Thermochemistry

Chapter 6

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Energy, nature & types

Energy is the capacity to do work. [work = force x distance]

Chemists define ***work*** as *directed energy change resulting from a process.*

- ***Kinetic energy*** the energy produced by moving object.
- ***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.

Energy Changes in Chemical Reactions

Chemical reactions absorbs or release energy in the form of heat.

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

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

"*heat absorbed*" or "*heat released*" describe energy change during a process.

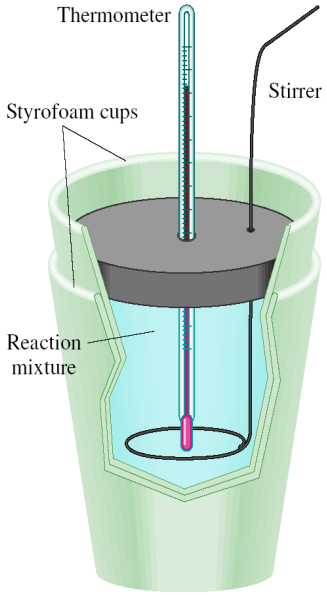
Temperature ≠ Thermal Energy

(intensive) (extensive)

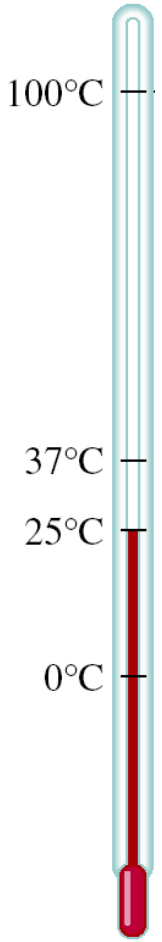
70°C

40°C

greater **temperature** greater **thermal energy**



Calorimeter



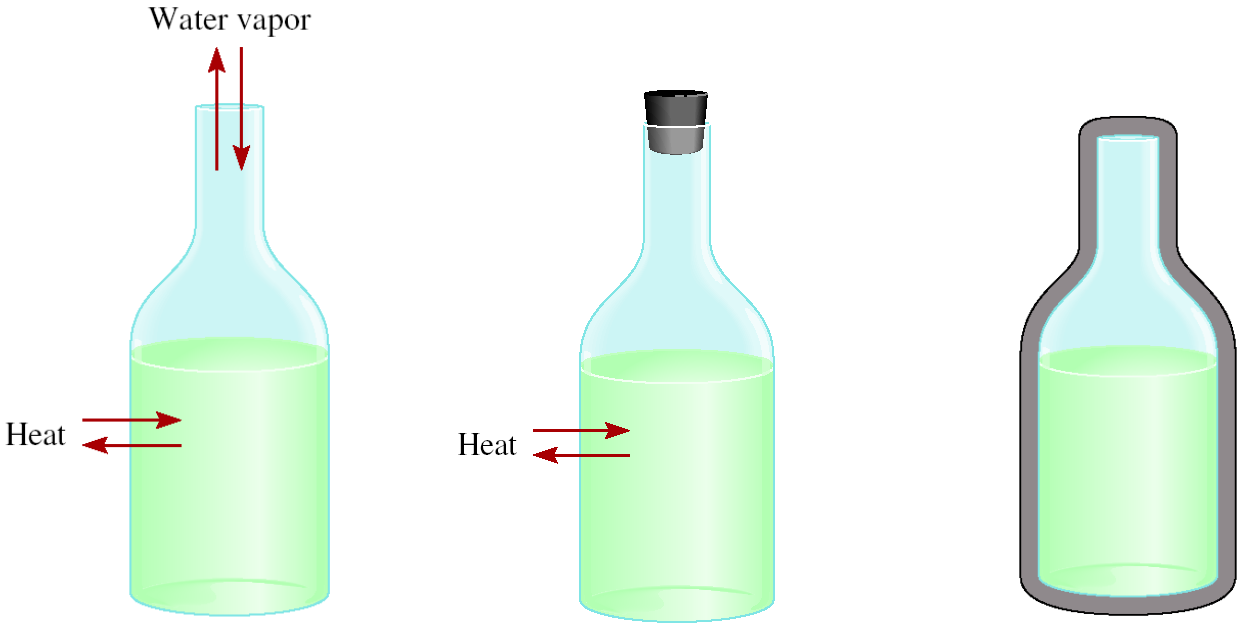
Thermometer

Thermochemistry, System & Surrounding

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.

Three types of systems



open	closed	isolated
Exchange: mass & energy	energy	nothing

Exothermic and Endothermic Processes

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

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l) + \text{energy}$$

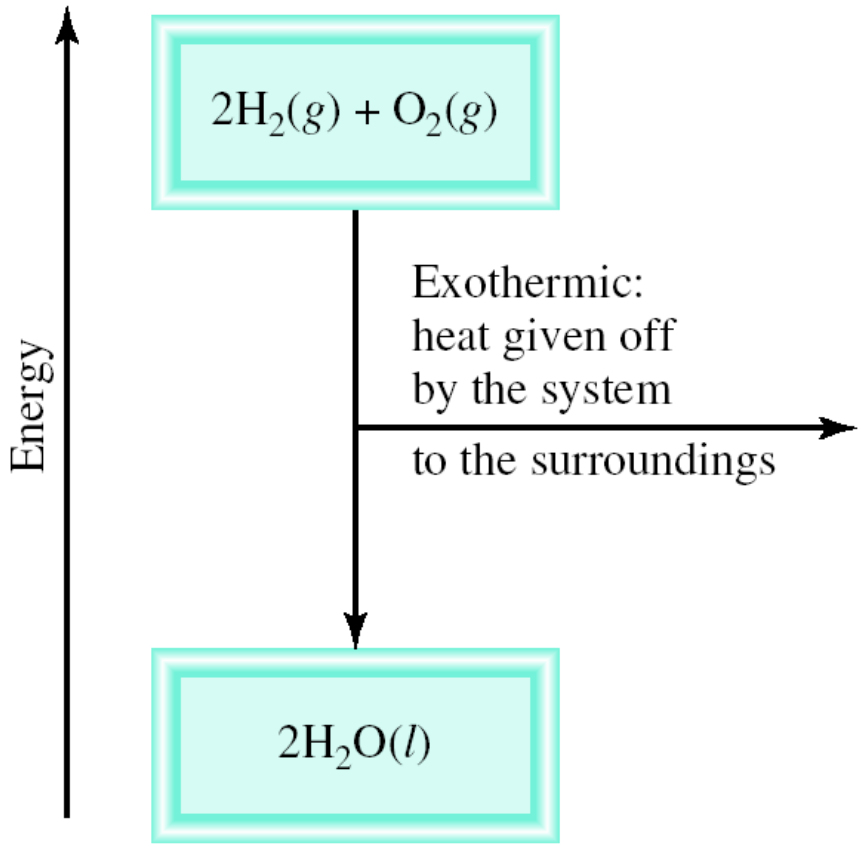
$$H_2O\,(g) \longrightarrow H_2O\,(l) + \text{energy}$$

