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Thermodynamic Properties by Levitation Calorimetry— V. High-Temperature Heat Content of Liquid Gallium[1]

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The heat content (enthalpy) of liquid gallium relative to the supercooled liquid state at 298.15 K has been measured by levitation calorimetry over the temperature range 1412–1630 K. Thermal energy increments were determined using an aluminum block calorimeter of conventional design. The sharp decrease of C_p with increasing temperature observed just above the melting point does not persist up to the high temperatures of the present work. When combined with recent laser-flash calorimetry results from the literature, the present work indicates that $\bar{C}_p$ is 26.46 ± 0.71 $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ over the temperature range 587–1630 K.

KEY WORDS: emissivity; enthalpy; gallium; heat capacity; high temperature; levitation calorimetry.

1. INTRODUCTION

High-temperature enthalpy and/or heat capacity data for liquid gallium are scarce. In fact, there are only two sets of data for temperatures above 993 K [1, 2] and they disagree with data extrapolated from lower temperatures by Hultgren et al. [3]. Data for liquid gallium at temperatures below 993 K show a constant-pressure heat capacity C_p that decreases with increasing temperature. None of the data at these lower temperatures shows an unequivocal leveling out of the heat capacity versus temperature curve, which is expected to begin around 700 K [3].

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Levitation calorimetry has previously been applied to metals that melt at rather high temperatures. For such metals, accurate values of the normal spectral emissivity (required for optical pyrometer) may be obtained with the levitation calorimetry apparatus alone. If the metal can be levitated at its melting point and observed at that temperature with the optical pyrometer, the known melting point can be used to calculate the required emissivity [4]. A description and history of levitation calorimetry, including a table showing which liquid metals have been studied, will be given in a forthcoming review [5].

Gallium melts at a temperature too low for observation with a visible-range optical pyrometer. Furthermore, even if its emissivity could be determined with an infrared pyrometer at the melting point, extrapolation to the high temperatures of levitation calorimetry would be subject to large uncertainties. Otherwise, gallium is quite suitable for levitation calorimetry, since there is an appreciable temperature range between the minimum temperature observable with the visible-range pyrometer and the maximum temperature, where vaporization of the gallium begins to interfere with the light emitted toward the pyrometer.

The emissivity of gallium can be calculated from data on the optical constants of liquid gallium in the literature [6, 7] at temperatures of about 298, 873, and 1133 K. The relationship between emissivity and temperature is linear, permitting a reliable extrapolation to the required temperature range.

Another reason for performing experiments by levitation calorimetry is the severity of the container problems with liquid gallium. The corrosive action of gallium on container materials is summarized by Sheka *et al.* [8]. The use of levitation eliminates the container, a likely source of error in enthalpy measurements.

2. APPARATUS

The measurements were made using apparatus similar to that described by Bonnell [4] and Chaudhuri *et al.* [9]. The calorimeter, its quartz thermometer, radiation gates, and jacket were the same as in earlier experiments. The levitation chamber was a "cross" of Kimax brand conical end process pipe, made from glass, with four openings, all of 6 inch (15 cm) nominal diameter. Each opening was covered with a thick plate of transparent poly(methyl methacrylate). The plates were shaped like conical ends of glass pipe and were attached using Kimax brand clamps. The necessary connections, ports, and windows were installed in the plates. A sample holder made from glass supported a sample in the coil until levitation was established. The sample holder was then withdrawn by its handle, a plastic rod, which passed through a Cajon fitting in the top plate.

The levitation chamber was not "vacuum tight," but could be pumped to about 1 Torr pressure. The chamber was pumped out prior to admitting inert gas (argon, helium, or a mixture of the two) for levitation experiments. This avoided the extremely long purging procedures that would have been necessary without the ability to pump out the air.

The gas purification train was the same as that described by Bonnell [4] but without the calcium trap. The same gas mixture flowed to both the calorimeter and the levitation chamber. The flow rates to calorimeter and chamber could be measured separately, but the argon and helium were mixed ahead of the flowmeters. When mixtures of the two gases were used, the composition of the mixture was estimated by shutting each gas off for a short time and observing the resultant change in flow rate. A filter of glass wool was installed in the gas outlet line between the levitation chamber and the Nujol bubbler to prevent metal-bearing dusts formed in the chamber from passing into the bubbler and/or into the room.

