

THERMOCHEMISTRY

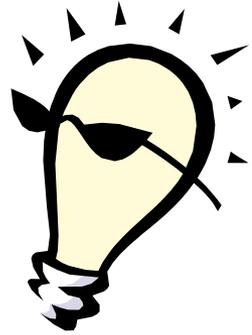
Chapter

7

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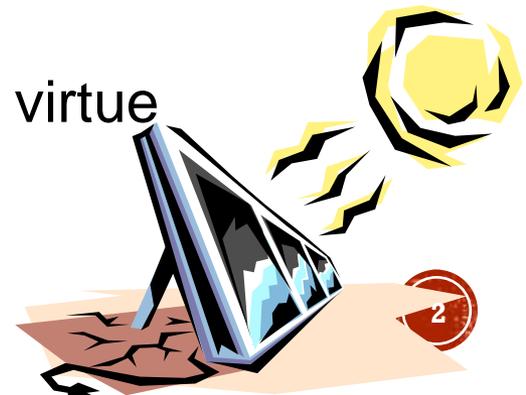
FACULTY OF MECHANICAL ENGINEERING

The Nature & Types of Energy



Energy is the capacity to do work

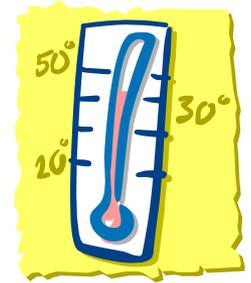
- **Thermal energy** is the energy associated with the random motion of atoms and molecules
- **Chemical energy** is the energy stored within the bonds of chemical substances
- **Nuclear energy** is the energy stored within the collection of neutrons and protons in the atom
- **Electrical energy** is the energy associated with the flow of electrons
- **Potential energy** is the energy available by virtue of an object's position



Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature is a measure of the **thermal energy**.



