

the correction  $\Delta\eta = 0.000205 \eta$ . The results are shown in Table I.

It is remarkable that although the absolute viscosity of butanol is reduced by one half in going from 0 to 25°, the viscosity relative to that of water is almost unchanged.

Previous determinations of the viscosity are shown below.

	0°	25°
T. Thorpe and J. Rodger, interpolated from other temp., <i>Phil. Trans. London</i> , <b>185A</b> , 537 (1894)	(0.0520)	(0.02577)
W. Herz and P. Schuftan, <i>Z. physik. Chem.</i> , <b>101</b> , 284 (1922)		0.02463
J. Timmermans and F. Martin, interpolated from other temp., <i>J. chim. phys.</i> , <b>25</b> , 428 (1925)		(0.02640)
R. C. Ernst, E. E. Litkenhous and J. W. Spanyer, Jr., <i>J. Phys. Chem.</i> , <b>36</b> , 842 (1932)		0.02465
V. C. G. Trew and G. M. C. Wat-		

kins, <i>Trans. Faraday Soc.</i> , <b>29</b> , 1310 (1933)		0.025641
Jones and Christian, this paper	0.05216	0.02605

Trew and Watkins give a low boiling point (117.25°) and a high density ( $d_{25}^{25}$  0.80849,  $d_{25}^{25}$  0.80613) which indicates that their material may have contained water. Ernst, Litkenhous and Spanyer actually give 0.002465, which is presumably a misprint for 0.02465. Their boiling point and density indicate that their material was of good quality. The figures ascribed to Thorpe and Rodger and to Timmermans and Martin are obtained by interpolation from measurements at other temperatures.

### Summary

The density and viscosity of normal butanol have been determined at 0 and 25°.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE PURE OIL CO.]

## Organic Sulfides: Specific Gravities and Refractive Indices of a Number of Aliphatic Sulfides

By GEORGE W. AYERS, JR., AND M. S. AGRUSS

During the course of an investigation involving the simple aliphatic sulfides, most of the values given in the literature for the specific gravities and refractive indices of these substances were found to be in error. It was therefore necessary to prepare these substances in a pure state for the determination of the constants mentioned above.

The specific gravities<sup>1</sup> and refractive indices of ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl and isoamyl sulfides are shown in Tables I and II. All specific gravity values have been corrected for the buoyancy of air and, wherever necessary, for the cubical expansion of glass. Practically all of the values reported represent averages of three separate determinations in 5-cc. glass pycnometers. The refractive indices were determined by means of an Abbe refractometer. Calibrated thermometers were used throughout the present work.

It is of interest to note that the specific gravities of the normal sulfides at 0° are very nearly identical. The values for the iso-aliphatic sulfides are

(1) Findlay, "Practical Physical Chemistry," Fourth Edition, 1929, p. 38.

TABLE I  
SPECIFIC GRAVITIES OF ALIPHATIC SULFIDES

Sulfide	$d_4^4$	$d_{20}^{20}$	$d_{25}^{25}$	Expansion	
				$V_t = V_0(1 + At + Bt^2)$ (for range 0 to 25°)	$\frac{A}{B}$ ( $\times 10^{-4}$ )
Ethyl	0.8524	0.8331	0.8299	1.439	-14.2
<i>n</i> -Propyl	.8525	.8358	.8319	1.042	-2.0
Isopropyl	.8306	.8135	.8092	1.039	0.8
<i>n</i> -Butyl	.8535	.8386	.8348	0.864	1.2
Isobutyl	.8427	.8262	.8232	1.182	-9.4
<i>n</i> -Amyl	.8532	.8390	.8350	0.745	5.0
Isoamyl	.8476	.8323	.8284	.899	1.0

TABLE II  
REFRACTIVE INDICES OF ALIPHATIC SULFIDES

Sulfide	$n_D^{20}$	$n_D^{25}$	$M_{RD}$ (Found)		$M_{RD}$ (Calcd.)	$n_D^{7D}$ Sulfur (Found)
			20°	25°		
Ethyl	1.4428	1.4395	28.69	28.61	28.64	7.98
<i>n</i> -Propyl	1.4481	1.4456	37.88	37.87	37.88	7.97
Isopropyl	1.4381	1.4354	38.16	38.15	37.88	8.25
<i>n</i> -Butyl	1.4529	1.4504	47.14	47.13	47.11	7.99
Isobutyl	1.4463	1.4439	47.24	47.19	47.11	8.07
<i>n</i> -Amyl	1.4556	1.4532	56.44	56.46	56.35	8.07
Isoamyl	1.4520	1.4499	56.51	56.55	56.35	8.15

Average 8.07

much smaller than those for the normal aliphatic sulfides. These relations are shown in Fig. 1.

