dure in order to freeze out the ammonia. After generating ammonia for several hours the bomb tube is transferred to a Dry Ice-bath, sealed off and then heated in a hot water-bath at 90–100° for four hours.

Following these directions carefully we were able to make many successful runs. Then, without explanation, the procedure began to result in explosion of the bomb tube and loss of its contents. We have had bomb tubes explode in the water-bath and in the Dry Ice-bath. After the loss of several dewar flasks we omitted the Dry Ice-bath and sealed the bomb tube in the liquid nitrogen bath. We observed that after the bomb tube had been sealed and removed from the bath, the tube first became covered with frost and that suddenly this frost began to melt. This suggested that a highly exothermic reaction had begun. If the bomb tube did not explode shortly thereafter, it usually did not explode at all.

Two possible explanations for the explosions suggested themselves. One was that due to the efficiency of the cooling system around the bomb tube and the duration of the process, there might have been some slight condensation of the sweeping nitrogen. A small amount of liquid nitrogen inside the bomb tube after it had been sealed off could give rise to many atmospheres of pressure when the tube was warmed. The other explanation was that tank nitrogen and ammonia, in the presence of copper and an organic compound might give rise to traces of an unstable compound which would detonate spontaneously as the temperature rose.

It was felt that sweeping with tank helium ("Medical Helium Gas," Liquid Carbonic Corp.) rather than tank nitrogen might eliminate both of these possibilities since helium liquifies well below the boiling point of nitrogen and is not known to form compounds. Since this modification was adopted, thirty successful runs have been made. Insofar as we can determine, no other conditions have been altered.

Drs. Cavalieri and Brown have indicated in a personal communication a third possible explanation which should be offered for these explosions. They point out that "oxygen is readily condensed from the air in tubes cooled with liquid nitrogen, and a small amount of oxygen condensed with organic matter can lead to violent explosions. Condensation of oxygen could thus occur; if the vessel is cooled before the flow of inert gas is begun, if the tank nitrogen contains appreciable oxygen, or if the period of time and length of tubing is such that there is appreciable diffusion of air oxygen through the tubing leading from the tank. Commercial nitrogen invariably contains small amounts of oxygen and this may vary from tank to tank, but helium seems less likely to contain it."

Whether these explanations are valid remains to be seen. We offer this communication so that others may be aware of the potential danger which may be involved in this synthesis and in the hope of obtaining a more rigorous explanation.

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Physical Properties of Thioacetic Acid and Diacetyl Sulfide

BY W. W. CROUCH

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In the course of experimental work on sulfur compounds, products were isolated which were believed to be thioacetic acid and diacetyl sulfide (thioacetic anhydride); however, considerable disagreement is found in the literature regarding even the boiling points of these commonplace materials and little information is available as to other physical properties. In the purification of the thioacetic acid by fractionation at atmospheric pressure, nearly all of the product was recovered at an overhead temperature of 86°, uncorrected, and further refractionation of the purest cuts led to no change in the boiling point. The boiling point for this product listed in Beilstein, Heilbron and the other conventional chemical handbooks is 93°, apparently based on the data of Kekulé,[1] although Clark and Hartman[2] reported a boiling range of 88 to 91.5° for their product. It was suspected that an azeotrope-forming agent might be present in our acid; however, no such impurity could be separated, and after purifying the product further by dissolving in caustic, extracting with ether to remove any inert material and recovering the acid, no change in boiling point was observed. Furthermore, fractionation of samples of Eastman thioacetic acid and thioacetic acid prepared in the conventional way by the reaction of hydrogen sulfide with acetic anhydride[2] also gave products boiling at an overhead temperature of 86°, uncorrected. Since their behavior during distillation, sulfur contents, neutral equivalents and infrared analyses all indicated the products to be uncontaminated by appreciable quantities of other materials, it was concluded that the boiling point of 93° reported in the literature is in error. The properties of the purified thioacetic acid are as follows: b.p. (corrected) 87.5° (760 mm.); d^{20}_4 1.0696; and $n^{20}\text{D}$ 1.4636. It freezes sharply to a white, crystalline solid at a temperature of approximately −75°.

Anal. Calcd. for C_2H_4OS: S, 42.12; neut. equiv., 76.11. Found: S, 42.03; neut. equiv., 75.62.

The infrared examination[3] of thioacetic acid was of particular interest. A strong absorption band was found at 3.9 microns characteristic of the sulfhydryl group, but no bands were obtained at 2.9 and 10.4 μ indicating the absence of the —OH and $-\underset{|}{C}{=}S$ groups, respectively. It was concluded that the acid is substantially completely in the thiol rather than the thion form, confirming the observations of Bloch.[4]

The boiling point of diacetyl sulfide at atmospheric pressure has been reported as 121°,[1] 119–120°[5] and 156–158°.[6] The last figure was found to be approximately correct; how-

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[1] F. A. Kekulé, *Ann.*, **90**, 311.

[2] H. T. Clarke and W. W. Hartman, THIS JOURNAL, **46**, 1731 (1924).

[3] Infrared studies were performed and interpreted by Vernon Thornton of the Physics Branch of this Laboratory.

[4] F. Bloch, *Compt. rend.*, **206**, 679 (1938).

[5] H. Tarugi, *Gazz. chim. ital.*, **27**, II, 157 (1897).

[6] S. H. Davies, *Ber.*, **24**, 3548 (1891).

ever, as a result of the rapid decomposition of the sulfide at that temperature, the material could not be distilled successfully at atmospheric pressure. By repeated fractionation in packed columns at reduced pressure, the sulfide was recovered as a constant boiling, water-white, lachrymatory liquid; b.p. 62° (20 mm.); b.p. 82° (50 mm.); n^{20}_D 1.4826; d^{20}_4 1.1317.

