Thermochemistry

Chapter 6

Thermochemistry

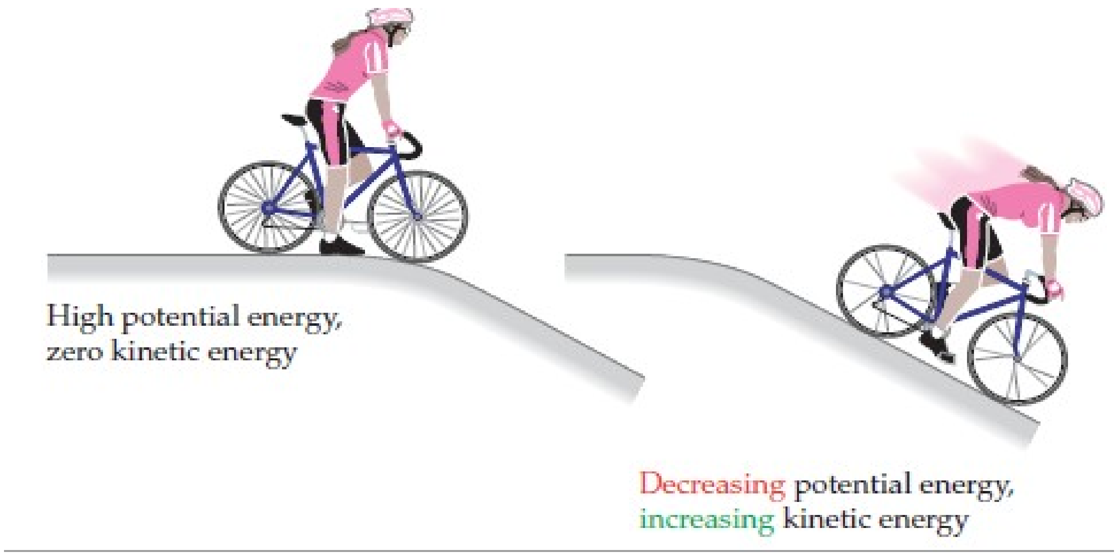
Introduction and Some Definitions
Internal Energy
The First Law of Thermodynamics
Enthalpy and Enthalpy Changes
Calorimetry
Hess's Law
Using Enthalpy's of Formation

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

Energy

- Energy is the ability to do work or transfer heat.
  - Energy used to cause an object that has mass to move is called **work**.
  - Energy used to cause the temperature of an object to rise is called **heat**.

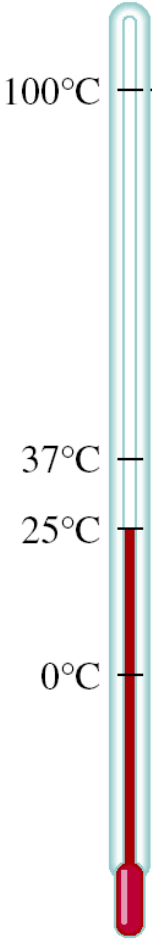


Energy Changes in Chemical Reactions

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



Units of Energy

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

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

shows that a mass of 2 kg moving at a speed of 1m/s possesses a kinetic energy of 1 J:

$$E_k = \tfrac{1}{2}mv^2 = \tfrac{1}{2}(2\ \mathrm{kg})(1\ \mathrm{m/s})^2 = 1\ \mathrm{kg\text{-}m^2/s^2} = 1\ \mathrm{J}$$

Kilojoule (kJ)   1 kJ = 1000 J

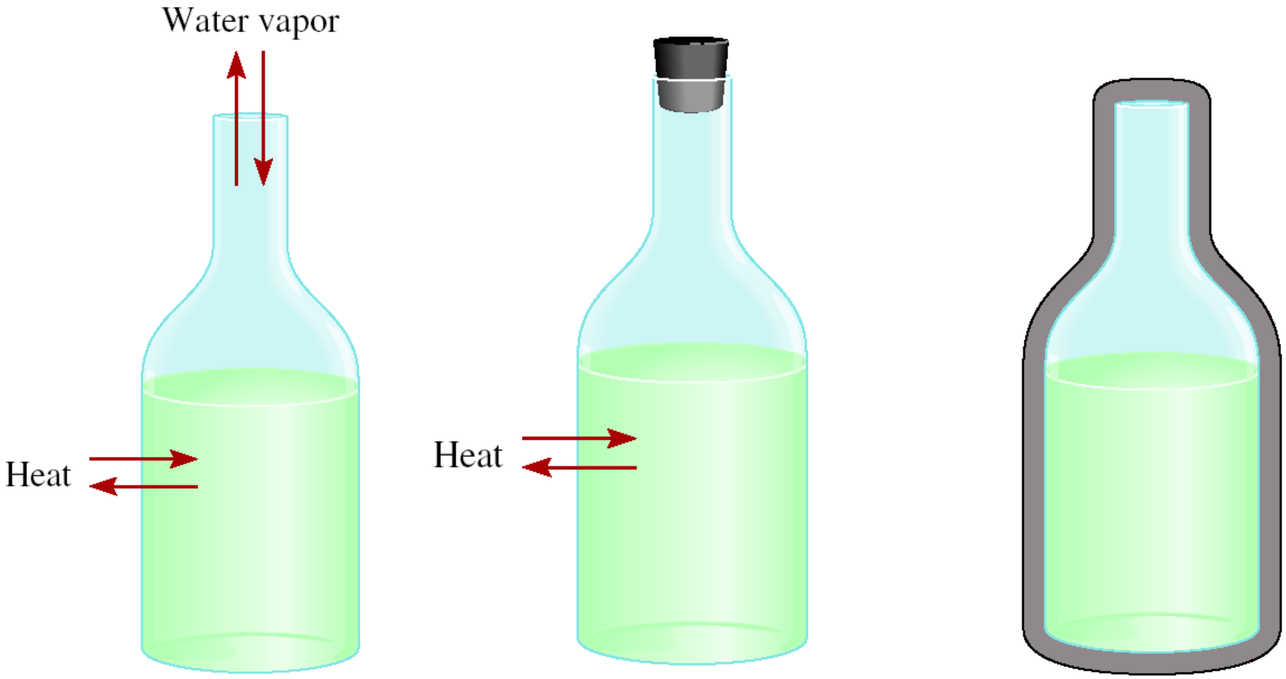
- **An older, non-SI unit is still in widespread use: the calorie (cal). Originally defined as the amount of energy needed to raise the temperature of 1 g of water from 14.5^{o}C to 15.5^{o}C**

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

Kilocalories (kcal)   1 kcal = 1000 cal

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.



	open	closed	isolated
Exchange:	mass & energy	energy	nothing

System:

The part of the universe singled out for study

Typically the chemicals involved in the reaction or process. The system is usually the chemicals in the flask/reactor.

Surroundings:

Everything else

A system can be either open or closed.

Open system:

A system that can exchange both matter and energy with the surroundings

Closed system:

A system that can exchange energy with the surroundings but not matter.

An isolated system is one in which neither energy nor matter can be exchanged with the surroundings.

Exchange of Heat between System and Surroundings

- **When heat is absorbed by the system from the surroundings, the process is endothermic.**

- **When heat is released by the system into the surroundings, the process is exothermic.**

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.

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

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

Examples of endothermic and exothermic reactions

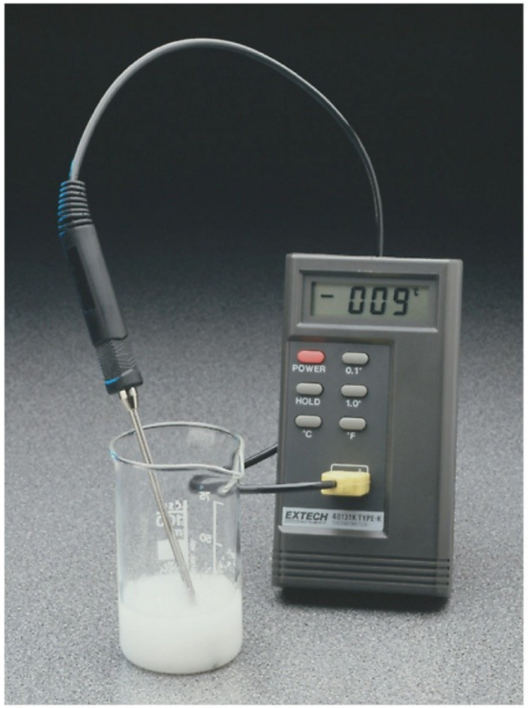
The reaction of powdered aluminum with Fe_2O_3 is highly exothermic. The reaction proceeds vigorously to form Al_2O_3 and molten iron:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l).$$

Heat flows (violently) from system into surroundings (exothermic reaction), temperature of surroundings increases

Exothermic reaction

Examples of endothermic and exothermic reactions



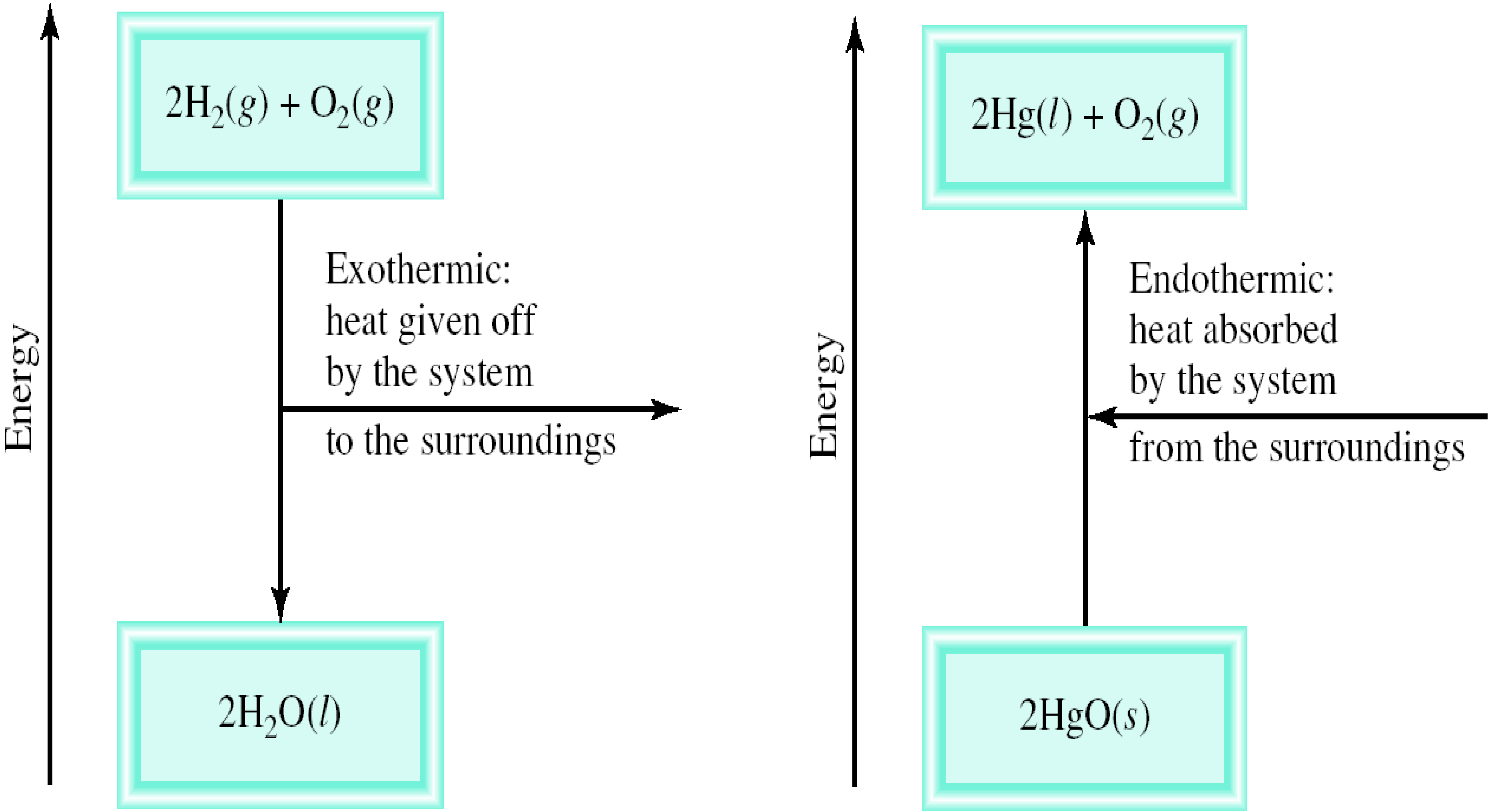
$2\ NH_4SCN(s) + Ba(OH)_2 * 8\ H_2O(s) \rightarrow Ba(SCN)_2(aq) + 2\ NH_3(aq) + 10\ H_2O(l)$.

As a result, the temperature of the system drops from about 20 °C to -9 °C.

Heat flows from surroundings into system (endothermic reaction), temperature of surroundings drops, thermometer reads temperature well below room temperature

Endothermic reaction

Schematic of Exothermic and Endothermic Processes



Energy

$2H_2(g) + O_2(g)$

Exothermic:
heat given off
by the system

to the surroundings

$2H_2O(l)$

Energy

$2Hg(l) + O_2(g)$

Endothermic:
heat absorbed
by the system

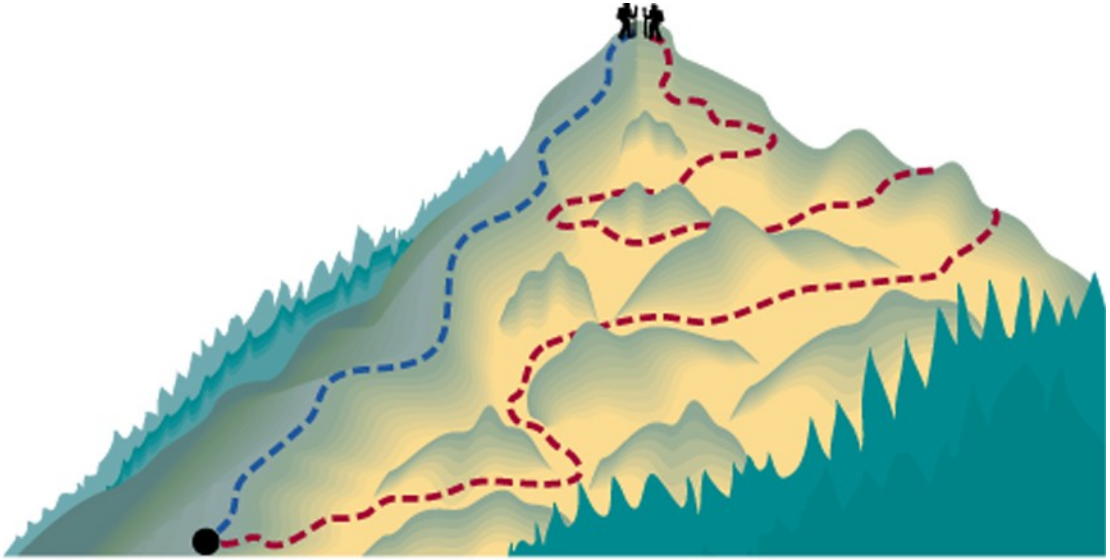
from the surroundings

$2HgO(s)$

Thermodynamics is the scientific study of the inter conversion 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



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

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

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

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

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

First Law of Thermodynamics

Energy can be transferred between the system and the surroundings as heat and/or work.

Energy can also be converted from one form to another.

Kinetic energy ←→ Potential energy

First Law of Thermodynamics: Energy can be converted from one form to another, but it cannot be created or destroyed.

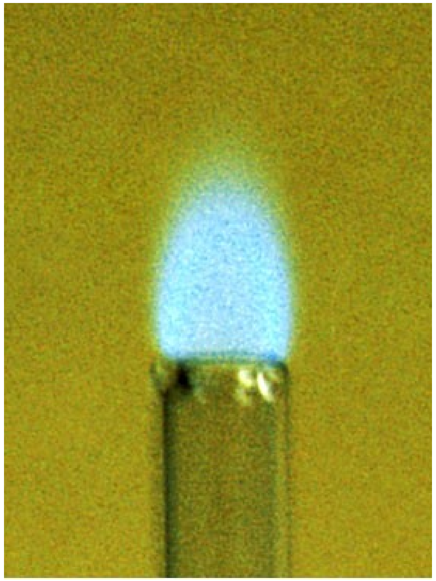
Any energy lost by the system must be gained by the surroundings and vice versa.

