Lecture 20: Maxwell Relations

Context of Maxwell Relations

- We just derived a bunch of state functions
- To solve harder problems, we need differentials and calculus
- Some differentials are hard to evaluate: $\left(\frac{\partial S}{\partial V}\right)_T$ $\left(\frac{\partial P}{\partial S}\right)_V$
- Maxwell relations allow us to transform these hard partials to something easy

Maxwell relations will 100% show up on the next exam

Recall Clairaut's Theorem

Suppose we have a function $f(x, y)$ and consider their second derivatives:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x$$

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y$$

Clairaut's Theorem

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

Maxwell Relation: Internal Energy

First Law:

$$dU = dq + dw$$

Plug in expressions for heat ($dq = T\,dS$) and work ($dw = -P\,dV$):

$$dU = T\,dS - P\,dV$$

Write the total differential of $U(S, V)$:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Recognize $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $-P = \left(\frac{\partial U}{\partial V}\right)_S$, take mixed second derivatives:

$$\frac{\partial^2 U}{\partial V\,\partial S} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial V}(T) = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S = \frac{\partial}{\partial S}(-P) = -\left(\frac{\partial P}{\partial S}\right)_V$$

Maxwell Relations

Maxwell Relations

State Function	Differential	Maxwell Relation
$U(S,V)$	$dU = T\,dS - P\,dV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$H(S,P) = U + PV$	$dH = T\,dS + V\,dP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$A(T,V) = U - TS$	$dA = -S\,dT - P\,dV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$G(T,P) = U - TS + PV$	$dG = -S\,dT + V\,dP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Entropy of Reversible Isothermal Gas Expansion

$$\Delta S = \int_{S_i}^{S_f} dS$$

$$= \int_{V_i}^{V_f} \left(\frac{\partial S}{\partial V}\right)_T dV$$

Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$:

$$= \int_{V_i}^{V_f} \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V}$$

$$\Delta S = \int_{V_i}^{V_f} \left(\frac{nR}{V}\right) dV$$

$$= nR\left(\ln(V_f) - \ln(V_i)\right) = nR \ln \frac{V_f}{V_i}$$