stance in glacial acetic acid is treated with potassium cyanate by the method described above in the preparation of the ethyl ester of 1-isobutyric acid amino-5-dimethylhydantoin. The reaction mixture is allowed to stand twelve hours, and is then diluted to eight times its volume, whereupon the difficultly soluble 1-benzylidene amino-5-dimethylhydantoin separates. Working with 5 g. of benzylidene hydrazinoisobutyric acid in 50 cc. of glacial acetic acid, 4.6 g. of the condensation product were obtained, and this proved identical with the product described in the foregoing preparation. The benzylidene compound thus obtained for further confirmation of its constitution was submitted to steam distillation in the presence of one mol of sulfuric acid. Benzaldehyde collected in the receiver and 1-amino-5-dimethylhydantoin was isolated from the solution in the distillation flask by the method employed above in the preparation of this substance. All attempts to condense cyanic acid with benzylidene hydrazinoisobutyric acid in water solution failed.

Action of Potassium Cyanate on the Hydrochloride of Ethyl Hydrazino-isobutyrate.—To 2.9 g. of ethyl hydrazinoisobutyrate, prepared according to the method of Thiele and Heuser,[1] was added the calculated amount of hydrochloric acid, and then 1.8 g. of potassium cyanate. After standing overnight, the solution did not react with benzaldehyde, a proof that no aminodimethylhydantoin is formed. Extraction with chloroform yielded a product that proved to be ethyl semicarbazinoisobutyrate,

$$NH_2CONHNHC(CH_3)_2COOC_2H_5.[2]$$
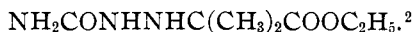
As further confirmation, a nitrogen determination was made.

Calc. for $C_7H_{15}O_3N_3$: N, 22.22. Found: N, 22.13.

AUSTIN, TEXAS.

THE VAPOR PRESSURE OF ETHANE AND ETHYLENE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.[3]

By G. A. BURRELL AND I. W. ROBERTSON.

The authors of this report have needed at various times, in working on the condensation of the constituents in natural gas, and in studying the separation of gas mixtures by fractionally distilling them, certain

(1896)) may be used to remove the benzalazine. Stir the mixture of benzaldehyde compounds with a little dilute ammonia, and after the benzylidene hydrazinoisobutyric acid has completely dissolved, filter from the undissolved benzalazine. Finally extract the last traces of benzalazine from the ammonia solution with ether and then precipitate the benzylidene hydrazino acid by neutralizing with dilute acetic acid. The yield obtained was about 42% of the theoretical (Bailey and Mikeska).

[1] Loc. cit.

[2] Am. Chem. J., 28, 386 (1902).

[3] Published by permission of the Director of the Bureau of Mines.

vapor-pressure measurements of gases at low temperatures. These have not been determined in the case of ethylene, and only for a limited range (20° below the normal boiling point) in the case of ethane. Hence in this paper are shown observations from 760 mm. down to 1 mm. Vapor pressures of propane, propylene, N-butane, iso-butane, butylene and acetylene will follow in subsequent articles.

Experimental.

The apparatus with which the work was performed is shown at Figs. 1 and 2. Referring to Fig. 1: The gas whose vapor pressure was measured was confined in the glass bulb b. The latter communicated on one side with a manometer and on the other side with a Töpler pump. The bath liquid was confined in a·Dewar flask about 35 cm. high and 10 cm. wide, inside measurements. It was not silvered, hence temperatures on pentane
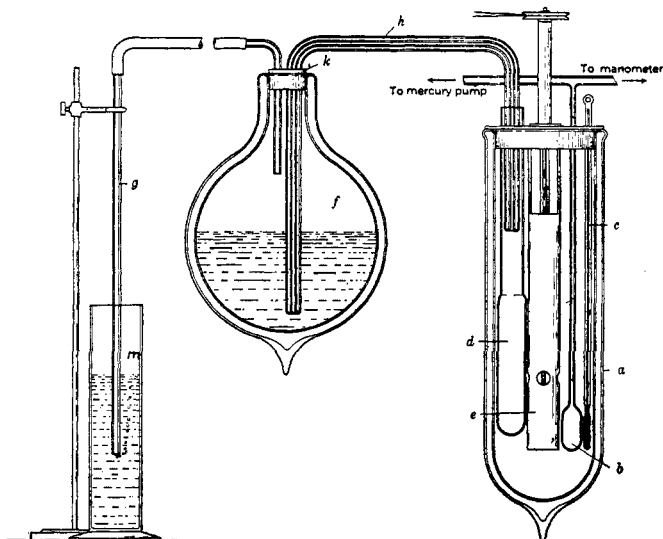

Fig. 1.—Vapor-pressure apparatus and cooling arrangement.

thermometers could be observed through its walls. e is a circulatory pump operated by a small electric motor. The bath liquid (natural-gas gasoline) was drawn into the pump at the base and discharged through four holes in the casing. By this means vigorous and efficient stirring was accomplished. c is a pentane thermometer for registering temperatures. d is a glass test-tube open at the top into which liquid air was forced from the Dewar flask through the tube h, for the purpose of cooling the bath. This arrangement of cooling and maintaining constant temperatures was devised by Henning.[1] The tube h is double-walled and evacuated. At one end it passes through the two-hole stopper k and dips

---

[1] F. Henning, Z. Instrumentkunde, **33,** 33 (1913).

beneath the surface of the liquid air in f. Another glass tube is shown passing through the stopper k. It was not immersed in liquid air. A rubber tube joined it to g. The latter is shown dipping beneath a cylinder of water, m. By lowering or raising g more or less pressure was exerted in f and varying quantities of liquid air could be forced through h into d. The depth of immersion of the tube g could be so regulated that just enough liquid air could be forced into d to compensate for the heat absorption of the bath, thereby maintaining the temperature of the bath constant within $0.04°$, although temperatures could not be determined with that degree of precision. However, close to the normal boiling point of ethane, the temperature changes about $4°$ for each 100 mm., or $0.04°$ per mm., and no trouble was experienced in maintaining pressures constant to 1 mm., close to the boiling point of ethane (or ethylene) for as long as 15 minutes, the maximum length of time the bath was kept constant at one observation. By constantly dropping a little water into the glass cylinder m, to keep the water level therein always at the same height above the liquid-air level in f,[1] constant temperatures could be maintained as long as the liquid air lasted. The bath liquid was casing-head gasoline obtained at a "plant" where gasoline is extracted from natural gas by subjecting it to a pressure of 250 lbs. per square inch and cooling, at ordinary temperatures. This condensate contained a large proportion of the liquid butanes and propane, besides some of the ordinary gasoline constituents, the pentanes, hexanes, etc., and did not jelly when the lighter portions were used, until a temperature of $-175°$ was reached.[2]

Fig. 2.—Mercury manometer.

Two views of the manometer are shown at Fig. 2. In some respects it is similar to one described by Germann.[3]

[1] As the liquid air in f evaporates its level changes, and hence the difference in height between its level and the water level in m changes.

[2] A steel tank such as is used for confining gases under heavy pressure was shipped to the natural-gas-gasoline plant of the Bessemer Gas Engine Co. at Follansbee, W. Va., where it was filled under pressure with the gasoline.

[3] A. F. O. Germann, "A modified precision barometer," THIS JOURNAL, **36**, 2456, 2459 (1914).
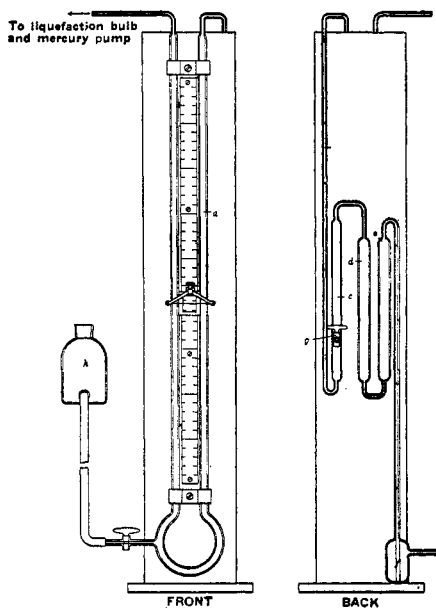
The glass parts were thoroughly cleaned and dried and purified mercury[1] poured into the leveling bottle h. The latter was then raised high enough to force mercury into the capillary b and reservoir c. Next, h was lowered, whereupon the mercury column fell, leaving a mercury seal in b and c and a vacuum above the column in a. The precaution recommended by Germann to clear the space above the mercury of traces of air was followed out as follows: Several days after the filling of the manometer, a water pump was attached to the mercury trap f and the trace of air that had accumulated in a removed. d and e were filled with soda lime. The scale of the manometer was made of steel, and graduated in 0.5 mm. It was checked against a cathetometer[2] with a rod of carefully ground steel, carrying a scale divided into millimeters and fitted with a vernier to read to 0.1 mm. It was also checked against a precision barometer owned by the Bureau of Mines.

Preparation of Gases.—Ethylene was prepared by heating sulfuric acid and ethyl alcohol together at a temperature of 165°. The evolved gases were passed through caustic potash and phosphorus pentoxide. Next they were fractionated at the temperature of liquid air, and air, together with any carbon monoxide or hydrogen formed in the reaction, was withdrawn with a Töpler pump.[3] Fractionation at this temperature was repeated until no more gas was removed by the pump. The gas was further fractionated at a temperature not higher than —140°. At this temperature ethylene was withdrawn by means of the pump, and traces of water vapor or other gases of much higher boiling point than ethylene remained frozen. In addition to this preliminary purification, the gas was cooled at the temperature of liquid air after it had been introduced into the vapor-pressure apparatus and the apparatus evacuated to make sure that air had not been trapped in the transfer. As a further check on the purity of the gas, portions of it were allowed to boil off during the vapor-pressure measurements, which were repeated with the remaining portions. In addition, pressure observations were made with both a rising and a falling mercury level in the manometer.

Ethane was prepared by the electrolysis of a saturated solution of sodium acetate, and purified in essentially the same manner as the ethylene.

Temperature Measurements.—It was originally intended to measure temperatures with a platinum resistance thermometer, but so much delay was experienced in obtaining the necessary equipment that it was decided to perform the work with a pentane thermometer. With this thermometer temperatures as low as —195° could be measured. The scale divisions

[1] Purified by the method of Hulett, *Phys. Rev.*, **34**, 307 (1911).

[2] This cathetometer is described by Wm. Gaertner & Co., their catalog M-L, No. M-902.

[3] See THIS JOURNAL, **36**, 1537 (1914); also *J. Ind. Eng. Chem.*, **7**, 17 (1915).

were 1°, but were so widely spaced that two different observers could easily make readings at a particular temperature which checked to 0.2°, and in most cases to 0.1°.

Holborn,[1] who devised the pentane thermometer, found that it followed the fluctuations of a hydrogen thermometer, in most cases to 0.1°, if properly used.

Calibration of Thermometers.—The authors calibrated their pentane thermometers against certain fixed points established by F. Henning.[2] This scale, together with observations by others, follows. With the exception of Siemen's[3] values, the data given were all cited by Henning.

BOILING AND MELTING POINTS OF DIFFERENT SUBSTANCES BY DIFFERENT OBSERVERS.

