too narrow. To secure a regular movement of the mercury it must be pure and the column must not be broken by small drops of water.

The advantage of this apparatus over the original apparatus described by Krogh is that an analysis can never be lost on account of a gas bubble parting from the rest in the measuring tube, as bubbles can always be collected again, either in the bulb beneath the measuring tube or in the absorption bulb, but of course one must be very careful not to drive the gas too near the tip, and thus incur losses. Another advantage is that the absorption liquids are protected against the influence of the air, and also that the operation is cleaner. A disadvantage is, that it works somewhat more slowly than Krogh's apparatus, a complete analysis being performed in one-half to three-quarters of an hour. The accuracy in the determinations by absorption is the same as with Krogh's apparatus, namely, about 0.1% absolute, when 10 cu. mm. can be disposed of. When the precautions mentioned above are taken the analyses by combustion also have about the same degree of accuracy.

Summary

A simple form of apparatus is described for the convenient micro analysis of quantities of mixed gases up to 20 cu. mm.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. VIII. THE PHYSICAL PROPERTIES OF MONOGERMANE[1]

BY ROBERT B. COREY AND A. W. LAUBENGAYER WITH L. M. DENNIS

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Introduction

In 1923 Dennis, Corey and Moore[2] prepared and isolated digermane, Ge_2H_6 and trigermane, Ge_3H_8. In the course of that investigation, about two liters of monogermane, GeH_4, was obtained, which was identified and stored in gas holders. This compound has already been studied by Voegelen,[3] Müller and Smith,[4] Paneth and Schmidt-Hebbel,[5] and Schenck.[6] Schenck obtained the gas in considerable amount and showed by analysis and vapor-density determinations that its composition was represented by

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

[3] Voegelen, *Z. anorg. Chem.*, **30**, 325 (1902).

[4] Müller and Smith, THIS JOURNAL, **44**, 1909 (1922).

[5] Paneth and Schmidt-Hebbel, *Ber.*, **55**, 2615 (1922).

[6] Schenck, *Rec. trav. chim.*, **41**, 569 (1922).

the formula GeH_4. He found the freezing point to be —165°, the boiling point, —126°, and he measured the vapor tension from —164° to —125°.

When considering the boiling points of the analogous hydrides, CH_4, —160°, SiH_4, —112°, GeH_4, —126°, attention is immediately attracted to the fact that the value for monogermane is much lower than would have been predicted from its relationship to the other hydrides of the group. This inconsistency suggested the advisability of further study of the compound, using the large quantity of material that was at our disposal.

Experimental Part

About two liters of the crude monogermane was dried by passage over calcium chloride and phosphorus pentoxide and was then introduced into the fractionation apparatus. This apparatus was similar to that already used in the separation and purification of the higher hydrides of germanium.[7] Distillation at —148° for 100 minutes yielded 2 cc. of liquid. The homogeneity of this distillate was proved by separating it into three fractions by redistillation and comparing the vapor tensions of these fractions at the same temperature. Concordant results were obtained.

Density of Monogermane as Gas.—Vapor-density determinations were made in a manner similar to that described in connection with digermane.[8] Two determinations gave for the weight of 1 liter under standard conditions 3.416 g. and 3.424 g.; av., 3.420 g. The calculated density is 3.416.

Analysis.—Analysis of the sample by thermal decomposition[9] gave the following results.

Weight of sample G.	Weight of Ge Calcd. G.	Weight of Ge Found G.	Weight of H Calcd. G.	Weight of H Found G.
0.13675	0.12954	0.1298	0.007210	0.007223
.13414	.12707	.1275	.007067	.007048

The sample was thus proved to consist of pure monogermane. It was used in determining the physical constants.

Melting Point.—Schenck had already reported that the melting point of monogermane is —165°. For the determination of a melting point at this temperature, a bath is required that is transparent and mobile at —170°. Schenck recommends the use of mixtures of Kahlbaum's "pentane for thermometers" with liquid air. Attempts to prepare a satisfactory bath in this way proved fruitless. A cooling bath for the accurate measurement of temperature must be constantly and vigorously agitated. Kahlbaum's "pentane for thermometers" when agitated and cooled to —155° became opaque, and at —160° solidified. Pentane obtained from

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[7] Ref. 2, p. 660.

[8] Ref. 2, p. 663.

[9] Ref. 2, p. 665.

the Atlantic Refining Company, through the kindness of Dr. A. B. Hoel, behaved in practically the same way. This pentane was then subjected to fractional distillation in the apparatus shown in Fig. 1. The pentane was placed in the flask A. The Hempel column B was filled with Raschig rings made from glass tubing by cutting it into lengths equal to its diameter. F is a reflux condenser through which cold water can be circulated. The Hempel column is connected through the adapter C to the spiral condenser D. The latter was surrounded with an ice-salt freezing mixture. The distillate was collected in the Dewar vessel E.

