

SHORT COMMUNICATIONS

ON THE TEMPERATURE DEPENDENCE OF FREE ENERGY OF CRYSTALLISATION

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AN accurate description of the temperature dependence of the free energy difference between the liquid and solid phases ΔG is important for an understanding of the kinetics of nucleation in the undercooled regime. From first principles, ΔG can be related to temperature T through ΔC_p , the heat capacity difference between the liquid and solid phases at constant pressure. We then have

$$\Delta G = \Delta S^m \cdot \Delta T - \int_T^{T_m} \Delta C_p dT + T \int_T^{T_m} (\Delta C_p/T) dT, \quad (1)$$

where ΔS^m is the entropy of fusion at the melting temperature, T_m . Many attempts have been made¹⁻⁷ to approximate ΔC_p and its temperature dependence for arriving at a simple expression for ΔG . In some of these, ΔC_p is taken to be zero or constant^{1,3} while in others ΔC_p at T_m , ΔC_p^m , is made proportional to ΔS^m on the basis of certain physical constraints⁴⁻⁶. In the present communication, we attempt to arrive at an unambiguous relationship through a Taylor series expansion of ΔG around its value ΔG^m at T_m . It will also be shown that the result is consistent with a hyperbolic expression for the temperature dependence of ΔC_p .

Expanding ΔG around ΔG^m by Taylor's method we have

$$\begin{aligned} \Delta G = \Delta G^m - \left[\frac{\partial \Delta G}{\partial T} \right]_{T_m} \cdot \Delta T \\ + \frac{1}{2!} \left[\frac{\partial^2 \Delta G}{\partial T^2} \right]_{T_m} \cdot \Delta T^2 \\ - \frac{1}{3!} \left[\frac{\partial^3 \Delta G}{\partial T^3} \right]_{T_m} \cdot \Delta T^3 + \dots \quad (2) \end{aligned}$$

where $\Delta T = (T_m - T)$ represents the undercooling and all derivatives are taken at $T = T_m$ and constant pressure. Noting that $\Delta G^m = 0$ and using the appropriate

thermodynamic parameters for the derivatives of ΔG we obtain:

$$\begin{aligned} \Delta G = \Delta S^m \cdot \Delta T - \frac{\Delta C_p^m \cdot \Delta T^2}{2T_m} \left[1 + \frac{\Delta T}{3T_m} \right. \\ \left. + \frac{\Delta T^2}{6T_m^2} + \frac{\Delta T^3}{10T_m^3} + \dots \right] + \left[\frac{\partial \Delta C_p}{\partial T} \right]_{T_m} \\ \times \frac{\Delta T^3}{6T_m} \left[1 + \frac{\Delta T}{4T_m} + \frac{3\Delta T^2}{10T_m^2} \dots \right]. \quad (3) \end{aligned}$$

Subsequent terms have higher order derivatives of ΔC_p . Each of the series in the square brackets is based on logarithmic series and can be summed to yield:

$$\begin{aligned} \Delta G = \Delta S^m \cdot \Delta T - \frac{\Delta C_p^m \cdot \Delta T^2}{T_m + T} \\ + \left[\frac{\partial \Delta C_p}{\partial T} \right]_{T_m} \cdot \frac{\Delta T^3}{2(T_m + T)}. \quad (4) \end{aligned}$$

While summing the series, where necessary, the approximation

$$\ln(T_m/T) = 2\Delta T/(T_m + T) \quad (5)$$

has been used. Neglect of the third and subsequent terms in (4) is effectively equivalent to ignoring temperature dependence of ΔC_p . Hence the similarity of the resultant expression

$$\Delta G = \Delta S^m \cdot \Delta T - \frac{\Delta C_p^m \cdot \Delta T^2}{(T_m + T)} \quad (6)$$

to that derived by Jones and Chadwick³ on the basis of temperature independent but finite ΔC_p is not surprising. However, it may be noted that Jones and Chadwick do not explicitly state the value of ΔC_p to be used. Dubey and Ramachandrarao⁷ have already shown that (6) is the most accurate amongst all expressions derived to-date on the basis of approximations with respect to ΔC_p . Hence, no fit with experiment is being attempted here.

From (3), it may be observed that the series in ΔG will converge if the magnitude of the n th differential is less than $T_m^{-(n+1)}$. In case ΔC_p is expressible as a finite polynomial in T , the above condition is expected to be easily satisfied. When ΔC_p is expressed in terms of hyperbolic form of the type

$$\Delta C_p = A + (B/T) \quad (7)$$

the convergence condition is immediately met. Battezzati and Garrone⁶ have recently discussed the usefulness of the hyperbolic type of representation vis-a-vis the linear dependence of ΔC_p on T . In the present context, the use of a linear equation in T for ΔC_p in conjunction with (4) shows that only the third term need be considered since all further terms vanish.

Substituting (7) in (1) and rearranging we have:

$$\Delta G = \Delta S^m \cdot \Delta T - \frac{\Delta C_p^m \cdot \Delta T^2}{(T_m + T)} + B \left(\frac{T_m + T}{T_m} \right) \left[\frac{2 \cdot \Delta T}{(T_m + T)} - \ln(T_m/T) \right] \quad (8)$$

If the approximation given by (5) is employed, (8) reduces to (6). This can be interpreted to mean that the contribution of the third and higher terms in (4) cancel each other. Thus, even when the temperature dependence is taken into account through (7), ΔG can still be expressed by (6) which is devoid of the parameters A and B . Further, the curvature in the ΔC_p versus T plots^{6,7} as well as the condition for the convergence of (3) warrant the use of (7).

Equation (6) can also be derived by a Taylor expansion of ΔC_p around ΔC_p^m . The second term in (6) can be viewed as a correction to the commonly used expression $\Delta G = \Delta S^m \cdot \Delta T$ due to Turnbull¹. Such corrections are important in arriving at the magnitude of solid/liquid interfacial energies from undercooling measurements as well as the nucleation rates and estimating the critical cooling rates for the suppression of homogeneous nucleation. All these considerations point to an urgent need for the experimental determination of ΔC_p^m . Further, whenever measurements of ΔC_p are made over limited range of temperature in the undercooled regime of the liquid, attempts should be made to test if the data fit (7) so that (6) for ΔG can be used without any constraints over a larger range of temperature.

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