## Multiple Transforms

$$y^{(j)}(\xi_1, \xi_2, \ldots \xi_j, x_{j+1}, \ldots) = y^{(0)}(x_1, x_2, \ldots x_j, x_{j+1} \ldots) - \sum_{i=1}^{j} x_i \xi_i$$

## Applications to Thermodynamics

| $\underline{U} = y^{(0)}$ | | $\underline{A} = y^{(1)}$ | | $\underline{G} = y^{(2)}$ | | Gibbs-Duhem relat. $y^{(n+2)} = \phi$ | |
|---|---|---|---|---|---|---|---|
| var. | der. | var. | der. | var. | der. | Var. | Der. |
| $\underline{S}$ | $T$ | $T$ | $-\underline{S}$ | $T$ | $-\underline{S}$ | $T$ | $-\underline{S}$ |
| $\underline{V}$ | $-P$ | $\underline{V}$ | $-P$ | $-P$ | $-\underline{V}$ | $-P$ | $-\underline{V}$ |
| $N_1$ | $\mu_1$ | $N_1$ | $\mu_1$ | $N_1$ | $\mu_1$ | $\mu_1$ | $-N_1$ |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | | $\vdots$ | $\vdots$ |
| $N_n$ | $\mu_n$ | $N_n$ | $\mu_n$ | $N_n$ | $\mu_n$ | $\mu_n$ | $-N_n$ |

### Different Ordering

| $\underline{U} = y^{(0)}$ | | $\underline{H} = y^{(1)}$ | |
|---|---|---|---|
| $\underline{V}$ | $-P$ | $-P$ | $-\underline{V}$ |
| $\underline{S}$ | $T$ | $\underline{S}$ | $T$ |
| $N_1$ | $\mu_1$ | $N_1$ | $\mu_1$ |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ |
| $N_n$ | $\mu_n$ | $N_n$ | $\mu_n$ |

### Different basis

| $\underline{G} = y^{(0)}$ | | $\underline{H} = y^{(1)}$ | |
|---|---|---|---|
| $T$ | $-\underline{S}$ | $-\underline{S}$ | $-T$ |
| $-P$ | $-\underline{V}$ | $-P$ | $-\underline{V}$ |
| $N_1$ | $\mu_1$ | $N_1$ | $\mu_1$ |
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ |
| $N_n$ | $\mu_n$ | $N_n$ | $\mu_n$ |

## What good is all this formalism?

* Differential and Integral relationships for fundamental functions: e.g.,

$$d\underline{G} = -\underline{S}\,dT + \underline{V}\,dP + \sum_i \mu_i\,dN_i$$

$$\underline{G} = \underline{U} - T\underline{S} + P\underline{V}$$

* "Recipes" for expressing derivatives of transforms with respect to derivatives of the basis function:

e.g. Table 5.3

$$y_{11}^{(1)} = -\frac{1}{y_{11}^{(0)}} \qquad y_{1i}^{(1)} = \frac{y_{1i}^{(0)}}{y_{11}^{(0)}} \quad i \neq 1$$

$$y_{ij}^{(1)} = y_{ij}^{(0)} - \frac{y_{1i}^{(0)}\, y_{1j}^{(0)}}{y_{11}^{(0)}} \quad i, j \neq 1$$

* There are also (complex) expressions for second derivatives of higher-order transforms with respect to second derivatives of $y^{(0)}$

- Table 5.5. $y_{ij}^{(k)} = f\left(y_{ij}^{(0)}\right)$

Of particular interest are the second-order derivatives of $\underline{G}$, which are experimentally measurable

$$dG = -S\,dT + V\,dP \qquad \text{(1-component, intensive)}$$

$$G_{TT} = \frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T} = -\frac{1}{T} C_P \qquad \text{Const-}P \text{ heat capacity}$$

$$G_{PP} = \frac{\partial^2 G}{\partial P^2} = \frac{\partial V}{\partial P}\Big)_T = \left(\frac{\partial V}{\partial P}\right)_T = -V \kappa_T$$

where $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ , isothermal compressibility

$$G_{PT} = \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T}\Big)_P = \left(\frac{\partial V}{\partial T}\right)_P = V \alpha_P$$

where $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ , thermal expansion coefficient

For example, let us obtain $\left(\frac{\partial S}{\partial V}\right)_P$ in terms of experimentally measurable properties:

P and V are "conjugate variables" — not amenable to transformations

$$\left(\frac{\partial S}{\partial V}\right)_P = \left[\left(\frac{\partial V}{\partial S}\right)_P\right]^{-1}$$

Which fundamental function has variables S and P?

