

STATISTICAL MOLECULAR THERMODYNAMICS

Christopher J. Cramer

Video 8.4

Maxwell Relations from G

WORKING WITH GIBBS FREE ENERGY

$$G = U - TS + PV$$

differentiate $\Rightarrow dG = dU - TdS - SdT + PdV + VdP$

using $dU = TdS - PdV \Rightarrow dG = -SdT + VdP$

compare with the formal
derivative of $G = G(P, T)$:

$$dG = \left(\frac{\partial G}{\partial T} \right)_P dT + \left(\frac{\partial G}{\partial P} \right)_T dP$$

$$\text{Thus } \left(\frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

EQUATING KEY CROSS DERIVATIVES

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

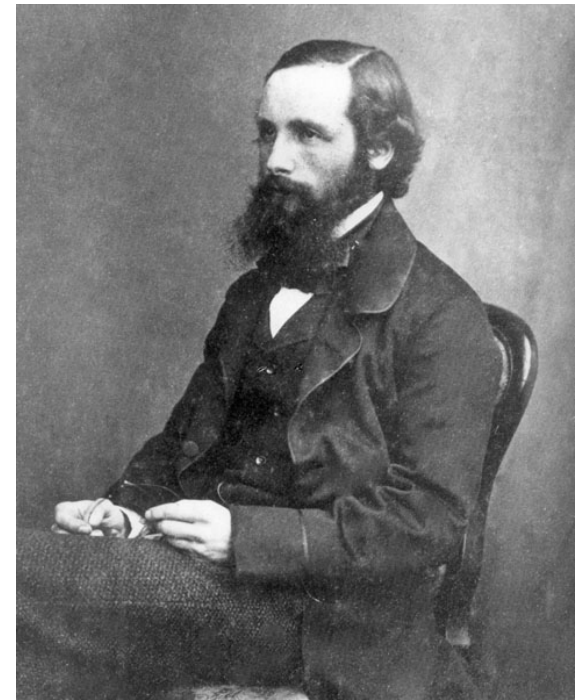
As $\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)$ *equality of mixed partial derivatives*

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \longrightarrow \quad \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \longrightarrow \quad \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = -\left(\frac{\partial S}{\partial P}\right)_T$$

Another of many Maxwell relations

$$\longleftarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$



James Clerk Maxwell

UTILITY OF THE MAXWELL RELATION

$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ From this Maxwell relation we can see how S changes with P given an equation of state

Integrate at constant T : $\Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$ *Note that T is held constant during integration over P*

Get P dependence of S from P - V - T data.

