

filled with ether to prevent the salt going into solution on account of the alcohol present. The salt dried in a vacuum desiccator to a white, yellow-tinted, flaky, crystalline compound. The salt cannot be prepared by passing dry ammonia into a solution of the acid in methyl alcohol, ethyl alcohol, propyl alcohol, acetone, benzene, toluene, pyridine, carbon tetrachloride or carbon disulfide on account of its great solubility in these solvents. It is also soluble in acetic acid and ethyl acetate. It is only slightly deliquescent. It does not lose ammonia in dry air, but gives it off slowly in moist air.

Calc. for $C_7H_{10}N_2O_2$: 18.18%. Found: 18.12% total N.

Ammonium *p*-Aminobenzoate.—Likewise no mention of this salt can be found. When ammonia is passed into an ether solution of the acid, the salt forms as a white, amorphous precipitate. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid and acetone. It is only slightly soluble in ether. The salt is not deliquescent, and its aqueous solution is neutral to sensitive litmus paper. It is stable in dry air, and slowly loses its ammonia in moist air.

Calc. for $C_7H_{10}N_2O_2$: 18.18%. Found: 18.17% total N.

The ammonium salts of the three aminobenzoic acids can be prepared in an ether solution by the general method described, modifying the method in the case of the *m*-salt by pouring the saturated alcoholic solution into an excess of ether. The three salts are soluble in water, the alcohols, acetone and acetic acid.

Ammonium 3,5-Diaminobenzoate.—After having so easily prepared the ammonium salts of the nitrobenzoic acids, the 3,5-dinitrobenzoic acid, and the aminobenzoic acids, an attempt was made to prepare the ammonium salt of 3,5-diaminobenzoic acid by passing dry ammonia into a solution of the acid in different organic solvents. Saturated solutions of the acid in methyl alcohol, ethyl alcohol, ether, benzene and carbon tetrachloride were tried, but no precipitate formed, owing evidently to the extreme solubility of the salt in these solvents. Further attempts will be made to prepare this salt and study its properties.

This investigation is being continued with other organic acids, especially the substituted acids.

St. Louis, Mo.

THE VAPOR PRESSURES OF PROPANE, PROPYLENE AND NORMAL BUTANE AT LOW TEMPERATURES.¹

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

Received July 1, 1915.

In this paper, one of a series dealing with the vapor pressures of liquid at low temperatures, are shown the vapor pressures of propane, propylene

¹ Presented with the permission of the Director of the Bureau of Mines.

and normal butane. A previous communication by the authors gave vapor pressures for ethane and ethylene. The method of experimentation was detailed in that communication. The same method was followed in this later work. The thermometers were calibrated at additional points in order to measure the higher temperatures demanded. These points are the melting points of chloroform, mercury and ice. Henning¹ found the following values for chloroform and mercury: Mercury, -38.89° ; chloroform, -63.7° .

The temperature readings as made by the authors with their pentane thermometers at the melting points of chloroform, mercury and ice are as follows:

Therm. No. 504: Chloroform -64.0 ; Mercury -36.5 ; Ice $+1.4$.

Therm. No. 707: Chloroform -67.1 ; Mercury -38.4 ; Ice $+1.3$.

These readings are uncorrected and are simply given to show how the thermometers varied among themselves.

In addition to using pentane thermometers, a calibrated mercury thermometer² was used in determining the normal boiling point and a few other points on the vapor-pressure curve of *N*-butane.

The chloroform used was Kahlbaum's purest reagent. Mercury was prepared by fractionating it by the method of Hulett.³ No differences in the melting points of these substances were found by additional fractionation of them.

Preparation of Gases.

Propane was prepared by the action of propyl iodide on a zinc-copper couple. It was purified by fractional distillation in a vacuum at the temperature of liquid air to rid it of air or other substances of high vapor pressure at that temperature, and at a temperature of -110° to remove water vapor and other substances whose vapor pressures are practically negligible at -110° . Phosphorus pentoxide was also used to remove water vapor. Propylene was prepared by dropping propyl alcohol on phosphorous pentoxide at ordinary temperature. *N*-Butane was prepared by the action of *N*-butyl iodide on a zinc-copper couple. Both of these gases were purified in essentially the same manner as the propane. Purification was carried to a point at which the entire liquid distilled at a temperature constant to $\pm 0.2^{\circ}$.

In the tables are shown the vapor pressures of the three substances, the equations of the curves, pressures calculated from the equations,

¹ Henning, F., "The Fixation of the Temperature Scale between 0° and -193° ," *Ann. Physik.*, [4] **43**, 282-94 (1914).

² Calibrated by J. K. Clement, physicist of this Bureau.

³ *Phys. Rev.*, **34**, 34 (1911).

observations with different thermometers, and average temperatures. ° C. and ° Abs. (ice point on Absolute scale = 273.1°).