Temperature \neq Thermal Energy



90°C



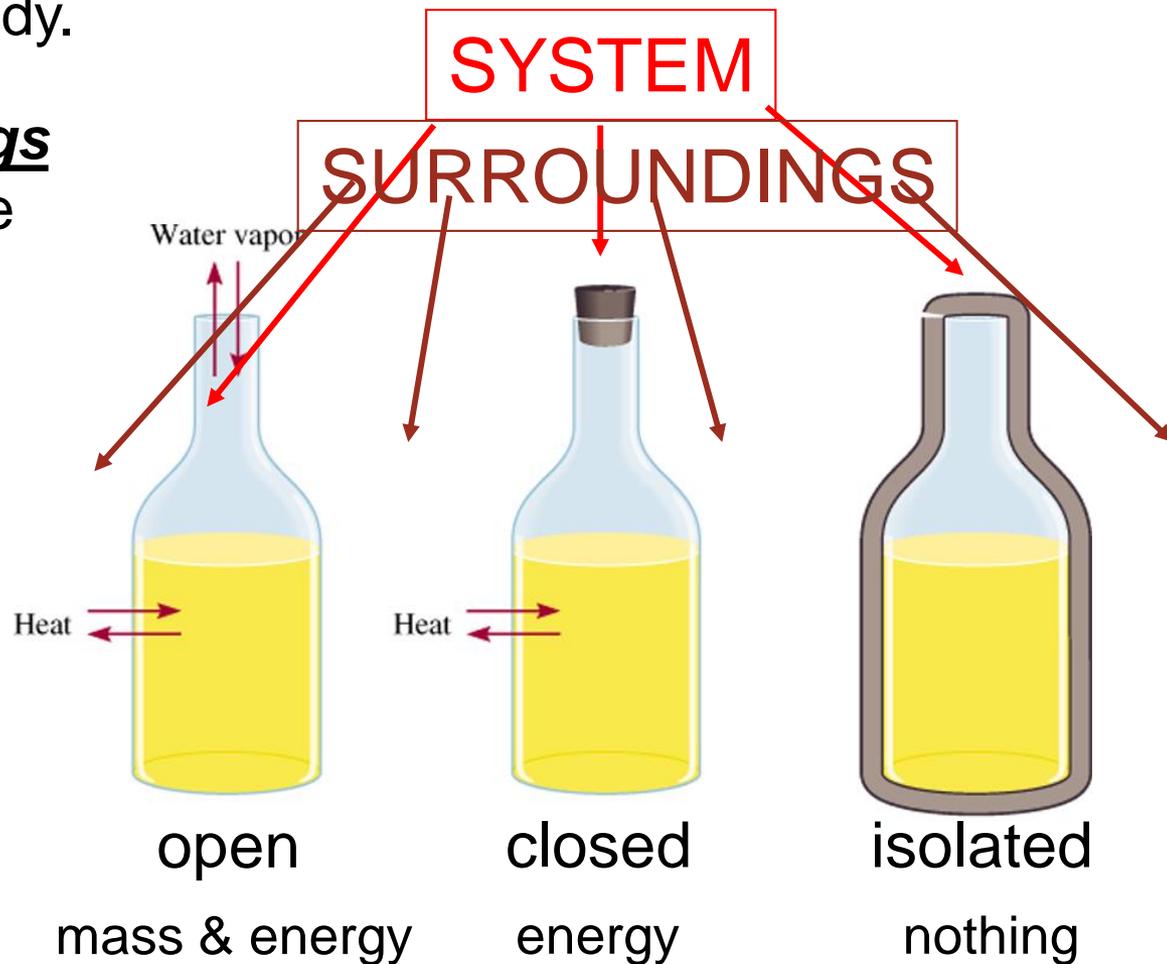
40°C

greater thermal energy

Thermochemistry is the study of heat change in chemical reactions.

The **system** is the specific part of the universe that is of interest in the study.

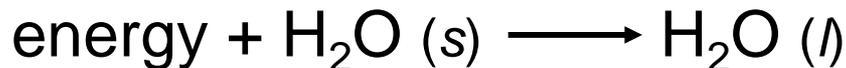
The **surroundings** are the rest of the universe outside the system.



Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.



Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

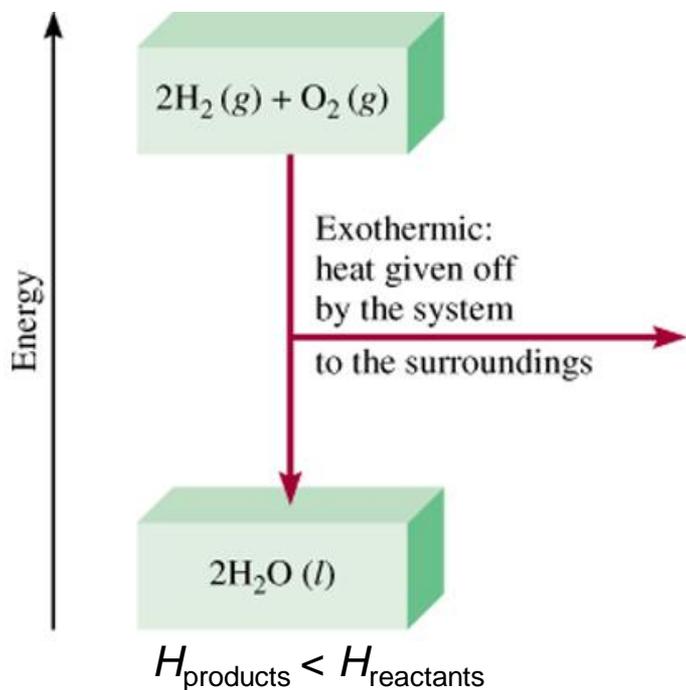


Enthalpy

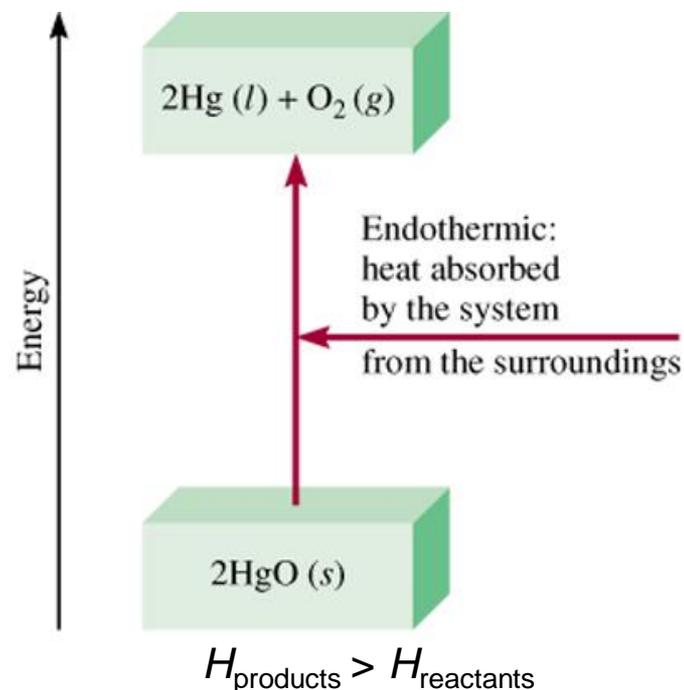
Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**

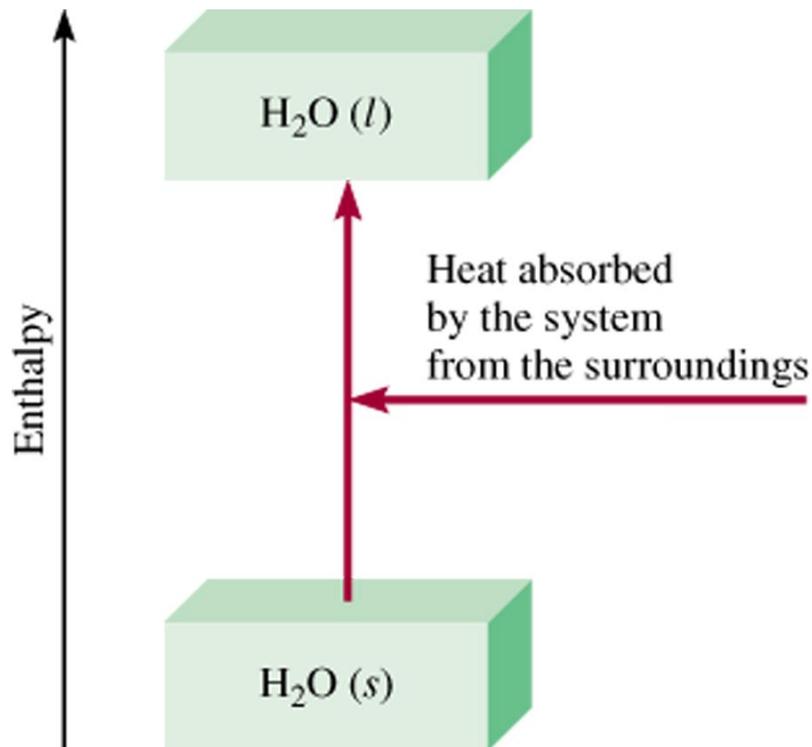


$$\Delta H < 0$$



$$\Delta H > 0$$

Thermochemical Equations



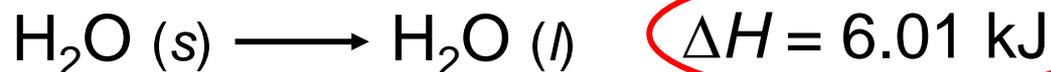
Is ΔH negative or positive?

