Extrapolation below 53.1° was made by use of this combination of functions, but only the first term has much significance. The entropy results are in Table II.

TABLE II

ENTROPIES AT 298.16°K.

	B_2O_3	B_4C	SiC
0–53.1°, extrapolation	0.68	0.047	0.043
53.1–298.16°, graphical	12.36	6.427	3.905
$S_{298.16}$	13.0 ± 0.1	6.47 ± 0.07	3.95 ± 0.04

The present value of the entropy of silicon carbide is, rather fortuitously, only 0.05 unit different from that (3.90 ± 0.2)[13] calculated from the older data of Nernst and Schwers and Günther.

The entropy of crystalline boron has not yet been determined. From the result for B_4C in comparison with those for SiC and Si[13] and TaC[14] and Ta[15] it may be estimated that $S_{298.16} = 1.7 \pm 0.2$ for B. This value is suggested for us until an experimental result is available.

Related Thermal Data.—The heats of formation of crystalline boric oxide and B_4C have not been determined; consequently it is not possible to derive free-energy values for these substances, although Roth and Börger's[16] $\Delta H = -349{,}000$ for B_2O_3 glass at room temperature might be used to set an upper limit for the free energy of formation of boric oxide crystals.

Heat of formation values for silicon carbide have been reported by von Wartenberg and Schütte[17] ($\Delta H = -31{,}000 \pm 6000$), Ruff and Grieger[18] ($\Delta H = -26{,}700 \pm 2100$), Ruff and Konschak[19] ($\Delta H = -25{,}000$), and Brunner[20] ($\Delta H = -39{,}000$). If the value of Ruff and Grieger is employed, then $\Delta F^\circ_{298.16} = -26{,}100$ is calculated, the entropies[13] of silicon and graphite being, respectively, 4.50 and 1.36. However, in view of the wide discrepancies in the ΔH results but little reliance can be placed on this free energy value.

Summary

Specific heat measurements of crystalline boric oxide, boron carbide and silicon carbide were made, covering the temperature range 51 to 298°K.

The entropies at 298.16°K. are 13.0 ± 0.1 for boric oxide, 6.47 ± 0.07 for boron carbide and 3.95 ± 0.04 for silicon carbide.

The value $S_{298.16} = 1.7 \pm 0.2$ is suggested for crystalline boron.

BERKELEY, CALIF. RECEIVED JANUARY 30, 1941

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[13] Kelley, *Bureau of Mines Bulletin*, 394, 1936, 55 pp.

[14] Kelley, THIS JOURNAL, **62**, 818 (1940).

[15] Kelley, *J. Chem. Phys.*, **8**, 316 (1940).

[16] Roth and Börger, *Ber.*, **70B**, 48 (1937).

[17] Von Wartenberg and Schütte, *Z. anorg. Chem.*, **211**, 222 (1933).

[18] Ruff and Grieger, *ibid.*, **211**, 145 (1933).

[19] Ruff and Konschak, *Z. Elektrochem.*, **32**, 515 (1926).

[20] Brunner, *Z. anorg. allgem. Chem.*, **217**, 157 (1934).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF HOWARD COLLEGE]

The Absorption of Oxygen by Mercaptans in Alkaline Solution[1]

BY J. XAN, E. A. WILSON, L. D. ROBERTS AND N. H. HORTON[2]

It has been known for some time that air or oxygen oxidizes sodium thioethylate in water or alcohol solution to ethyl disulfide.[3] The investigation herewith deals with the absorption of oxygen by alkaline solutions of representative aliphatic and aromatic mercaptans at several temperatures and concentrations of alkali.

The disulfides, which are insoluble in the aqueous alkali, separate as the reaction progresses. *n*-Butyl, phenyl and benzyl disulfides were identified by their physical properties. An unexpected result was found: more oxygen disappears than can be accounted for by the oxidation of the mercaptan to disulfide. This excess absorption is trifling if the alkali is weak, but rises to about 50% of the theoretical for the disulfide as the strength of the alkali is increased to 2.71. This indicates a further reaction, perhaps to a sulfonic acid, but its nature has not been determined.

It was realized from the first that the experimental method adopted, shaking a solution with a gas, is not suited to measurements of extreme accuracy, since the disappearance of the oxygen depends on the rate of diffusion as well as on the re-

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[1] Read at the Cincinnati A. C. S. meeting, April 1940. Original manuscript received May 13, 1940.

[2] We wish to express our appreciation to Dr. E. Emmet Reid, research advisor, Howard College, for his interest and helpful suggestions during the course of this investigation.

[3] P. Klason, *Ber.*, **20**, 3412 (1888).

action rate. However, it gave closely reproducible results when the conditions were kept constant. This was proved by the concordance of the results of duplicate runs. The rate of shaking was 300 times per minute. It was found that an increase of this rate to 750 did not change the absorption rate preceptibly, thus eliminating diffusion as a limiting factor. To avoid crowding only every second or third reading is plotted.

