GENERAL CHEMISTRY SECTION IV: THERMODYNAMICS

LECTURE 19: GETTING READY FOR THERMODYNAMICS

Up to this point, we've learned how to draw chemical structures, and we've learned that there are products and reactants that balance stoichiometrically because of **conservation of mass and charge**.

During class, you've seen this reaction happen…

$$2H_2 + O_2 \rightarrow 2H_2O \quad …\textbf{Big hydrogen balloon explosion!}$$

But in understanding the stoichiometry, we've paid no attention to the explosion and heat given off when that balloon blows up. We just counted up stuff to make sure mass and charge were conserved.

But now we are learning about **thermodynamics**, and will need to account for all the energy change that occurs. Sure, we want to conserve matter, but we also want to account for all that energy in the reaction.

Thermodynamics is the study of the energy change in a system – whether it's energy in the form of heat (as with the exploding balloon), or mechanical work, or the creation of order in a system.

ENERGY CHANGE IN A CHEMICAL REACTION

Simply put, chemical reactions' **changes in energy** happen because of **bonds breaking** and **bonds forming**. So consider hydrogen and oxygen:
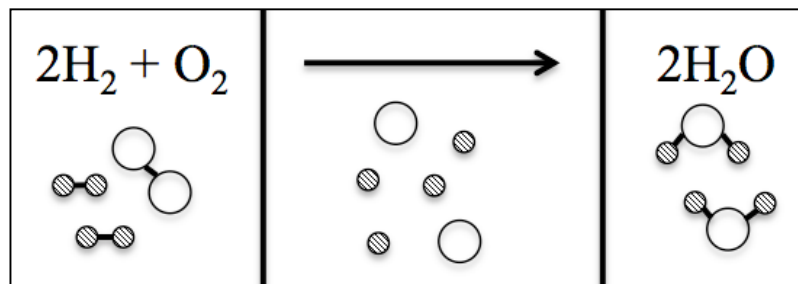
This **ΔE** is what we study, and we'll end up seeing that there are a variety of **energy-related changes** for us to measure as we work our way through thermodynamics:

ΔG	**ΔH**	**ΔE**	**ΔS**	**w**	**q**
Free energy	Enthalpy	Internal energy	Entropy	Work	Heat

## OUR PLAYGROUND FOR THERMODYNAMICS: UNIVERSE, SYSTEM, AND SURROUNDINGS

Before starting thermo, we need to define our territory:

We are in a **universe** (which is everything).

But we are only concerned with **the system** (which, in chemistry, is the **chemical reaction**).

And we like to isolate the chemical reaction/system by putting it in a **closed environment**; everything outside of that closed environment is **the surroundings**.

$$\text{Universe} = \text{System} + \text{Surroundings}$$
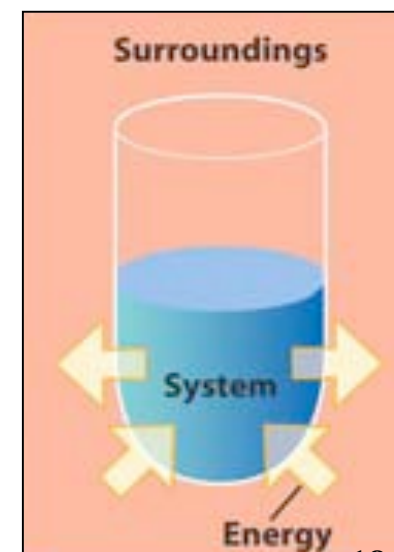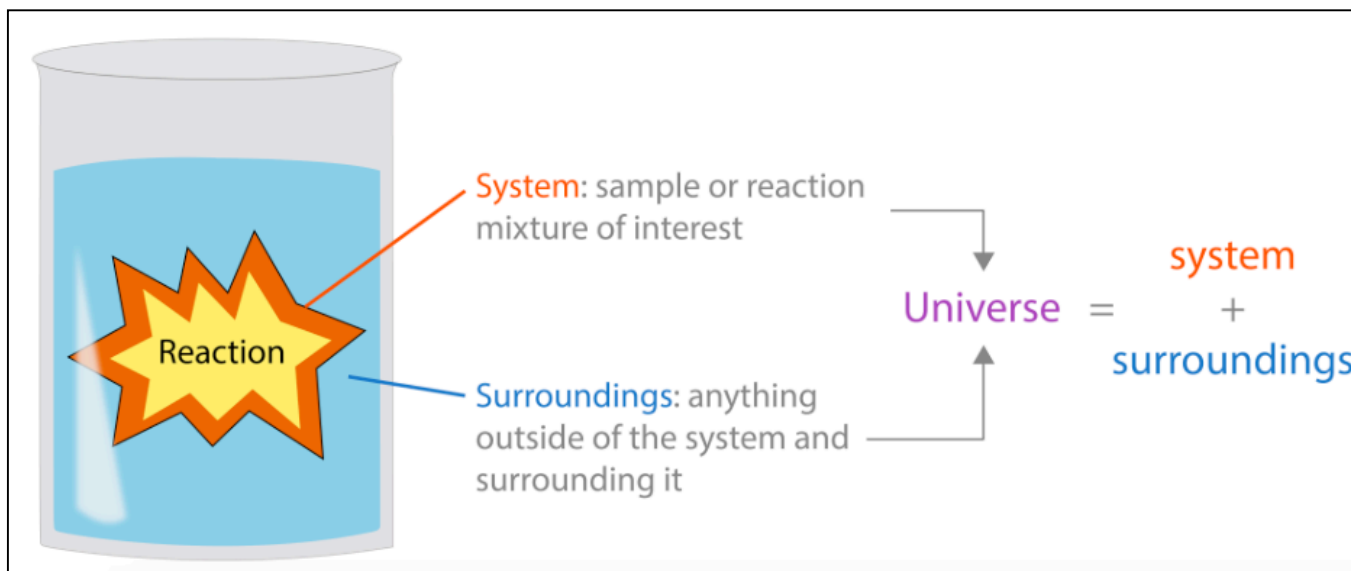
Many of the properties of systems that we're interested in are called **state functions** – properties of a system about which we care only the starting and ending states/values. Some of these we've already learned about in the context of **gases**:

Temperature (T)   **Pressure (P)**   **Volume (V)**   **Moles (n)**

And we'll learn about a few more in the coming **thermo** lectures:

**Internal energy (E *or* U)**   **Enthalpy (H)**   **Entropy (S)**   **Gibbs free energy (G)**

Here's another way to think of state functions: any information about what happened to a state function *during* the reaction is irrelevant – like how quickly it reacted, or the phases it went through. Take temperature, for example: if you're given the starting (T_1) and final (T_2) temperatures, then right away you have everything you need to know for T; nothing else matters about temperature once you know the values of T_1 and T_2. What it did between T_1 and T_2 – we couldn't care less about that.

So in a system, we can measure any of those state functions.

And actually, it isn't the state of the system that we care about – it's the **change in state** that matters.

BEFORE

P_1, V_1, T_1,
S_1, E_1, G_1,
H_1, n_1

Δ

AFTER

P_2, V_2, T_2,
S_2, E_2, G_2,
H_2, n_2
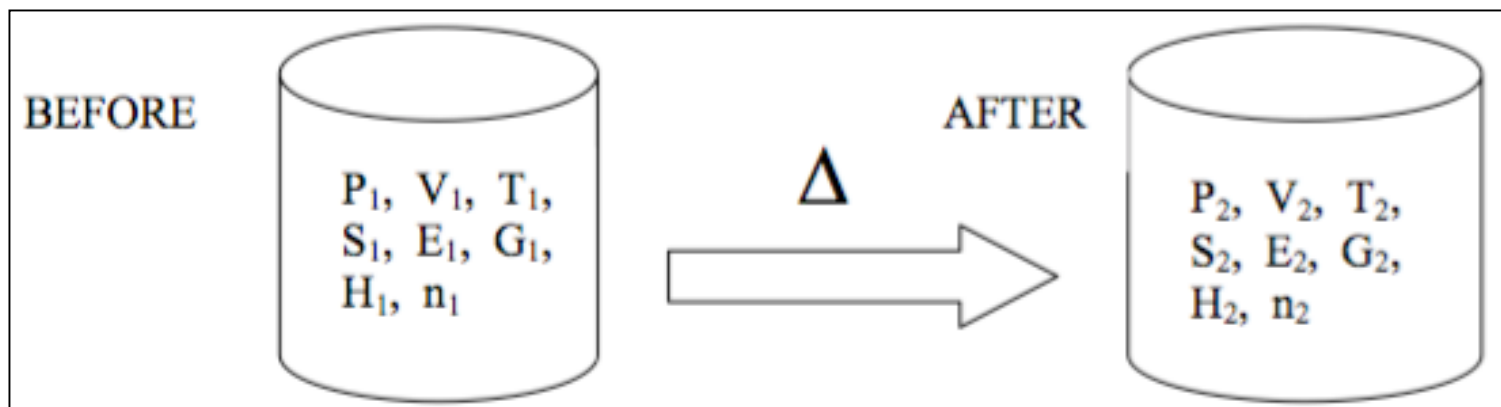
So basically we'll spend the rest of the semester calculating lots of changes in the states of systems:

$$\Delta V, \ \Delta P, \ \Delta T, \ \Delta n, \ \Delta S, \ \Delta G, \ \Delta H, \ \Delta E$$

Although state functions make up the majority of the thermodynamic properties we study, we are also interested in two things that are *not* state functions – __work (w)__ and __heat (q).__ Whereas state functions are completely independent of path, **w and q are *dependent* upon path.** See, we can ignore state functions because they are properties of the system, so we can just observe them before and after the reaction to figure out what they did. On the other hand, w and q are *not* system properties – they are actually part of the *processes* involved in a reaction. That means instead of checking them before and after the reaction, we must observe them *during* it.

THERMODYNAMIC LAWS ARE COMING

Just like in the quantum mechanics we discussed at the beginning of this semester, there are some **boundaries,** or **laws,** that govern the big picture of thermodynamics. We are already used to one of these notions – that of **conservation**. For example, when you discussed stoichiometry in high school, you learned that:

<div align="center">

All the <u>mass</u> in the universe is conserved.

…And…

All of the <u>charge</u> in the universe is conserved.

</div>

This made it easy to do things like balance chemical reactions. But we won't stop there: brace yourselves because ~~winter is coming~~ a **new conservation law** is coming:

<div align="center">

The <u>first</u> law of thermodynamics – all of the <u>energy</u> is the universe is <u>conserved</u>.

</div>

And we will also learn about a couple of other laws that bound what happens in our thermodynamic universe:

<div align="center">

The <u>second</u> law of thermodynamics – the <u>entropy</u> in the universe is always <u>increasing</u>.

The <u>third</u> law of thermodynamics – there is an <u>absolute lowest temperature</u>.
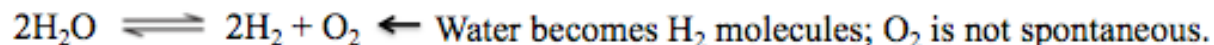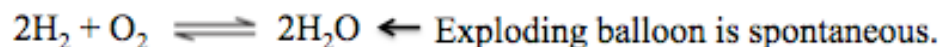
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So let's get started.

LECTURE 20: THERMODYNAMIC OVERVIEW – A QUALITATIVE APPROACH

Today's lecture is a general overview of thermodynamics from a qualitative perspective. To really be able to understand thermo, you need to look at a chemical reaction and talk about it in the context of **relative changes in state functions**.

HOW TO KNOW IF A REACTION WILL HAPPEN

First, one of the important consequences of thermodynamics is the ability to explain whether a reaction occurs or not. Note that **for every spontaneous reaction, there is a reverse non-spontaneous reaction**, and it would be nice to look at a reaction and tell whether it is going to happen as it's written or as the reverse.

