THE LATENT HEAT OF PRESSURE VARIATION OF LIQUID AMMONIA

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I. INTRODUCTION

When a fluid undergoes a change of pressure, there occurs a transformation of energy into heat or vice versa, which results in a change of temperature of the substance unless a like amount of heat is abstracted or added. This change expressed as the heat so transformed per unit change of pressure will be called "latent heat of pressure variation." For most liquids under usual conditions of temperature and pressure this quantity, which depends on the thermal expansivity, is small compared with the other quantities of heat which are usually observed, but for liquid ammonia in the range -40 to $+40°$ C and corresponding saturated vapor pressures it is sufficiently large to be taken into account in calorimetric determinations of specific heat; and, in consequence, the measurements here described were made as a supplement to a series of such determinations in order to correlate measurements of specific heat of liquid ammonia [1] made at constant pressure with others made under saturation conditions.

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[1] This Bulletin, **14**, p. 397; 1917.

The latent heat of pressure variation has been determined in two ways, namely, by direct calorimetric observations and by computation from the expansivity, using for the latter two independent sources of experimental data. Thus, three independent determinations were obtained. On account of the fact that the determinations of specific heat at constant pressure were, when made, regarded as secondary in importance to the others, these measurements of the latent heat of pressure variation as well as the specific heat at constant pressure were not executed with the nicety of which the method finally proved worthy, and, in consequence, the accuracy, while sufficient for the intended purpose, could probably have been considerably bettered with moderate additional refinements in the control and measurement of pressures.

II. NOTATION

M = mass, in grams, of ammonia in the calorimeter.

θ = temperature, in centigrade degrees, of the thermodynamic scale.

Q = heat added in joules.

N = heat capacity, in joules per degree, of calorimeter.

$\Delta\theta$ = total change of temperature in any experiment from initial equilibrium temperature to final equilibrium temperature.

θ' = temperature at which overflow of liquid leaves the calorimeter.

p = pressure, in kilograms per square centimeter.

C_p = specific heat at constant pressure, p, and temperature, θ.

l = latent heat of pressure variation, in joules per gram per unit pressure change.

v = specific volume in cubic centimeters per gram of liquid at pressure p.

III. DETERMINATIONS BY COMPUTATION FROM VOLUMETRIC DATA

The latent heat of pressure variation is quantitatively defined by the equation

$$l = \frac{1}{M}\left(\frac{\partial Q}{\partial p}\right)_\theta$$

where ∂Q is the heat added to mass M to maintain constant temperature simultaneously with a change of pressure ∂p. The latent heat of pressure variation may be computed by means of the general relation:

$$l = -\theta\left(\frac{\partial v}{\partial \theta}\right)_p \tag{1}$$

if the expansivity, $\left(\dfrac{\partial v}{\partial \theta}\right)_p$, is known. This was obtained in two ways from independent experimental sources—first, from the specific volumes of the saturated liquid and the compressibilities at various temperatures and, second, from the direct observations of the thermal expansion at constant pressure made with a dilatometer specially designed for use in connection with the calorimeter in the measurements of specific heat and described therewith.[2]

The compressibilities were obtained from the determinations of mass contained in the calorimeter at various temperatures and pressures, corrected for the expansion of the calorimeter itself. The values for specific volume of the liquid are preliminary values from measurements made at this Bureau by Messrs. Harper, Cragoe, and O'Connor, the final results of which will be published in a separate paper. By this method of computation it was found that within the range of temperature and pressure covered by the present experimental work the expansivity, $\left(\dfrac{\partial v}{\partial \theta}\right)_p$, and, consequently, the latent heat of pressure variation, l, were independent of the pressure to the degree of accuracy sought.[3] The results of the direct dilatometric observations, while covering too limited a range of pressure to permit this same conclusion independently, were found to be in agreement with it over the range actually covered. From each independent series of values of $\left(\dfrac{\partial v}{\partial \theta}\right)_p$, determined as described above, the corresponding values of l were computed, using equation (1). Only the final results appear in the appended Table 4.

