in the different directions in the altering crystal with the result that the spherulites are no longer round but are flattened ellipsoids. The application of X-ray analysis to inversion phenomena of this kind promises a deeper insight into the mechanics of inversion phenomena of this and other types.

Summary.

The crystallization of menthol is interesting not only to the crystallographer but also to the physical chemist. Menthol appears in four different forms, α, β, γ, δ; three of these bear apparently monotropic relations to the stable α-form. Because of pronounced undercooling the melting temperatures of all four forms can be realized and their mutual relations can be studied directly under the microscope. On crystallization all forms of menthol show a pronounced tendency to the development of radial spherulites; these are roughly spherical in shape in the case of crystallization from the melt, but noticeably ellipsoidal on inversion of one crystal form into a second. The four forms of menthol are readily distinguished under the petrographic microscope. α-Menthol shows dextrorotatory polarization while the melt is laevorotatory. In the formation of the different monotropic forms the initial temperature of crystallization appears to be the determinative factor.

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THE THERMODYNAMIC CONSTANTS OF AMMONIA.

I. THE HEAT-CAPACITY OF LIQUID AMMONIA.

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1. Introduction.

Although liquid ammonia has been in use for many years as a practical refrigerating agent, its various physical constants have not been hitherto completely determined with any considerable degree of precision. The practical as well as the scientific importance of an accurate body of data relating to the physical properties of the substance is very considerable. Aside from the use of ammonia in the refrigerating art the Haber process of atmospheric nitrogen fixation requires data for the gas phase which at present are lacking. From a scientific point of view, on the other hand, ammonia is very similar to water having a high dielectric constant and quite general solvent properties, thus rendering a study of the physical properties of the liquid phase of especial interest. In fact as will be shown in a later paper, ammonia furnishes an example of another substance which in the liquid state contains polymers of the molecule NH_3.

The work[1] carried out at this laboratory will be presented in a series of papers which will present the results of measurements of the vapor pressures, the specific volumes of both phases and the compressibilities of the phases. The equation of state of the gas phase has resulted from the study of the gaseous phase which thus permits the specific heat capacity to be calculated for any pressure and temperature by the application of the equation to the thermodynamic equation

$$C_p = C_v + T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p.$$

The present paper presents the results obtained for the mean heat capacity of the liquid between 0° and 20° and between 20° and 50°.

2. Previous Investigations.

Experimental values, all obtained by the method of mixtures, for the specific heat capacity of liquid ammonia have been obtained by von Strombeck,[2] Ludeking and Starr,[3] Elleau and Ennis[4] and H. Drewes.[5] The specific heat capacity has been computed from thermodynamic data by Ledoux, Zeuner and Wood. The results of such computations will be presented later.

Von Strombeck used a steel container in which the weight ration of steel to ammonia was 10.7 to 1. Temperatures were read to 0.01°, the total temperature change being 10°. No mention is made of the method used to obtain the true rise in temperature. Ludeking and Starr used a steel container in which the ratio of steel to ammonia was somewhat better, being 7.1 to 1.

The Ludeking and Starr measurements give the value of the heat capacity between 20° and 0° and 56° and 20°. The calorimeter capacity in these measurements was only 150 cc. and the weight of ammonia scarcely large enough in proportion to the heat capacity of the container, the container absorbing one calorie for an absorption of 1.4 calories by the ammonia.

The importance of transferring the ammonia and its container rapidly and reproducibly from the thermostat to the calorimeter is a matter of very great moment from the point of view of accuracy. Ludeking and Starr do not describe the method employed and the precise procedure

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[1] The experimental data have already been used as a partial basis for the computation of a new Table of Properties, see "The Thermodynamic Properties of Ammonia," by Frederick G. Keyes and Robert B. Brownlee, Wiley & Sons, 1916.

[2] *J. Franklin Inst.*, **136**, 467 (1890).

[3] *Am. J. Sci.*, **145**, 200 (1893).

[4] *J. Franklin Inst.*, **145**, 189, 280 (1898).

[5] Landolt and Börnstein, *Physikalisch-chemisches Tabellen*, page 762.

used to reduce the measurements is not given. It is stated that the "Rumford" method of correcting the observed temperature changes was employed. The value deduced from the measurements is materially lower than the value obtained by others.

