Discussion

The activity coefficient data in dilute solutions are certainly compatible with the ion-pairing and dimerization equilibria. The close agreement of the constants with those obtained from λ_+ data lends added support to the assumption that these two equilibria are involved. As with the conductance data the results reported here cannot distinguish between an ion-pair and a monomer unit.

Figure 3 shows that the mean molar activity coefficient is nearly constant over a very large concentration region. The extremes are only 25% apart, from 0.64 to 3.76 molar. Over this range, the mean ionic activity is nearly proportional to the total concentration, and the solution behaves as a nearly "ideal" binary electrolyte.

Figure 4 shows the variation of total activity (on a semi-log scale) with concentration. The inflection in the curve reflects the fact that in this concentration range at a temperature only 8.5 degrees below this, the system separates into two phases.

These results permit calculation of the standard free energy change for the solution process. For the process, $Na_{(s)} \rightarrow Na^+_{(am)} + e^-_{(am)}$, the values are:

(1) To form the hypothetical ideal solution, $C = 1$; $\Delta F_1{}^0 = +0.3$ kcal. mole^{-1}. (2) To form the hypothetical ideal solution, $m = 1$; $\Delta F_2{}^0 = -0.1$ kcal. mole^{-1}. (3) To form the hypothetical ideal solution, $X_{Na} = 1$; $\Delta F_3{}^0 = +3.8$ kcal. mole^{-1}.

These data can be combined with heat of solution data,[2b] which give $\Delta H^0 = +4.4$ kcal. mole^{-1}, to yield $\Delta S_1{}^0 = 17.1$ cal. deg.$^{-1}$ mole^{-1}; $\Delta S_2{}^0 = 18.7$ cal. deg.$^{-1}$ mole^{-1}; $\Delta S_3{}^0 = 2.5$ cal. deg.$^{-1}$ mole^{-1}. Using the value of 12.6 cal. deg.$^{-1}$ mole^{-1} for the partial molal entropy of sodium ion[2] and 10.8 cal. deg.$^{-1}$ mole^{-1} for the entropy of sodium at $-33.5°$ [17] gives $\bar{S}^0 = 16.9$ cal. deg.$^{-1}$ mole^{-1} (hypothetical ideal, $m = 1$) for the solvated electron.

Since extrapolation and interpolation were used extensively and also because smoothed curves were used for ϵ and T_+, we attempted to estimate the error in the final result. The estimate of the probable error in the smooth T_- curve is $\pm 0.6\%$.[10] Since T_- varies from 0.86 to 0.94 over the range studied, the probable error in T_+ is about $\pm 7\%$. The error in ϵ is not easy to estimate, but it is certainly less than the error in T_+ at high concentrations. The root mean square deviation of $\frac{\Delta\epsilon}{\Delta \log C}$ from a smooth curve is $\pm 4.6\%$ (probable error $= \pm 3\%$). Combination of all effects leads to an estimated probable error in $y_\pm/y_{\pm\,ref}$ ranging from 0.8% at 0.01 molar to 9.6% for a 0.63 molar solution. Because of extrapolation errors, this increases to about 16% at the point of tie-in with the vapor pressure data. Another uncertainty is introduced by choosing α_{ref} from conductance data, with the magnitude of this error unknown because of the dependence upon the conductance function chosen to represent the behavior of the ions. However, a rough estimate may be made based upon the experimental error. The estimated probable error in α_{ref} (6%) leads to an error of 4.2% in $y_{\pm ref}$. The combined effects give a probable error in $y_\pm$ varying from 4.3% at 0.01 molar to 10.5% at 0.63 molar. Consideration of all of these effects leads to an estimate of the probable error of ΔF^0 of ± 0.36 kcal. mole^{-1} which gives an uncertainty of ± 1.8 cal. deg.$^{-1}$ mole^{-1} for ΔS^0 assuming ΔH^0 to be accurate to ± 0.1 kcal mole^{-1}.

Acknowledgment.—The authors express appreciation to the U. S. Atomic Energy Commission for financial support of this research.

[17] F. Simon and W. Zeidler, *Z. physik. Chem.* (*Liepzig*), **123**, 383 (1926); National Bureau of Standards, *Circular 500*, "Selected Values of Chemical Thermodynamic Properties," 1952, p. 447.

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Apparatus and Methods for Low Temperature Heat Capacity Measurements. The Heat Capacity of Standard Benzoic Acid

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RECEIVED OCTOBER 15, 1959

An apparatus and methods for the measurement of low temperature heat capacities of solids are described. The methods of correcting the data for heat interchange and for thermal gradients within the calorimetric system, as well as other necessary corrections, are discussed. The heat capacity of a Calorimetry Conference standard sample of benzoic acid has been measured in the temperature range between 10 and 300°K. and the results are compared with data from the National Bureau of Standards and from other laboratories.

For some ten years there has been in use in this Laboratory apparatus for measuring the heat capacity of solids in the temperature range between 10 and 320°K. Since the apparatus and particularly the method used for calculating the corrected heat capacities from the experimentally measured quantities differ in some respects from those described in the literature, they will be briefly described in the present paper. In order to check on the accuracy of our heat capacity measurements, we have measured the heat capacity of a standard sample of benzoic acid, and the results are presented in this paper.