The bottom 5 mm of the radiation gate was under the water in the constant-temperature bath to provide water cooling. The gate itself did not have cooling coils on it. Any heat produced in the gate by radiofrequency (rf) radiation was too slight to be detected by touching the gate.

The constant-temperature water bath was controlled to within ±0.015 K using a mercury-filled thermoregulator, but the temperature was not always kept close to 298.15 K, for two reasons. First, when the room temperature was too high, the refrigerated water capability was too low to permit operation at such a low temperature. More important, the use of a higher temperature helped reduce the risk of crystallization of the supercooled gallium.

The calorimetric apparatus was supported in the constant-temperature water bath by an aluminum framework. The bath itself was a 10-gallon aluminum cooking pot. The stirrer was the same as that used by Bonnell [4] and the motor was equivalent.

The quartz thermometer was used with an automatic digital interface which transmitted the temperatures to a Texas Instruments Model 733 ASR computer terminal. The data were printed and simultaneously recorded on magnetic tape. The interface required at least 1 h warmup time, as did the Keithley Model 195DMM multimeter.

The induction heater was a 30-kW Lepel unit, model T-30-3-KC-SW. In this application it operated at approximately 300 kHz. A radiofrequency transformer similar but not identical to that described by Chaudhuri *et al.* [9] was used to improve the coupling. The levitation coil was similar to coil number 2 in Fig. 2 of the paper by Chaudhuri *et al.* [9].

Temperatures of levitated gallium were measured using the Leeds and Northrup Model 8641 automatic pyrometer [4]. The operating wavelength was nominally 645 nm and the pyrometer was calibrated from 1000 to

2300°C using a Ribbon Strip Lamp No. 805 purchased from the Pyrometer Instrument Company. They had calibrated the lamp against their laboratory standards, which had been calibrated at the U.S. National Bureau of Standards. The calibration was given as brightness temperature at 650 nm versus lamp current, measured through the voltage across a shunt. No correction was attempted for the slight difference from the nominal operating wavelength of the pyrometer.

Seven points were obtained on the "low" scale of the pyrometer, one of which was rejected because of poor focusing of the pyrometer. Eight points were obtained on the "medium" scale, one of which was rejected because of a very large discrepancy with the other data. Nine points were obtained on the "high" scale, and none was rejected. Pyrometer voltage was a linear function of temperature on the "low" and "medium" scales and a quadratic function on the "high" scale. Least-squares equations fitted the calibration points within 4 K maximum deviation and 2–3 K average deviation.

During levitation experiments the pyrometer voltage was observed simultaneously with the digital multimeter and with the strip chart recorder used by Bonnell [4]. The two devices usually agreed within about 2°C except when the temperature was changing very rapidly. The pyrometer voltages were taken from the strip chart recorder because it responded more rapidly than the multimeter when the latter was used to record data over a period of several minutes (storing the data in its digital memory).

The transmittance of the optical glass window through which the pyrometer viewed the samples was determined by alternately placing it in and removing it from the line of sight between the pyrometer and the calibration lamp. The brightness temperature of the lamp as read from the pyrometer output was 1214–1284 K and dropped slightly when the window was inserted in the line of sight. The mean of seven values of $\Delta(1/T)$ from insertion of the window was 3.04×10^{-6} K^{-1}. From commonly used equations given by Bonnell [4], the transmittance of the window was calculated as 0.934. This agrees closely with Bonnell's measurement on a similar window, using a completely different technique.

3. ELECTRICAL CALIBRATION

Electrical calibration was performed using a new sleeve made entirely of aluminum alloy number 6061. The calibration heater was made from 95Ω of 40-gauge enameled manganin wire wound bifilarly in a groove around the outside of the sleeve. The circuit for electrical calibration was similar to that used by Bonnell [4]. The direct current was supplied from the alternating current line through a rectifier bridge, a resistance capacitance ripple filter, and a Zener diode voltage regulator. Voltages were measured to within 0.1% accuracy by the digital multimeter.

