

Module 4

Targets/Objectives

At the end of the lesson, students should be able to:

- Discuss the difference between exothermic and endothermic reactions.
- Define internal energy (E), enthalpy (h), ΔH , q_v , and q_p .
- Explain energy changes with each phase change when water is heated or cooled.
- Compute the total heat absorbed or evolved when a water is heated or cooled and undergoes phase changes
- Differentiate state functions and path functions
- Compute standard enthalpy of reaction ΔH_r° using standard enthalpies of formation ΔH_f° of reactants and products
- Compute the standard enthalpy of reaction ΔH_r° using Hess Law

Lecture Guide

ENTHALPY

By using the definition of internal energy, under constant volume conditions, the change in internal energy equals the heat flow.

$$\Delta E = q + w$$

When gas expands, it does an amount of work equal to $P\Delta V$ on its surroundings, but if the expanding gas is our system, we want w to be the work done on the gas, and that will be $-P\Delta V$.

So, we can replace w in the equation:

$$\Delta E = q - P\Delta V$$

If the volume is held constant, $\Delta V = 0$, so the equation becomes

$$\Delta E = q_v$$

The equation shows how internal energy is related to heat, where the subscript “v” is added to denote that the equation is correct only under constant volume conditions.

When heat flow under constant pressure condition, the function is known as enthalpy, is defined as

$$H = E + PV$$

Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

From this definition, the change in enthalpy (ΔH) will be equal to the heat flow under constant pressure conditions. The change in enthalpy (ΔH) must be

$$\Delta H = \Delta E + \Delta(PV)$$

Expand by substituting for $\Delta E = q - P\Delta V$

$$\Delta H = (q - P\Delta V) + \Delta(PV)$$

If pressure is held constant, then the $\Delta(PV)$ term will simply become $P\Delta V$

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q - P\Delta V + P\Delta V$$

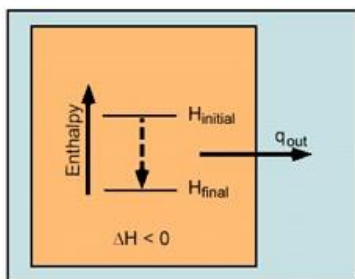
$$\Delta H = qp$$

Enthalpy change therefore equals the heat flows under constant pressure, denoted by the subscript "p".

For a process at constant volume, the measurable heat flow is equal to ΔE , the change in internal energy. For a process at constant pressure, the measurable heat flow is equal to the change in enthalpy, ΔH .

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

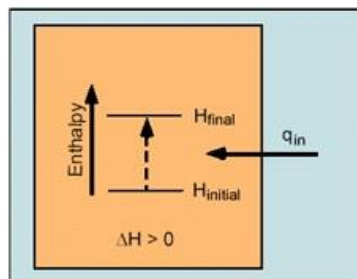
When heat evolves from a system....



If $\Delta H < 0$, then $q_p < 0$

The reaction is **Exothermic**.

Heat goes from the system
surroundings into the system.



If $\Delta H > 0$, then $q_p > 0$

The reaction is **Endothermic**.

Heat goes from the into the surroundings.

Phase Diagrams

A **phase diagram** is a graph of pressure versus temperature that shows in which phase a substance will exist under different conditions of temperature and pressure.

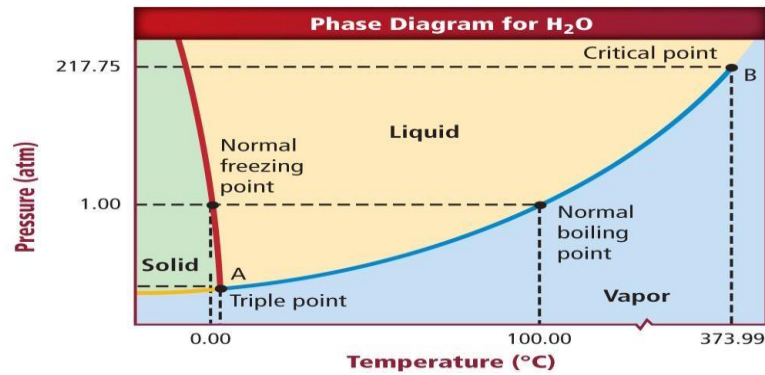


Figure 1. Phase Diagram for Water

The triple point (fig. 1) is the point on a phase diagram that represents the temperature and pressure at which all three phases of a substance can coexist.