Apparatus

Cryostat and Calorimeter.—The heat capacity apparatus is of the "isothermal" type consisting of a vacuum insulated calorimeter surrounded by a massive shield (called the "block") whose temperature remains nearly constant during a heat capacity measurement. The construction of this block and of the outer parts of the cryostat is similar to that described by Giauque and Egan[1] and by Johnston and Kerr.[2] The details of the construction of the cryostat, calorimeter and resistance-thermometer are available elsewhere.[3] The calorimeter is a copper cylinder, of 0.025 cm. wall thickness and having an axially located well into which the thermometer-heater is inserted. In the calorimeter used for heat capacity measurements of benzoic acid, amino acids and proteins, six radial fins, 0.040 cm. thick, are attached with 50-50 PbSn solder to the outside of the thermometer-heater well. The empty weight of this calorimeter, including the thermometer-heater, is 124.4 g. The sample volume is 145 cm.[3] In other calorimeters,[4] used with materials of greater thermal conductivity, the fins have been omitted without seriously lengthening the thermal relaxation time within the calorimeter. The outside of all calorimeters was covered with 0.0005 cm. thick dull gold plate.

The Thermometer-Heater.—The resistance thermometer-heater was made of pure platinum wire, 0.07 mm. diameter. It is of strain free construction, similar to that described by Meyers[5] and Catalano and Stout.[4] The details of the construction are given elsewhere.[3] The thermometer, wound on a mica cross, was sealed inside a case containing helium gas at one atmosphere pressure. The thermometer case was soldered into the well of the calorimeter with indium solder.[4] The weight of the thermometer and case was 11.39 g.

The resistance of the thermometer was measured at the triple point[6] of water and it was then calibrated over the range 10 to 300°K. against a laboratory standard Leeds and Northrup 25 ohm platinum resistance thermometer which had been calibrated by the National Bureau of Standards. This calibration is based on the International Temperature Scale of 1948 between the boiling points of sulfur and of oxygen and on the NBS scale of Hoge and Brickwedde[7] below the oxygen boiling point. There is a discontinuity in the derivative of resistance *versus* temperature at the junction of the International Temperature Scale and the scale of Hoge and Brickwedde and in constructing the table of resistance *versus* temperature for our thermometer this discontinuity was arbitrarily smoothed out. A correction was also made to put the scale on the basis of the ice-point temperature of 273.15°K. A typical resistance-thermometer heater had at the triple point of water a resistance of 127.734 ohms and $\mathrm{d}R/\mathrm{d}T = 0.5078$ ohm deg^{-1}. At 10°K. the resistance had dropped to 0.1122 ohms and $\mathrm{d}R/\mathrm{d}T$ was 0.0134 ohm $\mathrm{deg.}^{-1}$.

Electrical Measurements.—All measurements of the resistance of the thermometer and of electrical energy introduced into the calorimeter were made with a calibrated 100,000 microvolt White Double Potentiometer in conjunction with a Leeds and Northrup HS galvanometer. The illuminated galvanometer scale was at a distance of 9 meters and was read through a telescope directed at the mirror of the galvanometer. At all except the lowest temperatures the resistance of the thermometer could be read to a precision of a few parts per million. A calibrated unsaturated Weston standard cell was used as the standard of electromotive force and the heating current was calculated from the potential drop across a calibrated standard resistance. The energy input was automatically started and stopped by a timer driven by a pendulum clock. The timer was checked by comparison with a 1000 cycle standard frequency and found to have errors of less than 0.01%.

Redetermination of the triple-point resistance of two thermometers after use for periods of up to 30 months showed changes of less than 0.02°. The resistance of the thermometer at the boiling point of hydrogen was routinely measured during each cooling to hydrogen temperatures. Within the experimental uncertainty of about 0.03 degrees the resistance observed agreed with that obtained from the original calibration.

Experimental Procedure

The calorimeter is filled with sample and with He gas at one atmosphere and then sealed off. Careful account is kept of the weights during the filling of the calorimeter in order to obtain an accurate weight of the sample and to know the amounts of solder and helium in the filled calorimeter compared to the empty calorimeter whose heat capacity is determined in a separate series of experiments. The calorimeter is hung from the top of the block and electrical connections between the two 0.66 mm. diameter Pt leads of the thermometer-heater and the No. 16 copper wires imbedded in the top of the block which are used for current and potential leads are made with four Pt leads about 2.6 cm. long. The two current leads are 0.10 mm. diameter and the two potential leads are 0.07 mm. diameter. The length of these leads is measured in order to permit correction for the energy developed in them during the heating periods. The cryostat is then assembled and the insulating vacuum space pumped for several days at room temperature. The pressure read on an ionization gauge with a liquid N_2 trap is less than 10^{-6} mm.

