

Unit 4 Review 2

THERMODYNAMICS: ENTHALPY, CALORIMETRY, HESS' LAW

NEXT WEEK: ENTROPY, FREE ENERGY, & EQUILIBRIUM

Goals for Today

- There are two types of calorimetry:
 1. **Coffee cup calorimetry measures heat at constant pressure ($q_p = \Delta H$) in an insulated, open-air container**

$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

2. **Bomb calorimetry measures heat at constant volume ($q_v = \Delta U$) in a rigid, isolated container**

$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

Goals for Today

- There are three ways of using Hess' Law to solve for enthalpy:
 1. **The first technique is the one where you algebraically rearrange multiple steps that will equal the total enthalpy change of a single reaction**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

2. **Formation reactions take the sum of the formation enthalpy of products minus the reactants**

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

3. **Bond dissociation enthalpy is the weird one that takes the bond strength of the reactants minus the products**

$$\Delta H_{rxn} = \sum BE(\text{react}) - \sum BE(\text{prod})$$

Definition of Enthalpy

- **Enthalpy (H):** a state function that describes the heat content of a system, given by the equation:

$$H = U + PV$$

- **However, in chemistry we are more concerned with the change in enthalpy, ΔH , which is simply the heat flow at constant pressure, q_p**

$$\Delta H = q_p$$

Change in enthalpy derivation at constant pressure:

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = (q - \cancel{P\Delta V}) + \cancel{P\Delta V} + \Delta PV$$

$$\Delta P = 0$$

$$\Delta H = q$$

PS: if you want to think of reactions in our environment as occurring at constant pressure, change in enthalpy is a great term for determining the heat flow of reactions “IRL”

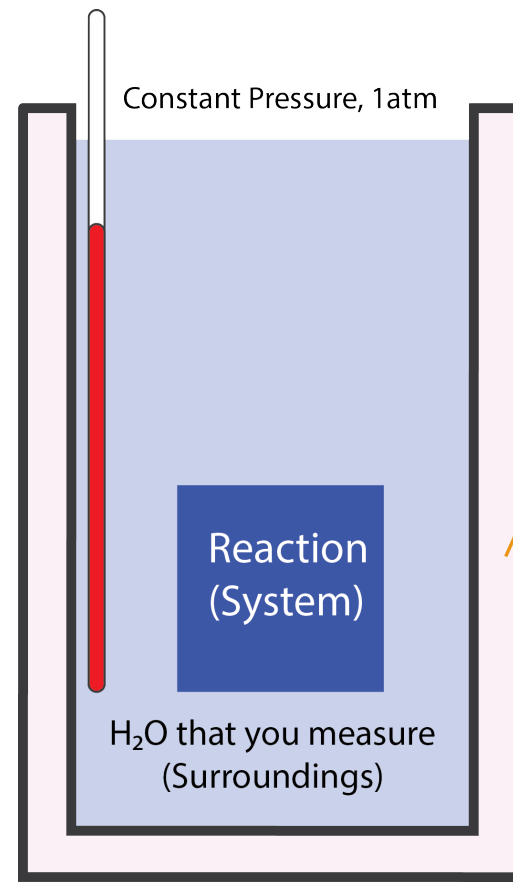
Coffee Cup Calorimetry

Coffee Cup: the goal is to get the enthalpy change (ΔH) of a reaction by measuring the ΔT of the water surrounding the reaction system

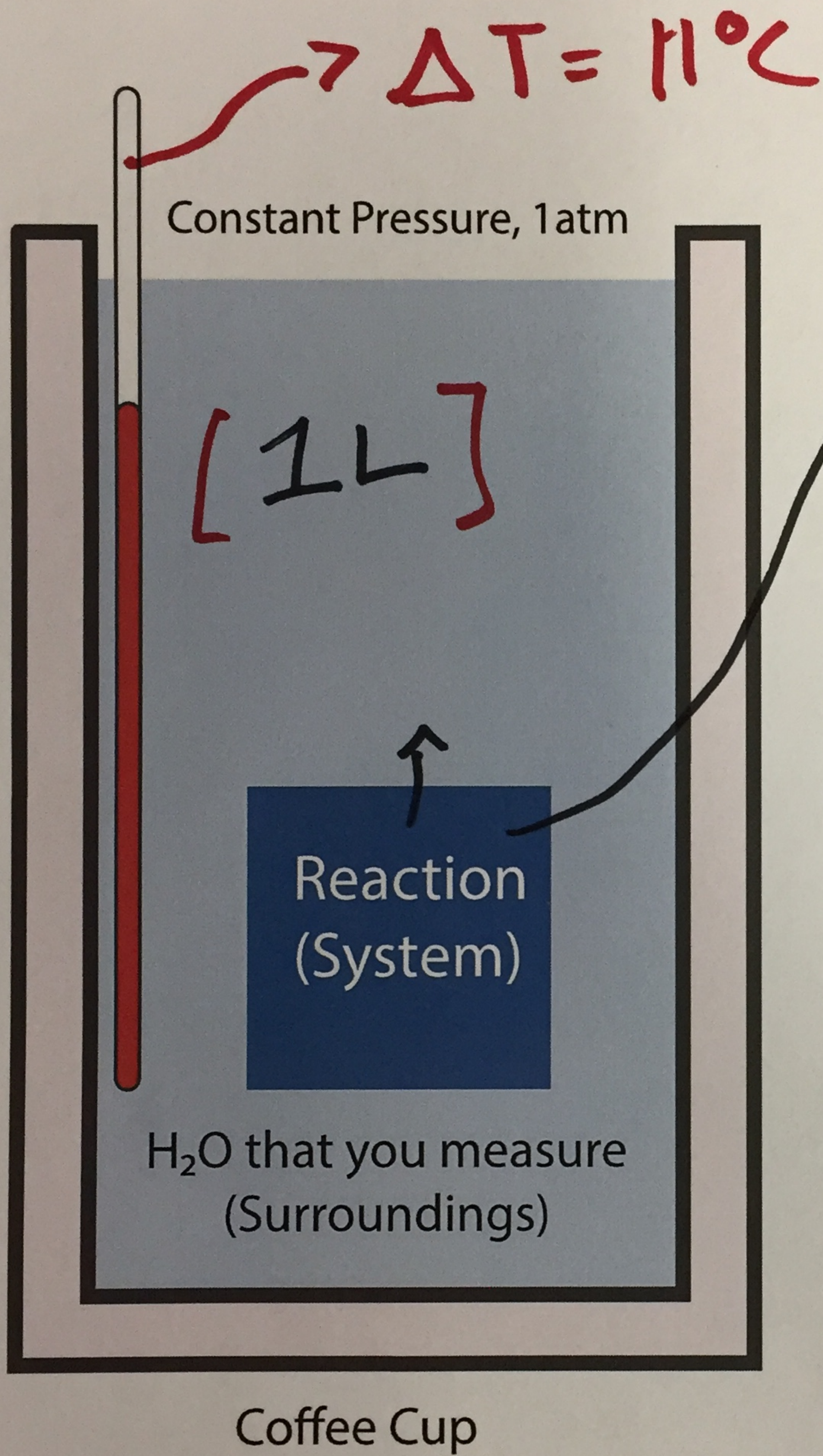
$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

