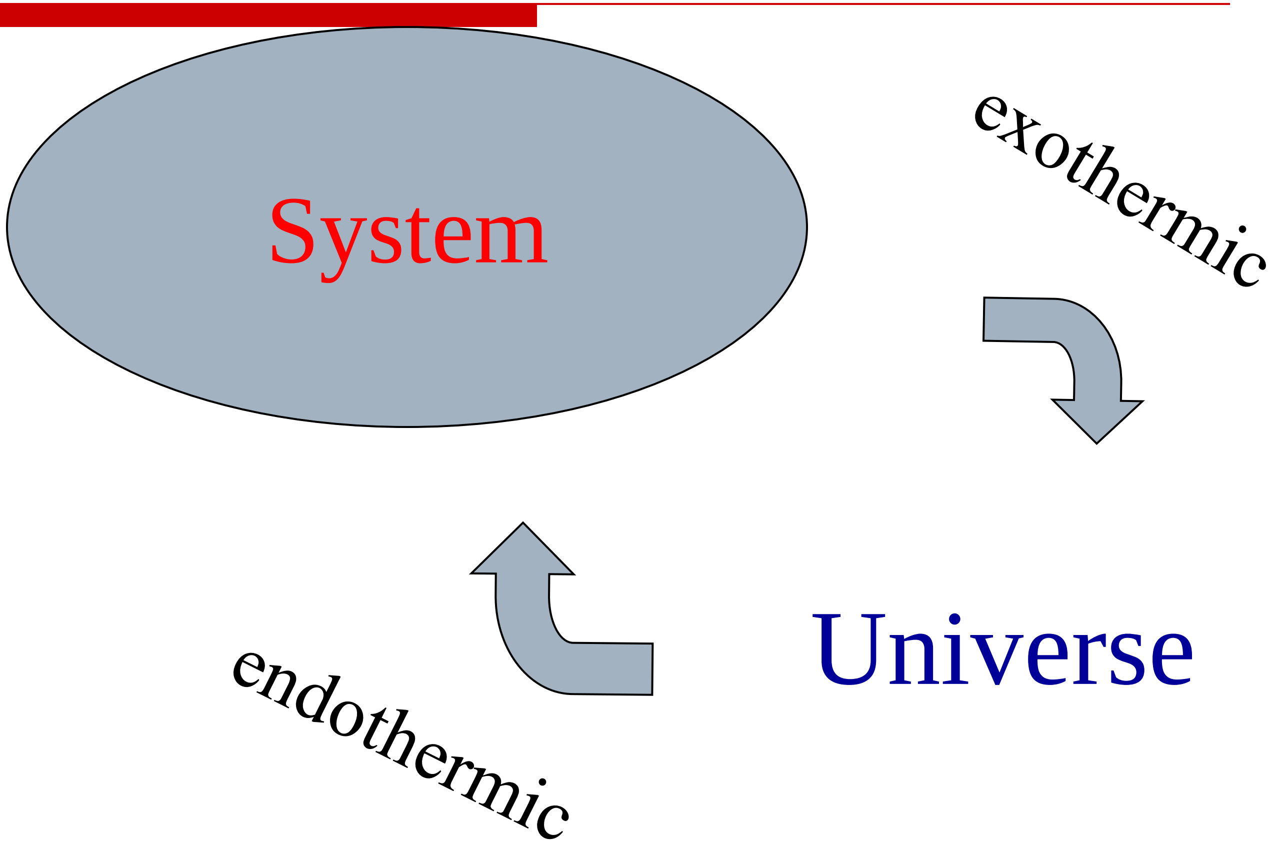
THERMOCHEMISTRY

Chemical Thermodynamics

The chemical science dealing with the relationships between heat and other forms of energy known as work.



