Experimental Determination of the P–T Melting Curves of Kr, Ne, and He*

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Pressure–temperature melting data have been obtained at pressures of 0–8 kbar for Kr, 0–10 kbar for Ne, and 1–10 kbar for He. The estimated accuracy of the data is ± 1 bar and ± 0.002 to $\pm 0.011°$K. Use of a modified Simon melting equation of the form $P = A(T+D)^c + B$ to represent the data removes nearly all of the systematic deviations which are observed when the usual Simon melting equation $P = AT^c + B$ is applied. The modified form of the equation also provides much better high pressure extrapolations from the melting curve data.

In an earlier paper[1] (subsequently referred to as I) apparatus and techniques for the precise measurement of the P–T melting curves of gases were described and the data for argon were presented. The same apparatus and techniques have now been applied to the measurement of the P–T melting curves of krypton, neon, and helium at pressures up to 10 kbar and the results are reported below. The degree to which the data are fit by the semiempirical Simon equation

$$P = AT^c + B \tag{1}$$

and by the modified form of this equation, introduced in I,

$$P = A(T+D)^c + B \tag{2}$$

is also discussed. [In Eqs. (1) and (2), A, B, c, and D are empirically determined constants.]

EXPERIMENTAL

In the experimental method used, a pressure vessel was held at a selected temperature and filled with the gas being studied. The vessel was connected to the external pressure generating and measuring system with a length of small diameter high pressure tubing (0.79 mm o.d., 0.15 mm i.d.) which was kept open during the experiment. The temperature of the vessel was measured with a platinum resistance thermometer, while the pressure in the system was measured using a precision manganin resistance manometer calibrated against the mercury melting curve as described in I. The presence of coexisting solid and fluid phases in the vessel was verified by slightly increasing or decreasing the pressure in the external system to change the amount of material in the vessel. When two phases were present the pressure would return to its initial value when equilibrium was again attained after such an operation. Further details of the experimental apparatus and procedures can be found in I.

The data for krypton, neon, and helium are presented in Table I. (Triple point data[2,3] for krypton and neon are included.) The data shown are from one run each for krypton and neon and from two different runs for helium. An additional short run was made for neon to check the reproducibility of the results. The pressure

measurements have an estimated accuracy of ± 1.0 bar, based on the provisional "mercury melting line" pressure scale discussed in I. The temperature measurements are based on the "1968 International Practical Temperature Scale" and are estimated to be accurate to within $\pm 0.002°$K at temperatures above 25°K. At lower temperatures the sensitivity of the platinum
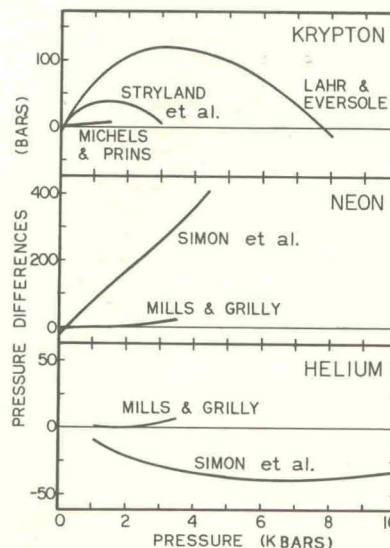

FIG. 1. Comparison of previously published P–T melting curve data with those presented here. The differences shown are the other data (represented by the Simon equations published in Refs. 6–12) minus the present data. The data of Holland, Huggill, and Jones (Ref. 13), Dugdale and Simon (Ref. 6), and Langer (Ref. 14) are represented within their experimental uncertainty by the curve for helium labeled Simon *et al.*

thermometer decreases so the temperature measurements decrease in accuracy, reaching an estimated maximum uncertainty of about $\pm 0.011°$K at 13.4°K which was the lowest temperature measured.

After completion of each data run a sample of gas was collected from the system and a mass-spectroscopic analysis was performed.[4] The results of these analyses are shown in Table II along with the estimated maximum effects of the impurities on the respective

TABLE I. Experimental $P–T$ melting data. The column labeled "Dev." gives the deviation of the experimental data point from Eq. (2) with constants given in Table III.

