Thermodynamics

Energy can be used

- to provide heat
- for mechanical work
- to produce electric work
- to sustain life

Thermodynamics is the study of the transformation of energy into heat and for doing work

Why is propane (C_3H_8) a better fuel than benzene (C_6H_6)?

What compound are feasible as alternate fuels or clean fuels?

Why are carbohydrates, proteins and fats fuels for our bodies?

Why is ATP (adenosine triphosphate) an “energy-rich” molecule?

Terminology - System, Surroundings & State Functions

System: object(s) under observation.

In a chemical reaction, the reaction mixture is the system.

Surrounding - everything else not considered to be the system.

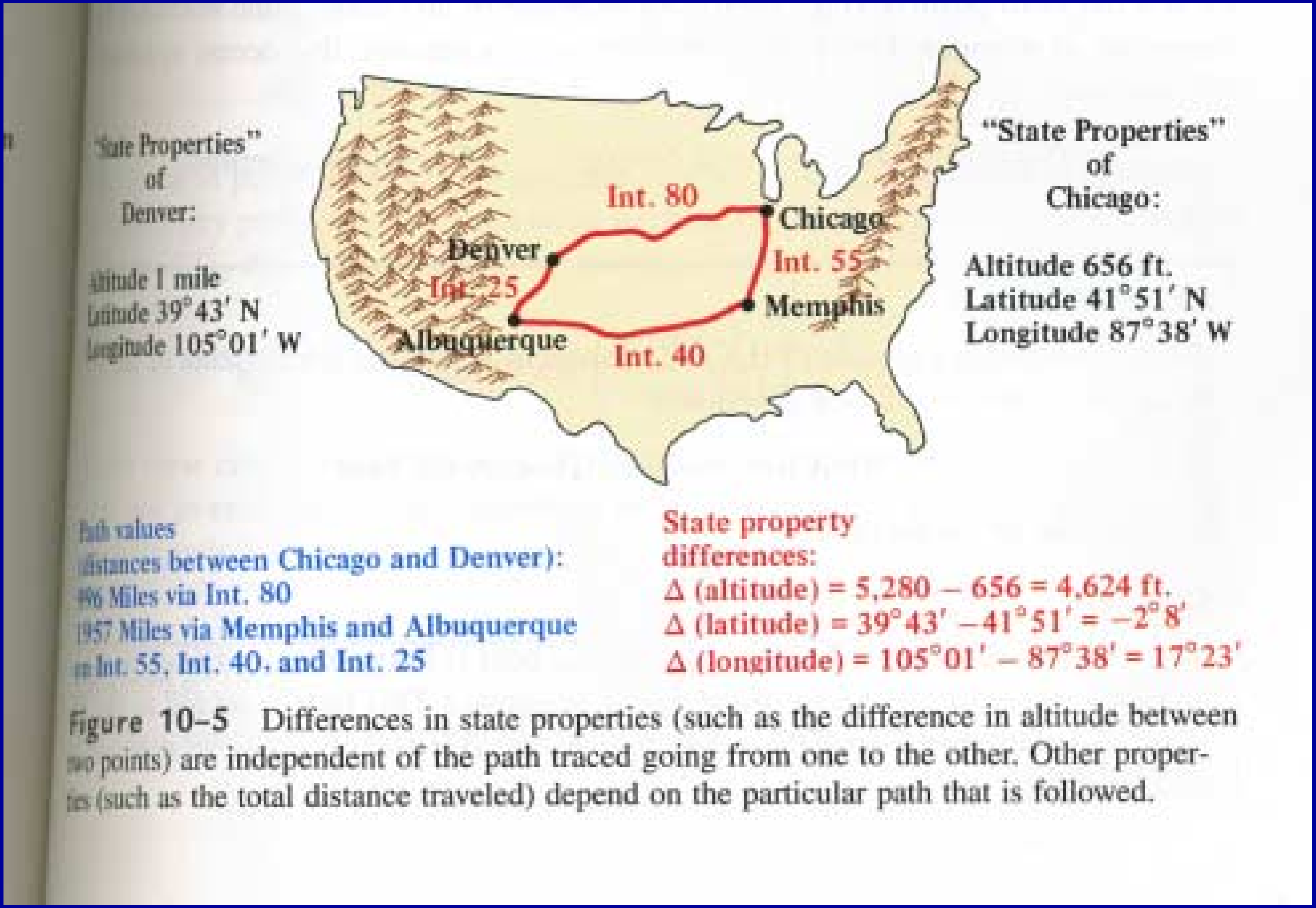
Transfer between system and surrounding

System	Energy	Matter
Open	Yes	Yes
Closed	Yes	No

State: macroscopic, measurable properties, like composition, volume, pressure, temperature, which define a system.

Process - the path the system undergoes to change from an initial state to a final state.

State function: depend on initial and final values and not the path that the system underwent in changing the values of these variables. The variables V, P, T and n are state functions.



tate Properties”
of
Denver:

ltitude 1 mile
atitude 39°43′ N
ongitude 105°01′ W

“State Properties”
of
Chicago:

Altitude 656 ft.
Latitude 41°51′ N
Longitude 87°38′ W

ath values
distances between Chicago and Denver):
96 Miles via Int. 80
1957 Miles via Memphis and Albuquerque
a Int. 55, Int. 40, and Int. 25

State property
differences:
Δ (altitude) = 5,280 – 656 = 4,624 ft.
Δ (latitude) = 39°43′ – 41°51′ = –2°8′
Δ (longitude) = 105°01′ – 87°38′ = 17°23′

Figure 10–5 Differences in state properties (such as the difference in altitude between o points) are independent of the path traced going from one to the other. Other properes (such as the total distance traveled) depend on the particular path that is followed.

Energy

Objects can posses energy either as kinetic energy (KE) or potential energy (PE).

The total energy, or the INTERNAL energy of the system

$$E = KE + PE$$

Units of energy - calorie (cal) or joule (J)

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

The nutritional calorie (Cal) = 1000 cal = 4184 J or 4.184 kJ

Energy, Work and Heat

Energy is the capacity to do work or transfer heat.

Work: Energy used to move an object.

Heat: Energy transferred from a hotter body to a colder body.

Work

mechanical work = force x distance

If the direction of the applied force is in the same direction as the displacement, work is done on the body; $w > 0$

If the direction of the applied force is opposite to the direction of the motion of the body, work is done against the body ; $w < 0$

Energy and Work in a Mechanical System

The work done in stopping a moving object, or pushing an object causes a change in the kinetic energy of the system

$$w = \Delta KE = \Delta \left(\frac{1}{2} m\, v^2\right)$$

The work done in raising an object from one height to another changes the potential energy of the object

$$w = \Delta PE = m\, g\, \Delta h$$

Pressure-Volume Work

Work done in expanding a gas against an external pressure, or to compress a gas causes a change in volume.

$w = - P_{ext}\ \Delta V$ (constant P)

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

If the gas expands $\Delta V > 0$ => work done by the gas (pushes against surrounding); work < 0

If the gas is compressed $\Delta V < 0$ => work done on the gas (by the surrounding); work > 0

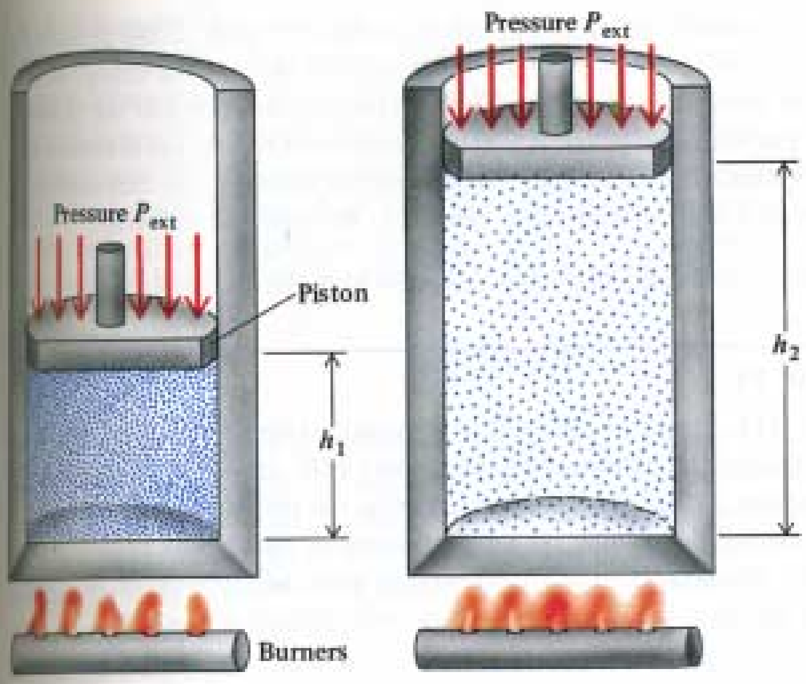


Figure 10–12 Heating the gas inside the cylinder causes it to expand, pushing the piston against the pressure exerted by the gas outside (P_{ext}). As the piston is displaced over a distance $h_2 - h_1 = \Delta h$, the volume of the cylinder increases by an amount $A\Delta h$, where A is the surface area of the piston.

