Energy Relationships in Chemical Reactions

Chapter 6

Energy is the capacity to do work.

- ***Radiant energy*** comes from the sun and is earth's primary energy source

- ***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

- ***Potential energy*** is the energy available by virtue of an object's position

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Energy Changes in Chemical Reactions

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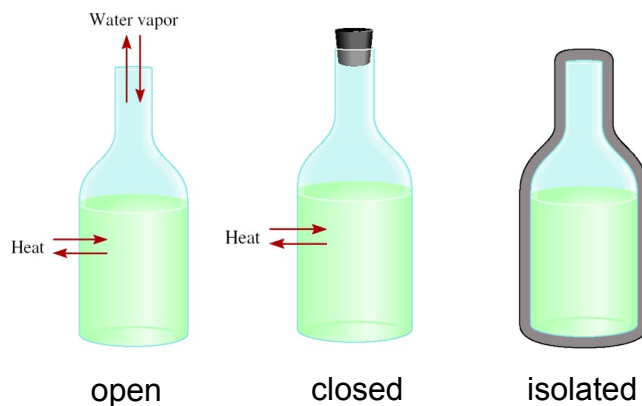
Temperature is a measure of the **thermal energy**.

Temperature ✗ Thermal Energy

100°C

37°C
25°C

0°C

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Thermochemistry is the study of heat change in chemical reactions.

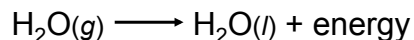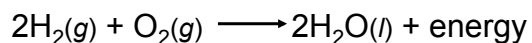The *system* is the specific part of the universe that is of interest in the study.

Water vapor

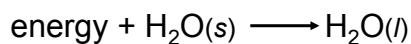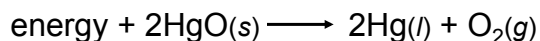Heat

Heat

open | closed | isolated

Exchange: mass & energy | energy | nothing 4

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

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) + energy$$

$$H_2O(g) \longrightarrow H_2O(l) + energy$$

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

$$energy + 2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

$$energy + H_2O(s) \longrightarrow H_2O(l)$$

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Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature

$$\Delta U = U_{final} - U_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

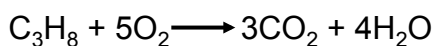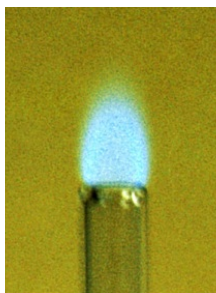Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

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First law of thermodynamics – energy can be converted from one form to another, but cannot be created or destroyed.

$$\Delta U_{system} + \Delta U_{surroundings} = 0$$

or

$$\Delta U_{system} = -\Delta U_{surroundings}$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Exothermic chemical reaction!

Chemical energy **lost** by combustion = Energy **gained** by the surroundings
          system   surroundings

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Another form of the *first law* for ΔU_{system}

$\Delta U = q + w$

ΔU is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

TABLE 6.1	Sign Conventions for Work and Heat	
Process		**Sign**
Work done by the system on the surroundings		−
Work done on the system by the surroundings		+
Heat absorbed by the system from the surroundings (endothermic process)		+
Heat absorbed by the surroundings from the system (exothermic process)		−

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Work Done On the System

$w = F \times d$

$w = -P \, \Delta V$

$P \times V = \dfrac{F}{d^2} \times d^3 = F \times d = w$

$\Delta V > 0$

$-P\Delta V < 0$

$w_{sys} < 0$

Work is not a state function.

