# [CONTRIBUTION FROM THE BUREAU OF STANDARDS.]

## LATENT HEAT OF VAPORIZATION OF AMMONIA.

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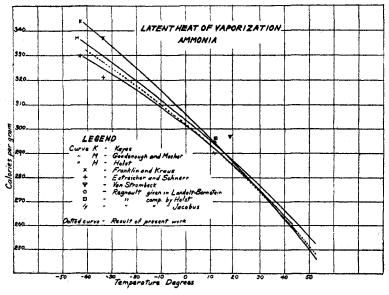
CONTENTS.—I. Introduction. II. Previous Determinations. III. General Description of Method. IV. Results of Measurements. V. Form of Empirical Equation. VI. Conclusions. VII. Summary. Appendix.—Specific Heat of Saturated Ammonia Vapor.

### I. Introduction.

In tables of heat content of ammonia such as engineers require, the latent heat of vaporization constitutes the major part. Nevertheless, the direct measurements of this property are among the rarest of the available experimental data. This is attributable probably to the fact that the latent heat of vaporization may, by thermodynamic formulas, be computed from other properties, more easily measurable; however, the data which have heretofore been available for this calculation have not been of a precision such as to yield satisfactory values for the latent heat. The measurements here presented have been carried out in response to the requests of the associations of refrigerating engineers in this country for more accurate data upon which to base calculations for machinery using ammonia in the production of artificial refrigeration.

## II. Previous Determinations.

Results of previous determinations of the latent heat of vaporization of ammonia are represented graphically in Fig. 1. The three curves also



shown in this figure represent values computed from other data by Keyes,<sup>1</sup> Goodenough and Mosher,<sup>2</sup> and Holst.<sup>3</sup>

Regnault<sup>4</sup> published a record of 12 experiments saved from the ruins of his laboratory, destroyed during the siege of Paris in 1870. The apparatus consisted of two calorimeters, the first, or evaporation calorimeter, in which the ammonia was allowed to evaporate from a steel container and flow through a chamber containing baffle plates, and the second, or expansion calorimeter, in which the ammonia vapor from the first calorimeter was allowed to expand to atmospheric pressure.

Regnault's results have been variously interpreted by different writers. Holst computed the latent heat of vaporization from the observation in the first calorimeter and ignored the partial expansion below saturation pressure which occurred there. As a mean result he obtained 296 calories per g. at 12°. Jacobus<sup>5</sup> computed the latent heat of vaporization from the observations in both calorimeters and obtained as a mean value 290 calories per g. at 12°. Landolt and Börnstein<sup>6</sup> give values from Regnault's data, the mean value at 12° being 294.5 calories per g.

Von Strombeck<sup>7</sup> used the same type of apparatus as Regnault and obtained from 12 experiments a mean value of 296.5 calories per g. at  $18^{\circ}$ .

Estreicher and Schnerr<sup>8</sup> (original paper unobtainable), according to Landolt and Börnstein, determined the heat of vaporization at the normal boiling point and obtained a value of 321 calories per gram at  $-33.4^{\circ}$ .

Franklin and Kraus<sup>9</sup> determined the heat of vaporization at the normal boiling point. The apparatus consisted of a Dewar flask containing a liquid bath and a glass evaporating cell, each supplied with a platinum heating coil. The energy required to evaporate a certain volume of liquid ammonia was measured and the mass computed from the volume evaporated, using the value 0.604 for the density. The mean result from three experiments was 341 calories per g. Recomputed, using more recent date for the density (0.683), the mean value becomes 337 calories per g. This result is the same as that deduced by Franklin and Kraus from the absolute boiling point and the molecular elevation by vant Hoff's formula.

#### III. General Description of Method.

The calorimeter used in making the experimental determinations is the same as that described in a paper<sup>10</sup> on specific heat of liquid ammonia.

<sup>1</sup> "Thermodynamic Properties of Ammonia," John Wiley & Sons, 1916.

<sup>2</sup> Univ. of Ill., Bull. 66 (1913).

<sup>3</sup> Association Internationale du Froid, Bull. 51 (1915).

