Some Heat Capacities of Argon in Ranges 5–1000 Atm and 180–450° K

Examination and Correction Using Sonic Velocity Data

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A compilation by Din of various properties of gaseous argon, including *pvT* data and heat capacities calculated from their second derivatives, represents the only literature source of C_p and C_v at high pressures. Sonic velocity data from two other sources have been utilized to compute heat capacities using only first derivatives, implying improved precision. Improvement is not significant below 200 atm but becomes increasingly appreciable in the 200–1000 atm range where failure of the second derivative method is attributable to a more complex deviation of argon from ideality. New, smoothed values of C_p and C_v are listed for the ranges 200–1000 atm and 300–400° K.

Because of experimental difficulties, gaseous heat capacities at constant pressure (C_p) and constant volume (C_v) are seldom measured directly. They can usually be calculated with higher precision from other, more measurable quantities combined with thermodynamic relationships. One method is to utilize pressure-volume-temperature (pvT) data to evaluate the integrands in the expression

$$C_p = C_{p_0} - T\int_0^p (\partial^2 v/\partial T^2)_p dp \qquad (1)$$

Din (*1*) followed this procedure in his careful and extensive work on the thermodynamic properties of argon, using the resulting C_p values to compute entropies and finally determining C_v's from slopes of the entropy curves. A shortcoming in this sequence is the loss of precision incurred in computing the second derivative in Equation 1. Even for conditions where the gas is close to ideal the pvT data must be highly accurate to yield reliable C_p values, while for nonideal gas states, implying large values of or sharp changes in the "curvature" $(\partial^2 v/\partial T^2)_p$, the fundamental data must be extraordinary. Hence heat capacities derived in this way tend to be less reliable, particularly for high pressures.

Another procedure for computing heat capacities, utilizing sonic velocity data, involves only first derivatives of the pvT network, thus avoiding the difficulty described above and implying more accurate results, which should be expected since an additional fundamental measurement has been added. The calculations reported here combine the pvT compilation of Din with sonic velocity data from two other sources, yielding sets of heat capacity values for argon which are compared with those listed by Din.

PROCEDURE AND TABULATED CALCULATIONS

The ratio and difference of the heat capacities are given by the two thermodynamic relationships

$$C_p/C_v = -(c_0^2/v^2)(\partial v/\partial p)_T M \qquad (2)$$

$$C_p - C_v = -T[(\partial v/\partial T)_p]^2(\partial p/\partial v)_T \qquad (3)$$

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where c_0 is the plane-wave sonic velocity and M the atomic weight. By evaluating the right-hand sides of these equations at selected values of p and T, the two heat capacities at these conditions may be calculated. The thermal expansion derivatives $(\partial v/\partial T)_p$ were obtained numerically by first fitting values of v along isobars in the Din tables to local power series of the form

$$v = a_0 + a_1 T + a_2 T^2 \qquad (4)$$

where the sets of empirical constants a_i are functions of pressure only, and then using these constants in the following formula, obtained by differentiating Equation 4:

$$(\partial v/\partial T)_p = a_1 + 2\, a_2 T \qquad (5)$$

Although the computer program could easily accommodate series of any order, three data points were adequate for the accuracy required here—i.e., taking one value of v at the desired p,T and the two flanking v values along an isobar—reflecting the close approach to linearity of the isobars for the ranges studied. The isothermal compressibility derivatives $(\partial v/\partial p)_T$ were computed from Din isotherms, using the formulas

$$pv = b_0 + b_1 p + b_2 p^2 \qquad (6)$$

$$[\partial(pv)/\partial p]_T = b_1 + 2\, b_2 p \qquad (7)$$

$$(\partial v/\partial p)_T = 1/p\,\{[\partial(pv)/\partial p]_T - v\} \qquad (8)$$

where the sets of constants b_i are functions of temperature only. Again, three term series were adequate because of the small deviations from linearity of the relationship pv vs. T throughout the ranges of interest. As shown in columns 5 and 6 of Tables I and II, calculated derivatives are listed to four-figure precision. The use of five terms (and hence five data points) in Equations 4 and 6 would have changed the fourth figure for some of these values. However, this refinement was not justified since the final calculated values of the heat capacities were made to only three figures.

