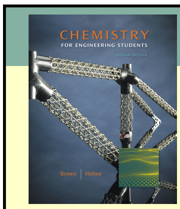

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Chapter 9
Energy and Chemistry

Jacqueline Bennett • SUNY Oneonta

Chapter Objectives

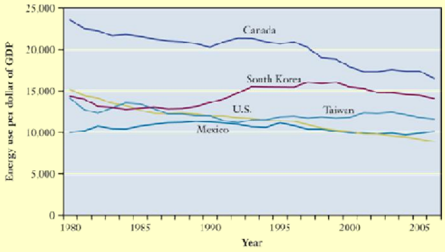
- Explain the economic importance of conversions between different forms of energy and the inevitability of losses in this process.
- Define work and heat using the standard sign conventions.
- Define state functions and explain their importance.
- State the first law of thermodynamics in words and as an equation.

Chapter Objectives

- Use calorimetric data to obtain values of ΔE and ΔH for chemical reactions.
- Define ΔH_f^o and write formation reactions for compounds.
- Explain Hess's law in your own words.
- Calculate ΔH^o for chemical reactions from tabulated data.
- Describe some important design considerations in choosing a battery for a specific application.

Energy Use and the World Economy

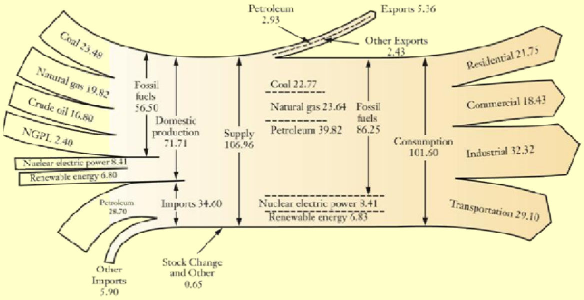
- A nation's energy consumption is an indicator of economic growth.
  - There is a direct relationship between Gross Domestic Product and energy consumption.



Energy Use and the World Economy

- In 2003, the total energy supply for the United States was 102.20 quadrillion Btu.
  - Quadrillion = 10^{15}
  - Btu = British thermal unit, 1 Btu = 1054.35 J.
- Energy supply can be broken down into coal, natural gas, crude oil, NGPL, nuclear energy, and renewable energy.
  - Domestic production, 70.47 quadrillion Btu
  - Imports, 31.02 quadrillion Btu.

Energy Use and the World Economy

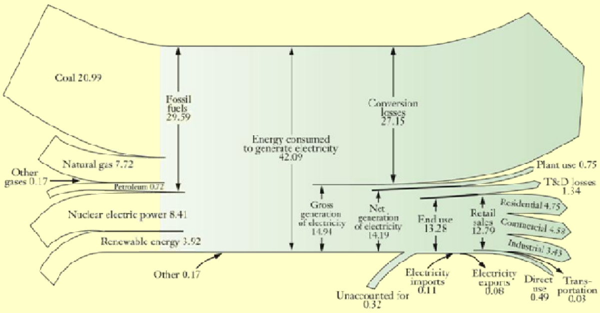


- Energy production and consumption (in quadrillion Btu) in the United States during the year 2003.

Energy Use and the World Economy

- Energy consumption is broken down into four main components.
  - Residential, 22%
  - Commercial, 18%
  - Industrial, 33%
  - Transportation, 27%
- Nearly half of all domestic energy use is in the production of electricity.
  - “Conversion losses” account for nearly two-thirds of the energy consumed to generate electricity.

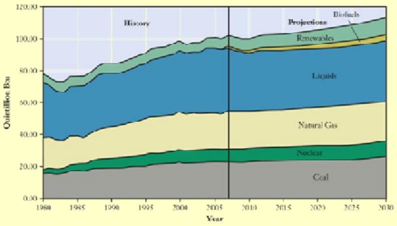
Energy Use and the World Economy



- Summary of the generation and consumption of electricity in the United States during the year 2003.

Energy Use and the World Economy

- U.S. domestic consumption has increased over the last 50 years.
  - The consumption of various energy sources fluctuates due to availability of raw material and the price and availability of imported fuels.



