Thermodynamics of materials

11. Thermodynamic Calculations of Material Process - III

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

September 17, 2024

Table of Contents

Table of Contents

Changes in Thermodynamic Properties for Phase Transitions

- Let's consider a phase transition at T, p

$$\alpha \to \beta$$

the finite changes are given by

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

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

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

Changes in Thermodynamic Properties for Phase Transitions

- The change in the chemical potential can be given by

$$\Delta\mu(T,p) = \Delta h(T,p) - T\Delta s(T,p)$$

- The chemical energy ($-\Delta\mu$), the thermodynamic driving force D, and the amount of entropy produced Δs^{ir} for a phase transition at constant T, p are related by

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

- If $\Delta\mu$ is negative, the driving force D is positive, and the transition is irreversible, producing Δs^{ir} amount of entropy. The larger the driving force D is, the greater amount of the entropy Δs^{ir} is produced, and thus the higher the degree of irreversibility for the phase transition.

Changes in Thermodynamic Properties for Phase Transitions

- The equilibrium transition temperature and pressure for a phase transition are T_e and p_e, the driving force is

$$D(T_e, p_e) = T_e \Delta s^{\mathrm{ir}}(T_e, p_e) = -\Delta\mu^\circ(T_e, p_e) = 0$$

- At equilibrium temperature and pressure,

$$\Delta\mu^\circ(T_e, p_e) = \Delta h^\circ(T_e, p_e) - T_e \Delta s^\circ(T_e, p_e) = 0$$

- The enthalpy of phase transition,

$$\begin{aligned}
\Delta h(T) &= h^\beta(T) - h^\alpha(T) \\
&= h^\beta(T_e) + \int_{T_e}^{T} c_p^\beta dT - \left[h^\alpha(T_e) + \int_{T_e}^{T} c_p^\alpha dT \right] \\
&= \Delta h^\circ(T_e) + \int_{T_e}^{T} c_p^\beta dT - \int_{T_e}^{T} c_p^\alpha dT
\end{aligned}$$

Changes in Thermodynamic Properties for Phase Transitions

- Let

$$\Delta c_p = c_p^\beta - c_p^\alpha$$

then

$$\Delta h(T) = \Delta h^\circ(T_e) + \int_{T_e}^{T} \Delta c_p dT$$

- For the chemical potential,

$$\left[\frac{\partial\left[\Delta\mu(T)/T\right]}{\partial T}\right]_p = -\frac{\Delta s(T)}{T} - \frac{\Delta\mu(T)}{T^2} = -\frac{\Delta h(T)}{T^2}$$

- By integrating the equation,

$$\frac{\Delta\mu(T)}{T} = \frac{\Delta\mu^\circ(T_e)}{T_e} - \int_{T_e}^{T} \left[\frac{\Delta h(T)}{T^2}\right] dT$$

- Under the equilibrium under (T_e, p_e),

$$\Delta h^\circ(T_e, p_e) = T_e \Delta s^\circ(T_e, p_e) = Q_e$$

where Q_e is the heat of transition under constant pressure and temperature.

- Therefore, the entropy of the heat generation for irreversible process,

$$\Delta s^\circ(T_e, p_e) = \frac{Q_e}{T_e}$$

- For the temperature T,

$$\Delta s(T, p_e) = \Delta s^\circ(T_e, p_e) + \int_{T_e}^{T} \frac{\Delta c_p}{T} dT$$

Changes in Thermodynamic Properties for Phase Transitions

- Since

$$d\mu = -sdT + vdp \rightarrow \left(\frac{\partial \mu}{\partial T}\right)_p = -s$$

therefore,

$$\Delta\mu(T, p_e) = \Delta\mu^\circ(T_e, p_e) - \int_{T_e}^{T} \Delta s(T, p_e) dT$$

