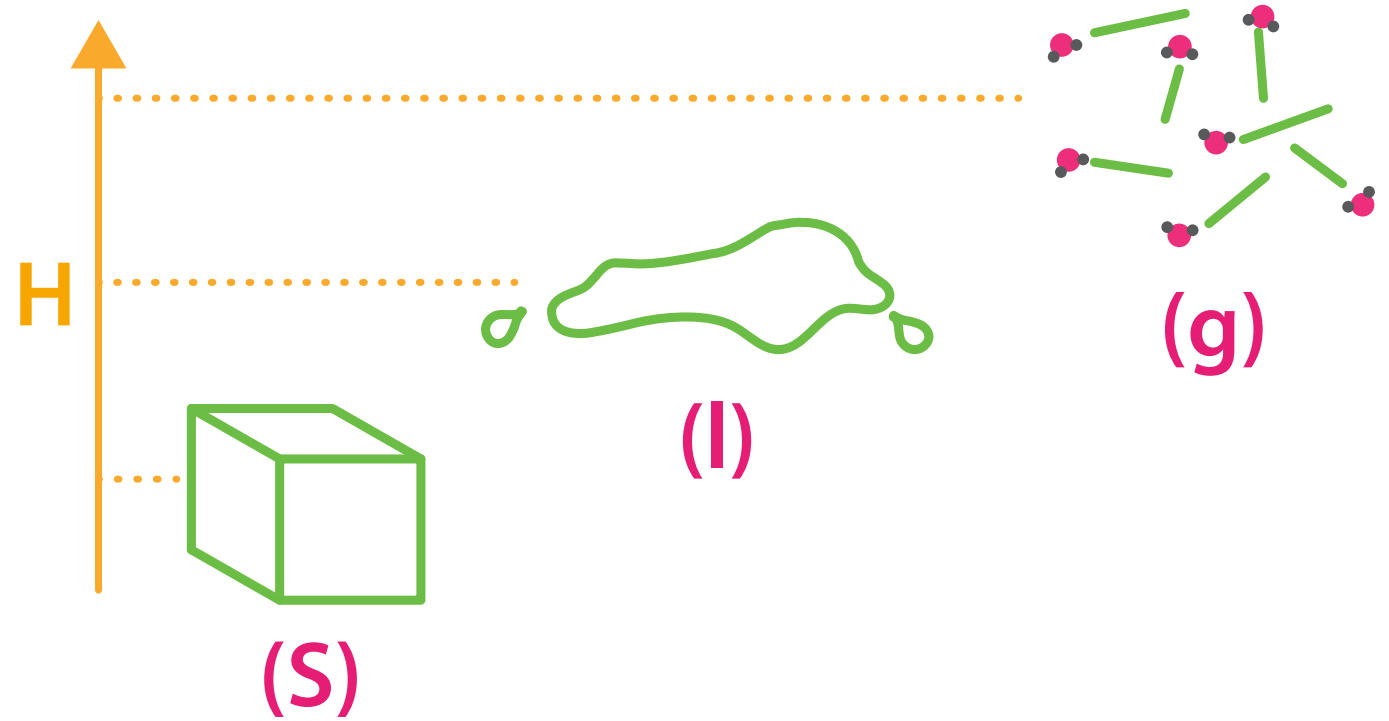


Standard Enthalpy Changes



Lesson Objectives

You will be able to

- ▶ define and describe the enthalpy of fusion, solidification, vaporization, and condensation and the relationship between them,
- ▶ identify the location of the enthalpy of fusion and vaporization from heating curves or tabulated data,
- ▶ define the enthalpy of solution and explain that dissolution results in a change in enthalpy,
- ▶ relate enthalpy of dilution to the difference between two enthalpies of solution with differing quantities of solvent,
- ▶ define and describe the enthalpy of combustion,
- ▶ define and describe the enthalpy of formation and how it relates to a compound's stability,
- ▶ use the standard enthalpies of formation to calculate change in enthalpy for a reaction.

Enthalpy Changes

Chemical reactions happen when bonds are broken in reactant molecules and new bonds are made in product molecules.

The chemical potential energy of the reactant and product molecules must be different because they contain different types of chemical bonds and potential energy is stored in chemical bonds.

The chemical potential energy has to change during a chemical reaction.

The change in energy of a system can be described as a change in enthalpy (ΔH) or a change in heat content.

Bond-breaking and bond-making processes depend on temperature and pressure.

The enthalpy change for the combustion of methane at room temperature might be entirely different from the enthalpy change for the combustion of methane at 100°C.

Enthalpy changes can also be applied to physical changes such as dissolution or a change in state.

Definition: Enthalpy Change (ΔH)

The enthalpy change describes the change in energy of a system.

Recap: Standard Conditions

Chemists can only compare enthalpy changes in a meaningful way if the measurements are all conducted at the same temperature and pressure.

In other words, a set of standard conditions are required, against which enthalpy changes can be measured.

The standard enthalpy change is the enthalpy change that happens at standard pressure and temperature.

A standard enthalpy change is indicated in chemical notation using a symbol called a plimsoll (\ominus) (the degree symbol is also commonly used (\circ)), which is written as a superscript term next to the enthalpy symbol, H :

$$\Delta H^{\ominus}.$$

Recap: Standard Conditions (Continued)

Chemists determined that the standard pressure for chemical reactions should be 1 atm.

A pressure of 1 bar is sometimes used instead because 1 bar is essentially equivalent to 1 atm:

$$1 \text{ atm} = 1.01325 \text{ bar.}$$

Chemists also determined that the standard temperature should be 298.15 K (25.15°C), but there has been some dispute about this value, and some chemists argue that a temperature of 0°C or 20°C would be more appropriate.

The standard concentration was determined to be one mole per litre (1 mol/L), which can also be written as 1 M.

Recap: Standard Conditions (Continued)

Chemists have also stated that standard enthalpy change values should only be determined when reactants and products are in their standard state.

The standard state is determined as the physical state of a substance at standard temperature and pressure.

The standard state for water is liquid (*l*) and the standard state for carbon dioxide is the gaseous state (*g*).

The following table shows the standard state of some familiar elements.

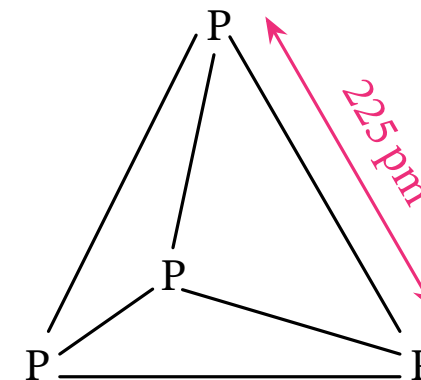
Hydrogen	H ₂ (g)
Helium	He(g)
Oxygen	O ₂ (g)
Sodium	Na(s)
Mercury	Hg(<i>l</i>)

Recap: Standard Conditions (Continued)

Some elements can exist as different allotropes and scientists have had to select just one allotropic form as the element's standard physical state.

Phosphorus has at least 10 different allotropic forms.

Chemists have determined that the standard state of phosphorus is solid white phosphorus, which has the chemical formula P_4 .



It is sometimes necessary to specify the standard allotropic form of an element when describing standard enthalpy change equations.