The calibration procedure was as described by Bonnell [4]. The measured voltages were constant within ±0.3% during each individual calibration experiment. Pure argon gas was supplied to the calorimeter, and the lower gate (on top of the calorimeter) was kept closed. During the electrical calibration experiments the bath temperature T_b remained at 25.179°C within ±0.006°C variation, as determined by a Beckmann-type thermometer calibrated against a quartz thermometer at 25°C. The quartz thermometer used for calibrating the Beckmann-type thermometer had recently been calibrated by the Hewlett–Packard Company.

The calorimeter cooling constant k (in Newton's law of cooling) determined from all the rating periods in the electrical calibration taken together was $(8.23 \pm 0.05) \times 10^{-5}\ \mathrm{s}^{-1}$ in the argon atmosphere. The uncertainty given is ±2 sdm, where sdm is the standard deviation of the mean. (A rating period is a period during which the variation of calorimeter temperature is observed as a function of time, and during which there is no heat input intentionally provided to the calorimeter. The temperature change during a rating period is thus due entirely to the heat exchange of the calorimeter with its surroundings. The rates of heat exchange observed in the rating periods are used to correct for heat exchange during the temperature rises caused by intentional heat inputs, such as electrical heat or the heat brought by dropping hot gallium into the calorimeter. Rating periods must begin only after the calorimeter has come to a steady state following the last previous disturbance. Periods during which heat inputs are provided intentionally to be measured are called "main" periods. The rating period before a main period is the "initial" period and the rating period after a main period is the "final" period.)

The calorimeter thermometer was recalibrated by assuming that the interpolated temperature at zero heat exchange was equal to the bath temperature. All the rating periods in the electrical calibration were used together for the interpolation.

The heat energy delivered to the calorimeter was evaluated as described by Bonnell [4]. For each individual calibration experiment, the value of calorimeter cooling constant observed in that experiment was used for calculation. Each rating period consisted of 38 readings of temperature at 15-s intervals. Each main period consisted of the heating time plus 28 more readings of temperature at 15-s intervals while the calorimeter temperature came to a steady state.

Calibration data are summarized in Table I. The new symbols in this table are $\bar{V}$, the average heater voltage; $\bar{I}$, the average heater current; Δt, the time of electrical heating; u, the "stirring constant" (calculated rate of

Table I. Electrical Calibration of the Calorimeter

$\bar{V}$ (V)	$\bar{I}$ (A)	Δt (s)	$k \times 10^5$ (s^{-1})	$u \times 10^6$ ($K \cdot s^{-1}$)	ΔT (K)	ΔT_c (K)	ε_s ($J \cdot K^{-1}$)	$\bar{T}$ (°C)
11.81244	0.1236615	970.832	8.50	−4.67	1.20254	0.98147	1444.911	22.9885[a]
11.81550	0.1236720	967.610	8.13	0.12	1.05967	0.97694	1447.292	24.1947
11.81418	0.1237242	968.779	8.17	−0.46	0.94553	0.97805	1447.844	25.2125
11.81775	0.1236609	967.611	8.22	0.21	0.84571	0.97589	1448.996	26.0727
						Mean:	1447.3	24.62
					Precision,	2 sdm:	±1.7	

[a] In this experiment the variation of temperature versus time in the rating periods was noticeably nonlinear. The beginning and ending temperatures of the main period (obtained from the usual linear equations) were corrected for this curvature, assuming that the calorimeter followed Newton's law of cooling. The corrected temperatures agreed with the observed temperatures at the same times within 0.00008°C.

calorimeter temperature change at T_b); ΔT, the change of calorimeter temperature during the main period; ΔT_c, that change of temperature after correction for heat exchange; ε_s, the standard energy equivalent of the calorimeter; and $\bar{T}$, the average of the beginning and ending temperatures in the main period. The ε_s is defined as the heat absorbed by the calorimeter per unit temperature rise during the electrical calibration. The value of ε_s is 1447.3 $J \cdot K^{-1}$.

The change of ε_s with changes in $\bar{T}$ is neglected. The temperature coefficient of the heat capacity of aluminum is about 7×10^{-4} fractional change per °C at 298.15 K [3]. This corresponds to about 1 $J \cdot K^{-1}$ per K in ε_s. (A least-squares fit of ε_s versus $\bar{T}$ would show a slope of 1.3 $J \cdot K^{-1}$ per K, and ε_s would be 1447.7 $J \cdot K^{-1}$ at 25°C. The variation of ε_s versus $\bar{T}$ is not statistically significant at the 95% level.) The value of ε_s is less than in previous calibrations [4, 9], probably because of changes in the thermometer (including the readout instrument and its adjustment as well as the thermometer probe itself.)

