

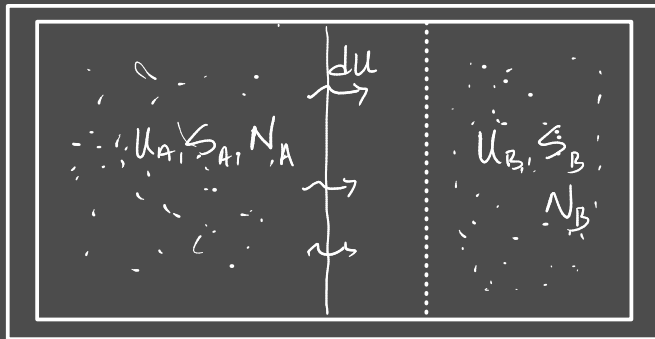
Chapter 5 - Free energy and chemical thermodynamics

↳ available

Goal: Apply laws of thermodynamics to non-cyclic processes like chemical reactions, phase changes, and other transformations.

Previously:

$$\rightarrow dU = TdS - pdV + \mu dN$$



total U was fixed
total V was fixed
total N was fixed

What if T is fixed but not U ?

What if p is fixed but not V ?

Constant T + Constant p processes

(u)
Enthalpy - energy plus the work to make room for a system under constant pressure from the surroundings

$$H \equiv U + pV$$

Helmholtz Free Energy \rightarrow total energy to create a system
minus the heat you can extract
from the surroundings at constant T .

$$F \equiv U - TS$$

\hookrightarrow all work done on the system
by us and the surroundings.

Gibbs Free Energy

$$G \equiv U - TS + pV$$

$$G = H - TS$$

$U, H, F, G \rightarrow$ thermodynamic potentials

What about changes in $F + G$?

$$dF = dU - TdS$$

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

for a reversible process

$$\pm Q_{\text{rev}} = T \cdot dS$$

$$dF = \cancel{TdS} + \pm W - \cancel{TdS}$$

$$dF = \pm W$$

↳ amount of work done on the system

otherwise,

$$dF \leq \pm W$$

$$dG = dU - TdS + p dV$$

$$= \pm Q + \pm W - \cancel{TdS} + \cancel{p dV}$$

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

$$\pm W = \cancel{-p dV} + \pm W_{\text{other}}$$

↳ electrical, etc.

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

ΔG is very useful, how is it measured.

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

↓
Then calculate ΔS from initial and final states.

$$S_{\text{react}} = \int_0^{T_f} \frac{C_p}{T} dT \quad \swarrow \text{react}$$

$$S_{\text{prod}} = \int_0^{T_f} \frac{C_p}{T} dT \quad \swarrow \text{product}$$

$$\Delta S = S_{\text{prod}} - S_{\text{react}}$$

Then $\underline{\Delta G} = \Delta H - T \cdot \Delta S$

Problem 5.2

Calculate ΔG , from ΔH + S .

$$T = 298 \text{ K}$$

$$p = 1 \text{ bar} = 10^5 \text{ Pa} \approx 1 \text{ atm} = 1.013 \cdot 10^5 \text{ Pa}$$



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

$$\begin{aligned} \Delta H &= 0 \text{ kJ} \\ S &= 191.61 \text{ J/Kmol} \end{aligned}$$

$$\begin{aligned} \Delta H &= 0 \text{ kJ} \\ S &= 130.68 \text{ J/Kmol} \end{aligned}$$

$$\begin{aligned} \Delta H &= -46.11 \text{ kJ/mol} \\ S &= 192.45 \text{ J/Kmol} \end{aligned}$$

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

$$\Delta S = S_{\text{prod}} - S_{\text{react}} = 2 \text{ mol} \cdot 192.45 \text{ J/Kmol} - 191.61 \text{ J/Kmol} - 3 \text{ mol} \cdot 130.68 \text{ J/Kmol}$$

$$\Delta S = -198.75 \text{ J/K}$$

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

$$= \underline{-92.22 \text{ kJ}} - (298 \text{ K})(\underline{-198.75 \text{ J/K}})$$

+ 59.23 kJ

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

the energy
out of the
system

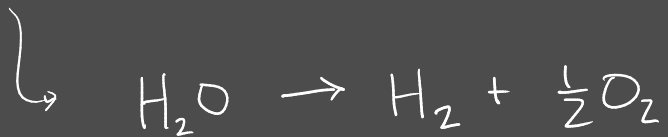
Compare to: ΔG_{NH_3}

$$\rightarrow -16.45 \text{ kJ/mol} \times 2 \text{ mol} =$$

$$\boxed{-32.9 \text{ kJ}}$$

back tabulated
value

Electrolysis, Fuel Cells, Batteries



How much electrical work?

$$\Delta H = \underline{286 \text{ kJ}} \rightarrow \begin{array}{l} \text{heat out to run} \\ \text{in reverse} \end{array}$$

\rightarrow to push atmosphere away

$$p\Delta V = \underline{\Delta n \cdot R \cdot T} = 1.5 \text{ mol} (8.31 \text{ J/Kmol}) (300 \text{ K})$$
$$= \underline{\underline{3.7 \text{ kJ}}} \sim 4 \text{ kJ}$$

\rightarrow 282 kJ will remain in the system in the form of potential energy

\rightarrow do we need to do all of this work?
heat from the environment?

