

Chapter 5 + Section 1.6 (end) → Free Energies

Enthalpy → energy plus the work to make room for the system under constant pressure from the environment

$$H \equiv U + PV \quad \leftarrow \text{total energy to create the system and put it into an environment}$$

But, the system can get its thermal energy from the surroundings, so all we really need to do is provide to the system any additional work

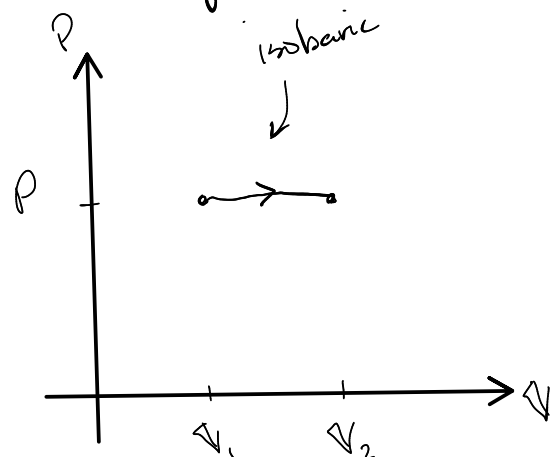
Gibbs Free Energy

$$\begin{array}{l} G \equiv H - TS \\ G \equiv U + PV - TS \end{array} \quad \leftarrow \begin{array}{l} \text{energy to make the system and make} \\ \text{room for the system minus the heat} \\ \text{we get to extract from surroundings.} \end{array}$$

Helmholtz Free Energy → total energy to create the system minus the heat we can extract from the surroundings

$$F = U - TS$$

Enthalpy



#1.34

$$W = -P(V_2 - V_1)$$

$$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} P \Delta V = \frac{f}{2} P(V_2 - V_1)$$

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

$$Q = \frac{f}{2} P(V_2 - V_1) + P(V_2 - V_1)$$

$$Q = \left(\frac{f}{2} + 1\right) P \Delta V$$

$$H \equiv U + PV$$

$$\Delta H = \Delta U + P \Delta V = Q$$

$$N k_B \Delta T = P \Delta V$$

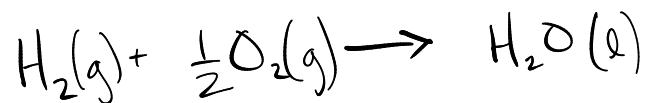
— or —

$$= \Delta P \cdot V$$

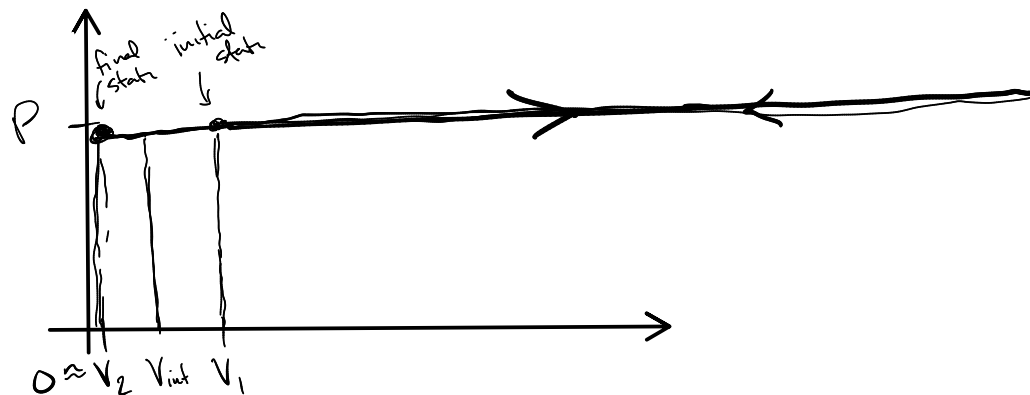
— but not —

$$= \underline{\underline{\Delta P \cdot \Delta V}}$$

Another example, what if we cause something to happen inside the tube & we measure the heat given off at constant pressure.