Carbon has several different allotropic forms, and it is not uncommon to state the standard allotropic form of carbon in standard enthalpy change equations.

Chemists might write the following term into an equation that describes the standard enthalpy change for a reaction involving pure carbon:



Standard Enthalpy of Fusion

There are many different types of enthalpy change processes.

One of the simplest is the melting of a substance from a solid to a liquid.

The standard enthalpy of fusion ($\Delta H^{\ominus}_{\text{fus}}$), also known as the standard heat of fusion, is the change in enthalpy when one mole of a substance transforms from a solid to a liquid.

The melting of ice is one of the most familiar examples of a system transitioning from a solid to a liquid.

The standard enthalpy of fusion for water is +6.01 kJ/mol at a pressure of 1 atm and a temperature of 0°C.

The enthalpy change could not be measured at 25.15°C because water changes to a liquid state at 0°C.

We can write this as follows:



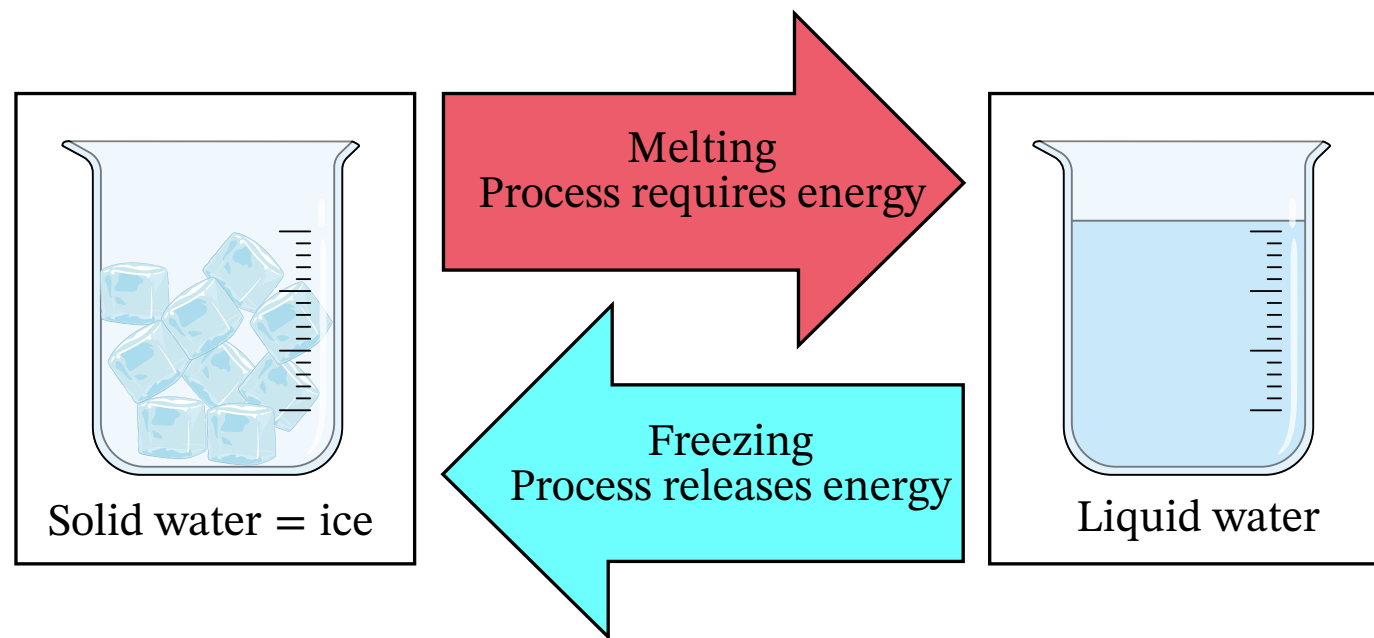
Standard Enthalpy of Fusion (Continued)

The standard enthalpy change will also change if the coefficients in front of the substance change.

For example, the standard enthalpy of fusion for two moles of water can be written as shown in the opposite equations.

We can determine that the melting of ice is an endothermic process because the enthalpy change is positive.

The water molecules absorb energy as they melt and transform from a solid to a liquid.



Definition: Standard Enthalpy of Fusion ($\Delta H^{\ominus}_{\text{fus}}$)

The standard enthalpy of fusion is the enthalpy change when one mole of a substance transforms from a solid state to a liquid state under standard conditions.

Example 1: Choosing the Statement That Best Describes Enthalpy of Fusion

Which of the following statements best describes the enthalpy of fusion, ΔH_{fus} ?

- A. The change in enthalpy resulting from the combining of two atoms to create a molecule
- B. The change in enthalpy resulting from the energy released by a substance when burned in oxygen
- C. The change in enthalpy resulting from the release of energy by a substance to change its state from solid to gas at constant pressure
- D. The change in enthalpy resulting from the taking in of energy by a substance to change its state from solid to liquid at constant pressure
- E. The change in enthalpy resulting from the mixing of two solutions together

Example 1 (Continued)

Answer

One of the dictionary definitions of the word fusion talks about different objects coming together and combining; however, it is important in chemistry when discussing enthalpy changes to remember that fusion almost means the exact opposite.

The standard enthalpy of fusion is the energy change when one mole of the substance transforms from a solid to a liquid under standard conditions.

Answer A seems to relate to an enthalpy change of formation, answer B relates to an enthalpy change of combustion, answer C relates to a sublimation, and finally, answer E relates to the enthalpy change of two substances mixing.

The answer not yet discussed is answer D, which relates to the enthalpy change that results from a substance turning from a solid into a liquid and is the correct answer.

Standard Enthalpy of Solidification

The standard enthalpy of solidification ($\Delta H^{\ominus}_{\text{solid}}$) describes the opposite physical transformation process.

The standard enthalpy of solidification is the enthalpy change that happens when a liquid transforms into a solid.

The standard enthalpy of solidification for water is the enthalpy change that happens when water freezes and forms ice.

The standard enthalpy of solidification for water is the negative of the standard enthalpy of fusion for water.

Therefore, the standard enthalpy of solidification for water is -6.01 kJ/mol at a pressure of 1 atm and a temperature of 0°C :



Definition: Standard Enthalpy of Solidification ($\Delta H^{\ominus}_{\text{solid}}$)

The standard enthalpy of solidification is the enthalpy change when one mole of a substance transforms from a liquid state to a solid state under standard conditions.

Standard Enthalpy of Vaporization and Condensation

The standard enthalpy of vaporization ($\Delta H^{\ominus}_{\text{vap}}$) is the enthalpy change that happens when a system of atoms vaporizes and changes from a liquid to a gas.

The standard enthalpy of vaporization for water is the enthalpy change that happens when one mole of water molecules is changed from a liquid into a gas.

The standard enthalpy of condensation is the enthalpy change that happens when a system of atoms is converted from a gas into a liquid.

The standard enthalpy of vaporization of water is the enthalpy change when one mole of water molecules is changed from a liquid into a gas, under standard conditions.

Standard Enthalpy of Vaporization and Condensation (Continued)

Similar to the standard enthalpies of fusion and solidification, the standard enthalpy of condensation for water is the negative of the standard enthalpy of vaporization for water:



The values are determined at a temperature of 100°C because water transitions between liquid and gas states at 100°C.