Heat

When the temperature of a system changes, the internal energy of the system changes.

$$\Delta E = E_f - E_i$$

If heat flows into the system, at constant volume, and there is no phase change, the temperature increases and ΔE is positive.

If ΔE is negative (at constant volume), heat has flown out of the system and its temperature decreases.

Heat, and hence changes in energy, accompany almost all chemical reactions.

When a chemical reaction occurs by absorbing heat from its surroundings, the reaction is said to be ENDOTHERMIC.

When a chemical reaction is accompanied by the release of heat, the reaction is said to be EXOTHERMIC.

Energy, Work and Heat

Heat exchange between the system and surrounding is one way of changing the energy of the system

Work done by the system or on the system also changes the energy of the system.

The energy of the system changes when the system undergoes a process in which heat is exchanged between the system and the surroundings and/or work is performed.

Energy Conservation and The First Law of Thermodynamics

1) Energy is conserved

2) Heat and work can produce equivalent effects

3) The only way that energy can be transferred is through heat and work.

First Law

$$\Delta E = q + w$$

where

ΔE is the change in internal energy of the system

q is the heat involved during the process

w work done during the process

Sign convention

The sign of ΔE indicates whether the final energy is less than or more than the initial energy.

The sign of ΔE depends on relative magnitudes and signs of q and w

If heat flows into the system	$q > 0$
Heat flows out of the system	$q < 0$

Work done by the system	$w < 0$
Work done on the system	$w > 0$

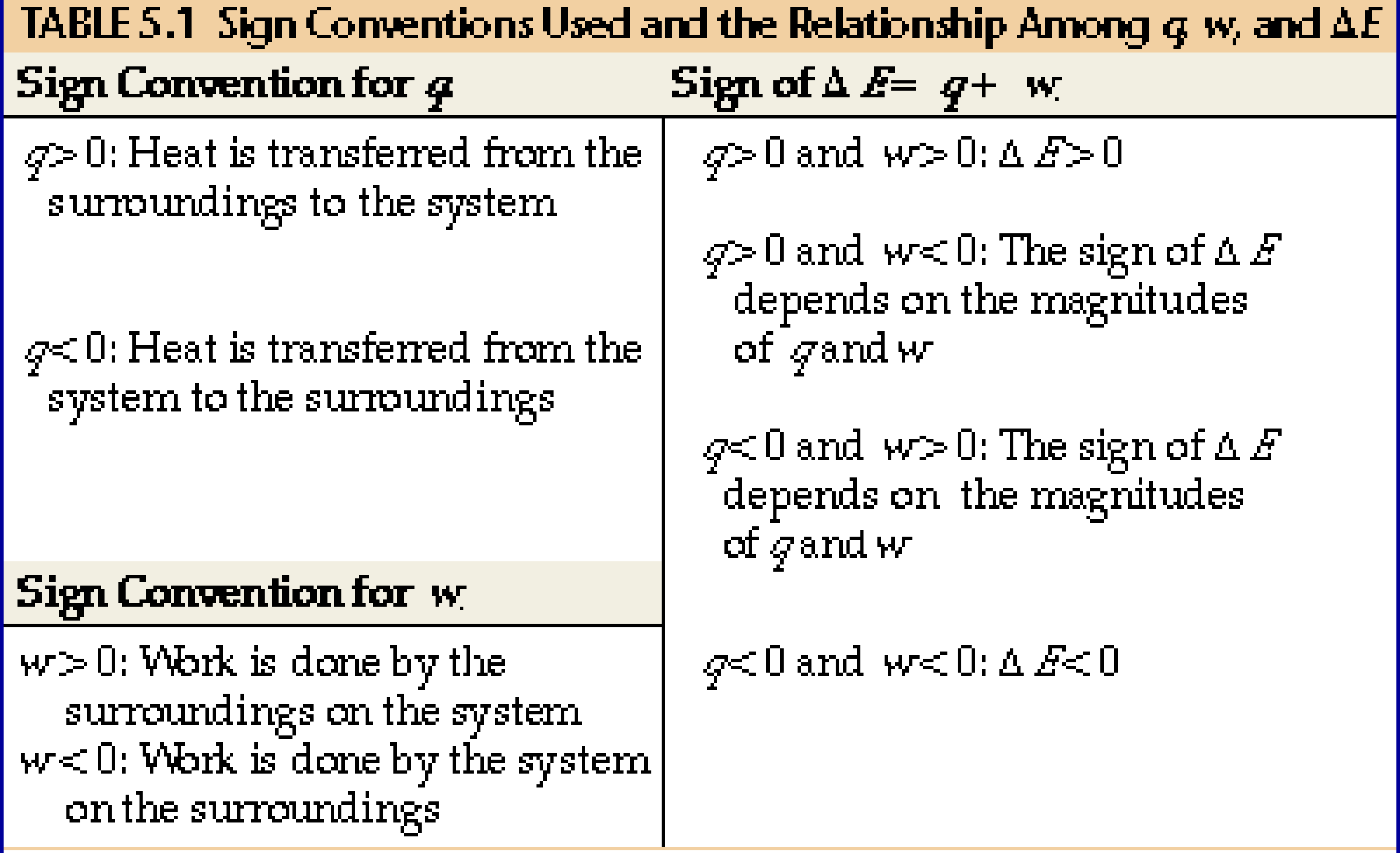


TABLE 5.1 Sign Conventions Used and the Relationship Among q, w, and ΔE

Sign Convention for q	Sign of $\Delta E = q + w$
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
$q < 0$: Heat is transferred from the system to the surroundings	$q < 0$ and $w > 0$: The sign of ΔE depends on the magnitudes of q and w
Sign Convention for w	
$w > 0$: Work is done by the surroundings on the system	$q < 0$ and $w < 0$: $\Delta E < 0$
$w < 0$: Work is done by the system on the surroundings	

Like P, V, T, and n, ΔE is a state function since the change in ΔE depends only on the initial and final energies of the system and not on the details of the process the system underwent.

However changes in q and w take place during the process and hence depend on the nature of the process.

q and w are path dependent and called **PATH FUNCTIONS**.

Note: the 1st law does not give any indication how ΔE is divided between q and w.

Problem:

A gas expands against a constant pressure of 5 atm, from 10 to 20 L, absorbing 2kJ of heat. Calculate the work done and the change in the internal energy of the gas.

1 L-atm = 101.3 J

For a process which takes place at constant volume

$w = -P_{ext}\,\Delta V = 0$; if volume is constant

$\Delta E = q + w$

For constant volume processes, no work can be done

$\Delta E = q_v$

where q_v is the heat exchanged at constant volume

Enthalpy

Most physical and chemical changes take place under the constant pressure of the Earth’s atmosphere.

The heat lost or gained by a system undergoing a process under constant pressure is related to the change in ENTHALPY (ΔH) of the system

$$\Delta H = H_{final} - H_{initial} = q_p$$

Note: ΔH is a state function

Enthalpies of Chemical Reactions

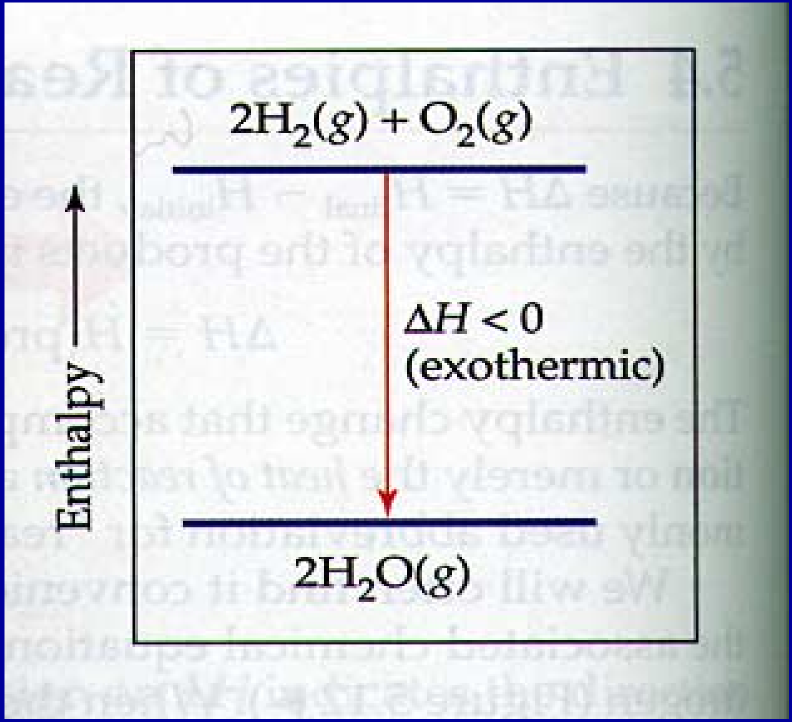
The enthalpy change for a chemical reaction is given by

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

For example:

$2H_2(g) + O_2\ (g) \dashrightarrow 2H_2O(g)$ $\Delta H = -\ 483.6$ kJ

Thermochemical reaction



In a chemical reaction, the enthalpy change during the reaction indicates whether the reaction releases energy or consumes energy.

