

Thermodynamics of materials

21. Phase Equilibrium of Single-Component Materials I

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General T and p dependencies of Chemical Potential

- From the Gibbs-Duhem relation of single component system,

$$d\mu = -sdT + vdp$$

and we can derive the relation for the condition when p is constant,

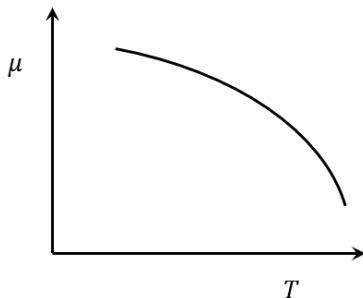
' and

$$\left(\frac{\partial\mu^2}{\partial T^2}\right)_p = -\frac{c_p}{T} < 0$$



General T and p dependencies of Chemical Potential

- The schematic sketch of T - μ relation is



General T and p dependencies of Chemical Potential

- At constant T ,

$$\left(\frac{\partial\mu}{\partial p}\right)_p = v > 0$$

$$\left(\frac{\partial^2\mu}{\partial p^2}\right)_p = -v\beta_T < 0$$

General T and p dependencies of Chemical Potential]

- The schematic sketch of p - μ relation is

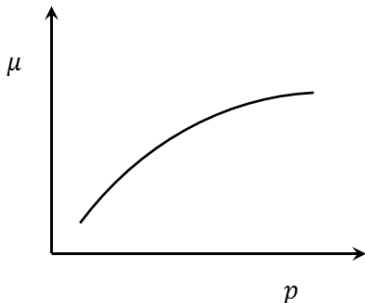


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Thermodynamic Driving Force for Phase Transition

- Consider the phase transition,



when number of moles of α and β phases are N^α and N^β . The Gibbs free energy of two-phase mixture is

$$G = G^\alpha + G^\beta = N^\alpha \mu^\alpha + N^\beta \mu^\beta$$

- From the fundamental equation,

$$dG^\alpha = -s^\alpha N^\alpha dT + v^\alpha N^\alpha dp + \mu^\alpha dN^\alpha$$

$$dG^\beta = -s^\beta N^\beta dT + v^\beta N^\beta dp + \mu^\beta dN^\beta$$

where s^α , s^β are molar entropies of α and β phases and v^α and v^β are molar volumes of α and β phases.



Thermodynamic Driving Force for Phase Transition

- Neglecting the interface energy, the differential form of free energy of α , β phase mixture is

$$dG = -(s^\alpha N^\alpha + s^\beta N^\beta)dT + (v^\alpha N^\alpha + v^\beta N^\beta)dp + (\mu^\alpha dN^\alpha + \mu^\beta dN^\beta)$$

- At constant T and p ,

$$dG = \mu^\alpha dN^\alpha + \mu^\beta dN^\beta$$

- Introduce a parameter of degree of transition, ξ ,

$$\xi = \frac{N^\beta}{N} \quad N = N^\alpha + N^\beta$$

then

$$G(N, T, p, \xi) = N\mu^\alpha(T, p) + N\xi[\mu^\beta(T, p) - \mu^\alpha(T, p)]$$



Thermodynamic Driving Force for Phase Transition

- The chemical potential is

$$\mu(T, p, \xi) = \frac{G(N, T, p, \xi)}{N} = \mu^\alpha(T, p) + \xi \Delta\mu(T, p)$$

where

$$\Delta\mu(T, p) = \mu^\beta(T, p) - \mu^\alpha(T, p)$$

- The differential form is

$$d\mu(T, p) = \Delta\mu(T, p)d\xi$$

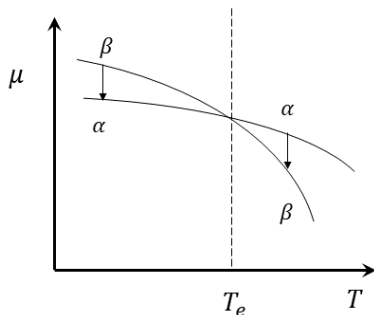
- The driving force for the phase transition is

$$D = -\left(\frac{d\mu}{d\xi}\right)_{T,p} = -\Delta\mu$$



Thermodynamic Driving Force for Phase Transition

- At given p , when the transition temperature is T_e ,
 - If $T < T_e$, $\Delta\mu > 0 \rightarrow D < 0$, α phase is stable against β phase.
 - If $T = T_e$, $\Delta\mu = 0 \rightarrow D = 0$, α phase is under equilibrium with β phase.
 - If $T > T_e$, $\Delta\mu < 0 \rightarrow D > 0$, α phase is unstable against β phase.



