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:

ΔH	(-)	Exothermic, Heat Released, Hot
	(+)	Endothermic, Heat Absorbed, Cold
ΔG	(-)	Spontaneous
	(+)	Non Spontaneous
ΔS	(+)	Disordered
	(-)	Ordered
w	(-)	A Bomb, Work Done on Surroundings
	(+)	"Arming a Bomb" Work Done on System

But now we will be adding numbers:

$$\mathbf{C_3H_8 + 5O_2 \rightleftharpoons 3C0_2 + 4H_2O}$$

Is **NOT** just ΔG = (-)   It **IS** ΔG = -2070kJ which means it is really spontaneous.

(Still, while we learn to do these calculations, don't forget the importance of simply looking at a reaction and being able to assign the signs! It is 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, $\Delta n_{gas,}$ w, ΔS, and ΔG. At the least provide a sign, but if you can offer a guess of the magnitude without using a calculator, that is even better.

First the signs. Can you explain how you know them?

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

And now the calculations.

Chemical Reaction	ΔH (kJ)	BE (kJ)	Δn_{gas}	w(kJ)= -ΔnRT	Δn_{sys}	TΔS (kJ)	ΔG (kJ)
$CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ Combustion reaction, would predict large heat and spontaneous reaction. Δn = 0 means no work, small entropy change	-802	-802	0	0	0	-1	-801
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ Spontaneous combustion reaction, would predict large heat. Δn = negative which means entropy decreases and work on system	-484	-482	-1	+2.5	-1	-27	-458

Two central concepts to remember as we do calculations:

1. Why signs are what they are. Remember, it is not just arbitrary to say **ΔH** is **(-)** for exothermic. It is a consequence of our having identified with energy flow to and from the system.

2. The fundamental concept behind calculations is Hess' Law, which says the path does not matter, it is just Δ = (how it ended - how it started.) Which is why there will be more than one way to calculate Δ state functions for a reaction.

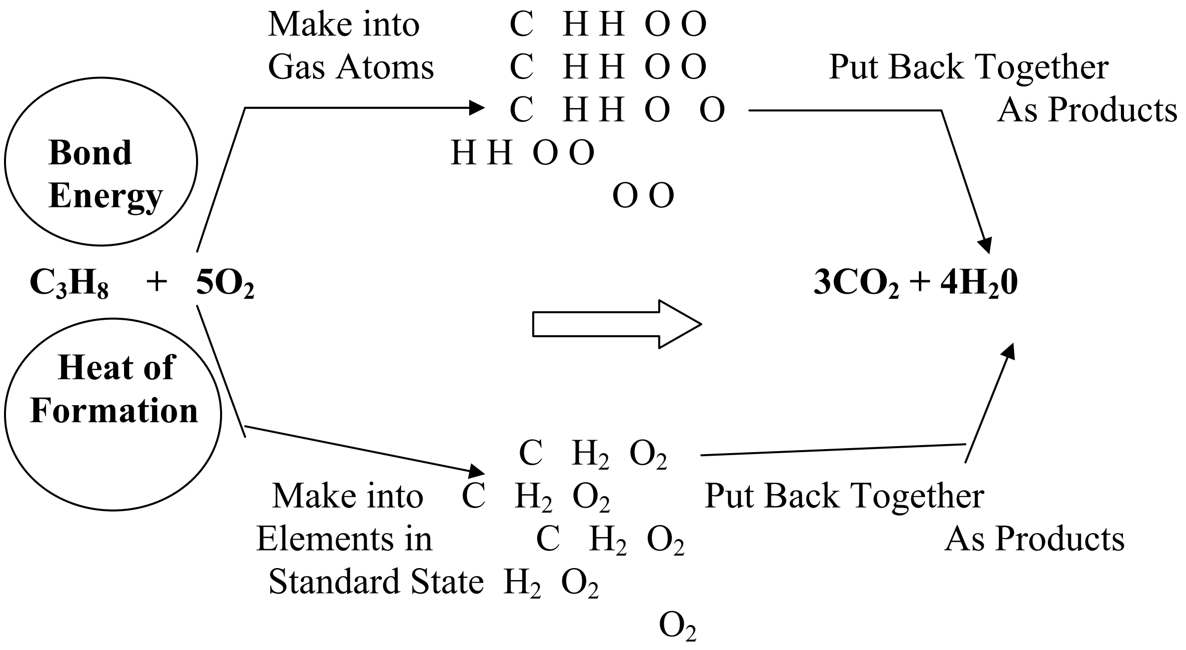
First Thermodynamic calculation: Measuring Heat of the System, ΔH

For example, in calculating enthalpy change, ΔH, Hess' Law says that these 3 very different methods all yield the same answer for ΔH_{rxn} and you will need to learn how to do each of them

Three calculations of ΔH

ΔH_f°	Heat of Formation
BE	Bond Energy
$\Delta H_{calorimeter}$	Bomb Calorimeter

Let's apply Hess' Law here: Consider three ways to determine heat of reaction for a propane explosion



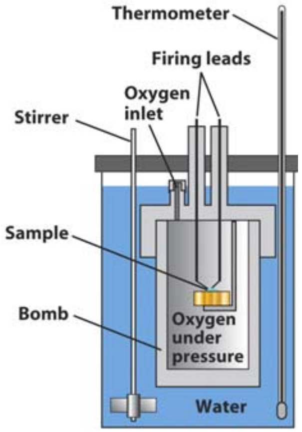
The Bomb Calorimeter Calculation.