For example:

$2H_2 + O_2 \rightleftharpoons 2H_2O$ ← Exploding balloon is spontaneous.

$2H_2O \rightleftharpoons 2H_2 + O_2$ ← Water becomes H_2 molecules; O_2 is not spontaneous.

The state function that **determines spontaneity** is $\underline{\Delta G}$, the **free energy**. So if you know the **sign of ΔG**, an easy way of knowing whether a reaction will happen is just to look at that sign:

If ΔG = (+):
The reaction is **non-spontaneous**.

If ΔG = (-):
The reaction is **spontaneous**.

Similarly, if you know from experience that the reaction happens or not, you already know the sign of ΔG.

Example:

Consider the reaction: $AgNO_3 + NaCl \rightleftharpoons AgCl + Na^+ + NO_3^-$.

You know from solubility rules that AgCl is insoluble, so the reaction must happen as it's written (in the forward direction, meaning it shifts to the right). So you know that for this reaction, ΔG is (–).

SIGNS IN THERMO – "BE THE SYSTEM"

So what is the source of this idea about thermodynamic signs? Why does ΔG = (–) mean that a reaction is spontaneous? Is it arbitrary? *No!*

Thermodynamic terms (i.e., state functions, as well as q and w – we'll learn these distinctions later) are given their (+) and (–) signs based on whether the **_system_** is **gaining or losing** whatever it is that that term represents:

If the system gains, the sign is (+).
If the system loses, the sign is (–).
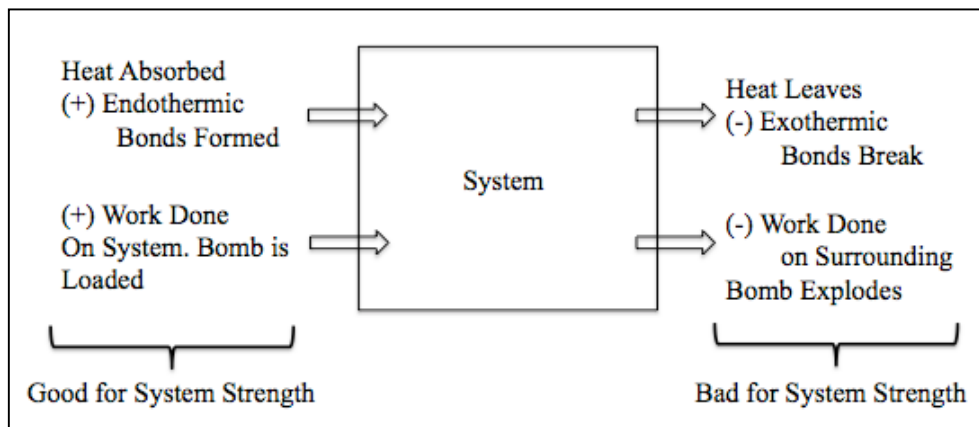
To keep straight whether the **system is gaining or losing** something, we use a **"be the system"** philosophy. But "being the system" can be hard because **us humans are the _surroundings_**, but we tend to think of things from our own perspectives. So **if you're thinking of whether _you_ are losing or gaining** something (like heat, for instance), you'll be thinking of **every sign in thermo backwards**, because as the surroundings, if you gain something, the system must have lost it, and vice versa. Which means that **a sign from your own perspective is opposite the sign from the system's perspective**.

Example:
    A fire burns down a house – is the process exothermic or endothermic? Is work being done on the system, or is it being done on the surroundings?

Answer:
    Exothermic: the sign is (–). Heat is being released into the surroundings, and the wood itself gets cold from that loss of heat (did you know that?!). The strong bonds in the wood become weak bonds: $CO_2 + H_2O$.
    Work is being done on the surroundings: the sign is (–). As the wood becomes $CO_2 + H_2O$, gas is produced, and a bomb forms as the volume of the house expands.

MORE THOUGHTS ON WORK AND SIGNS

A first equation:

$$w = -P\Delta V = -\Delta nRT$$
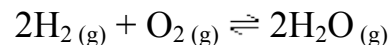
w = work
P = pressure
ΔV = change in volume
Δn = change in the number of moles of gas
R = ideal gas constant = 8.3 J/mol·K, when…
…T = temperature = 300K

With this ideal gas constant:
$RT = 2.5$ kJ/mol

Why the negative sign in that equation? Note that in the reaction:

$$2H_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(g)}$$

…$\Delta n = -1$, so ΔV is getting smaller. Work is being done **on** the system. That means **work is (+)** (as in, work is being **added** to the system). For the equation to reflect that, we need the minus signs in order to correct the sign that work ends up with.

$$w = -\Delta nRT = -(-RT) = (+)\,RT$$

Understanding signs is vital, because every thermo answer has a sign. You can do the math correctly and end up with the right number, but choose the wrong sign and you get the entire problem wrong.

TEMPERATURE DEPENDENCE OF FREE ENERGY

As we will learn, there are two quantities that can be measured to determine free energy in a temperature-dependent reaction: enthalpy (ΔH), and entropy (ΔS). These are included in an equation to tell you whether a reaction happens:

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

Depending on the combination of signs you have for these two state functions, you'll be able to determine whether a reaction is spontaneous or non-spontaneous, or whether that depends on temperature.

Case #1: The reaction is *always* **spontaneous**.
This is the case when:
$\Delta H = (–)$ and $\Delta S = (+)$.
Plugging these into the equation, ΔG will always be (–), regardless of T:
(–) = (–) - T(+).

Case #2: The reaction is *never* **spontaneous**.
This is the case when:
$\Delta H = (+)$ and $\Delta S = (–)$.
Plugging these into the equation, ΔG will always be (+), regardless of T:
(+) = (+) - T(–).

<u>Case #3: The reaction's spontaneity *depends upon temperature.*</u>

This is the case when you have either:

$$\Delta H = (+) \; and \; \Delta S = (+)$$
or
$$\Delta H = (-) \; and \; \Delta S = (-).$$

When ΔH and ΔS are **both positive**, the reaction will only be spontaneous at ***high* temperatures**.

ΔG will only be (–) if the second term (–TΔS; which will be (–) overall, since ΔS = (+)) has a higher magnitude than the first term (ΔH) →
(+ or –) = (+) - T(+).

When ΔH and ΔS are **both negative**, the reaction will only be spontaneous at ***low* temperatures**.

ΔG will only be (–) if the first term (ΔH) has a higher magnitude than the second term (–TΔS; which will be (+) overall, since ΔS = (–)) has a higher magnitude than the first term (ΔH) → (+ or –) = (–) - T(–).

Example of temperature-dependent spontaneity (case #3):

Consider the case of ice melting: $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$

Is it spontaneous? – Yes, if it's in a high T environment. Not, for example, a freezer. So it must be the high T spontaneous case, where both ΔH and ΔS are (+).

PUTTING 'EM ALL TOGETHER

ΔH	ΔS	ΔG	Reaction Characteristics	Example
+	+	+ at low T; – at high T	Nonspontaneous at low T; Spontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	–	Always +	Nonspontaneous at all T, Reverse rxn is spontaneous	$3O_2(g) \longrightarrow 2O_3(g)$
–	+	Always –	Spontaneous at all T	$2O_3(g) \longrightarrow 3O_2(g)$
–	–	– at low T; + at high T	Spontaneous at low T; Nonspontaneous at high T	$H_2O(s) \longrightarrow H_2O(l)$

ENERGY IN THREE FORMS: ENTHALPY, ENTROPY, AND WORK

Enthalpy (ΔH): State function that describes the **heat** of a reaction.	**Entropy (ΔS):** State function that describes the **disorder** of a reaction.	**Work (w):** *Not* a state function; describes how the reaction's **gas molecules** behaved.

ENTHALPY – ΔH

Enthalpy, **ΔH**, is a state function that describes the **heat** of the reaction. It tells whether the system **lost or gained heat** during the reaction. It can be either (+) or (–).
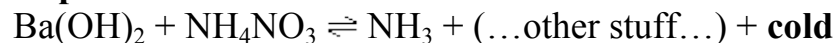
> If ΔH = (+), the reaction is **endothermic**:
> The **system gains** heat (which means the **surroundings lose** heat).
>
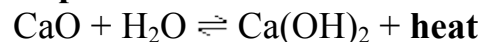> If ΔH = (–), the reaction is **exothermic:**
> The **system loses** heat (which means the **surroundings gain** heat).

Example – endothermic reaction:
   $Ba(OH)_2 + NH_4NO_3 \rightleftharpoons NH_3 + (\ldots\text{other stuff}\ldots) + \textbf{cold}$
We know that this reaction is **endothermic (ΔH = (+))** because, since heat is being used up as it reacts, the system must be **absorbing heat**.

Example – exothermic reaction:
   $CaO + H_2O \rightleftharpoons Ca(OH)_2 + \textbf{heat}$
We know this reaction is **exothermic (ΔH = (–))** because, since heat is produced as it reacts, the system must be **releasing heat**.

In general, combustion reactions are exothermic, and most spontaneous reactions are exothermic. But that's not to say endothermic reactions can't be spontaneous – see the example above.

So we can say that **exothermicity promotes spontaneity**, but is **not a necessary condition** for spontaneity. In our next lecture, we will learn about four ways to determine ΔH.

ENTROPY – ΔS

Entropy, **ΔS**, is a state function that describes the disorder of the reaction. It tells whether the system became more or less disordered/chaotic during the reaction. It can be either (+) or (–).

> ## If ΔS = (+):
> The **system becomes more disordered**.
>
> ## If ΔS = (–):
> The **system becomes less disordered**.

As we can see from the equation "ΔG = ΔH – TΔS," **spontaneity is more likely if ΔS = (+)**. And this makes sense – reactions happen because they ultimately make something easier (like energy being lowered in something); increasing disorder (such as dirtying a room) is easier than creating order (cleaning up the room).

So can we predict the sign of ΔS? – Yes, we just need to use common sense:

1. Raising the temperature increases ΔS. Why? – When heat increases, kinetic energy goes up, making velocity go up, and this molecules end up separating more frequently.
2. Increasing the volume increases ΔS. Why? – Molecules bouncing around in a cup will become more disordered if they're moved and let loose in a bucket.

3. Molecules changing to a higher-energy phase (solid → liquid → gas) get higher in ΔS. Why? – Imagine the collection of blocks being a solid on the left and a gas on the right:
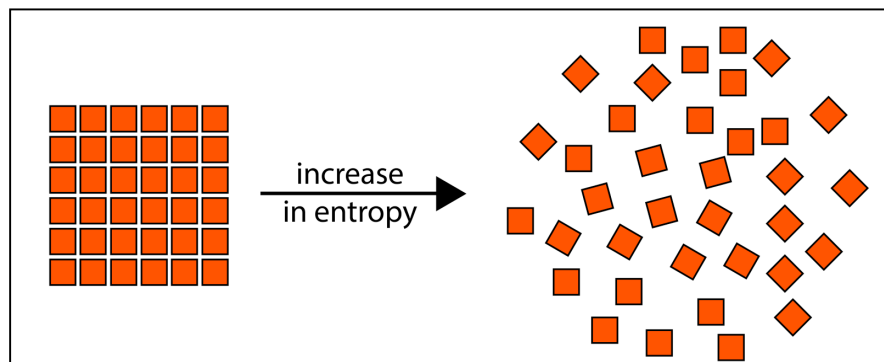
4. Increased Δn_{gas} increases ΔS. Why? – More molecules, more mess.

So we can look at a chemical reaction and predict ΔS:

$$2H_{2\ (g)} + O_{2\ (g)} \rightleftharpoons 2H_2O_{\ (l)}$$
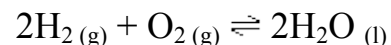
In this reaction, ΔS = (–). We know this for two reasons:
1. We see Δn_{gas} = -3; this means fewer gas molecules, and therefore less disorder.
2. Both reactants are gases, and the product is a liquid; this phase change indicates a decrease in disorder.

