

# Lecture 16

## Thermodynamics II

Calorimetry

Hess's Law

Enthalpy of Formation

# Four Methods for Finding $\Delta H$

- 1) Calculate it using average bond enthalpies
- 2) Measure it using a calorimeter.**
- 3) Calculate it using Hess's Law.
- 4) Calculate it using enthalpies of formation

# Calorimetry

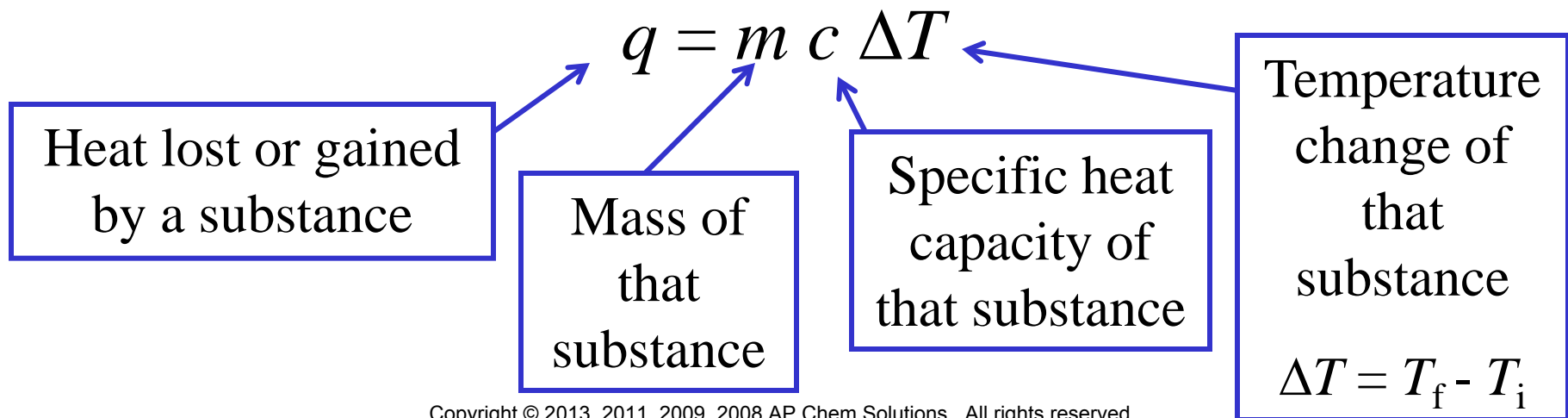
- Calorimetry
  - The measurement of heat transfer
- Calorimeter
  - A device used to determine the amount of heat transferred