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

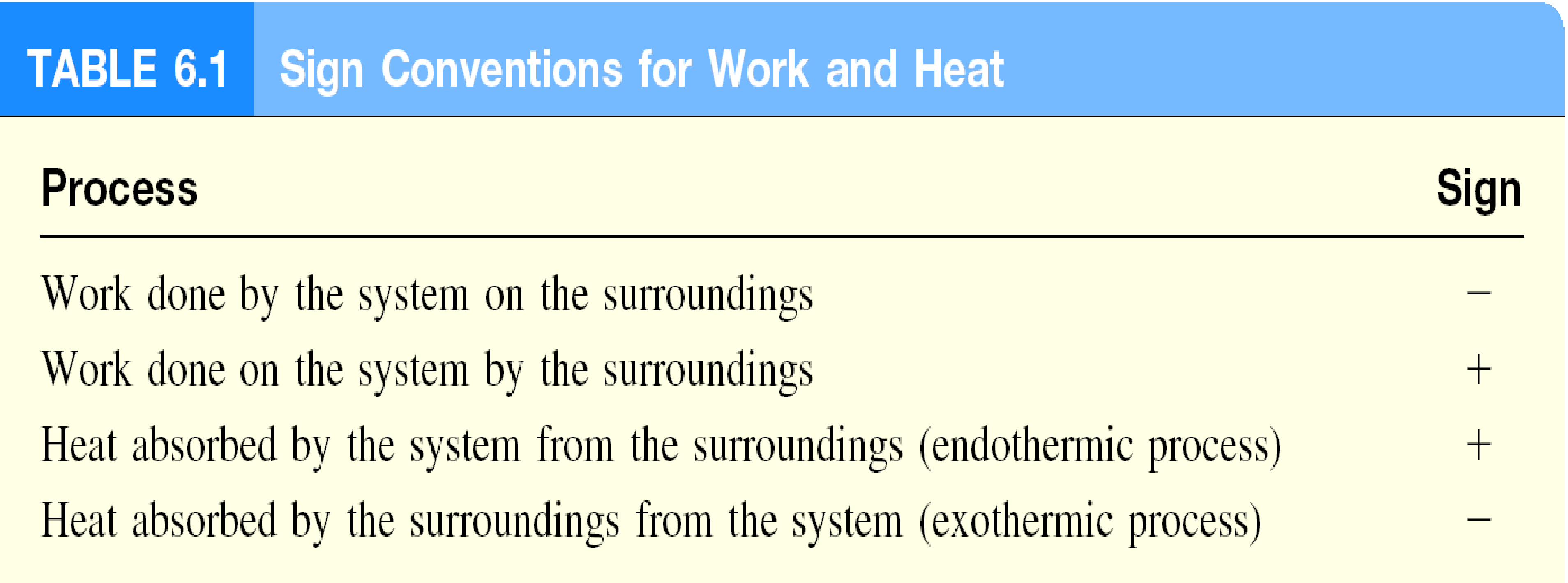


TABLE 6.1 Sign Conventions for Work and Heat

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 On the System

$$w = F \times d$$

$$w = -P\,\Delta V$$

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

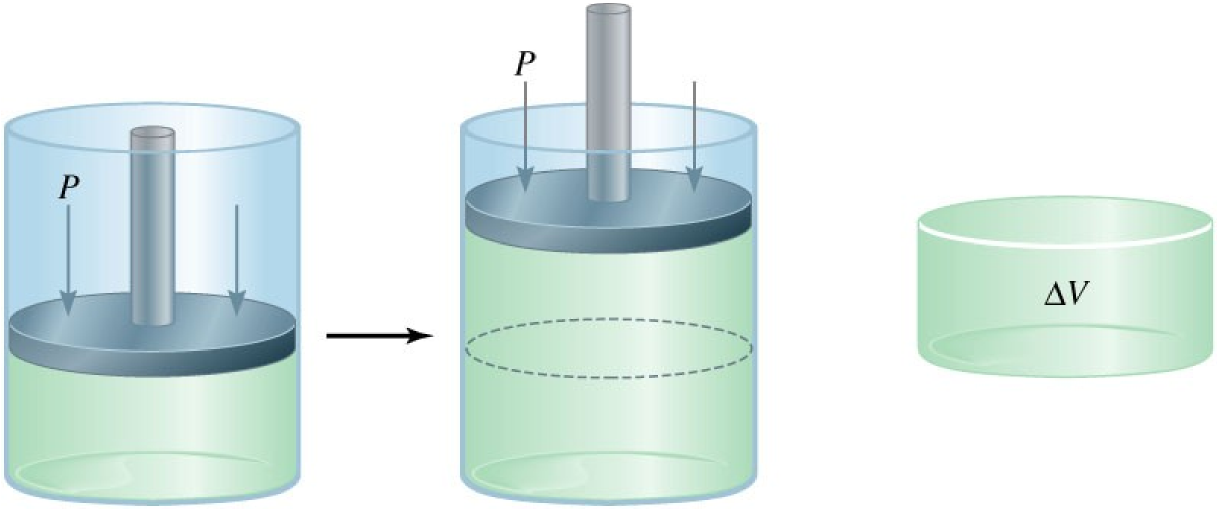
$$\Delta V > 0$$

$$-P\Delta V < 0$$

$$w_{sys} < 0$$

Work is not a state function.

$$\Delta w \cancel{=} w_{final} - w_{initial}$$



Example 6.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature.
Calculate the work done by the gas if it expands

- **a-against a vacuum**
- **b- against a constant pressure of 1.2 atm**

Solution

a)Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0)(6.0 - 2.0)\text{ L} = 0$$

b) The external, opposing is 1.2 atm, so

$$w = -P\Delta V = -(1.2\text{ atm})(6.0 - 2.0)\text{ L}$$

$$= -4.8\text{L} \cdot \text{atm}$$

Example 6.2

The work done when a gas is compressed in a cylinder is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

Solution

$$\Delta E = q + w$$

$$= -128\ \text{J} + 462\ \text{J} \qquad = 334\ \text{J}$$

As a result, the energy of the gas increases by 334 J.

Two Methods of *Energy* Exchange Between System and Surroundings

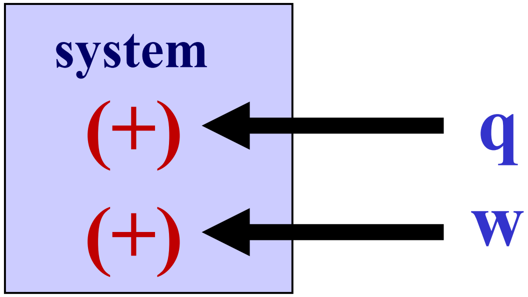
- Heat q Work w

∀ $\Delta E = q + w$

- **Conventions of heat and work**

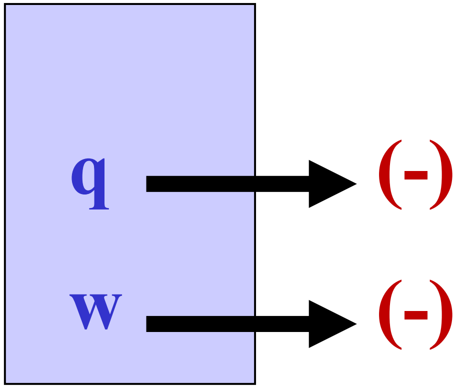
q	+	Heat **absorbed** by system	E_{system} ↑
q	–	Heat **released** by system	E_{system} ↓
w	+	Work done **on** system	E_{system} ↑
w	–	Work done **by** system	E_{system} ↓

Energy can be transferred between the system and the surroundings as either heat or work.



Energy gained by the system is always designated using a positive sign.

A reaction or process in which the system gains heat from the surroundings is endothermic.



Energy lost by the system is always designated using a negative sign.

A reaction or process in which the system loses heat to the surroundings is exothermic.

A reaction or process that experiences a net gain of energy from the surroundings is referred to as endergonic.

$E_{final} > E_{initial}$

$\Delta E > 0$ (positive)

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

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

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

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

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

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!

Enthalpy and the First Law of Thermodynamics

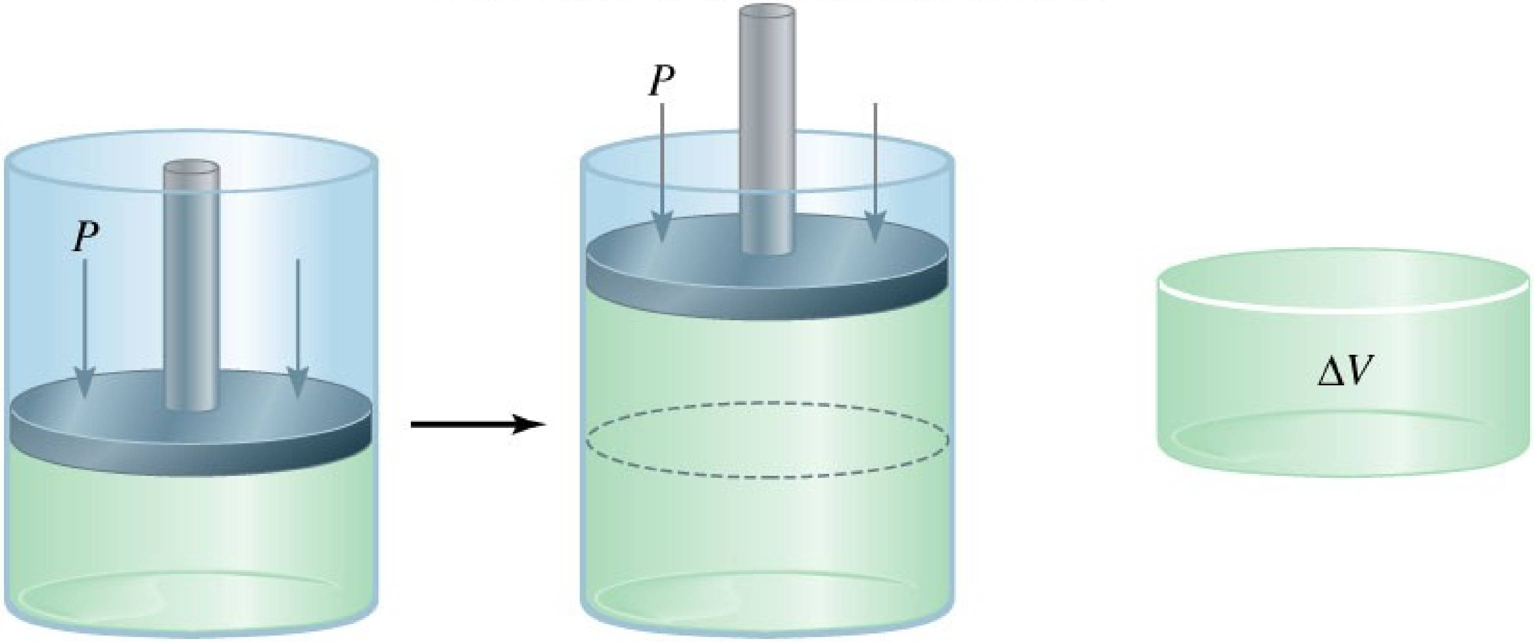
$$\Delta E = q + w$$

At constant pressure:

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

$$\boldsymbol{\Delta E = \Delta H - P\Delta V}$$

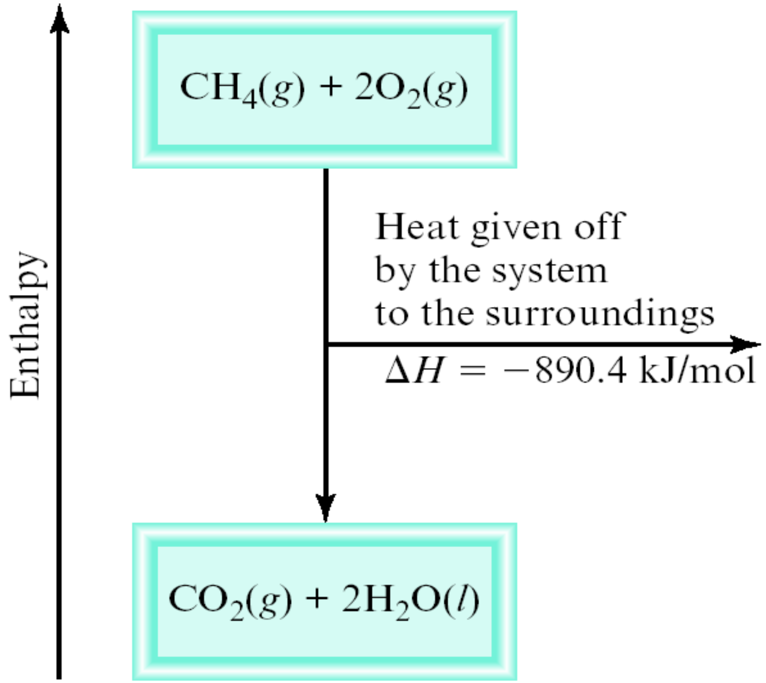
$$\boldsymbol{\Delta H = \Delta E + P\Delta V}$$