$\Delta w \neq w_{final} - w_{initial}$

P

P

ΔV

initial   final

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A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P\Delta V$$

(a) ΔV = 5.4 L – 1.6 L = 3.8 L P = 0 atm

W = -0 atm x 3.8 L = 0 L•atm = 0 joules

(b) ΔV = 5.4 L – 1.6 L = 3.8 L P = 3.7 atm

w = -3.7 atm x 3.8 L = -14.1 L•atm

w = -14.1 L•atm x $\dfrac{101.3 \text{ J}}{1\text{L•atm}}$ = -1430 J

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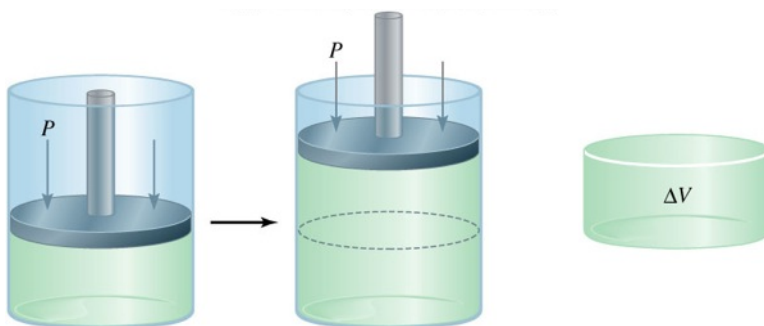## Enthalpy and the First Law of Thermodynamics

$$\Delta U = q + w$$

At constant pressure:

$$q = \Delta H \text{ and } w = -P\Delta V$$

$$\Delta E = \Delta H - P\Delta V$$

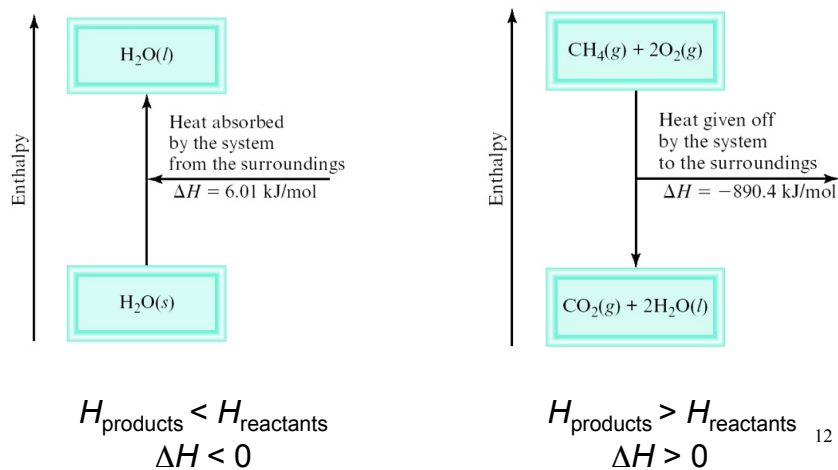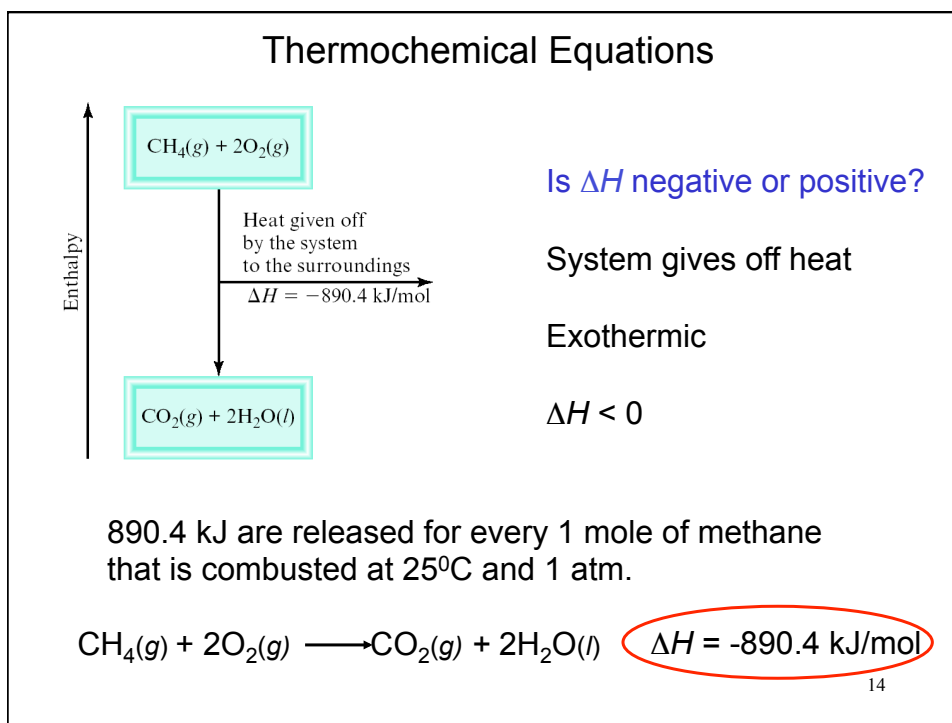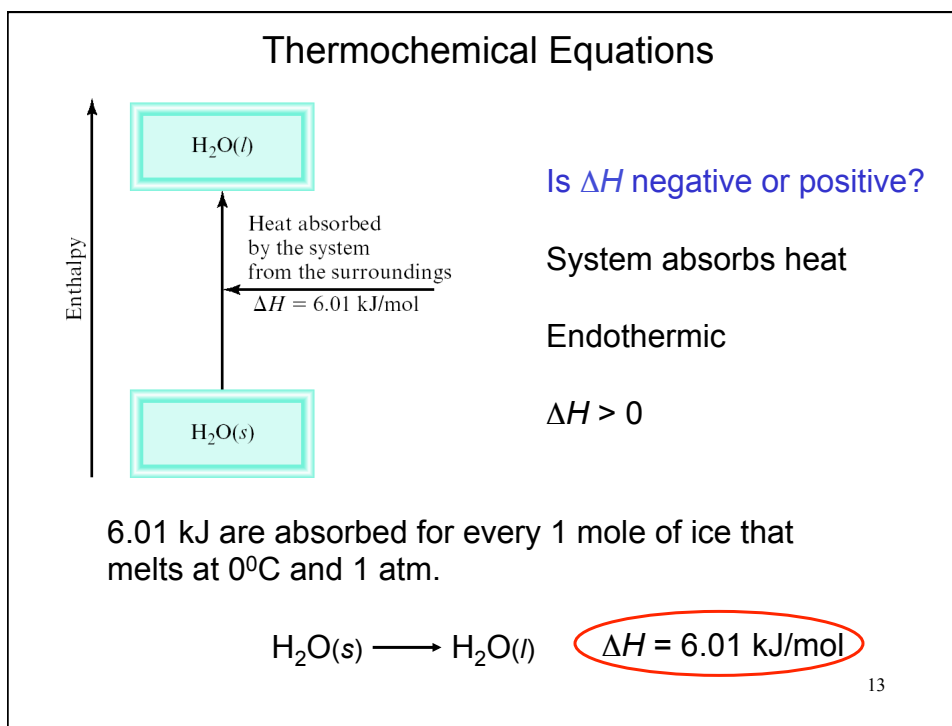$$\Delta H = \Delta U + P\Delta V$$

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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**

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

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

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Thermochemical Equations

Enthalpy →

$H_2O(l)$

Heat absorbed
by the system
from the surroundings
$\Delta H = 6.01$ kJ/mol

$H_2O(s)$

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.

