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THE LOW-TEMPERATURE HEAT CAPACITIES OF SOLID
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Leonard Finegold and Norman E. Phillips

August 1968

The Low-Temperature Heat Capacities of
Solid Argon and Krypton.*

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ABSTRACT

The specific heats of high-purity argon and krypton have been measured between 0.4 and 12°K, permitting a reliable extrapolation to 0°K. The higher-temperature results are in agreement with those of Morrison et al., but for argon the extrapolation to 0°K is not. At the lowest temperatures the heat capacities are represented by $C = (12/5) \pi^4 R(T/\theta_0)^3$, with $\theta_0 = 92.0^\circ\text{K}$ for argon and 71.9°K for krypton. The apparatus and techniques are described, and the results are compared with theoretical estimates.

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INTRODUCTION

The noble gas solids, with their relatively simple van der Waals attractive forces, are one of the best experimental systems for testing theories of lattice dynamics. A measure of current interest in the field is the number of recent review articles: Since Dobbs and Jones' review¹ of a decade ago, Pollack,² Boato,³ Horton,⁴ and Simmons⁵ have also reviewed the field. Although these reviews treat mainly the perfect crystalline state, there is also now an interest, both theoretical and experimental, in various defect states of the noble gas solids (see e.g., Hartmann and Elliott⁶ and Maradudin⁷). In general, the theories are at their best with the heavier noble gases (argon, krypton, xenon) where one does not have the large zero-point energy effects of helium and neon, and at the lowest temperatures where thermal vibrations are of small amplitude. The Debye characteristic temperature θ and Grüneisen "constant",⁸ and their values θ_0 and γ_0 at 0°K, are convenient parameters for describing experimental or theoretical results.

The comparison between theories and experimental results of the lowest-temperature properties of the heavier noble solidified gases has been much improved during recent years due to the following advances: The availability of high-speed computing machines has allowed the theoretician to test the validity of the mathematical approximations which are necessary to reduce the problem to manageable proportions, and also to

compute more accurate results. On the experimental side, large single crystals of neon, argon, and krypton have been grown^{9,10}--though at the expense of great effort. Dispersion curves for solid neon and krypton have been measured under pressure by Daniels and his associates.^{10,11} Improved experimental techniques, of exceedingly high accuracy in the case of the x-ray work, have determined the Grüneisen γ at zero pressures and temperatures which are effectively 0°K.

The lattice parameter (and hence, the density ρ), the coefficient of thermal expansion, α , and the isothermal compressibility κ have been measured for neon¹² and argon¹³ by Simmons and his associates, who have also measured α and κ for krypton.¹⁴ The specific heat at constant pressure C_p has been measured for neon and xenon by Fenichel and Serin¹⁵ and Fagerstroem and Hollis Hallett.¹⁶ Excellent specific heat measurements for argon from 2° to 86°K, and for krypton from 2° to 115°K were made by Flubacher, Leadbetter, and Morrison¹⁷ and Beaumont, Chihara, and Morrison.¹⁸ To establish θ_0 well, however, one must have measurements at temperatures below $\theta_0/50$, and preferably¹⁹ below $\theta_0/100$, i.e., at below 2°K for argon and krypton. Hence it was decided to measure the heat capacities of argon and krypton to 0.4°K in a helium-3 cryostat, and to overlap the higher-temperature measurements of Morrison et al.^{17,18} for comparison purposes. Below 0.4°K, the heat capacities of solid argon and krypton are so small that they are difficult to measure. However, it is considered that the measurements presented in this paper are of more than sufficient accuracy in θ_0 for existing theories.

