

to be obvious, especially when Guthnick's light curves for this star are recalled, that we have here an extraordinary case of Cepheid variation and one that should be taken into account in theories of this perplexing type of variable star. Doubtless this is not the only example of its kind.

Among the sixteen papers in this volume two others, at least, are especially noteworthy. Under the title: "New silicon lines in Class B stars," W. C. Rufus, R. A. Sawyer and R. F. Paton identify many lines of hitherto unknown origin in the spectra of helium stars. These disclosures originated in recent laboratory investigations with the vacuum spark, in the course of which the known number of silicon lines was increased fivefold. In the closing paper, R. H. Curtiss and D. B. McLaughlin discuss the results of their spectroscopic observations of comets, especially Delavan's comet of 1913. An advance in this field is marked by their success in deriving accurate radial velocities from the reflected solar spectrum of the comet.

Excellent enlargements of stellar spectra illustrate the volume, among them a beautiful series of Nova Geminorum II by Professor Curtiss and a very valuable sequence of typical spectra by Dr. Rufus.

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## SPECIAL ARTICLES

### EVIDENCE OF A SPARK LINE IN THE LITHIUM SPECTRUM<sup>1</sup>

EXPERIMENTS in this laboratory<sup>2</sup> have shown that the thermionic discharge in gas at low pressure is an effective means of exciting spark lines and that these lines are relatively strong at potentials only slightly greater than the critical voltage. The method has been applied to lithium vapor in an attempt to discover spark lines in this element. The design of discharge tube has been described elsewhere.<sup>3</sup>

Electrons from a tungsten cathode are accelerated by the potential applied between it and a nearby anode and the larger part of the electron path is in an equipotential region. The discharge is concentrated by the magnetic field (about 200 ampere turns) of a copper helix surrounding the tube. In this case the helix served at the same time as a heater to vaporize the lithium. Temperatures between 500° C. and

600° C. were used. The discharge was photographed with a large Hilger quartz spectrograph.

Spectra were obtained at applied potentials ranging from 8 to 200 volts. The only noticeable change in the spectrum (apart from lines of known impurities) was the appearance near 50 volts of a line  $\lambda 2934.15 \pm .1$  Å. This line appeared in one very long exposure at 45 volts. It was very faint at 55 and strong at 60 and above. The photographic density of the line at 100 volts was less than that of the fifth line of the principal series and greater than the sixth. Between 100 and 200 volts the intensity was only slightly increased.

The lithium used was not exceptionally pure. Sodium and hydrogen were always present. No likely impurity of the observed wave length is listed in Kayser's table of principal lines. A faint spark line of sodium is listed by Foote, Meggers and Mohler (*l. c.*) at  $\lambda 2934.4$ , but the absence of other stronger lines on the lithium plates excludes the possibility that the new line belongs to sodium. In one tube the lithium was contaminated with magnesium. The magnesium spark lines  $\lambda 2936.496$  and  $\lambda 2928.625$  were faintly visible on either side of the new line and served as convenient comparison standards. The plates were not, however, suitable for measurements of high precision.

To excite the spark spectrum of lithium the valence electron and one of the K electrons must be removed from the atom. Removal of the valence electron alone requires 5.3 volts and the potential for removal of the K electron alone we will call  $V_K$ . Removal of both by a single collision will require a potential greater than the sum of the two. The spark spectra of other alkalis are visible at the second ionization potential of the normal atom under conditions of current density comparable with those used with lithium, but are greatly enhanced at a potential four or five volts greater than this. This indicates that  $V_K = 50$  volts with a probable error of at least 5 volts.

Holtmark<sup>4</sup> and McLennan and Clark<sup>5</sup> have published critical potentials for the excitation of K radiation from solid lithium oxide and lithium. The former gives 52.8, the latter 42.4 volts. As the experiment is very difficult the results may be questioned without discrediting the ability of these physicists. However, the value here estimated for  $V_K$  is in agreement with Holtmark's results.

The spark spectrum of lithium must resemble the arc spectrum of helium, but will have series terms from two to four times as great. Few lines will fall within the range of the quartz spectrograph. The line  $\lambda 2934$  may correspond to the strong helium

<sup>1</sup> Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

<sup>2</sup> Foote, Meggers and Mohler, "Enhanced spectrum of Mg," *Phil. Mag.*, 42, p. 1002, 1921; "Enhanced spectra of Na and K," *Astro. Phys. J.*, 55, p. 145, 1922.

<sup>3</sup> Mohler and Ruark, "JOSA and R. S. I.," 7, p. 819, 1923.

<sup>4</sup> Holtmark, *Phys. Zeits.*, 24, p. 225, 1923.

<sup>5</sup> McLennan and Clark, *Proc. Roy. Soc. A.*, 102, p. 389, 1923.

doublet  $2s - 2p_{1,2}$ ,  $\lambda\lambda$  10829.1, 30.3. Until we have a satisfactory theory of the helium arc spectrum speculation as to the new line will be useless.

