Thermodynamics of materials

09. Thermodynamic Calculations of Material Process - I

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Changes with Temperature at Constant Volume

- The infinitesimal changes under constant volume is

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT \qquad dh = \left(\frac{\partial h}{\partial T}\right)_v dT \qquad ds = \left(\frac{\partial s}{\partial T}\right)_v dT$$

$$df = \left(\frac{\partial f}{\partial T}\right)_v dT \qquad d\mu = \left(\frac{\partial \mu}{\partial T}\right)_v dT$$

- The rates of change may have different name,

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v$$

$$\left(\frac{\partial h}{\partial T}\right)_v = \left(\frac{Tds + vdp}{dT}\right)_v = T\left(\frac{ds}{dT}\right)_v + v\left(\frac{dp}{dT}\right)_v$$

$$= c_v + v\left(\frac{\partial p}{\partial T}\right)_v$$

Changes with Temperature at Constant Volume

- Also,

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \qquad \left(\frac{\partial f}{\partial T}\right)_v = -s$$

$$\left(\frac{\partial \mu}{\partial T}\right)_v = \left(\frac{-sdT + vdp}{dT}\right)_v = -s + v\left(\frac{dp}{dT}\right)_v$$

where c_v is the molar constant volume heat capacity.

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{ds}{dT}\right)_v$$

- We have

$$\left(\frac{dp}{dT}\right)_v = -\frac{\left(\frac{dv}{dT}\right)_p}{\left(\frac{dv}{dp}\right)_T} = \frac{\alpha}{\beta_T}$$

where

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad \beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

Changes with Temperature at Constant Volume

- Therefore,

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v \qquad \left(\frac{\partial h}{\partial T}\right)_v = c_v + \frac{v\alpha}{\beta_T} \qquad \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{\beta_T}$$

$$\left(\frac{\partial f}{\partial T}\right)_v = -s \qquad \left(\frac{\partial \mu}{\partial T}\right)_v = -s + \frac{v\alpha}{\beta_T}$$

- The finite change is

$$\Delta u = u(T, v_0) - u(T_0, v_0) = \int_{T_0}^{T} \left(\frac{\partial u}{\partial T}\right)_v dT = \int_{T_0}^{T} c_v dT$$

$$\Delta h = h(T, v_0) - h(T_0, v_0) = \int_{T_0}^{T} \left(\frac{\partial h}{\partial T}\right)_v dT$$

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

- The finite change is

$$\Delta s = s(T, v_0) - s(T_0, v_0) = \int_{T_0}^{T} \left(\frac{\partial s}{\partial T}\right)_v dT = \int_{T_0}^{T} \frac{c_v}{T} dT$$

$$\Delta f = f(T, v_0) - f(T_0, v_0) = \int_{T_0}^{T} \left(\frac{\partial f}{\partial T}\right)_v dT = -\int_{T_0}^{T} s dT$$

$$\Delta \mu = \mu(T, v_0) - \mu(T_0, v_0) = \int_{T_0}^{T} \left(\frac{\partial \mu}{\partial T}\right)_v dT$$

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

Changes with Temperature at Constant Volume

- Proceed to

$$s(T, v_0) = s(T_0, v_0) + \Delta s = s(T_0, v_0) + \int_{T_0}^{T} \frac{c_v}{T} dT$$

- Therefore,

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

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

Changes with Temperature at Constant Volume

- By integration by parts,

$$\Delta f = -s(T_0, v_0)(T - T_0) + \int_{T_0}^{T} c_v dT - T \int_{T_0}^{T} \frac{c_v}{T} dT$$

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

- The value with measurable properties,

$$\Delta u = \int_{T_0}^{T} c_v dT \qquad \Delta h = \int_{T_0}^{T} \left(c_v + \frac{v_0 \alpha}{\beta_T} \right) dT \qquad \Delta s = \int_{T_0}^{T} \frac{c_v}{T} dT$$

$$\Delta f = -s(T_0, v_0)(T - T_0) + \int_{T_0}^{T} c_v dT - T \int_{T_0}^{T} \frac{c_v}{T} dT$$

