[Contribution from the Chemical Laboratory of the University of Illinois]

THE HEAT CAPACITIES OF LIQUID METALS

By Alfred L. Dixon[1] with Worth H. Rodebush

Received February 7, 1927 Published May 10, 1927

The heat capacities of liquid metals are necessary for an accurate calculation of the entropies of monatomic vapors. It is seldom that measurements of the vapor pressure can be made over a sufficient temperature range with sufficient accuracy to establish the vapor-pressure equation itself satisfactorily, and the calculation of heat capacities from vapor-pressure data is still more uncertain.[2] This is, perhaps, because the saturated vapor may not be assumed to be a perfect gas. The greater portion of the data which have been obtained by direct measurement of the heat capacities of liquid metals is to be found in the paper by Wüst, Meuthen and Durrer.[3] In their method the metal was sealed in a quartz bulb, heated to a high temperature and dropped into a Bunsen ice calorimeter. A correction was made for the heat capacity of the quartz, and the total heat content of the sample was expressed as a function of the temperature by an empirical equation. The specific heat is obtained by differentiation with respect to the temperature. The data of Wüst[3] appear to be reliable in some cases and doubtful in others. Iitaka, Bernini and Rengade[4] have used modifications of the above method to obtain data for a few molten metals including sodium, potassium and lead. The data obtained by the experimenters, mentioned above, however, are not in good agreement and it would appear that the method calls for a very considerable amount of experimental technique, although it has been used by investigators on solid metals with excellent results in many cases.[5]

A very reliable method appears to be that of Barnes[6] who obtained data for mercury and water by a continuous-flow calorimeter. Griffiths and Griffiths[7] obtained a few measurements upon molten sodium by the method of electrical heating in a vacuum. This method is not suited for high temperatures because of radiation effects.

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[1] This communication is an abstract of a thesis submitted by Alfred L. Dixon in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Thus, Poindexter [*Phys. Rev.*, **26**, 859 (1925)] was led to infer that the temperature coefficient of the heat of vaporization of mercury was 10 cal. per degree.

[3] Wüst, Meuthen and Durrer, *Verh. deut. Ing. Forsch.*, 204, **1918.**

[4] (a) Iitaka, *Sci. Rep. Tohoku Univ.*, **8**, 99 (1919). (b) Bernini, *Physik. Z.*, **7**, 168 (1906); **8**, 150 (1907). (c) Rengade, *Compt. rend.*, **156**, 1897 (1913).

[5] For references to work on solids see White [*Am. J. Sci.*, **47**, 1 (1919)] and Eastman, Williams and Young [This Journal, **46**, 1178 (1924)].

[6] Barnes, *Rep. Brit. Assoc. Winnipeg*, 403, **1909.** Barnes and Cooke, *Phys. Rev.*, **16**, 65 (1903).

[7] Griffiths and Griffiths, *Proc. Roy. Soc.*, **89A**, 561 (1914).

After a review of the methods which had been used it seemed that the most promising method at high temperatures would be one which did not involve the direct measurement of heat quantities at all. Such a method has been proposed by Lewis[8] for liquids. Barus[9] has employed a modification of this method, and a similar method has frequently been used, measuring the specific heats of gases.[10]

Experimental Part

In the method proposed by Lewis, the pressure on a liquid is changed suddenly and the corresponding change in temperature noted by means of a thermocouple. If the experiment is properly performed, the entropy remains constant and we have

$$(\partial T/\partial P)_s = (T/C_p)(\partial V/\partial T)_p \tag{1}$$

We need only the coefficient of expansion, for which data are to be found in the literature, to calculate C_p, the heat capacity. In order to meet the condition of Equation 1, namely, that the entropy remain constant, it is necessary that no currents be produced in the liquid by the change in pressure and that the heat exchange with the surroundings be negligible in the time required by the thermocouple to come to equilibrium with the liquid. In order to meet the latter condition it is necessary that the liquid be placed in a thermostat which is held very nearly at constant temperature. This made necessary the use of a double thermostat at elevated temperatures. The liquid metal was placed in a glass bulb with a thermocouple junction at its center with sealed-in leads, and the bulb was placed in the inner thermostat. When it had come to constant temperature, a pressure was applied to the liquid by admitting gas through a stopcock and the rise in temperature was observed by means of the thermocouple. The reverse operation was found to be equally satisfactory for the measurement of $(\partial T/\partial P)_s$.

