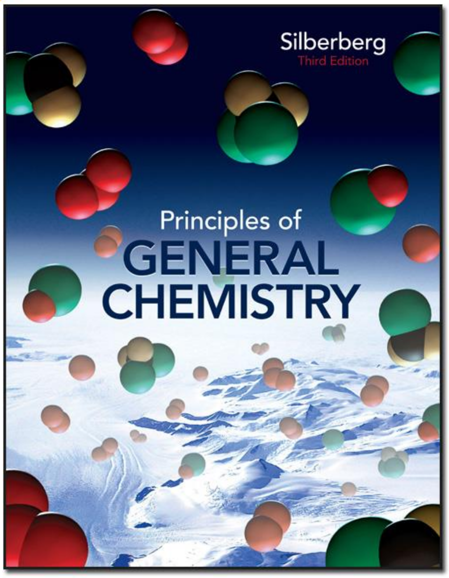


Chapter 06

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 6

Thermochemistry:
Energy Flow and Chemical Change

Thermochemistry: Energy Flow and Chemical Change

Transfer and Interconversion of Energy

Thermodynamics is the study of energy and its transformations.

Thermochemistry is a branch of thermodynamics that deals with the heat involved in chemical and physical changes.

When energy is transferred from one object to another, it appears as ***work*** and ***heat***.

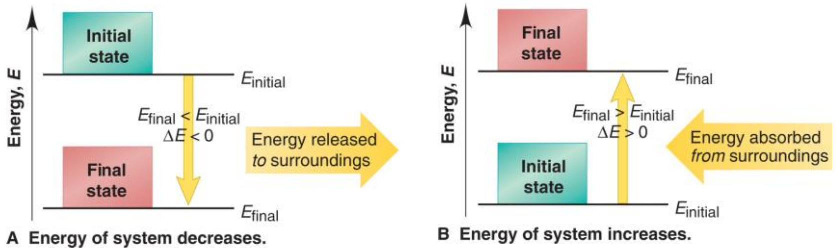
The System and Its Surroundings

A meaningful study of any transfer of energy requires that we first clearly define both the ***system*** and its ***surroundings***.
System + Surroundings = Universe

The ***internal energy***, ***E***, of a system is the sum of the potential and kinetic energies of all the particles present.

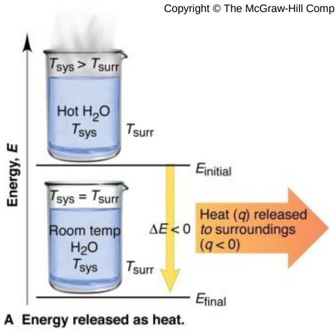
The total energy of the universe remains ***constant***.
A change in the energy of the system must be accompanied by an ***equal*** and ***opposite*** change in the energy of the surroundings.

Figure 6.1 **Energy diagrams for the transfer of internal energy (*E*) between a system and its surroundings.**



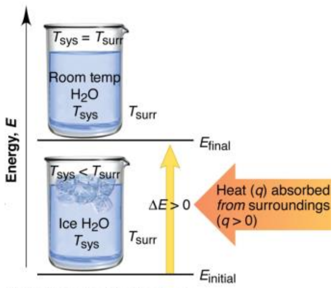
$$\boxed{\Delta E = E_{final} - E_{initial} = E_{products} - E_{reactants}}$$

Figure 6.2 **The two cases where energy is transferred as heat only.**



A Energy released as heat.

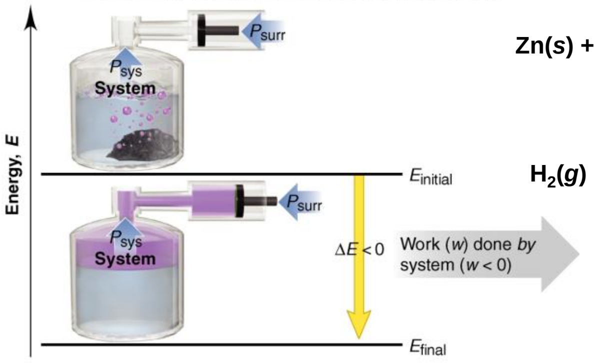
The system releases heat



B Energy absorbed as heat.

