

Heats of Reaction

Heat changes often accompany chemical reactions. If heat is absorbed in a chemical reaction (**endothermic change**), the products will have more energy than the reactants and the change in enthalpy (ΔH°) will have a positive value. If heat is released in a chemical reaction (**exothermic change**) the products will have less energy than the reactants and ΔH° will have a negative value. Regardless of whether a chemical reaction is endothermic or exothermic, all reactions require activation energy in order to begin. **Activation energy** (E_a) is defined as **the amount of energy needed to start a chemical reaction**. A **catalyst** is sometimes used to reduce the amount of activation energy needed to start a reaction. Catalysts are used to speed up reactions but are not used up in the chemical reaction.

Standard Enthalpies of Formation

- The standard enthalpy of formation (ΔH_f°) of a compound is defined as **the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states**.
- The degree symbol ($^\circ$) on a thermodynamic function indicates that the corresponding process has been carried out under **standard conditions**.
- Conventional Definitions of Standard Conditions (Standard State)
 - For a Compound
 - The standard state for a gaseous substance is a pressure of exactly **1 atmosphere**.
 - For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
 - For a substance present in a solution, the standard state is a **concentration of exactly 1 Molar**.
 - All compounds have heat of formation values.
 - For An Element
 - The standard state of an element is the form in which the element exists under conditions of a pressure of **1 atmosphere and a temperature of 25°C (298 K)**.
 - Elements in their standard state have $\Delta H_f^\circ = 0$.**
- Consider this reaction:

$$\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_f^\circ = 34 \text{ kJ/mol}$$
- Note that the reaction is written so that both elements are in their standard states and 1 mole of the product is formed. (This is why a fraction is used to balance nitrogen.) Enthalpies are always given **per mole of the product with the product in standard state**.
- To calculate the change in enthalpy for a reaction (ΔH°) you must find the difference between the **heats of formation** of the reactants and the products. $\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

For example: Calculate the change in enthalpy for the following reaction:



First balance the equation:



Determine the enthalpy for the products and the reactants:



Substance	ΔH_f° (kJ/mol)
Ca (s)	0
H ₂ O (l)	-285.8
Ca(OH) ₂ (s)	-986.6
H ₂ (g)	0

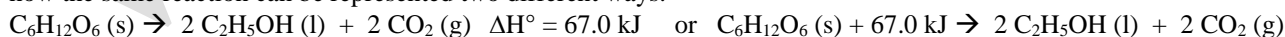
Calculate the ΔH for the reaction using the formula from above:

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\Delta H^\circ = -986.6 - (-571.6)$$

$$\Delta H^\circ = -415.0 \text{ kJ; this is an exothermic reaction}$$

The change in enthalpy (ΔH°) for a reaction can be written **at the end of an equation** or **as part of the equation**. Look below how the same reaction can be represented two different ways.



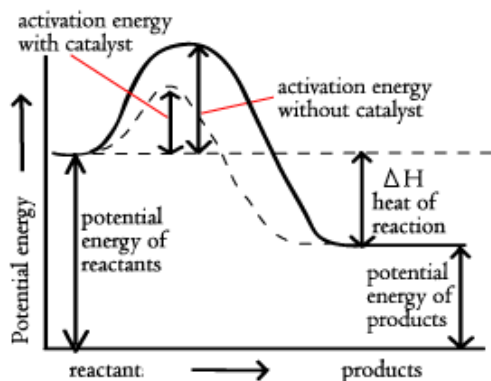
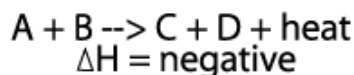
If a reaction is **endothermic**, the ΔH° will be **positive** in value and the energy value can be written as a **reactant**, as seen above. If a reaction is **exothermic**, the ΔH° value will be **negative** and the energy value can be written as part of the **product** as seen here:

$$\text{C} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ = -394 \text{ kJ} \quad \text{or} \quad \text{C} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 394 \text{ kJ}$$

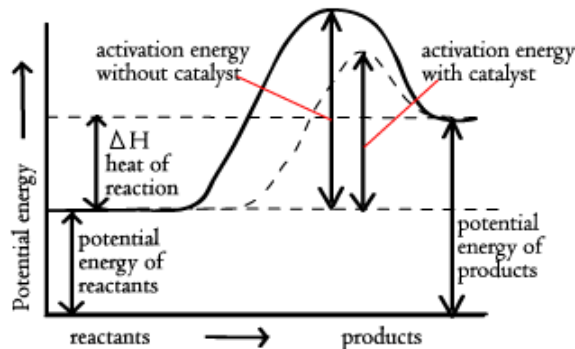
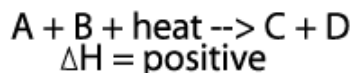
Energy Diagrams

Energy diagrams are used to give a graphic representation of a chemical reaction. The energy diagrams for endothermic and exothermic reactions are shown below.