In order to cool the calorimeter, liquid N_2 is added to the dewar and a pressure of about 1 mm. of He gas admitted to the insulating vacuum space. By pumping on the N_2 in the dewar the temperature of the calorimeter can be lowered to about 50°K. The inner can is then evacuated and a series of heat capacity measurements may be started. If measurements are to be made at liquid hydrogen temperatures, the calorimeter is cooled as above to 50°K. and the insulating vacuum pumped. The bath pressure is then raised to one atmosphere N_2 and after standing overnight the solid N_2 in the dewar will have melted and the liquid N_2 may be removed through the blowout tube. The calorimeter and block, protected by the insulating vacuum, will not rise in temperature by more than a degree in this period. After removing liquid nitrogen from the dewar and flushing the dewar space with hydrogen gas, liquid hydrogen is added to the dewar. A small pressure of He gas is again put in the insulating vacuum space and by pumping on the hydrogen bath the temperature of the calorimeter can be lowered to between 10 and 11°K. The insulating vacuum space is then pumped out and a series of measurements begun.

In an individual measurement the temperature of the block is approximately adjusted a little above the midpoint between the expected initial and final temperatures of the calorimeter. A series of measurements of the resistance of the thermometer is made in the fore rating period, the electrical energy introduced during a heating period, and the resistance again measured in an after rating period. The times used for the heating periods vary from five to fifteen minutes (generally 7-10 minutes). The total time for an individual measurement varies from 30 minutes to an hour. In addition to measurements of the electrical resistance in the rating periods and the current and potential during the heating period, thermocouple readings to determine the temperatures of the top and bottom of the block and top and bottom of the vacuum can are taken. During a series of measurements the temperature of the can is adjusted so as to minimize the temperature drift of the block.

Treatment of Experimental Data

Correction for Heat Interchange.—In a measurement of heat capacity, electrical energy, measured to an accuracy of a few hundredths of 1%, is introduced by means of the thermometer-heater. The thermal leakage between the calorimeter and the surrounding isothermal shield during the heating period is estimated from the variation with time of the thermometer readings in the fore and after rating periods. In Fig. 1 is shown the temperature-time curve for a measurement on an

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(1) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(2) H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

(3) Material supplementary to this article giving the details of construction of the cryostat, calorimeter and thermometer-heater has been deposited as Document number 6248 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints or $1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress. A more detailed form of this paper may also be obtained by writing to the authors.

(4) E. Catalano and J. W. Stout, *J. Chem. Phys.*, **23**, 1284 (1955).

(5) C. H. Meyers, *J. Research Natl. Bur. Standards*, **9**, 807 (1932).

(6) H. F. Stimson, *ibid.*, **24**, 209 (1949).

(7) H. G. Hoge and F. J. Brickwedde, *ibid.*, **22**, 351 (1939).

empty calorimeter (Laboratory designation III) near 12.5°K. This example is chosen to illustrate the non-linear temperature–time curves that may be found for a calorimeter of low heat capacity at low temperatures and therefore represents the most difficult conditions encountered. The correction for heat interchange is given by the following analysis. Let T indicate the temperature of the calorimeter and T^{B} that of the isothermal shield (block). Then the change of temperature with time is given by

$$\mathrm{d}T/\mathrm{d}t = \beta + \alpha(T^{\mathrm{B}} - T) \qquad (1)$$

where β is the ratio of the electrical power introduced to the heat capacity of the calorimeter and α is the ratio of the Newton's law coefficient of heat-interchange between calorimeter and block (called B_{N}) to the heat capacity of the calorimeter. α^{-1} is the thermal relaxation time between the calorimeter and the block. The times of the beginning and end of the heating period are designated as $t = -\tau$ and $t = \tau$ respectively so $t = 0$ corresponds to the midpoint of the heating period. The drift in temperature of the block is found from observations of the block thermocouple which suffice to determine the temperature drift even though the absolute temperature of the block is not known to high precision. To sufficient accuracy the temperature of the block may be represented by a linear function of time.

$$T^{\mathrm{B}} = T_0^{\mathrm{B}} + kt \qquad (2)$$

Let T' represent the calorimeter temperature in the fore rating period (including the extrapolation of this temperature to the midpoint of the heating period), T'' the temperature in the after rating period and T the actual temperature of the calorimeter during the heating period. During the rating periods $\beta = 0$. (In our calorimeters the heating by the thermometer current was ordinarily negligible. At the lowest temperatures a thermometer current of 2.5 ma., compared to the usual current of 0.9 ma or less, was sometimes used to increase the sensitivity. In such a case a separate correction, amounting at the most to 0.1%, is made to take account of the fact that the thermometer current is not passing through the thermometer-heater during the heating period. The fractional correction to the heat capacity is one minus the square of the ratio of the thermometer current to the heating current.) The solution of eq. 1 is then

$$T' = T'_0 + kt + (1/\alpha)[(\mathrm{d}T'/\mathrm{d}t)_0 - k](1 - e^{-\alpha t}) \qquad (3)$$

and a similar expression with T'' substituted for T'. The value of α used is an average over the temperature rise of the heating period and is given by the expression, following from eq. 1

$$\alpha = [(\mathrm{d}T'/\mathrm{d}t)_1 - (\mathrm{d}T''/\mathrm{d}t)_2]/[T_2'' - T_1' - k(t_2 - t_1)] \qquad (4)$$

where t_1 is a time in the fore period near the beginning of the energy input and t_2 a time in the after period soon after the end of the energy input. The constants T_0', T_0'', $(\mathrm{d}T'/\mathrm{d}t)_0$ and $(\mathrm{d}T''/\mathrm{d}t)_0$ in eq. 3, chosen for convenience at the midpoint of the energy input, are evaluated from the observed temperatures in the fore and after rating periods. These four constants also must be consistent with the value of α since, by putting $t_1 = t_2 = 0$ in eq. 4, α is determined by them. If β is taken as constant, the solution of eq. 1 during the heating period is

