Statistical Molecular Thermodynamics

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Video 8.3

Maxwell Relations from A

Interrelated Thermodynamic Quantities

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

$$dA = dU - TdS - SdT \qquad \text{(general)}$$

for a reversible process $\quad dU = TdS - PdV$

$$dA = -PdV - SdT$$

compare with the formal derivative of $A = A(V,T)$: $\quad dA = \left(\dfrac{\partial A}{\partial V}\right)_T dV + \left(\dfrac{\partial A}{\partial T}\right)_V dT$

Thus $\left(\dfrac{\partial A}{\partial V}\right)_T = -P$ and $\left(\dfrac{\partial A}{\partial T}\right)_V = -S$

EQUATING KEY CROSS DERIVATIVES

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$
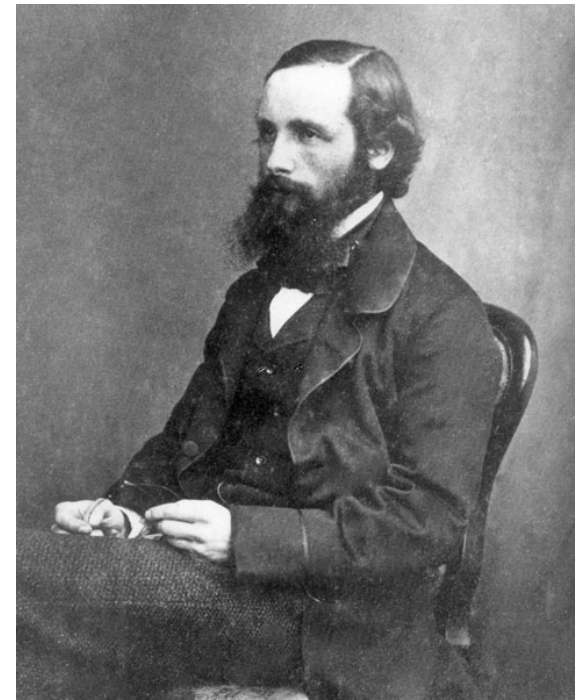
As
$$\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right) = \frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)$$
equality of mixed partial derivatives

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \longrightarrow \frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right) = -\left(\frac{\partial P}{\partial T}\right)_V$$

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

James Clerk Maxwell

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 ρ) dependence of S from P-V-T data.
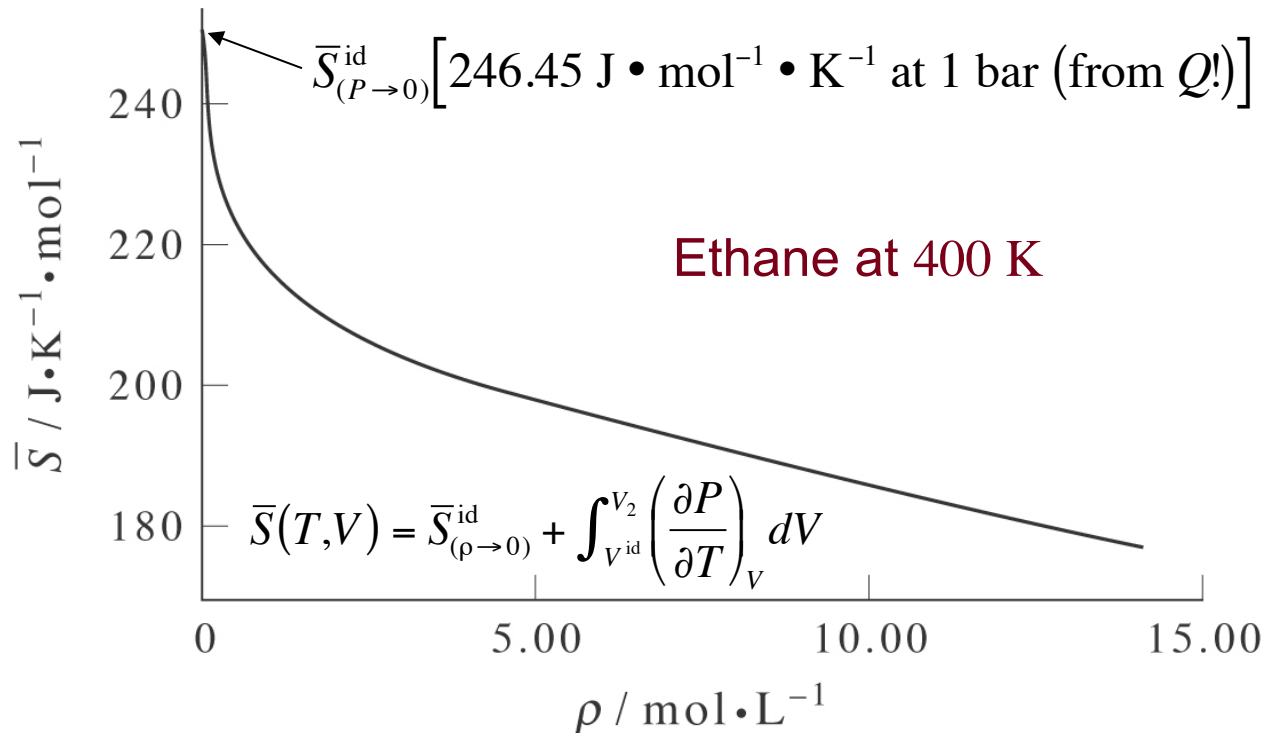
Example: Ideal gas

