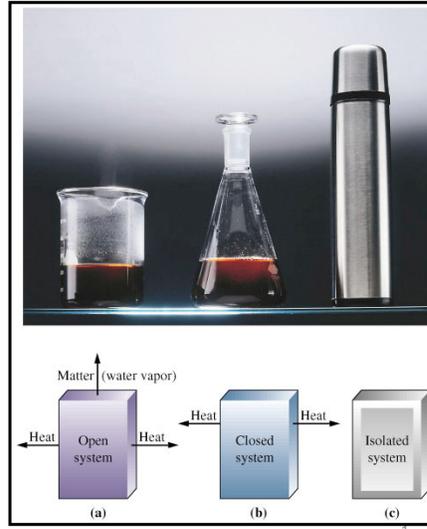


Thermodynamics

- **Thermodynamics** is the study of energy.
- **Thermochemistry** is the study of energy changes that occur during chemical reactions



Energy

- **energy** - the ability to do work or transfer heat
 - **work** - energy used to cause an object with mass to move
 - **heat** - energy used to cause the temperature of an object to increase
- **kinetic energy** - energy of motion
- **potential energy**
 - energy due to position
 - energy associated with forces of attraction and repulsion between objects



Units of Energy

- The SI unit of energy is the **joule (J)**.

$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

- An older, non-SI unit is still in widespread use called the **calorie (cal)**.

$$1 \text{ cal} = 4.184 \text{ J}$$

3

Law of conservation of energy

- The energy of the universe is constant.
- Energy is neither created nor destroyed.
- It can only be transformed from one kind into another.

4

Atoms & Molecules Possess Energy

- **kinetic energy**
 - proportional to the absolute temperature
- **potential energy**
 - chemical bonds hold atoms together, forces of attraction give rise to a compound's potential energy (chemical energy)
 - bonds break - increase PE of system
 - bonds made - lower PE of system

So we observe changes in chemical energy during chemical reactions.

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Heat Energy

- molecular kinetic energy
- ability to change temperature of colder object
- all forms of energy can be converted into heat

6

Heat Capacity

- the amount of energy required to raise the temperature of a substance by 1 K (1 °C)

$$C = \text{heat capacity} = \frac{\text{heat absorbed}}{\Delta T}$$

- depends on amount of substance (extensive property)

7

Specific Heat Capacity

- the amount of energy required to raise the temperature of **1 g** of a substance by **1 K**.

$$\text{specific heat capacity} = \frac{\text{heat capacity}}{\text{mass}}$$

$$C_s = \frac{q}{m \times \Delta T}$$

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Specific Heat Capacities

Substance	$C_s / \text{J K}^{-1} \text{mol}^{-1}$
Hg(l)	0.14
Fe(s)	0.45
Al(s)	0.90
CaCO ₃ (s)	0.82
CO ₂ (g)	0.84
CH ₄ (g)	2.20
H ₂ O(l)	4.18

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Heat Capacity & Specific Heat Capacity

To calculate a quantity of heat (q):

heat = specific heat \times mass \times temperature change

$$q = C_s \times m \times \Delta T$$

$$\text{J} = \text{J g}^{-1} \text{K}^{-1} \times \text{g} \times \text{K}$$

For water:

$$209 \text{ J} = 4.18 \text{ J g}^{-1} \text{K}^{-1} \times 50.0 \text{ g} \times 1 \text{ K}$$

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Example

- How much heat is given off when an 869 g iron bar cools from 94 °C to 5 °C?

(specific heat of Fe = 0.444 J g⁻¹ K⁻¹)

$$q = m \times C_s \times \Delta t$$

$$\begin{aligned} \Delta t &= t_{\text{final}} - t_{\text{initial}} \\ &= 5 \text{ }^\circ\text{C} - 94 \text{ }^\circ\text{C} \\ &= -89 \text{ }^\circ\text{C} \end{aligned}$$

$$\begin{aligned} q &= 869 \text{ g} \times 0.444 \text{ J g}^{-1} \text{ K}^{-1} \times -89 \text{ K} \\ &= -34000 \text{ J} \\ &\text{(} q < 0, \text{ heat lost!)} \end{aligned}$$

