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Specific Heats of Solid Natural Neon at Five Molar Volumes and of the Separated Neon Isotopes at P = 0

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Direct measurements of the constant volume specific heat C_v are reported for solid natural neon at several molar volumes (13.39–12.39 cm³/mole) at temperatures from 1 K to the melting line. All samples were solidified in a high-pressure bomb at the melting line (maximum conditions of 53 K and 2.5 kbar) and molar volumes for the melting line are given. The extrapolations of these data to 0 K result in a $\Theta_0(V)$ relation for which $\Theta_0(P = 0, T = 0) = 75.1 \pm 0.1$ K and an average Grüneisen parameter $\gamma_0 = 2.51 \pm 0.03$. These data can be represented at all temperatures and for all volumes by a single reduced curve as $C_v[T/\Theta_0(V)]$, with a maximum deviation of $\pm 0.8\%$ near $T/\Theta_0 = 0.12$. The deviations are systematic with volume and consistent with a temperature-dependent contribution to the Grüneisen parameter of $1 \pm 1\%$. The melting line parameters are used to test the Lindeman melting relation, and systematic deviations are found. Much less complete measurements of C_v for the separated neon isotopes ${}^{20}Ne$ and ${}^{22}Ne$ are consistent with the reduced curve for natural neon, and with an M^{-0.5} dependence for Θ_0 , where M is the isotopic mass.

1. INTRODUCTION

The thermodynamic properties of the weakly bound rare gas solids are of particular interest because of large anharmonic contributions to their lattice dynamics. Solid helium represents an extreme case where short-range correlation effects become very important, while conventional perturbation techniques may be used to treat the effects of anharmonicity in the heavier solids (argon, krypton, and xenon) at low temperatures.¹ For neon, the amplitude of the zero-point vibrations (approximately 6% of the nearestneighbor distance) is sufficiently great so as to make the use of perturbation techniques questionable even near 0 K.² The three-body triple–dipole interactions which are important for argon,³ krypton,⁴ and xenon probably

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are not important for neon, although the commonly used Lennard–Jones 6–12 potential² very likely is not correct.⁵ The very factors which cause neon to be of considerable theoretical interest also result in a solid which is very compressible and which has large thermal expansions and relatively low melting temperatures.

The present experiments were undertaken to provide direct measurements of the constant-volume heat capacity C_{ν} for solid natural neon at several molar volumes and for the separated isotopes ²⁰Ne and ²²Ne near the equilibrium volume. C_{ν} data can be correlated directly with the density of states function for the lattice and hence with inelastic neutron scattering data,⁶ while the limiting value of the Debye temperature Θ_0 represents an average over the elastic constants of the solid.⁷⁻⁹ The volume dependence of Θ_0 can be used to understand, to first order, the volume dependence of C_{ν} in terms of a reduced temperature, $C_{\nu}(T/\Theta_0)$, where the only volume dependence occurs through $\Theta_0(V)$. In effect, this model assumes that the shape of the density-of-states function is independent of volume, so deviations from such a reduced temperature dependence can be interpreted in terms of the actual volume dependence of the frequency spectrum. The combined volume and temperature dependences of C_{ν} can be related directly to the Grüneisen parameter γ , the volume thermal expansion coefficient, and to the equation of state P(V, T) if a single pressure-volume relation (such as that along the melting line) is known.10

Constant-pressure specific heat C_P measurements on natural neon by Fagerstroem and Hollis–Hallet¹¹ and Fenichel and Serin¹² have been summarized by Batchelder *et al.*⁷ These data are in basic agreement, and earlier uncertainties in the conversion of C_P to C_V can be removed through the use of recent elastic constant data.^{8,9} The most direct comparisons of C_V data and theoretical calculations are made for constant volume conditions, so the 4.4% volume expansion of solid neon between 0 K and the triple point 24.5 K requires that a rather large correction be made to C_V values which have been obtained from a constant-pressure experiment. This correction can be made relatively much smaller in an experiment which is conducted under almost constant-volume conditions.

Previous direct measurements of C_v at constant volume have been reported for helium (Ref. 13 is typical of work with this solid, which exists only under pressure), for hydrogen,¹⁴ and more recently for argon and xenon.¹⁵ In all of these experiments, the calorimeter which contains the solid is in the form of a high-pressure bomb which must be filled at the melting line under conditions where the molar volume of the solid is at least as small as the equilibrium volume at absolute zero, V_0 . The heat capacity of the relatively massive bomb (which must be designed to withstand at least 2 kbar pressure) is not a serious factor for helium where the heat capacities and

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compressibilities are large and the melting temperatures are low, although bomb design considerations limited the pressure and hence temperature range for work on the heavier solidified gases.¹⁵ The present experiments on solid neon extend to melting temperatures and pressures of up to 53.5 K and 2.5 kbar, and cover a range of molar volumes from 13.39 cm³/mole to 12.39 cm³/mole. The precision of these measurements does not appear to be limited by the heat capacity of the bomb which was used.

The separated neon isotopes have a relatively large (10%) mass difference, and hence should exhibit appreciably different thermodynamic properties. The lattice parameters and thermal expansions of these isotopes have been studied by Batchelder et al.,¹⁶ while Clusius et al.¹⁷ and more recently Somoza and Fenichel¹⁸ have reported C_P measurements for ²⁰Ne and ²²Ne.

2. EXPERIMENTAL DETAILS

These experiments utilize the conventional heat-pulse method of isothermal calorimetry, and the details (as well as the raw data) will be found elsewhere.¹⁹ A completely metal system is used, in part because of potential hazards due to the high pressure in the bomb calorimeter. The bomb, which contains the solid neon and hence is the most important part of the system, is connected to the outside of the cryostat by a fine stainless-steel capillary. The capillary and the bomb are isolated from their surroundings by vacuum spaces (and are kept warm by heaters) while the bomb is filled with solid neon at the melting line. The latent heat of fusion is removed by means of a direct connection to a liquid-helium bath through a mechanical heat switch, so a liquid-solid interface moves slowly upwards in the bomb after freezing has started until the capillary is blocked. The upper part of the capillary is kept filled with solid neon at 4 K throughout the specific heat measurements until all of the data have been taken. The melting temperature which corresponds to the molar volume of the neon is determined at least twice by measuring the rapid increase of the heat capacity of the solid neon in the bomb as the sample is warmed through the melting temperature. This temperature is used to calculate the pressure of the neon in the bomb (and hence the volume of the bomb)²⁰ at this temperature. The number of moles of neon in the sample is determined by expanding the gas into calibrated, temperature-controlled standard volumes at the end of the measurements with the cryostat at room temperature. The measurements of electrical quantities (for calculating the heat input to the sample and the resistance of the germanium thermometer) are sufficiently precise so that they introduce no appreciable error into the results, and the final precision at intermediate

temperatures (2-30 K) is estimated at 0.2%. The errors increase slightly at lower temperatures where the heat capacity of the bomb is relatively more important, and at higher temperatures where the small thermal diffusivity of the neon causes relatively long relaxation times.

