Heats of Reactions (ΔH)

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YALE UNIVERSITY

CHEMISTRY 161

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Conservation of Energy

Because of the law of conservation of energy (energy cannot be created or destroyed), any energy *lost* from the system is energy *gained* by the surroundings. $q_{surr} = -q_{sys}$

Because of the law of conservation of energy (energy cannot be created or destroyed), any energy *gained* by the system is energy *lost* from the surroundings. $q_{surr} = -q_{sys}$

Q1: Is this endothermic or exothermic relative to the system?

A1: Exothermic.

Q2: Will the system be warmer or cooler than it was?

A2: Cooler, lost energy.

SURROUNDINGS

SYSTEM

$q_{sys} < 0$ $q_{sys} > 0$

$q_{surr} > 0$ $q_{surr} < 0$
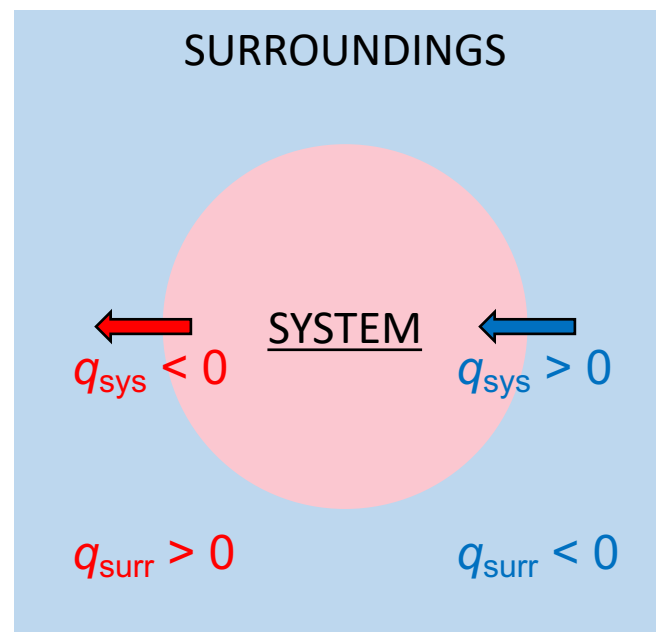
Q1: Is this endothermic or exothermic relative to the system?

A1: Endothermic.

Q2: Will the system be warmer or cooler than it was?

A2: Warmer, gained energy.

Enthalpy

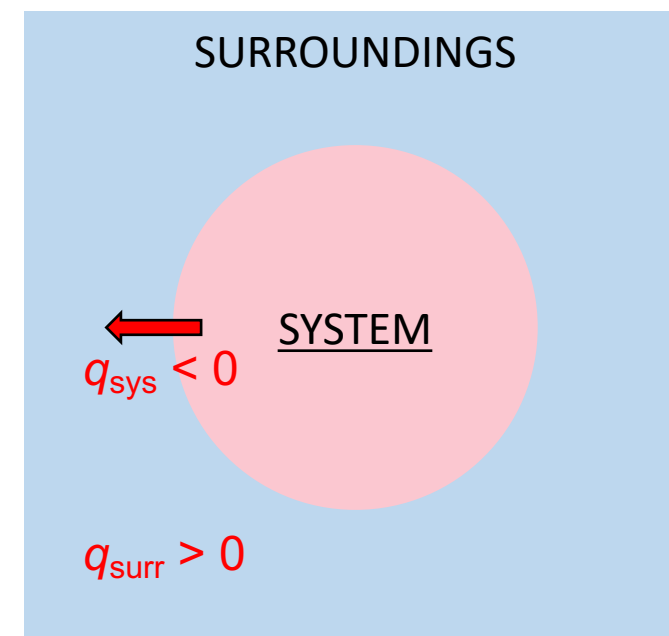Typically, we don't measure the energy of a system directly (it's hard to do so).

Usually, we measure the change in the energy (or heat) as the system undergoes a change, like a chemical reaction. This is called the <u>change in enthalpy or heat of a reaction</u>, denoted ΔH.

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Also, we usually measure the surroundings and not the system itself.

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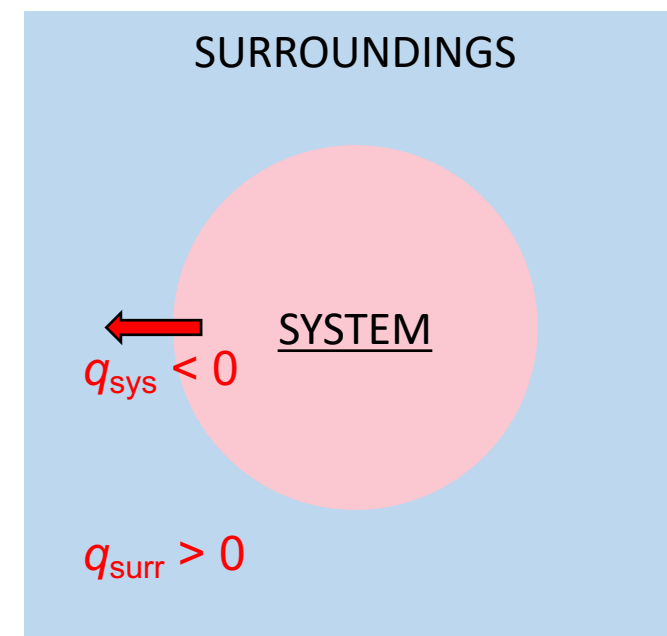
<u>SYSTEM</u>

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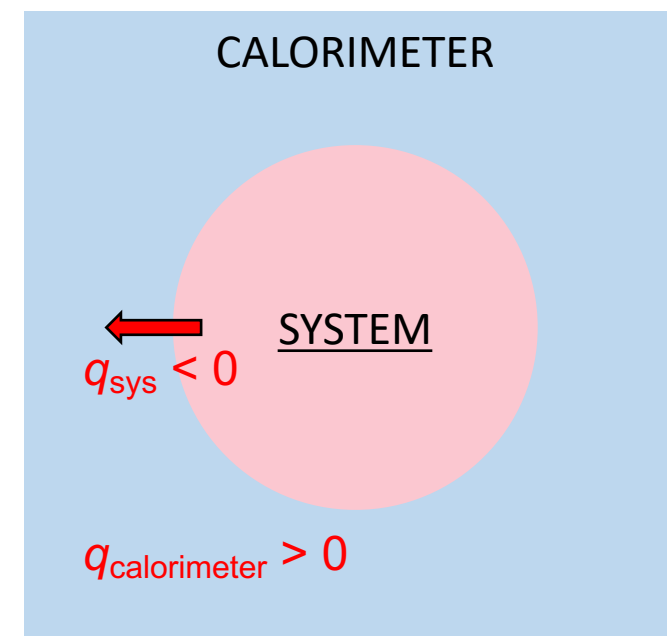
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More specifically, we use a <u>calorimeter</u> as the surroundings.