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

$$\underset{\textbf{Of System}}{\textbf{Heat Change}} \longrightarrow \Delta H = \underset{\underset{\textbf{Mass of System}}{\uparrow}}{m}\overset{}{\underset{\nwarrow\,\textbf{Specific Heat}}{C}}\Delta T \longleftarrow \textbf{Temperature Change}$$

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

Balloon in a Sealed Container



But we still need to make sure ΔT is accurate and that we know C. So here is a trick that uses conservation laws.

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

Then

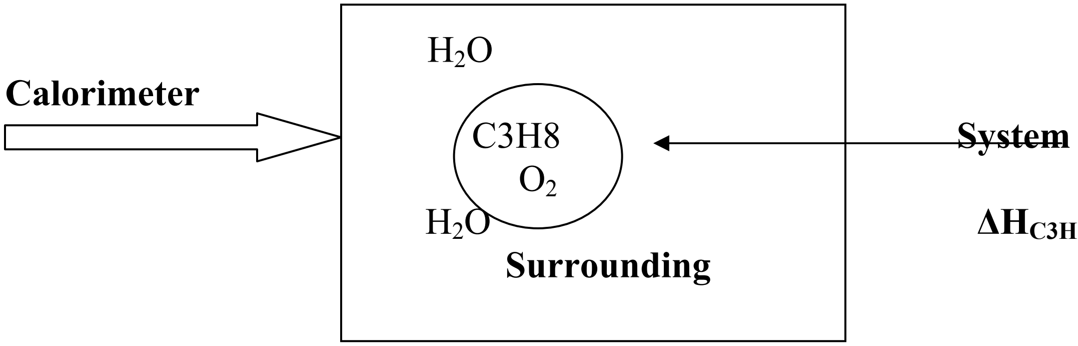
$$\Delta H_{universe} = 0 = \Delta H_{system} + \Delta H_{surrounding}$$

So

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

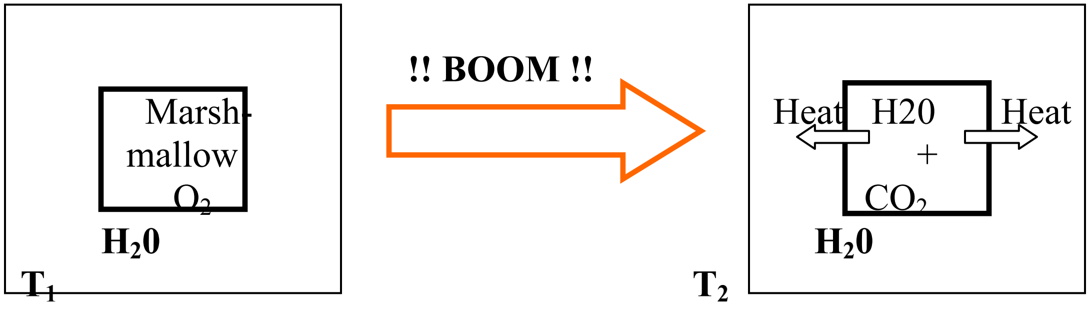
Why is this good?

Make the surroundings something you know, like H_2O. for which you can measure ΔT. It is easy to find $\mathbf{T_1 + T_2}$ of H_2O and mass of water and $\mathbf{C_{H20} = 1\ cal/\ 1°C}$



$$\Delta H_{C3H8} = \Delta H_{H2O} = mC\Delta T_{H2O}$$

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



So we find ΔH marshmallow using the **Calorimetry Equation**

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

On to to other methods to measure ΔH

Method 2: B.E. (Bond Energy): In this method the molecules become gas atoms and you calculate ΔH from differences in energy to tear apart and reform molecules like a tinker toy set.

Method 3: ΔH_f (Heat of Formation): In this method the molecules become elements in standard states (298K, 1atm) and then reform products.

A comparison:

B.E.	**ΔH_f**
1. Easy conceptually	1. Tougher Conceptually
2. Uses tables of bond energy	2. Uses Appendixes of formation data
3 Only correct for gases	3. Applicable for all states of matter (g,l,s)
	4. Can be used for ΔH_f, ΔS_f, ΔG_f (See Appendix)

Now let’s perform **BE** and **ΔH_f** calculations on

$$C_3H_8 + 5O_2 \quad 3CO_2 + 4H_2O$$

First find values for B.E. of various bonds as well as ΔH_f, ΔS_f, ΔG_f (this information is in the text in appendices and on the web—you will always be given this info on an exam.)