WORK – w

Now we move on to **work, w**, which is the ability of a chemical reaction to **move objects** around; you probably learned about it in high school physics as "force × distance = work." If you think about it, it makes sense that gas molecules under growing pressure will exert a greater and greater force as they reach a larger and larger volume:

$$w = -P\Delta V$$

We will spend our time learning about work in the context of **pressure-volume work**, but you should be aware that there are many other forms of it, like mechanical and magnetic work. We focus on its P-V form simply because it allows us to calculate the work involved in **combustion reactions**, which are a big deal in chemistry. In fact, **bombs** are really nothing more than combustion reactions that take place under specific pressure and volume conditions:

1. The reaction taking place in an **enclosed container**.
2. An **increase** in gas **pressure**.

Note that for work, we only talk about gases, because solids and liquids only ever have a negligible change in volume.

So can we calculate w? Yes – from the ideal gas law:
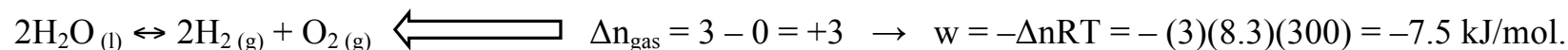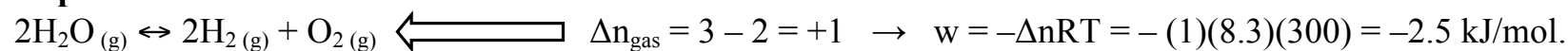
$$w = -P\Delta V = -\Delta nRT$$
$$R = 8.3 \text{ J/ mol·K}$$
$$T = 300 \text{ K}$$
$$RT = 2.5 \text{ kJ}$$

All we need to do is find Δn_{gas} and, at room temperature (300 K, or 25°C), work for a gas will be a multiple of 2.5 kJ/mol.

Examples:

$2H_2O_{(g)} \leftrightarrow 2H_{2(g)} + O_{2(g)}$ ⟸ $\Delta n_{gas} = 3 - 2 = +1$ → $w = -\Delta nRT = -(1)(8.3)(300) = -2.5$ kJ/mol.

$2H_2O_{(l)} \leftrightarrow 2H_{2(g)} + O_{2(g)}$ ⟸ $\Delta n_{gas} = 3 - 0 = +3$ → $w = -\Delta nRT = -(3)(8.3)(300) = -7.5$ kJ/mol.

See how easy it is to do a work calculation?

LECTURE 21: THERMODYNAMICS – LET'S GET QUANTITATIVE

Today we will examine the quantitative side of thermodynamics, while actually coming up with **numerical values** for ΔH, ΔS, etc. Up to this point we have been more concerned with the signs of thermo data and what they mean. These are summarized below and should be as much a part of you as your own name:

Energy Type	Symbol	Sign	Interpretation
Change in Enthalpy	ΔH	−	Exothermic, Heat Released
		+	Endothermic, Heat Absorbed
Change in Entropy	ΔS	−	System becomes more ordered
		+	System becomes less ordered
Change in Free Energy	ΔG	−	Spontaneous
		+	Non-spontaneous
Work	w	−	Work done by the system
		+	Work done on the system

But now we'll be adding numbers. For example, the reaction:

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$
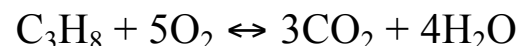
…We know that, **qualitatively**, it's **ΔG = (-)**.
But now we'll learn that, **quantitatively**, it's **ΔG = -2070 kJ**, which means it is **really spontaneous**.

(Still, while we learn to do these calculations, don't forget the importance of simply being able to look at a reaction and assign the signs! It's knowing the signs that proves you understand thermo – anyone can put numbers in a calculator, but since half the questions I put on tests don't require a calculator…)

HOW TO COMPLETE THE THERMODYNAMIC REACTION WORKSHEET

Predict the values for ΔH, Δn_{gas}, w, ΔS, and ΔG. At the very least provide a sign, but if you can offer a guess of the magnitude without using a calculator, you're ahead of the game.

First, we'll look at the signs. Can you explain how you know them?

Reaction	ΔH	Δn_{gas}	w	ΔS	ΔG
$CH_{4\,(g)} + O_{2\,(g)} \leftrightarrow CO_{2\,(g)} + 2H_2O_{\,(g)}$	(-)	0	0	(-)	(-)
$2H_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2H_2O_{\,(g)}$	(-)	(-)	(+)	(-)	(-)

Before we do **calculations**, here are **two central concepts** to remember as we do them:

1. Why the **signs** are what they are. Remember, it's not just arbitrary that $\Delta H = (-)$ in **exothermic reactions** – it's a consequence of us learning about the **energy's flow** into and out of the system.
2. The fundamental concept behind calculations is **Hess' Law**, which says the **path does not matter**, it's just:

$$\Delta = (\text{how it ended}) - (\text{how it started})$$

…which is why there will be **more than one way to calculate** the changes in state functions for a reaction.

Let's cut to the chase – here we go with some calculations:

Reaction	ΔH (kJ)	BE (kJ)	Δn_{gas}	w = nRT (kJ)	Δn_{sys}	$T\Delta S$ (kJ)	ΔG (kJ)
$CH_{4\,(g)} + O_{2\,(g)} \leftrightarrow CO_{2\,(g)} + 2H_2O_{\,(g)}$ Combustion reaction → we'd predict lots of heat and a very spontaneous reaction. Also, $\Delta n_{gas} = 0$ → this means no work and a small ΔS.	-802	-802	0	0	0	-1	-801
$2H_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2H_2O_{\,(g)}$ Spontaneous combustion reaction → we can predict high heat. Also, $\Delta n_{gas} = (-)$ → $\Delta S = (-)$ and work is done on system (w = +).	-484	-482	-1	+2.5	-1	-27	-458

OUR FIRST THERMO. CALCULATION: MEASURING THE HEAT OF THE SYSTEM, ΔH

In calculating a reaction's **change in enthalpy**, **ΔH**, Hess' Law says that the following four different methods all yield the same answer for **ΔH$_{rxn}$**, and you will need to learn how to do each of them:

> 1. Mixed reaction enthalpies
> 2. Heats of formation
> 3. Bond energy
> 4. Bomb calorimeter

BOND ENERGY AND HEATS OF FORMATION

Our methods behind **bond energy (BE)** and **heats of formation (ΔH$_f^\circ$)** calculations:

Bond energy: after the **molecules** (as gases) **break** apart to become **individual atoms**, we find the **difference** between the energy needed to **break** the bonds and the energy needed to **reform** them, thus giving us ΔH.

Heats of formation: the molecules become elements in their standard states (298K, 1atm) and then reform as products.

A quick comparison of BE and ΔH$_f^\circ$:

BE	**ΔH$_f^\circ$**
1. Easy conceptually	1. Tougher conceptually
2. Uses **tables of bond energy**	2. Uses **appendixes of formation data**
3. Only applicable for **gases**	3. Applicable for **all states** of matter
4. Can only be used for **ΔH$_f^\circ$**	4. Can be used for **ΔH$_f^\circ$** , and **ΔS$_f^\circ$** , and **ΔG$_f^\circ$**

Now, using our **BE** and ΔH_f° methods, let's find ΔH for this combustion of propane (C_3H_8):

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$
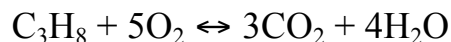
For the **BE** calculation, we'll first find the **BE values** for **all types of bonds** in every molecule. For the ΔH_f° calculation, we'll use **appendices** (you can find them on the web, and you'll always get them on exams) to find the values we need to calculate ΔH_f°, ΔS_f°, and ΔG_f°.

Propane combustion data, from appendices:

B.E. Values	
Bond	**Energy (kJ)**
C—C	346
C—H	413
O=O	458
C=O	799
O—H	463

$\Delta H_f^\circ, \Delta S_f^\circ, \Delta G_f^\circ$				
Molecule	C_3H_8	O_2	CO_2	H_2O
ΔH (kJ/mol)	-104	0	-374	-242
ΔS (J)	270	205	-214	-189
ΔG (kJ/mol)	-23	0	-394	-229

And of course, your equations are **variations on Hess's Law**:

For bond energies:

$$BE = \Sigma\ BE_{reactants} - \Sigma\ BE_{products}$$

For heats of formation:

$$\Delta H_f^\circ = \Sigma\ \Delta H_{products} - \Sigma\ \Delta H_{reactants}$$

Note that **the equation for BE calculations is the *one and only exception* to the convention in thermo equations of subtracting products from reactants.** The reason is, though the BE values should actually be negative to reflect the release of energy, they're conventionally positive in BE tables, so the equation for the BE calculation is reversed.

The calculations for this are shown on the next page.

Determine the ΔH_{sys} for the combustion of propane: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

According to Hess, you can do this by any path you like. We will use two $- \Delta H_f^\circ$ and bond energies.

For $\Delta H_f^\circ \rightarrow$ use the data given and: $\Delta H_{rxn}^\circ = \Sigma\, n\Delta H_f^\circ{}_{products} - \Sigma\, n\Delta H_f^\circ{}_{reactants}$

For BE $\rightarrow$ use the data below and: $\Delta H_{rxn}^\circ = \Sigma\, BE_{reactants} - \Sigma\, BE_{products}$

For $\Delta H_f^\circ \rightarrow$ The path is through the elements in their **standard states:** $C_{(s,\,graphite)}, O_{2\,(g)}, H_{(g)}$

$$\begin{array}{cccc} CO_2 & H_2O & C_3H_8 & O_2 \end{array}$$
$$\Delta H_f^\circ = [3(-394) + 4(-242)] - [1(-104) + 5(0)]$$

$$\Delta H_f^\circ = \text{-2046 kJ} \rightarrow \text{Very exothermic}$$

For BE $\rightarrow$ the path is through **breaking all bonds** to form **gas** phase atoms.

$$\begin{array}{ccccc} C\text{-}H & C\text{-}C & O\text{=}O & C\text{=}O & O\text{-}H \end{array}$$
$$BE = [8(413) + 2(346) + 5(458)] - [6(755) + 8(463)]$$

$$\Delta H_f^\circ \approx BE = \text{-2012 kJ} \rightarrow \text{Very exothermic}$$

Determine the ΔS for that same reaction.

What about entropy? Just because we know ΔH_f°, we can't say for sure whether the reaction is spontaneous. For that we need to look at the value of ΔS. Can you make a good guess as to whether entropy increases or decreases in the combustion reaction?

$$\Delta S_f = ([4(189) + 3(214)] - [5(205) + 1(189)])$$

$$\Delta S_f = \text{+100.7 J}$$

Determine the ΔG_f for the reaction.

With what we've already calculated, what can be said about ΔG and the spontaneity of the reaction?

$$\Delta G_f = [3(-394) + 4(-229)] - [1(23.5) + 5(0)]$$

$$\Delta G_f = \text{-2074 kJ} \rightarrow \text{really spontaneous.}$$

THE BOMB CALORIMETER CALCULATION

Remember that exploding balloon? We want to know the **energy released as heat** by that balloon.

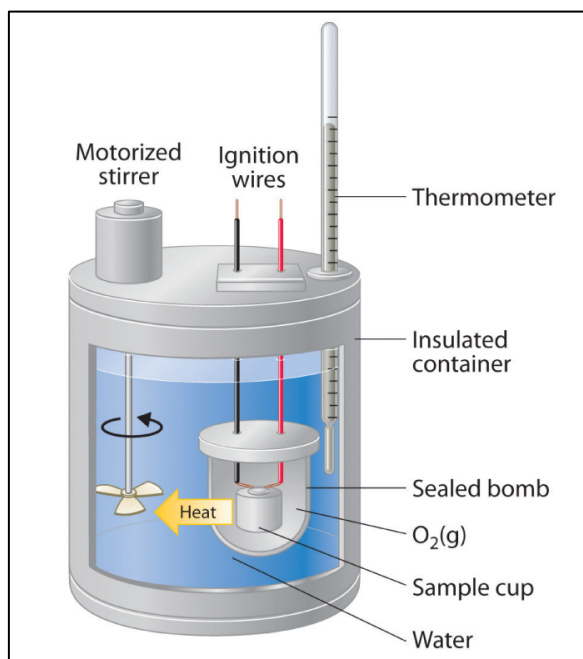$$\Delta H = mC\Delta T$$
ΔH = heat change of system
m = mass of system
C = specific heat
ΔT = temperature change

But this is hard to measure directly because the heat is given off in every direction, so the ΔT is not representative of the total energy. So why not **isolate the system** in a container?

Let's take our balloon and put it in a **sealed container**. The figure on the left shows a **bomb calorimeter**, which we use as that sealed container we need for **isolating the system**. But we still need to make sure ΔT is accurate and that we know C. Considering all of this, here's a trick that uses our conservation laws:

Motorized stirrer
Ignition wires
Thermometer
Insulated container
Sealed bomb
Heat
$O_2(g)$
Sample cup
Water

Since $\Delta E_{universe} = 0$ (and assuming the only E is heat)

Then
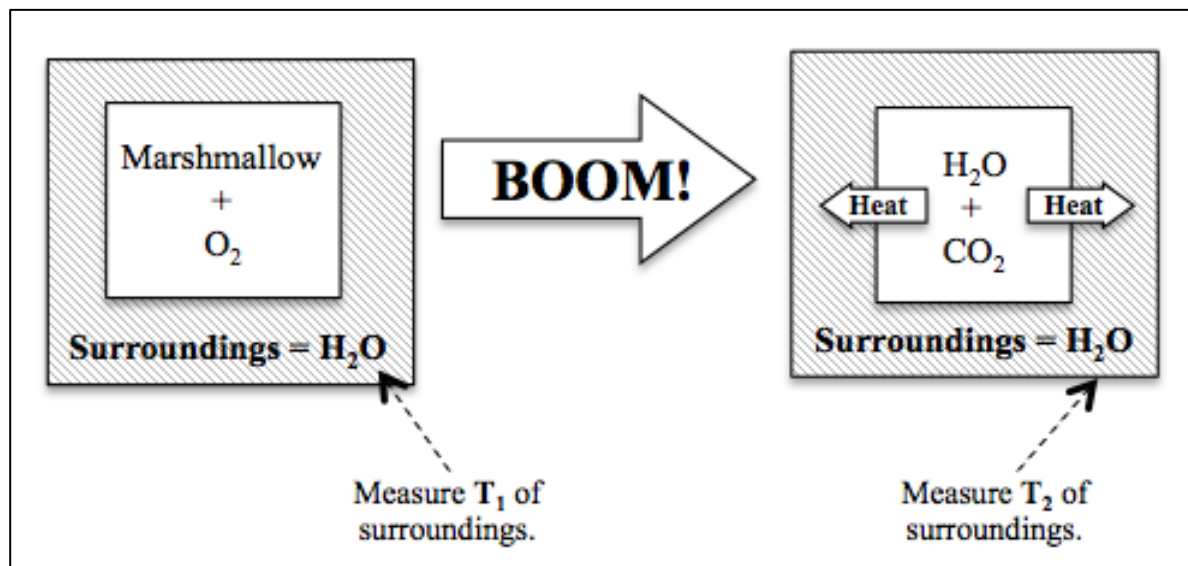
$$\Delta H_{universe} = 0 = \Delta H_{system} + \Delta H_{surrounding}$$

So

$$\Delta H_{system} = mC\Delta T = \Delta H_{surrounding} = mC\Delta T_{surrounding}$$

Why is this good? – Because if we choose as our surroundings something we're familiar with, like H_2O, then we have all the info we need to use the equation $\Delta H_{H_2O} = mC\Delta T$: the specific heat (**C**) of water is a known constant ($C_{H_2O} = 1$ **cal/1°C**); the **mass** of the water is whatever we set it as in our system; and we can measure ΔT from our reaction.

This is how they measure caloric content in food: put a marshmallow in a calorimeter, surround it with water, and explode the marshmallow. All the heat goes to the water surrounding it.

And then we just find $\Delta H_{marshmallow}$ using the calorimetry equation:

$$\Delta H_{marshmallow} = \Delta H_{system} = \Delta H_{surroundings} = mC\Delta T_{water}$$

LECTURE 22: STATISTICAL THERMODYNAMICS

So far we have discussed thermo in fairly simple terms that allowed us to do two useful things:

- Predict reaction spontaneity from:

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

- Perform simple calculations of:

$$\Delta G, \Delta H, \Delta S, \text{ bond energy, and work.}$$

This was all put together in worksheets and let us quickly feel competent in thermodynamics. But…it really played fast and loose with the underlying theory of thermo. It's all fine – it was just sloppy. Kind of like you didn't earn it.

So now you will earn it, with more sophisticated lectures on thermodynamic theory:

- Statistical thermodynamics
- Internal energy
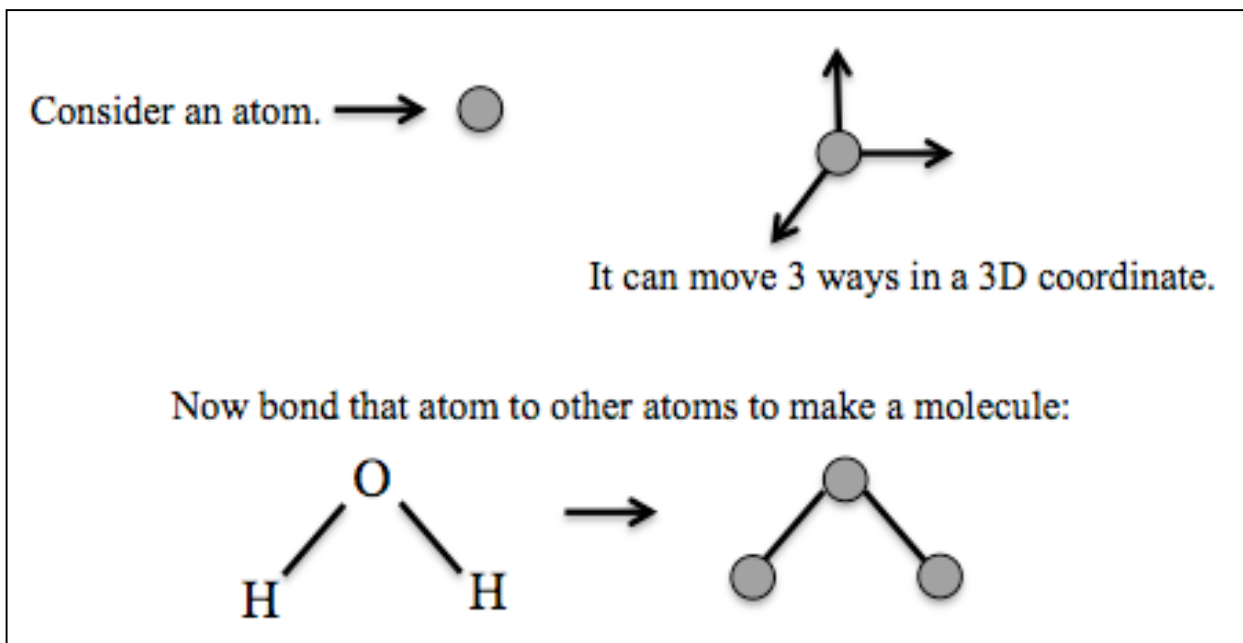- Entropy, equilibria, and free energy

STATISTICAL THERMO

To this point in thermo we have dealt entirely with bulk properties of a system: volume, temperature, pressure, free energy, enthalpy, entropy, and internal energy.

But what if we were to deal with the system **one molecule at a time** and ask questions about *its* **internal energy or entropy**? This is the study of **statistical thermodynamics.** And the short answer to that question is this:

To find **internal energy:**
$$E = \tfrac{1}{2}\, kT$$
…Which is the **energy per molecule, per degree of motional freedom** in a system.

To find **internal entropy:**
$$S = k\cdot\ln(W)$$
…Which is the **absolute entropy per molecule** in a system.

In both equations, the constant, **k,** is the **Boltzmann constant:**

$$k = 1.38 \times 10^{-23} \text{ J/K}$$
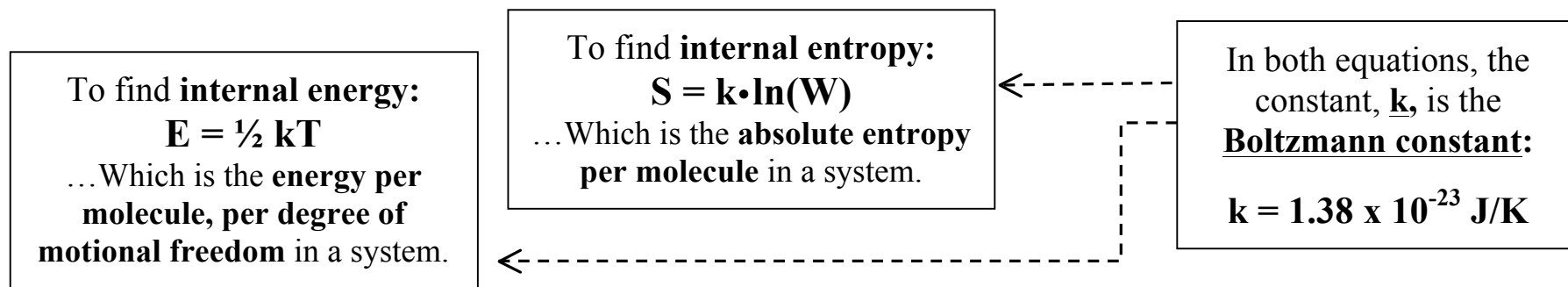
THE ORIGIN OF INTERNAL ENERGY

Consider an atom. → ◯

It can move 3 ways in a 3D coordinate.

Now bond that atom to other atoms to make a molecule:

O

H   H   →

If **each atom** has **three directions** in which to move, then **"N" atoms will have "3N" ways to move.** So for example, water has 9 total different kinds of movement. If you start playing with the vectors, you see that some times all the vectors for the atom are going in the same direction, and the molecule can **translate**. Other times the vectors oppose each other, and you get **vibrations**.

In fact there are three fundamentally different kinds of motion:

Translation: the molecule changes location.

Rotation: the molecule spins.

Vibration: the molecule twists.