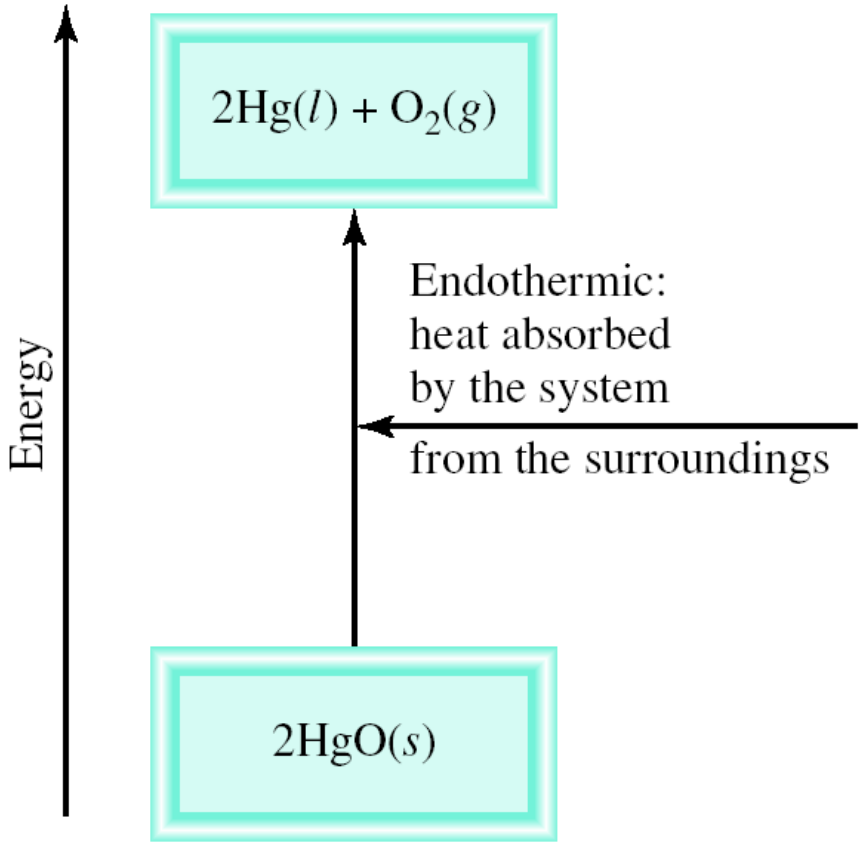
Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

$$\text{energy} + 2HgO\,(s) \longrightarrow 2Hg\,(l) + O_2\,(g)$$

$$\text{energy} + H_2O\,(s) \longrightarrow H_2O\,(l)$$

Schematic of Exothermic and Endothermic Processes



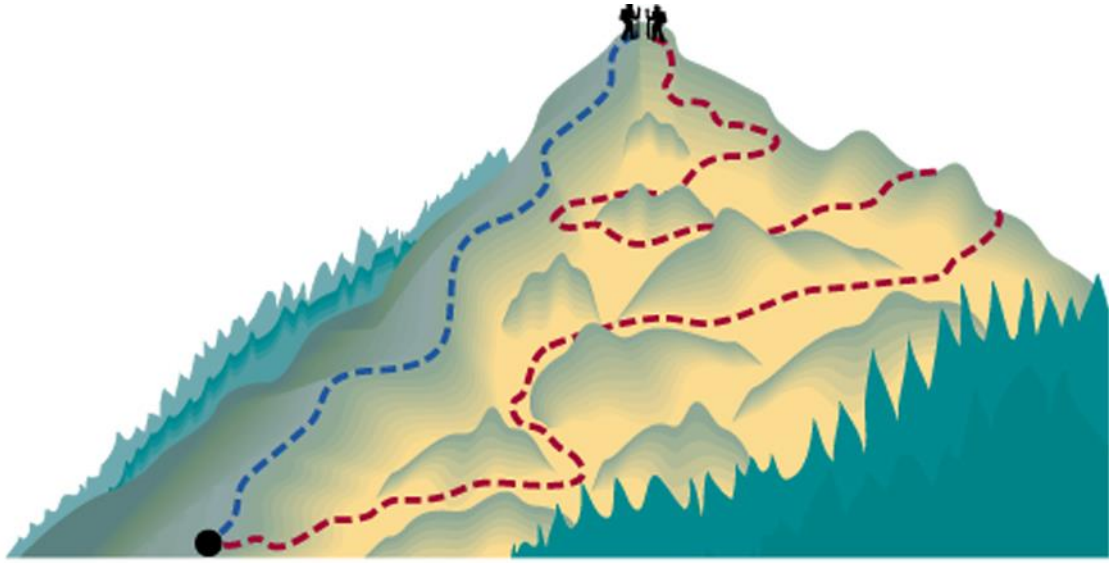


Thermodynamics & State function

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



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

$$\Delta E = E_{final} - E_{initial}$$

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

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

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

First law of thermodynamics

Energy can be converted from one form to another, but cannot be created or destroyed.

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

or

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

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

Exothermic chemical reaction!

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

System **Surroundings**

Another form of the first law for ΔE_{system}

$$\Delta E = q + w$$

ΔE 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)	−

Work Done by the System

$w = F \times d$

$w = -P \Delta V$

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

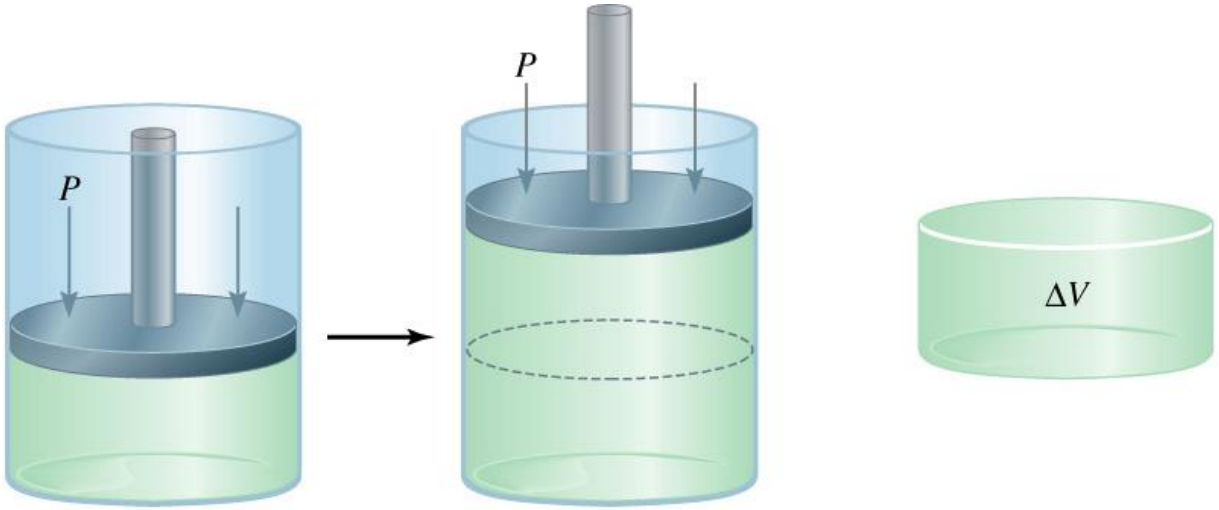
$\Delta V > 0$

$-P\Delta V < 0$

$w_{sys} < 0$

Work is not a state function.

