

Lecture 16

Thermodynamics II

Calorimetry
Hess's Law
Enthalpy of Formation

Four Methods for Finding ΔH

- 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

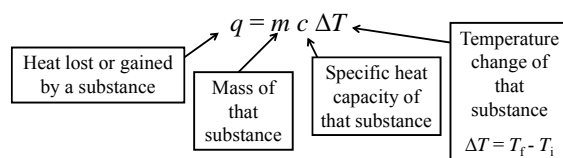
Calorimetry

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

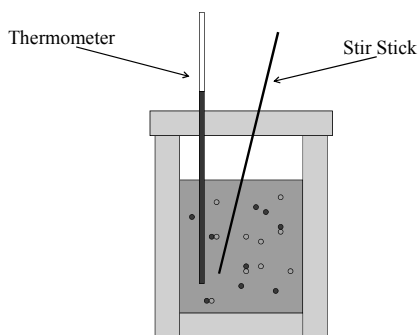
Heat flow cannot be measured directly.
We measure the temperature before and after a reaction, and use that data to calculate heat transfer.

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.

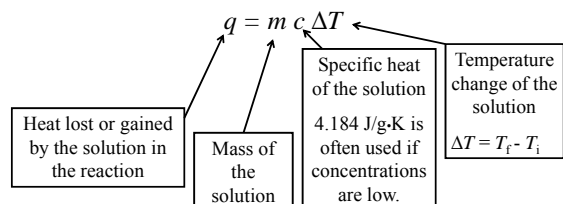


Coffee Cup Calorimeter



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 ($q_{\text{rxn}} = -568 \text{ J}$).

Ex1) Calorimetry

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

c) What is the specific heat of iron?

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 AgNO₃ 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.

- a) Write the net ionic equation for this reaction.
- b) Calculate ΔH for the reaction.

Ex2) Calorimetry (cont.)

Step 1) Calculate q_{sol} .

Step 2) Calculate q_{rxn} .

Ex2) Calorimetry (cont.)

Step 3) Calculate Moles of Ag^+ or Cl^- .

Step 4) Calculate ΔH_{rxn} .

q_{rxn} vs. ΔH_{rxn}

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

ΔH_{rxn} = The heat lost or gained in the balanced chemical equation

Four Methods for Finding ΔH

- 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.

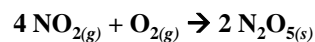
Hess's Law

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 ΔH for the following reaction using the information in the table below.



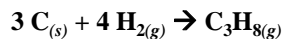
Reaction	Chemical Equation	Enthalpy Change
1	$2 \text{NO}_{(g)} + \frac{3}{2} \text{O}_{2(g)} \rightarrow \text{N}_2\text{O}_{5(s)}$	$\Delta H = - 223.7 \text{ kJ}$
2	$2 \text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{NO}_{2(g)}$	$\Delta H = - 114.2 \text{ kJ}$

Ex1) Hess's Law (cont.)

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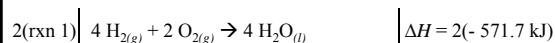
Ex2) Hess's Law

Ex2) Calculate ΔH 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.)

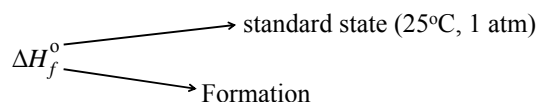


Four Methods for Finding ΔH

- 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.

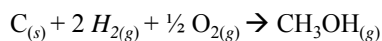
Standard Enthalpy of Formation

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 ΔH_f° value for the most stable form of any element in its standard state is **zero**.

Element	ΔH_f°	Element	ΔH_f°
Ca(s)	0	Cl ₂ (g)	0
Ag(s)	0	H ₂ (g)	0
Na(s)	0	Fe(s)	0
O ₂ (g)	0	N ₂ (g)	0

Formula for Calculating the Enthalpy of a Reaction under Standard Conditions

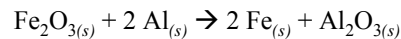
$$\Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

Sum of

stoichiometric
coefficients

Ex1) Enthalpy of Formation

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



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

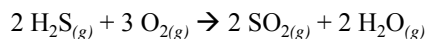
$$\Delta H_{\text{rxn}}^{\circ} = [2 (\Delta H_{\text{f}}^{\circ}(\text{Fe}_{(s)})) + 1 (\Delta H_{\text{f}}^{\circ}(\text{Al}_2\text{O}_{3(s)}))] - [2 (\Delta H_{\text{f}}^{\circ}(\text{Al}_{(s)})) + 1 (\Delta H_{\text{f}}^{\circ}(\text{Fe}_2\text{O}_{3(s)}))]$$

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

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

Ex2) Enthalpy of Formation

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



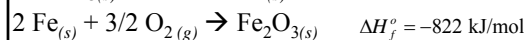
$$\Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

Enthalpy of Formation

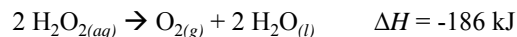
Reaction	$\Delta H_{\text{f}}^{\circ}$ kJ/mol	Elemental metal 1 st used by humans
$2 \text{Au}_{(s)} + 3/2 \text{O}_{2(g)} \rightarrow \text{Au}_2\text{O}_{3(s)}$	+131	~6000 BCE
$2 \text{Ag}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{Ag}_2\text{O}_{(s)}$	-31	~4000 BCE
$\text{Cu}_{(s)} + 1/2 \text{O}_{2(g)} \rightarrow \text{CuO}_{(s)}$	-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 ΔH_{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 H_2O_2 in the balanced equation.