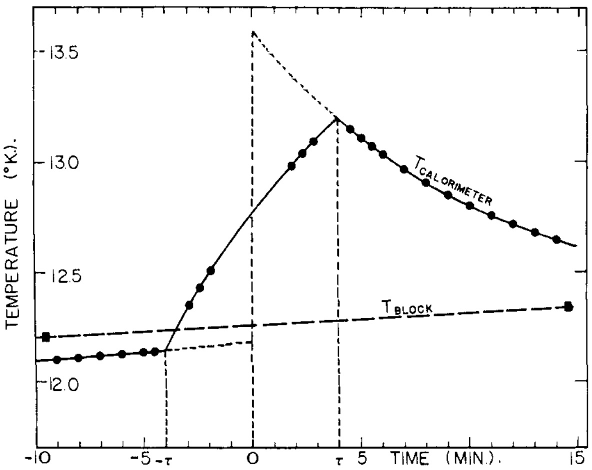

Fig. 1.—Temperature–time curve for a heat capacity measurement of the empty calorimeter.

$$T = T_0^{\mathrm{B}} + (1/\alpha)(\beta - k) + kt + Ke^{-\alpha t} \qquad (5)$$

β and the constant of integration, K are determined by the requirements that at $t = -\tau$, $T' = T$ and at $t = \tau$, $T'' = T$. (6)

The total energy added to the calorimeter between $t = -\tau$ and $t = \tau$ is

$$E + \int_{-\tau}^{\tau} B_{\mathrm{N}}(T^{\mathrm{B}} - T)\,\mathrm{d}t = E + \alpha(\Delta H/\Delta T)\int_{-\tau}^{\tau}(T^{\mathrm{B}} - T)\,\mathrm{d}t \qquad (7)$$

Here E is the electrical energy and B, is experimentally found to be sufficiently constant to be taken outside the integral sign. It is convenient to calculate the energy needed to heat the calorimeter instantaneously from T_0' to T_0''. This is

$$E + \alpha(\Delta H/\Delta T)\int_{-\tau}^{0}(T' - T)\mathrm{d}t + \int_{0}^{\tau}(T'' - T)\mathrm{d}t] \qquad (8)$$

The integrals may be evaluated by combining eq. 1, 3, 5 and 6. This gives

$$\alpha[\int_{-\tau}^{0}(T' - T)\,\mathrm{d}t + \int_{0}^{\tau}(T'' - T)\,\mathrm{d}t] = (T_0'' - T_0')(1 - (\alpha\tau/\sinh\alpha\tau)] \qquad (9)$$

and by substitution in eq. 8 one obtains the expression for the mean heat capacity

$$\frac{\Delta H}{\Delta T} = \frac{E}{T_0'' - T_0'}\,\frac{\sinh\alpha\tau}{\alpha\tau} \qquad (10)$$

The approximation $(\sinh\alpha\tau)/\alpha\tau = 1 + (\alpha\tau)^2/6$ is valid to 0.01% for $\alpha\tau < 1/3$ and may be used for all except the lowest temperature measurements.

Above a temperature of from 15 to 20°K., depending on the heat capacity of the calorimeter, the extrapolation of the rating period drifts may be made by taking the temperature to vary quadratically with time and from 30 to 200°K. a linear extrapolation is adequate. However, at the lowest temperatures and with a low heat capacity (*e.g.* with an empty calorimeter) serious errors may be introduced by approximating eq. 3 by a quadratic expression. Usually the resistance R of the thermometer may be substituted for T in the equations above, but below about 25°K. the non-linearity of the R–T curve makes it desirable to convert the resistance to temperature before making the extrapolation to the midpoint. In order to minimize uncertainties in the extrapolation to $t = 0$, it is desirable to minimize the heating time. In measurements below 20°K. we ordinarily use a six minute heating time. Typical values of α for an empty calorimeter (in min.$^{-1}$) are in °K.: 0.11 at 12°, 0.022 at 20°, 0.0043 at 30°, 0.0006 at 100°, 0.0029 at 200° and 0.013 at 300°. The values of α for a filled calorimeter are smaller by factors ranging from 2 to 6 depending on the sample and temperature.

In the above derivation it was assumed that α and β are constant over the heating period. Because of the variation of heat capacity and thermal conductance with temperature, they will vary somewhat. A correction, described below, is made for the variation of β. The maximum variation in α is at the lowest temperatures and at 10–15° K. amounts to about 10% per degree K. More elaborate calculations taking into account the variation in α show that even at the lowest temperatures the error in using the mean α given by eq. 4 is small compared to other experimental errors. It should be realized, however, that the extrapolation to the midpoint of the heating period using this mean α is only a mathematical device for evaluating the heat exchange of the real calorimeter during the heating period and that the temperature to which the heat capacity should be assigned is $^1/_2(T_{-\tau} + T_{\tau})$ rather than the average of the fore and after period temperatures extrapolated to $t = 0$.