EXPERIMENTAL PROCEDURES

The present experimental methods differ from those of Morrison et al. in the following chief particulars: The apparatus was designed to give good specific heat results in the lowest temperature range, whereas that of Morrison et al. was designed to cover the range 2° - 300° K and also to measure vapor pressures. At the lower temperatures, the careful adiabatic shielding, which is required for heat capacity measurements at high temperatures, is not necessary. Advantage was taken of the availability of stable germanium resistance thermometers of high reproducibility,²⁰ usable to 0.3° K,^{21,22} thus avoiding the problems of calibration shifts which Morrison et al. experienced¹⁷ with carbon resistance thermometers. The samples of argon and krypton used were larger than those of Morrison et al. (2.1 moles of argon compared with .16 to .24 moles; 1.6 moles of krypton compared with .11 to .16 moles) so that the unavoidable "background," due to the calorimeter, would not be excessive even at the lowest temperatures. The thermal diffusivity of the samples was not expected to get appreciably worse at temperatures below 1° K.

Calorimeter Vessel

Since the specific heat measurements were to be extended to the lowest possible temperature, it was important to choose a calorimeter material with a low heat capacity. Since the heat capacity of the sample varies approximately as T^3 , a metal

calorimeter, with an electronic heat capacity falling only as T , would appear at first sight to be not as good a choice as a nonmetallic calorimeter. A study was made of possible materials, including glass, polymethyl methacrylate,²³ and beryllium, which has a high θ and low electronic specific heat. A glass calorimeter was actually constructed, but was considered to be too fragile for use. Polymethyl methacrylate and beryllium presented construction problems, especially in their attachment to a gas input capillary of low thermal conductivity, and beryllium is also toxic, requiring special precautions in machining. Finally, it was decided to make the calorimeter of gold-plated copper.

The calorimeter walls were made as thin as possible (.004") consistent with adequate strength, and a spherical shape was chosen (see Fig. 1) for minimum weight and reasonably good heat transfer characteristics. Two spun hemispheres, 2" in diameter, were hard-soldered together: at the (lap) joint were soldered three equally-spaced loops of copper wire, to which were later attached cotton threads. To improve thermal contact with the sample inside, a set of eight semi-circular vanes, at 45° intervals was mounted concentrically with, but not directly touching, the sphere. At their mutual line of contact, the vanes were silver-soldered to each other and to a straight copper wire of .040" diameter. This wire, which was then a diameter of the sphere, was held in position at its lower end by a short concentric stainless steel pin, .005" diameter. The upper part of the wire emerged from the sphere through a .005" thick stainless steel collar: to the portion of the wire outside

the sphere was attached the heater for specific heat measurements. The outermost end of the .040" diameter wire was silver-soldered to one end of a two-inch length of flexible copper braid, of roughly equal cross-sectional area. To the upper end of the braid was silver-soldered half an inch of gold-plated .063" diameter copper wire, which lay between the jaws of the mechanical heat switch by means of which the calorimeter was cooled. The copper braid prevented damage to the fragile calorimeter from stresses due to the operation of the heat switch. The germanium resistance thermometer was attached to the outer surface of the sphere by a copper foil cemented with "7031" varnish,²⁴ and the electrical leads to the thermometer were also thermally anchored to the surface of the sphere with the same varnish. It is well known, for example, from ultrasonic measurements,^{25,26} that the large volume contraction on cooling a noble-gas solid is enough to considerably weaken the fragile van der Waals bond of the solid to the walls of its container, and the construction just described was chosen because, (a) the large contact areas would improve thermal contact to the argon, and (b) the heat pulse from the heater would be delivered more directly to the sample, minimizing the undetected heat loss through the gas input capillary, electrical leads and supports that would result from superheating of the calorimeter wall. The calorimeter was suspended by the gas input capillary (stainless steel .050" o.d. x .006" wall). Lateral motion was prevented by cotton threads and small wedges of expanded polystyrene foam (which had previously been

found useful in specific heat work down to 0.1°K ²⁷). The heater was wound from .0009" diameter 9% tungsten-91% platinum alloy wire²⁸ and was of 1744.8 ohms effective resistance at 4°K . Each end of the heater wire was connected to a length of fine copper wire, wound round the .040" diameter copper wire which was connected to the vanes inside the calorimeter, as a thermal anchor. The other ends of these fine copper wires were attached to one end of a free-standing spiral lead of the same wire used in the heater, which provided thermal insulation. The other ends of the spiral leads were each attached to two copper wires, thermally anchored to the cage surrounding the calorimeter, which were ultimately connected to a current source and a potentiometer. For this conventional arrangement, the usual approximation was made that half of the total resistance (here half of 53.2 ohms) of the 9% W/91% Pt spiral leads was added to the actual heater resistance to provide the effective heater resistance.²⁹