System

exothermic

endothermic

Universe

System

The substance under study

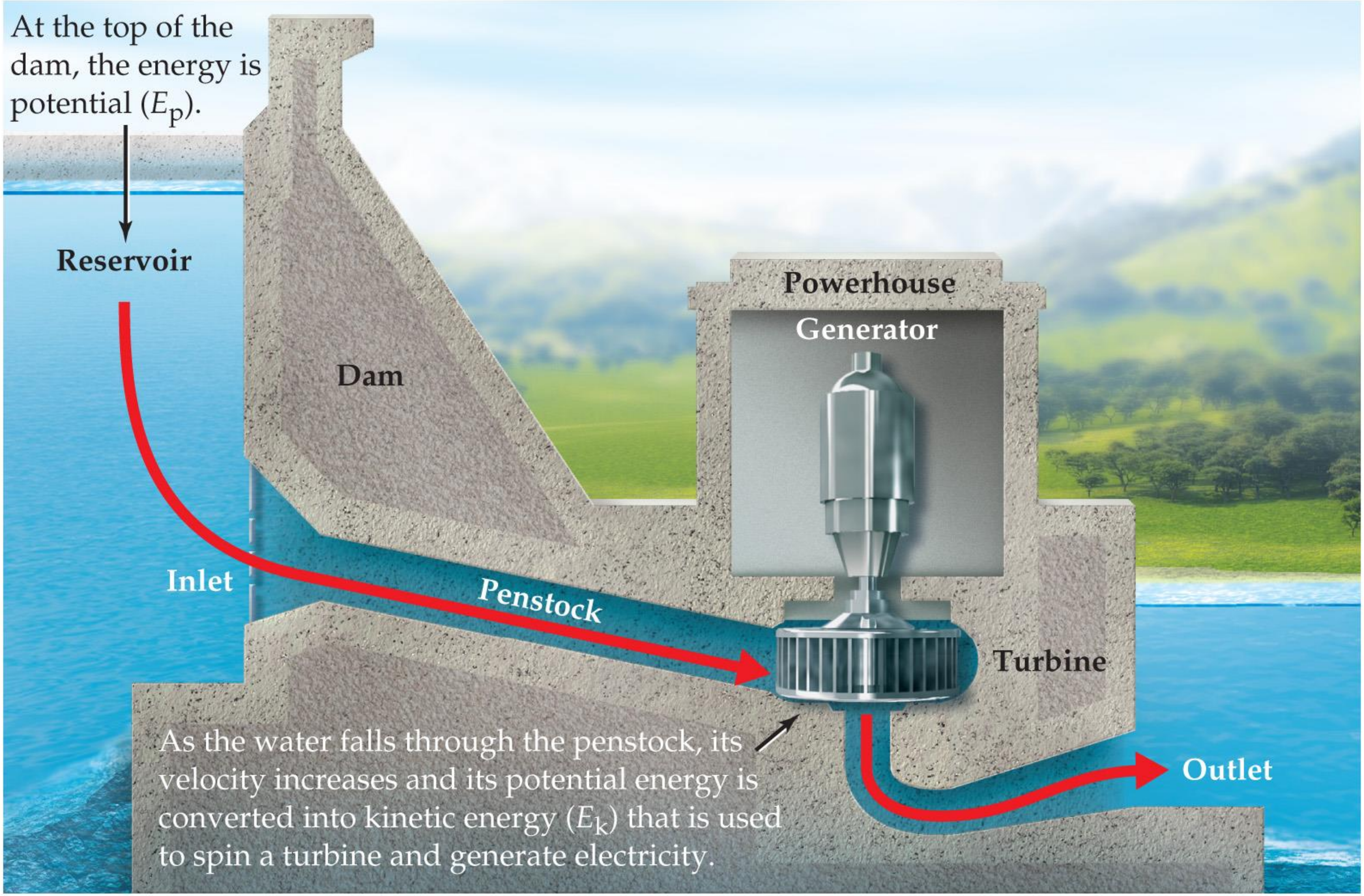
Universe (Surroundings)

Everything except the substance under study

Internal Energy

The total of all forms of energy present in a substance

- Energy is transferred out of a system when heat is lost from the system or when the system does work on the surroundings
- Energy is transferred into the system when heat is gained by the system or when the surroundings do work on the system



At the top of the dam, the energy is potential (E_p).

As the water falls through the penstock, its velocity increases and its potential energy is converted into kinetic energy (E_k) that is used to spin a turbine and generate electricity.

Thermochemistry

A branch of thermodynamics dealing with the determination and study of heat absorbed or evolved during chemical reactions or during phase changes

Energy: The capacity to supply heat or do work.