CALORIMETER

<u>SYSTEM</u>

$q_{sys} < 0$

$q_{calorimeter} > 0$

Enthalpy

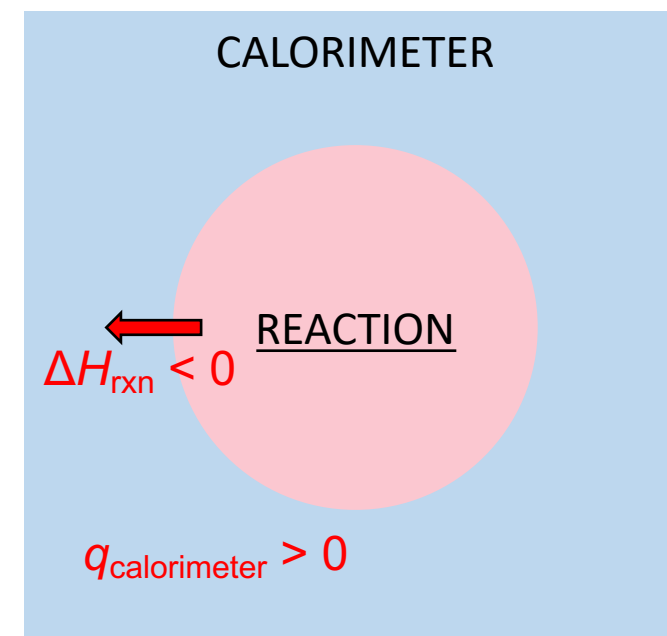Typically, we don't measure the energy of a system directly (it's hard to do so).

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<u>REACTION</u>

$\Delta H_{rxn} < 0$

$q_{calorimeter} > 0$

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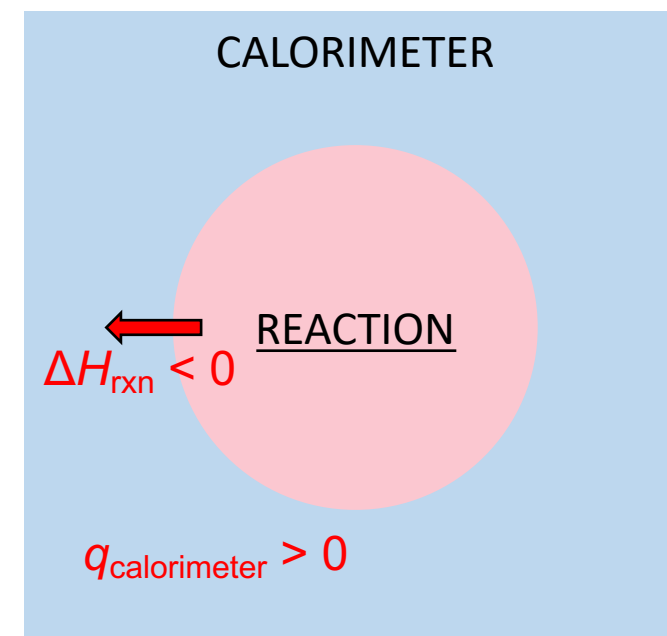Also, we usually measure the surroundings and not the system itself.

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A <u>calorimeter</u> is a well-insulated water bath, such that:

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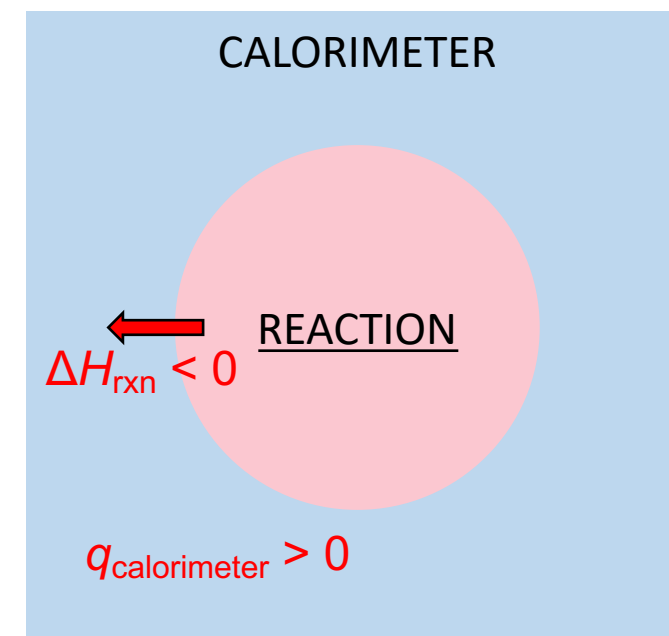Also, we usually measure the surroundings and not the system itself.

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CALORIMETER

$\Delta H_{rxn} < 0$ ← <u>REACTION</u>

$q_{calorimeter} > 0$

Note: Hopefully, you understand (a little better at least) why we went through those heating curves!

There are a few other ways to calculate the heat of a reaction.
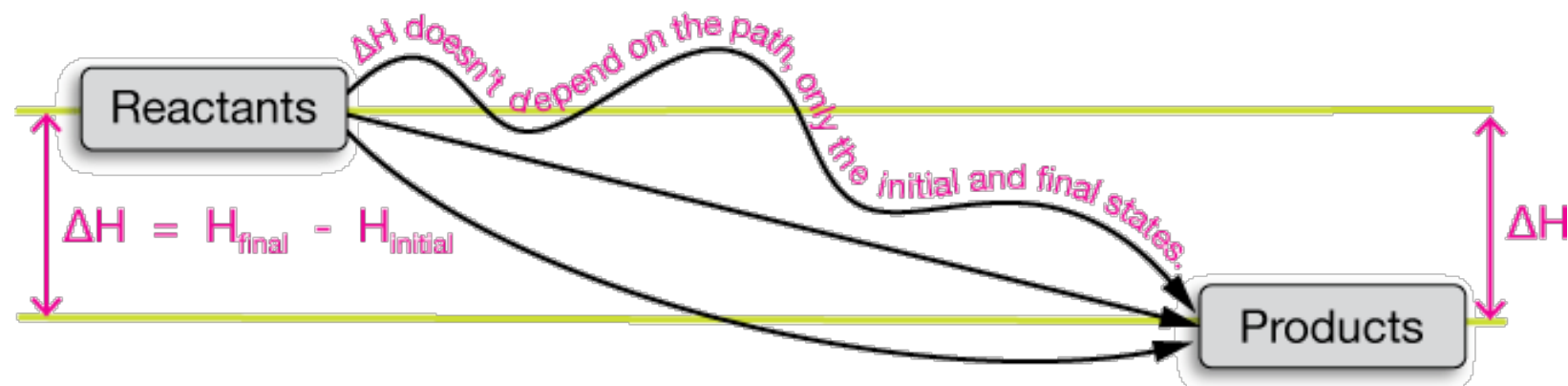
Hess's Law

Enthalpy is a state function, which means we only care about the *initial* and *final* states.

