Thermodynamics of materials

22. Phase Equilibrium of Single-Component Materials II

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October 30, 2024

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Gibbs Phase Rule

- There are restrictions on the maximum number of phases that can coexist at a given T and p or on the number of thermodynamic variables that can be independently varied at equilibrium.
- When n number of components, ψ number of phases, there are $(n-1)\psi$ number of independent chemical potentials because there is one Gibbs-Duhem relation that relates the n chemical potentials of the n components within each phase.
- There are two additional thermodynamic variables T, p, therefore, number of degree of freedom (NDF) of multicomponent multiphase mixture is

$$\text{NDF} = (n-1)\psi + 2 - n(\psi - 1) = n - \psi + 2$$

- A triple point of a $p - T$ phase diagram for a material with a fixed chemical composition,

$$\text{NDF} = n - \psi + 2 = 1 - 3 + 2 = 0$$

Gibbs Phase Rule

- Since

  $$\mathsf{NDF} = n - \psi + 2 \geq 0 \rightarrow \psi \leq n + 2$$

  so

  $$\psi_{\mathsf{max}} = n + 2$$

- For a single-component system, $n = 1$, the maximum number of phases that can coexist at thermodynamic equilibrium is 3.
- Along the phase boundaries of a one-component $p - T$ phase diagram,

  $$\mathsf{NDF} = n - \psi + 2 = 1 - 2 + 2 = 1$$

- Within the single-phase field of a phase diagram

  $$\mathsf{NDF} = n - \psi + 2 = 1 - 1 + 2 = 2$$

  which implies that one can vary both T and p simultaneously without leaving a single-phase field.

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Claperyon Equation

- In $p - T$ plot, at α/β phase boundary, we have

$$\mu^{\alpha}(T, p) = \mu^{\beta}(T, p)$$

- Since we have,

$$d\Delta\mu = -\Delta s dT + \Delta v dp$$

  at phase boundary,

$$0 = -\Delta s^{\alpha\to\beta} dT + \Delta v^{\alpha\to\beta} dp$$

- Therefore,

$$\frac{dp}{dT} = \frac{\Delta s^{\alpha\to\beta}}{\Delta v^{\alpha\to\beta}} = \frac{s^{\beta} - s^{\alpha}}{v^{\beta} - v^{\alpha}}$$

Claperyon Equation

- By second law, for a reversible process,

$$\Delta s^{\alpha\to\beta} = \frac{Q^{\alpha\to\beta}}{T_e^{\alpha\to\beta}}$$

  where $Q^{\alpha\to\beta}$ is the heat released or absorbed for the transition of one mole of α phase and β phase, and $T_e^{\alpha\to\beta}$ represents the equilibrium transition temperature at a given pressure.

- At constant pressure,

$$Q^{\alpha\to\beta} = \Delta h^{\alpha\to\beta}$$

  therefore,

$$\frac{dp}{dT} = \frac{\Delta h^{\alpha\to\beta}}{T\Delta v^{\alpha\to\beta}}$$

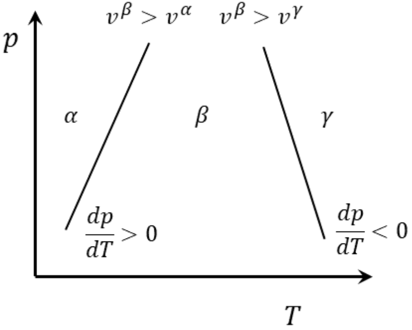
  which is the Clapeyron equation.

Claperyon Equation

- In general, for a transition of a lower temperature phase to a higher temperature phase, the heat of the transition is positive,

$$\Delta h^{\alpha\to\beta} > 0 \qquad \Delta h^{\beta\to\gamma} > 0$$

if $\Delta v > 0$, then slope of phase boundary at $p - T$ diagram is positive, and when $\Delta v < 0$, then it is negative.



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Clausius-Claperyon Equation

- Considering a phase transition of a liquid(l) to vapor(v). Since

  $$\Delta v^{l\to v} = v^v - v^l \simeq v^v$$

  proceed to

  $$\frac{dp}{dT} \simeq \frac{\Delta h^{l\to v}}{T v^v}$$

- From 1 mol ideal gas law,

  $$v^v = \frac{RT}{p}$$

  proceed to

  $$\frac{d\ln p}{dT} = \frac{\Delta h^{l\to v}}{RT^2}$$

  which is the Clausis-Clapeyron equation.