Forms of Energy

- Two broad categories of energy: potential energy and kinetic energy.
  - Potential energy - associated with the relative position of an object.
  - Kinetic energy - associated with motion.

$$\text{Kinetic energy} = \frac{1}{2}mv^2$$

Forms of Energy

- Internal energy - the combined kinetic and potential energies of atoms and molecules that make up an object or system.
- Chemical energy - energy released or absorbed during a chemical reaction.
- Other forms of energy include radiant, mechanical, thermal, electrical, and nuclear.
- Thermochemistry - the study of the energetic consequences of chemistry

Heat and Work

- Heat is the flow of energy between two objects because of a difference in temperature.
  - Heat flows from the warmer object to the cooler object.
- Work is the transfer of energy accomplished by a force moving a mass some distance against resistance.
  - Pressure-volume work (PV-work) is the most common work type in chemistry.
    - Releasing an inflated balloon before it is tied off illustrates an example of PV-work.

Energy Units

- The Joule is the SI unit of energy.
    - 1 Joule = 1 kg m^2/s^2

$$W = \text{mass} \times \text{acceleration} \times \text{distance} = \text{kg} \times \frac{\text{m}}{\text{s}^2} \times \text{m}$$

- Other energy units include the Btu and the calorie.
    - 1 Btu is the energy required to raise 1 lb of water 1°F. 1 Btu = 1055 J
    - 1 calorie is the energy required to raise 1 g water from 14.5 to 15.5 °C. 1 calorie = 4.184 J

Energy Transformation and Conservation of Energy

- During energy transformation, the total energy must be conserved.
    - The sum of all energy conversions and energy transfers must equal the total energy present which must remain constant.
- To account for energy transformations and conversions, the system and surroundings must be specified.
    - System - the part of the universe being considered.
    - Surroundings - the remainder of the universe.
    - System + Surroundings = Universe
    - System and surroundings are separated by a boundary.

Energy Transformation and Conservation of Energy

- For a system or surroundings, the only possible forms of energy flow are heat, *q*, and work, *w*.
- The delta, Δ, means "change in" and is defined as the difference in the final and initial states.

$$\Delta E = q + w$$

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

Example Problem 9.1

- If 515 J of heat is added to a gas that does 218 J of work as a result, what is the change in the energy of the system?

Energy Transformation and Conservation of Energy

- The sign resulting from the difference in the final and initial states indicates the direction of the energy flow.
    - Negative values indicate energy is being released.
    - Positive values indicate energy is being absorbed.

Energy Transformation and Conservation of Energy

- First law of thermodynamics states that energy can be transformed from one form to another but cannot be created or destroyed.

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

Waste Energy

- A common way to obtain work from a system is to heat the system. Heat flows in and is converted to work.
  - It is impossible to completely convert all heat to work.
  - Heat not converted to work is considered waste energy, which may contribute to thermal pollution.
    - Thermal pollution is the temperature change in a body of water from hot or cold waste streams resulting in temperatures different from normal seasonal ranges.
- The efficiency of conversion from heat to work can be expressed as a percentage.
  - Increases in energy consumption can be offset by increasing energy efficiencies.

Waste Energy

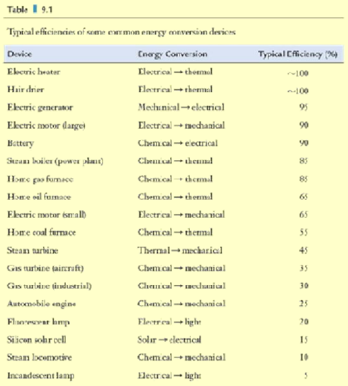


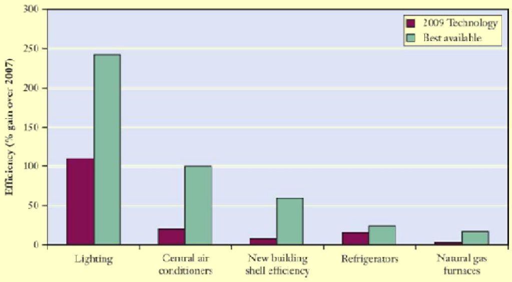
Table 9.1

Typical efficiencies of some common energy conversion devices

Device	Energy Conversion	Typical Efficiency (%)
Electric heater	Electrical → thermal	~100
Hair drier	Electrical → thermal	~100
Electric generator	Mechanical → electrical	95
Electric motor (large)	Electrical → mechanical	90
Battery	Chemical → electrical	90
Steam boiler (power plant)	Chemical → thermal	85
Home gas furnace	Chemical → thermal	85
Home oil furnace	Chemical → thermal	65
Electric motor (small)	Electrical → mechanical	65
Home coal furnace	Chemical → thermal	55
Steam turbine	Thermal → mechanical	45
Gas turbine (aircraft)	Chemical → mechanical	35
Gas turbine (industrial)	Chemical → mechanical	30
Automobile engine	Chemical → mechanical	25
Fluorescent lamp	Electrical → light	20
Silicon solar cell	Solar → electrical	15
Steam locomotive	Chemical → mechanical	10
Incandescent lamp	Electrical → light	5

- Typical efficiencies of some common energy conversion devices.