Kinetic energy (E_K): Energy of motion

vs.

Potential Energy (E_p): Stored energy

Conservation of Energy Law

Energy cannot be created or destroyed; it can only be converted from one form into another.

Heat

A measure of molecular motion which moves from one body to another due to a difference in temperature

Temperature

A measure of transferable heat energy

-degree Fahrenheit

-degree Celsius

-Kelvin

Heat Measurement Units

- Calorie
  - The energy needed to raise one gram of water by one degree Celsius
  - kilocalorie (kcal)
- Joule
  - The SI unit for all forms of energy including heat energy
  - Kilojoule
  - 4.184 J = 1 cal

First Law of Thermodynamics

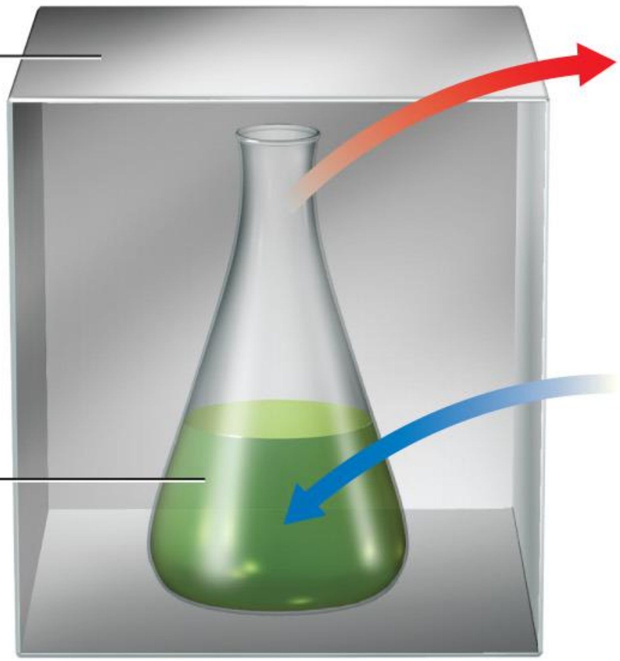
- The energy of the universe is constant.

First Law

- $\Delta E = q + w$
- ΔE = *change in system's internal energy*
- q = *heat*
- w = *work*

The energy change is the difference between final and initial states.

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



Surroundings

Energy out of system to surroundings: − sign because $E_{\text{final}} < E_{\text{initial}}$.

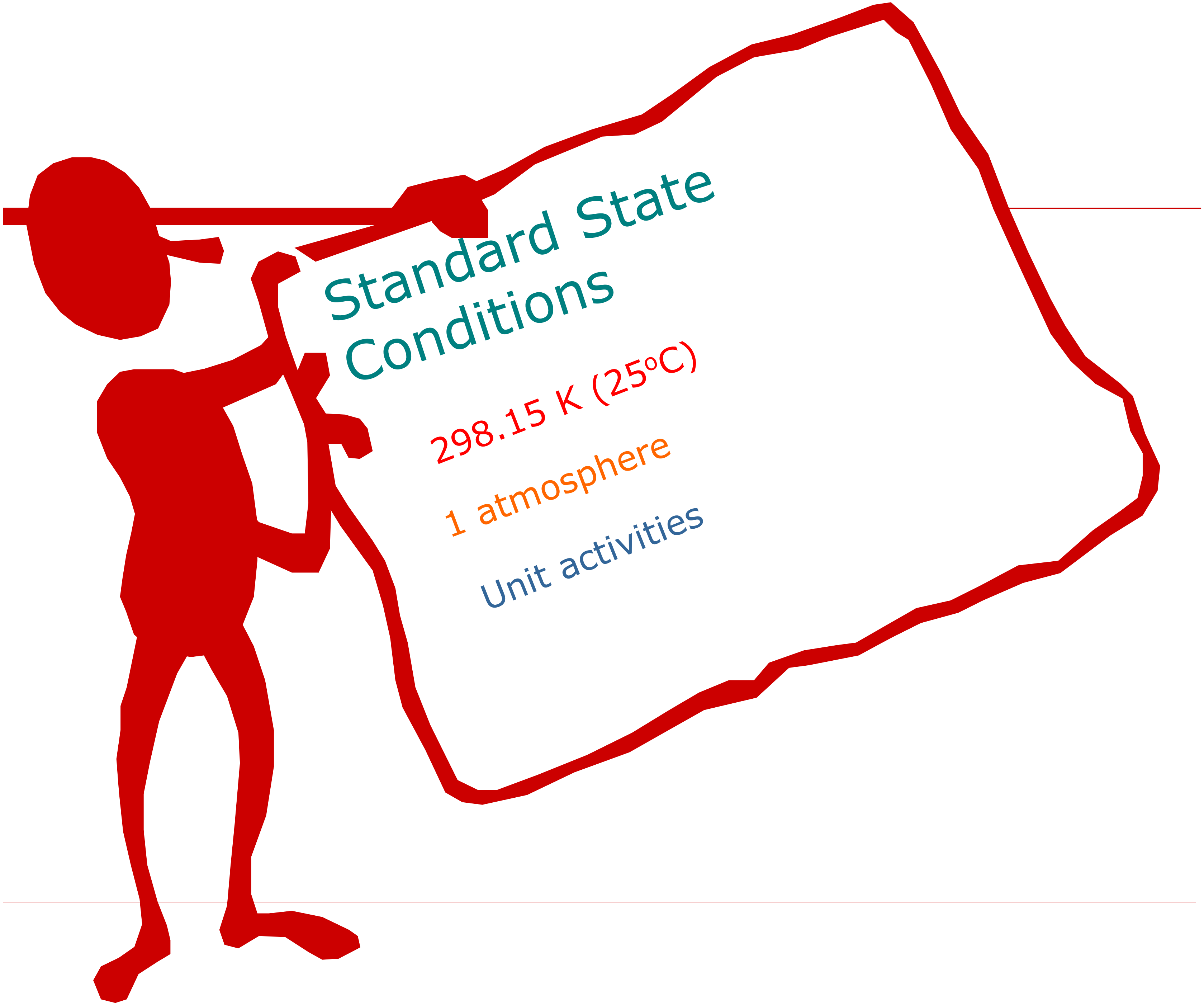
The *system* is the reaction mixture, and the *surroundings* are the flask, the room, the air, and the rest of the universe.

Energy into system from surroundings: + sign because $E_{\text{final}} > E_{\text{initial}}$.

System

State Function

- Depends only on the present state of the system - not how it arrived there.
- It is independent of pathway.



Standard State Conditions

298.15 K (25°C)

1 atmosphere

Unit activities

Work

- work = force × distance
- since pressure = force / area,
- work = pressure × volume
- $w_{system} = -P\Delta V$

$$\underbrace{C_3H_8(g) + 5\,O_2(g)}_{\text{6 mol of gas}} \longrightarrow \underbrace{3\,CO_2(g) + 4\,H_2O(g)}_{\text{7 mol of gas}}$$

$$\overset{\text{A negative value}}{w} = -P\overset{\text{A positive value}}{\Delta V}$$

Work done during expansion

$$\underbrace{3\,H_2(g) + N_2(g)}_{\text{4 mol of gas}} \longrightarrow \underbrace{2\,NH_3(g)}_{\text{2 mol of gas}}$$

$$\overset{\text{A positive value}}{w} = -P\overset{\text{A negative value}}{\Delta V}$$

Work gained during contraction

Calculating the amount of PV work

Example 8.1

Calculate the work in kilojoules done during a reaction in which the volume expands from 12.0 L to 14.5 L against an external pressure of 5.0 atm.

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$$(-12.5\,\text{L}\cdot\text{atm})(101\,{}^{\text{J}}\!/_{\text{L}\cdot\text{atm}}) = -1.3\times10^{3}\ \text{J} = -1.3\ \text{kJ}$$

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Conversion factor to convert to kJ

Enthalpy Changes
ΔH

The heat lost or gained by a system under constant pressure, with the only work done being due to expansion or contraction of the system under this constant pressure

Enthalpy (H)

- Also known as heat of reaction
- Enthalpy change (ΔH)
- $\Delta H = E + PV$

Change in Enthalpy

- Can be calculated from enthalpies of formation of reactants and products.