2.1. Cryostat and Calorimetric Details

The bomb (which will be described below) is suspended inside the sample chamber by a stainless-steel capillary (0.018 in. o.d. and 0.010 in. i.d. containing a 0.009-in.-stainless-steel wire) which passes from the sample chamber to room temperature through a separate vacuum jacket. The copper walls of the sample chamber form an isothermal shield. The temperature of this shield can be monitored with either a germanium or a platinum resistance thermometer and can be kept constant anywhere between 0.9 and 77 K with either pumped liquid helium in a 100-cm³ pot or a heater. This shield is surrounded by a second vacuum jacket which is attached to a 2-liter liquid-helium reservoir at 4 K. The main cryostat vacuum is common to both the helium reservoir and a liquid-nitrogen container-77 K radiation shield. Thus, there are four distinct vacuum systems: one for the main cryostat (which is sealed-off during an experiment), a second to isolate the isothermal shield from the 4 K shield (this vacuum can be maintained with an oil diffusion pump), a third (which is pumped continuously with an ion pump) to isolate the calorimeter from the isothermal shield, and a fourth (which again is pumped by an ion diffusion pump) to isolate the fill capillary from the liquid-helium bath as the sample is being formed.

The design of the bomb is shown to scale in Fig. 1. The bomb is constructed from hardened beryllium copper (Berlyco 25, half-hard initially) primarily because this material contains no transition metals and hence has a small electronic heat capacity. In addition, these alloys can be machined easily as received, after which they can be heat treated to have a yield strength of approximately 2×10^5 psi at 77 K. Early attempts to construct a bomb by silver soldering this material were unsuccessful, since we were not able to carry out this operation and at the same time retain this yield strength. The final design (Fig. 1) uses a Bridgman-type unsupported area indium seal at the top end for the main seal, and indium solder for supplementary pressure seals. Extrusion of the indium is prevented by the triangular extrusion rings. The capillary is silver soldered to a beryllium copper disc which in turn is indium soldered to the top seal. This design unfortunately leaves a dead space above the bottom of the capillary, and we never were able to fill the bomb completely with solid neon at the melting line. This problem could be remedied easily by a slight modification. The internal copper fins (four at 90°) which are relied upon to conduct heat to the sample are silver soldered



Fig. 1. The details of the high-pressure bomb which contains the solid neon.

to a high purity copper post (2 mm in diameter as it passes through the bomb) which in turn is indium soldered to the bomb for a pressure seal. The hemispherical bottom end of the bomb reduces stress concentrations which were found to be serious in previous purely cylindrical designs. This bomb, which has a diameter ratio of 1.25, was used to 2.5 kbar at 77 K; a previous version with a diameter ratio of 1.23 burst at room temperature at 2.6 kbar.

The room-temperature volume of the bomb was determined by weighing it before and after filling with degassed distilled water. The result as corrected to 0 K^{21} is $2.902 \pm 0.002 \text{ cm}^3$. The bomb was immersed in a pyncnometer in an ice bath in a second experiment, and its volume was found to change reversibly and linearly with internal pressures of up to 2.5 kbars with a coefficient $\kappa' = V^{-1} (\partial V / \partial P)_T = 7.36 \times 10^{-6} \text{ bar}^{-1}$. The assumption is made that the volume of the metal does not change with pressure. This parameter should be proportional to the Young's modulus for beryllium copper,^{22,23} and hence should decrease to $\kappa = 6.62 \times 10^{-6} \text{ bar}^{-1}$ for temperatures below 77 K.

The sample heater (550 Ω , 0.001-in.-diam Pt-8% wire) and the germanium resistance thermometer are attached directly to the copper wire which comes from the fins (Fig. 1). This wire also leads directly to a mechanical heat switch which is operated from the top of the cryostat and which is identical with one which we have used previously.¹³ Initially, sample heat was supplied by a 1000- Ω heater wound on the heavy top portion of the bomb. Rather long time constants were observed when this heater was used and all data eventually were taken using the sample heater on the wire. The

initial heater proved to be useful, however, to prevent the capillary from blocking prematurely while the sample solidified at constant pressure.

The heater power and the thermometer resistance are determined using conventional potentiometric techniques with current reversal. These, and the timing methods, are almost identical except for a few details with those which we have used previously.²⁴ The major improvements have involved the use whenever possible of constant current supplies of the type described by Kroeger and Rhinehart.²⁵ These give indicated thermometer current stabilities of at least 0.001% (as determined by potentiometer readings across a standard resistance), and allow a choice of 20 different sample heater currents (which vary discretely from 1 μ A to 14.5 mA) which are reproducible to 0.01%. Chart recorders indicate the off-balance readings of null detectors that are associated with the various potentiometers.

The germanium thermometer is calibrated from 0.9 to 20 K in terms of a paramagnetic salt temperature scale²⁶ that is referenced to the NBS-1955 platinum resistance thermometer scale above 20 K. The thermometer calibration is in terms of this platinum resistance scale from 20 K to 77 K, and a check after these experiments were completed showed it to be unchanged to 0.01 %. The thermometer leads are anchored to the bomb walls to ensure that the thermometer indicates the bomb temperature.

2.2. Procedures and Ancillary Apparatus

Gas pressures of up to 4 kbar can be produced with an air-driven hydraulic pump and a 2-in.-i.d. by 37-in.-stroke, O-ring piston, gas-oil separator manufactured by Autoclave Engineers, Inc. Great care is taken that no oil is transmitted over with the gas, and a special proximity gauge indicates the exact position of the piston for the last two inches of its travel. The bomb is purged with clean neon several times at room temperature, and then is sealed off at approximately 2 kbar pressure prior to cooling to 77 K. Liquid helium then is transferred to the main reservoir and the sample shield is cooled to 25 K where its temperature is held constant. During this time, the desired freezing pressure has been maintained in the separator (as indicated by a Heise gauge in the oil side) and the bomb, and the capillary and the bomb have been heated to prevent their being blocked. The bomb is cooled slowly from the bottom by adjusting the heat-switch pressure, and the onset of freezing is marked by a rapid decrease in the cooling rate of the bomb at a temperature which corresponds with published values.^{19,20} The sample again cools rapidly when freezing is completed. Helium exchange gas then is admitted into the capillary vacuum space to block the capillary over a major portion of its length. The melting temperature is redetermined at this point by measuring the heat capacity of the bomb at small intervals of temperature through the expected region; the data show a sharp increase at the temperature where melting first occurs in the neon. This temperature invariably is lower than the temperature which is observed during freezing at constant pressure because the dead space in the bomb above the end of the capillary (Fig. 1) causes a small portion of the freezing to occur at constant volume.

The bomb is cooled slowly to 4 K over a period of 12 hours or so to prevent the generation of strains. Data taking begins at 1 K, with temperature changes during a heat pulse which are of the order of or less than 0.05 T, where T is the average temperature. The shield temperature always is maintained constant midway between the initial and the final temperature of the heat pulse so that drift rates are positive (warming) before heat is applied and negative (cooling) afterwards. This procedure also makes it plausible to assume that one-half of the heat generated in each of the heater current leads flows into the sample, and indeed we have calculated heat inputs by assuming that one of these leads is a part of the heater. The maximum drift rate is 0.5 mK/min at 1 K, which corresponds to less than 10 erg/min stray heat input. The major source of heat leak is the neon-filled stainlesssteel capillary, and a rough estimate suggests that the conductivity of the neon²⁸ (a cylindrical shell 5×10^{-4} in. average thickness, 0.0095 in. in diameter) predominates from 2 to 8 K, with the stainless steel being more important at other temperatures. Data are analyzed graphically using chartrecorder traces from which temperature increments can be determined to better than 0.1%, and the scatter of the experimental results (see below) typically is of this order of magnitude. Above 20 K the measured heat capacities increase by as much as 1 % for high rates of heating and for large temperature increments during a heat pulse. The thermal diffusivity of neon is small at these temperatures and the time constants which we observed (that is, the time to achieve a linear drift rate after a heat pulse) become several minutes long, so perhaps local heating occurs under extreme conditions with excess heat leaks during the heat pulses. Data in this region are taken with small heater currents (long time intervals) and small temperature intervals to minimize these effects.

