Enthalpy

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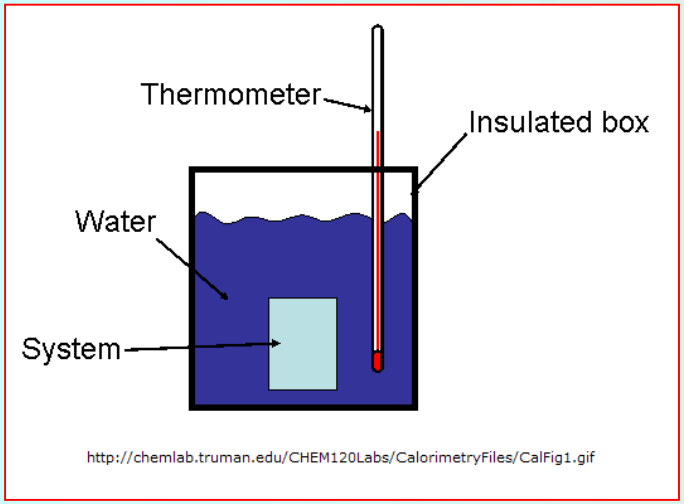

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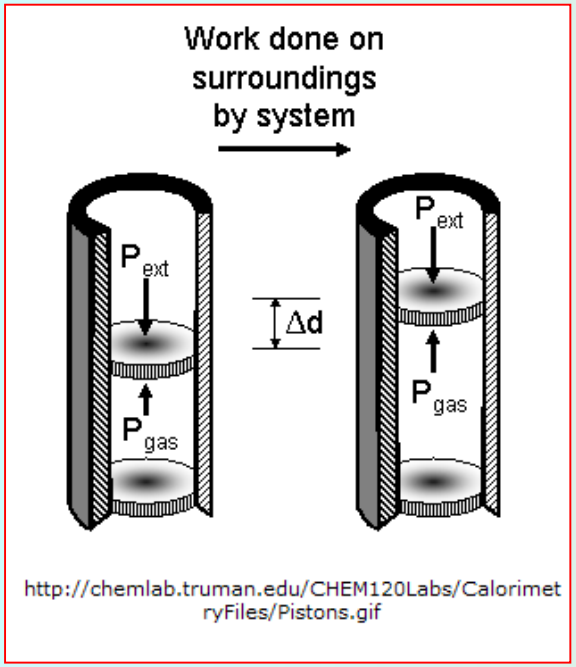

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Definition

Most physical and chemical changes occur at virtually constant atmospheric pressure.

We define a thermodynamic variable called enthalpy as the expression

$$H = E + P * V$$

where

H ... enthalpy of the system
E ... internal energy of the system
P ... external pressure on the system
V ... volume of the system

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The Meaning of Enthalpy

To determine the change in the internal energy of a system (ΔE) we must measure both heat and work:

$$\Delta E = Q + W$$

WORK DONE BY AN EXPANDING GAS

When the volume (V) of a system increases by an amount ΔV against an external pressure (P), the system does **PV work** on the surroundings:

$$W = -P * \Delta V = -P * (V_{final} - V_{intial})$$

The enthalpy of a system is defined as the internal energy plus the product of the pressure and the volume.

$$H = E + P * V$$

The change in enthalpy (ΔH) is the heat gained or lost by the system at constant pressure (Q_p):

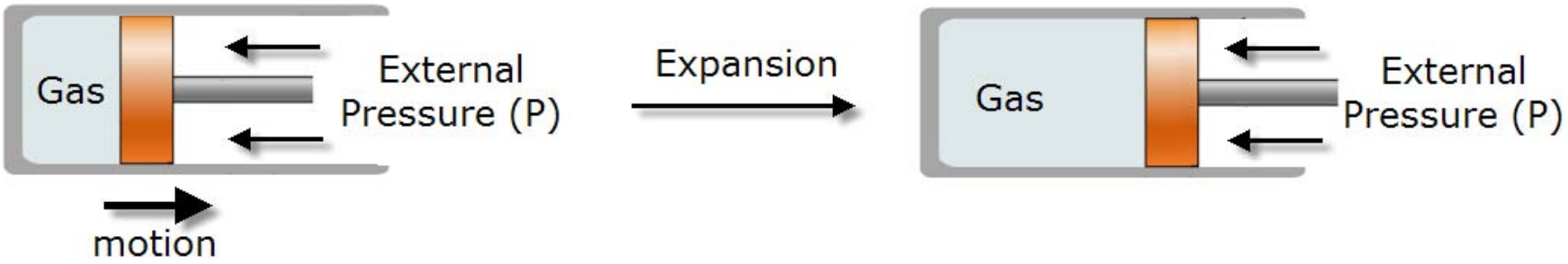
When P = constant:

$$Q_p = \Delta E - W = \Delta E - (-P * \Delta V)$$

$$Q_p = (E_{final} - E_{initial}) + P * (V_{final} - V_{initial})$$

$$Q_p = (E_{final} + P * V_{final}) - (E_{initial} + P * V_{initial})$$

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



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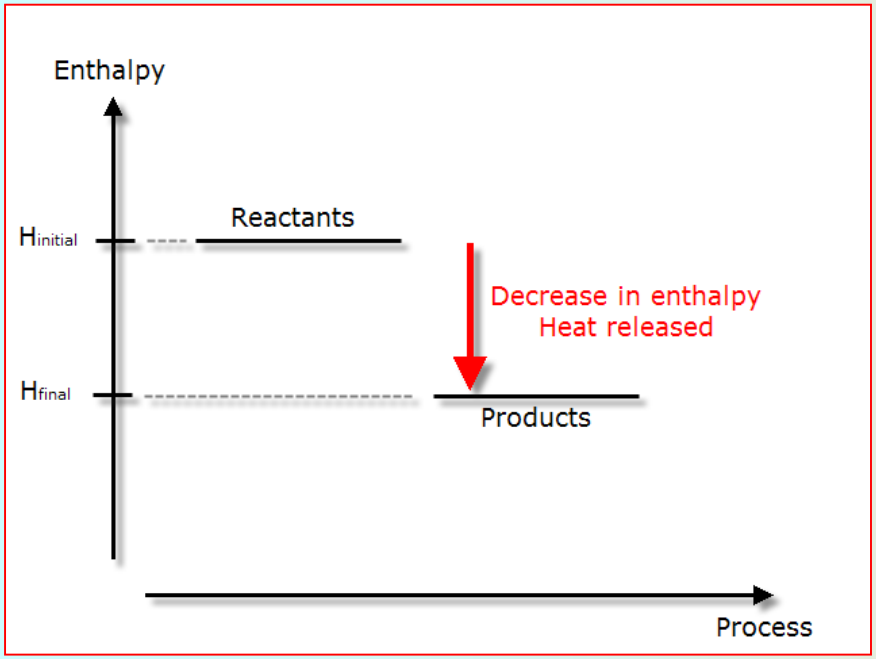

Exothermic and Endothermic Processes

The enthalpy change of a reaction (also called heat of reaction, ΔH_{rxn}) is:

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

The sign of ΔH indicates whether heat is absorbed or released in the change.

EXOTHERMIC PROCESSES

An exothermic process releases heat and results in a decrease in the enthalpy of the system.

Exothermic:

$\Delta H = H_{products} - H_{reactants} < 0$

$H_{products} < H_{reactants}$

Heat released

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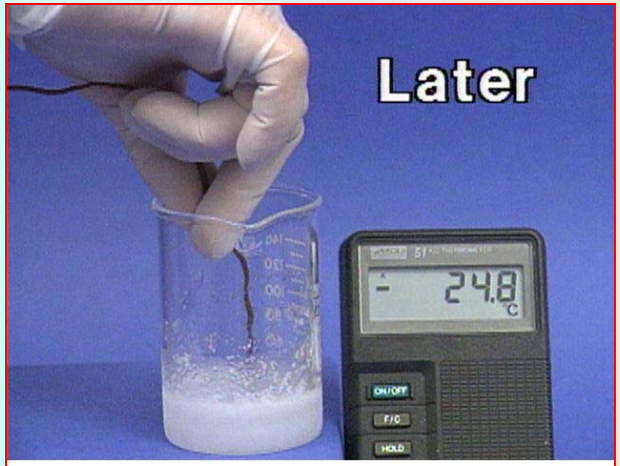