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Molar Heat Capacity

- Molar heat capacity** is the product of specific heat times the molar mass of a substance (units are J K⁻¹ mol⁻¹)

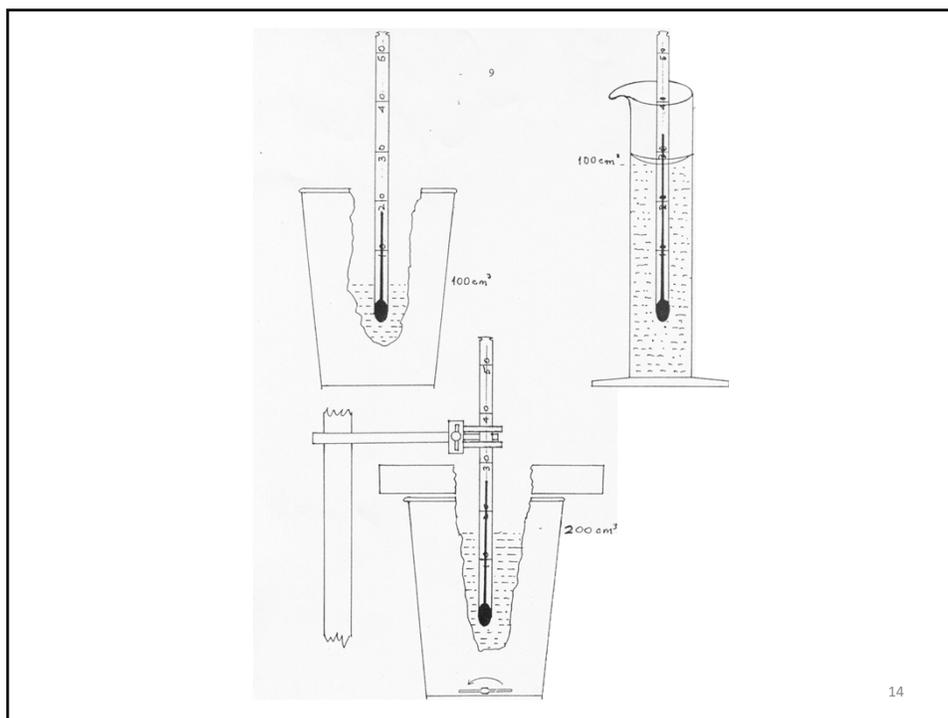
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Calorimetry

- **Calorimetry** is a technique used to measure heat exchange in chemical reactions
- A **calorimeter** is the device used to make heat measurements.
- Calorimetry is based on the law of **conservation of energy**.
- $q_{soln} = -q_{reaction}$

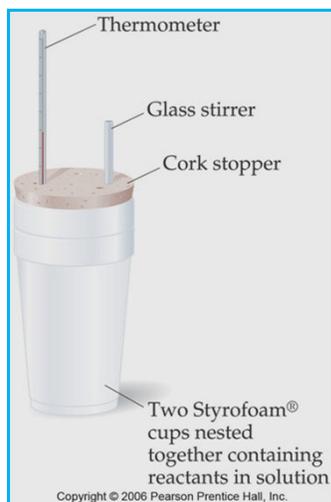


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Coffee Cup Calorimeter



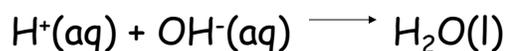
- We indirectly measure the heat change for the **system** by measuring the heat change for the **water** in the calorimeter
- The specific heat for water is well known ($4.184 \text{ J K}^{-1} \text{ mol}^{-1}$)
- We can measure ΔH for the reaction with this equation:

$$q = m \times C_s \times \Delta T$$

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Example

In a neutralisation reaction between a strong acid and a strong base, the following reaction forms water.



If 25.00 cm^3 of 2.50 mol dm^{-3} HCl and 25.00 cm^3 of 2.50 mol dm^{-3} NaOH, both at $21.1 \text{ }^\circ\text{C}$ react and the final temperature is $37.8 \text{ }^\circ\text{C}$, determine the heat of the neutralisation reaction expressed per mole of H_2O formed.

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Solution:

The total volume of solution is 50.00 cm^3 , we need to calculate its mass.

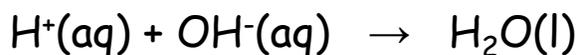
$$\text{Heat of reaction} = q_{\text{neutr}} = -q_{\text{soln}}$$

$$\begin{aligned} q_{\text{soln}} &= m \times C_s \times \Delta T \\ &= (50.00 \text{ cm}^3 \times 1.00 \text{ g cm}^{-3}) \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \\ &\quad \times (37.8 - 21.1) \text{ K} \\ &= 3.5 \times 10^3 \text{ J} \end{aligned}$$

$$q_{\text{neutr}} = -q_{\text{soln}} = -3.5 \text{ kJ}$$

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$$\begin{aligned} n(\text{H}^+) &= C \times V \\ &= 2.50 \text{ mol dm}^{-3} \times 25.00 \times 10^{-3} \text{ dm}^3 \\ &= 0.0625 \text{ mol H}^+ \end{aligned}$$



$$n(\text{H}^+) = n(\text{OH}^-) = n(\text{H}_2\text{O}) = 0.0625 \text{ mol}$$

Amount of heat produced per mole of H_2O is

$$\begin{aligned} q_{\text{neutr}} &= -3.5 \text{ kJ} / 0.0625 \text{ mol} \\ &= -56 \text{ kJ mol}^{-1} \text{ H}_2\text{O} \end{aligned}$$

(Since $q < 0$, heat is lost, that is neutralisation reaction is exothermic!)

[Do practice exercise on top of page 519 of textbook.]

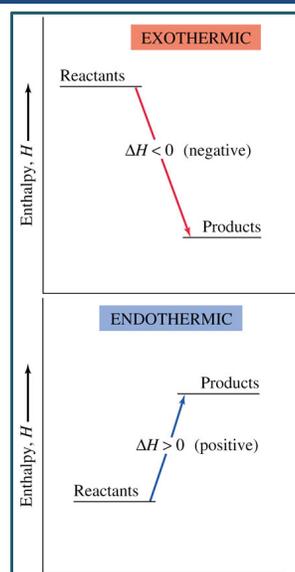
Heat of reaction (ΔH)

- The total amount of heat released or absorbed between the beginning of a reaction and the return of the substances present to the original temperature
- Depends on:
 - the specific reaction
 - the amounts of substances
 - the temperature

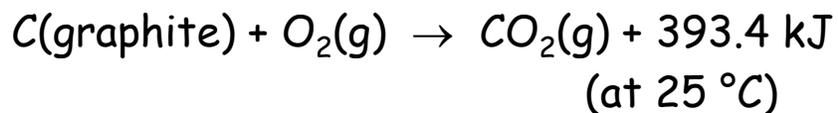
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Endothermic and exothermic processes

- **Exothermic reaction**
 - Liberates heat
 - ΔH -ve
- **Endothermic reaction**
 - Requires heat
 - ΔH +ve



Example



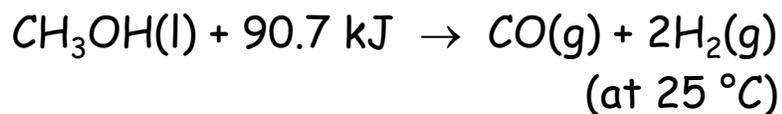
Heat is a product.

$$\Delta H (298 \text{ K}) = -393.4 \text{ kJ}$$

N.B. Physical state of the reactants and products is given.

21

Example



Heat is a reactant.

$$\Delta H (298 \text{ K}) = +90.7 \text{ kJ}$$

N.B. Physical state of the reactants and products is given.

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Standard State

- Standard state is the **reference state** for the material's thermodynamic state properties.
- Required for **comparison** purposes.
- Standard state of any substance – the physical state at which it is most stable at **1 bar**.
- The **usual** specified temperature for the standard state is 298 K.
- For substances that are solids at this temperature and pressure, and can also have **different crystalline forms**, it is necessary to specify for which form the heat of reaction is given.