System absorbs heat

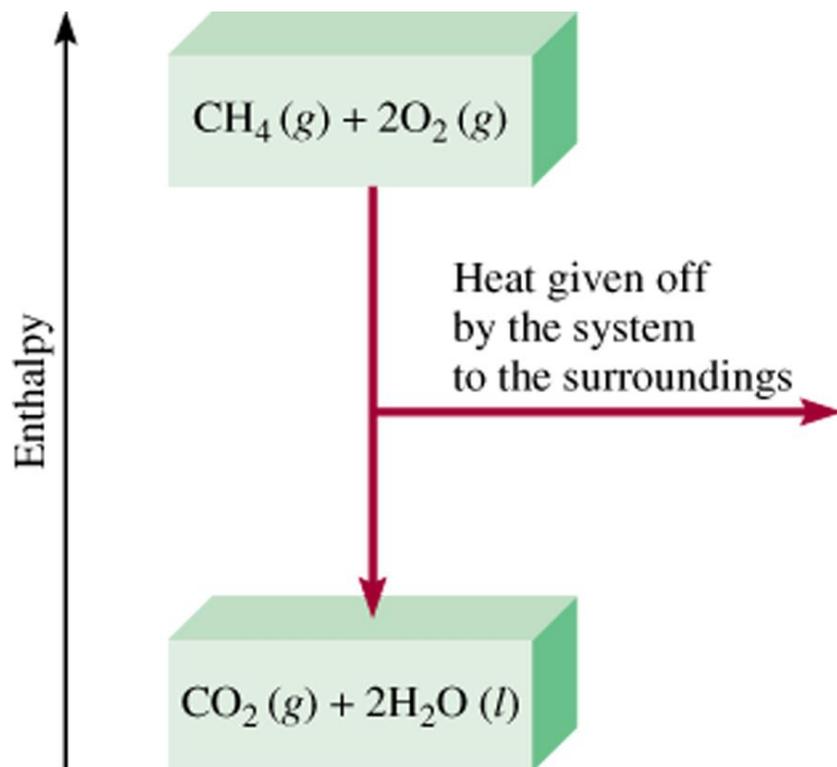
Endothermic

$$\Delta H > 0$$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0°C and 1 atm.



Thermochemical Equations



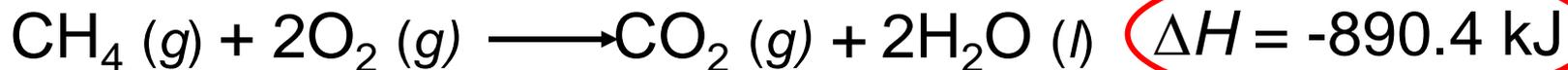
Is ΔH negative or positive?

System gives off heat

Exothermic

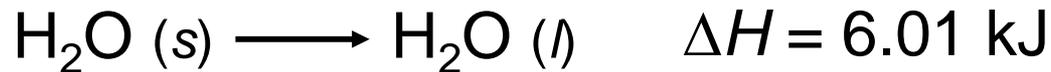
$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25⁰C and 1 atm.



Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance



- If you reverse a reaction, the sign of ΔH changes



- If you multiply both sides of the equation by a factor n , then ΔH must change by the same factor n .



Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.



How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

Calorimetry

The **specific heat** (s) of a substance is the amount of heat (q) required to raise the temperature of **one gram** of the substance by **one degree Celsius**.

The **heat capacity** (C) of a substance is the amount of heat (q) required to raise the temperature of **a given quantity** (m) of the substance by **one degree Celsius**.

$$C = ms$$

Heat (q) absorbed or released:

$$q = ms\Delta t$$

$$q = C\Delta t$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

Table 6.1 The Specific Heats of Some Common Substances

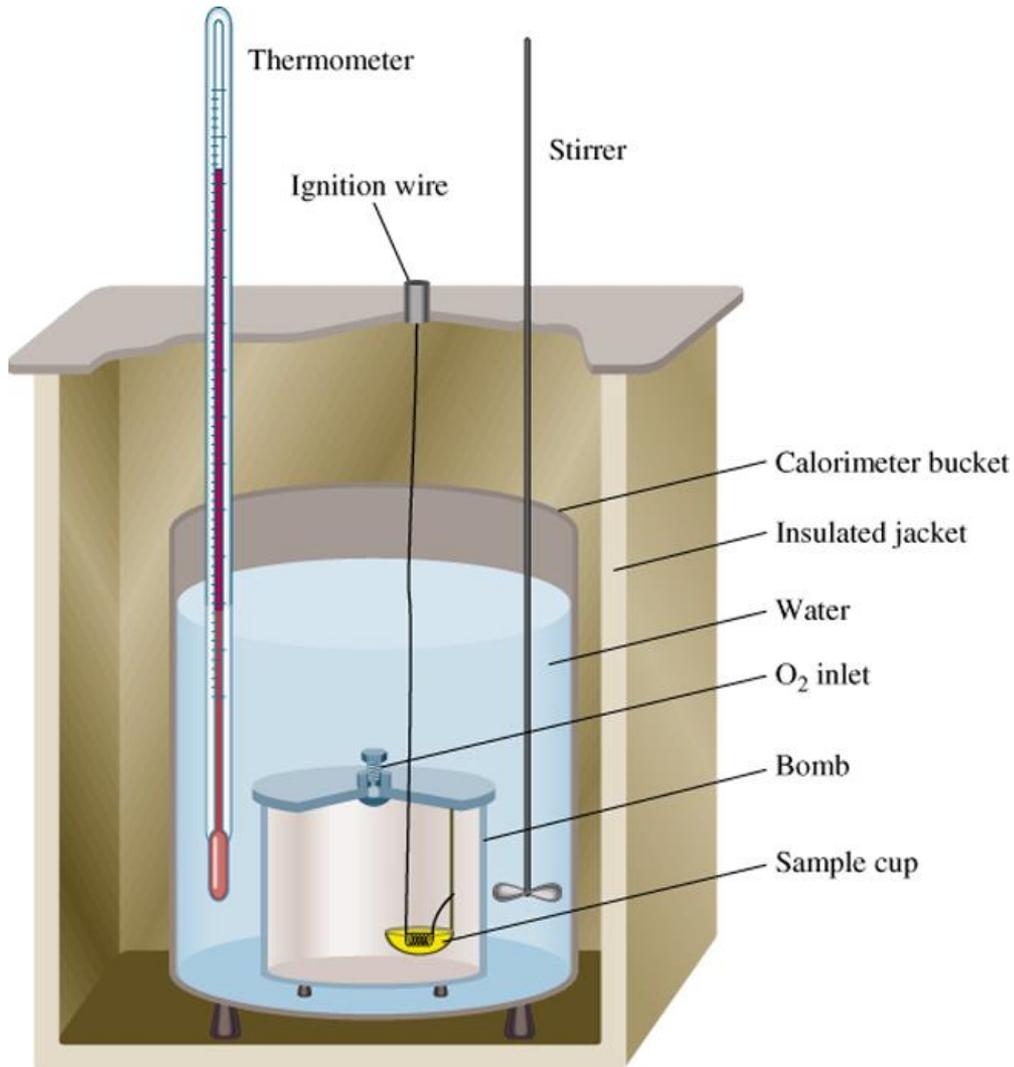
Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
C ₂ H ₅ OH (ethanol)	2.46