Waste Energy



- Predicted efficiency gains by the year 2030 for various technologies.

Heat Capacity and Calorimetry

- Calorimetry is a laboratory method for observing and measuring the flow of heat into and out of a system.
- Different systems will absorb different amounts of energy based on three main factors.
  - The amount of material, *m* or *n*.
    - *m* is mass and *n* is number of moles
  - The type of material, as measured by *c* or C_p.
    - *c* is the specific heat capacity, or specific heat, and C_p is the molar heat capacity.
  - The temperature change, ΔT.

Heat Capacity and Specific Heat

- The specific heat capacity, or specific heat, is a physical property of a substance that describes the amount of heat required to raise the temperature of one gram of a substance by 1˚C.
  - Represented by *c*.
  - Specific heat is compound and phase specific.
- The molar heat capacity is a physical property of a substance that describes the amount of heat required to raise the temperature of one mole of a substance by 1˚C.
  - Represented by C_p.
  - Molar heat capacity is compound and phase specific.

Heat Capacity and Specific Heat

- The amount of heat energy absorbed can be quantified.

$$q = mc\Delta T$$

$$q = nC_p\Delta T$$

Heat Capacity and Specific Heat

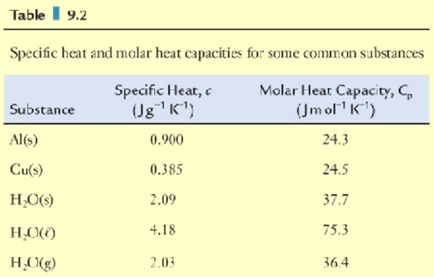


Table 9.2

Specific heat and molar heat capacities for some common substances

Substance	Specific Heat, *c* ($J g^{-1} K^{-1}$)	Molar Heat Capacity, C_p ($J mol^{-1} K^{-1}$)
Al(s)	0.900	24.3
Cu(s)	0.385	24.5
$H_2O(s)$	2.09	37.7
$H_2O(\ell)$	4.18	75.3
$H_2O(g)$	2.03	36.4

- Specific heat and molar heat capacities for some common substances.

Example Problem 9.2

- Heating a 24.0 g aluminum can raises its temperature by 15.0°C. Find the value of *q* for the can.

Example Problem 9.3

- The molar heat capacity of liquid water is 75.3 J/mol K. If 37.5 g of water is cooled from 42.0 to 7.0°C, what is *q* for the water?

Calorimetry

- Heat flow is measured using a calorimeter.
- A calorimeter measures the heat evolved or absorbed by the system of interest by measuring the temperature change in the surroundings.

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

$$q_{\text{gained}} = -q_{\text{lost}}$$

Example Problem 9.4

- A glass contains 250.0 g of warm water at 78.0°C. A piece of gold at 2.30°C is placed in the water. The final temperature reached by this system is 76.9°C. What was the mass of gold? The specific heat of water is 4.184 J/g°C, and that of gold is 0.129 J/g°C.

Calorimetry

- There are two steps in a calorimetric measurement.
  - Calibration - the calorimeter constant, $C_{\text{calorimeter}}$, is determined by dividing the known amount of heat released in the calorimeter by the temperature change of the calorimeter.
  - Actual Measurement - heat released or absorbed in a reaction of known quantity of material is measured.

$$q = C_{\text{calorimeter}} \times \Delta T$$

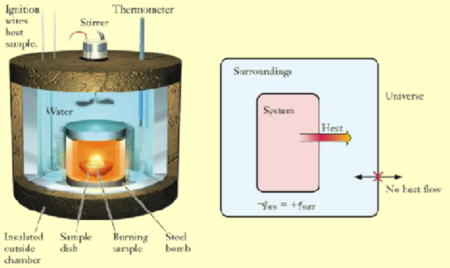
Calorimetry

- Actual Measurement - temperature change for the calorimeter and the calorimeter constant are used to determine the amount of heat released by a reaction.

$$q_{\text{calorimeter}} = C_{\text{calorimeter}} \times \Delta T_{\text{calorimeter}}$$

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

Calorimetry



- Diagram of a bomb calorimeter and standard choice for system and surroundings in a bomb calorimetry experiment.

