LECTURE 24. ENTROPY—THE TRUTH BEHIND SPONTANEITY

We have defined spontaneity through ΔG

ΔG	-	spontaneous
ΔG	+	non spontaneous

But we have seen that reactions can occur

- whether a rxn is endo or exothermic
- whether the entropy of a system increases or decreases

Clearly something more profound than simple energy conservation from the first law is at work.

What is the deeper insight?
The second law of thermodynamic says that:

> "A reaction is spontaneous if the entropy of the isolated system increases."

(an isolated system is the universe in most examples)

We are quite accustomed to disorder in natural environments as the direction of physical processes

- Food coloring distributes in a beaker of water
- A hot block of metal cools to room temperature

We are less accustomed to understanding this with chemical processes, <u>especially</u> when considering reactions that increase the energy of a system (endothermic) or decrease the entropy of a system (the system gets more ordered). Like, why do we exist?

The answer rests in a deeper appreciation of entropy on a global level.

But first, we need a quantitative measure of entropy

Entropy Defined Quantitatively

$$\Delta S = \frac{Q}{T}$$ in a reversible process, at constant temperature

Example: What is the entropy change if we dump 100 J of heat into a cube of melting ice?

$\Delta S = 100\ J / 273\ K = 0.366\ J/K$

Is there a way to describe $\Delta S = Q / T$ that makes physical sense?

The key is to realize that is we dump a lot of energy into a system, it increases the disorder. For example when we explode a hydrogen balloon, stuff starts flying everywhere. We see the balloon parts all over the ground. We feel the rush of hot air past us. So increasing Q in a system makes sense for ΔS increasing.

But why an inverse relationship to T?

The equation says:

100 J makes a lot bigger mess at 1 ºK than at 1,000 ºK, ΔS is a lot larger at 1 K than 1,000 K

The famous analogy is to sound during an exam versus sound at a concert. At a concert, if someone coughs it is barely noticed (the change in sound is minor). But in a quiet room, a cough makes you want to punch the guy with a cold.

Global Changes in Entropy

To obtain a quantitative understanding of how entropy affects spontaneity, we need to better define a few terms.

$\Delta S_{total} \equiv$ change in entropy of the isolated system
$\Delta S_{surr} \equiv$ change in entropy of surroundings
$\Delta S \equiv$ change in entropy of system

So $\Delta S_{total} = \Delta S_{surr} + \Delta S$

And from the second law, a reaction is only spontaneous if $\Delta S_{total} > Ø$

This suggests that ΔS for the system can be negative and a rxn spontaneous
BUT ONLY IF $|\Delta S_{surr}| > |\Delta S|$

Famous examples of ΔS negative reactions are phase changes like

$$H_2O_{(aq)} \rightarrow H_2O_{(l)} \rightarrow H_2O_{(s)}$$

which we see happen all the time. So we know that if
$H_2O_{(l)} \rightarrow H_2O_{(s)}$ has an increase in ΔS_{surr} driving the rxn

Table S° for H_2O

Phase	T (°C)	S° (J/kmol)
Solid	-273	3.4
	0	43
Liquid	0	65
	50	75
	100	87
Vapor	100	197
	200	204

we estimate this with stat. thermo!!!

ice freezing has a $\Delta S° = -22$ J/kmol

So according to the second law, if ice freezing is spontaneous below 0 º (and we see this to be true), then

$\Delta S^{o}_{surr} > 22$ J/kmol at < 0 ºK

We know $\Delta S_{surr} = \frac{\Delta H}{T}$ so at -10º , the ΔH_{fusion} of ice becomes heat in surroundings

$= \frac{6{,}000 \text{ J/mole}}{263}$

$= 23$ J/mole K

$\boxed{\Delta H_f = -6 \text{ kJ/mole for } H_2O}$

So $\Delta S_{surr} > \Delta S_{sys}$ below T=0ºC. And thus water freezing is spontaneous.

Can we make sense of this qualitatively? Yes.

The heat that leaves the system when ice freezes is going into the surroundings (conservation of energy). But it is going into a colder environment. Remember that in a colder place (quieter room) the disruption is greater. Hence the 6,000 J of heat are making a bigger relative mess in the surroundings (-10 ºC) than in the system (0ºC).

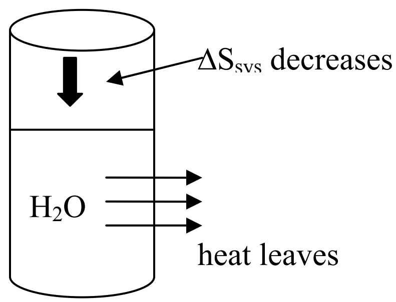
Exothermic Processes.

Water freezing is exothermic. (Heat leaves the system).

This means that there will <u>ALWAYS</u> be an increase in ΔS_{surr} when heat leaves, which aids spontaneity, even when ΔS_{system} is negative.

Example 1 Exothermic rxn, ΔS_{system} decreases

$H_2O_{(g)} \rightarrow H_2O_{(l)}$

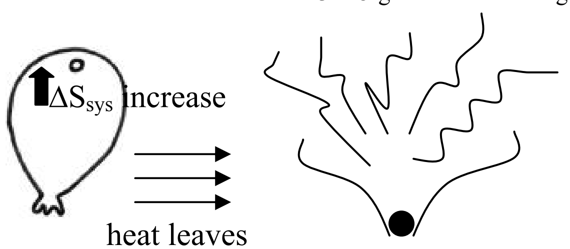


ΔS_{surr} increases ΔS_{tot} is > Ø

So even though ΔS_{sys} goes the wrong way,
ΔH makes ΔS_{surr} overcome it.

Example 2 Exothermic rxn, ΔS_{system} increases

combustion rxn $C_3H_{8\,g} + 5\ O_{2\,g} \rightleftharpoons 3\ CO_{2\,g} + 4\ H_2O_g$



ΔS_{surr} increases ΔS_{tot} is > Ø

here ΔS_{sys} helps spont.
and ΔH exothermic makes ΔS_{surr} increase. Both
$\Delta S_{sys} + \Delta H_{sys}$ make ΔS_{tot} > Ø

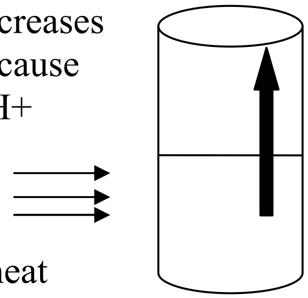
But what about endothermic processes? How can they be spontaneous? How can a reaction happen if ΔE for the system gets stronger? Isn't the energy going the wrong way?

Answer? It's the entropy (not the energy) stupid.
Entropy drives spontaneity.

Example 3 Endothermic Process, ΔS_{system} increases

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ ice melts

ΔS_{surr} decreases because $\Delta H+$



heat enters

ΔS_{sys} increases because
T in system ↑
and solid → liquid

↑ ΔS_{tot} is > 0 spontaneous

So we now look at these cases of $\Delta G-$ in a new light where the ΔH being endo or exothermic changes $\Delta S = \Delta H/T$ and either drive or stalls spontaneity.