**Heat flow cannot be measured directly.**

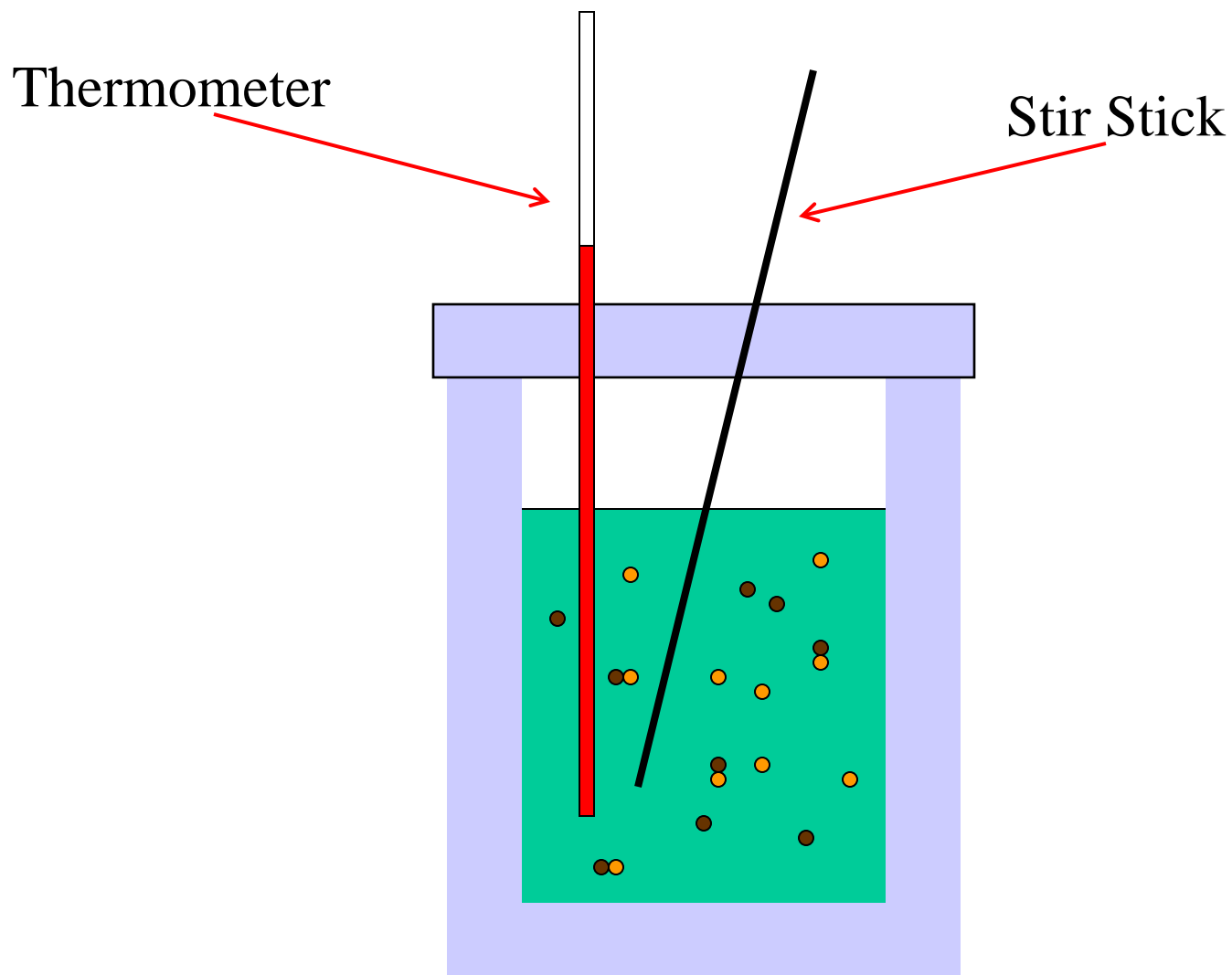
**We measure the temperature before and after a reaction, and use that data to calculate heat transfer.**

# Calorimetry

- Specific Heat Capacity ( $c$ )
  - The amount of heat required to raise the temperature of 1 g of a substance by 1 K.
  - A large value for water (4.184 J/g•K)
    - It takes a lot of heat to increase the temperature of water.
  - A small value for iron (0.45 J/g•K)
    - It takes much less heat to raise the temperature of iron.