If $\Delta H < 0$, the reaction releases heat and is EXOTHERMIC

If $\Delta H > 0$, the reaction absorbs heat and is ENDOTHERMIC

The magnitude of ΔH for a reaction is directly proportional to the amount of reactants consumed by the reaction.

$$CH_4(g) + 2O_2(g) \text{-->} CO_2(g) + 2H_2O(l) \qquad \Delta H = -890\ kJ$$

Calculate the amount of heat that would be released when 4.50 g of $CH_4(g)$ is burned in an oxygen atmosphere at constant pressure.

4.50g CH_4 => 0.28 mole CH_4

=> (0.28 mol CH_4)(-890 kJ/mol CH_4) = -250 kJ

The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction

$CH_4(g) + O_2(g) \text{ --> } CO_2(g) + 2H_2O(l)$ $\Delta H = -890\ kJ$

$CO_2(g) + 2H_2O(l) \text{ --> } CH_4(g) + O_2(g)$ $\Delta H = +890\ kJ$

The enthalpy change for a reaction depends on the phase of the reactants and products.

1) $CH_4(g) + O_2(g) \text{ --> } CO_2(g) + 2H_2O(l)$ $\Delta H = -890\ kJ$

2) $CH_4(g) + O_2(g) \text{ --> } CO_2(g) + 2H_2O(g)$ $\Delta H = -802\ kJ$

3) $2H_2O(g) \text{ --> } 2H_2O(l)$ $\Delta H = -88 kJ$

Enthalpy and Internal Energy

We know that $\Delta H = q_p$ (at constant pressure)

Since, $\Delta E = q + w$, if the volume is held constant, no pressure-volume work can be done on that system or by that system.

$$\text{work} = - P_{ext}\Delta V = 0 \text{ at constant volume}$$

Hence, for constant volume processes, $\Delta E = q_v$

Enthalpy is defined as

$$H = E + PV$$

For a system undergoing pressure-volume work, the change in enthalpy in the system is

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

If the pressure is a constant external pressure, P_{ext},

$$\Delta H = \Delta E + P_{ext}\Delta V$$

From the 1st law: $\Delta E = q + w$

For constant P: $\Delta H = q_p + w + P_{ext}\Delta V$

Since $w = - P_{ext}\ \Delta V$

$$\Delta H = q_p - P_{ext}\ \Delta V + P_{ext}\Delta V = q_p$$

For experiments carried out at constant volume, ΔE is the quantity to use since changes in internal energy equal the amount of heat involved in the process.

However, chemical reactions are typically conducted under constant pressure conditions and hence ΔH is the more commonly used quantity.

Relationship between ΔH and ΔE

$C(s) + 1/2\ O_2(g) \dashrightarrow CO(g)$ $\Delta H = -110.5$ kJ

Determine the change in internal energy accompanying this reaction.

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

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

$$\Delta(PV) = \Delta\ (nRT) = RT(\Delta n_g)$$

$$\Delta E = \Delta H - RT(\Delta n_g) \quad \text{or} \quad \Delta H = \Delta E + RT\Delta n_g$$

For this reaction $\Delta n_g = 0.5$ mol; hence $\Delta E = -111.7$ kJ

Calorimetry

Calorimetry is the measurement of the amount of heat flow and change in temperature accompanying a process.

Heat capacity (at constant pressure), C_P, of a body, is the amount of heat required to raise the temperature of the body by one degree at constant pressure.

$$\text{Heat capacity} = C_P = \frac{q}{\Delta T}$$

q is the amount of heat absorbed by the body

ΔT is the rise in temperature

Units of C_P: joule/K or cal/K

Molar heat capacity, c_P: amount of heat absorbed per mole of sample

$$\text{Molar heat capacity} = c_P = \frac{C_P}{n}$$

Units of c_P joule/(mole K)

$$q = n\, c_P\, \Delta T$$

Specific heat capacity, c_s: the amount of heat absorbed per unit mass of body

$$\text{specific heat capacity} = c_s = \frac{C_P}{m}$$

Units of c_s joule/(g K)

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

Problem: How much heat is needed to warm 250g (~ 1 cup) of water from 22^{o}C to near its boiling point 98^{o}C. The specific heat of water is 4.18 J/(g-K)?

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

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

1st Law: $\Delta E = q + w$

Work = $- P_{ext} \Delta V$

At constant volume, $w = 0$; $\Delta E = q_v$

At constant pressure, $\Delta H = q_p$

$\Delta H > 0$ endothermic $\Delta H < 0$ exothermic

$\Delta H = \Delta E + RT \Delta n_g$

Calorimetry:

heat gained by colder object = heat lost by warmer object

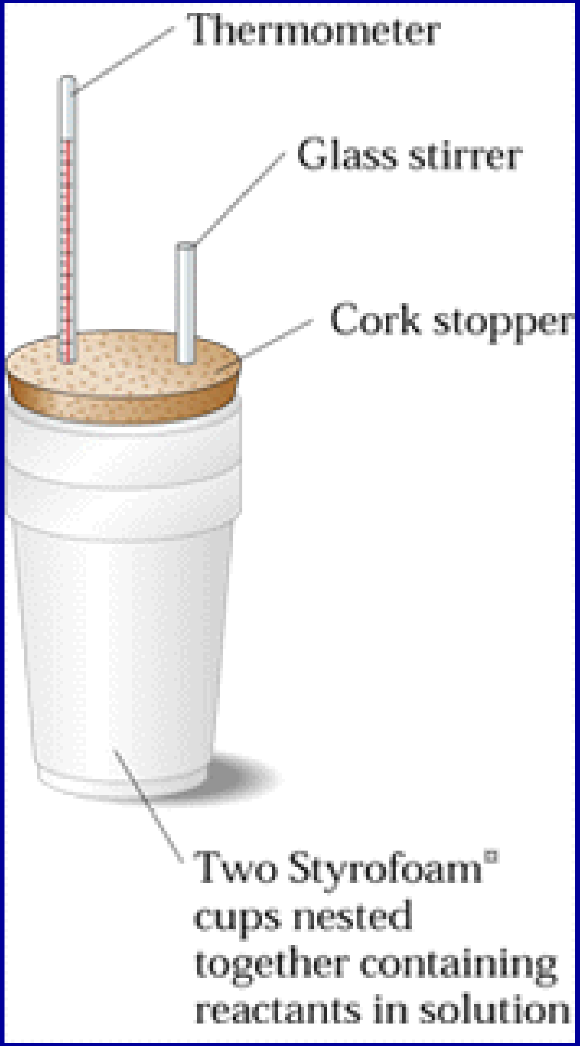
If two objects at different temperatures are in contact with one another, heat flows from the hotter body to the colder body in an attempt for the system to reach an equilibrium.

