Thermodynamics of materials

12. Construction of Fundamental Equation of Thermodynamics

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Table of Contents

Table of Contents

Choice of Fundamental Equation of Thermodynamics

- In the materials science, the commonly chosen natural variables are (T, s) and (p, v), therefore, the most commonly employed fundamental equations in molar quantities are

$$f(T, v) = u - Ts = -pv + \mu \rightarrow df = -sdT - pdv$$

$$g(T, p) = u - Ts + pv = \mu \rightarrow dg = d\mu = -sdT + vdp$$

Table of Contents

Molar Helmholtz Free energy change

- We have

$$f(T,v) = f^\circ(T_0,v_0) - \int_{T_0}^{T} s\,dT - \int_{v_0}^{v} p\,dv$$

with

$$f^\circ(T_0,v_0) = u^\circ(T_0,v_0) - T_0 s^\circ(T_0,v_0)$$

$$f(T,v) = u(T,v) - Ts(T,v)$$

- We have

$$u(T,v) - u^\circ(T_0,v_0) = \int_{T_0}^{T} c_v\,dT + T\int_{v_0}^{v} \alpha B_T\,dv - \int_{v_0}^{v} p\,dv$$

$$s(T,v) - s^\circ(T_0,v_0) = \int_{T_0}^{T} c_v\,d(\ln T) + \int_{v_0}^{v} \alpha B_T\,dv$$

Molar Helmholtz Free energy change

- Proceed to

$$f(T,v) - f^\circ(T_0,v_0) = u(T,v) - u^\circ(T_0,v_0) - Ts(T,v) + T_0 s^\circ(T_0,v_0)$$

- RHS is

$$\int_{T_0}^{T} c_v dT + T\int_{v_0}^{v} \alpha B_T dv - \int_{v_0}^{v} p dv + T_0 s^\circ(T_0,v_0) \\ - T\left[s^\circ(T_0,v_0) + \int_{T_0}^{T} c_v d(\ln T) + \int_{v_0}^{v} \alpha B_T dv\right]$$

- Therefore,

$$-\int_{T_0}^{T} s dT = \int_{T_0}^{T} c_v dT - s^\circ(T_0,v_0)\big(T - T_0\big) - T\int_{T_0}^{T} c_v d(\ln T)$$

Table of Contents

Chemical Potential change

- Since we have at reference state,

$$\mu^\circ(T_0, p_0) = h^\circ(T_0, p_0) - T_0 s^\circ(T_0, p_0)$$

and at state (T, p)

$$\mu(T, p) = h(T, p) - Ts(T, p)$$

- The enthalpy and entropy are given by

$$h(T, p) = h^\circ(T_0, p_0) + \int_{T_0}^{T} c_p dT + \int_{p_0}^{p} v(1 - T\alpha) dp$$

$$s(T, p) = s^\circ(T_0, p_0) + \int_{T_0}^{T} \frac{c_p}{T} dT - \int_{p_0}^{p} v\alpha dp$$

Chemical Potential change

- Then

$$\mu(T,p) = \mu^\circ(T_0,p_0) + \int_{T_0}^{T} \left[c_p - s^\circ(T_0,p_0)\right] dT + \int_{p_0}^{p} v(1 - T\alpha) dp$$
$$- T\left[\int_{T_0}^{T} \frac{c_p}{T} dT - \int_{p_0}^{p} v\alpha dp\right]$$

therefore,

$$\mu(T,p) = \mu^\circ(T_0,p_0) + \int_{T_0}^{T} \left[c_p - s^\circ(T_0,p_0)\right] dT - T\int_{T_0}^{T} \frac{c_p}{T} dT + \int_{p_0}^{p} v dp$$

- The volume is given by

$$v(T,p) = v_0(T_0,p_0) \exp\left[\alpha(T - T_0) - \beta_T(p - p_0)\right]$$

Table of Contents

Chemical Potential change with phase change

- At $T = T_e$, α and β phases are under equilibrium, for α phase,

$$h^\alpha(T, p_0) = h^{\circ,\alpha}(T_0, p_0) + \int_{T_0}^{T} c_p^\alpha dT$$

$$s^\alpha(T, p_0) = s^{\circ,\alpha}(T_0, p_0) + \int_{T_0}^{T} \frac{c_p^\alpha}{T} dT$$

$$\mu^\alpha(T, p_0) = \mu^{\circ,\alpha}(T_0, p_0) + \int_{T_0}^{T} c_p^\alpha dT - T\int_{T_0}^{T} \frac{c_p^\alpha}{T} dT$$

- For β phase,

$$h^\beta(T, p_0) = h^\alpha(T_e, p_0) + \Delta h_e^\circ(T_e, p_0) + \int_{T_e}^{T} c_p^\beta dT$$

$$s^\beta(T, p_0) = s^\alpha(T_e, p_0) + \Delta s_e^\circ(T_e, p_0) + \int_{T_e}^{T} \frac{c_p^\beta}{T} dT$$

Chemical Potential change with phase change

- The chemical potential of β phase,

$$\begin{aligned}\mu^{\beta}(T,p_0) &= h^{\beta}(T,p_0) - Ts^{\beta}(T,p_0)\\ &= h^{\alpha}(T_e,p_0) - Ts^{\alpha}(T_e,p_0) + \Delta h_e^{\circ}(T_e,p_0) - T\Delta s_e^{\circ}(T_e,p_0)\\ &+ \int_{T_e}^{T} c_p^{\beta} dT - T\int_{T_e}^{T} \frac{c_p^{\beta}}{T} dT\end{aligned}$$