Calculation of Enthalpy Change

$$\Delta H = \sum \Delta H_{\text{product(s)}} - \sum \Delta H_{\text{reactant(s)}}$$

Types of Enthalpy

Enthalpy of Fusion (ΔH_{fus})

The amount of heat required to change 1 mol of substance from the solid to the liquid state at constant temperature

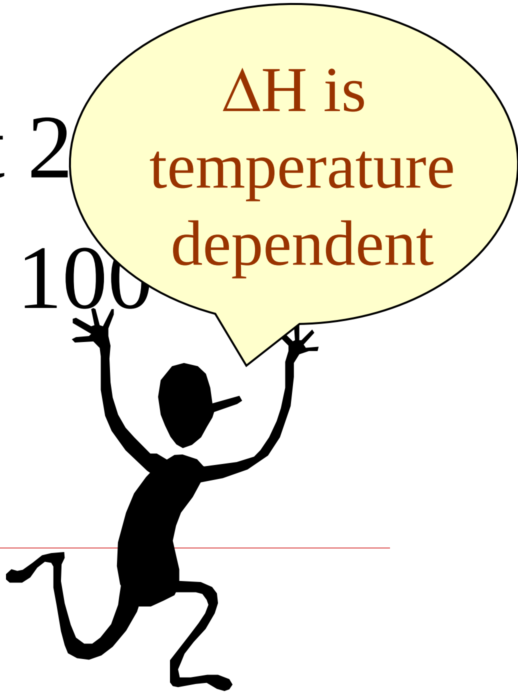
ΔH_{fus} for water is 6.01 KJ/mol at 0^oC

Enthalpy of Vaporization (ΔH_{vap})

The amount of heat required to evaporate 1 mol of a liquid at a constant temperature

ΔH_{vap} of water is 44.01KJ/mol at 2

ΔH_{vap} of water is 40.67KJ/mol at 100



ΔH is temperature dependent

Enthalpy of Combustion

The enthalpy change for the combustion of 1 mol of substance under standard state conditions

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH°_{298}(kJ mol $^{-1}$)
Carbon	$C(s) + \frac{1}{2}\,O_2(g) \longrightarrow CO(g)$	– 111
	$C(s) + O_2(g) \longrightarrow CO_2(g)$	– 394
Hydrogen	$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(g)$	– 242
	$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l)$	– 286
Magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	– 602
Sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	– 297
Carbon monoxide	$CO(g) + \frac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$	– 283
Methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$	– 802
Acetylene	$C_2H_2(g) + \frac{5}{2}\,O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$	– 1256
Methanol	$CH_3OH(l) + \frac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$	– 638
Isooctane	$C_8H_{18}(l) + \frac{25}{2}\,O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$	– 5460

Standard Molar Enthalpy of Formation ΔH^o

The heat absorbed or released during the formation of 1 mol of a pure substance from free elements in their most stable states under standard state conditions

Calculating the amount of Heat Released during a Chemical Reaction

Example 8.3

How much heat in kilojoules is evolved when 5.00 g of aluminum reacts with a stoichiometric amount of Fe_2O_3?

- How much heat in kilojoules is evolved when 5.00 g of aluminum reacts with a stoichiometric amount of Fe_2O_3?

$$2\,Al(s) + Fe_2O_3(s) \rightarrow 2\,Fe(s) + Al_2O_3(s) \qquad \Delta H^o = -852\,kJ$$