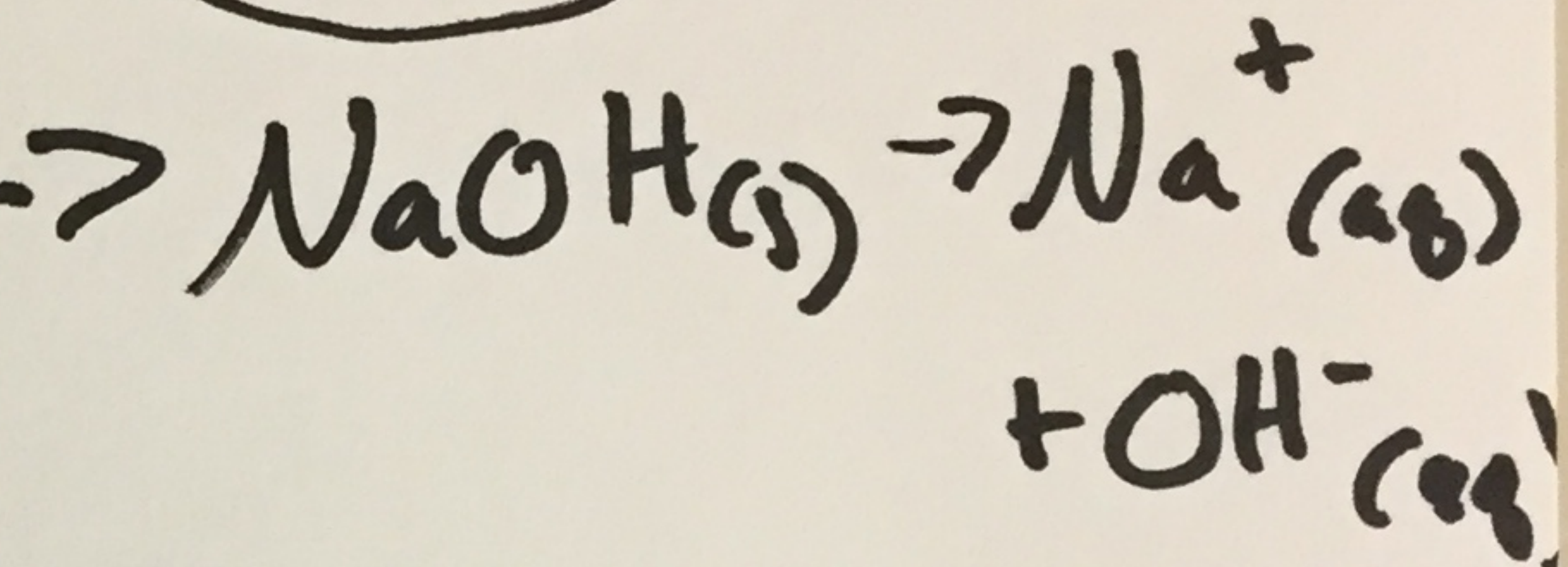
The sign switches to get the heat flow for the system



Insulated hardware does not absorb heat, so we don't care about the $C\Delta T$ term for the calorimeter



1 mol



$$q_{\text{cal}} = \underbrace{mC}_{\text{Water}} \Delta T$$

$$1000 \text{ g} \times 4.184 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

$$\times 11^\circ\text{C}$$

$$q_{\text{sur}} = 46,024 \text{ J/mol}$$

$$\underline{\Delta U} = \Delta H = q_{\text{sys}} = -46,024 \text{ J/mol}$$

↳ not always

~~endothermic~~
exothermic

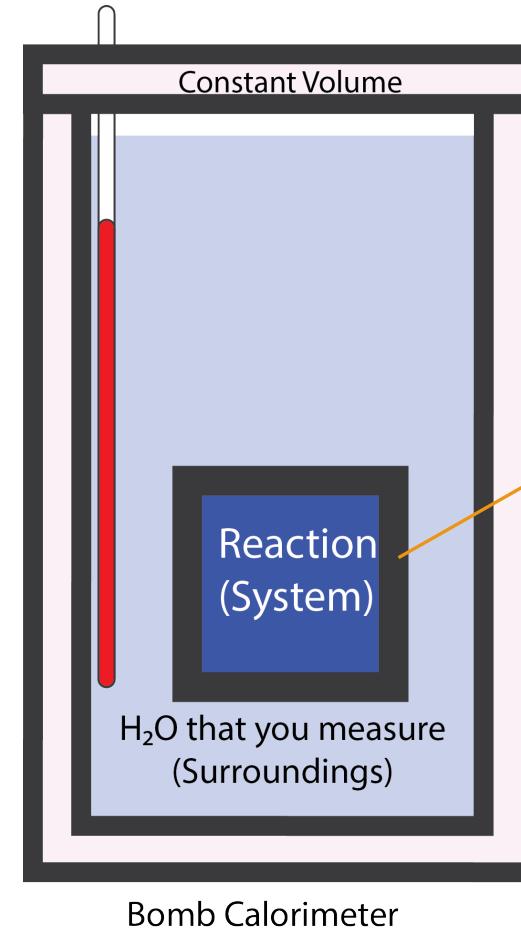
Bomb Calorimetry

Bomb Calorimetry: the goal is to get the internal energy change (ΔU) of a combustion reaction by measuring the ΔT of both the surrounding water and the hardware of the calorimeter