http://jchemed.chem.wisc.edu/jcesoft/cca/CCA3/STILLS/ENDO2/ENDO2/64JPG48/16.JPG

Exothermic and Endothermic Processes

ENDOTHERMIC PROCESSES

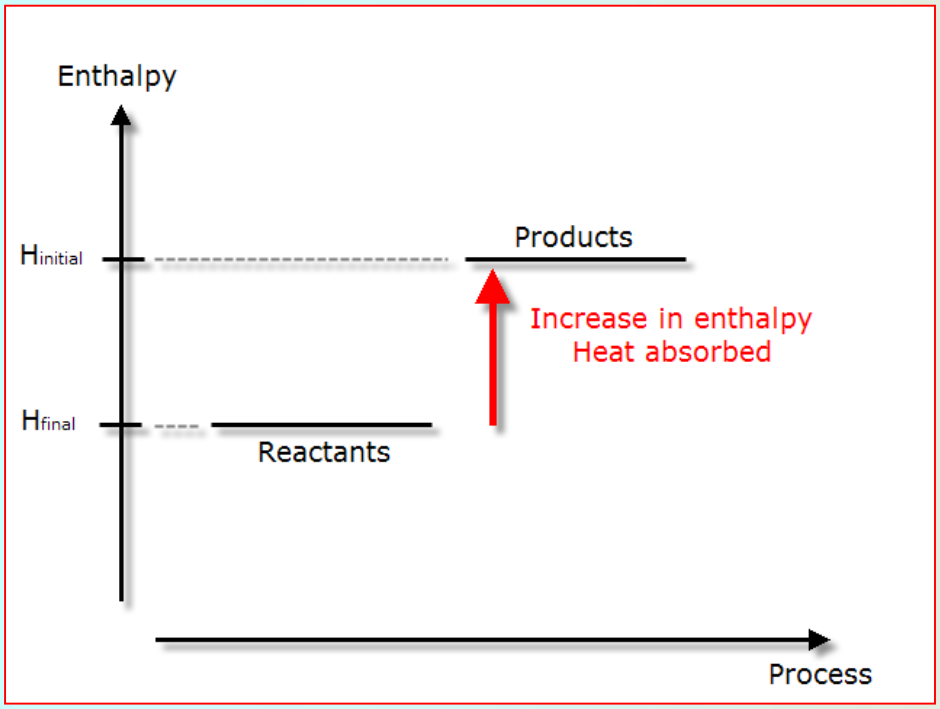
An endothermic process absorbs heat and results in a increase in the enthalpy of the system.

Endothermic

$\Delta H = H_{products} - H_{reactants} > 0$

$H_{products} > H_{reactants}$

Heat absorbed



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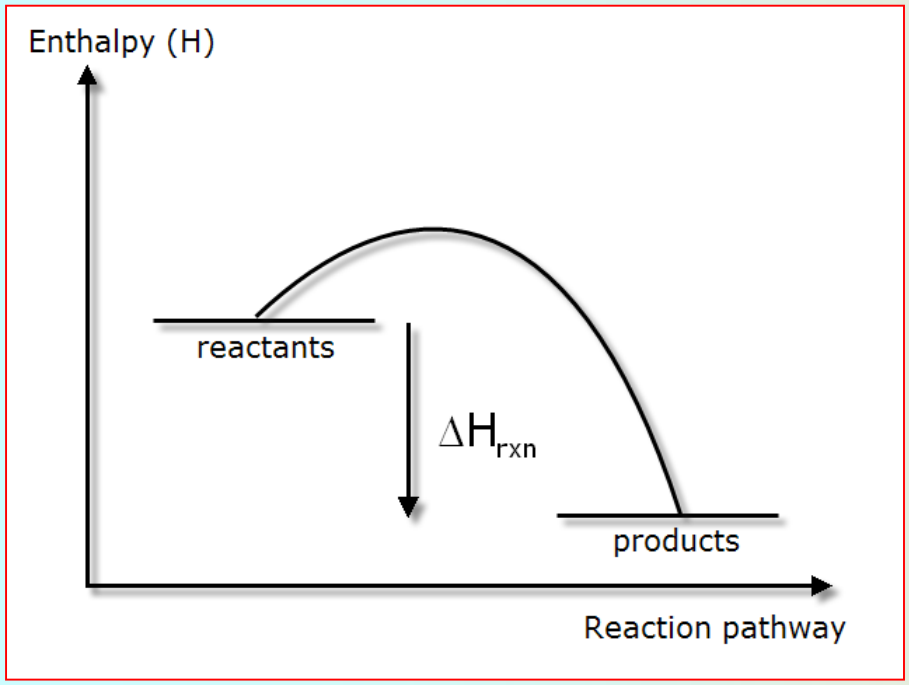

Enthalpies of Reaction

Because the enthalpy change can be expressed as

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

the enthalpy change for a chemical reaction is given by the enthalpy of the products (final state) minus that of the reactants (initial state):

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

The enthalpy change that accompanies a reaction is called the enthalpy of reaction or merely the heat of reaction (ΔH_{rxn}).

