

TABLE II

THE SOLUBILITY OF CO<sub>2</sub> IN H<sub>2</sub>O AND IN SATURATED Li<sub>2</sub>CO<sub>3</sub> SOLUTIONS AT 250°

CO <sub>2</sub> pressure, atm.	CO <sub>2</sub> wt. % evolved from Li <sub>2</sub> CO <sub>3</sub> soln.	CO <sub>2</sub> tot. wt. % in Li <sub>2</sub> CO <sub>3</sub> soln.	CO <sub>2</sub> tot. wt. % in H <sub>2</sub> O
22.9	0.90	2.05	
29.7	1.07	2.29	
36.7	1.34	2.63	
52.7	1.87	3.26	
52.7	1.98	3.37	
52.7	1.92	3.32	
65.3			2.686
107.1			3.881
123.1			4.473

solubility of CO<sub>2</sub> in H<sub>2</sub>O and in solutions saturated with solid Li<sub>2</sub>CO<sub>3</sub> at 250°. Curve AB fits data for CO<sub>2</sub> in pure water (determined by the gravimetric method) and for non-ionic CO<sub>2</sub> in the saturated Li<sub>2</sub>CO<sub>3</sub> solution (determined by the gas-liquid ratio method). This indicates the solubility of non-ionic CO<sub>2</sub> in the lithium carbonate solution is essentially independent of the concentration of the ionic species. Curve C gives the total CO<sub>2</sub> content of the Li<sub>2</sub>CO<sub>3</sub> saturated solutions calculated by adding the HCO<sub>3</sub><sup>-</sup> equivalent of the Li<sup>+</sup> analysis to the CO<sub>2</sub> determined by the gas-liquid ratio method.

The Henry's law constant  $k'$  ( $k' = m_{\text{CO}_2}/P_{\text{CO}_2}$ , where  $m_{\text{CO}_2}$  = molality of non-ionic CO<sub>2</sub> and  $P_{\text{CO}_2}$  is the partial pressure of CO<sub>2</sub> in atmospheres) is calculated from line AB to be  $8.69 \times 10^{-3}$  at 250°. Substituting for  $P_{\text{CO}_2}$  in equation 2, we obtain

$$K' = \frac{K_m}{k'} = \frac{(m_{\text{Li}^+})^4}{m_{\text{CO}_2}} = 2.38 \times 10^{-2} \text{ (at } 250^\circ \text{)} \quad (3)$$

The adherence to Henry's law at elevated temperatures is not paralleled at lower temperatures<sup>4,5</sup> where there are significant deviations from linearity at comparable pressures. This observation concurs with our previous comment supporting an isothermal constancy of the activity coefficient in this aqueous system at high temperature. If approximate Henry's law constants calculated from the data of Wiebe and Gaddy are plotted, along with the value of the constant at 250°, a minimum in the solubility of CO<sub>2</sub> in H<sub>2</sub>O occurs at approximately 180°.

In conclusion, the data presented give evidence that, in general, aqueous solutions at high temperature are probably much simpler to interpret than similar systems at low temperature, as had been pointed out previously by Gibson and Loeffler.<sup>6</sup>

(4) R. Wiebe and V. L. Gaddy, *THIS JOURNAL*, **63**, 475 (1941).

(5) R. Wiebe and V. L. Gaddy, *ibid.*, **62**, 815 (1940).

(6) R. E. Gibson and O. H. Loeffler, *Ann. N. Y. Acad. Sci.*, **51**, 727 (1949).

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## Water Vapor Pressures above Sodium Hydroxide and Mixtures of Sodium Hydroxide and Sodium Oxide in the Vicinity of 300°

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An effusion study of the NaOH-Na<sub>2</sub>O-H<sub>2</sub>O system between 260 and 310° yields water pressures significantly higher than expected from reported thermodynamic properties. Vaporization of NaOH was not detected below 310°. Limited solubility of Na<sub>2</sub>O in NaOH in the solid phase, less than 10% at 305°, is indicated.

Published thermodynamic data predict that the decomposition of sodium hydroxide to sodium oxide will give an equilibrium pressure of water vapor of *ca.* 10<sup>-11</sup> atmosphere in the vicinity of 300°, if both solid phases are at unit activity. Hence direct study of this equilibrium below the melting point of sodium hydroxide (319°) does not appear practical. However, on investigation of the behavior of sodium hydroxide in effusion cells, water pressures above 10<sup>-8</sup> atmosphere have been observed for prolonged periods. An extended study of the system between 260 and 310° has been made in an effort to ascertain whether pressures of this magnitude actually are established by the decomposition equilibrium.