The phase diagram for different substances are different from water.

This type of graph is called a heating curve because it shows the temperature change of water as thermal energy, or heat, is added.

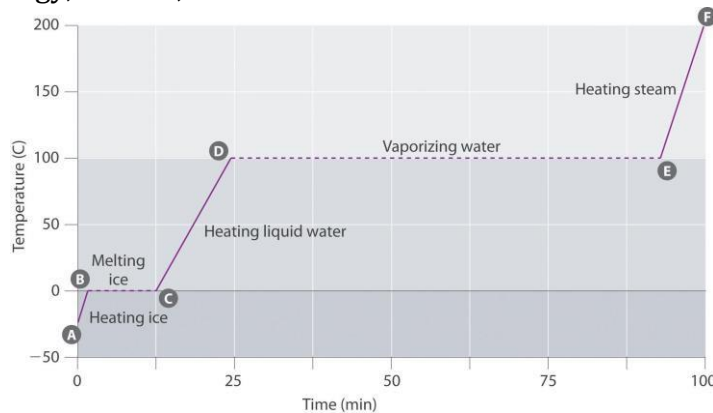


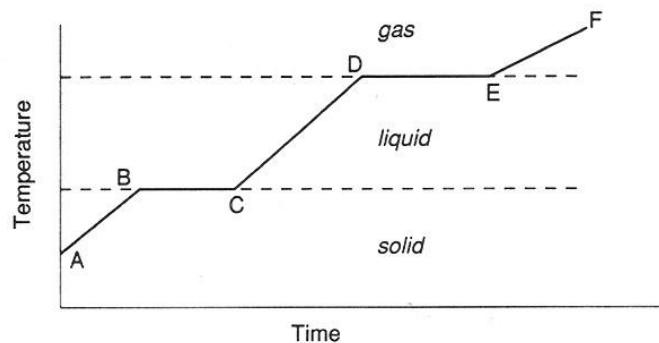
Figure 2. Heating Curve for Water

Notice the two areas on the graph where the temperature does not change.

At 0°C, ice is melting.

At 100°C, water vaporizes.

Heating and cooling curve for water heated at a constant rate



Analysis of a Heating Curve

Looking from left to right on the graph, there are five distinct parts to the heating curve:

1. **A→B = solid ice.** Solid ice is heated and the temperature increases until the normal freezing/melting point of zero degrees Celsius is reached. The amount of heat added, q , can be computed by $q = mC_{H_2O(solid)}\Delta T$, where m is the mass of the sample of water, C is the specific heat capacity of solid water, or ice, and ΔT is the change in temperature during the process.
2. **B→C = Solid starts to change state from solid to liquid.** The first phase change is melting; as a substance melts, the temperature stays the same. For water, this occurs at 0 °C. The above equation (described in part 1 of the curve) cannot be used for this part of the curve because the change in temperature is zero. Instead, use the heat of fusion (ΔH_{fusion}) to calculate how much heat was involved in that process: $q = m \cdot \Delta H_{fusion}$, where m is the mass of the sample of water. $H_2O_{(s)} \rightarrow H_2O_{(l)}$ energy required \square 6.01 kJ/mol
3. **C→D = temperature starts to rise once all the solid has melted.** After all of the solid substance has melted into liquid, the temperature of the liquid begins to increase as heat is absorbed. It is then possible to calculate the heat absorbed by $q = mC_{H_2O(l)}\Delta T$. Note that the specific heat capacity of liquid water is different than that of ice.
4. **D→E = Liquid starts to vaporize, turning from liquid to gas.** The liquid will begin to boil when enough heat has been absorbed by the solution that the temperature reaches the boiling point, where again, the temperature remains constant until all of the liquid has become gaseous water. At the atmospheric pressure of 1 atm, this phase transition occurs at 100°C (the normal boiling point of water). Liquid water becomes water vapor or steam when it enters the gaseous phase. Use the heat of vaporization (ΔH_{vap}) to calculate how much heat was absorbed in this process: $q = m \cdot \Delta H_{vap}$, where m is the mass of the sample of water. $H_2O_{(l)} \rightarrow H_2O_{(g)}$ energy required \square 40.67 kJ/mol
5. **E→F = temperature starts to rise once all liquid is vaporized.** After all of the liquid has been converted to gas, the temperature will continue to increase as heat is added. Again, the heat added that results in a certain change temperature is given by: $q = mC_{H_2O(gas)}\Delta T$. Note that the specific heat capacity of gaseous water is different than that of ice or liquid water.
6. Water has a high boiling point because of the presence of extensive hydrogen bonding interactions between the water molecules in the liquid phase (water is both a strong hydrogen bond donor and acceptor). When heat is first applied to water, it must break the intermolecular hydrogen bonds within the sample. After breaking the bonds, heat is then absorbed and converted to increased kinetic energy of the molecules in order to vaporize them.

Phase Changes

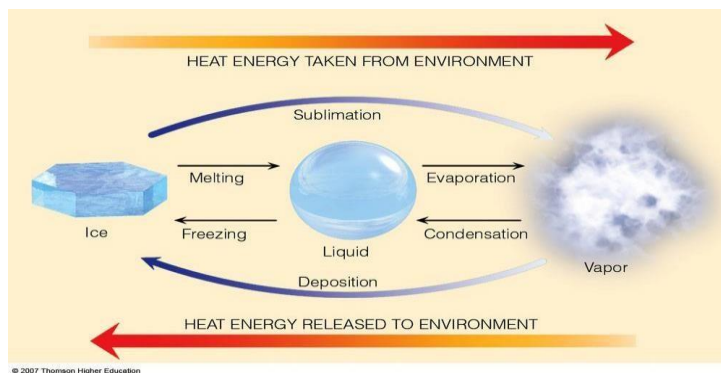


Figure 3. Changes of State of Water

Melting occurs when heat flows into a solid object. The melting point of a crystalline solid is the temperature at which the forces holding the crystal lattice together are broken and it becomes a liquid.

Sublimation is when a solid phase goes directly into a gaseous phase without first becoming a liquid.

Deposition is the process by which a gas or vapor changes directly to a solid, and is the reverse of sublimation.

Frost is an example of deposition.

Snowflakes are also formed in the upper atmosphere by deposition of ice crystals.

Freezing, or solidification, is a phase transition in which liquid turns into a solid when its temperature is lowered to or below its freezing point. **Condensation** is the process by which a gas or vapor becomes a liquid.

Condensation is the reverse of evaporation.

Vaporization is a phase transition from the liquid phase to the gas phase.

Fusion is when a solid melt to form a liquid **Energy Changes**

Accompanying Phase Changes

Sublimation: $\Delta H_{\text{sub}} > 0$ (endothermic).

Vaporization: $\Delta H_{\text{vap}} > 0$ (endothermic).

Melting or Fusion: $\Delta H_{\text{fus}} > 0$ (endothermic).

Deposition: $\Delta H_{\text{dep}} < 0$ (exothermic).

Condensation: $\Delta H_{\text{con}} < 0$ (exothermic).

Freezing: $\Delta H_{\text{fre}} < 0$ (exothermic).