Clausius-Claperyon Equation

- The normal boiling point T_b of a liquid is the temperature at which the liquid is at equilibrium with its vapor phase at $1\,\text{bar}$. The heat of evaporation at the normal boiling point is labeled as Δh_b°.
- Assume the heat of evaporation only depends on temperature,

$$\Delta h^{l\to v}(T) = \Delta h_b^\circ + \int_{T_b}^{T} \left(c_p^v(T) - c_p^l(T)\right) dT = \Delta h_b^\circ + \int_{T_b}^{T} \Delta c_p(T) dT$$

- When $\Delta c_p(T) = 0$ then $\Delta h^{l\to v}(T) = \Delta h_b^\circ$, the heat of evaporation is independent of temperature, then

$$\frac{d\ln p}{dT} = \frac{\Delta h_b^\circ}{RT^2} \to \int d\ln p = \frac{\Delta h_b^\circ}{R} \int \frac{dT}{T^2}$$

proceed to

$$\ln p = -\frac{\Delta h_b^\circ}{RT} + c$$

Clausius-Claperyon Equation

- At $p = 1$ bar and $T = T_b$,

$$\ln(1) = -\frac{\Delta h_b^\circ}{RT_b} + c = 0 \to c = \frac{\Delta h_b^\circ}{RT_b}$$

  then

$$\ln p = \frac{\Delta h_b^\circ}{R}\left(\frac{1}{T_b} - \frac{1}{T}\right)$$

- When Δc_p is assumed to be a constant rather than 0,

$$\Delta h^{l\to v} = \Delta h_b^\circ + \Delta c_p (T - T_b)$$

  The Clausis-Clapeyron equation becomes

$$\frac{d\ln p}{dT} = \frac{\Delta h_b^\circ + \Delta c_p (T - T_b)}{RT^2} = \frac{a}{T^2} + \frac{b}{T}$$

  where

$$a = \frac{\Delta h_b^\circ - \Delta c_p T_b}{R} \qquad b = \frac{\Delta c_p}{R}$$

Clausius-Claperyon Equation

- Then we have

$$\ln p = -\frac{a}{T} + b\ln T + c$$

- At triple point, we have

$$\mu^s(T,p) = \mu^l(T,p) = \mu^v(T,p)$$

and we have

$$\ln p_{tr} = -\frac{a^{l\to v}}{T_{tr}} + b^{l\to v}\ln T_{tr} + c^{l\to v}$$

$$\ln p_{tr} = -\frac{a^{s\to v}}{T_{tr}} + b^{s\to v}\ln T_{tr} + c^{s\to v}$$

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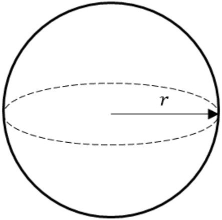
Size Effect on Phase Transition Temperature

- For a nano-scale material, the contribution of surface energy to the phase transition temperature cannot be ignored. The chemical potential of a spherical particle is

$$\mu_r^s = \frac{2\gamma_{sl} v}{r} + \mu_\infty^s$$

where μ_r is the chemical potential of a particle with radius r, μ_∞ is the chemical potential of a solid with infinite size, γ_{sl} is solid-liquid interfacial energy, and v is the molar volume of the solid.



Size Effect on Phase Transition Temperature

- At the solid-liquid equilibrium, with labeling the melting temperature T_m for infinite particle size as T_∞ at which

  $$\mu^s_\infty = \mu^l$$

  where μ^l is the chemical potential of atoms in the liquid.
- The entropy of melting is given by

  $$\Delta s_m = \frac{\Delta h_m}{T_\infty}$$

  where Δh_m is the enthalpy or heat of melting.
- A solid particle of size r, the chemical potential of atoms inside the particle must be equal to the chemical potentials of atoms in the liquid,

  $$\mu^s_r = \mu^s_\infty + \frac{2\gamma_{sl} v}{r} = \mu^l$$

Size Effect on Phase Transition Temperature

- Assuming that the heat Δh_m and entropy Δs_m of melting are independent of temperature, we have the melting temperature T_r of particle size r,

$$\mu^l - \mu^s_\infty = \Delta h_m - T_r \frac{\Delta h_m}{T_\infty} = \Delta h_m \frac{T_\infty - T_r}{T_\infty}$$

then

$$\mu^l - \mu^s_\infty = \Delta h_m \frac{T_\infty - T_r}{T_\infty} = \frac{2\gamma_{sl} v}{r}$$

therefore,

$$T_r = \left(1 - \frac{2\gamma_{sl} v}{r \Delta h_m}\right) T_\infty$$

As r increases, T_r approaches to T_∞.