The measurements due to Elleau and Ennis were carried out between 0° and 20° only and a very large ratio of steel to the weight of ammonia in the container was employed making the heat capacities of steel and ammonia nearly equal. The container in these measurements was transferred by hand from the thermostat to the calorimeter and the data obtained treated graphically to obtain the temperature rise corrected for loss of heat due to radiation. The procedure adopted consisted in taking the vertical distance on the temperature-time plot, drawn from the instant of introducing the bomb to the intersection of the final cooling curve projected toward the temperature axis. The method is evidently incapable of yielding the true temperature rise. The value given by Elleau and Ennis is likewise low though greater than the Ludeking and Starr datum.

H. Drewes' original paper was inaccessible, but the final values as given in the Landolt and Börnstein tables will be presented for comparison with the values obtained in the present investigation.

3. The Experimental Method and Apparatus.

In carrying out specific heat measurements by the method of mixtures, it is necessary to provide for a large difference of temperature between the thermostat and the calorimeter in order that a sufficiently large temperature change may be obtained. The specific heat thus obtained is consequently the mean value between the temperature of the thermostat and the calorimeter.

It is a disadvantage of the method of mixtures that it yields only the mean values, whereas to calculate the true value of the specific heat, defined by $\left(\frac{\partial Q}{\partial T}\right)_{\text{sat.}}$, requires a knowledge of $\left(\frac{\partial Q}{\partial T}\right)_{\text{sat.}}$ as a function of the temperature. The form of this function is at present unknown and it appears in any case that it cannot be a simple function since the specific heat increases with extreme rapidity as the critical temperature of a liquid is approached. At low temperatures on the other hand, the quantity becomes very small in the case of those substances which remain liquid at low temperatures. The range of temperature throughout which the heat capacity of saturated liquid ammonia is required for practical purposes is far enough removed from the critical point so that the heat capacity may be represented by a comparatively simple empirical temperature function. Methods which will give the specific heat values over a very small temperature interval as for example one degree, are very much needed, but unfortunately such methods as have been studied are not applicable to liquids at temperatures at which the saturation pressures are large.

There is also considerable difficulty entailed in obtaining the precise value for the water equivalent of the calorimeter with the method of mixtures, and also in obtaining the value of the specific heat of the steel container or other receptacle containing the ammonia to be experimented on. Since an error in either of these quantities affects the determination directly the precision of the measurements will depend on a number of difficult secondary measurements.

A further difficulty is that there is no method available for determining precisely the temperature of the hot body just before it enters the calorimeter. The temperature of the body may be quite different from that of the thermostat and since the temperature difference affects the rise in temperature of the calorimeter directly when the body is introduced, especial care must be exercised to make at least the process of introduction as exactly reproducible as possible.

The principle of the method here used to measure the specific heat capacity of liquid ammonia, is due to Charles A. Kraus, formerly of this laboratory. The method consists in making strictly comparable measurements with water and ammonia. This was affected by constructing two steel containers or bombs as nearly identical in shape as possible and of the same weight. The weight of water in the water bomb was subsequently adjusted by trial experiments until its heat capacity was identical with that of the ammonia.[1] Because of the equality of the heat capacities of the two bombs together with their contents, the temperature rise produced in the calorimeter will be the same for each, provided every detail with respect to the thermostat temperature and calorimeter is the same in the parallel experiments.

The method has many advantages but like the usual "method of mixtures," procedure requires a considerable temperature difference between the temperature of the thermostat and the calorimeter. The uncertainty regarding the temperature of the bomb at the instant it passes into the calorimeter is removed however, provided a reproducible method of introducing the bomb into the calorimeter is employed, because the surface and heat capacity of the bombs are identical. The water equivalent of the calorimeter is eliminated by the improved procedure and were it not for the slightly different calorimeter temperature-time curves due to the different rates of temperature equalization of the two substances, any consistent method of treating the curves would suffice for obtaining the corrected temperature rise. In the present instance the convection currents in the bomb containing the ammonia were much more vigorous

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[1] The weight of liquid present is of course dependent upon the temperature of the bomb but in the experiments here undertaken the error caused by assuming the weight of liquid invariable is smaller than the accuracy attained.

than in the water bomb and accordingly a more rapid equalization of the temperature in the calorimeter was effected. Evidently this circumstance made it necessary to consider very accurately the radiation correction.