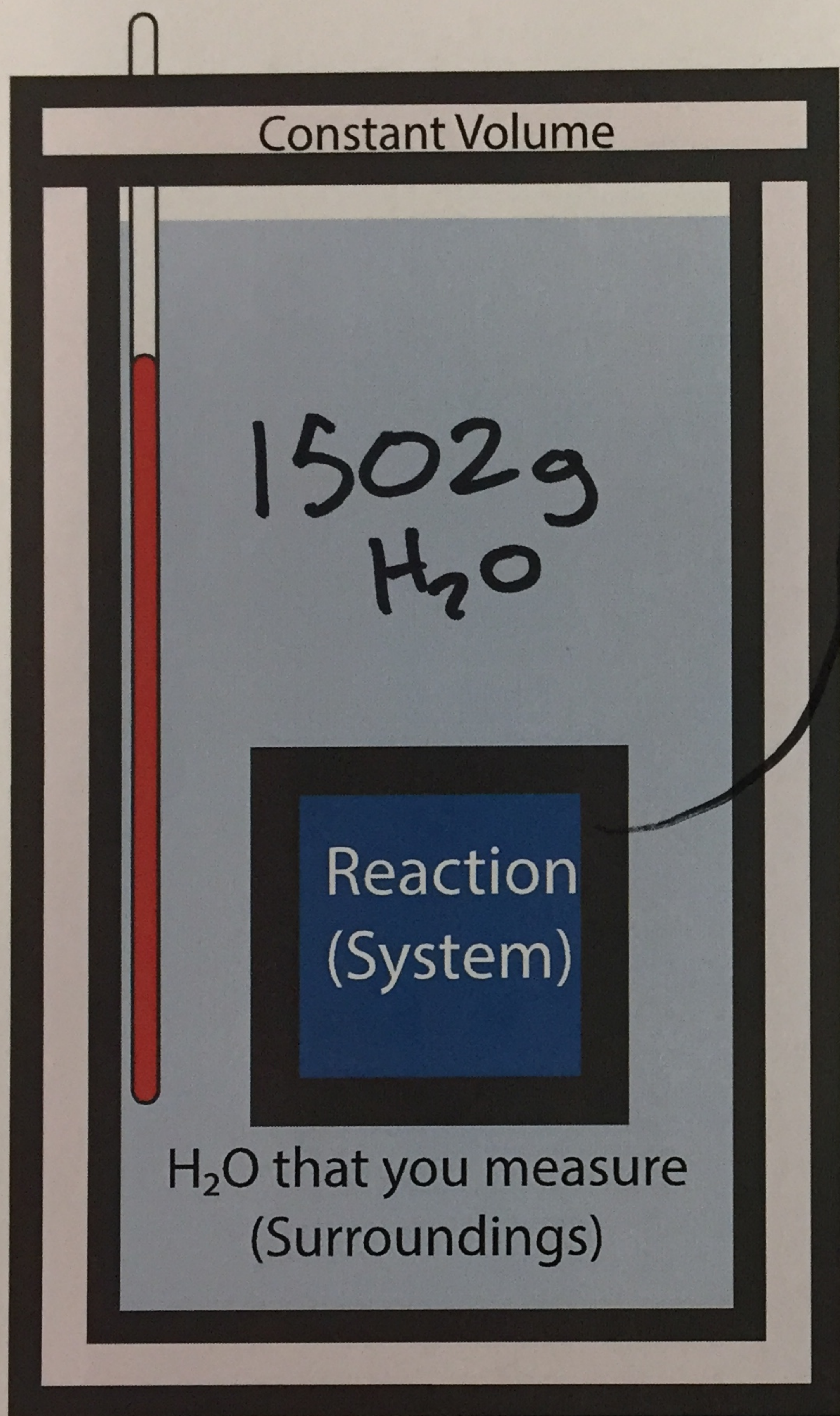
$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

The sign switches to get the heat flow for the system



Stainless steel hardware **does** absorb heat, so we **do** care about the $C\Delta T$ term for the calorimeter



Bomb Calorimeter

ΔU \rightarrow KJ/mol

water hardware

$$q = mC\Delta T + C\Delta T$$

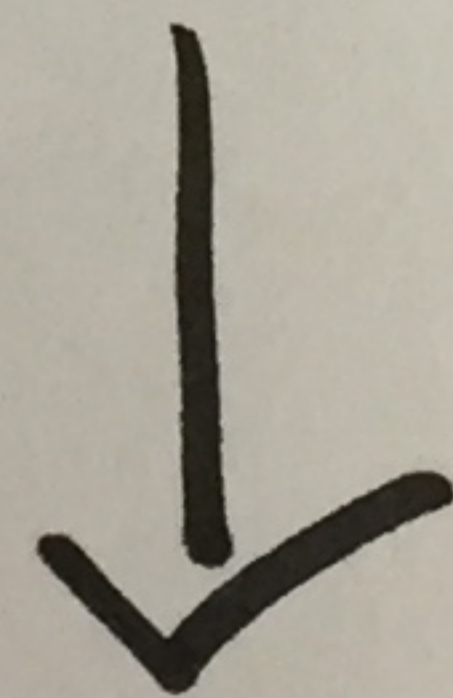
$n = C_6H_{14}$ combustion

(1g)

$$\Delta T = 6.66^\circ C$$

$$C_{\text{hard}} = 4042 \frac{J}{^\circ C}$$

$$C_{\text{water}} = 4.184 \frac{J}{g^\circ C}$$



$$q = 1502g \times 4.184 \times 6.66^\circ C + 4042 \times 6.66^\circ C$$

$q_{\text{sys}} = \underline{68.8 \text{ KJ}}$ — $q = 68,773 \text{ J}$

$$-\frac{68.8 \text{ KJ}}{g \text{ hexane}} \times \frac{86.1g}{mol} = -6 \times 10^3 \text{ KJ/mol}$$

Bomb Calorimetry – ΔU to ΔH

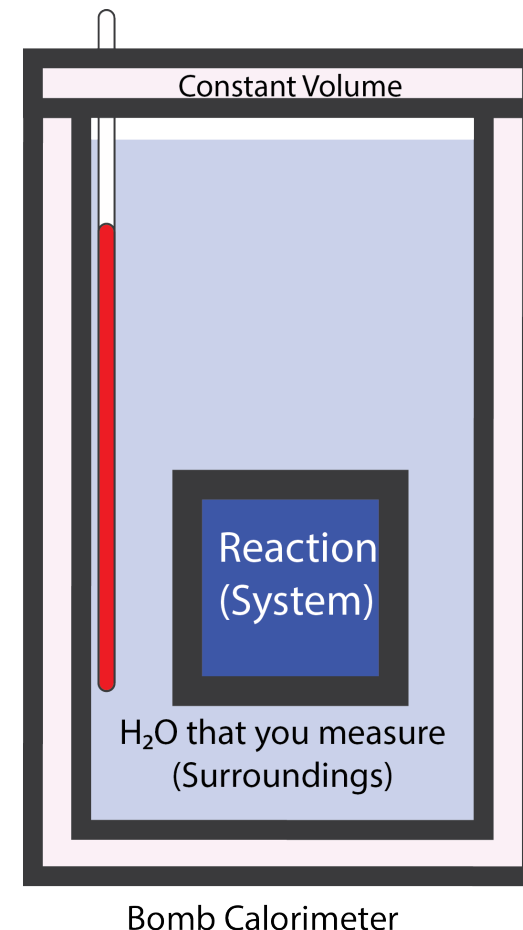
If we are interested in finding the ΔH° of the combustion reaction, two additional steps are necessary.