	Henning.	Timmermans.	Baly.	Dewar.	Travers.	Onnes.	Siemens.
Oxygen (b. p.) 760 mm.	—183.01		—181.9	—182.5	—182.8	—182.99	—182.99
Oxygen (b. p.) 740 mm.	—183.27						
Carbon dioxide (b. p.)..	— 78.52						—78.44
Mercury (m. p.).......	— 38.89	— 38.6					—38.77
Ethyl ether (m. p.)	—123.6	—123.3					
Carbon bisulfide (m. p.)	—112.0	—111.6					—112.16
Chloroform (m. p.).....	— 63.7	— 63.3					
Chlorobenzol (m. p.)....	— 45.5	— 45.0					
Nitrogen (b. p.)........							—195.84

It will be observed that Henning, Onnes and Siemens agree fairly well. For the boiling point of oxygen the agreement is striking, the variation being only 0.02°, which is the utmost precision obtainable with the hydrogen thermometer.

The pentane thermometers used by the authors were calibrated at four points: the normal boiling point of carbon dioxide, the melting points of carbon bisulfide and ethyl ether, and at —183.27° (the temperature of liquid oxygen boiling at 740 mm.). The carbon dioxide was prepared in two ways: first, by using that furnished commercially in steel tanks, after thoroughly fractionating it at low temperatures and passing it over phosphorus pentoxide to remove water vapor; and, second, by the action of dilute sulfuric acid on potassium bicarbonate. It also was thoroughly purified in the same way as the carbon dioxide obtained from the commercial tanks. The ethyl ether and carbon disulfide were the purest reagents commercially obtainable. No difference was found in their melting points after redistilling them over phosphorus pentoxide.

The oxygen was prepared by heating potassium permanganate in an evacuated hard-glass tube, discarding the first portions of gas that came off, then liquefying the remainder with liquid air, and pumping it into

[1] *Ann. Phys.*, **6**, 242 (1901).

[2] *Ibid.*, **43**, 294 (1913).

[3] H. V. Siemens, *Ibid.*, **42**, 871–878 (1913).

another container. When calibrating against the vapor pressure of liquid oxygen, liquid oxygen was used for the temperature bath.

The following table shows the observations as made with the different pentane thermometers. They are uncorrected readings and show how the thermometers varied among themselves. For instance, at the normal boiling point of carbon dioxide, thermometer No. 8161 read—77.8°, thermometer No. 707 read —81.8°, and thermometer 504 read —78.8°

TEMPERATURE OBSERVATIONS WITH DIFFERENT PENTANE THERMOMETERS.

Therm. No.	CO_2 (from tank), b. p.760.	CO_2 (from K_2CO_3), b. p.760.	CS₂, m. p.		Ethyl ether, m. p.		O₂, b. p.740.
8161	—77.8	—77.7	—111.0	—111.0	—122.8	—122.8	
707	—81.8	—81.9	—114.0	—114.0	—125.5	—122.5	—182.0
507	—78.8	—78.6	—111.6	—111.6	—123.5	—123.5	—183.0

In making independent observations of the vapor pressures of both ethylene and ethane with different thermometers (as noted later) and then correcting them according to their respective calibrations, it was found that the same results were obtained with the different thermometers, thus sho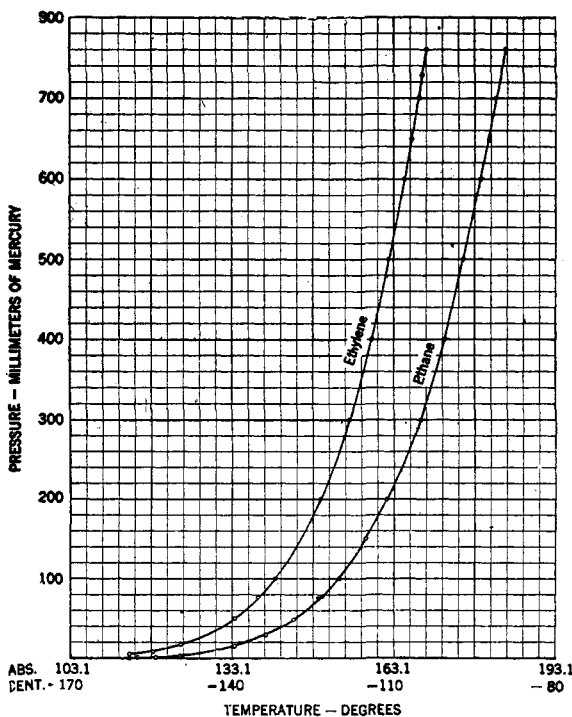wing that the thermometers did not vary seriously (at uncalibrated points) from a straight line drawn between calibrated points,