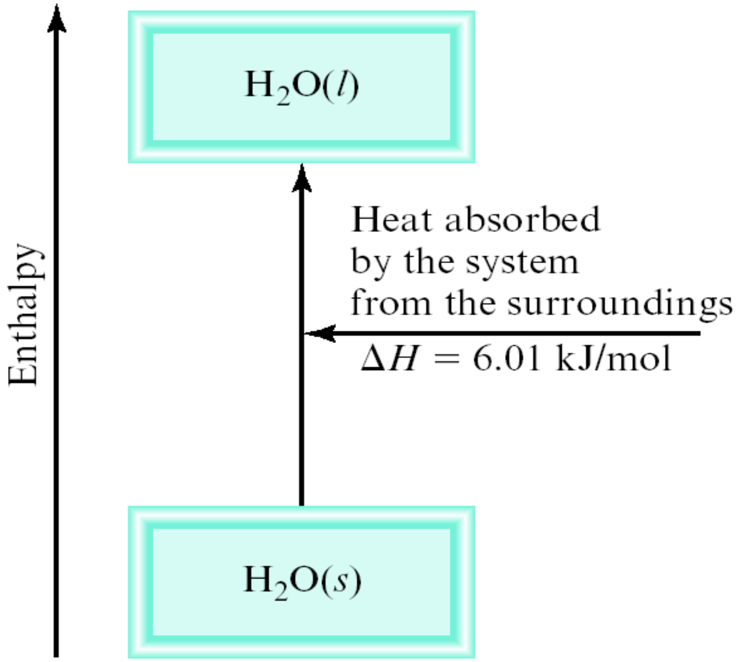


Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

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





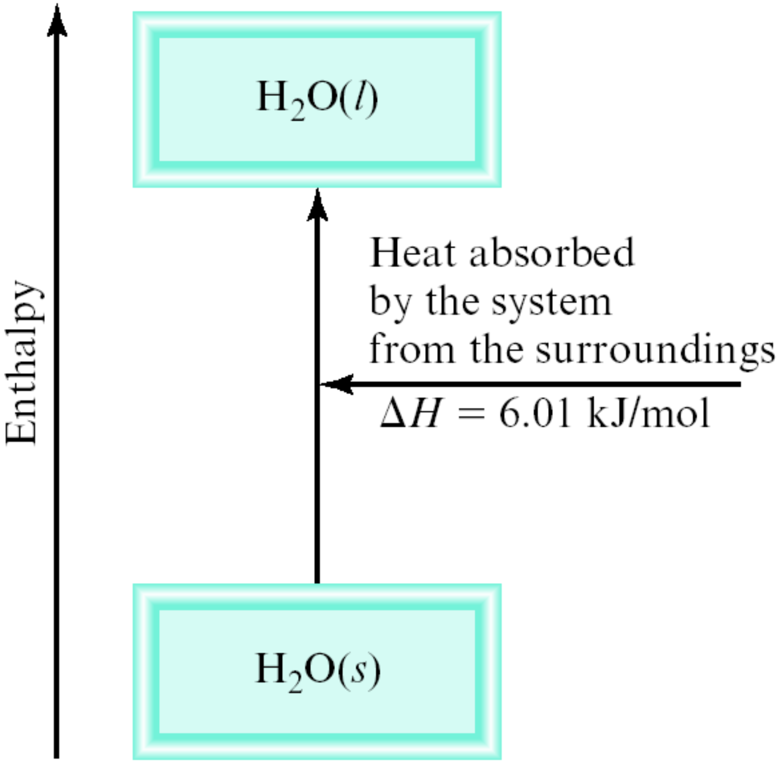
$H_{\text{products}} < H_{\text{reactants}}$

$\Delta H < 0$

$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$

Thermo chemical Equations



Is ΔH negative or positive?

System absorbs heat

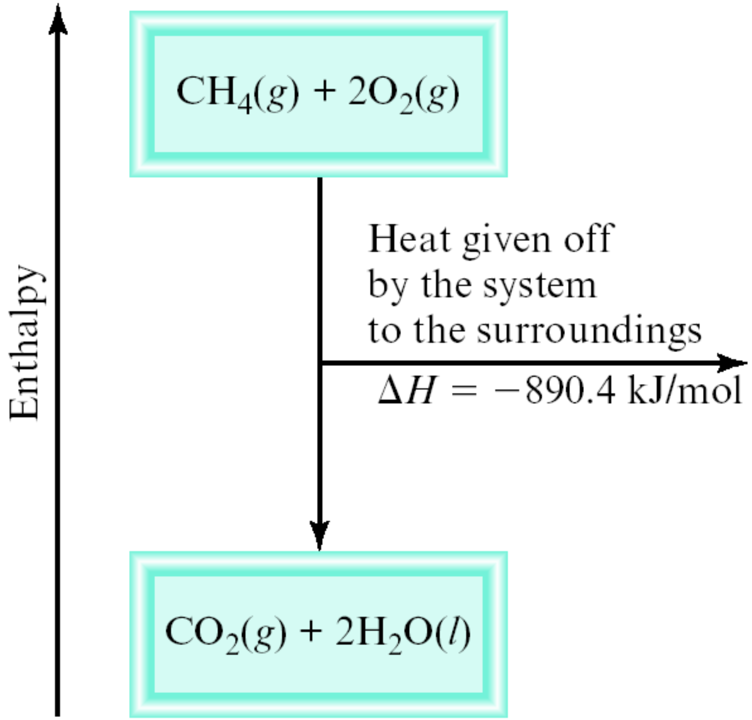
Endothermic

$\Delta H > 0$

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

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

Thermo chemical 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.

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

Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

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

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

- So, at constant pressure, the change in enthalpy *is* the heat gained or lost.

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

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

For Gas Materials

$$P\Delta V = n_f RT - n_i RT = (n_f - n_i)RT = \Delta n\ RT$$

Where n is the numbers of moles of gas molecules

Olive oils is completely burned in oxygen at 100.3 ˚C according to:

$$C_{57}H_{104}O_6\ (l) + 80O_2\ (g) \longrightarrow 57CO_2\ (g) + 52H_2O\ (g)$$

$\Delta H = -31150$ kJ

Calculate the change in the internal energy ΔE (in kJ) for this combustion process.

$$\Delta n = n_f - n_i = (52+57) - 80 = 29$$

$$P\Delta V = \Delta n\, RT = 29 \text{ x } 8.314 \text{ x } 373 = 89932.5\ J = 89.93\ kJ$$

$$\Delta E = \Delta H - P\Delta V = -31150 - 89.93 = -31240\ kJ$$

Thermo chemical 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.

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

Thermo chemical 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?

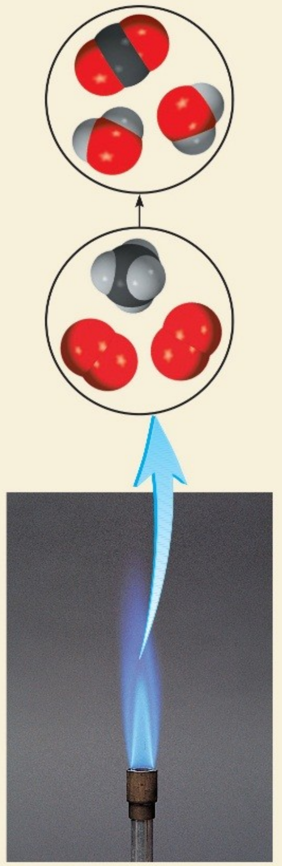
$$\mathbf{P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s) \quad \Delta H = -3013\ kJ/mol}$$

$$266\ \cancel{\text{g P}_4} \times \frac{1\ \cancel{\text{mol}}\ \text{P}_4}{123.9\ \cancel{\text{g P}_4}} \times \frac{3013\ \text{kJ}}{1\ \cancel{\text{mol P}_4}} = -\ 6470\ \text{kJ}$$

Example 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:

$$2CO_2(g) + O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -566.0 \text{ kJ/mol}$$



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Carbon monoxide burns in air to form carbon dioxide

Solution

From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

Δn = number of moles of product gas – number of moles reactant gases

$= 2 - 3 \quad = -1$

Using 8.314 J/K· mol for *R* and T = 298K in Equation , we write

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

$$= -566.0\,\text{kJ} / \text{mol} - (8.314\text{J/K} \cdot \text{mol})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(298\,\text{K})(-1) = -563.6\,\text{kJ} / \text{mol}$$

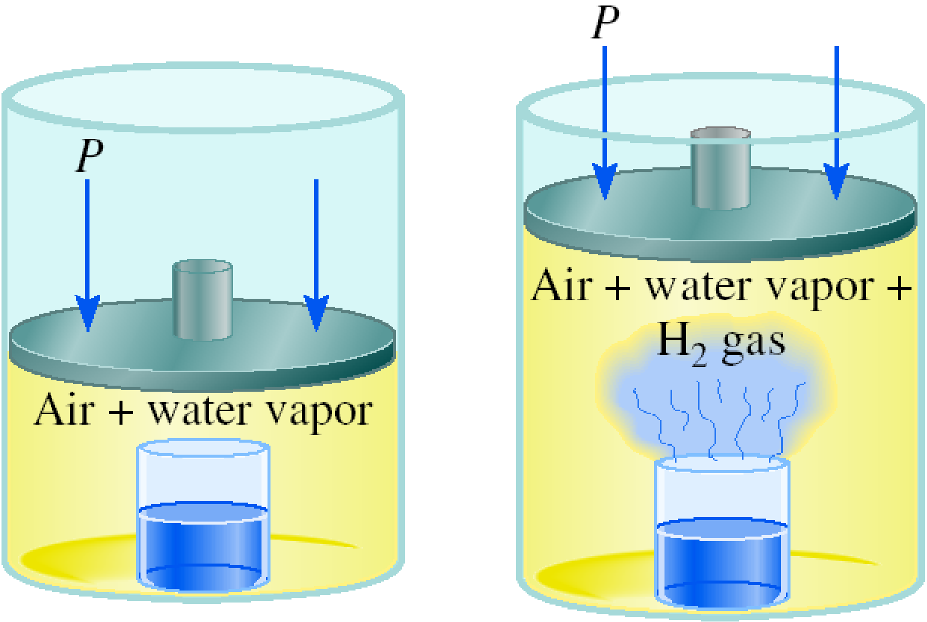
A Comparison of ΔH and ΔE

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

$\Delta E = \Delta H - P\Delta V$ At 25 ^{o}C, 1 mole $\mathrm{H_2}$ = 24.5 L at 1 atm

$P\Delta V = 1\ \mathrm{atm} \times 24.5\ \mathrm{L} = 2.5\ \mathrm{kJ}$

$\Delta E = -367.5\ \mathrm{kJ/mol} - 2.5\ \mathrm{kJ/mol} = -370.0\ \mathrm{kJ/mol}$



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.