$\Delta U = q + w$; remember that at standard conditions and constant pressure:

$$q = \Delta H^\circ \text{ and } w = - \Delta nRT$$

If you can write out your balanced combustion reaction, you can easily solve for ΔH°

$$\Delta U + \Delta nRT = \Delta H^\circ$$



Hess' Law – 3 Calculations

- For any state function, the path does not matter as long as you have final and initial values.
- Suppose you have a reaction but no way to directly calculate its enthalpy. You can “create” a path for your reaction using one of three techniques:
 1. Sum of hypothetical reactions that serve as “steps” from your initial to your final
 2. The standard enthalpy of formation for your reaction (products minus reactants)
 3. The bond energies of the molecules that make up your reaction (reactants minus products)

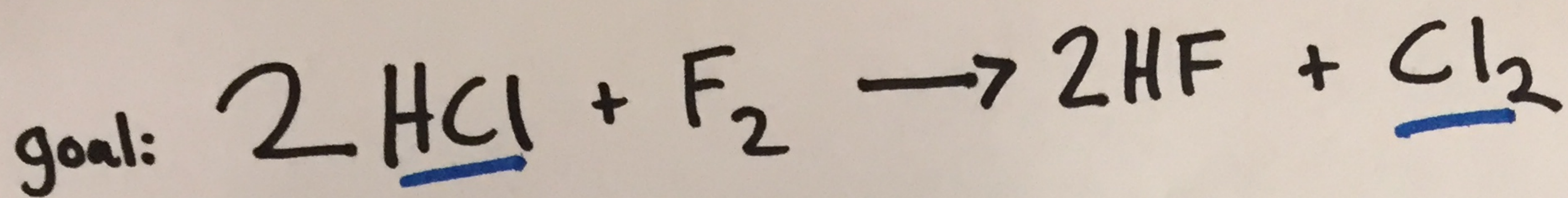
$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

Hess' Law – Sum of Reactions

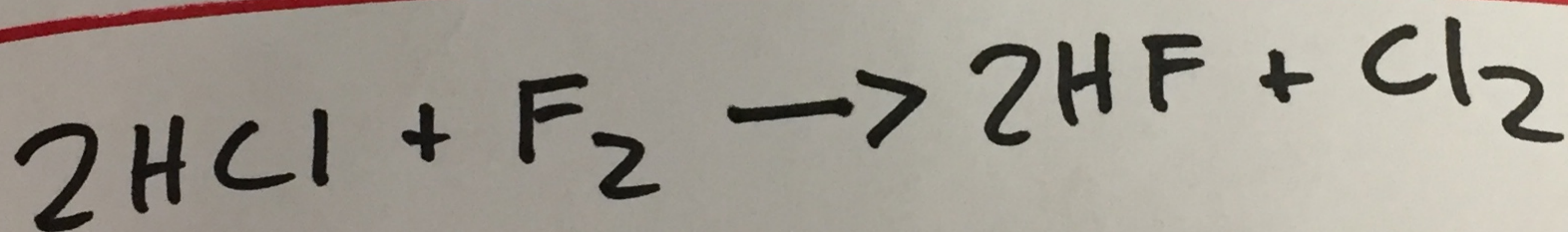
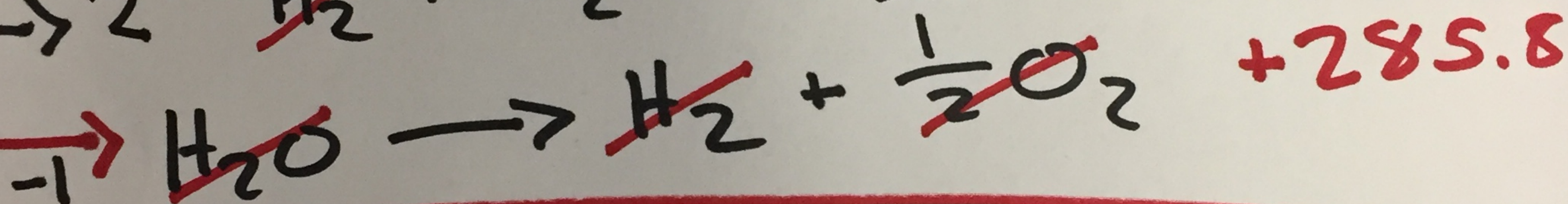
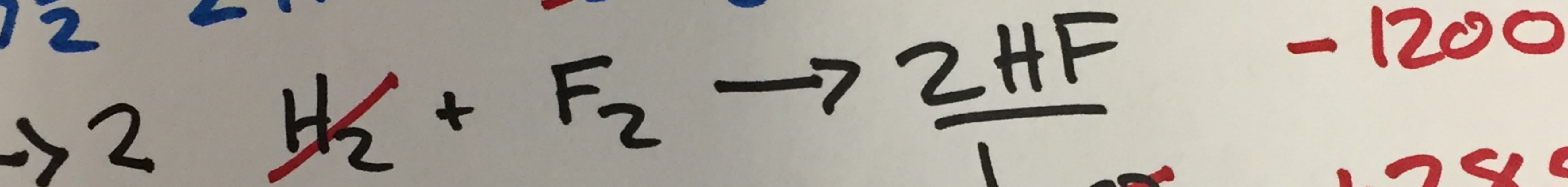
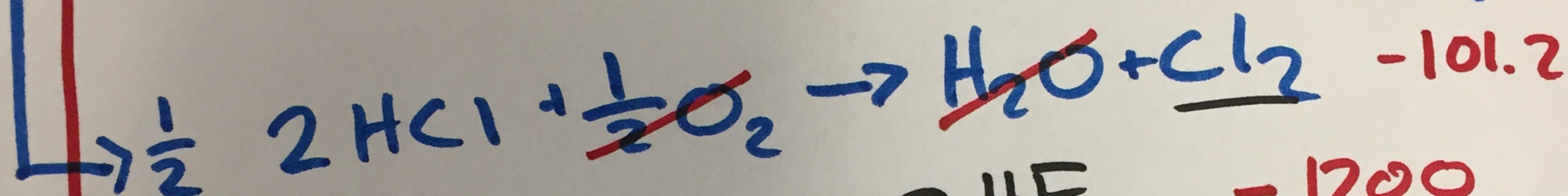
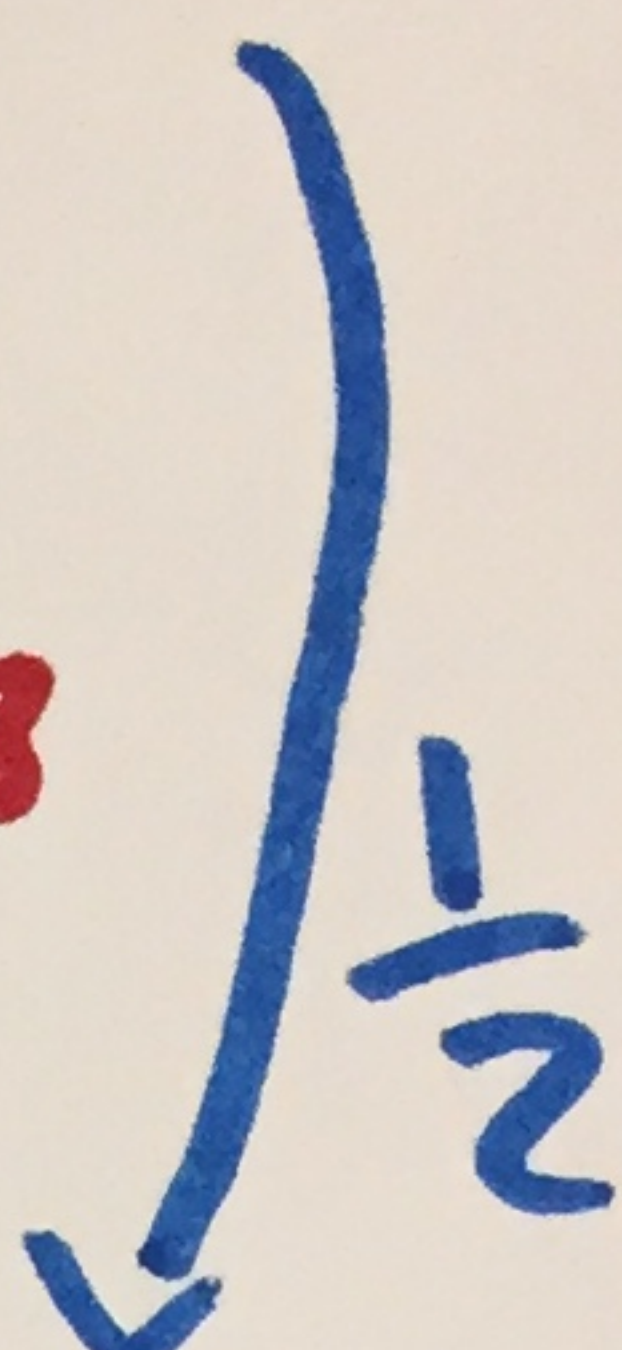
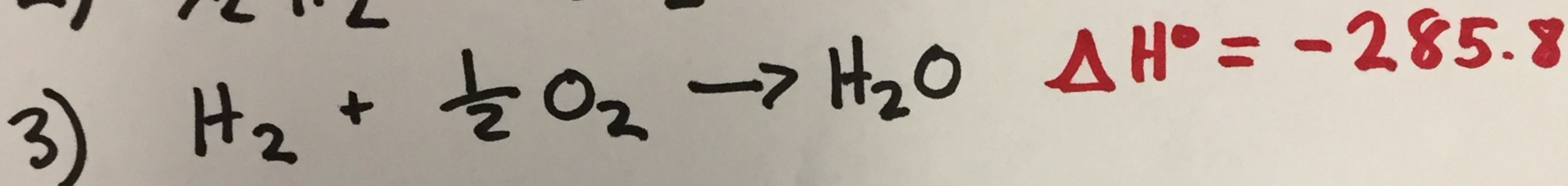
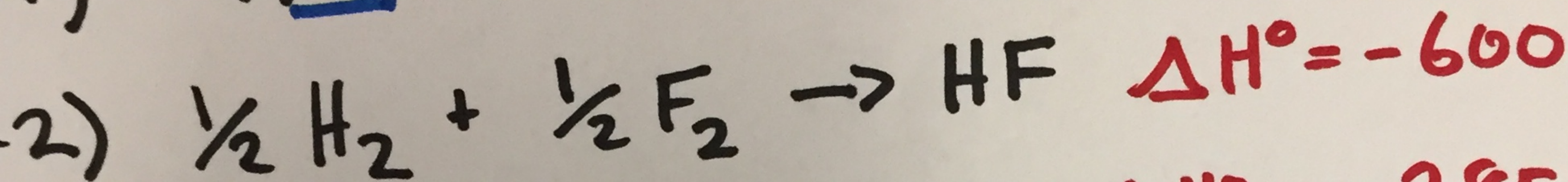
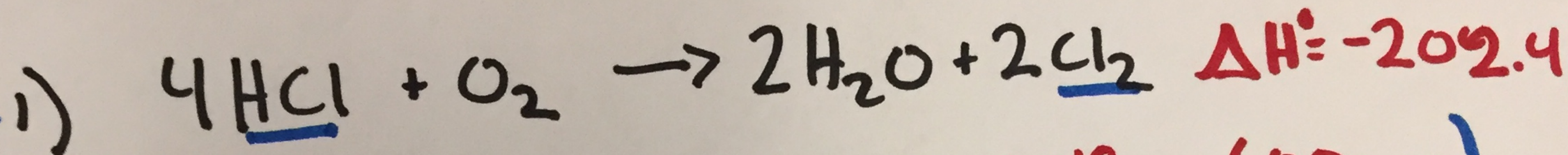
- **Goal: create your desired equation using a given set up hypothetical steps**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