There are shown in Tables I and II saturated vapor-pressure measurements for ethane and ethylene, also the plotted curves (Fig. 3) for the values as found.

Near the normal boiling points a very small temperature change is represented by large pressure change. For instance, in the case of ethane, 1.6° (90.9–89.3°) = 60 mm. Therefore, 0.2 (the limit of our thermometrical accuracy) corresponds to 7.5 mm. In the case of ethylene, 0.2° corresponds to about 7 mm. at the normal boiling point. In the case

Fig. 3.—Curves showing absolute temperatures plotted against pressures in mm. of mercury.

of ethane 0.2° corresponds to almost 1 mm. between —128.5° and —133.7°
and at the lowest temperatures given (—157.7° and —159.8°) 1 mm. =
2.1° or 0.2° = 0.09 mm.

TABLE I.—SATURATED VAPOR PRESSURES OF ETHYLENE AT TEMPERATURES BELOW
THE NORMAL BOILING POINT.

Thermometer 707.	Thermometer 8161.	Thermometer 504.	Average temperature °C.	Average temperature °Abs.[1]	Observed pressure, mm.	Calculated pressure, mm.
—103.7	—103.9	—104	—103.9	169.2	760	760
—104.8		—104.9	—104.8	168.3	730	726
—105.3	—105.4	—105.5	—105.4	167.7	700	701
—106.8	—106.8		—106.8	166.3	650	643
—107.9	—108.0	—108.2	—108.0	165.1	600	595
—111.0	—111.0		—111.0	162.1	500	512
—114.1	—114.1		—114.1	159.0	400	400
—118.2	—118.1		—118.2	154.9	300	300
—123.5	—123.7		—123.6	149.5	200	200
—132.0		—132.3	—132.2	140.9	100	98
—135.2		—135.3	—135.3	137.8	75	74
—139.5		—139.7	—139.6	133.5	50	49
—144.2		—144.4	—144.3	128.8	31	30
—149.3		—149.6	—149.4	123.7	17	17
—154.7		—154.9	—154.8	118.3	9	9
—159.8		—160.0	—159.9	113.2	4	4

[1] Ice point on the absolute scale is 273.1°. Equation of the curve is $\log P = -762.52/T + 1.75 \log T - 0.00532 T + 4.3910$.

TABLE II.—SATURATED VAPOR PRESSURES OF ETHANE AT TEMPERATURES BELOW THE
NORMAL BOILING POINT.

Thermometer 707.	Thermometer 8161.	Thermometer 504.	Average temperature °C.	Average temperature °Abs.	Observed pressure, mm.	Calculated pressure, mm.
—89.3	—89.4		—89.3	183.8	760	760
—90.8	—90.9		—90.9	182.2	700	711
—92.2	—92.3		—92.3	180.8	650	651
—93.7	—93.7		—93.7	179.4	600	604
—97.0	—96.8		—96.9	176.2	500	495
—100.4	—100.5	—100.6	—100.5	172.6	400	410
—105.2	—105.0	—105.1	—105.1	168.0	300	307
—111.4	—111.2	—111.3	—111.3	161.8	200	200
—115.3		—115.4	—115.3	157.8	150	149
—120.3	—120.1	—120.2	—120.2	152.9	100	100
—123.1		—123.2	—123.2	149.9	77	77
—124.0		—124.2	—124.1	149.0	74	73
—128.4		—128.7	—128.5	144.6	49	47
—133.6		—133.9	—133.7	139.4	29	28
—138.9		—139.2	—139	134.1	15	15
—149.4		—149.7	—149.5	123.6	4	4
—154.6		—154.7	—154.6	118.5	3	2
—157.7		—157.8	—157.7	115.4	2	1.2
—159.8		—159.9	—159.8	113.4	1	0.8

Equation of the curve is $\log P = -1050.85/T + 1.75 \log T - 0.01342T + 7.10217$.