Thermodynamic Driving Force for Phase Transition

- When a phase transition takes place with a driving force of D , an amount of chemical energy of D is dissipated due to the transition and converted to thermal energy.
- The amount of entropy produced due to a phase transition is

$$\Delta S^{\text{ir}} = \frac{D}{T} = -\frac{\Delta\mu}{T}$$



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T and p dependence of Driving Force

- The chemical potential of α and β phases

$$d\mu^\alpha = -s^\alpha dT + v^\alpha dp \quad d\mu^\beta = -s^\beta dT + v^\beta dp$$

therefore,

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

where

$$\Delta\mu = \mu^\beta - \mu^\alpha \quad \Delta s = s^\beta - s^\alpha \quad \Delta v = v^\beta - v^\alpha$$

- By integration,

$$\Delta\mu(T, p) = - \int_{T_e}^T \Delta s(T, p = 1 \text{ bar}) dT + \int_{1 \text{ bar}}^p \Delta v(T, p) dp$$



T and p dependence of Driving Force

- Assuming Δc_p is a constant, $\beta_T = \alpha = 0$,

$$\Delta s(T, p) = \Delta s^\circ(T_e, 1 \text{ bar}) + \Delta c_p \ln \left(\frac{T}{T_e} \right)$$

and

$$\Delta v(T, p) = \Delta v(T, 1 \text{ bar}) = \Delta v^\circ(T_e, 1 \text{ bar})$$

therefore,

$$\begin{aligned} \Delta \mu(T, p) &= - \int_{T_e}^T \left[\Delta s^\circ + \Delta c_p \ln \left(\frac{T}{T_e} \right) \right] dT + \Delta v^\circ \Delta p \\ &= [\Delta c_p - \Delta s^\circ] \Delta T - \Delta c_p T \ln \left(1 + \frac{\Delta T}{T_e} \right) + \Delta v^\circ \Delta p \end{aligned}$$

where

$$\Delta T = T - T_e \quad \Delta p = p - 1 \text{ bar}$$



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Classification and Order of Phase Transitions

- According to Ehrenfest's classification, A first-order transition is one at which the first-order derivatives of chemical potential with respect to T and p , i.e., molar entropy and molar volume, are discontinuous. The jumps or changes in molar entropy and molar volumes at the transition temperature and pressure are called entropy and volume of transition. The enthalpy change at the transition is equal to the product of entropy change and transition temperature, which is assumed as latent heat of transition.
- Melting, solidification, phase separation, precipitation, structural transitions, ferroelectric transitions etc., are first-order phase transitions.



Classification and Order of Phase Transitions

- A second-order phase transition is one at which the first derivatives of chemical potential with respect to T and p , i.e., the molar entropy and molar volume, are continuous, but the second derivatives of chemical potential with respect to T and p , i.e., heat capacity, or compressibility, are discontinuous. The example of second-order phase transition is ferromagnetic phase transition.



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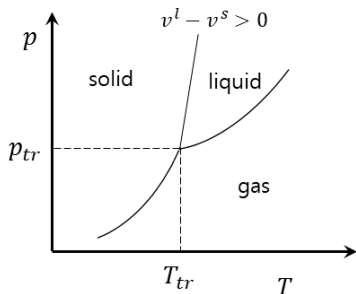
$T - p$ Phase Diagram

- According to the thermodynamic equilibrium principle, at constant T and p , an equilibrium state is obtained by minimizing the Gibbs free energy.
- A diagram that collects all the phase boundaries separating the regions of stable phases in material is called a phase diagram. For a material with a fixed chemical composition, the graphical representation of stable phases at different T and p is also called a $T - p$ diagram.
- It is also possible to construct other types of phase diagrams, e.g., phase diagrams of equilibrium states represented on diagrams, such as, $T - v$, $p - v$ and $T - s$.



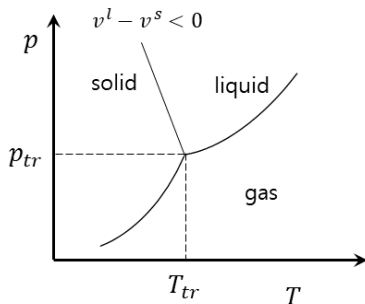
$T - p$ Phase Diagram

- When $v^l > v^s$, the typical $T - p$ diagram is shown as below. The slope of phase boundary between solid-liquid phase is positive.



$T - p$ Phase Diagram

- When $v^l < v^s$, the typical $T - p$ diagram is shown as below. The slope of phase boundary between solid-liquid phase is negative.



$T - p$ Phase Diagram

- Single phase region: The ranges of T and p within which one of the phases has the lowest chemical potential are called single-phase regions.
- Two-phase coexistence boundaries: If there are two phases that have the same chemical potential at certain T and p , therefore two phases are at thermodynamic equilibrium.
- Triple points: Three different phases that have the same chemical potential at given T and p , all three phases are at equilibrium.