Wire Corrections.—During the heating period energy is developed in the two platinum wires, 0.01 cm. in diameter and about 2.5 cm. long, through which the heating current is led from the block to the calorimeter. This energy is not included in the measured electrical energy since the two potential leads are attached directly to the heavy leads of the thermometer–heater. Half of this energy goes into the calorimeter and half to the shield. The heat capacities must be multiplied by a correction factor $1 + r/R$ where r is the resistance of *one* platinum wire lead and R is the resistance of the thermometer–heater. Since the wires are of the same material as the thermometer–heater, the correction is independent of temperature. It amounts to 0.2 to 0.3% for our thermometers.

Non-constant Heating Correction.—In deriving eq. 10 β was assumed constant. Actually the heating rate will vary because of variations in the resistance of the thermometer–heater and of the heat capacity of the calorimeter. A correction to the heat interchange during energy input must therefore be made. In measurements below about 100° K. the heating current is kept nearly constant with a large series resistance and the electrical power into the heater increases as its resistance rises. The heat capacities must be multiplied by a factor

$$1 + (^1/_6)\alpha\tau\Delta T\ [\mathrm{d}\ \ln R/\mathrm{d}T - \mathrm{d}\ \ln\,(\Delta H/\Delta T)/\mathrm{d}T] \quad (11)$$

where ΔT is the temperature rise in a measurement. This correction reaches a maximum value of about 0.3% between 10 and 15°K. and is down to 0.02% at 30°K. and above. Above about 100°K. the heater voltage is kept constant during energy input and the sign of d ln $R/\mathrm{d}T$ in (11) must be changed. The correction in this range never exceeds 0.02%.

Transient Heating Correction.—During energy input the heater wire is hotter than the calorimeter. In extreme cases this temperature difference may amount to as much as 15°K. After an initial brief period following the beginning of energy input this temperature difference remains approximately constant. Then, in measurements where the heating current is kept approximately constant the current may be represented with sufficient accuracy by a linear, and the potential difference by a quadratic, function of time. In "constant voltage" measurements the potential difference is linear and the current quadratic in time. Advantage is taken of these facts in scheduling the measurement of current and potential difference during energy input, the linear one being read at $t = 0$ and the quadratic one at $t = \pm\ \tau/\sqrt{3}$, two times so chosen that their average is equal to the mean value of a quadratic function. A correction to the energy is necessary to account for the rapid change in current or voltage in the transient period before the steady state has been reached. The transient change in current or voltage may be adequately represented by an exponential function with a characteristic time called t_{w}, the thermal relaxation time between the heater wire and the calorimeter. t_{w} is determined at a few temperatures in special experiments where the transient change of the current is read on an ammeter of short time constant. t_{w} is proportional to the product of the heat capacity of the heater wire plus some of the mica support and the thermal resistance (called A/E) between the heater wire and the calorimeter. This thermal resistance is calculated for every measurement as the ratio of the steady state temperature difference between the heater and calorimeter to the electrical power, $A/E = \delta R/P$. $\delta R = R_{\mathrm{w}} - R_{\mathrm{av}}$ where R_{w} is the resistance of the heater wire and R_{av} the resistance corresponding to the mean calorimeter temperature, both at the midpoint of the heating period. In addition to its use in the transient heating correction, A/E is very useful in detecting numerical errors in the calculation of the heating current or potential difference. The value of the effective heat capacity of wire plus mica is deduced, at a few temperatures, from the special experiments and a curve drawn, taking into account the shape of the heat capacity–temperature curves of these substances. To correct for the initial transient change in current, the heat capacities must be multiplied by

$$1 + (\delta R/R_{\mathrm{w}})(t_{\mathrm{w}}/2) \quad (12a)$$

for measurements at constant voltage and by

$$1 - (\delta R/R_{\mathrm{av}})\,(t_{\mathrm{w}}/2) \quad (12b)$$

for measurements at constant current. When the case enclosing the thermometer-heater is filled with pure helium, the maximum value of t_{w} observed is about 5 sec. and the correction does not exceed

0.1%. However if the helium in the case is contaminated with air, as once occurred,[4] t_w may increase by a factor of three or four with a corresponding increase in the correction.