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



Constant-Volume Calorimetry



$$q_{\text{sys}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{bomb}})$$

$$q_{\text{water}} = ms\Delta t$$

$$q_{\text{bomb}} = C_{\text{bomb}}\Delta t$$

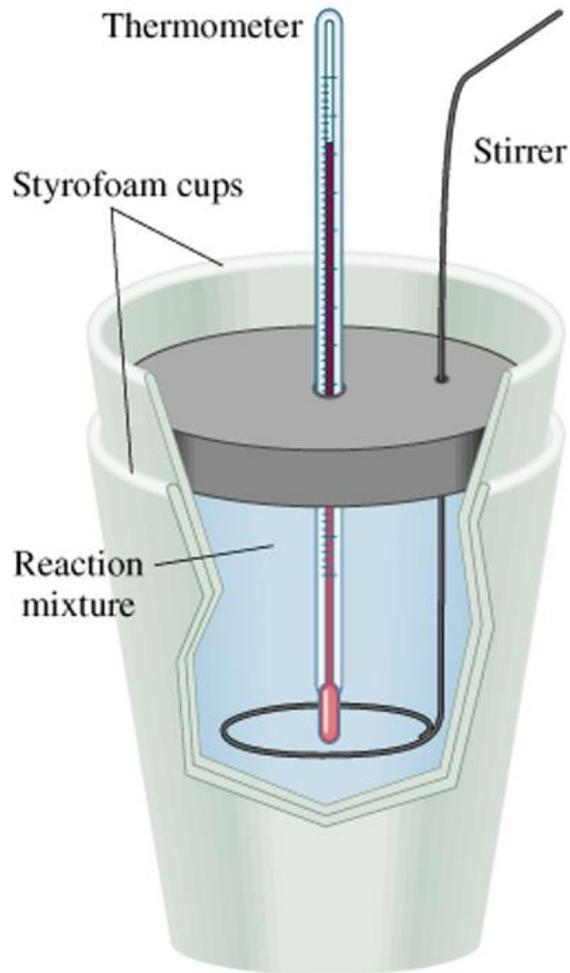
Reaction at Constant V

$$\Delta H \neq q_{\text{rxn}}$$

$$\Delta H \sim q_{\text{rxn}}$$

No heat enters or leaves!

Constant-Pressure Calorimetry



$$q_{\text{sys}} = q_{\text{water}} + q_{\text{cal}} + q_{\text{rxn}}$$

$$q_{\text{sys}} = 0$$

$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{cal}})$$

$$q_{\text{water}} = ms\Delta t$$

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$

Reaction at Constant P

$$\Delta H = q_{\text{rxn}}$$

No heat enters or leaves!

Standard Enthalpy of Formation & Reaction

Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.

$$\Delta H_f^0 (\text{O}_2) = 0$$

$$\Delta H_f^0 (\text{C, graphite}) = 0$$

$$\Delta H_f^0 (\text{O}_3) = 142 \text{ kJ/mol}$$

$$\Delta H_f^0 (\text{C, diamond}) = 1.90 \text{ kJ/mol}$$

Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.04	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.94
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-268.61	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-347.98
H ₂ O(l)	-285.8		

[Back to Q & A](#)

The **standard enthalpy of reaction** (ΔH_{rxn}^0) is the enthalpy of a reaction carried out at 1 atm.



$$\Delta H_{\text{rxn}}^0 = [c\Delta H_{\text{f}}^0(\text{C}) + d\Delta H_{\text{f}}^0(\text{D})] - [a\Delta H_{\text{f}}^0(\text{A}) + b\Delta H_{\text{f}}^0(\text{B})]$$

$$\Delta H_{\text{rxn}}^0 = \sum n\Delta H_{\text{f}}^0(\text{products}) - \sum m\Delta H_{\text{f}}^0(\text{reactants})$$



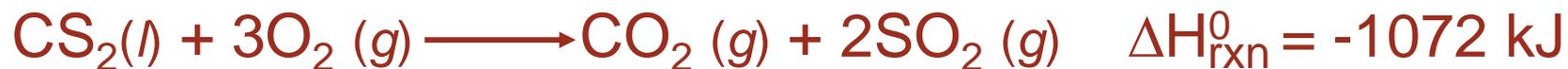
Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released **per mole** of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

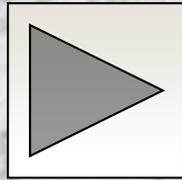
(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)



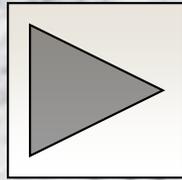
Calculate the standard enthalpy of formation of $\text{CS}_2(l)$ given that:



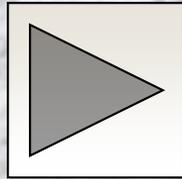
Q & A session



Question **1**



Question **2**



Question **3**

Calculate the quantity of heat required to raise the temperature of 2.10 gram of water from 2.0 °C to 6.0 °C.

Calculate the specific heat if a 36.9 gram sample of a metal at 57.2 °C is immersed in 50.1 gram of water at 16.0 °C, warming the water to 20.5 °C.

Calculate the enthalpy change for the reaction of one mole of CH₄ with oxygen gas to yield carbon dioxide and water.

$$\Delta H_f^\circ \text{CH}_4(\text{g}) = -74.5 \text{ kJ}$$

Table 6.3

Calculate the enthalpy of the following reaction based on the enthalpies of combustion in equation given:

