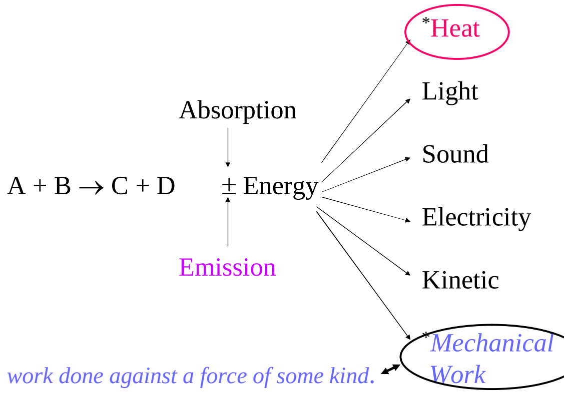
CHAPTER 5

Thermochemistry



$A + B \rightarrow C + D$ ± Energy

Absorption

Emission

*Heat

Light

Sound

Electricity

Kinetic

*Mechanical Work

work done against a force of some kind.

Definitions

Thermodynamics:

Transformation of energy from one form to another.

Thermochemistry:

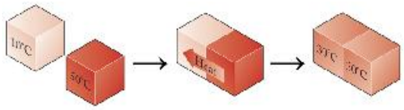
Energy in the form of heat consumed or produced by chemical reactions.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ ± heat energy

Energy: Heat and/or Work

Heat:

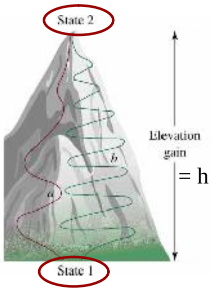
Energy transferred between objects because of a difference in their temperatures.



Work: $w = F \times d$

Mechanical work (w) is done when a force (F) moves an object through a distance (d).

Work and Energy (PE)



Gain in gravitational potential energy (PE) = mgh

Moving from the bottom to top of the mountain results in the gain of PE, and vice versa.

Potential Energy: is due to position in a force field (or chemical composition in a chemical system) and PE can be converted to work:

$$PE = m \; g \; h$$

m = mass, g = force of gravity, and h = vertical distance

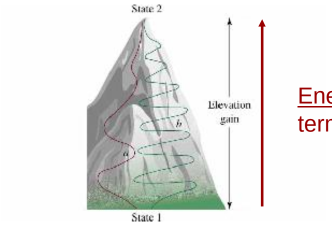
Kinetic Energy: is due to the motion of the object(s).

$KE = {}^1/_2\, mu^2$ (m = mass, u = velocity)

Chemical energy is a form of potential energy

Potential Energy: A State Function

PE depends only on the difference between initial and final state of the system. Independent of path between states.



Energy 'stored' is termed potential energy.

The Nature of Energy

Law of Conservation of Energy:

Energy can be neither created nor destroyed.

However energy can be converted from *one form to another* (technology accomplishes this task).

Potential energy → kinetic energy (KE), …..

Chemical Potential energy → heat, …..

Energy at the Molecular Level

KE at molecular level depends on:

mass and velocity of the particle, molecular motion changes with *T* .

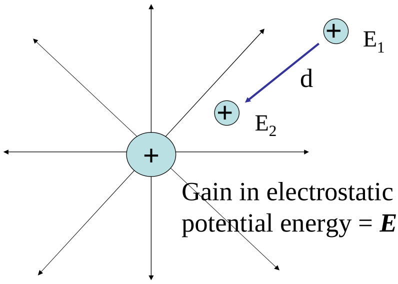
$$KE = \frac{1}{2}mu^2 = \frac{3}{2}kT$$

PE at molecular level: depends on electrostatic attractions:

$$E_{el} \sim \frac{Q_1 Q_2}{d}$$

E_{el} is electrostatic energy, Q_1 and Q_2 are charges, separated by distance, *d*.

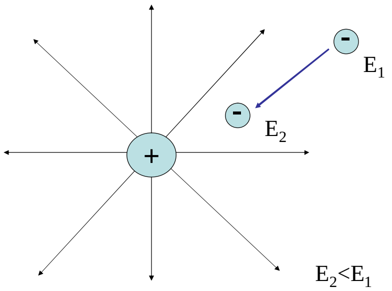
Unit charge



Gain in electrostatic potential energy = ***E***d

$E_2 > E_1$

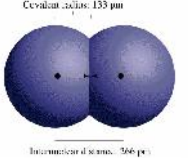
Unit charge



$E_2 < E_1$

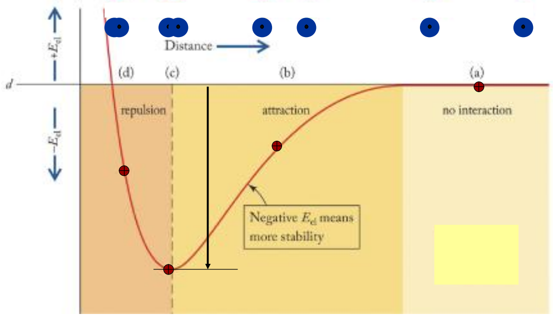
Attractions leads to lowering of energy and stability. All processes seek stability.