4 Ann. chim. phys., 24, 375 (1871).

<sup>b</sup> Trans. Am. Inst. Mech. Eng., 12, 307 (1890).

<sup>6</sup> Phys. Chem. Tabellen, 1912.

<sup>7</sup> J. Franklin Inst., 131, 470 (1891).

<sup>8</sup> Bull. de l'Ac. de Cracovie, p. 345 (1910); Phys. Chem. Tables (1912).

<sup>9</sup> J. Phys. Chem., 11, 553 (1907).

<sup>10</sup> THIS JOURNAL, **40**, 1 (1918).

A system of baffle plates in the top of the calorimeter is provided for drying the vapor during its removal in evaporation experiments. The method employed in the determinations of heat of vaporization was to evaporate, slightly superheat, and withdraw from the calorimeter a measured amount of the ammonia. The approximate amount of heat required to effect this change was added and measured electrically, the small balance being due to the thermal leakage and the resulting change in temperature of the remainder of the system, both of which were kept relatively small and were measured. The jacket was kept at a constant temperature during the experiment. The withdrawn vapor passed into the reservoir, where it was condensed. The rate of outflow of the vapor was governed by the difference between the vapor pressures in the calorimeter and condenser and by the throttling at the needle valve in the connecting tube outside the calorimeter. This valve was provided with a graduated circle and index for facilitating fine adjustment. The vapor pressure in the condenser was controlled approximately by regulating its temperature. The balance between heat added and heat extracted from the system could be maintained in two independent ways-either by control of the outflow, using the regulating valve, or by control of the heat added electrically.

The temperature of the vapor withdrawn was determined with reference to the initial temperature of the experiment by means of the thermocouples attached to the outflow tube, the common reference junction being on the jacket. Three junctions equidistant along the length of the tube are available for this observation.

The pressure within the calorimeter was indicated by means of a closed manometer, the connection to the interior being similar to that used for transfer of ammonia. This manometer might have been calibrated in terms of actual pressures; but it was found, instead, more convenient to calibrate and use it as a vapor-pressure thermometer to indicate the temperature at the free surface of the liquid in the calorimeter, especially as the evaporation temperature—that is, the free surface temperature during evaporation—enters as a correction factor into the calculation of the final result.

Initially, the system consisting of the calorimeter and the ammonia sample is in thermal equilibrium, the contents comprising both liquid and vapor phases. A portion is withdrawn as superheated vapor with the addition of heat electrically and the remaining portion allowed to resume equilibrium; the aim being to adjust the rate of adding heat and the rate of evaporation so as to avoid large temperature changes throughout the process and to make the final temperature approximately equal to the initial. The initial and final temperatures and amount removed are ob-

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served, and periodic observations made throughout the experiment of the following quantities:

- 1. Current in electric heating coil.
- Potential drop in heating coil. 2.
- 3. Temperature difference between calorimeter and jacket surfaces.
- Vapor pressure in calorimeter. 4.

5. Temperature of vapor as it leaves the calorimeter at the pressure existing therein.

Given these data and the necessary additional data from independent sources, the problem is to compute the latent heat of vaporization.

The process which goes on in the calorimeter cannot be followed in detail, for during the period while heat is being added and vapor is being withdrawn the temperature is certainly not uniform and, furthermore, the temperature distribution in the ammonia is unknown. The observations during this period furnish merely knowledge at any instant of the temperature  $\theta_e$  of the liquid surface at which the evaporation is occurring, and the temperature  $\theta$ , to which the vapor is superheated when withdrawn. It is thus evidently impossible to analyze in detail the phenomena which actually occur and recourse must therefore be had to some other method of interpreting the observations quantitatively. By assuming an ideal process which would, if carried out, lead from the observed initial to the observed final state and involve the same amount of external work as the actual process, the amount of heat required can be expressed in terms of known data and of the unknown latent heat of vaporization which is to be determined. If this expression be equated to the observed quantity of heat supplied during the actual experiment, the result after making certain minor approximations, is an equation from which the unknown latent heat L may be found. The notation used and the equation are as follows:

- V= volumetric capacity of calorimeter in cubic centimeters.
- $M_1, M_2$  = initial and final mass in calorimeter.

= mass, in grams, removed from calorimeter as superheated  $\Delta M$ vapor.  $\Delta M = M_1 - M_2$ .

- $\theta_1, \theta_2$ = initial and final temperatures of calorimeter and contents when in equilibrium.
  - = average temperature of free surface in calorimeter.
- $\frac{\overline{\theta}_e}{\overline{\theta}_s}$ = average temperature of superheated vapor as it leaves the calorimeter.
- $\Delta O$ = heat added to contents of calorimeter during an experiment.
- C,' = specific heat at constant pressure p and temperature  $\theta$ .
- = specific heat, in joules per gram per degree, of the saturated σ liquid—that is, the liquid in equilibrium with the vapor.

- = specific heat, in joules per gram per degree, of the saturated vapor.
- u = specific volume in cm.<sup>3</sup>/g. of the saturated liquid.
- u' = specific volume in cm.<sup>3</sup>/g. of the saturated vapor.
- $\pi$  = saturation pressure.

 $\sigma'$ 

L = latent heat of vaporization at temperature  $\theta$  in joules per gram, defined as the heat required to change I gram of saturated liquid to saturated vapor at a constant temperature and pressure.

$$L_{1} = \frac{\Delta Q}{\Delta M} - L_{1} \frac{u_{1}}{u'_{1} - u_{1}} - \left(\sigma + \frac{dL}{d\theta} + \frac{L}{\theta} \frac{u}{u' - u}\right) (\bar{\theta}_{e} - \theta_{1}) - C'_{p} (\bar{\theta}_{s} - \bar{\theta}_{e}) \\ - \left\{ \frac{M_{2}}{\Delta M} \left[\sigma - \theta \frac{d}{d\theta} \left(\frac{L}{\theta} \frac{u}{u' - u}\right)\right] + \frac{V}{\Delta M} \theta \frac{d}{d\theta} \left(\frac{L}{\theta} \frac{u}{u' - u}\right) \right\} (\theta_{2} - \theta_{1}).$$
(1)

The expression,  $\frac{\Delta Q}{\Delta M} = L_1 \frac{u_1}{u'_1 - u_1}$ , in Equation 1 represents the quantity

of heat which would be added to the ammonia per gram evaporated at the initial temperature  $\theta_1$ . It would equal the latent heat of vaporization at that temperature if the experiment proceeded under ideal conditions, such that the heat added was instantaneously distributed over the free surface so as to avoid any change in temperature and pressure whatever, for then all the other terms would vanish. The remaining terms in the right member of Equation 1 represent corrections to the above expression for the departure of the actual experiment from the ideal conditions just specified.

Considerable variation in the manipulation was possible and such variations were purposely introduced as a means of detecting possible systematic errors. Experiments were made in which the aim was to keep the temperature of evaporation as nearly as possible equal to the initial temperature. In these experiments the thermal leakage was relatively large. Usually the thermal leakage was kept small by keeping the average surface temperature of the calorimeter nearly constant, and permitting the temperature of evaporation to vary. Different rates of evaporation were used as a test for the dryness of the vapor, on the supposition that if spray were carried out with the vapor the amount would vary with the rate. Different parts of the heating coil were used, that part usually being used which would develop the heat nearest to the place where evaporation occurred.

Some significant discrepancies in the earlier results were found to be due to the condensation of ammonia in the outflow tubes previous to beginning an experiment. Such an occurrence would result in transferring to the condenser more material than was evaporated during the period in which the heat added was measured and would therefore lead to a too low result for the latent heat of vaporization. This source of error was detected through the peculiarity that the initial experiment of a series frequently gave a result lower than those immediately following, the discrepancy in some cases being as much as 0.3 per cent. An error of this magnitude might be tolerated, but after identifying the cause an effective remedy was evident, namely, to precede the first determination in a day's series with a blank experiment by which all liquid condensed in the outflow tube during the preliminary cooling would be expelled and the tube dried. The results of all previous initial experiments where this procedure had been omitted should, of course, be excluded from the authentic determinations because, even when operating at low temperatures, although the natural tendency would be for the tube ultimately to become dry, nevertheless there was no assurance that sufficient time had elapsed for this to occur, and therefore all unpreceded experiments in a series are open to doubt.

The sample of ammonia used in these determinations was similar to Sample C, described in preceding paper.

## IV. Results of Measurements.

The data obtained from the calorimetric measurements are given in Table I.  $\Delta Q$ , the heat added to the ammonia, is computed according to the formula

$$\Delta Q = \Sigma (IEt') + Bht_2 - N(\theta_2 - \theta_1).$$

The total energy supplied electrically,  $\Sigma(IEt')$ , is the sum of the amounts for all the periods of heating during the experiment. In most of the experiments the energy was supplied during a single period, t', the current I and potential drop E being very nearly constant, so that the product of the average values obtained from the periodic readings of the potentiometer multiplied by the time t' gives the total energy within the limit of significant error. For the few experiments where the energy was supplied in several installments, each portion was computed separately and the sum taken. The thermal leakage was computed on the basis of the coefficient of thermal leakage B, determined by supplementary experiments, the average deflection of the galvanometer h and the total time  $t_2$  elapsing between the initial and final readings of temperature  $\theta_1$ and  $\theta_2$ . The energy absorbed by the calorimeter was computed on the basis of the heat capacity of the calorimeter N, determined by supplementary experiments, and the total change in temperature  $\theta_2 - \theta_1$  during the experiment.

In Table II is given the computation of the latent heat of vaporization L from the experimental data in Table I, and accessory data from other sources. The computation in Table II is made according to Equation 1. This equation involves in addition to the data of the present experiments only the specific volumes u and u' of the two phases and the specific heat  $C_{p'}$  of the vapor at constant pressure.

Experi- ment No.	Heat to ammonia ΔQ. Joules.	Mass ammonia removed $\Delta M$ . G.	Final mass in calorimeter $M_2$ . G.	$\frac{M_2}{\Delta M}$ C	$\frac{V}{\Delta M}$ m. <sup>s</sup> /G.	Initial tem- perature $\theta_1$ . °C.	θ <sub>2</sub> — θ <sub>1</sub> . ° C.	$\theta_{e} - \theta_{1}.$ ° C.	$\theta_{s} - \theta_{e}$ ° C.
I	25 272	19.619	176.72	9.008	26	-5.39	-0.004	-0.10	+o.66
2	25 354	19.610	157.11	8.012	26	-5.40	+0.127	—I.23	+1.11
3	25 578	19.950	137.16	6.875	25	-5.27	-0.142	—1 , IO	10.1+
4	17 864	13.940	108.48	7.782	36	-4.84	-0.143	-2.23	+1.61
5	24 800	19.285	54.76	2 . 839	26	-4 . 98	+0.018	—1.17	+0.99
6	24 777	19.228	35.53	1.848	26	-4.96	+0.150	—o.69	+0.75
7	24 150	18.188	211.03	11.603	28	-21.83	-0.169	—1.95	+1.55
8	14 239	10.625	157.14	14.790	47	-22.09	+0.033	-0.29	+0.53
9	13 432	10.079	137.62	13.654	50	-22.48		-0.50	+o.68
10	27 821	20.775	116.84	5.624	24	-22.58	-0.004	—1.32	+1.30
11	26 606	19.297	78.38	4.062	26		+0.034	-0.95	+1.05
12	20 370	17.035	28.65	1.682	30	+22.23	+0.047		+0.85
13	22 664	18.976	210.97	11.122	27	+20.84		0.77	+0.60
14	23 605	19.667	170.90	8.690	26	+20.38	-0.026	-o.85	+o.98
15	23 432	19.521	151.38	7.755	26	+20.35	-0.041	-o.33	+0.79
16	22 676	18.870	-	6.704	27	+19.74	-0.020		+0.53
17	25 003	20.110	103 . 89	5.166	26	+7.60	o.o68	0.54	+0.59
18	24 436	19.612	84.28	4.297	26	+7.53	+0.021	-0.63	+0.69
19	16 220	13.014	50.51	3.881	39	+7.38	100.00	-0.25	+0.52
20	22 303	17.367	15.85	0.913	29	-4.09	+0.059	o.35	+0.64
21	11 150	8.684	7.16	0.824	58	-4.03	+0.021	-o.48	+0.73
22	13 004	9.323	226.66	24.312	54	-42.01	-0.007	—0.63	+0.79
23	13 067	9.494	217.17	22.874	53	-42 .01	—0.184	-0.43	+0.65
24	14 954	11.036	195.05	17.674	46	-28.28	-0.031	0.39	+0.60
25	14 913	11.002	184.05	16.730	46	-28.31	-0.005		+0.68
26	12 310	9.396	165.51	17.615	53	—14.93	-0.091	-0.44	+0.78
27	12 313	9.394	156.11	16.618	54	-14.70	-0.071	-0.60	+o.8o
									θ <sub>s</sub> — θ1
28	11 921	10.485	134.94	12.870	48	+36.43		• • • •	+0.36
29	11 589	10.807	113.17	10.472	46	+51.80	-0.054	• • • •	-0.02
30	11 989	11.112	90.92	8.182	45	+50.61	-0.042	••••	-0.01
31	11 926	11.049		7.229	46	+50.56	+0.037		+0.03
32	11 831	10.934	68.94	6.305	46	+50.53	+0.006		+0.07
33	11 618	10.185	46.49	4.565	49	+36.21	+0.018		+0.19
34	11 652	10.214	36.28	3.551	49	+36.22	-0.012	••••	+0.24

#### TABLE I.-CALORIMETRIC DATA.

The following abbreviations are employed in the computations:

$$\frac{dH'}{d\theta} = \frac{dL}{d\theta} + \sigma + \frac{L}{\theta} \frac{u}{u' - u}$$
$$Y = \theta \frac{d}{d\theta} \left[ \frac{L}{\theta} \frac{1}{u' - u} \right]$$
$$Z = \sigma - \theta \frac{d}{d\theta} \left[ \frac{L}{\theta} \frac{u}{u' - u} \right]$$

The values used for the specific volumes of the liquid and vapor phases of ammonia are preliminary values from the measurements made at this Bureau by Messrs. Harper, Cragoe, and O'Connor, the final results of which will be published in a separate paper.

Table	II.—CALCULATION	OF $L_1$	•
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Experiment No.	<u>Δ0</u> . <u>ΔM</u> Joules/g.	$L_1 \frac{u_1}{u'_1 - u_1}$	$\bigcup_{i=1}^{dH'} \frac{dH'}{d\theta} = -\frac{1}{\theta_e - \theta_i};$ i Joules/g.	$C_{\hat{P}'}(\overline{\theta}_e - \overline{\theta}_e).$ Joules/g.	$\frac{M_1}{\Delta M}Z(\theta_1-\theta_1).$	$ \stackrel{V}{\circ} \frac{V}{\Delta M} Y(\theta_{1} - \theta_{1}). $	Lı. Joules/g.	ට • ස්	Deviation from Equation. Parts in 10,000.
1	1288.1	5.7	o.1	1.5	-0.2	-0.0	1281.2	-5.33	+3
2	1293.0	5.7	1.5	2.6	+4.4	+0.4	1281.4	5.40	+2
3	1282.1	5.7	1.3	2.4	-4.3	o.4	1280.0	-5.27	-5
4	1281.5	5.8	2.7	3.8	-4.9	o.6	1280.1	-4.84	+8
5	1286.0	5.8	1.4	2.3	+0.2	+0.0	1279.1	-4.98	4
6	1288.6	5.8	o.8	1.7	+1.2	+0.5	1280.2	-4.96	+5
7	1327.8	3.0	2.8	3.4	-8.6	-0.3	1333.1	<b>—2</b> 1.83	8
8	1340.1	3.0	0.4	1.1	+2.1	+0.1	1333.2	-22.09	7
9	1332.7	2.9	0.8	1.5		0.4	1335.2	<b>—22</b> .48	7
10	1339.2	2.9	1.9	2.8	0.1	<b>0</b> .0	1335.5	-22.58	7
11	1378.8	1.6	1.5	2.2	+0.7	+0.0	1375.8	-35 . 75	+3
12	1195.8	14.2	0.5	2.2	+0.3	+0.3	1179.3	+22.23	+8
13	11 <b>94</b> .6	13.7	0.5	1.6	-3.9	0.4	1184.1	+20.84	+1
14	1200.2	13.5	0.6	2.5	-1.0	0.4	1186.2	+20.38	+3
15	1200.3	13.5	0.2	2.1	—1.4	-0.2	1186.5	+20.35	+7
16	1201.7	13.2	0.3	1.4	0.7	0.1	1188.2	+19.74	2
17	1243.3	8.9	0.5	1.5	—1.5	0.3	1235.2	+7.60	+1
18	1246.0	8.9	0.6	1.7	+0.4	+0.1	1235.5	+7.53	+1
19	1246.3	8.9	0.2	1.3	<b>0</b> .0	0.0	1236.3	+7.38	+3
20	1284.2	6.0	0.4	1.5	+0.2	+0.2	1276.7	-4.09	+1
21	1284.0	6.0	0.6	1.7	+0.1	+0.1	1276.7	-4.03	+2
22	1394.8	1.2	1.0	1.6	0.7	0.0	1393.7	-42.01	+6
23	1376.3	1.2	0.7	1.3	—18.4	-0.3	1393.2	-42.01	+3