Try to visualize a water molecule moving in these ways:

Translation – Imagine the water molecule moving to the left, because all 3 atoms are moving to the left. There are **3 directions** in which **all** molecules can translate: **up/down, left/right, and forward/backward.**
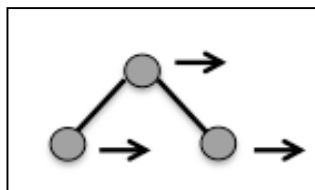
Rotation – Now imagine the water is spinning counterclockwise. There are **3 ways non-linear** molecules (the majority of molecules) can rotate. **Linear** molecules are the exception, as they can only rotate in **2 ways**.
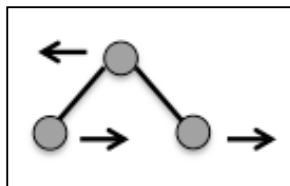
Vibration – Finally, imagine the molecule is vibrating. **Non-linear** molecules can vibrate in **3N – 6 ways** (6 = 3 translations + 3 rotations). **Linear** molecules can only vibrate in **3N – 5 ways** (5 = 3 translations + 2 rotations).
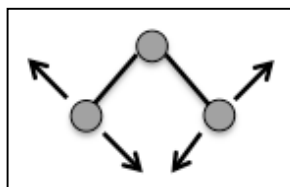
How much energy is associated with each movement? The amount is dependent upon temperature. **Equipartition theory** tells us that, for an average molecule, the **motional energy** is:

$$E = \tfrac{1}{2}\, kT$$

T = temperature, in degrees Kelvin (K)
k = Boltzmann constant = 1.38×10^{-23} J/K

Which means:

Translational energy of any molecule: $3 \times \frac{1}{2}kT = \frac{3}{2}kT$

Rotational energy of a non-linear molecule is: $3 \times \frac{1}{2}kT = \frac{3}{2}kT$

Rotational energy of a linear molecule is: $2 \times \frac{1}{2}kT = \frac{3}{2}kT$

So a **non-linear molecule** (most molecules) has:

$$\frac{3}{2}kT + \frac{3}{2}kT = 3kT \text{ of motional energy at room temperature.}$$

A **linear molecule** (like CO_2 or I_3^-) has:

$$\frac{3}{2}kT + \frac{2}{2}kT = \frac{5}{2}kT \text{ of motional energy at room temperature.}$$

But what about **vibrational energy**? – For our purposes, **room temperature doesn't provide enough energy** to excite vibrations, so we ignore energy produced by them.

So how do you calculate motional energy when you have **more than one molecule**? – Just **add up the motional energies** of the individual atoms. Look at the example below for a mole of molecules.

Time out for something utterly fascinating. Did you know that:

$$\mathbf{R = kN}$$

…Where **R** is the **ideal gas constant** (R = 8.3 J/mol·K), and **N** is **Avogadro's number** (N = 6.02 x 10^{23}).
(Recall from our unit on gases that, at **room temperature** (T = 300K), **RT = 2.5 kJ/mol**.)

So **one molecule's** motional energy is:

$$\frac{3}{2}kT + \frac{3}{2}kT = 3kT$$

While **one mole's** motional energy is:
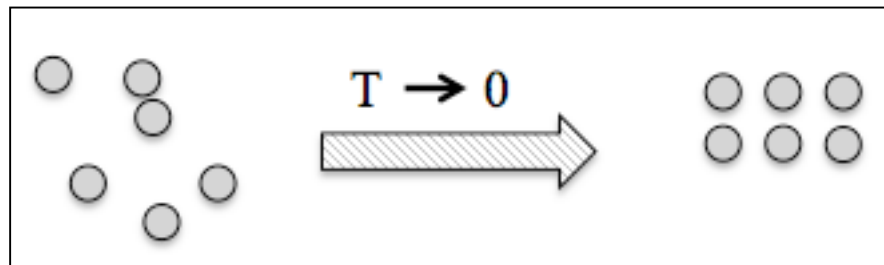
$$\frac{3}{2}RT + \frac{3}{2}RT = 3RT$$

Therefore, a **mole of non-linear gas molecules** at room temperature has **3RT = 7.5 kJ of motional energy**.

(Time in.)

ABSOLUTE ENTROPY

As **temperature decreases**, the **motional energy** of matter **decreases**. At that point, in the absence of motion, we start to form **perfectly ordered** crystals:

…And we see that **S decreases** as well.

We can think, though, about how the complexity of an individual molecule figures into the order. **Flip a symmetrical molecule 180°, and the molecule looks identical**; do that to an **asymmetrical molecule, however, and it no longer looks the same**:

Symmetrical Molecules	Asymmetrical Molecules
$O=O$, when flipped, is still $O=O$	$C\equiv O$, when flipped, is now $O\equiv C$
$O=C=O$, when flipped, is still $O=C=O$	

So in terms of the ability to order a compound, we would say that **O_2 and CO_2 have a** *lower* **absolute entropy than CO** – there is only **one orientation** for molecules of **O_2 and CO_2**, but there are **two orientations** for molecules of **CO**.

Boltzmann generalized the extent of **absolute entropy (S)**:

$$S = k \cdot \ln(W)$$

…**where W = the number of possible orientations = # of orientations$^{(\text{# of molecules})}$**

Example:
The number of orientations of different molecules:
- 4 molecules of O_2 → $1^4 = 1$ orientation
- 4 molecules of CO → $2^4 = 16$ orientations

Calculating the absolute entropy for those molecules:
- For O_2 → $S = k \cdot \ln W = (1.38 \times 10^{-23} \text{ J/K}) \cdot \ln(1) = 0 \text{ J/K}$
- For CO → $S = k \cdot \ln W = (1.38 \times 10^{-23} \text{ J/K}) \cdot \ln(16) = 3.8 \times 10^{-23} \text{ J/K}$

And if I have a mole of molecules it works the same way.

Example:
What is the S for a mole of BH_3, which has 1 possible orientation?

Solution:
$S = 1.38 \times 10^{-23} \cdot \ln(1^{(6.02 \times 10^{23})}) = 0 \text{ J/K}$

So we now have a way to find the absolute entropy of a system just by knowing how many particles are involved, as well as how they can orient themselves. But unfortunately, their orientations are not quite so simple: even though looking at a molecule's symmetry can tell us about its orientations, it might actually have a **"preferred" orientation** in the physical system. For example, HCl has two possible orientations:
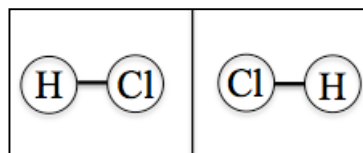
…So we would **expect $W = 2^n$**.

But **H-bonding** makes it more likely for the molecules to align themselves as H-Cl $\cdots\cdots$ H-Cl (with their δ- and δ= regions aligned), so an HCl molecule actually has **$W < 2^n$**.

We can find out a lot of interesting information about how packing occurs in solids by comparing experimentally-measured entropy to statistical thermodynamic values.
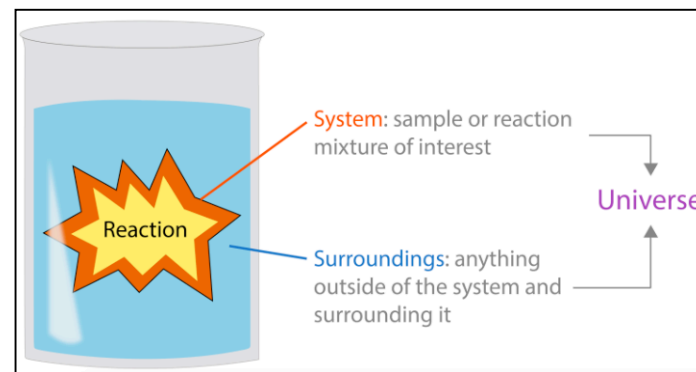
LECTURE 23: INTERNAL ENERGY

To begin studying **internal energy** (Δ**E**, or Δ**U**), we need to distinguish concepts of system and define state functions more precisely.
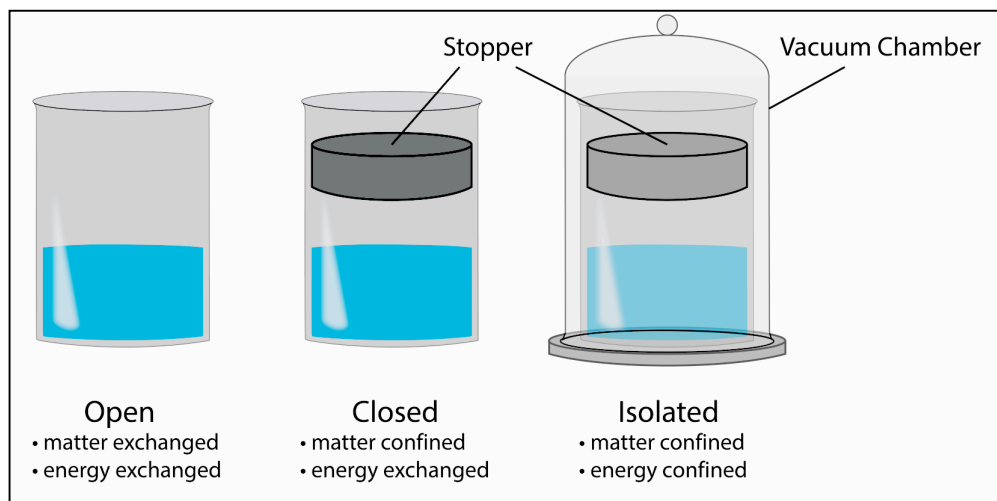
Recall:

Universe = System + Surroundings

Thermo studies the **flow of energy** – in **all forms** – between the chemical **system and its surroundings**.

To investigate the internal energy of the system, we need to think about different ways to create systems experimentally:

Open	Closed	Isolated
• matter exchanged	• matter confined	• matter confined
• energy exchanged	• energy exchanged	• energy confined

Open system:
The way we normally do reactions.
- Constant P
- ΔV

Closed system:
The equivalent of a bomb.
- Constant V
- ΔP

Isolated system:
Surroundings = a vacuum.
- Constant E
- Constant H
- Constant V

WORK (w)

We have discussed **work (w)** in past thermo lectures as the result of **gas molecules expanding against an external force**.
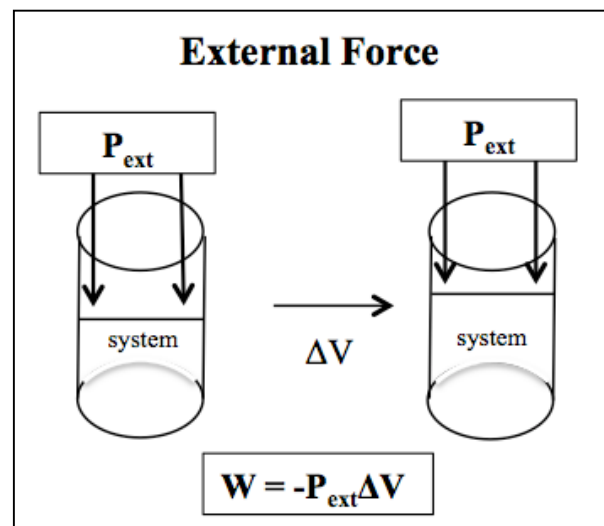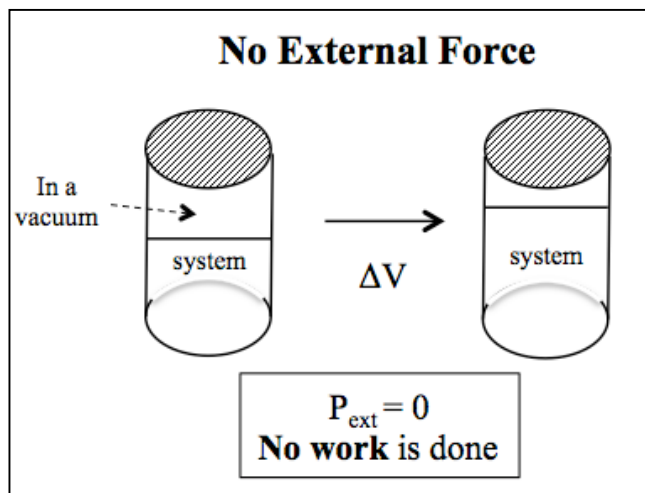
$$w = -P\Delta V = -\Delta nRT$$

But we haven't developed the source or limitations of this expression – until now.