Apparatus

The thermostat used in these experiments is shown in Fig. 1. A sheet-iron can D, 41 cm. in diameter and 61 cm. deep, was constructed of material 3 mm. in thickness. All of the seams were welded. Before this can was mounted in place it was plastered over with alundum cement 1 cm. thick. Over this was uniformly wound 36 turns of No. 16 B. and S. Chromel-A wire, which was then fastened on by another coat of alundum cement. This winding was divided into three equal parts by two taps. Outside the winding was a thick layer of insulation. Centrally located, inside of the thermostat, was the double-walled vessel M made of two concentric No. 24 gage sheet-iron cans. The space between the two was filled with insulation. This vessel was supported by an iron tripod (not shown) and weighted down with lead N. The space between the inner vessel and the outer can was filled with the thermostat bath to the level shown. This

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[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 137.

[9] Barus, *Carnegie Inst. Pub.*, **4**, 39 (1919).

[10] See Partington and Howe, *Proc. Roy. Soc.*, **109**, 286 (1925).

bath, which will be referred to as the outer bath, was provided with two stirrers HH. Inside of the inner vessel was the inner bath O, as shown, provided with a stirrer I. The bulb J, containing the liquid to be investigated, was supported in the inner bath by the 3mm. Pyrex capillary *L*. All of the rods and tubes leading from the thermostat were arranged in a plane, and both the inner and the outer vessels were furnished with insulated covers PP, made in halves with holes along the diameter for these rods and tubes. For temperatures between room temperature and 170°, the bath liquid used was a light grade of lubricating oil (Polarine E). Between the temperatures of 310 and 550° fused sodium nitrate was used.

The main part of the heating current was supplied to the outer resistance winding of the thermostat can, and an intermittent current controlled by the regulating devices, described below, was supplied to a heating coil immersed in the outer bath. The outer bath was the only one that was regulated. The temperature of the inner bath was allowed to come to equilibrium with the outer one, and since the two were rather well insulated from each other the fluctuations of temperature of the inner bath were very slight.

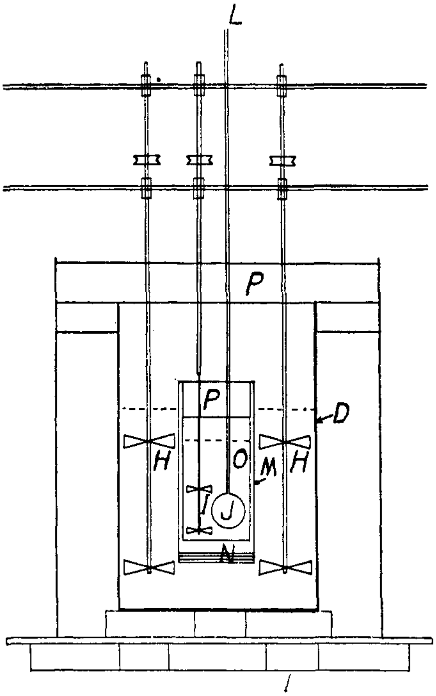

Fig 1.

The temperature control of the bath was effected by means of a platinum-resistance thermometer which formed one arm of a Wheatstone bridge and thus actuated a galvanometer and relay which turned an auxiliary heating current on or off. This method of temperature control has been used by others and the details will not be given here. It was possible to hold the outer bath temperature constant within a few hundredths of a degree. In the oil-bath, the wires of the resistance thermometer and auxiliary heating coil were bare. In the nitrate bath, the heating coil and the platinum-resistance thermometer were copper-enclosed and mica-insulated. Thermocouples were placed in the inner and outer baths for control purposes and for measuring the temperatures at which experiments were performed.

The bulbs in which the samples of the liquids were placed were made from thick-walled, 150cc. Pyrex extraction bulbs. For use in the oil-bath at the lower temperatures, the arrangement was as shown in Fig. 2. A was the supporting tube of 3 mm. Pyrex capillary through which the pressure was applied; R was an enlargement to provide space for the expansion and contraction of the liquid; B was the tube through which the liquid was admitted; CC were capillary side tubes, each with a slight enlargement as shown, through which the thermocouple was sealed. These seals were made by pressing a thick paste of alundum cement around the wire and, when dry, fused orange shellac was driven into the clay from the inside, by heat and pressure. This type of seal proved to be perfectly liquid-tight at temperatures up to 200°. Heavy copper wire was wound around the two tubes CC, and the ends of the thermocouple wires were soldered to these with pure tin. The copper lead wires also were soldered to these lugs which constituted the fixed junctions of the thermocouple. When filling the bulb, both tubes A and B were connected to a pump, and the arrangement connected to B permitted the liquid to be filtered in through an ungreased stopcock until R was half filled. B was then sealed off while the low pressure was maintained and subsequently the pressure in A was raised to atmospheric by pure dry nitrogen. For use in the sodium nitrate bath it was necessary that the lead-in wires be insulated by Pyrex tubing, which complicated the construction of the bulb to a considerable extent.