24	1355.0	2.3	0.6	1.3	-2.4	-0.1	1354.5	-28.28	+7
25	1355.5	2.3	0.7	1.4	0.4	0.0	1352.9	-28.31	6
26	1310.1	4.0	0.6	1.7	-7.I	-0.4	1312.5	-14.93	≠o
27	1310.8	4.0	0.8	1.8	-5.2	-0.3	1311.3	-14.70	-4
28	1137.0	21.3	0.1	2.5	-3.4	0.8	1117.5	+36.43	+3
29	1072.4	32.2	+0.1	1.5	<b>—2</b> .4	-0.9	1041.9	+51.80	6
30	1078.9	31.0	0.0	1.5	<b>—1</b> .5	—o.6	1048.5	+50.61	— <b>1</b>
31	1079.4	31.0	0.0	1.5	<u> </u>	0.6	1048.6	+50.56	—3
32	1082.0	31.0	0.0	1.8	+0.1	+0.1	1049.0	+50.53	—1
33	1140.8	21.1	0.1	2.0	+0.3	+0.2	1117.3	+36.21	-7
34	1140.8	21.1	0.1	2.0	0.2	0.2	1118.2	+36.22	+ 1

For the experiments where  $\theta_e - \theta_1$  was not observed on account of the temperature being higher than would allow the use of the manometer, the value of  $\theta_e - \theta_1$  was taken equal to 0.5°, this being the mean value in

previous experiments. The greatest deviation from this value in the preceding experiments was not more than  $0.3^\circ$ , and this amount would not change the computed value of L more than 1 part in 1000. The final results probably are affected less than one-third this amount.

## V. Form of Empirical Equation.

An empirical equation the form of which is consistent with the behavior of substances at the critical point should give a value of zero at the critical point for L, and for the derivative  $dL/d\theta$  should give a value of  $-\infty$ . An equation of the form

$$L = A \left(\theta_{c} - \theta\right) + B \left(\theta_{c} - \theta\right)^{\frac{1}{2}},$$

in which  $\theta_c$  = the critical temperature, was found to meet these requirements and to represent the experimental results closely. The equation has the further advantage of giving no real roots above the critical temperature.

## VI. Conclusions.

An inspection was made to ascertain whether the results were affected by such variations as occurred in the experiments. The following conditions which might conceivably independently affect the results are: (a) Rate of evaporation; (b) thermal leakage; (c) average deviation of evaporation temperature from initial temperature; (d) maximum deviation of evaporation temperature from initial temperature; (e) portion of heating coil used; (f) amount removed; (g) amount in calorimeter (mean during experiment); and (h) temperature of experiment.