Temperature (°K)	Pressure (bar)	Dev. (bar)	Temperature (°K)	Pressure (bar)	Dev. (bar)
			Krypton		
115.773[a]	0.73[a]	0.03	215.873	4 087.30	−0.46
138.270	788.25	−0.08	215.874	4 087.42	−0.38
138.284	788.87	0.02	228.296	4 687.23	−0.20
138.286	788.79	−0.13	228.302	4 687.63	−0.08
152.379	1324.95	−0.12	240.685	5 302.93	0.04
165.790	1863.60	0.49	253.143	5 939.51	0.75
165.790	1863.18	0.03	253.150	5 939.79	0.71
178.297	2388.24	0.26	265.674	6 594.43	−0.47
178.303	2388.12	−0.11	279.160	7 318.88	−0.24
190.430	2917.30	0.03	279.161	7 319.00	−0.15
190.431	2917.24	−0.10	291.695	8 008.52	0.06
202.696	3471.70	0.06	291.695	8 008.51	0.04
			Neon		
24.555[b]	0.43[b]	−0.85	78.900	5 555.66	−0.13
33.144	629.03	0.41	82.311	6 002.54	−0.15
33.146	629.24	0.44	82.312	6 003.62	0.81
41.530	1355.20	0.90	87.519	6 702.30	−0.25
41.530	1355.19	0.88	87.520	6 702.55	−0.15
48.497	2027.63	0.10	93.615	7 548.49	0.93
48.498	2027.81	0.15	93.615	7 548.04	0.47
54.513	2653.57	−0.30	96.716	7 988.15	0.36
54.513	2653.64	−0.25	96.716	7 989.44	1.61
59.873	3243.72	−0.38	99.962	8 456.69	0.76
59.874	3243.80	−0.45	100.023	8 465.09	0.42
64.665	3794.87	−0.80	105.253	9 234.66	0.34
64.665	3794.96	−0.74	105.253	9 234.65	0.31
69.476	4370.20	−0.62	109.870	9 928.11	−0.69
69.477	4370.26	−0.64	109.876	9 929.21	−0.53
74.168	4951.52	0.06	110.040	9 953.55	−1.15
74.170	4951.34	−0.30	110.041	9 953.58	−1.21
78.896	5555.34	0.07			
			Helium		
13.417	944.17	−1.17	31.140	3 544.98	−0.13
13.975	1008.96	0.40	31.236	3 561.51	−0.67
14.459	1065.41	0.87	37.092	4 653.24	0.65
15.060	1134.88	−0.63	37.095	4 653.39	0.19
16.536	1317.19	0.98	42.385	5 722.97	0.71
16.541	1317.19	0.28	42 386	5 722.72	0.20
16.541	1317.00	0.07	47.105	6 739.59	0.10
21.365	1967.90	−1.04	47.106	6 739.81	0.12
21.366	1968.75	−0.45	51.511	7 739.51	−0.70
26.361	2734.49	−0.21	51.514	7 740.17	−0.67
26.362	2734.76	−0.13	56.004	8 809.02	−0.47
26.447	2748.89	0.25	58.429	9 406.51	0.04
26.450	2749.40	0.25	60.863	10 019.53	0.46
31.139	3545.16	0.20	60.864	10 019.19	−0.18

[a] Triple point values taken from Ref. 2. [b] Triple point values taken from Ref. 3.

melting curves.[5] For krypton and neon the maximum shifts are within the experimental uncertainty, but for the first data run for helium this is not the case. Because of the relatively large impurity content of the original helium sample, a few points on the helium melting curve were reproduced using helium of a much higher purity (30 ppm of neon; no other detectable impurities). These points, which are included with the data in Table I, were all found to lie within the experimental scatter of the original helium data, indicating that impurity effects were also negligible in this case.