Formation of a covalent bond: H-H

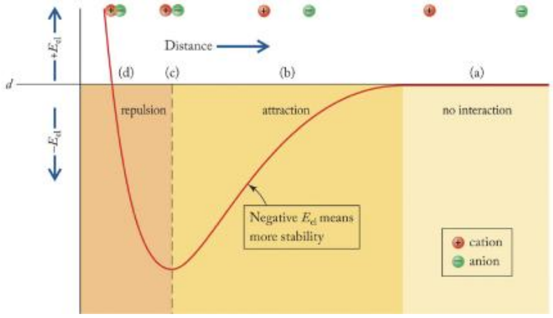


Chemical Potential Energy is due to attractions and repulsions between electrons and nuclei in the molecule; by virtue of their positions in the molecule.

Energetics of Bond Formation: e.g. H_2 molecule



Electrostatic Potential Energy; ionic solids



Terms Describing Energy Transfer

System: The part of the universe that is the focus of a thermodynamic study.

Classified as; isolated / open / closed

Surroundings: Everything in the universe that is not part of the system.

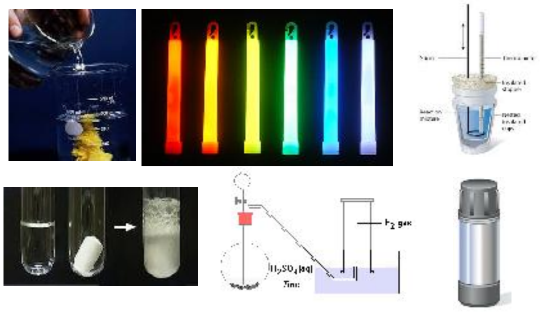
Universe = System + Surroundings

Examples

(a) Isolated system: A thermos bottle containing hot soup with the lid screwed on tightly

(b) Closed system: A cup of hot soup with a lid

(c) Open system: An open cup of hot soup



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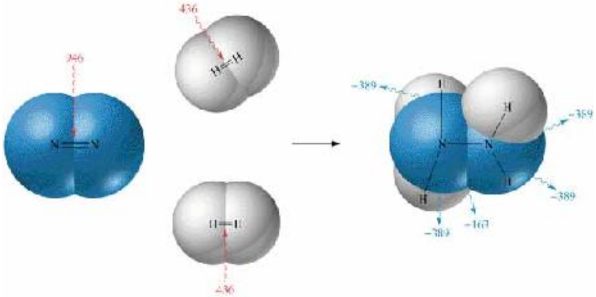
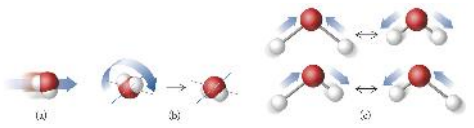
Example of a chemical reaction



$$N_2 + 2H_2 \rightarrow N_2H_4$$

Internal Energy, E (PE + KE)

Internal energy of a system = sum of all motional energy and PE of all components of the system.



Different types of molecular motion contribute to overall internal energy: (a) translational (KE), (b) rotational, and (c) vibrational.

The chemical potential energy (due to the attractions and repulsions between electrons and nuclei) of the reactants *will be different from* that of the products.

Reactants → Products

$E_{reactants}$ $E_{products}$

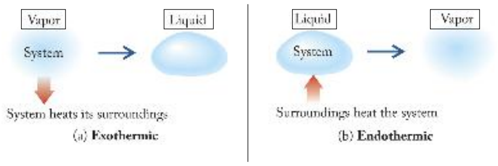
If $E_p \neq E_r$ then ΔE $= E_p - E_r$

The ΔE is the energy ***associated*** with the reaction.

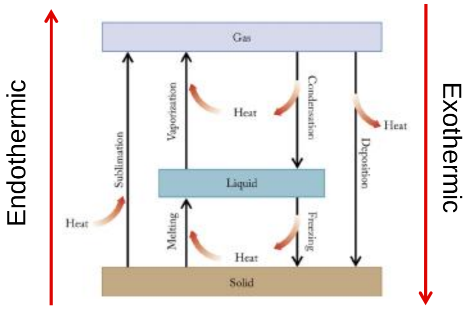
Heat Flow

Exothermic process: Heat flows out of the system to surroundings ($q < 0$).

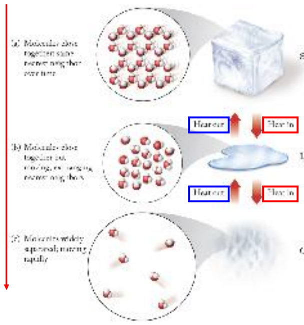
Endothermic process: Heat flows into the system from surroundings ($q > 0$).