Since the accuracy of thermometer readings was 0.2° and of pressure readings 1 mm., the observations at the higher temperatures were made by adjusting the thermostat until the mercury in the manometer remained constant to 1 mm. Then the thermometer was read. In the case of ethane at the lower temperatures (below —128.5°) the thermostat was adjusted until the pentane thread in the thermometer remained constant to 0.2°. Next the pressure was read. The same procedure was followed in the case of ethylene, the object being to remain within the experimental error, at all times, in reading temperatures and pressures.

Calculation of the Curves of the Vapor Pressure.

This may be done with the aid of the approximate and empirical formula of Nernst:[1]

$$\log P = -\frac{\lambda_0}{4.571 T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C$$

in which the constants λ_0, ϵ, and C may be found by taking values of P at three different temperatures. In the case of ethane, taking as the values of P at three different temperatures the following, 760 mm., 183.8° Abs.; 200 mm., 161.8°; 4 mm., 123.6°; the equation of the curve becomes:

$$\log P = -\frac{1050.85}{T} + 1.75 \log T - 0.01342 T + 7.10217.$$

In the case of ethylene, taking as the values of P at three different temperatures the following, 700 mm., 167.7° Abs.; 300 mm., 154.9° 17 mm., 123.7°; the equation of the curve becomes:

$$\log P = -\frac{762.52}{T} + 1.75 \log T - 0.00532 T + 4.39100.$$

From these equations one can calculate the vapor pressure of ethane and ethylene at any temperature. This has been done as shown in Tables I and II. It will be noted that in the case of ethylene there is one discrepancy outside the error of experimentation, 12 mm. (the —111° point) corresponding to 0.65°. In the case of ethane, 11 mm. (the —90.9° point) corresponds to 0.3°; 10 mm. (the —100.5° point) corresponds to 0.4°; and 7 mm. (the —105.1° point) corresponds to 0.3°. The agreement is not as good as in the case of ethylene.

The results may also be expressed by plotting the common logarithm of the pressure against the reciprocal of the absolute temperature (Fig. 4). The results lie on a straight line. The straight lines were drawn by obtaining an equation from the average of all the results computed by the method of least squares and drawing the lines according to these equations. For ethylene the equation is:

[1] "Theoretical Chemistry," 1911, p. 719.

$$\text{Log } P = -\frac{767.8}{t} + 7.433 \qquad (1)$$

For ethane:

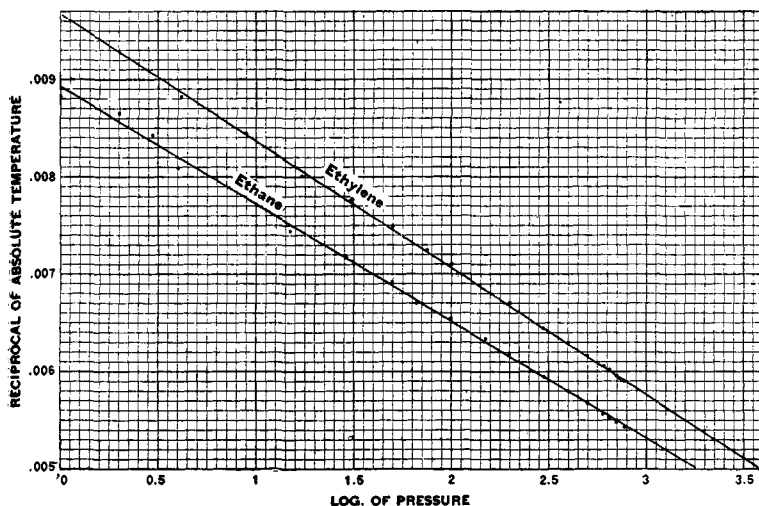$$\text{Log } P = -\frac{831.4}{t} + 7.42 \qquad (2)$$

Fig. 4.—Curve showing common logarithm of vapor pressure plotted as a function of the reciprocal of the absolute temperature.