The heat equation may be written $(W_1 + B)\, t_1 + Q_1 = (W + K)\Delta T_1$ plus heat due to stirring radiation and conduction where w_1 is the total heat capacity of the water, B the total heat capacity of the steel container, t_1 the equilibrium temperature difference between the thermostat and the calorimeter, Q the vaporization correction for the water, W the weight of water in the calorimeter, K the water equivalent of the calorimeter and ΔT_1 the calorimeter temperature change.

And

$(w + B)\, t + Q = (W + K)\Delta T$ plus heat due to stirring radiation and conduction for the ammonia container. Since the heat introduced by stirring, conduction and radiation is the same for both the water and the ammonia, if $\Delta T_1 = \Delta T$, $(w_1 + B)t_1 + Q_1 - (w + B)t - Q = 0$.

But the temperature of equilibrium of the calorimeter is nearly the same in both cases and the two steel bombs are identical whereupon

$$(w_1 - w)t + (Q_1 - Q) = 0,$$

or

$$w = G\,\bar{C}_s = w_1 + \frac{Q_1 - Q}{t}.$$

$$\bar{C}_s = \frac{w_1}{G} + \frac{(Q_1 - Q)}{Gt},$$

where $\bar{C}_s$ is the mean saturation specific heat of liquid ammonia.

The specific heat is therefore equal to the weight of water in the bomb multiplied by its specific heat and divided by the weight of ammonia plus a small correction due to vaporization or condensation.

If V_2 and V_1 are the specific volumes, respectively, of the liquid and gas phases at saturation and M_2 and M_1 the weights, the total volume of the two phases will be $V = M_2V_2 + M_1V_1$. The total weight M is equal to $M_2 + M_1$ and therefore the weight of the liquid phase will always be equal to $\frac{V - MV_1}{V_2 - V_1}$.

Now let the subscripts t_1 and t_2 represent any two different temperatures. Then the vaporization correction in passing from t_1 to t_2 will be

$$Q = R\,[(M_2)_{t_1} - (M_2)_{t_2}]$$

where R is the heat of evaporation per gram of substance. Substituting the value of M_2 there is obtained for the the vaporization correction

$$Q = R\left[\left(\frac{V - MV_2}{V_1 - V_2}\right)_{t_1} - \left(\frac{V - MV_1}{V_1 - V_2}\right)_{t_2}\right].$$

Essentially the apparatus used in this work consisted of a thermostat, a calorimeter, and a thermometer to measure the temperature change

(Fig. 1). The thermostat consisted of a galvanized iron can. Into the bottom of the thermostat was a bored hole and soldered to the edge of this hole and standing vertically in the thermostat was a copper tube closed at its upper end, except for a very small brass tube which extended beyond the top of the thermostat. Within the thermostat was a long copper tube coiled so as to expose a larger surface to the liquid in the thermostat; this tube connected with the bottom of the upright copper tube. The bomb chamber was closed at the bottom by means of a cork in the upright copper tube, while air under a slight pressure was passed through the coiled copper tube leading finally into the copper tube of the bomb chamber. In the 0–20 determination the thermostat was filled with melting ice, while in the 20–50 determination the thermostat was filled with water maintained at 50 by an electrical heating coil. A mercury regulator was used to keep the temperature constant. The air forced through the coiled copper tube with a low velocity came to the same temperature as the thermostat and in passing up around the bomb, thereby shortened the time required for the bomb to assume the temperature of the thermostat.[1]

The calorimeter consisted of a large Dewar tube. In this type of calorimeter losses due to radiation and conduction are reduced to a very small value. The Dewar tube was submerged in a bath maintained to within 0.1° of constant temperature. The calorimeter or Dewar tube was provided with a tight vulcanite cover which supported the stirrer and four small brass rods which formed a cage to receive the bomb on its descent into the calorimeter. The vulcanite cover to the calorimeter

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[1] An estimate of the time required for the cylinder to come to equilibrium may be readily calculated by solving the equation $\frac{\partial V}{\partial t} = a^2\left(\frac{\partial^2 V}{\partial r^2} + \frac{1}{r}\frac{\partial V}{\partial r}\right)$ where V is the temperature and $a^2 = \lambda/\rho c$, λ being the conductivity for heat for the particular substance, ρ its density, and c its specific heat. In the present case it is desired to estimate the length of time required for the axis of the bomb to come to within 0.01° of the thermostat temperature. The constant a^2 is of the same order for various liquids, varying from 8.4×10^{-4} to 11.9×10^{-4}. For the present computation 1.0×10^{-3} was chosen. The solution satisfying the present boundary conditions for a 20° difference in temperature between the thermostat and the bomb at the instant it is placed in the thermostat is

