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 ($P^* \sim 0$), while the data for helium extend only down to $P^* \sim 11$. 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 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.

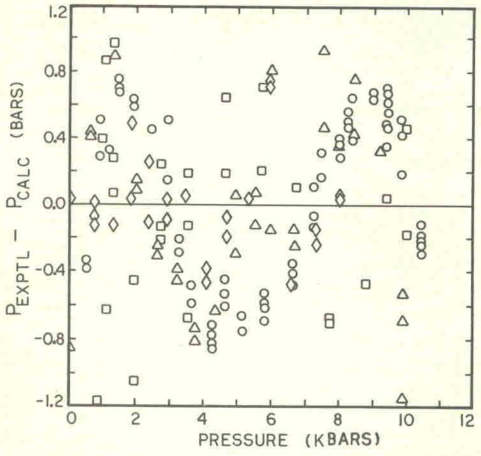

FIG. 4. Deviations from Eq. (2) using constants given in Table III. The symbols are the same as for Fig. 2. The deviation at the triple point for argon which is not shown is −1.7 bar.

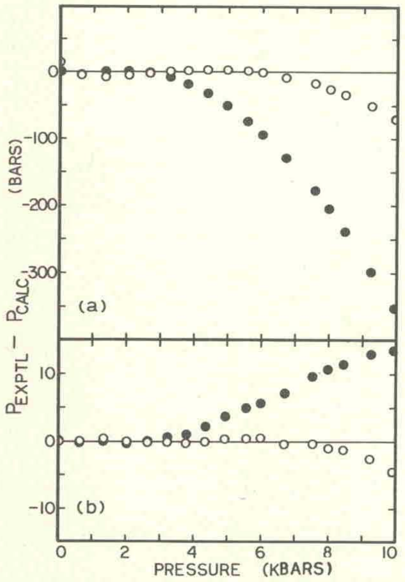

FIG. 5. Extrapolations of (a) Eq. (1) and (b) Eq. (2) for neon. Constants in the equations were determined by least-squares fits to all data below 7 kbar (open circles) and to all data below 3 kbar (solid circles). Extrapolated curves varied smoothly between the types of behavior shown as the range of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

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

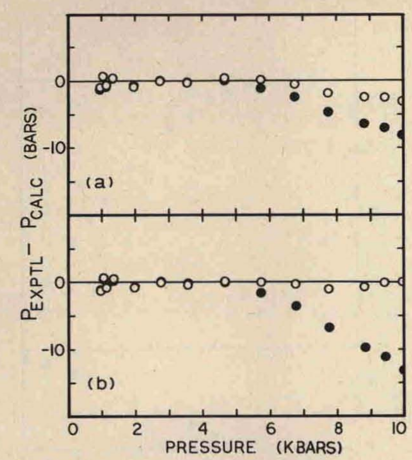

FIG. 6. Extrapolations of (a) Eq. (1) and (b) Eq. (2) for helium. Constants in the equations were determined by least-squares fits to all data below 7 kbar (open circles) and to all data below 5 kbar (solid circles).

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 extrapolation 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 $\Delta T = RT^2x/L$, 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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