The system absorbs heat

Figure 6.3A **The two cases where energy is transferred as work only.**

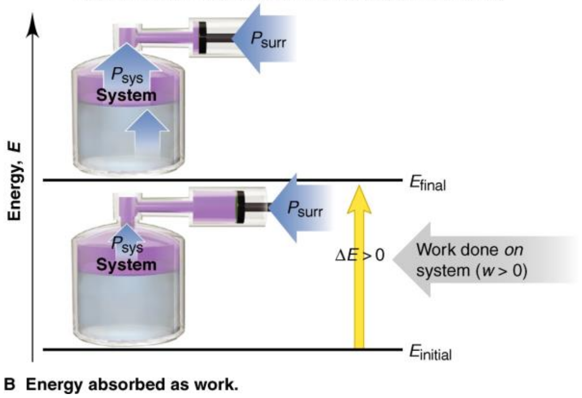


A Energy released as work.

$$Zn(s) + 2H^+(aq) + 2Cl^-(aq) \longrightarrow H_2(g) + Zn^{2+}(aq) + 2Cl^-(aq)$$

The system does work *on* the surroundings.

Figure 6.3B The two cases where energy is transferred as work only.



B Energy absorbed as work.

The system has work done on it *by* the surroundings.

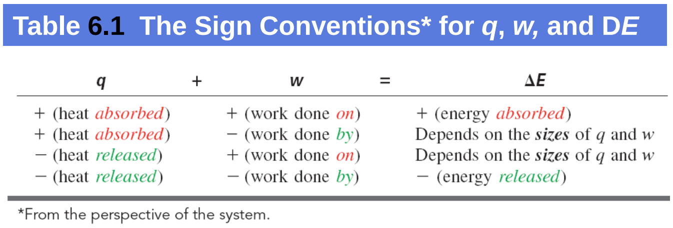


Table 6.1 The Sign Conventions* for *q*, *w*, and DE

q	+	w	=	ΔE
+ (heat *absorbed*)		+ (work done *on*)		+ (energy *absorbed*)
+ (heat *absorbed*)		− (work done *by*)		Depends on the *sizes* of q and w
− (heat *released*)		+ (work done *on*)		Depends on the *sizes* of q and w
− (heat *released*)		− (work done *by*)		− (energy *released*)

*From the perspective of the system.

Which of these are **not state functions**?

A) volume B) temperature C) pressure **D) heat** E) energy

A) internal energy B) volume C) work D) pressure E) enthalpy

A system which undergoes an adiabatic change (i.e., $q = 0$)

A system which undergoes an isothermal change (**i.e., *constant temperature***)

The Law of Energy Conservation

The first law of Thermodynamics states that *the total energy of the universe is constant*.

Energy is conserved, and is neither created nor destroyed.
Energy is transferred in the form of heat and/or work.

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

◀ ▶

Units of Energy

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

$1\ J = 1\ kg{\cdot}m^2/s^2$

The **calorie** was once defined as the quantity of energy needed to raise the temperature of 1 g of water by 1°C.

1 cal = 4.184 J

The **British Thermal Unit (Btu)** is often used to rate appliances.

1 Btu is equivalent to 1055 J.

◀ ▶

Sample Problem 6.1

Determining the Change in Internal Energy of a System

PROBLEM: When gasoline burns in a car engine, the heat released causes the products CO_2 and H_2O to expand, which pushes the pistons outward. Excess heat is removed by the car's radiator. If the expanding gases do 451 J of work on the pistons and the system releases 325 J to the surroundings as heat, calculate the change in energy (ΔE) in J, kJ, and kcal.

PLAN: Define the system and surroundings and assign signs to ***q*** and ***w*** correctly. Then $\Delta E = q + w$. The answer can then be converted from J to kJ and to kcal.

Sample Problem 6.1

SOLUTION:

Heat is given out by a chemical reaction, so it makes sense to define the system as the reactants and products involved. The pistons, the radiator and the rest of the car then comprise the surroundings.

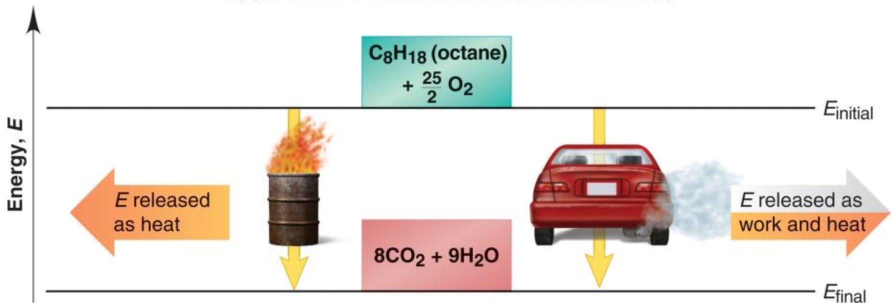
Heat is given out by the system, so ***q* = - 325 J**

The gases expand to push the pistons, so the system does work on the surroundings and ***w* = - 451 J**

$$\Delta E = \mathbf{q} + \mathbf{w} = \quad -325\ \text{J} + (-451\ \text{J}) = \boxed{\mathbf{-776\ J}}$$

$$-776\ \cancel{\text{J}} \times \frac{1\ \text{kJ}}{10^3\ \cancel{\text{J}}} \boxed{\mathbf{= -0.776\ kJ}} \qquad -0.776\ \cancel{\text{kJ}} \times \frac{1\ \text{kcal}}{4.184\ \cancel{\text{kJ}}} \boxed{\mathbf{= -0.185\ kcal}}$$

Figure 6.4 Two different paths for the energy change of a system.



Even though *q* and *w* for the two paths are different, the total ΔE is the same for both.

Enthalpy:
Chemical Change at Constant Pressure

$$w = -P\Delta V$$

$$H = E + PV$$

where H is enthalpy

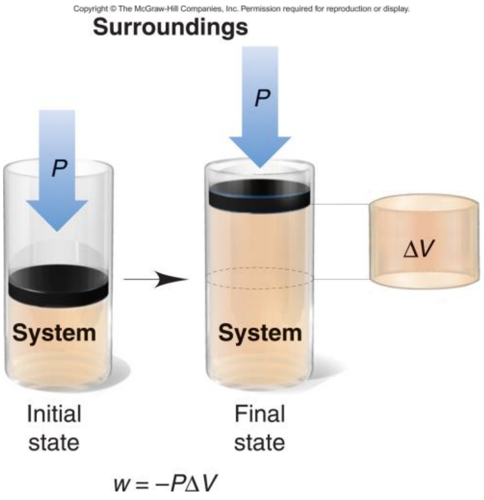
$$\Delta H = \Delta E + P\Delta V$$

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

$\Delta H \approx \Delta E$ in

1. Reactions that do not involve gases.
2. Reactions in which the number of moles of gas does not change.
3. Reactions in which the number of moles of gas does change but q is >>> $P\Delta V$.

Figure 6.5 **Pressure-volume work.**



An expanding gas pushing back the atmosphere does *PV* work (*w* = -*P*Δ*V*).

ΔH as a measure of ΔE

- Δ*H* is the change in heat for a system at ***constant pressure***.

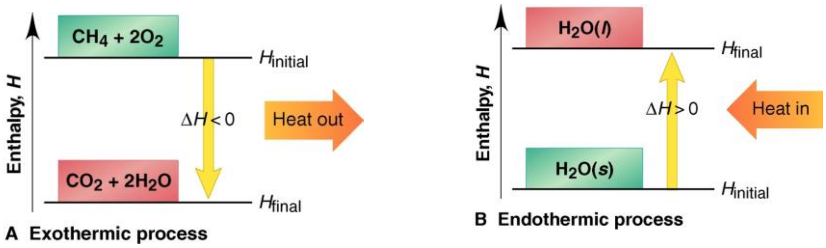
  $$q_P = \Delta E + P\Delta V = \Delta H$$

- $\Delta H \approx \Delta E$
  - for reactions that do not involve gases
  - for reactions in which the total amount (mol) of gas does **not** change
  - for reactions in which q_P is much larger than $P\Delta V$, even if the total mol of gas does change.

Figure 6.6

Enthalpy diagrams for exothermic and endothermic processes.

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



A Exothermic process
Heat is given out.

B Endothermic process
Heat is taken in.

Sample Problem 6.2 **Drawing Enthalpy Diagrams and Determining the Sign of ΔH**

PROBLEM: In each of the following cases, determine the sign of ΔH, state whether the reaction is exothermic or endothermic, and draw an enthalpy diagram.

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 285.8\ \text{kJ}$

(b) $40.7\ \text{kJ} + H_2O(l) \longrightarrow H_2O(g)$

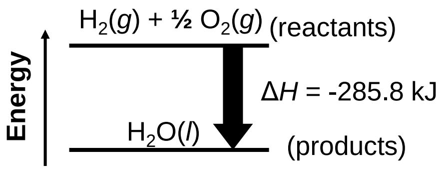
PLAN: From each equation, note whether heat is a “reactant” or a “product”. If heat is taken in as a “reactant”, the process is endothermic. If heat is released as a “product”, the process is exothermic.

For the enthalpy diagram, the arrow always points from reactants to products. For endothermic reactions, the products are at a higher energy than the reactants, since the reactants take in heat to form the products.

Sample Problem 6.2

SOLUTION: **(a)** $H_2(g) + ½O_2(g) \longrightarrow H_2O(l) + 285.8\ kJ$

Heat is a “product” for this reaction and is therefore given out, so the reaction is exothermic. The reactants are at a higher energy than the products.



$H_2(g)$ + ½ $O_2(g)$ (reactants)

Energy

ΔH = -285.8 kJ

$H_2O(l)$

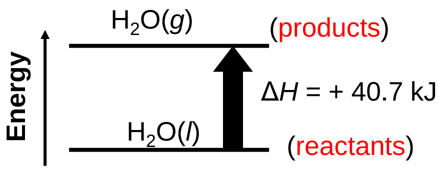
(products)

EXOTHERMIC

Sample Problem 6.2

SOLUTION: **(b)** $40.7\ kJ + H_2O(l) \longrightarrow H_2O(g)$

Heat is a “reactant” in this reaction and is therefore absorbed, so the reaction is endothermic. The reactants are at a lower energy than the products.



$H_2O(g)$

(products)

Energy

ΔH = + 40.7 kJ

$H_2O(l)$

(reactants)

ENDOTHERMIC

Calorimetry

$$q = c \text{ x } m \text{ x } \Delta T$$

q = heat lost or gained
c = specific heat capacity
m = mass in g
$\Delta T = T_{\text{final}} - T_{\text{initial}}$

The ***specific heat capacity*** (***c***) of a substance is the quantity of heat required to change the temperature of ***1 gram*** of the substance by ***1 K***. **(J/g·K)**

Table 6.2 Specific Heat Capacities (*c*) of Some Elements, Compounds, and Materials

Substance	Specific Heat Capacity (J/g·K)	Substance	Specific Heat Capacity (J/g·K)*
Elements		**Solid materials**	
aluminum, Al	0.900	wood	1.76
graphite,C	0.711	cement	0.88
iron, Fe	0.450	glass	0.84
copper, Cu	0.387	granite	0.79
gold, Au	0.129	steel	0.45
Compounds			
water, $H_2O(l)$	4.184		
ethyl alcohol, $C_2H_5OH(l)$	2.46		
ethylene glycol, $(CH_2OH)_2(l)$	2.42		
carbon tetrachloride, $CCl_4(l)$	0.862		

* At 298 K (25°C).

Sample Problem 6.3

Finding the Quantity of Heat from a Temperature Change

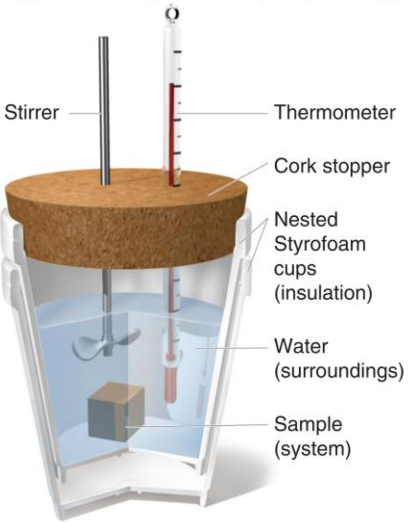
PROBLEM: A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300.°C? The specific heat capacity (*c*) of Cu is 0.387 J/g·K.

PLAN: We know the mass (125 g) and *c* (0.387 J/g·K) of Cu and can find ΔT in °C, which equals ΔT in K. We can use the equation $q = c \text{ x } m \text{ x } \Delta T$ to calculate the heat.

SOLUTION: $\Delta T = T_{\text{final}} - T_{\text{initial}} = 300. - 25 = 275°\text{C} = 275 \text{ K}$

$$q = c \text{ x } m \text{ x } \Delta T = \frac{0.387 \text{ J}}{\cancel{\text{g}\cdot\text{K}}} \text{ x } 125 \cancel{\text{ g}} \text{ x } 275 \cancel{\text{ K}} \boxed{= 1.33\text{x}10^4 \text{ J}}$$

Figure 6.7 **Coffee-cup calorimeter.**



This device measures the heat transferred at constant pressure (q_P).

Sample Problem 6.4

Determining the Specific Heat Capacity of a Solid

PROBLEM: A 22.05 g solid is heated in a test-tube to 100.00°C and added to 50.00 g of water in a coffee-cup calorimeter. The water temperature changes from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

PLAN: Since the water and the solid are in contact, heat is transferred from the solid to the water until they reach the same T_{final}. In addition, the heat given out by the solid ($-q_{\text{solid}}$) is equal to the heat absorbed by the water (q_{water}).

SOLUTION:

$$\Delta T_{\text{water}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 25.10°\text{C}) = 3.39°\text{C} = 3.39\ \text{K}$$

$$\Delta T_{\text{solid}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 100.00°\text{C}) = -71.51°\text{C} = -71.51\ \text{K}$$

Sample Problem 6.4

$$c_{solid} = \frac{c_{\text{H}_2\text{O}} \times \text{mass}_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}}{\text{mass}_{\text{solid}} \times \Delta T_{\text{solid}}}$$

$$= \frac{4.184\ \text{J/g·K} \times 50.00\ \text{g} \times 3.39\ \text{K}}{22.05\ \text{g} \times (-71.51\ \text{K})} \quad \boxed{= 0.450\ \text{J/g·K}}$$

Sample Problem 6.5 Determining the Enthalpy Change of an Aqueous Reaction

PROBLEM: 50.0 mL of 0.500 *M* NaOH is placed in a coffee-cup calorimeter at 25.00ºC and 25.0 mL of 0.500 *M* HCl is carefully added, also at 25.00ºC. After stirring, the final temperature is 27.21ºC. Calculate q_{soln} (in J) and the change in enthalpy, ΔH, (in kJ/mol of H_2O formed).

Assume that the total volume is the sum of the individual volumes, that d = 1.00 g/mL and c = 4.184 J/g·K

PLAN: Heat flows from the reaction (the system) to its surroundings (the solution). Since $-q_{rxn} = q_{soln}$, we can find the heat of the reaction by calculating the heat absorbed by the solution.

Sample Problem 6.5

SOLUTION:

(a) To find q_{soln}:

Total mass (g) of the solution = (25.0 mL + 50.0 mL) x 1.00 g/mL = 75.0 g

ΔT_{soln} = 27.21°C – 25.00°C = 2.21°C = 2.21 K

$q_{soln} = c_{soln} \times \text{mass}_{soln} \times \Delta T_{soln}$ = (4.184 J/g·K)(75.0 g)(2.21 K) $\boxed{= 693\ \text{J}}$

(b) To find ΔH_{rxn} we first need a balanced equation:

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

Sample Problem 6.5

For HCl:

$$25.0\text{ mL HCl} \times \frac{1\text{ L}}{10^3\text{ mL}} \times \frac{0.500\text{ mol}}{1\text{ L}} \times \frac{1\text{ mol }H_2O}{1\text{ mol HCl}} = 0.0125\text{ mol }H_2O$$