EXOTHERMIC



ENDOTHERMIC

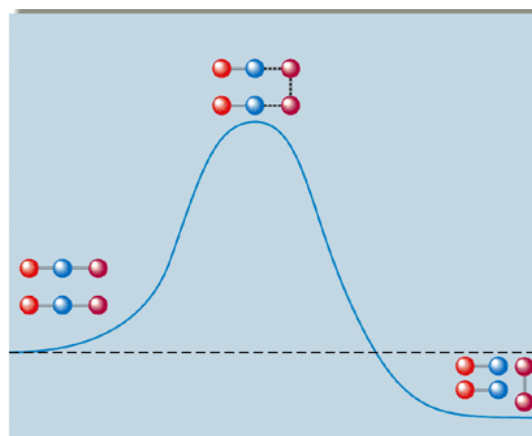
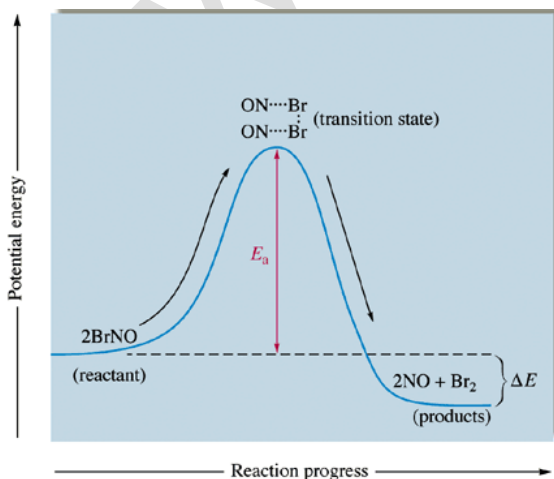


In Summary:

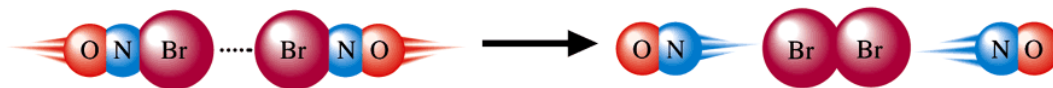
ΔH° Value	Endothermic/Exothermic	Higher Enthalpy	In Equation, write ΔH° value as:	Example
Positive (+)	Endothermic	Products	Reactant	$X + Y + \Delta H^\circ \rightarrow Z$
Negative (-)	Exothermic	Reactant	Product	$X + Y \rightarrow Z + \Delta H^\circ$

A Model for Chemical Kinetics

- Chemical reactions speed up when the temperature is increased. Experiments have shown that virtually all rate constants show an exponential increase with absolute temperature.
- The **collision model** is built around the central idea that molecules must collide to react.
- The kinetic molecular theory of gases predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecules. This agrees with the observation that reaction rates are greater at higher temperatures qualitatively. However, it is found that the rate of reaction is much smaller than the calculated collision frequency in a collection of gas particles. This means only a fraction of the collisions produces a reaction.
- In 1880 Svante Arrhenius proposed the existence of a *threshold energy*, called **activation energy** that must be overcome by a chemical reaction.
- Strong bonds between molecules results in high activation energy for a chemical reaction.**
- The arrangement of atoms found at the potential energy “hill,” or barrier, is called the **activated complex**, or **transition state**.
- A certain minimum energy is required for molecules to “get over the hill” so that products can form. This energy is furnished by the energy of the collision.
- Only collisions with energy greater than the activation energy are able to react (get over the barrier).



- Experiments show that the observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier. This means that many collisions, even though they have the required energy, still do not produce a reaction. The reason for this is that in some collisions the molecular orientation is not correct for a reaction to occur. (See the diagram to the below. The first reaction occurs but the second reaction does not.



(b)



c)

Summarize: Two requirements must be satisfied for reactants to collide successfully:

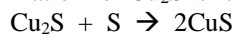
- The collision must involve enough energy to produce the reaction; the collision energy must equal or exceed the activation energy.
- The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

Homework:

- Define activation energy –
- Define catalyst –
- Define standard enthalpy of formation (ΔH_f°) –
- The degree symbol ($^\circ$) on a thermodynamic function indicates:
- Define Standard Conditions for:
 - pressure -
 - temperature -
 - molarity (M) -
- What is the heat of formation value for elements in their standard state?
- Circle if the reaction is **endothermic** or **exothermic**. Rewrite the following equations with energy included as either a reactant or product.

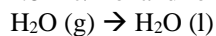
<p>a. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $\Delta H^\circ = -27 \text{ kcal}$ endothermic or exothermic</p> <p>c. $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ $\Delta H^\circ = 571.6 \text{ kJ}$ endothermic or exothermic</p> <p>e. $2\text{K} + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2$ $\Delta H^\circ = -393 \text{ kJ}$ endothermic or exothermic</p>	<p>b. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ $\Delta H^\circ = -890 \text{ kJ}$ endothermic or exothermic</p> <p>d. $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ $\Delta H^\circ = 2870 \text{ kJ}$ endothermic or exothermic</p> <p>f. $\text{TiO}_2 + 2\text{Cl}_2 \rightarrow \text{TiCl}_4 + \text{O}_2$ $\Delta H^\circ = 140.5 \text{ kJ}$ endothermic or exothermic</p>
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8. The heat of formation for Cu_2S is -79.5 kJ/mol , for S its 0 kJ/mol and for CuS its -53.1 kJ/mol .