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

(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 ($=V_{id}$),

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

$\overline{S}^{id}_{(P \to 0)} \left[246.45 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \text{ at 1 bar (from } Q!) \right]$

Ethane at 400 K

$$\overline{S}(T,V) = \overline{S}^{id}_{(\rho \to 0)} + \int_{V^{id}}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV$$
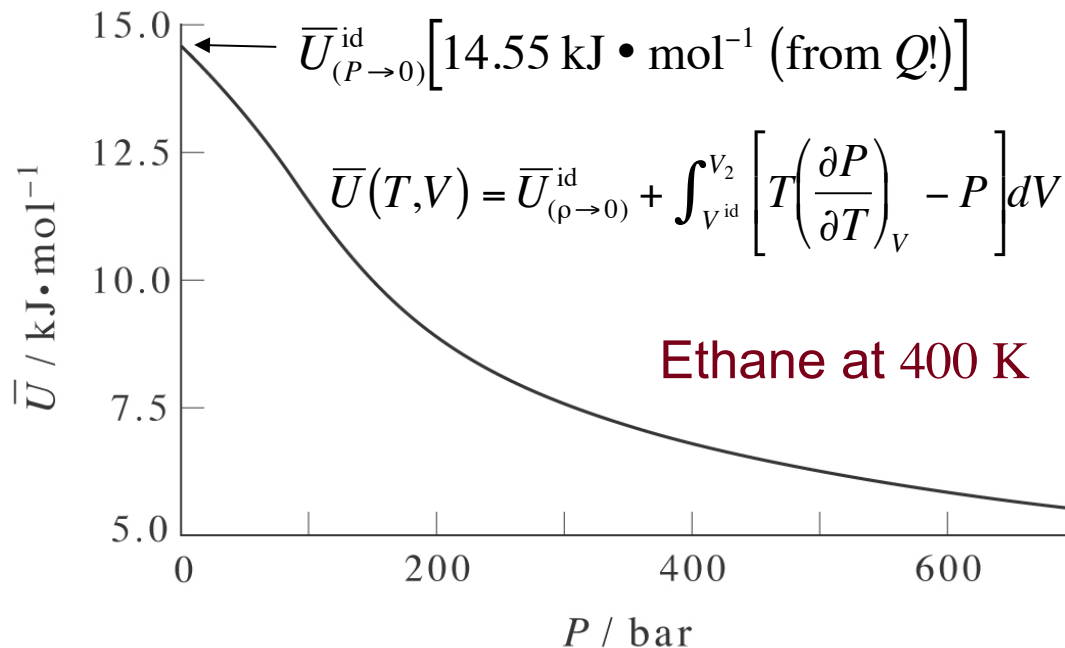
For real gases, i.e., those having no readily available, analytical equation of state, this requires data for how pressure varies with temperature over a full range of volumes (or densities, since density is equal to $\overline{V}^{-1}$)

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 $\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$ and $\boxed{\left(\frac{\partial A}{\partial V}\right)_T = -P}$

  Maxwell relation   *previously derived*

$$\Longrightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

$\overline{U}^{\text{id}}_{(P \to 0)}\left[14.55 \text{ kJ} \bullet \text{mol}^{-1} \left(\text{from } Q!\right)\right]$

$$\overline{U}(T,V) = \overline{U}^{\text{id}}_{(\rho \to 0)} + \int_{V^{\text{id}}}^{V_2}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$$

Ethane at 400 K

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*

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

Ideal gas example, $P = nRT/V$:

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

Compare this to a previous result for an ideal gas at constant T: $\qquad \Delta S = nR \ln \frac{V_2}{V_1}$

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*