Example Problem 9.5

- In the calibration of a calorimeter, an electrical resistance heater supplies 100.0 J of heat and a temperature increase of 0.850˚C is observed. Then, 0.245 g of a particular fuel is burned in this same calorimeter and the temperature increases by 5.23˚C. Calculate the energy density of this fuel, which is the amount of energy liberated per gram of fuel burned.

Enthalpy

- The conditions under which heat flow, *q*, occurs will have an impact on the measurement that is made.
  - Combustion of octane releases 5.45 x 10^3 kJ under constant volume conditions, represented as q_V.
  - Combustion of octane releases 5.48 x 10^3 kJ under constant pressure conditions, represented as q_p.

Defining Enthalpy

- The internal energy change for a reaction equals the sum of the heat flow and the work.

$$\Delta E = q + w$$

  - During an expansion, $w = -P\Delta V$.

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

  - Under constant volume conditions, $\Delta V = 0$, and $\Delta E = q_V$.

$$\Delta E = q_v$$

Defining Enthalpy

- Enthalpy is the heat flow under conditions of constant pressure.
  - The enthalpy change can be expressed as

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = (q - P\Delta V) + \Delta(PV)$$

$$\Delta H = q - P\Delta V + P\Delta V$$

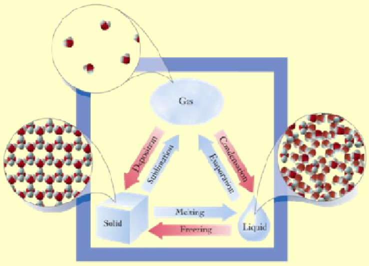
$$\Delta H = q_p$$

Defining Enthalpy

- When a system releases heat, the process is said to be exothermic.
    - The value of ΔH is less than zero; the sign on ΔH is negative.
- When a system absorbs heat, the process is said to be endothermic.
    - The value of ΔH is greater than zero; the sign on ΔH is positive.

ΔH of Phase Changes

- Phase changes occur under constant pressure conditions.
    - The heat flow during a phase change is an enthalpy change.
    - During a phase change, temperature does not change with heat flow due to formation or breaking of intermolecular attractive forces.



ΔH of Phase Changes

- The heat required to convert a liquid to a gas is the heat of vaporization, ΔH_{vap}.
    - ΔH_{vap} is endothermic with a positive value.
- The heat released to convert a gas to a liquid is the heat of condensation, ΔH_{cond}.
    - ΔH_{cond} is exothermic with a negative value.
- $\Delta H_{cond} = -\Delta H_{vap}$
    - The values of enthalpy changes in opposite directions have equal numeric values and differ only in their signs.
    - The magnitude of enthalpy change depends on the substance involved.

ΔH of Phase Changes

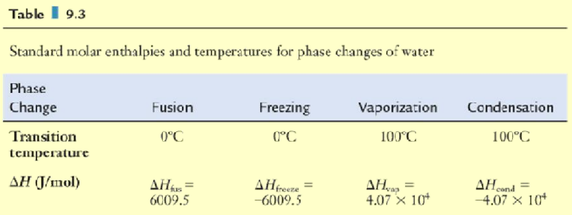


Table 9.3

Standard molar enthalpies and temperatures for phase changes of water

Phase Change	Fusion	Freezing	Vaporization	Condensation
Transition temperature	0°C	0°C	100°C	100°C
ΔH (J/mol)	$\Delta H_{fus} =$ 6009.5	$\Delta H_{freeze} =$ −6009.5	$\Delta H_{vap} =$ 4.07×10^4	$\Delta H_{cond} =$ -4.07×10^4

- Standard molar enthalpies and temperatures for phase changes of water.