$H_2O(s) \longrightarrow H_2O(l)$ $\Delta H = 6.01$ kJ/mol

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Thermochemical Equations

Enthalpy →

$CH_4(g) + 2O_2(g)$

Heat given off
by the system
to the surroundings
$\Delta H = -890.4$ kJ/mol

$CO_2(g) + 2H_2O(l)$

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 25°C and 1 atm.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.4$ kJ/mol

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Thermochemical Equations

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

$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H = 6.01 \text{ kJ/mol}$$

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

$$H_2O(l) \longrightarrow H_2O(s) \quad \Delta H = -6.01 \text{ kJ/mol}$$

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

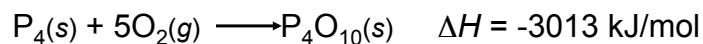$$2H_2O(s) \longrightarrow 2H_2O(l) \quad \Delta H = 2 \times 6.01 = 12.0 \text{ kJ}$$
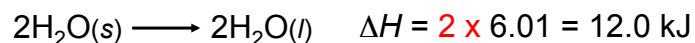
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Thermochemical Equations

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

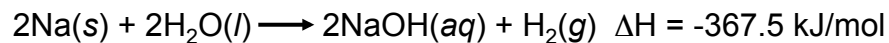$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H = 6.01 \text{ kJ/mol}$$

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = 44.0 \text{ kJ/mol}$$

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

$$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) \quad \Delta H = -3013 \text{ kJ/mol}$$

$$266 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.9 \text{ g } P_4} \times \frac{3013 \text{ kJ}}{1 \text{ mol } P_4} = 6470 \text{ kJ}$$
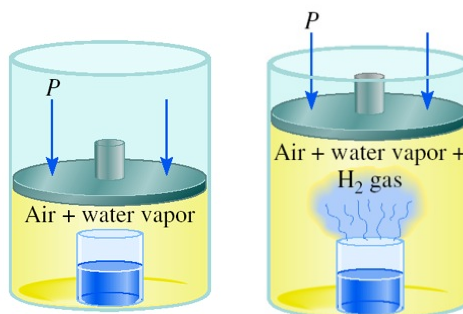
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A Comparison of ΔH and ΔU

$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$ $\Delta H = -367.5$ kJ/mol

$\Delta U = \Delta H - P\Delta V$ At 25 $^\circ$C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V$ = 1 atm x 24.5 L = 2.5 kJ

ΔU = -367.5 kJ/mol – 2.5 kJ/mol = -370.0 kJ/mol

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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.

TABLE 6.2	
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_2O	4.184
C_2H_5OH (ethanol)	2.46

$C = m \times s$

Heat (*q*) absorbed or released:

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

$q = C \times \Delta t$

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

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

s of Fe = 0.444 J/g · °C

$\Delta t = t_{final} - t_{initial}$ = 5°C – 94°C = -89°C

$q = ms\Delta t$ = 869 g x 0.444 J/g · °C x –89°C = -34,000 J

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Constant-Volume Calorimetry

Thermometer

Stirrer

Ignition wire

Calorimeter bucket

Insulated jacket

Water

O_2 inlet

Bomb

Sample cup
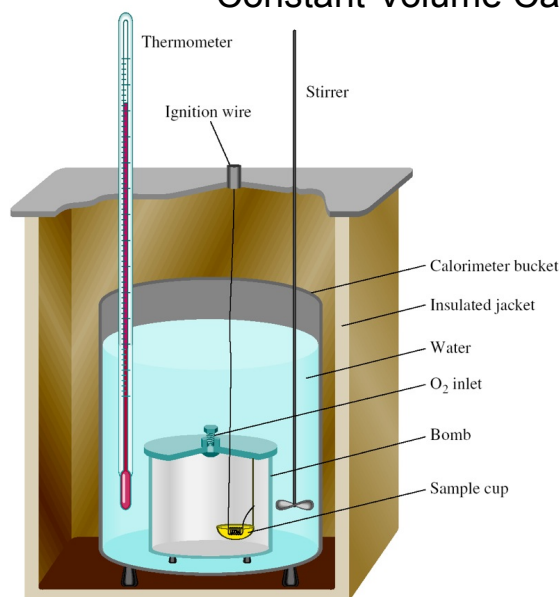
$q_{sys} = q_{water} + q_{bomb} + q_{rxn}$

$q_{sys} = 0$

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

$q_{water} = m$ x s x Δt

$q_{bomb} = C_{bomb}$ x Δt

Reaction at Constant V

$\Delta H \neq q_{rxn}$

$\Delta H \sim q_{rxn}$

No heat enters or leaves!