### Experimental

The effusion apparatus and techniques used were basically those described for a study of magnesium hydroxide<sup>1</sup> with the exception that the sample was not subjected to continuous evacuation but remained isolated in a closed vacuum system during the short time necessary for deter-

mination of the quantity of effusate collected in a given run. Water vapor removed from the cell at reaction temperature during the measurement was collected in a liquid oxygen cooled trap. The trap was then isolated from the effusion cell by means of a large bore stopcock and the collected water transferred to a small calibrated volume where it was allowed to vaporize and the quantity determined by *PVT* measurements near room temperature. The identity of the vapor frequently was confirmed by checking the vapor pressure of the condensate at the ice point. Thus the water leaving the cell was determined directly, independent of any other species which may also have effused.

Baker C.P. sodium hydroxide sticks (analyzed lot no. 4231, 98.9% NaOH, 0.9% Na<sub>2</sub>CO<sub>3</sub>) were used. Sodium oxide was prepared by reaction of sodium (present in excess) with sodium peroxide at 500° in an argon atmosphere. After the reaction the excess sodium was distilled away *in vacuo*. Weighed samples of oxide, hydroxide and mixtures of the two were analyzed by titration with standard HCl solution to phenolphthalein and methyl orange end-points and Na<sub>2</sub>O, NaOH and Na<sub>2</sub>CO<sub>3</sub> contents evaluated in the conventional way. For several samples, Na<sub>2</sub>CO<sub>3</sub> also was determined independently by release of carbon dioxide, the latter measured gravimetrically in a standard Ascarite absorption train. Carbonate content was generally between 1 and 2%. When samples of sodium oxide were dissolved in water in evacuated containers, no gas was

(1) E. Kay and N. W. Gregory, *J. Phys. Chem.*, **62**, 1079 (1958).

liberated, showing the absence of significant amounts of sodium peroxide. Identity of the oxide and hydroxide was also established by X-ray powder patterns.

Two recent papers<sup>2,3</sup> describe the interaction of NaOH with various metals at temperatures up to 1000°. Nickel and Monel appear best suited as metallic container materials at lower temperatures and were used to construct several effusion cells. No loss in weight after cleaning or change in appearance of these metal cells was noted in our experiments with solid NaOH. After several days at higher temperatures, 350–450°, slight reaction was indicated by a green coloration of NaOH and a roughening of the metal surface. To assure that water pressures measured at the lower temperatures were not associated with a reaction involving metal, the majority of experiments were conducted with an effusion cell ground in a single crystal of magnesium oxide. Brewer and Margrave<sup>4</sup> found no evidence of reaction of Na<sub>2</sub>O with MgO at temperatures as high as 1200°.

Brass grinding tools and carborundum powder were used to form the various parts of the MgO cell. The lid, containing the effusion hole, was fitted into a hole made in the single crystal constituting the main body of the cell by forming a tapered finely finished ground joint. Both MgO and metal cells were from 2 to 5 cm. in length with cross-sectional areas between 2 and 4 cm.<sup>2</sup>. Orifice areas are given in the legend of figures presenting results. Samples of NaOH, Na<sub>2</sub>O, etc., were finely ground and transferred into the effusion cells (and subsequently into a movable section of the vacuum line, closed off by a stopcock) in a carbon dioxide-free dry box.

Reliable measurements were not obtained from MgO cells above the melting point of NaOH. Within a relatively short time (a day or so) liquid NaOH would creep out of the cell orifice; its appearance on the outside of the cell was detected easily by abnormally high apparent water pressures. Creeping also occurred slowly at temperatures just below the melting point. However, measurements could be made below 310° for periods as long as a month without difficulty. The liquid does not creep as rapidly on nickel or Monel surfaces.