ΔH of Phase Changes

- The value of ΔH for a phase change is compound specific and has units of kJ/mol.
    - The heat flow can be calculated using the number of moles of substance, n, and the value of the enthalpy change.

$$\Delta H = n \times \Delta H_{\text{phase change}}$$

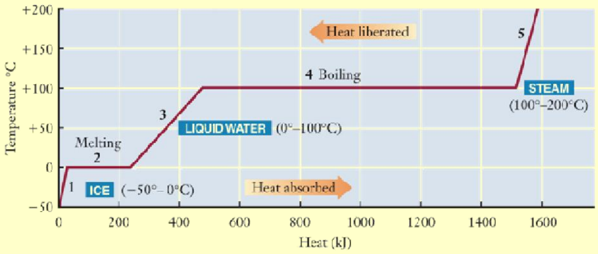
Example Problem 9.6

- Calculate the enthalpy change when 240. g of ice melts.

Vaporization and Electricity Production

- The enthalpy change for the conversion of ice to liquid and then to steam can be calculated.
  - A heat curve breaks the calculation down into specific heat calculations (sections of the heat curve where temperature changes) and phase change enthalpy calculations (sections of the heat curve where temperature does not change).

ΔH of Phase Changes

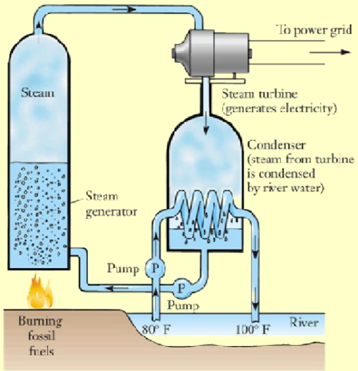


- Heat curve for the heating of 500-g of ice at -50^{o}C to 200^{o}C.

Vaporization and Electricity Production

- The large amount of energy required to convert water from a liquid to a gas is exploited in converting chemical energy into electricity.
  - The goal of the power plant is to convert as much chemical energy as possible into electricity.
  - The large heat of vaporization for water is ideal for "trapping" the heat energy given off in the combustion reaction.

Vaporization and Electricity Production



- Schematic diagram of the important elements of a standard electric power plant.

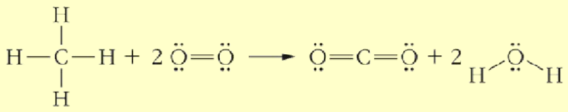
Heat of Reaction

- Enthalpy changes can be calculated for chemical reactions, in addition to temperature changes and phase transitions.
  - The enthalpy change is commonly referred to as the heat of reaction.

Bonds and Energy

- The enthalpy change for a reaction can be estimated using bond energies.
- During a chemical reaction, reactant bonds are broken and product bonds are made.
  - Breaking bonds requires energy.
  - Making bonds releases energy.
- If the amount of energy released making product bonds is greater than the amount of energy required to break reactant bonds, the reaction is exothermic. If the energy released is less than the energy required, the reaction is endothermic.

Bonds and Energy



$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- The combustion of methane breaks 4 C-H bonds and 2 O=O bonds. 2 C=O bonds and 4 O-H bonds are made.

Bonds and Energy

- The accuracy of enthalpy changes calculated from tabulated bond energies is not very good.
  - The bond energies used are averages.
  - Bond energy method used to estimate enthalpy changes for reactions involving compounds with no available thermochemical data.
- A thermochemical equation summarizes the overall energetics for a chemical reaction.
  - The sign on the ΔH indicates whether the reaction is endothermic or exothermic

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

Bonds and Energy

- The combustion of methane is an exothermic reaction and releases 890.4 kJ of heat energy when 1 mole of methane reacts with 2 moles of oxygen.

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

- For thermochemical equations, if the stoichiometric coefficients are multiplied by some factor, the heat of reaction must also be multiplied by the same factor.

$$2CH_4(g) + 4O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$
$$\Delta H = -1780.8 \text{ kJ}$$

Heats of Reaction for Some Specific Reactions

- Some classes of chemical reactions are given their own labels for heats of reactions.
  - Heat of combustion, ΔH_{comb}
  - Heat of neutralization, ΔH_{neut}
  - Heat of formation, ΔH_f, is the heat of reaction for formation of substances.

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$$

  - Fractional coefficients are allowed for formation reactions because only one mole of product can be formed.