The thermocouple materials used were copper, constantan, Chromel P, Alumel and Copel. The copper, No. 36 B. and S. gage, and constantan, Ideal No. 35 B. and S. gage, were from spools that had been used in this Laboratory for a number of years. In these experiments four pieces of each, about 1 meter long, were made up into thermocouples and calibrated at the temperatures of melting mercury, melting ice, boiling water and boiling naphthalene. The differences between these four couples, and between these and previous calibrations of the spools were less than one part in a thousand. The thermo-electric power was uniformly 1% higher than in the standard table of Adams.[11] All of the copper-constantan thermocouples used in the specific-heat bulbs were made from the wire from these four couples. The silk insulation was taken off with concd. sulfuric acid and a small junction was made by twisting the ends for 3 mm. This junction was then soldered with pure tin and the whole wire was insulated by repeated coats of enamel baked on at 350°. It was then mounted in the bulb by alundum cement, as described above. The Chromel P, Alumel and Copel wires No. 28 B. and S. gage were part of a special lot obtained from the Hoskins Manufacturing Company. The combinations Chromel P-Alumel and Chromel P-Copel were calibrated against a platinum platinum-10%-rhodium thermocouple which in turn had been calibrated at the temperatures of boiling water, boiling naphthalene and boiling sulfur. From these calibrations, thermo-electric power-temperature curves were drawn which were used as reference curves, as will be described later. Chromel P-Copel insulated with glass was used in the experiments on liquid sodium and liquid potassium. Chromel P-Alumel, sealed in glass, was used in the experiments on liquid lead. The potentiometer used was a modification of the one devised by Rodebush[12] for freezing-point work; it has the advantage that it is self-calibrating and has a galvanometer circuit free from parasitic e.m.f.'s.

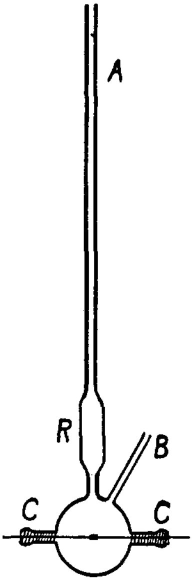

Fig. 2.

All wiring in the thermocouple circuit consisted of twisted pairs of cotton-enamel insulated copper wire. The twisting was found to be necessary, because no matter how tightly the wires were stretched, the air currents caused them to move and electromotive forces were generated by the cutting of the earth's magnetic field. The galvanometer was a Leeds and Northrup high-sensitivity instrument with an all-copper circuit. It had the following constants: sensitivity, 238 megohms; period, 5.6 sec.; res., 17.5 ohms; CDRX, 10 ohms. The galvanometer was supported upon a spring suspension placed upon a pier. The light from a single straight-wire filament passed through a lens, was reflected from the galvanometer mirror, and was re-reflected from a stationary mirror to a ruled, ground-glass plate. The image of the filament was about 1 mm. wide at a total scale distance of about 4 meters. However, if the image was thrown out of focus

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[11] Adams, "Pyrometry," *Am. Inst. Min. Metallurg. Eng.*, New York, **1920.**

[12] Hovorka and Rodebush, THIS JOURNAL, **47,** 1614 (1925).

slightly, a dark line appeared in it approximately 0.2 mm. wide. This line was used in taking the readings.

The pressure used was obtained from a tank of compressed nitrogen. The gas was admitted from one high-pressure tank to another, to which was connected a mercury manometer 3.5 meters high. A motor-driven, two-way, 3mm. Pyrex stopcock connected the 3mm. capillary tube, which led to the bulb in the thermostat, alternately to the atmosphere or to the pressure cylinder, as desired. Since the volume of gas required for each application of pressure was small and the volume of the tank was comparatively large, the pressure was quite constant. It was regulated at intervals to exactly the pressure desired.

Mercury

The first metal used was mercury. It was chosen because of the obvious advantages of low melting point and also, because of the careful work of Barnes and others, its specific heat is known quite accurately. Much preliminary work was done with mercury in developing the construction of the apparatus and the technique of using it. The mercury was electrolytically purified and then distilled twice under low pressure in a current of air. Finally, it was filtered through cloth and dried by boiling in a vacuum. The bulbs were evacuated while they were being filled in order to prevent the presence of air bubbles. These were undesirable because their collapse under pressure would allow convection currents to be set up in the liquid.

The data obtained for the specific heat of mercury are shown in Table I. ΔP is the pressure change in centimeters of mercury; s is the sensitivity of the galvanometer in millimeters per microvolt; T. E. P. is the thermo-electric power in microvolts per degree; $(\partial V/\partial T)$ is in cubic centimeters per gram atom per degree; d is the galvanometer deflection in millimeters, and n is the number of observations averaged to give this result; C_p is the heat capacity at constant pressure per gram atom. Nos. 1 to 9 were taken on one bulb and Nos. 10 to 17 were taken on a second. The group, Nos. 5 to 9, is a series taken consecutively to test the linearity of the relation between ΔP and d. The curvature, if any, was much less than the experimental error. Readings were taken both by application and by release of the pressure. After each change of pressure, the whole was allowed three to five minutes to attain constant temperature before the next reading was taken by reversing the pressure. There was no systematic difference between the values obtained by application of pressure and those obtained by release of pressure. However, if there was a constant slow drift of the temperature of the inner bath of the thermostat, there was a difference. For example, if the temperature of the inner bath were rising at a constant rate, the temperature of the junction of the thermocouple in the bulb would be rising at the same rate as the temperatures of those in the thermostat. The galvanometer would show a constant deflection corresponding to the lag of the temperature of the center of the bulb behind the temperature of the thermostat. Under these conditions the deflections obtained upon applications of pressure were greater than those obtained when the pressure was released. The average of the two, however, was very nearly the value obtained under constant-temperature conditions. After the change of pressure was effected, the galvanometer required about seven seconds to attain the full deflection. It remained stationary for one or two seconds before the heat-conduction wave reached the center of the bulb and then started back toward its original position.

TABLE I

MERCURY

No.	Temp., °C.	Temp., °K.	ΔP, cm.	s mm./mv.	T. E. P., mv./deg.	$(\partial V/\partial T)_p$, cc./g. at./deg.	n	d, mm.	C_p
1	70	343	350	39.3	44.8	0.002695	13	27.6	6.59
2	70	343	350	39.4	44.8	.002695	5	27.3	6.67
3	157	430	353	38.8	50.8	.002750	22	39.8	6.59
4	100	373	426	38.8	47.2	.002712	14	37.7	6.68
5	101	374	345	38.8	47.2	.002713	4	30.95	6.63
6	101	374	295	38.9	47.2	.002713	8	26.7	6.57
7	101	374	253	38.9	47.2	.002713	4	22.9	6.56
8	103	376	222	38.9	47.4	.002714	6	20.2	6.58
9	103	376	143	38.9	47.4	.002714	4	13.0	6.60
10	102	375	314	48.2	47.3	.002714	17	35.2	6.60
11	103	376	313	48.0	47.4	.002714	6	34.6	6.69
12	103	376	353	48.2	47.4	.002714	4	39.45	6.65
13	103	376	353	48.0	47.4	.002714	10	39.2	6.66
14	103	376	233	48.0	47.4	.002714	4	25.9	6.66
15	143	416	284	47.9	50.0	.002740	13	37.4	6.61
16	143	416	324	47.9	50.0	.002740	6	42.4	6.65
17	41	314	325	48.0	42.4	.002681	8	26.65	6.66

The data are plotted in Fig. 3, together with the data of Barnes. The data for the volume expansion were taken from the work of Callendar and Moss,[13] whose values agree quite well with those of Regnault.[14] Both of these authors measured the coefficients of expansion of mercury for temperatures up to 300°, using connecting-tube methods. The equation which fits their data does not differ by more than 1% from that of Chappius,[15] or from that of Thiesen, Scheel and Sell[16] in the interval of their measurements, namely, up to 100°. The extrapolated values of these latter authors, however, differ greatly from the experimental values of Callendar and Moss at the higher temperatures. The data of the latter were chosen because of the longer temperature interval of measurement.

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[13] Callendar and Moss, *Phil. Trans. Roy. Soc.*, **211A**, 1 (1912).

[14] Regnault, *Mem. acad. roy. sci. inst. France*, **21**, 271 (1847).

[15] Chappius, *Trav. mem. bur. inter. Poids Mes.*, 13, **1907.**

[16] Thiesen, Scheel and Sell, *Wis. Abh. Phys.-Tech. Reich.*, **2**, 73 (1895).

The maximum variation between our results and those of Barnes and Cooke is about 1%, which is probably not greater than the actual experimental error.

