

Unit 4 Review 2

CALORIMETRY AND HESS' LAW

Thanksgiving Break

- We will be posting ~92 questions for you to work from old exams and Quest homework
- Historically, students who honestly do these problems do better on the exam

YouTube Videos:


- Bomb Calorimetry I and II

Thermodynamics - Calorimetry

1.112 grams of a hydrocarbon fuel source are combusted in a bomb calorimeter. The calorimeter hardware has a heat capacity equal to $1.580 \text{ kJ/}^\circ\text{C}$ and is filled with 1.900 L water ($C_p = 4.184 \text{ J/g}^\circ\text{C}$). You measure a change in temperature equal to 2.865°C .

a. What is the change in internal energy (ΔU) for the combustion of 1.112 grams of this fuel? Answer in kJ.

b. After further analysis of the hydrocarbon, the molecular weight of the fuel source is found to be equal to 86 g/mol. What is the molar internal energy of combustion (ΔU_{comb})? Answer in kJ/mol.



Bomb Calorimeter
Measures heat at constant volume
 $q_{\text{cal}} = mC_p\Delta T + C_{\text{calorimeter}}\Delta T$
 $q_{\text{cal}} = -q_{\text{rxn}}$

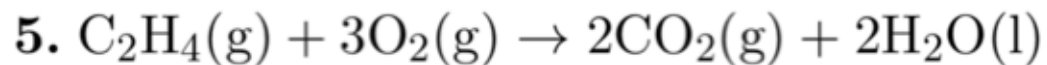
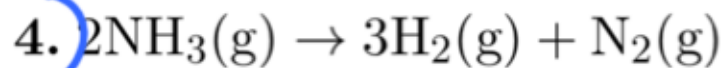
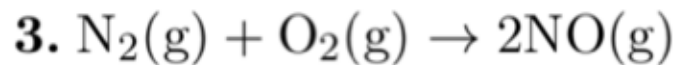
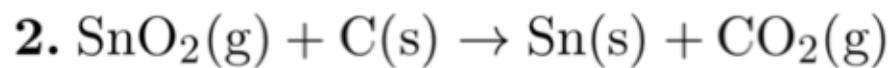
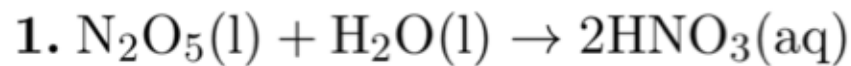
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Thermodynamics - Calorimetry Pt II - Bomb Calorimeter Example

$$\Delta U = \Delta H - \Delta nRT$$

Conceptual Question II (last week)

For which of the following reactions is $\Delta U_{\text{sys}} < \Delta H_{\text{sys}}$ at constant external pressure?



} $\Delta n = \phi, \Delta U = \Delta H$

Intensive vs Extensive Properties

Intensive properties are **i**ndependent on amount, meaning the value is constant no matter how much you have.

- Specific Heat Capacity (J/ g ° C) ^{xg}
- Molar enthalpy of combustion (kJ/ mol) ^{xmol}
- Standard enthalpy of reaction
($\Delta H^\circ_{\text{rxn}} = \text{kJ/mol rxn}$)

Extensive properties are dependent on amount, meaning the value itself accounts for the mass, volume, etc.

- Heat Capacity (J/° C)
- Enthalpy of combustion for a process (kJ)
- Enthalpy for a limiting reagent problem
($\Delta H_{\text{rxn}} = \text{kJ}$)

Why does this matter?

1. You have equal masses of each of the following substances at room temperature:

$$C_{\text{lithium}} = 3.58 \frac{\text{J}}{\text{g}^\circ\text{C}} \quad C_{\text{iron}} = 0.450 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

$$C_{\text{air}} = 1.012 \frac{\text{J}}{\text{g}^\circ\text{C}} \quad C_{\text{helium}} = 5.193 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

$$C_{\text{mercury}} = 0.140 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

Assuming no phase change occurs, which substance will have the highest final temperature after 22.7 J heat is added to each?

1. Lithium
2. Air
3. Iron
4. Helium
5. Mercury **correct**

$$2. q = \underline{mC_s\Delta T} + C\Delta T$$

intensive = $\frac{\text{J}}{\text{g}^\circ\text{C}}$

extensive

$\frac{\text{J}}{^\circ\text{C}}$

3. If ΔH_f is -266 kJ/ mol rxn, but you make 4 moles of products, you need to account for the amount (convert intensive, ΔH_f to extensive, ΔH).