What is the change in entropy for this system?

$$S_{H_2O} = 70 \text{ J/K} \quad S_{H_2} = 131 \text{ J/K} \quad S_{O_2} = 205 \text{ J/K}$$

$$\underbrace{\hspace{10em}}_{\text{products}} \quad \begin{array}{c} H_2 \\ \downarrow \end{array} \quad \begin{array}{c} \frac{1}{2} O_2 \\ \downarrow \end{array}$$
$$S_{\text{prod}} = 131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K} = 233.5 \text{ J/K}$$

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

entropy increase
so the most heat that
can enter the system
will be

$$\Delta Q \leq T \Delta S$$

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

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

So of the 286 kJ that go in, 48.7 kJ come from heat from surroundings.
 $286 \text{ kJ} - 48.7 \text{ kJ} = \underline{237.3 \text{ kJ}} \rightarrow$ come from electrical work
matches ΔG from the book

In reverse, we can extract 237 kJ of electrical work!

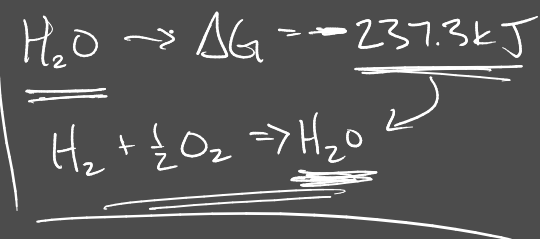
→ 49 kJ of waste heat to surrounding.

→ $\Delta H = 282 \text{ kJ}$ → from chemical reaction

→ $P\Delta V = 4 \text{ kJ}$ → from collapse of gas to liquid

→ Fuel Cell

$$\text{efficiency} = \frac{\text{what we get}}{\text{what we pay for}} = \frac{273 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$



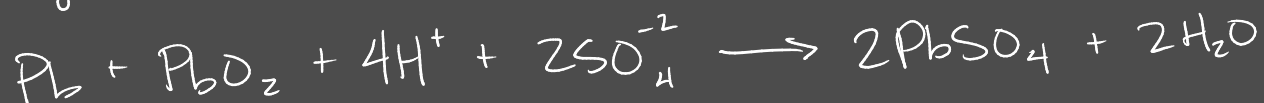
Compare to chapter 4

→ prob. 4.2 → 66%

↳ car (theoretical)
~50%

(practical)
20-30%

Battery



Start w/ ΔH → heat to accomplish this reaction

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

↑ energy out from this
reaction at constant pressure

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

↑ electrical energy out

more than ΔH !

How? Heat coming into the system from the surroundings

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

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

increase!

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

increase in entropy
means the system can
absorb heat from
the surroundings

What about the energy/charge = voltage

↳ $2e^-$ are given up at the - electrode

↳ $2e^-$ are taken up at the + electrode

$$\text{voltage} = \frac{W_e}{q} = \frac{394 \text{ kJ}}{2e^- \cdot N_A \cdot 1.6 \cdot 10^{-19} \text{ C/e}} = \underline{\underline{2.04 \text{ V}}}$$

voltage of reaction

Thermodynamic Identity

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

$\underbrace{\quad\quad\quad}_{\text{variables}}$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N}$$

Enthalpy

• $H = U + pV$

$$dH = dU + \cancel{p dV} + V dp$$

$$\uparrow T dS - \cancel{p dV} + \mu dN$$

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

$$\left| \begin{array}{l} \text{Ex. } dp = 0 \\ dN = 0 \end{array} \right.$$

$$dH = T dS \quad \leftarrow \begin{array}{l} \text{for reversible} \\ \text{isobaric process} \\ \pm Q = dH \end{array}$$

Helmholtz Free Energy

$$F = U - TS$$

$$dF = dU - T dS - S dT$$

$$\rightarrow dF = -S dT - p dV + \mu dN$$

T, V, N

$$\left| \begin{array}{l} \text{Ex. } dT = 0 \quad \text{isothermal process} \\ dN = 0 \end{array} \right.$$

$$dF = -p dV$$

\rightarrow reversible

$$\pm W = -p dV$$

$$dF = \pm W$$

Gibbs Free Energy

$$\rightarrow dG = -SdT + Vdp + \mu dN$$

$T, p, N \rightarrow$ very natural variables
for experiments

take $dF = -SdT - pdV + \mu dN$

- hold $V + N$ constant

$$dV = 0$$

$$dN = 0$$

$$dF = -SdT$$

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

← entropy is the
rate of change of
F w.r.t. T.

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

Similarly for Gibbs

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

$$1 \text{ mol of C} \Rightarrow 5.3 \cdot 10^{-6} \text{ m}^3$$

(graphite)

$G = 0 \text{ kJ}$ ← most stable elemental form of C

Gibbs increases by $5.3 \cdot 10^{-6} \text{ J}$ per Pa of pressure above atmospheric pressure

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

Gibbs at 30°C (303 K)

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

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

$$S = \left(\frac{\partial G}{\partial T} \right)_{P,N} \Rightarrow \Delta G = S \cdot \Delta T = 69.91 \text{ J/K} \cdot 5 \text{ K} = 349.55 \text{ J}$$
$$\begin{array}{r} + (-237.13 \text{ kJ}) \\ \hline -236.78 \text{ kJ} \end{array}$$