Sonic velocities were obtained from two sources: (1) Itterbeek (*2*), who employed an ultrasonic interferometer having a nominal frequency of 500 kHz to obtain data on argon within 174–300° K and 2–72 atm. His values were reported to four-figure precision, as shown in column four of Table I. (2) Lacam (*3*), who utilized a monochromatic light diffraction technique and an acoustic pulse of 2–5 MHz

Table I. Heat Capacities of Argon in Ranges 180–290° K and 5–50 Atm

(Summarized calculations and comparison)[a]

	Primary data			Calcd derivatives		C_p, cal/g atom °K		C_v, cal/g atom °K	
Pressure, atm	Temp, °K	Vol, Din (*1*), cc/g atom	Sonic velocity Itterbeek (*2*), m/sec	$(\partial v/\text{-}p)_T$, Eq 8, cc/g atom atm	$(\partial v/\partial T)_p$, Eq 5, cc/g atom °K	Calcd, Eqs 2 & 3	Lit, Din (*1*)	Calcd, Eqs 2 & 3	Lit, Din (*1*)
%	180	2894	248.0	−590.9	17.15	5.22	5.22	3.05	3.03
	200	3235	261.0	−656.5	16.95	5.16	5.18	3.04	3.01
	220	3572	275.6	−722.1	16.80	5.08	5.10	3.00	3.00
	240	3907	288.5	−787.6	16.70	5.02	5.05	2.96	3.00
	260	4242	300.4	−853.2	16.75	5.09	5.03	3.01	3.00
	290	4742	317.6	−951.8	16.65	5.03	5.02	2.99	3.00
10	180	1417	246.6	−147.8	8.900	5.39	5.52	3.05	3.06
	200	1593	261.1	−164.2	8.750	5.31	5.37	3.05	3.04
	220	1767	275.2	−180.5	8.650	5.25	5.25	3.0−	3.03
	240	1938	288.4	−196.9	8.550	5.15	5.15	3.00	3.03
	260	2109	300.7	−213.3	8.500	5.14	5.10	3.01	3.02
	290	2363	318.3	−237.8	8.400	5.05	5.07	2.97	3.01
20	180	678	243.8	−37.07	4.850	5.87	6.26	3.11	3.13
	200	772	260.0	−41.05	4.700	5.72	5.85	3.12	3.10
	220	864	274.8	−45.07	4.500	5.39	5.56	3.00	3.08
	240	954	288.4	−49.10	4.500	5.51	5.36	3.11	3.07
	260	1043	301.1	−53.25	4.400	5.34	5.24	3.05	3.05
	290	1174	319.4	−59.45	4.350	5.27	5.18	3.04	3.05
30	180	430	241.3	−16.51	3.600	6.67	7.14	3.26	3.20
	200	499	259.9	−18.20	3.350	6.14	6.40	3.15	3.15
	220	564	274.5	−20.00	3.200	5.85	5.89	3.12	3.12
	240	627	288.5	−21.84	3.050	5.48	5.57	3.00	3.10
	260	688	301.7	−23.64	3.050	5.60	5.40	3.12	3.09
	290	777	320.7	−26.42	2.950	5.30	5.29	2.98	3.08
50	180	229	237.7	−+.260	2.950	9.71	9.40	3.65	3.31
	200	280	260.6	−6.580	2.300	7.01	7.67	3.12	3.24
	220	324	275.8	−7.200	2.150	6.65	6.63	3.23	3.20
	240	364.9	289.5	−7.836	1.985	6.01	6.02	3.09	3.17
	260	404.3	304.0	−8.510	1.940	5.88	5.72	3.10	3.15
	290	461.1	323.2	−9.490	1.860	5.61	5.53	3.05	3.13

[a] Constants and conversion factors used: atomic weight of argon = 39.944 g/g atom, 1 liter atm = 101.325 J, 1 cal = 4.1868 J.

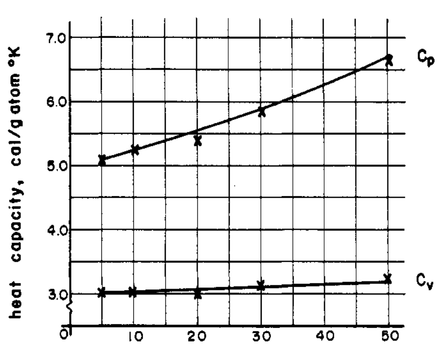

Figure 1. Comparison of argon heat capacities at 220° K
x Calculated from Itterbeek (2) sonic velocity data
—Literature values from Din (1)

to cover the ranges 298–473°K and 50–1100 atm. His measurements, as shown in column four of Table II, were to three-figure precision.