- In sum, the finite changes are

$$\Delta h(T, p_e) = \Delta h^\circ(T_e, p_e) + \Delta c_p(T - T_e)$$

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

$$\Delta\mu(T, p_e) = \Delta h^\circ(T_e, p_e) - T\Delta s^\circ + \Delta c_p(T - T_e) - \Delta c_p T \ln\left(\frac{T}{T_e}\right)$$

- When $\Delta c_p = 0$

$$\Delta\mu(T, p_e) = \Delta h^\circ(T_e, p_e) - T\Delta s^\circ(T_e, p_e)$$

- Since we have

$$\Delta h^\circ(T_e, p_e) - T_e\Delta s^\circ(T_e, p_e) = 0 \to \Delta s^\circ(T_e, p_e) = \frac{\Delta h^\circ(T_e, p_e)}{T_e}$$

proceed to

$$\Delta\mu(T, p_e) = \Delta h^\circ(T_e, p_e) - T\frac{\Delta h^\circ(T_e, p_e)}{T_e} = -\frac{\Delta h^\circ(T_e, p_e)\Delta T}{T_e}$$

where

$$\Delta T = T - T_e$$

Changes in Thermodynamic Properties for Phase Transitions

- For the process at p at constant temperature T,

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

- For arbitrary pressure p,

$$\mu^{\alpha}(T,p) = \mu^{\alpha}(T,p_e) + \int_{p_e}^{p} v^{\alpha} dp$$

$$\mu^{\beta}(T,p) = \mu^{\beta}(T,p_e) + \int_{p_e}^{p} v^{\beta} dp$$

therefore,

$$\Delta\mu^{\alpha\rightarrow\beta}(T,p) = \Delta\mu(T,p_e) + \int_{p_e}^{p} \Delta v dp$$

Changes in Thermodynamic Properties for Phase Transitions

- Combining the temperature and pressure dependence of chemical potential change for a phase transition,

$$\Delta\mu(T,p) = \Delta h^\circ - T\Delta s^\circ + \int_{T_e}^{T} \Delta c_p dT - T\int_{T_e}^{T} \frac{\Delta c_p}{T} dT + \int_{p_e}^{p} \Delta v dp$$

- When Δc_p and Δv are independent of temperature and pressure,

$$\Delta\mu(T,p) = \Delta h^\circ - T\Delta s^\circ + \Delta c_p\left[T - T_e - T\ln\left(\frac{T}{T_e}\right)\right] + \Delta v(p - p_e)$$

- Introduce, $\Delta p = p - p_e$, $\Delta T = T - T_e$ under the equilibrium,

$$\Delta p = \left[\Delta T\Delta s^\circ - \Delta c_p\left[\Delta T - (T_e + \Delta T)\ln\left(\frac{T_e + \Delta T}{T_e}\right)\right]\right]/\Delta v$$

- If $\Delta T \ll T_e$,

$$\Delta p = \frac{\Delta T}{\Delta v}\left(\frac{\Delta h^\circ + \Delta c_p \Delta T}{T_e}\right)$$

it is known as Clapeyron equation.

- For a phase transition in a crystal, incorporating effect of an applied stress,

$$\begin{aligned}\Delta\mu(T,\sigma_{ij}) = \Delta h^\circ - T\Delta s^\circ + \int_{T_e}^{T} \Delta c_p dT \\ - T\int_{T_e}^{T} \frac{\Delta c_p}{T} dT + \int_{\sigma_{ij}^e}^{\sigma_{ij}} v\varepsilon_{ij}^\circ d\sigma_{ij}\end{aligned}$$

where ε_{ij}° is the stress-free transition strain which is a measure of the relative stress-free lattice parameter change from the parent to the produce phase and σ_{ij} is the applied stress.