$$\Delta H = -286 \text{ kJ/mol}$$



1.4a) $\frac{1 \text{ mol H}_2(\text{g})}{0.5 \text{ mol O}_2}$
 $1.5 \text{ mol} \rightarrow n_m$

$$PV = n \cdot R \cdot T \leftarrow 298 \text{ K}$$

\uparrow \uparrow \nwarrow
 10^5 Pa 1.5 mol 8.31

$1 \text{ mL} = 1 \text{ cm}^3$
 $1000 \text{ L} = 1 \text{ m}^3$

$$V = \frac{nRT}{P} = \frac{1.5 \cdot 8.31 \cdot 298}{10^5} = 0.037 \text{ m}^3 = 37 \text{ L}$$

n_m after the reaction?

$$V_{\text{int}} = \frac{1 \cdot 8.31 \cdot 298}{10^5} = 0.0248 \text{ m}^3$$

↓ this condenses
to give ~ 0 L
of liquid, giving
up heat along the way

$$V = \frac{nRT}{P} \xrightarrow{\text{constant}} V \propto n \rightarrow \frac{V_{\text{int}}}{V_1} = \frac{n_2}{n_1} = \frac{1}{1.5}$$

$V_{\text{int}} = 0.0248 \text{ m}^3$

So what total work has been done?

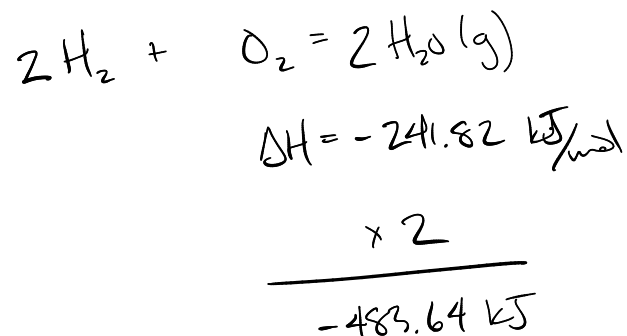
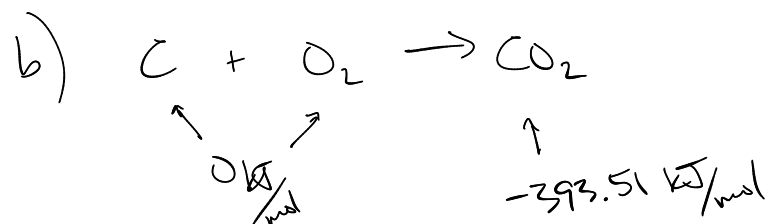
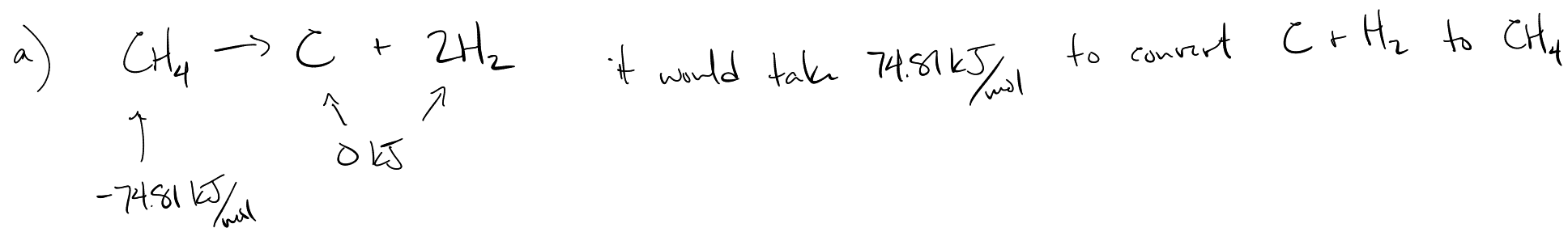
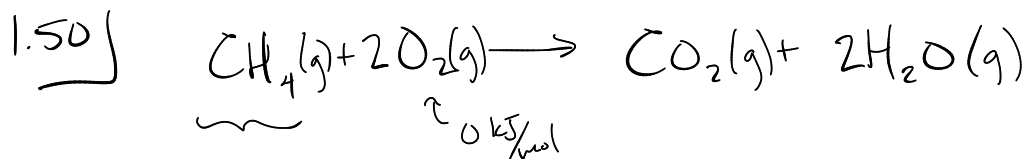
$$W = - \int_{0.037 \text{ m}^3}^{0 \text{ m}^3} P dV = -10^5 \text{ Pa} (0 - 0.037 \text{ m}^3)$$