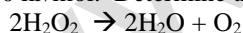
- What is the change in enthalpy for this reaction? _____
 - Is this reaction: exothermic or endothermic? Circle One.
 - Draw an energy diagram for this reaction. Label potential energy of the reactants, potential energy of the products, ΔH° , and activation energy.
-
- Which has higher enthalpy? reactants or products Circle One.
 - Re-write the equation from above with the ΔH° value as a reactant or product, which ever is correct.

9. Determine the heat of reaction for the following reaction as water vapor cools to form liquid water. The heat of formation for $\text{H}_2\text{O}(\text{g})$ is -241.82 kJ/mol and for $\text{H}_2\text{O}(\text{l})$ it is -285.83 kJ/mol .



- What is the change in enthalpy for this reaction? _____
 - Is this reaction: exothermic or endothermic? Circle One.
 - Draw an energy diagram for this reaction. Label potential energy of the reactants, potential energy of the products, ΔH° , and activation energy.
-
- Which has higher enthalpy? reactants or products Circle One.
 - Re-write the equation from above with the ΔH° value as a reactant or product, which ever is correct.

10. The heat of formation of H_2O_2 is -187.6 kJ/mol , the heat of formation of H_2O is -285.83 kJ/mol , and the heat of formation of O_2 is 0 kJ/mol . Determine the heat of reaction for the decomposition of H_2O_2 . Draw an energy diagram for this reaction.



- What is the change in enthalpy for this reaction? _____
 - Is this reaction: exothermic or endothermic? Circle One.
 - Draw an energy diagram for this reaction. Label potential energy of the reactants, potential energy of the products, ΔH° , and activation energy.
-
- Which has higher enthalpy? reactants or products Circle One.
 - Re-write the equation from above with the ΔH° value as a reactant or product, which ever is correct.

11. In the engine of your car, nitrogen and oxygen combine to form nitrogen oxides, chemicals that contribute to pollution. Below is a reaction where nitrogen dioxide decomposes to form nitrogen monoxide and oxygen. Determine the ΔH value for this reaction using the heats of formation given.



Substance	ΔH_f° (kJ/mol)
$\text{NO}_2(\text{g})$	+33.2
$\text{NO}(\text{g})$	+90.2

- What is the change in enthalpy for this reaction? _____
 - Is this reaction: exothermic or endothermic? Circle One.
 - Draw an energy diagram for this reaction. Label potential energy of the reactants, potential energy of the products, ΔH° , and activation energy.
-
- Which has higher enthalpy? reactants or products Circle One.
 - Re-write the equation from above with the ΔH° value as a reactant or product, which ever is correct.

12. At constant temperature and pressure, the heats of formation for $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{C}_2\text{H}_6(\text{g})$ are given to the right. What is the ΔH° for **1 mole of C_2H_6** gas to oxidize to carbon dioxide gas and water vapor (temperature and pressure are held constant)?

Species	ΔH_f° (kJ/mole)
$\text{H}_2\text{O}(\text{g})$	-251
$\text{CO}_2(\text{g})$	-393
$\text{C}_2\text{H}_6(\text{g})$	-84

13. $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ $\Delta H^\circ = -889.1 \text{ kJ}$
 What is the standard heat of formation of methane, $\Delta H_f^\circ \text{CH}_4(\text{g})$, as calculated from the data above?

Species	ΔH_f° (kJ/mole)
$\text{H}_2\text{O}(\text{l})$	-285.8 kJ / mole
$\text{CO}_2(\text{g})$	-393.3 kJ / mole

14. $\text{O}_3(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{NO}_2(\text{g})$
 Consider the reaction represented above. Referring to the data in the table to the right, calculate the standard enthalpy change, ΔH° , for the reaction at 25°C . Be sure to show your work.

Species	ΔH_f° (kJ/mole)
$\text{O}_3(\text{g})$	143
$\text{NO}(\text{g})$	90.
$\text{NO}_2(\text{g})$	33

15. $\text{C}_7\text{H}_{16}(\text{l}) + 11\text{O}_2(\text{g}) \rightarrow 7\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$
 The heat of combustion, $\Delta H_{\text{comb}}^\circ$, for one mole of $\text{C}_7\text{H}_{16}(\text{l})$ is $-4.85 \times 10^3 \text{ kJ}$. Using the information in the table below, calculate the value of ΔH_f° for $\text{C}_7\text{H}_{16}(\text{l})$ in kJ mol^{-1} .

Species	ΔH_f° (kJ/mole)
$\text{H}_2\text{O}(\text{l})$	-285.8 kJ / mole
$\text{CO}_2(\text{g})$	-393.3 kJ / mole