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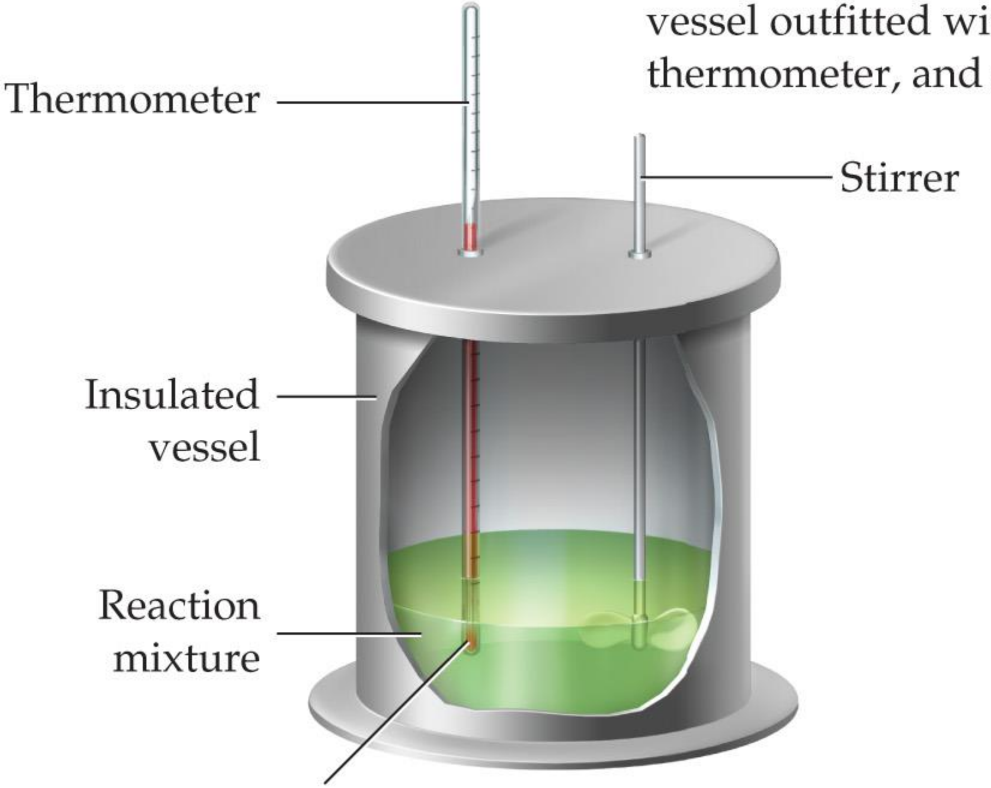
$$5\,g\ Al \times \frac{1\,mol\ Al}{26.98\,g\ Al} \times \frac{-852\ kJ}{2\ mol\ Al} = -78.8\,kJ$$

Calorimetry

- The process of measuring the amount of heat involved in a chemical or physical change
- Calorimeter
  - C_{cal} -- calorimeter constant
- $q_{reaction} + q_{soln} + q_{calorimeter} = 0$

The Bomb Calorimeter



The reaction takes place inside an insulated vessel outfitted with a loose-fitting top, a thermometer, and a stirrer.

Measuring the temperature change that accompanies the reaction makes it possible to calculate Δ*H*.

Heat Capacity (C)

- The amount of heat required to raise the temperature of an object or substance by a given amount.

$$C = \frac{q}{\Delta T}$$

Specific Heat(C)

- The amount of heat required to raise the temperature of 1 gram of a substance by 1 ^{o}C.

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

TABLE 8.1 Specific Heats and Molar Heat Capacities for Some Common Substances at 25 °C

Substance	Specific Heat J/(g · °C)	Molar Heat Capacity J/(mol · °C)
Air (dry)	1.01	29.1
Aluminum	0.897	24.2
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.449	25.1
Mercury	0.140	28.0
NaCl	0.859	50.2
Water(*s*)*	2.03	36.6
Water(*l*)	4.179	75.3

*At −11 °C

Example 8.4

What is the specific heat of silicon if it takes 192 J to raise the temperature of 45.0 g of Si by 6.0 ^{o}C?

What is the specific heat of silicon if it takes 192 J to raise the temperature of 45.0 g of Si by 6.0 °C?

amount of heat = specific heat × mass of substance × temperature

soo....

$$q = Cm\Delta T$$

What is the specific heat of silicon if it takes 192 J to raise the temperature of 45.0 g of Si by 6.0 ^{o}C?

since: $q = Cm\Delta T$

$$then:\ C = \frac{q}{m \cdot \Delta T}$$

What is the specific heat of silicon if it takes 192 J to raise the temperature of 45.0 g of Si by 6.0 ^{o}C?

and....