Assuming that there is no heat lost to the surroundings, then:

heat lost by hotter object = heat gained by cooler object

$$n_1c_{P1}\Delta T_1 = n_2c_{P2}\Delta T_2$$

$$n_1c_{P1}\,(T_{f1} - T_{i1}) = n_2c_{P2}\,(T_{f2} - T_{i2})$$


Thermometer
Glass stirrer
Cork stopper
Two Styrofoam® cups nested together containing reactants in solution

Problem

When 50.mL of 1.0M HCl and 50.mL of 1.0M NaOH are mixed in a calorimeter, the temperature of the resultant solution increases from 21.0°C to 27.5°C. Calculate the enthalpy change per mole of HCl for the reaction carried out at constant pressure, assuming that the calorimeter absorbs only a negligible quantity of heat, the total volume of the solution is 100. mL, the density of the solution is 1.0g/mL and its specific heat is 4.18 J/g-K.

q_{rxn} = - (c_s solution J/g-K) (mass of solution g) (ΔT K)

= - (4.18 J/g-K) [(1.0g/mL)(100 mL)] (6.5 K)

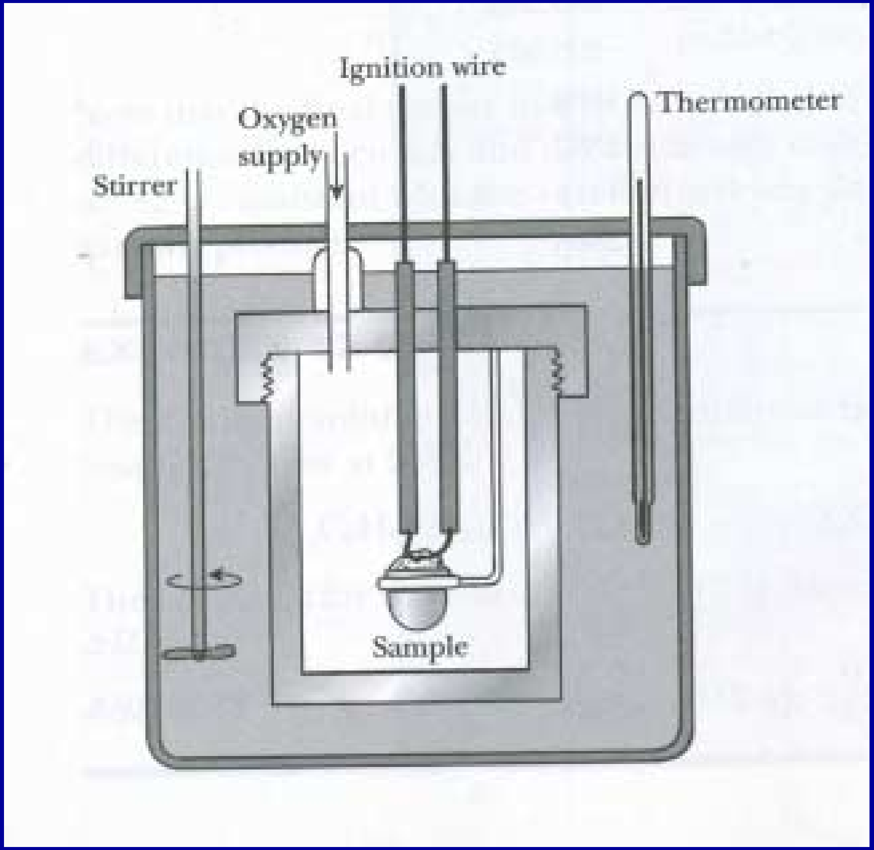
= - 2700 J or 2.7 kJ

ΔH = 2.7 kJ

Enthalpy change per mole of HCl = (-2.7 kJ)/(0.050 mol)

= - 54 kJ/mol

Bomb calorimeter: used to determine heats of combustion and caloric values of foods.



Experimentally determine heat capacity of calorimeter

$$q_{rxn} = - C_{calorimeter}\, \Delta T$$

Problem

When methylhydrazine, CH_6N_2, a rocket fuel, undergoes combustion the following reaction occurs:

$$CH_6N_2(l) + 5\ O_2(g) \dashrightarrow 2N_2(g) + 2CO_2(g) + 6H_2O(g)$$

When 4.00 g of $CH_6N_2(l)$ is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00°C to 39.50°C. In a separate experiment, the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. What is the heat of reaction for the combustion of a mole of $CH_6N_2(l)$?

$$q_{rxn} = -\ C_{calorimeter}\ \Delta T$$

$$= -\ (7.794\ kJ/^{o}C)\ (14.50^{o}C) = -113.0\ kJ$$

Heat of reaction per mole of $CH_6N_2(l)$

$$(-113.0\ kJ)/(0.0868\ mol) = 1.30 \times 10^3\ kJ/mol$$

Calorimetry of Foods

Most of the energy our bodies need comes from the metabolism of carbohydrates, fats and proteins.

Carbohydrates decompose into glucose, $C_6H_{12}O_6$.

Metabolism of glucose produces CO_2 and H_2O and energy

$$C_6H_{12}O_6(s) + 6O_2\ (g) \dashrightarrow 6CO_2\ (g) + 6H_2O(l)$$

$$\Delta H = -2803\ \text{kJ}$$

The combustion of tristearin $C_{57}H_{110}O_6$, a typical fat:

$2C_{57}H_{110}O_6 + 163O_2\text{ (g)} \text{ --> } 114\ CO_2\text{(g)} + 110\ H_2O\text{(l)}$

$\Delta H = -75{,}520\text{ kJ}$

On average, the metabolism of

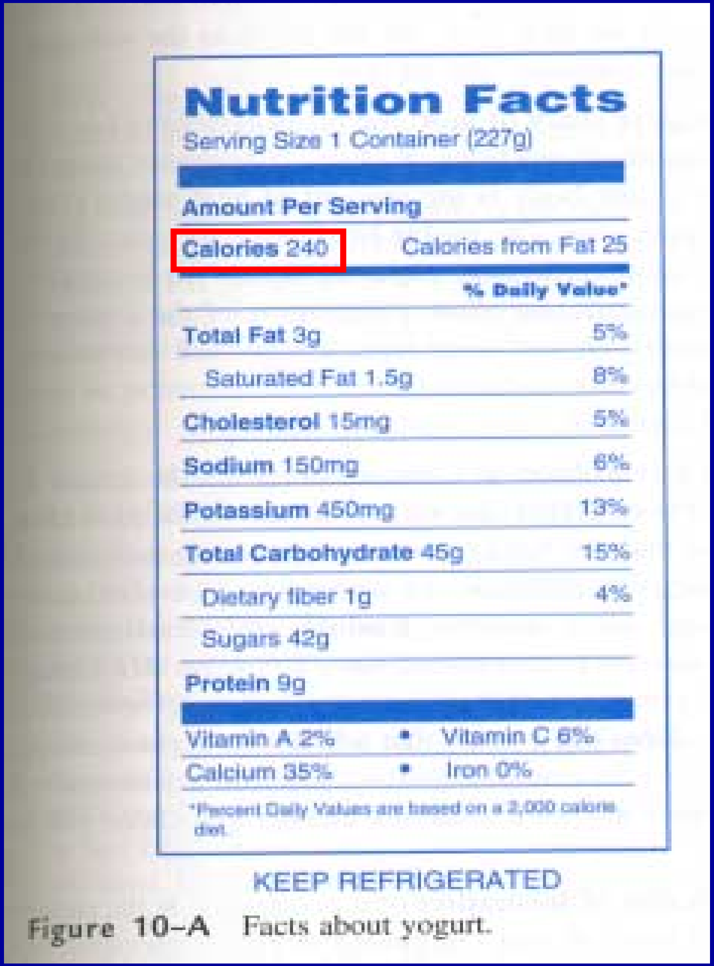
proteins produces ~ 4 Cal/g

carbohydrates produces ~ 4Cal/g

fats produces about ~ 9 Cal/g

(1 Cal = 1000 cal; I Cal = 4.184 kJ)

Calculate Calories from amount of carbohydrate, protein and fats



Nutrition Facts

Serving Size 1 Container (227g)

Amount Per Serving

Calories 240	Calories from Fat 25
	% Daily Value*
Total Fat 3g	5%
Saturated Fat 1.5g	8%
Cholesterol 15mg	5%
Sodium 150mg	6%
Potassium 450mg	13%
Total Carbohydrate 45g	15%
Dietary fiber 1g	4%
Sugars 42g	
Protein 9g	

Vitamin A 2%	• Vitamin C 6%
Calcium 35%	• Iron 0%

*Percent Daily Values are based on a 2,000 calorie diet.

KEEP REFRIGERATED

Figure 10-A Facts about yogurt.