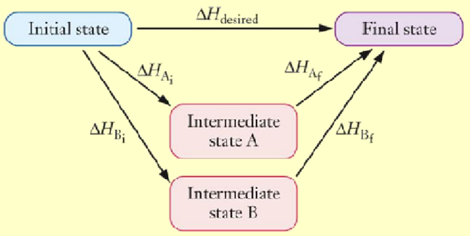
Heats of Reaction for Some Specific Reactions

- A formation reaction is the chemical reaction by which one mole of a compound is formed from its elements in their standard states.
- The standard state is the most stable form of an element at room temperature, 25ºC, and pressure, 1 atm, indicated with a superscript º.
- $\Delta H_f^o = 0$ for an element in its standard state.

Hess's Law and Heats of Reaction

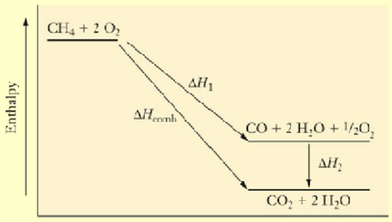
- Direct calorimetric determinations of some reactions may be too difficult or dangerous to perform.
  - An indirect method is needed to obtain heats of reaction.
- Hess's law: the enthalpy change for any process is independent of the particular way the process is carried out.
  - Enthalpy is a state function.
  - A state function is a variable whose value depends only on the state of the system and not its history.

Hess’s Law



- Conceptual diagram representing Hess’s law. Enthalpy is a state function, so any convenient path can be used to calculate the enthalpy change.

Hess’s Law



- Enthalpy diagram for the combustion of methane. The CH_4 is converted to CO, then the CO is converted to CO_2. The ΔH for each step is used to calculate the ΔH for the overall reaction. The ΔH will be the same for both paths.

Example Problem 9.7

- One origin of SO_3 is the combustion of sulfur, which is present in small quantities in coal, according to the following equation.

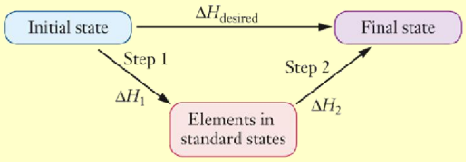
$$\mathrm{S(s)} + \frac{3}{2}\mathrm{O_2(g)} \rightarrow \mathrm{SO_3(g)}$$

- Given the thermochemical information below, determine the heat of reaction for this reaction.

$$\mathrm{S(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{SO_2(g)} \qquad \Delta H^\circ = -296.8\ \mathrm{kJ}$$

$$2\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{SO_3(g)} \qquad \Delta H^\circ = -197.0\ \mathrm{kJ}$$

Formation Reactions and Hess’s Law



- Conceptual diagram showing how to use tabulated enthalpies of formation to calculate the enthalpy change for a chemical reaction.

Formation Reactions and Hess’s Law

- The enthalpy change for a reaction can be calculated using Hess’s law and heats of formation.

$$\Delta H^\circ = \sum_i \nu_i \Delta H_f^\circ(\text{products})_i - \sum_j \nu_j \Delta H_f^\circ(\text{reactants})_j$$

Example Problem 9.8

- Use tabulated data to find the heat of combustion of one mole of propane, C_3H_8, to form gaseous carbon dioxide and liquid water.

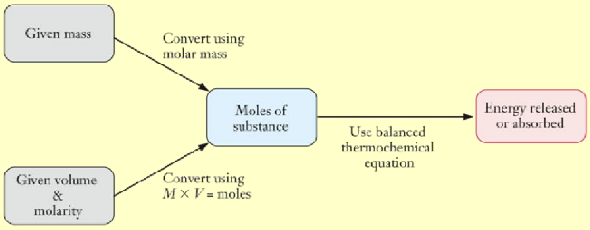
Example Problem 9.9

- Ethanol, C_2H_5OH, is used to introduce oxygen into some blends of gasoline. It has a heat of combustion of 1366.8 kJ/mol. What is the heat of formation of ethanol?

Energy and Stoichiometry

- A thermochemical equation allows for the stoichiometric treatment of energy.
  - For an exothermic reaction, energy is treated as a product.
  - For an endothermic reaction, energy is treated as a reactant.
- The thermochemical equation is used to convert between the number of moles of a reactant or product and the amount of energy released or absorbed.
  - The stated value of ΔH for a thermochemical equation corresponds to the reaction taken place exactly as written, with the indicated numbers of moles of each substance reacting.

Energy and Stoichiometry



- Flow chart detailing the sequence of steps needed to calculate the amount of energy released or absorbed when a chemical reaction is carried out using a given amount of material.