Considerable pumping time was necessary to remove what appeared to be surface water from sodium hydroxide samples. About a week of continuous evacuation (pressure in the system maintained below 10<sup>-6</sup> mm.) at 250° was required before no measurable amount of water (ca. 5 × 10<sup>-8</sup> mole) was collected in a period of ten hours. Most of the surface water appeared to be removed in the first few hours, with the pressure continuously decreasing thereafter. Hydrates of NaOH would be expected to decompose quickly as their decomposition vapor pressures are in the millimeter range near room temperature.<sup>5-7</sup> After the pump-out period, temperatures were increased to the measuring range, 260–310°; measured pressures then showed a typical temperature dependent equilibrium-like behavior. Blank runs were made periodically to ensure that water collected came from the effusion cell.

### Results and Discussion

Data shown in Fig. 1 were obtained from the first experiments, conducted in metal and magnesium oxide cells, with NaOH initially at unit mole fraction (except line 2-P, to be discussed later). For similar orifice areas, pressures from metal cells are comparable with those from MgO cells, indicating that reaction of NaOH with metal is not primarily responsible for the release of water. Sample temperatures were varied randomly between successive measurements in each series; pressures appear markedly dependent on cell orifice area.

Free evaporation experiments also were conducted in the same apparatus (same diffusion path

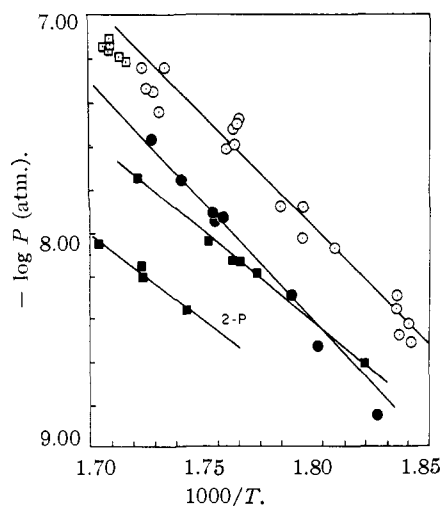


Fig. 1.—Steady-state pressure dependence on temperature and cell geometry:  $N_{\text{NaOH}} \approx 0.99$  (except line 2-P).

Monel cells	○	$A_0 = 6.28 \times 10^{-3} \text{ cm.}^2$ ; $f = \frac{A_0}{A_s} = 2.93 \times 10^{-3}$
	●	$A_0 = 1.48 \times 10^{-2} \text{ cm.}^2$ ; $f = 6.90 \times 10^{-3}$
MgO cell	□	$A_0 = 3.7 \times 10^{-3} \text{ cm.}^2$ ; $f = 3.0 \times 10^{-3}$
	■	$A_0 = 1.4 \times 10^{-2} \text{ cm.}^2$ ; $f = 1.1 \times 10^{-2}$

between sample and trap) and after the preliminary pump-out period gave rates of release of water in agreement with effusion results if a condensation (accommodation) coefficient ca. 10<sup>-3</sup> is assumed. A coefficient of this magnitude also is indicated by the change of steady-state pressure with orifice area, seen in Fig. 1 and in later experiments, Fig. 2.

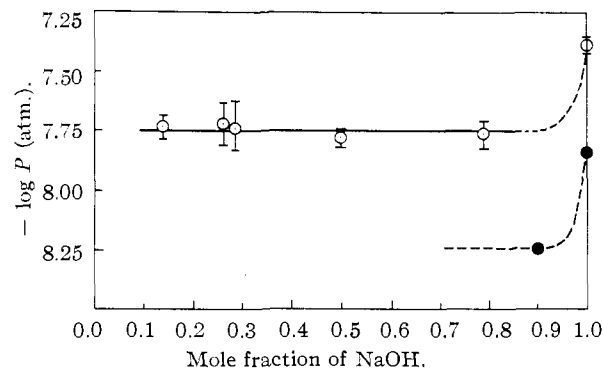


Fig. 2.—Steady-state water pressures above various mixtures of NaOH and Na<sub>2</sub>O at 305°: ○, MgO cell,  $A_0 = 3.7 \times 10^{-3} \text{ cm.}^2$ ;  $f = 3.0 \times 10^{-3}$ ; ●, MgO cell,  $A_0 = 1.4 \times 10^{-2} \text{ cm.}^2$ ;  $f = 1.1 \times 10^{-2}$ .

When free evaporation experiments from a given sample of NaOH were continued for a considerable period of time, a gradual decrease in the apparent equilibrium pressure of water became evident. This observation suggested, if water pressures are attributed to the reaction  $2\text{NaOH(s)} = \text{Na}_2\text{O(s)} + \text{H}_2\text{O(g)}$ , that sodium oxide may form a solid solution with NaOH, and that the fall in water pressure corresponded to an increasing activity of the oxide. Solid solution formation could be responsible for the high water pressures observed in the beginning stages of the decomposition, when the activity of the oxide is very small, and the long initial pump-out period.