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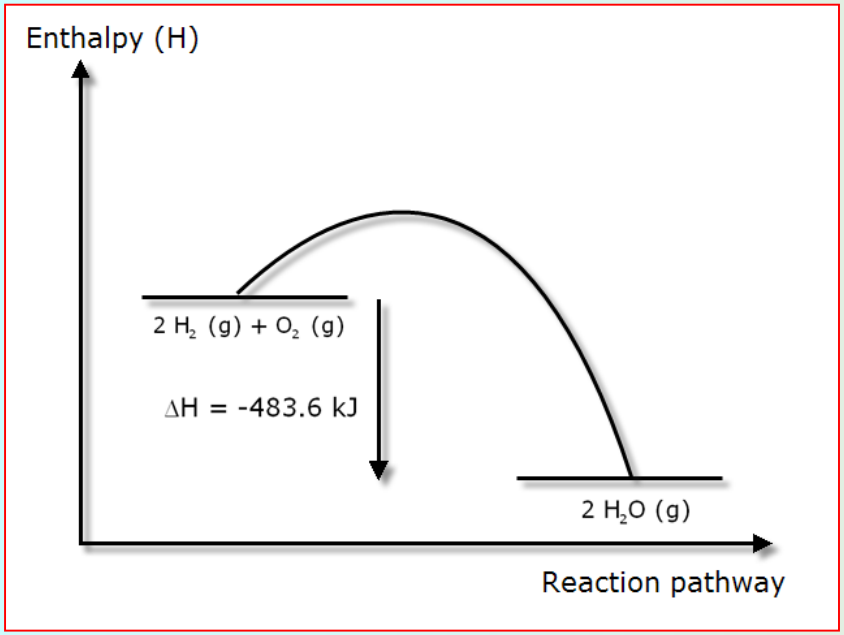
Thermochemical equation

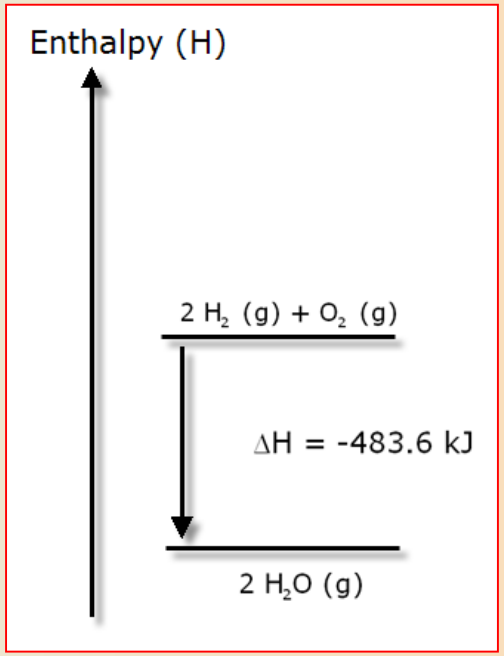
Balanced chemical equations that show associated enthalpy changes are called **thermochemical equations**.

In the case of the synthesis of water, the corresponding thermochemical equation is:

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \qquad \Delta H = -483.6\ kJ$$

The enthalpy change can be represented in an enthalpy diagram





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Properties of enthalpies of reaction

1. **Enthalpy is an extensive property. It means that its magnitude is directly proportional to the amount of reactant consumed.**

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g) \qquad \Delta H = -890\ kJ$$

When 1 mol of methane is burned, the enthalpy change is –890 kJ
When 2 mol of methane are urned, the enthalpy change is –1780 kJ

2. **The enthalpy change for a reaction is equal in magnitude but opposite in sign to the enthalpy change for the reverse equation**

From the previous thermochemical equation we get:

$$CO_2\ (g) + 2\ H_2O\ (g) \rightarrow CH_4\ (g) + 2\ O_2\ (g) \qquad \Delta H = +890\ kJ$$

3. **The enthalpy change for a reaction depends on the state of the reactants and the products**

In the case of water we have that:

$$2\ H_2O\ (l) \rightarrow 2\ H_2O\ (g) \qquad \Delta H = +88\ kJ$$