- What you can do to “make” your sum of reactions equal your goal reaction: multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!) or reverse the entire reaction (changing the sign of the enthalpy value associated with that step).



KJ/mol



$-101.2 + (-1200) + 285.8$

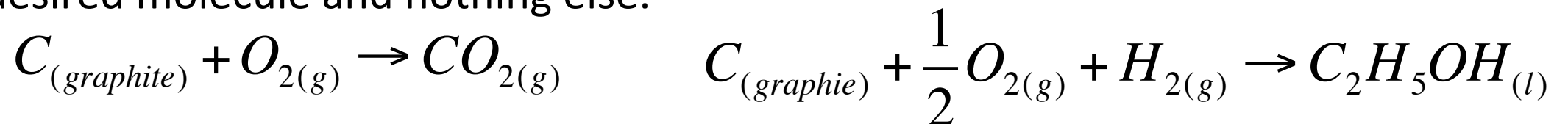
$= -1015.4 \text{ kJ/mol}$

Hess' Law – Formation Reactions

- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.**

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

- Phase and number of moles are important!
- Note: a formation reaction for a molecule is a balanced chemical reaction that shows the constituent elements combining to form a single mole of your desired molecule and nothing else.

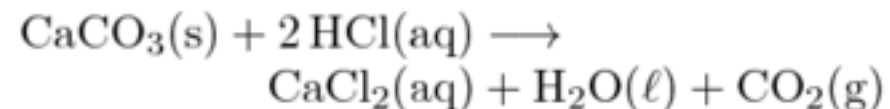


Hess' Law – Formation Reactions Example

- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.**
- Number of moles are important!