$$V = 40\left\{e^{-\mu_1^2 a^2 t}\frac{1}{\mu_1 c J_1(c\mu_1)} + e^{-\mu_2^2 a^2 t}\frac{1}{\mu_2 c J_1(c\mu_2)} + \ldots\right\}$$

where μ_1, μ_2..are the roots of $J_1(c\mu_1)$..a Bessel's function of the first kind and first order and C is the radius (1.3 cm.) of the cylinder. The conductivity of the steel shell may be neglected since it is many times greater than the liquid. The time required is between 20 and 25 minutes. It will be observed that this estimate gives the maximum time required. The presence of convection currents in the liquid ammonia shorten the time very considerably. Tests were of course made by varying the length of time the bomb remained in the thermostat, and half an hour proved to be ample time.

was provided with a thin vulcanite disc so arranged as to swing over the opening in the top for the reception of the bomb. A hole was also provided in the cover for the Beckmann thermometer. An electric bell tapper was so arranged as to tap gently and continuously on the top of the thermometer thus obviating the difficulty of the mercury sticking in the capillary. This tapping device was found to be quite essential to accuracy, as it was found that without the tapper errors as large as 0.005° were made due to the stiction of the mercury. An ordinary thermometer telescope was used to read the temperatures which were probably read with a precision of 0.002°.

The water in the calorimeter was measured in a 500 cc. flask brought to a constant temperature in one of the laboratory thermostats. It was filled with distilled water, placed in the thermostat which was maintained at 18°, and after it had come to temperature the water was adjusted to the proper level and poured into the calorimeter. The weight of this water used was 502.7 g. In order to adjust the temperature of the water in the calorimeter to a definite point before starting a measurement, use was made of a small heating coil placed in the water until it had come to the desired temperature.

Owing to the complicated nature of the apparatus between the thermostat and the calorimeter it was found impracticable to remove the calorimeter after each experiment. The water was therefore siphoned out by means of a glass tube, and then compressed air blown into the calorimeter until it was found that the calorimeter was dry.

Fig. 1 shows the method of lowering the bomb from the thermostat into the calorimeter. The bomb A is supported in the thermostat by means of a thread passing over the pulleys P and down to the trigger J. The thermostat is shown at B and the cork closing the opening at C. A movement of the lever L downward causes a small metal ring to slip from the trigger F, thus the spring E is brought into play, which, acting through the lever arm, pulls the cork out and allows it to swing out of the way. As the lever L is being pulled down, it trips the cord from the nail G, and allows the tube D to be pulled by the spring H into position lining up the hole in the thermostat with the hole in the top of the calorimeter cover, thus forming a guide for the bomb in its descent. As the tube D swings into place, it slackens the cord I, and due to the weight of the bomb the trigger J is upset and the bomb is free to fall down the glass tube D. The movement of the lever L acts on the cord, passing around the pulleys N, and opens the cover O, and at the same time stretches the spring K. The bomb has a free fall until it reaches the point where it is four inches above the surface of the water in the calorimeter M. Here the cord attached to the spring Q comes taut. This spring stretches until the bomb nearly touches the surface of the water in the calorimeter; then its tension overcomes the tension of the spring S upon which the trigger R trips and permits the bomb to drop freely the remaining short distance down to the bottom of the wire cage in the calorimeter, thus breaking the fall of the bomb and preventing any splash of water or injury to the calorimeter.

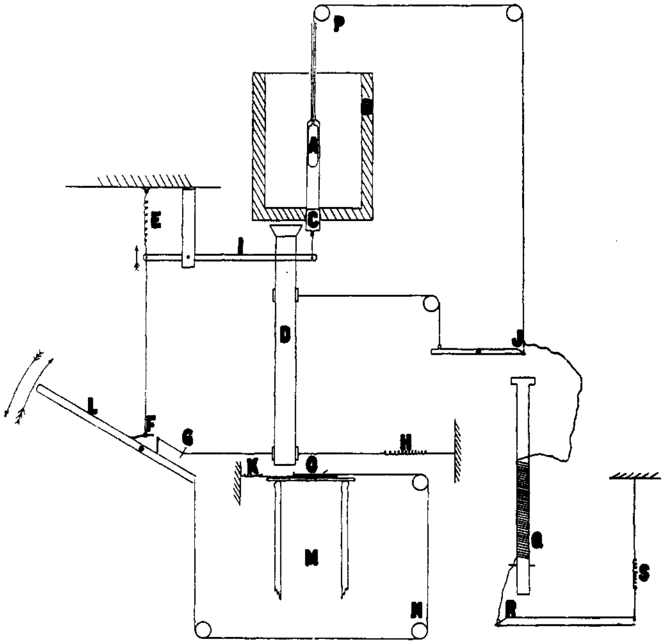

Fig. 1.