Correction for Thermal Gradients within the Calorimeter.—In the derivation of eq. 10 it is assumed that thermal equilibrium between the resistance thermometer, the calorimeter shell and the sample is reached in a time which is short compared to the thermal relaxation time between calorimeter and shield so that it is justifiable to assume the temperature read by the thermometer is that of the entire calorimeter and contents. At the lowest temperatures the time for establishment of thermal equilibrium within the calorimetric system is very short and the first measurement of the resistance thermometer, taken one-half minute after the end of the energy input, represents an equilibrium temperature. At higher temperatures nonequilibrium thermometer drifts are normally observed for three to six minutes after the energy input. However, the time for establishment of steady state drifts may, with a sample of large heat capacity and not too good thermal conductivity, rise to about ten minutes at 150°K. and fifteen minutes near room temperature. Even after steady state drifts are established, the temperature read by the resistance thermometer will not be exactly equal to the mean temperature of the sample. In an empty calorimeter, for example, during the fore rating period, when the calorimeter is warming, the mean temperature of the calorimeter is higher than that of the thermometer, and in the after period, when the calorimeter is cooling, the temperature of the thermometer will be the higher. Consequently the true rise in temperature of the calorimeter corresponding to the electrical energy introduced is less than that deduced from the thermometer readings. In a filled calorimeter the temperature rise indicated by the thermometer readings may be either greater or less than that corresponding to complete thermal equilibrium in the calorimetric system depending on the heat capacities and thermal conductivities within the system. A further correction to the heat interchange between calorimeter and shield during the heating period is required since the temperature of the outside of the calorimeter which is exchanging heat with the shield is not identical with that corresponding to complete thermal equilibrium in the calorimetric system. The steady state temperature gradients within the calorimetric system and the correction to the heat interchange during energy input will both be proportional to the thermal conductance between calorimeter and shield (B_N). We may write the correction by which the heat capacity must be multiplied as

$$1 - 2\gamma B_N = 1 - 2\gamma\alpha(dH/dT) \qquad (13)$$

where γ is to be experimentally determined and the other symbols are defined above. $\gamma(dH/dT)$ has the dimensions of time and the correction may be thought of as involving the ratio of the thermal relaxation time within the calorimeter to that between the calorimeter and shield. Catalano and Stout[4] determined the value of γ by observing the effect of a change in shield temperature on the resistance of the thermometer and using a simple model for the thermal connections between different parts of the calorimetric system. An alternative method, which we now employ, is to measure the heat capacity at the same temperature with two different values of B_N and use these data to calculate γ. The two methods give concordant results. In practice some helium gas, sufficient to increase B_N by a factor of two or three, is admitted to the insulating vacuum space separating the calorimeter and shield and a series of measurements of heat capacity is made. The values of γ calculated are plotted against temperature and points read off the curve are used to correct the heat capacity measurements taken with a good vacuum. In essence the method consists of extrapolating the measured heat capacities to those that would be obtained if the thermal insulation between calorimeter and shield were perfect. With an empty calorimeter the γB_N correction amounts to about 1% at 300°K. and with a filled calorimeter the correction is considerably smaller, usually amounting to no more than 0.3%. The correction diminishes rapidly at lower temperatures since B_N varies approximately as T^3 and γ does not change rapidly with temperature. It is estimated that at 300°K. uncertainties in the γB_N correction can introduce a maximum uncertainty of 0.2% in the heat capacity data and this error drops rapidly at lower temperatures.

Corrections for Empty Calorimeter, Solder and Helium.—The heat capacity of the empty calorimeter is measured over the entire temperature range. To obtain the heat capacity of the sample the heat capacity of the filled calorimeter is corrected for that of the empty and for the changes in weights of solder and helium of the filled calorimeter compared to those of the empty. The heat capacities obtained are values of $\Delta H/\Delta T$ and must be corrected for curvature if the differential heat capacity, $C_p = dH/dT$, is desired. In most substances this correction is significant only at the lowest temperatures.

The Heat Capacity of Benzoic Acid.—The benzoic acid sample was a Calorimetry Conference Standard sample[8] obtained from the Thermochemistry Section of the National Bureau of Standards. The sample was transferred directly to the calorimeter from the bottle in which it was received, without further purification. The weight of the sample (*in vacuo*) was 100.99 g. (0.8270 mole). The fraction of the total heat capacity of the filled calorimeter contributed by the empty calorimeter was 0.10 at 11°K., 0.36 at 100°K. and 0.27 at 300°K. The experimental heat capacities, listed in Table I, are the ratios of the increase in enthalpy, ΔH to the rise in temperature, ΔT. In benzoic acid the correction for curvature, to change to the differential heat capacity, C_p, is for all points less than a change of one in the last place entered in the table and so the table entries are also, to well within the experimental error, values of C_p at the mean temperature T. The heat capacities are expressed in terms of the defined calorie

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[8] D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953).

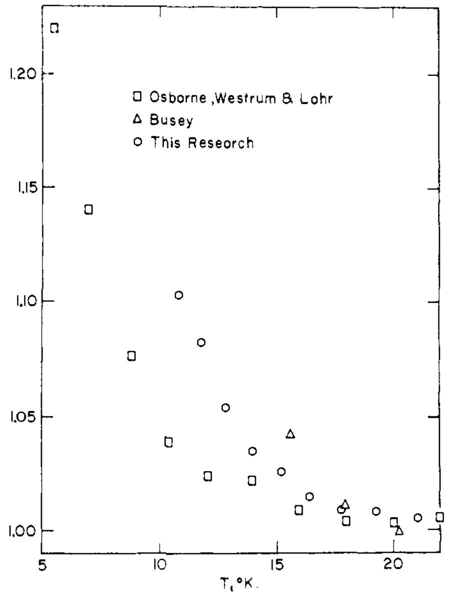

Fig. 2.—Ratio of heat capacity of benzoic acid measured by various observers to the table of Furukawa, McCoskey and King, *versus* temperature.