TABLE III  
 YIELD DATA AND TESTS ON PURIFIED ALIPHATIC SULFIDES

Aliphatic sulfide prepared	Aliphatic bromide, g.	Sodium sulfide (Na <sub>2</sub> S·9H <sub>2</sub> O), g.	Approx. yield of sulfide, <sup>b</sup> % (based on bromide)	Boiling range (corr.) °C.		1st Result	% Sulfur 2nd Result	Theoretical
				°C.	Mm.			
Ethyl <sup>a</sup>				91.2-91.5	746	35.29	35.27	35.55
<i>n</i> -Propyl	99.0	120.8	71	141.6-142.1	749	27.02	26.97	27.11
Isopropyl	99.0	120.8	49	118.7-118.9	749	27.89	27.89	27.11
<i>n</i> -Butyl <sup>a</sup>				186.4-187.0	750	21.72	21.70	21.91
Isobutyl	106.0	116.7	71	168.2-168.8	749	21.71	21.71	21.91
<i>n</i> -Amyl	100.8	198.8	74	227.1-227.5	754	18.22	18.30	18.39
Isoamyl	98.9	195.0	59	214.3-214.8	754	18.37	18.43	18.39

<sup>a</sup> Obtained from Eastman Kodak Co. and further purified. <sup>b</sup> Approximately 500 cc. of alcohol was used per 100 g. of aliphatic bromide.

Likewise, the refractive indices are smaller for the iso series than for the normal series, as shown in Fig. 2.

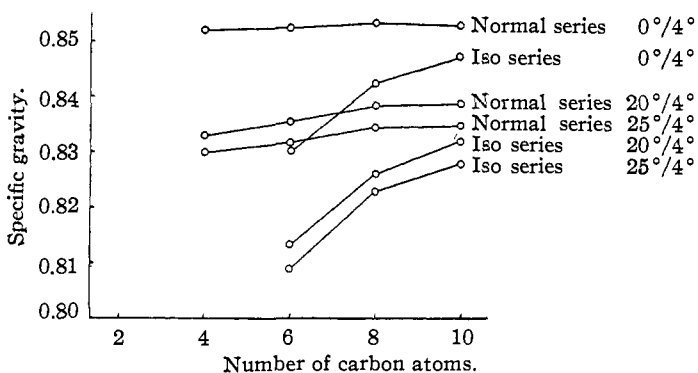


Fig. 1.

Figure 3 gives comparisons of the specific gravities and refractive indices of the aliphatic sulfides and ethers.

The molecular refraction values (*MR<sub>D</sub>*) were determined by means of the Lorentz-Lorenz equation. The calculated values were obtained by use of 2.418 and 1.100 for the atomic refractivities of carbon and hydrogen,<sup>2</sup> respectively, and of 7.97 for the atomic refractivity of sulfur<sup>3</sup> in the sulfide state.

The ethyl and *n*-butyl sulfides were Eastman products, but both were further purified by fractionation through a 14-inch (36-cm.) Hempel column filled with glass beads. The other sulfides were prepared in this Laboratory by a modification of the Bost and Conn<sup>4</sup> method for *n*-propyl sulfide. The aliphatic bromide was dropped slowly into a solution of Na<sub>2</sub>S·9H<sub>2</sub>O in alcohol (Formula 30 or 95% ethyl alcohol). The reaction mixture was refluxed on the

(2) Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911).

(3) Price and Twiss, *J. Chem. Soc.*, **401**, 1259 (1912).

(4) *Org. Syntheses*, **18**, 72 (1935).

steam-bath for two hours, then cooled to room temperature. An oil separated during the preparation of *n*-amyl and isoamyl sulfides. This oil was separated and added to the organic sulfide precipitated after the reaction mixture was added to the sodium chloride solution. In some cases emulsions separated from the salt solutions instead of oils; these emulsions were readily broken down by centrifuging, with or without the use of anhydrous sodium sulfate. To prevent contamination, the salt solutions were not extracted with petroleum ether. The crude organic sulfides, after drying over anhydrous sodium sulfate, were fractionated twice through a 14-inch (36-cm.) Hempel column filled with glass beads. Yield data on the preparation of the organic sulfides are shown in Table III.

In order to determine the purity of the sulfides, the sulfur content was determined by a modifica-

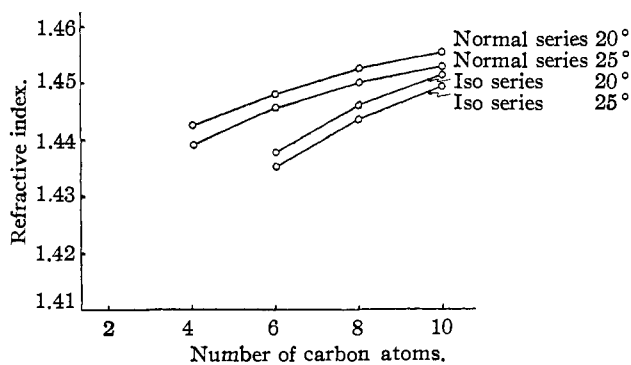


Fig. 2.

tion of the method proposed by Sampey, Slagle and Reid.<sup>5</sup> The results are given in Table III. Approximately 0.2-0.3 g. of the sulfide was added

(5) Sampey, Slagle and Reid, *This Journal*, **54**, 3401 (1932).

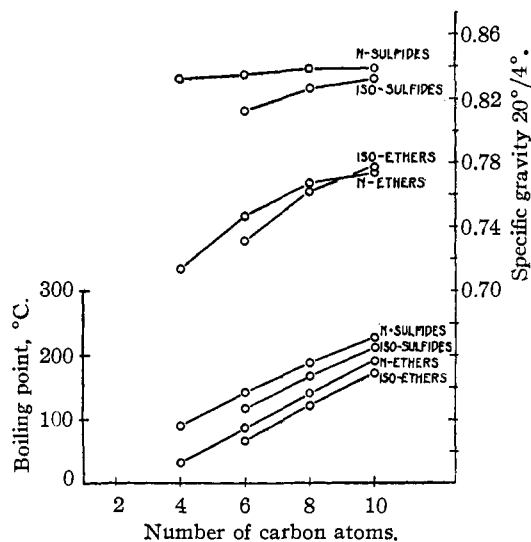


Fig. 3.

from a dropping bottle to 50 cc. of c. p. benzene

and 50 cc. of distilled water contained in a 250-cc. separatory funnel. The acid obtained by the above procedure was titrated with approximately 0.1 *N* sodium hydroxide solution, using methyl red indicator. All corrections due to reagents were found to be negligible. This method was very satisfactory except for isopropyl sulfide, which, according to Sampey, Slagle and Reid, gives slightly high results.

### Summary

Specific gravities at 0°/4°, 20°/4° and 25°/4° were determined for pure samples of ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl and isoamyl sulfides. Refractive indices at 20 and 25° for the D sodium line were also determined for the same sulfides. From these values the molecular refraction values were calculated.

CHICAGO, ILL.

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## Residual Paramagnetism in Compounds of Lanthanum<sup>1</sup>

BY ROBERT B. HALLER AND P. W. SELWOOD<sup>2</sup>

Some years ago one of the writers<sup>3</sup> pointed out an apparent anomaly in the magnetic susceptibility of lanthanum oxide. On theoretical grounds the lanthanum ion may be expected to be diamagnetic with no temperature coefficient of susceptibility. Nevertheless, the purest lanthanum oxide contained a small paramagnetic residue which became evident as the temperature was lowered. Further study of this problem is desirable because magnetic susceptibility is often used as a criterion of purity of lanthanum compounds, and because the small but measurable ortho-para hydrogen conversion on pure lanthanum oxide surfaces<sup>4</sup> is inexplicable unless some paramagnetism on or in the compound is postulated.

### Experimental Part

**Preparation of Materials.**—The lanthanum used in this work had been prepared under the direction of Dr. Frank

(1) Presented in part under the title "Magnetic Measurements in Rare Earth Chemistry" at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry on the Less Familiar Elements, Cleveland, Ohio, December 27, 28, and 29, 1937.

(2) The authors are indebted to the National Research Council for funds for the construction of a magnet, and to the Penrose Fund of the American Philosophical Society for funds for research assistance.

(3) Selwood, *THIS JOURNAL*, **55**, 3161 (1933).

(4) Taylor and Diamond, *ibid.*, **57**, 1251 (1935).

T. Gucker, of Northwestern University, through whose courtesy the authors received a sample sufficient for their purposes. This material had been separated from other rare earths by prolonged fractional crystallization of the ammonium double nitrates. Cerium had been removed by alkaline oxidation with potassium permanganate. The lanthanum had been precipitated repeatedly as oxalate, and then as sulfate enneahydrate.<sup>3</sup>

The present authors reprecipitated the lanthanum as hydrated sulfate. The material now showed no selective absorption in the visible through a 10-cm. layer of saturated nitrate solution in water, indicating the absence of praseodymium and neodymium. The familiar peroxide test for cerium also was negative. Careful qualitative tests failed to reveal the presence of any impurity.

Part of this material was reserved for susceptibility measurements. The remainder was divided into two portions, one of which was converted directly into oxide by ignition at 1000° for sixty hours. The sulfate decomposes slowly but the final sample of oxide obtained gave no cloudiness when dissolved in nitric acid and treated with barium chloride.

The remaining sulfate hydrate was dissolved in a large volume of water at room temperature and was precipitated as oxalate by addition of oxalic acid. The oxalic acid had been purified by repeated recrystallization from redistilled hydrochloric acid followed by recrystallization from distilled water. Part of the lanthanum oxalate was converted to oxide by ignition for one hour at 920°.

Care was taken throughout to prevent the oxide samples