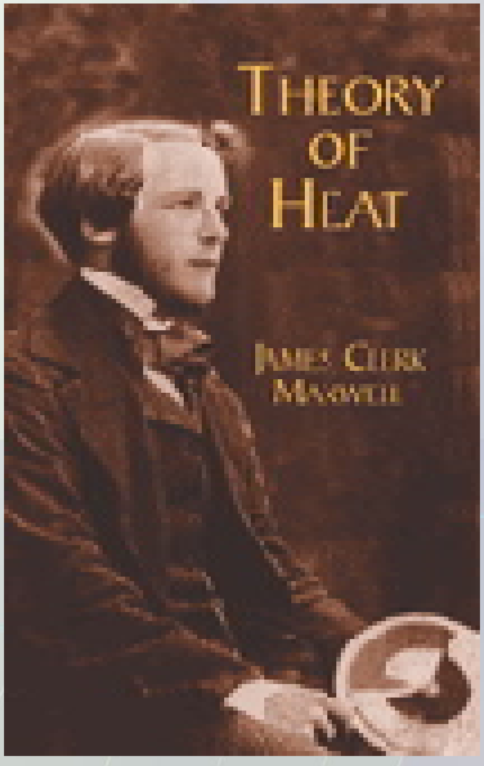
Maxwell Relations

James Clerk Maxwell (1831-1879)

- **Born in Edinburgh, Scotland**
- **Physicist well-known for his work in electromagnetism and field theory**
- **Also known for his work in thermodynamics and kinetic theory of gases**

Theory of Heat



Zoom

- **Written by Maxwell and published first in 1870**
- **Describes his views of the limitations of the Second Law of Thermodynamics**
- **Maxwell Relations were first introduced in this book**

Why Use Maxwell Relations?

- **Certain variables in thermodynamics are hard to measure experimentally such as entropy**
- **Maxwell relations provide a way to exchange variables**

What are some examples of Maxwell Relations?

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

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

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

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

Deriving Maxwell Relations

First, start with a known equation of state such as that of internal energy

$$dU = TdS - PdV$$

Next, take the total derivative of with respect to the natural variables. For example, the natural of internal energy are entropy and volume.

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

Deriving Maxwell Relations Continued

Now that we have the total derivative with respect to its natural variables, we can refer back to the original equation of state and define, in this example, T and P.

$$dU = TdS - PdV$$

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

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

Deriving Maxwell Relations Continued

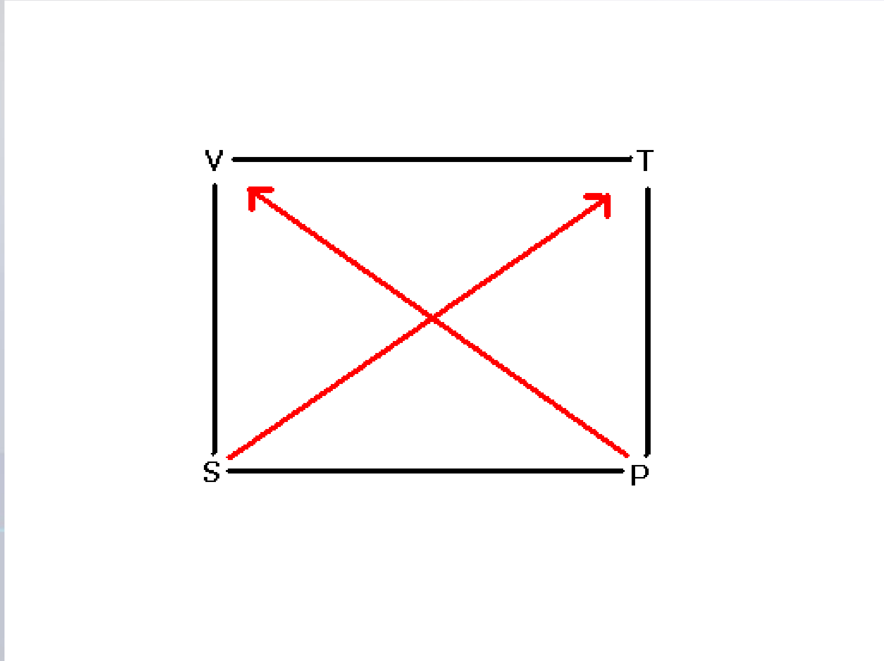
We must now take into account a rule in partial derivatives

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

When taking the partial derivative again, we can set both sides equal and thus, we have derived a Maxwell Relation

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

Mnemonic Device for Obtaining Maxwell Relations



The partial derivative of two neighboring properties (e.g. V and T) correspond to the partial derivative of the two properties on the opposite side of the square (e.g. S and P). The arrows denote the negative sign; if both are pointed the same way, then the sign is negative.

Using Maxwell Relations

Maxwell Relations can be derived from basic equations of state, and by using Maxwell Relations, working equations can be derived and used when dealing with experimental data.

basic equations	Maxwell relations	working equations
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$dH = C_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$
$dA = -PdV - SdT$	$\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$	$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$
$dG = VdP - SdT$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$	$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$