Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.
Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

Chapter L. Maxwell Relations. We can derive many useful relations from the following table of state functions.

State Function Name	Function Symbol	Differential	Variables
specific energy	u	$du = Tds - pd\alpha$	s, α
specific enthalpy	$h = u + p\alpha$	$dh = Tds + \alpha dp$	s, p
specific Helmholtz free energy	$f = u - Ts$	$df = -sdT - pd\alpha$	T, α
specific Gibbs free energy	$g = u - Ts + p\alpha$	$dg = -sdT + \alpha dp$	T, p

We start with specific energy.

$$du = Tds - pd\alpha$$

From this equation we immediately find

$$\left(\frac{\partial u}{\partial s}\right)_\alpha = T \quad \text{and} \quad \left(\frac{\partial u}{\partial \alpha}\right)_s = -p\,.$$

We now take the partial derivate with respect to the other variable in each case.

$$\left[\frac{\partial}{\partial \alpha}\left(\frac{\partial u}{\partial s}\right)_\alpha\right]_s = \left(\frac{\partial T}{\partial \alpha}\right)_s \qquad \left[\frac{\partial}{\partial s}\left(\frac{\partial u}{\partial \alpha}\right)_s\right]_\alpha = -\left(\frac{\partial p}{\partial s}\right)_\alpha$$

Since partial derivatives can be taken in any order

$$\left[\frac{\partial}{\partial \alpha}\left(\frac{\partial u}{\partial s}\right)_\alpha\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial u}{\partial \alpha}\right)_s\right]_\alpha$$

and therefore,

$$\left(\frac{\partial T}{\partial \alpha}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_\alpha\,.$$

This equation is one of the Maxwell relations.

Each differential in our above table leads to a Maxwell relation.

For the shortcut, look at $du = Tds - pd\alpha$ and $\left(\frac{\partial T}{\partial \alpha}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_\alpha$.

Do you see the pattern?

You take a partial of the variable in front of a differential with respect to the other variable.

From this pattern, three other Maxwell relations immediately follow.

State Function Name	**Function Symbol**	**Differential**	**Maxwell Relation**
specific energy	u	$du = Tds - pd\alpha$	$\left(\frac{\partial T}{\partial \alpha}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_\alpha$
specific enthalpy	$h = u + p\alpha$	$dh = Tds + \alpha dp$	$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial \alpha}{\partial s}\right)_p$
specific Helmholtz free energy	$f = u - Ts$	$df = -sdT - pd\alpha$	$\left(\frac{\partial s}{\partial \alpha}\right)_T = \left(\frac{\partial p}{\partial T}\right)_\alpha$
specific Gibbs free energy	$g = u - Ts + p\alpha$	$dg = -sdT + \alpha dp$	$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial \alpha}{\partial T}\right)_p$

The Maxwell relation we need is the one found from the specific Gibbs free energy.

$$(22)\quad \boxed{\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial \alpha}{\partial T}\right)_p}$$

Be careful to never refer to the Maxwell relations as Maxwell equations because the Maxwell equations refer to a different set of equations found in electromagnetism.