These sonic velocity data dictated the ranges of pressure and temperature over which calculations were performed. As shown above, the ranges vary widely for the two sources, particularly for the pressure variable, the calculations falling naturally into two separate categories which are presented in Tables I and II. The points chosen for calculation are at even increments of p and T, conforming to the arrangement in the Din tables. This made it necessary to interpolate the sonic velocities, which posed no difficulty since both the Lacam and Itterbeek data fall on smooth curves which approach linearity. Tables I and II present the pressure ranges of 5–50 and 50–1000 atm, respectively, giving primary data, calculated derivatives, and, finally, C_p and C_v values which are listed just as calculated and are unsmoothed. Adjacent columns of C_p and C_v from Din (*1*) are listed for comparison. As shown, the precision of the calculated heat capacities for both pressure ranges is given uniformly to three figures, or ± 0.01 cal/g atom °K, which is the same as the literature (Din) values. Although some of the primary data and intermediate calculated values are listed to higher precision, four figures being characteristic of most of the volumes, the derivatives, and some of the sonic velocities, this was done merely to accommodate rounding off the calculated heat capacities.

DISCUSSION

Rough inspection of the two pairs of columns on the right side of Table I shows that agreement between calculated (based on sonic velocities) and literature (based on second derivatives—i.e., Equation 1) values is quite good for both C_p and C_v. This impression is substantiated by isotherms such as Figure 1 which shows both calculated points and literature values (solid curves) at a temperature of 220°K or about the midrange of the Itterbeek data set. The scatter of the calculated points is minimal, at this and the other temperatures, and it must be concluded,

Table II. Heat Capacities of Argon in Ranges 300–450° K and 50–1000 Atm

(Summarized calculations and comparison)

