

Thermodynamics of small phases. Equation of Thompson Gibbs

Specific Surface energy, Specific edge energy, Specific Vertex energy
 Position of half crystal
 Equilibrium form of crystals

Heterogeneous systems differ from homogeneous ones in that phase interfaces are present. The properties of substances and the distribution of components in thin layers adjacent to the surface differ from their bulk values. The extra free energy on the surface stems from the unbalance of the intermolecular forces in the surface region. Therefore, between the two bulk phases there is an intermediate region in which the properties are gradually changing. Gibbs (1875-1878) developed a consistent thermodynamic theory that took into account the properties related to the surface. If two phases (having volumes V_1 and V_2) are in contact with an interfacial area O the internal energy U is:

$$U = u_1 V_1 + u_2 V_2 + u^* O$$

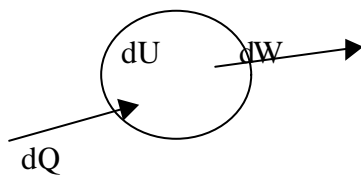
In similar way are determined all excess properties related to the surface. The excess of the free energy is denoted by σ

The I Thermodynamic Principle states:

$$dQ = dU + pdV - TdS - s dO$$

The sign (-) denotes that external work is needed to increase the interface with dO

$$dF = dU - TdS - SdT = dU - dQ - SdT$$



$$dQ = dU + dW$$

$$dQ = dU + pdV - s dO$$

$$dF = -pdV - SdT + s dO$$

$$F = F(V, T, O)$$

$$dF = \left(\frac{\partial F}{\partial V} \right)_{O, T} dV + \left(\frac{\partial F}{\partial T} \right)_{O, V} dT + \left(\frac{\partial F}{\partial O} \right)_{V, T} dO$$

$$p \quad s = \left(\frac{\partial F}{\partial O} \right)_{V, T} \quad \text{in analogy} \quad s = \left(\frac{\partial G}{\partial O} \right)_{p, T}$$

Dimensions and magnitude:

$$s \approx 10^2 \left[\frac{\text{erg}}{\text{cm}^2} \right] = 10^2 \frac{10^{-7}}{10^4} = 0.1 \left[\frac{\text{J}}{\text{m}^2} \right]$$

According to Scapski-Turnbull rule the ratio of the specific surface energy and the molar melting enthalpy is a dimensionless parameter α :

$$\alpha = \frac{s V_m^{2/3} N_a^{1/3}}{\Delta H_m} = \frac{s d_o^2 N_a}{\Delta H_m}$$

According to Zanotto, α generally varies between 0.5 and 0.55.

EQUILIBRIUM FORM OF CRYSTALS

Equilibrium is the form with minimum free energy ($F = \min$) at a given volume V and temperature T

$$\left\{ \begin{array}{l} F = \min \\ V = \text{const} \\ T = \text{const} \end{array} \right.$$

In deriving the equilibrium form it is assumed that all surfaces are flat (although there are some rounded regions in the vicinity of the melting point)

Let a face i has surface O_i specific surface energy s_i and is at a distance from the midpoint of the crystal r_i

The overall volume is a sum of volumes of small pyramids

$$\left\{ \begin{array}{l} F = \sum s_i O_i = \min \\ V = \frac{1}{3} \sum r_i O_i = \text{const} \end{array} \right.$$

$$dV = \frac{1}{3} (\sum O_i dr_i + \sum r_i dO_i)$$

On the other hand with accuracy to second order small parameter the change of volume is equal to O_i times dh_i

Therefore

$$\sum O_i dr_i = \frac{1}{2} \sum r_i dO_i$$

$$dV = \frac{1}{2} \sum r_i dO_i$$

Finally the condition of Gibbs-Curie becomes:

$$\sum \mathbf{s}_i dO_i = 0$$

$$\sum r_i dO_i = 0$$

The problem is solved using the method of Lagrange : Let multiply to λ and sum two conditions

$$\sum_{i=1}^s (\mathbf{s}_i - \lambda O_i) dO_i = 0 \quad \text{Let } \mathbf{l} = \frac{\mathbf{s}_i}{r_i}$$

$$\mathbf{l} = \frac{\mathbf{s}_i}{r_i}$$

But there are $s-1$ independent variables so that

Equation of Thompson- Gibbs:

$$G = n_{liq} \mathbf{m}_{liq} + n_c \mathbf{m}_c + \sum \mathbf{s}_i O_i + \sum \mathbf{k}_i l_i = \min$$

Example: cubic crystal with flat faces

$$\begin{cases} (dG)_{p,T} = \mathbf{m}_{liq} dn_{liq} + \mathbf{m}_c dn_c + \sum \mathbf{s}_i \frac{O_i}{dn_c} dn_c = 0 \\ dn_{liq} + dn_c = 0 \end{cases}$$

$$\mathbf{m}_{liq} - \mathbf{m}_c - \mathbf{s} \frac{dO}{dn_c} = 0$$

$$\text{For cube of side } a ; O=6a^2 ; V=a^3 ; \frac{dO}{dn_c} = \frac{4v_c}{a}$$

$$\Delta \mathbf{m} = \frac{4\mathbf{s}v_c}{a}$$

In isotropic approximation

$$\Delta \mathbf{m} = \frac{2\mathbf{s}v}{r}$$

Construction of equilibrium form, illustrations, half crystal position, two dimensional nucleus