(45g carb x 4 Cal/g carb) +

(9g protein x 4 Cal/g protein) +

(3g fat x 9 Cal/g fat) = 243 Cal

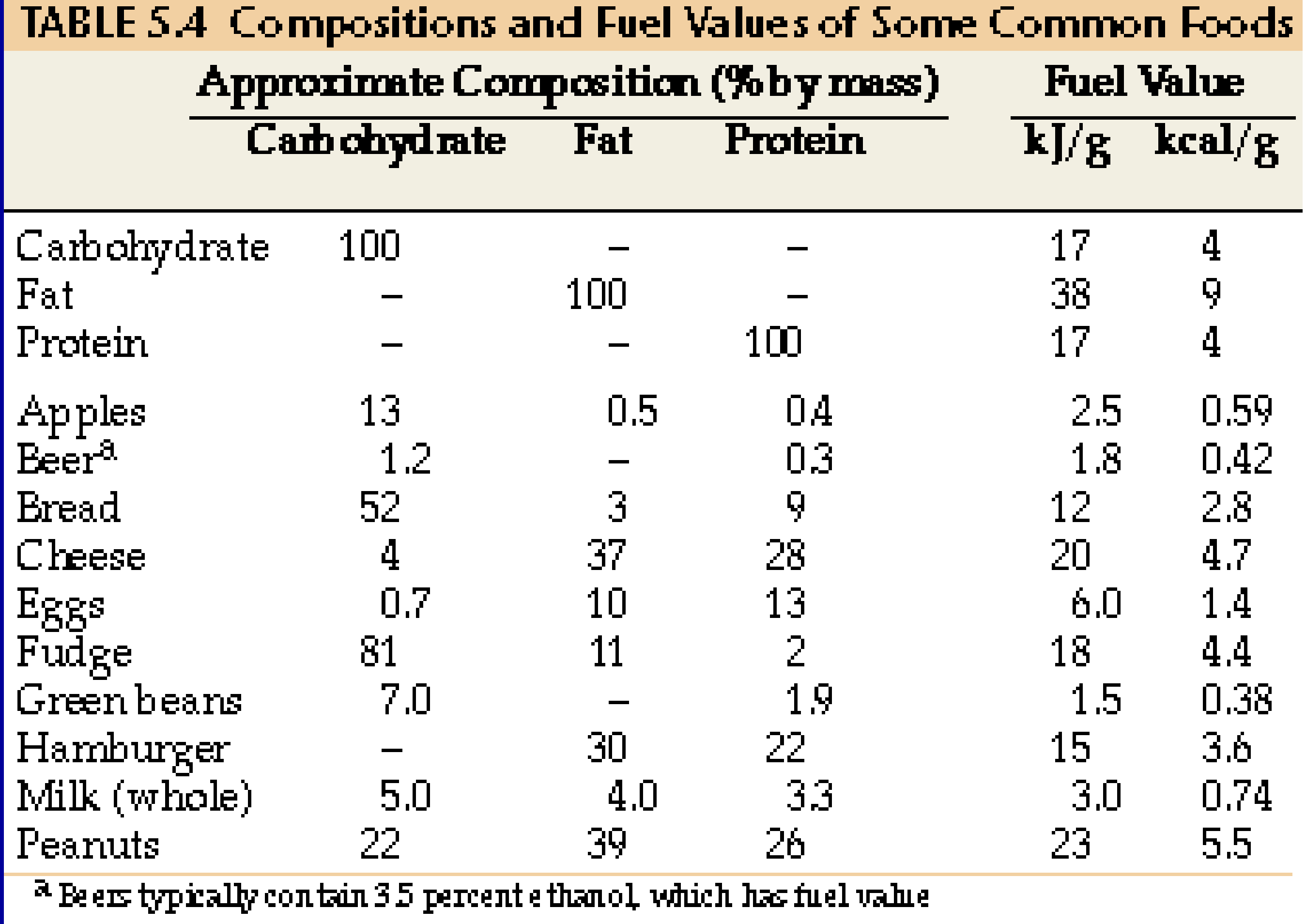


TABLE 5.4 Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g
Carbohydrate	100	–	–	17	4
Fat	–	100	–	38	9
Protein	–	–	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer[a]	1.2	–	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	–	1.9	1.5	0.38
Hamburger	–	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

[a] Beers typically contain 3.5 percent ethanol, which has fuel value

Hess’s Law

Known values of ΔH for reactions can be used to determine ΔH’s for other reactions.

ΔH is a state function, and hence depends only on the amount of matter undergoing a change and on the initial state of the reactants and final state of the products.

If a reaction can be carried out in a single step or multiple steps, the ΔH of the reaction will be the same regardless of the details of the process (single vs multi- step).

$$\begin{tikzcd}
A \arrow[rrr, "\Delta H_6"'] \arrow[d, "\Delta H_1"] & & & F \\
B \arrow[dr, "\Delta H_2"] & & & E \arrow[u, "\Delta H_5"'] \\
& C \arrow[r, "\Delta H_3"] & D \arrow[ur, "\Delta H_4"'] &
\end{tikzcd}$$

$$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

$$CH_4(g) + O_2(g) \dashrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890\ kJ$$

If the same reaction was carried out in two steps:

$$CH_4(g) + O_2(g) \dashrightarrow CO_2(g) + \cancel{2H_2O(g)} \qquad \Delta H = -802\ kJ$$

$$\cancel{2H_2O(g)} \dashrightarrow 2H_2O(l) \qquad \Delta H = -88\ kJ$$

$$CH_4(g) + O_2(g) \dashrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890\ kJ$$

Net equation

Hess's law : if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy change for the individual steps.

The enthalpy of combustion of C to CO_2 is -393.5 kJ/mol, and the enthalpy of combustion of CO to CO_2 is -283.0 kJ/mol CO.

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(2) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0$ kJ

Use this data to calculate the enthalpy change of combustion of C to CO

(3) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ $\Delta H = ?$

To calculate ΔH for (3) need to rearrange equations (1) & (2)

Need C(s) and $1/2 O_2(g)$ on the left and CO on the right

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5\ kJ$

$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$ $\Delta H = 283.0\ kJ$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H = -110.5\ kJ$

Calculate ΔH for the reaction:

$$2C(s) + H_2(g) \dashrightarrow C_2H_2\,(g)$$

given the following reactions and their respective enthalpy changes:

(1) $C_2H_2\,(g) + \frac{5}{2} O_2\,(g) \text{-->} 2CO_2\,(g) + H_2O(l)$ $\Delta H = -1299.6 kJ$

(2) $C(s) + O_2\,(g) \text{-->} CO_2\,(g)$ $\Delta H = -393.5\ kJ$

(3) $H_2\,(g) + \frac{1}{2} O_2\,(g) \text{-->} H_2O(l)$ $\Delta H = -285.8\ kJ$

To solve this problem, note that given reaction involves 2 moles of C(s).

Reaction (2) must be multiplied by 2 and the ΔH for 2 moles of C(s) will be twice the ΔH for 1 mole C(s) reacting

Also, need the reverse of equation (1)

(1) $2CO_2\,(g) + H_2O(l) \text{-->} C_2H_2\,(g) + \frac{5}{2}O_2\,(g)$ $\Delta H = 1299.6\text{kJ}$

(2) $2C(s) + 2O_2\,(g) \text{-->} 2CO_2\,(g)$ $\Delta H = -787.0\text{ kJ}$

(3) $H_2\,(g) + \frac{1}{2}O_2\,(g) \text{-->} H_2O(l)$ $\Delta H = -285.8\text{ kJ}$

$2C(s) + H_2\,(g) \text{-->} C_2H_2\,(g)$ $\Delta H = -226.8\text{ kJ}$

Enthalpies of Formation

$$\Delta H = \Sigma H_{products} - \Sigma H_{reactants}$$

The enthalpy of formation, ΔH_f, or heat of formation, is defined as the change in enthalpy when one mole of a compound is formed from its stable elements.

$H_2(g) + 1/2\ O_2\ (g) \rightarrow H_2O(g) \qquad \Delta H_f = -242\ kJ$

In order to compare the enthalpies of different reactions, it is necessary to define a set of conditions called the standard state.

The standard state of a substance is its pure form at atmospheric pressure of 1 atm and the temperature of interest (usually 298 K).

The most stable form of an element at 1 atm is defined as the standard state of that element.

The standard state of oxygen at 1 atm is O_2(g), for nitrogen, N_2(g).

The **standard enthalpy of formation (ΔH_f^o)** of a compound is defined as the enthalpy change for the reaction that forms 1 mole of compound from its elements, with all substances in their standard states.

The standard enthalpy of formation for ethanol, C_2H_5OH, is the enthalpy change accompanying the following reaction.

$$C(s) + O_2(g) + H_2(g) \text{ --> } C_2H_5OH(l) \qquad \Delta H_f^o = -277.7 \text{ kJ}$$

The standard enthalpy of formation of the most stable form of an element under standard conditions is ZERO.