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Constant-Pressure Calorimetry

Thermometer

Stirrer

Styrofoam cups

Reaction mixture
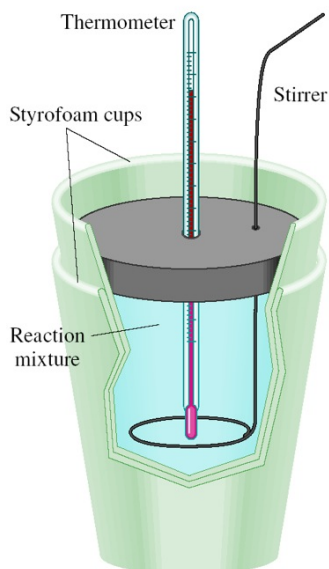
$q_{sys} = q_{water} + q_{cal} + q_{rxn}$

$q_{sys} = 0$

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

$q_{water} = m \times s \times \Delta t$

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

Reaction at Constant P
$\Delta H = q_{rxn}$

No heat enters or leaves!

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TABLE 6.3	Heats of Some Typical Reactions Measured at Constant Pressure	
Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	-56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	$44.0*$
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	-180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

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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°) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f°) 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.

ΔH_f°(O$_2$) = 0

ΔH_f°(O$_3$) = 142 kJ/mol

ΔH_f°(C, graphite) = 0

ΔH_f°(C, diamond) = 1.90 kJ/mol

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TABLE 6.4	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)	−127.0	Hg(l)	0
Al(s)	0	I$_2$(s)	0
Al$_2$O$_3$(s)	−1669.8	HI(g)	25.9
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(g)	81.56
CaCO$_3$(s)	−1206.9	N$_2$O$_4$(g)	9.66
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)	−271.6	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	Zn(s)	0
H$_2$O(l)	−285.8	ZnO(s)	−348.0

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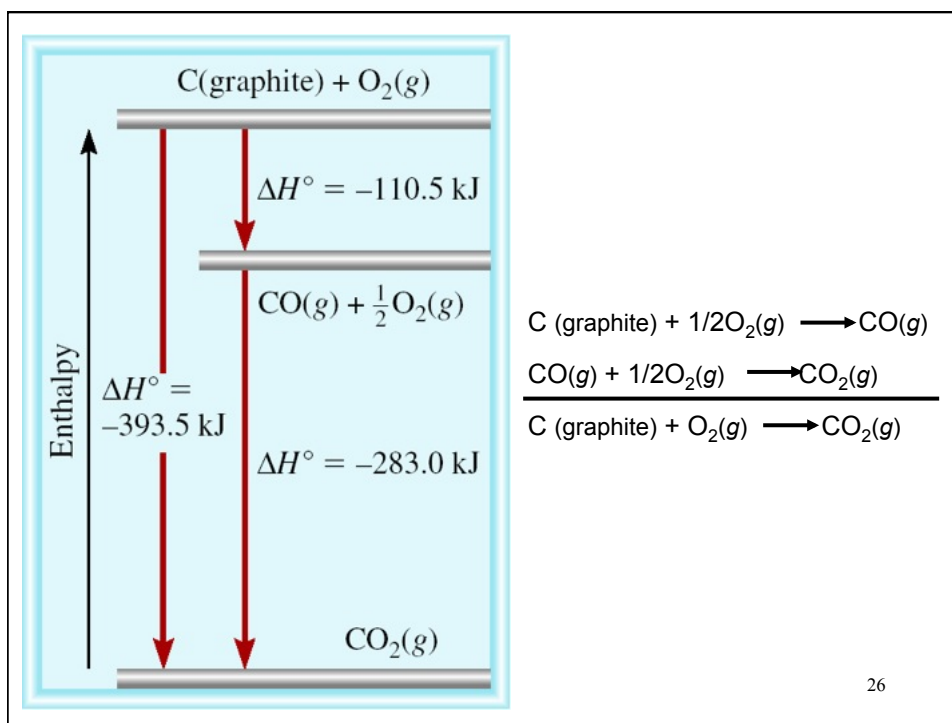The **standard enthalpy of reaction** (ΔH_{rxn}°) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$
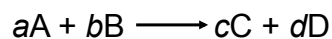
$$\Delta H_{rxn}^{\circ} = [c\Delta H_f^{\circ}(C) + d\Delta H_f^{\circ}(D)] - [a\Delta H_f^{\circ}(A) + b\Delta H_f^{\circ}(B)]$$