The bombs used to hold the water and ammonia in these experiments were made from 1″ mild steel tubing having a wall thickness of 0.028″. The length of the bombs was 5″. The ends were spun down to a hemispherical shape and the lower end silver soldered. In the upper end was soldered a short steel tube having a diameter of about 3/32″ and a length of 3/8″. Soldered to this short tube was a piece of steel having a 1/8″ tapped hole at its upper end and a 1/16″ hole connecting the tapped hole with the tube. A gold washer 1/32″ thick was used to lock the bomb being compressed by a screw plug. The device made a gas-tight closing which permitted no perceptible leakage. There was a small hole drilled transversely in the plug to permit of the insertion of a small wire hook to connect the bomb with the supporting thread The two steel bombs, while of not exactly the same volume and dimensions, were adjusted as to weight within 0.2 mg.

The methods ordinarily used to obtain the corrected temperature rise in a calorimeter reaction seem to have been in general: (1) to extend the final radiation curve back toward the axis of temperatures and take the temperature change as equivalent to the length of the ordinate through the initial temperature point; (2) to assume the curve obtained previous to the reaction as due to radiation alone, and then by Newton's Law of Cooling to compute the radiation correction.[1]

The latter procedure would hold rigorously, provided the change in heat capacity of the calorimeter due to the introduction of the substance and the heat introduced by the stirrer were allowed for. The error due to the lag of the Beckmann[2] thermometer must remain and affect the determination, because adequate correction for it appears impossible. W. P. White[3] has discussed with considerable completeness the effect of the various temperature lags which occur in a calorimetric measurement and concludes that the thermometric lag may be entirely neglected. This would be especially true in the comparison method here adopted.

