Thermodynamics of materials

22. Phase Equilibrium of Single-Component Materials II

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October 21, 2024

Table of Contents

Table of Contents

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

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

  so

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

- 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,

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

- Within the single-phase field of a phase diagram

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

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

Table of Contents

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.

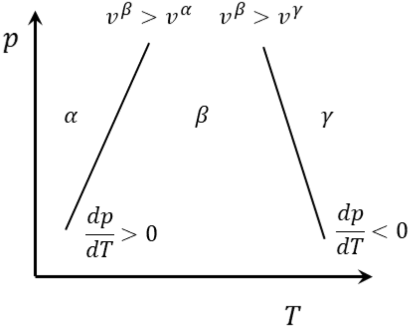


Table of Contents

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 $1\,\mathrm{bar}$. The heat of evaporation at the normal boiling point is labeled as Δh_b°.
- Assume the heat of evaporation only depends on temperature,

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

- 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 $T = T_b$,

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

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,

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

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

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

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

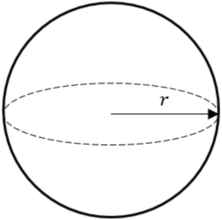
Table of Contents

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_∞.

Table of Contents

Landau Theory of Phase Transitions

- Any phase transition can be characterized by physically well-defined other parameters that distinguish the parent and new transformed phases.
- An order parameter is typically defined to zero in the high-temperature phase and has a finite value in the low-temperature phase.
- Example: Compositional phase separation etc.

Landau Theory of Phase Transitions

- For a phase transition described by a single order parameter η, we can express the free energy density as

$$f(\eta) = f(0) + \left(\frac{\partial f}{\partial \eta}\right)_0 \eta + \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{3!}\left(\frac{\partial^3 f}{\partial \eta^3}\right)_0 \eta^3 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4 + \cdots$$

considering the symmetry of the system, we vanish all odd-order terms,

$$f(\eta) = f(0) + \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4 + \cdots$$

keeping terms up to fourth order,

$$f(\eta) - f(0) = \frac{1}{2}\left(\frac{\partial^2 f}{\partial \eta^2}\right)_0 \eta^2 + \frac{1}{4!}\left(\frac{\partial^4 f}{\partial \eta^4}\right)_0 \eta^4$$

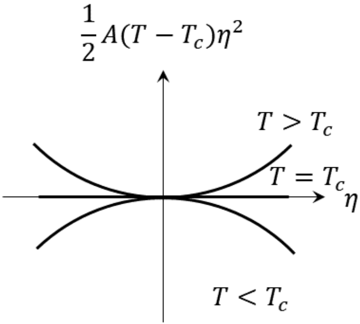
Landau Theory of Phase Transitions

- If we assume only the coefficient in the first term is temperature-dependent,

$$f(\eta) - f(0) = \frac{A(T - T_c)}{2}\eta^2 + \frac{B}{4}\eta^4$$

  where A and B are positive coefficients, and T_c is the critical temperature for the phase transition.

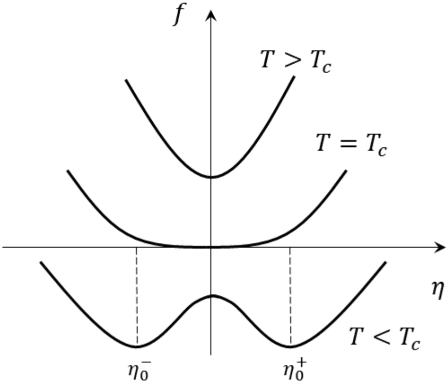
Landau Theory of Phase Transitions



- When $B = 0$, and $T < T_c$, the parent phase with $\eta = 0$ is unstable since a finite value of order parameter η has a lower energy density.

Landau Theory of Phase Transitions

- When $B \neq 0$,



Landau Theory of Phase Transitions

- At temperatures higher than T_c, the state with $\eta = 0$ has the lowest free energy density and this the stable state.
- Below T_c the states with finite values of the order parameter, η_0^- and η_0^+, are the stable phases. For minimizing free energy,

$$\left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = A(T - T_c)\eta_0 + B\eta_0^3 = 0$$

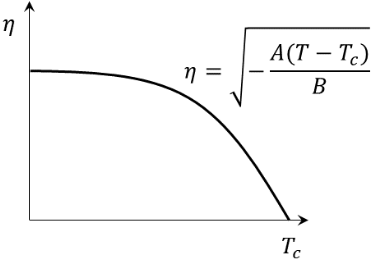
proceed to

$$\eta_0^+ = \sqrt{-\frac{A(T - T_c)}{B}} \qquad \eta_0^- = -\sqrt{-\frac{A(T - T_c)}{B}}$$

- At $T = T_c$,

$$\eta_0^+ = \eta_0^- = 0 \qquad \left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = 0$$

Landau Theory of Phase Transitions



- Schematic dependence of η_0^+ as a function of temperature. The magnitude of order parameter gradually goes to zero as the temperature approaches to the critical temperature, i.e., there is no jump in the order parameter value at the transition temperature.
- A phase transition at which the order parameter value is continuous is called a second-order phase transition or simply a continuous transition.

Landau Theory of Phase Transitions

- To describe a first-order phase transition, it is necessary to add either a cubic or a sixth-order term. Let's first look at the $\eta^2 - \eta^3 - \eta^4$ free energy density model,

$$f(\eta) - f(0) = \frac{A(T - T_c)}{2}\eta^2 - \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4$$

- To obtain the equilibrium order parameter,

$$\left.\frac{\partial f(\eta)}{\partial \eta}\right|_{\eta_0} = A(T - T_c)\eta_0 - B\eta_0^2 + C\eta_0^3 = 0$$

the solutions are

$$\eta_{0,1} = 0$$

$$\eta_{0,2} = \frac{B + \sqrt{B^2 - 4AC(T - T_c)}}{2C}$$

$$\eta_{0,3} = \frac{B - \sqrt{B^2 - 4AC(T - T_c)}}{2C}$$

Landau Theory of Phase Transitions

- At the critical temperature T_c,

$$\eta_{0,1} = 0 \qquad \eta_{0,2} = \frac{B}{C} \qquad \eta_{0,3} = 0$$

- At the transition temperature T_0,

$$B^2 - 4AC(T_0 - T_c) = 0 \rightarrow T_0 = T_c + \frac{B^2}{4AC}$$

Landau Theory of Phase Transitions