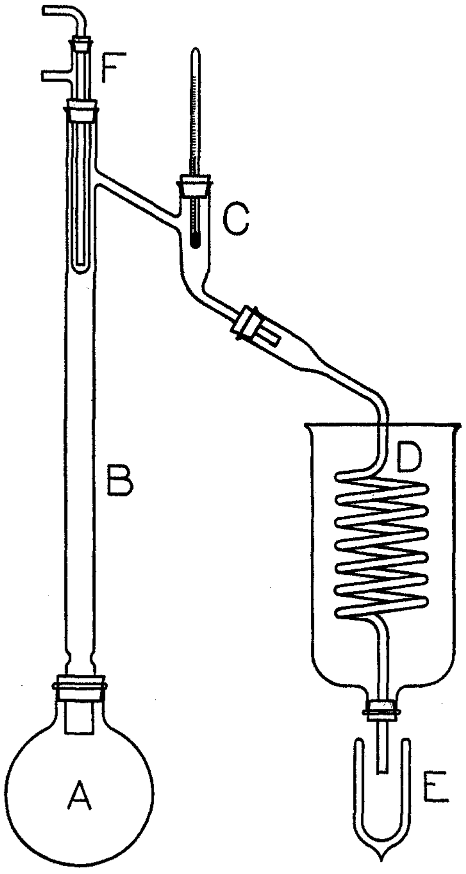

Fig. 1.

Since the room was warm, it was found that fairly rapid distillation resulted without the application of heat to the flask A. The water running through F was kept at 7°, and the thermometer in C never indicated a temperature above 23°. The distillate that was obtained could be cooled to —171° before solidifying. It remained sufficiently clear at —168° to permit readings to be made and was consequently quite satisfactory for our purpose.

The melting point of monogermane, as determined by the dropping-ring method,[10] was found to be —165°, which coincided exactly with the value given by Schenck.

Density of Monogermane as Liquid.—The density of the liquid sample was determined[11] at —142°. Two determinations gave 1.520 g. and 1.526 g. per cc.; av., 1.523 g. per cc.

Thermal Decomposition.—A sample of the gas was placed in a quartz tube at a pressure of about 350 mm., and the tube was very gradually heated.[12] A germanium mirror was formed at 280° and at 285° the de-

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[10] Ref. 2, p. 665.

[11] Ref. 2, p. 666.

[12] Ref. 2, p. 671.

composition proceeded rapidly. It is interesting to note here that the sample of monogermane that had been stored for more than one year over mercury at room temperature gave no evidence of appreciable decomposition during that period.

Table I

Vapor Tension of Monogermane

Temp., °C........	−145.3	−142.1	−140.0	−138.5	−136.3	−134.3	−131.6	−129.3	...
Press., mm.......	13.8	18.3	22.7	27.0	33.3	39.4	50.0	63.3	...
Temp., °C........	−126.6	−124.7	−123.0	−118.0	−115.1	−111.3	−107.5	−105.8	...
Press., mm.......	81.6	92.6	106.1	148.1	178.8	224.9	289.7	330.3	...
Temp., °C........	−103.5	−101.7	−99.5	−97.5	−96.3	−94.0	−92.7	−90.6	−89.3
Press., mm.......	375.1	420.2	461.4	527.8	569.1	628.4	681.9	739.7	787.5

Vapor Tension.—The vapor tension of monogermane from —145° to —90° was determined.[13]

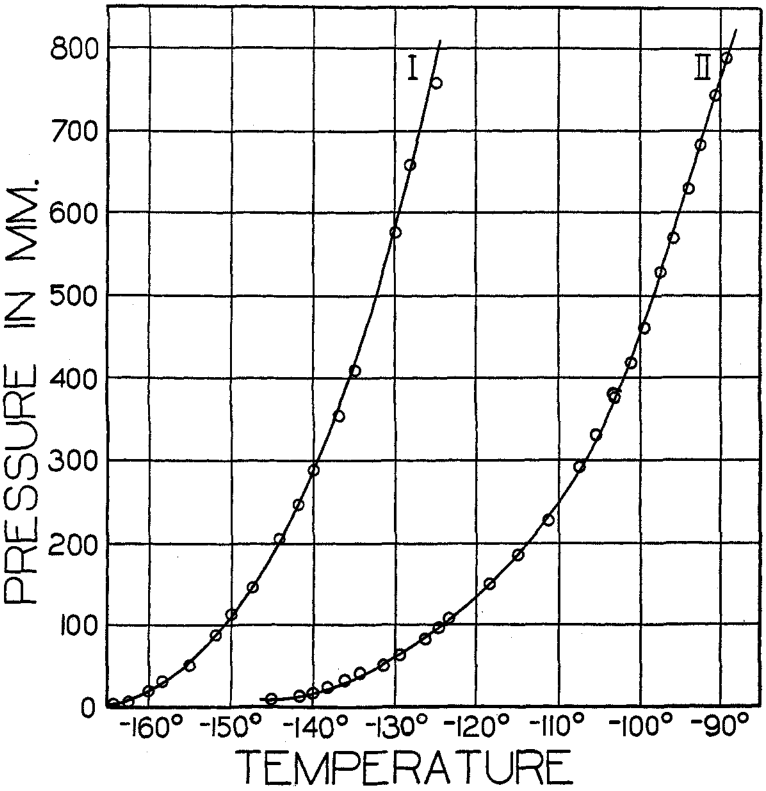

Fig. 2.