Time out: be familiar with the +/- signs that tell whether **work is being done *to* or *by* a system**:
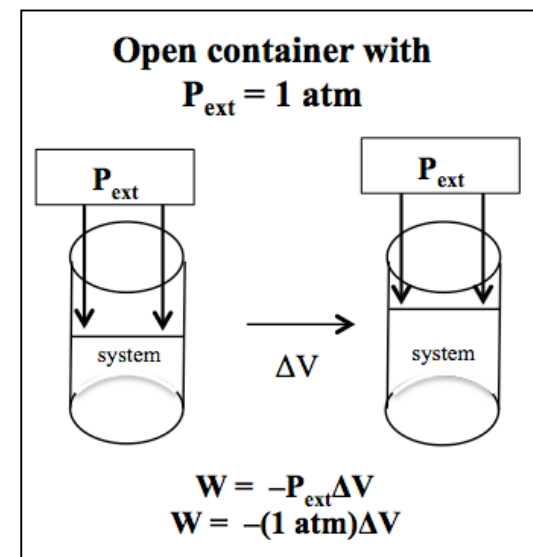
> ### If **w = (+)**:
> Work is done **on** the system.
> "Arming the bomb."
>
> ### If **w = (–)**:
> Work is done **by** the system.
> "Exploding the bomb."

Time in. Consider the idea of a **gas expansion** (**change in ΔV of a gas**), in the **presence or absence of external pressure** (P_{ext}):

No External Force

In a vacuum

system

ΔV

system

$P_{ext} = 0$
No work is done

External Force

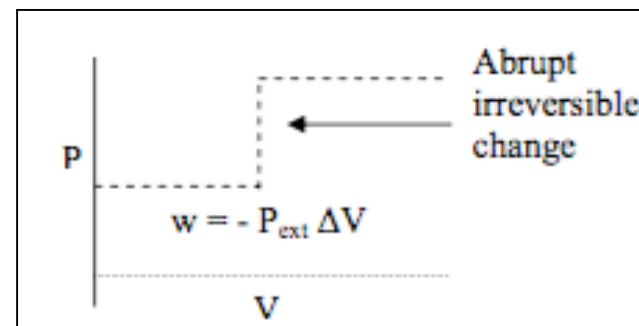P_{ext}

P_{ext}

system

ΔV

system

$W = -P_{ext}\Delta V$

Note that P_{ext} even happens in an **open container** because of the **1 atm** of **external pressure** we experience on the ground:

Open container with $P_{ext} = 1$ atm

P_{ext} P_{ext}

system   ΔV   system

$$W = -P_{ext}\Delta V$$
$$W = -(1\ atm)\Delta V$$
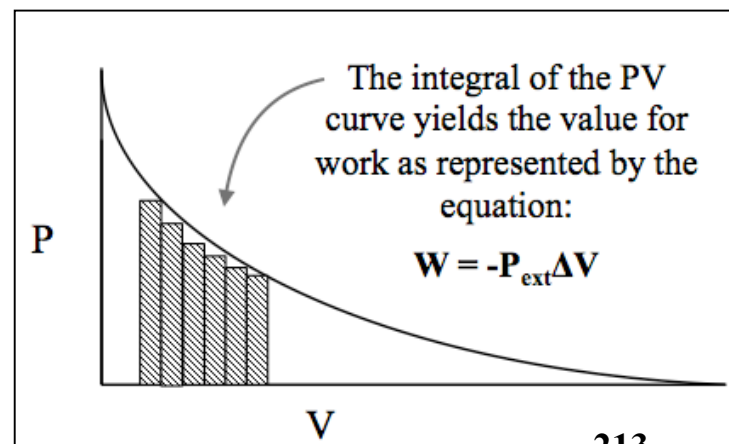
REVERSIBLE VS. IRREVERSIBLE WORK

Up to this point, we've only considered systems in which P_{ext} is **constant**, like atmospheric pressure or the force created by putting a cap on the system. Now it's time for a change:

Irreversible work: work done when a **system's pressure (P_{sys})** abruptly changes to **no longer match P_{ext}** (which is usually constant).

P

Abrupt irreversible change

$$w = - P_{ext}\,\Delta V$$

V
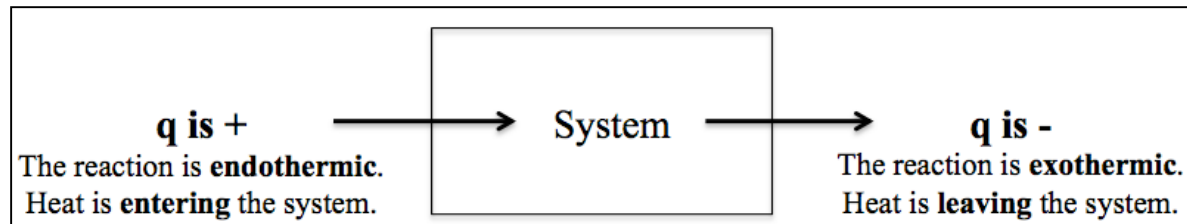
Reversible work: imagine a **changing P_{ext}** and a P_{sys} that matches it. Under these conditions, a reaction could **reverse** itself by an *infinitesimal change in P_{sys}*. We can create this scenario with a piston that is varied so that P_{ext} changes gradually when system pressure changes, either because of changes in T, n, etc.

P

The integral of the PV curve yields the value for work as represented by the equation:

$$W = -P_{ext}\Delta V$$

V

HEAT (q)

Not only can work change a system's energy – a transfer of **heat (q)** between the system and surroundings changes the amount of energy in the system, resulting in a temperature change.

Recall that in **endothermic** reactions, **q is (+)** because **heat is entering** the system. The reverse is true for exothermic reactions.

q is +
The reaction is **endothermic.**
Heat is **entering** the system.

System

q is -
The reaction is **exothermic.**
Heat is **leaving** the system.

Every material has its own capacity for transferring heat energy, and this is called the material's **specific heat (C):** the amount of heat needed to raise the temperature of the system by 1°C.

$$C = q / \Delta T$$

Two things matter in raising the temperature of a material: kind of material, and amount of material. For example, copper's $C = 0.38$ J/g °C; and water's $C = 4.18$ J/g °C.

THE FIRST LAW'S USE IN CALORIMETRY

Recall that we applied the first law of thermodynamics to calorimetry, to devise a method for finding foods' heat capacities.

The **first law** says that the total internal energy (ΔE_{sys}) of an **isolated system** is **conserved**:

$$\Delta E_{sys} = q + w$$

ΔE_{sys} **cannot change – but q and w** *can.* So we can **indirectly determine** ΔE_{sys} by measuring the amount of **energy** that moves **from system to surroundings**:

$$\Delta E_{sys} = -\Delta E_{surr \text{ (calorimeter)}} = -C\Delta T_{H_2O} + (-C\Delta T_{calorimeter})$$

HEAT (q) AND WORK (w) – NOT STATE FUNCTIONS

Recall that our definition of a **state function** was that its value depended solely on its **final quantity minus the initial quantity**. So, for example:

$$\Delta E = E_f - E_i \qquad \qquad \Delta T = T_f - T_i \qquad \qquad \Delta H = H_f - H_i$$

…And the same for **ΔV, ΔP, ΔG, ΔS**. All are state functions.

But **q and w are *not* state functions**.

Why, you ask? – Because the **path *does* matter** for the amounts of **q and w** in the reaction. That's the case, even though their combined total (ΔE; remember: $\Delta E = q + w$) *is* a state function and doesn't itself depend upon path.

Here are examples of a reversible process and an irreversible process as they relate to w and q:
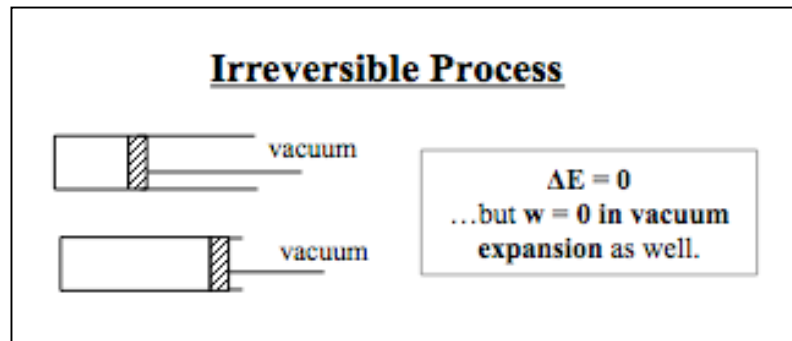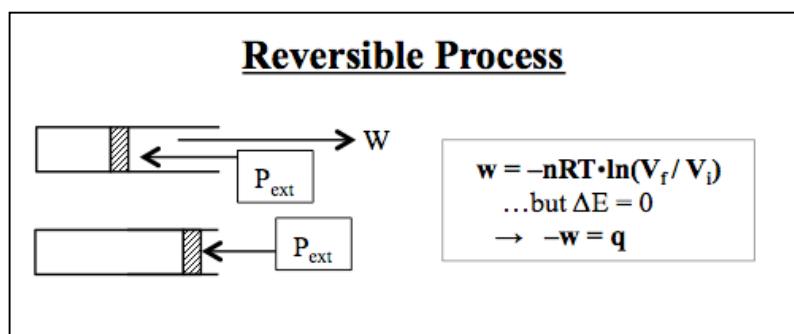
Before moving on from work and heat, let's remind ourselves one more time of their signs, and what those signs tell us about whether things are entering or leaving the system:
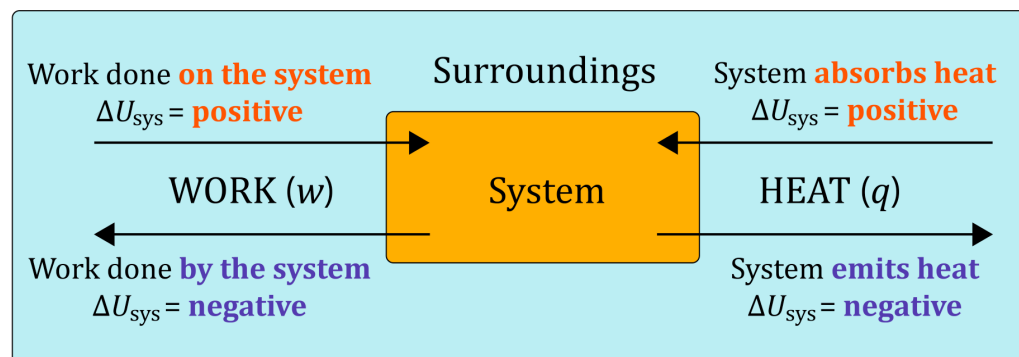
ENTHALPY

We sure have spent a lot of time on ΔE and ignored ΔH, which seems odd since we use ΔH to determine a reaction's spontaneity from $\Delta G = \Delta H - T\Delta S$. But worry not about ΔH – now it returns.

We know that $\mathbf{\Delta E}$ is really useful in **closed environments**, because a sealed system has $\mathbf{\Delta V = 0}$, which means that $\mathbf{w = 0}$. This is why $\mathbf{\Delta E = q}$ in a **bomb calorimeter**. But we do most experiments in **open containers**, so there typically is **expansion work**, and $\mathbf{P\Delta V \neq 0}$. Which means we need a way to keep track of both that **expansion work** and $\mathbf{\Delta E}$:

$$\mathbf{\Delta H = \Delta E + P\Delta V}$$
ΔE = system energy
$P\Delta V$ = expansion work

From here, we can perform an exciting derivation of ΔH at atmospheric pressure:

$\Delta H = \Delta E + P\Delta V$
$\Delta H = q + w + P\Delta V$
$\Delta H = q - P_{ext}\Delta V + P\Delta V$
…But $P_{ext} = P_{sys}$ in open container.
So $\Delta H = q$ when P is constant.

So…drum roll, please!

In a **bomb calorimeter**, where **V is constant**:

$$\mathbf{\Delta E = q}$$

In a **coffee cup calorimeter**, where **P is constant**:

$$\mathbf{\Delta H = q}$$

EPILOGUE: RELATING ΔH TO ΔE

- If there is no gas present $\rightarrow$ $P\Delta V$ is negligible $\rightarrow$ $\Delta H \approx \Delta E$.
- If there is gas present, and the reaction is at a constant P $\rightarrow$ $\Delta H = \Delta E + P\Delta V$ $\rightarrow$ $\Delta H = \Delta E + \Delta nRT$ $\rightarrow$ the work quantity (ΔnRT) comes into play.