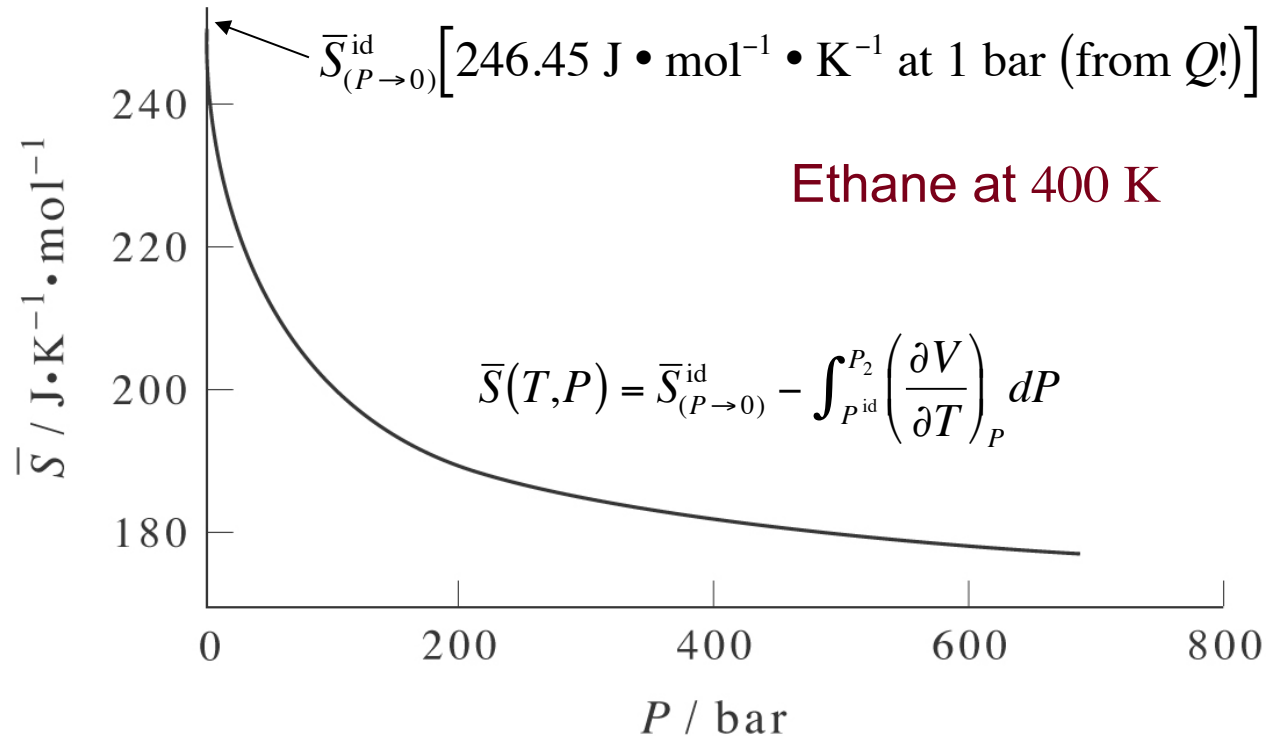
Example: Ideal gas

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \Delta S = -nR \int_{P_1}^{P_2} \frac{dP}{P} = -nR \ln \frac{P_2}{P_1} \quad (\text{isothermal})$$

ENTROPY OF ETHANE AGAIN

If P_1 is chosen to be so small that a gas behaves ideally ($P \rightarrow 0$),

$$\Delta S = S(T, P_2) - S_{(P \rightarrow 0)}^{\text{id}} = - \int_{P^{\text{id}}}^{P_2} \left(\frac{\partial V}{\partial T} \right)_P dP \quad (\text{constant } T)$$



*For real gases, i.e., those having no readily available, analytical equation of state, this requires data for how **volume** varies with **temperature** over a full range of **pressures***

ENTHALPY DEPENDENCE ON P

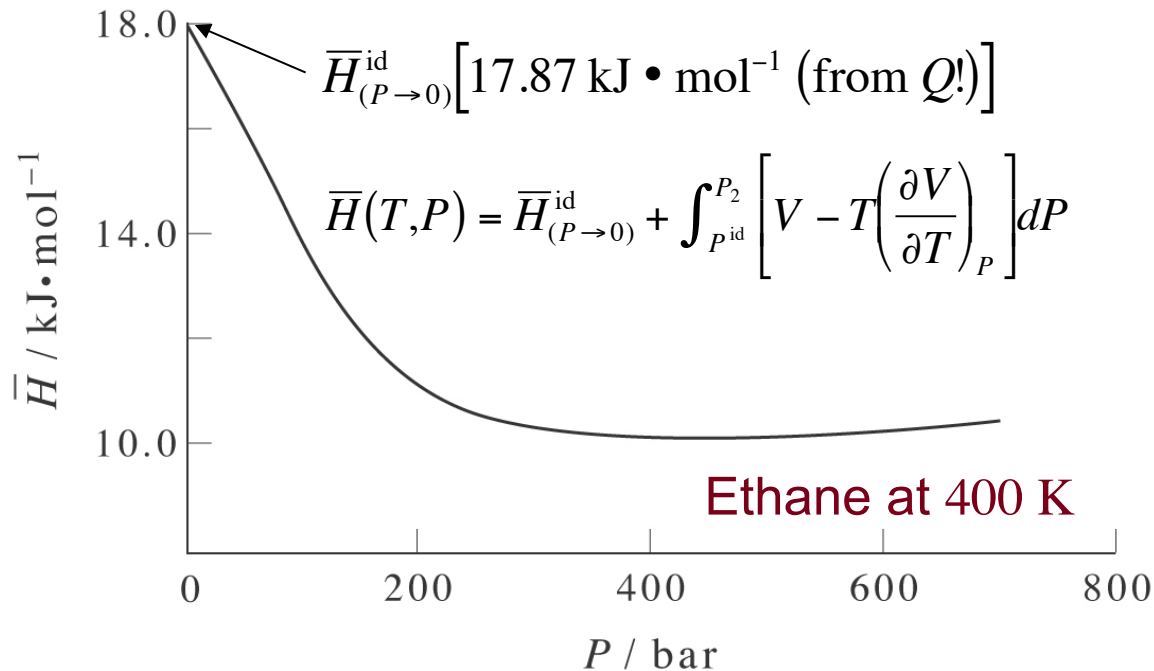
Differentiating $G = H - TS$ wrt P : $\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$ (isothermal)

using $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$

Maxwell relation

previously derived
➔

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$



*For real gases, i.e., those having no readily available, analytical equation of state, this again requires data for how **volume** varies with **temperature** over a full range of **pressures***

PRESSURE DEPENDENCE OF G

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \xrightarrow{\text{integrate}} \quad \Delta G = \int_{P_1}^{P_2} V dP \quad (\text{constant } T)$$

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

$$\Delta G = nRT \int_{P_1}^{P_2} \frac{1}{P} dP = nRT \ln \frac{P_2}{P_1} \quad (\text{constant } T)$$

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

$$\Delta S = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{P_2}{P_1}$$

As expected, $\Delta G = \Delta H - T\Delta S$ is equal simply to $-T\Delta S$ since $\Delta H = 0$ at constant T *for an ideal gas*