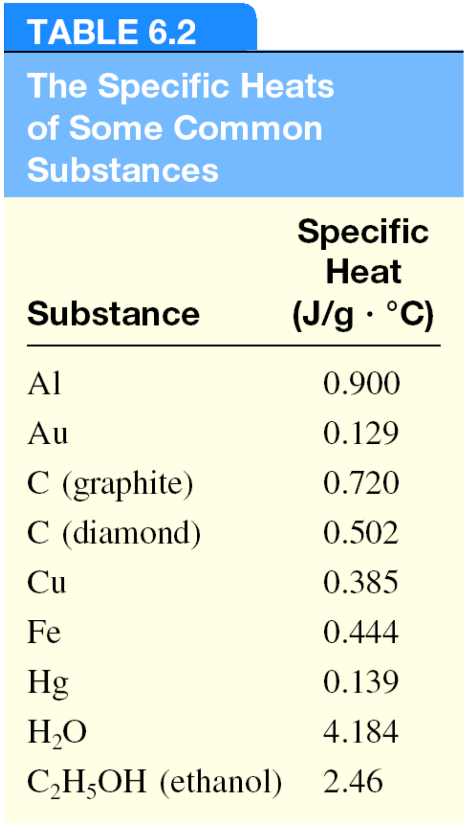


TABLE 6.2

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

$$C = m \text{ x } s$$

<u>Heat (*q*) absorbed or released:</u>

$$q = m \text{ x } s \text{ x } \Delta t$$

$$q = C \text{ x } \Delta t$$

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

Heat Capacity and Specific Heat

Specific heat, then, is

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

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

(a) How much heat is needed to warm 250 g of water from 22 °C to 98 °C? (b) What is the molar heat capacity of water?

(a) $\Delta T = 98\,^{o}C - 22\,^{o}C = 76\,^{o}C = 76\ K$

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

$q = (4.18\ J/g\text{-}K)(250\ g)(76\ K) = 7.9 \times 10^4\ J$

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

(b) 1 mol H_2O = 18 g H_2O

$C_m = (4.18\ J/g\text{-}K)(18\ g/mol) = 75.2\ J/mol\text{-}K$

Example 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C.

Calculate the amount of heat absorbed (in kilojoules) by the water.

Solution

Using Equation , we write

$$q = ms\,\Delta\text{t}$$

$$= (466\text{ g})(4.184\text{ J}/\text{g}\cdot{}^{\circ}\text{C})(74.60^{\circ}\text{C} - 8.50^{\circ}\text{C})$$

$$= 1.29\times 10^{5}\text{ J}\times\frac{1\text{ kJ}}{1000\text{ J}}$$

$$= 129\text{ kJ}$$

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

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

$$q = ms\Delta t = 869\ \cancel{\text{g}}\ \text{x}\ 0.444\ \text{J/}\cancel{\text{g}}\bullet{}^{\circ}\text{C}\ \cancel{\text{x}} -89^{\circ}\text{C}\ \ \diagup\ \ = -34{,}000\ \text{J}$$

- **What is the specific heat of a substance if 1560 cal are required to raise the temperature of a 312g sample by 15°C?**

A) 0.033 cal/g°C

B) 0.33 cal/g°C

C) 1.33 cal/g°C

D) 0.99 cal/g°C

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.

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 Formation and Reaction

How to calculate ΔH_f^o

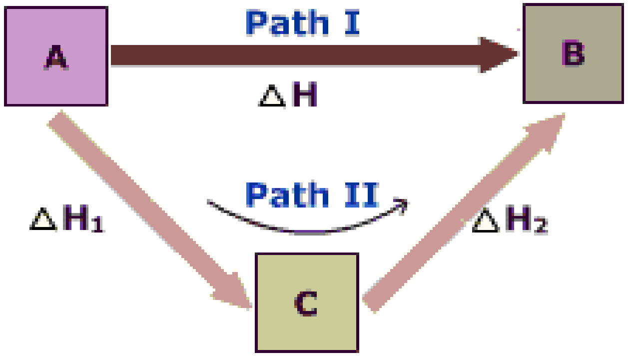
1- Direct method **2- indirect method**

1- Direct method: by standard heat of formation

$$\Delta H^o = \sum n\ \Delta H_f^o\ (\text{products}) - \sum n\ \Delta H_f^o\ (\text{reactants})$$

n = no. of moles in the balanced thermochemical equation

2- The Indirect Method (Hess's Law)



Standard Enthalpy of Formation and Reaction

1- The direct Method

- **Suppose we want to know the enthalpy of formation of carbon dioxide.**
- **We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:**

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

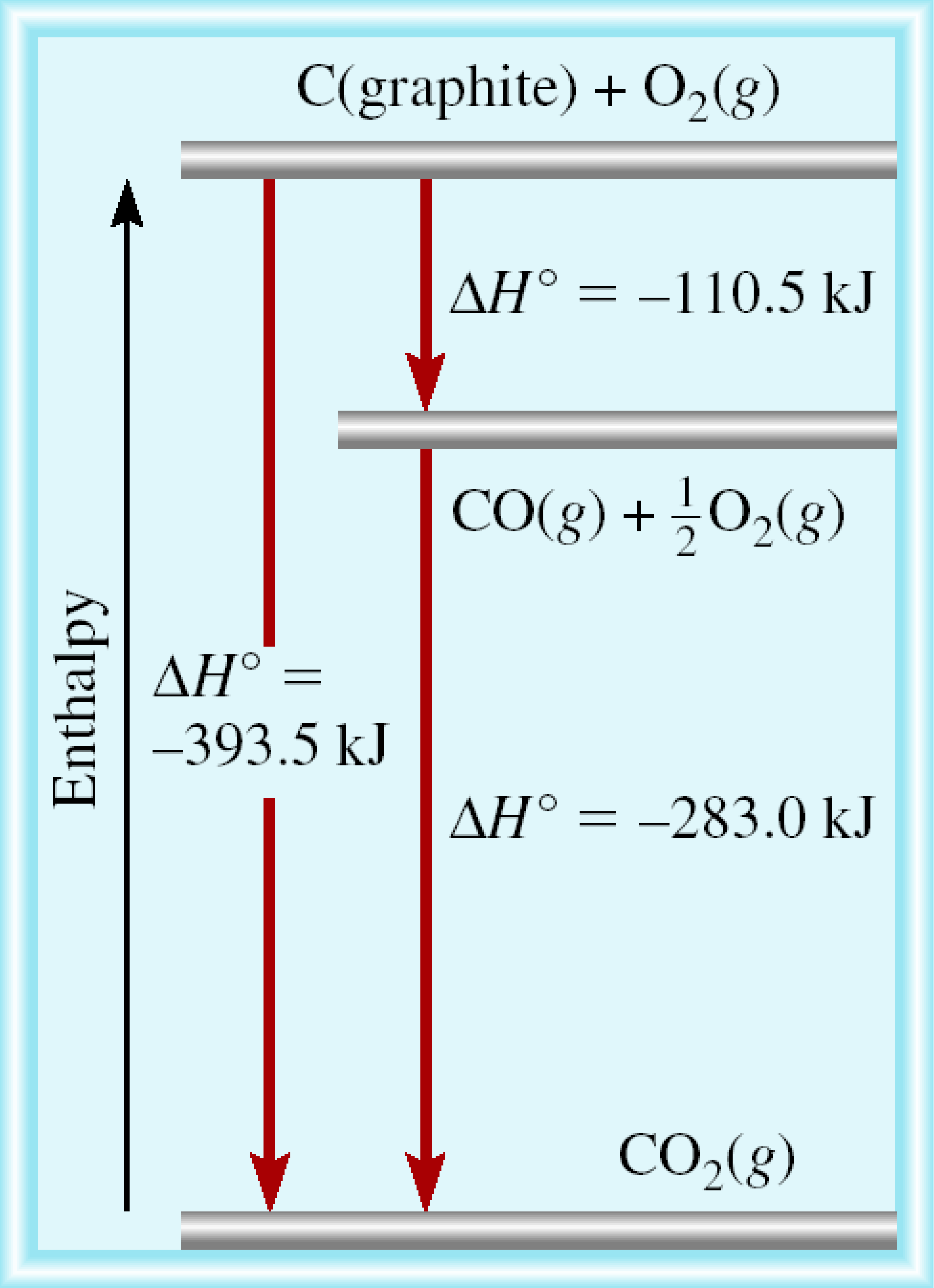
$$\Delta H^0_{\mathrm{rxn}} = \Sigma n \Delta H^0_f\,(\mathrm{products}) - \Sigma m \Delta H^0_f\,(\mathrm{reactants})$$

$$\begin{aligned}\Delta H^\circ_{\mathrm{rxn}} &= \Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) - [\Delta H^\circ_{\mathrm{f}}(\mathrm{C, graphite}) + \Delta H^\circ_{\mathrm{f}}(\mathrm{O_2}, g)] \\ &= -393.5\ \mathrm{kJ/mol}\end{aligned}$$

$$\Delta H^\circ_{\mathrm{rxn}} = \Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) = -393.5\ \mathrm{kJ/mol}$$

or

$$\Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) = -393.5\ \mathrm{kJ/mol}$$



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

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

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

Standard Enthalpy of Formation and Reaction

2- The Indirect Method (Hess's Law)

- **Many compounds cannot be directly synthesized from their elements.**
- **The reaction proceeds too slowly, or side reactions produce substances other than the desired compound.**

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.)