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



initial final

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) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 0$ atm

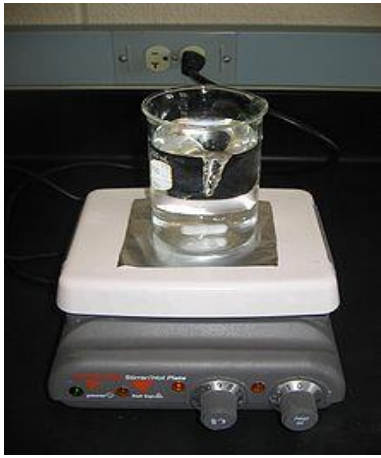
$$W = -0\text{ atm} \times 3.8\text{ L} = 0\text{ L•atm} = 0\text{ joules}$$

(b) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $P = 3.7$ atm

$$w = -3.7\text{ atm} \times 3.8\text{ L} = -14.1\text{ L•atm}$$

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

Heat, not a state function



- Raising temperature of 100 g of water in different way from 20°C to 30°C at 1 atm.
  - **Path 1**: Bunsen burner, Δt = 10°C,
    $q = ms\Delta t$
    = 100g×4.184J/g•°C×10°C = 4184 J
  - **Path 2**: magnetic stirrer, Δt = 10°C,
    $q = ms\Delta t = 0$
  - **Path 3**: Bunsen burner from 20 to 25°C, stirrer from 25 to 30°C, Δt = 10°C,
    q is in between 0 and 4184 J
- Heat change depends on how the process is carried out, ~~$\Delta q = q_f - q_i$~~
- ***q*** and ***w*** **not** state function but $\boldsymbol{q + w = \Delta E}$ is a state function

Chemistry in Action: Making Snow

$\Delta E = q + w$

$q = 0$

$w < 0$, $\Delta E < 0$

$\Delta E = C\Delta T$

$\Delta T < 0$, SNOW!

Internal Energy and the First Law of TD

- How first law of TD can be applied to processes carried out under different conditions.
- Two situations most commonly encountered in the laboratories:
  - ***Volume*** of the system kept **constant**
  - ***Pressure*** on the system kept **constant**

At constant volume:

$\Delta V = 0$ and no $P-V$ work; from 1st law

$$\Delta E = q + w$$
$$= q_v - P\Delta V$$
$$= q_v$$

$$\boxed{\Delta E = q_v}$$

Enthalpy and the First Law of TD

$$\Delta E = q + w$$

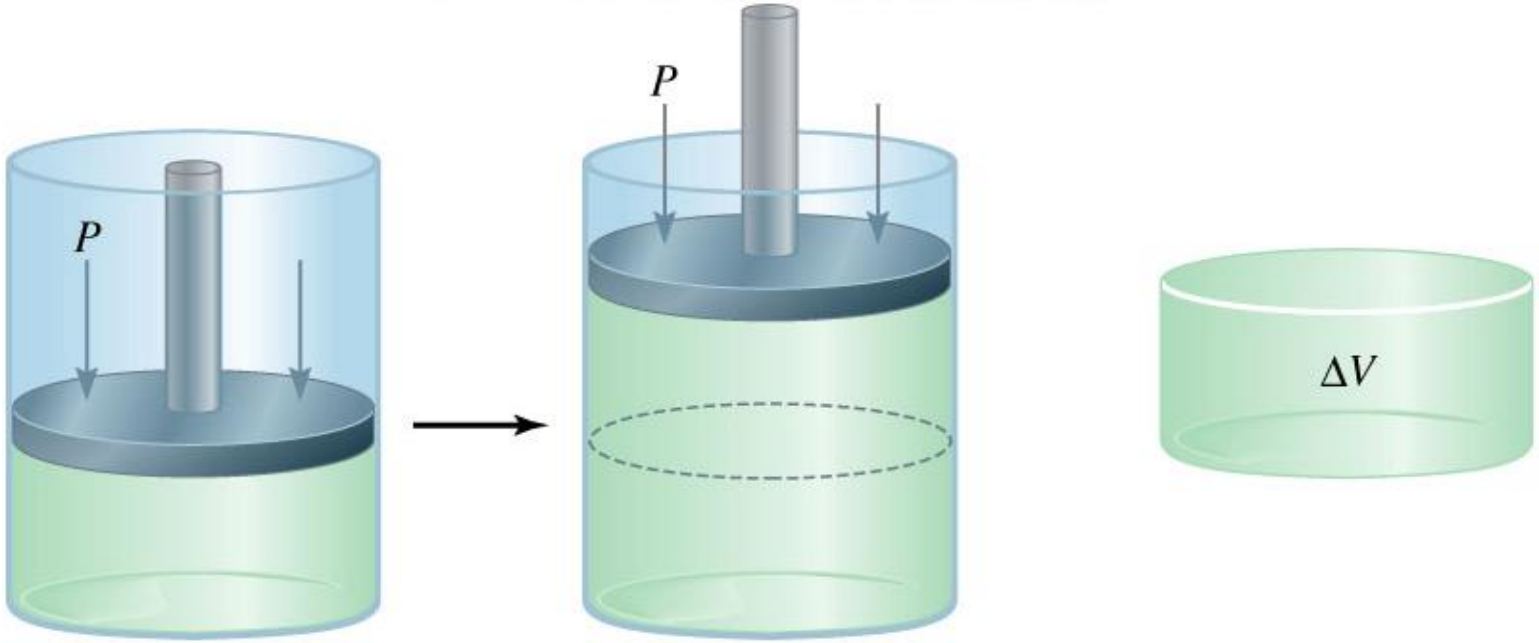
At constant pressure:

$$\Delta E = q + w$$
$$= q_p - P\Delta V$$
$$q_p = \Delta E + P\Delta V$$

Enthalpy (*H*) a new function:

$$H = E + PV$$
$$\Delta H = \Delta E + \Delta(PV), \text{ at const. } P$$
$$\Delta H = \Delta E + P\Delta V$$

