Maxwell Relations from $A$
Interrelated Thermodynamic Quantities

When you are not able to directly measure a given thermodynamic property, it is very useful to express it in terms of other properties.

\[ dA = dU - TdS - SdT \]  \hspace{1cm} \text{(general)}

for a reversible process \[ dU = TdS - PdV \]

\[ dA = -PdV - SdT \]

compare with the formal derivative of \( A = A(V,T) \):

\[ dA = \left( \frac{\partial A}{\partial V} \right)_T \, dV + \left( \frac{\partial A}{\partial T} \right)_V \, dT \]

Thus \[ \left( \frac{\partial A}{\partial V} \right)_T = -P \] and \[ \left( \frac{\partial A}{\partial T} \right)_V = -S \]
**Equating Key Cross Derivatives**

\[
\left( \frac{\partial A}{\partial V} \right)_T = -P \quad \text{and} \quad \left( \frac{\partial A}{\partial T} \right)_V = -S
\]

As

\[
\frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right) = \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)
\]

equality of mixed partial derivatives

\[
\left( \frac{\partial A}{\partial V} \right)_T = -P \quad \rightarrow \quad \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right) = -\left( \frac{\partial P}{\partial T} \right)_V
\]

\[
\left( \frac{\partial A}{\partial T} \right)_V = -S \quad \rightarrow \quad \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right) = -\left( \frac{\partial S}{\partial V} \right)_T
\]

One of *many* Maxwell relations

\[
\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T
\]
Utility of a Maxwell Relation

\[
\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T
\]

From this Maxwell relation we can determine how \( S \) changes with \( V \) given an equation of state.

Integrate at constant \( T \):

\[
\Delta S = \int_{V_1}^{V_2} \left( \frac{\partial P}{\partial T} \right)_V \, dV
\]

Note that \( T \) is held constant during integration over \( V \).

Get \( V \) (or \( \rho \)) dependence of \( S \) from \( P-V-T \) data.

Example: Ideal gas

\[
\left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \quad \Delta S = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1} \quad \text{(isothermal)}
\]

(a previous result derived another way, cf. Video 6.2)
Entropy of Ethane

If $V_1$ is chosen to be so large that a gas behaves ideally ($=V_{id}$),

$$\Delta S = S(T, V_2) - S_{(\rho \to 0)}^{id} = \int_{V_{id}}^{V_2} \left( \frac{\partial P}{\partial T} \right)_V dV \quad \text{(constant } T)$$

Ethane at 400 K

For real gases, i.e., those having no readily available, analytical equation of state, this requires data for how pressure varies with temperature over a full range of volumes (or densities, since density is equal to $V^{-1}$)

\[ \bar{S}_{(P \to 0)}^{id} [246.45 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{ at 1 bar (from Q!)}] \]
**Internal Energy of Ethane**

Differentiating $A = U - TS$ wrt $V$:

\[
\left( \frac{\partial A}{\partial V} \right)_T = \left( \frac{\partial U}{\partial V} \right)_T - T \left( \frac{\partial S}{\partial V} \right)_T \quad \text{(isothermal)}
\]

using \( \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T \)

and \( \left( \frac{\partial A}{\partial V} \right)_T = -P \)

\( \text{Maxwell relation} \)

\( \text{previously derived} \)

\[
\left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V
\]

For real gases, i.e., those having no readily available, analytical equation of state, this again requires data for how pressure varies with temperature over a full range of volumes (although the plot here is over pressures, which are obviously readily measured for each volume)
**Volume Dependence of \( A \)**

\[
\left( \frac{\partial A}{\partial V} \right)_T = -P \quad \text{integrate} \quad \Delta A = -\int_{V_1}^{V_2} P \, dV \quad \text{(constant } T\text{)}
\]

Ideal gas example, \( P = \frac{nRT}{V} \):

\[
\Delta A = -nRT \int_{V_1}^{V_2} \frac{1}{V} \, dV = -nRT \ln \frac{V_2}{V_1} \quad \text{(constant } T\text{)}
\]

Compare this to a previous result for an ideal gas at constant \( T \):

\[
\Delta S = nR \ln \frac{V_2}{V_1}
\]

As expected, \( \Delta A = \Delta U - T \Delta S \) is equal simply to \( -T \Delta S \) since \( \Delta U = 0 \) at constant \( T \) for an ideal gas.