When data taking is completed for a given sample, the melting point is redetermined and a few low-temperature points are retaken to verify that no annealing effects have occurred. The bomb then is maintained at 4 K while the capillary vacuum space is evacuated and the neon in the capillary is released to a set of calibrated volumes as the capillary is heated. As a result, the neon in the "dead space" (room-temperature valves and the major cold portions of the capillary) is released and measured before the solid in the bomb is released, leaving only a small correction (less than 0.1 %) to be made for the 5 cm or so of capillary between the end of the vacuum jacket and the bomb itself.

The two standard volumes (nominally 5 liters and 0.5 liters) are maintained at 25°C in a water bath, the temperature of which can be read and kept constant to 2×10^{-3} °C. The temperature is monitored with a platinum resistance thermometer which has been compared to this precision with an NBS-calibrated platinum resistance thermometer. Gas pressures of less than 1 bar are measured to 0.005% with a wide-bore mercury manometer and a Wild cathetometer, with readings reduced to the density of mercury at 0°C. The ideal gas law is assumed to calculate the number of moles *n* in the sample since second virial coefficient effects²¹ amount to only 0.03% at 0.9 bar and 25°C. The accuracy with which *n* can be determined is assumed to be $\pm .08\%$, or ± 0.01 cm³/mole for solid molar volumes of 12.5 cm³.

The natural neon gas was purchased from Cryogenic Rare Gases, Inc., of Newark, New Jersey, and is specified to have been purified over titanium, with all impurities (N₂, O₂, Ar, CO₂, He) in a concentration of less than 10 ppm. The gas from one of the samples was analyzed by mass spectrometry* after the experiment and was found within the limits of detection to satisfy these specifications, which suggests that our experiments did not contaminate it. The limits for H₂ (less than 0.01%) and O₂ (less than 0.02%) are set by the analytical methods. The relative abundances of the neon isotopes are found to be; ²⁰Ne, 91.2; ²¹Ne, 0.3; ²²Ne, 8.5. These differ somewhat from those given by Furukawa²⁹ (90.5, 0.3, 9.2) in his summary of natural neon isotope concentrations from various sources, and the reasons for the differences are difficult to understand.

3. EXPERIMENTAL RESULTS

Experimental specific heat data were obtained for five natural neon samples. The physical data for each of these samples are given in Table I. In each case, an addenda or evacuated bomb heat capacity is subtracted from the raw heat capacities to obtain the heat capacity of the neon, and a molar quantity $C_{meas}(T)$ is calculated. This heat capacity is not C_V since the bomb expands slightly during a heat pulse as the internal pressure increases. The resulting correction is very similar to that which must be applied to convert C_P measurements to C_V , except that the expansivity of the bomb κ (see the Section 2) replaces the compressibility of the solid. As a result, C_V can be calculated as

$$C_V = C_{\text{meas}} - T(\partial P/\partial T)_V^2 \simeq C_{\text{meas}} - \kappa T(\gamma C_V/V)^2$$
(1)

where the Grüneisen relation $(\partial P/\partial T)_V = \gamma C_V/V$ has been used. The present experiments can be used to show that the Grüneisen parameter γ for neon

*This analysis was carried out by Mr. G. Flesch of the Ames Laboratory Mass Spectrometry Group.

Sample	No. moles	$V, \text{cm}^3/\text{moles}^a$	P_0 , bar	P_m , bar ^b	θ_0, \mathbf{K}^c	T_m, \mathbf{K}^d
Ned	0.2142	13.60	_	521	_	31.75
INC 4	0.2142	(13.39)	0	(768)	75.1	(34.8)
NI C	0.0105	13.30		885		36.20
Ne 5	0.2195	(13.23)	147	(976	77.7	(37.25)
NT (0.00(1	12.95		1364	_	41.80
Ne 6	0.2261	(12.87)	511	(1514)	83.1	(43.2)
21.7	0.0010	12.67		1862		46.80
Ne /	0.2318	(12.59)	841	(2033)	87.6	(48.5)
N. 0	0.00(1	12.48		2301		51.10
Ne 8	0.2361	(12.39)	1192	(2555)	91.5	(53.5)

TABLE I								
Physical	Data	for	the	Five	Natural	Neon	Samples	

^aValues are uncertain by $\pm 0.01 \text{ cm}^3/\text{mole}$. The first volume for each sample is for the melting line. The volume in parenthesis is the calculated value for that sample at T = 0, with the corresponding estimated T_m and P_m which would be observed in a constant-volume experiment. The Ne 4 sample pulled away from the bomb walls at approximately 15 K.

^bValues are uncertain by ± 3 bar.

Values are uncertain by ± 0.1 K.

^dValues without parentheses are uncertain by ± 0.05 K.

is equal to approximately 2.55 ± 0.03 at high temperature, so $\gamma^2 = 7$ was assumed in a self-consistent calculation of C_V from the data. The correction term in Eq. (1) is less than 1 % below 20 K for all of the samples, and increases to approximately 4% for the Ne 8 sample at 50 K, so the volume V also was assumed to be constant for a given sample.

The resulting values of $C_{\nu}(T)$ for each sample are not true values for constant volume, since the internal pressure in the bomb and hence its volume increase with increasing temperature. The molar volume of the sample rather than the bomb volume will be used in the following discussion since these differ only by a proportionality factor. Thus, the molar volume given in Table I for the melting temperature and pressure for a sample must be greater than the molar volume at 0 K (in parentheses). The change in internal pressure for neon can be estimated from the Mie–Grüneisen equation of state

$$P^* = \gamma U^* / V \tag{2}$$

where γ , the Grüneisen parameter, is a slight function of volume and $C_V = (\partial U^*/\partial T)_V$. The increase in the internal pressure of the neon with increasing temperature at constant volume $(\partial P^*/\partial T)_V$ will be decreased slightly due to the finite expansivity of the bomb κ and the bulk modulus B_T of the neon, with a resulting relation $(dP/dT)_{\text{homb}} = (1 + \kappa B_T)^{-1} (\partial P^*/\partial T)_V$, which is

analogous with Eq. (1). As a result, the actual pressure in the bomb at a given temperature can be calculated from the melting line parameters as

$$P(T, V) = P_m(T_m, V_m) + (\gamma/V)(1 + B_T \kappa)^{-1} \int_{T_m}^T C_V(T, V) dT$$
(3)

In this equation V is the actual volume of the bomb and will be a slight function of the temperature, and C_V is as calculated from Eq. (1). The present experiments do not supply sufficient information to allow the precise determination of the pressure from Eq. (3), and the values of P_0 and hence of $V(P_0)$ given in Table I are calculated using this relation and a combination of the heat-capacity results and piston-displacement equation-of-state data.¹⁰ One problem, for instance, is that while B_T is only slightly temperature dependent at constant volume, it increases by 50% with the change in volume from Ne 5 to Ne 8. The major volume decrease occurs for the highest melting Ne 8 sample, but even then is only 0.7%. The volume change indicated in Table I for the Ne 4 sample is misleading since the pressure in

<i>T</i> , K	C_V , J/mole·K	Θ, Κ	U*, J/mole	S, J/mole·K
0	0	77.71	0	0
1.0	4.155×10^{-3}	77.64	1.038×10^{-3}	1.383×10^{-3}
2.0	3.376×10^{-2}	77.24	1.675×10^{-2}	1.115×10^{-2}
3.0	1.189×10^{-1}	76.14	8.692	3.846
4.0	3.041	74.24	2.877×10^{-1}	9.45
5.0	6.446	72.21	7.471	1.961×10^{-1}
6.0	$1.175 \times 10^{\circ}$	70.77	1.641×10^{0}	3.576
7.0	1.895	69.96	3.161	5.906
8.0	2.776	69.57	5.845	8.996
9.0	3.778	69.42	8.755	$1.284 \times 10^{\circ}$
10.0	4.855	69.41	13.07	1.738
12.0	7.069	69.66	25.00	2.821
14.0	9.179	70.10	41.27	4.077
16.0	11.081	70.59	61.57	5.436
18.0	12.743	71.09	85.44	6.851
20.0	14.154	71.69	112.37	8.281
22.0	15.336	72.41	141.90	9.702
24.0	16.326	73.22	173.6	11.100
26.0	17.168	73.97	207.1	12.460
28.0	17.90	74.86	242.2	13.47
30.0	18.54	75.57	278.6	15.06
32.0	19.11	76.10	316.3	16.30
34.0	19.61	76.60	355.1	17.50
36.0	20.02	77.33	394.7	18.66
37.3	(20.24)	(78.)	(421.)	(19.2)

TABLE II

Smoothed Thermodynamic Functions for the Ne 5 Sample as Corrected to Constant Volume, $V = 13.23 \text{ cm}^3/\text{mole}$

T	A	R	r.	F	T	II
		D	-	E.		

<i>T</i> , K	C_V , J/mole·K	Θ, Κ	U^* , J/mole	S, J/mole·K
0	0	83.05	0	0
1.0	3.398×10^{-3}	83.02	8.49×10^{-4}	1.132×10^{-3}
2.0	2.747×10^{-2}	82.73	1.367×10^{-2}	9.100
3.0	9.615	81.73	7.055	3.124×10^{-2}
4.0	2.437×10^{-1}	79.93	2.321×10^{-1}	7.672
5.0	5.147	77.86	5.992	1.575×10^{-1}
6.0	9.441	76.23	1.315×10^{0}	2.868
7.0	$1.542 \times 10^{\circ}$	75.20	2.544	4.752
8.0	2.295	74.64	4.450	7.287
9.0	3.172	74.39	7.175	$1.049 \times 10^{\circ}$
10.0	4.133	74.35	10.82	1.433
12.0	6.158	74.66	21.10	2.366
14.0	8.164	75.14	35.44	3.471
16.0	10.052	75.56	53.68	4.692
18.0	11.736	76.03	75.51	5.985
20.0	13.191	76.61	100.47	7.309
22.0	14.43	77.31	128.13	8.641
24.0	15.49	78.06	158.1	9.960
26.0	16.41	78.81	190.0	11.256
28.0	17.20	79.41	223.6	12.522
30.0	17.90	80.17	258.8	13.76
32.0	18.51	80.87	295.1	14.96
34.0	19.03	81.59	332.7	16.12
36.0	19.47	82.40	371.2	17.24
38.0	19.85	83.25	410.6	18.34
40.0	20.23	83.75	450.7	19.40
4.20	(20.65)	83.3	(492.)	(20.4)
43.2	(20.9)	82.9	(509.)	(20.9)

Smoothed Thermodynamic Functions for the Ne 6 Sample as Corrected to Constant Volume, $V = 12.87 \text{ cm}^3/\text{mole}$

this sample actually became zero at approximately 15 K and the sample did not fill the bomb at 0 K. Hence, the above discussion applies only to the Ne 5 to Ne 8 samples.

Once the temperature dependence of the volume is obtained for a given sample, the average derivative $(\partial C_V / \partial V)_T$ can be calculated for neon as a function of temperature, and the experimental $C_V[T, V(T)]$ data can be converted to more meaningful $C_V(T, V = \text{const})$ values. The maximum adjustment of 0.4% occurs again at the highest temperatures. Tables II through V give the resulting values of $C_V(T)$ at constant volume for each of the samples, Ne 5 through Ne 8, together with the equivalent Debye temperatures Θ (which are useful for interpolation), the internal energy $C_V = (\partial U^* / \partial T)_V$, and the entropy $C_V = T(\partial S / \partial T)_V$ for each of the samples, Ne 5 through Ne 8. Table VI contains a summary of the same functions for solid natural neon at its T = 0 equilibrium volume, $V_0 = 13.39 \text{ cm}^3/\text{mole}$. The actual

TA	BI	Æ	IV
			-

Smoothed	Thermodynamic	Functions	for the	Ne 7	Sample a	as Corrected	to Constant	Volume,
		L	' = 12	59 cm	³ /mole			

<i>T</i> , K	C_{ν} , J/mole·K	Θ, Κ	U*, J/mole	S, J/mole·K
0	0	87.63	0	0
1.0	2.894×10^{-3}	87.58	7.23×10^{-4}	9.64×10^{-4}
2.0	2.336×10^{-2}	87.33	1.163×10^{-2}	7.75×10^{-3}
3.0	8.104	86.53	5.98	2.649×10^{-2}
4.0	2.040×10^{-1}	84.81	1.955×10^{-1}	6.468
5.0	4.289	82.74	5.019	1.321×10^{-1}
6.0	7.888	80.99	$1.098 \times 10^{\circ}$	2.399
7.0	$1.298 \times 10^{\circ}$	79.81	2.130	3.979
8.0	1.952	79.12	3.744	6.125
9.0	2.729	78.76	6.075	8.866
10.0	3.601	78.63	9.234	$1.219 \times 10^{\circ}$
12.0	5.492	78.80	18.31	2.043
14.0	7.412	79.25	31.22	3.037
16.0	9.247	79.73	47.90	4.153
18.0	10.918	80.25	68.10	5.348
20.0	12.404	80.79	91.45	5.987
22.0	13.70	81.37	117.6	7.844
24.0	14.82	82.02	146.2	9.101
26.0	15.78	82.73	176.8	10.344
28.0	16.61	83.48	209.2	11.565
30.0	17.34	84.15	243.2	12.76
32.0	17.97	85.02	278.5	13.92
34.0	18.53	85.79	314.9	15.05
36.0	19.03	86.41	352.6	16.15
38.0	19.48	86.92	391.1	17.22
40.0	19.87	87.47	430.4	18.16
42.0	20.22	88.08	470.3	19.27
44.0	20.54	88.59	511.3	20.25
46.0	20.85	88.83	552.6	21.20
(48.0	(21.15)	(88.9)	(595.)	(22.1)
(48.5)	(21.2)	(89.2)	(605.)	(22.3)

Ne 4 data are used for these calculations below 6 K, while the values above 6 K are obtained from the Ne 5 results by extrapolation at constant temperature.

All of the calculations, beginning with the raw data, are carried out using an IBM 360–65 digital computer. Heat-capacity and addenda results are represented in limited ranges by expressions of the form

$$C = \sum_{n} A_{n} T^{n} \tag{4}$$

with the choices of the *n*'s being determined by the temperature region and the function (addenda heat capacity or neon) being represented. The resulting

expressions for the neon samples are used to generate the smooth heatcapacity values in the tables, as well as the thermodynamic functions.