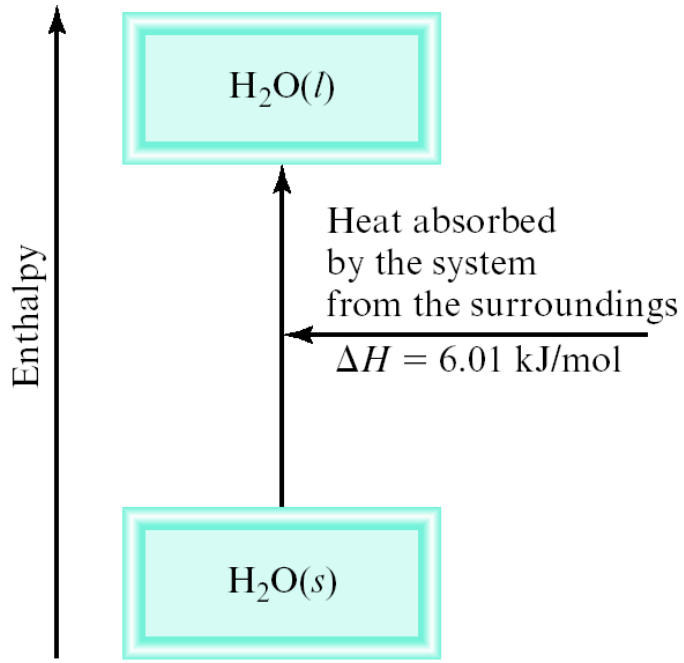
$$\boxed{\Delta H = q_p}$$



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

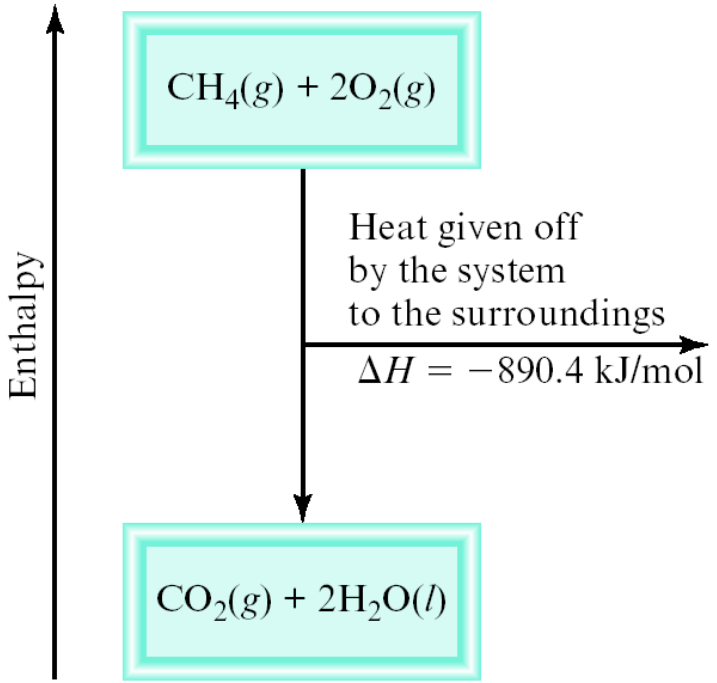
$$\Delta H = H \text{ (products)} - H \text{ (reactants)}$$

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



$H_{products} > H_{reactants}$

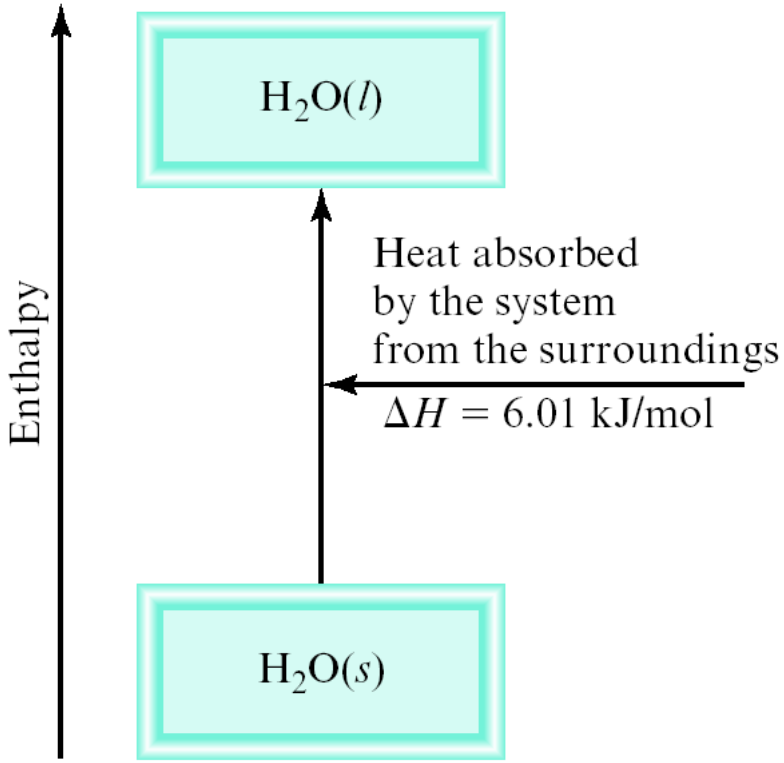
$\Delta H > 0$



$H_{products} < H_{reactants}$

$\Delta H < 0$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

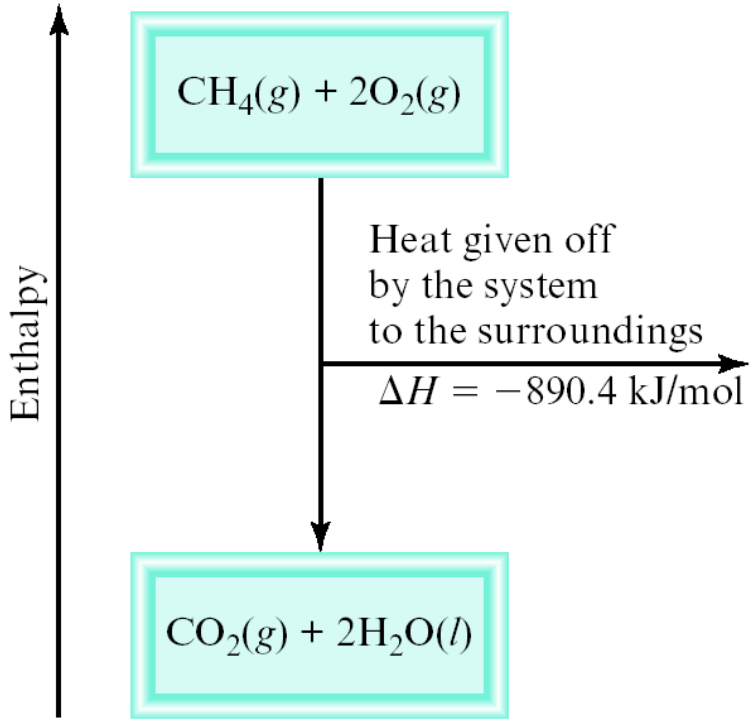
Endothermic

$\Delta H > 0$

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

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

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 25^0C and 1 atm.

