Helmholtz and Gibbs Free Energy

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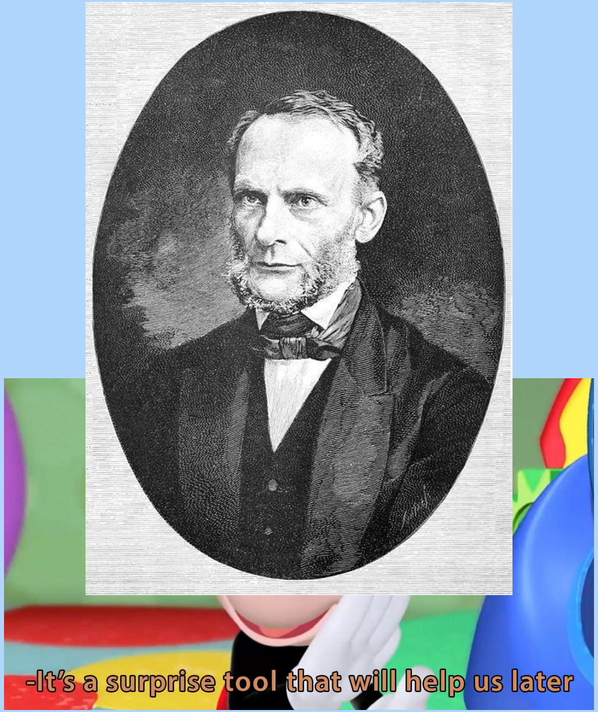
But first, review

- Clausius' definition of entropy:

  $\Delta S = Q/T$

- Heat is different from work
- First Law of Thermodynamics:

  $\Delta U = Q - P\Delta V$



Can rewrite in terms of entropy → $\Delta U = T\Delta S - P\Delta V$

Remember this guy? → Enthalpy

- What is enthalpy again? Defined as:

  H = U + PV

- Ok, but what does that mean?
  - Enthalpy is the total energy required to create a system out of nothing and make space for it in the environment
  - OR if you're annihilating a system, enthalpy is the energy you get out, plus the work done by the atmosphere collapsing back in

Using Enthalpy

More useful to do a process and see how things change! → find ΔH

$$H = U + PV \quad \rightarrow \quad \Delta H = \Delta U + V\Delta P + P\Delta V$$

But for a constant pressure process this is: $\Delta H = \Delta U + P\Delta V$

Our new ΔU is: $\Delta U = T\Delta S - P\Delta V$

Plugging this into ΔH → $\Delta H = T\Delta S - P\Delta V + P\Delta V$

Which gives, $\Delta H = T\Delta S$ → this is equal to the heat

If you can measure ΔH, you can learn about the change in entropy or about the heat created by your process

Something New! → Helmholtz free energy

- This is defined as:

  F = U - TS

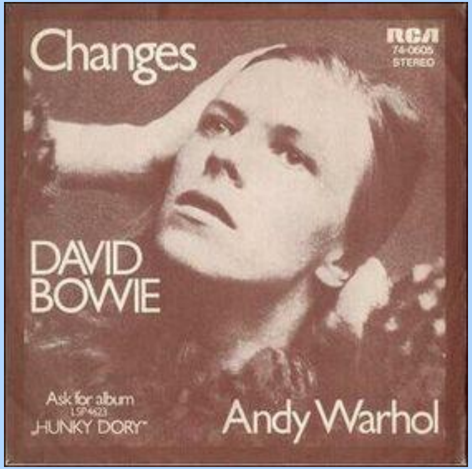
- What does this mean?
  - F is the energy needed to create a system MINUS the energy that the environment gives through temperature → like a reservoir
  - OR, if you're annihilating your system, F is the work you get out of destruction plus you have to dump the entropy of that system into the environment

Zero Entropy??