As will be discussed in detail below, the scatter and reproducibility of these data indicate that the precision for any given sample is between 0.1 and 0.2% for temperatures below 30 K. The smooth variation of C_V from one sample to another at constant temperature, and also on reduced plots at common values of a reduced temperature, suggest that systematic errors are small, and that the accuracy of these C_V data are close to ± 0.3 %. The addenda contribution becomes larger and the precision begins to deteriorate above 30 K so that these data are perhaps reliable to only ± 1 %.

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Smoothed Thermodynamic Functions for the Ne 8 Sample as Corrected to Constant Volume, $V = 12.39 \text{ cm}^3/\text{mole}$

<i>T</i> , K	C_{ν} , J/mole·K	Θ, Κ	U*, J/mole	S, J/mole·K.
0	0	91.50	0	0
1.0	2.543×10^{-3}	91.45	6.38×10^{-4}	8.51×10^{-4}
2.0	2.051×10^{-2}	91.18	1.023×10^{-2}	6.82×10^{-3}
3.0	7.093	90.46	5.235	2.322×10^{-2}
4.0	1.768×10^{-1}	88.95	1.706×10^{-1}	5.650
5.0	3.702	86.90	4.353	1.148×10^{-1}
6.0	6.820	85.03	9.507	2.079
7.0	1.129×10^{0}	83.71	$1.845 \times 10^{\circ}$	3.449
8.0	1.710	82.89	3.254	8.322
9.0	2.413	82.45	5.306	7.733
10.0	3.211	82.25	8.111	$1.068 \times 10^{\circ}$
12.0	4.981	82.35	16.29	1.809
14.0	6.824	82.75	28.08	2.718
16.0	8.621	83.18	43.54	3.752
18.0	10.288	83.66	62.48	4.872
20.0	11.792	84.15	84.58	6.045
22.0	13.12	84.67	109.54	7.244
24.0	14.28	85.26	137.0	8.451
26.0	15.28	85.90	166.6	9.651
28.0	16.15	86.59	198.0	10.836
30.0	16.91	87.16	231.1	12.00
32.0	17.57	87.98	265.6	13.14
34.0	18.16	88.76	319.8	14.24
36.0	18.69	89.40	338.2	15.32
38.0	19.16	89.92	376.1	16.37
40.0	19.58	90.44	414.8	17.40
42.0	19.94	91.06	454.3	18.39
44.0	20.27	91.66	494.6	19.36
46.0	20.57	92.24	535.6	20.30
48.0	20.88	92.24	577.0	21.21
50.0	21.25	91.08	619.3	22.11
52.0	(21.7)	(88.1)	(662.)	(22.9)
53.5	(22.0)	(86.0)	(692.)	(23.6)

<i>T</i> , K	C_{ν} , J/mole·K	Θ, Κ	U*, J/mole	S, J/mole·K
0	0	75.1	0	0
1.0	4.62×10^{-3}	75.0	1.15×10^{-3}	1.53×10^{-3}
2.0	3.75×10^{-2}	74.6	1.863×10^{-2}	1.24×10^{-2}
3.0	1.327×10^{-1}	73.4	9.70	4.29
4.0	3.42	71.4	3.22×10^{-1}	1.062×10^{-1}
5.0	7.25	69.4	8.37	2.20
6.0	$1.318 \times 10^{\circ}$	68.0	$1.843 \times 10^{\circ}$	4.01
7.0	2.111	67.3	3.55	6.62
8.0	3.062	67.0	6.11	$1.004 \times 10^{\circ}$
9.0	4.13	66.9	9.71	1.426
10.0	5.27	66.9	14.42	1.921
12.0	7.55	67.3	27.2	3.08
14.0	9.70	67.7	44.5	4.41
16.0	11.61	68.1	65.9	5.84
18.0	13.25	68.7	90.7	7.30
20.0	14.62	69.4	118.7	8.77
22.0	15.76	70.2	149.1	10.22
24.0	16.71	71.0	182.	11.63
26.0	17.55	71.7	216.	13.01
28.0	18.3	72.2	252.	14.33
30.0	18.9	72.9	289.	15.6
32.0	19.4	73.5	327.	16.9
34.0	19.9	74.1	367.	18.0
34.8	20.1	74.4	383.	18.5

TABLE VI Smoothed Thermodynamic Functions for Neon at the T = 0 Equilibrium Molar Volume, $V_0 = 13.39 \text{ cm}^3/\text{mole}^a$

^aThe values below 7 K are as obtained from the Ne 4 data, while the higher temperature values are as derived from an extrapolation to V_0 of the specific heat data for smaller molar volumes.

3.1. The Addenda Heat Capacity

The addenda heat capacities were determined in several experiments before the natural neon data were taken and again after the Ne 8 sample had been measured. The calorimeter never was disassembled or modified in any manner in the course of the addenda and the solid neon measurements. Equation (3) (with n = 1, 3, 5, 7, ...) is used to represent the addenda heat capacity in three ranges; 1–3.41, 3.41–9.32, and 9.32–52 K. The scatter of the experimental data gives a rms deviation of approximately 0.2% for each range. The indium in the bomb gasket and seals becomes superconducting at 3.41 K, and hence contributes a slight anomaly (less than 1%) at this temperature, so the addenda representations are chosen to exclude this temperature and no heat pulses ever included it. The ratio of the addenda heat capacity C_{Add} to the total measured heat capacity C_{Tot} depends to some extent on sample density but even more so on the temperature. Near 1 K,

Specific Heats of Solid Natural Neon

the ratio C_{Add}/C_{Tot} varies from 0.4 to 0.5 with decreasing sample molar volume, but by 2 K is in the range from 0.16 to 0.26. This ratio reaches a minimum of approximately 0.06 for all samples at 10 K, and then increases to 0.11 at 20 K, 0.25 at 30 K, 0.37 at 40 K, and 0.46 at 50 K. Hence, it is only at very low temperatures (below 1.5 K) and at high temperatures (above 30 K) where the precision with which the addenda is determined has a significant effect on the accuracy of the data. Typically, many data points were taken at low temperatures both for the addenda and for the samples (see below) so some precision is gained through averaging. The high-temperature data are in general less reliable in all cases.

3.2. Typical Neon Data

The data for each of the samples Ne 5 through Ne 8 are represented by variations of Eq. (3) in three separate temperature ranges; roughly, 1–3.5 K, 3.5–15 K, and 15 K to the melting temperature. The Ne 4 data are analyzed only for temperatures below 5 K. The low-temperature expansions must approach T^3 behavior in the T = 0 Debye limit, and are chosen to include only odd values of n, beginning with n = 3. The two higher temperature expansions use all integer values of n (0, 1, 2, 3, ...) since the heat capacity is approximately linear in the temperature near 4 K and becomes roughly constant at high temperatures. The rms deviations for all of these representations are approximately 0.2% for the lowest range, 0.1% for the intermediate range, and 0.3% for the highest range.

The data for the Ne 7 sample are presented in Figs. 2, 3, and 4 as being typical of those for all four samples, both in number of data points and in the experimental scatter. Figure 2 contains a reduced plot $(C_V/T^3 \text{ vs. } T^2)$, which is useful for extrapolation to T = 0 of the low-temperature data. The least-squares fit of Eq. (3) to these data is represented by the solid line; the rms deviation of 0.26 % is somewhat greater than is found for the other samples at these temperatures, possibly due to the scatter below $T^2 = 2 \text{ K}^2$. The T = 0 intercept can be defined to better than ± 0.3 %, which suggests that Θ_0 (as calculated from the coefficient of the T^3 term) should be reliable to ± 0.1 %.