$\longrightarrow$ H

| $G = y^{(0)}$ | | $H = y^{(1)}$ | |
|---|---|---|---|
| $x$ | $\xi$ | $x$ | $\xi$ |
| $T$ | $-S$ | $-S$ | $+T$ |
| $P$ | $V$ | $P$ | $V$ |

$$\left(\frac{\partial V}{\partial S}\right)_P = -\frac{\partial^2 H}{\partial S \partial P} = -y_{12}^{(1)}$$

$$= -\frac{y_{12}^{(0)}}{y_{11}^{(0)}} = \frac{\alpha_P V T}{C_P}$$

(from Table 5-3)

Other useful "tricks" for transformations of derivatives (see §5.3 in T+M)

$$dy = \xi_1 dx_1 + \xi_2 dx_2 + \dots \Rightarrow \left(\frac{\partial \xi_2}{\partial x_1}\right)_{x_2 \dots} = \left(\frac{\partial \xi_1}{\partial x_2}\right)_{x_1 \dots}$$

(Maxwell's relationships)

XYZ -1 rule: $\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1$

$$\left(\frac{\partial a}{\partial b}\right)_c = \left(\frac{\partial a}{\partial d}\right)_c \cdot \left(\frac{\partial d}{\partial b}\right)_c \quad \text{Chain Rule}$$

Two ways to do this.

(a) $dy^{(0)} = dG = -S\,dT + v\,dP$

$dy^{(1)} = dH = (-T)\,d(-S) + v\,dP$ [not $TdS + vdP$!]

$$\left(\frac{\partial v}{\partial S}\right)_P = -H_{PS} = -y^{(1)}_{12} = -\frac{y^{(0)}_{12}}{y^{(0)}_{11}} = \frac{(\partial v/\partial T)_P}{(\partial S/\partial T)_P} = \frac{(\partial v/\partial T)_P}{c_P/T}$$

(b) $dy^{(0)} = dH = TdS + vdP$

$dy^{(1)} = dG = (-S)\,dT + v\,dP$

$$y^{(1)}_{12} = \frac{y^{(0)}_{12}}{y^{(0)}_{11}} \Rightarrow y^{(0)}_{12} = y^{(0)}_{11} \cdot y^{(1)}_{12} \Rightarrow \left(\frac{\partial v}{\partial S}\right)_P = \left(\frac{\partial T}{\partial S}\right)_P \cdot \left(\partial v/\partial T\right)_P$$

## Modifications to F.E. for non-simple systems

If external fields act on a system (e.g. a solid or elastic material under tension, a magnetic material under a magnetic field, the F.E. can be augmented by appropriate terms:

$$d\underline{u} = T d\underline{S} \left[ -P d\underline{V} + \sum_i \mu_i d N_i \right] + \underset{\uparrow\ \text{field}}{F} \cdot d\underset{\uparrow\ \text{extensive variable}}{\underline{x}}$$

For systems (e.g. a rubber band) under stress:

$F =$ Force exerted by band (pointing in)

$\underline{x} =$ Linear extension $\underline{L}$ (length)

For a magnetic material

$F = -\vec{H}$ (magnetic field strength)

$\underline{x} = \underline{\vec{B}}$ (magnetic moment)

Example: Principles of shrink-wrapping

An elastic material (e.g. a rubber band) cools when suddenly released from tension. Predict the sign of $\left(\frac{\partial F}{\partial T}\right)_{\underline{L}}$

Solution: $d\underline{u} = T d\underline{S} + F d\underline{L}$

$= \left.\frac{\partial F}{\partial T}\right)_L \cdot \left.\frac{\partial T}{\partial S}\right)_L$

Maxwell's relationship $\left(\frac{\partial T}{\partial \underline{L}}\right)_{\underline{S}} = + \left(\frac{\partial F}{\partial \underline{S}}\right)_L > 0$

Since $\left.\frac{dS}{dT}\right)_{\underline{L}} > 0 \Rightarrow \left(\frac{\partial F}{\partial T}\right)_{\underline{L}} > 0$ (shrink-wrapping)