

THERMOCHEMISTRY – 2

CALORIMETRY AND

HEATS OF REACTION

Dr. Sapna Gupta

HEAT CAPACITY

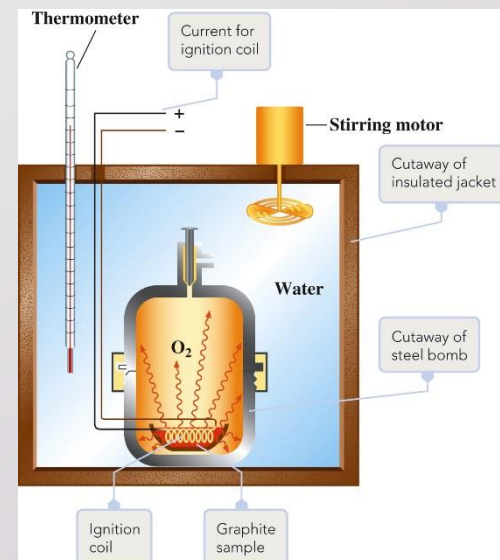
- **Heat capacity** is the amount of heat needed to raise the temperature of the sample of substance by one degree Celsius or Kelvin.

$$q = C\Delta t$$

- **Molar heat capacity:** heat capacity of one mole of substance.
- **Specific Heat Capacity:** Quantity of heat needed to raise the temperature of **one gram** of substance by one degree Celsius (or one Kelvin) at constant pressure.

$$q = m \cdot s \cdot \Delta t \text{ (final-initial)}$$

- Measured using a calorimeter – it absorbed heat evolved or absorbed.



EXAMPLES OF SP. HEAT CAPACITY

The higher the number the higher the energy required to raise the temp.

TABLE 5.2

Specific Heat Values of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al(<i>s</i>)	0.900
Au(<i>s</i>)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu(<i>s</i>)	0.385
Fe(<i>s</i>)	0.444
Hg(<i>l</i>)	0.139
H ₂ O(<i>l</i>)	4.184
C ₂ H ₅ OH(<i>l</i>) (ethanol)	2.46

CALORIMETRY: EXAMPLE - 1

Example:

A piece of zinc weighing 35.8 g was heated from 20.00°C to 28.00°C. How much heat was required? The specific heat of zinc is 0.388 J/(g°C).

Solution

$$m = 35.8 \text{ g}$$

$$s = 0.388 \text{ J/(g}^\circ\text{C)}$$

$$\Delta t = 28.00^\circ\text{C} - 20.00^\circ\text{C} = 8.00^\circ\text{C}$$

$$q = m \cdot s \cdot \Delta t$$

$$q = 35.8 \text{ g} \cdot \left(\frac{0.388 \text{ J}}{\text{g}^\circ\text{C}} \right) (8.00^\circ\text{C}) = 111 \text{ J}$$

CALORIMETRY: EXAMPLE - 2

Example:

Nitromethane, CH_3NO_2 , an organic solvent burns in oxygen according to the following reaction:



You place 1.724 g of nitromethane in a calorimeter with oxygen and ignite it. The temperature of the calorimeter increases from 22.23°C to 28.81°C . The heat capacity of the calorimeter was determined to be $3.044 \text{ kJ}/^\circ\text{C}$. Write the thermochemical equation for the reaction.

Solution:

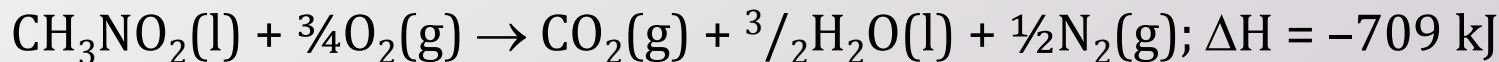
Heat evolved

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta t$$
$$q_{\text{rxn}} = -\left(\frac{3.044 \text{ kJ}}{^\circ\text{C}}\right)(28.81^\circ\text{C} - 22.23^\circ\text{C}) = -20.03 \text{ kJ}$$

Convert the heat evolved to per mol.

$$q_{\text{rxn}} = \frac{-20.03 \text{ kJ}}{1.724 \text{ g CH}_3\text{NO}_2} \cdot \frac{61.04 \text{ g CH}_3\text{NO}_2}{1 \text{ mol CH}_3\text{NO}_2} = -709 \text{ kJ}$$

Now the equation:



CALORIMETRY: EXAMPLE - 3

Example:

A metal pellet, 85.00 grams at an original temperature of 92.5°C is dropped into a calorimeter with 150.00 grams of water at an original temperature of 23.1°C. The final temperature of the water and the pellet is 26.8°C. Calculate the heat capacity and the specific heat for the metal.

