

## DISCUSSION

## Effect of Pressure on Melting

A number of melting experiments on a variety of polyethylene samples under pressure can be found in the literature. In most cases it is only possible to distinguish whether branched or linear polyethylene was measured, little further characterization is usually presented. Along with chemical information, the thermal history, density, morphology, and heating rate are necessary to discuss melting. Without this information, it is difficult to compare the results of various workers, since under the common name polyethylene they may actually be measuring quite different substances. In particular, on slow heating folded-chain crystals will reorganize to more perfect crystals and yield false data. Heating rates used in this research were shown to be sufficiently fast to convert metastable folded-chain crystals to metastable melt with a minimum of reorganization.<sup>24</sup> Complications from superheating for more perfect extended-chain crystals will be discussed below.

The results of all available investigations on linear polyethylene are included in Table IV. It was necessary to take graphical points from many of the papers, since numerical data were not tabulated. The graphical or numerical character of the data is indicated by "g" or "n," respectively, in column 1. The melting temperature versus pressure data for each reference were fitted to the same quadratic form:  $T_m = A + BP + CP^2$ . Examination of Table IV shows that the slope ( $B$ ) and curvature ( $C$ ) of the melting curves differs among the several sets of data. Experimental difficulties as well as difference in samples accounts for the wide spread. Apart from our measurements, only Baltenas and Igonin used differential thermal analysis; all other values were arrived at by slow volume measurements. In all the studies quoted, the melting curve of polyethylene decreases in slope with increasing pressure; on a  $T_m$  versus  $P$  graph the curves bend toward the  $P$  axis. Such behavior is typical of both polymers and nonpolymeric materials and is coupled to the observed decrease in compressibility with pressure.

It is difficult to evaluate the slope of the melting curve near atmospheric pressure because the curve rises steeply in this region. One procedure is to compute the slope by differentiating the least-squares expression and evaluating  $dT_m/dP$  at 1 bar. The results are shown in column 7 of Table IV. This may underestimate the steeper slope at low pressures. A better method is to calculate the slope from the point measured at atmospheric pressure and the point at the next highest measured pressure. Slopes calculated from our measurements by the latter method are listed in Column 8 of Table IV together with the published values of the slopes of other workers. In column 7 we list the slopes calculated by the least squares method.

To calculate  $dT_m/dP$  at 1 bar for equilibrium melting, it is only necessary to know the values entering the Clausius-Clapeyron expression. In the