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

Changes with Temperature at Constant Volume

- The change in the molar thermal energy Δu_{T}, molar mechanical energy Δu_{M}, and molar chemical energy Δu_{C} at constant volume and temperature from T to T_0 is

$$\Delta u_{\mathsf{T}} = \int_{T_0}^{T} d(Ts) = \int_{T_0}^{T} T ds + \int_{T_0}^{T} s dT = -\Delta f + \Delta u = -\Delta f + Q$$

  where Q is the amount of heat absorbed from the surrounding during the process.

$$\Delta u_{\mathsf{M}} = \int_{T_0}^{T} d(pv) = v_0 \int_{T_0}^{T} \left(\frac{\partial p}{\partial T} \right)_v dT$$
$$= -v_0 \int_{T_0}^{T} \frac{\alpha}{\beta_T} dT = \Delta f - \Delta \mu$$

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

Changes with Temperature at Constant Volume

- When c_v, β_T and α are constant,

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

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

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

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

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Changes with Temperature at Constant Pressure

- The infinitesimal changes under constant pressure are

$$du = \left(\frac{\partial u}{\partial T}\right)_p dT \qquad dh = \left(\frac{\partial h}{\partial T}\right)_p dT \qquad ds = \left(\frac{\partial s}{\partial T}\right)_p dT$$

$$df = \left(\frac{\partial f}{\partial T}\right)_p dT \qquad d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT$$

- Then, we have

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{Tds - pdv}{dT}\right)_p = c_p - p\left(\frac{\partial v}{\partial T}\right)_p = c_p - pv\alpha$$

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p \qquad \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$$

Changes with Temperature at Constant Pressure

- The infinitesimal changes under constant pressure are

$$du = \left(\frac{\partial u}{\partial T}\right)_p dT \qquad dh = \left(\frac{\partial h}{\partial T}\right)_p dT \qquad ds = \left(\frac{\partial s}{\partial T}\right)_p dT$$

$$df = \left(\frac{\partial f}{\partial T}\right)_p dT \qquad d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT$$

- Then, we have

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{Tds - pdv}{dT}\right)_p = c_p - p\left(\frac{\partial v}{\partial T}\right)_p = c_p - pv\alpha$$

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p \qquad \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$$

- Also,

$$\left(\frac{\partial f}{\partial T}\right)_p = \left(\frac{-sdT - pdv}{dT}\right)_p = -s - p\left(\frac{\partial v}{\partial T}\right)_p = -s - pv\alpha$$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -s$$

where c_p is the molar constant pressure heat capacity,

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

- The finite change

$$\Delta u = u(T, p_0) - u(T_0, p_0) = \int_{T_0}^{T} \left(\frac{\partial u}{\partial T}\right)_p dT = \int_{T_0}^{T} (c_p - p_0 v\alpha) dT$$

$$\Delta h = h(T, p_0) - h(T_0, p_0) = \int_{T_0}^{T} \left(\frac{\partial h}{\partial T}\right)_p dT = \int_{T_0}^{T} c_p dT$$

$$\Delta s = s(T, p_0) - s(T_0, p_0) = \int_{T_0}^{T} \left(\frac{\partial s}{\partial T}\right)_p dT = \int_{T_0}^{T} \frac{c_p}{T} dT$$

$$\Delta f = \int_{T_0}^{T} \left(\frac{\partial f}{\partial T}\right)_p dT = -\int_{T_0}^{T} (s + p_0 v\alpha) dT$$

$$\Delta \mu = \int_{T_0}^{T} \left(\frac{\partial \mu}{\partial T}\right)_p dT = -\int_{T_0}^{T} s dT$$

- The entropy is

$$s(T,p_0) = s(T_0,p_0) + \int_{T_0}^{T} \frac{c_p}{T} dT$$

$$\begin{aligned}\Delta f &= -\int_{T_0}^{T} (s + p_0 v\alpha) dT \\ &= -\int_{T_0}^{T} \left[s(T_0,p_0) + \int_{T_0}^{T} \frac{c_p}{T} dT + p_0 v\alpha \right] dT\end{aligned}$$

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

- By integrating by parts,

$$\Delta f = -s(T_0, p_0)(T - T_0) + \underbrace{\int_{T_0}^{T} \left(c_p - p_0 v\alpha\right) dT}_{\Delta u} - T \underbrace{\int_{T_0}^{T} \frac{c_p}{T} dT}_{\Delta s}$$

$$\Delta \mu = -s(T_0, p_0)(T - T_0) + \underbrace{\int_{T_0}^{T} c_p dT}_{\Delta h} - T \int_{T_0}^{T} \frac{c_p}{T} dT$$

- The change of energy

$$\Delta u_{\mathsf{T}} = \int_{T_0}^{T} d(Ts) = \int_{T_0}^{T} s dT + \int_{T_0}^{T} T ds = -\Delta\mu + \Delta h = -\Delta\mu + Q$$

$$\Delta u_{\mathsf{M}} = -\int_{T_0}^{T} d(pv) = -p_0 \int_{T_0}^{T} \left(\frac{\partial v}{\partial T}\right)_p dT$$

$$= -p_0 \int_{T_0}^{T} v\alpha dT = -p_0(v - v_0) = W$$

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

- The thermal expansion coefficient

$$\alpha = \frac{1}{v(T, p_0)} \frac{dv(T, p_0)}{dT} \to d \ln v(T, p_0) = \alpha dT$$

Changes with Temperature at Constant Pressure

- Integrating the equation

$$\int_{T_0}^{T} d\ln v(T, p_0) = \int_{T_0}^{T} \alpha dT$$

proceed to

$$\ln\left[\frac{v(T, p_0)}{v_0(T_0, p_0)}\right] = \alpha(T - T_0)$$

then

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

- With all parameters, such as c_p, α are constant, the finite change of internal energy is

$$\Delta u = c_p(T - T_0) - p_0\alpha v_0\int_{T_0}^{T}\exp\big[\alpha(T - T_0)\big]dT$$

- Also,

$$\Delta f = \left[c_p - s(T_0, p_0)\right](T - T_0) - p_0 \alpha v_0 \int_{T_0}^{T} \exp\left[\alpha(T - T_0)\right] dT - c_p T \ln\left(\frac{T}{T_0}\right)$$

- Carrying the integration,

$$\Delta u = c_p(T - T_0) - p_0 v_0 \Big[\exp\left[\alpha(T - T_0)\right] - 1\Big]$$

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

Changes with Temperature at Constant Pressure

- The finite difference of chemical potential,

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

- When α is small,

$$\exp\left[\alpha(T - T_0)\right] - 1 \simeq \alpha(T - T_0)$$

then

$$\Delta u \simeq \left[c_p - p_0 v_0 \alpha\right](T - T_0)$$

$$\Delta f \simeq \left[c_p - p_0 v_0 \alpha - s(T_0, p_0)\right](T - T_0) - c_p T \ln\left(\frac{T}{T_0}\right)$$

Changes with Temperature at Constant Pressure

- For ideal gases, c_p is constant, $\alpha = 1/T$, then

$$\Delta u = c_v(T - T_0) \qquad \Delta h = c_p(T - T_0) \qquad \Delta s = c_p \ln\left(\frac{T}{T_0}\right)$$

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

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

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Changes with Volume at Constant Temperature