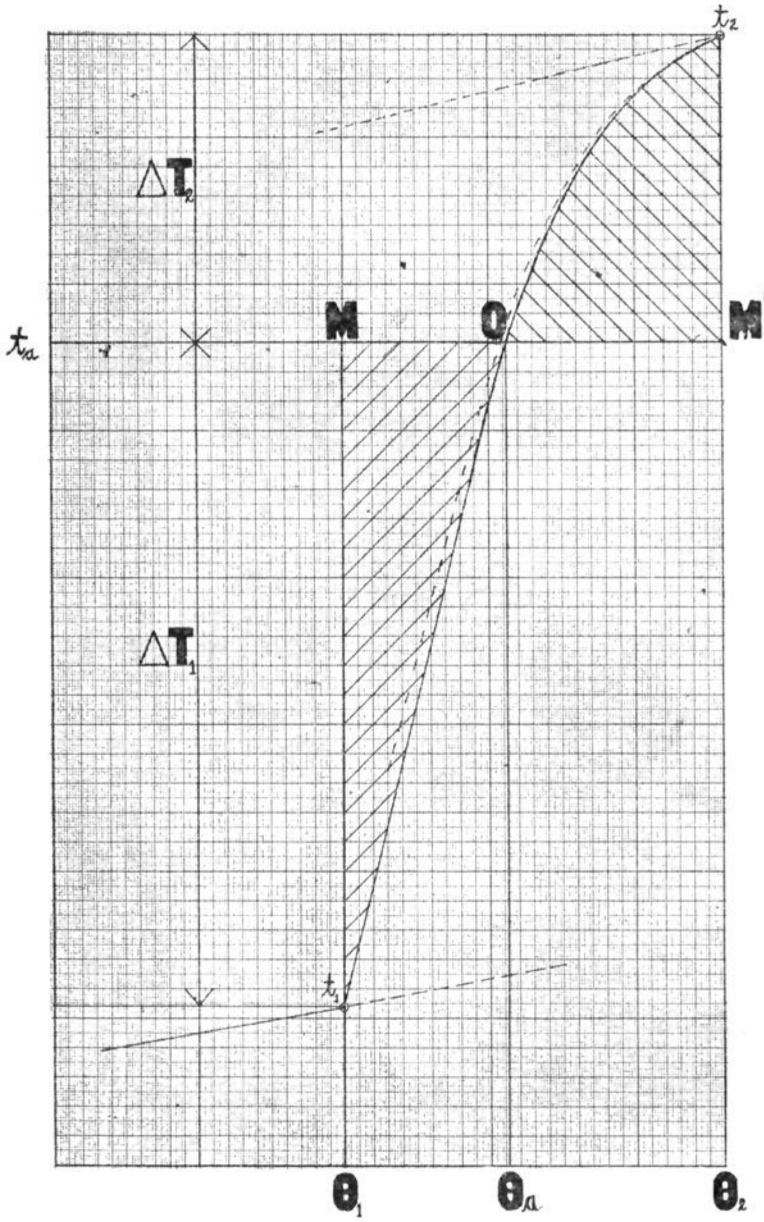

Fig. 2.

The following analysis of the typical calorimeter curves obtained gives the method of obtaining the temperature change in the calorimeter due to the introduction of the substance alone or corrected for temperature changes, due to radiation and stirring.

In considering a calorimeter curve, such as is shown in Fig. 2, the temperature rise will be taken in two parts:

(1) That obtained in passing from t_1 to O.

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[1] Ostwald Luther, "Physiko Chemische Messungen," p. 307.

[2] R. D. Harper, Bur. Standards, *Bull.* **8,** 683 (1912).

[3] W. P. White, *Phys. Rev.*, **31,** 562 (1910).

(2) That obtained in passing from O to t_2, where the point O is the intersection of the surroundings temperature t_a with the reaction curve $t_1\ t_2$.

If we consider the full line to be the observed temperatures plotted against time, it is evident that owing to the lag of the thermometer the true temperature at any instant is above that registered by the thermometer, and the true curve would follow the course shown in the dotted line. The lag of the thermometer as already stated may be probably assumed to be proportional to the difference in temperature of the calorimeter and the mean temperature of the thermometer, but it will be assumed in what follows that the observed curve is the true one.

Consideration of the conditions attending a measurement show that the observed temperature rise ($\Delta T_2 + \Delta T_1$) is due to the following additions of energy[1] to the calorimeter where the meaning of ΔT_1 and ΔT_2 is made clear from Fig. 2.

(1) Introduction of heat due to introduction of substance.

(2) Introduction of heat due to stirring.

(3) Introduction of heat due to radiation.

(4) Introduction of heat due to conduction.

(5) Introduction of heat due to convection currents between the cover and the surface of the water in the calorimeter. (3) and (4) follow the same general law and can be treated together, being referred to simply as the "radiation effect." The effect of (5) in this case was probably so small as to have no appreciable effect on the final result and will therefore be neglected.

The curve $t_1\ t_2$ is the resultant of the three curves: of stirring, radiation and heat, due to the bomb being introduced into the calorimeter. The equation for ΔT_1 may be written as

$$\Delta T_1 = \Delta T_1' + s_1 + r_1, \tag{1}$$

where $\Delta T_1'$ is the temperature change due to the substance and its container s_1 the temperature rise due to stirring, and r_1 the "radiation effect" in terms of temperature.

In general it is desired to know the temperature change $\Delta T_1'$, which from (1) is

$$\Delta T_1' = \Delta T_1 - s_1 - r_1. \tag{2}$$

Let t_s be the temperature at any instant on the stirring curve. Then

$$H dt = P d\theta \tag{3}$$

where H = heat capacity of the entire system, θ the time, and P is the power input of the stirrer. For s_1 there results accordingly

$$s_1 = \int_{\theta_1}^{\theta_a} \frac{P}{H}\, d\theta = \frac{P}{H}\ (\theta_a - \theta_1). \tag{4}$$

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[1] The heat capacity of the calorimeter remains constant and therefore all heat quantities have been interpreted in terms of the temperature change they produce.