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Enthalpies of Reaction

- When a reaction occurs at **constant pressure**, the heat of reaction is equal to the **enthalpy change**.
- The *change* in enthalpy, ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

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Enthalpy

- **standard enthalpy of reaction ($\Delta H^\circ_{\text{rxn}}$):** the enthalpy change for the transformation of reactants in their standard states to products **in their standard states**.
- There are many types of **heats of reaction**, e.g.
 - heat of formation
 - heat of combustion
 - heat of hydrogenation

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Heat of Formation

The **standard heat of formation** of a compound (ΔH°_f) is the heat change when one mole of the compound in its standard state is formed from its elements in their standard states at a specified temperature.

- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
 $\Delta H_f^\circ(298 \text{ K}) = -285.83 \text{ kJ}$
- The **standard enthalpy of formation** of an **element** in its standard state is taken to be **zero**.

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Heat of Combustion

The heat of combustion is the heat released in the reaction of **one mole** of a substance **in its standard state** with **oxygen**.

- The equation for the combustion of a compound must show the reaction of **one mole** of the **compound** with sufficient **oxygen** to convert all of the carbon and hydrogen present to **gaseous CO₂** and **liquid H₂O**.
- $C_6H_6(l) + 7\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l) \quad \Delta H_c^\circ = -3274 \text{ kJ}$
- $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H_c^\circ = -890.2 \text{ kJ}$

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Hess's Law

The enthalpy change of a chemical reaction is the same whether the reaction takes place in one step or several steps.

- i.e. the **heat change** in a reaction A to C is the **same** whether the reaction takes place in **one stage** as



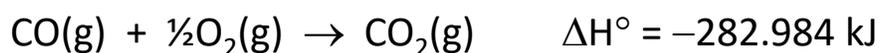
or in **two stages** as



(Consequence of law of conservation of energy.)

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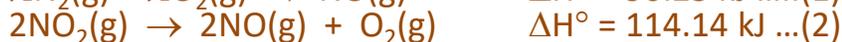
Example



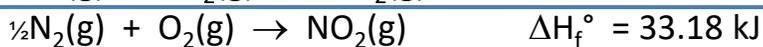
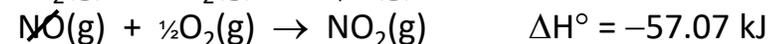
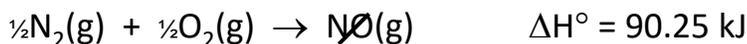
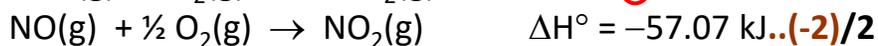
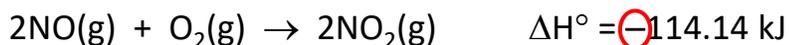
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Application of Hess's Law

Find ΔH_f° of $\text{NO}_2(\text{g})$ given that



Desired equation:



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Hess's Law

- ΔH for a reaction in one direction is equal in magnitude to ΔH for the reaction in the reverse direction, but is opposite in sign.
- For a given reaction, ΔH is directly proportional to the quantities of reactants or products.

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Calculation of ΔH

When the standard heats of formation are known for all of the reactants and products in a given reaction we can use Hess's law in this way:

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

where n and m are the stoichiometric coefficients.

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Example

The heat of combustion of ethane gas, $C_2H_6(g)$, is $-1560.1 \text{ kJ mol}^{-1}$. If ΔH_f° for $CO_2(g)$ and $H_2O(l)$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively, calculate the heat of formation of ethane.

combustion equation: $C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$$\begin{aligned}\Delta H_{rxn}^\circ &= \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) \\ &= [(2 \text{ mol})\Delta H_f^\circ(CO_2) + (3 \text{ mol})\Delta H_f^\circ(H_2O)] - \\ &\quad [(1 \text{ mol})\Delta H_f^\circ(C_2H_6) + (3\frac{1}{2} \text{ mol})\Delta H_f^\circ(O_2)]\end{aligned}$$

$$-1560.1 \text{ kJ} = (2 \times -393.5) + (3 \times -285.8) - \Delta H_f^\circ(C_2H_6) - 0 \text{ kJ}$$

$$\therefore \Delta H_f^\circ(C_2H_6) = -84.3 \text{ kJ mol}^{-1}$$

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Standard Enthalpies of Formation

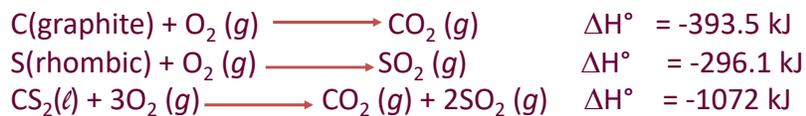
Standard enthalpies of formation, ΔH_f° , are measured under standard conditions (25°C and 1.00 bar pressure).