(2) D. D. Williams, J. A. Grand and R. R. Miller, *THIS JOURNAL*, **78**, 5150 (1958).

(3) D. M. Mathews and R. F. Kruh, *Ind. Eng. Chem.*, **49**, 55 (1957).

(4) L. Brewer and J. Margrave, *J. Phys. Chem.*, **69**, 421 (1955).

(5) G. P. Baxter and H. W. Starkweather, *THIS JOURNAL*, **38**, 2038 (1916).

(6) M. deForcrand, *Compt. rend.*, **133**, 223 (1901).

(7) P. Mauret, *ibid.*, **240**, 2151 (1955).

A solid solution effect is difficult to detect in effusion experiments because of the very slow rate of decomposition, only  $10^{-7}$  to  $10^{-8}$  mole in each measurement. The total water vapor removed during the entire pumping period, including bake-out, overnights, etc., for a series of measurements generally corresponded to decomposition of not more than 2-3% of the initial 1-g. NaOH sample. Since the same general preliminary pump-out procedure was used for all the samples shown on Fig. 1, it may be assumed that measurements were initiated at about the same degree of decomposition, perhaps 1-2%  $\text{Na}_2\text{O}$ ; hence data are in fair correspondence. However, some of the displacement of the various curves may well be associated with small differences in the composition of the solid phase. Since the activity of the oxide cannot be estimated, thermodynamic properties cannot be evaluated from these data.

To further investigate possible solid solution effects, various mixtures of  $\text{Na}_2\text{O}$  and NaOH were prepared and subjected to effusion study in MgO cells at  $305^\circ$ , Fig. 2. Each point on the upper line represents an average of about five measurements with the spread indicated by the vertical lines through the points. Mixtures containing less than 40% NaOH were prepared by adding measured amounts of water to a known quantity of  $\text{Na}_2\text{O}$  initially placed in the effusion cell. The oxide took up limited quantities of water very rapidly at  $305^\circ$ . Measurements were initiated as soon as all the water metered into the system had been absorbed by the sample. The first effusion experiment after the addition gave water pressures close to those shown in Fig. 1. However, after the sample was held at  $305^\circ$  for several hours, pressures dropped about a half an order of magnitude to values shown on Fig. 2 and then did not change perceptibly (measurements were made for several weeks with continuous pumping). Identical pressures (within experimental error) were observed above all mixtures studied.

Water take-up by  $\text{Na}_2\text{O}$  was surprisingly slow after about 40% of the oxide had been converted. It was found more convenient to prepare mixtures at 50, 80 and 90% by mixing weighed amounts of  $\text{Na}_2\text{O}$  and NaOH in the dry box; the composition of these mixtures was later confirmed by analysis.

Data in Fig. 2 suggest that solubility of  $\text{Na}_2\text{O}$  in NaOH is not greater than 10% at  $305^\circ$ . Richer mixtures appear to form a two solid phase system, above which water pressures are still  $10^2$  to  $10^3$  times higher than expected if the solids are assumed to be at unit activity. Only one series of experiments was conducted in which the temperature of the two-phase mixtures was varied appreciably (Fig. 1, curve labelled 2-P,  $N_{\text{NaOH}} = 0.9$ ). In Fig. 2 the effect of increasing the orifice area by a factor of 3.7 also is shown for the two-phase region.

Evidence for slight solubility of  $\text{Na}_2\text{O}$  in NaOH could not be detected on X-ray powder patterns of the mixtures. Lines of both pure constituents were observed in mixtures between 10 and 90% without perceptible shift in spacings. Lines of  $\text{Na}_2\text{O}$  could not be detected on patterns of the solid having mole fraction of NaOH near one. One free

evaporation experiment was specifically designed to provide evidence that  $\text{Na}_2\text{O}$  was formed as water was removed; a 0.1-g. sample of NaOH was held at  $300^\circ$  and water pumped off continuously for a period of several weeks. An X-ray powder pattern showed the residual material to still be primarily NaOH but the strongest line characteristic of  $\text{Na}_2\text{O}$  was clearly visible also.<sup>8</sup>