Today's Equations

$$H = U + PV$$

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta U = \Delta H - P\Delta V$$

$$\Delta U = \Delta H - \Delta nRT$$

$$\Delta H = q_p$$

$$\Delta U = q_v$$

$$q_{\text{cal}} = -q_{\text{sys}}$$

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

$$q_{\text{cal}} = m_{\text{water}} \cdot C_{s,\text{water}} \cdot \Delta T + C_{\text{hardware}} \cdot \Delta T$$

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

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

$$\Delta H_{\text{rxn}}^\circ \approx \sum n\Delta H_{\text{bond}}^\circ (\text{breaking}) - \sum n\Delta H_{\text{bond}}^\circ (\text{making})$$

Hess

cal

Calorimetry

$$\Delta U = q + w$$

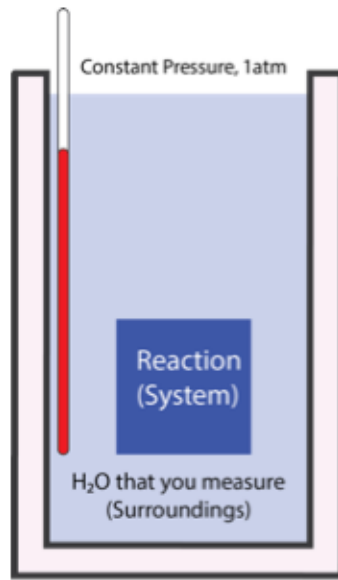
Calorimetry Overview

$$q_{cal} = \underbrace{mC_s\Delta T}_{\text{H}_2\text{O}} + \underbrace{C\Delta T}_{\text{hardware}}$$

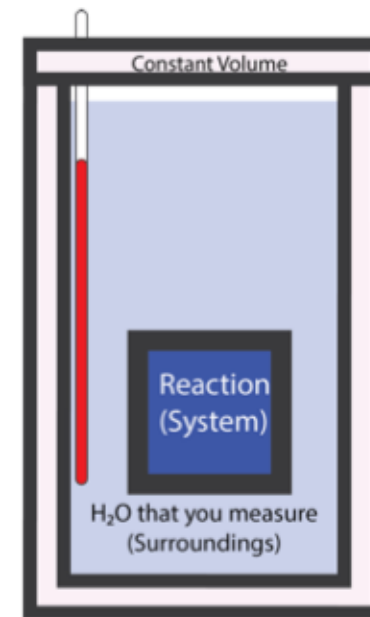
$$q_{cal} = q_{surr}$$

$$q_{surr} = -q_{sys}$$

$$\Delta H \leftarrow q_p \leftarrow q_{sys} \rightarrow q_v \rightarrow \Delta U$$



Coffee Cup



Bomb Calorimeter

Calorimetry Overview

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**

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

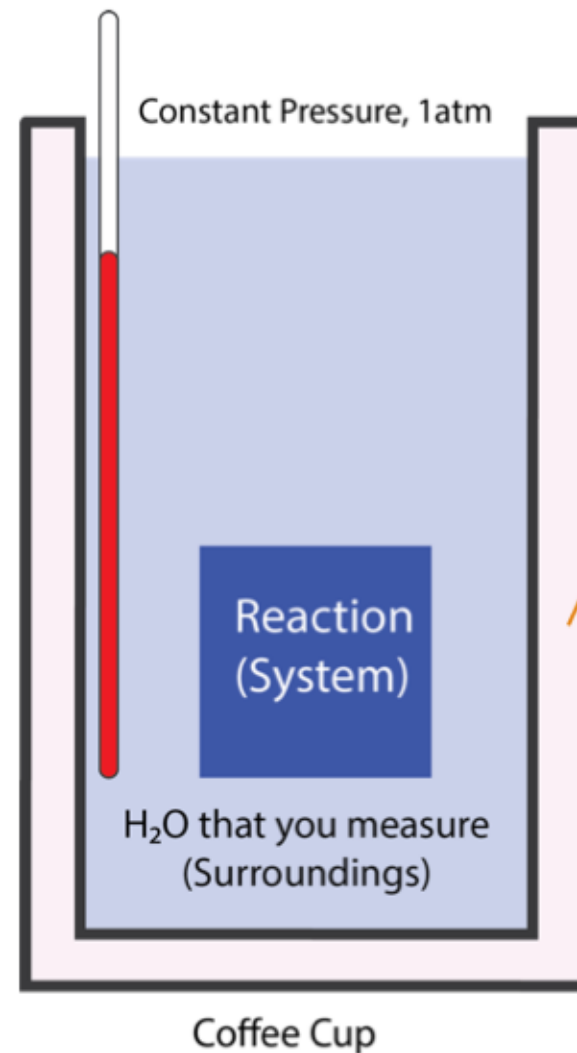
Coffee Cup Calorimetry

Coffee Cup: the goal here is to measure heat at constant pressure. This directly gives us the enthalpy (ΔH) for a reaction.