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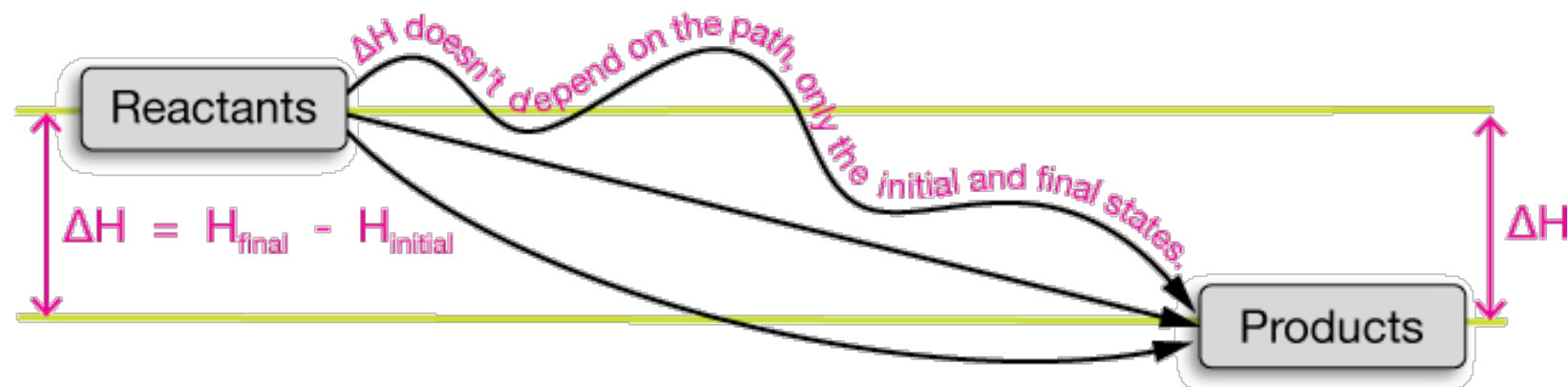Enthalpy is a state function, which means we only care about the *initial* and *final* states.

Pictorially, imagine starting with "Reactants" and getting to "Products" any of the three drawn black lines. It does not matter which pathway (line) you follow because the enthalpy change (ΔH_{rxn}) will be the same.

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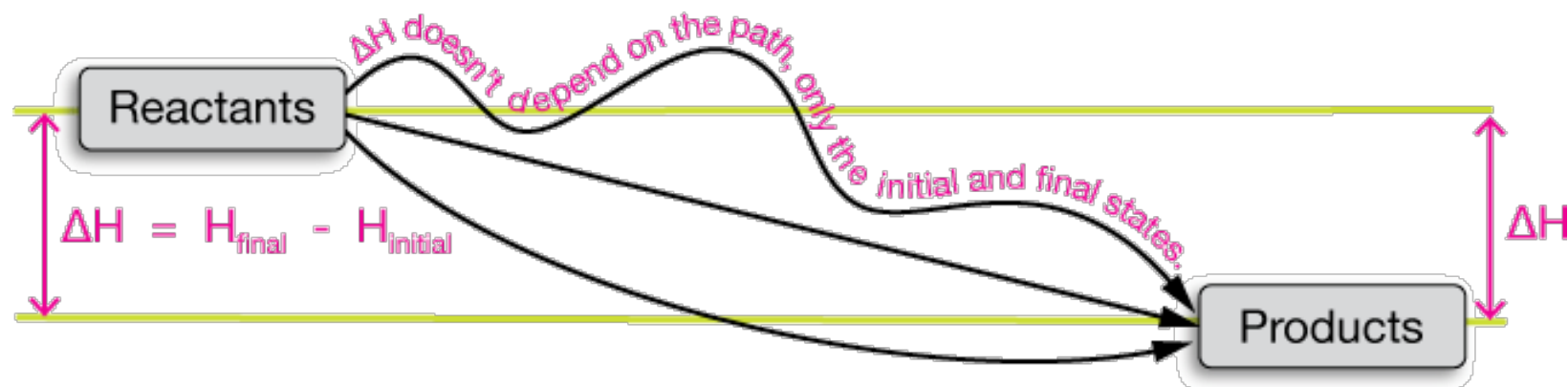

Q: Why is this information helpful though?

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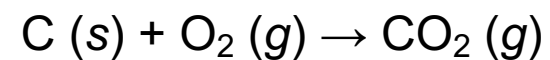

Q: Why is this information helpful though?

A: Because it means that we don't necessarily have to carry out the exact reaction in order to determine its change in enthalpy. We just have to find a set of reactions in which the products and reactants are exactly the same as those of the reaction we are interested in! This is a shortcut because you may not have access to every single reaction imaginable, but you may have enough to get what you want.
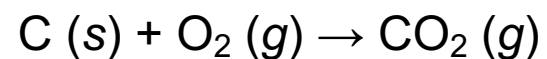
Hess's Law: A Guided Example

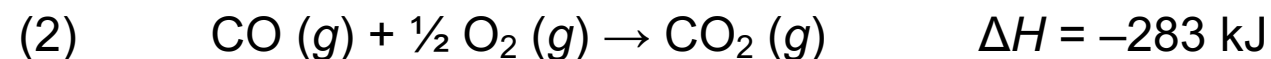Let's say you want to calculate the heat of reaction for the following reaction:

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(1) $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$ $\Delta H = -111$ kJ

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Since enthalpy is a state function, if you add up (in some manner) these two reactions to get the reaction you are interested in, then you can also get the heat of reaction.