$$C_{Si} = \frac{q}{m \cdot \Delta \mathrm{T}} = \frac{192\,J}{(45.0\,\mathrm{g})(6.0\,{}^{o}C)} = 0.71\ {}^{J}\!\big/_{(g\,\cdot\,{}^{o}C)}$$

Calculations in a Calorimetry Experiment

Example 8.5

Aqueous silver ion reacts with aqueous chloride ion to yield a white precipitate of solid silver chloride:

$$\mathrm{Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)}$$

When 10.0 mL of 1.00 M $AgNO_3$ solution is added to 10.0 mL of 1.00 M NaCl solution at 25.0 ^{o}C in a calorimeter, a white precipitate of AgCl(s) forms and the temperature of the aqueous mixture increases to 32.6 ^{o}C. Assuming that the specific heat of the aqueous mixture is 4.18 J/g·^{o}C, that the density of the mixture is 1.00 g/mL, and that the calorimeter itself absorbs a negligible amount of heat, calculate ΔH in kilojoules for the reaction.

$$q_{Rx} + q_{soln} = 0$$

Then: $q_{Rx} = -q_{soln}$

Sooo…

$$q_{Rx} = -Cm\Delta T$$

$$q_{Rx} = -Cm\Delta T$$

$$q_{Rx} = -(4.18\ {}^{J}\!/_{g\cdot{}^{o}C})(20.0g)(32.6^{o}C - 25.0^{o}C)$$

$$q_{Rx} = -635\ J$$

Hess’s Law

If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes for each step.

Step 1 $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow \cancel{CO_{(g)}} \qquad \Delta H^{o}_{298} = -111\text{KJ}$

Step 2 $\cancel{CO_{(g)}} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^{o}_{298} = -283\text{KJ}$

Overall reaction $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^{o}_{298} = -394\text{KJ}$

The Reaction of Hydrogen & Nitrogen

$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \qquad \Delta H_{Rx}^{o} = -92.2\mathrm{KJ}$

The Reaction of Hydrogen & Nitrogen

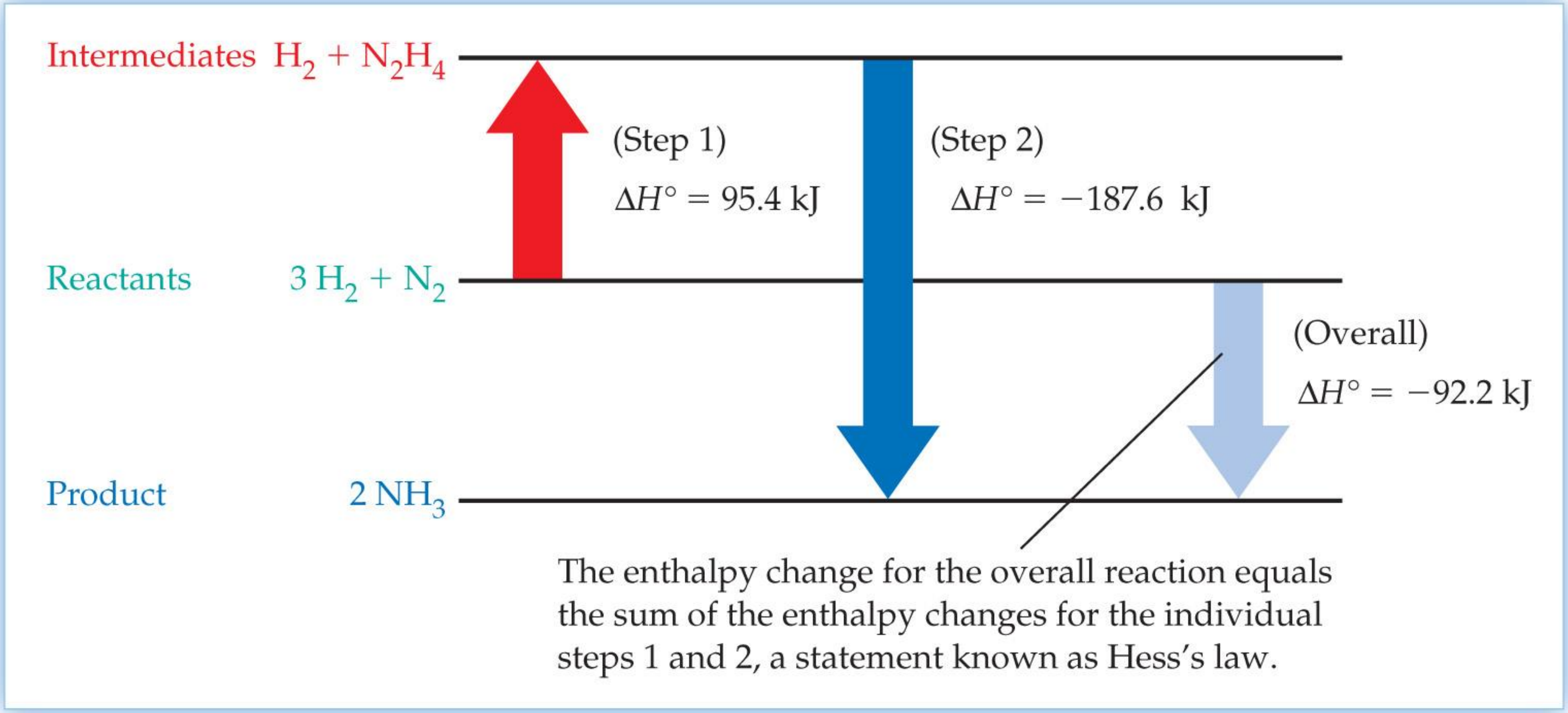
Step 1	$2H_2(g)+N_2(g)\rightarrow \cancel{N_2H_4}(g)$	$\Delta H_1^o = ?$
Step 2	$\cancel{N_2H_4}(g)+H_2(g)\rightarrow 2NH_3(g)$	$\Delta H_2^o = -283\text{KJ}$
Overall reaction	$3H_2(g)+N_2(g)\rightarrow 2NH_3(g)$	$\Delta H_{Rx}^o = -92.2\text{KJ}$