$$q_{\text{cal}} = m C_s \Delta T$$

$$q_{\text{cal}} = -q_{\text{sys}}$$

$$q_{\text{sys}} = \Delta H$$



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

Bomb Calorimetry

* Combustion:

$$\underline{\underline{\Delta U < 0}}$$

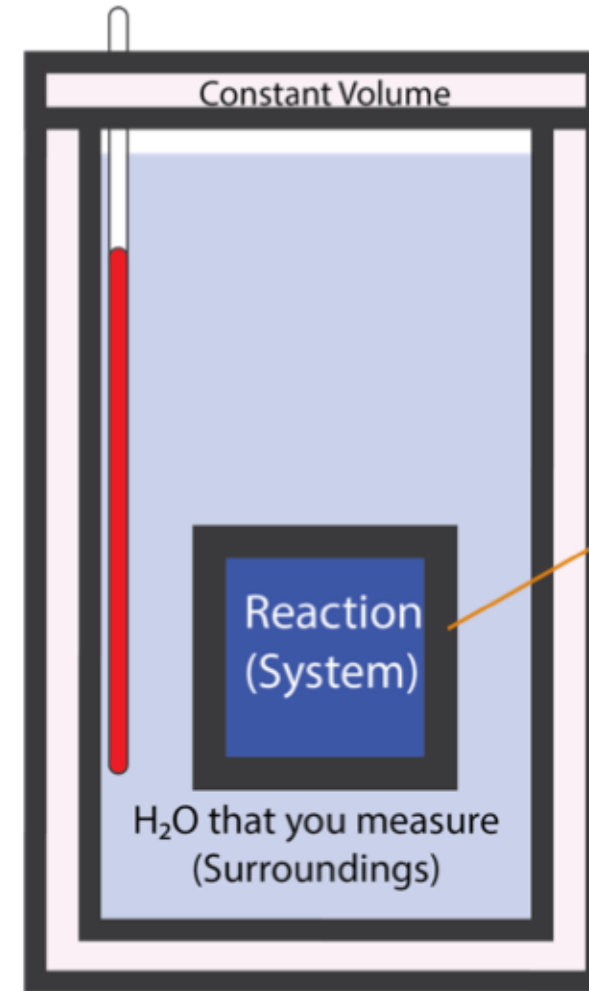
The goal is to get the internal energy change (ΔU) of a combustion reaction by measuring the ΔT of both the surrounding water and the hardware of the calorimeter

$$q_{cal} = mC_s \Delta T + \underline{\underline{C \Delta T}}$$

$$q_{cal} = -q_{sys}$$

$$q_{sys} = \Delta U$$

↳ then to $\Delta U / \text{mol} \dots$



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

Bomb Calorimeter

Bomb Calorimeter Exam Question

Methyl tert-butyl ether or MTBE is an octane booster for gasoline. The combustion of 0.9211 grams of MTBE ($C_5H_{12}O$ 88.15 g/mol) is carried out in a bomb calorimeter. The calorimeter's hardware has a heat capacity of 1.540 kJ/°C and is filled with exactly 2.022 L of water. The initial temperature was 26.336°C. After the combustion, the temperature was 29.849°C.

Analyze this calorimeter data and determine the molar internal energy of combustion (ΔU) for this octane booster. Answer in kJ/mol.

$$q_{cal} = \underbrace{m C_s \Delta T}_{H_2O} + \underbrace{C \Delta T}_{hardware}$$

$$4.184 \times 10^{-5} \frac{kJ}{g \cdot ^\circ C} \leftarrow C_s = 4.184 \frac{J}{g \cdot ^\circ C} \quad m = 2,022g \quad C = 1.540 \frac{kJ}{^\circ C} \quad \Delta T = 3.513^\circ C$$

$$q_{cal} = 35.130 \frac{kJ}{\cancel{g}} = \left(2,022 \cancel{g} \right) \left(4.184 \times 10^{-3} \frac{kJ}{\cancel{g} \cdot ^\circ C} \right) \left(3.513 \cancel{^\circ C} \right) + \left(1.540 \frac{kJ}{\cancel{^\circ C}} \right) \left(3.513 \cancel{^\circ C} \right)$$

