Maxwell Relations

- Take a function $f(x, y)$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Now we have

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

- Let's see what this means

$$dU = đQ - dW_{out} = T\,dS - p\,dV$$

So

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad -p = \left(\frac{\partial U}{\partial V}\right)_S$$

Now use the result ★ relating cross derivatives

$$\bigstar \quad \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V \quad \bigstar$$

Leading to a neat relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

The importance of this "Maxwell Relation" is that it relates various derivatives to experimental observables. For instance $(\partial T/\partial V)_S$ is the change in temperature per change in volume, when no heat leaves the system. It is readily measured. $-(\partial p/\partial S)_V$ is hard to interpret and measure.

- Each thermodynamic function U, H, F, G leads to a maxwell relation

For example

$$dF = -S\,dT - p\,dV$$

Comparing the cross derivatives

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

← We will use this below!

A table of the Maxwell Relations is given on the slide below.

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

We derived this first from the

Energy, $E(S, V)$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Enthalpy, $H(S, p)$

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

We derived this next from the

Free Energy, $F(T, V)$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Gibbs Free Energy $G(T, P)$

Example: Using Maxwell Relations

- Suppose you want to know the entropy of a substance as a function of temperature and volume. You can measure the specific heats $C_V(T,V)$ and the pressure $p(T,V)$

First keep the volume fixed

$$T\,dS_V = \text{đ}Q_V = C_V\,dT$$

- So at fixed volume we can integrate to find S:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \Delta S = \int_{T_i}^{T_f} C_V(T,V)\,\frac{dT}{T}$$

- Now consider temperature and volume changes

$$dS = \left(\frac{\partial S}{\partial T}\right)_T dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Use maxwell Relation!

$$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

So at fixed temperature

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV$$

measured Equation of State

- So by using Maxwell Relations we are able to relate all thermodynamic derivatives, e.g. $(\partial S/\partial V)_T$ in this example, to measurable quantities such as the pressure. This is the general result.

All physical results are related to specific heats and the pressure through maxwell relations.

For an ideal gas Equation of State we have $p = NkT/V$ and

$$\Delta S = \int_{V_1}^{V_2} Nk \frac{dV}{V} = Nk \ln\left(\frac{V_2}{V_1}\right)$$