

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Atomic Oxygen as a Reducing Agent

The reducing action of hydrogen peroxide on certain metallic oxides is well known and the analogous reaction might be predicted for atomic oxygen. The authors have spent a considerable amount of time in this laboratory trying to obtain a reducing action by exposing various metallic oxides to a beam of oxygen atoms produced in the electrodeless discharge. No reaction was obtained except in the case of molybdenum trioxide where a reaction was obtained which appears to be identical with the reaction produced by atomic hydrogen. A target which has been covered with a finely divided deposit of molybdenum trioxide, which is light yellow in color, shows the characteristic slate blue trace where the oxygen beam impinges. Not only were traces of atomic hydrogen and atomic oxygen beams produced side by side on the same target, but beams of atomic hydrogen and atomic oxygen were impinged on the same spot in alternation. No change in the appearance of the blue discoloration could be observed on changing from the oxygen to the hydrogen beam, which seems to eliminate the possibility that the reaction with oxygen is the formation of a higher oxide.

Elaborate precautions were taken to free the oxygen from all impurities including water. In order to make certain of the active species the beam was passed through an inhomogeneous magnetic field. The central undeviated line characteristic of atomic oxygen (Phipps and Kurt, Phys. Rev. **34**, 1357, 1929) was readily obtained but no trace of side lines was observed. This is probably due to lack of intensity since the side lines should be fainter than the central line. It may be that the oxygen atom only reacts with the trioxide when it is in the 3P_0 state or it may be of course that the active species is not the atom but an activated molecule, the $^1\Sigma$ state for instance. It should be noted that the molybdenum trioxide is reduced only when it is separated by two slits from the discharge. If only one slit is used or the target is introduced into the discharge the blue coloration disappears almost instantly.

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A Generalization of the Rydberg Formula

On the basis of the old quantum theory it was known that by carrying on a perturbation calculation one arrived successively at the Rydberg and then the Ritz formulas for the terms of a hydrogen-like atom. In the quantum mechanics it has been shown by Hartree (Proc. Camb. Phil. Soc. **24**, 1929) that for an atom with one electron in a central field a generalized Ritz formula holds at least for large values of N . This formula can be written (the series limit is here taken as the zero of frequency).

$$\nu_n = R / (n + \sum_0^{\infty} q_i \nu_n^i)^2. \quad (1)$$

The ordinary Ritz formula is the approximation obtained when only the first two powers (0 and 1) of ν_n are used. To use more than two constants q_0 and q_1 would make the formula unwieldy and would scarcely help in the complicated cases while in the simpler cases additional constants are unnecessary. The two-constant formula of Ritz is however wholly inadequate to describe certain series of terms especially in the complex atoms.

If one follows the perturbation calculation of the quantum mechanics to two approximations admitting the possibility of more than one optical electron, one is led to suggest a substitute for the Ritz formula which has sometimes important advantages and in the other cases reduces to the Ritz expression. The theoretically derived energy equation can be put into the simple form:

$$\nu_n = R / [n + \sum_0^{\infty} p_{in} / (\nu_i - \nu_n)]^2. \quad (2)$$

This form involves perhaps a slightly artificial but quite harmless definition of the term for which $i = n$ —so that the first approximation (i.e. Rydberg correction) is taken into account without spoiling the appearance of the formula. For all other terms the ν_i are by no means arbitrary constants but are the observable spectroscopic terms. These as well as the properties of the p_{in} will be described in detail elsewhere. For the present only two remarks will be made.

I. In the most usual case there will be no term difference, ν_i with $p_{in} \neq 0$ small enough to be important. That is, all the terms in the sum can be expanded in powers of ν_n and the ordinary Ritz formula results if one uses only the first two terms in the expansion.

II. If there is more than one electron a possibility arises which has heretofore been left out of account. An electron configuration not belonging to a particular series may have

an energy level for which $\nu_i - \nu_n$ changes sign with varying n while the corresponding p_{in} 's are not zero. The conditions for such a case are too complicated to be described in the present letter further than to say that they are stringent enough to explain why this case is not more common than it is found to be. In the neighborhood of such a ν_i the terms will be given by

$$\nu_n = R / [n + q_0 + P / (\nu_i - \nu_n)]^2 \quad (3)$$

and will show a remarkable irregularity which was first observed by Schrödinger (Ann. d. Physik **77**, 1925).

This case which arises, e.g. in Pb I, Ca I, Hg I, Al II, Si III, etc. is possibly the most common form of irregularity and in the past has invariably led to misidentification of terms. If one takes the theory into account and reassigns quantum numbers accordingly the applicability of Eq. (3) is obvious. The term ν_i is incidently located and because of the conditions on p_{in} is fairly definitely identified.

The chief contribution of this work is the satisfaction one gets from the elimination of an apparent flaw in our notions of line spectra. It permits a temporary relief from the feeling that our present theory is not complete enough.

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The Reflection of Hydrogen Atoms From Crystals of Lithium Fluoride

The work on the reflection of hydrogen atoms is now being extended to a study of the reflection from LiF crystals. These crystals were grown from the melt by a modification of the method of Ramsperger and Melvin, (Jour. Opt. Soc. **15**, 359, 1927). A freshly cleaved surface was mounted in the apparatus formerly used in the study of the reflection from NaCl and KCl, (Frank. Inst. **206**, 301, 1928), and bombarded with a sharply defined beam of hydrogen atoms issuing from a discharge tube.

Under favorable conditions the reflection in the specular beam from LiF was as high as 50% of the incident beam, as compared with 5% from NaCl, and 0.5% from KCl. As in the case of the other alkali halides which have been studied, the specularly reflected beam

from LiF is confined to within the same angular breadth as the incident beam.

During the course of the investigation some peculiar fan-shaped patterns consisting of a central spot with radial streamers appeared on the molybdenum oxide coated detecting plate. Simultaneous with the appearance of these patterns the LiF crystal lost its atomic reflecting power and acquired a brownish tinge similar to what is usually observed on glass when bombarded by ions or electrons. If the copper crystal holder was maintained at +110 volts with respect to the surrounding case, these patterns disappeared. Furthermore, it was found that when the crystal holder was insulated similar patterns appeared on the plate even though the crystal was removed from the holder. It was therefore dem-