Definitions

Standard Enthalpy of Vaporization ($\Delta H^{\ominus}_{\text{vap}}$)

The standard enthalpy of vaporization is the enthalpy change that happens when one mole of a substance transforms from a liquid to a gas.

Standard Enthalpy of Condensation ($\Delta H^{\ominus}_{\text{cond}}$)

The standard enthalpy of condensation is the enthalpy change that happens when one mole of a substance transforms from a gas to a liquid, under standard conditions.

Example 2: Calculating the Heat Released during the Condensation of Methanol

How much heat, in kilojoules, is released when 0.13 moles of methanol(g) at 64.7°C are converted to methanol(l)? Take the ΔH_{vap} of methanol to be +35.2 kJ/mol. Give your answer to 2 decimal places.

Answer

In this question, we are asked to calculate how much heat is released when a certain amount of gaseous methanol is converted to liquid methanol.

As the physical change is from a gas to a liquid, we need to calculate the standard enthalpy change of condensation.

The standard enthalpy change of condensation is the enthalpy change when one mole of a substance transforms from a gas to a liquid under standard conditions.

Example 2 (Continued)

However, the data given in the question is for ΔH_{vap} , the standard enthalpy change of vaporization.

The standard enthalpy change of vaporization is the enthalpy change when one mole of a substance transforms from a liquid to a gas under standard conditions.

As the standard enthalpy of condensation is the reverse process of the standard enthalpy of vaporization, then, for the same substance, these two values are equal in magnitude, but with a change in sign.

For methanol, the standard enthalpy change of vaporization is $+35.2 \text{ kJ/mol}$. This would mean that the standard enthalpy change of condensation is -35.2 kJ/mol .

However, in this question, we do not have a mole of methanol; we only have 0.13 moles.

As such, we will need to do some simple arithmetic to work out the enthalpy change for 0.13 moles:

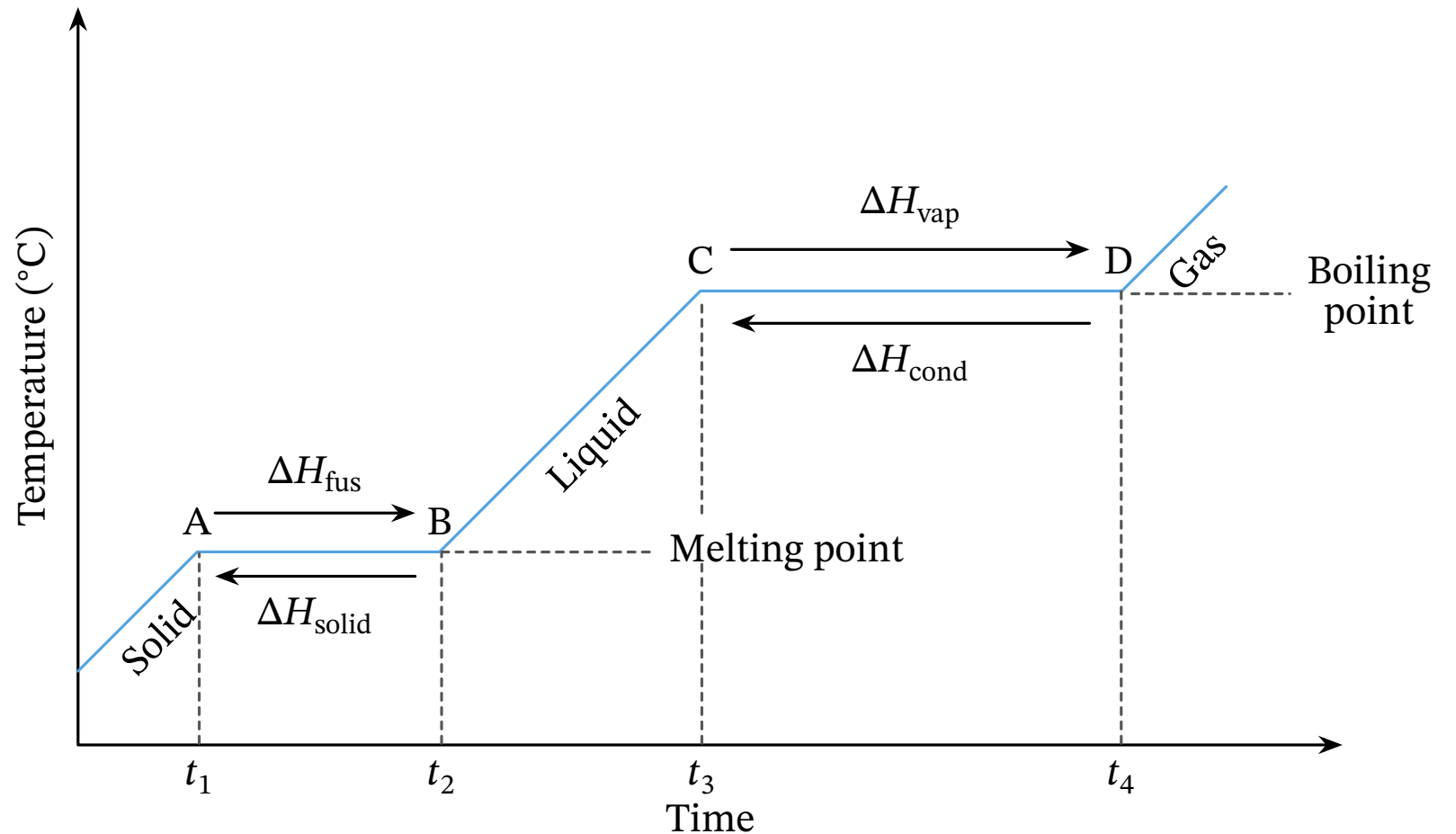
$$= -35.2 \times 0.13 = -4.58 \text{ kJ/mol} \quad (\text{correct to two decimal places}).$$

Estimating Standard Enthalpy from Heating Curves

It is sometimes preferable to describe enthalpy change processes through simple schematic illustrations.

The opposite illustration shows how the temperature of a system changes when it interacts with a heat source such as an open flame.

The flat lines correspond to when the physical state of the system is changing, and the slanted lines represent times when the temperature of the system is increasing.