IV. DETERMINATIONS BY DIRECT CALORIMETRIC OBSERVATIONS

The apparatus used for these determinations was identical with that used in the measurements of specific heat at constant pressure [4] and has been previously described.[5]

As used in the measurements here described, the essential features consist of a metal shell containing the material, suspended for thermal insulation in an air space within a thermally controlled

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[2] This Bulletin, 14, p. 397; 1917.

[3] The expansivity was computed by means of the formula:

$$\left(\frac{\partial v}{\partial \theta}\right)_p = \frac{du}{d\theta} + \left(\frac{\partial v}{\partial p}\right)_{\theta,\pi}\frac{d\pi}{d\theta} - \int_\pi^p \frac{\partial}{\partial \theta}\left(\frac{\partial v}{\partial p}\right)_\theta dp$$

where u is specific volume of saturated liquid and π is saturation pressure at temperature θ.

[4] This Bulletin, 14, p. 397; 1917.

[5] This Bulletin, 14, p. 133; 1917.

jacket.   A platinum resistance thermometer located in the center
serves to indicate the temperature of the system when in equilib-
rium.   A heating coil likewise in the center may be used to add
heat electrically in order to determine the heat capacity of the
system.   For evaluating the thermal leakage thermocouples with
multiple junctions distributed on the surfaces indicate temperature
differences between calorimeter and jacket surfaces.   By keeping
the average jacket and calorimeter surface temperatures equal the
thermal leakage is annulled.   The calorimeter full of the liquid
connects with a reservoir outside, which is immersed in a thermally
controlled bath and contains both liquid and vapor   The tempera-
ture of the free surface in the reservoir determines the vapor
pressure therein, and, therefore, the pressure in the calorimeter
may be controlled by manipulation of the aforementioned bath.
The measurements of the heat of pressure variation, l, could readily
have been made by simultaneously adding heat electrically and
decreasing the pressure at such a rate that no change in tempera-
ture occurred, the heat added and the change in pressure being
observed and the determination would then be independent of the
heat capacity of the system.   Since the actual quantity of heat
transformed was small in the present experiments, it was found
more convenient practically to observe the small change in tem-
perature produced by a change of pressure with the addition of no
heat electrically.   The change in pressure was produced by chang-
ing the temperature of the outside reservoir in which the free surface
of the liquid was maintained.   By observing this temperature when
the calorimeter was in equilibrium at the beginning and again at
the end of an experiment, and using data for the relation between
temperature and pressure of saturated ammonia vapor, the change
in pressure Δp was obtained. $\Delta \theta$ was obtained from observations
of the initial and final temperatures of the calorimeter when in
equilibrium, just as in the specific-heat determinations.   The
quantity l was then computed, using the heat capacity of the
calorimeter and contents determined in separate experiments.
The method of making this computation is as follows:

The quantity of heat, dq, added to the calorimeter and contents
to produce a given change in temperature, $d\theta$, accompanied by a
change in pressure, dp, can be expressed in three parts as follows:

1. Amount required to produce the change, $d\theta$, dp, in the amount
M, in the calorimeter at any mean temperature θ of the contents

$$dQ_1 = M (C_p d\theta + l d_p)$$

2. Amount required to heat from θ to θ' the amount dM expelled during the change $d\theta$, dp

$$dQ_{\text{II}} = C_p \, dM \ (\theta' - \theta)$$

3. Amount required to heat the calorimeter through the temperature increment $d\theta$

$$dQ_{\text{III}} = N d\theta$$

The entire amount is, therefore, by addition of the above separate parts

$$dQ = (MC_p + N) \ d\theta + Mldp + C_p dM \ (\theta' - \theta) \qquad (2)$$

The total amount of heat, ΔQ, added to the system during an experiment is obtained by integrating equation (2) over the corresponding increments of temperature, pressure, and mass experienced. For such small increments of temperature and pressure as were observed the quantities M, C_p, N and l were all found to be so nearly linear functions of θ and p that for the purpose of this integration they may without significant error be regarded as constants and taken equal to their respective values at the mean temperature of the experiment. Furthermore the term $C_p \, dM (\theta' - \theta)$ is neglible in comparison with the other terms, since dM and $\theta' - \theta$ are each small. By integrating after making these approximations equation (2) then becomes