Generally, heat of fusion (enthalpy of fusion) is less than heat of vaporization:

It takes more energy to completely separate molecules, than partially separate them. It takes more energy to vaporize water than to melt it. This is because in melting you weaken

the intermolecular forces. Here about 1/6 of the hydrogen bonds are broken. In vaporization you totally break them. All the hydrogen bonds are broken

ΔH_{vap} is always greater than ΔH_{fus}

Values of ΔH

	kJ/mol	kJ/kg	Kcal/kg
ΔH_{fusion}	6.01	334	79.6
$\Delta H_{\text{vaporization}}$	40.67	2258	539.2

Sample Problems

Example 1. Calculate the amount of energy needed to convert 55.0 grams of ice to all liquid water at its normal melting point.

Solution:

$$\Delta H = \text{mass} \times \Delta H_{\text{fus}}$$

$$\Delta H = (55.0 \text{ g})(334 \text{ J/g})$$

$$\Delta H = 18400 \text{ J}$$

Example 2. Using the same amount of water calculate the energy needed to completely vaporize the water at its normal boiling point.

Solution:

$$\Delta H = \text{mass} \times \Delta H_{\text{vap}}$$

$$\Delta H = (55.0 \text{ g})(2258 \text{ J/g})$$

$$\Delta H = 124190 \text{ J}$$

Why is there such a large difference in energy needed?

Answer: because more energy is needed to completely break the bonds

Example 3. How much energy is required to heat 25 g of liquid water from 25°C to 100°C and change it to steam?

Solution:

$$\Delta H_1 = mC_p\Delta T$$

$$\Delta H_1 = 25 \text{ g} \times 4.186 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (100 - 25)^\circ\text{C}$$

$$\Delta H_1 = 7,848.75 \text{ J or } 7.848 \text{ kJ}$$

To solve for n= number of moles

$$n = 25 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 1.387 \text{ mol}$$

$$\Delta H_2 = n \times \Delta H_{\text{vap}}$$

$$\Delta H_2 = 1.387 \text{ mol} \times 40.67 \frac{\text{kJ}}{\text{mol}}$$

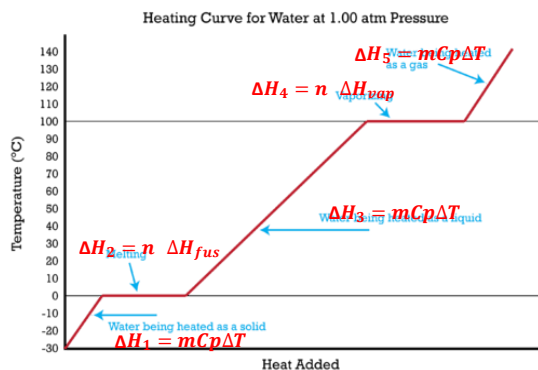
$$\Delta H_2 = 56.409 \text{ kJ}$$

$$\Delta H_{total} = \Delta H_1 + \Delta H_2$$

$$\Delta H_{total} = 7.848 \text{ kJ} + 56.409 \text{ kJ}$$

$$\Delta H_{total} = 64.257 \text{ kJ}$$

Example 4. Calculate the total amount of heat absorbed (in kJ) when 2.00 mol of ice at -30.0°C is converted to steam at 140.0°C Solution:



$$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

To get the mass of water given the number of moles

$$18.02 \text{ g H}$$

$$\text{Mass of } H_2O = 2.00 \text{ mol } H_2O \times \frac{18.02 \text{ g}}{1 \text{ mol } H_2O} = 36.04 \text{ g}$$

Compute for ΔH_1

$$\Delta H_1 = mC_p\Delta T$$

$$\Delta H_1 = 36.04 \text{ g} \times 2.100 \frac{\text{J}}{\text{g}^\circ\text{C}} (0 - (-30))^\circ\text{C} \times$$

$$\Delta H_1 = 2,270.52 \text{ J} \approx 2.270 \text{ kJ}$$

Compute for ΔH_2

$$\Delta H_2 = n\Delta H_{fus}$$

$$\Delta H_2 = 2.00 \text{ mol} \times 6.01 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_2 = 12.02 \text{ kJ}$$