For t_r, or the temperature change due to radiation and conduction at any instant on the radiation curve, Newton's Law of Cooling gives

$$\frac{dt_{r_1}}{d\theta} = \mathrm{K}(t_a - t) = \mathrm{K}\,(t_a - f(\theta)), \tag{5}$$

where $t = f\ (\theta)$ and t_a is the temperature of the surroundings. There is obtained by integrating (5), the equation for r_1

$$r_1 = \mathrm{K}\int_{\theta_1}^{\theta_a} [t_a - f(\theta)]\, d\theta = \mathrm{K}t_a\,(\theta_a - \theta_1) - \mathrm{K}\int_{\theta_1}^{\theta_a} f(\theta)d\theta, \tag{6}$$

substituting Equations 6 and 4 in 1 gives

$$\Delta\mathrm{T}_1' = \Delta\mathrm{T}_1 - \frac{\mathrm{P}}{\mathrm{H}}\,(\theta_a - \theta_1) - k\,[t_a\,(\theta_a - \theta_1) - \int_{\theta_1}^{\theta_a} f(\theta)d\theta]. \tag{7}$$

For the second part of the curve, similarly

$$\Delta\mathrm{T}_2' = \Delta\mathrm{T}_2 - \frac{\mathrm{P}}{\mathrm{H}}\,(\theta_2 - \theta_a) - k\,[t_a(\theta_2 - \theta_a) - \int_{\theta_a}^{\theta_2} f(\theta)d\theta]. \tag{8}$$

Combining (7) and (8) we have

$$\Delta\mathrm{T}_1' + \Delta\mathrm{T}_2' = \Delta\mathrm{T}_1 + \Delta\mathrm{T}_2 - \frac{\mathrm{P}}{\mathrm{H}}\,(\theta_2 - \theta_1) - k\,(t_1\mathrm{MO} - \mathrm{O}t_2\mathrm{M}').$$

The terms $\Delta\mathrm{T}_1$ and $\Delta\mathrm{T}_2$ are taken directly from the plot. The terms $\mathrm{K}(t_1\mathrm{MO})$ and $\mathrm{K}(\mathrm{O}t_2\mathrm{M}')$ are seen to be the shaded areas in the figure.

In order to determine P experimentally, we have by Equation 3

$$\mathrm{P} = \mathrm{H}\,\frac{dt_s}{d\theta},$$

and knowing H, the heat capacity of the system, it is only necessary to note that rate of temperature change when the calorimeter is at the same temperature as the surroundings.

K by Equation 5 is $\frac{dt_r}{d\theta}\,\frac{1}{t_a - t}$ and by combining any curve where the observed slope is $dt/d\theta$ with the slope $\frac{dt_s}{d\theta}$ (obtained above) it is possible to obtain $\frac{dt_r}{d\theta}$ and hence K.

4. The Experimental Data.

In computing the mean specific heat capacity of liquid ammonia from the data tabulated in Tables I and II the equation for the specific heat of water as given by Bousfield and Bousfield[1] was employed. It is very desirable to obtain the specific heat capacity of liquid ammonia at higher temperatures, but as already stated the method is badly suited to the case where the specific heat changes rapidly with the temperature. Continuous flow calorimeters are undoubtedly the best adapted for liquids

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[1] *Phil. Trans.*, 211, 199 (1911). $\mathrm{C} = 1/4.17911\ (4.2085 - 0.003022t + 7.833 \times 10^{-5}\,t^2 - 4.9 \times 10^{-7}\,t^3)$.

TABLE I.

0° to 20° Measurements.

Water Bomb Volume = 52.15 cc.

	Wt. steel bomb.	Wt. water in bomb.	Corrected temp. change.	Temp. of equilib.
	70.507	33.52	...	...
1	....	...	1.462	19.34
2	....	...	1.462	19.32
3	....	...	1.460	19.35
		Mean,	1.4613	19.34

Ammonia Bomb Volume = 52.65 cc.

	Wt. steel bomb.	Wt. NH_3 in bomb.	Corrected temp. change.	Temp. of equilib.
	70.507	29.26	...	...
1	....	...	1.457	19.35
2	....	...	1.464	19.32
3	....	...	1.454	19.34
4	....	...	1.466	19.31
5	....	...	1.461	19.32
		Mean,	1.4604	19.32

Ammonia Vaporization Correction Per g. 0.0042.

$$\bar{C}_{0-19.32} = 1.152$$

TABLE II.

20–50° Measurements.

Water Bomb.

	Wt. steel bomb.	Wt. water in bomb.	Corrected temp. change.	Temp. of equilib.
	70.507	34.30	...	...
1	....	...	2.305	20.74
2	....	...	2.307	20.84
3	....	...	2.303	20.83
		Mean,	2.3050[1]	20.80

Ammonia Bomb.

	Wt. steel bomb.	Wt. NH_3 in bomb.	Corrected temp. change.	Temp. of equilib.
	70.507	29.24	...	...
1	..	...	2.301	20.82
2	..	...	2.302	20.81
3	..	...	2.298	20.84
		Mean,	2.3003	20.82

Ammonia Vaporization Correction Per g. 0.00521.

$$\bar{C}_{s\;50-20.8} = 1.172$$

$$C_{s\;\text{true}} = 1.144 + 0.0008t$$

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[1] Instead of making a further adjustment of the weight of water, interpolation of the several weights of water used was made, giving a correction of 0.16 g. of water which must be subtracted from the weight given in the table.

or gases, however, such calorimeters have not been developed for use at the higher saturation pressures. A flow calorimeter for studying liquid specific heats at higher saturation pressures has been under consideration for some time. A very valuable increase of the relation between the liquid state and the gaseous state will no doubt result from a study of reliable saturation specific heats over a long temperature range, which, when combined with suitable compressibility data, can be computed over to constant volume by means of the equation $C_v = C_s - T\left(\frac{\partial p}{\partial T}\right)_v \frac{dv}{dT}$ where C_s denotes the specific heat at saturation and C_v the specific heat at constant volume. In the case of ether, for example, the specific heat at constant volume is nearly the same numerical magnitude in both liquid and gaseous phase at zero. Water on the other hand has approximately twice the value at zero compared to the gaseous phase. Ammonia at zero is similar in this respect to water, for in the latter case the ratio of the liquid constant volume specific heat to the gaseous is almost exactly two.

Table III has been drawn up to exhibit the relation of the earlier values of other investigators to the values of the specific heat capacity calculated by the linear equation $C_s = 1.144 + 8.0 \times 10^{-4}t$. The linear equation is not strictly reliable because the specific heat capacity along the saturation line augments with increased rapidity as the critical point is approached. One of the later papers, however, will give a method of approximating calculating the true values of the heat capacity from compressibility data along the gas and liquid phase saturation line when a few liquid heat capacities are known as well as any constant pressure heat capacity curve of the gas phase.[1]

TABLE III.

		S. H. capacity linear equation, K. & B.	T.
Drewes	0.876	1.144	0
Drewes	1.140	1.152	10
Elleau and Ennis	1.02	1.152	10
Drewes	1.19	1.160	20
Ludeking & Starr	0.886	1.166	28
Drewes	1.218	1.168	30
Drewes	1.231	1.178	40
von Strombeck	1.229	1.180	45
Drewes	1.239	1.184	50
Drewes	1.240	1.192	60

5. Summary.

In this article a new modification of the calorimetric method of mixtures has been described, which eliminates many of the conditions which

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[1] Equation 42, p. 31 of the Keyes and Brownlee's "Thermodynamic Properties of Ammonia" resulted from the two heat capacity measurements contained in the present paper together with an estimated heat capacity value for 100°.

have hitherto limited the precision of measurements by the mixtures method. The method consists in making strictly comparable measurements with a substance of known heat capacity. The containers for the two substances are made identical, and the quantity of the reference substance used is so adjusted that the same temperature change is obtained in the calorimeter as with the substance under examination. Water has been used as the reference substance in this investigation, and the values of its heat capacity as determined by Bousfield have been employed in the calculations.

An automatic device has been described, whereby the substance whose heat capacity is to be determined may be lowered rapidly from the thermostat into the calorimeter under strictly reproducible conditions.

The mean specific heat capacity of liquid ammonia has been measured for the temperature intervals 0°–20°, and 20°–50°. Its value expressed in 15° calories is 1.152 between 0°–20° and 1.172 between 20°–50°. The equation for the true specific heat capacity obtained from these data (assuming it to be linear function of the temperature) is

$$C_s = 1.144 + 0.0008t.$$

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THE RELATIVE ELECTRODE POTENTIALS OF TIN AND LEAD DETERMINED BY EQUILIBRIUM MEASUREMENTS WITH THEIR PERCHLORATES.

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1. Purpose of the Investigation.

The specific electrode potential of tin is shown by previous determinations to be not far different from that of lead, but its value is not accurately established. A satisfactory method of determining the difference between this electrode potential and that of lead would seem to be to allow one of these metals to come to equilibrium with an aqueous solution of some salt of the other metal. As the electrode potentials are nearly equal, both metallic elements would be found in solution at the end in amounts large enough to determine by chemical methods. The study of this