Representations of this type were used to calculate the values of Θ_0 for the Ne 4, Ne 5, Ne 6, and Ne 7 samples which are given in the tables. The determination of Θ_0 for Ne 8 is not as straightforward since the extrapolation to T = 0 is dominated by two data points near 1 K which appear to be 1% too high. The computer fit which includes these data points gives $\Theta_0 =$ 91.1 K, instead of the 91.5 K which appears in Tables I and V. We find that all of the data (Ne 4 through Ne 7) for temperatures up to 4 K can be represented within the experimental scatter as a single curve on a reduced





plot of $C_{\nu}(\Theta_0/T)^3$ vs. $(T/\Theta_0)^2$, while the Ne 8 data lie roughly 1 % below this curve when $\Theta_0 = 91.1$ K is used. If, however, Θ_0 for Ne 8 is increased to 91.5 K, the Ne 8 data also lie on this common curve to better than ± 0.5 % except for the two points near 1 K. It is interesting to speculate that an orthohydrogen impurity of approximately 10 ppm could produce an effect of this magnitude.

Figures 3 and 4 present the experimental data in the form of deviations from smooth least-square fits of Eq. (3) to the C_{meas} (molar heat capacity



Fig. 3. Typical deviations of experimental data from a smooth curve for intermediate temperatures. The rms deviation is 0.07 %.



Fig. 4. Typical deviations of high-temperature data from a smooth curve. The rms deviation is 0.33 %.

uncorrected for bomb expansion) results. The rms deviation for the intermediate region (Fig. 3) is 0.07%, while that for the high-temperature region is 0.33%, with the major scatter occurring above 30 K.

4. DISCUSSION, NATURAL NEON

The plot of $\ln \Theta_0$ vs. $\ln V$ in Fig. 5 can be used to evaluate the limiting average value of the Grüneisen parameter, $\gamma_0 = -d \ln \Theta_0/d \ln V = 2.51$ (± 0.03) . The error bars on this figure correspond to approximately ± 0.1 % uncertainties in both Θ_0 and V. The value of Θ_0 , which we obtain for the 0 K equilibrium state $\Theta_0(13.39 \text{ cm}^3/\text{mole}) = 75.1 (\pm 0.1)$ K, is in good agreement with that given by Fagerstroem and Hollis-Hallet [75.0 (± 0.5) K]¹¹





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and by Fenichel and Serin [74.6 (\pm 1) K].¹² γ_0 also can be calculated from the extrapolation of low-temperature thermal expansion data to T = 0, but the only available data⁷ are not sufficiently precise to carry out this extrapolation. Our value of γ_0 does appear to be consistent with those values calculated from the higher temperature data, although, as we argue in Ref. 10, a more reasonable procedure involves the assumption of a volume dependence for γ , with one possibility being $\gamma_0 = 0.194 \pm 0.002 \text{ cm}^{-3} \text{ V}$. This representation is not unique, and gives a $\Theta_0(V)$ relation which differs from the straight line of Fig. 5 by the width of the line. On this basis, we would predict γ_0 (13.39 cm³/mole) = 2.60 \pm 0.03.

The volume dependence of the lattice vibrational properties for a solid can be expected to a first approximation to scale with Θ_0 ; that is, in this approximation all lattice frequencies scale identically with volume, and the shape of the density of states curve is not a function of volume. This assumption is equivalent to that of a temperature-independent thermodynamic Grüneisen parameter

$$\gamma = \beta B_T V/C_V = V(\partial S/\partial V)_T/C_V = \sum_i \gamma_i c_i/C_V$$
(5)

at constant volume. The right-hand side of Eq. (5) gives the result for γ in the quasiharmonic approximation, with $\gamma_i = -d \ln \omega_i / d \ln V$ and c_i being, respectively, the Grüneisen parameters and specific heats for the individual modes. The present data indeed can be represented by a common curve to better than $\pm 1\%$ at all temperatures when C_{ν} is plotted as a function of $T/\Theta_0(V)$. Small deviations exist, however, and these are illustrated in Fig. 6, where the smoothed results from Tables II through VI are plotted in reduced form as $\Theta(T, V)/\Theta_0(V)$ vs. $T/\Theta_0(V)$. The internal consistency of the results is quite evident in this figure, with a maximum difference between the four experimental curves (the curve for 13.39 cm³/mole is extrapolated) of 1.5% near $T/\Theta_0 = 0.12$. This difference appears to be systematic and smooth to within our estimated experimental accuracy of ± 0.3 % and to disappear for temperatures below roughly $0.08\Theta_0$ (6.5 K) and above $0.3\Theta_0$ (25 K). These results suggest that the higher frequency modes have γ_i 's which are slightly larger than those for lower frequencies, and hence that γ [Eq. (5)] should show a slight increase with increasing temperature at constant volume.

The magnitude of this increase can be estimated in the following manner. If C_V can be represented approximately as a universal function $C_V(T/\Theta_0)$, then the entropy also can be represented in the same fashion and to the same approximation as $S(T/\Theta_0)$. In particular, the entropy curve for Ne 6 is chosen for the reduced expression, since these results are for an "average" volume, and the entropies for the other volumes are considered to deviate



Fig. 6. A plot vs. reduced temperature of the smoothed specific heat results of Tables II–VI as expressed in terms of equivalent reduced Debye Θ 's. The values of Θ_0 are given in Table I and are plotted in Fig. 5.

linearly from it as

$$S(T/\Theta_0, V) = S_{\operatorname{Ne}6}(T/\Theta_0) + [(\partial S/\partial V)_{T/\Theta_0}]_{\operatorname{Ne}6}(V - V_{\operatorname{Ne}6})$$
(6)

The derivative, which must be evaluated at the molar volume of the Ne 6 data, is a function of (T/Θ_0) and is zero for temperatures below $0.08\Theta_0$. Equation (3) then can be used to calculate γ at this molar volume as

$$\gamma(T, V_{\operatorname{Ne} 6}) = (V/C_V) [(\partial S/\partial V)_T + (\partial S/\partial V)_{T/\Theta_0}]_{\operatorname{Ne} 6}$$
$$= \gamma_0(\operatorname{Ne} 6) [1 + \alpha(T)]$$
(7)

since the first term in the brackets is the temperature-independent value of γ_0 given in Fig. 5. Hence, the relative temperature-dependent contribution to γ , $\alpha(T)$, is equal to the ratio $(\partial S/\partial V)_{T/\Theta_0}/(\partial S/\partial V)_T$. The entropies given in Tables II through V were plotted as a function of T/Θ_0 for the various volumes, and no systematic differences greater than $\pm 0.5 \%$ were found at any temperature. This result is combined with the average values of $(\partial S/\partial V)_T$, which can be calculated from these tables to conclude that the magnitude of

the temperature-dependent contribution to γ is no greater than 1%. Figure 6 can be interpreted in terms of a temperature dependence for γ , so we will assume that γ changes from γ_0 to a high-temperature value γ_{∞} between temperatures of $0.08\Theta_0$ and $0.2\Theta_0$, with γ_{∞} differing from γ_0 by $+1 (\pm 1)$ %. This postulate is in excellent agreement with the independent analysis which is carried out in Ref. 10.