The propane combustion data from Tables and Appendices:

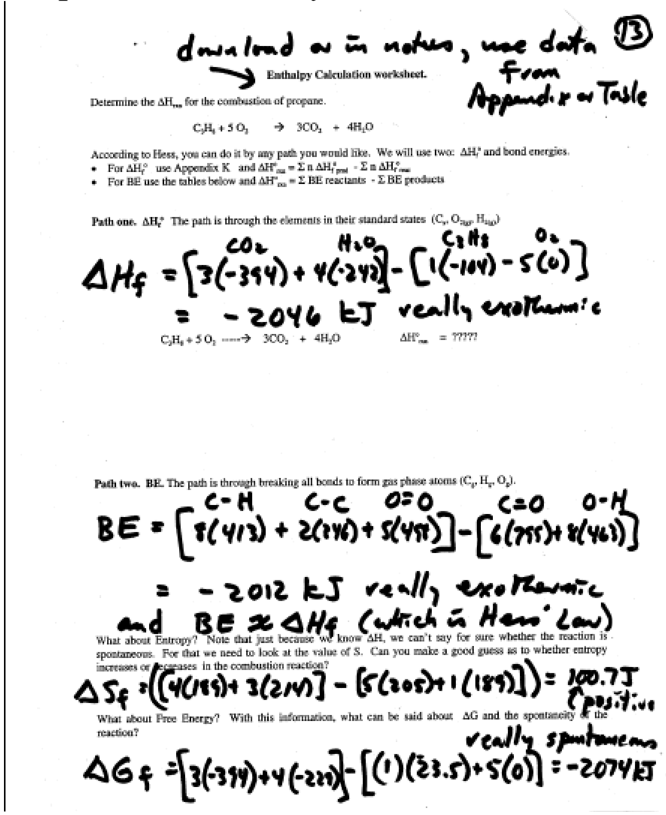
B.E. values	ΔH_f, ΔS_f, ΔG_f				
C-C, **C-H**, **O=O**,	C_3H_8		O_2	CO_2	H_2O
346kJ, 413kJ, 458kJ	**ΔH (kJ)**	-104	0	-374	-242
C=O **O-H**	**S (J)**	270	205	-214	-189
799kJ 463kJ	**ΔG (kJ)**	-23	0	-394	-229

And of course you have equations that are variations on Hess's Law.

For Bond Energies: $\text{B.E.} = \boldsymbol{\Sigma}\text{BE}_{\text{react}} - \boldsymbol{\Sigma}\text{BE}_{\text{prod}}$

For Heats of Formation: $\Delta H_f = \Delta H_{\text{prod}} - \Delta H_{\text{reac}}$

And the calculations are done below. Note that BE calculations are the one exception to the convention of subtracting products from reactants. The reason is that the BE values should actually be a negative sign reflecting energy release, but because they are positive values by convention in the BE tables, the equation for the BE calculation is reversed.



download or in notes, use data from Appendix or Table ⑬

→ Enthalpy Calculation worksheet.

Determine the ΔH_{rxn} for the combustion of propane.

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

According to Hess, you can do it by any path you would like. We will use two: $\Delta H_f°$ and bond energies.

- For $\Delta H_f°$ use Appendix K and $\Delta H°_{rxn} = \Sigma n \Delta H_f°_{prod} - \Sigma n \Delta H_f°_{react}$
- For BE use the tables below and $\Delta H°_{rxn} = \Sigma$ BE reactants $- \Sigma$ BE products

Path one. $\Delta H_f°$ The path is through the elements in their standard states (C_s, $O_{2(g)}$, $H_{2(g)}$)

$$\Delta H_f = [\overset{CO_2}{3(-394)} + \overset{H_2O}{4(-242)}] - [\overset{C_3H_8}{1(-104)} - \overset{O_2}{5(0)}]$$

$$= -2046 \text{ kJ}$$ really exothermic

$C_3H_8 + 5O_2 \dashrightarrow 3CO_2 + 4H_2O$ $\Delta H°_{rxn}$ = ?????

Path two. BE. The path is through breaking all bonds to form gas phase atoms (C_g, H_g, O_g).

$$BE = [\overset{C-H}{8(413)} + \overset{C-C}{2(348)} + \overset{O=O}{5(498)}] - [\overset{C=O}{6(799)} + \overset{O-H}{8(463)}]$$

$$= -2012 \text{ kJ}$$ really exothermic

and $BE \approx \Delta H_f$ (which is Hess' Law)

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

$$\Delta S_f = ([4(189) + 3(214)] - [5(205) + 1(189)]) = 100.7 \text{ J}$$ (positive

What about Free Energy? With this information, what can be said about ΔG and the spontaneity of the reaction?

really spontaneous

$$\Delta G_f = [3(-394) + 4(-229)] - [(1)(23.5) + 5(0)] = -2074 \text{ kJ}$$