



Fig. 2. PDTA traces of melting and crystallization under pressure.

because the temperature of the cell has been rising during fusion as indicated by the positive slope of the plateau in the T trace. The breadth of the plateau, $T_B - T_A$, varies with the heat of fusion, mass, and thermal diffusivity of the substance which is melting and depends upon the heating rate, the temperature gradient across the sample, and any heat leakage along the thermocouple.

The melting process is somewhat complicated in the case of a polymer. The polymer sample chosen is larger than the small amount of sharp melting material used for calibration. Thus in the PDTA cell, T_A is the temperature at which melting begins on the outer surface of the cylindrical polymer specimen. A second complicating factor in polymer DTA is inherent in the melting behavior of polymeric materials. In calorimetric experiments, even slowly crystallized polyethylene has exhibited a temperature range of about 15°C in which 90% of the crystalline portion fused.⁷ Some evidence suggests that slight melting may occur far below the range in which major melting is observed.⁸ For folded-chain polyethylene of high crystallinity, T_B has been shown to be close to the temperature at which all of the heat of fusion of the sample has been absorbed.⁹ This observed peak temperature must be corrected by adding the thermocouple calibration constant. From the peak, return of the ΔT trace to the baseline is not instantaneous but exhibits an exponential characteristic.⁹ Point (C) in Figure 2 indicates the return to steady-state conditions.

Crystallization of the fully melted polymer can be followed in the PDTA cell by merely turning off the heater current which results in a cooling rate