$$\Delta Q = (M \ C_p + N)\Delta\theta + M \ l \ \Delta p \qquad (3)$$

Solving for l

$$l = \frac{\Delta Q}{M \Delta p} - \frac{MC_p + N}{M} \frac{\Delta\theta}{\Delta p} \qquad (4)$$

In the experiments ΔQ was made zero. The equation, therefore, may be written

$$l = -\left(\frac{N}{M} + C_p\right)\frac{\Delta\theta}{\Delta p} \qquad (5)$$

which is suited for the computation of l from the observed quantities.

The results of these direct determinations upon liquid ammonia are given in the following table. The adjusted values of the mean of the three independent methods are also given in this table, equal weight being assigned to each series of values.

V. RESULTS

Latent Heat of Pressure Variation of Liquid Ammonia

Temperature of calorimeter θ	Initial pressure p_1	Final pressure p_2	Pressure change Δp	Mean pressure $\dfrac{p_1+p_2}{2}$	Change in temperature of calorimeter $\Delta\theta$	Energy transformed $\left(\dfrac{N}{M}+C_p\right)\Delta\theta$ a	l determined calorimetrically b	l computed from specific volumetric data	l computed from dilatometer data	l adjusted value c
°C	Kg/cm²	Kg/cm²	Kg/cm²	Kg/cm²	°C	J/g	$\dfrac{J}{g}\Big/\dfrac{Kg}{cm^3}$	$\dfrac{J}{g}\Big/\dfrac{Kg}{cm^3}$	$\dfrac{J}{g}\Big/\dfrac{Kg}{cm^2}$	$\dfrac{J}{g}\Big/\dfrac{Kg}{cm^2}$
−44.1	11.41	7.67	− 3.74	9.54	−0.029	+0.206	−0.055	−0.056	−0.054	−0.055
−39.0	7.67	.86	− 6.81	4.26	− .053	+ .377	− .055	− .059	− .057	− .057
−24.2	16.12	2.01	−14.11	9.06	− .065	+ .920	− .065	− .069	− .068	− .068
− .2	12.03	18.85	+ 6.82	15.44	+ .079	− .599	− .088	− .089	− .089	− .088
− .2	18.85	4.58	−14.27	11.71	− .161	+1.219	− .085	− .089	− .089	− .088
− .2	4.58	18.80	+14.22	11.69	+ .166	−1.262	− .088	− .089	− .089	− 0.88
+16.5	20.94	8.17	−12.77	14.55	− .175	+1.372	− .107	− .109	− .109	− .107
+26.5	20.83	11.04	− 9.79	15.93	− .149	+1.191	− .122	− .124	− .124	− .123
+35.4	20.83	14.30	− 6.53	17.56	− .112	+ .923	− .141	− .141	− .141	− .140
+40.3	20.83	16.18	− 4.65	18.50	− .085	+ .705	− .152	− .152	− .151	− .150

a $N = 1000$ J/deg. approximately; $M = 300$ g. approximately; $C_p = 4.5$ J/g. deg. approximately.

b Certain observations with smaller pressure increments than those here given appeared to indicate an increase in the numerical value of l with pressure, in apparent contradiction to the result of the computations from the data on specific volume and compressibility. Since the discrepancy was only of the order of the precision of the measurements and was not significant in the application of the results to the specific heat measurements, its investigation was postponed. In future measurements by this method, with better provision for control and observation of the pressure, better concordance could be expected.

c The adjusted value of l is that given by the empirical equation $l = 0.0371 - \dfrac{14.97}{120 - \theta}$.

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