- Since

$$du = Tds - pdv$$

we have

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

- Also

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad \beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

therefore,

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

Changes with Volume at Constant Temperature

- Also since

$$dh = Tds + vdp$$

we have

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

- For Helmholtz free energy,

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

Changes with Volume at Constant Temperature

- For chemical potential, we have

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

therefore,

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T = -\frac{1}{\beta_T}$$

Changes with Volume at Constant Temperature

- The finite changes are

$$\Delta u = u(T_0, v) - u(T_0, v_0) = \int_{v_0}^{v} \left(\frac{\partial u}{\partial v}\right)_T dv = \int_{v_0}^{v} \left(\frac{T\alpha}{\beta_T} - p\right) dv$$

$$\Delta h = \int_{v_0}^{v} \left(\frac{\partial h}{\partial v}\right)_T dv = \int_{v_0}^{v} \frac{T\alpha - 1}{\beta_T} dv$$

$$\Delta s = \int_{v_0}^{v} \left(\frac{\partial s}{\partial v}\right)_T dv = \int_{v_0}^{v} \frac{\alpha}{\beta_T} dv$$

$$\Delta f = \int_{v_0}^{v} \left(\frac{\partial f}{\partial v}\right)_T dv = -\int_{v_0}^{v} p\, dv$$

$$\Delta \mu = \int_{v_0}^{v} \left(\frac{\partial \mu}{\partial v}\right)_T dv = -\int_{v_0}^{v} \frac{1}{\beta_T} dv$$

Changes with Volume at Constant Temperature

- The finite changes of energies are

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

$$\Delta u_{\mathsf{M}} = -\int_{T_0}^{T} \left[\frac{\partial(pv)}{\partial v}\right]_T dv = -\int_{v_0}^{v} p dv + \int_{v_0}^{v} \frac{dv}{\beta_T} = W - \Delta\mu$$

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

where Q is the amount of heat absorbed from the surrounding during the process.

Changes with Volume at Constant Temperature

- From the definition of isothermal compressibility

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

integrating,

$$v(T_0, p) = v(T_0, p_0)\exp\big[-\beta_T(p - p_0)\big]$$

in other forms,

$$p = p_0 - \frac{1}{\beta_T}\ln\left(\frac{v}{v_0}\right)$$

Changes with Volume at Constant Temperature

- With assumption that β_T and α are constant, integrating the equation,

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

  integrating by parts,

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

- Also the finite differences are

$$\Delta h = \int_{v_0}^{v} \frac{1}{\beta_T} (T_0 \alpha - 1) dv = \frac{(T_0 \alpha - 1)(v - v_0)}{\beta_T}$$

$$\Delta s = \int_{v_0}^{v} \frac{\alpha}{\beta_T} dv = \frac{\alpha}{\beta_T} (v - v_0)$$

Changes with Volume at Constant Temperature

- Additionally,

$$\Delta f = -\int_{v_0}^{v} p dv = -\left(\frac{1}{\beta_T} + p_0\right)(v - v_0) + \frac{1}{\beta_T}\left[v \ln \frac{v}{v_0}\right]$$

$$\Delta \mu = -\int_{v_0}^{v} \frac{dv}{\beta_T} = \frac{v_0 - v}{\beta_T}$$

Changes with Volume at Constant Temperature

- For ideal gas,

$$\alpha = \frac{1}{T} \qquad \beta_T = \frac{1}{p}$$

we have

$$\Delta u = \int_{v_0}^{v} \left(\frac{T\alpha}{\beta_T} - p \right) dv = 0 \qquad \Delta h = \int_{v_0}^{v} \frac{T\alpha - 1}{\beta_T} dv = 0$$

$$\Delta s = \int_{v_0}^{v} \frac{p dv}{T} = \int_{v_0}^{v} \frac{R dv}{v} = R \ln \left(\frac{v}{v_0} \right)$$

$$\Delta f = -\int_{v_0}^{v} p dv = -RT_0 \ln \left(\frac{v}{v_0} \right)$$

$$\Delta \mu = -\int_{v_0}^{v} \frac{dv}{\beta_T} = -RT_0 \ln \left(\frac{v}{v_0} \right)$$