$$= 3700 \text{ J} = 3.7 \text{ kJ}$$

$$\rightarrow \Delta H = -286 \text{ kJ} = \Delta U - W$$

$$-286 \text{ kJ} = \Delta U - 3.7 \text{ kJ}$$

$$\boxed{\Delta U = -282.3 \text{ kJ}}$$



c) $\Delta H_{\text{reaction}} = 74.81 - 393.51 \text{ kJ/mol} - 483.64 \text{ kJ}$

$\Delta H_{\text{reaction}} = -802.34 \text{ kJ} \rightarrow$ heat given to the surroundings

d) 802.34 kJ

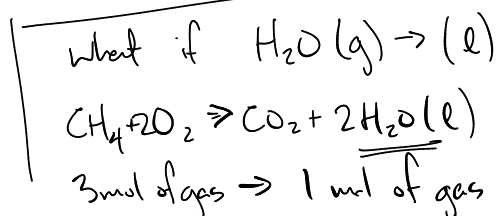
e) $\Delta H = U + p\Delta V$

\uparrow \nwarrow find this

$\Delta H = U$ when final mixture is a gas

$pV = nRT \rightarrow p\Delta V = \Delta n R \cdot T$

$= 0 \text{ mol} \cdot 8.31 \cdot 298 \text{ K}$



$p\Delta V = -2 \text{ mol} \cdot 8.31 \cdot 298 \text{ K}$

$= -4.9 \text{ kJ}$

$$\Delta H_{\text{reaction}} = ?$$

f) ?

also do 1.55

Gibbs Free Energy

$$G = U + PV - TS$$

$$G = H - TS$$

$$dG = dU - TdS + pdV$$

$$dG = \pm Q + \pm W - TdS + pdV$$

- for a reversible process
(no new entropy is created)

- $\pm Q_{\text{rev}} = TdS$

- $\pm W = -pdV + \pm W_{\text{other}}$
↳ electrical

$$dG = \cancel{TdS} - \cancel{pdV} + \pm W_{\text{other}} - \cancel{TdS} + \cancel{pdV}$$

$$dG = \pm W_{\text{other}}$$

not reversible

$$dG \leq \pm W_{\text{other}} \text{ at constant } T, p$$

Thermodynamic Potentials

$$dF = dU - TdS$$

$$dF = \pm Q + \pm W - TdS$$

for a reversible process
(no new entropy is created)

$$\pm Q_{\text{rev}} = TdS$$

$$dF = TdS + \pm W - TdS$$

$$dF = \pm W$$

↳ amount of work done
on the system by
you or by surroundings

otherwise, (not a reversible process)

$$dF \leq \pm W$$

How is ΔG_f measured?

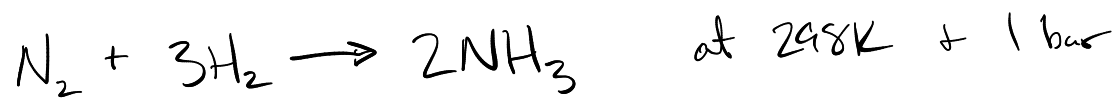
First measure $\Delta H \rightarrow$ heat absorbed or released for a reaction at constant pressure & no other work has been done