An interesting feature of the spectrum of the thermionic discharge in lithium is the unusual development of the subordinate series. Eleven lines of the sharp series and 16 of the diffuse were plainly seen on one of the plates. Only six and seven, respectively, are listed in tables of series lines. The principal series was recorded to the tenth line.

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### ON THE DISPERSITY OF SILVER HALIDES IN RELATION TO THEIR PHOTO- GRAPHIC BEHAVIOR

IN an article appearing in *SCIENCE* for October 26, 1923, under the above heading, Dr. Frank E. Germann and Mr. Malcolm Hylan query a conclusion reached by Wightman, Trivelli and Sheppard, on the relation of grain size and photographic sensitivity. Their first questioning of the conclusion that the sensitivity increases with the grain size is based on an example quoted in "Monographs on the theory of photography," No. 1, p. 104, where comparison of two emulsions showed that the one having grains one third the linear dimensions was more than 19 times as fast and that the same was true of individual grains in the same emulsion. The explanation of this discrepancy has been amply provided subsequently by discoveries concerning the function of sensitive specks in the silver halide grains.<sup>1</sup>

They quote further the conclusion of Koch and DuPre that "it is not possible to formulate any definite relationship between the grain size and sensitivity with the information at present available," to which it may be replied that very much more data are now available than were at hand at the time that Koch and DuPre made their statement.

With regard to the theoretical considerations they advance, we find ourselves in considerable disagreement with them. They conclude, on the nuclear theory (without specifying what they mean by the nuclear theory), that the speed depends on the *number of grains affected* without reference, therefore, to the size of the grains. It can be seen from the work of Svedberg and others that this argument is entirely in contradiction with the present nuclear theory, since the number of specks or nuclei increase with the size of grain and, therefore, the chance of a grain being made develop-

able by light increases with its size. As we have pointed out in other papers,<sup>2</sup> this result is independent of whether the continuous wave theory or the quantum theory of the constitution of light be adopted. The decision between these two theories must be reached on other grounds. Consequently, we can not agree that "theoretically the smaller grained emulsion should be the more sensitive," but rather the reverse. We may point out in this connection that the writers have not defined exactly what they mean by "sensitivity." Speed, in the usual photographic significance of the term, depends on density measurements, that is, on the number and size of the developed grains conjointly. Sensitivity can be determined microscopically from counts of grains independently of density measurements and the sensitivity of grains of a given size can therefore be specified in a manner independent of such density measurements.

It does not appear necessary, therefore, to discuss their explanation of a discrepancy between experimental results and those theoretically expected, which discrepancy does not in our opinion exist.

We shall await publication of their experiments on removing adsorbed halide from silver bromide grains with interest, but prefer to postpone discussion of this until we have their fuller data.

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### THE AMERICAN CHEMICAL SOCIETY

(Continued)

DIVISION OF ORGANIC CHEMISTRY

Frank C. Whitmore, *chairman*

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*The uses of acetylene in synthesis:* J. A. NIEUWLAND. The evolution of acetylene in organic syntheses began with the introduction of catalytic agents to effect reactions. Some of the following important types of catalytic syntheses were discussed: A—The halogenation reactions, typified by (a) catalytic  $AlCl_3$  reactions; (b) catalytic  $SbCl_5$  reactions. B—Catalysis with mercury salts, as (a) acetaldehyde, glacial acetic acid and acetone; (b) paraldehyde synthesis; (c) synthesis of ethylidene diacetate, acetic anhydride, formaldehyde and methyl acetate; (d) synthesis of acetals and cyclic acetals; (e) synthesis of acetylene with aryl hydrocarbons; (f) synthesis of acetylene with phenols (bake-lite), and the dinaphthylols; (g) synthesis with reacting substances in solution, aldehyde blue, and green, acridine and xanthene dyes. Quinaldine, indole, cinnamic aldehyde, nitro cinnamic aldehyde and indigo. C—Syntheses with  $Cu_2Cl_2$ , as (a) divinyl acetylene, and derivatives ( $HCHO$ ); (b) quinaldine and quinoxaline de-

<sup>1</sup> See papers of Svedberg, *Phot. Journ.*, 62, 186, 316 (1923); Toy, *Phil. Mag.*, 44, 352 (1923); *ibid.*, 45, 715 (1923); Silberstein, *Phil. Mag.*, 44, 252, 955 (1923); *ibid.*, 45, 1062 (1923); S. E. Sheppard and E. P. Wightman on "The theory of photographic sensitivity," *SCIENCE*, 1923, pp. 89-91.

<sup>2</sup> *J. Franklin Inst.*, 194, 485 (1922); *J. Phys. Chem.*, 27, 141 (1923).