Let's simply add reactions (1) and (2) to get reaction (3) below:

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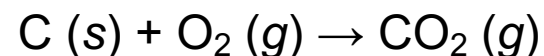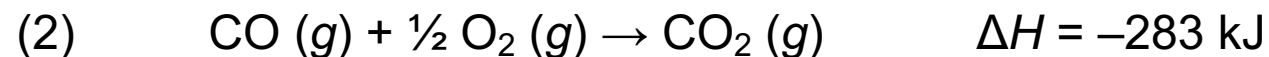Let's say you want to calculate the heat of reaction for the following reaction:

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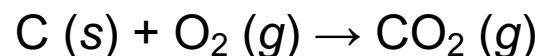
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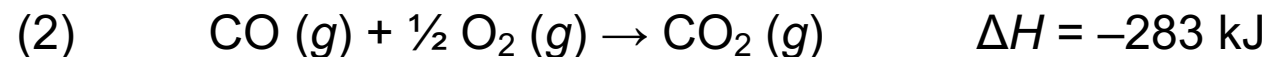
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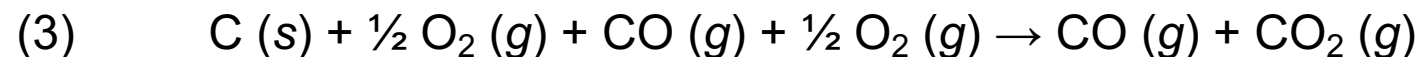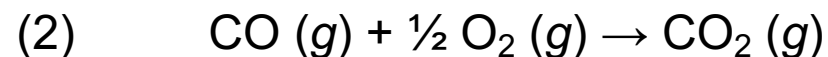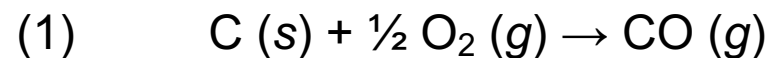$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$$

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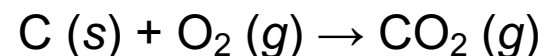
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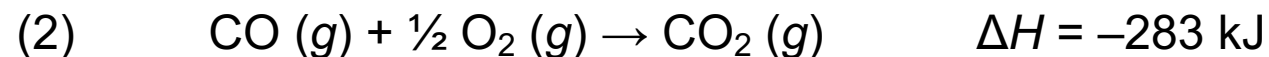
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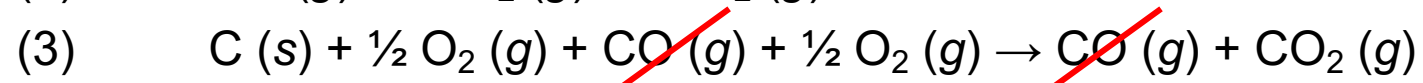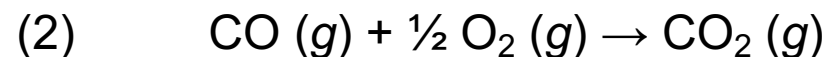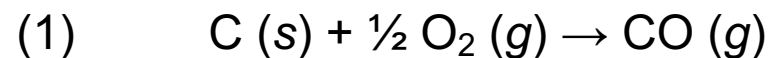
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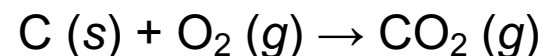
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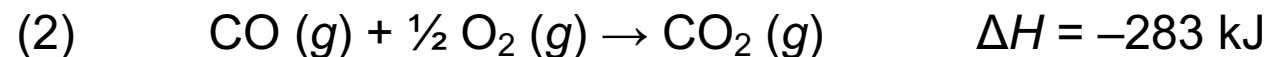
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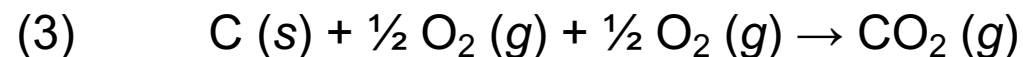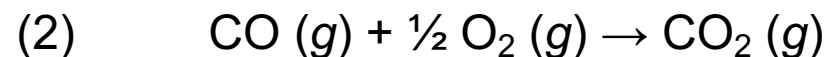
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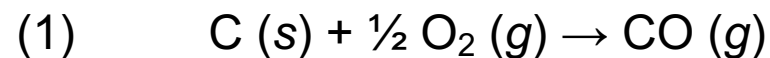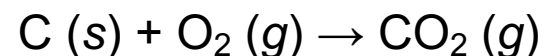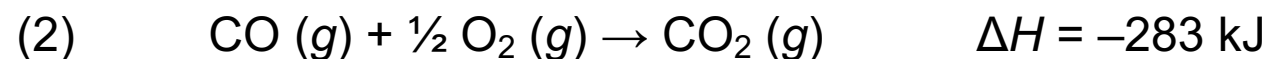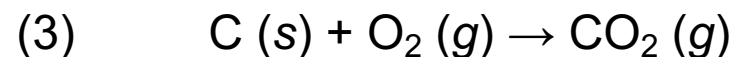
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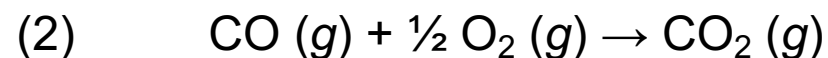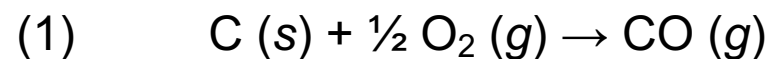
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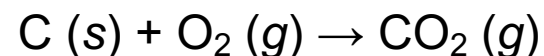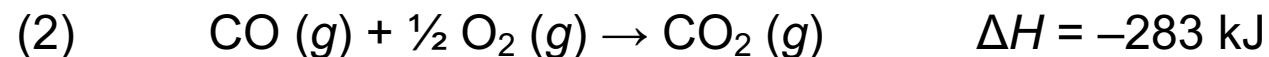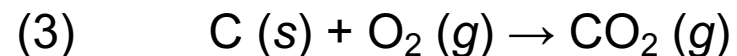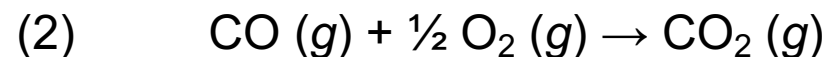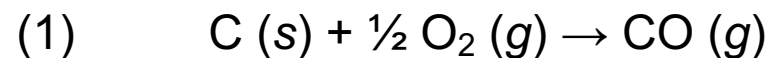
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(3) $C \ (s) + O_2 \ (g) \rightarrow CO_2 \ (g)$ $\Delta H_{rxn} = -111$ kJ + $(-283$ kJ$) = -394$ kJ

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Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:

$$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$$

You have access to the heats of reactions of some related reactions:

(1)	$2OF_2\ (g) \rightarrow O_2\ (g) + 2F_2\ (g)$	$\Delta H = -49.4$ kJ
(2)	$2ClF\ (g) + O_2\ (g) \rightarrow Cl_2O\ (g) + OF_2\ (g)$	$\Delta H = +205.6$ kJ
(3)	$ClF_3\ (g) + O_2\ (g) \rightarrow 1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g)$	$\Delta H = +266.7$ kJ

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Let's say you want to calculate the heat of reaction for the following reaction:

$$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$$

You have access to the heats of reactions of some related reactions:

(1)	$2OF_2\ (g) \rightarrow O_2\ (g) + 2F_2\ (g)$	$\Delta H = -49.4$ kJ
(2)	$2ClF\ (g) + O_2\ (g) \rightarrow Cl_2O\ (g) + OF_2\ (g)$	$\Delta H = +205.6$ kJ
(3)	$ClF_3\ (g) + O_2\ (g) \rightarrow 1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g)$	$\Delta H = +266.7$ kJ

You need to be a little creative with how you want to manipulate these equations. I like to start with the first reactant, which is ClF, which is found in reaction (2), but we need to multiply it by ½ first:

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$$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$$
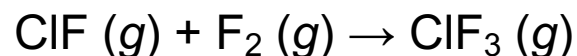
You have access to the heats of reactions of some related reactions:

(1) $2OF_2\ (g) \rightarrow O_2\ (g) + 2F_2\ (g)$ $\Delta H = -49.4\ kJ$

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(3) $ClF_3\ (g) + O_2\ (g) \rightarrow 1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g)$ $\Delta H = +266.7\ kJ$

You need to be a little creative with how you want to manipulate these equations. I like to start with the first reactant, which is ClF, which is found in reaction (2), but we need to multiply it by ½ first:

(2)   ½ × [$2ClF\ (g) + O_2\ (g) \rightarrow Cl_2O\ (g) + OF_2\ (g)$]   ½ × [$\Delta H = +205.6\ kJ$]

Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:

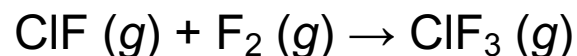$$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$$

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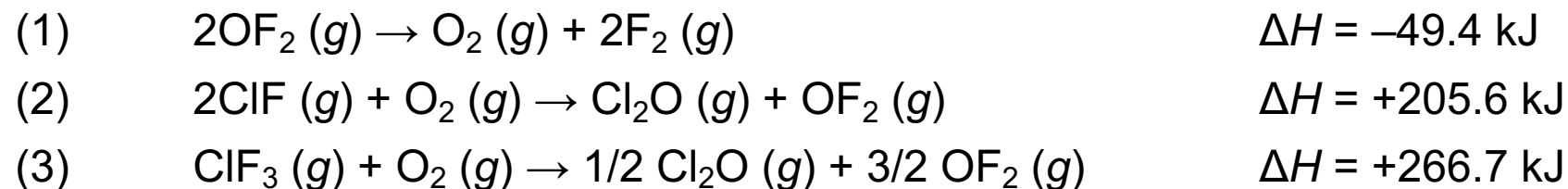
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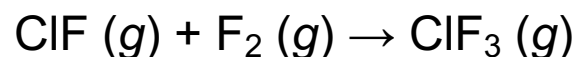
(2) $ClF\ (g) + ½\ O_2\ (g) \rightarrow ½\ Cl_2O\ (g) + ½\ OF_2\ (g)$ $\Delta H = ½\ (+205.6$ kJ$)$

Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:

$$ClF \ (g) + F_2 \ (g) \rightarrow ClF_3 \ (g)$$

You have access to the heats of reactions of some related reactions:

    (1) $2OF_2 \ (g) \rightarrow O_2 \ (g) + 2F_2 \ (g)$ $\Delta H = -49.4$ kJ

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Now, you should see that you also need F_2 as a reactant, which can be found in reaction (1), but you have to invert it to get it on the correct side and multiply by ½:

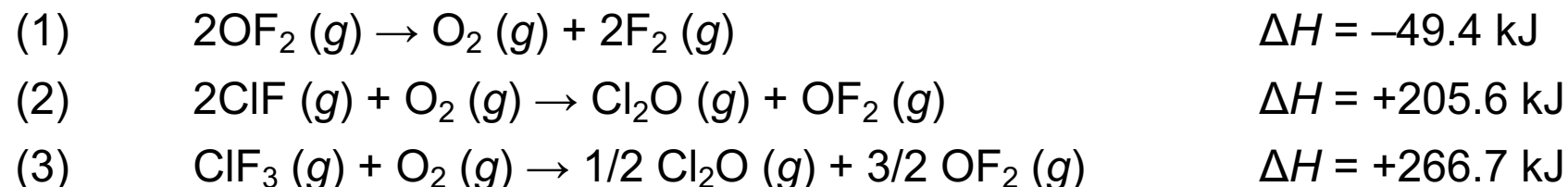   (2) $ClF \ (g) + \frac{1}{2} O_2 \ (g) \rightarrow \frac{1}{2} Cl_2O \ (g) + \frac{1}{2} OF_2 \ (g)$ $\Delta H = \frac{1}{2} (+205.6$ kJ$)$

Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:

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Now, you should see that you also need F_2 as a reactant, which can be found in reaction (1), but you have to invert it to get it on the correct side and multiply by ½:

(2)	$ClF\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow \frac{1}{2}\ Cl_2O\ (g) + \frac{1}{2}\ OF_2\ (g)$	$\Delta H = \frac{1}{2}\ (+205.6$ kJ$)$
(1)	$\frac{1}{2} \times [2F_2\ (g) + O_2\ (g) \rightarrow 2OF_2\ (g)]$	$\frac{1}{2} \times [\Delta H = +49.4$ kJ$]$

Note: Flip sign when you invert reaction!

Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:
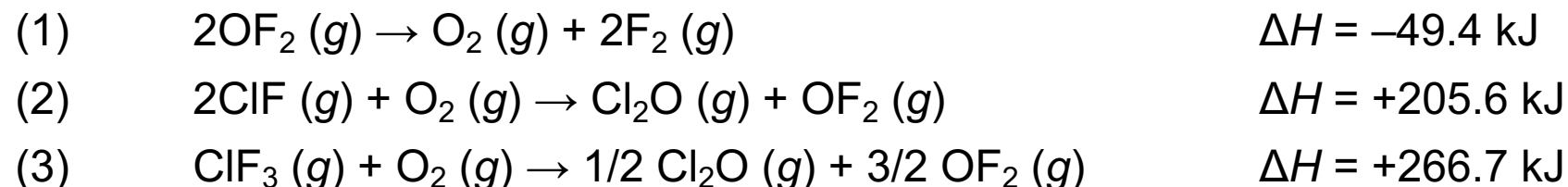
$$ClF \ (g) + F_2 \ (g) \rightarrow ClF_3 \ (g)$$

You have access to the heats of reactions of some related reactions:

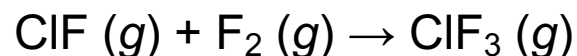|		
(1)	$2OF_2 \ (g) \rightarrow O_2 \ (g) + 2F_2 \ (g)$	$\Delta H = -49.4$ kJ
(2)	$2ClF \ (g) + O_2 \ (g) \rightarrow Cl_2O \ (g) + OF_2 \ (g)$	$\Delta H = +205.6$ kJ
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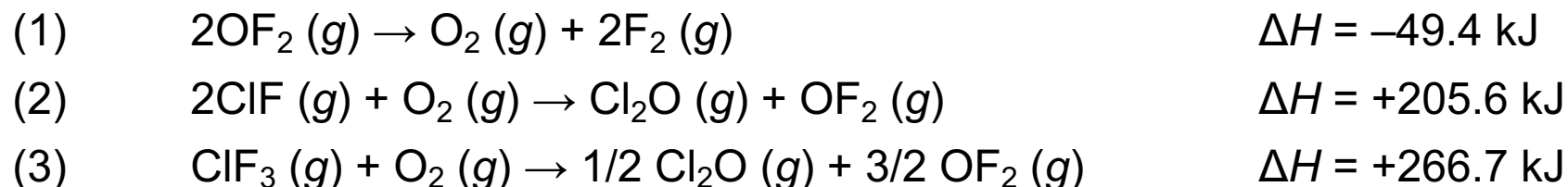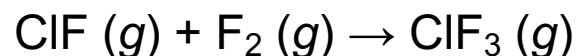
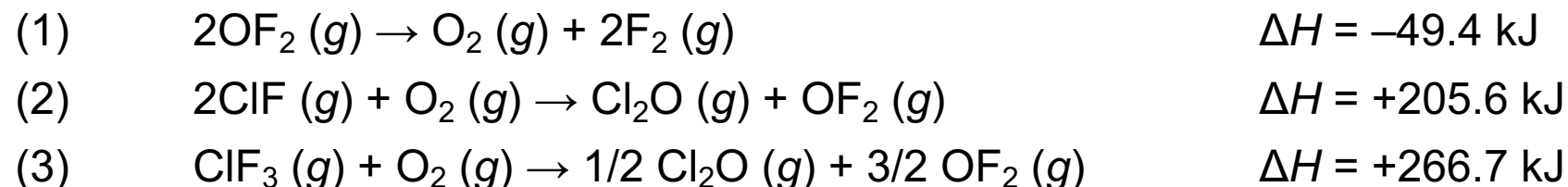|		
(2)	$ClF \ (g) + ½ \ O_2 \ (g) \rightarrow ½ \ Cl_2O \ (g) + ½ \ OF_2 \ (g)$	$\Delta H = ½ \ (+205.6$ kJ$)$
(1)	$F_2 \ (g) + ½ \ O_2 \ (g) \rightarrow OF_2 \ (g)$	$\Delta H = ½ \ (+49.4$ kJ$)$

Hess's Law: A More Difficult Example

Let's say you want to calculate the heat of reaction for the following reaction:

$$\text{ClF } (g) + F_2 (g) \rightarrow \text{ClF}_3 (g)$$

You have access to the heats of reactions of some related reactions:

(1)	$2OF_2 (g) \rightarrow O_2 (g) + 2F_2 (g)$	$\Delta H = -49.4 \text{ kJ}$
(2)	$2\text{ClF } (g) + O_2 (g) \rightarrow Cl_2O (g) + OF_2 (g)$	$\Delta H = +205.6 \text{ kJ}$
(3)	$\text{ClF}_3 (g) + O_2 (g) \rightarrow 1/2\ Cl_2O (g) + 3/2\ OF_2 (g)$	$\Delta H = +266.7 \text{ kJ}$

Finally, you should see that you need ClF_3 as a product, which can be found in reaction (3), but you have to invert it to get it on the correct side:

(2)	$\text{ClF } (g) + \frac{1}{2} O_2 (g) \rightarrow \frac{1}{2} Cl_2O (g) + \frac{1}{2} OF_2 (g)$	$\Delta H = \frac{1}{2}\ (+205.6 \text{ kJ})$
(1)	$F_2 (g) + \frac{1}{2} O_2 (g) \rightarrow OF_2 (g)$	$\Delta H = \frac{1}{2}\ (+49.4 \text{ kJ})$

Hess's Law: A More Difficult Example
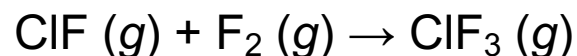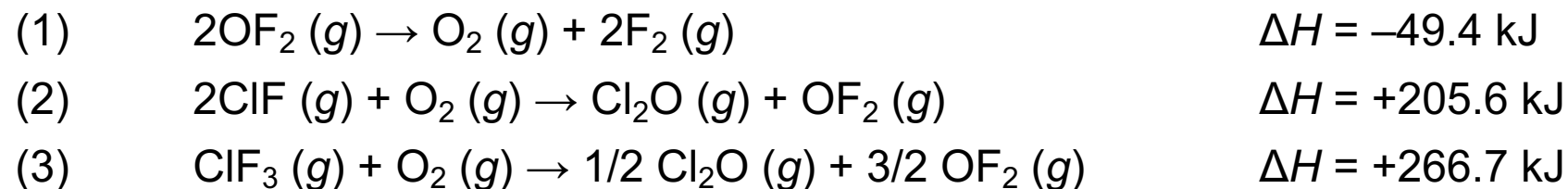
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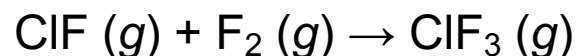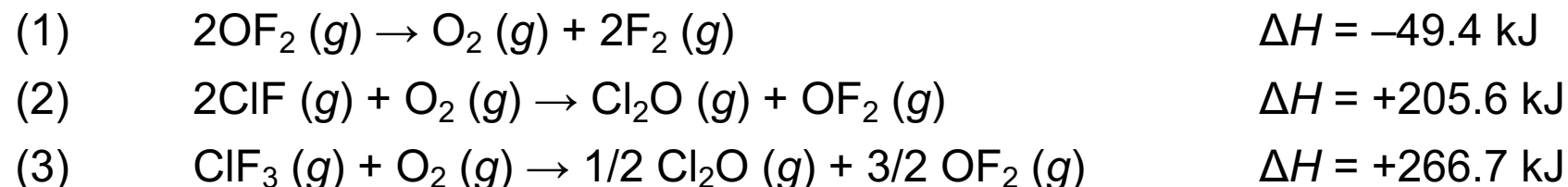
(2)	$ClF\ (g) + ½\ O_2\ (g) \rightarrow ½\ Cl_2O\ (g) + ½\ OF_2\ (g)$	$\Delta H = ½\ (+205.6$ kJ$)$
(1)	$F_2\ (g) + ½\ O_2\ (g) \rightarrow OF_2\ (g)$	$\Delta H = ½\ (+49.4$ kJ$)$
(3)	$1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g) \rightarrow ClF_3\ (g) + O_2\ (g)$	$\Delta H = -266.7$ kJ

Note: Flip sign when you invert reaction!

Hess's Law: A More Difficult Example

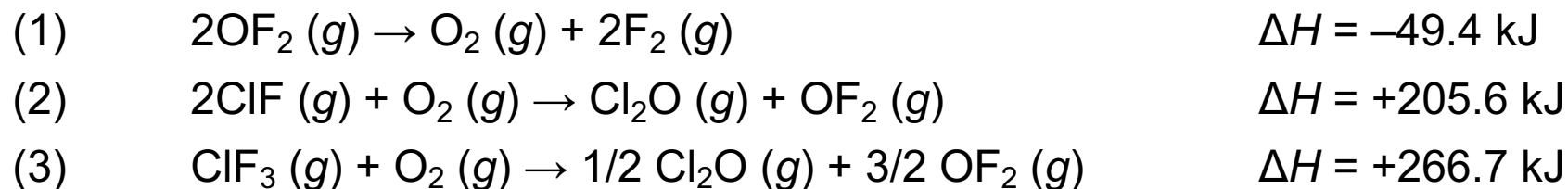Let's say you want to calculate the heat of reaction for the following reaction:

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Now sum up reactions (2), (1), and (3):

(2)	$ClF\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow \frac{1}{2}\ Cl_2O\ (g) + \frac{1}{2}\ OF_2\ (g)$	$\Delta H = \frac{1}{2}\ (+205.6$ kJ$)$
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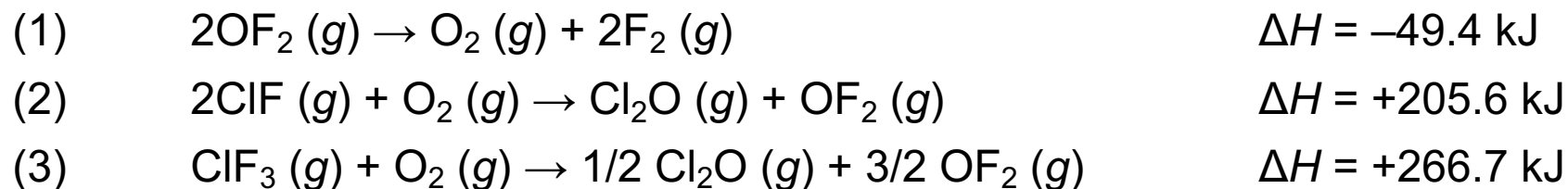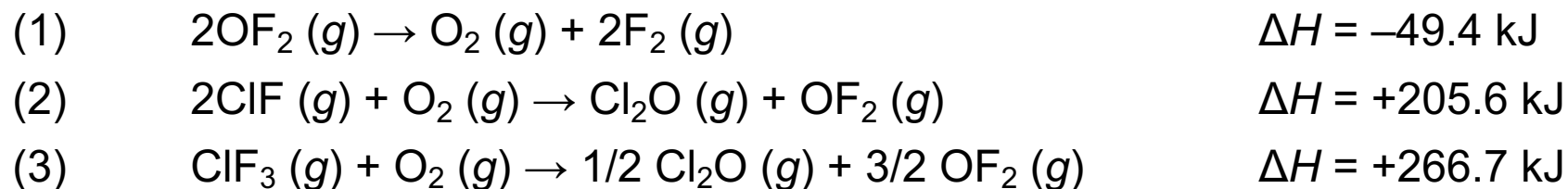|		
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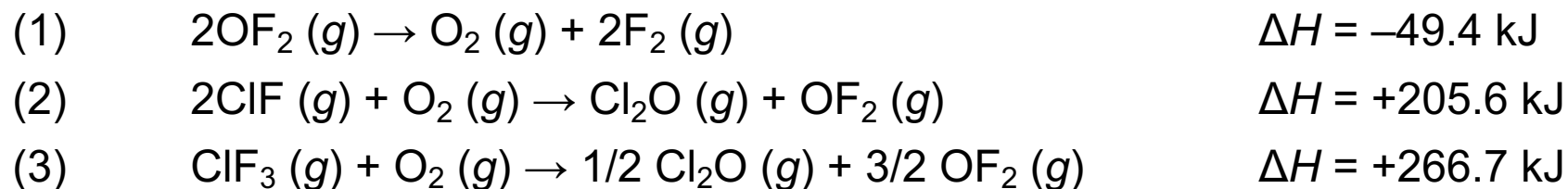|		
(2)	$ClF\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow \frac{1}{2}\ Cl_2O\ (g) + \frac{1}{2}\ OF_2\ (g)$	$\Delta H = \frac{1}{2}\ (+205.6$ kJ$)$
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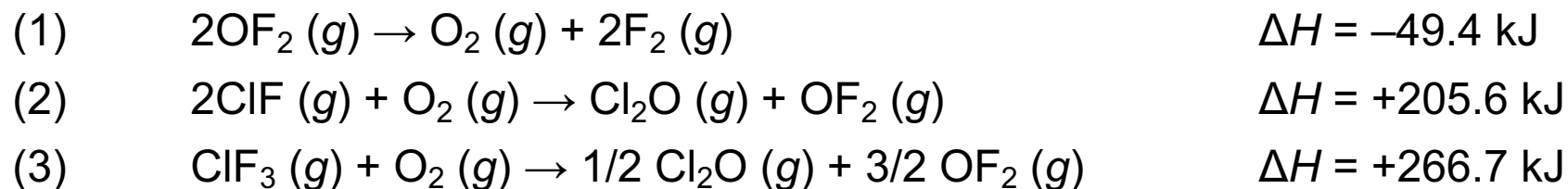|		
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(1)	$F_2\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow OF_2\ (g)$	$\Delta H = \frac{1}{2}\ (+49.4$ kJ$)$
(3)	$1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g) \rightarrow ClF_3\ (g) + O_2\ (g)$	$\Delta H = -266.7$ kJ
	$ClF\ (g) + F_2\ (g) \rightarrow ClF_3\ (g)$	$\Delta H_{rxn} = -139.2$ kJ

Note: Flip sign when you invert reaction!