Example 6.9

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

$$2\mathrm{C}(\text{graphite}) + \mathrm{H_2}(g) \rightarrow \mathrm{C_2H_2}(g)$$

The equations for each step and the corresponding enthalpy changes are

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

$$(\mathrm{b})\ \ \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{H_2O}(l) \qquad \Delta H^{\circ}_{\text{rxn}} = -285.8\ \text{kJ/mol}$$

$$(\mathrm{c})\ \ 2\mathrm{C_2H_2}(g) + 5\mathrm{O_2}(g) \rightarrow 4\mathrm{CO_2}(g) + 2\mathrm{H_2O}(l) \quad \Delta H^{\circ}_{\text{rxn}} = -2598.8\,\text{kJ/mol}$$

Example 6.9

Solution

Looking at the synthesis of C_2H_2, we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get

$$(d)\ \ 2C(\text{graphite}) + 2O_2(g) \rightarrow 2CO_2(g)\ \ \Delta H^\circ_{\text{rxn}} = 2(-393.5\ \text{kJ/mol})$$

$$= -787.0\ \text{kJ/mol}$$

Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole C_2H_2 of as a product.

Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:

$$(e)\qquad 2CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + \frac{5}{2}O_2(g)\ \ \Delta H^\circ_{\text{rxn}} = \frac{1}{2}(2598.8\ \text{kJ/mol})$$

$$= 1299.4\ \text{kJ/mol}$$

Adding Equations (d), (b), and (e) together, we get

$$2\mathrm{C}(\text{graphite}) + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(\mathrm{g}) \qquad \Delta H^\circ_{\mathrm{rxn}} = -787.0\ \mathrm{kJ/mol}$$

$$\mathrm{H}_2(g) + \frac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{H}_2\mathrm{O}(l) \qquad \Delta H^\circ_{\mathrm{rxn}} = -285.8\ \mathrm{kJ/mol}$$

$$\underline{2\mathrm{CO}_2(g) + \mathrm{H}_2\mathrm{O}(l) \rightarrow \mathrm{C}_2\mathrm{H}_2(g) + \frac{5}{2}\mathrm{O}_2(g) \quad \Delta H^\circ_{\mathrm{rxn}} = 1299.4\ \mathrm{kJ/mol}}$$

$$2\mathrm{C}(\text{graphite}) + \mathrm{H}_2(g) \rightarrow \mathrm{C}_2\mathrm{H}_2(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = 226.6\ \mathrm{kJ/mol}$$

Therefore,

$$\Delta H^\circ_{\mathrm{f}} = 226.6\,\mathrm{kJ/mol}$$

This value means that when 1mole of C_2H_2 is synthesized from 2 moles of C(graphite) and 1mole of H_2, 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

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

$C(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g) \qquad \Delta H^0_{rxn} = -393.5\ \text{kJ/mol}$

$S(\text{rhombic}) + O_2\,(g) \longrightarrow SO_2\,(g) \qquad \Delta H^0_{rxn} = -296.1\ \text{kJ/mol}$

$CS_2(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g) \qquad \Delta H^0_{rxn} = -1072\ \text{kJ/mol}$

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.

$C(\text{graphite}) + \cancel{O_2}\,(g) \longrightarrow \cancel{CO_2}\,(g) \qquad \Delta H^0_{rxn} = -393.5\ \text{kJ/mol}$

$2S(\text{rhombic}) + 2\cancel{O_2}\,(g) \longrightarrow 2\cancel{SO_2}\,(g) \qquad \Delta H^0_{rxn} = -296.1\ \text{kJ/mol} \times 2$

$+\ \cancel{CO_2}(g) + 2\cancel{SO_2}\,(g) \longrightarrow CS_2\,(l) + 3\cancel{O_2}\,(g) \qquad \Delta H^0_{rxn} = +1072\ \text{kJ/mol}$

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

$$\Delta H^0_{rxn} = -393.5 + (2x-296.1) + 1072 = 86.3\ \text{kJ/mol}$$

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.

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

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f\,(\text{products}) - \Sigma m\Delta H^0_f\,(\text{reactants})$$

$$\Delta H^0_{rxn} = [12\Delta H^0_f\,(CO_2) + 6\Delta H^0_f\,(H_2O)] - [2\Delta H^0_f\,(C_6H_6)]$$

$$\Delta H^0_{rxn} = [12\text{x}{-393.5} + 6\text{x}{-187.6}] - [2\text{x}49.04] = -5946\text{ kJ}$$

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

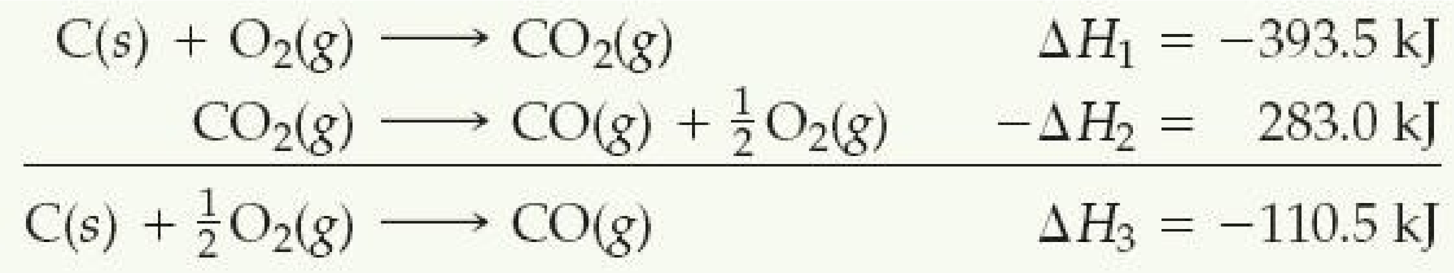
The enthalpy of reaction for the combustion of C to CO_2 is –393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is –283.0 kJ/mol CO:

(1) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H_1 = -393.5$ kJ

(2) $CO_{(g)} + 0.5\ O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H_2 = -283.0$ kJ

Using these data, calculate the enthalpy for combustion of C to CO:

(3) $C_{(s)} + 0.5\ O_{2(g)} \longrightarrow CO_{(g)}$ $\Delta H_3 = ?$ kJ



$$\begin{array}{llr}
C(s) + O_2(g) \longrightarrow CO_2(g) & & \Delta H_1 = -393.5\text{ kJ} \\
CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) & & -\Delta H_2 = 283.0\text{ kJ} \\
\hline
C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) & & \Delta H_3 = -110.5\text{ kJ}
\end{array}$$

Example 6.10

© Orgo-Thermite

The thermite reaction involves aluminum and iron(III) oxide

$$2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(l)$$

This reaction is highly exothermic and the liquid iron formed is used to weld metals.

The molten iron formed in a thermite reaction is run down into a mold between the ends of two railroad rails. On cooling, the rails are welded together.

Calculate the heat released in

per gram of Al reacted with Fe_2O_3.

The ΔH_f° for Fe (l) is 12.40 kJ / mol.

Example 6.10

Solution

Using the given $\Delta \mathrm{H}_f^\circ$ value for Fe(*l*) and other ΔH_f° values in Appendix 3 and Equation (6.18), we write

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= \left[\Delta H_f^\circ(\mathrm{Al_2O_3})\right] + 2\Delta H_f^\circ(\mathrm{Fe}) - \left[2\Delta H_f^\circ(\mathrm{Al}) + \Delta H_f^\circ(\mathrm{Fe_2O_3})\right] \\ &= \left[(-1669.8\ \mathrm{kJ/mol}) + 2(12.40\,\mathrm{kJ/mol})\right] - \left[2(0) + (-822.2\,\mathrm{kJ/mol})\right] \\ &= -822.8\ \mathrm{kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. We use the following ratio

$$\frac{-822.8\,\mathrm{kJ}}{2\,\mathrm{mol\,Al}}$$

to convert to kJ/g Al.

The molar mass of Al is 26.98 g, so

$$\text{heat released per gram of Al} = \frac{-822.8\ \mathrm{kJ}}{2\ \mathrm{mol\ Al}} \times \frac{1\ \mathrm{mol\ Al}}{26.98\ \mathrm{g\ Al}}$$

$$= 15.25\ \mathrm{kJ/g}$$

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Chemistry in Action: Bombardier Beetle Defense

$C_6H_4(OH)_2\ (aq) + H_2O_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + 2H_2O\ (l)\quad \Delta H^0 = ?$

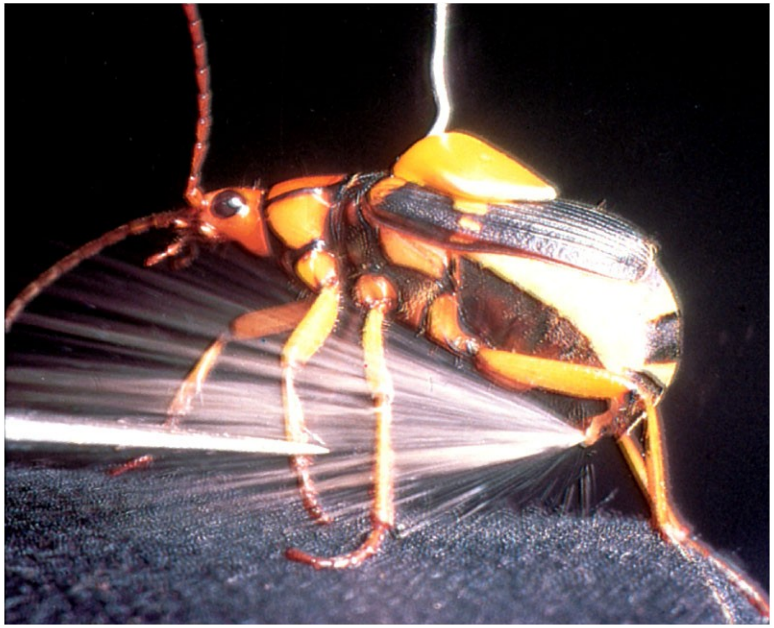
$C_6H_4(OH)_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + H_2\ (g)\quad \Delta H^0 = 177$ kJ/mol

$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \tfrac{1}{2}O_2\ (g)\quad \Delta H^0 = -94.6$ kJ/mol

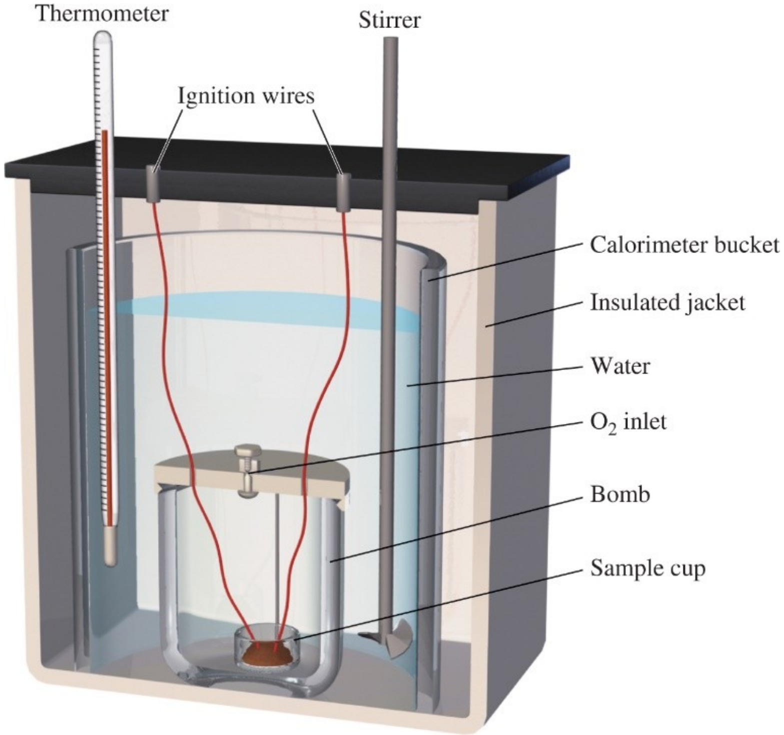
$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \longrightarrow H_2O\ (l)\quad \Delta H^0 = -286$ kJ/mol

$\Delta H^0 = 177 - 94.6 - 286 = -204$ kJ/mol

Exothermic!



Constant-Volume Calorimetry



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

$$q_{sys} = 0$$

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

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

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

No heat enters or leaves!

Reaction at Constant V

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

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

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EXAMPLE 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C. If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta t \\ &= (10.17\ \text{kJ/°C})(25.95\text{°C} - 20.28\text{°C}) \\ &= 57.66\ \text{kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is -57.66 kJ. This is the heat released by the combustion of 1.435 g of $C_{10}H_8$; therefore, we can write the conversion factor as

$$\frac{-57.66\ \text{kJ}}{1.435\ \text{g}\ C_{10}H_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66\ \text{kJ}}{1.435\ \cancel{\text{g}\ C_{10}H_8}} \times \frac{128.2\ \cancel{\text{g}\ C_{10}H_8}}{1\ \text{mol}\ C_{10}H_8} \\ &= -5.151 \times 10^3\ \text{kJ/mol} \end{aligned}$$

Chemistry in Action:

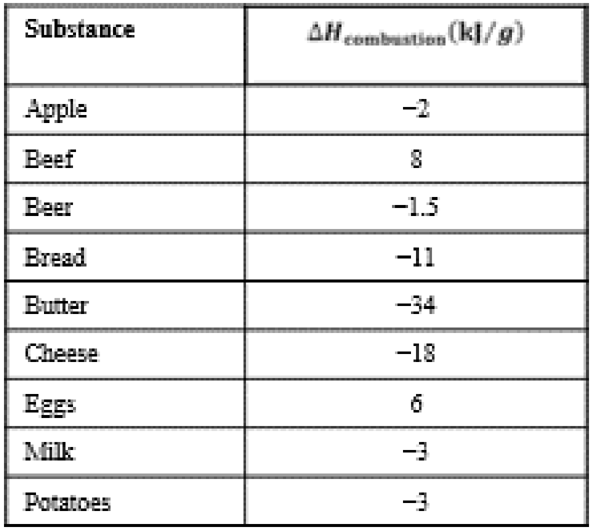
Fuel Values of Foods and Other Substances

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

1 cal = 4.184 J

1 cal = 1000 cal = 4184 J

Fuel Values of Foods



Substance	$\Delta H_{\text{combustion}}$ (kJ/g)
Apple	−2
Beef	8
Beer	−1.5
Bread	−11
Butter	−34
Cheese	−18
Eggs	6
Milk	−3
Potatoes	−3

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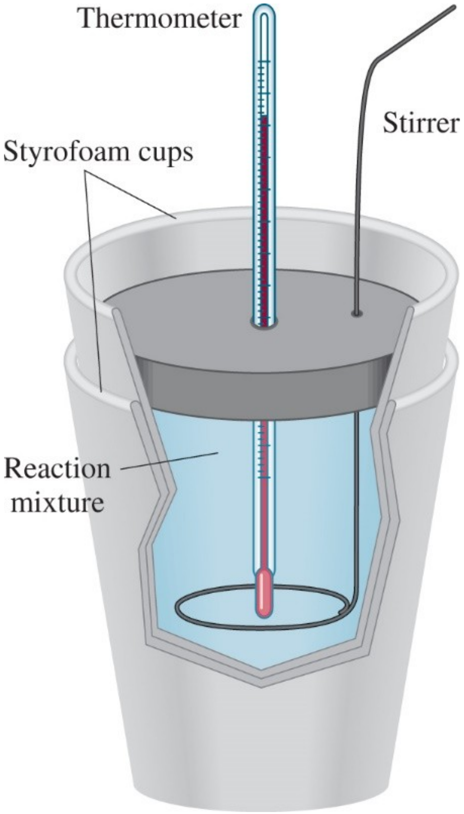
Constant-Pressure Calorimetry



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

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

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

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

Reaction at Constant *P*

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

No heat enters or leaves!

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EXAMPLE 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{Pb} + q_{H_2O} = 0$$

or

$$q_{Pb} = -q_{H_2O}$$

The heat gained by the water is given by

$$q_{H_2O} = ms\Delta t$$

where m and s are the mass and specific heat and $\Delta t = t_{final} - t_{initial}$. Therefore,

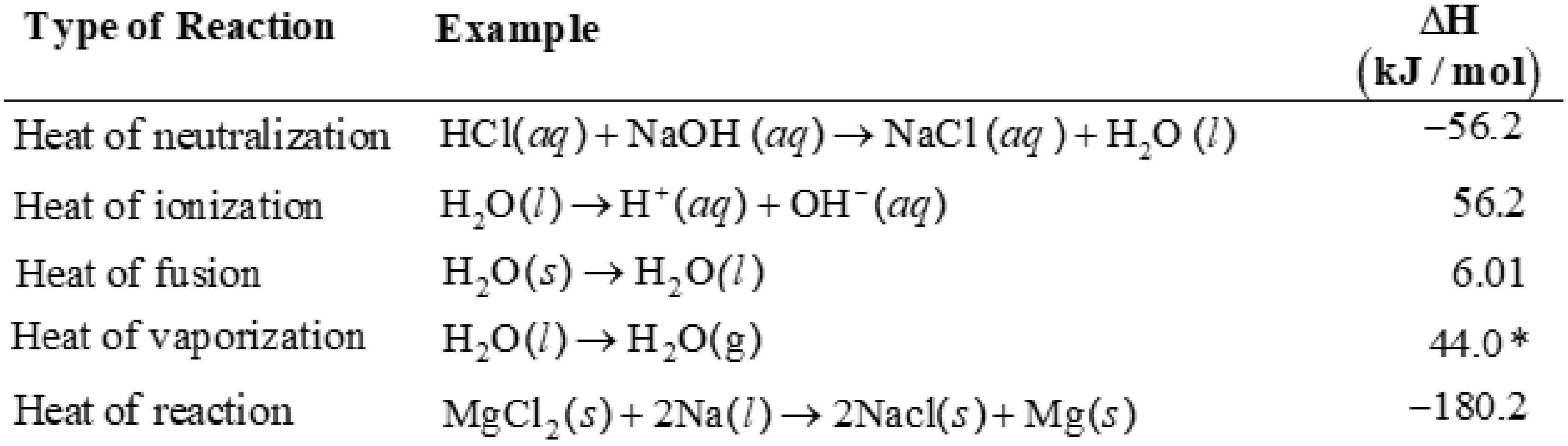
$$\begin{aligned} q_{H_2O} &= (100.0\ g)(4.184\ J/g \cdot °C)(23.17°C - 22.50°C) \\ &= 280.3\ J \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, so $q_{Pb} = -280.3$ J. Solving for the specific heat of Pb, we write

$$\begin{aligned} q_{Pb} &= ms\Delta t \\ -280.3\ J &= (26.47\ g)(s)(23.17°C - 89.98°C) \\ s &= 0.158\ J/g \cdot °C \end{aligned}$$

Some Heats of Reaction

Table 6.3 Heats of Some Typical Reactions Measured at Constant Pressure



Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$	-56.2
Heat of ionization	$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \rightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \rightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \rightarrow 2Nacl(s) + Mg(s)$	-180.2

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EXAMPLE 6.8

A quantity of 1.00×10^2 mL of 0.500 *M* HCl was mixed with 1.00×10^2 mL of 0.500 *M* NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g · °C, respectively).