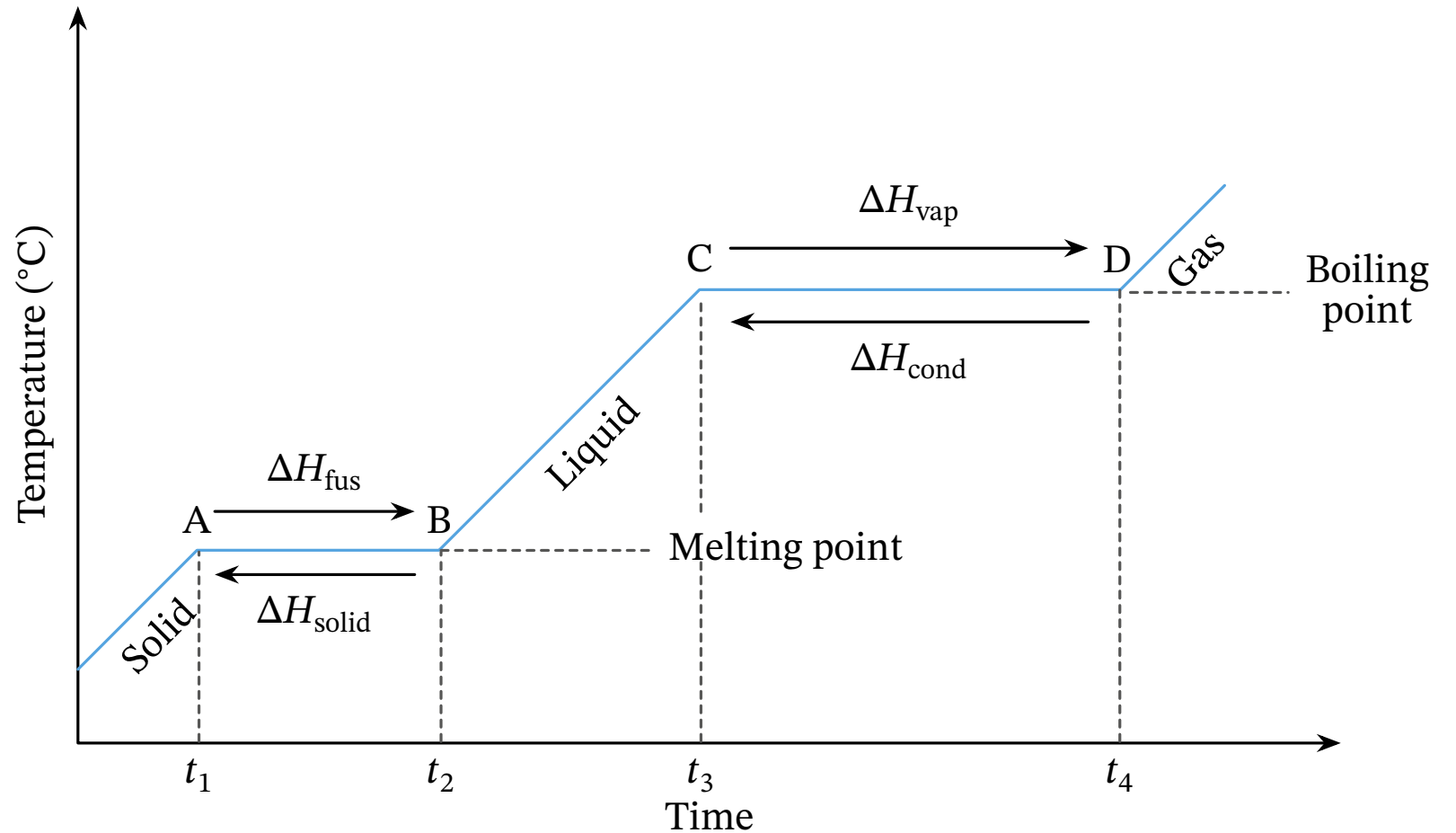


Estimating Standard Enthalpy from Heating Curves (Continued)

Melting is represented by the flat line that spans from points A to B, and evaporation is represented by the flat line that spans from points C to D.

The enthalpy of fusion is the enthalpy change that happens between times t_1 and t_2 .

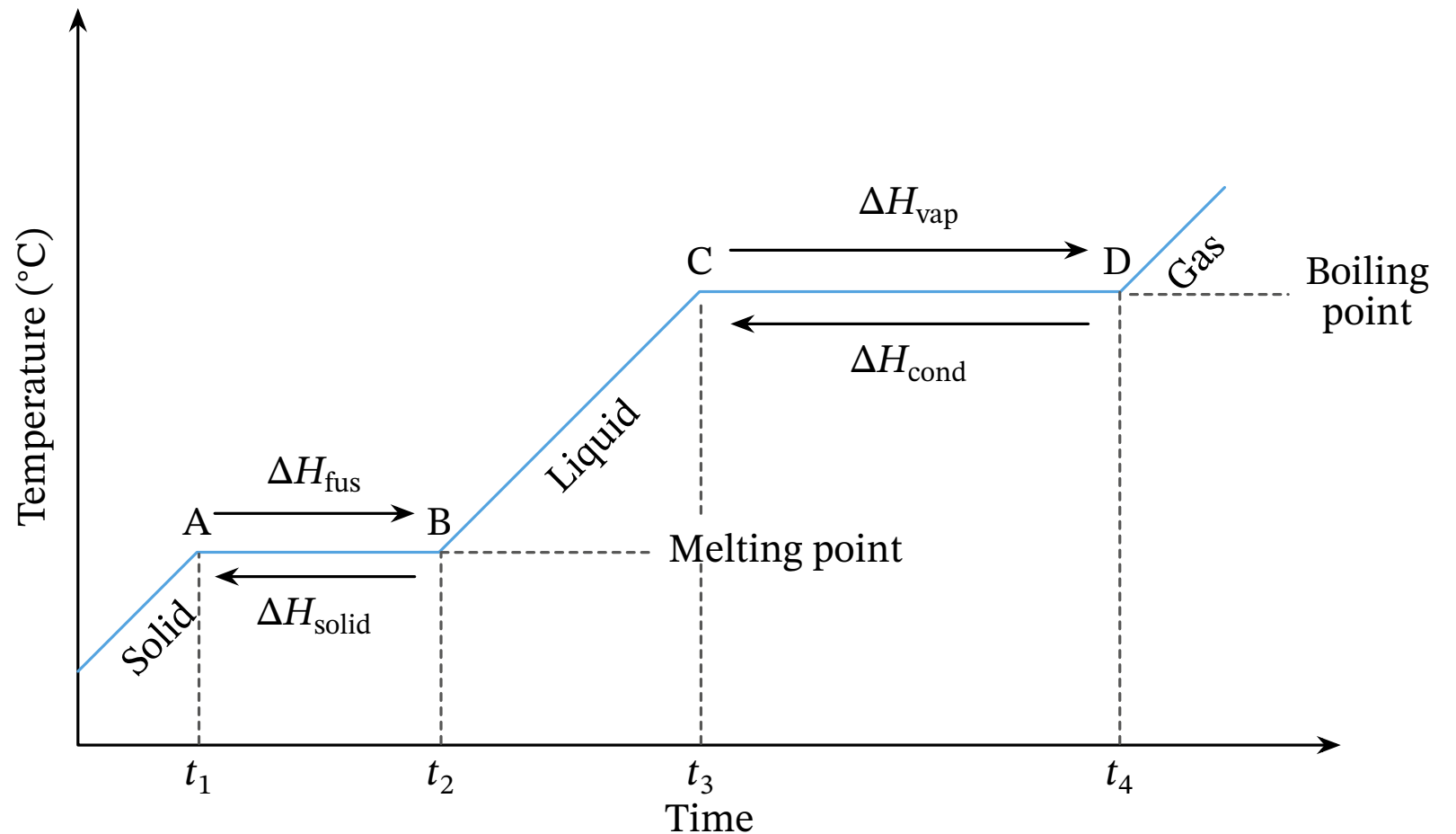
The enthalpy of vaporization is the enthalpy change that happens between times t_3 and t_4 .



Estimating Standard Enthalpy from Heating Curves (Continued)

The temperature does not increase between times (t_1 and t_2) and (t_3 and t_4) because all of the added heat energy is being used to break down intermolecular interactions that are responsible for holding either a solid or a liquid substance together.

