONOXIDE REACTION

Sir:

We have been studying the photochemical oxygen–carbon monoxide reaction and wish to announce some of our results. At room temperature in a mixture of oxygen and carbon monoxide and with light-producing

---

[2] Carothers and Van Natta, This Journal, **52**, 318 (1929); Carothers, Dorough and Arvin, *ibid.*, **52**, 3292 (1930).

[3] Voermann, *Rec. trav. chim.*, [2] **23**, 265 (1904); Farmer and Kracovski, *J. Chem. Soc.*, 680 (1927).

oxygen atoms, the reaction goes almost quantitatively with the formation of ozone. A comparison with equivalent mixtures of oxygen and nitrogen shows that of the two possible reactions of initially formed oxygen atoms, $O + O_2 + X = O_3 + X$ and $O + CO + X = CO_2 + X$, the first goes at least 100 times faster. As both reactions are exothermic and probably do not require activation energy the above result should be attributed to the necessity for the oxygen atom and the carbon monoxide molecule to be properly oriented at the moment of collision, while the oxygen atom and the oxygen molecule can react more independently of their relative orientation in a similar triple collision.

Some years ago Coehn and Tramm [*Ber.*, **54,** 1148 (1920)] reported that at room temperature water vapor has no influence on the rate of the photochemical oxygen–carbon monoxide reaction. We have repeated their experiments at 575° with the result that at this temperature water vapor has a very pronounced accelerating effect on the rate. This action is probably due to setting up of semi-thermal chains and may be linked with the well-known action of water in the thermal explosions of the carbon monoxide–oxygen mixtures. Further experiments on this subject are in progress and will be reported later in THIS JOURNAL.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

W. F. JACKSON
G. B. KISTIAKOWSKY

RECEIVED JULY 5, 1930
PUBLISHED AUGUST 5, 1930

THE OXIDATION OF LACTAL

Sir:

M. Bergmann[1] states that when lactal is oxidized with perbenzoic acid 4-galactosido-mannose is produced in good yield. His experimental results indicate that solely this sugar is formed in the reaction. For the pure sugar he finds the value $[\alpha]_D^{23} + 23.04$ in water five minutes after solution, the rotation becoming constant at +30.0 after about eighty minutes. In the autumn of 1929 we undertook the preparation of a considerable quantity of 4-galactosido-mannose for the purpose of studying the rotations of the sugar and some of its derivatives. The beautifully crystalline lactal which was prepared showed $[\alpha]_D^{20} + 27.69$ in water, in full agreement with Bergmann's measurement (+27.70). The substance did not reduce Fehling's solution and was therefore free of sugar. Its oxidation by a solution of perbenzoic acid in ethyl acetate, following Bergmann's directions, gave a good yield of a crystalline sugar the initial and final rotations of which corresponded well with his data, previously quoted. When the product, which absorbed no bromine and therefore contained no residual

[1] M. Bergmann, *Ann.*, **434**, 79 (1923).

lactal, was fractionally recrystallized it proved to be a mixture of at least two sugars, one having a final $[\alpha]_D$ less than 30° and the other a greater value. Many repetitions of the work gave the same result. The mixture of sugars was dissolved in the minimum amount of water and allowed to crystallize slowly after the addition of methyl alcohol, thus separating the product into two fractions. After five such fractionations the extreme values for the high and low fractions were $[\alpha]_D$ 34.6 and 26.9 (stable aqueous solutions). It is evident therefore that a review of Bergmann's data for 4-galactosido-mannose is required. We suppose that this sugar predominates in the lower-rotating fraction. What then is the identity of the higher-rotating sugar? It is apparently not lactose because it shows upward mutarotation and is very soluble in cold water. The separation of the sugars by fractional crystallization is tedious and considerable time will probably be required for the completion of the work. We are accordingly publishing this record of our year's studies on the subject. The experiments will be resumed in the fall of 1930, and it is also planned to make a similar study of the oxidation of cellobial and similar substances.

National Institute of Health
Washington, D. C.

Andrew J. Watters
C. S. Hudson

Received July 9, 1930
Published August 5, 1930

NEW BOOKS

The Analytical Expression of the Results of the Theory of Space Groups. By Ralph W. G. Wyckoff. Second edition. Carnegie Institution of Washington, Washington, D. C., 1930. 239 pp. 222 figs. 17.5 × 25.5 cm.

The tabulation of the special positions of the space groups has been useful in facilitating the determinations of atomic arrangements in crystals. The second edition of this work has been modified to include a graphical presentation of the symmetry elements of the space groups together with statements of the symmetry properties of the special positions. C. Hermann's recently proposed nomenclature is included in the outline of the derivation of the space groups. The majority of the errors in the tables of the first edition have been corrected.

Sterling B. Hendricks

Trattato di Chimica Organica. (Treatise on Organic Chemistry.) By Giuseppe Oddo, Professor of Chemistry at the University of Palermo. Casa Editrice Remo Sandron, Palermo, Italy, 1930. xv + 949 pp. 101 figs. 17.5 × 25 cm. Price, L. 90.

It is doubtful whether or not an elementary textbook of organic chemistry can be expected to serve at the same time as a reference work for the advanced student. Most American textbook writers have contented themselves with a brief survey of the subject and have placed much