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

Thermochemical Equations

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

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

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

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

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

$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ/mol}$$

Thermochemical Equations

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

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

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

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

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

$$266 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.9 \text{ g } P_4} \times \frac{-3013 \text{ kJ}}{1 \text{ mol } P_4} = -6470 \text{ kJ}$$

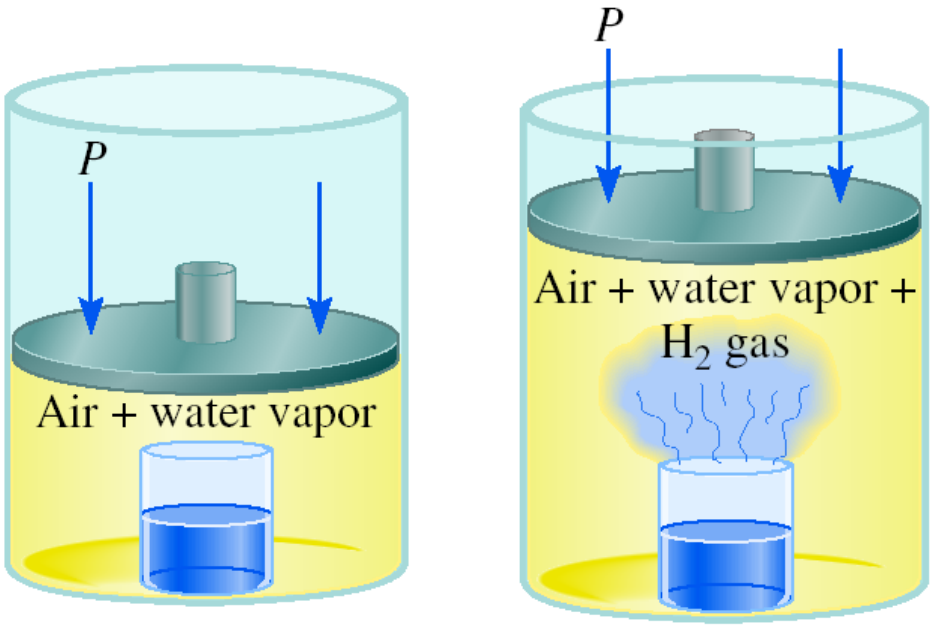
A Comparison of ΔH and ΔE

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

$\Delta E = \Delta H - P\Delta V$ At 25 °C, 1 mole H_2 = 24.5 L at 1 atm

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

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



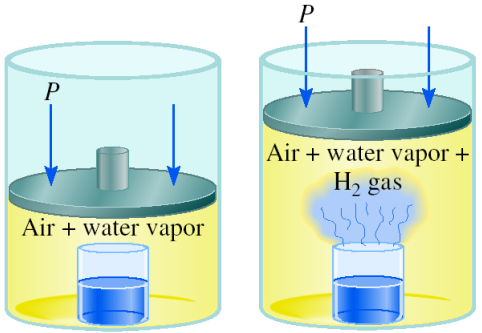
A Comparison of ΔH and ΔE

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

$\Delta E = -370.0$ kJ/mol

- ΔE and ΔH are approximately same
- ΔH smaller than ΔE, some internal energy used to do expansion work
- Reactions do not involve gases, ΔV is very small so ΔE is practically same as ΔH
- For gaseous reactions ΔE can be calculated assuming ideal behaviour:

$$\Delta E = \Delta H - \Delta(PV)$$
$$= \Delta H - \Delta(nRT)$$
$$= \Delta H - RT\Delta n$$



Δn = no. of moles of product – no. of moles of reactant

Calorimetry: measurement of heat changes

- 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:

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

$$q = C \times \Delta t$$

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

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

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

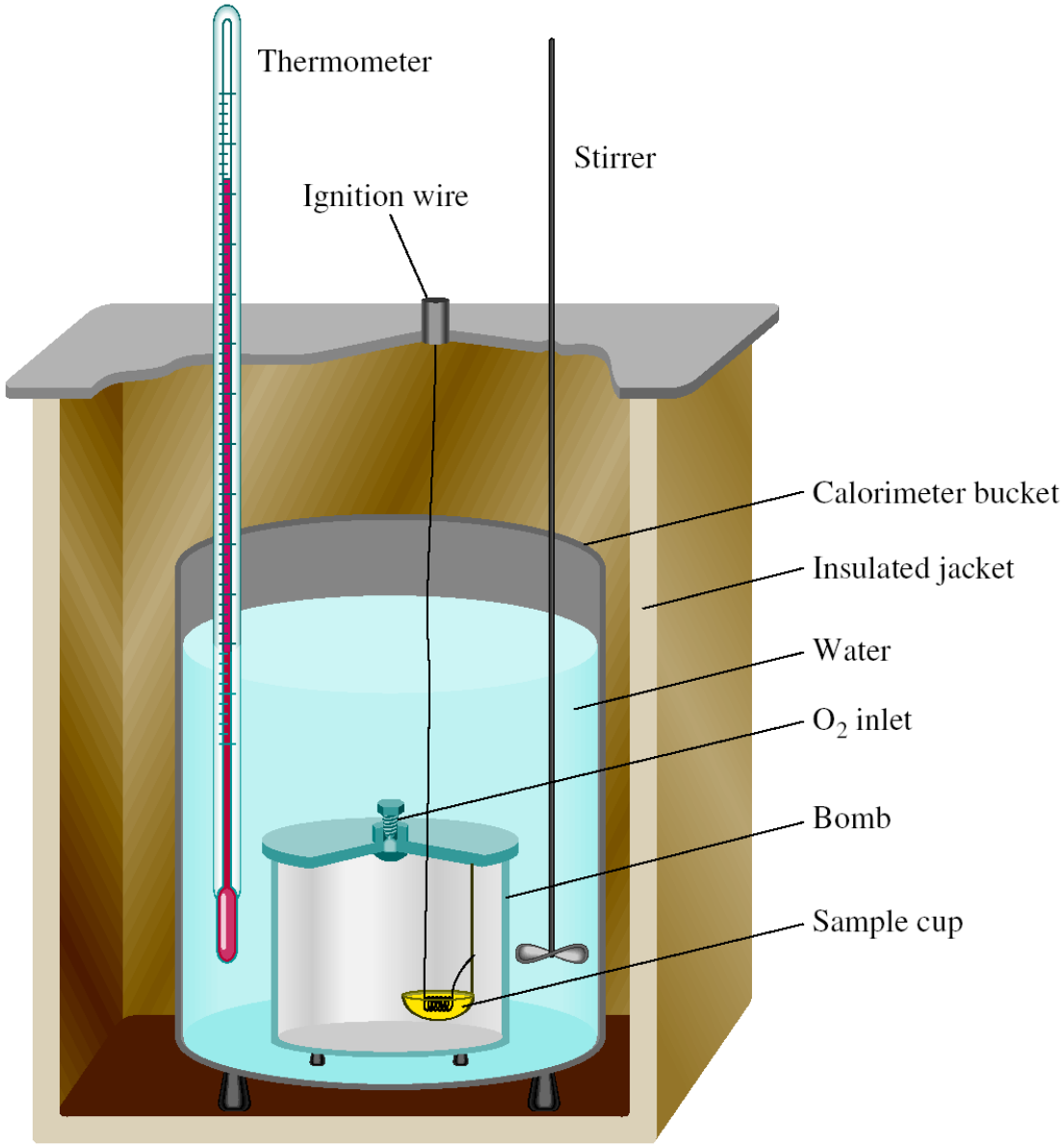
$= 5°C - 94°C = -89°C$

$q = ms\Delta t$

$= 869\ g \times 0.444\ J/g \cdot °C \times -89°C$

$= -34{,}000\ J$

Constant-Volume Calorimetry



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

$q_{sys} = 0$

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

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

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

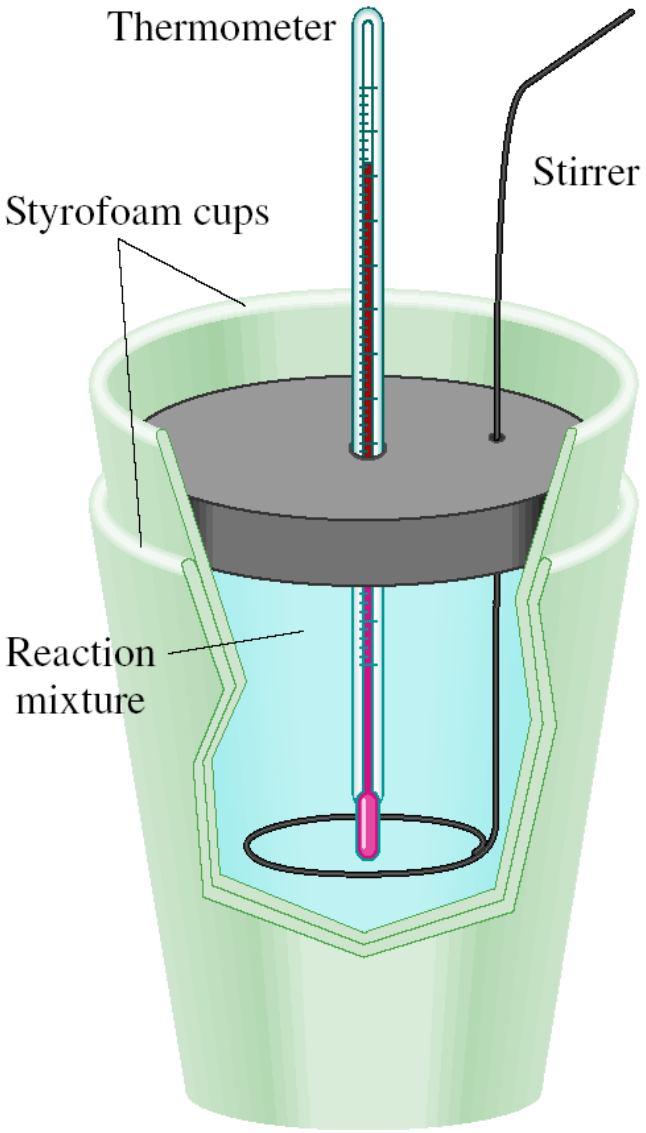
Reaction at Constant V

$\Delta H \neq q_{rxn}$

$\Delta H \sim q_{rxn}$

No heat enters or leaves!

Constant-Pressure Calorimetry



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

$q_{sys} = 0$

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

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

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

Reaction at Constant P

$\Delta H = q_{rxn}$

No heat enters or leaves!

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.

Chemistry in Action:

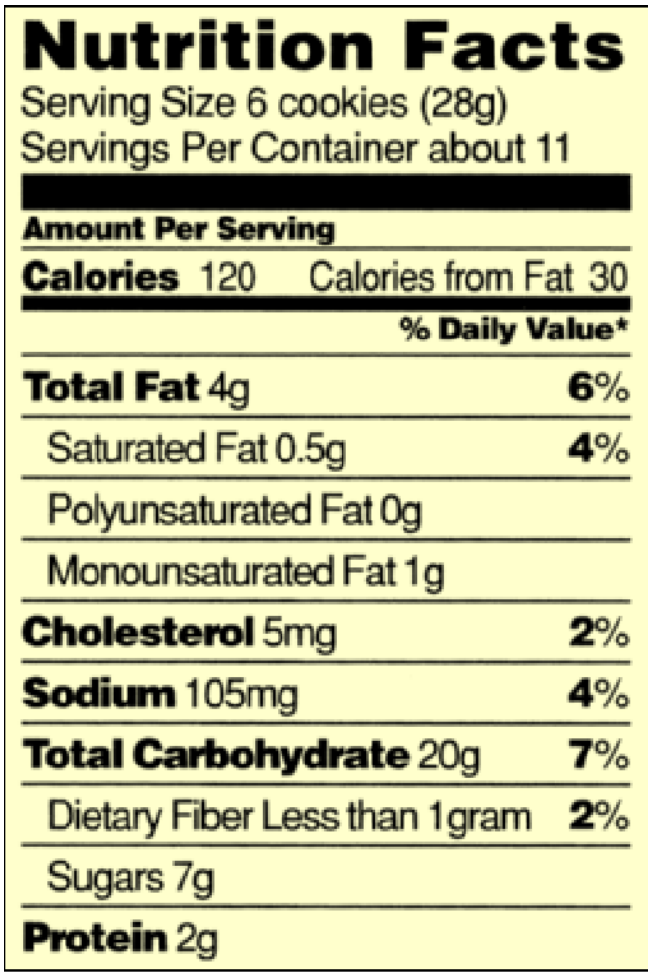
Fuel Values of Foods and Other Substances

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \longrightarrow 6CO_2\,(g) + 6H_2O\,(l) \quad \Delta H = -2801\ \text{kJ/mol}$$

1 cal = 4.184 J

1 Cal = 1000 cal = 4184 J

Substance	$\Delta H_{combustion}$ (kJ/g)
Apple	-2
Beef	-8
Butter	-34
Gasoline	-34



Nutrition Facts

Serving Size 6 cookies (28g)
Servings Per Container about 11

Amount Per Serving

Calories 120 Calories from Fat 30

% Daily Value*

Total Fat 4g	**6%**
Saturated Fat 0.5g	**4%**
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
Cholesterol 5mg	**2%**
Sodium 105mg	**4%**
Total Carbohydrate 20g	**7%**
Dietary Fiber Less than 1gram	**2%**
Sugars 7g	
Protein 2g	

Standard Enthalpy of Formation

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^o) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^o) 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**.

$\Delta H_f^o (O_2) = 0$ $\qquad$ ΔH_f^o (C, graphite) = 0

$\Delta H_f^o (O_3) = 142$ kJ/mol $\qquad$ ΔH_f^o (C, diamond) = 1.90 kJ/mol

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	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−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	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	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	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$Zn(s)$	0
$H_2O(l)$	−285.8	$ZnO(s)$	−348.0

Standard Enthalpy of Reaction

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

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

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

$$\Delta H^{o}_{rxn} = \Sigma n\Delta H^{o}_{f}(\text{products}) - \Sigma m\Delta H^{o}_{f}(\text{reactants})$$

To calculate ΔH^{o}_{rxn} we must know ΔH^{o}_{f} values of the compounds that take place in the reaction.