The energy equivalent ε is defined as the heat absorbed by the calorimeter per unit temperature rise in a levitation experiment. The ε_s and ε are different because for levitation experiments the calibration sleeve was absent and was replaced by a sleeve of aluminum alloy number 6061 containing tantalum foil and sometimes gallium from previous levitation experiments. The value of ε was calculated from ε_s using the measured weights of materials and the following heat capacity values in $J \cdot g^{-1} \cdot K^{-1}$ at 298.15 K: aluminum alloy number 6061, 0.8941 [4]; manganin, 0.447 [4]; varnish, 1.7 [4]; copper, 0.385 [3]; solder (60 wt % Sn), 0.188 [3], assuming molar additivity of C_p; tantalum, 0.140 [3]; gallium, as determined during this work or taken from the literature (see below for numerical values).

4. LEVITATION TESTS ON LIQUID COPPER

Experiments were performed on pure copper to demonstrate that the apparatus was operating satisfactorily. A measurement of the normal spectral emissivity of liquid copper at 645 nm was made at its melting point as described by Bonnell [4]. A value of 0.109 was found, as compared with Bonnell's result of 0.15. It was difficult to control the temperature and rate of heating of copper in the present apparatus, so the present value of normal spectral emissivity is probably less accurate than Bonnell's result. Two measurements of the heat content of copper relative to the solid at 298.15 K made with the present levitation apparatus yielded 59,590 $J \cdot g\text{-atom}^{-1}$ at 1831.6 K and 56,578 $J \cdot g\text{-atom}^{-1}$ at 1783.0 K. The deviations from the least-squares line representing Bonnell's smoothed results are $+84$ and -1246 $J \cdot g\text{-atom}^{-1}$, respectively. Their rms deviation is ± 883, as compared with Bonnell's standard deviation of ± 848 $J \cdot g\text{-atom}^{-1}$. If the results are recalculated using 0.15 for the normal spectral emissivity, the deviations become $+1504$ and $+99$ $J \cdot g\text{-atom}^{-1}$, respectively; the rms deviation is then ± 1066, only slightly worse than with the emissivity value 0.109. We conclude that the present apparatus gives correct results for the enthalpy of liquid copper.

5. CALCULATION OF EMISSIVITY

The emissivity of gallium cannot be determined by observing the metal at its melting point with the visible-range optical pyrometer, as described by Bonnell [4]. Even if it could be observed, there would be considerable uncertainty in extrapolating the emissivity to the much higher temperatures of the levitated samples.

The emissivity of gallium has been calculated from data on its optical constants given by Schulz [6] and Comins [7]. Both authors treat the data by the Drude theory, in which the optical properties depend upon two parameters, N, the number of free electrons per unit volume, and σ, the direct current electrical conductivity. The complex index of refraction $n - ik$ is calculated from these parameters and the frequency of the light waves using equations given by Schulz. (In this section, k always refers to k as defined by Schulz.) The dielectric constant at optical frequency is negative and is given by $n^2 - k^2$. The conductivity at optical frequency is given by n times k times the frequency [10]. Using an equation given by Schulz, the reflectivity at normal incidence can be calculated from n, k, the frequency, and the index of refraction of the medium in contact with the gallium. This index of refraction is unity for low-pressure argon and/or helium. The normal spectral emissivity $\varepsilon_{n\lambda}$ is then given by one minus the reflectivity at normal incidence for the same frequency or wavelength.

Table II. Normal Spectral Emissivities Calculated for Liquid Gallium at 645 nm

Temperature T (K)	$N \times 10^{-23}$ (cm^{-3})	$\sigma \times 10^{-5}$ ($\Omega^{-1} \cdot \mathrm{m}^{-1}$)	$\varepsilon_{n\lambda}$	$\varepsilon_{n\lambda}$ from least-squares equation	Deviation of the equation
298.15	1.58	38.5	0.0971	0.0975	+ 0.0004
873.15	1.594	26.0	0.1383	0.1369	− 0.0014
1133.15	1.60	23.0	0.1538	0.1547	+ 0.0009

From Schulz's data [6] we have calculated the normal spectral emissivity at 645 nm and ambient temperature, which we took to be 25°C. Comins [7] gives plots of conductivity and dielectric constant as functions of photon energy (which is directly proportional to frequency) at 600°C and 860°C. We chose values of N and σ that reproduced these data reasonably well and used them to calculate normal spectral emissivities at 645 nm. The results are shown in Table II.