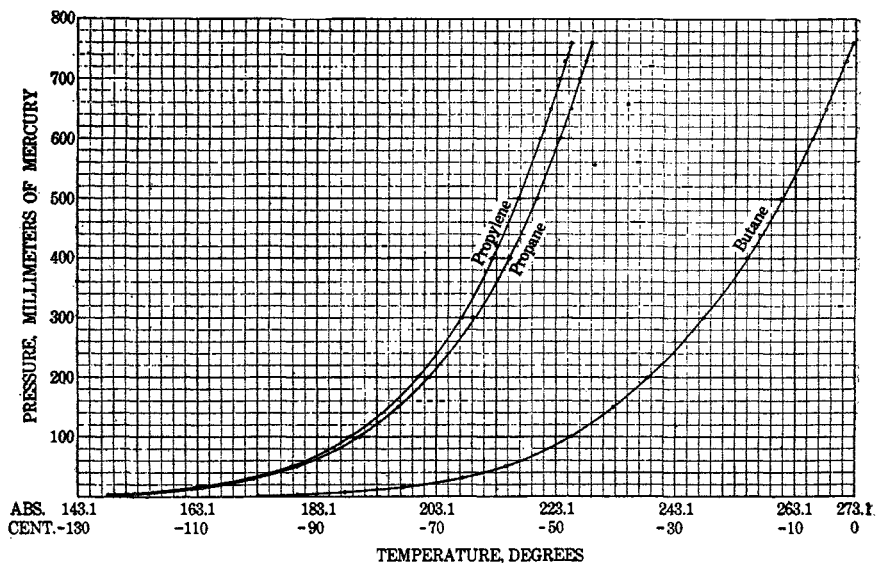


Fig. 1.—Curves showing the temperature plotted against the pressure.

Calculation of the Curve of the Vapor Pressure.—This was done with the aid of the empirical, approximate 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 the values of P at three different temperatures.

The following table shows the values of P and T that were taken in the case of each gas:

	P. Mm. of Hg.	T. ° Abs.		P. Mm. of Hg.	T. ° Abs.		P. Mm. of Hg.	T. ° Abs.
Propane...	600	223.7	Propylene...	730	224.4	<i>N</i> -Butane...	760	272.8
	200	202.0		300	207.4		300	247.8
	15	163.9		15	162.7		15	197.5

For propane, the equation of the curve is $\log P = -863.6/T + 1.75 \log T - 0.000702 T + 2.684$.

For propylene: $\log P = 709.6/T + 1.75 \log T + 0.003947 T + 1.0256$.

For *N*-butane: $\log P = -1633/T + 1.75 \log T - 0.01094 T + 7.590$.

From these equations one can calculate the vapor pressures at different temperatures.

¹ *Theoretical Chemistry*, 1911, p. 719.

VAPOR PRESSURE OF PROPANE AT LOW TEMPERATURES.

Temperature.				Pressure.	
Thermometer. 707 °C.	Thermometer. 504 °C.	Average.		Observed. Mm. Hg.	Calculated. Mm. Hg.
		°C.	° Abs.		
-44.1	-44.2	-44.1	229.0	760	761
-45.1	-45.2	-45.1	228.0	730	729
-46.0	-46.2	-46.1	227.0	700	697
-47.6	-47.7	-47.6	225.5	650	651
-49.4	-49.3	-49.4	223.7	600	600
-53.2	-53.2	-53.2	219.9	500	502
-57.8	-57.7	-57.7	215.4	400	403
-62.9	-62.9	-62.9	210.2	300	309
-71.1	-71.0	-71.1	202.0	200	200
-76.6	-75.9	-76.3	196.8	150	149
-83.0	-82.6	-82.8	190.3	100	101
-93.4	-93.2	-93.3	179.8	50	51
-100.6	-100.3	-100.5	172.6	30	30
-109.2	-109.3	-109.2	163.9	15	15
-118.2	-118.4	-118.3	154.8	6	5.7
-124.1	-124.2	-124.2	148.9	3	3.7
.....	-136.1	137.0	...	1.05
.....	-143.1	130.0	...	0.45

VAPOR PRESSURE OF PROPYLENE AT LOW TEMPERATURES.

Temperature.				Pressure.	
Thermometer. 707 °C.	Thermometer. 504 °C.	Average.		Observed. Mm. Hg.	Calculated. Mm. Hg.
		°C.	° Abs.		
-47.8	-47.8	-47.8	225.3	760	763
-48.7	-48.7	-48.7	224.4	730	730
-49.6	-49.6	-49.6	223.5	700	706
-51.1	-51.1	-51.1	222.0	650	648
-52.8	-52.8	-52.8	220.3	600	595
-56.4	-56.2	-56.3	216.8	500	497
-60.6	-60.5	-60.6	212.5	400	396
-65.8	-65.6	-65.7	207.4	300	300
-73.5	-72.9	-73.2	199.8	200	196
-78.4	-77.7	-78.0	195.1	150	147
-84.6	-84.1	-84.4	188.7	100	98
-94.4	-94.1	-94.2	178.9	50	51
-101.5	-101.3	-101.4	171.7	30	30
-110.4	-110.3	-110.4	162.7	15	15
-120.3	-120.4	-120.3	152.8	6	6.4
-127.3	-127.5	-127.4	145.7	3	3.3
.....	-138.1	135	...	1.07
.....	-143.1	130	...	0.59

VAPOR PRESSURE OF *N*-BUTANE AT LOW TEMPERATURES.
 Temperature.

