Heat Capacity of Gallium Arsenide

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The heat capacity at constant pressure of gallium arsenide over the temperature range 310–980K was determined with a differential scanning calorimeter, and the smoothed results were given by $(5.35 + 1.16 \times 10^{-3} T)$ cal K^{-1} g atom^{-1}. These results are compared with previous determinations of the same function.

There is considerable current interest in the electronic properties of the important semiconductor gallium arsenide, but little definitive work has been reported on the thermodynamic properties. There are two conflicting literature reports (*1*, *3*) on the heat capacity of GaAs as a function of temperature in the temperature range 300–1000K, both sets of results obtained by use of a drop calorimeter. This note reports corresponding results over the range 310–980K obtained with a differential scanning calorimeter.

Experimental

A Perkin-Elmer differential scanning calorimeter (Model DSC 2) was used with gold sample pans and a sapphire calibrant. The heat capacity of sapphire is well established (2). Temperature measurement was accurate to ±0.2K, and for measurements below 323K, an auxiliary cooling system was used. Temperature scans of 60K were made at a scan speed of 10K min^{-1} and a range setting corresponding to a full-scale deflection of 2×10^{-3} cal s^{-1}. Equilibrium isothermal base lines were recorded for each scan for the sapphire calibrant, for the empty sample pans, and for the GaAs. These were coincident to within ±0.5% of full-scale deflection above 700K, whereas superior coincidence was noted at lower temperatures and exact coincidence between 300 and 400K. Heat capacities were extracted at 10K intervals up to 500K and 20K intervals thereafter.

The sapphire and GaAs (semiconductor grade, 99.999%, M.C.P. Electronics Ltd., Alperton, Wembley, UK) were in the form of thin discs weighing 30.045 and 87.790 mg, respectively.

Results and Discussion

The accuracy of heat capacities obtained by the scanning calorimeter depends on the uncertainty in the heat capacity of the sapphire calibrant (±0.02 cal K^{-1} mol^{-1} at 300K to ±0.03 cal K^{-1} mol^{-1} at 1000K) and on the random error in measuring pen displacement. This is ±1% which corresponds to ±0.06 cal K^{-1} g atom^{-1} for GaAs. Inclusion of the error for the noncoincidence of the isothermal base lines gives an estimated overall accuracy of ±0.1 cal K^{-1} g atom^{-1}. However, in view of

Table I. Experimental and Calculated Heat Capacities for Gallium Arsenide in cal K^{-1} g atom^{-1}

T, K	C_p, exptl	C_p, calcd	T, K	C_p, exptl	C_p, calcd
310	5.60	5.71	540	5.99	5.98
320	5.65	5.72	560	6.04	6.00
330	5.67	5.74	580	6.08	6.03
340	5.69	5.75	620	6.11	6.07
350	5.72	5.76	640	6.16	6.09
360	5.76	5.77	660	6.16	6.12
370	5.79	5.78	680	6.18	6.14
380	5.81	5.79	700	6.19	6.16
390	5.82	5.81	720	6.17	6.19
400	5.84	5.82	740	6.18	6.21
410	5.85	5.83	760	6.20	6.23
420	5.89	5.84	780	6.30	6.26
430	5.91	5.85	800	6.31	6.28
440	5.92	5.86	820	6.26	6.30
450	5.91	5.88	840	6.27	6.33
460	5.93	5.89	860	6.30	6.35
470	5.86	5.90	880	6.29	6.37
480	5.90	5.91	920	6.38	6.42
490	5.94	5.92	940	6.38	6.44
500	5.95	5.93	960	6.47	6.47
520	5.98	5.96	980	6.54	6.49

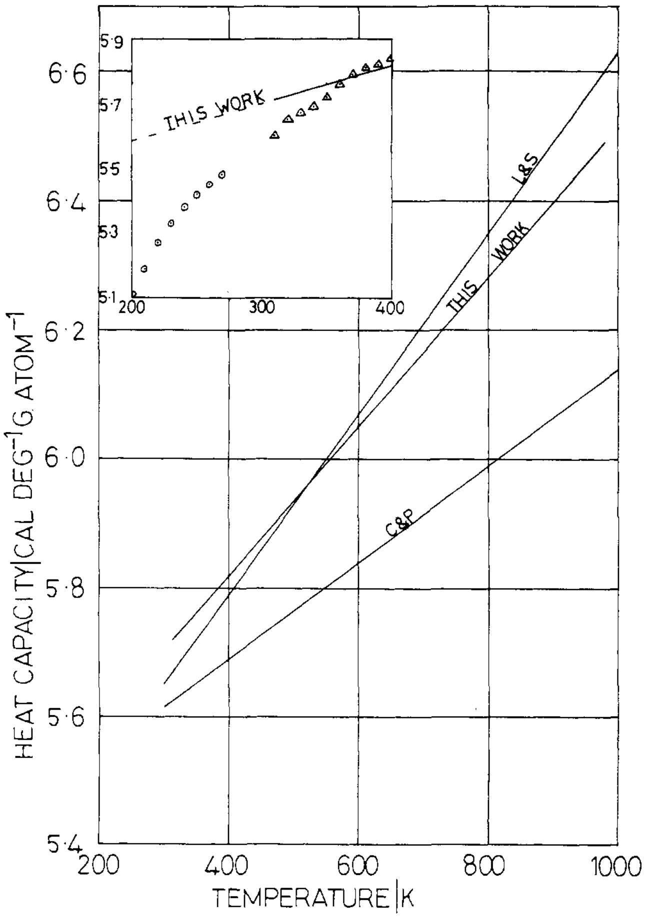

Figure 1. Smoothed heat capacity results for GaAs of Cox and Pool (*1*) (C&P), Lichter and Sommelet (*3*) (L&S), and present results. Inset: Piesbergen's (*4*) results from 200 to 270K and our results from 310 to 400K