These values can be determined by:

- The **direct** method
- The **indirect** method

Standard Enthalpy of Reaction

- **The direct method**

  For compounds that can be readily synthesized from their elements in standard state:

  $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^o_{rxn} = -393.5 \text{ kJ/mol}$

  $\Delta H^o_{rxn} = \Delta H^o_f(CO_2,g) - [\Delta H^o_f(C, \text{graphite}) - \Delta H^o_f(O_2,g)]$

  $= -393.5 \text{ kJ/mol}$

  $\Delta H^o_{rxn} = \Delta H^o_f(CO_2,g) = -393.5 \text{ kJ/mol}$

  $\Delta H^o_f(CO_2,g) = -393.5 \text{ kJ/mol}$

  Similarly,

  $S(\text{rhombic}) + 3F_2(g) \rightarrow SF_6(g)$

  $P_4(\text{white}) + 5O_2(g) \rightarrow P_4O_{10}(s)$

  $C(\text{graphite}) + 2S(\text{rhombic}) \rightarrow CS_2(l)$

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.

$$2C_6H_6\,(l) + 15O_2\,(g) \longrightarrow 12CO_2\,(g) + 6H_2O\,(l)$$

$$\Delta H^o_{rxn} = \Sigma n \Delta H^o_f \text{ (products)} - \Sigma m \Delta H^o_f \text{ (reactants)}$$

$$\Delta H^o_{rxn} = [12\Delta H^o_f\,(CO_2) + 6\Delta H^o_f\,(H_2O)] - [\,2\Delta H^o_f\,(C_6H_6)]$$

$$\Delta H^o_{rxn} = [\,12x{-}393.5 + 6x{-}187.6\,] - [\,2x49.04\,] = -5946 \text{ kJ}$$

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

Standard Enthalpy of Reaction

- **The indirect method**

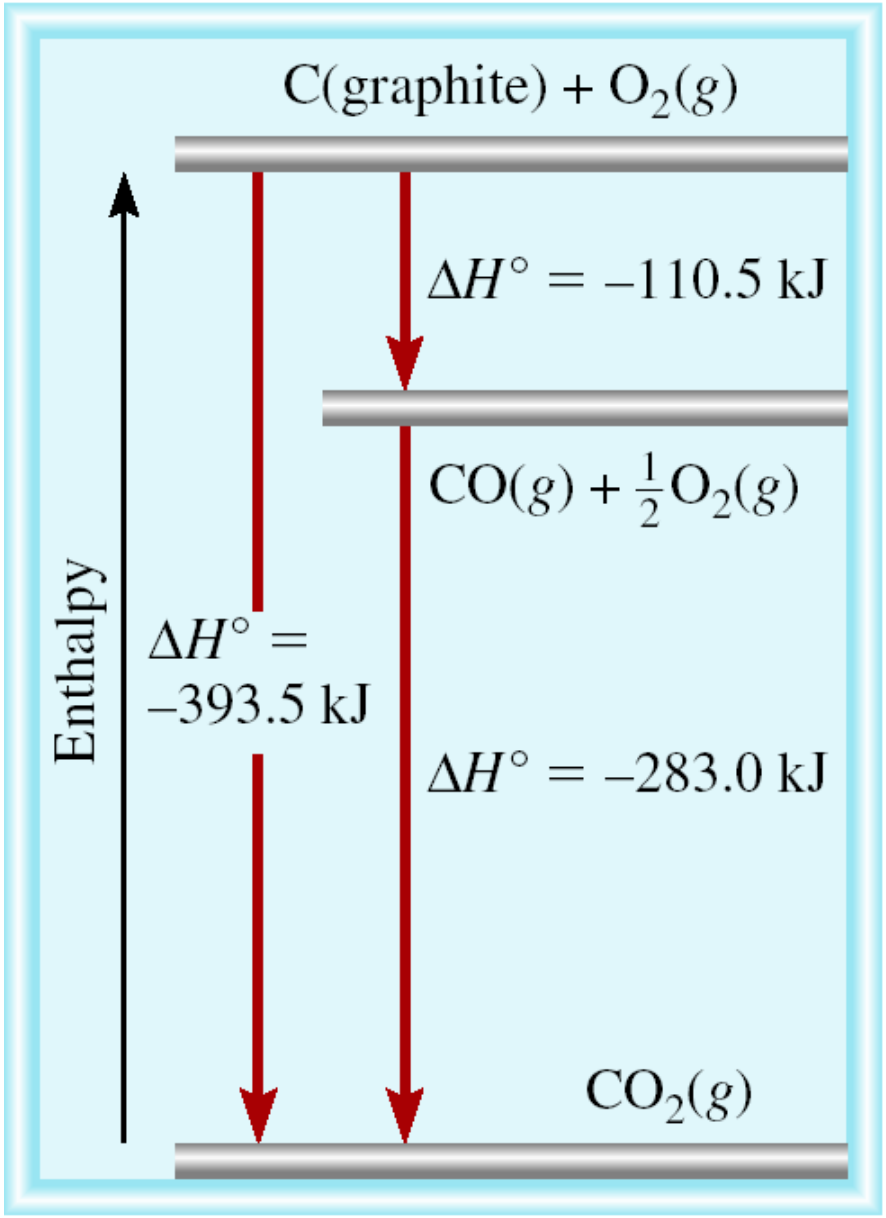
  Many compounds can not be directly synthesized from their elements,

  – reaction does not go to completion
  – reaction proceeds too slowly
  – side reactions produce undesired products

  ΔH^{o}_{f} can be determined by indirect method based on Hess's law of heat summation

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.)



$C(graphite) + O_2(g) \longrightarrow CO_2(g)$

$CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$

$C(graphite) + 1/2O_2(g) \longrightarrow CO(g)$ **?**

$C(graphite) + O_2(g) \longrightarrow CO_2(g)$

$+ CO_2(g) \longrightarrow CO(g) + 1/2O_2(g)$

$C(graphite) + 1/2O_2(g) \longrightarrow CO(g)$

$\Delta H^o_f(CO) = -393.5 + 283.0$

$= -110.5$ kJ/mol

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

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ_{rxn} = -393.5$ kJ/mol

$S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g)$ $\quad \Delta H^\circ_{rxn} = -296.1$ kJ/mol

$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ $\quad \Delta H^\circ_{rxn} = -1072$ kJ/mol

1. Write the enthalpy of formation reaction for CS_2

$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2(l)$

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

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ_{rxn} = -393.5$ kJ/mol

$2S(\text{rhombic}) + 2O_2(g) \longrightarrow 2SO_2(g)$ $\quad \Delta H^\circ_{rxn} = -296.1$ kJ/mol x 2

$+ \; CO_2(g) + 2SO_2(g) \longrightarrow CS_2(l) + 3O_2(g)$ $\quad \Delta H^\circ_{rxn} = +1072$ kJ/mol

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$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2(l)$

$\Delta H^\circ_{rxn} = -393.5 + (2x-296.1) + 1072 = 86.3$ kJ/mol

Chemistry in Action: Bombardier Beetle Defense

$C_6H_4(OH)_2\ (aq) + H_2O_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + 2H_2O\ (l)\ \Delta H^o = ?$

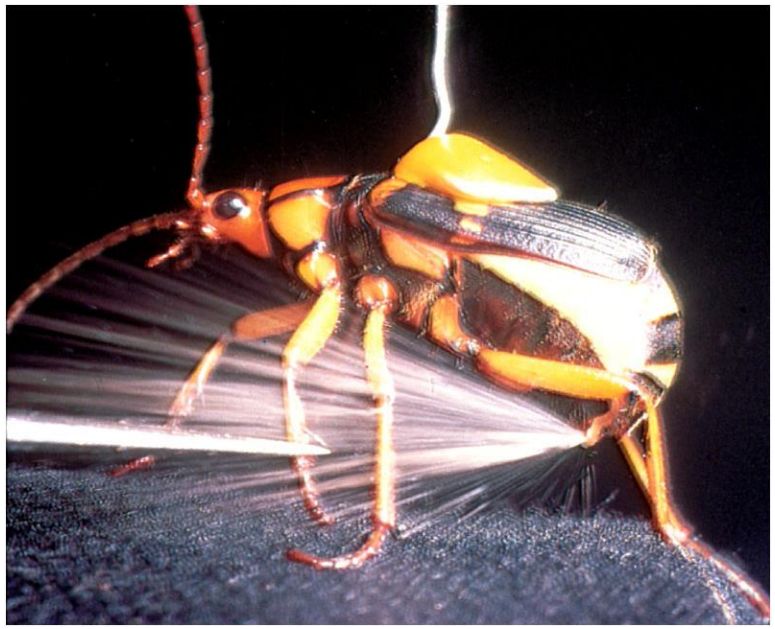
$C_6H_4(OH)_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + H_2\ (g)\ \Delta H^o = 177\ kJ/mol$

$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \frac{1}{2}O_2\ (g)\ \Delta H^o = -94.6\ kJ/mol$

$H_2\ (g) + \frac{1}{2}\ O_2\ (g) \longrightarrow H_2O\ (l)\ \Delta H^o = -286\ kJ/mol$

$\Delta H^o = 177 - 94.6 - 286 = -204\ kJ/mol$

Exothermic!



Heat of Solution

The ***heat of solution*** or ***enthalpy of solution*** (ΔH_{soln}) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

TABLE 6.5

Heats of Solution of Some Ionic Compounds

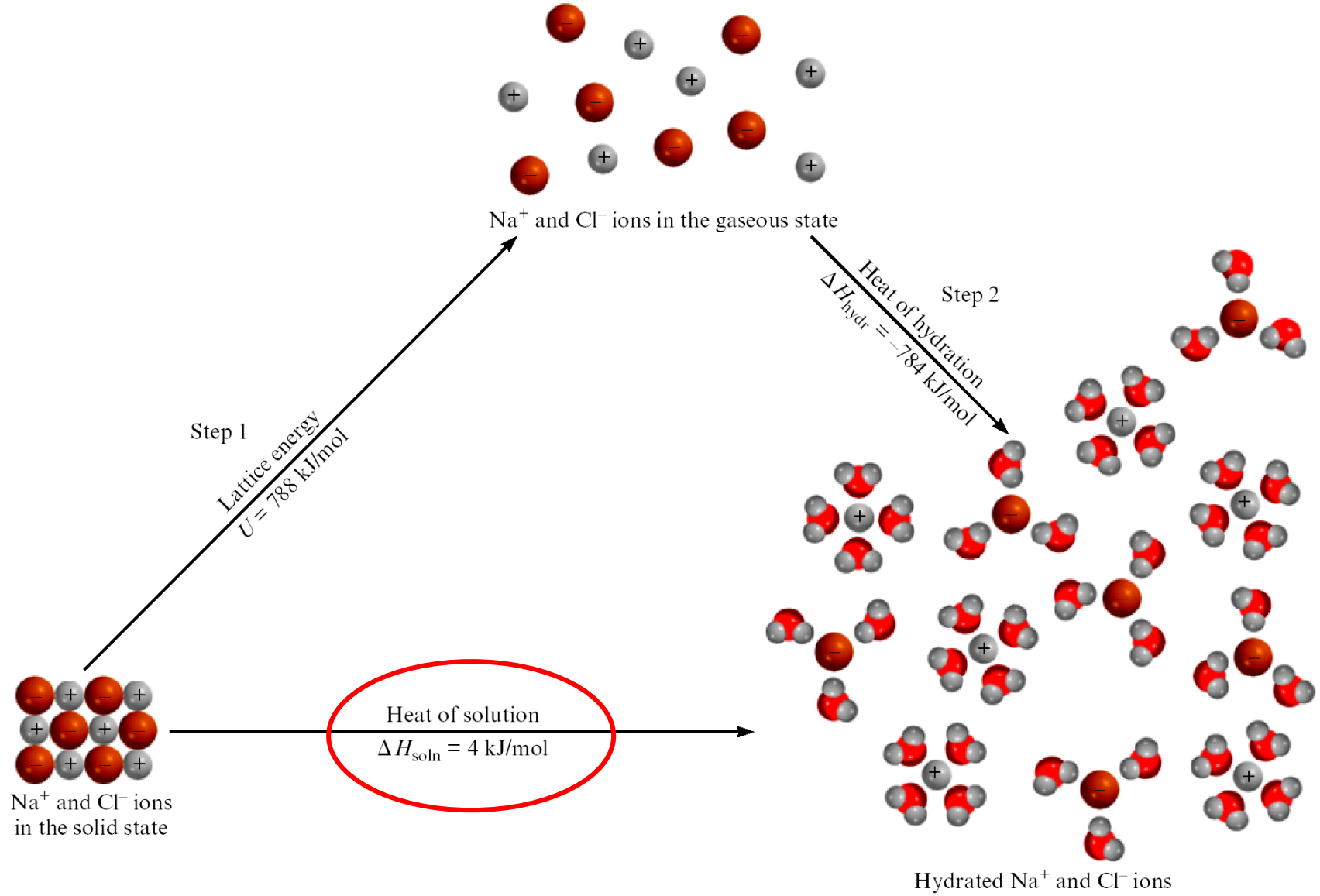
Compound	ΔH_{soln} (kJ/mol)
LiCl	−37.1
$CaCl_2$	−82.8
NaCl	4.0
KCl	17.2
NH_4Cl	15.2
NH_4NO_3	26.2

$$\Delta H_{soln} = H_{soln} - H_{components}$$

Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

Solution Process for NaCl



ΔH_{soln} = Step 1 + Step 2 = 788 – 784 = 4 kJ/mol