Pentane thermometer. 707 °C.	Pentane thermometer. 504 °C.	Mercury thermometer. °C.	Average.		Pressures.	
			°C.	°Abs.	Observed. Mm. Hg.	Calculated. Mm. Hg.
-0.3	-0.3	-0.2	-0.3	272.8	760	760
-1.6	-1.5	-1.4	-1.5	271.6	730	731
-2.9	-2.8	-2.7	-2.8	270.3	700	701
-4.9	-5.1	...	-5.0	268.1	650	652
-7.2	-7.1	...	-7.2	265.9	600	604
-12.2	-12.3	...	-12.3	260.8	500	504
-18.2	-18.0	...	-18.1	255.0	400	404
-25.3	-25.3	...	-25.3	247.8	300	300
-34.6	-34.7	...	-34.6	238.5	200	196
-40.4	-40.3	...	-40.3	232.8	150	148
-47.4	-47.6	...	-47.5	225.6	100	100
-58.3	-58.2	...	-58.3	214.8	50	52
-65.5	-65.3	...	-65.4	207.7	31	32
-76.1	-75.2	...	-75.6	197.5	15	15
-85.4	-85.1	...	-85.3	187.8	7	7
-93.3	-93.1	...	-93.2	179.9	3	3
-100.0	-99.8	...	-99.9	173.2	1	1
.....	-113.1	160.0	...	0.31

The results may also be expressed by plotting the logarithm of the pressure against the reciprocal of the absolute temperature, (Fig. 2). The

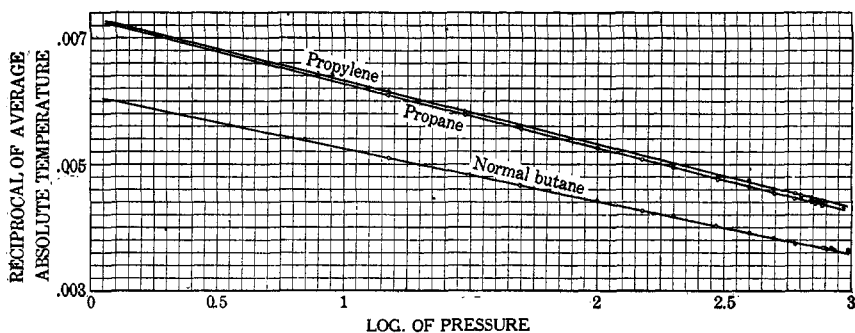


Fig. 2.—Curves showing the logarithm of the pressure plotted against the reciprocal of the absolute temperature.

straight lines shown 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.

$$\text{For propylene the equation is: } \log P = -\frac{1006.1}{T} + 7.173.$$

$$\text{For propane: } \log P = -\frac{983.7}{T} + 7.3402.$$

For normal butane: $\log P = -\frac{1224.5}{T} + 7.3948$.

Heats of Evaporation of Propane, Propylene and Normal Butane.

The heats of evaporation over the temperature range studied (calories per gram molecule) were calculated from the Clausius-Clapeyron equation:

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

By integrating this equation and assuming that Q is a constant, one obtains:

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

Using the values 1006.1, 983.7 and 1224.5 in the above equation and from common to natural logarithms, one finds:

For propylene: $Q = (1006.1 \times 4.571) = 4599$ calories.

For propane: $Q = (983.7 \times 4.571) = 4496$ calories.

For normal butane: $Q = (1224.5 \times 4.571) = 5597$ calories.

Summary.

The vapor pressures of propane, propylene and *N*-butane at low temperatures are shown. For propane the vapor pressure ranges from 760 mm. at -44.1° to 3 mm. at -124.2° . For propylene the vapor pressure ranges from 760 mm. at -47.8° to 3 mm. at -127.4° . For *N*-butane the vapor pressure ranges from 760 mm. at -0.3° to 1 mm. at -99.9° .

LABORATORY, GAS INVESTIGATIONS, BUREAU OF MINES,
PITTSBURGH, PA.

THE ESTIMATION OF RAFFINOSE BY ENZYMOTIC HYDROLYSIS.

By C. S. HUDSON AND T. S. HARDING,¹

Received April 26, 1915.

In a recent article² we have called attention to the fact that it is possible to prepare from top-fermentation yeast by a specified procedure an extract which is rich in the enzyme invertase but contains no melibiase, while bottom-fermentation yeast yields an extract which contains both enzymes. Each extract hydrolyzes sucrose to invert sugar, and each also has a hydrolyzing action upon raffinose, but the top yeast extract produces melibiase and fructose from it, while the bottom yeast extract converts it to galactose, glucose and fructose. These relations are better understood from the accompanying diagram which indicates the various steps in the hydrolysis of raffinose by enzymes.

¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² THIS JOURNAL, 36, 1570 (1914).