Phase Changes and Heat Flow



Energy and Phase Changes

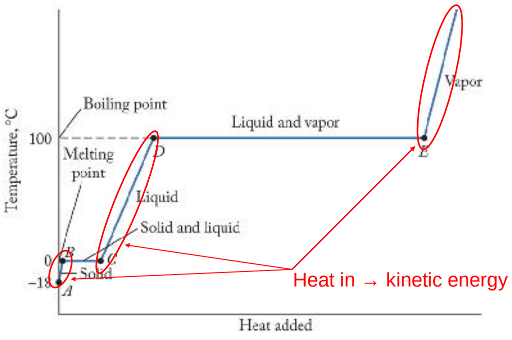


Absorbed heat increases kinetic energy of molecules.

Release of heat decrease kinetic energy molecules.

$$\frac{1}{2}m(u_2^2 - u_1^2) = \frac{3}{2}k(T_2 - T_1)$$

Heating Curves



Heat in → kinetic energy

First Law of Thermodynamics

First Law of Thermodynamics is the
Law of Conservation of Energy!

Energy of the universe is constant!

$E_{Universe} = E_{system} + E_{surroundings}$ = constant

So the energy *gained or lost by a system* must ***equal*** the energy *lost or gained by surroundings*.

Law of Conservation of energy.

All processes involve energy changes.

Overall sum of energy change however is zero.

The loss of energy by one part is equal to the energy gained by another part; overall, energy is conserved (meaning neither created/destroyed)

The energy can, and often changes it’s form; thermal, kinetic, light, mechanical work, etc. and its ‘form’.

Units of Energy

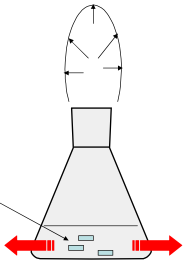
Calorie (cal):

The amount of heat necessary to raise the temperature of 1 g of water 1°C.

Joule (J):

The SI unit of energy. 4.184 J = 1 cal.

Energy = heat and/or work (same units!).



System

Surrounding

Pushes air outward
System works against the atmosphere = w, system expends (loses) energy.
w<0

Loss of heat.
System loses energy in the form of heat.
q<0

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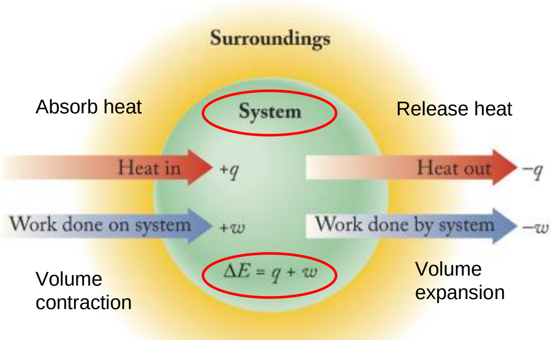


Absorb heat

Release heat

Volume contraction

Volume expansion

Net change in internal energy, ΔE, of a process is the sum of heat exchanges, q, and work exchanges, w, of the system with the surroundings.

Change in Internal Energy

$\Delta E = q + w$:

ΔE = change in system's internal energy

q = heat; $q<0$ for loss from system

w = work; $w<0$ for work done by system

Work (mechanical) : $w = -P\Delta V = -P(V_f - V_i)$

where P = pressure, ΔV = change in volume.

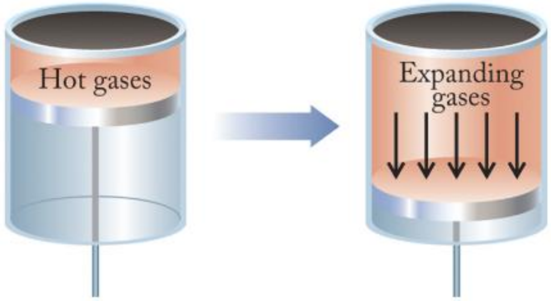
Work done by the system is energy lost by the system (added to the surroundings), hence the negative sign.

Problem: Calculation of Work

Calculate the work in L·atm and joules associated with the expansion of a gas in a cylinder from 54 L to 72 L at a constant external pressure of 18 atm. (Note: 1 L·atm = 101.32 J)

Sample Exercise 5.2

Figure shows a simplified version of a piston and cylinder in an engine. Suppose combustion of fuel injected into the cylinder produces 155 J of energy. The hot gases in the cylinder expand, pushing the piston down. In doing so, the gases do 93 J of *P–V* work on the piston. If the system is the gases in the cylinder, what is the change in internal energy of the system?



Chemistry: The Science in Context 3/e Figure 5.19
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Sample Exercise 5.2 (cont.)

- The system (gases in the cylinder) absorbs energy, so $q > 0$, and the system does work on the surroundings (the piston), so $w < 0$.

$$\Delta E = q + w = (155\ \text{J}) + (-93\ \text{J}) = 62\ \text{J}$$

- More energy enters the system (155 J) than leaves it (93 J), so a positive value of ΔE is reasonable.

