

A similar development may be applied to the piezometric data to obtain the expanded form (9):

$$-\ln N_1 = (\Delta V_0/RT) (P-P_0) \left\{ (1 + 1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c] (P-P_0) \right\}, \quad (4)$$

$$= A'\Delta P [1 + B'\Delta P], \quad (4a)$$

where

$$A' = \Delta V_0/RT$$

$$B' = (1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c]$$

(dV/dP) = molar compressibility coefficient of the liquid (*l*) or solid (*c*) phase at the pressure P_0 and temperature T .

Equation 4 takes into account the change in volumes of the solid and liquid phases during the changing pressure of the fusion. The similarity of the forms of equation 3 and 4 seemed to justify the extrapolation of the time-pressure data by hyperbolic equations similar to those used for the time-temperature data.

The pressure, P , and time, t_a , at which an infinitesimal amount of solid is in equilibrium with liquid were obtained by fitting the values in the liquid-solid region to a curve and extrapolating to the intersection with the time-pressure curve for the liquid. The time, t_b , when the sample would have been completely solid, if pure, was obtained by extrapolating the time-pressure curve for the solid to the pressure, P . The interval $(t_a - t_b)$ was taken as the duration of the transition and was used to calculate ΔV_0 (the volume change for the transition).

(9) A derivation of this equation follows:

The basic differential equation at constant temperature is:

$$-d\ln N_1 = \left(\frac{V_l - V_c}{RT} \right) dp = (\Delta V/RT) dp \quad (a)$$

$$\text{Let: } \Delta V = \Delta V_0 + (k_l - k_c) (P - P_0), \quad (b)$$

where: P_0 is the pressure when $N_1 = 1$; P is the pressure when $N_1 = N_1$; and k is dV/dP for each phase.

Substitute for ΔV into equation (a):

$$-d\ln N_1 = \frac{\Delta V_0 + (k_l - k_c) (P - P_0)}{RT} dP. \quad (c)$$

$$\text{Integrate: } -\ln N_1 = \frac{\Delta V_0}{RT} (P - P_0) + \frac{(k_l - k_c) (P - P_0)^2}{2RT}$$

Rearrange and substitute for k :

$$-\ln N_1 = (\Delta V_0/RT) (P - P_0) \left\{ 1 + (1/2\Delta V_0) [(dV/dP)_l - (dV/dP)_c] (P - P_0) \right\}. \quad (d)$$