The values of N and σ at 298.15 K in Table II are from Schulz's paper. The other values of N and σ have been derived from Comins' data. The calculated values of $\varepsilon_{n\lambda}$ at 645 nm shown in Table II are a linear function of temperature, and the least-squares equation

$$\varepsilon_{n\lambda} = 0.0771 + 6.852 \times 10^{-5} T \tag{1}$$

was used to extrapolate the spectral emissivity of gallium to higher temperatures for use in optical pyrometry. It would be possible to compute the total hemispherical emissivity ε_T by computing spectral emissivity as a function of wavelength and angle of emission, then integrating it over both angle and wavelength, and extrapolating to high temperatures. Instead, we have simply estimated that ε_T is equal to the normal spectral emissivity at 645 nm.

6. LEVITATION MEASUREMENTS ON LIQUID GALLIUM

The experimental apparatus and procedures were as described by Bonnell [4] and Chaudhuri *et al.* [9], except for changes specifically mentioned. The calorimeter was not cooled with dry ice. The sleeve was inserted into and removed from the calorimeter without removing the calorimeter from the constant-temperature water bath. The cooling water supply for the levitation coil was on whenever the induction heater filament was on. Tantalum foil was used as the lining for the aluminum alloy sleeve because tantalum reacts only slightly with gallium, even at moderately high temperatures [8]. Since the gallium could be expected to cool very quickly upon impact in the calorimeter, no significant reaction was expected. Inspection of the calorimeter sleeve after each experiment showed that all of the gallium was liquid. Inspection after the last experiment showed no visible reaction between gallium and the tantalum or the aluminum alloy sleeve.

The initial rating period was begun after levitation had been established. The sample was dropped at any convenient time after 38 temperature observations at 15-s intervals had been obtained showing an apparently constant temperature drift rate. The beginning of the initial period was established by counting back 38 observations before the drop time. If least-squares computations later showed that the calorimeter had not reached a steady state at the beginning of the initial period, all temperature observations preceding the establishment of a steady rate were dropped from the initial period. The radiation gate was opened for as short a time as possible to permit dropping the gallium, which was done by momentarily shutting off the rf power. The rf power was turned on again as quickly as possible. This procedure kept the rf power level, and thus its possible effects on temperature readings, constant throughout most of the experiment. Any temperature readings obviously affected by the temporarily high level of rf power (when it was raised to bring the gallium to the required high temperature) were deleted and replaced by interpolated values. The final rating period contained 38 measurements of temperature and was begun as soon as a steady-state rate of temperature change was reached after the drop.

The lower gate (on top of the calorimeter) was kept open before the drop and closed after the drop, making the conditions of heat exchange slightly different in the two rating periods, and perhaps increasing the error slightly. However, it was a necessary precaution to reduce the risk of dropping gallium onto the lower gate, where it would have splashed and possibly damaged the apparatus. During and after these experiments, the calorimeter was inspected carefully for splashes of gallium, which is corrosive to aluminum. No splashes were found.

Corrections for heat losses from the gallium during its drop were made as described by Bonnell [4] with an additional term added to the conduction loss correction to account for the conduction loss when the sample is moving slowly, i.e., just as it starts to fall. The additional term is described by Eckert and Drake [11] in discussing their Eq. (9-34). Viscosities, thermal conductivities, and the mixing rules for low pressure gases were taken from the fifth edition of the *Chemical Engineers' Handbook* [12].

