

THERMOCHEMISTRY

3: HESS'S LAW AND STANDARD HEAT OF FORMATION

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CALCULATING ENTHALPY

There are many ways of calculating enthalpy. It depends on what data available to us.

Calorimetry: We have learned this previously. It can be experimentally determined in the lab in a Styrofoam cup calorimeter or bomb calorimeter. We do this when there is new data to be collected.

Thermochemical Equations: Recall that we have learned about manipulating thermochemical equations. We could do this because enthalpy is a state function. We will take this one step further in this portion by learning Hess's law. In this we can use several equations to find the enthalpy for the reaction we want because going from point A to point B requires the same amount of energy no matter how many steps you take. This is possible only when data for all equations is given.

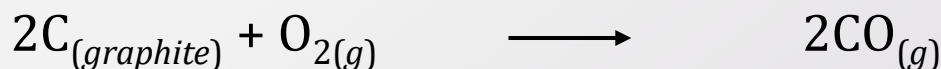
Heat of Formation: This method is used under standard conditions when data is available to us. We can calculate heat of reaction for any reaction, provided that standard heats of formation for those chemicals is given.

HESS'S LAW

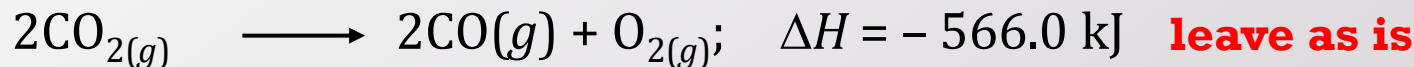
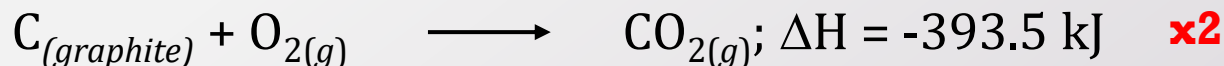
Hess's law states that the change in enthalpy when reactants are converted to products is the same whether the reaction occurs in one step or a series of steps.

- 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.

Example: Suppose you want the ΔH for the reaction:



However, two other reactions are known:

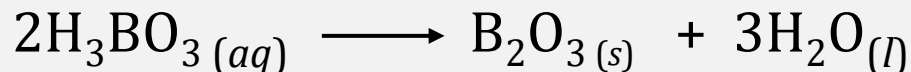


For these to add to give the reaction we want, we must multiply the first reaction by 2 (Note that we also multiply ΔH by 2.)

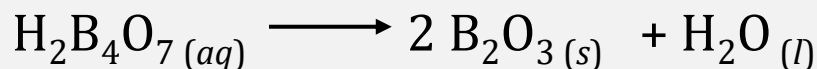
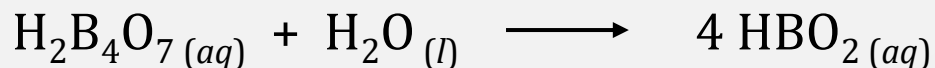
Then add the two heat of reactions along with the ΔH . $(-787 + (-566.0)) = -1353 \text{ kJ}$

EXAMPLE 1: HESS'S LAW

Find the ΔH for this overall reaction using the equations given below.



Equations given.

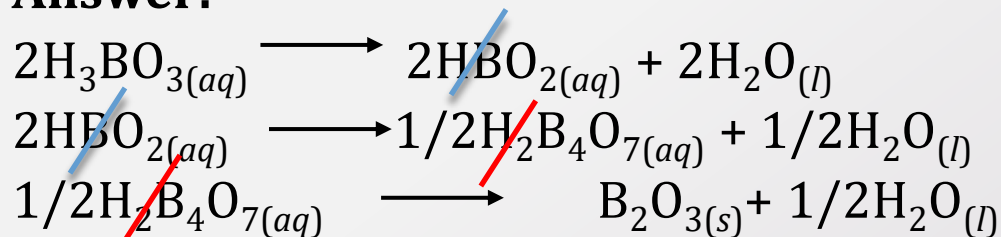


$$\Delta H_{\text{rxn}} = -0.02 \text{ kJ} \quad \times 2$$

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

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

Answer:



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

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

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

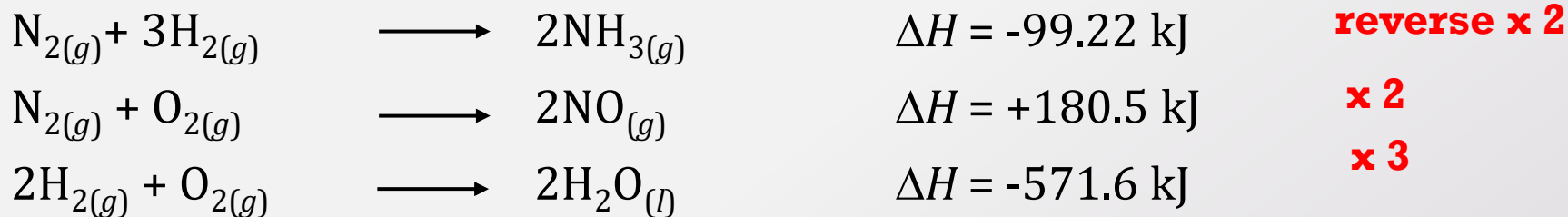
$$\Delta H_{\text{rxn}} = 14.36 \text{ kJ}$$

EXAMPLE 2: HESS'S LAW

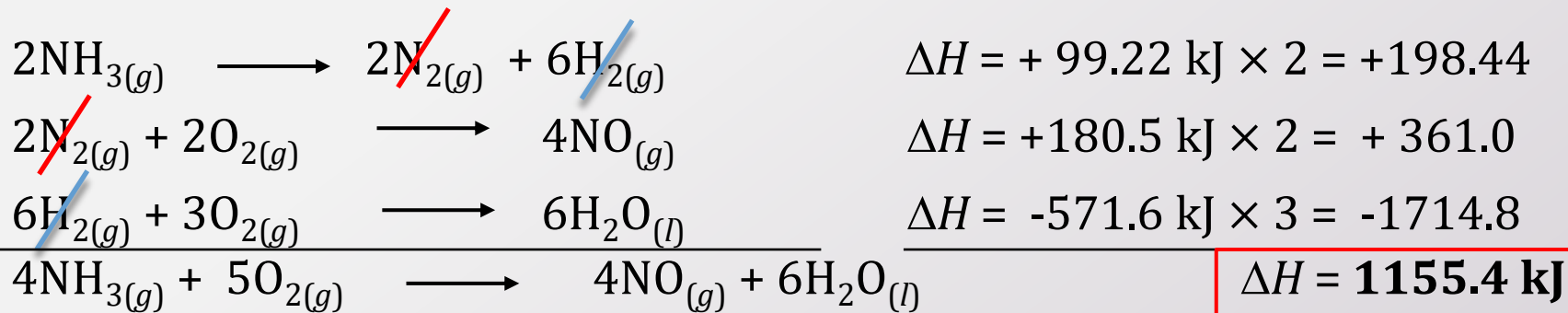
Find the ΔH for this overall reaction using the equations given below.



Equations given.



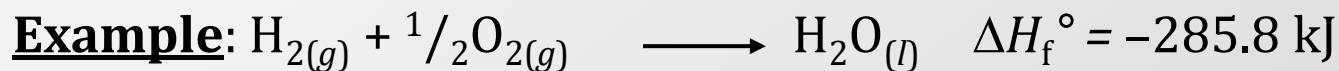
Answer:



STANDARD ENTHALPY OF FORMATION

Standard state refers to the standard thermodynamic conditions for the pure substances when listing thermodynamic data, the atmospheric pressure is 1 atm and temperature is 25 °C. Standard conditions are indicated with a degree sign “°”: e.g., ΔH is simply enthalpy while ΔH° is the standard enthalpy at 1 atm and 25 °C.

- Elements can exist in more than one physical state e.g., carbon as solid, liquid or gas; carbon as graphite or diamond (allotropes) and these all have their own standard enthalpy values.
- 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.

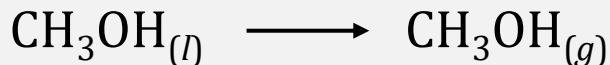


The equation below can be used to calculate the enthalpy. (n = number of moles)

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_{\text{products}} - \sum n \Delta H^\circ_{\text{reactants}}$$

EXAMPLE 3: STANDARD ENTHALPY

Calculate the ΔH° for the following reaction:



Answer:

Find the ΔH_f° values for all the compounds from data tables (found at the end of any general chemistry textbook) and subtract product from reactant.

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

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

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

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

EXAMPLE 4: STANDARD ENTHALPY

Methyl alcohol, CH_3OH , is toxic because liver enzymes oxidize it to formaldehyde, HCHO , which can coagulate protein. Calculate ΔH° for the following reaction: $2\text{CH}_3\text{OH}_{(aq)} + \text{O}_{2(g)} \longrightarrow 2\text{HCHO}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$

Answer: Standard enthalpies of formation, ΔH_f° :

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

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

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

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

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

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

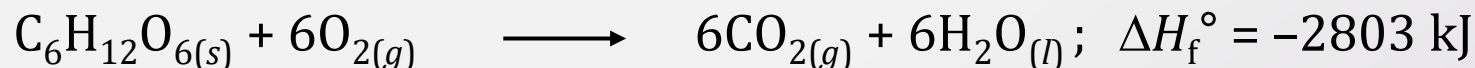
$$\Delta H_{\text{reaction}}^\circ = (-872.0 \text{ kJ}) - [-491.8 \text{ kJ}]$$

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

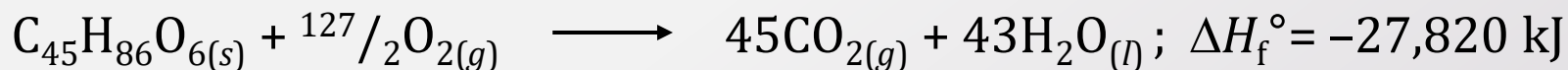
APPLICATIONS: FOOD

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