ΔH_f^o for C(graphite), $H_2(g)$, $O_2(g)$ are zero

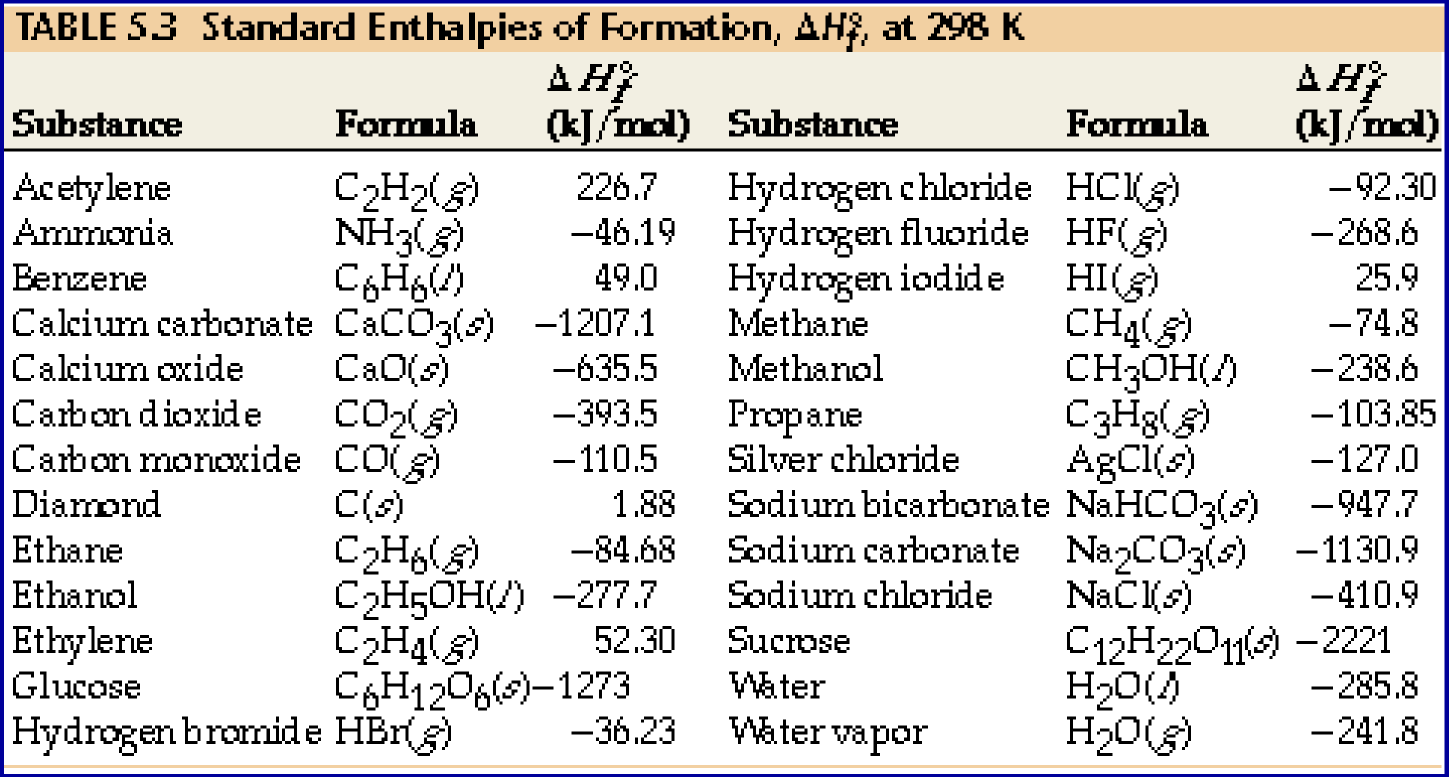


TABLE 5.3 Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.6
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.8
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

The stoichiometry for formation reactions indicate the formation of 1 mole of the desired compound, hence enthalpies of formation are always listed as kJ/mol.

Using Enthalpies of Formation to calculate Standard Enthalpies of Reactions

Consider the combustion of propane (C_3H_8) gas to form $CO_2(g)$ and $H_2O(l)$

$$C_3H_8\ (g) + 5\ O_2\ (g) \dashrightarrow 3CO_2\ (g) + 4H_2O(l)$$

This equation can be written as the sum of the following three equations

$C_3H_8(g) \dashrightarrow 3C(s) + 4H_2(g)$ $\qquad \Delta H_1 = -\ \Delta H_f^o\ (C_3H_8(g)\ )$

$+\ 3C(s) + 3O_2(g) \dashrightarrow 3CO_2(g)$ $\qquad \Delta H_2 = 3 \times \Delta H_f^o\ (CO_2(g)\ )$

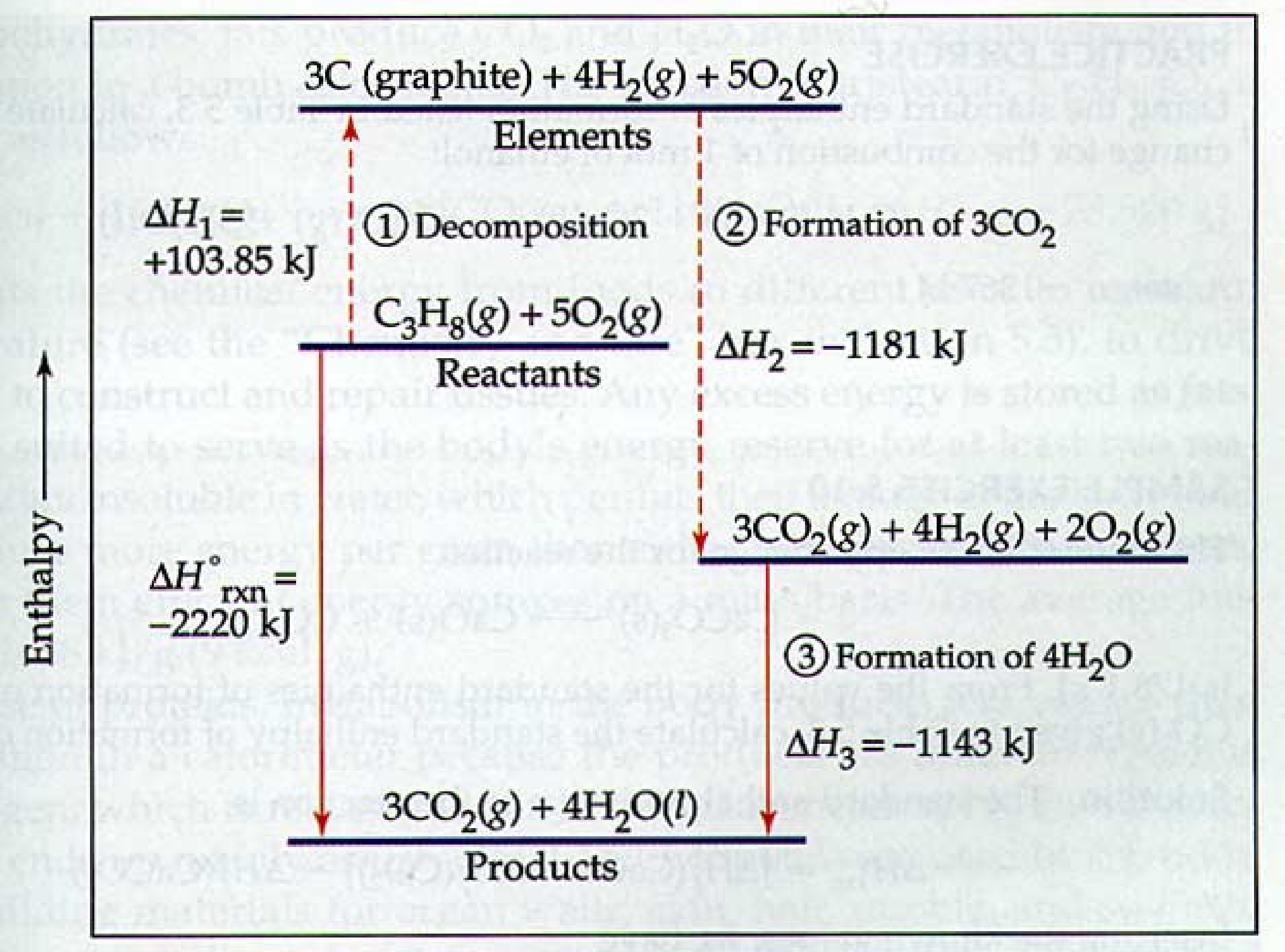
$+\ 4H_2(g) + 2O_2(g) \dashrightarrow 4H_2O(l)$ $\qquad \Delta H_3 = 4 \times \Delta H_f^o\ (H_2O\ (l)\ )$

$$C_3H_8\ (g) + 5\ O_2\ (g) \dashrightarrow 3CO_2\ (g) + 4H_2O(l)$$

$$\Delta H^o_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Looking up the table for the standard heats of formation for each equation

ΔH^o_{rxn} = -(-103.85) + 3(-393.5) + 4(-285.8)) = -2220 kJ



In general,

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

where

n and m are the stoichiometric coefficients in the reaction,

and assuming that the ΔH_f^o's are per mole

Calculate the standard enthalpy change for the combustion of 1 mole of benzene (C_6H_6 (l)) to CO_2(g) and H_2O(l). Compare the quantity of heat produced by the combustion of 1.00 g of propane (C_3H_8(g)) to that produced by 1.00 g of C_6H_6 (l)

First write a balanced equation for the combustion of 1 mole of C_6H_6 (l)

$$C_6H_6\,(l) + \frac{15}{2}\,O_2\,(g) \dashrightarrow 6CO_2\,(g) + 3H_2O(l)$$

$$\Delta H^o_{rxn} = [6\,\Delta H_f^o(CO_2) + 3\Delta H_f^o(H_2O)] - [1\Delta H_f^o(C_6H_6) + (15/2)\Delta H_f^o(O_2)]$$

$$= 6(-393.5\text{ kJ}) + 3(285.8\text{ kJ}) - 49.0\text{ kJ} - 7.5(0\text{ kJ})$$

$$= -3267\text{ kJ}$$

For the combustion of 1 mole of propane ΔH^o_{rxn} = -2220 kJ

Hence for 1.00g propane, which corresponds to 0.0227 mol propane, ΔH^o_{rxn} = 0.0227mol x -2220 kJ/mol = - 50.3 kJ/g

For C_6H_6 (l) => ΔH^o_{rxn} = - 41.8 kJ/g

The combustion of propane results in more energy released per gram compared to the combustion of benzene.

