Thermodynamics of materials

10. Thermodynamic Calculations of Material Process - II

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

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- Since

$$du = Tds - pdv$$

the variation under constant temperature,

$$\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T = -Tv\alpha + pv\beta_T$$

- Since

$$dh = Tds + vdp$$

the variation under constant temperature,

$$\left(\frac{\partial h}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v = -Tv\alpha + v = v(1 - T\alpha)$$

Changes with Pressure at Constant Temperature

- Since

$$df = -sdT - pdv$$

the variation under constant temperature,

$$\left(\frac{\partial f}{\partial p}\right)_T = -p\left(\frac{\partial v}{\partial p}\right)_T = pv\beta_T$$

- Also,

$$\left(\frac{\partial s}{\partial p}\right)_T = -v\alpha$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v$$

- The finite changes

$$\Delta u = u(T_0, p) - u(T_0, p_0) = \int_{p_0}^{p} \left(\frac{\partial u}{\partial p}\right)_T dp = \int_{p_0}^{p} v\big(p\beta_T - T_0\alpha\big) dp$$

$$\Delta h = h(T_0, p) - h(T_0, p_0) = \int_{p_0}^{p} \left(\frac{\partial h}{\partial p}\right)_T dp = \int_{p_0}^{p} v\big(1 - T_0\alpha\big) dp$$

$$\Delta s = s(T_0, p) - s(T_0, p_0) = \int_{p_0}^{p} \left(\frac{\partial s}{\partial p}\right)_T dp = -\int_{p_0}^{p} v\alpha dp$$

$$\Delta f = f(T_0, p) - f(T_0, p_0) = \int_{p_0}^{p} \left(\frac{\partial f}{\partial p}\right)_T dp = \int_{p_0}^{p} pv\beta_T dp$$

$$\Delta \mu = \mu(T_0, p) - \mu(T_0, p_0) = \int_{p_0}^{p} \left(\frac{\partial \mu}{\partial p}\right)_T dp = \int_{p_0}^{p} v dp$$

- The finite change of energies are

$$\Delta u_{\mathsf{T}} = T_0 \Delta s = Q$$

$$\Delta u_{\mathsf{M}} = -\int_{p_0}^{p} \left[\frac{\partial (pv)}{\partial p}\right]_T dp = -\int_{p_0}^{p} \left[v + pv\beta_T\right] dp = -\Delta\mu + W$$

$$\Delta u_{\mathsf{C}} = \Delta\mu$$

Changes with Pressure at Constant Temperature

- For constant isothermal compressibility independent of pressure,

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

therefore,

$$\int_{p_0}^{p} v dp = -\frac{v_0}{\beta_T}\left[\exp\left[-\beta_T(p - p_0)\right] - 1\right]$$

proceed to

$$\int_{p_0}^{p} vp\beta_T dp = \beta_T v_0 \int_{p_0}^{p} p \exp\left[-\beta_T(p - p_0)\right] dp$$

Changes with Pressure at Constant Temperature

- Performing the integration by parts,

$$\beta_T \int_{p_0}^{p} v p dp = -v_0 \Big[p \exp\big[-\beta_T (p - p_0) \big] - p_0 \Big] - \frac{v_0}{\beta_T} \Big[p \exp\big[-\beta_T (p - p_0) \big] - 1 \Big]$$

- When thermal expansion coefficient and the isothermal compressibility are constant,

$$\Delta u = v_0 \Bigg[\Bigg[p_0 - \frac{T_0 \alpha - 1}{\beta_T} \Bigg] - \Bigg[p - \frac{T_0 \alpha - 1}{\beta_T} \Bigg] \exp\big[-\beta_T (p - p_0) \big] \Bigg]$$

$$\Delta h = \frac{(T_0 \alpha - 1) v_0}{\beta_T} \Big[\exp\big[-\beta_T (p - p_0) \big] - 1 \Big]$$

- Also,

$$\Delta s = \frac{\alpha v_0}{\beta_T}\Big[\exp\big[-\beta_T(p-p_0)\big]-1\Big]$$

$$\Delta f = -v_0\left[\left(p\exp\big[-\beta_T(p-p_0)\big]-p_0\right)+\frac{\exp\big[-\beta_T(p-p_0)\big]-1}{\beta_T}\right]$$

$$\Delta \mu = -\frac{v_0}{\beta_T}\exp\big[-\beta_T(p-p_0)\big]$$

Changes with Pressure at Constant Temperature

- When the condensed phase is incompressible, $\beta_T = 0$,

$$\Delta u = -T_0 \alpha v_0 (p - p_0) \qquad \Delta h = (1 - T_0 \alpha) v_0 (p - p_0)$$

$$\Delta s = -\alpha v_0 (p - p_0) \qquad \Delta f = 0 \qquad \Delta \mu = v_0 (p - p_0)$$

- For ideal gas,

$$\Delta u = \int_{p_0}^{p} v(p\beta_T - T_0 \alpha) dp = 0 \qquad \Delta h = -\int_{p_0}^{p} v(1 - T_0 \alpha) dp = 0$$

$$\Delta s = -\int_{p_0}^{p} v \alpha dp = -R \ln\left(\frac{p}{p_0}\right) \qquad \Delta \mu = \int_{p_0}^{p} v dp = RT \ln\left(\frac{p}{p_0}\right)$$

$$\Delta f = \int_{p_0}^{p} p v \beta_T dp = RT \ln\left(\frac{p}{p_0}\right)$$

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Changes with Temperature and Volume

- Assume the initial state (T_0, v_0) and the final state (T, v)

$$\Delta u = \int_i^f \left[\left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \right]$$

$$= \int_{T_0}^{T} c_v dT + \int_{v_0}^{v} \left(\frac{T\alpha}{\beta_T} - p \right) dv$$

$$\Delta h = \int_{T_0}^{T} \left(c_v + v_0 \frac{\alpha}{\beta_T} \right) dT + \int_{v_0}^{v} \frac{T\alpha - 1}{\beta_T} dv$$

$$\Delta s = \int_{T_0}^{T} \frac{c_v}{T} dT + \int_{v_0}^{v} \frac{\alpha}{\beta_T} dv$$

$$\Delta f = \int_{T_0}^{T} \left[c_v - s(T_0, v_0) \right] dT - T \int_{T_0}^{T} \frac{c_v}{T} dT - \int_{v_0}^{v} p dv$$

- Also,

$$\Delta\mu = \int_{T_0}^{T} \left[c_v + \frac{v_0\alpha}{\beta_T} - s(T_0, v_0)\right] dT - T\int_{T_0}^{T} \frac{c_v}{T} dT - \int_{v_0}^{v} \frac{dv}{\beta_T}$$

- When c_v, β_T and α are constant,

$$\Delta u = c_v(T - T_0) + \left(\frac{T\alpha - 1}{\beta_T} - p_0\right)(v - v_0) + \frac{v}{\beta_T}\ln\left(\frac{v}{v_0}\right)$$

$$\Delta h = \left(c_v + \frac{v_0\alpha}{\beta_T}\right)(T - T_0) + \frac{1}{\beta_T}(T\alpha - 1)(v - v_0)$$

Changes with Temperature and Volume

- When c_v, β_T and α are constant,

$$\Delta s = c_v \ln\left(\frac{T}{T_0}\right) + \frac{\alpha(v - v_0)}{\beta_T}$$

$$\begin{aligned}\Delta f = {} & \left[c_v - s(T_0, v_0)\right](T - T_0) \\ & - c_v T \ln\left(\frac{T}{T_0}\right) - \left(\frac{1}{\beta_T} + p_0\right)(v - v_0) + \frac{v}{\beta_T}\ln\left(\frac{v}{v_0}\right)\end{aligned}$$

$$\begin{aligned}\Delta \mu = {} & \left[c_v + \frac{v_0\alpha}{\beta_T} - s(T_0, v_0)\right](T - T_0) \\ & - c_v T \ln\left(\frac{T}{T_0}\right) - \frac{v - v_0}{\beta_T}\end{aligned}$$

- For ideal gases,

$$\Delta u = c_v(T - T_0) \qquad \Delta h = c_p(T - T_0)$$

$$\Delta s = c_v \ln\left(\frac{T}{T_0}\right) + R\ln\left(\frac{v}{v_0}\right)$$

$$\Delta f = \left[c_v - s(T_0, v_0)\right](T - T_0) - c_v T\ln\left(\frac{T}{T_0}\right) - RT\ln\left(\frac{v}{v_0}\right)$$

$$\Delta \mu = \left[c_p - s(T_0, v_0)\right](T - T_0) - c_v T\ln\left(\frac{T}{T_0}\right) - RT\ln\left(\frac{v}{v_0}\right)$$

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- Assume the initial state (T_0, p_0) and the final state (T, p)

$$\Delta u = \int_i^f \left[\left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial p} \right)_T dp \right]$$
$$= \int_{T_0}^{T} (c_p - pv\alpha) dT + \int_{p_0}^{p} v(p\beta_T - T\alpha) dp$$

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

$$\Delta s = \int_{T_0}^{T} \frac{c_p}{T} dT - \int_{p_0}^{p} v\alpha dp$$

Changes with Temperature and Pressure

- Assume the initial state (T_0, p_0) and the final state (T, p)

$$\Delta f = \int_{T_0}^{T} \left[c_p - s(T_0, p_0) - pv\alpha\right] dT - T \int_{T_0}^{T} \frac{c_p}{T} dT + \int_{p_0}^{p} pv\beta_T dp$$

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

- When α and β_T are constant,

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

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

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

Changes with Temperature and Pressure

- When α, c_p and β_T are constant,

$$\Delta u = c_p(T - T_0) - p_0 v_0\Big[\exp\big[\alpha(T - T_0)\big] - 1\Big]$$
$$+ v_0 \exp\big[\alpha(T - T_0)\big]\Bigg[\Big[p_0 + \frac{1 - T\alpha}{\beta_T}\Big] -$$
$$\Big[p + \frac{1 - T\alpha}{\beta_T}\Big]\exp\big[-\beta_T(p - p_0)\big]\Bigg]$$

$$\Delta h = c_p(T - T_0)$$
$$- \frac{v_0 \exp\big[\alpha(T - T_0)\big](1 - T\alpha)}{\beta_T}\Big[\exp\big[-\beta_T(p - p_0)\big] - 1\Big]$$

$$\Delta s = c_p \ln\left(\frac{T}{T_0}\right) + \frac{v_0 \exp\big[\alpha(T - T_0)\big]\alpha}{\beta_T}\Big[\exp\big[-\beta_T(p - p_0)\big] - 1\Big]$$

Changes with Temperature and Pressure

- When α, c_p and β_T are constant,

$$\Delta f = \left[c_p - s(T_0, p_0)\right](T - T_0) - p_0 v_0 \Big[\exp\left[\alpha(T - T_0)\right] - 1\Big]$$
$$- c_p T \ln\left(\frac{T}{T_0}\right) - v_0 \exp\left[\alpha(T - T_0)\right] \times$$
$$\Bigg[\Big[p \exp\left[-\beta_T(p - p_0)\right] - p_0\Big] + \frac{1}{\beta_T}\Big[\exp\left[-\beta_T(p - p_0)\right] - 1\Big]\Bigg]$$

$$\Delta \mu = \left[c_p - s(T_0, v_0)\right](T - T_0) - c_p T \ln\left(\frac{T}{T_0}\right)$$
$$- \frac{v_0 \exp\left[\alpha(T - T_0)\right]}{\beta_T}\Big[\exp\left[-\beta_T(p - p_0)\right] - 1\Big]$$

Changes with Temperature and Pressure

- For ideal gases,

$$\Delta u = c_v(T - T_0) \qquad \Delta h = c_p(T - T_0)$$

- Since

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp \\ &= \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp \end{aligned}$$

- For ideal gas,

$$v = \frac{RT}{p} \rightarrow \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$$

therefore,

$$ds = \frac{c_p}{T} dT - \frac{R}{p} dp$$

Changes with Temperature and Pressure

- The finite difference of the properties are

$$\Delta s = c_p \ln\left(\frac{T}{T_0}\right) - R\ln\left(\frac{p}{p_0}\right)$$

$$\Delta f = \big[c_v - s(T_0, p_0)\big](T - T_0) - c_p T\ln\left(\frac{T}{T_0}\right) + RT\ln\left(\frac{p}{p_0}\right)$$

$$\Delta \mu = \big[c_p - s(T_0, p_0)\big](T - T_0) - c_p T\ln\left(\frac{T}{T_0}\right) + RT\ln\left(\frac{p}{p_0}\right)$$