$-q_{sys} \rightarrow -35.130 \text{ kJ}$

$\Delta U \rightarrow$

$$0.9211g \times \frac{mol}{88.15g} = 0.01045 \text{ moles}$$

$$= \boxed{-3362 \frac{kJ}{mol}}$$

Bomb Calorimetry – ΔU to ΔH

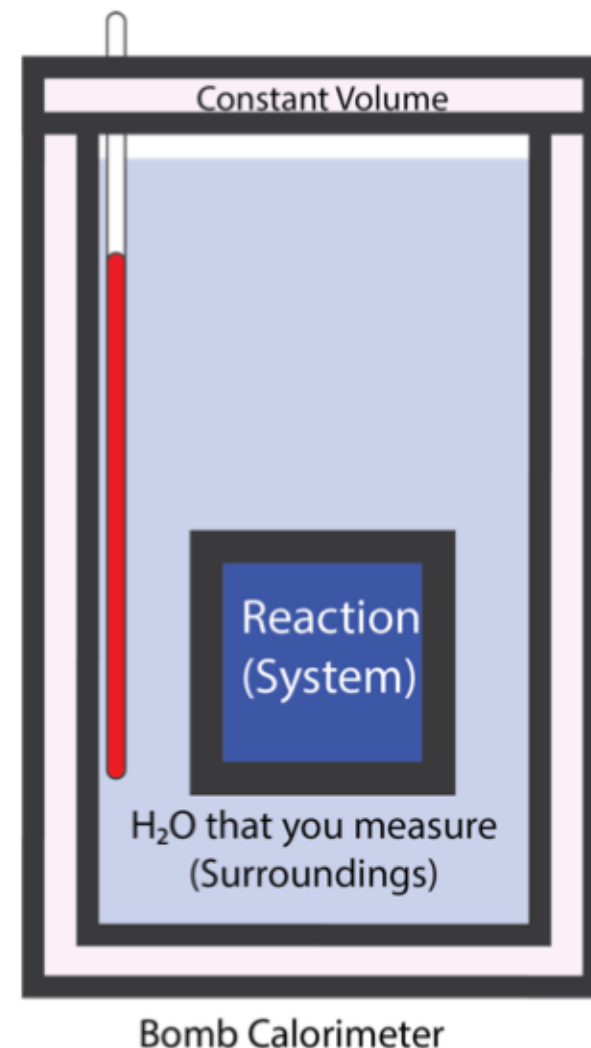
If we are interested in finding the ΔH° of the combustion reaction, two additional steps are necessary.

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

$$q_p = \Delta H \text{ and } w = -P\Delta V = -\Delta nRT$$

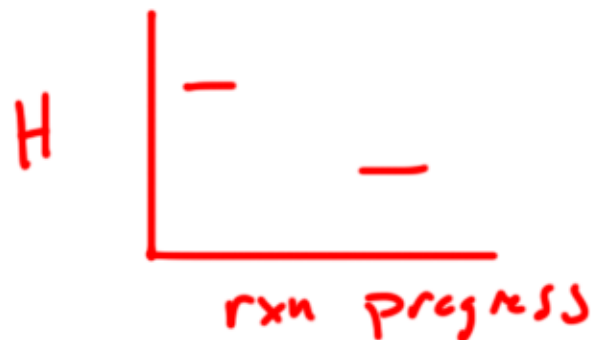
If you can write out your balanced combustion reaction, you can easily solve for ΔH

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



Enthalpy

Goals for Today



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. The first technique is the one where you algebraically rearrange multiple steps that will equal the total enthalpy change of a single reaction

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

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

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

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



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

Reactants - Products

Hess' Law – Sum of Reactions

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

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

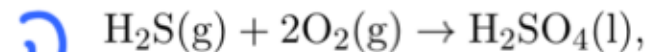
- What you can do to “make” your sum of reactions equal your goal reaction: **multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!)** or **reverse the entire reaction (changing the sign of the enthalpy value associated with that step).**
- I prefer going step-by-step to determine what adjustments need to be made (start at step one, make necessary adjustments, etc.)

