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 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.

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.

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

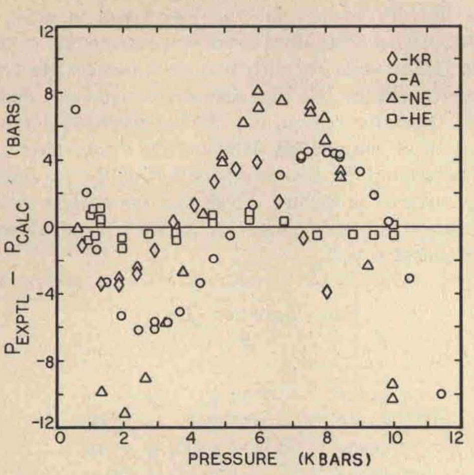

FIG. 2. Deviations from Eq. (1) using constants given in Table III. The deviations at the triple points which are not shown are +9.4 bar for krypton, +22.8 bar for argon, and +30.9 bar for neon. Some graph symbols represent multiple data points in this and in subsequent figures.

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 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.

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.

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 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 $T^*=T/T'$.

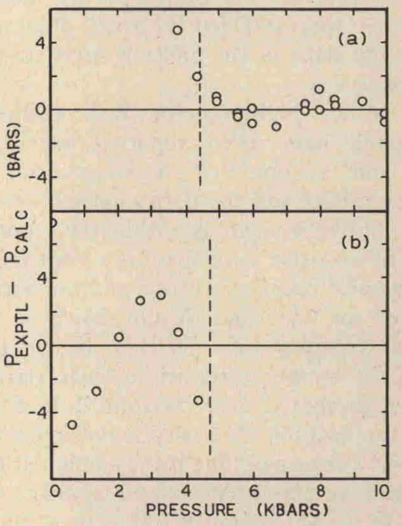

FIG. 3. Deviations from Eq. (1) for neon. (a) All points to the left of the vertical dashed line were weighted zero and the remainder of the points were least-squares fit to determine the constants in Eq. (1). The deviations at low pressures increased monotonically with decreasing pressure to a maximum 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.

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