Then calculate ΔS from initial & final states using heat capacity data

$$\Delta S = \int_0^{T_f} \frac{C_p}{T} dT$$

$$\Delta G = \Delta H - T\Delta S$$

So lets do an example: (5.2)



$$\downarrow$$
$$\Delta H = 0 \text{ kJ}$$

$$S = 191.61 \text{ J/K mol}$$

$$\downarrow$$
$$\Delta H = 0 \text{ kJ}$$

$$S = 130.68 \text{ J/K mol}$$

$$\rightarrow \Delta H = -46.11 \text{ kJ}$$

$$S = 192.45 \text{ J/K mol}$$

$$\Delta H = 2 \text{ mol} \cdot (-46.11 \text{ kJ/mol}) = -92.22 \text{ kJ}$$

$$\Delta S = S_f - S_i = 2 \cdot 192.45 \text{ J/K mol} - 3(130.68) - 191.61$$
$$= -198.75 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{watch out for kJ!}$$

$$= -92.22 \text{ kJ} - 298(-0.19875 \text{ kJ/K})$$

$$\underline{\underline{\Delta G = -32.99 \text{ kJ}}}$$

compare!

from the book

$$\Delta G = -16.45 \text{ kJ/mol}$$

for this reaction

$$\Delta G = 2 \text{ mol.} (-16.45 \text{ kJ/mol}) = \underline{\underline{-32.9 \text{ kJ}}}$$

Electrolysis, Fuel Cells, Batteries (another example)



↑ electrical work must be done

$$\Delta H = \underline{286 \text{ kJ}} \rightarrow \text{heat out when we run in reverse}$$

To run this reaction forward we need to put in 286 kJ of energy

→ some of this will push aside the atmosphere

$$p\Delta V = \Delta n RT = \underset{\substack{\uparrow \text{gas form}}}{1.5 \text{ mol.}} (8.31 \text{ J/Kmol}) (298 \text{ K}) = 3714 \text{ J}$$

$$= 3.7 \text{ kJ}$$

→ so, 282 kJ will remain in the system in the form of potential energy in the chemical bonds $\sim 4 \text{ kJ}$

Do we need to do all of this work, or can we get some help from surroundings?

What is the change in entropy?

$$S_{H_2O} = 70 \text{ J/K}$$

$$S_{H_2} = 131 \text{ J/K}$$

$$S_{O_2} = 205 \text{ J/K}$$

← from the back of the book

products

$$S_{\text{prod}} = 131 \text{ J/K} + \frac{1}{2} (205 \text{ J/K}) = 233.5 \text{ J/K}$$

$$\Delta S = S_p - S_r = 233.5 \text{ J/K} - 70 \text{ J/K} = 163.5 \text{ J/K}$$

entropy increased

$$dQ \leq T dS$$

$$Q = T \Delta S = 298 \text{ K} \cdot 163.5 \text{ J/K}$$

$$Q = \underline{48.7 \text{ kJ}}$$

So of the 286 kJ that go in, 48.7 kJ can come from heat from surroundings

$$286 \text{ kJ} - 48.7 \text{ kJ} = \underline{\underline{237.3 \text{ kJ}}} \rightarrow \text{come from } \underline{\underline{\text{electrical work}}}$$

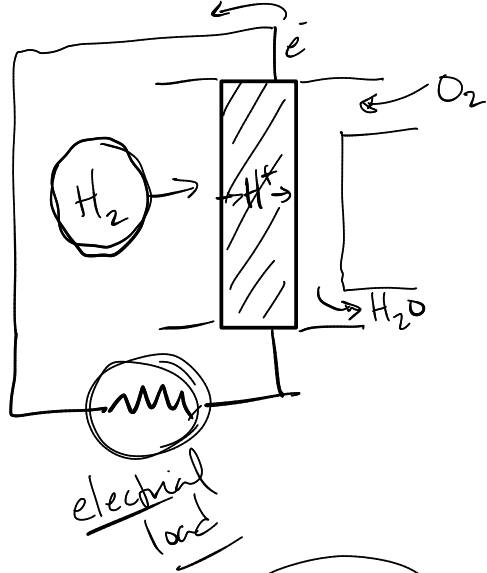
$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G_{H_2O} = -228.57 \text{ kJ} \quad \Delta G_{H_2} = 0 \text{ kJ} \quad \Delta G = 0 \text{ kJ}$$

HW 5.1 + 5.5

$$\Delta G = \Delta G_{\text{prod}} - \Delta G_{\text{react}} = 0 - 228.57 \\ = \underline{\underline{228.57 \text{ kJ}}}$$