The variation with volume of the lattice frequency spectrum or the dispersion relations also has been determined directly at 4.7 K using inelastic neutron scattering techniques.⁶ These measurements give γ 's for the longitudinal acoustic and transverse acoustic modes as $\gamma_{LA} = 4.2 \pm 0.6$ and $\gamma_{TA} = 2.9 \pm 0.5$, respectively. While these results can be compared with the present data only after a suitable average over all modes, the small temperature dependence of γ which we observe and the magnitude of $\gamma_0 = 2.6$ suggest that the value of γ_{LA} is perhaps a bit high.

The present extrapolated results for $V_0 = 13.39 \text{ cm}^3/\text{mole}$ are compared in Fig. 7 with theoretical calculations,² with previous calorimetric results^{11,12} (as reduced to this same molar volume by Batchelder *et al.*⁷), and with C_V as calculated from the neutron scattering results.⁶ The agreement between the calorimetric results is quite good, although we do not observe the systematic oscillations which Fenichel and Serin¹² report for the Θ -vs.-*T* curve. The values from the neutron experiments⁶ appear to scale very well with ours, with a systematic difference of 1.3%, about one-half of which could be



Fig. 7. A plot of equivalent Debye Θ 's for $V_0 = 13.39 \text{ cm}^3/\text{mole}$ for the present results (Table VI) (solid line), for the data from Refs. 11 (FH) and 12 (FS) as analyzed in Ref. 7, as calculated from inelastic neutron scattering experiments of Ref. 6, and as given by theoretical calculations in Ref. 2 (dashed lines).

explained if their molar volume were to coincide with the smallest extreme of their lattice parameter uncertainty (4.462 \pm 0.002 Å vs. the x-ray value of 4.4638 Å).⁷ The agreement with the theoretical calculation is good above 7 K for the n = 12 model, although the volume dependence of C_V as calculated on this model is not correct.³⁰ The difficulty most likely lies in the form of the two-body potential which was used for these calculations, and there are prospects for better potentials in the near future.⁵

The comparison in Fig. 7 of the present results and the values of Θ which are derived from C_P data is not very satisfactory since the earlier data have been processed in two ways. First, the smoothed values of C_P have been converted to C_V using

$$C_P = C_V (1 + \beta \gamma T) \tag{8}$$

where γ is given by Eq. (5), and second, the values of C_V for each temperature have been adjusted to make them correspond to the 0 K equilibrium volume. The present results suggest a simple model for solid neon in which C_V is a function only of the reduced temperature $T/\Theta_0(V)$. Hence, the known thermal expansion for solid neon⁷ can be used to determine the molar volume and Θ_0 at P = 0 for each temperature, after which C_V can be obtained from the reduced curve. In practice, the relationships of Figs. 5 and 6 are used together with a tabulation of the Debye function. The values of Θ_0 which result from the use of the equation-of-state expression for γ_0 ($\gamma_0 = 0.197 \pm 0.002$ cm⁻³. V) range from 75.1 K at $V_0 = 13.391$ cm³/mole to 66.8 \pm 0.5 K at the triple point (24.6 K, 14.02 cm³/mole), where $T/\Theta_0 = 0.37$. The use of a constant value $\gamma_0 = 2.51$ would not alter these results appreciably. C_P then is calculated from Eq. (8), using Eq. (5) to calculate γ and the x-ray values⁷ for the thermal expansion coefficient β .

The resulting relationship for $C_P(T, P = 0)$ is given as the solid line in Fig. 8, where it is compared with direct determinations of C_P .^{11,12,17} The



Fig. 8. A comparison of C_P as calculated from the present results and as obtained from the smoothed results of Refs. 11 (FH), 12 (FS), and 17 (Clusius).

agreement below 20 K is well within the experimental uncertainties, especially if the data of Clusius *et al.*¹⁷ (taken for the pure isotope ²⁰Ne, T > 8 K) are increased slightly to compensate for the 1% isotopic mass difference between their sample and natural neon. Above 20 K, the smoothed results of Fenichel and Serin¹² begin to deviate systematically from the other data, as do the data of Fagerstroem and Hollis-Hallet¹¹ above 23 K. The latter authors give only a plot for this temperature region, and the points in Fig. 8 were read from the smooth curve in this plot. If the values of γ which are used in Eq. (8) to calculate C_P from our model for C_V are calculated from experimental thermodynamic quantities⁷⁻⁹ in a self-consistent fashion instead of using our equation of state, the predicted curve for C_P would tend to bend over above 21 K to a value of roughly 24 J/mole-K at the triple point.

The agreement for C_p between the relation which is calculated from our C_V data and the results of Clusius *et al.*¹⁷ is excellent at all temperatures, as is the agreement with Fagerstroem and Hollis-Hallet¹¹ at 23 K and below. The reason for the rapid increase in C_p , which both Fenichel and Serin¹² and Fagerstroem and Hollis-Hallet¹¹ observe near the melting point, is not clear. None of our samples show a premelting anomaly of this magnitude (see Fig. 4, for instance, where the melting temperature is 46.8 K, and Fig. 6), in basic agreement with the results of Clusius *et al.*¹⁷ Schoknecht and Simmons³¹ have shown recently that vacancy effects should be quite small in C_p for solid neon near these temperatures. Our calculated values of C_p also are in excellent agreement with those given by Goldman *et al.*² for their m = 12 ISC calculation.

The present data can be used to test the Lindeman melting relation which associates the melting temperature T_m with the relative mean square amplitude $x^2 = \langle \delta r^2 \rangle / r_s^2$, $(4\pi r_s^3/3) = V_m$ of the atomic vibrations in the solid at the melting line. The usual relation³³

$$x^{2} = (9\hbar^{2}/mk_{B})(T_{m}/\Theta^{2}r_{s}^{2}) = 41.11 \,(\text{cm}^{2}\cdot\text{K})(T_{m}/\Theta^{2}V_{m}^{2/3})$$
(9)

(where \hbar and k_B are the Planck and Boltzmann constants, respectively, and m is the mass of the atom) is applicable only for $T_m > \Theta$, whereas the melting temperatures of solid neon in Table I all are less than $0.6\Theta_0$. Hence, we have calculated a Debye model generalization of Eq. (9) following Ziman's approach,³² in which x^2 becomes [with $x^2_{\text{classical}}$ given by Eq. (9)]

$$x^{2} = x_{\text{classical}}^{2} [1 + (z^{2}/36) - (z^{4}/3600) + (z^{6}/2.12 \times 10^{5}) - \cdots]$$
(10)

where $z = \Theta/T_m$. This expression is valid for the present range of z and is based on a series expansion³³ of the integrand of Ziman's equation (2.111).³²

Figure 9 gives a plot of x as calculated from the present data (Table I) for both Eqs. (9) and (10), with $\Theta = \Theta_0$. This plot is given in terms of T_m/Θ_0



Fig. 9. A test of the Lindeman melting relation, with the reduced atomic vibration amplitude x plotted as a function of reduced melting temperature. See the text for details. "Classical" refers to the use of Eq. (9); "Exact" refers to the use of Eq. (10).

to emphasize the range of the reduced melting temperature for our data. A calculation for the triple point also is included which uses the extrapolation to the triple point volume which is described in the previous paragraphs. The value of x appears to be relatively constant over a wide range of temperature (24.6–53.5 K) and volume (14–12.4 cm³/mole), and close to the values for other solids,³² especially when the modified expression is used. The deviations are systematic, however, so extrapolations to higher temperatures are of doubtful validity.