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

Calculate the standard reaction enthalpy for the reaction of calcite with hydrochloric acid



The standard enthalpies of formation are:

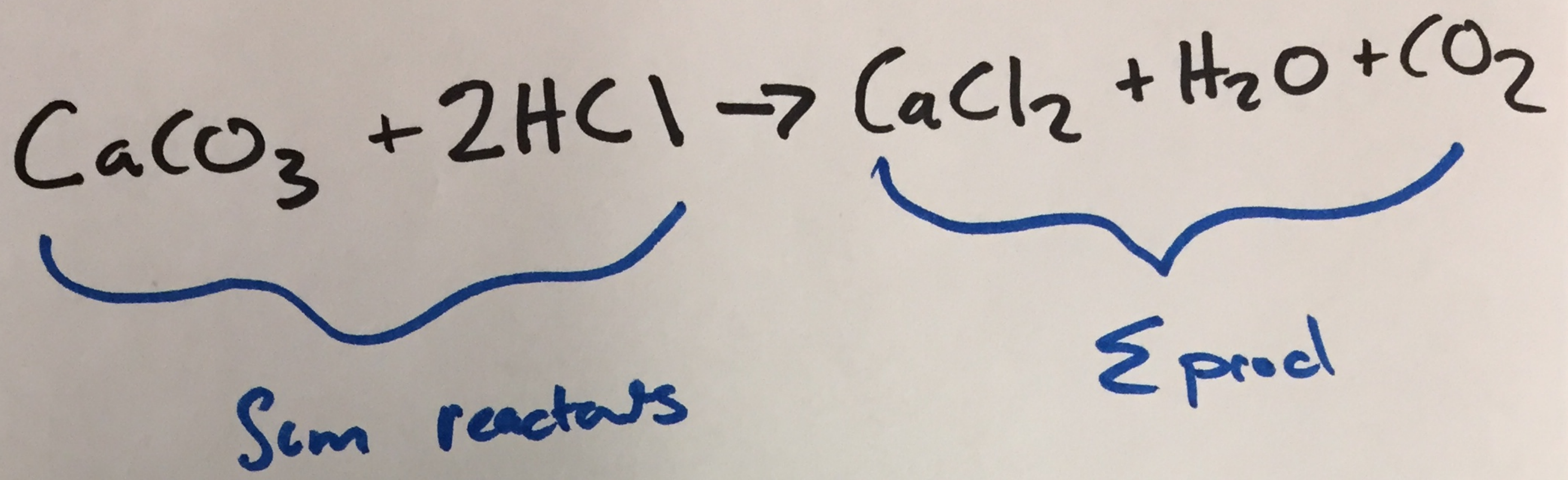
for $\text{CaCl}_2(\text{aq})$: -877.1 kJ/mol;

for $\text{H}_2\text{O}(\ell)$: -285.83 kJ/mol;

for $\text{CO}_2(\text{g})$: -393.51 kJ/mol;

for $\text{CaCO}_3(\text{s})$: -1206.9 kJ/mol;

and for $\text{HCl}(\text{aq})$: -167.16 kJ/mol.



$$\Sigma n(\text{prod}) - \Sigma n(\text{react})$$

prod

$$-877 + (-285.83) + (-393.51)$$

react

$$-(-1206.9) + 2(-167.16)$$

$$-15.22 \text{ kJ/mol}$$

Hess' Law – Bond Energy Data

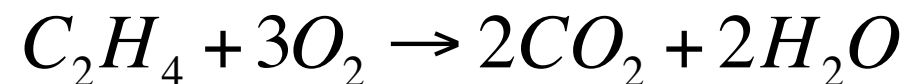
- **Goal: determine the energy difference between all bonds breaking and all bonds forming**
- You must draw a proper Lewis structure, determine what kind of bonds are breaking (reactants) and what kind of bonds are forming (products), and take the difference.

$$\Delta H_{rxn} = \sum BE(react) - \sum BE(prod)$$

- Hint: you will only be drawing very simple Lewis Structures that follow these rules:
 - Carbon makes 4 bonds
 - Nitrogen makes 3 bonds
 - Oxygen makes 2 bonds
 - Hydrogen makes 1 bond

Hess' Law – Bond Energy Data Example

- What is the standard enthalpy for the combustion of ethylene given the following data?



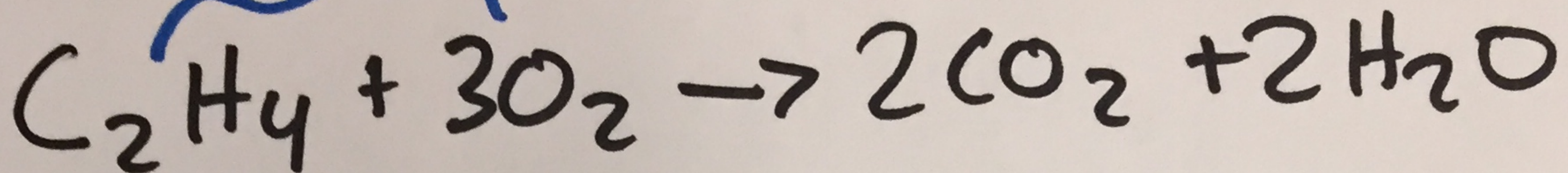
hydrogen	
H-H	432
H-C	413
H-N	391
H-O	467
H-F	565
H-Cl	427
H-Br	363
H-I	295
H-S	347
H-Si	393

carbon	
C-H	413
C-C	347
C-N	305
C-O	358
C-F	485
C-Cl	339
C-Br	276
C-I	240
C-Si	360
C-S	259