Example Problem 9.10

- An engine generates 15.7 g of nitric oxide gas during a laboratory test. How much heat was absorbed in producing this NO?

Energy Density and Fuels

- When deciding the economic merits of a fuel, several factors must be considered.
  - Technology available to extract the fuel.
  - The amount of pollution released by its combustion.
  - The fuel's relative safety.
  - The ease of transporting the fuel.
  - The fuel's energy density.

Energy Density and Fuels

- Energy density is the amount of energy that can be released per gram of fuel burned.
  - The higher the energy density of a fuel, the less fuel that must be transported to the customer.

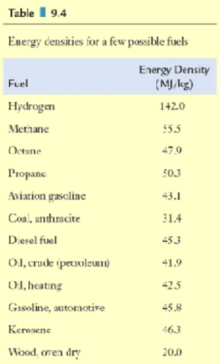


Table 9.4

Energy densities for a few possible fuels

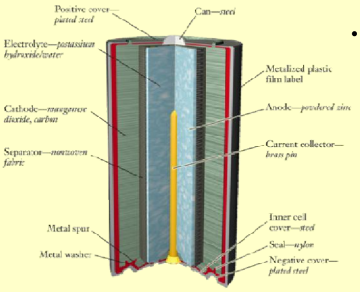
Fuel	Energy Density (MJ/kg)
Hydrogen	142.0
Methane	55.5
Octane	47.9
Propane	50.3
Aviation gasoline	43.1
Coal, anthracite	31.4
Diesel fuel	45.3
Oil, crude (petroleum)	41.9
Oil, heating	42.5
Gasoline, automotive	45.8
Kerosene	46.3
Wood, oven dry	20.0

Batteries

- Many reactions interconvert between chemical energy and forms of energy other than heat.
  - Energy can be released as light.
  - Energy can be released as electrical energy.
    - Electrical energy arises from moving a charge.
- Oxidation-Reduction or redox reactions convert chemical energy to electrical energy by transferring electrons between chemical species.
- Batteries are constructed such that electrons flow through an external circuit as they are transferred from one species to another.

Batteries

$$\mathrm{Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s)}$$



- The construction of a typical alkaline battery.
  - Zn gets oxidized from 0 to 2+
  - Mn gets reduced from 4+ to 2+

Batteries

- Batteries can be classified as either primary or secondary.
  - Primary batteries become useless once the redox reaction has run its course. An alkaline battery is a primary battery.
    - The lifetime of a primary battery is determined by the amounts of reactants present.
  - Secondary batteries can be recharged.

Batteries

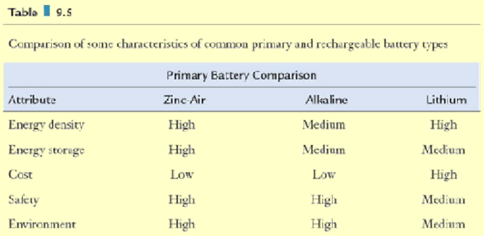


Table 9.5

Comparison of some characteristics of common primary and rechargeable battery types

	Primary Battery Comparison		
Attribute	Zinc-Air	Alkaline	Lithium
Energy density	High	Medium	High
Energy storage	High	Medium	Medium
Cost	Low	Low	High
Safety	High	High	Medium
Environment	High	High	Medium

- Comparisons of energy density, energy storage, cost, safety, and environmental characteristics for various primary batteries.

Batteries

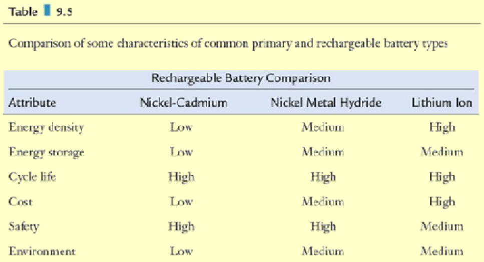


Table 9.5

Comparison of some characteristics of common primary and rechargeable battery types

	Rechargeable Battery Comparison		
Attribute	Nickel-Cadmium	Nickel Metal Hydride	Lithium Ion
Energy density	Low	Medium	High
Energy storage	Low	Medium	Medium
Cycle life	High	High	High
Cost	Low	Medium	High
Safety	High	High	Medium
Environment	Low	Medium	Medium

- Comparisons of energy density, energy storage, cost, safety, and environmental characteristics for various rechargeable batteries.