Changes in Thermodynamic Properties for Phase Transitions

- If the chemical potential change $\Delta\mu$ for a phase transition in known as a function of T and p, then

$$\Delta s(T,p) = -\left[\frac{\partial \Delta\mu(T,p)}{\partial T}\right]_p$$

- Similarly, the enthalpy change or heat of transition is

$$\Delta h(T,p) = -T^2\left[\frac{\partial(\Delta\mu(T,p)/T)}{\partial T}\right]_p = \Delta\mu(T,p) + T\Delta s(T,p)$$

- Finally, the volume difference is

$$\Delta v(T,p) = \left[\frac{\partial \Delta\mu(T,p)}{\partial p}\right]_T$$

Changes in Thermodynamic Properties for Phase Transitions

- The amount of entropy produced during a phase transition is

$$\Delta s^{\mathrm{ir}}(T,p) = -\frac{\Delta\mu(T,p)}{T}$$

For spontaneous reaction, chemical potential reduces, therefore, the irrerversible entropy increases.

Table of Contents

Changes in Properties for Chemical Reactions

- For the chemical reaction at T and p,

$$\nu_A A + \nu_B B \Leftrightarrow \nu_C C + \nu_D D$$

where ν_i is the stoichiometric reaction coefficient.

- H^R, S^R and G^R are the properties of reactants and H^P, S^P and G^P are properties of products. At T and p,

$$\Delta G(T,p) = G^P(T,p) - G^R(T,p)$$

$$\Delta H(T,p) = H^P(T,p) - H^R(T,p) = Q$$

$$\Delta S(T,p) = S^P(T,p) - S^R(T,p)$$

- Since we can write

$$G^R(T,p) = \nu_A \mu_A(T,p) + \nu_B \mu_B(T,p)$$

$$H^R(T,p) = \nu_A H_A(T,p) + \nu_B H_B(T,p)$$

$$S^R(T,p) = \nu_A S_A(T,p) + \nu_B S_B(T,p)$$

$$G^P(T,p) = \nu_C \mu_C(T,p) + \nu_D \mu_D(T,p)$$

$$H^P(T,p) = \nu_C H_C(T,p) + \nu_D H_D(T,p)$$

$$S^P(T,p) = \nu_C S_C(T,p) + \nu_D S_D(T,p)$$

- From thermodynamic relations,

$$\mu_i(T,p) = h_i(T,p) - T s_i(T,p)$$

$$\Delta G(T,p) = \Delta H(T,p) - T\Delta S(T,p)$$

Changes in Properties for Chemical Reactions

- At $T = 298\,\mathrm{K}$ and $p = 1\,\mathrm{bar}$, we put circle to the right top,

$$\Delta G^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} = \left[\nu_C \mu^\circ_C + \nu_D \mu^\circ_D\right] - \left[\nu_A \mu^\circ_A + \nu_B \mu^\circ_B\right]$$

$$\Delta H^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} = \left[\nu_C H^\circ_C + \nu_D H^\circ_D\right] - \left[\nu_A H^\circ_A + \nu_B H^\circ_B\right]$$

$$\Delta S^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} = \left[\nu_C S^\circ_C + \nu_D S^\circ_D\right] - \left[\nu_A S^\circ_A + \nu_B S^\circ_B\right]$$

  also

$$\Delta G^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} = \Delta H^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} - T\Delta S^\circ_{298\,\mathrm{K},1\,\mathrm{bar}}$$

- If the reaction is irreversible,

$$\Delta G^\circ_{298\,\mathrm{K},1\,\mathrm{bar}} \neq 0$$

Changes in Properties for Chemical Reactions

- The change of enthalpy of the reaction at T and $p = 1\,\text{bar}$,

$$\Delta H(T, 1\,\text{bar}) = \Delta H(298\,\text{K}, 1\,\text{bar}) - \int_{298K}^{T} C_p^R dT + \int_{298K}^{T} C_p^P dT$$
$$= \Delta H(298\,\text{K}, 1\,\text{bar}) + \int_{298K}^{T} \Delta C_p dT$$

where

$$C_p^R = \nu_A C_{p,A} + \nu_B C_{p,B}$$
$$C_p^P = \nu_C C_{p,C} + \nu_D C_{p,D}$$
$$\Delta C_p = C_p^P - C_p^R$$