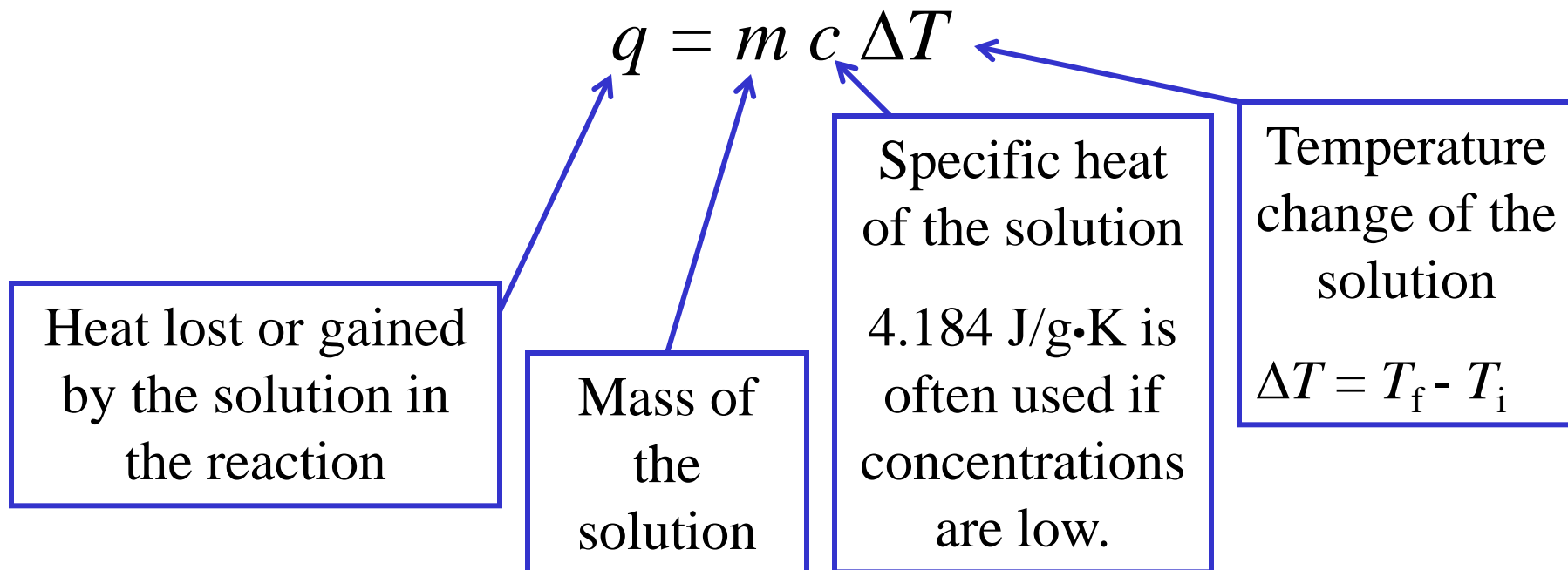


# Coffee Cup Calorimeter



# Coffee Cup Calorimetry

When measuring the heat lost or gained in a chemical reaction that takes place in a coffee cup calorimeter, we use the solution as the basis for our calculations.



# Coffee Cup Calorimetry

- The reactants and products are the system.
- The water which they are dissolved in and calorimeter make up the surroundings.
- The heat lost or gained by the solution is equal to the heat lost or gained by the reaction.

e.g.) If you calculated  $q_{solution}$  to be +568 J, the solution gained heat. This means the reaction was exothermic, as the heat gained by the solution is equal to the heat lost by the reaction ( $q_{rxn} = -568$  J).

# Ex1) Calorimetry

Ex1) A 97 g iron bar was heated to  $143^{\circ}\text{C}$  and placed in a coffee cup calorimeter containing 350.0 g of water at  $25.00^{\circ}\text{C}$ . The maximum temperature of the water was measured to be  $28.40^{\circ}\text{C}$ .

- a) How much heat was gained by the water?
- b) How much heat was lost by the iron bar?
- c) What is the specific heat of iron?



# Ex1) Calorimetry (cont.)

a) How much heat was gained by the water?

b) How much heat was lost by the iron bar?

# Ex1) Calorimetry (cont.)

a) How much heat was gained by the water?

$$q_w = mc\Delta T$$

b) How much heat was lost by the iron bar?

# Ex1) Calorimetry (cont.)

a) How much heat was gained by the water?

$$q_w = mc\Delta T$$

$$q_w = (350.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(28.40 ^\circ \text{C} - 25.00 ^\circ \text{C})$$

b) How much heat was lost by the iron bar?

# Ex1) Calorimetry (cont.)

a) How much heat was gained by the water?

$$q_w = mc\Delta T$$

$$q_w = (350.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(28.40 ^\circ \text{C} - 25.00 ^\circ \text{C})$$

$$q_w = +4979 \text{ J}$$

Gaining heat is endothermic

b) How much heat was lost by the iron bar?

# Ex1) Calorimetry (cont.)

a) How much heat was gained by the water?

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Gaining heat is endothermic

b) How much heat was lost by the iron bar?

$$q_w = -q_{\text{Fe}}$$

# Ex1) Calorimetry (cont.)

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$$q_w = +4979 \text{ J}$$

Gaining heat is endothermic

b) How much heat was lost by the iron bar?

$$q_w = -q_{\text{Fe}}$$

$$q_{\text{Fe}} = -4979 \text{ J}$$

Losing heat is exothermic

As energy is conserved, the heat gained by the water is equal in magnitude to the heat lost by the iron bar.

# Ex1) Calorimetry (cont.)

c) What is the specific heat of iron?

# Ex1) Calorimetry (cont.)

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$$q_{\text{Fe}} = mc\Delta T$$



# Ex1) Calorimetry (cont.)

c) What is the specific heat of iron?

$$q_{\text{Fe}} = mc\Delta T$$

$$c = \frac{q_{\text{Fe}}}{m\Delta T}$$

# Ex1) Calorimetry (cont.)

c) What is the specific heat of iron?

$$q_{\text{Fe}} = mc\Delta T$$

$$c = \frac{q_{\text{Fe}}}{m\Delta T}$$

$$c = \frac{-4979 \text{ J}}{(97 \text{ g})(28.40 \text{ }^{\circ}\text{C} - 143 \text{ }^{\circ}\text{C})}$$

# Ex1) Calorimetry (cont.)

c) What is the specific heat of iron?

$$q_{\text{Fe}} = mc\Delta T$$

$$c = \frac{q_{\text{Fe}}}{m\Delta T}$$

$$c = \frac{-4979 \text{ J}}{(97 \text{ g})(28.40 \text{ }^\circ\text{C} - 143 \text{ }^\circ\text{C})}$$

$$c = 0.45 \text{ J / g} \cdot ^\circ \text{C}$$

## Ex2) Calorimetry

Ex2) When 20.0 mL of 1.00 *M* NaCl at 22.00°C is mixed with 20.0 mL of 1.00 *M* AgNO<sub>3</sub> at 22.00°C in a calorimeter, a white precipitate forms and the temperature of the mixture reaches 29.60°C.

Assume that the specific heat capacity of the mixture is 4.184 J/g·K, its density is 1.00 g/mL, and the volumes are additive.

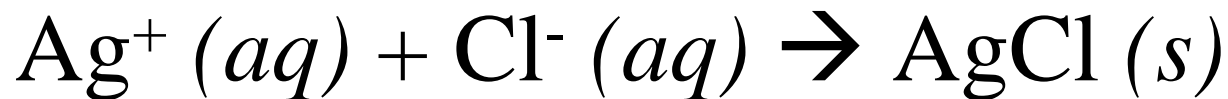
- Write the net ionic equation for this reaction.
- Calculate  $\Delta H$  for the reaction.

## Ex2) Calorimetry

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Assume that the specific heat capacity of the mixture is 4.184 J/g·K, its density is 1.00 g/mL, and the volumes are additive.

- Write the net ionic equation for this reaction.
- Calculate  $\Delta H$  for the reaction.



# Ex2) Calorimetry (cont.)

Step 1) Calculate  $q_{sol}$ .

Step 2) Calculate  $q_{rxn}$ .

# Ex2) Calorimetry (cont.)

Step 1) Calculate  $q_{sol}$ .

$$q_{sol} = mc\Delta T$$

Step 2) Calculate  $q_{rxn}$ .

## Ex2) Calorimetry (cont.)

Step 1) Calculate  $q_{sol}$ .

$$q_{sol} = mc\Delta T$$

$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(29.60^\circ \text{C} - 22.00^\circ \text{C})$$

Step 2) Calculate  $q_{rxn}$ .



## Ex2) Calorimetry (cont.)

Step 1) Calculate  $q_{sol}$ .

$$q_{sol} = mc\Delta T$$

$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(29.60^\circ \text{C} - 22.00^\circ \text{C})$$

$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(7.60^\circ \text{C})$$

Step 2) Calculate  $q_{rxn}$ .

## Ex2) Calorimetry (cont.)

Step 1) Calculate  $q_{sol}$ .

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$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(29.60^\circ \text{C} - 22.00^\circ \text{C})$$

$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(7.60^\circ \text{C})$$

$$q_{sol} = +1270 \text{ J}$$

Step 2) Calculate  $q_{rxn}$ .

## Ex2) Calorimetry (cont.)

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$$q_{sol} = (40.0 \text{ g})(4.184 \text{ J / g} \cdot ^\circ \text{C})(7.60^\circ \text{C})$$

$$q_{sol} = +1270 \text{ J}$$

Step 2) Calculate  $q_{rxn}$ .

$$q_{rxn} = -q_{sol}$$

$$q_{rxn} = -1270 \text{ J}$$

The reaction is **exothermic** as heat is released to the water.

## Ex2) Calorimetry (cont.)

Step 3) Calculate Moles of  $\text{Ag}^+$  or  $\text{Cl}^-$ .

Step 4) Calculate  $\Delta H_{rxn}$ .

## Ex2) Calorimetry (cont.)

Step 3) Calculate Moles of  $\text{Ag}^+$  or  $\text{Cl}^-$ .

$$0.0200 \text{ L} \times \frac{1.0 \text{ moles Ag}^+}{1 \text{ L}} = 0.0200 \text{ moles Ag}^+$$

Step 4) Calculate  $\Delta H_{rxn}$ .

## Ex2) Calorimetry (cont.)

Step 3) Calculate Moles of  $\text{Ag}^+$  or  $\text{Cl}^-$ .

$$0.0200 \text{ L} \times \frac{1.0 \text{ moles Ag}^+}{1 \text{ L}} = 0.0200 \text{ moles Ag}^+$$

Step 4) Calculate  $\Delta H_{rxn}$ .

$$\Delta H_{rxn} = \frac{q_{rxn}}{n_{\text{AgCl}}}$$

$$\Delta H_{rxn} = \frac{-1270 \text{ J}}{0.0200 \text{ moles AgCl}}$$

## Ex2) Calorimetry (cont.)

Step 3) Calculate Moles of  $\text{Ag}^+$  or  $\text{Cl}^-$ .

$$0.0200 \text{ L} \times \frac{1.0 \text{ moles Ag}^+}{1 \text{ L}} = 0.0200 \text{ moles Ag}^+$$

Step 4) Calculate  $\Delta H_{rxn}$ .

$$\Delta H_{rxn} = \frac{q_{rxn}}{n_{\text{AgCl}}}$$

$$\Delta H_{rxn} = \frac{-1270 \text{ J}}{0.0200 \text{ moles AgCl}}$$

$$\Delta H_{rxn} = -63500 \text{ J/mol} = -63.5 \text{ kJ/mol}$$

# $q_{\text{rxn}}$ vs. $\Delta H_{\text{rxn}}$

$q_{\text{rxn}}$  = The heat lost or gained in the experiment that took place in the calorimeter

$\Delta H_{\text{rxn}}$  = The heat lost or gained in the balanced chemical equation



# Four Methods for Finding $\Delta H$

- 1) Calculate it using average bond enthalpies.
- 2) Measure it using a calorimeter.
- 3) Calculate it using Hess's Law.**
- 4) Calculate it using enthalpies of formation.

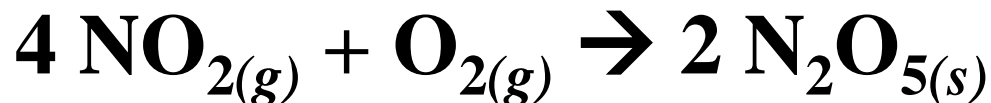
# Hess's Law

If a reaction is carried out in a series of steps, the overall change in enthalpy will be equal to the sum of the enthalpy changes for the individual steps.

- The overall enthalpy change will be the same if a reaction is carried out in one step or in several steps.

# Ex1) Hess's Law

Ex1) Calculate  $\Delta H$  for the following reaction using the information in the table below.



Reaction	Chemical Equation	Enthalpy Change
1	$2 \text{NO}_{(g)} + \frac{3}{2} \text{O}_{2(g)} \rightarrow \text{N}_2\text{O}_{5(s)}$	$\Delta H = - 223.7 \text{ kJ}$
2	$2 \text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{NO}_{2(g)}$	$\Delta H = - 114.2 \text{ kJ}$

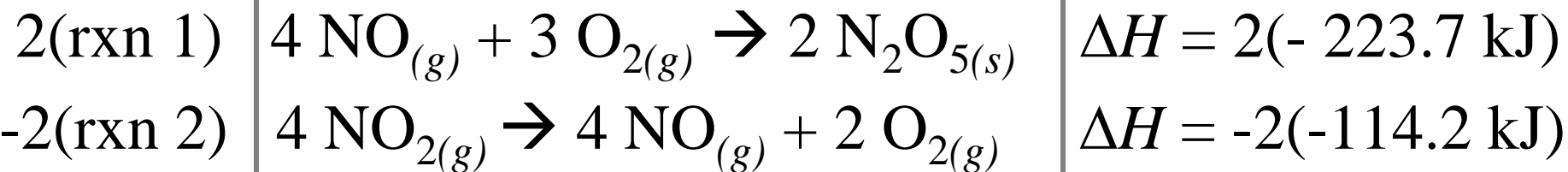
# Ex1) Hess's Law (cont.)

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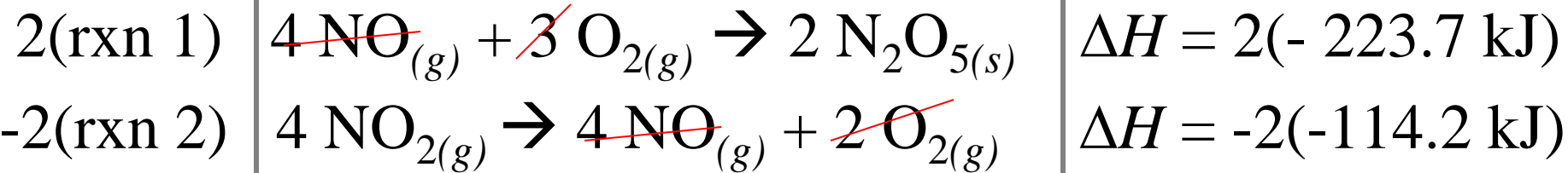
# Ex1) Hess's Law (cont.)



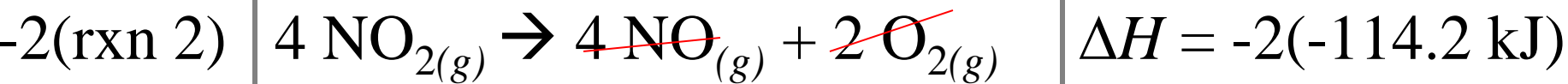
# Ex1) Hess's Law (cont.)