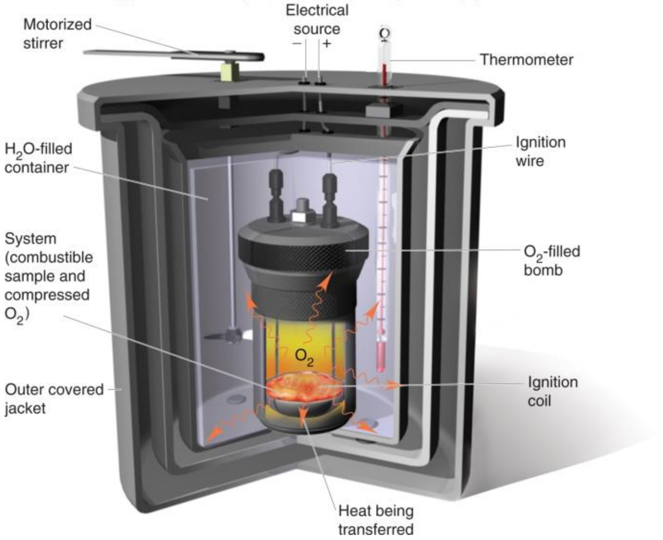
For NaOH:

$$50.0\text{ mL NaOH} \times \frac{1\text{ L}}{10^3\text{ mL}} \times \frac{0.500\text{ mol}}{1\text{ L}} \times \frac{1\text{ mol }H_2O}{1\text{ mol NaOH}} = 0.0250\text{ mol }H_2O$$

HCl is limiting, and the amount of H_2O formed is 0.0125 mol.

$$\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol }H_2O} = \frac{-693\text{ J}}{0.0125\text{ mol}} \times \frac{1\text{ kJ}}{10^3\text{J}} \quad \boxed{\mathbf{= -55.4\text{ kJ/mol }H_2O}}$$

Figure 6.8 **A bomb calorimeter.**



This device measures the heat released at constant volume (q_V).

Sample Problem 6.6

Calculating the Heat of a Combustion Reaction

PROBLEM: A manufacturer claims that its new dietetic dessert has “fewer than 10 Calories per serving.” To test the claim, a chemist at the Department of Consumer Affairs places one serving in a bomb calorimeter and burns it in O_2. The initial temperature is 21.862°C and the temperature rises to 26.799°C. If the heat capacity of the calorimeter is 8.151 kJ/K, is the manufacturer’s claim correct?

PLAN: When the dessert (system) burns, the heat released is absorbed by the calorimeter:

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

To verify the energy provided by the dessert, we calculate $q_{\text{calorimeter}}$.

Sample Problem 6.6

SOLUTION:

$$\Delta T_{\text{calorimeter}} = T_{\text{final}} - T_{\text{initial}}$$
$$= 26.799°\text{C} - 21.862°\text{C} = 4.937°\text{C} = 4.937\ \text{K}$$

$$q_{\text{calorimeter}} = \text{heat capacity} \times \Delta T = 8.151\ \text{kJ/K} \times 4.937\ \text{K} = 40.24\ \text{kJ}$$

$$40.24\ \text{kJ} \times \frac{\text{kcal}}{4.184\ \text{kJ}} \quad \boxed{\mathbf{= 9.63\ kcal\ or\ Calories}}$$

The manufacturer’s claim is true, since the heat produced is less than 10 Calories.

Stoichiometry of Thermochemical Equations

- A ***thermochemical equation*** is a balanced equation that includes ΔH_{rxn}.
- The sign of ΔH indicates whether the reaction is exothermic or endothermic.
- The magnitude of ΔH is ***proportional to the amount of substance***.
- The value of ΔH can be used in a calculation in the same way as a mole ratio.

Figure 6.11

The relationship between amount (mol) of substance and the energy (kJ) transferred as heat during a reaction.

Sample Problem 6.7

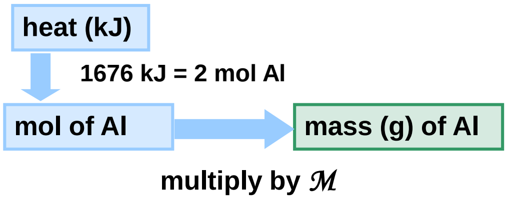
Using the Enthalpy Change of a Reaction (ΔH) to Find Amounts of Substance

PROBLEM: The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by the equation

$$Al_2O_3(s) \longrightarrow 2Al(s) + \frac{3}{2}O_2(g) \quad \Delta H_{rxn} = 1676 \text{ kJ}$$

If aluminum is produced this way, how many grams of aluminum can form when 1.000×10^3 kJ of heat is transferred?

PLAN: From the balanced equation and ΔH, we see that 2 mol of Al is formed when 1676 kJ of heat is absorbed.



heat (kJ)

1676 kJ = 2 mol Al

mol of Al

mass (g) of Al

multiply by $\mathcal{M}$

Sample Problem 6.7

SOLUTION:

$$1.000 \times 10^3 \text{ kJ} \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \boxed{= 32.20 \text{ g Al}}$$

Hess' Law

Hess's law states that *the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.*

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \dots\dots\dots + \Delta H_n$$

ΔH for an overall reaction can be calculated if the ΔH values for the individual steps are known.

Calculating ΔH for an overall process

- Identify the target equation, the step whose ΔH is unknown.
  - Note the amount of each reactant and product.
- Manipulate each equation with known ΔH values so that the target amount of each substance is on the correct side of the equation.
  - Change the sign of ΔH when you reverse an equation.
  - Multiply amount (mol) and ΔH by the same factor.
- Add the manipulated equations and their resulting ΔH values to get the target equation and its ΔH.
  - All substances except those in the target equation must cancel.

Sample Problem 6.8

Using Hess's Law to Calculate an Unknown Δ*H*

PROBLEM: Two gaseous pollutants that form in auto exhausts are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following reaction:

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2}N_2(g) \quad \Delta H = ?$$

Given the following information, calculate the unknown Δ*H*:

Equation A: $CO(g) + \tfrac{1}{2} O_2(g) \longrightarrow CO_2(g) \quad \Delta H_A = -283.0\text{ kJ}$

Equation B: $N_2(g) + O_2(g) \longrightarrow 2NO(g) \quad \Delta H_B = 180.6\text{ kJ}$

PLAN: Manipulate Equations A and/or B and their Δ*H* values to get to the target equation and its Δ*H*. All substances except those in the target equation must cancel.

Sample Problem 6.8

SOLUTION:

Multiply Equation B by ½ and reverse it:

$$NO(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g); \ \Delta H = -90.3\text{ kJ}$$

Add the manipulated equations together:

Equation A: $CO(g) + \tfrac{1}{2} O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -283.0\text{ kJ}$

½ Equation B: (reversed) $NO(g) \longrightarrow \tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \quad \Delta H = -90.3\text{ kJ}$

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2} N_2(g)$$

$$\boxed{\Delta H_{rxn} = -373.3\text{ kJ}}$$

Table 6.3 Selected Standard Enthalpies of Formation at 25°C (298K)

Formula	ΔH°_f (kJ/mol)	Formula	ΔH°_f (kJ/mol)	Formula	ΔH°_f (kJ/mol)
Calcium		$Cl_2(g)$	0	Silver	
$Ca(s)$	0	$HCl(g)$	-92.3	$Ag(s)$	0
$CaO(s)$	-635.1	Hydrogen		$AgCl(s)$	-127.0
$CaCO_3(s)$	-1206.9	$H(g)$	218	Sodium	
Carbon		$H_2(g)$	0	$Na(s)$	0
C(graphite)	0	Nitrogen		$Na(g)$	107.8
C(diamond)	1.9	$N_2(g)$	0	$NaCl(s)$	-411.1
$CO(g)$	-110.5	$NH_3(g)$	-45.9	Sulfur	
$CO_2(g)$	-393.5	$NO(g)$	90.3	S_8(rhombic)	0
$CH_4(g)$	-74.9	Oxygen		S_8(monoclinic)	0.3
$CH_3OH(l)$	-238.6	$O_2(g)$	0	$SO_2(g)$	-296.8
$HCN(g)$	135	$O_3(g)$	143	$SO_3(g)$	-396.0
$CS_s(l)$	87.9	$H_2O(g)$	-241.8		
Chlorine		$H_2O(l)$	-285.8		
$Cl(g)$	121.0				

Sample Problem 6.9 **Writing Formation Equations**

PROBLEM: Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include ΔH°_f.