(4.1840 joules). The temperature rise in an individual measurement may be inferred from the spacing in temperature between successive measurements. In Table I the measurements are listed in chronological order. The last three points, marked with an asterisk, were made with helium gas in the vacuum space in order to determine the correction for thermal gradients within the calorimeter. These points are less accurate than the usual ones with a good vacuum and should be given no weight.

TABLE I

HEAT CAPACITY OF BENZOIC ACID

0°C. = 273.15°K. Molecular weight 122.12

T, °K.	$\Delta H/\Delta T$, cal. deg.$^{-1}$ mole^{-1}	Dev. from NBS table, %	T, °K.	$\Delta H/\Delta T$, cal. deg.$^{-1}$ mole^{-1}	Dev. from NBS table, %
300.65	35.50	0.39	234.53	28.15	− .01
			240.44	28.74	− .05
53.88	10.074	.15	245.82	29.35	− .03
58.63	10.773	.01	251.63	29.93	− .17
63.86	11.492	.09	257.49	30.63	.04
69.10	12.131	− .10	262.26	31.12	− .04
74.09	12.688	− .04	268.00	31.78	.06
78.42	13.179	.05	273.87	32.46	.15
83.34	13.721	.04	279.82	33.12	.16
88.49	14.248	.11	285.88	33.75	.06
93.75	14.734	.13	291.94	34.34	− .16
99.09	15.202	.02	297.20	35.00	.05
104.47	15.683	.00	303.28	35.65	− .02
109.83	16.174	.07			
114.97	16.631	− .01	10.78	0.630	10
120.08	17.081	− .10	11.76	0.792	8.2
125.23	17.535	− .14	12.80	0.977	5.4
130.34	18.005	− .08	13.95	1.208	3.5
133.18	18.266	− .08	15.14	1.469	2.6
138.62	18.762	− .08	16.39	1.750	1.5
143.99	19.231	− .18	17.78	2.080	0.9
149.21	19.705	− .19	19.28	2.462	0.8
154.42	20.20	− .09	21.00	2.900	.5
160.02	20.69	− .25	22.91	3.404	.2
165.62	21.26	− .02	25.07	3.982	.3
171.27	21.79	−0.06	27.62	4.649	.4
176.86	22.31	− .09	30.35	5.348	.37
182.55	22.86	− .07	33.30	6.074	.16
188.32	23.43	− .06	36.71	6.873	.12
194.18	23.99	− .08	40.39	7.650	− .01
200.07	24.57	− .11	44.32	8.424	.04
205.99	25.17	− .09	48.65	9.219	.09
211.94	25.78	− .09			
217.57	26.36	− .07	259.38	30.94*	.38
223.20	26.93	− .11	264.35	31.37*	.03
228.76	27.51	− .13	269.94	31.98*	.03

Also listed in Table I are the deviations, in per cent, of each of our experimental points from the table of Furukawa, McCoskey and King.[9] This table is not smooth to the number of figures given in it, and we have interpolated in it as it is printed rather than changing it to a smooth table. The error in our heat capacity measurements is estimated as not exceeding 5% at 10°K., 2% at 15°K., 1% at 20°K. and 0.2% between 40 and 250°K. Above 250°K. the error increases, reaching about 0.4% at 300°K. The observed scatter in heat capacity data is less than the above errors by a factor of two or more and the estimated error includes an allowance for possible uncertainties in the NBS temperature scale relative to the thermodynamic scale. The agreement of our data with the table of Furukawa, McKoskey and King[9] is well within the estimated error except at the lowest temperatures where our measurements are higher than those of the NBS workers, reaching a maximum deviation of 10% for our lowest point. Measurements of the heat capacity of the Calorimetry Conference Standard benzoic acid have been reported by Osborne, Westrum and Lohr[10] and by Busey.[11] A plot of the ratio of the heat capacities of benzoic acid to the table of Furukawa, McCoskey and King, as measured by the above two sets of workers and by us is shown in Fig. 2. Below 16°K. the heat capacity given by the NBS table appears to be too low by more than the estimated uncertainties of the various experiments. In this temperature range the thermal relaxation time between the calorimeter and its surrounding becomes short and the corrections for heat interchange must be carefully made. We believe that in this range our isothermal calorimeter, with the heat interchange corrections calculated as indicated earlier in this paper is capable of more accurate results than many adiabatic calorimeters where the adiabatic condition is determined by a copper–constantan thermocouple which becomes quite insensitive at low temperatures. The thermal relaxation time between the calorimeter and its surroundings, the reciprocal of α in eq. 1, may be used as a figure of merit in comparing various calorimeters in the low temperature region. If this time becomes too short, so that the thermal contact between the calorimeter and its surroundings is good, the elimi-

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[9] G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Research Natl. Bur. Standards*, **47**, 256 (1951).

[10] D. W. Osborne, E. F. Westrum, Jr., and H. R. Lohr, THIS JOURNAL, **77**, 2737 (1955) and private communication.