Heats of Evaporation of Ethane and Ethylene.

The heats of evaporation of ethane and ethylene for the temperature range studied may be calculated from the Clausius-Clapeyron equation:

$$Q = \frac{(d \ln p)\ RT^2}{dT} \qquad (3)$$

in which Q is the heat of evaporation in calories per gram molecule, ln p is the natural logarithm of the vapor pressure, T the absolute temperature, and R the gas constant (1.985).

Integrating Equation 3 and assuming that Q is a constant (which is permissible, however, only for a limited temperature range), one obtains:

$$\ln p = -\frac{Q}{RT} + \text{const.}$$

The values 767.8 and 831.4 in Equations 1 and 2 represent the average of all the determined points on the curve.

Using these values in the Clausius-Clapeyron equation, and changing from common to natural logarithms one finds in the case of ethylene:

$$Q = R(767.8 \times 4.571) = 3510 \text{ calories}$$

and in the case of ethane:

$$Q = R(831.4 \times 4.571) = 3800 \text{ calories}$$

The only other vapor-pressure values at low temperatures for ethane or ethylene (aside from normal boiling points) are those of Maas and McIntosh,[1] who worked out values for ethane from —88.5° (the normal boiling point found by them) to —107.8°. At this temperature they found a pressure of 287 mm., or 2.3° from the value the authors found at 287 mm.

The normal boiling point of ethylene has been found by Olszeswki and by Ramsey and Travers to be 170.5° abs.[2] Travers believes both of these values to be about 1° too low and places greater faith in the value 169.5° abs. found by Wroblewski and Witkowski.[3] The authors of this paper found the normal boiling point to be 169.2° abs.

Thermometer and Manometer Corrections.

The thermometer measurements could be reproduced within 0.2° and pressure readings within 1 mm. Stem corrections on the thermometers were not necessary because they were calibrated with the same depth of immersion as during the vapor-pressure measurements. Corrections for the expansion of the mercury in the manometer and for the steel scale, all fell within the error of experimentation.

Summary.

Saturated vapor pressures for ethane and ethylene at low temperatures are shown. In the case of ethane the vapor pressures range from 760 mm. at —89.3° to 1 mm. at —159.8°. In the case of ethylene the vapor pressures range from 760 mm. at —103.9° to 4 mm. at —159.9°.

The authors' experience with a bath devised by Henning for maintaining constant low temperatures is described.

CHEMICAL LABORATORY, BUREAU OF MINES,
    PITTSBURGH, PA.

ON THE REACTIONS OF BOTH THE IONS AND THE MOLECULES OF ACIDS, BASES AND SALTS.

THE REACTIONS OF SODIUM ETHYLATE WITH METHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25°.[4]

[TWENTY-FIRST[5] COMMUNICATION ON CATALYSIS.]

BY H. C. ROBERTSON, JR., AND S. F. ACREE.

When Brunel and Acree began, in March, 1905, work on the theory that *both the ions and the nonionized form of acids, bases and salts must be considered*

¹ O. Maas and McIntosh, THIS JOURNAL, **36**, 737 (1914).
² M. W. Travers, "The Experimental Study of Gases," p. 243 (1901).
³ *Loc. cit.*
⁴ We are indebted to the Carnegie Institution of Washington for aid in this work.
⁵ For references see *Am. Chem. J.*, **49**, 474 (1913).