Hess' Law – Sum of Reactions

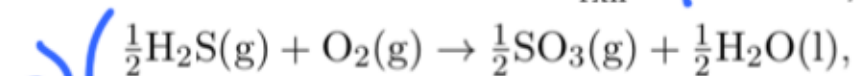
Consider the following balanced chemical reaction:



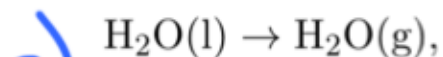
To solve for the $\Delta H_{\text{rxn}}^\circ$ for this reaction, you collect the following data in the lab:



$$\Delta H_{\text{rxn}}^\circ = +241.3 \text{ kJ/mol}$$

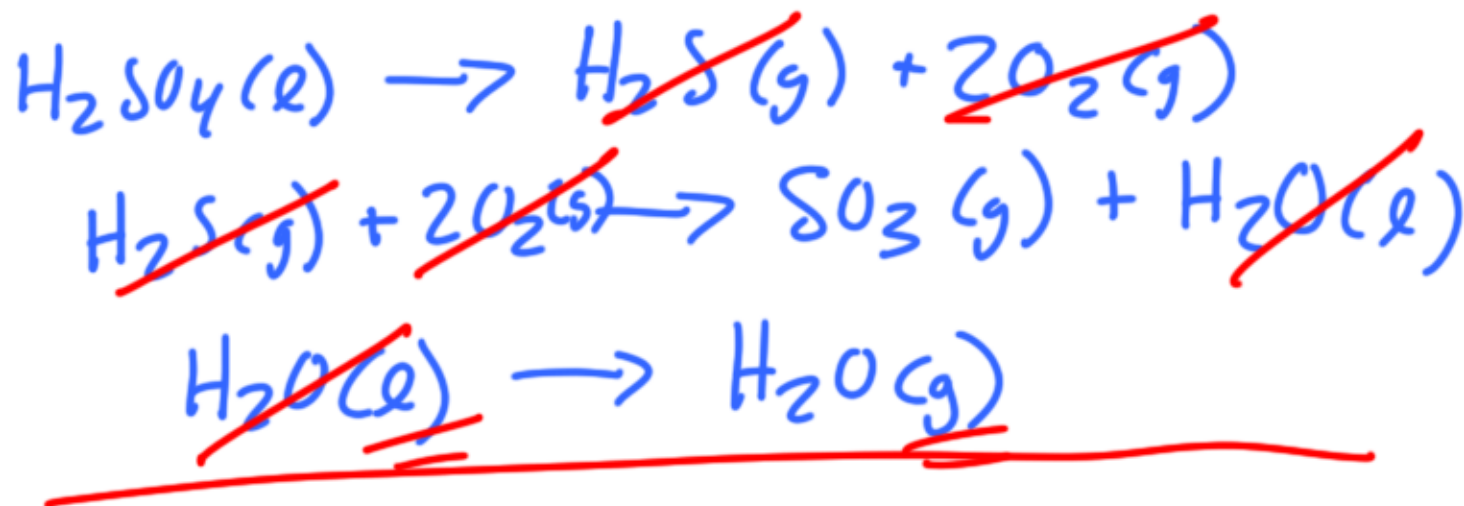


$$\Delta H_{\text{rxn}}^\circ = -100.6 \text{ kJ/mol}$$



$$\Delta H_{\text{rxn}}^\circ = 41.9 \text{ kJ/mol}$$

What is the $\Delta H_{\text{rxn}}^\circ$ of the overall balanced reaction?



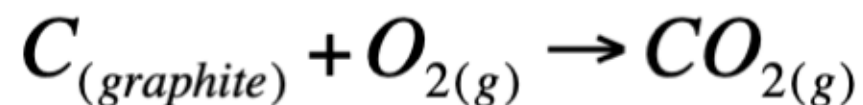
$$\Delta H_{\text{rxn}} = +241.3 + (2 \cdot -100.6) + 41.9 = 82 \text{ kJ/mol}$$

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.**

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

- 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

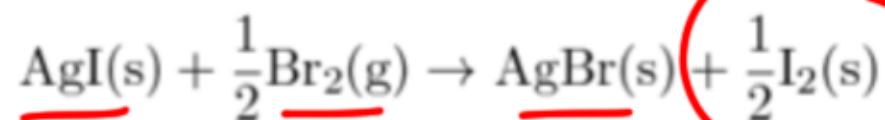
- **Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.**
- Number of moles are important!