Table III. Calorimetric Data for Liquid Gallium

Gas (Ar and/or He, mole %)	n_{init}	n_{main}	$\varepsilon - \varepsilon_s$ $(\mathrm{J \cdot K^{-1}})$	$k \times 10^4$ $(\mathrm{s^{-1}})$	$u \times 10^5$ $(\mathrm{K \cdot s^{-1}})$	ΔT (K)	ΔT_c (K)
Ar	26	29	1.9	1.179	− 8.063	0.15600	0.06428
65% Ar	38	27	2.1	2.721	0.207	0.10931	0.08910
He	38	47	2.3	5.090	4.977	0.06845[a]	0.08360
He	38	25	2.5	4.614	4.525	0.08068[a]	0.08703
He	32	47	2.6	4.622	7.722	0.18036	0.12909
He	37	63	2.7	4.277	3.518	0.09775	0.11562

[a] Corrected for stoppage of the thermometer by the rf (35 s and 11 s, respectively).

The gallium metal was obtained from Alfa Products, Ventron Division of Thiokol Corp., as ingots in polyethylene, Catalog Number 128, Lot Number 101879. The nominal purity of the gallium was 99.99999%.

"Oxide," possibly Ga_2O [13], escaped from the gallium as a black vapor and/or dust during the early stages of levitation, leaving behind a bright, mirrorlike surface. Traces of white scum on the gallium after dropping were assumed to be the result of oxidation occurring while the gallium was exposed to air. Traces of black "oxide" were assumed to have fallen in from the coil, where they collected as small particles during levitation. The weights of such oxides were too small to have affected the results significantly. This was confirmed in the case of black "oxide" by removing the particles and weighing the sleeve again.

Results from six experiments on liquid gallium are given in Table III in chronological order. Auxiliary data used are as follows: atomic weight of gallium, 69.72; density of gallium at ambient temperature, $6.097\ \mathrm{g \cdot cm^{-3}}$ at 25°C [14] (extrapolated); density of gallium at drop temperature, by linear extrapolation using the density and its temperature coefficient at 600°C from Köster *et al.* [14]; temperature of the gas in the levitation chamber, taken as the bath temperature; and drop distance, 50 cm (measured). The high-temperature densities agree within 0.3% with results of Bykova and Shevchenko [15].

In Table III n_{init} represents the number of calorimeter temperature observations in the initial rating period; n_{main} represents the number of such observations in the main period; T represents the temperature of the gallium at the time it was dropped; T_{calor} represents the calorimeter temperature at the end of the main period (that is, the effective temperature to which the gallium was dropped); m represents the mass of gallium dropped; E represents the energy delivered to the calorimeter by the

Table III. (Continued)

T (K)	T_{calor} (K)	m (g)	T_b (°C)	E (J)	E_{rad} (J)	E_{conduc} (J)	$H_T - H_{298.15}$ ($\text{J} \cdot \text{g-atom}^{-1}$)
1629.9	297.66	0.19001	26.967	93.157	1.243	1.453	35158
1417.1	299.97	0.30194	26.972	129.144	0.889	2.456	30641
1450.2	300.26	0.29930	26.975	121.189	0.983	4.377	29535
1412.0	300.37	0.32176	27.071	126.173	0.912	4.278	28524[b]
1552.8	300.17	0.39128	26.967	187.163	1.615	5.594	34688
1545.6	300.35	0.36315	27.077	167.652	1, 503	5.369	33565

[b] A small piece of copper fell into the sleeve when the apparatus was opened before shutting off the gas flow. It was removed before weighing and took no visible gallium with it.

gallium dropped; E_{rad} represents the radiation loss correction; E_{conduc} represents the conduction loss correction; and $H_T - H_{298.15}$ represents the enthalpy of the gallium at temperature T less that of supercooled liquid gallium at 298.15 K. The mass m was determined by the change in weight of the sleeve plus tantalum plus gallium and was corrected for air buoyancy.

The correction from $H_T - H_{T_{\text{calor}}}$ to $H_T - H_{298.15}$ was calculated from

$$H_T - H_{298.15} = H_T - H_{T_{\text{calor}}} + (T_{\text{calor}} - 298.15)C_{p(\text{Ga},298.15\ \text{K})} \tag{2}$$

where $C_{p(\text{Ga},298.15\ \text{K})}$ represents the heat capacity of gallium at 298.15 K in the supercooled liquid state. Here the variation with temperature of C_p is neglected over the small range from T_{calor} to 298.15 K. The value of C_p used for Table III was that found in this study. [The final calculations for Table III were made after Eq. (4) was derived.]

7. DISCUSSION

A preliminary evaluation can be performed by applying the assumption of constant heat capacity. (Since the heat capacity is not constant [3], an average heat capacity is obtained.) A least-squares line constrained to pass through $H_T - H_{298.15} = 0$ at $T = 298.15$ yields the result

$$H_T - H_{298.15} = 26.628T - 7939.1 \tag{3}$$

The rms (root mean square) deviation from this line is $\pm 927\ \text{J} \cdot \text{g-atom}^{-1}$ or $\pm 2.97\%$; the standard deviation for five degrees of freedom is ± 1016

$\mathrm{J \cdot g\text{-}atom^{-1}}$ or 3.26%. The standard deviation of the mean for heat capacity is ±1.33%. The average heat capacity with 2 sdm uncertainty is therefore

$$\bar{C}_p = 26.63 \pm 0.71\ \mathrm{J \cdot g\text{-}atom^{-1} \cdot} K^{-1} \qquad \text{for} \quad T = 298.15\text{–}1629.9\ K \quad (4)$$

This is in good agreement with selected values of Hultgren *et al.* [3], which show an average heat capacity of 26.69 $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ for the range 302.9 K (the melting point) to 1629.9 K. The difference in $\bar{C}_p$ is 0.2%.

A further evaluation can be made by using literature data to define the heat capacity up to about 700 K (above which Hultgren *et al.* assumed C_p to be constant). The present data can then be used to determine the average value of C_p above the temperature at which it presumably becomes constant.

The laser-flash calorimetric data of Takahashi *et al.* [16] agree approximately with selected values of Hultgren *et al.* Both show a heat capacity decreasing rapidly with increasing temperature from the melting point to about 600 K. The values of $H_{600} - H_{302.93}$ are 8064 $\mathrm{J \cdot g\text{-}atom^{-1}}$ calculated from data of Takahashi *et al.* and 8046 $\mathrm{J \cdot g\text{-}atom^{-1}}$ from Hultgren *et al.*, a difference of 0.2%.

Smoothed heat capacities for liquid gallium from data of Takahashi *et al.* are given by

$$C_p = 27.49 - 2.426 \times 10^{-3}T + 1.361 \times 10^5/T^2 \quad (5)$$

in which we have corrected a decimal point misplaced in the original paper [16]. The equation covers the temperature range 250–600 K.

Integration of the heat capacity equation gives the enthalpy equation

$$H_T - H_{298.15} = 27.49T - 1.213 \times 10^{-3}T^2 - 1.361 \times 10^5/T - 7631.8 \quad (6)$$

fitting data of Takahashi *et al.* on liquid gallium up to 600 K. At 587 K the enthalpy $H_{587} - H_{298.15}$ is 7855 $\mathrm{J \cdot g\text{-}atom^{-1}}$ and the heat capacity is 26.46 $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$.

The present experimental data were fitted to a least-squares line constrained to pass through $H_T - H_{298.15} = 7855$ $\mathrm{J \cdot g\text{-}atom^{-1}}$ at $T = 587$ K. They were then recalculated using $C_{p(\mathrm{Ga},298.15\ \mathrm{K})} = 28.30$ $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ from data of Takahashi *et al.* The high-temperature C_p used in the recalculation was determined in the present study. [The final recalculation was made after Eq. (8) was derived.] The values of $H_T - H_{298.15}$ from Table III changed by a maximum of 4 $\mathrm{J \cdot g\text{-}atom^{-1}}$, about 0.01%. The new values, in chronological order, were 35,157; 30,644; 29,539; 28,528; 34,692; and 33,569 $\mathrm{J \cdot g\text{-}atom^{-1}}$ and are plotted in Fig. 1 along with the data of

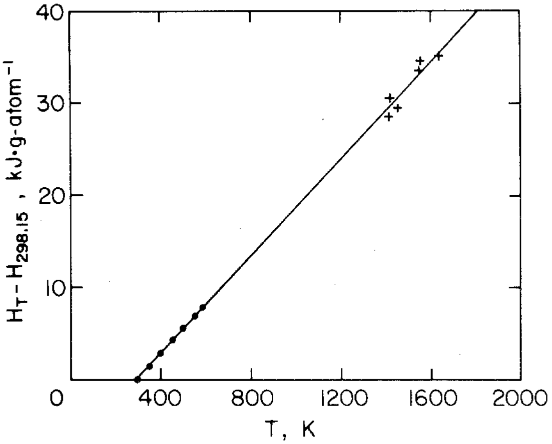

Fig. 1. Enthalpy of liquid gallium relative to the supercooled liquid state at 298.15 K. (●) Takahashi *et al.* (smoothed data); (+) present work.

Takahashi *et al.* The final least-squares line was

$$H_T - H_{298.15} = 26.460T - 7677.0 \tag{7}$$

The rms deviation from this line is ±931 J · g-atom^{-1} or ±2.99%; the standard deviation for five degrees of freedom is ±1020 J · g-atom^{-1} or ±3.27%. The standard deviation of the mean for heat capacity is ±1.34%. The average heat capacity with 2 sdm uncertainty is therefore

$$\bar{C}_p = 26.46 \pm 0.71 \text{ J} \cdot \text{g-atom}^{-1} \cdot \text{K}^{-1} \qquad \text{for} \quad T = 587\text{–}1629.9 \text{ K} \tag{8}$$

Hultgren *et al.* estimated $\bar{C}_p = 26.58$ J · g-atom^{-1} · K^{-1} for the same range, a difference of 0.5%. And, of course, the value of C_p from Takahashi *et al.* at 587 K is 26.46 J · g-atom^{-1} · K^{-1}. The present data confirm that the sharp decrease of heat capacity with increasing temperature up to 600 K does not persist and imply that C_p is constant over the range 600–1630 K, and probably up to the boiling point.

Both x-ray diffraction [17] and neutron diffraction [18] studies of liquid gallium confirm short-range order in the liquid at low temperatures, but the degree of order diminishes as the temperature increases. Such order is not detectable at 838 K, a little above the temperature at which C_p seems to become constant. The heat capacity of liquid gallium must obviously include a component representing the entropy increase involved in the loss of short-range order. This component should disappear at the temperature where short-range order disappears.

Akhmatova [1] reports C_p in $\mathrm{J \cdot cm^{-3} \cdot K^{-1}}$ for liquid copper (1463–1638 K) and liquid gallium (1283–1623 K). Her data for copper, converted to $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ using densities of liquid copper from Frohberg and Weber [19], are, on the average, 22% less than the value found by Bonnell [4]. The uncertainty of measurement stated by Akhmatova is less than 7%. If her data for gallium are converted to $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ by linearly extrapolating the density data of Köster *et al.* [14] (as in the calculations for Table III), the resulting C_p values are, on the average, 5% less than the present result of 26.46. Akhmatova's data for gallium show a peak in the curve of C_p versus temperature. She noted that the liquid metals may have penetrated the walls of their containers, and most liquid copper C_p values from the literature [4, 20–24] are substantially higher than hers. Therefore it is possible that the apparent peak results from experimental errors greater than the 7% estimate.

Novikov and Mardykin [2] reported values of C_p for liquid copper (1400–1600 K) about 21% lower than that found by Bonnell and 8–21% lower than those found by numerous others [20–24]. They [2] report that the C_p of gallium is about 9% greater than the present result of 26.46 $\mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}}$ in the range 1173–1450 K.

Kochetkova and Rezukhina [25] measured the enthalpy of gallium at 588–993 K relative to the supercooled liquid state at 293.15 K. They used drop calorimetry with the gallium enclosed in quartz ampules. Their smoothed enthalpy data are 1.2–1.7% lower than values from Eq. (7). Their data are therefore consistent with the present results and with those of Takahashi *et al.* to within 1.7%.

In view of the excellent agreement of the high-temperature levitation measurements with those from laser-flash calorimetry and those other data for which container reactions are not significant, we recommend the following enthalpy equation for liquid gallium:

$$H_T - H_{298.15} = 26.460T - 7677.0\ \mathrm{J \cdot g\text{-}atom^{-1}} \qquad \text{for} \quad 587 < T < 1630\ \mathrm{K} \tag{9}$$

and thus

$$C_p = 26.46 \pm 0.71\ \mathrm{J \cdot g\text{-}atom^{-1} \cdot K^{-1}} \tag{10}$$

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