

The Second Law of Thermodynamics (II)



The Fundamental Equation

We have shown that:

$$dU = dq + dw$$

plus

$$dw_{\text{rev}} = -pdV \quad \text{and} \quad dq_{\text{rev}} = TdS$$

We may write:

$$dU = TdS - pdV$$

(for constant composition)

Properties of the internal energy

In chapter 3 we discussed total integrals.

$$\text{If } z = f(x, y) \text{ then: } dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

We can express U as a function of S and V , i.e. $U = f(S, V)$

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

$$\text{c.f. } dU = TdS - pdV$$

We have discovered that $\left(\frac{\partial U}{\partial S} \right)_V = T$ $\left(\frac{\partial U}{\partial V} \right)_S = -p$

Properties of the internal energy

Recall the test for exactness:

$$Fdx + Gdy = dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

If the differential is exact then:

$$\left(\frac{\partial F}{\partial y} \right)_x = \left(\frac{\partial G}{\partial x} \right)_y$$

All state functions have exact differentials

Properties of the internal energy

Therefore:

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

Where:

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

Because this is exact we may write:

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

We have obtained our first **Maxwell relation!**

Relationships between state functions: Be prepared!

U and S are defined by the first and second laws of thermodynamics, but H , A and G are defined using U and S .

The four relationships are:

$$H = U + pV$$

$$G = H - TS$$

$$A = U - TS$$

$$G = A + pV$$

We can write the fundamental thermodynamic equation in several forms with these equations

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Gibbs Equations

Properties of the internal energy

Also consider $dH = TdS + Vdp$, and writing $H = f(S, p)$

$$MdS + Ndp = dH = \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dp$$

Where: $M = \left(\frac{\partial H}{\partial S} \right)_p = T$ $N = \left(\frac{\partial H}{\partial p} \right)_S = V$

Because this is exact we may write:

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

We have obtained our second **Maxwell relation!**

The Maxwell Relations

$$\begin{aligned}
 \text{(a)} \quad & DU = q + w \\
 \text{(b)} \quad & DS = q_{\text{rev}}/T \\
 \text{(c)} \quad & H = U + pV \\
 \text{(d)} \quad & A = U - TS \\
 \text{(e)} \quad & G = H - TS
 \end{aligned}$$

$$\left(\frac{\partial T}{\partial V} \right)_S \stackrel{1.}{=} - \left(\frac{\partial p}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial p} \right)_S \stackrel{2.}{=} \left(\frac{\partial V}{\partial S} \right)_p$$

$$\left(\frac{\partial S}{\partial V} \right)_T \stackrel{3.}{=} \left(\frac{\partial p}{\partial T} \right)_V$$

$$\left(\frac{\partial S}{\partial p} \right)_T \stackrel{4.}{=} - \left(\frac{\partial V}{\partial T} \right)_p$$



$$\begin{aligned}
 1. \quad & dU = TdS - pdV \quad \text{(a)+(b)} \\
 2. \quad & dH = TdS + Vdp \quad \text{(a)+(b)+(c)} \\
 3. \quad & dA = -SdT - pdV \quad \text{(a)+(b)+(d)} \\
 4. \quad & dG = -SdT + Vdp \quad \text{(a)+(b)+(e)}
 \end{aligned}$$