Fuels

During the complete combustion of fuels, carbon is completely converted to CO_2 and hydrogen to H_2O, both of which have large negative enthalpies of formation.

$\Delta H_f^o (CO_2) = -393.5$ kJ/mol

$\Delta H_f^o (H_2O) = -242$ kJ/mol

The greater the percentage of carbon and hydrogen in a fuel, the higher its fuel value.

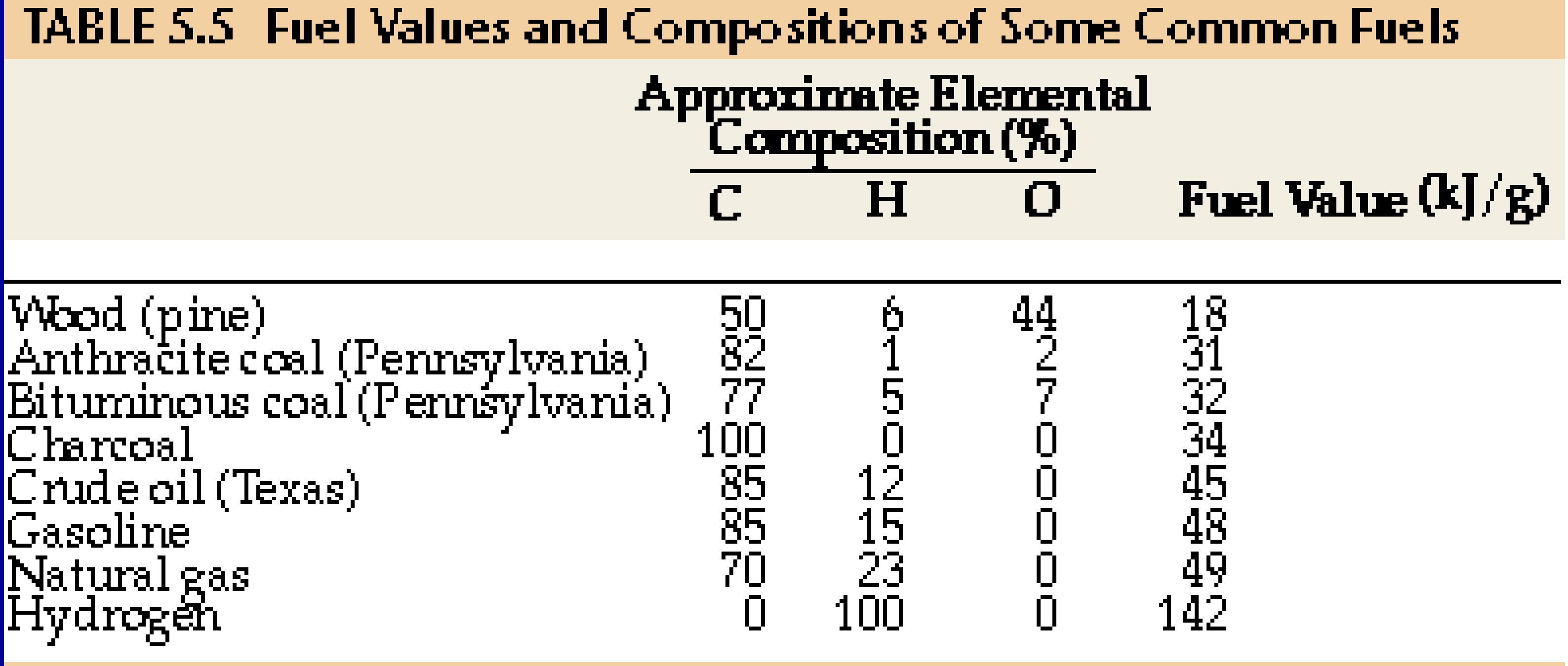


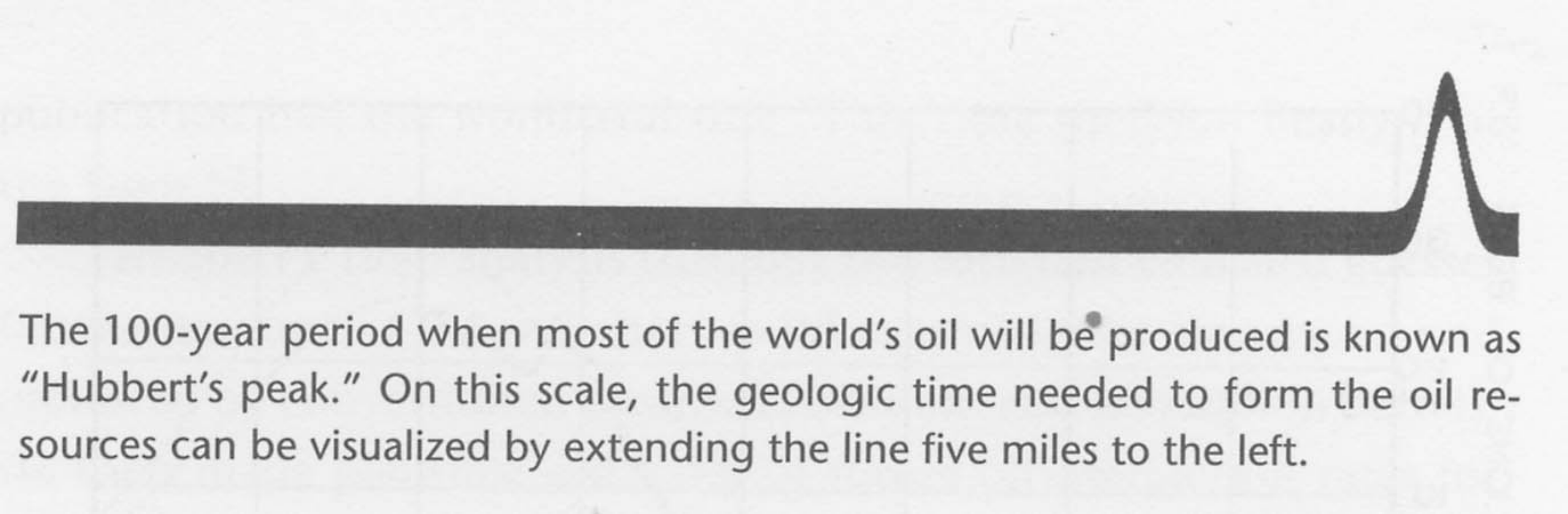
TABLE 5.5 Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (%)			
	C	H	O	Fuel Value (kJ/g)
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142

Global Energy Reserves (1988) (units of $Q = 10^{21}$ J)