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-130.9
Ethanol	$C_2H_5OH(l)$	-277.7	Sodium chloride	$NaCl(s)$	-410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	-2221
Glucose	$C_6H_{12}O_6(s)$	-1273	Water	$H_2O(l)$	-285.8
Hydrogen bromide	$HBr(g)$	-36.23	Water vapor	$H_2O(g)$	-241.8

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Example

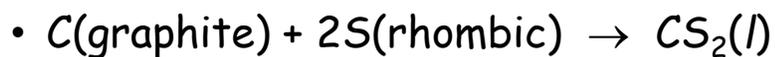
Calculate the standard enthalpy of formation of $CS_2(l)$ given that:



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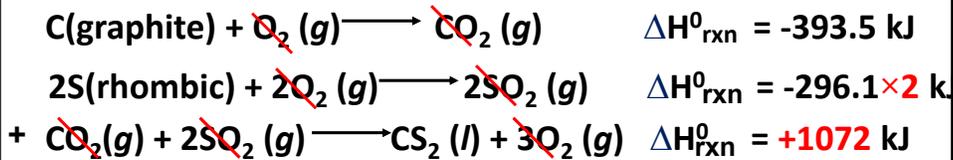
Example

1. Write the enthalpy of formation reaction for CS_2 :



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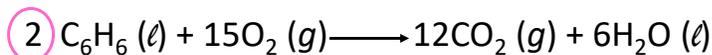
2. Add the given reactions so that the result is the desired reaction. (N.B. molar ratios!)



$$\Delta H_{\text{rxn}}^{\circ} = -393.5 + (2 \times -296.1) + 1072 = 86.3 \text{ kJ}$$

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 Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene burnt? The standard enthalpy of formation of benzene is $49.04 \text{ kJ mol}^{-1}$.



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

$$\Delta H_{\text{rxn}}^{\circ} = [12\Delta H_{\text{f}}^{\circ}(\text{CO}_2) + 6\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})] - [2\Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_6)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [12 \times -393.5 + 6 \times -285.8] - [2 \times 49.04] = -6535 \text{ kJ}$$

$$\frac{-6535 \text{ kJ}}{2 \text{ mol}} = -3267 \text{ kJ mol}^{-1} \text{ C}_6\text{H}_6$$

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Bond Energies

- bond breaking - endothermic
- bond formation - exothermic
- Bond energies indicate the amount of **energy required to break a particular bond** and are therefore **positive**.

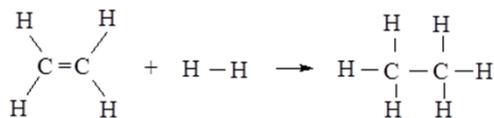
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Bond Energies

$$\Delta H^\circ = (\text{sum of heats of breaking all bonds in reactants}) + (\text{sum of heats of forming all bonds in products})$$
$$\Delta H^\circ = [\text{sum of bond energies of all bonds in reactants (bonds broken)}] - [\text{sum of bond energies of all bonds in products (bonds formed)}]$$

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Example - hydrogenation reaction



$$\begin{aligned}
 \text{Bond energies of reactants} &= E_{\text{C}=\text{C}} + 4E_{\text{C}-\text{H}} + E_{\text{H}-\text{H}} \\
 &= 606.1 + 4(409.64) + 430.5 \text{ kJ} \\
 &= 2675.16 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{Bond energies of products} &= E_{\text{C}-\text{C}} + 6E_{\text{C}-\text{H}} \\
 &= 334.4 + 6(409.64) \text{ kJ} \\
 &= 2792.24 \text{ kJ}
 \end{aligned}$$

$$\Delta H^\circ = 2675.16 - 2792.24 \text{ kJ} = -117.08 \text{ kJ mol}^{-1}$$

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