Similarly, the enthalpy of condensation occurs between t_4 and t_3 , and the enthalpy of solidification occurs between t_2 and t_1 .



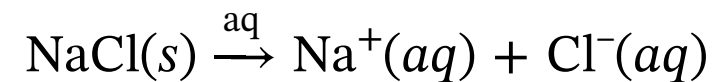
Standard Enthalpy of Solution

Another physical change for which the enthalpy change can be determined is the standard enthalpy of solution, ΔH_{soln} .

The standard enthalpy of solution is the enthalpy change when one mole of a substance dissolves to form an infinitely dilute solution.

An infinitely dilute solution is a theoretical construct that cannot exist, and scientists have to use a very large body of water as an acceptable substitute for an infinitely large body of water.

The following equation describes the enthalpy of solution for the dissolution of sodium chloride in water at a temperature of 25°C:



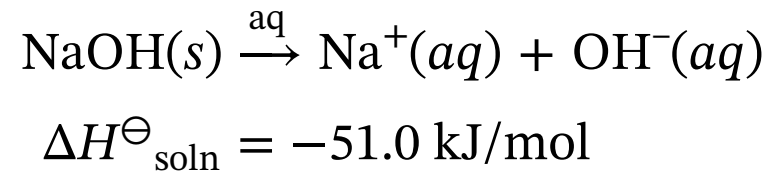
$$\Delta H^{\ominus}_{\text{soln}} = +3.9 \text{ kJ/mol}$$

Standard Enthalpy of Solution (Continued)

The standard enthalpy of solution is clearly an endothermic reaction because it has a positive value (+3.9 kJ/mol).

The system of atoms has to absorb energy for the reaction to happen because the enthalpy of the products is higher than the enthalpy of the reactants.

However, the standard enthalpy of solution for sodium hydroxide in water at a temperature of 25°C is



The negative value for standard enthalpy of solution for sodium hydroxide clearly indicates that this process is exothermic.

Definition: Standard Enthalpy of Solution ($\Delta H^{\ominus}_{\text{soln}}$)

The standard enthalpy of solution is the enthalpy change when 1 mole of a substance dissolves to produce an infinitely dilute solution.

Standard Enthalpy of Solution (Continued)

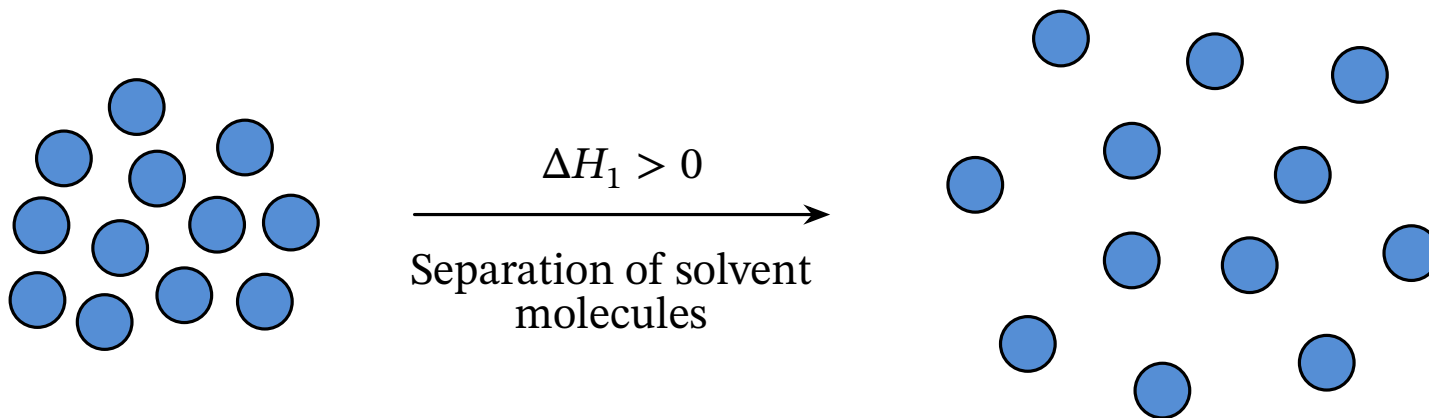
The overall process of dissolution can be broken down into three separate stages, each of which has its own enthalpy change associated with it.

The enthalpy change of solution can be determined by summing up the enthalpy changes of these three steps:

$$\Delta H^{\ominus}_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

The first step (ΔH_1) involves separation of the solvent molecules, as shown in the image below.

As this separation requires energy, then ΔH_1 is an endothermic process and so has a positive enthalpy.

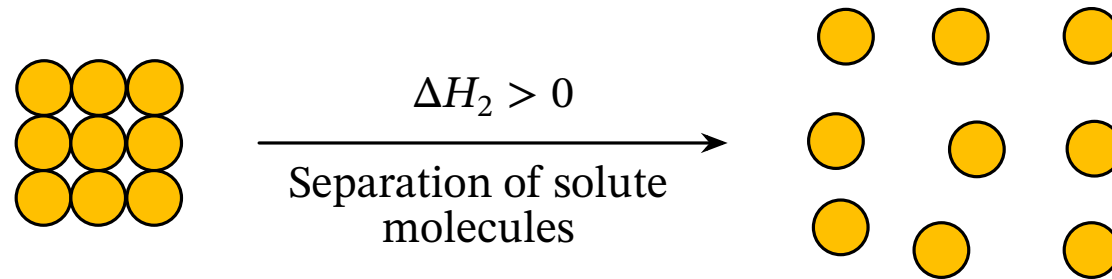


Standard Enthalpy of Solution (Continued)

The second step (ΔH_2) involves separation of the solute molecules, as shown in the image below.

In this example, the crystal lattice needs to be separated into ions.

As this separation requires energy, then ΔH_2 is an endothermic process and so has a positive enthalpy.