- In the equation **F = U - TS**, Schroeder says that this **S** is the final entropy of the created system
- This comes from heat → **ΔS**
- If $S_{initial}$ = 0 , **ΔS = S**
- But why would $S_{initial}$ = 0 ? → Remember Julia's grapes!
- There is only way to have zero energy → zero, because the wizard hasn't created it yet

Chchchanges in Helmholtz Free Energy

$F = U - TS$ → $\Delta F = \Delta U - T\Delta S - S\Delta T$



However, we're probably working at a constant T environment (like a lab):
$\Delta F = \Delta U - T\Delta S$

Now, plug in our **ΔU (= $T\Delta S - P\Delta V$):**

$\Delta F = T\Delta S - P\Delta V - T\Delta S$

This gives: **$\Delta F = - P\Delta V$** → This is the work!! (W)

If we can measure **ΔF**, we can learn about the work

Warning, I was confused

$F = U - TS$ → $\Delta F = \Delta U - T\Delta S - S\Delta T$

However, we're probably working at a constant T environment (like a lab):
$\Delta F = \Delta U - T\Delta S$

If the process creates new entropy IN ADDITION to the heat included in ΔU,

Now, plug in our ΔU (**$= T\Delta S - P\Delta V$**):

$\Delta F = T\Delta S - P\Delta V - T\Delta S$

→ This **$T\Delta S$** doesn't fully cancel and subtracts some energy of $-P\Delta V$

Giving the inequality: $\Delta F \leq W = -P\Delta V$

This gives: **$\Delta F = -P\Delta V$** → However this is only true if no NEW entropy is created during the process

Ok, so we've been lying to you

- We've been using this definition of the first law: $\Delta U = Q - P\Delta V$
- However, this is only true for purely compression work
- Remember that the first law of thermodynamics also includes other forms of work: $\Delta U = Q - P\Delta V + W_{other} = T\Delta S - P\Delta V + W_{other}$

Ex. Electrical work

Another one! Gibbs Free Energy

- The Gibbs Free Energy is defined as:

  $$\mathbf{G = U - TS + PV}$$

- Combo of F and H → includes the corrections from F and H

Let's do a process → Changes in G

$$G = U - TS + PV \quad \rightarrow \quad \Delta G = \Delta U - T\Delta S - S\Delta T + P\Delta V + V\Delta P$$

At constant T and P, can get rid of some terms:

$$\Delta G = \Delta U - T\Delta S + P\Delta V$$

Plug in the REAL first law: $\Delta U = Q - P\Delta V + W_{other}$

$$\rightarrow \Delta G = T\Delta S - P\Delta V + W_{other} - T\Delta S + P\Delta V$$

Notice that things cancel and....

$$\Delta G = W_{other}$$

If you can measure ΔG you can learn about the non-compression work in your process

Tricky Inequalities…

$G = U - TS + PV \quad \rightarrow \Delta G = \Delta U - T\Delta S - S\Delta T + P\Delta V + V\Delta P$

At constant T and P, can get rid of some terms:

$\Delta G = \Delta U - T\Delta S + P\Delta V$

Plug in the REAL first law….

$\rightarrow \Delta G = T\Delta S - P\Delta V + W_{other} - T\Delta S + P\Delta V$

Notice that things cancel:

$\Delta G = W_{other}$

Again, if your process creates entropy this is not completely true….

$\rightarrow \Delta G \leq W_{other}$

What did we learn?

Happy Halloween!

Helmholtz Free Energy: $\mathbf{F = U - TS}$ OR

$\mathbf{\Delta F = \Delta U - T\Delta S}$ & $\mathbf{\Delta F \leq W = -P\Delta V}$ (at constant T)

If you can measure **ΔF**, you can learn about work

Gibbs Free Energy: $\mathbf{G = U - TS + PV}$ OR

$\mathbf{\Delta G = \Delta U - T\Delta S + P\Delta V}$ & $\mathbf{\Delta G \leq W_{other}}$ (at constant T and P)

If you can measure **ΔG**, you can learn about the non-compression work in your process