[11] R. H. Busey, (a) *ibid.*, **78**, 3263 (1956); (b) ORNL-1828 (Jan. 26, 1955).

nation of corrections for heat interchange by controlling the temperature of a shield becomes very difficult. In the temperature range above 250°K., on the other hand, where a difference thermocouple is very sensitive and where the corrections for thermal relaxation times within the calorimetric system become important, we believe that an adiabatic calorimeter is capable of more accurate results than our isothermal calorimeter. Even in this region, however, a comparison of our measurements of the heat capacity of benzoic acid with those of the other laboratories indicates that our estimate of a possible error of 0.4% at 300°K. is a generous one.

Acknowledgments.—We are indebted to the Atomic Energy Commission for the support of this research. The research was also supported in part by the Office of Naval Research.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSIOLOGY AND THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

Heat Capacities from 11 to 305°K. and Entropies of *l*-Alanine and Glycine[1]

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RECEIVED OCTOBER 15, 1959

The heat capacities of *l*-alanine and glycine have been measured from 11 to 305°K. The entropies at 298.15°K. were found to be 30.88 cal. deg.$^{-1}$ mole^{-1} for *l*-alanine and 24.74 cal. deg.$^{-1}$ mole^{-1} for glycine. The heat capacities, entropies, $(H^\circ - H^\circ_0)/T$ and $-(F^\circ - H^\circ_0)/T$ are tabulated for both substances from 10 to 310°K. The values of $S^\circ_{298.15} - S^\circ_{90}$ found are in good agreement with previous work by Huffman and Borsook on *d*-alanine and by Parks, *et al.*, on glycine. However, extrapolation procedures employed below 90°K. by previous workers led to too high an estimate for S°_{90} for both amino acids.

One of the most obvious deficiencies in present day knowledge of the metabolism of living organisms is the lack of information concerning energetic changes associated with the synthesis of proteins. For several years we have been engaged in measuring the heat capacities of the naturally occurring amino acids and some selected proteins to establish the entropies of these compounds. Concurrently Tsuzuki and Hunt[2] have been measuring the heats of combustion of these same compounds. The projects were undertaken to supplement work on the few amino acids studied in the 1930's by Huffman, Borsook and others.[3]

We present here our data on glycine and *l*-alanine. *d*-alanine has been studied previously[4] as has glycine[5] but not below 90°K. Estimates of the entropies of these amino acids must be revised as a result of extending heat capacity measurements below 90°K. Furthermore, over the entire range of temperatures employed, our data offer a greater degree of precision than the previous studies.

Experimental

Amino Acids.—The glycine and *l*-alanine used in these studies were provided by the late Jesse P. Greenstein of the National Institutes of Health. Both were free of other amino acids as indicated by unidirectional paper chromatography using five different solvent systems (formix, MeOH-pyridine, ketone mix, phenol and butanol-acetic acid). The *l*-alanine was 99.9% free of the *d*-isomer by the criteria of Meister, *et al.*[6] Both amino acids were crystalline as evidenced by examination in polarized light. Both materials were dried at room temperature for several days at 10^{-4} mm. in a system trapped with liquid nitrogen. After loading the calorimeter they were subjected to pumping at $<10^{-6}$ mm. pressure for 48 hr. No weight losses which could be considered significant occurred. Nonetheless the heat capacity measurement on glycine at 269.27°K. is 1.1% high and was ignored in drawing the curve from which the thermodynamic functions were derived. We believe the high value probably arises from the melting of water in the sample. To produce the excess heat observed in this measurement, 0.022 g. H_2O per mole of glycine would be required. At other temperatures the effect on the heat capacity of this amount of water is always less than 0.06%, and since it is small compared to the experimental error, no correction has been made.

Experimental Methods and Calculations.—The methods for measuring heat capacities and for calculating the results have been described in detail.[7] As an additional detail, the method used to extrapolate the heat capacity curve below 11°K. was as follows. Values of $(\Delta H/\Delta T)/T^2$ were plotted as a function of T and this curve extrapolated in such a fashion that $\Delta H/\Delta T$ was proportional to T^3 as T approached zero. The fractional error involved is no doubt appreciable, but since S°_{10} is less than 0.2% of $S^\circ_{298.15}$ the absolute error is tolerable. The calorimeter used was the one with six radial fins and the heater-thermometer was the one bearing the laboratory designation "H" described in the previous paper. The sample weight was 47.431 g. for *l*-alanine and 98.129 g. for glycine. The heat capacity of the empty calorimeter represented 40–50% of the total heat capacity over most of the temperature range employed, falling to 25% at 300°K. in the case of glycine.

Results

The experimentally measured quantities ($\Delta H/\Delta T$) are given in Table I for glycine and in Table II for *l*-alanine. The individual values are listed in the chronological order in which they were obtained and the thermal history of the compounds can be deduced from the table. Glycine had an exceptionally stormy history as a result of a broken vacuum line. In general the temperature rise in individual experiments can be deduced from the intervals between the points. Where an occasional run was lost or where cooling overnight led to overlapping of points, the following applies: From 11–50°K. ΔT was approximately 0.1 T. From 50–150°K., ΔT <5.5°, from 150–200°K., ΔT <6°;

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[1] This work was supported by the U. S. Atomic Energy Commission.

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[5] G. S. Parks, H. M. Huffman and M. Barmore, *ibid.*, **55**, 2733 (1933).

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