# Thermodynamics of materials
## 06. Relations Among Thermodynamic Properties

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# Table of Contents

# Table of Contents

# Maxwell Relations

- The thermodynamic properties obtained from the fundamental equations of thermodynamics through first and second derivatives are related each other. The representative relations are Maxwell relations.

- The differential form for the Gibbs free energy as an example,

$$dG = -SdT + Vdp + \mu dN$$

then we have

$$\left( \frac{\partial G}{\partial T} \right)_{p,N} = -S \quad \left( \frac{\partial G}{\partial p} \right)_{T,N} = V \quad \left( \frac{\partial G}{\partial N} \right)_{T,p} = \mu$$

# Maxwell Relations

- The mixed second derivatives of $G$,

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

$$\left[\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial p}\right)_{T,N}\right]\right]_{p,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

- Since $G$ is a state function, the order of derivative does not matter,

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

- Using the definition of volume thermal expansion coefficient $\alpha$, we have

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} = -V\alpha$$

# Maxwell Relations

- The change of entropy can be computed by

$$\Delta S = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right)_{T,N} dp = -\int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_{p,N} dp = -\int_{p_1}^{p_2} V\alpha \, dp$$

- Similarly,

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

$$\left[\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial N}\right)_{T,p}\right]\right]_{p,N} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N}$$

- We get another Maxwell relation

$$-\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -s$$

where $s$ is the molar entropy.

# Maxwell Relations

- We can also write down additional Maxwell relation,

$$\left[\frac{\partial}{\partial N}\left[\left(\frac{\partial G}{\partial p}\right)_{T,N}\right]\right]_{T,p} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = v$$

$$\left[\frac{\partial}{\partial p}\left[\left(\frac{\partial G}{\partial N}\right)_{T,p}\right]\right]_{T,N} = \left(\frac{\partial \mu}{\partial p}\right)_{p,N} = v$$

hence

$$\left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{p,N} = v$$

where $v$ is the molar volume.

# Maxwell Relations

- Also, we can obtain the consistent relation by

$$dU = TdS - pdV + \mu dN \qquad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

$$dF = -SdT - pdV + \mu dN \qquad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}$$

$$dH = TdS + Vdp + \mu dN \qquad \left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N}$$

# Table of Contents

# Euler Relation

- For the thermodynamic quantity $z$, we can represent

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- For constant $z$,

$$-\left(\frac{\partial z}{\partial x}\right)_y dx = \left(\frac{\partial z}{\partial y}\right)_x dy$$

then proceed to

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{(\partial z/\partial x)_y}{(\partial z/\partial y)_x}\checkmark$$

# Ratio of derivatives

- For the thermodynamic quantity $z$ and $x$, we can represent

$$dz = \left( \frac{\partial z}{\partial w} \right)_y dw + \left( \frac{\partial z}{\partial y} \right)_w dy$$

$$dx = \left( \frac{\partial x}{\partial w} \right)_y dw + \left( \frac{\partial x}{\partial y} \right)_w dy$$

- For constant $y$,

$$dz = \left( \frac{\partial z}{\partial w} \right)_y dw \qquad dx = \left( \frac{\partial x}{\partial w} \right)_y dw$$

proceed to

$$\left( \frac{\partial z}{\partial x} \right)_y = \frac{(\partial z/\partial w)_y}{(\partial x/\partial w)_y} \checkmark$$

# Table of Contents

# Barocaloric Effect

- For adiabatic process, when temperature and pressure changes,

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = 0$$

Therefore,

$$dT = -\frac{\left(\partial S/\partial p\right)_T}{\left(\partial S/\partial T\right)_p} dp = -\frac{-V\alpha}{C_p/T} dp = \frac{TV\alpha}{C_p} dp$$

the barocaloric effect is proportional to the thermal expansion coefficient or the rate volume change with temperature change.

- Therefore, we have

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{TV\alpha}{C_p} dp$$

which is positive, in general.

# Isothermal Volume Dependence of Entropy

- Isothermal dependence of entropy can be rewritten by

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{(\partial S/\partial p)_T}{(\partial V/\partial p)_T}$$

- By Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{(\partial S/\partial p)_T}{(\partial V/\partial p)_T} = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\beta_T}$$

- Joule Expansion Effect represents the temperature change with respect to volume change under constant internal energy,

$$\left(\frac{\partial T}{\partial V}\right)_U$$

- By Euler relation,

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = -\frac{(\partial U/\partial V)_T}{C_V} = -\frac{1}{C_V}\left(\frac{T\alpha}{\beta_T} - p\right)$$

- The Joule-Thompson expansion effect can be rewritten by Euler Relation

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\partial H/\partial p\right)_T}{\left(\partial H/\partial T\right)_p} = -\frac{\left(\partial H/\partial p\right)_T}{C_p}$$

- The differential enthalpy is

$$dH = TdS + Vdp$$

- Take partial derivative with respect to $p$ at constant $T$,

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

# Joule-Thompson Expansion Effect

- By Maxwell relation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

we have

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

- Using the definitions for the isobaric volume thermal expansion,

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha)$$

- Therefore, the magnitude of the Joule-Thomson effect of a fluid is

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} = \frac{V(T\alpha - 1)}{C_p}$$

# Grüneisen parameter

- The Grüneisen parameter represents the temperature increase of a material as the material is adiabatically compressed.

$$\gamma = -\left[\frac{(\partial T/T)}{(\partial V/V)}\right]_S = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = -\frac{V}{T}\left(\frac{\partial T}{\partial V}\right)_S = V\left(\frac{\partial p}{\partial U}\right)_V$$

- Using Maxwell relation and so on,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{(\partial S/\partial p)_T}{(\partial V/\partial p)_T}$$

# Grüneisen parameter

- Therefore,

$$\gamma = -\left[\frac{(\partial T/T)}{(\partial V/V)}\right]_S = \frac{V}{T}\frac{(\partial S/\partial p)_T}{(\partial V/\partial p)_T} = \frac{V}{T}\frac{-(\partial V/\partial T)_p}{(\partial S/\partial T)_V(\partial V/\partial p)_T}$$

- For monoatomic ideal gas,

$$\alpha = \frac{1}{T} \qquad c_v = \frac{3R}{2} \qquad \beta_T = \frac{1}{p}$$

then

$$\gamma = \frac{\alpha}{cc_v\beta_T} = \frac{1/T}{c(3R/2)(1/p)} = \frac{pV}{NT(3R/2)} = \frac{2}{3}$$

# Thermal Strain and Elastocaloric Effect

- The thermal strain and elastocaloric effects involve thermomechanical coupling. The differential form for the Gibss free energy per unit volume $g$ including only the thermal and mechanical contributions is

$$dg = -sdT - \varepsilon_{ij}d\sigma_{ij}$$

where $s$ is the entropy per unit volume.

- The Maxwell relation is

$$\left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_{\sigma,E,H} = \alpha_{ij} = \left(\frac{\partial s}{\partial \sigma_{ij}}\right)_{T,E,H} = \alpha'_{ij}$$

where $\alpha_{ij}$ is the second-rank thermal expansion coefficient tensor, and $\alpha'_{ij}$ is the second-rank elastocaloric coefficient tensor.