

Thus (4.3), (4.7) and (5.3) are the equations in tensor form which give as first approximation the equations which Einstein proposes as a substitute for Maxwell's equations of empty space. To these must be added also equations (4.4) and (4.9).

When  $\varphi_{ij}$  are identified as the electric and magnetic intensities, they are not the components of the curl of a vector as in the classical theory, unless an additional condition is added.

<sup>1</sup> *Berlin Sitzungsberichte*, 22, 1925, 414-420.

---

## EVIDENCE FOR THE EXISTENCE OF ACTIVATED MOLECULES IN A CHEMICAL REACTION

BY OLIVER R. WULF

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated January 14, 1925

It is known that when ozone decomposes rapidly radiation is emitted, part of which at least lies in the visible and ultra-violet. Stuchtey<sup>1</sup> has photographed the spectrum of the radiation using a quartz spectrograph. The radiation is scattered across the visible and extends well out into the ultra-violet. In particular, the well known bands of ozone in the vicinity of 2450 Ångstrom units come in definitely in the spectrum of the luminescence of the decomposition; there is also radiation of still higher frequency extending to approximately 2200Å which seems to have been the limit of observation of Stuchtey's work.<sup>2</sup> It is the purpose of this article to give the probable explanation of the emission of this remarkably short wave-length radiation, which, as will be shown, requires for its excitation energy quantities much larger than can be afforded by the ordinary heat of reaction.

The heat of decomposition of ozone is well known, the best value being that given by Jahn,<sup>3</sup> who found 34,500 calories per mol. The decomposition can under no circumstances be in entirety a simple monomolecular process, for we cannot obtain an even number of oxygen atoms from one of ozone. The interaction of three molecules is impossible as the complete mechanism; for this also does not yield an even number of oxygen atoms. The interaction of four molecules, while leading to possible mechanisms, is so improbable that we shall not consider it here.

We hence conclude that the process leading to the decomposition of ozone involves the interaction of two molecules and thus would make available not more than the energy of decomposition of two molecules. This does not mean that the mechanism which determines the rate of

decomposition is bimolecular, and indeed from our knowledge of the kinetics of this decomposition it may be said with considerable certainty that such is not the case. It does mean, however, that the energy available as a result of a single complete decomposition process will not exceed the energy of decomposition of two molecules of ozone.

The individual process in the case of the decomposition of two molecules of ozone would only liberate  $2 \times 34,500/6.06 \times 10^{23}$  calories. Expressing this in terms of the frequency of a light quantum of the same energy, or better still in terms of the corresponding wave-length, we have 4120 Å. Hence, if the decomposition results from the interaction of two ozone molecules of normal energy content, and if the energy liberated in decomposition were in certain of the elementary processes liberated as light, the shortest wave-length that could possibly be emitted would be in the blue at 4120 Å.

Actually wave-lengths corresponding to an energy of practically two times this value are observed to be emitted. Now, the spectrum of the emitted light agrees closely with the emission spectrum of ozone molecules. We must accordingly conclude that ozone molecules have been raised from the normal state to states of excitation of much greater energy, the reversion of which again to the normal state being the process of the emission of the observed radiation. Our interest lies in discovering the source of this energy. If we reject the highly improbable possibility of this excitation occurring in steps, then it is a consequence<sup>4</sup> of the experimental facts that at least a part of the *decomposing* ozone molecules be in an activated<sup>5</sup> state, a state of energy-content higher than the normal state, so that the total energy available as the result of the decomposition is the energy represented by *the reversion of two normal ozone molecules to oxygen plus the energy of activation of the reacting molecules*. That is, at least a part of the ozone molecules do not revert to oxygen directly from their normal state; instead these molecules first become activated to states of higher energy content. These molecules may then revert to oxygen, the total energy liberated, a quantity greater than that corresponding to the transformation of two normal ozone molecules into oxygen being available for the excitation of ozone molecules. These excited ozone molecules then constitute the source of the radiation that is observed.

This seems to be a first case where in a homogeneous chemical reaction, there is direct evidence of the formation of activated molecules prior to reaction.

It should be noted that there is still uncertainty as to whether perfectly pure ozone emits radiation when it decomposes.<sup>6</sup> This might be thought to seriously limit the conclusions drawn above, since in a reaction between ozone and impurity there might be sufficient energy liberated to account for the very short radiation that is observed to be emitted. It is possible

that ozone could react with a compound of carbon (for example, acetylene) where the heat of reaction would be sufficient to account for the observed radiation. But it does not appear at all probable that such a possible reaction could occur in a single step. Moreover, the phenomenon has been observed by several investigators under conditions of gas purity which must have varied widely. It appears very probable that the influence of the impurity is a catalytic one, accounting in this way for the bringing out of the luminescence at lower temperatures than those at which it appears in purer ozone. For with increased rate of decomposition the luminescence would be expected to become visible at a lower temperature than that at which it appears in the uncatalyzed reaction. Stuchtey finds no change in the spectrum when it is excited by purely thermal means, or when excited partially by the introduction of an oxidizable impurity, the luminescence spectrum in all cases showing far-reaching agreement with the emission spectrum of ozone. No bands are observed that would have to be ascribed to the impurity. The existence of activated reactants is of course just as necessary a consequence of the catalyzed decomposition as of the normal decomposition, since no more energy is available in the individual process in the former case than in the latter. Therefore the ideas expressed in this paper seem to rest upon grounds of sufficient certainty to allow of the conclusion that in ozone decomposition we have experimental evidence that at least some of the ozone molecules suffer activation before they revert to oxygen.<sup>7</sup>

*Summary.*—It is shown in this article that the radiation emitted when ozone decomposes into oxygen, considered in relation to the quantum theory, makes it necessary to assume that ozone gas, under conditions favorable for its decomposition, contains ozone molecules in activated states of much higher energy content than that of the normal molecule. The existence of molecules as well as atoms in states of energy content higher than that of the state in which they are normally found, has of course been common experience in the study of the physical processes of the absorption and emission of radiation. But such molecules have hitherto in no case been identified with the activated molecules postulated by Arrhenius to explain the temperature coefficient of chemical reactions. This article is believed to give the first direct evidence which has been offered of the existence of these activated molecules.

The author gratefully acknowledges the suggestions and helpful criticism received from Professors A. A. Noyes and R. C. Tolman and Dr. Linus Pauling.

<sup>1</sup> Stuchtey, *Zs. wiss. Photogr.*, 19, 161 (1920).

<sup>2</sup> The important question as to whether the oxygen bands in the vicinity of 1900 Å which are active in converting oxygen to ozone also are present in the luminescence spectrum remains as yet unanswered. •

<sup>3</sup> Jahn, *Zs. anorg. Chem.*, **60**, 337 (1908). Kailan and John, *Zs. anorg. Chem.*, **68**, 243 (1910).

<sup>4</sup> It must be pointed out that this is a consequence only if we also reject chain reactions in which consecutively normal ozone molecules are decomposed for the activation of some molecule in successive steps, which, after a sufficient number of such steps, may clearly be made to possess enough energy to account for the observed excitation energies. Chain mechanisms of this type, and of such a design as to actually account for the observed radiation appear, from energy considerations and our knowledge of the kinetics of ozone decomposition, to be highly improbable.

<sup>5</sup> By this activation there is understood any passage of the ozone molecule to a form of higher energy. Thus a possible form of activation would be  $O_3 \longrightarrow O_2 + O$ .

<sup>6</sup> Trautz and Seidel, *Ann. Physik*, **67**, 527 (1922).

<sup>7</sup> In regard to the possibility of reaction between ozone and impurity affording sufficient energy to account for the luminescence observed without any activation of these reactants, it may be pointed out that if it be assumed, in view of the work of Trautz and Seidel referred to above, that it is the reaction between ozone and carbon monoxide which yields the energy that excites the luminescence, the conclusions of this paper remain substantially unchanged. For, while this reaction affords more energy than the reaction of two normal ozone molecules, it does not give a sufficient amount to account for the short wave-length radiation that is observed. Thus from thermochemical data it may readily be computed that the reaction  $O_3 + CO = CO_2 + O_2$  is attended by an energy liberation of 102,500 calories. This might account for radiation of wave-lengths as short as 2780Å, but not shorter. As has been said above, Stuchtey finds an important part of the total radiation to be of considerably shorter wave-length than this, namely that lying in the vicinity of 2540Å, and radiation extending even farther in the direction of shorter wave-length than this latter is also observed. Therefore the conclusions of this paper can be applied equally as well to the reaction between ozone and carbon monoxide, if this reaction be thought responsible for the luminescence.

---

### CRYSTALLINE INSULIN\*

BY JOHN J. ABEL

FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY  
AND THE DEPARTMENT OF PHARMACOLOGY, JOHNS HOPKINS UNIVERSITY

Communicated February 6, 1926

In two preceding communications<sup>1,2</sup> it has been told how my collaborators and I were induced to attack the problem of the isolation of insulin and what progress had been made towards its solution to within a few months past. It was there pointed out that a clue had been found, the following out of which promised to lead to the desired goal. This clue eventuated from the observation that when the highly impure and complex, though therapeutically serviceable insulin extracts of commerce are boiled for a short time with  $N/10$  sodium carbonate the resulting physiological inactivation of the extracts is always associated with an alteration of a part of their sulphur, an element which our experiments justified us in believing to be an integral constituent of the hormone itself. After