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# Ex1) Hess's Law (cont.)





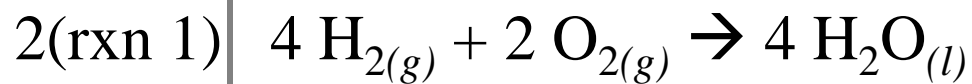
## Ex2) Hess's Law

Ex2) Calculate  $\Delta H$  for the following reaction using the information in the table below.



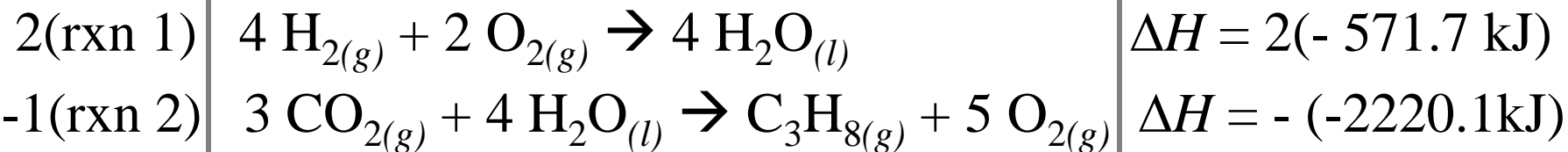
Reaction	Chemical Equation	Enthalpy Change
1	$2 \text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2 \text{H}_2\text{O}_{(l)}$	$\Delta H = - 571.7 \text{ kJ}$
2	$\text{C}_3\text{H}_{8(g)} + 5\text{O}_{2(g)} \rightarrow 3\text{CO}_{2(g)} + 4\text{H}_2\text{O}_{(l)}$	$\Delta H = - 2220.1 \text{ kJ}$
3	$\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$	$\Delta H = - 393.5 \text{ kJ}$

## Ex2) Hess's Law (cont.)

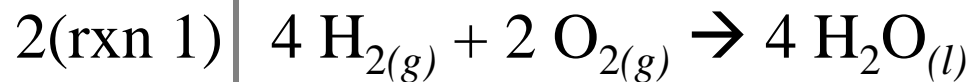


$$\Delta H = 2(-571.7 \text{ kJ})$$

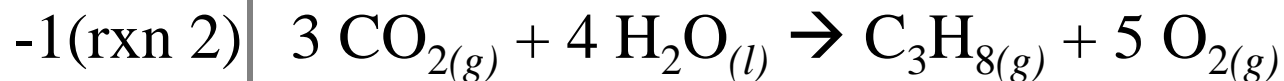
## Ex2) Hess's Law (cont.)



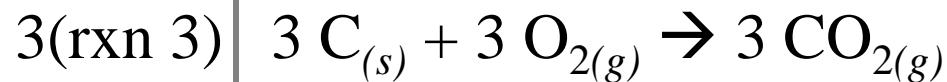
## Ex2) Hess's Law (cont.)



$$\Delta H = 2(-571.7 \text{ kJ})$$

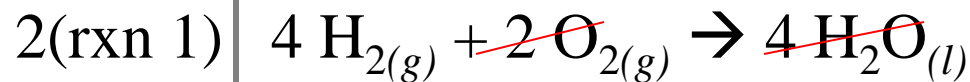


$$\Delta H = -(-2220.1 \text{ kJ})$$



$$\Delta H = 3(-393.5 \text{ kJ})$$

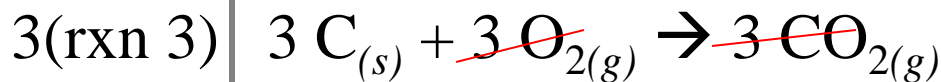
## Ex2) Hess's Law (cont.)



$$\Delta H = 2(-571.7 \text{ kJ})$$



$$\Delta H = -(-2220.1 \text{ kJ})$$



$$\Delta H = 3(-393.5 \text{ kJ})$$



$$\Delta H = -103.8 \text{ kJ}$$

# Four Methods for Finding $\Delta H$

- 1) Calculate it using average bond enthalpies.
- 2) Measure it using a calorimeter.
- 3) Calculate it using Hess's Law.
- 4) **Calculate it using enthalpies of formation.**

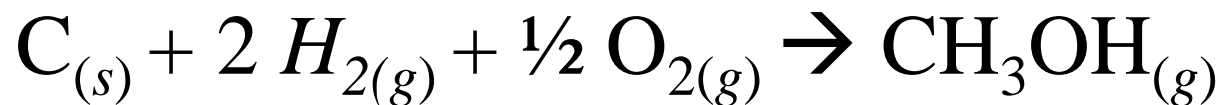
# Standard Enthalpy of Formation

A hypothetical value that indicates how much heat would be lost or gained during the formation of one mole of a compound from the most common form of its elements in their standard states.