The tension-temperature curve plotted from these data is shown in Fig. 2, Curve II. Curve I was obtained by plotting the vapor-tension values

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[13] Ref. 2, p. 667.

already reported by Schenck. The marked difference in the data, as shown by these curves, led the authors to repeat the determinations. The results that were obtained closely agreed with those given in Table I.

To test the correctness of our data further, the logarithm of the vapor tension was plotted against the reciprocal of the absolute temperature. It has been shown[14] that for normal liquids, assuming the molar heat of vaporization to be a constant, the logarithm of the vapor tension is a straight-line function of the reciprocal of the absolute temperature. Since the molar heat of vaporization is nearly constant at ordinary pressures, this relationship is useful in testing the accuracy of experimental data.[15]

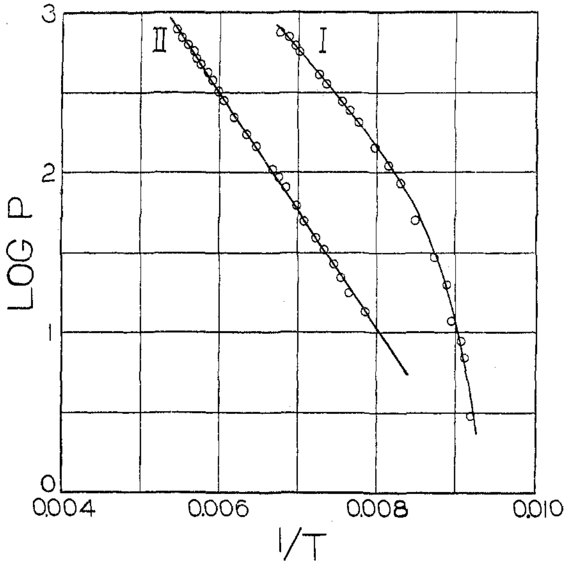

Fig. 3.

In Fig. 3, Curve I shows the result of applying this relationship to the values obtained by Schenck and Curve II to the data given in Table I. This evidence indicates that the latter values more nearly represent the true vapor tension of monogermane.

Boiling Point.—The boiling point of monogermane, as taken from the vapor-tension curve, is —90°, which is much higher than the value given by Schenck, namely, —126°.

Summary

Monogermane that had been prepared in a previous investigation was carefully purified. The density as gas, the density as liquid, the melting

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[14] Hildebrand, "Solubility," Chemical Catalog Co., **1924**, pp. 32–34.

[15] Hildebrand, This Journal, **37**, 970 (1915).

point and the boiling point of the compound were determined, and the vapor-tension curve was plotted. Vapor-tension values quite different from those previously published by Schenck were obtained.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE OF SWANSEA]

THE RELATION BETWEEN DEVIATIONS FROM RAOULT'S LAW AND THE PARTIAL HEATS OF SOLUTION

BY J. A. V. BUTLER

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In the attempts which have been made to account for the deviations of liquid mixtures from Raoult's law, both chemical and physical effects have been taken into account.[1] Dolezalek and his school saw in all deviations evidence of chemical change, that is, combination between the components, or association. Although it appears to be possible by means of suitable assumptions of this kind to account for any deviation, it has been shown that in their efforts to explain all deviations in this way the exponents of this view were led to postulate effects for other reasons that were absurd or contrary to other evidence.[2] On the other hand, it has been shown that purely physical causes can give rise to deviations. Van der Waals[3] and Van Laar[4] attempted to apply the underlying ideas of van der Waals' equation of state to binary mixtures and showed that it is possible to account in this way for the various kinds of vapor-pressure curves met. More recently, Hildebrand[5] has referred deviations to differences in the internal pressures of the components. However, this theory has been developed for the purpose of giving comprehensive indications of the kind and amount of deviation over a wide field rather than a quantitative explanation of the deviations in individual cases.

It can be shown that if a binary mixture obeys Raoult's law, the heat effect of mixing the components must be zero.[6] Further, it has long been known that a general correspondence exists between the deviations from Raoult's law and the heat of mixing and also with the volume change on mixing.[7] The thermodynamical relation between the partial heat of solu-

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[1] For a complete bibliography see (a) Lecat, "L'azeotropisme," Brussels, **1918**; also (b) Hildebrand, "Solubility," Chemical Catalog Co., **1924**.

[2] Ref. 1 b, Chap. VII.

[3] Van der Waals, *Z. physik. Chem.*, **5**, 133 (1890).

[4] Van Laar, *ibid.*, **72**, 723 (1910); **83**, 599 (1913).

[5] Hildebrand, THIS JOURNAL, **38**, 1452 (1916).

[6] Schroeder, *Z. physik. Chem.*, **11**, 449 (1893).

[7] Compare Young, "Fractional Distillation," MacMillan, **1922**, p. 34.