The data for helium extend to temperatures somewhat below 14.9°K, the temperature at which solid helium transforms from the fcc structure to the hcp structure.[6] However, the scatter in the data at low temperatures was sufficiently great that no sharp change in the slope of the melting curve at this point could be observed.

Several other high-pressure P–T melting curve measurements have been reported for krypton,[7–9] neon,[10,11] and helium.[6,11–14] A comparison between these other results and the data reported here is given in Fig. 1. The agreement is within the reported error estimates of the other investigators except for the data of Michels and Prins[7] for krypton and the data of Mills and Grilly[11] for neon and helium. Michels and Prins report an accuracy of ±0.01% in pressure and ±0.001°K in temperature, while their results differ from those presented here by from 1 to 8 bar. The purity of the krypton they used is not known since no analysis was performed, but if it is assumed that their krypton had an impurity content similar to that of the argon they used (about 0.16%), then the resulting melting curve shift could account for nearly all the difference indicated in Fig. 1. However, the fact that the Michels and Prins melting measurements differ in almost identical fashion from the present measurements for krypton and from the measurements for

TABLE II. Impurity concentrations.

Sample	Impurity[a]	Concentration (ppm)	Maximum ΔT (°K)[b]
Kr	Ne	53	0.012
Ne	Ar	18	0.002
He (Run 1)	Ne	1000	
	Ar	15	
	N_2	12	0.090
He (Run 2)	Ne	30	0.002

[a] Only the detectable impurities are listed. Concentration of any other impurity is less than 4 ppm.

[b] These values are estimated using the usual formula for the lowering of the melting point by dilute impurities (see Ref. 5). The numbers given are for the highest temperatures at which measurements were made for each gas. The values of the latent heats needed in the calculations were estimated from the low pressure values and known trends along the melting curve.

TABLE III. Parameters for the Simon and modified Simon melting equations determined from least-squares fits to the data of Table I. The units are such that pressures are given in bars and temperatures in °K. The number of significant figures retained in this table reflects the number necessary for accurate reproduction of the melting data and does not reflect the statistical uncertainty in the determination of the parameters by the least-squares procedure. Since the parameters were very highly correlated, other choices of parameters might represent the data almost as well.

	Simon Equation [Eq. (1)]		
	A	B	c
Kr	1.61845	−2532.72	1.54729
Ar[a]	2.67348	−2293.25	1.52299
Ne	8.90498	−1174.85	1.51708
He	17.83518	−31.86	1.54171

	Modified Simon Equation [Eq. (2)]			
	A	B	c	D
Kr	3.36253	−1778.71	1.44084	−38.096
Ar[a]	4.99313	−1484.94	1.43057	−30.179
Ne	15.70774	−587.70	1.41852	−11.685
He	18.17612	−16.24	1.53805	−0.218

[a] Data taken from Ref. 1.

argon reported in I suggests that some systematic factor (for example a difference in the pressure scales used in the two laboratories) may also be present.

Mills and Grilly report an accuracy of ±0.05% in pressure and a temperature accuracy of ±0.03°K except in the range 31–55°K where they state that their temperature uncertainty may reach ±0.1°K. The helium they used had less than 0.08% impurities, while their neon had between 0.09% and 0.19% impurities. The discrepancy between their helium data and that reported here (about 7 bar at most) could be accounted for entirely by impurities and temperature errors within the stated limits. However the maximum shift in the neon data which can be accounted for by the combined effects of the impurity content and the temperature uncertainty is only about 15 bar, which is much less than the maximum observed disagreement of 25 bar. The reason for the disagreement in this case is not known at present.

THE SIMON EQUATION

The Simon equation [Eq. (1)] has long been used to represent P–T melting curve data, and for this reason many attempts have been made to derive this equation from first principles. However, significant systematic deviations from the Simon equation were found for the argon data presented in I, casting some doubt upon the fundamental significance of this
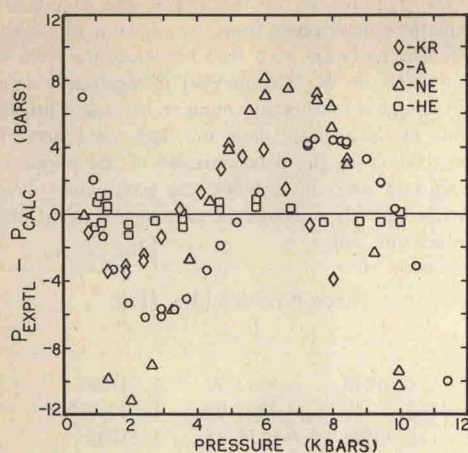
FIG. 2. Deviations from Eq. (1) using constants given in Table III. The deviations at the triple points which are not shown are +9.4 bar for krypton, +22.8 bar for argon, and +30.9 bar for neon. Some graph symbols represent multiple data points in this and in subsequent figures.

equation. To check whether this behavior is a more general feature of $P-T$ melting curves, Eq. (1) was least-squares fit to the data of Table I for krypton, neon, and helium. The values obtained for the constants are listed in Table III along with the constants for argon which were determined in I. The extent to which the equation fits the data is best exhibited in a plot showing the deviation of each experimental point from the calculated function. These deviation plots are presented in Fig. 2. (The results from I for argon are also shown for comparison.) First, one should note that the deviations are much larger than the experimental accuracy except in the case of helium. Second, one can see that the deviations are systematic; that is they are not randomly distributed about zero, but rather follow curves which appear remarkably similar for krypton, argon, and neon. (Since the deviations for helium lie within the experimental scatter, little can be said about

TABLE IV. Corresponding states data. The column labeled "Range" gives the range of reduced pressures spanned by the data.

	ϵ (erg)[a]	σ (Å)[a]	T' (°K)	P' (bar)	Range
Kr	2.384×10^{-14}	3.591	172.7	515	0–16
Ar	1.654	3.405	119.8	419	0–27 [b]
Ne	0.491	2.749	35.6	237	0–42
He	0.141	2.556	10.22	84	11–119

[a] The parameters given are for an intermolecular potential of the Lennard-Jones form $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ and were obtained from Ref. 15.

[b] Data for argon from Ref. 1.

their systematicity.) These systematic deviations are a typical result of a least-squares analysis whenever the functional form used does not match the shape of the "best" curve which could be drawn through the experimental points. Thus it can be said that Eq. (1) is not the "best" functional form which could be fit to the melting data for these gases.

The data for helium are in some sense anomalous in that they are fit by the Simon equation much better than are the other data. In order to investigate the reasons for this anomaly, it is instructive to look at the range of "reduced" pressures and temperatures spanned by the data for the different substances. According to
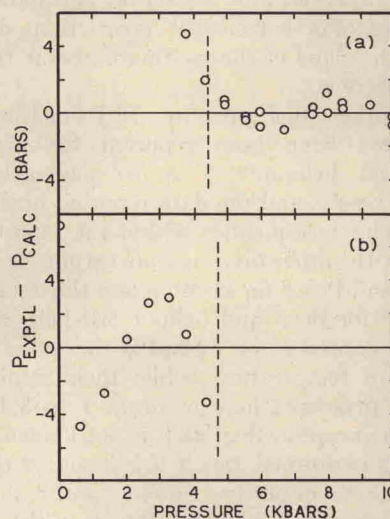

FIG. 3. Deviations from Eq. (1) for neon. (a) All points to the left of the vertical dashed line were weighted zero and the remainder of the points were least-squares fit to determine the constants in Eq. (1). The deviations at low pressures increased monotonically with decreasing pressure to a maximum of 146.8 bar at the triple point. (b) All points to the right of the vertical dashed line were weighted zero and the remainder of the points were least-squares fit to determine the constants in Eq. (1). The magnitude of the negative deviations at high pressures increased monotonically with increasing pressure, reaching a deviation of −172.3 bar at 9.95 kbar.

to the theory of corresponding states,[15] if the intermolecular potential for several substances can be put in the form $\phi(r) = \epsilon f(r/\sigma)$, where ϵ and σ are characteristic energies and lengths, then a characteristic pressure $P' = \epsilon/\sigma^3$ and a characteristic temperature $T' = \epsilon/k$ can be defined for each substance (here k is Boltzmann's constant). The theory then states that the melting curves for all such corresponding materials should coincide when expressed in terms of the reduced pressures $P^* = P/P'$ and temperatures $T^* = T/T'$.

Although the law of corresponding states is not exact for the noble gases due to quantum effects and possibly to differences in the intermolecular potentials, nevertheless it is sufficiently well satisfied so that comparison

of the reduced ranges of the data for these materials is meaningful. A set of values for the parameters ϵ and σ and the corresponding characteristic temperatures and pressures for krypton, argon, neon, and helium are given in Table IV. Also given in the table are the reduced pressure ranges covered by the experimental data for these cases. (Since the intermolecular potential parameters are not known exactly, the values in Table IV are only approximate, but they are sufficient for the present purposes.) It can be seen that the data for helium cover a much greater reduced pressure range than do the data for the other gases. Also the data for the other gases extend to their triple points ($P^*\sim0$), while the data for helium extend only down to $P^*\sim11$. Thus in terms of reduced units, the lowest data point for helium lies *above* most of the data for the other gases. This suggests that the reason the Simon equation fits the data for helium much better than it does for the other gases may be that the Simon equation is a good representation of the melting curve in the high pressure region (say above $P^*=15$), but that it doesn't quite represent the data at lower pressures ($P^*=0-15$).

If this hypothesis is correct then a least-squares fit of only the high pressure portion of the data for the other gases should yield substantially reduced deviations with little or no systematicity remaining. Fig. 3(a) shows what happens to the deviations from Eq. (1) for neon when only the high pressure portion of the data (above $P^*=15$) is fit. The deviations are reduced essentially to within the noise level of the data although a slight systematic trend can still be discerned. To check whether this improved fit is due only to the smaller range of the fitted data, the low pressure data for neon were fit over a range of approximately equivalent length. The resulting deviations are displayed in Fig. 3(b). These deviations are

FIG. 5. Extrapolations of (a) Eq. (1) and (b) Eq. (2) for neon. Constants in the equations were determined by least-squares fits to all data below 7 kbar (open circles) and to all data below 3 kbar (solid circles). Extrapolated curves varied smoothly between the types of behavior shown as the range of data used in determining the constants was varied between the above limits.

much greater and are obviously systematic. The results for argon are found to be similar although less conclusive due to the much smaller reduced range of the argon data. Nearly all of the krypton data points lie below $P^*=15$ so those data could not be used in checking the hypothesis.

MODIFIED SIMON EQUATION

In I it was discovered that a modified Simon equation, Eq. (2), fit the argon data much better than did the Simon equation, Eq. (1). This modified equation has now been fit to the other data as well, and the constants are listed in Table III. The deviations from this equation are displayed in Fig. 4 and tabulated in Table I. Since the Simon equation already fit the data for helium to within the experimental uncertainty the modified equation results in little improvement in that case, but it seems to provide a much improved representation of the melting curves of neon, argon, and krypton. It should be noted, however, that the deviations still exhibit some systematicity.

Another test of the degree to which the Simon and modified Simon equations represent the melting curves of the noble gases is to fit these equations to only the low pressure portions of the melting curve data and then to see how well the equations extrapolate to the higher pressure regions. This is a question of some interest, since one of the most important uses for
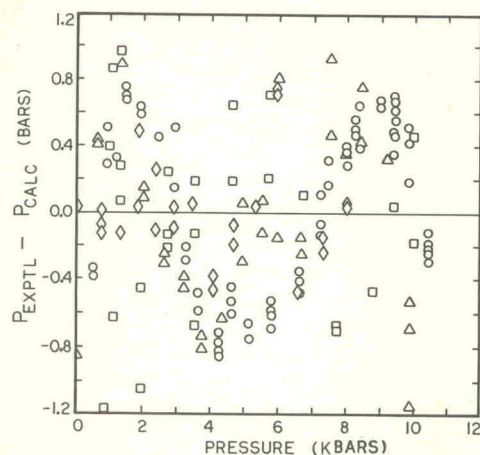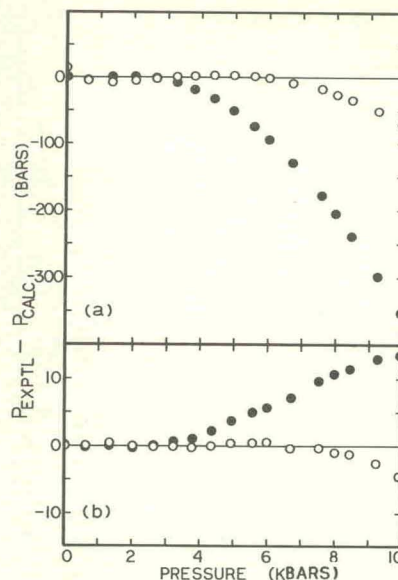

FIG. 4. Deviations from Eq. (2) using constants given in Table III. The symbols are the same as for Fig. 2. The deviation at the triple point for argon which is not shown is −1.7 bar.
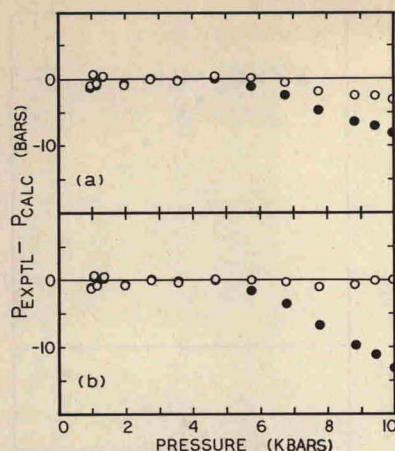
FIG. 6. Extrapolations of (a) Eq. (1) and (b) Eq. (2) for helium. Constants in the equations were determined by least-squares fits to all data below 7 kbar (open circles) and to all data below 5 kbar (solid circles).

empirical equations such as these is in extrapolating to pressures above those accessible in the laboratory. Such fits have been performed and the results for neon and for helium are shown in Figs. 5 and 6. The results for argon and krypton are qualitatively the same as those for neon. For these gases the Simon equation begins to diverge rapidly while the modified Simon equation shows very little divergence even when extrapolating to pressures more than twice the maximum used in determining the constants in the equation. For helium, however, the modified Simon equation shows essentially no improvement over the Simon equation, with both of them diverging somewhat at high pressures.

These various results lead to the conclusion that (1) the modified Simon equation [Eq. (2)] provides a better representation of the melting curves of the noble gases than does the Simon equation [Eq. (1)] particularly for the low pressure portions of these curves; (2) when only low pressure melting data is available to determine the constants in the equation, the modified Simon equation provides a much more reliable extrap-

olation than does the Simon equation, but if higher pressure data is available there is little reason for preferring one of these equations over the other; (3) neither of these equations provides exact representation of the melting curves since all extrapolations show some divergences from the data and there is evidence of systematicity in the deviations of the data from both equations. Thus although Eq. (1) and Eq. (2) are quite useful for purposes of extrapolation and interpolation, it is not certain at present whether the functional forms or the empirically determined constants for these equations have any definite fundamental significance.

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[3] The triple point temperature for neon was taken from a table of secondary temperature reference points, Metrologia **5**, 35 (1969). The triple point pressure was taken from Ref. 2.
[4] Mass spectroscopic analyses were performed by Gollob Analytical Service Corp., Berkeley Heights, N.J.
[5] The usual formula for impurity effects on melting $\Delta T = RT^2 x/L$, where R is the molar gas constant, x is the impurity concentration, and L is the latent heat of fusion, is derived in many standard texts. See, for example, J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939), p. 288. This formula is derived by assuming the impurity is completely soluble in the fluid phase and completely insoluble in the solid phase, so, in most cases, it should provide an upper limit for the melting curve shift which could be caused by a given impurity concentration.
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