oxygen	
O-H	467
O-O	146
O-C	358
O-N	201
O-F	190
O-Cl	203
O-I	234
O-Si	452

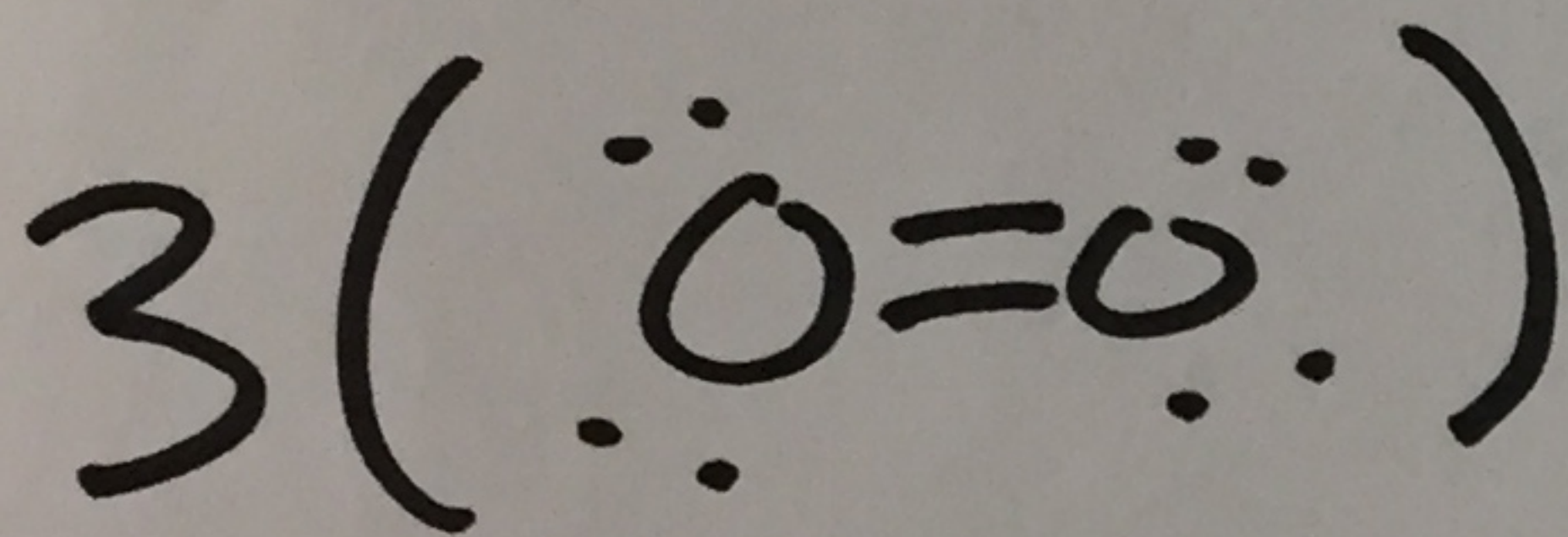
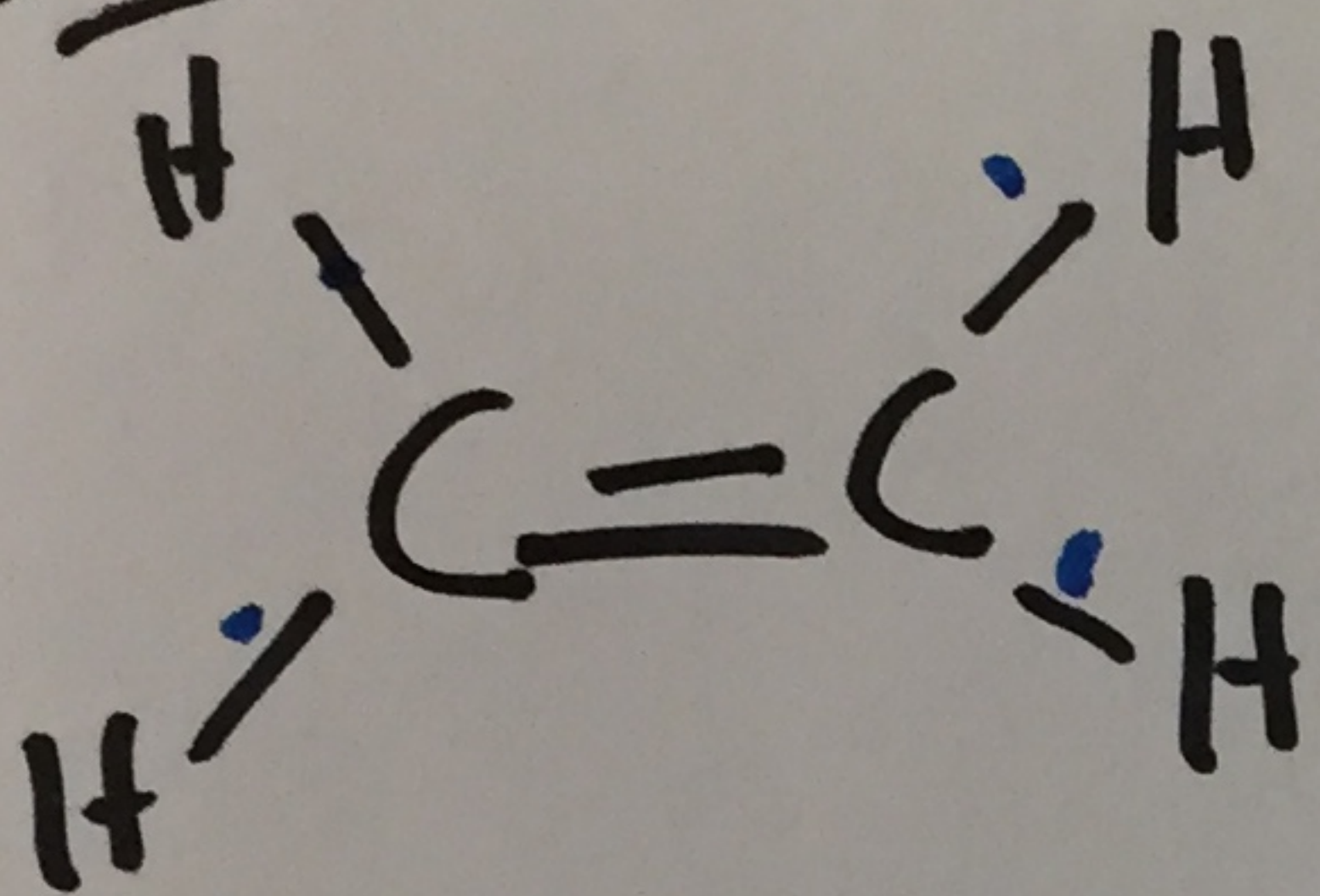
multiple-bond	
C=C	614
C≡C	839
O=O	495
C=O	745
C=O (CO ₂)	799
C≡O	1072
C=S (CS ₂)	577
N=O	607
N=N	418
N≡N	941
C=N	615
C≡N	891

