

- $R$  = gas constant per mole,  
 $T$  = observed absolute temperature of equilibrium, at a fixed pressure  $P'$ ,  
 $T_0$  = absolute temperature of the freezing point of the pure substance at fixed pressure  $P'$ ,  
 $P$  = observed equilibrium pressure at fixed temperature  $T'$ ,  
 $P_0$  = equilibrium pressure of pure substance at  $T'$ .

The heat of fusion is a function of temperature and pressure; at ordinary pressures the effects of changes in pressure are usually negligible. The temperature dependence may be included by incorporating terms involving the specific heats of the two phases, as below. In a similar manner,  $\Delta V$  is a function of temperature and pressure. However, the effects of both temperature and pressure are significant, especially at higher pressures. These effects may be included with terms involving the compressibility and the thermal expansion coefficient; if these are not available, the values of  $\Delta V$  must be measured at each temperature of interest.

In the evaluation of purity from thermometric data, the change in the temperature of the liquid-solid transition, as the substance becomes more impure is more adequately expressed [14,15] as :

$$\begin{aligned}
 -\ln N_1 &= (\Delta H_0/RT_0^2) \Delta T \left[ 1 + \left( 1/T_0 - \frac{\Delta C_{P_0}}{2\Delta H_0} \right) \Delta T + \dots \right], \quad (3) \\
 &= A\Delta T [1 + B\Delta T + \dots], \quad (3a)
 \end{aligned}$$

where

- $N_1$  = mole fraction of substance in the liquid phase,  
 $\Delta T$  =  $(T_0 - T)$   
 $\Delta C_{P_0}$  = molar heat capacity of liquid less that of solid for the pure substance at  $T_0$ ,  
 $A$  =  $\Delta H_0/RT_0^2$ , main cryoscopic constant,  
 $B$  =  $(1/T_0 - \Delta C_{P_0}/2\Delta H_0)$ , secondary cryoscopic constant.

Equation 3 takes into account the change in the heat of fusion with temperature. Taylor and Rossini, by making certain assumptions, were able to express [16] equation 3 as a rectangular hyperbola; this was used to extrapolate the time-temperature data from freezing and melting point measurements to obtain values for the freezing points of the sample and the pure material. Saylor [17] has recently used an optical method of fitting a skewed hyperbola to such data.