Primary data				Calcd derivatives		C_p, cal/g atom °K		C_v, cal/g atom °K	
Pressure, atm	Temp, °K	Vol, Din (1), cc/g atom	Sonic velocity Lacam (3) m/sec	$(\partial v/\partial p)_T$, Eq 8, cc/g atom atm	$(\partial v/\partial T)_p$, Eq 5, cc/g atom °K	Calcd, Eqs 2 & 3	Lit, Din (1)	Calcd, Eqs 2 & 3	Lit, Din (1)
50	300	479.6	327	−9.792	1.842	5.68	5.50	3.16	3.12
	320	516.1	339	−10.47	1.805	5.50	5.43	3.09	3.11
	340	551.8	350	−11.12	1.778	5.38	5.38	3.04	3.10
	360	587.2	362	−11.80	1.760	5.28	5.34	2.99	3.09
	380	622.2	372	−12.45	1.743	5.21	5.30	2.97	3.08
	400	656.9	381	−13.11	1.731	5.20	5.28	2.99	3.08
	450	743.0	403	−14.73	1.715	5.24	5.24	3.07	3.08
100	300	235.4	335	−2.419	1.003	6.25	6.09	3.23	3.24
	320	255.2	349	−2.590	0.9775	6.00	5.93	3.14	3.22
	340	274.5	360	−2.756	0.9550	5.86	5.81	3.13	3.20
	360	293.4	371	−2.922	0.9350	5.69	5.71	3.08	3.19
	380	311.9	382	−3.087	0.9100	5.46	5.64	2.99	3.17
	400	329.8	391	−3.250	0.8976	5.41	5.58	3.01	3.16
	450	375.0	414	−3.672	0.8930	5.47	5.51	3.11	3.14
200	300	117.4	368	−0.5607	0.5483	7.20	7.22	3.31	3.43
	320	128.3	380	−0.6078	0.5350	6.95	6.89	3.31	3.39
	340	138.8	389	−0.6568	0.5175	6.59	6.64	3.24	3.36
	360	149.0	398	−0.7025	0.5050	6.41	6.42	3.24	3.34
	380	159.0	407	−0.7475	0.4950	6.26	6.26	3.25	3.32
	400	168.8	416	−0.7925	0.4843	6.07	6.14	3.21	3.30
	450	192.3	437	−0.9064	0.4610	5.56	5.94	3.01	3.26
300	300	82.1	418	−0.2198	0.3733	8.28	7.78	3.68	3.58
	320	89.3	424	−0.2460	0.3575	7.43	7.39	3.40	3.54
	340	96.4	430	−0.2713	0.3500	7.01	7.07	3.29	3.51
	360	103.3	436	−0.2947	0.3425	6.72	6.82	3.26	3.48
	380	110.1	442	−0.3192	0.3375	6.48	6.62	3.20	3.45
	400	116.8	450	−0.3417	0.3284	6.11	6.45	3.05	3.43
	450	132.4	467	−0.3963	0.3050	5.26	6.17	2.70	3.38
400	300	66.3	471	−0.1128	0.2683	8.35	8.15	3.71	3.71
	320	71.6	471	−0.1272	0.2600	7.64	7.72	3.52	3.68
	340	76.7	473	−0.1427	0.2550	7.05	7.36	3.30	3.64
	360	81.8	475	−0.1570	0.2500	6.66	7.05	3.19	3.61
	380	86.7	479	−0.1709	0.2450	6.28	6.81	3.05	3.58
	400	91.6	485	−0.1848	0.2401	5.92	6.62	2.89	3.56
	450	103.0	498	−0.2162	0.2230	5.03	6.25	2.53	3.51
500	300	57.7	524	−0.06740	0.2083	8.59	8.39	3.92	3.84
	320	61.8	518	−0.07700	0.2000	7.57	7.95	3.55	3.80
	340	65.7	516	−0.08600	0.1950	6.98	7.54	3.34	3.77
	360	69.6	515	−0.09560	0.1925	6.55	7.20	3.17	3.74
	380	73.4	516	−0.1042	0.1900	6.27	6.92	3.08	3.71
	400	77.2	520	−0.1128	0.1866	5.92	6.69	2.94	3.68
	450	86.1	529	−0.1324	0.1760	5.18	6.29	2.63	3.63
600	300	52.2	575	−0.04567	0.1683	8.32	8.56	3.81	3.95
	320	55.5	566	−0.05211	0.1625	7.38	8.11	3.46	3.92
	340	58.7	560	−0.05800	0.1575	6.78	7.65	3.26	3.89
	360	61.8	556	−0.06422	0.1550	6.36	7.28	3.10	3.86
	380	64.9	555	−0.07011	0.1550	6.24	6.96	3.09	3.83
	400	68.0	556	−0.07600	0.1524	5.91	6.72	2.96	3.81
	450	75.3	559	−0.08889	0.1450	5.33	6.31	2.76	3.52
800	300	45.4	660	−0.02556	0.1200	7.71	8.81	3.62	4.17
	320	47.7	648	−0.02881	0.1175	7.13	8.31	3.42	4.14
	340	50.1	642	−0.03206	0.1150	6.55	7.78	3.15	4.12
	360	52.4	635	−0.03513	0.1125	6.17	7.33	3.03	4.10
	380	54.6	629	−0.03838	0.1100	5.77	6.99	2.87	4.08
	400	56.8	627	−0.04131	0.1100	5.71	6.72	2.87	4.06
	450	62.3	623	−0.04131	0.1100	5.69	6.30	3.00	4.02
1000	300	41.3	735	−0.01669	0.09833	8.08	8.88	3.87	4.36
	320	43.2	723	−0.01863	0.09250	6.92	8.36	3.36	4.35
	340	45.0	713	−0.02057	0.09000	6.37	7.81	3.13	4.34
	360	46.8	703	−0.02243	0.08750	5.96	7.31	2.98	4.33
	380	48.5	696	−0.02437	0.08750	5.84	6.95	2.95	4.32
	400	50.3	693	−0.02603	0.08643	5.71	6.68	2.93	4.31
	450	54.7	686	−0.03046	0.08600	5.63	6.25	2.98	4.29

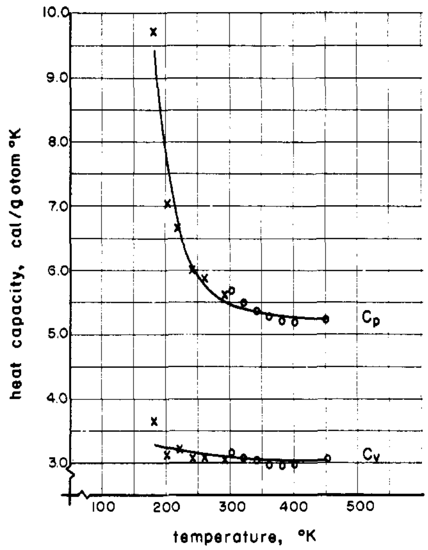

Figure 2. Comparison of argon heat capacities at 50 atm
x Calculated from Itterbeek (2) sonic velocity data
O Calculated from Lacam (3) sonic velocity data
— Literature values from Din (1)

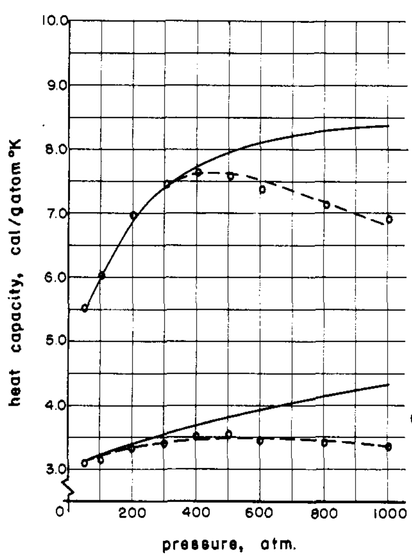

Figure 3. Comparison of argon heat capacities at 320° K
O Calculated from Lacam (3) sonic velocity data
— Literature values from Din (1)

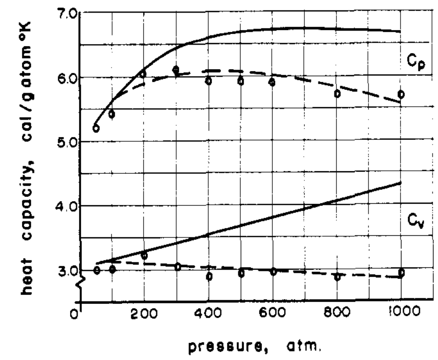

Figure 4. Comparison of argon heat capacities at 400° K
O Calculated from Lacam (3) sonic velocity data
— Literature values from Din (1)

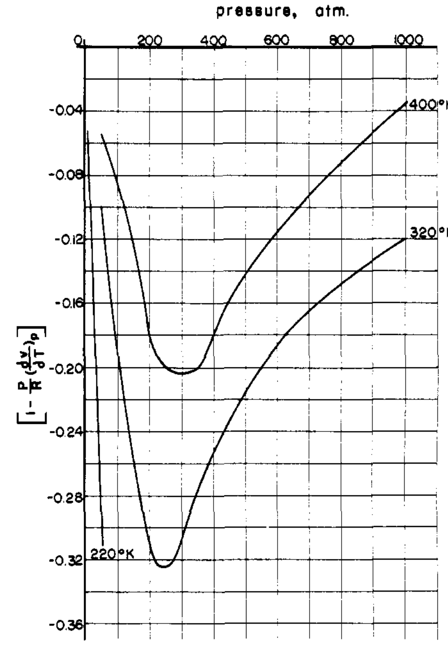

Figure 5. Deviation from ideality of argon over the pressure and temperature ranges shown in Figures 1, 3, and 4

at least for these ranges, that both sonic velocity-pvT and pvT alone are equally reliable bases for computing argon heat capacities.

A link between the low and high pressure data—i.e., Tables I and II, respectively—is furnished by the 50-atm isobar, which spans both sets. Figure 2 presents calculated and literature values for this pressure, and demonstrates again that the agreement is quite good. This supports not only the reliability of the Itterbeek and Lacam sonic measurements and the Din pvT compilation, but also the calculation procedure featured here. There appears to be no reason to modify the Din values of C_p and C_v for this range.

The higher pressure results given in Table II, however, display marked and systematic differences. At a lower temperature of 320° K (Figure 3), the calculated and literature values for both C_p and C_v again agree almost exactly at the lower end of the pressure range, 50–200 atm, but diverge sharply for the upper portion of the range, 300–1000 atm. Furthermore, the calculated values show maxima with increasing pressure while the literature values do not. At a higher temperature of 400° K (Figure 4), the characteristics are qualitatively similar except that divergence starts at a lower pressure for C_p (it is notable that the literature values also show a gentle maximum here) and becomes cumulatively greater for C_v, decreasing to about 35% below the literature value at 1000 atm.

These significant discrepancies are explainable by Figure 5 which reveals, at least qualitatively, the source of errors which must have been accumulated by Din in using Equation 1 over certain ranges. The modulus $[1 - (P/R)(\partial v/\partial T)_p]$, where R is the gas constant, expresses the deviation of the gas from ideality, becoming zero for the ideal state. Figure 5 is a plot of this modulus vs. pressure with the three temperatures previously discussed in detail—i.e., 220, 320, and 400° K—as parameters, and spanning only the pressure ranges for which sonic data are available at these temperatures. The profiles show a rather remarkable behavior, particularly at the two higher temperatures where Equation 1 fails.

Furthermore, the minima in these two higher isotherms occur in the range 200–300 atm or approximately at the level where divergence between calculated and literature values begins in Figures 3 and 4. The straight portions of the three isotherms in Figure 5, on the low pressure sides of the 320 and 400° K minima and the entire curve for 220° K, represent regions of concurrence between calculated and literature values of the heat capacities. Hence, apparently, it is not the magnitude of the deviation from ideality which causes accumulation of errors in using Equation 1, but rather the inability of the *pvT* data alone to follow drastic changes in this deviation.

Such changes describe a second derivative. The behavior of the particular second derivative appearing in Equation 1, $(\partial^2 v/\partial T^2)_p$, can only be inferred from Figure 5, aided by noting that it also becomes zero for the ideal gas. It is qualitatively clear, however, merely from inspection of the scatter resulting from calculations using only first derivatives (Figures 3 and 4), that computations based on $(\partial^2 v/\partial T^2)_p$ or any second derivative would involve considerable uncertainty. They could not be expected to follow the complex changes implied by the 320° and 400° K isotherms of Figure 5. Furthermore, since $(\partial^2 v/\partial T^2)_p$ occurs under an integral sign in Equation 1, the errors are cumulative, a characteristic which is reflected in the increasing divergence of the calculated and literature values plotted in Figures 3 and 4.

It should also be mentioned here that the marked deviations shown for the higher pressures are in no way attributable to systematic errors in the Lacam sonic velocity data. In the first place, the precision of the Lacam experimental technique increases with pressure, so that the high-pressure data, where the deviations are observed, are actually more reliable than the low-pressure data, where concurrence is observed. Another consideration is the correction for the acoustic wave being nonplanar, since the use of Equation 2 assumes a plane acoustic wave. The well-known Helmholtz expression (*4*) for the ratio of a measured sonic velocity c to the free-space or planar velocity c_0 in a gas of density ρ and viscosity μ is

$$c/c_0 = 1 - (1/r)(\mu/2\nu\rho)^{1/2} \quad (9)$$

where r is the radius of the containing cylinder and ν the frequency of the acoustic wave. Since for the Lacam apparatus ν = 3 MHz and r = 1.0 cm, it may easily be shown, inserting representative values for μ and ρ into Equation 9, that c/c_0 is of the order of 0.9999, which is completely negligible for the calculations presented in this paper. Furthermore, since density appears in the denominator of the modulus in Equation 9, increased pressure would reduce any such correction rather than augment it. Hence the deviations in heat capacities at high pressures appear to be completely attributable to other effects, as discussed previously.

Table III. Heat Capacities of Argon in Ranges 300–400° K and 200–1000 Atm

(Smoothed values calculated from sonic velocities to replace existing literature values)

Pressure, atm	Temp, ° K	Cal/g atom ° K C_p	Cal/g atom ° K C_v
200	340		3.25
	360		3.20
	380	6.00	3.15
	400	5.90	3.10
300	340	6.90	3.30
	360	6.60	3.20
	380	6.20	3.15
	400	6.05	3.05
400	320	7.60	3.50
	340	7.00	3.30
	360	6.70	3.20
	380	6.25	3.10
	400	6.10	3.00
500	320	7.60	3.50
	340	6.95	3.30
	360	6.60	3.20
	380	6.25	3.10
	400	6.10	3.00
600	320	7.50	3.50
	340	6.85	3.30
	360	6.50	3.20
	380	6.20	3.10
	400	6.00	2.95
800	300	8.25	3.85
	320	7.15	3.45
	340	6.60	3.20
	360	6.25	3.10
	380	6.05	2.95
	400	5.85	2.90
1000	300	7.90	3.80
	320	6.80	3.40
	340	6.30	3.10
	360	5.90	2.95
	380	5.75	2.85
	400	5.60	2.85

SMOOTHED RESULTS

For the temperature and pressure ranges represented in Table I and portions of the ranges in Table II, the use of sonic velocities does not improve the heat capacity values already tabulated in the literature by Din. For the higher pressure regions of Table II, however, the literature data should be replaced by values obtained from curves such as the dotted portions of Figures 3 and 4. These smoothed results are given in Table III which has the same format as Table II but omits those entries for which calculated and literature values fall on the same smoothed curves. As indicated, the precision of the smoothed values is given as ±0.05 cal/g atom ° K, which is the lowest spread justified by the scatter of the plotted data. The 450° K isotherm has been omitted entirely since the scatter of the calculated values is too great to justify smoothing (although their bias still conforms to the generalizations discussed above).

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