

determinations indicating variations corresponding to the atomic weights reported. These were omitted in the published article, as well as several of the crudities noted in other parts of the work. In the paper as published the experimental details are lacking that should be considered if critical comment were to be made. The most charitable view, however, would be that he attempted the application of procedures to unknown material before he had tested them sufficiently to understand their behavior on known material, a not uncommon mistake in analytical work.

### Summary

1. Muzaffar reported atomic weights of 121.14 and 122.37, respectively, for specimens of antimony derived from stibnites from Hungary and from Bolivia.

2. Specimens of metallic antimony have been prepared from stibnites from Hungary and Bolivia, the ores being obtained from the supply house that furnished the material for Muzaffar.

3. These specimens have been compared with each other and with Kahlbaum's antimony by density determinations and by titration with potassium bromate.

4. The densities of the three specimens lie within one-tenth of one per cent. of one another.

5. The ratios of potassium bromate to antimony lie within five-hundredths of one per cent. of each other,

6. There is no evidence of variation in the atomic weight of antimony from different sources.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE  
CHEMICAL LABORATORY OF THE UNITED GAS IMPROVEMENT COMPANY]

## THE SHIFT IN THE $1.14\mu$ ABSORPTION BAND OF SOME BENZENE DERIVATIVES

By JAMES BARNES AND W. H. FULWEILER

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In an earlier paper<sup>1</sup> by the authors it was shown that the frequencies of the absorption bands (at approximately  $0.87\mu$ ) of benzene and some of its derivatives are shifted progressively toward lower values as methyl and ethyl groups are added to the benzene ring. This note is to report that a similar effect has been observed in benzene, toluene, *p*-xylene and mesitylene in their next outstanding absorption band toward the infra-red, which has a wave length of approximately  $1.14\mu$ . The amount of the shift is the same within the limit of error as that observed in the  $0.87\mu$  band.

The apparatus used, namely, source of continuous radiation, six-foot

<sup>1</sup> Barnes and Fulweiler, THIS JOURNAL, 49, 2034 (1927).

Rowland concave grating and thalofide cell, as well as the method of measurement, were the same as those described in the *Physical Review*, **32**, 618 (1928). In addition, a No. 87 Wratten filter was placed in front of the slit of the grating spectrometer.

The results obtained with an absorption cell 30 mm. in length are recorded by small circles on the curves of Fig. 1. These curves show the variation in the transmission ratio with wave length for the hydrocarbons used. In order clearly to separate the curves the zeros of the transmission

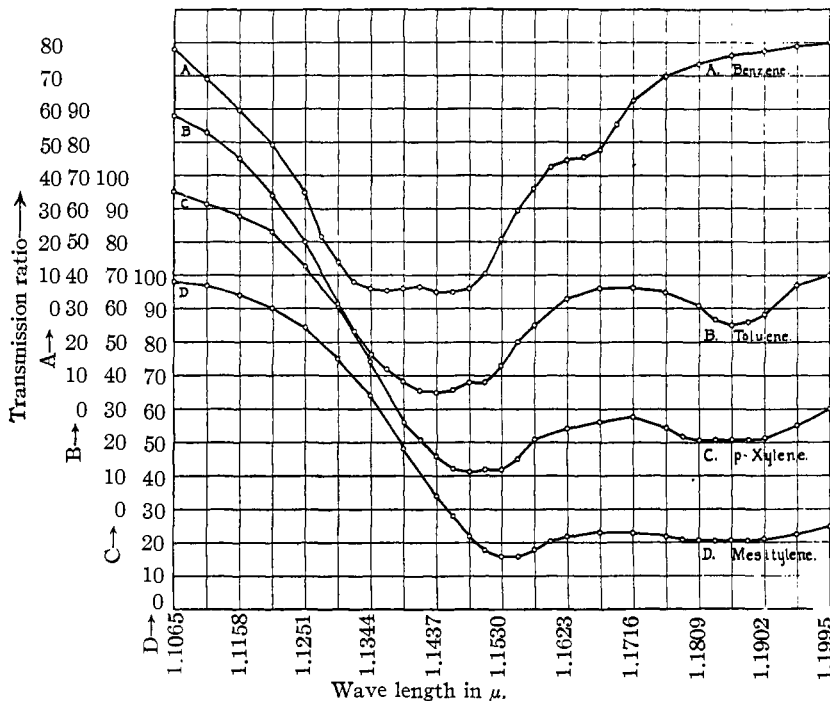


Fig. 1.—Variation of transmission ratio with wave length for benzene derivatives.

ratio for the different liquids are uniformly raised along the ordinate axis. The wave-length scale is, however, in the same position for each liquid.

Inspection of these curves shows that the wave length of the center of the outstanding absorption band is shifted toward the region of longer wave length and hence the frequency of the oscillator is decreased as methyl groups are added to the benzene ring. They also show that the addition of this group appreciably lowers the transmission in the region from 1.16 $\mu$  to 1.20 $\mu$ , with a broad and weak absorption band at approximately 1.185 $\mu$ .

The following table gives the wave length,  $\lambda(\mu)$ , of the center of this outstanding absorption band for each of the liquids investigated. The values are believed to be accurate within  $\pm 0.001\mu$ .

TABLE I  
WAVE LENGTHS OF ABSORPTION BANDS OF BENZENE DERIVATIVES

Derivative $\lambda(\mu)$	Benzene	Toluene	<i>p</i> -Xylene	Mesitylene
	1.1409	1.1442	1.1498	1.1539

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## THE EFFECT OF AIR ON THE POTENTIAL OF THE MERCURY-MERCUROUS SULFATE ELECTRODE

BY MERLE RANDALL AND HENRY A. STONE

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Vosburgh<sup>1</sup> has shown that the potential of Weston standard cells with slight additions of basic mercuric sulfate to the mercury-mercurous sulfate electrode in neutral or slightly acid saturated cadmium sulfate solutions or prepared with the materials in contact with air is about 0.03 mv. higher than that of cells prepared out of contact with the air. Randall and Young<sup>2</sup> found relatively large errors of the order of 1.5 mv. in acid calomel electrodes prepared in the presence of air. We shall here study the effect of air on the hydrogen-mercurous sulfate-mercury cell.

**The Reaction between Dilute Sulfuric Acid and Mercury.**—Redistilled mercury and 0.1 *M* sulfuric acid were sealed in pyrex flasks<sup>2</sup> and rotated for twenty-four hours in a thermostat at 25°. In some of the flasks the air was displaced with a current of pure nitrogen and acid which had been freed from air by boiling in a current of pure nitrogen was used. There was no evidence of the formation of a precipitate but upon the addition of air-free dilute hydrochloric acid a precipitate of mercurous chloride appeared in the acid from the flasks in which no precautions had been taken to exclude air.

**Materials.**—The sulfuric acid was prepared and analyzed as described by Randall and Scott.<sup>3</sup> Nitrogen was prepared by passing commercial nitrogen over three feet of reduced copper turnings at a bright red heat, or by adding a small amount of hydrogen and passing the mixed gas over white-hot platinum wire. The dilute acids were prepared from the stock acid by dilution with conductivity water (weight burets, concentration in moles per 1000 g. of water in vacuum) and traces of air were removed by bubbling through pure nitrogen for eight hours. The acids were stored in quartz flasks.

Mercurous sulfate was prepared by precipitation in the dark from mercurous nitrate.<sup>4</sup> It was washed six to eight times with air-free acid in an atmosphere of nitrogen in the pipet (Fig. 1) and introduced into the cell by a slight adaptation of the method of Vosburgh.<sup>1</sup> Considerable care was taken to shield the mercurous sulfate from the light. We found that mercurous sulfate in contact with 0.1 *M* sulfuric acid

<sup>1</sup> Vosburgh, *THIS JOURNAL*, **47**, 1255 (1925).

<sup>2</sup> Randall and Young, *ibid.*, **50**, 989 (1928).

<sup>3</sup> Randall and Scott, *ibid.*, **49**, 636 (1927).

<sup>4</sup> Prepared by the method of Randall and Frandsen (unpublished); see ref. 2.