Table I

Time given in minutes; per cent. in vol. of O_2 calcd. for $2RSH \longrightarrow R_2S_2$

NaOH 0.0576 *N*				NaOH 0.346 *N*			
Mg. moles BuSH	10.68		10.69	Mg. moles BuSH	10.87		10.70
Theoretical	5.99		5.99	Theoretical	6.12		6.03
1		2		1		2	
Time	%	Time	%	Time	%	Time	%
2	34.4-	2	33.2-	2	41.4-	2	42.5
4	50.1	4	49.8	4	64.7-	4	63.1
6	60.4-	6	58.6	6	79.8	6	77.9-
8	66.8-	8	65.7-	8	89.5	8	87.2

The absorption of oxygen by *n*-butyl mercaptan in various strengths of alkali is shown in Fig. 1.

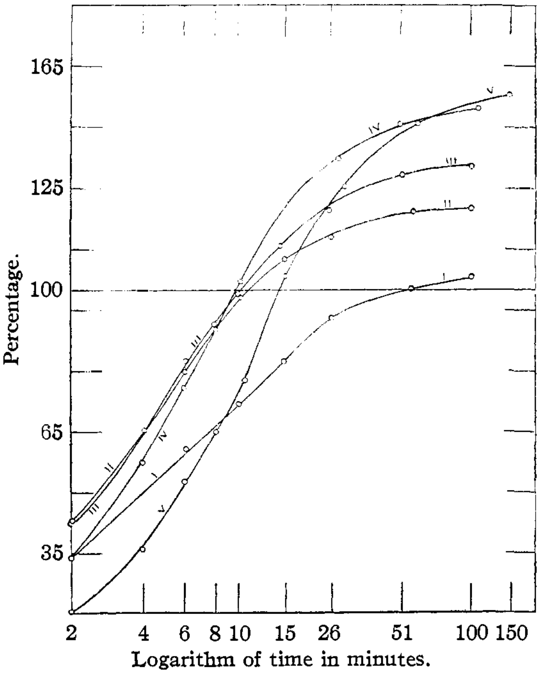

Fig. 1.—Absorption of oxygen by butylthiol in 20 ml. of sodium hydroxide solution at 29.03°, 100% is volume of oxygen calculated for $2RSH \rightarrow R_2S_2$: Curve I, concn. of sodium hydroxide 0.0576 *N;* Curve II, 0.346 *N;* Curve II, 0.548 *N;* Curve IV, 1.07 *N;* Curve V, 2.71 *N.*

With weak alkali, the absorption is practically the theoretical, but it increases with the strength of the alkali to 152% of that calculated for the conversion to the disulfide. In the earlier part of the absorption the rate increases with the strength of the alkali up to 0.5 *N* and then decreases. This decrease may be explained by the markedly lower solubility of oxygen in the stronger alkali.[4] If this is considered, the rate increases all the way. In the latter part the rate increases continually.

Figure 2 shows the same relationship at a higher temperature; for the same strength of alkali the excess absorption of oxygen is practically the same but the rate is faster.

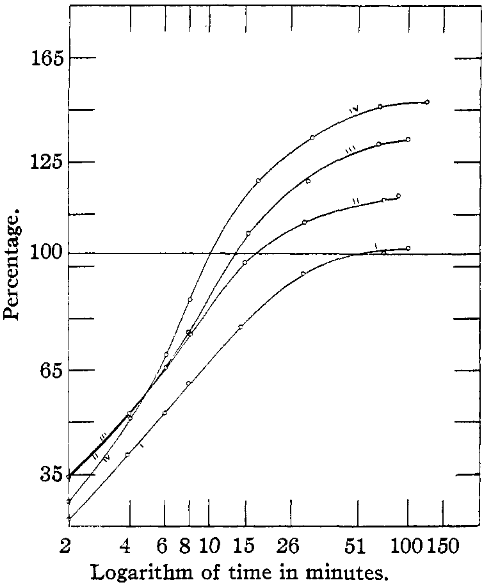

Fig. 2.—Absorption of oxygen by butylthiol in 30 ml. of sodium hydroxide solution at 34.66°, 100% is volume calculated for $2RSH \rightarrow R_2S_2$: Curve I, concn. of sodium hydroxide is 0.098 *N;* Curve II, 0.315 *N;* Curve III, 0.856 *N;* Curve IV, 0.985 *N.*

In Fig. 3 different mercaptans are contrasted. In 2.71 *N* alkali, propyl goes faster and further than *n*-butyl, while amyl goes much slower. The curves for benzyl and phenyl differ greatly from those for the aliphatic mercaptans.

Experimental

Materials.—Mercaptans from the Eastman Kodak Company were refractionated and only the middle fractions with boiling point ranges from 0.5 to 1° were used. The sodium hydroxide solutions were standardized against potassium acid phthalate and stored in waxed bottles.