Note: I used C=O as 745kJ instead of the 799kJ on this table



Σ breaking - Σ Forming

Breaking



kJ

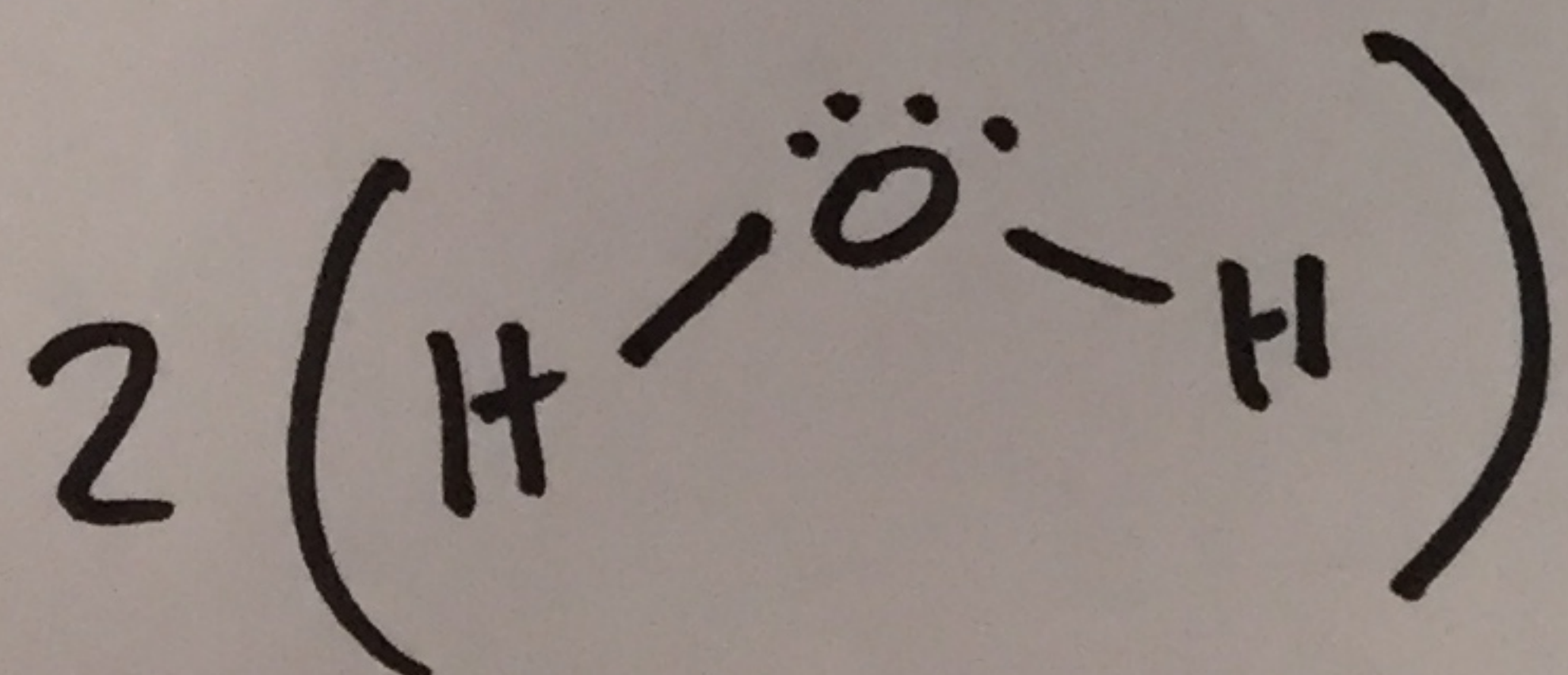
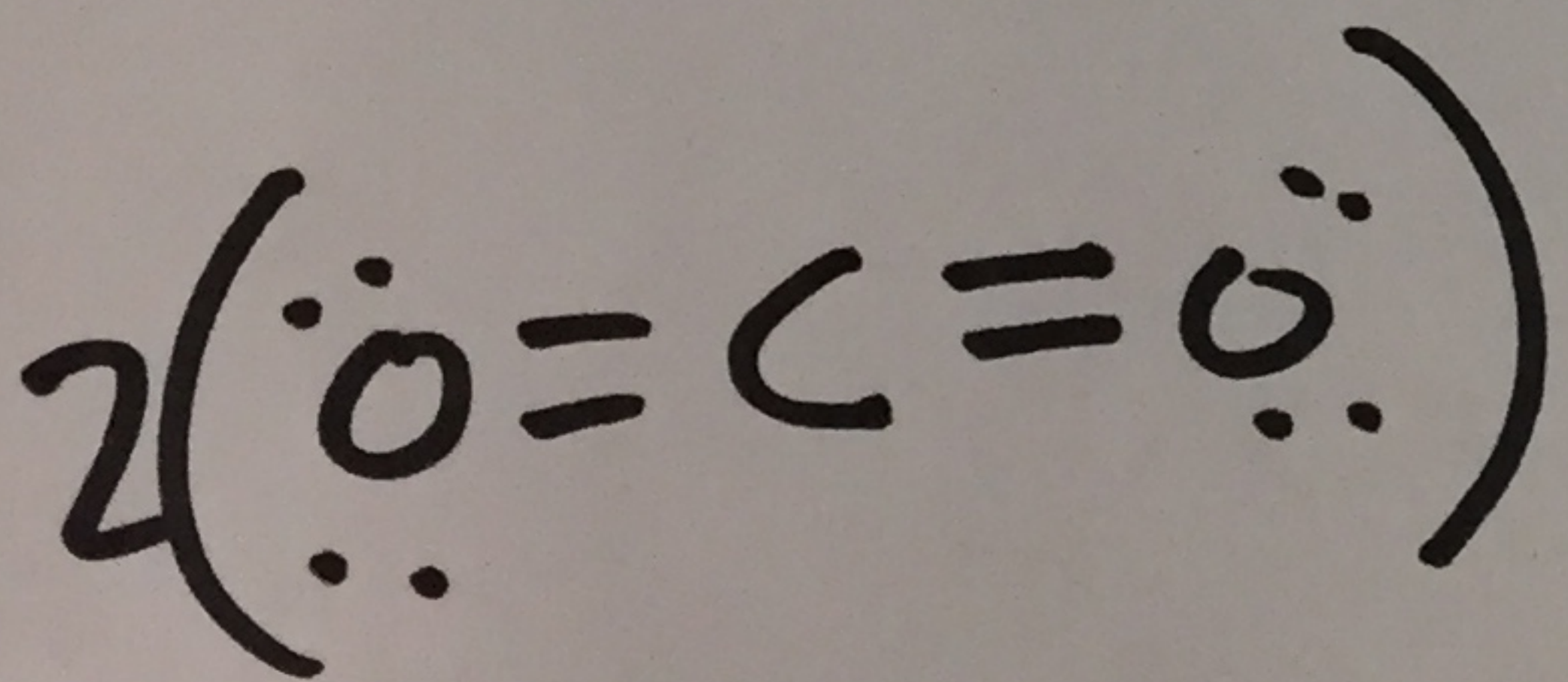
$$\text{C}=\text{C}: 1 \times \underline{614}$$

$$\text{C}-\text{H}: 4 \times 413 = \underline{1652}$$

$$\text{O}=\text{O}: 3 \times 495 = \underline{1485}$$

$$\text{Total} = 3751 \text{ kJ}$$

Forming



$$\text{C}=\text{O}: 4 \times 745 = 2980$$

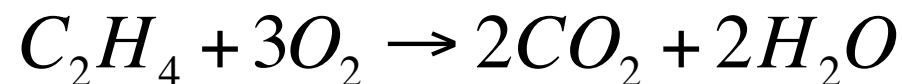
$$\text{H}-\text{O}: 4 \times 467 = 1868$$

$$\text{Total} = 4848 \text{ kJ}$$

$$3751 - 4848 = -1097 \text{ kJ/mol}$$

Hess' Law – Bond Energy Data Example

- What is the standard enthalpy for the combustion of ethylene given the following data? Ans: $3751\text{kJ} - 4848\text{kJ} = -1097\text{kJ}$



hydrogen	
H-H	432
H-C	413
H-N	391
H-O	467
H-F	565
H-Cl	427
H-Br	363
H-I	295
H-S	347
H-Si	393

carbon	
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C-Si	360
C-S	259

oxygen	
O-H	467
O-O	146
O-C	358
O-N	201
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multiple-bond	
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