LECTURE 24: ENTROPY – THE TRUTH BEHIND SPONTANEITY

We have defined spontaneity through ΔG:

$$\text{If } \Delta G = (–) \rightarrow \text{ Reaction is \textbf{spontaneous}}$$
$$\text{If } \Delta G = (+) \rightarrow \text{ Reaction is \textbf{non-spontaneous}}$$

And we have seen that reactions can occur:
- Whether a reaction is endothermic or exothermic.
- Whether the entropy of a system increases or decreases.

Clearly something more profound is at work here than just the first law's concept of energy conservation. So what's the deeper insight?

The **second law of thermodynamics** says that:

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

(Note: in most examples, "the isolated system" is the **universe**.)

We're already familiar with seeing physical processes gradually increase in disorder:
- Food coloring distributes itself throughout a beaker of water.
- A hot block of metal cools to room temperature.

But we are less accustomed to understanding this in chemical processes, especially when considering reactions in which the system's energy increases (endothermic), or ones in which its entropy decreases (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

In a reversible process happening at a constant T:

$$\Delta S = \frac{q}{T}$$

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

Solution:
  $\Delta S = (100 \text{ J}) / (273 \text{ K}) = 0.366 \text{ J/K}$

Is there a way to describe $\Delta S = \frac{q}{T}$ that makes physical sense?

The key is to realize that, when 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**?

In the context of the above example, the equation says:

<div align="center">

100 J makes a bigger mess at 1 K than it would at 1,000 K

…which means…

ΔS is a lot larger at 1 K than 1,000 K

</div>

Here's a famous analogy: think about sound during an exam versus sound during a concert. At a concert, if someone coughs, it's barely noticed – he increases the noise level by a negligible amount. But when you're sitting in a quiet room taking a test, a cough of the exact same volume seems so loud that it makes you want to punch the guy with the cold.

GLOBAL CHANGES IN ENTROPY

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

ΔS_{total} = change in entropy of the **isolated system.**
ΔS_{surr} = change in entropy of the **surroundings.**
ΔS_{sys} = change in entropy of the **system.**

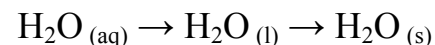So… $\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys}$

And we know from the second law that a reaction **only spontaneous if $\Delta S_{total} > 0$.**

This shows us that ΔS_{sys} **can be negative and a reaction still be spontaneous**… *But only if*:

$$|\Delta S_{surr}| \ > \ |\Delta S_{sys}|$$

Some famous examples of reactions in which $\Delta S_{sys} = (-)$ 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 when water turns from liquid to solid, there must be an **increase in** ΔS_{surr} **driving the reaction.**

Here is the $\Delta S°$ table 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 can calculate this with statistical thermo!
↓
Ice freezing: $\Delta S° = -22$ J/kmol

So according to the second law, if water freezes spontaneously at temperatures below 0°C (which we know to be true), then:

$$\Delta S°_{surr} > 22 \text{ J/kmol} \qquad \text{...at } T < 0°C$$

We know $\Delta S = \dfrac{\Delta H}{T}$ → so at -10°C (263K), the ΔH_{fusion} of ice becomes heat in its surroundings. Let's calculate that:

$\Delta S = \Delta H/T$ → $\Delta H = T\Delta S$ → $\Delta H = (-22 \text{ J/kmol}) \cdot 263K$ → $\Delta H \approx 6{,}000 \text{ J/mol·K}$ → $\Delta H_f \approx -6 \text{ kJ/mol·K}$ (for H_2O)
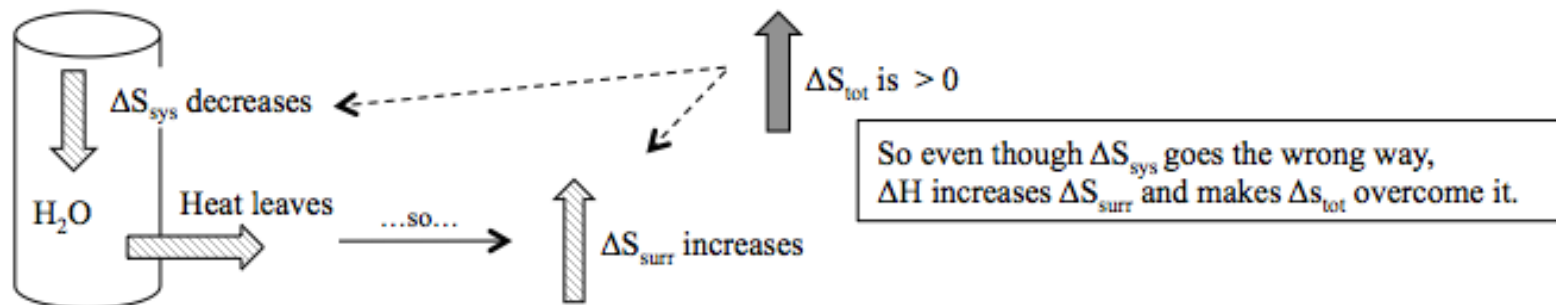
So $\Delta S_{surr} > \Delta S_{sys}$ **below T = 0°C**, which lets **water freeze spontaneously**. Can we make sense of this qualitatively? Yes – the **heat** that leaves the system when ice freezes is goes **into the surroundings** (conservation of energy), which is a colder environment. Remember that **disruption is greater** in a colder place or a quieter room than it would be in a warmer place or louder room. So the 6,000 J of **heat make a bigger relative mess in the surroundings** (-10°C) than in the system (0°C).
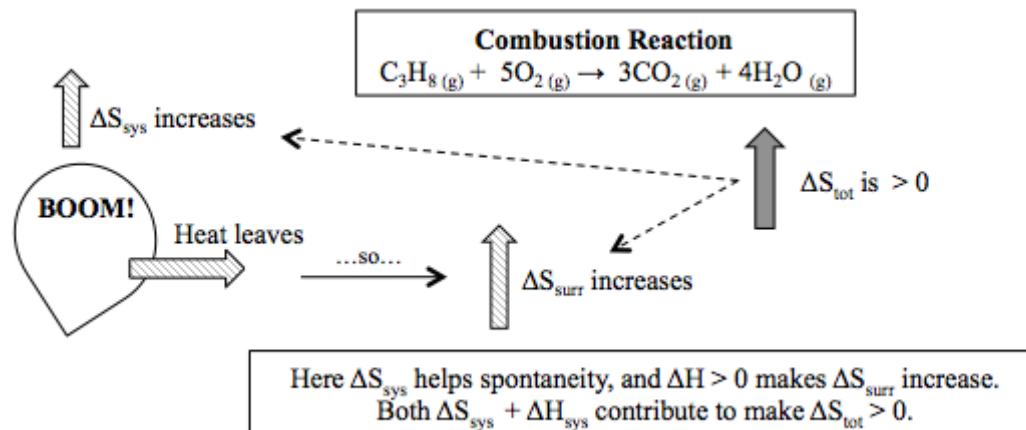
EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

The reaction of water freezing is an exothermic one (so heat is leaving the system). This means that there will **always** be an **increase in ΔS_{surr} when heat leaves, which aids spontaneity, even when ΔS_{sys} is negative.** Examples #1 and 2 are of exothermic reactions.

Example #1 – exothermic, ΔS_{sys} decreases:
    Water vapor condenses: $H_2O_{(g)}$ → $H_2O_{(l)}$

ΔS_{sys} decreases

H_2O Heat leaves   ...so... ΔS_{surr} increases

ΔS_{tot} is > 0

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

Example #2 – exothermic, ΔS_{sys} increases:

Combustion Reaction
$C_3H_{8\ (g)} + 5O_{2\ (g)} \rightarrow 3CO_{2\ (g)} + 4H_2O_{\ (g)}$

ΔS_{sys} increases

BOOM!

Heat leaves

...so...

ΔS_{surr} increases

ΔS_{tot} is > 0

Here ΔS_{sys} helps spontaneity, and $\Delta H > 0$ makes ΔS_{surr} increase.
Both $\Delta S_{sys} + \Delta H_{sys}$ contribute to make $\Delta S_{tot} > 0$.

But how can **endothermic processes** be spontaneous if ΔE_{sys} **gets stronger**? Isn't energy going the wrong way?

Answer? **It's entropy (not energy), and entropy drives spontaneity.** Example #3 is of an endothermic reaction.

Example #3 – endothermic, ΔS_{sys} increases:
   Ice melts: $H_2O_{\ (s)} \rightarrow H_2O_{\ (l)}$

ΔS_{sys} increases

Heat enters

...so...

ΔS_{surr} decreases

ΔS_{tot} is > 0
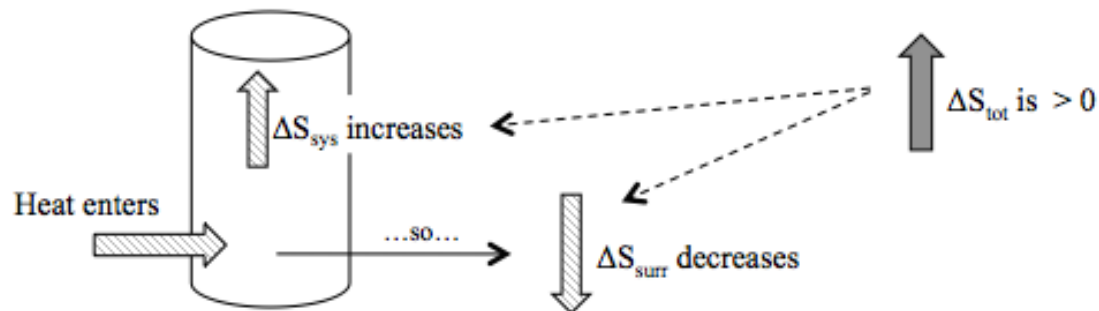
Now we can look at cases of $\Delta G = (-)$ in a new light, where $\Delta H = (\pm)$ affects $\Delta S = \Delta H/T$ and either drives or stalls spontaneity.

# LECTURE 25: EQUILIBRIUM, FREE ENERGY, AND TEMPERATURE

We'll use this lecture to expand upon three topics we've already discussed in thermo. Learning a bit more about each of these should help you in putting together all of our thermo topics, and building links between them.

EQUILIBRIUM

We hinted at **equilibrium** while discussing thermodynamics (for example, noting that at a phase change, like melting or boiling, a system is at equilibrium). But equilibrium is actually so useful that we will spend 90% of next semester's CH 302 course studying it!

A system at **equilibrium** is defined as having **no tendency to change its current state**. For a system at equilibrium, then its state functions – internal energy, pressure, volume, temperature, enthalpy, free energy, entropy – **retain the same value**.