Strategy Because the temperature rose, the neutralization reaction is exothermic. How do we calculate the heat absorbed by the combined solution? What is the heat of the reaction? What is the conversion factor for expressing the heat of reaction on a molar basis?

Solution Assuming no heat is lost to the surroundings, $q_{\mathrm{sys}} = q_{\mathrm{soln}} + q_{\mathrm{rxn}} = 0$, so $q_{\mathrm{rxn}} = -q_{\mathrm{soln}}$, where q_{soln} is the heat absorbed by the combined solution. Because

(Continued)

the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g. Thus,

$$\begin{aligned} q_{\text{soln}} &= ms\Delta t \\ &= (1.00 \times 10^2\ \text{g} + 1.00 \times 10^2\ \text{g})(4.184\ \text{J/g} \cdot {}^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3\ \text{J} \\ &= 2.81\ \text{kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81$ kJ.

From the molarities given, the number of moles of both HCl and NaOH in 1.00×10^2 mL solution is

$$\frac{0.500\ \text{mol}}{1\ \text{L}} \times 0.100\ \text{L} = 0.0500\ \text{mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

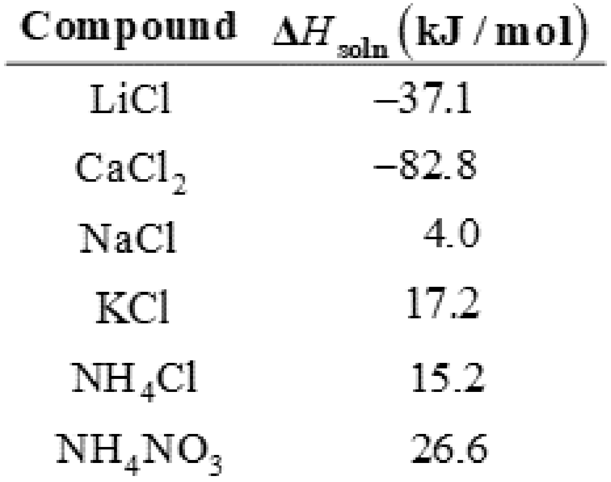
$$\text{heat of neutralization} = \frac{-2.81\ \text{kJ}}{0.0500\ \text{mol}} = -56.2\ \text{kJ/mol}$$

Enthalpy of Solution

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

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

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	26.6

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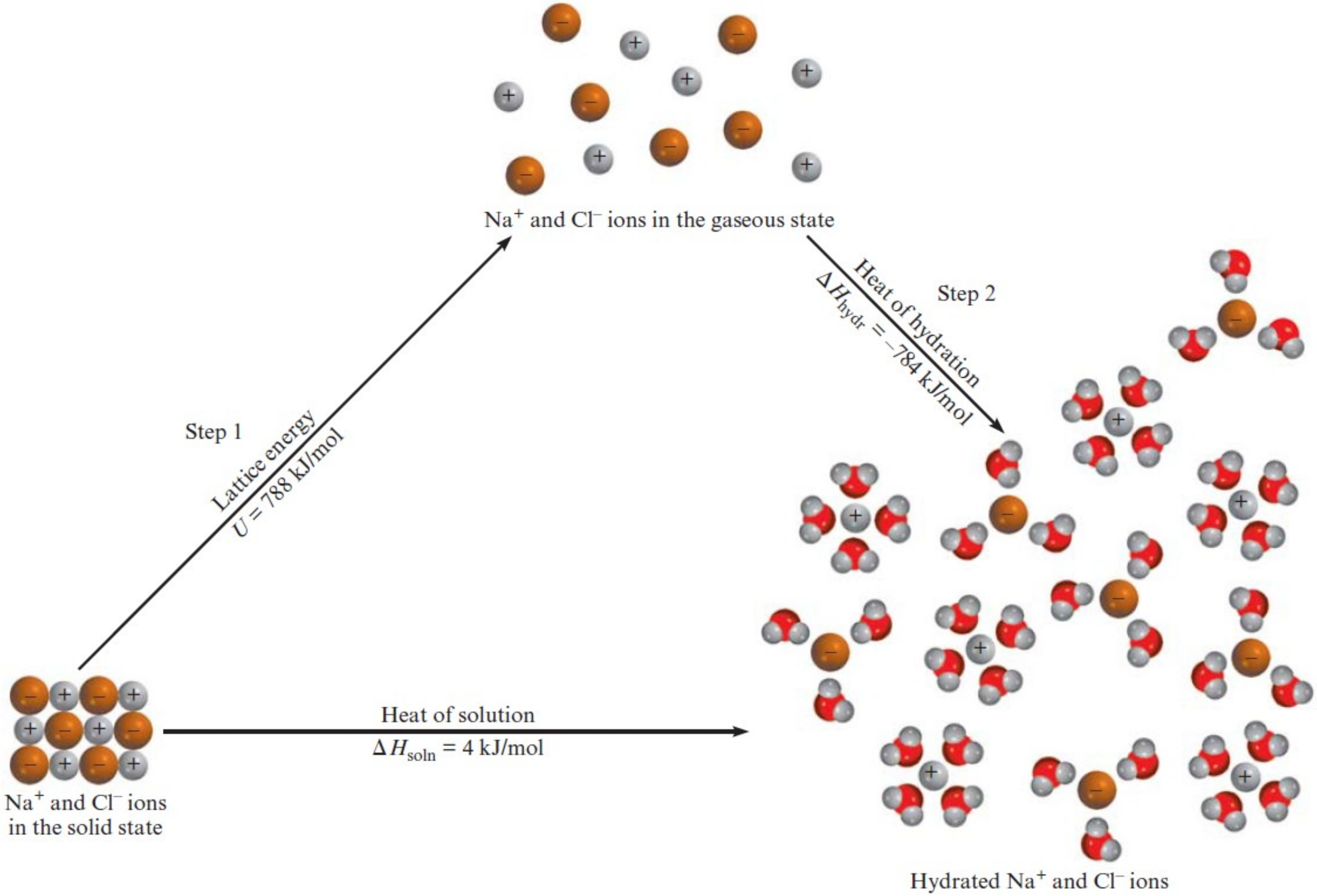
The Solution Process for NaCl



$$\Delta \boldsymbol{H}_{\text{sol}} = \text{step 1} + \text{step 2} = 788 - 784 = 4\ \text{kJ} / \text{mol}$$

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Question 1

An exothermic reaction causes the surroundings to:

A. become basic
B. decrease in temperature
C. condense
D. increase in temperature
E. decrease in pressure

Question 2

How much heat is evolved when 320 g of SO_2 is burned according to the chemical equation shown below?

$2\ SO_2(g) + O_2(g) \text{--->} 2\ SO_3(g)\ \Delta H^{o}_{rxn} = -198\ kJ$

A. 5.04×10^{-2} kJ
B. 9.9×10^{2} kJ
C. 207 kJ
D. -5.0×10^{2} kJ
E. None of the above

Question 3

The specific heat of aluminum is 0.214 cal/g.°C. Determine the energy, in calories necessary to raise the temperature of a 55.5 g piece of aluminum from 23.0 to 48.6°C.

A. 109 cal
B. 273 cal
C. 577 cal
D. 347 cal
E. 304 cal

Question 4

Energy is the ability to do work and can be:

A. converted to one form to another
B. can be created and destroyed
C. used within a system without consequences
D. none of the above

Question 5

To which one of the following reactions, occurring at 25°C, does the symbol ΔH^{o}_{f} $[H_2SO_4(l)]$ refer?

A. $H_2(g) + S(s) + 2\ O_2(g) \text{ ----> } H_2SO_4(l)$
B. $H_2SO_4(l) \text{ ----> } H_2(g) + S(s) + 2\ O_2(g)$
C. $H_2(g) + S(g) + 2\ O_2(g) \text{ ----> } H_2SO_4(l)$
D. $H_2SO_4(l) \text{ ----> } 2\ H(g) + S(s) + 4\ O(g)$
E. $2\ H(g) + S(g) + 4\ O(g) \text{ ----> } H_2SO_4(l)$

Question 6

Given:

$SO_2(g) + \frac{1}{2}O_2(g) \text{ ----> } SO_3(g)$ $\Delta H^{o}_{rxn} = -99$ kJ, what is the enthalpy change for the following reaction?

$2\ SO_3(g) \text{ ----> } O_2(g) + 2\ SO_2(g)$

A. 99 kJ
B. -99 kJ
C. 49.5 kJ
D. -198 kJ
E. 198 kJ

Question 7

Calculate ΔH^{o}_{rxn} for the combustion reaction of CH_4 shown below given the following:

$\Delta H^{o}f\ CH_4(g) = -74.8$ kJ/mol;
$\Delta H^{o}f\ CO_2(g) = -393.5$ kJ/mol;
$\Delta H^{o}f\ H_2O(l) = -285.5$ kJ/mol.
$CH_4(g) + 2\ O_2(g) \text{ ----> } CO_2(g) + 2\ H_2O(l)$

A. -604.2 kJ
B. 889.7 kJ
C. -997.7 kJ
D. -889.7 kJ
E. None of the above

Question 8

Find the standard enthalpy of formation of ethylene, $C_2H_4(g)$, given the following data:

$C_2H_4(g) + 3\ O_2(g) \text{ ----> } 2\ CO_2(g) + 2\ H_2O(l)$
$\Delta H^{o}_{rxn} = -1411$ kJ
$C(s) + O_2(g) \text{ ----> } CO_2(g)$ $\Delta H^{o}_{f} = -393.5$ kJ
$H_2(g) + \frac{1}{2}O_2(g) \text{ ----> } H_2O(l)$ $\Delta H^{o}_{f} = -285.8$ k

A. 731 kJ
B. 2.77 x 103 kJ
C. 1.41 x 103 kJ
D. 87 kJ