- By rearrangement,

$$\mu^{\beta}(T,p_0) = \mu^{\beta}(T_e,p_0) + \int_{T_e}^{T} \left[c_p^{\beta} - s^{\beta}(T_e,p_0)\right] dT - T\int_{T_e}^{T} \frac{c_p^{\beta}}{T} dT$$

- At (T_e, p_0),

$$\begin{aligned}\mu^{\beta}(T_e,p_0) &= \mu^{\alpha}(T_e,p_0)\\ &= h^{\circ,\alpha}(T_0,p_0) - T_e s^{\circ,\alpha}(T_0,p_0) + \int_{T_0}^{T_e} \frac{(T-T_e)c_p^{\alpha}}{T} dT\end{aligned}$$

Table of Contents

Reference State for Helmholtz free energy

- The reference state for molar Helmholtz free energy has almost always been associated with the state at $0\,\mathsf{K}$,

$$f(T = 0\,\mathsf{K}, v) = u(T = 0\,\mathsf{K}, v)$$

- By third law of thermodynamics,

$$\lim_{T\to 0\,\mathsf{K}} s(T, v_0) \to 0 \qquad \lim_{T\to 0\,\mathsf{K}} c_v(T) \to 0$$

$$\lim_{T\to 0\,\mathsf{K}} c_p(T) \to 0 \qquad \lim_{T\to 0\,\mathsf{K}} \alpha(T) \to 0$$

- The Helmholtz free energy is

$$\begin{aligned} f(T, v) = u(v) + \int_{0\,\mathsf{K}}^{T} c_v dT - T \int_{0\,\mathsf{K}}^{T} c_v d(\ln T) - p_0(v - v_0) \\ - \int_{v_0}^{v} B_T dv + v \int_{v_0}^{v} B_T d(\ln v) \end{aligned}$$

Reference State for Chemical Potential

- In general, the enthalpy of the pure element at $1\,\text{bar}$ and $T = 298\,\text{K}$,

$$h^\circ(298\,\text{K}, 1\,\text{bar}) = 0$$

Table of Contents

Fundamental Equations with Multiphysics Effects

- The differential internal energy of the system

$$dU = TdS - pdV + V_0(\sigma_{ij}^d d\varepsilon_{ij}^d + E_i dD_i) + \phi dq + \gamma dA + \mu dN_i$$

where σ_{ij}^d and ε_{ij}^d are deviatoric components of stress and strain and γ is the interface energy.

- The differential Helmholtz and Gibbs free energies are

$$dF = -SdT - pdV + V_0(\sigma_{ij}^d d\varepsilon_{ij}^d + E_i dD_i) + \phi dq + \gamma dA + \mu dN_i$$

$$dG = -SdT + Vdp + V_0(\varepsilon_{ij}^d d\sigma_{ij}^d + E_i dD_i) + \phi dq + \gamma dA + \mu dN_i$$

Fundamental Equations with Multiphysics Effects

- The volume densities at constant T and p are

$$du_v = T ds_v - p d\varepsilon + \sigma^d_{ij} d\varepsilon^d_{ij} + E_i dD_i + \phi d\rho_q + \gamma da_v + \mu_i dc_i$$

$$df_v = -p d\varepsilon + \sigma^d_{ij} d\varepsilon^d_{ij} + E_i dD_i + \phi d\rho_q + \gamma da_v + \mu_i dc_i$$

$$dg_v = -\varepsilon^d_{ij} d\sigma^d_{ij} + E_i dD_i + \phi d\rho_q + \gamma da_v + \mu_i dc_i$$

Electrochemical Potential

- At constant T and V and constant interface area and displacement,

$$\begin{aligned} dF = \phi dq + \mu_i dN_i &= \left(\phi \frac{dq}{dN_i} + \mu_i\right) dN_i \\ &= (\phi z_i e N_{\mathsf{A}} + \mu_i) dN_i = (\phi z_i \mathcal{F} + \mu_i) dN_i \end{aligned}$$

  where z_i is the valence of the species i, e is the elementary charge, N_{A} is Avogadro's number.

- Let the electrochemical potential of species i is

$$\tilde{\mu}_i = \mu_i + z_i \mathcal{F} \phi$$

Chemical Potential Including Surface

- At constant T and p,

$$dG = \gamma dA + \mu dN$$

Proceed to

$$dG = \gamma \left(\frac{\partial A}{\partial V}\right)\left(\frac{\partial V}{\partial N}\right) dN + \mu dN = \gamma v \left(\frac{\partial A}{\partial V}\right) dN + \mu dN$$

it becomes

$$dG = \left[\gamma v \left(\frac{\partial A}{\partial V}\right) + \mu\right] dN$$

Let

$$\mu_r = \gamma v \left(\frac{\partial A}{\partial V}\right) + \mu$$

For solid particle r,

$$\mu_r = \gamma v \left(\frac{\partial A/\partial r}{\partial V/\partial r}\right)_{T,p} + \mu$$

Chemical Potential Including Surface

- Assume the particle is spherical,

$$A = 4\pi r^2 \qquad V = \frac{4\pi}{3} r^3$$

therefore,

$$\mu_r = \frac{2\gamma v}{r} + \mu$$

- Since $r \to \infty$,

$$\mu = \mu_\infty$$