Sodium and Potassium

The sodium was commercial electrolytic metal, purified by melting in a vacuum and filtering twice through capillary tubing. The potassium was melted in a vacuum and filtered into distillation bulbs. The original containers were then sealed off, and when the vacuum improved the potassium was distilled into a reservoir from which it was filtered into the specific-heat bulb. It was found that the molten alkali metals attacked shellac and organic enamels very rapidly; consequently, glass-insulated Chromel P-Copel thermocouple wires were used. The manner of calibration of this thermocouple has been described but it was feared that the heating incident to the sealing-in process might change the thermo-electric power. Since a direct calibration could not be made on the thermocouple after it was sealed into the bulb, it was thought best to fill the bulb with mercury and repeat the determinations on mercury at various temperatures. This indirect recalibration gave a correction for the thermo-electric power which amounted to 2–3% in the thermocouples used on sodium and potassium. The actual uncertainty in the value for the thermo-electric power should be much less than the correction. Although the values of $(\partial V/\partial T)_p$ are large for the alkali metals, and large deflections were obtained, the heat conductivity of these metals was so great that the temperature at the center of the bulb began to drift back toward the equilibrium temperature before the galvanometer had time to attain its full deflection. In fact, the deflection obtained by a simple application

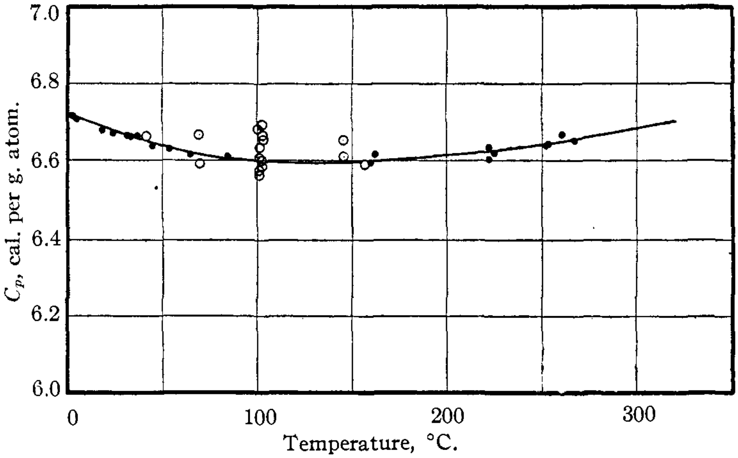

Fig. 3.—Specific heat of mercury. ●, Barnes and Cooke; ○, Rodebush and Dixon.

of pressure was usually only about 85% of the value finally accepted as corresponding to the true temperature change. At first, extrapolation of the deflection-time curve was attempted but the results were uncertain. Byerly[17] has worked out the theory of the heat conduction of a sphere. In Fig. 4 is plotted the theoretical variation in temperature at the center of the sphere after the temperature of its surface is suddenly changed to a new value. The curves obtained for the sodium and potassium bulbs were of the same general shape as the calculated one but the effect of the glass shell altered the quantitative characteristics. The method finally used was to guess the deflection and to balance it out by the potentiometer to the nearest tenth of a microvolt. The pressure was then suddenly changed with the galvanometer circuit open and a few seconds later the galvanometer circuit was closed. The resultant deflection of a few millimeters was added to that corresponding to the reading of the potentiometer. By this method values of the temperatures were determined as early as two seconds after the application of the pressure. In Fig. 5 is plotted a set of temperature readings of the bulb containing sodium as they changed with time after the application of pressure. The first temperature reading was obtained 0.03 minute after the pressure was applied. If no correction were made, the value would be 106 mm. and a tangential extrapolation would give a value 6 mm. greater. In consideration of the fact that the curve should have zero slope at zero time, as demanded by the theory of heat conduction, an intermediate value was chosen. The data for potassium were treated in a similar fashion to obtain the additive correction for heat conduction.

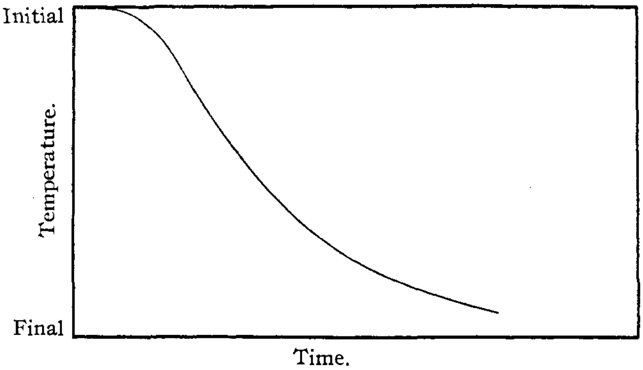

Fig. 4.—Temperature variation at the center of a sphere.

The data for the coefficients of expansion of liquid sodium and of liquid potassium were taken from the work of Hackspill.[18] His values were

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[17] Byerly, "Fourier Series and Spherical Harmonics," Ginn and Co., New York, 1893, p. 116.

[18] Hackspill, *Compt. rend.*, **152**, 259 (1911).

chosen arbitrarily in preference to the older ones of Hagen.[19] Bernini and Cantoni[20] made some measurements upon very small quantities of sodium and potassium and obtained values for the coefficients of expansion very much higher than those of Hagen or Hackspill. Their values are believed to be in error not only because of the disagreement with the other authors but also because the values of specific heat calculated from their data are unreasonable.

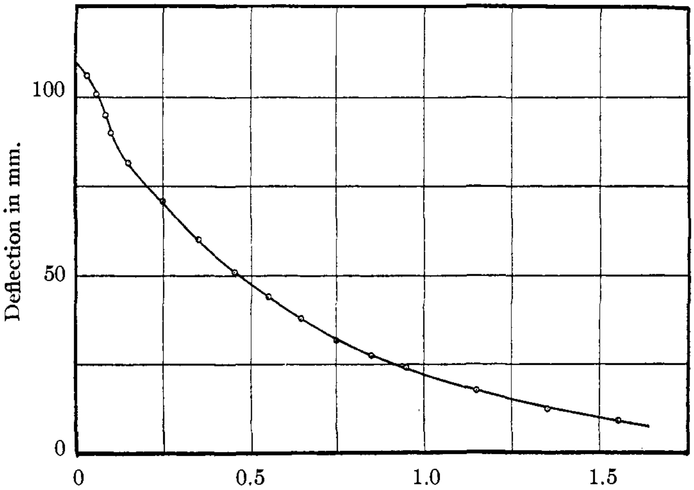

Fig. 5.—Experimental heat conductivity of sodium.

Table II gives the data obtained for sodium and potassium. The values are plotted in Figs. 6 and 7, together with those of Bernini,[4b] Rengade,[21] Iitaka[4a] and Griffiths.[7] Because of the uncertainty of the heat-conduction correction and the unknown accuracy of the coefficient of expansion data, the values for the specific heats of sodium and potassium may be in error by several per cent. However, a comparison of the data given here with

TABLE II

No.	Temp., °C.	Temp., °K.	ΔP	s	T. E. P.	$(\partial V/\partial T)_p$	d	n	C_p
				SODIUM					
1	121	394	282	50.5	68.1	0.006739	109	7	7.53
2	178	451	252	50.5	70.3	.006739	118	9	7.35
				POTASSIUM					
1	90	363	290	50.5	66.7	0.0133	193	11	7.80
2	136	409	200	51.0	70.1	.0136	165	11	7.68
3	181	454	200	50.5	71.7	.0138	188	10	7.69

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[19] Hagen, *Ann. Physik*, **19**, 436 (1883).

[20] Bernini and Cantoni, *Nuovo cimento*, [6] **8**, 241 (1914).

[21] Rengade, *Bull. soc. chim.*, **15**, 130 (1914).

those of other authors shows that the probable error is certainly less than the existing discrepancies, especially in the case of potassium.

Lead

The last metal investigated was lead. On account of the higher temperatures required, fused sodium nitrate was used for the thermostat baths and because of its electrical conductivity and the necessity of insulating the thermocouple leads, the bulb system was more complicated. It was found that Copel wire dissolved easily in liquid lead and consequently Chromel P-Alumel thermocouples were used. Much time was spent in developing a bulb which would withstand the temperature changes

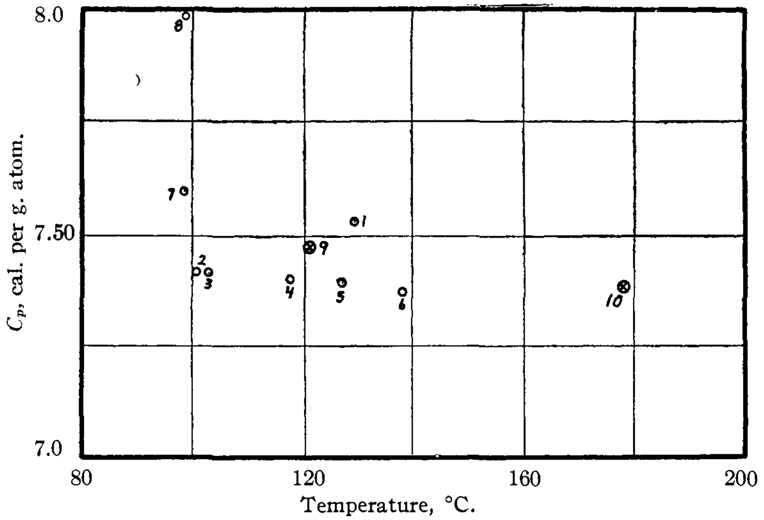

Fig. 6.—Specific heat of sodium. 1, Bernini; 2–6, Griffiths; 7, Rengade; 8, Iitaka; 9–10, Rodebush and Dixon.

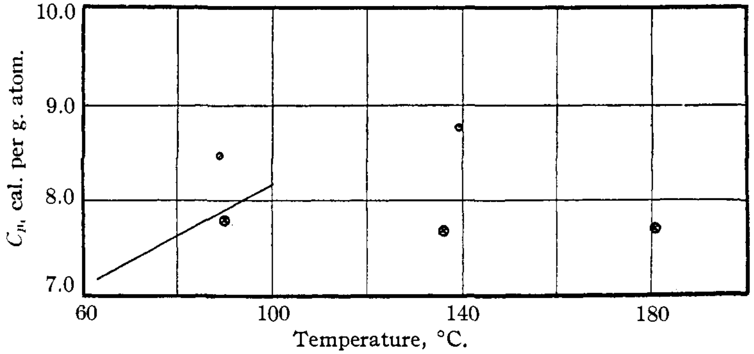

Fig. 7.—Specific heat of potassium. ○, Bernini; —, Rengade equation; ⊗, Rodebush and Dixon.

without cracking or leaking. After the type of bulb was perfected, no difficulty was experienced in obtaining the data except that at the highest temperatures used the Alumel wire of the thermocouple dissolved slowly. Because of this, no accurate data were obtained at temperatures above 460°. The lead was Merck's C. P. grade obtained in a granulated form. It was first fused in an atmosphere of nitrogen to a massive form and then kept molten in air for some time. This latter process, aided by stirring and skimming, served to oxidize any sulfide that might have been dissolved in the metal. The molten lead was then filtered into a reservoir in an atmosphere of dry nitrogen and from there it was filtered through a stopcock into the bulb. The bulb was placed in a furnace while it was being filled, in order to keep the lead molten. When the filling tube had been sealed off and the nitrogen had been admitted to atmospheric pressure, the bulb was transferred rapidly to the thermostat. About five or six hours were required for the temperatures in the thermostat to come to equilibrium at each temperature at which readings were taken.

The data for the coefficient of expansion of liquid lead were taken from the work of Day, Sosman and Hostetter,[22] who found that its value was constant throughout their interval of measurement, namely, from the melting point to 850°. A standard curve for the thermo-electric power of the Chromel-Alumel couple was used and corrected for the individual bulbs by a mercury calibration in a manner similar to that described for sodium and potassium. It was not possible to make a satisfactory check on mercury at temperatures above 311°, but the correction obtained in this way was less than 1% of the thermo-electric power and it may be assumed that the sealing-in process did not affect the thermocouple appreciably.

Expts. 1 to 5 (Table III) were made on one bulb and Expts. 6 to 9 were made on a second. In both cases the dissolving of the thermocouple prevented the taking of readings at higher temperatures, as was desired. However, the data obtained give a sufficient indication of the course of the specific heat to be of value. The points are plotted in Fig. 8, together

TABLE III

LEAD

No.	Temp., °C.	Temp., °K.	P	s	T. E. P.	$(\partial V/\partial T)_p$	d	n	C_p
1	365	638	350	48.5	42.0	0.00224	46.85	17	6.95
2	378	651	350	48.5	42.0	.00224	47.3	16	7.00
3	418	691	350	48.5	42.3	.00224	51.0	20	6.95
4	459	732	350	48.1	42.5	.00224	53.8	16	6.95
5	354	627	350	48.25	42.4	.00224	45.7	16	7.02
6	375	648	350	48.0	42.6	.00224	47.5	10	6.97
7	419	692	350	48.5	42.9	.00224	51.75	10	6.95

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[22] Day, Sosman and Hostetter, *Neues Jahrb. Mineral. Geol.*, **40**, 119 (1915).

with the equation of Wüst[3] and that of Iitaka.[4a] The agreement with Iitaka is very close but rather fortuitous, since his values depend upon somewhat uncertain calibration of his calorimeter. The discrepancy between our data and those of Wüst is very great and must be due to a serious error somewhere in his work, as his values are highly improbable.

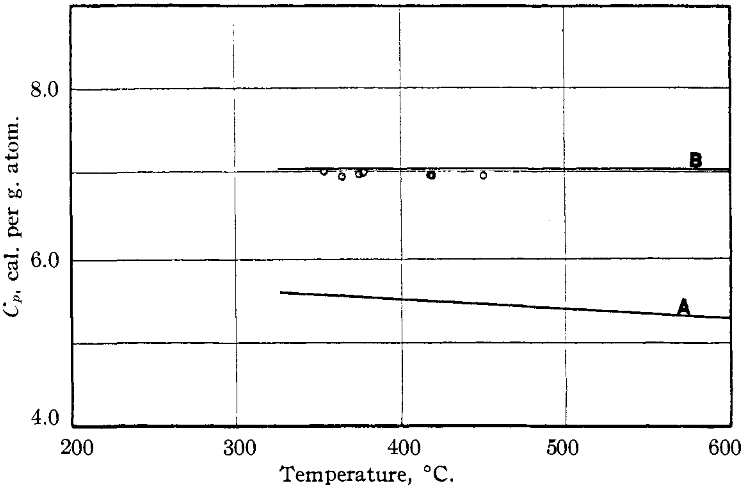

Fig. 8.—Specific heat of lead. *A*, Wüst; *B*, Iitaka.

Accuracy

The correction for the change in thermo-electric power of the thermocouples by the sealing-in process has been discussed. The copper-constantan thermocouples used in the original mercury experiments were accurately calibrated and had a small heat capacity. The Hoskins wires, together with their glass coverings, had a somewhat larger heat capacity and, consequently, the error due to that factor was greater. In the case of sodium and potassium, the high heat conductivity necessitated uncertain corrections which could have been minimized only by using bulbs of larger diameter. This change would have required the rebuilding of the thermostat and, consequently, was not made. The deflection readings were estimated to 0.1 mm., with a maximum reading error of perhaps 0.3 or 0.4 mm. The individual deflections usually did not vary more than 1% from the average value. The temperature and pressure were known to a comparatively high order of accuracy and no error should be asigned to them. The values of *s*, the galvanometer sensitivity, were taken repeatedly during the course of an experiment and were of the same order of accuracy as the temperature deflections. Considering these facts, it seems that the possible error in the individual measurements of the temperature rise in the case of mercury was about

2%; in sodium, potassium and lead about 3%. Of course, to these must be added the errors of the coefficient of expansion values, the magnitude of which errors are in most cases unknown. No attempt was made to measure the coefficients of expansion of any of the liquids used, although there were some large discrepancies in the literature. When more reliable data for this factor are obtained, the calculated values of the specific heats will be rendered more accurate.

So far as these experiments show, the method used was found to be entirely feasible and reliable. As a test of the method, the use of liquid metals was the most severe that could be attempted, since their coefficients of expansion are relatively low and their heat conductivities are high. Using this method, a comparatively simple apparatus could be set up which would measure the specific heats of organic liquids, for example. In such a case, fine, bare thermocouples could be used and by proper calibrations the coefficients of expansion of the liquids and the pressure-temperature increments could be measured on the same sample in the same bulb. With such an apparatus the measurements of the specific heats of pure liquids would be reduced to a routine with a probable error of 1% or less.

Summary

An apparatus has been constructed to measure the specific heats of molten metals by a method suggested by Lewis.

Satisfactory data have been obtained for sodium, potassium and lead at temperatures above their melting points.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 196]

A FIXED POINT FOR THE CALIBRATION OF PRESSURE GAGES. THE VAPOR PRESSURE OF LIQUID CARBON DIOXIDE AT 0°[1]

BY OSCAR C. BRIDGEMAN[2]

RECEIVED FEBRUARY 23, 1927 PUBLISHED MAY 10, 1927

For a considerable period of years, piston gages of various types have been used for measuring pressures greater than a few atmospheres in place of the more cumbersome mercury column. The procedure used in calibrating the piston gage ordinarily consists either of a direct comparison with a mercury column or a determination of the diameters of the piston

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[1] Professor F. G. Keyes suggested to the writer the advantage of utilizing the vapor pressure exerted by carbon dioxide at the ice point as a standard for the determination of piston gage constants. It is also a pleasure for the writer to express his indebtedness to Professor Keyes and the members of the Laboratory Staff for assistance and advice during the progress of this investigation.

[2] National Research Fellow in Chemistry.