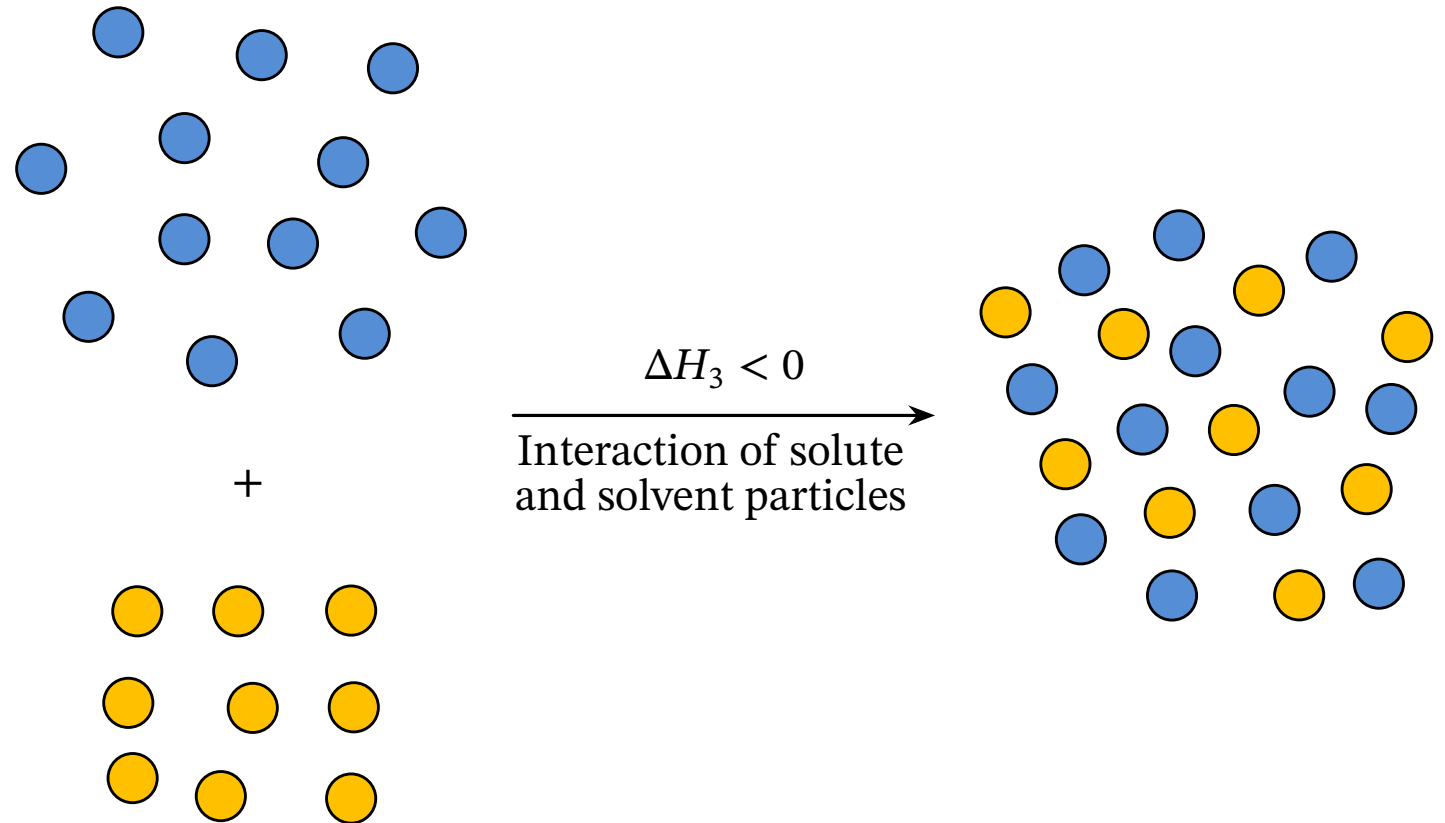


Standard Enthalpy of Solution (Continued)

In the third and final step (ΔH_3), the solute ions and solvent molecules are brought together and form bonds between each other.

This process is also known as the hydration energy if the solvent is water.

This process, shown in the opposite image, is exothermic and so ΔH_3 has a negative value.



Standard Enthalpy of Solution (Continued)

The standard enthalpy of solution therefore depends on the enthalpy values for each of these steps.

Since ΔH_1 and ΔH_2 are endothermic and ΔH_3 is exothermic, then

if $\Delta H_1 + \Delta H_2 > \Delta H_3$, $\Delta H^\ominus_{\text{soln}} > 0$ and the solution is endothermic;

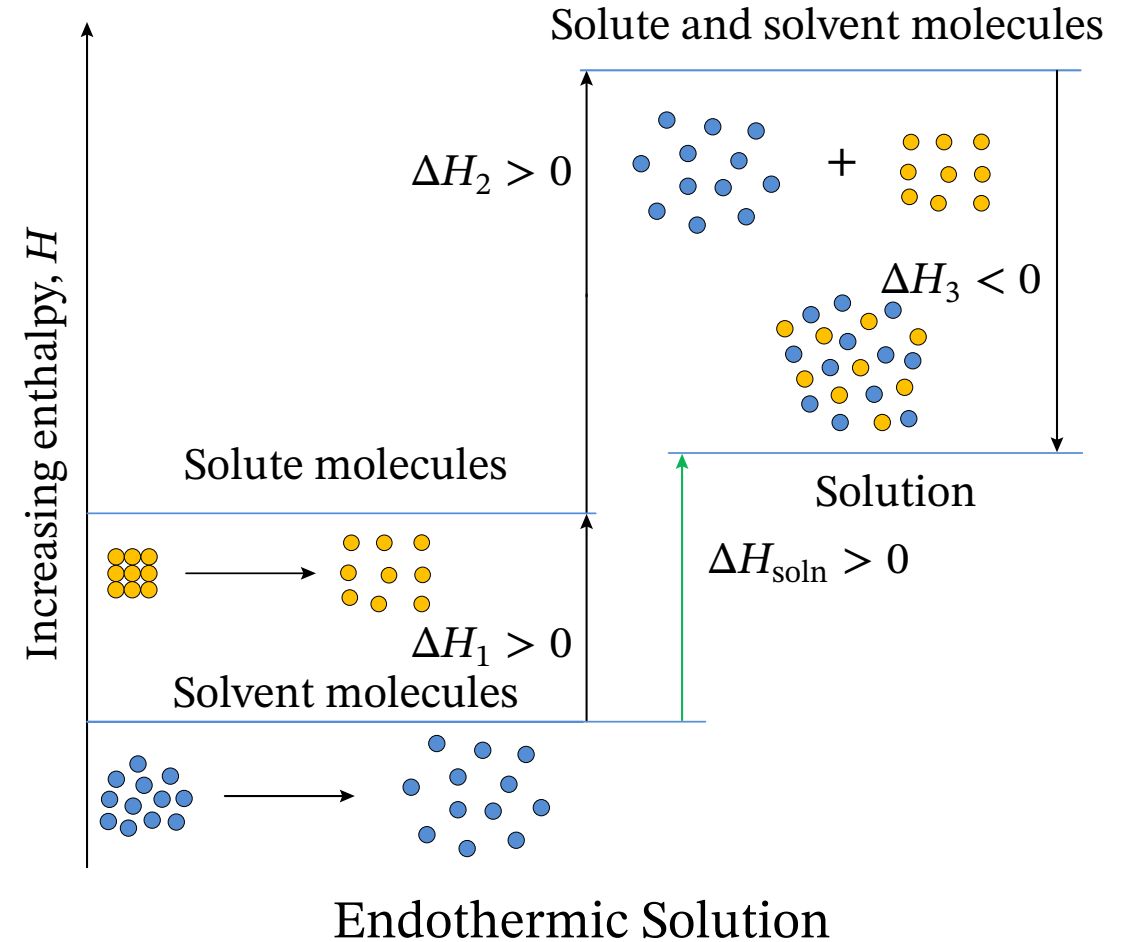
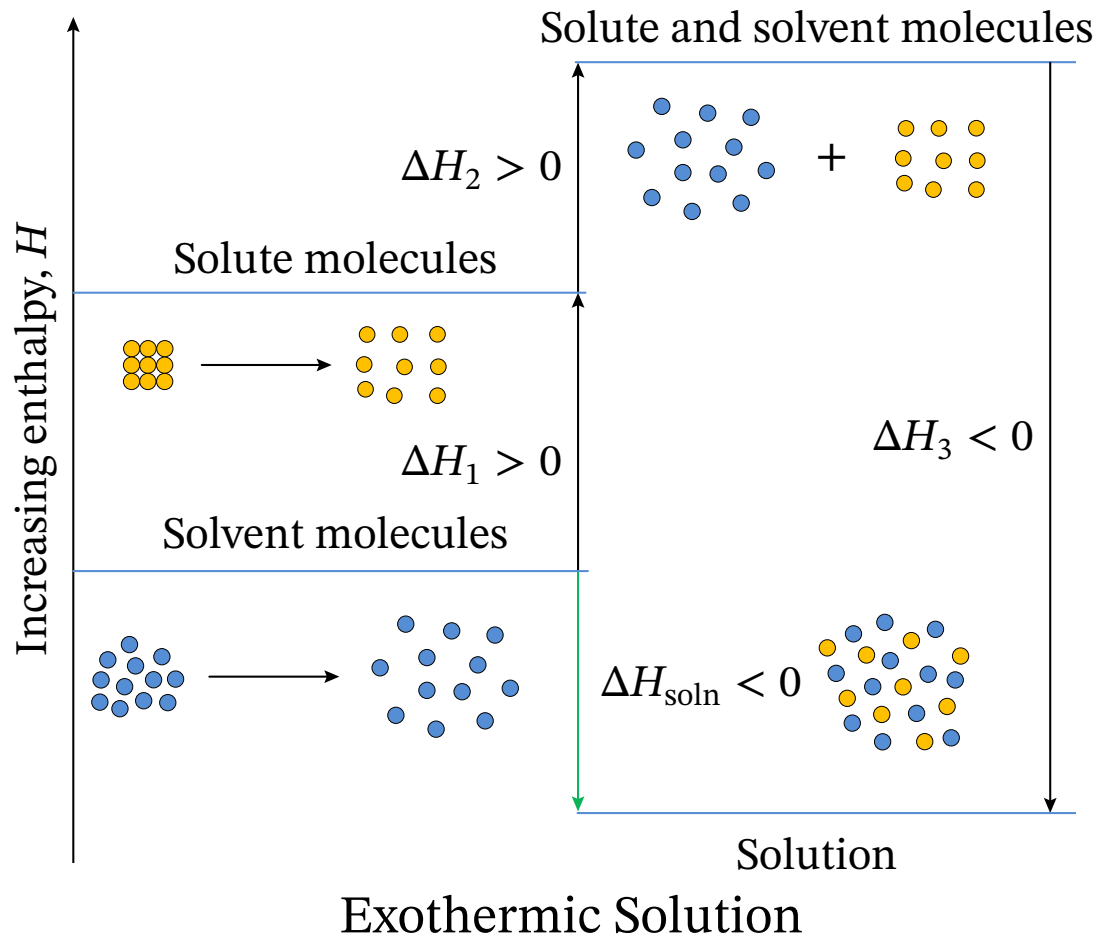
if $\Delta H_1 + \Delta H_2 < \Delta H_3$, $\Delta H^\ominus_{\text{soln}} < 0$ and the solution is exothermic.