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the superior base line stability at low temperatures (see Experimental section), the results between 300 and 400K are of significantly higher accuracy, probably ±0.05 cal K^{-1} g $atom^{-1}$. All the results were fitted to polynomials of successively higher degree, and the fit to a first degree polynomial ($C_1 + C_2\ T$) gave a residual mean square ($N^{-1}\ \Sigma\ [C_p(\text{calcd}) - C_p(\text{exptl})]^2$) of the same order as the RMS corresponding to the estimated accuracy (±0.1 cal K^{-1} g $atom^{-1}$) of the results. This polynomial, $C_p(\text{GaAs}) = (5.35 + 1.16 \times 10^{-3}\ T)$ cal K^{-1} g $atom^{-1}$, was used to calculate the smoothed results in Table I.

The smoothed results are compared in Figure 1 with the corresponding smoothed data of Cox and Pool (1) (298–1250K) and Lichter and Sommelet (3) (298–1513K, the melting temperature). Our results are systematically higher than those of Cox and Pool (given by $C_p = 5.4 + 7.3 \times 10^{-4}\ T$) and are in closer agreement with those of Lichter and Sommelet [Lichter and Sommelet's smoothed C_p results at 600 and 1300K are not linear with the other smoothed C_p results in their Table 3. Further, these smoothed results (given by C_p/cal K^{-1} g $atom^{-1} = 5.23 + 0.0014\ T$, except for those results at 600 and 1300K) are not in agreement with an analytical expression, given in the form $C_p = 3\ R(a' + b'T) = 5.66 + 8.34_5 \times 10^{-4}\ T$, contained in their Table 5], although our results display a significantly larger temperature coefficient. Confidence in our results is increased by the continuity of our values in the range 300–400K with the low temperature (10–273K) heat capacities of Piesbergen (4) (see inset to Figure 1).

Acknowledgment

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Vapor-Pressure Relations for 15 Hydrocarbons

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Experimental values of vapor pressure for 15 hydrocarbons are measured in the low-pressure range 0.1–25 mm Hg by means of the inclined-piston deadweight gage and in the range 71–2025 mm Hg by means of comparative ebulliometers. Correlations of the present results with selected literature values are given in terms of Cox equations.

Vapor pressure–temperature relations of liquid and solid phases are a requisite for comprehensive thermodynamic studies. The presently reported experimental vapor pressures and derived parameters of Cox's (4) vapor-pressure equations for 15 hydrocarbons are part of a larger project carried out by the Bureau of Mines Bartlesville (Okla.) Energy Research Center to determine the thermodynamic properties of hydrocarbons in or related to petroleum. Except for the vapor-pressure values of Willingham et al. (18), Forziati et al. (7), and Pitzer and Scott (14), which in some cases are correlated with present results, there are no experimental data of comparable quality for these compounds in the literature.

Materials

The samples were American Petroleum Institute (API) research-grade hydrocarbons, purified and made available by the API Research Project 58 at Carnegie-Mellon University, A. J. Streiff, Director. The purity of most of the compounds was determined from freezing temperatures vs. fraction melted data observed as a purity monitor by Project 58 or during low-temperature calorimetric measurements made in this laboratory under API Project 62. (Details of the freezing-point measurements carried out on individual compounds in connection with low-temperature thermal studies will appear in separate reports from this laboratory.) An additional check on the purity of seven of the samples was furnished by simultaneous observations of the boiling and condensing temperatures. The small observed differences in temperature (Table I, column 1) substantiate the calorimetric purity values for these compounds and suggest that the impurities present did not affect significantly the observed boiling points of the samples.

Experimental Methods

Static measurements. An inclined-piston manometer, described by Douslin and McCullough (5) and Douslin and Osborn (6), was used for low-pressure measurements below and slightly above room temperature. Briefly, the method consisted of balancing the known weight, W, of a free piston declined from the horizontal by a measured angle, θ, against the pressure exerted by the vapor of the sample placed in a thermostated bath. From the measured area and weight of the piston, the angle of declination, and the acceleration of gravity, the vapor pressure was calculated as a primary quantity, $p = (g/g_{\text{std}})(W \sin \theta)/A$. Corrections were applied, when significant, for vapor head between the piston face and the surface of the liquid.

Ebulliometric measurements. The comparative ebulliometric method described by Waddington et al. (17), and more recently by Osborn and Douslin (12), was used on seven of the hydrocarbons over a pressure range from 70 to 2025 mm Hg. Briefly, the ebulliometric method consisted of comparing boiling temperatures of the hydrocarbon with the boiling temperatures of standard water or standard benzene under equal pressure of a helium gas blanket. From the boiling temperature of the standard substance, the pressure in the ebulliometers was determined by reference to the International Steam

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