Solution:

$$\begin{aligned} \text{Energy} &= q_{\text{water}} = ms\Delta T = (150.00 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (3.7^\circ\text{C}) \\ &= 2300 \text{ J (water gained energy)} = -2300 \text{ J (pellet released energy)} \end{aligned}$$

Heat capacity of pellet: $q = C\Delta T$

$$C = q/\Delta T = -2300 \text{ J}/-65.7^\circ\text{C} = 35 \text{ J}/^\circ\text{C}$$

Specific heat of pellet:

$$s = \frac{35 \text{ J}/^\circ\text{C}}{85.00 \text{ g}} = 0.41 \text{ J/g}^\circ\text{C}$$

Note: we could have calculated the sp. heat of the pellet in one calculation using $q = m \cdot s \cdot \Delta t$,
But since the question was also about Heat Capacity, we calculated that first and then just divide that by mass to get the sp. heat of the metal.

CALORIMETRY: EXAMPLE - 4

Example:

A snack chip with a mass of 2.36 g was burned in a bomb calorimeter. The heat capacity of the calorimeter 38.57 kJ/°C. During the combustion the water temp rose by 2.70°C. Calculate the energy in kJ/g for the chip.

Solution:

$$\begin{aligned}q_{\text{rxn}} &= - C_{\text{cal}} \Delta T = -(38.57 \text{ kJ}/^{\circ}\text{C}) (2.70^{\circ}\text{C}) \\ &= - 104 \text{ kJ}\end{aligned}$$

Energy content is a positive quantity.

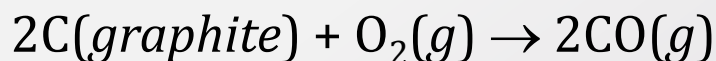
$$\begin{aligned}&= 104 \text{ kJ}/2.36 \text{ g} \\ &= 44.1 \text{ kJ/g}\end{aligned}$$

Convert J to Cal.

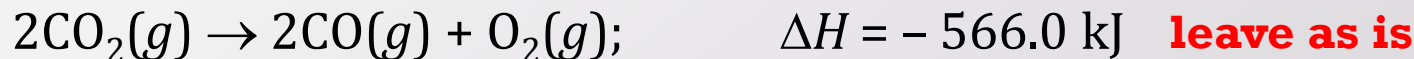
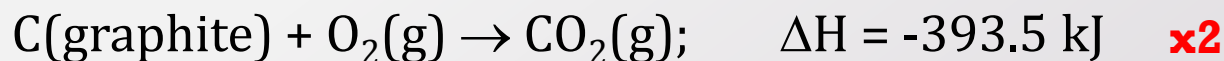
Food Calories: 10.5 Cal/g

HESS'S LAW

- The change in enthalpy when reactants are converted to products is the same whether the reaction occurs in one step or a series of steps.
- Usually used when heat of reaction cannot be determined directly.
- Manipulation of equations is the same as before.
- Add all the ΔH values after equations are manipulated.
- Suppose you want the ΔH for the reaction:



However two other reactions are known:



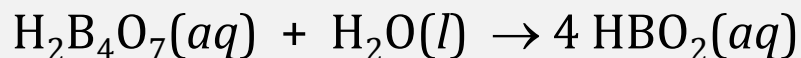
In order for these to add to give the reaction we want, we must multiply the first reaction by 2 (Note that we also multiply ΔH by 2.)

Then add the two heat of reactions along with the ΔH . $(-787 + (-566.0)) = -1353 \text{ kJ}$

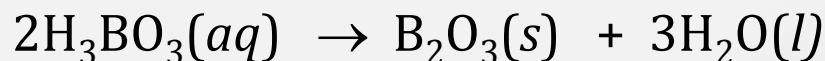
HESS'S LAW: EXAMPLE

Example:

Given the following equations:



Find the ΔH for this overall reaction.

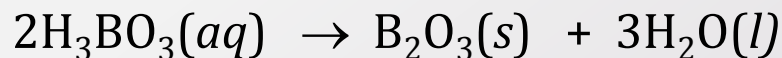
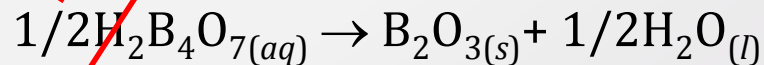


$$\Delta H_{\text{rxn}} = -0.02 \text{ kJ} \quad \times 2$$

$$\Delta H_{\text{rxn}} = -11.3 \text{ kJ} \quad \text{reverse, } \div 2$$

$$\Delta H_{\text{rxn}} = 17.5 \text{ kJ} \quad \div 2$$

Solution:



$$\Delta H_{\text{rxn}} = 2(-0.02 \text{ kJ}) = -0.04 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = +11.3 \text{ kJ}/2 = 5.65 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = 17.5 \text{ kJ}/2 = 8.75 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = 14.36 \text{ kJ}$$

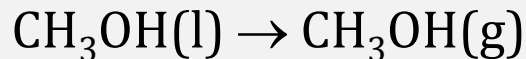
STANDARD ENTHALPY OF FORMATION

- Standard state refers to the standard thermodynamic conditions for the substances when listing or comparing thermodynamic data: the atm pressure and temperature (25 °C).
- Standard conditions are indicated with a degree sign “o”: eg ΔH and ΔH° – the second one is the standard enthalpy at 1 atm and 25 °C.
- Elements can exist in more than one physical state e.g. carbon as graphite or diamond (allotropes).
- The standard enthalpy of formation, ΔH_f° , is the enthalpy change for formation of one mole of substance from its elements in their reference forms and in their standard states. The ΔH_f° for an element in its reference state is zero.
- Example: $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_f^\circ = -285.8 \text{ kJ}$
- The equation below can be used to calculate the enthalpy. (n = number of moles)

$$\Delta H_{\text{reaction}}^\circ = \sum_{\text{products}} n\Delta H_f^\circ - \sum_{\text{reactants}} n\Delta H_f^\circ$$

STANDARD ENTHALPY: EXAMPLE

Calculate the ΔH° for the following reaction:



Solution:

Find the ΔH_f° values for all the compounds and subtract product from reactant.

$$\text{For liquid methanol : } \Delta H_f^\circ = -238.7 \frac{\text{kJ}}{\text{mol}}$$

$$\text{For gaseous methanol : } \Delta H_f^\circ = -200.7 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_{\text{vap}} = \left[1 \text{ mol} \left(-200.7 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[1 \text{ mol} \left(-238.7 \frac{\text{kJ}}{\text{mol}} \right) \right] = + 38.0 \text{ KJ}$$

STANDARD ENTHALPY: EXAMPLE

Methyl alcohol, CH_3OH , is toxic because liver enzymes oxidize it to formaldehyde, HCHO , which can coagulate protein. Calculate ΔH° for the following reaction:

$$2\text{CH}_3\text{OH}(\text{aq}) + \text{O}_2(\text{g}) \rightarrow 2\text{HCHO}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$

Standard enthalpies of formation, ΔH_f° :

$\text{CH}_3\text{OH}(\text{aq})$: -245.9 kJ/mol

$\text{HCHO}(\text{aq})$: -150.2 kJ/mol

$\text{H}_2\text{O}(\text{l})$: -285.8 kJ/mol

$$\Delta H_{\text{reaction}}^\circ = \sum_{\text{products}} n\Delta H_f^\circ - \sum_{\text{reactants}} n\Delta H_f^\circ$$

$$\Delta H_{\text{reaction}}^\circ = \left[2 \text{ mol} \left(-150.2 \frac{\text{kJ}}{\text{mol}} \right) + 2 \text{ mol} \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[2 \text{ mol} \left(-245.9 \frac{\text{kJ}}{\text{mol}} \right) + 1 \text{ mol} \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta H_{\text{reaction}}^\circ = [(-300.4 \text{ kJ}) + (-571.6 \text{ kJ})] - [-491.8 \text{ kJ}]$$

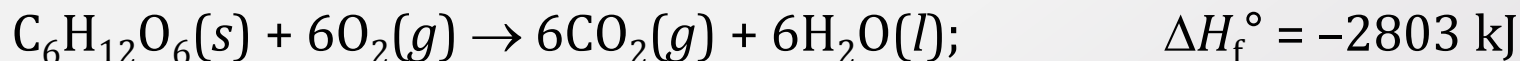
$$\Delta H_{\text{reaction}}^\circ = (-872.0 \text{ kJ}) - [-491.8 \text{ kJ}]$$

$$\Delta H_{\text{reaction}}^\circ = -380.2 \text{ kJ}$$

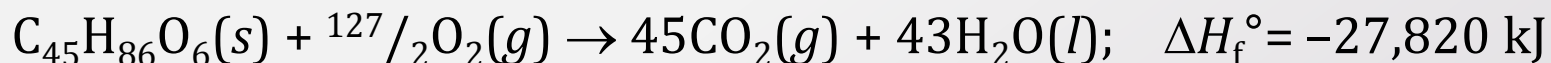
APPLICATIONS: FOOD

Foods are fuel needed for the body. They undergo a combustion process in the body.

For glucose, a carbohydrate:



For glycerol trimyristate, a fat:



The average value for carbohydrates is 4.0 Cal/g and for fats is 9.0 Cal/g.

APPLICATIONS: FUEL

- Fuels originate from organic substances: plants and animals, that have decayed over millions of years. This provides the coal, petroleum products and natural gas.
- Coal is about 30% of US energy consumption. Variety of coal determines how much carbon is in it: anthracite – 80% carbon; bituminous coal – 45-65% carbon.
- Natural gas is about 23% of energy. It is a fluid and easy to transport. Pure natural gas is methane, CH_4 with small amounts of ethane, propane and butane.
- Petroleum is a mixture of hydrocarbon compounds.
- Natural gas and petroleum products are in short supply while coal will last longer.
- All these are used for energy sources.

KEY CONCEPTS

- Measuring heats of reaction - calorimetry
- Hess's Law
- Standard enthalpy of formation