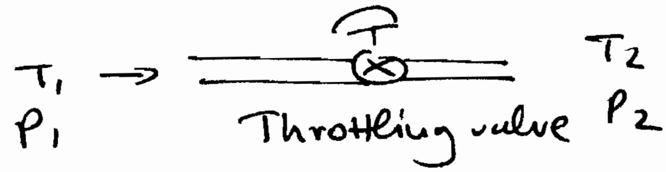
Derivatives at const $\underline{U}$, $\underline{H}$, ...

→ Use triple-product rule, inversion, chain rule etc:

e.g. Joule-Thompson coefficient, $\left.\frac{\partial T}{\partial P}\right)_{\underline{H}}$



$$\left(\frac{\partial T}{\partial P}\right)_{\underline{H}}\left(\frac{\partial \underline{H}}{\partial T}\right)_P\left(\frac{\partial P}{\partial \underline{H}}\right)_T = -1 \Rightarrow \left(\frac{\partial T}{\partial P}\right)_{\underline{H}} = -\frac{(\partial \underline{H}/\partial P)_T}{\underbrace{(\partial \underline{H}/\partial T)_P}_{\to C_p}}$$

$(\partial \underline{H}/\partial P)_T$ from $d\underline{H} = Td\underline{S} + \underline{V}dP \Rightarrow$

$$(\partial \underline{H}/\partial P)_T = T\left.\frac{\partial \underline{S}}{\partial P}\right)_T + \underline{V} \underbrace{=}_{\text{maxwell on } \underline{G}} -T\left.\frac{\partial \underline{V}}{\partial T}\right)_P + \underline{V}$$

$$\therefore \left.\frac{\partial T}{\partial P}\right)_{\underline{H}} = \frac{1}{C_p}\left[T\left(\frac{\partial \underline{V}}{\partial T}\right)_P - \underline{V}\right]$$

Example 5.5: Differentials for $\underline{U}(T,\underline{V})$ & $\underline{U}(T,P)$

$\underline{U}(T,\underline{V})$ or $\underline{U}(T,P)$ are not F.E.s.

need $d\underline{U} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} dT + \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_T d\underline{V}$ etc

$\left.\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} \equiv C_v$ ✓ $\quad d\underline{U} = Td\underline{S} - Pd\underline{V} \Rightarrow \left.\frac{\partial \underline{U}}{\partial \underline{V}}\right)_T = T\left.\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T - P$

$$= T\left.\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \checkmark$$

for $\left.\frac{\partial \underline{U}}{\partial T}\right)_P = T\left.\frac{\partial \underline{S}}{\partial T}\right)_P - P\left.\frac{\partial \underline{V}}{\partial T}\right)_P = C_p - P\left.\frac{\partial \underline{V}}{\partial T}\right)_P$ ✓

$$\left.\frac{\partial \underline{u}}{\partial P}\right)_T = T\left.\frac{\partial s}{\partial P}\right)_T - P\left.\frac{\partial \underline{v}}{\partial P}\right)_T = -T\left.\frac{\partial \underline{v}}{\partial T}\right)_P - P\left.\frac{\partial \underline{v}}{\partial P}\right)_T \quad \checkmark$$

More complex than "natural" derivatives but exper. measurable.

Example 5.6 $C_P - C_V$ from $P\underline{V}T$

From previous expressions for $\underline{u}(T,\underline{v})$ & $\underline{u}(T,P)$

$$d\underline{u} = c_v\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{v}} - P\right]d\underline{v} \qquad (i)$$

$$d\underline{u} = \left(c_P - P\left.\frac{\partial \underline{v}}{\partial T}\right)_P\right)dT - [\quad]\,dP \qquad (ii)$$

Take $\left.\frac{\partial (i)}{\partial T}\right)_P$ and set equal to

$$C_v + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{v}} - P\right]\left.\frac{\partial \underline{v}}{\partial T}\right)_P = c_P - P\left.\frac{\partial \underline{v}}{\partial T}\right)_P \Rightarrow$$

$$\Rightarrow \quad C_P - C_v = T\left.\frac{\partial P}{\partial T}\right)_{\underline{V}}\left.\frac{\partial \underline{v}}{\partial T}\right)_P$$

If a $P\underline{V}T$ relationship (an equation of state) is known, the R.H.S can be obtained.

for I.G. $\quad P\underline{V} = RT \quad \left.\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}} \quad \left.\frac{\partial \underline{v}}{\partial T}\right)_P = \frac{R}{P}$

$$\Rightarrow \quad C_P - C_v = T\cdot\frac{R^2}{P\underline{V}} = R \quad \text{as already known}$$