Changes in Properties for Chemical Reactions

- Since

$$\left[\frac{\partial(\Delta G(T,p)/T)}{\partial T}\right]_p = -\frac{\Delta H(T,p)}{T^2}$$

- By integrating,

$$\frac{\Delta G(T,1\,\text{bar})}{T} = \frac{\Delta G^\circ(298\,\text{K},1\,\text{bar})}{T=298\,\text{K}} - \int_{298\,\text{K}}^{T}\left[\frac{\Delta H(T,1\,\text{bar})}{T^2}\right]dT$$

- If $\Delta H(T,1\,\text{bar})$ is independent of the temperature,

$$\frac{\Delta G(T,1\,\text{bar})}{T} - \frac{\Delta G^\circ(298\,\text{K},1\,\text{bar})}{T=298\,\text{K}} = \Delta H^\circ(298\,\text{K},1\,\text{bar})\left(\frac{1}{T}-\frac{1}{298\,\text{K}}\right)$$

- The entropy change is

$$\Delta S(T, 1\,\text{bar}) = \Delta S^\circ(298\,\text{K}, 1\,\text{bar}) + \int_{298\,\text{K}}^{T} \frac{\Delta C_p}{T} dT$$

- The Gibbs energy change is

$$\begin{aligned}\Delta G(T, 1\,\text{bar}) &= \Delta G^\circ(298\,\text{K}, 1\,\text{bar}) - \int_{298\,\text{K}}^{T} \Delta S(T, 1\,\text{bar}) dT \\ &= \Delta H(T, 1\,\text{bar}) - T\Delta S(T, 1\,\text{bar})\end{aligned}$$

and we can have the entropy and enthalpy by

$$\Delta S(T, p) = -\left[\frac{\partial \Delta G(T, p)}{\partial T}\right]_p$$

$$\Delta H(T, p) = \Delta G(T, p) + T\Delta S(T, p)$$

Changes in Properties for Chemical Reactions

- If the difference in compressibility between reactants and products are negligible,

$$\Delta G(T,p) = \Delta G(T,p_0) + \int_{1\,\text{bar}}^{p} \Delta V \, dp$$

if ΔV is independent of the pressure,

$$\Delta G(T,p) = \Delta G(T, 1\,\text{bar}) + \Delta V\,(p - 1\,\text{bar}) = \Delta G(T, 1\,\text{bar}) + \Delta V\,\Delta p$$

- When reactant and product is under the equilibrium, $\Delta G(T,p) = 0$ at T_e and p_e,

$$\Delta H(T_e,p_e) - T_e \Delta S(T_e,p_e) = 0 \rightarrow T_e = \frac{\Delta H(T_e,p_e)}{\Delta S(T_e,p_e)}$$

Changes in Properties for Chemical Reactions

- The entropy produced ΔS^{ir} or the driving force D in a reaction at constant T and p,

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

  If a reaction is spontaneous, D as the amount of chemical energy that is converted to thermal energy, which is positive.

- At constant T and V, the entropy produced for a chemical reaction is

$$\Delta S^{\text{ir}} = \Delta S(T,V) - \frac{\Delta U(T,V)}{T} = -\frac{\Delta F(T,V)}{T}$$

  for the spontaneous reaction, $\Delta F(T,V) < 0$.

Changes in Properties for Chemical Reactions

- If a chemical reaction takes place adiabatically at constant pressure,

$$\Delta S^{\text{ir}} = \Delta S = S(T, 1\,\text{bar}) - S(T_0, 1\,\text{bar})$$

- If a chemical reaction takes place adiabatically at constant volume,

$$\Delta S^{\text{ir}} = \Delta S = S(T, V) - S(T_0, V)$$