In reverse, we can extract 237 kJ of electrical work



gray H₂ blue H₂ green H₂
↳ sdar

- 49 kJ of waste heat goes to the environment
- $\Delta U = 282 \text{ kJ}$ → comes from chemical reactions
- $P\Delta V = 4 \text{ kJ}$ → comes from the collapse of gas to liquid

$$\text{efficiency} = \frac{\text{get}}{\text{pay for}}$$

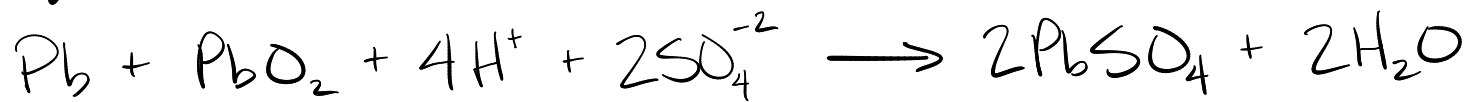
$$\text{fuel cell} \\ \frac{237 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$

compare to efficiencies
we would have
gotten in chapter 4

max theoretical
engine efficiency → 66%

max theoretical car
engine efficiency → 50%
↳ practically → 20-30%

Battery



start w/ $\Delta H = -316 \text{ kJ/mol}$

↑ energy out from reaction at constant pressure

what about $\Delta G = -394 \text{ kJ/mol}$

↑ electrical energy out

ΔG is more than the ΔH . How? Heat is coming in to the system from surroundings!

How much?

$$394 \text{ kJ/mol} - 316 \text{ kJ/mol} = 78 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S$$

$$-394 - (-316) = -298 \Delta S$$

$$\Delta S > 0$$

$$78 \text{ kJ/mol} = T\Delta S$$

increase in entropy

means the heat is being absorbed from surroundings

$$\Delta S = \frac{78 \text{ kJ}}{298 \text{ K}} = 261.7 \frac{\text{J}}{\text{K}}$$

watch out for units

Energy / charge \rightarrow potential (voltage)

$$\text{voltage} = \frac{\Delta W_E}{q} = \frac{394 \text{ kJ}}{2e \cdot N_A \cdot 1.6 \cdot 10^{-19} \frac{\text{C}}{e}} = 2.84 \text{ V} \quad \leftarrow \begin{array}{l} \text{per "cell" in a car battery} \\ 6 \text{ "cells"} \rightarrow \underline{12\text{V}} \end{array}$$

\uparrow
need to know how many electrons
are moved during the reaction
 $2e^-$

Thermodynamic identity

$$dU = T dS - P dV + \mu dN$$

but what about H, F, G ? How do these change when conditions change?

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

$$\hookrightarrow T dS - p dV + \mu dN$$

$$dH = T dS + V dp + \mu dN$$

\rightarrow So the variables have changed from dU
we tend to use enthalpy

when $dp = 0$

$dN = 0$

$dH = T dS \leftarrow$ heat at constant pressure

What about F ?

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = -S \underline{dT} - p \underline{dV} + \mu \underline{dN}$$

What about G ? \rightarrow you derive this

We can use these identities to derive many useful statements.

Ex: $dF = -SdT - pdV + \mu dN$

hold $V + N$ constant $\rightarrow dV + dN$ are 0

$$dF = -SdT$$

$$S = -\left(\frac{dF}{dT}\right)_{V,N}$$

\leftarrow what does this mean?
entropy is the rate of change of F w.r.t. T

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

What about Gibbs?