(a) Silver chloride, AgCl, a solid at standard conditions.

(b) Calcium carbonate, $CaCO_3$, a solid at standard conditions.

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

PLAN: Write the elements as reactants and 1 mol of the compound as the product formed. Make sure all substances are in their standard states. Balance the equations and find the value of ΔH°_f in Table 6.3 or Appendix B.

Sample Problem 6.9

SOLUTION:

(a) Silver chloride, AgCl, a solid at standard conditions.

$$Ag(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow AgCl(s) \qquad \Delta H^\circ_f = -127.0\ kJ$$

(b) Calcium carbonate, $CaCO_3$, a solid at standard conditions.

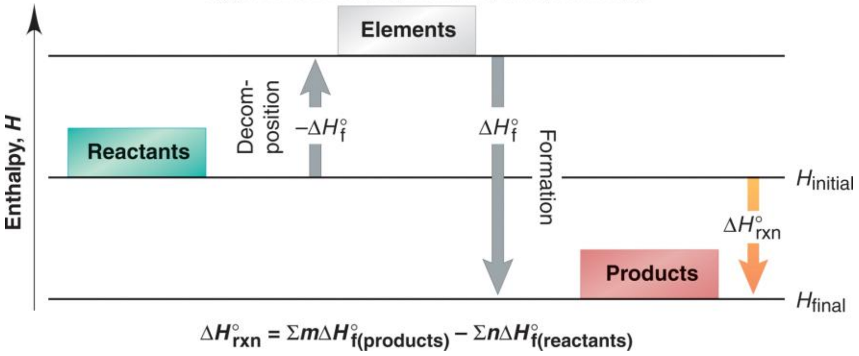
$$Ca(s) + C(graphite) + \frac{3}{2}O_2(g) \longrightarrow CaCO_3(s) \qquad \Delta H^\circ_f = -1206.9\ kJ$$

(c) Hydrogen cyanide, HCN, a gas at standard conditions.

$$\tfrac{1}{2}H_2(g) + C(graphite) + \tfrac{1}{2}N_2(g) \longrightarrow HCN(g) \qquad \Delta H^\circ_f = 135\ kJ$$

Figure 6.10

The two-step process for determining ΔH°_{rxn} from ΔH°_f values.



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

Sample Problem 6.10 Calculating ΔH°_{rxn} from ΔH°_f Values

PROBLEM: Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:

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

Calculate ΔH°_{rxn} from ΔH°_f values.

PLAN: Use the ΔH°_f values from Table 6.3 or Appendix B and apply the equation

$$\Delta H_{rxn} = \Sigma\, m\Delta H^\circ_f \text{ (products)} - \Sigma\, n\Delta H^\circ_f \text{ (reactants)}$$

Sample Problem 6.10

SOLUTION:

$$\Delta H_{rxn} = \Sigma\, m\Delta H^\circ_f \text{ (products)} - \Sigma\, n\Delta H^\circ_f \text{ (reactants)}$$

$$\Delta H_{rxn} = [4(\Delta H^o_f \text{ of } NO(g) + 6(\Delta H^o_f \text{ of } H_2O(g)] - [4(\Delta H \text{ of } NH_3(g) + 5(\Delta H \text{ of } O_2(g)]$$

$$= (4 \text{ mol})(90.3 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) – [(4 \text{ mol})(-45.9 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})]$$

$$= -906 \text{ kJ}$$

$$\boxed{\Delta H_{rxn} = -906 \text{ kJ}}$$

Figure 6.11 **The trapping of heat by the atmosphere.**