$$Mdx + Ndy = dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$



The Maxwell Relations: The Magic Square



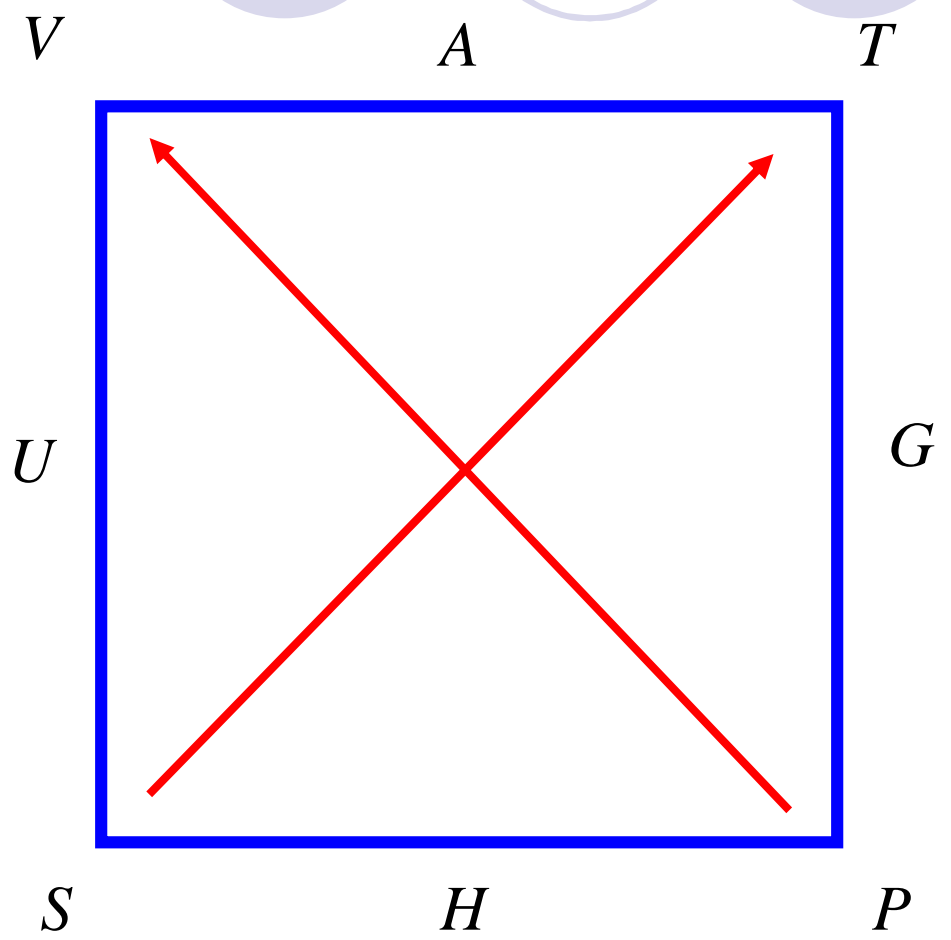
“Vat Ug Ship”

Each side has an *energy* (U, H, A, G)

Partial Derivatives from the sides

Thermodynamic Identities from the corners

Maxwell Relations from walking around the square





Example:

Calculate the change in enthalpy if the pressure on one mole of liquid water at 298 K is increased from 1 atm to 11 atm, assuming that V and α are independent of pressure. At room temperature α for water is approximately $3.0 \times 10^{-4} \text{ K}^{-1}$.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (\text{The expansion coefficient})$$

The volume of 1 mole of water is about 0.018 L.

Properties of the Gibbs energy

$$G = H - TS$$



$$dG = dH - TdS - SdT$$



$$dG = dU + pdV + Vdp - TdS - SdT$$



$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$



$$dG = Vdp - SdT \longrightarrow G = f(p, T)$$

$$H = U + pV$$



$$dH = dU + pdV + Vdp$$

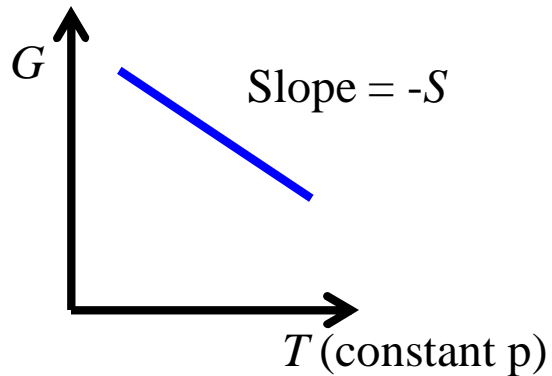
$$dU = TdS - pdV$$

Properties of the Gibbs energy

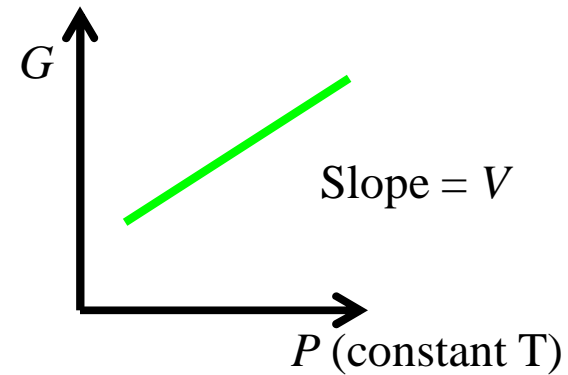
$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$



S is positive ($-S$ is negative)
so G is decreasing with
increasing T



V is positive so G is
increasing with
increasing p

Dependence of G on T

Using the same procedure as for the dependence of G on p we get:

$$\left(\frac{\partial G}{\partial T} \right)_p = -S$$

$$\int dG = -\int SdT$$

To go any further we need S as a function of T ?

Instead we start with: $G = H - TS$

$$-S = (G - H)/T$$

Dependence of G on T

$$-S = \frac{G - H}{T}$$



$$\frac{G}{T} = \frac{H}{T} - S$$



$$x = \frac{H}{T} - S$$



$$\left(\frac{\partial x}{\partial T} \right)_p = -\frac{H}{T^2}$$

Let $G/T = x$

$$\left(\frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2}$$

This is the **Gibbs-Helmholtz Equation**

$$\left(\frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2}$$