Dissolution processes can look similar for two salts but can involve very different bond-breaking processes and solvent–solute intermolecular interactions.

As a result, two dissolution processes can look similar, but they can have different standard enthalpy of dissolution values.

Standard Enthalpy of Solution (Continued)

The changes in energy for an endothermic and an exothermic solution are shown below.



Example 3: Identifying the Steps in the Dissolution of a Solid

The process of dissolution can be considered to involve three steps. Which of the following is not one of these steps?

- A. The separation of solvent–solute interactions
- B. The separation of solute–solute attractions
- C. The formation of solute–solvent interactions
- D. The separation of solvent–solvent intermolecular attractions

Answer

When a solid dissolves in a solvent, a number of different attractive forces must be overcome, an endothermic energy change, and new interactions and bonds are created that release energy, an exothermic change.

Example 3 (Continued)

As the solid dissolves, the attraction between the different particles in the solid must be overcome; think about the sodium and chloride ions in the NaCl lattice.

Answer B discusses these solute–solute attractions and so is an incorrect answer.

The intermolecular attractions between the different solvent molecules also need to be overcome for new intermolecular attractions to be made with solute particles. This concept relates to answer D, which is also incorrect.

Energy is released during the dissolution process due to the formation of solute and solvent interactions created as the solute dissolves. This idea is stated in answer C, which is therefore incorrect.

Answer A is the correct answer, as the statement incorrectly discusses the separation of solvent–solute interactions; however, these interactions cannot exist before the solute dissolves.

Standard Enthalpy of Dilution

The difference between an infinitely large and a very large solvent system is usually not significant.

Experimentally determined enthalpy of solution values usually mimic the enthalpy of dissolution value that would be calculated for an infinitely dilute solution.

There is sometimes a significant difference between the enthalpy change that accompanies dissolution to an infinitely dilute state and actual dissolution experiments that happen in the laboratory.

The standard enthalpy of dilution can be used to understand the difference between realistic dissolution experiments that occur in laboratories and dissolution processes that could happen in infinitely large systems of solvent.

Standard Enthalpy of Dilution (Continued)

We can consider a more dilute solution to result in a greater separation of solute ions.

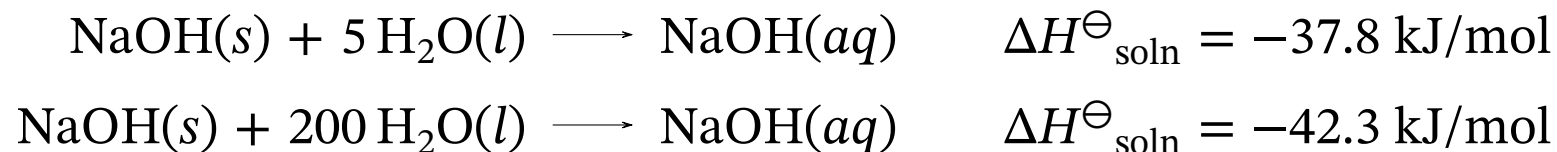
Since the separation of solute ions is an endothermic process, then more energy is required.

However, in a more dilute solution, the solute ions can form bonds with a greater number of solvent molecules.

This process is exothermic, and so the more dilute a solution, the greater the amount of energy released.

Hence, the enthalpy of dilution is a balance between the sum of the energy required to separate solute ions and the energy released from the bonds formed between solute and solvent molecules.

This can also be shown with the dilution of sodium hydroxide in water:



Definition: Standard Enthalpy of Dilution ($\Delta H^{\ominus}_{\text{dil}}$)

The standard enthalpy of dilution is the enthalpy change when a solution of a substance is diluted infinitely per mole of substance.

Standard Enthalpy of Combustion

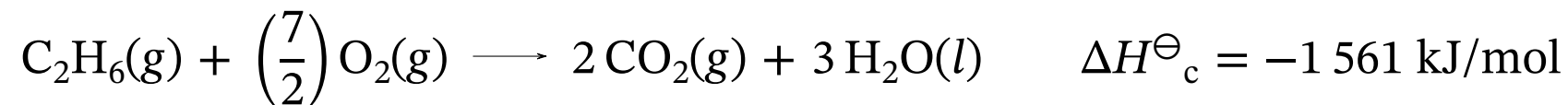
Next, we can look at the enthalpy changes associated with chemical reactions.

Specifically, we will consider the standard enthalpy for combustion and formation.

The standard enthalpy of combustion is the change in enthalpy that happens when a system of atoms burns completely in oxygen to produce chemical products.

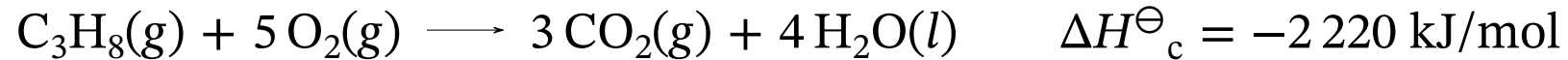
Standard enthalpies of combustion are used to compare the amount of energy that can be obtained from different types of combustible fuels.

The following equation shows the standard enthalpy of combustion for ethane:



Standard Enthalpy of Combustion (Continued)

Other examples include the standard enthalpy of combustion for propane, often used as a fuel:



And the standard enthalpy of combustion for glucose is shown:



The enthalpy change of combustion should be measured when the reactants are all in their standard state. This is sometimes very difficult to achieve, and it is easier to record the change in enthalpy when some reactants are in a gaseous state, even though they should be in a liquid state.

The standard enthalpy of combustion is calibrated to account for reactant molecules that are not in their standard state. This is achieved by including any energy that is needed to change reactants into their standard state.

Definition: Standard Enthalpy of Combustion (ΔH^{\ominus}_c)

The standard enthalpy of combustion is the enthalpy change when one mole of substance burns completely in oxygen under standard conditions and standard states.

Standard Enthalpy of Formation

The final standard enthalpy we will describe is the standard enthalpy of formation, $\Delta H^{\ominus}_{\text{formation}}$, sometimes shortened to $\Delta H^{\ominus}_{\text{f}}$.

The standard enthalpy of formation describes the enthalpy change when one mole of substance is formed from its elements, under standard conditions.

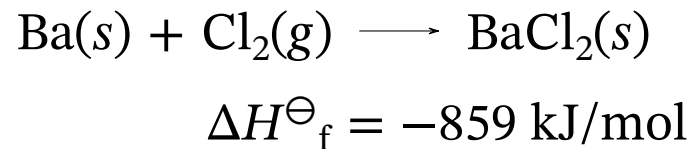
The standard enthalpy of formation has to be zero for any element in its standard state because it does not take any energy to convert an element into itself.

It does take energy to convert elements into chemical compounds, and this explains why the standard enthalpy of formation is nonzero for almost all chemical compounds.

Standard Enthalpy of Formation (Continued)

The more negative the standard enthalpy of formation for a substance is, the more stable that substance is.

The following equation describes the standard enthalpy of formation for barium chloride:



The barium and chloride elements are in their standard state, and the barium chloride product is in its standard state.

The reaction is exothermic, because energy is released from the system to its surroundings.

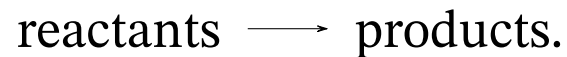
This statement could be reworded to say that the enthalpy of the products is lower than the enthalpy of the reactants.

Standard Enthalpy of Formation (Continued)

The barium chloride product must be more stable than the barium and chloride reactants because it has the lower enthalpy value.

We must not make the fatal mistake of assuming that all standard enthalpies of formation processes are exothermic, because we have already discussed how enthalpy change values vary from one system to another.

The standard enthalpies of formation can be used to determine the change in enthalpy for a chemical reaction:



Standard Enthalpy of Formation (Continued)

The enthalpy change for this reaction (ΔH^{\ominus}_r) can be calculated as the difference between the standard enthalpy of formation for the reactants and products. This statement is described in the following equation:

$$\Delta H^{\ominus}_r = \sum \Delta H^{\ominus}_f(\text{products}) - \sum \Delta H^{\ominus}_f(\text{reactants}).$$

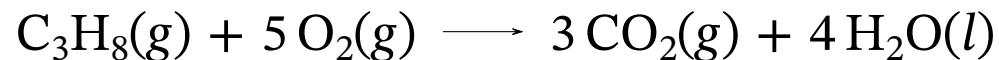
The equation can be used to determine the enthalpy of reaction for a chemical process.

The next table shows the enthalpy of formation for some reactant and product molecules.

Substance	ΔH^{\ominus}_f (kJ/mol)
Propane	-105
Oxygen	0
Carbon dioxide	-394
Water	-286

Standard Enthalpy of Formation (Continued)

The tabulated values can be used to determine the enthalpy of reaction for the combustion of propane:



We will determine the enthalpy of reaction by first writing out the standard enthalpy of reaction equation:

$$\Delta H^\ominus_{\text{r}} = \sum \Delta H^\ominus_{\text{f}}(\text{products}) - \sum \Delta H^\ominus_{\text{f}}(\text{reactants})$$

$$\Delta H^\ominus_{\text{r}} = [\Delta H^\ominus_{\text{f}}(3 \text{CO}_2(\text{g})) + \Delta H^\ominus_{\text{f}}(4 \text{H}_2\text{O}(\text{l}))] - [\Delta H^\ominus_{\text{f}}(\text{C}_3\text{H}_8(\text{g})) + \Delta H^\ominus_{\text{f}}(5 \text{O}_2(\text{g}))].$$

We will then substitute our tabulated numbers into this mathematical equation:

$$\Delta H^\ominus_{\text{r}} = ((3 \times -394) + (4 \times -286)) - ((-105) + (5 \times 0))$$

$$\Delta H^\ominus_{\text{r}} = -2\,221 \text{ kJ/mol.}$$

The enthalpy change of reaction for propane is $-2\,221 \text{ kJ/mol}$.

Definition: Standard Enthalpy of Formation (ΔH^{\ominus}_f)

The standard enthalpy of formation is the enthalpy change when one mole of substance is formed from its constituent elements in their standard states and under standard conditions.

Example 4: Determining the Standard Enthalpy of Formation of a Native Element

What is the value of the standard enthalpy of formation of any element in its standard state?

Answer

The standard enthalpy of formation is the enthalpy change when one mole of a substance is formed from its constituent elements in their standard states under standard conditions.

The standard enthalpy of formation for an element does not describe a chemical change as the element is already in its native state.

By definition, the standard enthalpy of formation of an element already in its standard state is zero.

If no energy is transferred, there can be no enthalpy change, and the value is 0 kJ/mol.

Key Points

- ▶ The enthalpy change for chemical reactions and physical processes can be standardized in terms of their conditions and the physical states of the chemicals involved.
- ▶ The standard enthalpy of fusion relates to a substance melting, and the standard enthalpy of solidification relates to a substance turning back into solid from a liquid.
- ▶ The standard enthalpy of vaporization relates to a substance boiling and turning from a liquid into a gas, whereas the standard enthalpy of condensation is the energy change of the reverse process.
- ▶ The enthalpy change of solution relates to the dissolution of a substance and the formation of an infinitely dilute solution.
- ▶ The standard enthalpy change of dilution defines the enthalpy change when one mole of a solution is infinitely diluted.
- ▶ The standard enthalpy of combustion relates to one mole of a substance being burned in excess oxygen under standard states and standard conditions.
- ▶ The standard enthalpy of formation relates to one mole of the substance being formed from its constituent elements under standard states and standard conditions.
- ▶ The standard enthalpies of formation can be used to calculate the change in enthalpy of a reaction.