Compute for ΔH_3

$$\Delta H_3 = mC_p\Delta T$$

$$\Delta H_3 = 36.04 \text{ g} \times 4.186 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (100 - 0)^\circ\text{C}$$

$$\Delta H_3 = 15,086.344 \text{ J} = 15.086 \text{ kJ}$$

Compute for ΔH_4

$$\Delta H_4 = n \times \Delta H_{vap}$$

$$\Delta H_4 = 2.00 \text{ mol} \times 40.67 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_4 = 81.34 \text{ kJ}$$

Compute for ΔH_5

$$\Delta H_5 = mC_p\Delta T$$

$$\Delta H_5 = 36.04 \text{ g} \times 2.010 \frac{\text{J}}{\text{g}^\circ\text{C}} \times (140 - 100)^\circ\text{C}$$

$$\Delta H_5 = 2,897.616 \text{ J} \approx 2.897 \text{ kJ}$$

Computing for ΔH_{total}

$$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

$$\Delta H_{total} = 2.270 + 12.02 + 15.086 + 81.34 + 2.897$$

$$\Delta H_{total} = 113.613 \text{ kJ}$$

*** The total heat absorbed as the ice at -30°C is heated to steam at 140°C is 113.613 kJ. The largest absorption of heat comes during the vaporization of the liquid water.

HEATS OF REACTIONS

Heat of reaction is the change in enthalpy during a reaction symbolized as ΔH_{rxn} .

$$\Delta H_{rxn} = H_{final} - H_{initial}$$

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

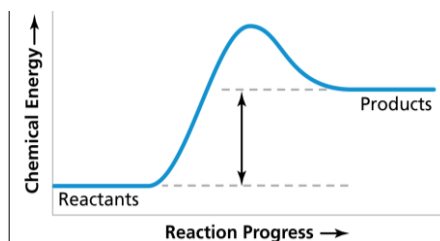
**The enthalpy change is commonly referred to as the heat of reaction

Activation Energy

The energy required to break the bonds in the reactants for a chemical reaction to occur.

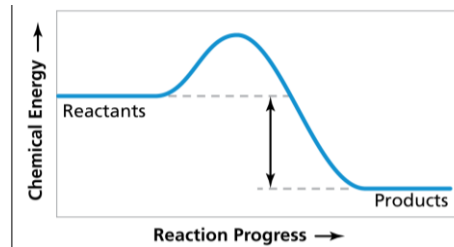
Endothermic and Exothermic Reactions

Endothermic – more energy is taken in to break the bonds in the reactants than released by the bonds being formed in the products. Therefore, energy is absorbed.





Exothermic – More energy is released when the products were formed than energy was used to break bonds in the reactants. Therefore, a net release of energy.



***A reaction is EXOTHERMIC if more energy is **RELEASED** than **SUPPLIED**. If more energy is **SUPPLIED** than is **RELEASED** then the reaction is ENDOTHERMIC

Enthalpy and enthalpy changes

Enthalpy (H) is a state function defined as

$$H = E + PV$$

At constant pressure $q_p =$

ΔH Enthalpy of reaction

$$\Delta H_{rxn} = \Delta H_{product} - \Delta H_{reactant}$$

ΔH is + for endothermic changes.

ΔH is – for exothermic changes.

A state function is a variable whose value depends only on the state of the system and not on its history. State functions do not depend on the path by which the system arrived at its present state.

Mass, pressure, density, energy, temperature, volume, enthalpy, entropy, Gibbs free energy and chemical composition are all examples of state functions in thermochemistry

Is heat and work a state function?

Heat and work, unlike temperature, pressure, and volume, are not intrinsic properties of a system. They have meaning only as they describe the transfer of energy into or out of a system. They appear only when there occurs any change in the state of system and the surroundings.

Work can't be a state function because it is proportional to the distance an object is moved, which depends on the path used to go from the initial to the final state. If the system process happens at constant volume then there is no work done on the surroundings and the heat change must be a state function

$$\Delta E = q_v$$

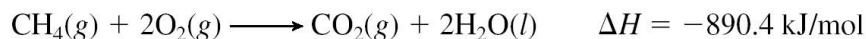
Thermochemical Equations

Equations that represent both mass and enthalpy changes



This is an endothermic process. It requires 6.01 kJ to melt one mole of ice, $\text{H}_2\text{O}_{(s)}$.

The enthalpy value will change if the number of moles varies from the 1:1 reaction stoichiometry.

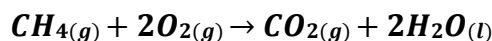


This is an exothermic process. It releases 890.4 kJ when one mole of methane, CH_4 , reacts

The enthalpy value will change if the number of moles varies from the 1:2:1:2 reaction stoichiometry.

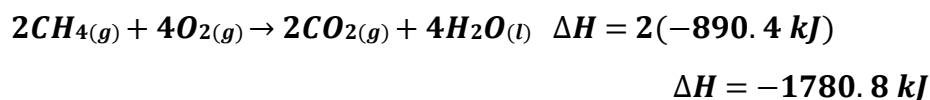
Thermochemical equation guidelines:

- Always specify state of reactants and products.

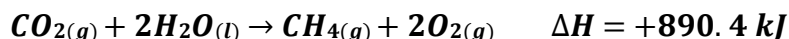
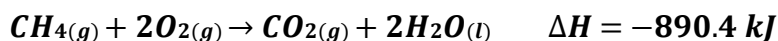


(g)- gaseous state, (l)- liquid state, (s)- solid state, (aq)- aqueous state

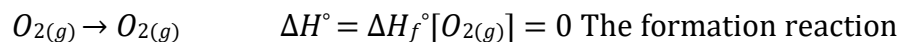
- When multiplying an equation by a factor (n), multiply the ΔH value by same factor.



- Reversing an equation changes the sign but not the magnitude of the ΔH .

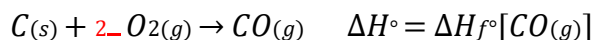


- 1 mole of $\text{O}_{2(g)}$ as the product and oxygen in its standard state as the reactant. But because the standard state of oxygen is $\text{O}_{2(g)}$, the formation reaction is really no reaction at all:



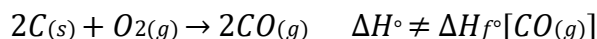
for carbon monoxide is

1



Because we require just 1 mole of CO on the right-hand side, we must use a fractional coefficient on the O_2 to balance the equation, even though this may look odd.

- Two very common errors when writing formation reactions :



Although both are valid chemical equations, they do not describe the formation reaction for CO. The first reaction is not correct because oxygen is not shown in its standard state, as a diatomic molecule. The second reaction is not correct, because 2 moles of carbon monoxide are formed. Formation reactions are quite useful for determining heats of reaction.

Standard reaction enthalpy, $\Delta H^\circ_{\text{rxn}}$: change in enthalpy when reactants in their standard states are changed to products in their standard states

Standard enthalpy of formation, $\Delta H^\circ_{\text{form}}$: change in enthalpy when one mole of product is formed from reactants in their standard states

Standard enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$: change in enthalpy when one mole of reactant is burned completely in oxygen

A **formation reaction** is the chemical reaction by which 1 mole of a compound is formed from its elements in their standard states. The **standard states** is the most stable form of the element at room temperature (25°C) and pressure (1atm).

Enthalpy values vary according to the condition a substance under these conditions is said to be in its standard state ...

Pressure: 100 kPa (1 atmosphere)

A stated temperature: usually 298K (25°C)

- as a guide, just think of how a substance would be under normal lab conditions assign the correct subscript [(g), (l) or (s)] to indicate which state it is in

- to tell if standard conditions are used, we modify the symbol for ΔH

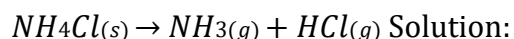
ΔH	ΔH°_f
Enthalpy Change	Standard Enthalpy Change(at 298K)

Sample Problems

Example1. Given the following standard enthalpies of formation ΔH_f (298K, 1 atm)

$$NH_{3(g)} - 46.2 \frac{kJ}{mol} ; HCl_{(g)} - 92.3 \frac{kJ}{mol} ; NH_4Cl_{(g)} - 315.0 \frac{kJ}{mol}$$

Calculate the standard enthalpy change for the reaction, ΔH_r°



$$\Delta H_{rxn} = \Delta H_{product} - \Delta H_{reactant}$$

$$\Delta H_{rxn} = [\Delta H_f[NH_{3(g)}] + \Delta H_f[HCl_{(g)}]] - \Delta H_f[NH_4Cl_{(s)}]$$

$$\Delta H_{rxn} = [(-46.2) + (-92.3)] - (-315.0)$$

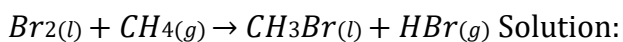
$$\Delta H_{rxn} = (-138.5) - (-315.0)$$

$$\Delta H_{rxn} = 176.5 \quad \text{kJ/mol}$$

Example 2. Given the following standard enthalpies of formation, ΔH_f° in kJ/mol (298K, 1 atm)

$$\text{CH}_4(g) - 74.9 ; \text{CH}_3\text{Br}(l) - 36.0 ; \text{HBr}(g) - 36.2$$

Calculate the standard enthalpy change for the reaction, ΔH_{rxn}°



$$\Delta H_{rxn} = \Delta H_{product} - \Delta H_{reactant}$$

$$\Delta H_{rxn} = [\Delta H_f[\text{CH}_3\text{Br}(l)] + \Delta H_f[\text{HBr}(g)]] - [\Delta H_f[\text{Br}_2(l)] + \Delta H_f[\text{CH}_4(g)]]$$

$$\Delta H_{rxn} = [(-36.0) + (-36.2)] - [(0) + (-74.9)]$$

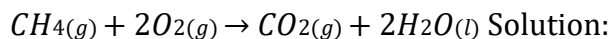
$$\Delta H_{rxn} = (-72.2) - (-74.9)$$

$$\Delta H_{rxn} = 2.7 \quad \text{kJ/mol}$$

Example 3. Given the following standard enthalpies of formation ΔH_f in kJ/mol (289K, 1 atm)

$$\text{CH}_4(g) - 74.8 ; \text{CO}_2(g) - 393.5 ; \text{H}_2\text{O}(l) - 285.8$$

Calculate the standard enthalpy change for the reaction, ΔH_{rxn}°



$$\Delta H_{rxn} = \Delta H_{product} - \Delta H_{reactant}$$

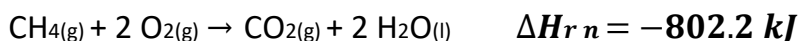
$$\Delta H_{rxn} = [\Delta H_f[\text{CO}_2(g)] + 2\Delta H_f[\text{H}_2\text{O}(l)]] - [\Delta H_f[\text{CH}_4(g)] + 2\Delta H_f[\text{O}_2(g)]]$$

$$\Delta H_{rxn} = [(-393.5) + 2(-285.8)] - [(-74.8) + 2(0)]$$

$$\Delta H_{rxn} = (-965.1) - (-74.8)$$

$$\Delta H_{rxn} = -890.3 \quad \text{kJ/mol}$$

Example 4. If 10.3 grams of CH_4 are burned completely, how much heat will be produced?



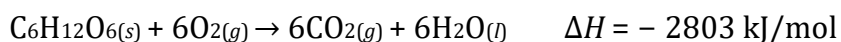
Convert to moles Convert moles to desired unit Start with known value

$$10.3 \text{ g CH}_4 \left(\frac{1 \text{ mol CH}_4}{16.05 \text{ g CH}_4} \right) \left(\frac{802.2 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -514 \text{ kJ}$$

Ratio from balanced equation

$\Delta H = -514 \text{ kJ}$, which means the heat is *released* for the reaction of 10.3 grams CH_4

Example 5. Given the following equation,



Calculate the energy released when 45.00 g of glucose is burned in oxygen.

Solution:

$$45.00 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{-2803 \text{ kJ}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} = -700.0 \text{ kJ}$$

Hess's Law

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

Used for calculating enthalpy for a reaction that cannot be determined directly.

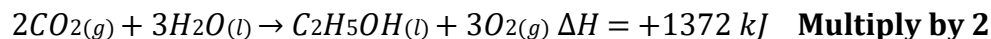
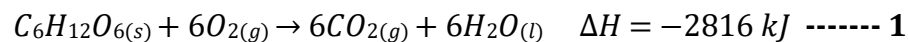
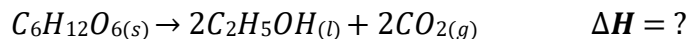
In using stepwise reactions to determine an overall reaction

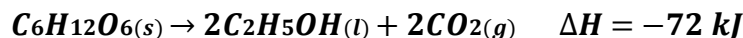
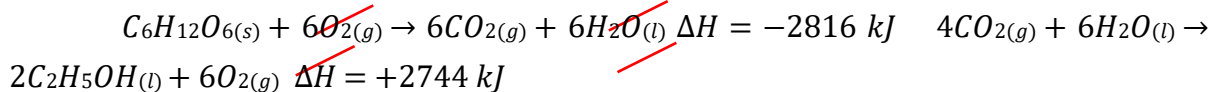
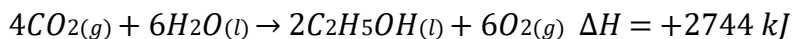
- Remember the rules for manipulating equations.
- Add the ΔH values for each step together after proper manipulation to obtain the overall enthalpy for the desired reaction.

Example 6. Given the combustion of glucose

$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \quad \Delta H = -2816 \text{ kJ}$ and the combustion of ethanol

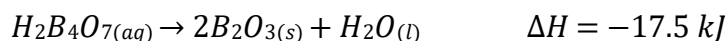
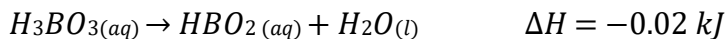
$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \quad \Delta H = -1372 \text{ kJ}$ Calculate ΔH (in kJ) for the fermentation of glucose:



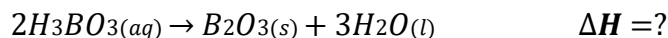


exothermic

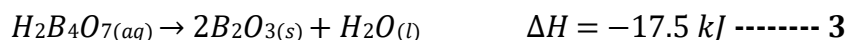
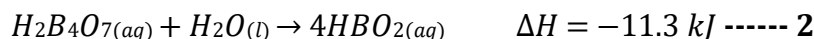
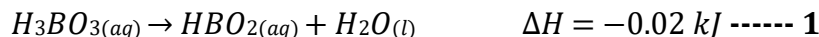
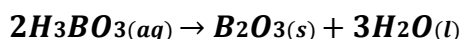
Example 7. Given the following equations



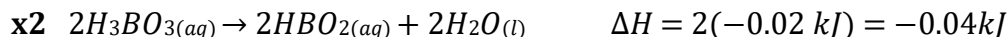
Find the ΔH for the overall reaction of



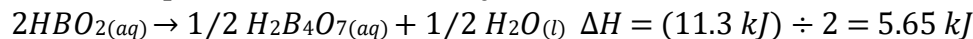
Solution:



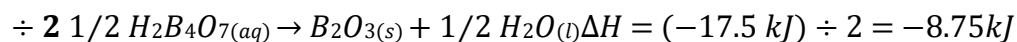
Multiply equation 1 by a factor of 2



Reverse equation 2 and divide by 2



Divide equation 3 by 2



Adding the equation:

