

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.

Absolute Value of X-ray Wave-lengths and e/m as Calculated from
X-ray Dispersion Measurements

Recently there have been published two investigations by Bearden^{1,2} the purpose of which is to determine the real value of e/m and the absolute wave-lengths of x-rays. The experimental part of this work is limited to the determination of the index of refraction ($\mu=1-\delta$) for Mo $K\mu$ and Cu K -lines in a quartz prism. The conclusions drawn from the results obtained are: (1) "There is now very little question about the real value of e/m ", and (2) "The grating measurements of x-ray wave-lengths are definitely in error".

Without entering into numerical particulars I shall here present only some general remarks in connection with these statements.

The principle of this method consists in a calculation of e/m or of λ by the employment of an experimentally determined value of δ and the x-ray dispersion theory. For a given medium this theory leads to a relation between the two variables δ and λ which contains also several physical constants (among others e/m and the density ρ). Solved for δ/λ^2 , the relation may be written:

$$\delta/\lambda^2 = e/m\rho K\Phi,$$

where the values of e/m and λ are in doubt, K is a product of some other constants and Φ is a function representing the atomic properties of the dispersing medium and according to Bearden almost insensible for small variations in λ within the wave-length interval here in question [$\lambda \leq (\lambda_K/4)$].

(a) This relation has been experimentally tested by the exceedingly careful, systematic investigation by Larsson,³ using several methods for the determination of δ . From the results it is clear that the deviations found

between theory and experiment hardly may be explained as due only to the values of the physical constants used by the calculation of the "theoretical" curve. In this λ -interval the theory reproduces the experimental results within the limits determined by the uncertainty of the numerical values used and by the experimental accuracy obtained (about ± 0.5 percent). The differences between the extreme e/m -values and the corresponding λ -values are respectively 0.5 and 0.3 percent.

To use the theory to clear up discrepancies of the same order of magnitude as that for which the theory itself has been tested seems to be somewhat hazardous.

(b) Since the agreement between the results of Bearden and those of Larsson has been claimed as a proof of reliability, the following may be noted.

It is pointed out by Larsson that on account of a slight inadvertency the density value (ρ) in his dissertation was somewhat too high. It has been corrected in Siegbahn's "Spektroskopie der Röntgenstrahlen" (Berlin 1931) and has no influence on the δ -values obtained, but only on the "theoretical" ones. Calculated from the differences between the two δ/λ^2 -curves in these books the ρ -value of Larsson must be lowered about 0.5 percent. Consequently the e/m -values calculated by Bearden from Larsson's δ -values comes out as 0.5 percent higher and the agreement is lost. The same correction applied to the λ -value for Larsson in the later paper by Bearden increases this value to about the grating λ obtained by Bearden and also here the agreement is lost.

(c) Looking at the relation above it is clear that we may use a value of δ to calculate one of the two quantities in doubt (e/m or λ) by the aid of a chosen value of the other one. Using different values of λ , we should get

¹ J. A. Bearden, Phys. Rev. **38**, 835 (1931).

² J. A. Bearden, Phys. Rev. **39**, 1 (1932).

³ A. Larsson, Inaug. Diss. Uppsala, 1929.

similar to Stauss,⁴ different values of e/m . Bearden has calculated a value of e/m with the assumption that his own grating λ is the correct one. Using, in the second paper, just this e/m -value, and the same δ -value as before he solves for λ . A priori, one had to expect the grating λ once inserted to come back again. But this is not the fact! Provided that the numerical calculations are correct the difference obtained must be due to the somewhat different form of the relation used in the two cases, and has nothing to do with absolute wave-lengths.

According to Bearden the e/m -value found in the first paper is based on a λ -value, which, according to the latter paper, is definitely in error!

From the above we may conclude that the conclusions (1) and (2) quoted above are both incorrect.

It has also been suggested that in similar cases where the differences between the existing values are considerably larger than the published limits of error, a new method, even

if not so accurate, may be sufficient to decide whether the one or the other value is the "real" one. When it happens, that by such a method, a result is obtained just between the two others, this result is judged as "very unsatisfactory".⁵

It seems to me that these differences ought to be considered as giving a better idea of the reliability of experimental results than is obtained by ordinary methods for calculations of errors. The reason for such frequently occurring discrepancies between calculated accuracy and that in reality obtained, may be found in the common use of the so-called "probable errors" without the necessary analysis to ascertain whether the conditions for the theory of errors are satisfied or not, and also in the tendency to underestimate or to neglect systematic errors.

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⁴ H. E. Stauss, Phys. Rev. **36**, 1101 (1930).

⁵ J. A. Bearden, Phys. Rev. **37**, 1210 (1931).

The Entropy of Nitrous Oxide and Carbon Dioxide

Wulf, (J. Am. Chem. Soc., **54**, 833, 1932) estimates the entropy of nitrous oxide by comparison with other triatomic molecules. The work of Plyler and Barker (Phys. Rev., **38**, 1827, 1931) makes possible an exact calculation of the entropy. According to their interpretation of the infrared spectrum nitrous oxide is a linear molecule, NNO. All but a few percent of the molecules are in the lowest vibrational state. The value obtained for the entropy at 298°K is 52.4 entropy units which is not greatly different from the value estimated by Wulf. The data reported by Martin and Barker (Phys. Rev., **37**, 1708, 1931) on

the infrared spectrum of carbon dioxide indicate that the entropy of carbon dioxide is 51.0 entropy units at 298°K.

The structure proposed for N₂O by Bailey and Cassie (Phys. Rev. **39**, 534, 1932) appears to agree well with the low vibrational frequencies observed and also with the absence of a large dipole moment. This structure assumes double bonds between each pair of atoms.

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The Crystal Lattice of Potassium Pyrosulphite, K₂S₂O₆, and the Structure of the Pyrosulphite Group

Pursuing my investigations on the structure of inorganic groups in crystals I have determined completely and uniquely the crystal lattice of K₂S₂O₆.

The dimensions of the monoclinic unit cell were found to be: $a=6.95\text{Å}$, $b=6.19\text{Å}$, $c=7.55\text{Å}$, $\beta=102^\circ 41'$.

The cell contains two molecules and the space group is C_{2h}^2 . Two sets of potassium atoms, two sets of sulphur atoms and one

set of oxygen atoms are lying in reflexion planes with coordinates $\pm(u\frac{1}{4}v)$. Two sets of four oxygen atoms lie in general positions $\pm(xy_2)$, $\pm(x, \frac{1}{2}-y, z)$. There are thus 16 parameters to determine.

The oscillating crystal method and the Laue method were used. The determination of the structure was based upon the observed intensities of the reflections from several hundred individual atomic planes. No as-