All these observations suggest that water pressures observed are, in fact, produced by the decomposition of NaOH to  $\text{Na}_2\text{O}$ . Appreciable vaporization of NaOH itself, or of sodium (possibly produced by a reduction reaction;  $\text{Na}_2\text{O}$  vaporizes by decomposition to sodium and oxygen only at much higher temperatures),<sup>4</sup> was not observed below  $310^\circ$ . Even after periods of continuous pumping for several weeks, during which a series of water measurements were made, detectable amounts of NaOH were not found on surfaces (glass in some cases, nickel in others) outside the effusion cell. Washings from these surfaces were tested for sodium by flame photometry as well as by conventional tests for alkalinity.

Several experiments were conducted above the melting point of NaOH in nickel cells to confirm the magnitude of expected water pressures as well as to estimate the magnitude of the vapor pressure of NaOH. At  $335^\circ$ , the water pressures were measured in five consecutive 30-minute runs, Fig. 3. The apparatus then was filled with helium and cooled; none of the NaOH liquid had crept out of the cell in this short period, nor could evidence be seen of attack on the metal. Again sodium containing compounds could not be detected on the nickel lined surfaces outside the cell. Considering the sensitivity of the flame photometric method, it was concluded that the pressure of NaOH in the cell could not be materially greater than  $10^{-8}$  atmosphere at  $335^\circ$ . If NaOH has an unusually low condensation (accommodation) coefficient for the vaporization process, or if its rate of vaporization is seriously lowered by the presence of ca. 1% sodium carbonate, this apparent limit on the vapor pressure may be too low; however, it is representative of our observations.

Vaporization of sodium hydroxide was frequently observed at higher temperatures, ca.  $400^\circ$ , but reliable vapor pressure data were not obtained because of the creeping problem. Evidence from mass spectrometric studies for the existence of  $(\text{NaOH})_2$  in the vapor phase above  $600^\circ\text{K}$ . has recently been reported.<sup>9</sup> Water pressures also were observed at ca.  $450^\circ$ , Fig. 3; a rather large uncertainty in sample temperature,  $\pm 5^\circ$ , and in composition (degree of decomposition at the time measurements were made) must be associated with these points.

The generally accepted heat of formation of NaOH is based on heat of solution data of Roth, *et al.*,<sup>10</sup>  $\Delta H_{298}^\circ = -102$  kcal. mole<sup>-1</sup>; NBS cir-

(8) For greater details of the free evaporation and other experiments, see the Doctoral Thesis of Eric Kay, University of Washington (1958).

(9) R. F. Porter and R. C. Schoonmaker, *J. Chem. Phys.*, **28**, 168 (1958).

(10) W. A. Roth, G. Wirths and H. Berendt, *Z. Elektrochem.*, **48**, 264 (1942).

cular 500<sup>11</sup> gives  $-99.4$  kcal. mole<sup>-1</sup> for the heat of formation of Na<sub>2</sub>O, based on heat of solution data of Rengade<sup>12</sup> and Matsui and Oka.<sup>13</sup> These values together with the well established value for water vapor give  $\Delta H_{298}^0 = 46.8$  kcal. for the reaction  $2\text{NaOH}(s) = \text{Na}_2\text{O}(s) + \text{H}_2\text{O}(g)$ . Heat capacity data of Douglas and Dever<sup>14</sup> for NaOH together with Kelley's estimate for sodium oxide<sup>15</sup> and the heat capacity of water vapor change  $\Delta H^0$  to 41.8 kcal. at 575°K., the mean temperature of our study. From entropy data for NaOH,<sup>14</sup> water vapor and Shomate and Kelley's estimate for Na<sub>2</sub>O,<sup>15</sup>  $\Delta S_{575}^0$  is calculated to be 22 e.u., leading to a predicted equilibrium pressure of water vapor of  $10^{-11}$  atmosphere (solids at unit activity).

Roth and Kaule<sup>16</sup> have revised the heat of formation of Na<sub>2</sub>O to  $-103$  kcal., based on measurement of the heats of solution of sodium and sodium oxide. This value reduces  $\Delta H_{575}^0$  for the decomposition to 38 kcal., and, with the entropy estimated above, increases  $P_{575}$  to  $10^{-9.7}$ , still one hundredth as large as our observed value, however.