# Standard Enthalpy of Formation

## For Methanol



$$\Delta H_f^\circ = -201 \text{ kJ/mol}$$

**Heat of formation reactions are always written so that all reactants exist as they would under standard conditions, and there is one mole of product.**



# Enthalpy of Formation

The  $\Delta H_f^\circ$  value for the most stable form of any element in its standard state is zero.

Element	$\Delta H_f^\circ$	Element	$\Delta H_f^\circ$
Ca(s)	0	Cl <sub>2</sub> (g)	0
Ag(s)	0	H <sub>2</sub> (g)	0
Na(s)	0	Fe(s)	0
O <sub>2</sub> (g)	0	N <sub>2</sub> (g)	0

# Formula for Calculating the Enthalpy of a Reaction under Standard Conditions

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

Sum of

stoichiometric  
coefficients

# Ex1) Enthalpy of Formation

Ex1) Find  $\Delta H_{\text{rxn}}^{\circ}$  for the thermite reaction under standard conditions.



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

$$\Delta H_{\text{rxn}}^{\circ} = [2 (\Delta H_{\text{f}}^{\circ} (\text{Fe}_{(s)})) + 1 (\Delta H_{\text{f}}^{\circ} (\text{Al}_2\text{O}_{3(s)}))] - [2 (\Delta H_{\text{f}}^{\circ} (\text{Al}_{(s)})) + 1 (\Delta H_{\text{f}}^{\circ} (\text{Fe}_2\text{O}_{3(s)}))]$$

$$\Delta H_{\text{rxn}}^{\circ} = [2(0) + 1(-1675.7)] - [2(0) + 1(-821.4)]$$

$$\Delta H_{\text{rxn}}^{\circ} = -854.3 \text{ kJ/mol}$$

# Ex2) Enthalpy of Formation

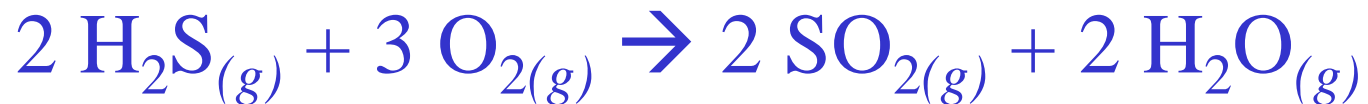
Ex2) Find  $\Delta H_{\text{rxn}}^{\circ}$  for this reaction at standard conditions.



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

# Ex2) Enthalpy of Formation

Ex2) Find  $\Delta H_{\text{rxn}}^{\circ}$  for this reaction at standard conditions.



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

$$\Delta H_{\text{rxn}}^{\circ} = [2 (\Delta H_{\text{f}}^{\circ}(\text{SO}_{2(g)})) + 2 (\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(g)}))] - [2 (\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{S}_{(g)})) + 3 (\Delta H_{\text{f}}^{\circ}(\text{O}_{2(g)}))]$$

# Ex2) Enthalpy of Formation

Ex2) Find  $\Delta H_{\text{rxn}}^{\circ}$  for this reaction at standard conditions.



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

$$\Delta H_{\text{rxn}}^{\circ} = [2 (\Delta H_{\text{f}}^{\circ}(\text{SO}_{2(g)})) + 2 (\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(g)}))] - [2 (\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{S}_{(g)})) + 3 (\Delta H_{\text{f}}^{\circ}(\text{O}_{2(g)}))]$$

$$\Delta H_{\text{rxn}}^{\circ} = [2(-296.8) + 2(-241.8)] - [2(-20.2) + 3(0)]$$

$$\Delta H_{\text{rxn}}^{\circ} = -1036.8 \text{ kJ/mol}$$

# Enthalpy of Formation

Reaction	$\Delta H_f^\circ$ kJ/mol	Elemental metal 1 <sup>st</sup> used by humans
$2 \text{Au}_{(s)} + 3/2 \text{O}_{2(g)} \rightarrow \text{Au}_2\text{O}_{3(s)}$	+131	~6000 BCE
$2 \text{Ag}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{Ag}_2\text{O}_{(s)}$	- 31	~4000 BCE
$\text{Cu}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{CuO}_{(s)}$	- 156	~4000 BCE
$\text{Pb}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{PbO}_{(s)}$	- 217	~3500 BCE
$\text{Sn}_{(s)} + \text{O}_{2(g)} \rightarrow \text{SnO}_{2(s)}$	- 581	~1800 BCE
$2 \text{Fe}_{(s)} + 3/2 \text{O}_{2(g)} \rightarrow \text{Fe}_2\text{O}_{3(s)}$	- 822	~1200 BCE

# Ex3) Enthalpy of Formation

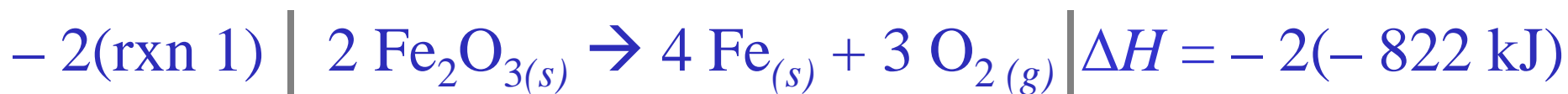
Ex3) Use the enthalpy of formation values below to determine  $\Delta H_{\text{rxn}}$  for the reaction between  $\text{C}_{(s)}$  and  $\text{Fe}_2\text{O}_{3(s)}$  to produce  $\text{Fe}_{(s)}$ .





# Ex3) Enthalpy of Formation

Ex3) Use the enthalpy of formation values below to determine  $\Delta H_{\text{rxn}}$  for the reaction between  $\text{C}_{(s)}$  and  $\text{Fe}_2\text{O}_{3(s)}$  to produce  $\text{Fe}_{(s)}$ .



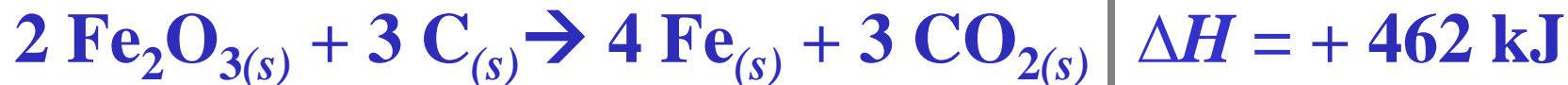
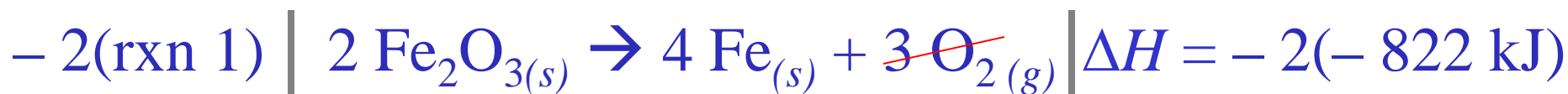
# Ex3) Enthalpy of Formation

Ex3) Use the enthalpy of formation values below to determine  $\Delta H_{\text{rxn}}$  for the reaction between  $\text{C}_{(s)}$  and  $\text{Fe}_2\text{O}_{3(s)}$  to produce  $\text{Fe}_{(s)}$ .

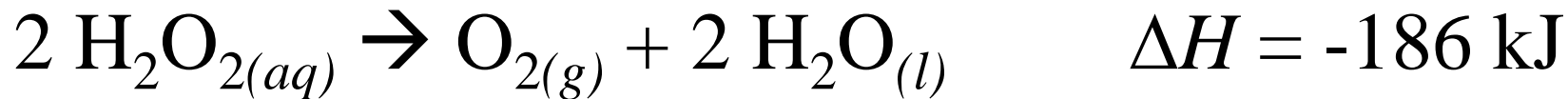


# Ex3) Enthalpy of Formation


Ex3) Use the enthalpy of formation values below to determine  $\Delta H_{\text{rxn}}$  for the reaction between  $\text{C}_{(s)}$  and  $\text{Fe}_2\text{O}_{3(s)}$  to produce  $\text{Fe}_{(s)}$ .



# Ex) Enthalpy and Stoichiometry



Ex) How much heat is released when 3.56 g  $\text{H}_2\text{O}_{2(aq)}$  decomposes into water and oxygen gas?

$$3.56 \text{g H}_2\text{O}_2 \times \frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \times \frac{-186 \text{ kJ}}{2 \text{ mol H}_2\text{O}_2} = -9.73 \text{ kJ}$$


**There are 2 moles  $\text{H}_2\text{O}_2$  in the balanced equation.**