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

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.

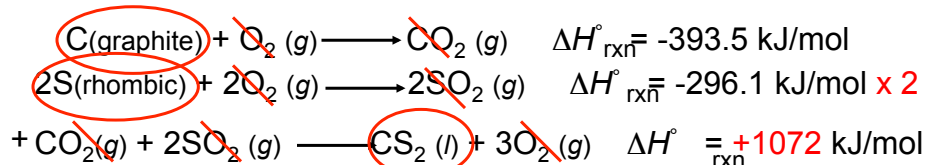(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

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C (graphite) + 1/2O$_2$(g) $\longrightarrow$ CO(g)

CO(g) + 1/2O$_2$(g) $\longrightarrow$ CO$_2$(g)

C (graphite) + O$_2$(g) $\longrightarrow$ CO$_2$(g)

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

C(graphite) + O_2 (*g*) ⟶ CO_2 (*g*) ΔH°_{rxn} = -393.5 kJ/mol

S(rhombic) + O_2 (*g*) ⟶ SO_2 (*g*) ΔH°_{rxn} = -296.1 kJ/mol

CS_2(*l*) + $3O_2$ (*g*) ⟶ CO_2 (*g*) + $2SO_2$ (*g*) ΔH°_{rxn} = -1072 kJ/mol

1. Write the enthalpy of formation reaction for CS_2

C(graphite) + 2S(rhombic) ⟶ CS_2 (*l*)

2. Add the given rxns so that the result is the desired rxn.

C(graphite) + O_2 (*g*) ⟶ CO_2 (*g*) ΔH°_{rxn} = -393.5 kJ/mol

2S(rhombic) + $2O_2$ (*g*) ⟶ $2SO_2$ (*g*) ΔH°_{rxn} = -296.1 kJ/mol x 2

+ CO_2(*g*) + $2SO_2$ (*g*) ⟶ CS_2 (*l*) + $3O_2$ (*g*) ΔH°_{rxn} = +1072 kJ/mol

_____

C(graphite) + 2S(rhombic) ⟶ CS_2 (*l*)

ΔH°_{rxn} = -393.5 + (2x-296.1) + 1072 = 86.3 kJ/mol   27

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.

$2C_6H_6$(*l*) + $15O_2$ (*g*) ⟶ $12CO_2$ (*g*) + $6H_2O$ (*l*)
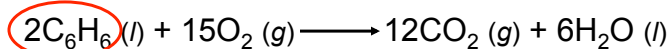
$\Delta H^{\circ}_{rxn} = \Sigma n \Delta H^{\circ}_{f}$ (products) - $\Sigma m \Delta H^{\circ}_{f}$ (reactants)

ΔH°_{rxn} = [$12\Delta H^{\circ}_{f}(CO_2)$ + $6\Delta H^{\circ}_{f}$ (H_2O)] - [$2\Delta H^{\circ}_{f}$ (C_6H_6)]

ΔH°_{rxn} = [12x–393.5 + 6x–187.6] – [2x49.04] = -5946 kJ

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

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