The thermometer was an encapsulated doped germanium resistance thermometer,³⁰ series MHSP-IV, resistance at 4°K of 27 ohms. The four leads were each attached to 9% W/91% Pt wire spirals. The thermometer was calibrated from 0.3°K to 25°K by a combination of magnetic, gas, and vapor-pressure thermometry in this laboratory.²²

Filling of Calorimeter

Ideally, one would like to make measurements on perfect single crystals of the solidified noble gases, but they are

extremely difficult to prepare. Fortunately, for the measurement of a bulk quantity like the specific heat, polycrystalline samples are adequate and at low temperatures the effect of vacancies in at least solid argon³¹ and krypton³² should be negligible. Liquid argon (not quite enough to fill the calorimeter), was condensed into the calorimeter and then frozen, keeping the input capillary warm enough by electrical heating so that no liquid would condense in it. (The capillary was conveniently self-heated by passing an electric current along its length.³³) During freezing, the internal vanes of the calorimeter were connected to the mechanical heat switch, and hence to the refrigerant in the cryostat, so that the sample would preferentially freeze to the vanes before freezing to the spherical surface of the calorimeter. In this way, thermal contact to the sample heater would be preserved as the sample was cooled to liquid helium temperatures. The thermometer response during the actual specific heat measurements showed that the thermal contact of the sample was quite satisfactory. As soon as the sample was completely frozen, as shown by a change in the resistance of the sample thermometer, the heating of the capillary was reduced, and the whole sample cooled further. Care was taken, by the addition of a heater to the capillary near the calorimeter, that the capillary would remain unblocked until the vapor pressure of the solid sample was low enough. The quantity of gas left in the capillary tubing and the filling system was then negligible.

Although the calorimeter, being spherical, had maximum strength for its mass, it was necessary to keep the filling pressure to below 2 atm. for fear of bursting it. The liquid range from the triple point to one atmosphere pressure is only 3.5°K for argon, and 4.0°K for krypton. Hence it was convenient to have an automatic pressure regulator to allow the (large amounts of) gas to condense at reasonable rates at pressures from 0 to 2 atm. To control the temperature of the calorimeter during condensation of the gas, it was easiest to fill the "helium" Dewar surrounding the apparatus with a suitable liquid refrigerant, and to adjust the temperature of the refrigerant by means of the same vapor-pressure controller which was later used to control the liquid helium temperature. For argon, the liquid refrigerant was liquid oxygen. For krypton, carbon tetrafluoride (commercial "Freon 14") was used. The gases were high purity cylinder gases.³⁴ The supplier's batch analysis of impurities, in parts per million was as follows:

Argon: O₂, 1; N₂, 1; H₂O, 0.4; hydrocarbons, <1; H₂, <1.

Krypton: O₂, 2.4; N₂, <50; H₂O, 9.2; hydrocarbons, <1; Xe, <10.

At the end of the measurements, the gases were stored in large metal bylinders at $\approx$ 2 atm. Samples were later analyzed on a mass spectrometer³⁵ and the following impurities (ppm) detected:

"Argon: N₂ (or CO) 26^{+0}_{-10} ; H₂O 10^{+0}_{-5} ; C₂H₄ 15^{+0}_{-5} ; C₂H₂ 11^{+0}_{-3}
CH₄ 10^{+0}_{-5} ; H₂ 110^{+0}_{-10} .

Krypton: O_2 1 ± 1 ; N_2 <25 ; H_2O <16 ; CH_4 15 ± 3 ; C_2H_2 ≤ 5 ;
 C_2H_4 ≤ 20 ; C_2H_6 ≤ 8 ; H_2 98 ± 6 ; CO ≤ 15 ; CO_2 10 ± 3 .

The limits on undetected impurities are, in general, less than 5 ppm for any single impurity. Owing to low sensitivity, the limit on detection of helium is 10 ppm and of neon is 40 ppm. Note that neon must be determined on mass 22, which isotope is only 10% abundant."

It is likely that much of these impurities were desorbed from the walls of the metal storage containers used after the measurements were completed, and hence, were not present in the specific heat samples.

Because the samples were large (approximately two gram moles), the measurement of mass by the conventional method (measurements of its pressure and volume at known temperature) would have been awkward. Hence, the mass was determined by direct weighing to well within 0.1% accuracy in a pressure vessel, which was also made part of the gas handling and retrieval system.³⁶ The numbers of gram-moles were 2.1385 for the argon sample (assuming a molecular weight 39.944) and 1.6055 for the krypton sample (molecular weight 83.80).

The cool-down procedure, after the argon or krypton sample had been well frozen, was briefly as follows: The liquid refrigerant was removed from the Dewar, and a flow of cool helium gas to the Dewar commenced. The temperature of the sample did not increase appreciably during this time. Liquid helium-4 was then transferred; care was taken that there was

no exchange gas surrounding the calorimeter. When the calorimeter was at 4.2°K , the pressure above the liquid helium-4 was reduced until the temperature was about 1.2°K . Helium-3 was then allowed to condense into its chamber: when it had condensed, its vapor pressure was reduced until a temperature below 0.3°K was attained.

Specific Heat Measurements

The well-known heat-pulse method of measuring specific heats³⁷ was used. The thermometer resistance was measured by the usual four-probe method, using a six-dial potentiometer³⁸ and a chopper amplifier with a few nano-volts resolution.³⁹ The output of the amplifier was fed to a variable-speed chart recorder. Temperature increments were from $T/20$ to $T/10$: There was no observable dependence of the results on heater power. The quantity of heat applied to the sample was measured to within 0.1%. Measurements could not be made reliably below about 0.4°K , because of electrical and vibrational noise (even though the cryostat was on anti-vibration supports).

The specific heat of the empty calorimeter was measured in a later run, and in the argon measurements accounted for 23% of the measured heat capacity at 0.5°K and 7% at 1°K . For the krypton measurements, the corresponding figures are 16% and 5%.

Possible Existence of Two Phases

Meyer, Barrett, and Haasen⁴⁰ discovered the existence of an hcp phase in solid argon in addition to the more usual fcc

structure. This discovery was encouraging, because theories based on central two-body forces of the Mie-Lennard-Jones type had predicted that the hcp structure would be slightly more stable than the fcc.⁴¹ However, of the noble gas solids only helium had previously been shown to exhibit polymorphism. Hence many authors have postulated noncentral many-body forces, but there is still discussion about the necessity of this postulate.⁴² Feldman⁴³ has calculated the difference between θ_0 for the hcp and fcc phases based on a Mie-Lennard-Jones all-neighbor model in the quasi-harmonic approximation, and found that $[\theta_0(\text{hcp}) - \theta_0(\text{fcc})]/\theta_0(\text{fcc})$ is of the order of 2% for argon. Present specific heat techniques are therefore sufficient to detect the difference between a completely hcp sample of solid argon and a completely fcc one. Should a sample be of mixed hcp and fcc phases--as is indeed more probable than hcp alone--then it is of course necessary to know, by independent means, the proportion of each phase present. (An analogous situation is well discussed in Martin's analysis of the martensitic change in sodium and lithium.⁴⁴) An attempt was made in this work to detect a difference of the above type. In Run I, an argon sample was cooled as rapidly as possible from 80°K to 4°K, in the hope that the rapid cooling would induce as much stress, and hence, as much hcp phase as possible.⁴⁰ After the specific heat measurements had been made, the same sample was annealed at 77°K for half a day, and then cooled slowly to 4°K, in the expectation that the sample would be mainly, if not all, fcc. The measurements of Run II were then

made. Care was taken that there were no changes in the apparatus, or in the sample mass, between Runs I and II. A comparison of the results of Run I and Run II shows that the low-temperature θ was unchanged, within the precision of the measurements. However, it is estimated, on the basis of the predicted 2% difference in θ_0 and a precision of 1% in C , that as much as 17% of the hcp phase could have been present. In the work Barrett and Meyer,^{40,45} the x-rays do not penetrate deeply into the solid, and so it is possible that the hcp phase existed only near the surface. In electron diffraction experiments on thin films of solidified noble gases, Curzon and Pawlowicz⁴⁶ found that when observed in transmission, argon, neon, krypton, and xenon crystallized in the fcc structure. However, when observed in reflection, krypton showed an hcp form. The possibility of a phase transformation occurring at a solid argon surface has been discussed by Burton and Jura.⁴⁷

ANALYSIS OF RESULTS

In Figs. 2 and 3, the heat capacities are plotted as C/T^3 vs T and compared with the measurements of Morrison and coworkers.^{17,18} Smoothed values of C/T^3 , corresponding to the curves of Figs. 2 and 3, are given in Table I, which also includes equivalent values of the effective Debye temperatures. As Fig. 2 shows, the results obtained in the two argon runs do not differ significantly. They have, therefore, been considered together in the following analysis, and no distinction between them is made in subsequent

figures. For both argon and krypton our results differ from the earlier work by an amount which is, over most of the common temperature range, qualitatively similar in temperature dependence and only slightly greater than the combined scatter of the points. However, the extension of the new results to 0.5°K and their greater precision at temperatures below 5°K define the extrapolation of 0°K more precisely, and, as will be shown, this leads to significant differences in the dependence of θ/θ_0 on T/θ_0 .

The data have been analysed on the usual assumption that the heat capacity can be expressed by a series of odd powers of T starting with T^3 ,

$$C = \sum_{i=1}^n A_{2i+1} T^{2i+1}. \quad (1)$$

The coefficients of the T^3 terms, and the values of θ_0 , were obtained by extrapolation of plots of C/T^3 vs T^2 to $T^2 = 0$, as shown in Figs. 4 and 5. Since the extrapolations are short, the θ_0 values, 92.0°K for argon and 71.9°K for krypton, are determined quite precisely. The value for krypton is close to that obtained by Beaumont, Chihara, and Morrison,¹⁸ 71.7°K, but there is a significant difference (corresponding to 4% in heat capacity) between our value for argon and the 93.3°K reported by Flubacher, Leadbetter, and Morrison.¹⁷ The coefficients of the T^5 terms, A_5 , which correspond to the slopes of the lines in Figs. 4 and 5, are not so well established--their values are small, and depend strongly on the temperature interval over

which the straight-line approximation is made. These conclusions were verified by making a number of least-squares fits of the data to Eq. (1) with different values of n and different high-temperature cutoffs. With a sufficient number of terms this equation fits all the data with an rms deviation of 0.8% for argon and 0.9% for krypton. (The difference is apparently associated with a relatively large number of low-precision low-temperature points in the krypton data.) All fits which gave an rms deviation of 1.25% or less gave values of A_3 within 0.5% of those determined graphically, but the corresponding values of A_5 differed from each other by considerably larger amounts. The inclusion of even powers to T in the expansion usually improved the fit obtained with a given number of terms but the magnitude and sign of the coefficients of terms other than the T^3 term fluctuated erratically with changes in the number of terms. The T^3 coefficients, however, were still substantially the same as those obtained graphically except for some of the fits to the krypton data with a series containing a T^4 term. The downturn in C/T^3 for the lowest-temperature krypton points and the dip at $T \approx 1.4^\circ\text{K}$ (which also occurs in the argon data and presumably reflects an irregularity in the temperature scale) is probably responsible for this exception.

DISCUSSION

The effective Debye temperature has been calculated from the heat capacities in the usual way. (No correction for the difference between C_p and C_v or for thermal expansion is

necessary at these temperatures.) As shown in Fig. 6, plots of θ/θ_0 vs T/θ_0 for argon and krypton in this temperature range are closely similar. Figure 6 also shows the results of calculations by Horton and Leech.⁴⁸ The approach of Horton and Leech, and of Grindlay and Howard in similar calculations,⁴⁹ was to consider a simplified model in which any mathematical approximations, necessary for the evaluation of the model, were well understood. They assumed a Mie-Lennard-Jones potential in the harmonic approximation, including zero-point energy only in the Boltzmann thermal distribution terms. They then tested the sensitivity of their model to the exact form of the Mie-Lennard-Jones potential chosen and to the number of atomic neighbors whose interactions are considered important. Even though the effects of anharmonicity were specifically not included, this approach appears at present to be more useful than one in which an attempt is made to include all effects, but in which the mathematical assumptions may have more influence than the physical assumptions. Horton and Leech present calculations for nearest neighbors only (1N), nearest- and next-nearest neighbors only (2N) and all neighbors (AN). For temperatures up to the minimum of the reduced θ -T curves, they find a law of corresponding states for argon and krypton, for 1N, 2N, and AN models. Our experimental results agree with such a law, in contrast with the earlier results in this temperature range. Since the assumption of a Mie-Lennard-Jones potential would be expected to give a law of corresponding states, in the absence of zero-point energy, it appears that zero-point energy effects

are indeed small here. Our experimental results fall midway between Horton and Leech's 1N and AN calculations for a 12-6 potential, and are in reasonable agreement with, but a little higher than, their 2N calculations. According to "commonly accepted folklore" the effect of anharmonicity is to raise the (harmonic) reduced θ -T curves with increasing temperature,⁴⁸ and so might bring the 2N calculated curves into better agreement with our results. Estimates of anharmonic effects are difficult to make. One such estimate, due to Klein,⁵⁰ would expand the T/θ_0 axis of Fig. 6 by approximately 4% for argon and 2% for krypton. However, the fact that the AN calculation does not give the best agreement with experiment implies that corrections are needed to the potential, either in its shape or by the inclusion of three-body interactions. Also, θ -T plots show that different potentials are needed to fit different temperature regions,⁵¹ confirming that the Mie-Lennard-Jones potential is still inadequate.

In summary, it would seem that these results are consistent with present views of this field: that whereas some years ago the theories were more advanced than the experimental data available, now the need is for a better understanding of the interatomic forces as well as for improved anharmonic theories.

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Table I. Smoothed values of C/T^3 and θ/θ_0 for argon and krypton. (θ_0 was taken as 91.953 and 71.896 for argon and krypton, respectively.)

T (°K)	Argon		Krypton	
	C/T^3 (mJ/mole-°K ⁴)	θ/θ_0	C/T^3 (mJ/mole-°K ⁴)	θ/θ_0
0.5	2.502	0.9997	5.237	0.9996
1.0	2.510	0.9987	5.265	0.9978
1.5	2.527	0.9964	5.331	0.9937
2.0	2.557	0.9925	5.447	0.9866
2.5	2.602	0.9868	5.622	0.9762
3.0	2.662	0.9793	5.868	0.9624
3.5	2.737	0.9703	6.170	0.9464
4.0	2.827	0.9599	6.488	0.9307
4.5	2.927	0.9488	6.784	0.9166
5.0	3.029	0.9380	7.013	0.9058
5.5	3.126	0.9282	7.158	0.8981
6.0	3.214	0.9192	7.227	0.8927
6.5	3.290	0.9114	7.225	0.8888
7.0	3.350	0.9048	7.159	0.8861
7.5	3.390	0.8993	7.039	0.8843
8.0	3.406	0.8953	6.867	0.8830
8.5	3.398	0.8925	6.657	0.8829
9.0	3.368	0.8908	6.421	0.8828
9.5	3.322	0.8897	6.169	0.8827
10.0	3.263	0.8888	5.910	0.8825
10.5	3.197	0.8881	5.648	0.8821
11.0	3.123	0.8871	5.386	0.8815
11.5	3.045	0.8860	5.124	0.8811
12.0	2.964	0.8845	4.862	0.8810
12.5	2.880	0.8828	4.600	0.8817

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APPENDIX I
Measured Heat Capacities of Argon

Run I

T(°K)	C(mJ/mole-°K)	T(°K)	C(mJ/mole-°K)
4.8913	354.0	1.8332	15.71
5.4764	510.9	1.9575	19.11
6.0978	731.8	2.1398	25.11
6.6429	971.6	2.3312	32.73
7.1685	1235.0	2.5233	41.68
8.0024	1735.0	2.7478	54.33
8.7131	2216.0	2.9965	71.17
4.4551	255.5	3.2243	89.91
0.4978	0.3083	3.4492	111.1
0.5334	0.3741	3.7407	143.8
0.5693	0.4690	4.0687	189.9
0.5960	0.5364	4.4499	255.7
0.6292	0.6176	4.8235	331.1
0.6587	0.7065	1.4206	7.212
0.6896	0.8131	1.5774	9.906
0.8283	1.423	1.6606	11.56
0.8817	1.725	1.7543	13.71
0.9578	2.237	1.8423	15.89
1.0376	2.826	1.9193	17.85
1.1253	3.584	1.9920	20.21
1.1735	4.020	2.0690	22.71
1.2253	4.603	0.5104	0.3368
1.2844	5.288	0.5576	0.4270
1.3414	6.050	0.6003	0.5313
1.4059	6.973	0.6052	0.5487
1.4735	7.958	0.6613	0.7315
1.5289	9.035	0.7147	0.9246
2.0727	22.85	0.7621	1.130
2.1614	25.94	0.8100	1.317
2.1183	24.42	0.8617	1.616
2.2907	31.12	0.9265	2.007
2.3979	35.85	0.9896	2.439
2.5257	41.72	0.9508	2.173
2.6255	47.21	1.0195	2.648
2.7569	55.02	1.0927	3.293
2.9071	64.64	1.2683	5.144
3.0710	76.88	1.3650	6.403
3.2732	94.38	4.3091	231.2
3.5483	121.5	4.8241	334.1
3.8604	160.2	5.3373	466.8
4.2258	216.1	5.8326	630.2

(Continued)

T(°K)	C(mJ/mole-°K)	T(°K)	C(mJ/mole-°K)
1.2105	4.507	6.3069	816.2
1.2989	5.480	6.9139	1103.0
1.3832	6.630	8.2931	1948.0
1.4828	8.167	9.0860	2480.0
1.5852	10.07	11.2261	4366.0
1.7119	12.77		

Run II

0.4367	0.2130	10.0900	3341.0
0.4840	0.2818	11.2269	4376.0
0.5332	0.3765	4.5362	275.1
0.5833	0.4976	4.9792	372.3
0.6374	0.6486	5.4175	495.7
0.6645	0.7397	5.9462	672.1
0.7100	0.8876	6.5000	906.8
0.7669	1.122	1.2380	4.785
0.8464	1.540	1.3722	6.523
0.8934	1.793	1.5863	10.13
0.9205	1.949	1.6516	11.42
1.0026	2.555	1.7380	13.42
1.1060	3.418	1.8316	15.75
1.2146	4.513	1.9309	18.43
1.2511	4.930	2.0162	21.19
1.3693	6.455	2.1260	24.72
1.4809	8.167	2.2769	30.53
0.3960	0.1553	2.4627	38.88
0.5527	0.4374	2.6562	49.03
0.6546	0.7025	2.8708	62.44
0.7183	0.9353	3.0846	78.30
0.7722	1.153	3.3288	99.79
0.8648	1.642	3.5949	127.9
0.9569	2.187	3.9063	167.0
1.0338	2.761	4.2602	222.1
1.1024	3.313	4.6114	289.6
1.1528	3.840	4.9798	375.1
1.2036	4.395	1.2428	4.838
1.3098	5.669	1.3559	6.299
1.3968	6.889	1.4604	7.863
1.4903	8.342	1.5269	9.020
0.4969	0.3041	1.6035	10.49
0.5910	0.5338	1.9228	18.24
0.6450	0.6813	2.0508	22.20
0.7042	0.8869	2.2399	29.21
0.7693	1.162	2.4571	38.78
0.8449	1.543	2.6673	49.92

(Continued)

T(°K)	C(mJ/mole-°K)	T(°K)	C(mJ/mole-°K)
4.1810	210.1	2.9187	66.09
4.6041	287.6	3.1743	86.27
5.1224	408.3	3.4365	111.5
5.6733	574.4	3.7313	144.6
6.2357	784.6	4.6987	310.2
7.5256	1456.0	5.1263	417.5
8.3630	1995.0	1.4946	8.44
9.1864	2598.0		

APPENDIX II

Measured Heat Capacities of Krypton

T(°K)	C(mJ/mole-°K)	T(°K)	C(mJ/mole-°K)
4.6496	688.7	0.8480	3.219
5.1110	942.5	0.9368	4.325
5.5990	1263.0	1.0076	5.412
5.9839	1552.0	1.1048	7.091
6.2566	1775.0	1.1996	9.140
6.5436	2017.0	1.2906	11.31
6.8930	2361.0	1.4011	14.58
7.2669	2726.0	1.5133	18.40
7.6586	3143.0	1.6322	23.33
8.1047	3648.0	0.5089	0.6796
8.6887	4334.0	0.5602	0.9173
9.3577	5105.0	0.6133	1.206
10.1437	6088.0	0.6721	1.576
12.2790	8738.0	0.3600	0.2390
11.0851	7270.0	0.3872	0.2970
1.2404	10.11	0.4198	0.3826
1.3379	12.67	0.4817	0.5904
1.4466	16.14	0.5269	0.7796
1.5450	19.69	0.5803	1.047
1.6552	24.39	0.6417	1.416
1.7768	30.39	0.6910	1.757
1.8961	36.79	0.7565	2.295
2.0212	45.13	0.8350	3.115
2.1616	55.42	0.9155	4.047
2.3144	68.84	1.0066	5.441
2.4920	86.53	1.1086	7.240
2.7118	113.5	1.2068	9.316
2.9379	147.1	1.3168	12.09
3.1875	193.2	1.4260	15.44
3.4782	258.5	1.5257	18.97
3.8040	348.5	1.6066	22.31
4.1726	479.3	1.7651	29.79
4.5926	658.3	1.9367	39.64
5.0652	913.0	2.1092	51.81
0.3684	0.2540	2.3038	68.21
0.4114	0.3683	2.5354	92.28
0.4581	0.5175	2.8180	129.2
0.4994	0.6347	3.1263	182.5
0.5452	0.8265	3.4622	256.5
0.5949	1.100	3.8311	357.9
0.6566	1.480	4.2416	505.7
0.7106	1.883	4.7103	723.5
0.7716	2.414		

Figure Captions

Fig. 1. The calorimeter.

Fig. 2. The heat capacity of argon between 0.4 and 12°K. FLM refers to Flubacher, Leadbetter, and Morrison (Ref. 17) and the dashed curve represents their smoothed values and extrapolation to 0°K. The solid curve corresponds to the smoothed values given in Table I.

Fig. 3. The heat capacity of krypton between 0.4 and 12°K. BCM refers to Beaumont, Chihara, and Morrison (Ref. 18) and the dashed curve represents their smoothed values and extrapolation to 0°K. The solid curve corresponds to the smoothed values given in Table I.

Fig. 4. The heat capacity of argon below ~3°K.

Fig. 5. The heat capacity of krypton below ~3°K.

Fig. 6. Reduced Debye temperature plots for the argon and krypton data. The solid curves represent calculations by Horton and Leech (Ref. 48). 1N, 2N, and AN refer to first-, first- and second-, and all-neighbor calculations, respectively.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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