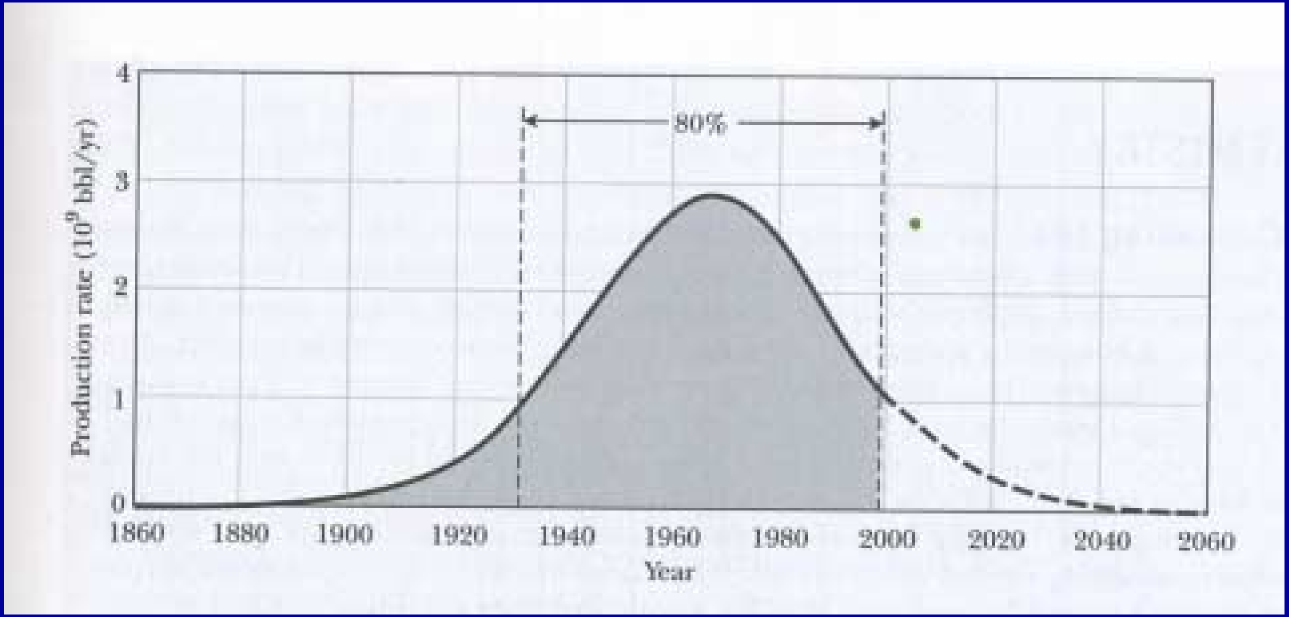
Fuel Type	Proven Reserves	Est. Reserves
Coal	25Q	118Q
Oil	5Q	9Q
Natural Gas	4Q	10Q

Note: Total amount of commercially energy currently consumed by humans ~ 0.5Q annually



The 100-year period when most of the world's oil will be produced is known as "Hubbert's peak." On this scale, the geologic time needed to form the oil resources can be visualized by extending the line five miles to the left.

Hubbert's Peak, K. S. Deffeyes



US crude oil production

Alternate Fuels

Natural Gas and Propane

$C(s) + O_2(g) \text{-->} CO_2(g) \quad \Delta H = -393.5 \text{ kJ/mol}$

$CH_4(g) + 2O_2(g) \text{-->} CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ/mol}$

$C_3H_8(g) + O_2(g) \text{-->} 3CO_2 + H_2O \quad \Delta H = -2213 \text{ kJ/mol}$

Natural gas, primarily methane with small amounts of ethane and propane used for cooking and heating.

Highly compressed natural gas (CNG) - commercial vehicles.

Liquid petroleum gas (LPG) - propane - also used as a fuel for vehicles

Name	Heat released per gram
C(s)	34 kJ
CH_4(g)	55.6 kJ
C_3H_8(g)	50.3 kJ

Name	Heat released per mole of CO_2(g) released
C(s)	393.5 kJ
CH_4(g)	890 kJ
C_3H_8(g)	738 kJ

CH_4(g) and C_3H_8(g) release more energy per gram and can be considered to be “cleaner” fuels.

Disadvantages: leakage of CH_4 from pipes, storage and transportation, need to be compressed

Methanol & Ethanol

Alcohols have the advantage over hydrogen and natural gas in that they are liquids at atmospheric pressure and temperature.

Compound	$\Delta H_{combustion}$ (kJ/g)
$CH_3OH(l)$	-22.7
$C_2H_5OH\ (l)$	-29.7
$CH_4(g)$	-55.6
C(s)	-34

Ethanol can be produced from plant material

Large scale production of methanol would likely start with coal

Hydrogen

$H_2(g) + 1/2O_2(g) \xrightarrow{\text{spark}} H_2O$ $\Delta H = -242$ kJ/mol

Compound	$\Delta H_{\text{combustion}}$ (kJ/g)
$CH_3OH(l)$	-22.7
$C_2H_5OH(l)$	-29.7
$CH_4(g)$	-55.6
C(s)	-34
$H_2(g)$	-120

Advantages of using H_2 as a fuel

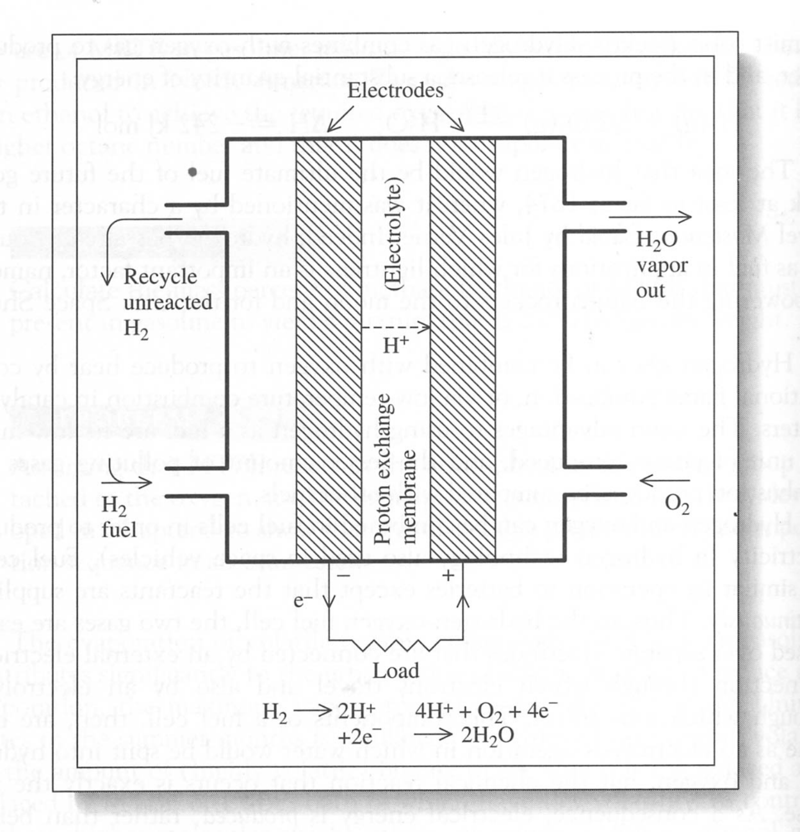
energy released per gram

low polluting

H_2/O_2 Fuel cells: Opposite of electrolysis of water

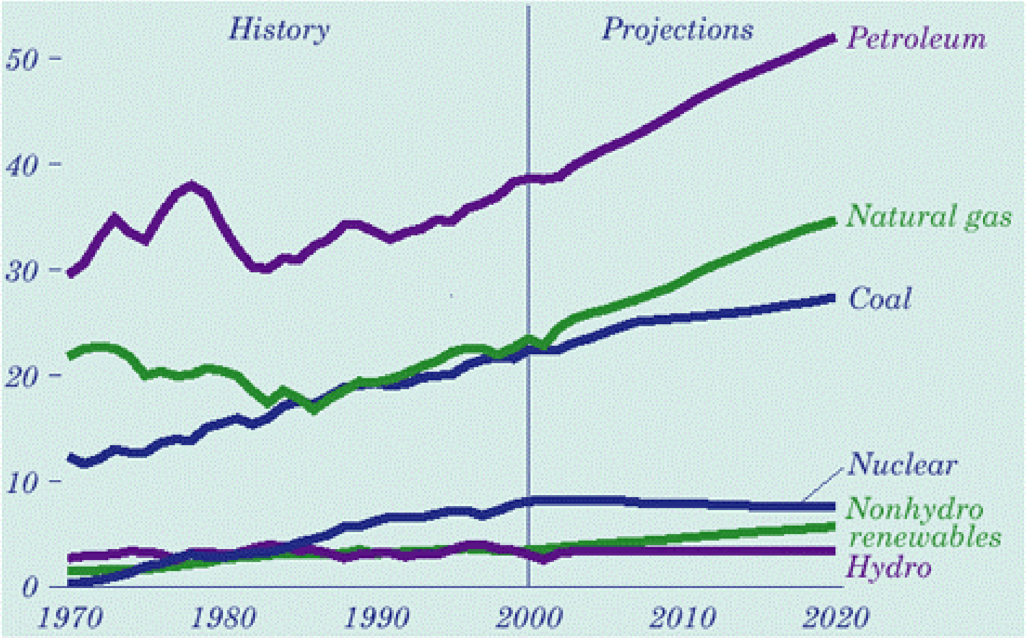
Electrical energy is produced when the following redox reaction occurs

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$



http://www.msnbc.com/news/248093.asp?cp1=1

Figure 2. Energy consumption by fuel, 1970-2020 (quadrillion Btu)



History: Energy Information Administration, *Annual Energy Review 2000*, DOE/EIA-0384(2000) (Washington, DC, August 2001). **Projections:** Tables A1 and A18.

Energy Information Administration, Dept. of Energy

http://www.eia.doe.gov/oiaf/aeo/index.html#production