Sample Exercise 5.3

A tank of compressed helium is used to inflate balloons for sale at a carnival on a day when the atmospheric pressure is 1.01 atm. If each balloon is inflated from an initial volume of 0.0 L to a final volume of 4.8 L, how much *P–V* work is done by 100 balloons on the surrounding atmosphere when they are inflated? The atmospheric pressure remains constant during the filling process.

Sample Exercise 5.3 (cont.)

- Each of 100 balloons goes from empty ($V = 0.0$ L) to 4.8 L, which means $\Delta V = 4.8$ L, and the atmospheric pressure P is constant at 1.01 atm. The identity of the gas used to fill the balloons doesn't matter, because under normal conditions all gases behave the same way, regardless of their identity. Our task is to determine how much P–V work is done by the 100 balloons on the air that surrounds them.

Sample Exercise 5.3 (cont.)

- Focus on the work done on the atmosphere (the surroundings) by the system; the balloons and the helium they contain are the system.
- The volume change (ΔV) as all the balloons are inflated I

100 balloons × 4.8 L/balloon = 480 L

The work (w) done by our system (the balloons) as they inflate against an external pressure of 1.01 atm is

$$w = -P\Delta V = 1.01\ \text{atm} \times 480\ \text{L}$$
$$= -480\ \text{L}\cdot\text{atm}$$

Because the work is done *by* the system on its surroundings, the work is negative from the point of view of the system:

$$w = -480\ \text{L}\cdot\text{atm.}$$

Enthalpy and Change in Enthalpy

Enthalpy $H = E + PV$

Change in Enthalpy $\Delta H = \Delta E + P\Delta V$

ΔH = change in enthalpy; energy flows as heat at constant pressure

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

$\Delta H > 0$, Endothermic; $\Delta H < 0$, Exothermic

Add subscripts to indicate ΔH for specific process or part of the universe; *e.g.*, ΔH_{vap}, ΔH_{rxn}, ΔH_{sys}.

$\Delta H < 0$ - exothermic

$\Delta H > 0$ - endothermic

Exothermic reactions are generally spontaneous when run at constant pressure.

Add subscripts to indicate ΔH for specific process or part of the universe; *e.g.*, ΔH_{vap}, ΔH_{sys}.ΔH_{f}, ΔH_{comb}, ΔH_{fus} (Usually per mole of substance).

ΔH_{rxn} for the reaction as written.

Heat Capacities

Molar heat capacity (c_p) is the heat required to raise the temperature of 1 mole of a substance by 1°C at constant pressure.

→ $q = nc_p\Delta T$ (c_p = J/(mol·°C)

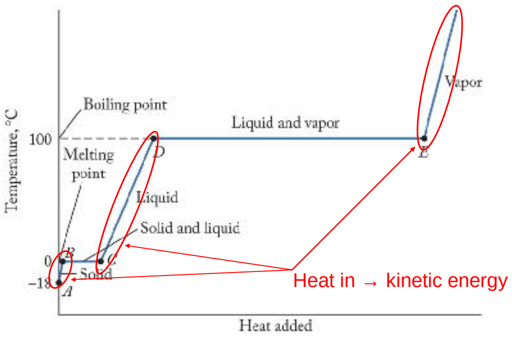
Specific heat (c_s) is the heat required to raise the temperature of 1 gram of a substance by 1°C at constant pressure.

→ $q = mc_s\Delta T$ (c_s = J/(g·°C)

Heat capacity (C_p) is the quantity of heat needed to raise the temperature of some specific object by 1°C at constant pressure.

→ $q = C_p\Delta T$ (C_p = J/°C)

Heating Curves



Heat in → kinetic energy

Calculating Energy Through a Change in State

Molar heat of fusion:

ΔH_{fus} = heat needed to convert 1 mole of a solid at its melting point to 1 mole of liquid.

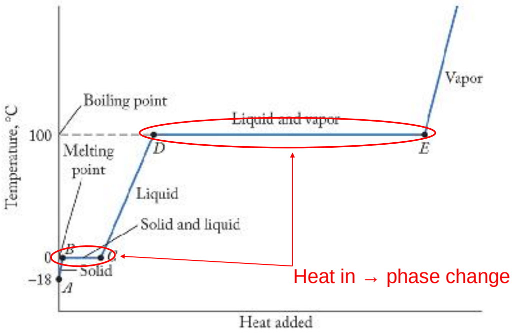
$q = n\Delta H_{fus}$

Molar heat of vaporization:

ΔH_{vap} = heat needed to convert 1 mole of a liquid at its boiling point to 1 mole of vapor.

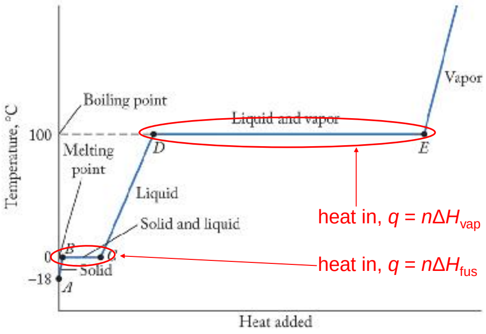
$q = n\Delta H_{vap}$

Heating Curves



Heat in → phase change

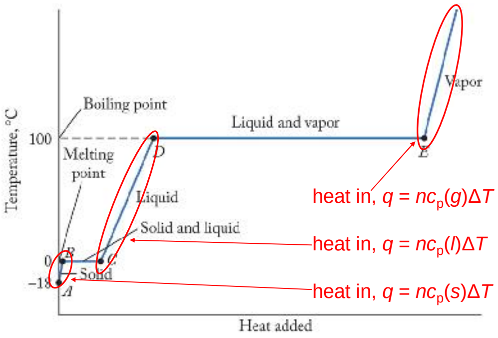
Heating Curves



heat in, $q = n\Delta H_{vap}$

heat in, $q = n\Delta H_{fus}$

Heating Curves

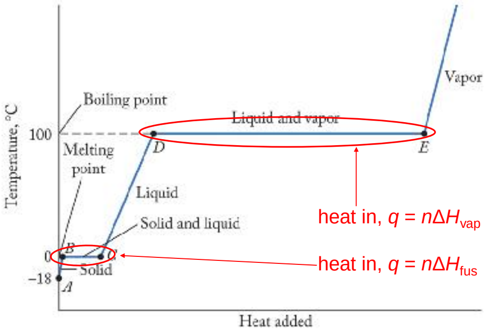


heat in, $q = nc_p(g)\Delta T$

heat in, $q = nc_p(l)\Delta T$

heat in, $q = nc_p(s)\Delta T$

Heating Curves



heat in, $q = n\Delta H_{vap}$

heat in, $q = n\Delta H_{fus}$

Calorimetry

Calorimetry = measurement of heat.

Typically, measuring change in heat that accompanies a physical change or chemical process.

A calorimeter is a device used to measure the absorption or release of heat, by a physical or chemical process (system).

$$-q_{system} = q_{calorimeter}$$

For objects the heat change is calculated using;

Heat = mass × specific heat × Change in Temperature

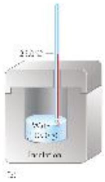
$q = m\, c_S\, \Delta T$

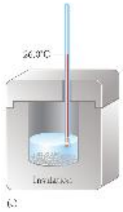
Example: Heat exchange measurements

(a) 23.5 g of Al beads are heated to 100.0°C in boiling water.

(heat transferred from water to Al until the final temp of Al beads = 100.0°C)

(b) The Al beads (at 100°C) are placed in a Styrofoam box calorimeter containing 130.0 g of water at 23.0°C.





(c) Heat is transferred from Al beads to water until they reach a thermal equilibrium at 26.0°C; heat lost by Al = heat gained by H_2O.

$$-q_{\text{aluminum}} = q_{\text{water}}$$

$$-m_{\text{Al}} c_{s(\text{Al})} \Delta T_{\text{Al}} = m_{\text{water}} c_{s(\text{water})} \Delta T_{\text{water}}$$

Heat (Enthalpy) of Reaction ΔH_{rxn}

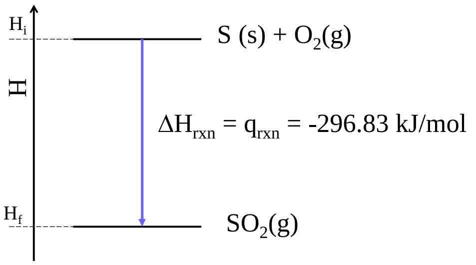
Heat of reaction:

Also known as enthalpy of reaction (ΔH_{rxn}).

The heat absorbed or released by a chemical reaction performed at constant pressure.

Enthalpies of Reactions: ΔH_{rxn}

$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H_{\text{rxn}} = -296.83$ kJ



H_i

H

$S(s) + O_2(g)$

$\Delta H_{\text{rxn}} = q_{\text{rxn}} = -296.83$ kJ/mol

H_f

$SO_2(g)$

For *exothermic* reactions, the *products are below the reactants* on an energy diagram; by an amount equal to the ΔH_{rxn} and vice versa.

$$\Delta H = H_f - H_i$$
$$\Delta H = \Delta H_{rxn}$$
$$\Delta H_{rxn} = H_f - H_i < 0$$
$$H_f < H_i$$

$$\Delta H_{rxn} = H_f - H_i$$
$$H_i = H_f - \Delta H_{rxn}$$

For *endothermic* reactions, the *products are above the reactants on an energy diagram*; by an amount equal to the ΔH_{rxn}.

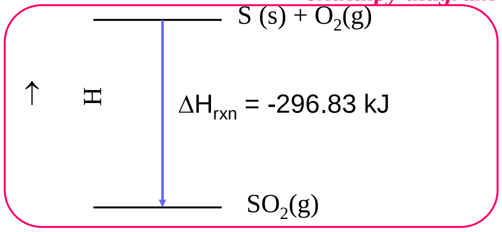
$$\Delta H = H_f - H_i$$
$$\Delta H = \Delta H_{rxn}$$
$$\Delta H_{rxn} = H_f - H_i > 0$$
$$H_f > H_i$$

Enthalpies of Reactions: ΔH_{rxn}

thermochemical equation

$$\boxed{S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H_{rxn} = -296.83\ \text{kJ}}$$

enthalpy diagram



S (s) + O_2(g)

↑ H

ΔH_{rxn} = -296.83 kJ

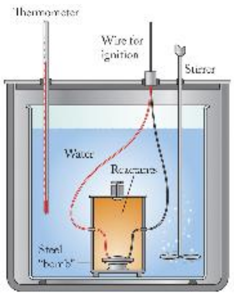
SO_2(g)

Measuring Heats of Reaction (ΔH_{rxn})

A calorimeter is a device used to measure the heat of a reaction. Mix known quantities of reactants in the calorimeter.

Heat produced by reaction = heat gained by calorimeter contents

$q_{rxn} = -q_{cal} = -C_{p.cal}\Delta T$



Calculation of q_{rxn} and ΔH_{rxn}

As a good approximation

- mass of the system = m_{water}
- specific heat capacity of water =4.184 J g^{-1} $^oC^{-1}$.

ΔT = temperature change of water

$q_{rxn} = - q_{water} = - c_s\, m_{water}\, \Delta T = - C_{p,cal}\, \Delta T$

$$\Delta H_{rxn} = \frac{q_{rxn}}{n}$$

n= # moles of limiting reactant

Heat of Reaction

Heat of reaction:

Also known as enthalpy of reaction (ΔH_{rxn}).

The heat absorbed or released by a chemical reaction.

Standard Heat of reaction:

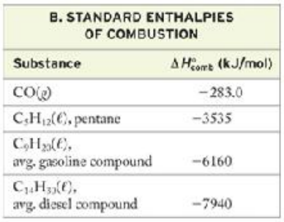
Also known as standard enthalpy of reaction (ΔH^0_{rxn}).

The heat absorbed or released by a chemical reaction where ractants and products are at standard state.

Heat of Combustion

Reaction = combustion

Some Standard Enthalpies of Combustion $\Delta H_{rxn} = \Delta H_{comb}°$



B. STANDARD ENTHALPIES OF COMBUSTION

Substance	ΔH°_{comb} (kJ/mol)
CO(*g*)	−283.0
C_5H_{12}(ℓ), pentane	−3535
C_9H_{20}(ℓ), avg. gasoline compound	−6160
$C_{14}H_{30}$(ℓ), avg. diesel compound	−7940

Enthalpy of Formation of Elements

The standard enthalpy of formation, $\Delta H_f°$:

Standard enthalpy of formation of elements at standard states is zero by definition.

(The standard state of a substance is its most stable form under 1 bar pressure and at 25°C.)

Enthalpy of Formation of a Compound

The standard enthalpy of formation, $\Delta H_f°$:

A formation reaction is the process of forming 1 mole of a substance in its standard state from its component elements in their standard states.

For example, formation reaction for water:

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$\Delta H_{rxn} = \Delta H_f°(H_2O)$

(The standard state of a substance is its most stable form under 1 bar pressure and at 25°C.)

Methods of Determining ΔH_{rxn}

1. From calorimetry experiments:

   $q_{rxn} = -C_{p,cal} \Delta T$ *then q/n* Ĝ ΔH_{rxn}

2. From enthalpies of formation:

   $\Delta H_{rxn}° = \Sigma n_p \Delta H_f°(\text{products}) - \Sigma n_r \Delta H_f°(\text{reactants})$

   $\Delta H_f°$ values for substances in Appendix 4.

3. Using Hess's Law (Section 5.8).

Problem: Using $\Delta H_f°$ to Find $\Delta H_{rxn}°$

Use Table 5.2 to calculate an approximate enthalpy of reaction for

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l).$$

$\Delta H_f°$ to Find $\Delta H_{rxn}°$

One step in the production of nitric acid is the combustion of ammonia. Use data in Appendix 4 to calculate the enthalpy of this reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Fuel Values

- Amount of energy (in kJ/g) from combustion reaction.

  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

  ΔH_{comb} = - 802.3 kJ/mol

  Fuel value = (802.3 kJ/mol)·(1 mol/16.04 g)
  = 50.02 kJ/g

- Fuel Density:

  For liquid fuels, energy released in kJ/L.

Fuel Values (cont.)

Compound	Molecular Formula	Fuel Value (kJ/g)*
Methane	CH_4	50.0
Ethane	C_2H_6	47.6
Propane	C_3H_8	46.3
Butane	C_4H_{10}	45.8
* Based on the formation of H_2O (*g*)		

Food Values

- Amount of energy produced when food is burned completely:
    - Determined by bomb calorimetry.
    - Nutritional Calorie = 1 kcal = 4.184 kJ.

Food Category	Food Value (Cal or kcal)	Food Value (kJ)
Proteins	4.0	16.7
Carbohydrates	4.0	16.7
Fats	9.0	37.7

Hess's Law:

Enthalpy (and enthalpy change) is a state function. Value of ΔH is independent of the steps taken to accomplish a process.

The overall ΔH_{rxn} of a reaction is therefore equal to the sum of the ΔH's for the steps/sequence of reactions that accomplishes the same overall reaction.

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + ...$$

Hess's Law of heat of summation: The Δ*H* of a reaction that is the sum of two or more reactions is equal to the sum of the Δ*H* values of the constituent reactions.

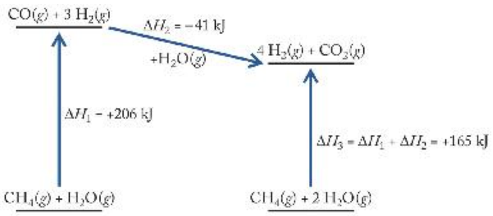
1. $CH_4(g) + H_2O(g) \rightarrow \cancel{CO}(g) + 3\cancel{H_2}(g)$ ΔH_1=206
2. $C\cancel{O(g)} + 3\cancel{H_2}(g) + H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$ ΔH_2= -41

---

3. $CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$ ΔH_3=

$$\Delta H_3 = \Delta H_1 + \Delta H_2 = 165$$

Hess's Law (cont.)



Calculations Using Hess's Law

1. If a reaction is reversed, Δ*H* sign changes.

   $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = 180$ kJ

   $2NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H = -180$ kJ

2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.

   $6NO(g) \rightarrow 3N_2(g) + 3O_2(g)$ $\Delta H = 3(-180 \text{ kJ})$

   $\Delta H = -540$ kJ

Strategy in using Hess's law;

Recognize how the 'target reaction' is made from the other reactions.

Manipulate(×, +, - or ÷) the balanced equations (and their associated ΔH values) to arrive at the target equation.

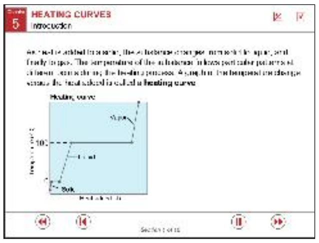
Problem: Using Hess's Law

Using the following data, calculate the enthalpy change for the reaction:

Target Reaction: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

	ΔH_{rxn}
$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	−285.8 kJ
$C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)$	−1411 kJ
$C_2H_6(g) + 7/2O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$	−1560 kJ

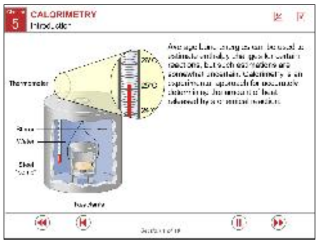
ChemTour: Heating Curves



Click here to launch this ChemTour

In this ChemTour, students use interactive heating curve diagrams to explore phase changes, heat of fusion, and heat of vaporization. Macroscopic views of ice melting and water boiling are shown in sync with the appropriate sections of the heating curve. It includes Practice Exercises.

ChemTour: Calorimetry



Click here to launch this ChemTour

This ChemTour demonstrates how a bomb calorimeter works and walks students through the equations used to solve calorimetry problems. It includes an interactive experiment.

Sample Exercise 5.8

Which of the following reactions are formation reactions at 25°C? For those that are not, explain why not.

a. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ ò

b. $C_{graphite}(s) - 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(\ell)$ Ĕ

(CH₃OH is methanol, a liquid in its standard state.)

c. $CH_4(g) - 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ $\Delta H^0_{comb,CH4}$

d. $P_4(s) + 2O_2(g) + 6Cl_2(g) \rightarrow 4POCl_3(\ell)$ x

(P_4 is a solid in its standard state; Cl_2 is a gas, and $POCl_3$ is a liquid.)

Sample Exercise 5.9

Using the appropriate values from Table 5.2, calculate $\Delta H°_{rxn}$ for the combustion of the fuel propane (C_3H_8) in air.

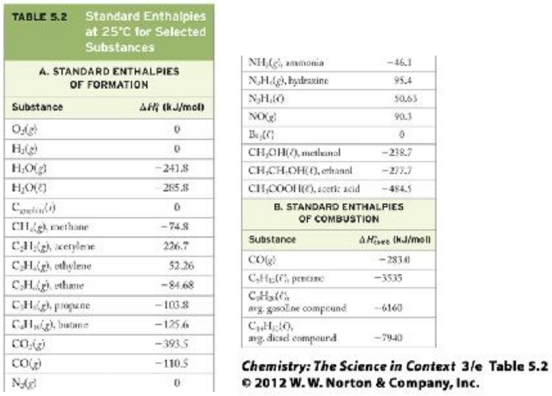


TABLE 5.2 Standard Enthalpies at 25°C for Selected Substances

A. STANDARD ENTHALPIES OF FORMATION	
Substance	ΔH°_f (kJ/mol)
$O_2(g)$	0
$H_2(g)$	0
$H_2O(g)$	−241.8
$H_2O(\ell)$	−285.8
$C_{graphite}(s)$	0
$CH_4(g)$, methane	−74.8
$C_2H_2(g)$, acetylene	226.7
$C_2H_4(g)$, ethylene	52.26
$C_2H_6(g)$, ethane	−84.68
$C_3H_8(g)$, propane	−103.8
$C_4H_{10}(g)$, butane	−125.6
$CO_2(g)$	−393.5
$CO(g)$	−110.5
$N_2(g)$	0
$NH_3(g)$, ammonia	−46.1
$N_2H_4(g)$, hydrazine	95.4
$N_2H_4(\ell)$	50.63
$NO(g)$	90.3
$Br_2(\ell)$	0
$CH_3OH(\ell)$, methanol	−238.7
$CH_3CH_2OH(\ell)$, ethanol	−277.7
$CH_3COOH(\ell)$, acetic acid	−484.5
B. STANDARD ENTHALPIES OF COMBUSTION	
Substance	ΔH°_{comb} (kJ/mol)
$CO(g)$	−283.0
$C_5H_{12}(\ell)$, pentane	−3535
$C_9H_{20}(\ell)$, avg. gasoline compound	−6160
$C_{14}H_{30}(\ell)$, avg. diesel compound	−7940

Chemistry: The Science in Context 3/e Table 5.2

Sample Exercise 5.9 (cont.)

. We need the balanced equation for combustion of propane:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(\ell)$$

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

Sample Exercise 5.9 (cont.)

- Inserting ΔH°_f values for the products [$CO_2(g)$ and $H_2O(\ell)$] and reactants [$C_3H_8(g)$ and $O_2(g)$] from Table 5.2 and the coefficients in the balanced chemical equation into last equation, we get

$$\begin{aligned}\Delta H_{rxn} &= [(3\,\cancel{mol}\,CO_2)(-393.5\text{ kJ}/\cancel{mol}) + (4\,\cancel{mol}\,H_2O)(-285.8\text{ kJ}/\cancel{mol})] \\ &\quad - [(1\,\cancel{mol}\,C_3H_8)(-103.8\text{ kJ}/\cancel{mol}) + (5\,\cancel{mol}\,O_2)(0.0\text{ kJ}/\cancel{mol})] \\ &= -2219.9\text{ kJ}\end{aligned}$$

Sample Exercise 5.12

Hydrocarbons burned in a limited supply of air may not burn completely, and CO(*g*) may be generated. One reason furnaces and hot-water heaters fueled by natural gas need to be vented is that incomplete combustion can produce toxic carbon monoxide:

Reaction A: $2\,CH_4(g) + 3\,O_2(g) \rightarrow 2\,CO(g) + 4\,H_2O(g) \quad \Delta H^\circ_{comb} = ?$

Use the reactions

Reaction B: $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \quad \Delta H^\circ_{comb} = -802\text{ kJ}$

Reaction C: $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g) \quad \Delta H^\circ_{comb} = -566\text{ kJ}$

to calculate the ΔH°_{comb} for reaction A.

Sample Exercise 5.12 (cont.)

- Start with reaction B as written and add the reverse of reaction C, remembering to change the sign of (C) ΔH°_{comb}:

B: $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \quad \Delta H^\circ_{comb} = -802\text{ kJ}$

C (reversed): $2\,CO_2(g) \rightarrow 2\,CO(g) + O_2(g) \quad -\Delta H^\circ_{comb} = -566\text{ kJ}$

Because methane has a coefficient of 2 in reaction A, we multiply all the terms in reaction B, including ΔH°_{comb} (B), by 2:

$$2 \times [CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)] \quad 2[\Delta H^\circ_{comb}(B) = -802\text{ kJ}]$$

Sample Exercise 5.12 (cont.)

Because the carbon monoxide in reaction A has a coefficient of 2, we do not need to multiply reaction C by any factor. Now we add (2 × B) to the reverse of C and cancel out common terms:

$$\begin{array}{lll} 2 \times B: & 2\,CH_4(g) + \overset{3}{\cancel{4}}\,O_2(g) \rightarrow \cancel{2\,CO_2(g)} + 4\,H_2O(g) & \Delta H^\circ_{comb} = -1604\text{ kJ} \\ C\text{ (reversed)}: & \cancel{2\,CO_2(g)} \rightarrow 2\,CO(g) + \cancel{O_2(g)} & \Delta H^\circ_{comb} = +566\text{ kJ} \\ \hline A: & 2\,CH_4(g) + 3\,O_2(g) \rightarrow 2\,CO(g) + 4\,H_2O(g) & \Delta H^\circ_{comb} = -1038\text{ kJ} \end{array}$$