Heats of Formation

Let's say we want to calculate the standard heat of reaction for the following reaction:

$$3NO_2\ (g) + H_2O\ (l) \rightarrow 2HNO_3\ (aq) + NO\ (g)$$

Instead of Hess's Law, you could also use the underlined standard heats of formations ($\Delta H_f°$) to calculate ΔH_{rxn}.

Heats of Formation

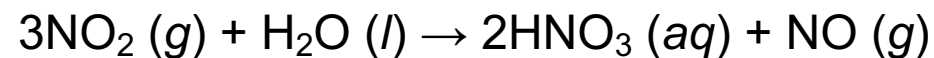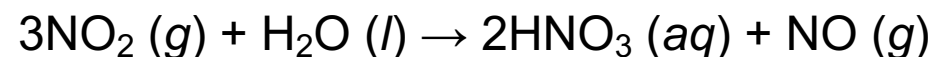Let's say we want to calculate the standard heat of reaction for the following reaction:

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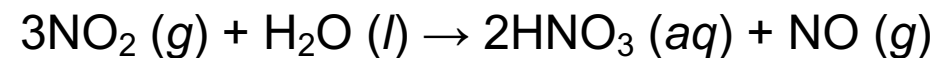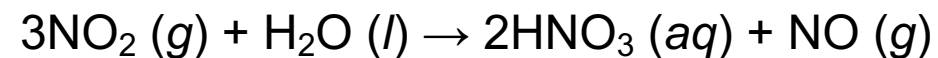
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Q: What is a heat of formation anyway?

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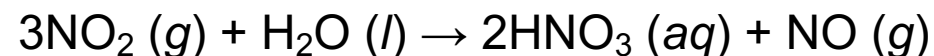Instead of Hess's Law, you could also use the standard heats of formations ($\Delta H_f°$) to calculate ΔH_{rxn}.

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A: *It's the amount of heat required to form 1 mole of a substance from its elements in standard states.*

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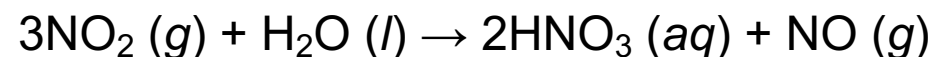
Q: What is a standard state?

A: *1 bar (~1 atm) of pressure and 25 °C. (This is NOT STP for gases!)*

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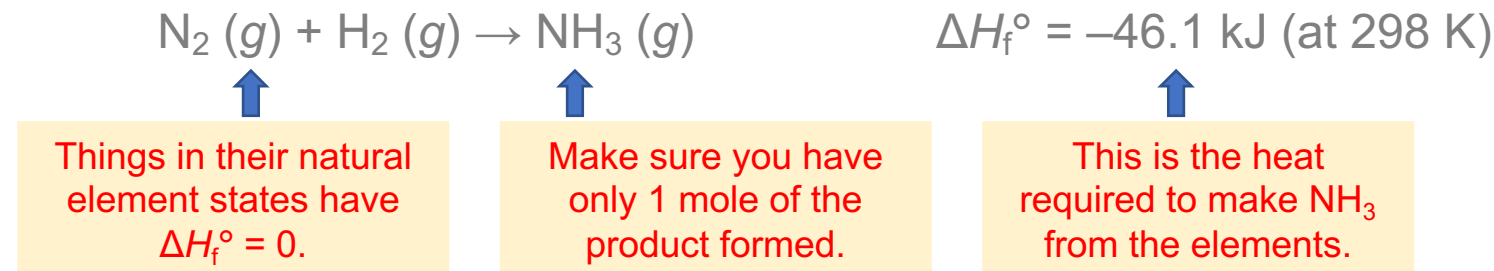
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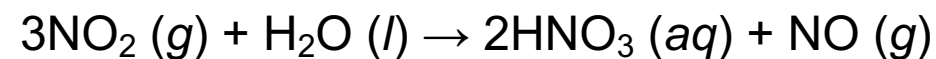
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| Things in their natural element states have $\Delta H_f° = 0$. | Make sure you have only 1 mole of the product formed. | This is the heat required to make NH_3 from the elements. |

Heats of Formation

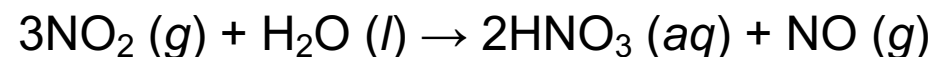Let's say we want to calculate the standard heat of reaction for the following reaction:

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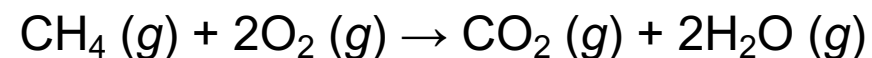
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Heats of Combustion

A <u>heat of combustion</u> (ΔH_{comb}) is the same thing as the heat of reaction but pertains to a combustion reaction, such as:

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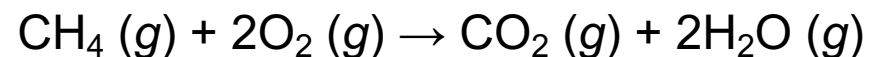
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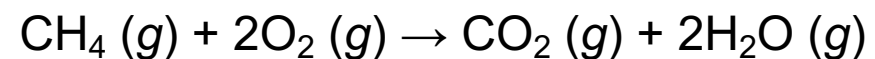
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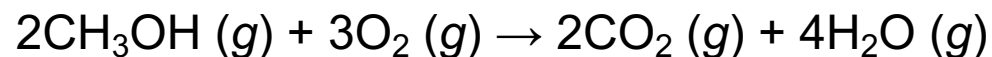
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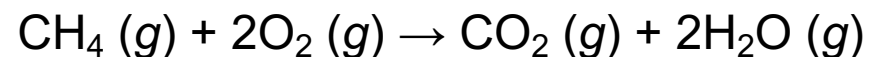
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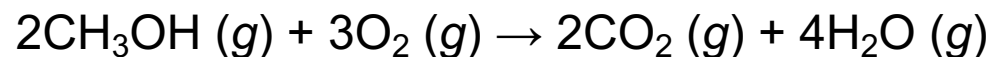
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The ΔH_{comb} is reported for 2 moles of CH_3OH gas being combusted.