You can imagine equilibrium in many ways, such as **thermal**, **mechanical**, and **chemical**:

Chemical equilibrium

Mechanical equilibrium

Thermal equilibrium
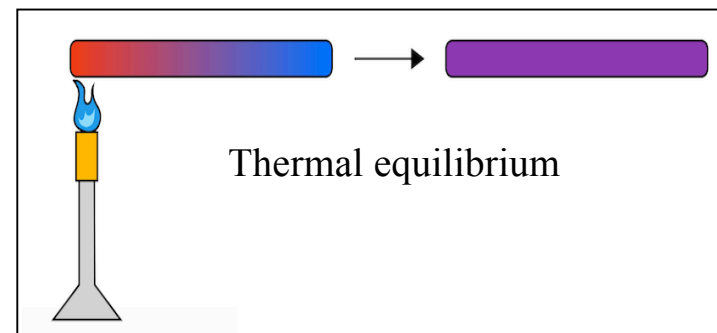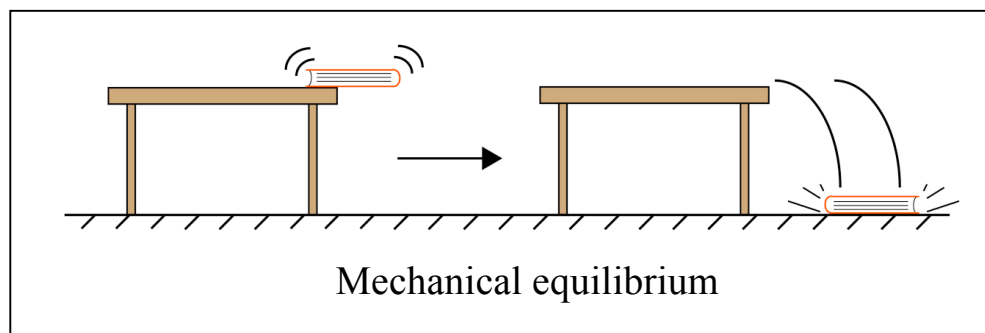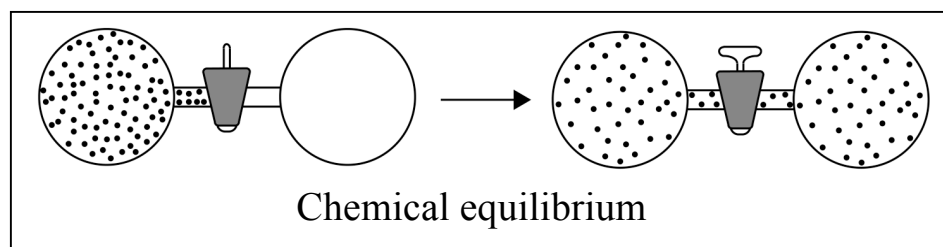
Note that even though a system's overall state functions don't change at when it's at equilibrium, on a **molecular level** there is plenty of action, as molecules are constantly transferring energy locally. For example, in a water-ice mixture, there are always ice molecules becoming liquid molecules, and liquid becoming ice. This is called **dynamic equilibrium**.

But the point of equilibrium is that the **rates** of both the **forward and reverse reactions don't change** (i.e., the relative numbers of water and ice molecules remain the same). So from **our external, macroscopic vantage, nothing is changing**.

Definition of **equilibrium:**

$$\Delta S_{univ} = 0$$

(Or as we will see soon: $\Delta G = 0$.)

We've already exploited this handy definition – recall that we are at equilibrium at a phase change (like ice melting). So:

$$\Delta G = 0 = \Delta H - T\Delta S \qquad \text{or, equivalently,} \qquad T_{boiling} \text{ or } T_{freezing} = \Delta H/\Delta S$$

Temperature of phase change

FREE ENERGY – ΔG

We have already learned that **ΔG** is a measure of reaction **spontaneity** and have come to appreciate that it gives a sense of a reaction's **drive to completion**. In the context of our new concept of equilibrium, we can construct a figure that shows us a reaction – from both the forward and reverse directions – being driven by a release of energy to the surroundings, which comes to a stop when $\Delta G = 0$. At that point, equilibrium has been reached, and the state functions remain constant.
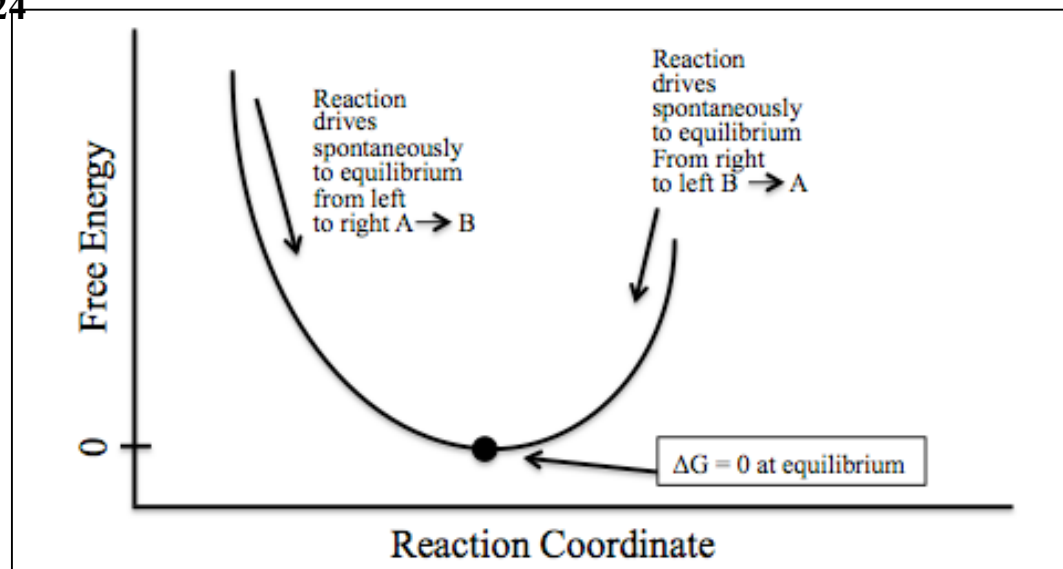
The $\Delta G = 0$ will correspond to aa specific ratio of reactant concentrations.

In this case it's A $\leftrightarrow$ B, where at some point, [A] and [B] are in equilibrium at $\Delta G \neq 0$.

So why bother with ΔG if the measure of spontaneity is $\Delta S_{univ} = 0$, as seen in the second law? The reason is that it's easier to take stock of the **system's – rather than the surroundings' – parameters** in determining spontaneity. For this equation:

$$\Delta S_{univ} = \Delta S_{surr} - \Delta S_{sys}$$

…Wouldn't it be better if ΔS_{univ} was a system function? The answer is yes, and that's what we use ΔG for – to tell us about spontaneity based on a system's state functions. Let's derive:

$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$	2nd law of Thermo.
$\Delta S_{univ} = \dfrac{-\Delta H_{sys}}{T} + \Delta S_{sys}$	$\Delta S_{surr} = \dfrac{-\Delta H_{sys}}{T}$
$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$	Multiply by $-T$
$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$	Define $\Delta G = -T\Delta S_{univ}$ (for constant T and P)

With **ΔH and ΔS as system parameters**!
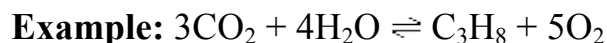
TEMPERATURE DEPENDENCE OF SPONTANEITY

Now for a bit of a review. Since we have $\Delta G = \Delta H - T\Delta S$ to determine spontaneity, we see that **temperature** controls the relative **magnitude of ΔH and ΔS**. Consider four cases:

1. **$\Delta H = (-)$, $\Delta S = (+)$** $\rightarrow$ exothermic; ΔS_{sys} increases $\rightarrow$ this means the reaction will ***always happen***, because $\Delta G = (-)$, no matter the temperature.

   **Example:** $C_3H_8 + 5O_2 \rightleftharpoons 3CO_2 + 4H_2O$
    …So ΔS is positive because more molecules formed, ΔH is negative because it is combustion.

2. **ΔH is $(+)$, ΔS is $(-)$** $\rightarrow$ endothermic; ΔS_{sys} decreases $\rightarrow$ this means the reaction will ***never happen***, because $\Delta G = (+)$ at all temperatures.

   **Example:** $3CO_2 + 4H_2O \rightleftharpoons C_3H_8 + 5O_2$
    …This is exactly the opposite/reverse reaction of case #1's, so it never happens. (Recall: if a reaction is spontaneous in one direction, it is nonspontaneous in the other.)

3. **ΔH is $(+)$, ΔS is $(+)$** $\rightarrow$ endothermic; ΔS_{sys} increases $\rightarrow$ this is a ***temperature-dependent*** process – at ***high T***, the **$(-)T\Delta S$ dominates the $(+)\Delta H$**, and the reaction occurs.
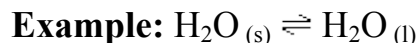
    Example: $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$
    … ΔS is $(+)$ because of the making of a liquid, and ΔH $(+)$ because heat enters system. If you didn't notice, this reaction is ice melting, and we all know that won't occur in the low temperature of the freezer.

4. **ΔH is $(-)$, ΔS is $(-)$** $\rightarrow$ exothermic; ΔS_{sys} decreases $\rightarrow$ this is ***temperature-dependent*** – at ***low T***, the **$(-)\Delta H$ dominates the $(+)T\Delta S$**, and the reaction occurs.
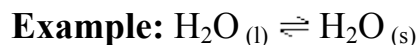
    Example: $H_2O_{(l)} \rightleftharpoons H_2O_{(s)}$
    …Opposite of case #3. In this reaction, liquid water is freezing, which only occurs at low temperatures, like those of a freezer.

GIBBS FREE ENERGY OF FORMATION (ΔG_f°) TELLS US COMPOUND STABILITY

We have learned the convenience of formation reactions by using heats of formation (ΔH_f°) – along with Hess' Law – to calculate the ΔH_{rxn} value for any reaction. Recall that these ΔH_f° values are compiled in tables.

We can do the same thing with ΔG_f° values, which are also pre-tabulated and found in tables. For example, the table below has the ΔG_f° value for each of the following reactions:
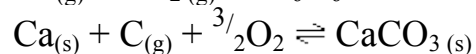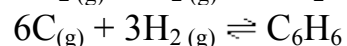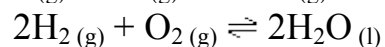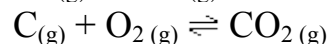
$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$

$C_{(g)} + O_{2\,(g)} \rightleftharpoons CO_{2\,(g)}$

$2H_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(l)}$

$6C_{(g)} + 3H_{2\,(g)} \rightleftharpoons C_6H_6$

$Ca_{(s)} + C_{(g)} + {}^3/_2O_2 \rightleftharpoons CaCO_{3\,(s)}$
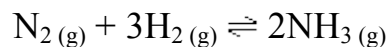
Table of ΔG_f° (kJ/mol)	
NH_3	-16
CO_2	-394
H_2O	-228
C_6H_6	+124
$CaCO_3$	-1128

We can use these values in any combination in the expression:

$$\Delta G^\circ{}_{rxn} = \sum \Delta G_f^\circ{}_{products} - \sum \Delta G_f^\circ{}_{reactants}$$

Similarly, we can calculate:

$$\Delta H^\circ{}_{rxn} = \sum \Delta H_f^\circ{}_{products} - \sum \Delta H_f^\circ{}_{reactants}$$

…and…

$$\Delta S^\circ{}_{rxn} = \sum \Delta S_f^\circ{}_{products} - \sum \Delta S_f^\circ{}_{reactants}$$

And you will see that in combination:

$$\Delta G^\circ{}_{rxn} = \Delta H^\circ{}_{rxn} - T\Delta S^\circ{}_{rxn}$$

IS A COMPOUND STABLE?

Wow, now we have a direct measure – ΔG_f° – of whether a compound has the tendency to degrade into its elemental form.

If $\Delta G_f^\circ = (+)$:
The compound is **stable** and will not degrade.

If $\Delta G_f^\circ = (-)$:
The compound is **unstable** and will degrade.

Examples from table above:

$\Delta G_f^\circ = (+)$:
NH_3, H_2O, CO_2, $CaCO_3$

$\Delta G_f^\circ = (-)$:
C_6H_6 (benzene)

Labile: means $\Delta G_f^\circ = (+)$ and compound **degrades quickly.**
Non-labile: means $\Delta G_f^\circ = (+)$ and compound **degrades slowly.**

So benzene – which is unstable – can spend time hanging around in bottles (albeit while causing cancer), so we describe it as non-labile. On the other hand, hydrogen peroxide – also unstable –goes bad just sitting on a kitchen counter, so we call it labile.