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad \underline{\underline{V = \left(\frac{\partial G}{\partial P}\right)_{T,N}}}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

How does the Gibbs Free Energy change w/ pressure

Use reference data \rightarrow 1 mol of C (graphite) $\Rightarrow 5.3 \cdot 10^{-6} \text{ m}^3$

$\Delta G_{\text{C}} = 0 \text{ kJ} \leftarrow$ most stable form

Gibbs will increase by $5.3 \cdot 10^{-6} \text{ J}$ for each additional Pa of pressure above atmospheric pressure

Ex: 1 mol of $\text{H}_2\text{O}(l)$ at 25°C (298K)

Gibbs at 30°C ? (303K) -

$G_{\text{H}_2\text{O}} = -237.13 \text{ kJ}$ at 298K and 1 atm

$$S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$$

$$S_{\text{H}_2\text{O}} = 69.91 \text{ J/K}$$

$$\Delta G = S \cdot \Delta T$$

$$= 69.91 \cdot 5 \text{ K} = 349.55 \text{ J}$$

$$+ \underline{-237.13 \text{ kJ}} \quad \underline{-236.78 \text{ kJ}}$$

units warning!



new
Gibbs
 \downarrow

5.14 → Monday

Now do 5.12 then come back to 5.14.

Thermodynamic identity

$$dU = T dS - P dV + \mu dN$$

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

$$\frac{\partial U}{\partial S} = T$$

$$\frac{\partial U}{\partial V} = -P$$

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

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

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

$$dS(U, V, N) = \underbrace{\left(\frac{\partial S}{\partial U} \right)_{V,N}}_{\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V} \right)_{U,N}}_{\frac{P}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N} \right)_{U,V}}_{-\frac{\mu}{T}} dN$$

$$T dS = dU + P dV - \mu dN$$

$$f(x, y)$$

$$\left(\frac{\partial f}{\partial x} \right)_y$$

$$\left(\frac{\partial f}{\partial y} \right)_x$$

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

Now do for Gibbs

$$dG = dU + p dV - T dS \quad (dN = 0)$$

$$dG = \frac{\partial G}{\partial U} dU + \frac{\partial G}{\partial V} dV + \frac{\partial G}{\partial S} dS$$

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

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

Now for Helmholtz + Enthalpy then back to 5.14...

5.2 / Free Energy as a

Force toward Equilibrium

$$dS_{\text{total}} = dS + dS_R$$

rewrite in
terms of system's
variables

$$dS_R = \frac{1}{T} dU_R + \frac{P}{T} dV_R + \frac{\mu}{T} dN_R$$

$$dV_R = 0$$

$$dN = 0$$

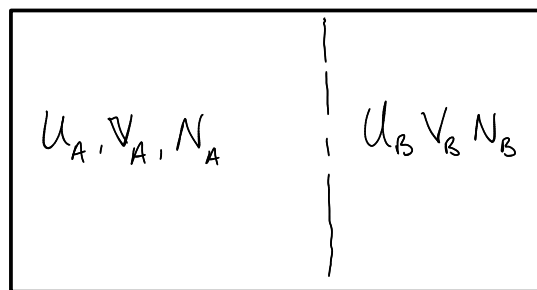
$$dU = -dU_R \leftarrow \text{energy is conserved}$$

$$dS_{\text{total}} = dS - \frac{1}{T} dU$$

$$= \frac{1}{T} (T dS - dU)$$

$$= -\frac{1}{T} (dU - T dS)$$

Helmholtz! dF



surrounding
(reservoir)

$$dS_{\text{total}} = -\frac{dF}{T}$$

↑ increase this

↓ decrease that

Conditions

$$dT = 0$$

$$dV = 0$$

$$dN = 0$$

So, the system will minimize
its Helmholtz free energy

What about keeping Pressure, temperature and number constant and letting V change?

$$dS_{\text{total}} = dS + dS_{\text{res}}$$

$$\hookrightarrow dS_{\text{res}} = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \rightarrow 0$$

$$dS_{\text{res}} = -dS$$

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV$$
$$= -\frac{1}{T} (dU - T dS + P dV)$$

Δ Gibbs free energy $\rightarrow dG$

Conditions:

$$dT = 0$$

$$dp = 0$$

$$dN = 0$$

$$dS_{\text{total}} = -\frac{dG}{T}$$

system will spontaneously minimize Gibbs

At constant energy & volume, S tends to increase

At constant temperature & volume, F tends to decrease.

At constant temperature & pressure, G tends to decrease

Is this intuitive from their definitions

$$G = U + PV - TS$$

$\downarrow \quad \downarrow \quad \uparrow$