5. RESULTS FOR ²⁰Ne AND ²²Ne

We initially had planned to repeat the V_0 (approximately 13.35 cm³/ mole) measurements with samples of pure ²⁰Ne and ²²Ne, and had purchased gas from the Mound Laboratories for this purpose. Measurements on ²⁰Ne, however, showed anomalies below 4 K and excessive warming rates, so extensive data were taken on this sample to outline the problems which were involved. The quantity of ²⁰Ne in the sample (0.2170 \pm 0.0002 moles) gave a molar volume in the bomb at T = 0 of 13.38 \pm 0.01 cm³, which is to be compared with the T = 0, P = 0 molar volume of 13.397 given by Batchelder *et al.*¹⁶ This suggests a minimum neon pressure of 20 bar. The low-temperature anomalies made it impossible to extrapolate the data directly to T = 0 to obtain a value for Θ_0 as was done for natural neon.

The ²⁰Ne was removed from the system and was replaced by ²²Ne. The quantity of this gas was inadequate to fill the bomb completely at T = 0, and because of experimental problems the number of moles (0.216 \pm 0.001) in the sample had to be estimated from the observed melting temperature and the natural neon V_m -vs.- T_m relation. This introduces an additional uncertainty in the experiment which should not be greater than that quoted above. Low-temperature anomalies also were observed for this sample, which unfortunately were somewhat greater in magnitude than for ²⁰Ne. The experiment was terminated after only a few heat-capacity measurements were

made when it was realized that the anomalous effects could be understood in terms of a hydrogen impurity of approximately 0.2% (well within the supplier's specifications). Normal hydrogen exhibits a very large lowtemperature heat-capacity anomaly below 4 K, and considerable heat is generated due to the ortho-parahydrogen conversion.^{34,35} Indeed, the anomaly and the heating both are consistent to within a factor of two or so with the postulate of a hydrogen impurity of this magnitude. Attempts to remove the hydrogen from the neon failed for various reasons, and the above experiments were not repeated.

One of the conclusions which follows from the experiments on natural neon is that the volume-dependent heat-capacity data scales very well with the reduced temperature T/Θ_0 , especially for temperatures less than $0.08\Theta_0$ (Fig. 6). If this same type of scaling applies to the measurements on the isotopes, the natural neon data can be used to determine values of Θ_0 for the isotopes from the high-temperature data for which the impurity effects are small. The common relationship between Θ/Θ_0 and $T(\Theta_0$ for the natural neon is plotted as the solid curve in Fig. 10, where the $V = 13.39 \text{ cm}^3/\text{mole}$



Fig. 10. The reduced equivalent Debye Θ plot (as derived from Fig. 6) which is used to determine Θ_0 for the neon isotopes. The symbols indicate the actual experimental data. See the text for details.

relation is used for $T/\Theta_0 > 0.08$. The data for ²⁰Ne and ²²Ne have been converted to Θ -vs.-*T* relations, and these relations have been normalized through the use of appropriate values of Θ_0 to make them fit onto this curve. The agreement is excellent, with uncertainties in the apparent values of Θ_0 of ± 0.1 K for ²⁰Ne and ± 0.2 K for ²²Ne, where the data are more limited. The low-temperature deviations are due to the onset of the anomalous behavior associated with the hydrogen. The heat-capacity data have not been corrected for the presence of the $0.2 \pm 0.1 \%$ hydrogen impurity since the thermal properties of solid hydrogen are similar to those of neon at temperatures well away from the anomaly (that is, above 3 or 4 K).³⁴ Table VII gives the values of Θ_0 which were used to scale the isotope data. The relatively large uncertainty in the ²²Ne value of Θ_0 occurs because of a greater uncertainty in the quantity of sample for these measurements.

We also have plotted in Fig. 10 the low-temperature results for the natural neon Ne 4 sample using $\Theta_0 = 75.1 \pm 0.1$ K. This sample did not fill the bomb completely due to a low initial pressure at the melting line, so a $C_P - C_V$ correction has been applied to the data above 6 K using the data of Batchelder *et al.*⁷ A similar correction has been applied to the highest temperature ²²Ne point, although not to the ²⁰Ne data since these were taken at constant volume.

The values of Θ_0 given in Table VII refer to the actual molar volumes of the samples; these are unambiguous for ²²Ne and natural Ne 4 since the samples had pulled away from the walls and were at zero pressure, so the molar volumes of ²²Ne (13.321 cm³) and natural Ne (13.391 cm³) as given by Batchelder *et al.*¹⁶ can be used. The molar volume of the ²⁰Ne sample is as given previously in this section.

These various experimental results can be compared most legitimately at a common molar volume, so we have made use of our value of γ_0 (= 2.6) for natural neon and the Grüneisen relation $\Delta\Theta_0 = -\gamma\Theta_0\Delta V/V$ to reduce the Θ_0 values to the molar volume of the natural neon (13.391 cm³). The uncertainty for the ²⁰Ne data increases in this calculation because of the

The Results for C_V at Low Temperatures for the Neon Isotopes							
- Mass, g/mole	Θ_0, K	V, cm ³ /mole	$\Theta_0(V_0),^a \mathrm{K}$	$\Theta_0 M^{0.5},$ K-(g/mole) ^{0.5}			
20.00 20.17 22.00	$75.9 \pm 0.1 75.1 \pm 0.1 73.5 \pm 0.3$	13.38 ± 0.01 13.391 13.321	$75.7^{5} \pm 0.2 75.1 \pm 0.1 72.5 \pm 0.3$	338.8 ± 1.0 337.3 ± 0.5 340.0 ± 1.5			

FABLE V	п
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 ${}^{a}V_{0} = 13.391 \text{ cm}^{3}/\text{mole.}$

somewhat greater uncertainty in the molar volume for this sample. An elementary picture suggests that Θ_0 should vary as the inverse square root of the isotopic mass, and this postulate is tested in the last column of Table VII where $\Theta_0 M^{0.5}$ is tabulated. The agreement appears to be within experimental error. The concentration of the major component for ²⁰Ne is 99.9% or better, while that for ²²Ne is 99% or better, in agreement with the Mound Laboratories specifications.

The present data can be compared directly with the results of Somoza and Fenichel,¹⁸ who performed constant-pressure heat-capacity measurements on separated neon isotopes. Our values appear to lie approximately 1.6 K higher than theirs for each of the isotopes, and this is slightly higher than the combined estimated uncertainties for the two experiments. A direct comparison with the data of Clusius *et al.*¹⁷ is not possible since their C_p data extended only down to 8 K.

The high temperature C_{ν} data (near 30 K) for the two isotopically pure samples tend to lie slightly higher (by 1-2%) than the data for the natural neon at the same values of T/Θ_0 . This perhaps is understandable in terms of the hydrogen impurities, since in each case we are approaching pressures and temperatures which are close to the hydrogen melting line. We know very little about the effect of dissolved hydrogen or neon on the melting properties. The observation can be made, based on the heating which we observed at low temperatures, that the hydrogen must exist in the solid neon as discrete (although perhaps very small) particles since the ortho-para conversion can take place only via the mechanism of an interaction between two orthomolecules. The conversion would be very unlikely if the H₂ molecules were distributed in random solution. If these particles exist, then local melting effects could be observed with an enhanced specific heat for the solid as a whole. Certainly, there do not appear to be any significant deviations of the neon isotope data from the reduced curves which we find for natural neon.

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