Anal. Calcd. for $C_4H_6O_2S$: S, 27.14; neut. equiv., 59.07. Found: S, 26.68; neut. equiv., 58.41.

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Further Applications for Egloff's Boiling Point Equation. II

BY W. DAVID ENGLISH[1]

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It was previously shown[2] that the equation derived by Egloff, *et al.*[3]

$$T = a \ln (n + b) + k$$

relating boiling points of hydrocarbons to their constitution is applicable to certain Group IV hydrides. In the equation, T is the boiling point in °K., n the number of atoms other than hydrogen, and a and b and k are empirical constants. k depends only on the structure of the molecule, while a and b do not vary with the structure, but are related to the Group IV element.

If the values of a and b previously reported for alkanes, silanes and germanes (Table VI) are plotted against the atomic weights of carbon, silicon and germanium smooth curves result. Extrapolation of the curves to the atomic weights of tin and lead gave values of a and b which were then substituted in the equation. When n was taken as 1, boiling points of stannane and plumbane were calculated (Table I). These values were about 18° higher than the observed values, the same discrepancy as was previously noted for methane,[3] silane[2] and germane.[2] A correction factor was introduced into the equation so that it read

$$T = a \ln (n + b) + k - \frac{18.0}{n^{\infty}}$$

The new term has the value of −18.0 when $n = 1$ and is 0 for any other value of n. In Table I there is a comparison of the boiling points calculated with the old and new forms of the equation and the observed values.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED BOILING POINTS FOR MH_4 COMPOUNDS

$$T = a \ln (1 + b) - 416.3 - \frac{18.0}{1}$$

Compound	Calcd. b.p. old eq., °K.	Calcd. b.p. new eq., °K.	Obsd. b.p., °K.	ΔT
Methane[a]	129.6	111.6	111.6	0
Silane[b]	179.0	161.0	161.6	+0.6
Germane[b]	202.1	184.1	183.0	−1.1
Stannane[c]	240	222	221	−1
Plumbane[d]	278	260	260	0

[a] Reference 3. [b] Reference 2. [c] Paneth, Haken and Rabinowitsch, *Ber.*, **57**, 1891 (1924). [d] Paneth and Rabinowitsch, *ibid.*, **58**B, 1138 (1925).

The correction factor is the equivalent of having a different k for compounds with the structure MH_4 compared to those with n-R-MH_3. The new k would equal −434.3. However, the extra term in the equation is more convenient than changing k.

Recent publication of physical properties of alkyl germanes (terminal Ge) alkyl stannanes (internal Sn) and disilyl alkanes (two terminal Si's) has made possible the calculation of Egloff equation constants for these families, Tables II, III, IV. The calculations were made using the k values derived by Egloff and determining a and b.

TABLE II

MONO-n-ALKYL GERMANES

$$T = 303.4 \ln (n + 7.0) - 416.3 - \frac{18.0}{n^{\infty}}$$

Compound	No. central atoms	T, °K. Obsd.[a]	T, °K. Calcd.	ΔT
Methylgermane	2	250	250	0
Ethylgermane	3	282.4	282.3	+0.1
n-Propylgermane	4	Above room temp.	311	...

[a] Teal and Kraus, THIS JOURNAL, **72**, 4706 (1950).

TABLE III

α,ω-DISILYL ALKANES

$$T = 342.2 \ln (n + 5.1) + k - \frac{18.0}{n_{\infty}}$$

Compound	No. central atoms	T, °K. Obsd.[a]	T, °K. Calcd.	ΔT
Normal compounds, $k = -416.3$				
Disilylmethane	3	299	299	0
1,2-Disilylethane	4	340	339	+1
2-Methyl compounds, $k = -424.5$				
1,1-Disilylethane	4	330	331	−1
1,2-Disilylpropane	5	368	367	+1

[a] English, Taurins and Nicholls, *Can. J. Chem.*, in press.

TABLE IV

POLYALKYL STANNANES

$$T = 324.7 \ln (n + 6.3) + k - \frac{18.0}{n^{\infty}}$$

Compound	No. central atoms	T, °K. Obsd.	T, °K. Calcd.	ΔT
Normal compounds, $k = -416.3$				
Dimethylstannane	3	308[a]	308	0
2-Methyl compounds, $k = -424.5$				
Trimethylstannane	4	332[b]	331	+1
Dimethylethylstannane	5	363[c]	363	0

[a] B.p. 35°, Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947). [b] B.p. 60°, Kraus and Greer, *ibid.*, **44**, 2629 (1922); b.p. 59°, Finholt, Bond, Wilzbach and Schlesinger, *ibid.*, **69**, 2692 (1947). [c] B.p. 90°, Bullard and Vingee, *ibid.*, **51**, 892 (1929).

By using the values of a and b previously derived for polyalkyl silanes[2] together with k's found by Egloff for 3- and 4-methyl compounds,[3] it was possible to calculate the boiling points of methyldiethyl- and methyldipropylsilane (Table V) to ±1°. This increases to four the number of structural constants (k) shown to apply to other Group IV hydrides as well as hydrocarbons.

The root mean square deviation for the compounds tabulated is ±0.71°, almost the same value as was found in the previous paper.

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(1) Defence Research Chemical Laboratories, Ottawa, Ont., Canada.

(2) W. D. English and R. V. V. Nicholls, THIS JOURNAL, **72**, 2764 (1950).

(3) G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).