It is noted that recent heat capacity measurements of Popov and Ginzburg<sup>17</sup> for sodium hydroxide are not in close agreement with those of Douglas and Dever. High precision measurements in the temperature interval 220 to 300° are made difficult by the occurrence of a slow transition. Data of Popov and Ginzburg lead to  $H_{575}^0 - H_{298}^0$  of 4325 cal. rather than 6130 cal. from the earlier work. This difference has a pronounced effect on the decomposition reaction, making  $\Delta H_{575}^0$  3.6 kcal. smaller and changing  $\Delta S^0$  from 22 to 29. The heat and entropy effects largely offset each other in calculating the expected decomposition pressure, however, giving  $10^{-9.5}$ .

If the ratio of activities of Na<sub>2</sub>O and NaOH is assumed to be near unity in the two solid phase region our water pressures may be used to calculate  $\Delta F^0$  for the decomposition reaction. Only a rough estimate can be made of  $\Delta H^0$  from curve 2-P, Fig. 1; 34 kcal. ( $\pm 10$ -20%). These points were obtained from a large orifice cell in which steady-state pressures were well below apparent equilib-

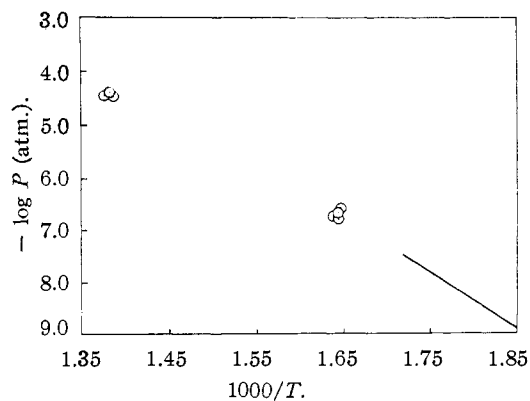


Fig. 3.—Steady-state water pressures from Ni effusion apparatus above the melting point of NaOH:  $\odot$ , Ni cell,  $A_0 = 1.0 \times 10^{-2}$  cm.<sup>2</sup>; —, MgO cell,  $A_0 = 1.4 \times 10^{-2}$  cm.<sup>2</sup> (data, Fig. 1).

rium values and cover only a small temperature interval. Using the estimated  $\Delta S^0$  of 22, and  $\Delta F^0$  calculated from  $P_{575} = 10^{-7.75}$  a heat of reaction of 33 kcal. is obtained. The larger  $\Delta S^0$  of 29 gives a correspondingly larger heat, 37 kcal. It is apparent, if our results do correspond to near equilibrium behavior, a careful re-examination of the thermodynamic properties of both sodium oxide and sodium hydroxide is necessary.

The difficulties frequently encountered with the effusion method<sup>1</sup> generally lead to observed pressures lower than true equilibrium values, in the opposite direction of the discrepancy noted here. It did not seem practical to attempt work with cells with materially smaller orifices, necessary for a reasonable extrapolation to a limiting pressure at zero orifice.

The difficulty experienced in getting water to convert Na<sub>2</sub>O to NaOH completely raises some doubt as to whether true solid phase equilibrium was established in our systems. If water molecules do not readily penetrate a NaOH film on Na<sub>2</sub>O particles, and if Na<sub>2</sub>O does not diffuse readily through this film, Na<sub>2</sub>O at the outer surface participating in the decomposition equilibrium might be at an appreciably lower activity than the majority of the material on the inside. However, data in Fig. 2 show general correspondence of pressures measured with relatively little NaOH in the system, in which case water take-up was rapid, and for those above mixtures rich in NaOH, suggesting that this diffusion problem is unimportant.

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(11) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circ. 500, U. S. Government Printing Office, Washington, D. C., 1952.

(12) M. Rengade, *Compt. rend.*, **145**, 236 (1907).

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(14) T. B. Douglas and J. L. Dever, *J. Research Natl. Bur. Standards*, **53**, 81 (1954).

(15) K. K. Kelley, *Bur. of Mines Bull.* **476**, U. S. Government Printing Office, Washington, D. C., 1949.

(16) W. A. Roth and H. L. Kaule, *Z. anorg. Chem.*, **253**, 353 (1947); W. A. Roth, *ibid.*, **255**, 324 (1948).

(17) M. M. Popov and D. M. Ginzburg, *J. Gen. Chem. (USSR)*, **26**, 4 (1956).