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

prod - react

$$(-100.4) - \left(-61.9 + \frac{1}{2} 30.9\right) = -54.0 \text{ kJ}$$

Consider the following reaction and standard heats of formation:



$$\Delta H_f^\circ \text{ for AgI(s)} = -61.9 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for AgBr(s)} = -100.4 \text{ kJ/mol}$$

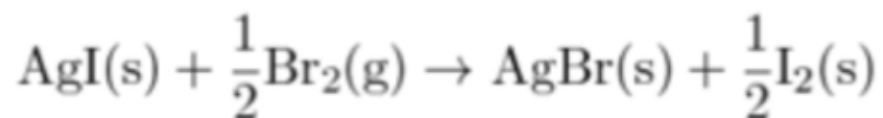
$$\Delta H_f^\circ \text{ for Br}_2(\text{g}) = +30.9 \text{ kJ/mol}$$

What is the ΔH_{rxn}° ?

Hess' Law – Formation Reactions Example

Bonus Challenge: Write the reactions for each ΔH_f° value provided in this question

Consider the following reaction and standard heats of formation:



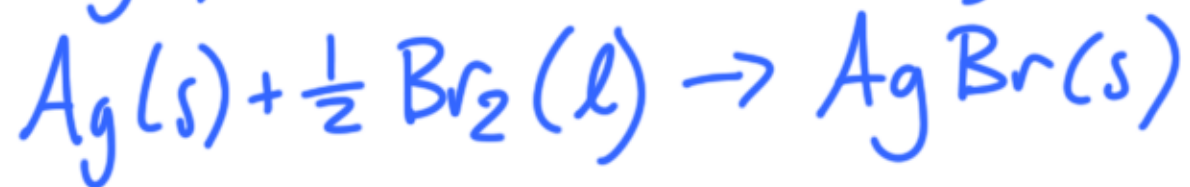
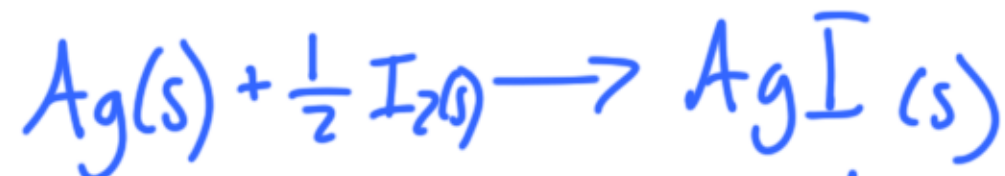
$$\Delta H_f^\circ \text{ for AgI}(s) = -61.9 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for AgBr}(s) = -100.4 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for Br}_2(g) = +30.9 \text{ kJ/mol}$$

What is the $\Delta H_{\text{rxn}}^\circ$?

↳ 1 mol product, 1 product
↳ reactants elements in their
std. state



Hess' Law – Bond Energy Data

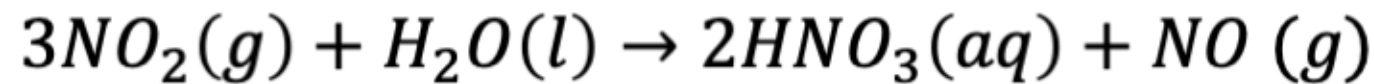
- **Goal: determine the energy difference between all bonds breaking and all bonds forming**
- You must draw a proper Lewis structure, determine what kind of bonds are breaking (reactants) and what kind of bonds are forming (products), and take the difference.

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

$$\Delta H_{\text{forward}} = -\Delta H_{\text{reverse}}$$

Final Challenge - ΔH_{rxn} Stoichiometry

As written, the following reaction has a $\Delta H_{\text{rxn}} = -137 \text{ kJ/mol rxn}$. \rightarrow intensive



5 moles of HNO_3 are added to 5 moles of NO gas to run the reverse reaction. What is the ΔH for this reaction?

$$\Delta H_{\text{rev}} = +137 \text{ kJ/mol rxn} \times \# \text{ rxns}$$

$$5 \text{ moles HNO}_3 \times \frac{\text{rxn}}{2 \text{ moles}} = \boxed{2.5 \text{ rxns}}$$

$$5 \text{ moles NO} \times \frac{\text{rxn}}{1 \text{ mol}} = 5 \text{ rxns}$$

$$+137 \text{ kJ/mol rxn} \times 2.5 \text{ mol rxns}$$

$$= \boxed{342.5 \text{ kJ}}$$

\downarrow
extensive