These various conditions were not all systematically changed one at a time, keeping all the others constant, as would have been necessary if large variations had been found to result from the changes. Except for the actual temperature of the determination, which is the primary independent variable, effects of variations in the other conditions are presumed to have been either eliminated experimentally or taken into account quantitatively in the computation of the results, supposing, of course, that such variations were kept within reasonable limits. If the results were dependent to a significant extent on these incidental conditions, it would scarcely be possible to avoid some effect being observed. By examination of the deviations from the value given by the empirical equation it has not been possible to trace any systematic deviation to any of the experimental conditions other than the temperature of the experiment. It may, therefore, be concluded that no systematic error resulted from these conditions which was not obscured by accidental errors.

Particular mention might be made of the rate of evaporation. If this rate were increased to the point where active boiling occurred, it is possible that the system of baffle plates might have failed to intercept all of the fine spray thrown up and the evaporation of the withdrawn material would have been incomplete, or, in other words, the vapor would have been wet. It is, therefore, of especial interest to note that considerable variation in rate occurred without causing any consequent effect upon the resulting value for latent heat, indicating that within the range of variation used the vapor was dry. Additional confirmation on this point is furnished by the fact that the temperature of the vapor withdrawn was, with rare exceptions, always higher than the temperature at which evaporation was proceeding within the calorimeter.

The results of the determinations may be expressed by means of the following empirical equation:

$$L = 137.91 \sqrt{133 - \theta} - 2.466 (133 - \theta)$$
  
VII. Summary.

Using a calorimeter of the aneroid type specially designed for the peculiar conditions, the latent heat of vaporization of ammonia has been determined throughout the temperature interval -42 to  $+52^{\circ}$ .

The instrument contains no special liquid for a calorimetric medium, the ammonia being the only liquid in the calorimeter. Heat developed and measured electrically in a coil is transmitted by conduction and convection to the surrounding ammonia and is utilized to effect the evaporation of a determined amount of the ammonia which is withdrawn as superheated vapor, at a determined temperature and pressure. Heat from other sources is minimized by reducing as far as practicable the avenues for heat transfer between the calorimeter and its environment, and by so manipulating as to keep the temperatures of the calorimeter and jacket surfaces nearly equal, means being provided for determining the amount of thermal leakage which is not thus annulled. Initial and final temperatures are measured by a platinum resistance thermometer.

An analysis of the process occurring in the calorimeter during an experiment leads to a method of calculation of the results whereby data from other sources than the direct calorimetric observations enter only in the computation of correction terms which can by careful manipulation be made small.

Variations in manipulation were introduced as a means of detecting possible systematic errors, particularly in regard to the matter of dryness of the vapor withdrawn.

The result of each of the 34 determinations agrees with the mean result as expressed by means of an empirical equation within 1 part in 1000. An empirical equation was found which, in addition to representing closely the results in the range of temperature covered experimentally, also conforms to what is known about the behavior of substances in general when approaching the critical point. As a final result the latent heat of vaporization of ammonia—that is, the heat in joules per g. required to convert saturated liquid into saturated vapor at constant temperature—is expressed in the range  $-42^{\circ}$  to  $+52^{\circ}$ by the equation

$$L = 137.91 \sqrt{133 - \theta} - 2.466 (133 - \theta).$$

If the latent heat of vaporization be expressed in calories<sub>20</sub> per g. taking 1 calorie<sub>20</sub> = 4.163 joules, the equation becomes

$$L = 32.968 \sqrt{133 - \theta} - 0.5895 (133 - \theta).$$

The values computed from this equation in every degree are as follows:

CALORIES PER GRAM.										
Tempera ture.	 0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
—40°	331.7	332.3	333.0	333.6	334 . 3	334 . 9	335.5	336.2	336.8	337.5
—30	324.8	325.5	326.2	326.9	327.6	328.3	329.0	329.7	330.3	331.0
-20	317.6	318.3	319.1	319.8	320.6	321.3	322.0	322.7	323.4	324.1
—10	309.9	310.7	311.5	312.2	313.0	313.8	314.6	315.3	316.1	316.8
—o	301.8	302.6	303.4	304.3	305 . 1	305.9	306.7	307.5	308.3	309 . 1
+0	301.8	300.9	300.1	299.2	298.4	297.5	296.6	295.7	294.9	294.0
+10	293.1	29 <b>2</b> .2	291.3	290.4	289.5	288.6	287.6	286.7	285.7	284.8
+20	283.8	282.8	281.8	280.9	279.9	278.9	277.9	276.9	275.9	274.9
+30	273.9	272.8	271.8	270.7	269.7	268.6	267.5	266.4	265.3	264.2
+40	263.1	262.0	260.8	259.7	258.5	257.4	256.2	255.0	253.8	252.6

# Appendix—Specific Heat of Saturated Ammonia Vapor.

If the latent heat of vaporization and the specific heat of the saturated liquid are known as functions of the temperature, it is possible to compute the specific heat of the saturated vapor by using the general relation

$$\sigma' - \sigma = \frac{dL}{d\theta} - \frac{L}{\theta} = \theta \frac{d}{d\theta} \left(\frac{L}{\theta}\right).$$

The data for the specific heat of saturated liquid ammonia are available from a previous investigation<sup>1</sup> the results of which are expressed by the empirical equation

$$\sigma = 3.1365 - 0.00057\theta + \frac{16.842}{\sqrt{133 - 6}}$$

in which  $\sigma$  is the specific heat in joules per g. degree at temperature  $\theta$  of the saturated liquid. The rate of change  $dL/d\theta$  of the heat of vaporization of ammonia with temperature and the quantity  $L/\theta$  can be calculated from the results of the present work. The computed values of the specific heat  $\sigma'$  in joules per g. degree of saturated ammonia vapor are given in the following table:

<sup>1</sup> This Journal, 40, 1 (1918).

Temperature. °C.	Specific heat of saturated vapor. Joules/g. deg.	Temperature. °C.	Specific heat of saturated vapor. Joules/g. deg.
-45	-4.42	0	-3.54
-40	-4.29	$+_{5}$	-3.48
-35	-4.17	+10	-3.43
—30	-4.05	+15	-3.40
-25	3.95	+20	<u> </u>
20	<u> </u>	+25	-3.34
—15	3.76	+30	-3.33
-10	<u> </u>	+35	-3.33
-5	<u> </u>	+40	-3.34
0	3.54	+45	-3.36
WASHINGTON, D. C.			

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 112.]

## THE VAPOR PRESSURE OF LIQUID AMMONIA UP TO THE CRITICAL TEMPERATURE.

[PART II.]

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CONTENTS.—1. Previous Investigations. 2. The Experimental Method and Description of the Apparatus. 3. Data and Method of Determining the Vapor Pressure as a Function of the Temperature. 4. Summary.

### 1. Previous Investigations.

The earliest attempt to measure the vapor pressure of liquid ammonia appears to be due to Faraday<sup>1</sup>. The measurements extend from -17.77 to +28.33. At that time precise thermometry had not been developed, and, moreover, no very great precautions were taken to avoid the presence of permanent gas or other impurities soluble in liquid ammonia. The presence of permanent gas such as air in a liquid is most difficult to remove. It is in fact not possible to remove it by simply pumping away vapor or even sufficiently by freezing and pumping the vapor from the crystals.<sup>2</sup> The Faraday measurements, while not as accurate as may now be obtained with modern experimental facilities, are nevertheless within a few per cent. of the values obtained by Regnault.<sup>3</sup>

Regnault's data are given in three series of measurements each under different experimental conditions. The third series were made by means of a closed air manometer, thus requiring an accurate knowledge of the pressures corresponding to the various volumes of compressed air read from the manometer. The pressures assigned to the volume readings of the manometer were not accurately known and in consequence the ammonia

<sup>&</sup>lt;sup>1</sup> Faraday, Phil. Trans., 135, 170 (1845).

<sup>&</sup>lt;sup>2</sup> Young, Phil. Mag., 20, 797 (1910).

<sup>&</sup>lt;sup>8</sup> Regnault, Mem. l'Inst. France, 26, 598 (1847).