Preparation of Mercaptan Solution.—Twenty ml. of standard alkali and the proper amount of mercaptans were weighed into a small glass-stoppered Erlenmeyer

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(4) According to Geffcken, *Z. physik. Chem.*, **49**. 254 (1904), the solubility of oxygen at 25° drops from 28.12 in water to 23 for 0.5 *N* NaOH and to 12.2 for 2 *N*.

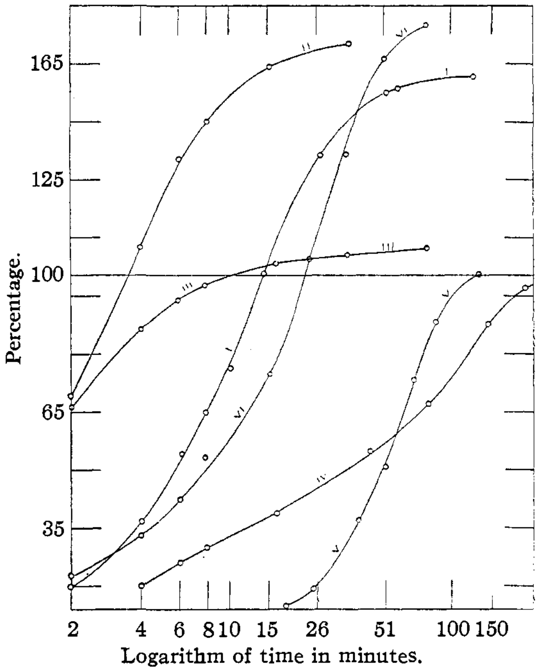

Fig. 3.—Absorption of oxygen by different thiols in 30 ml. of sodium hydroxide solution at 29.03°, 100% is volume of oxygen calculated for $2RSH \rightarrow R_2S_2$: Curve I is for butylthiol in 2.71 *N* sodium hydroxide; Curve II, propylthiol in 1.07 *N;* Curve III, propylthiol in 0.0576 *N;* Curve IV, amylthiol in 2.71 *N;* Curve V, phenylthiol in 2.71 *N;* Curve VI, benzylthiol in 2.71 *N*.

flask which had been swept out with a stream of nitrogen and brought to temperature. Five ml. was taken out with a pipet calibrated with the same solution. It was possible to duplicate the amount of mercaptan added to within two parts per thousand.

Apparatus.—The apparatus consisted of a constant-temperature bath (B) with a jacketed buret and manometer system (F) through which water from the bath was circulated by a centrifugal pump (A). The buret (L) was connected to the reaction flask (C) by heavy rubber connections and a capillary tube (M). The reaction flask consisted of a 100-ml. volumetric flask with a side arm connected to the capillary tube and through it to the buret. Another side arm tube with a stopcock (J) was provided for equalizing the pressure before starting a run. Constant pressure was maintained during each run by means of the mercury reservoir (G).

Procedure.—The absorption of oxygen by the solution was read on the buret. A typical run was carried out as follows. The bath (B) was brought to working temperature, controlled within ±0.005°. The buret (L) and the reaction flask (C) containing 25 ml. of standard alkali, were swept out with oxygen and connected through the side arm (M) by pressure tubing. A mechanical shaker agitated the reaction flask about 300 times per minute until vapor pressure equilibrium was established. The pressure in the buret and manometer system was then equalized and 5 ml. of mercaptan solution, prepared as indicated previously, was introduced into the reaction flask below the surface of the standard alkali. The stopper of the flask was then closed, stopcock (J) opened momentarily and the shaker started. Zero time was taken at the instant stopcock (J) was closed. Buret readings were taken at one-minute intervals for about ten minutes and at five-minute intervals for about one-half an hour. The reaction was considered to be complete when the absorption was 0.05 or less per hour.

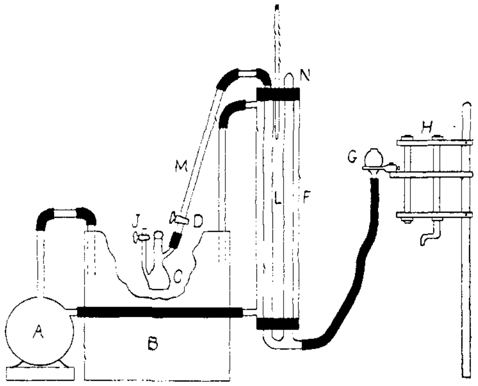

Fig. 4.

Further work on this investigation is being carried on.

Summary

1. Thiophenol and *n*-propyl, *n*-butyl, *n*-amyl and benzyl mercaptans were shown to be oxidized readily by oxygen in sodium hydroxide solution.

2. The absorption of oxygen by mercaptans in sodium hydroxide solution is greater than is accounted for by the formation of the disulfide. The excess absorption depends upon the concentration of the alkali.

3. If the solubility of oxygen in the different strengths of alkali is taken into account, the rate of absorption of oxygen increases with the increase in the concentration of alkali.

4. The relative rates of oxygen uptake by mercaptans in sodium hydroxide solution are as follows: *n*-propyl > *n*-butyl > *n*-amyl > benzyl > thiophenol.

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