Since: $$\Delta H_1^o + \Delta H_2^o = \Delta H_{Rx}^o$$

Then: $$\Delta H_1^o = \Delta H_{Rx}^o - \Delta H_2^o$$

Sooo…

$$\Delta H_1^o = (-92.2\,\mathrm{kJ}) - (-187.6\,\mathrm{kJ}) = +95.4\ \mathrm{kJ}$$



The enthalpy change for the overall reaction equals the sum of the enthalpy changes for the individual steps 1 and 2, a statement known as Hess's law.

☐ Example 8.6

Methane, the main constituent of natural gas, burns in oxygen to yield carbon dioxide and water:

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

Use the following information to calculate ΔH^o in kilojoules for the combustion of methane:

$CH_4(g) + O_2(g) \rightarrow CH_2O(g) + H_2O(g)$ $\Delta H^o = -275.6\ kJ$

$CH_2O(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ $\Delta H^o = -526.7\ kJ$

$H_2O(g) \rightarrow H_2O(l)$ $\Delta H^o = -\ 44.0\ kJ$

$$\begin{array}{ll}
CH_4(g) + O_2(g) \rightarrow \cancel{CH_2O(g)} + \cancel{H_2O(g)} & \Delta H^o = -275.6\ \text{kJ} \\
\cancel{CH_2O(g)} + O_2(g) \rightarrow CO_2(g) + \cancel{H_2O(g)} & \Delta H^o = -526.7\ \text{kJ} \\
\cancel{2H_2O(g)} \rightarrow 2H_2O(l) & (2)[\Delta H^o = -44.0\ \text{kJ}] = -88.0\ \text{kJ} \\
\hline
CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) & \Delta H^o = -890.3\ \text{kJ}
\end{array}$$

Entropy

- Standard entropy: The entropy content of exactly 1.0 mole of substance under standard state conditions.
- The driving force for a spontaneous process is an increase in the entropy of the universe.
- Entropy, *S, can be viewed as a measure of randomness, or disorder*.

Spontaneous Processes and Entropy

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

During a Spontaneous Chemical Change:

- Systems tend toward a state of lower energy
- Systems tend toward a state of maximum disorder

Entropy of Solids, Liquids and Gases

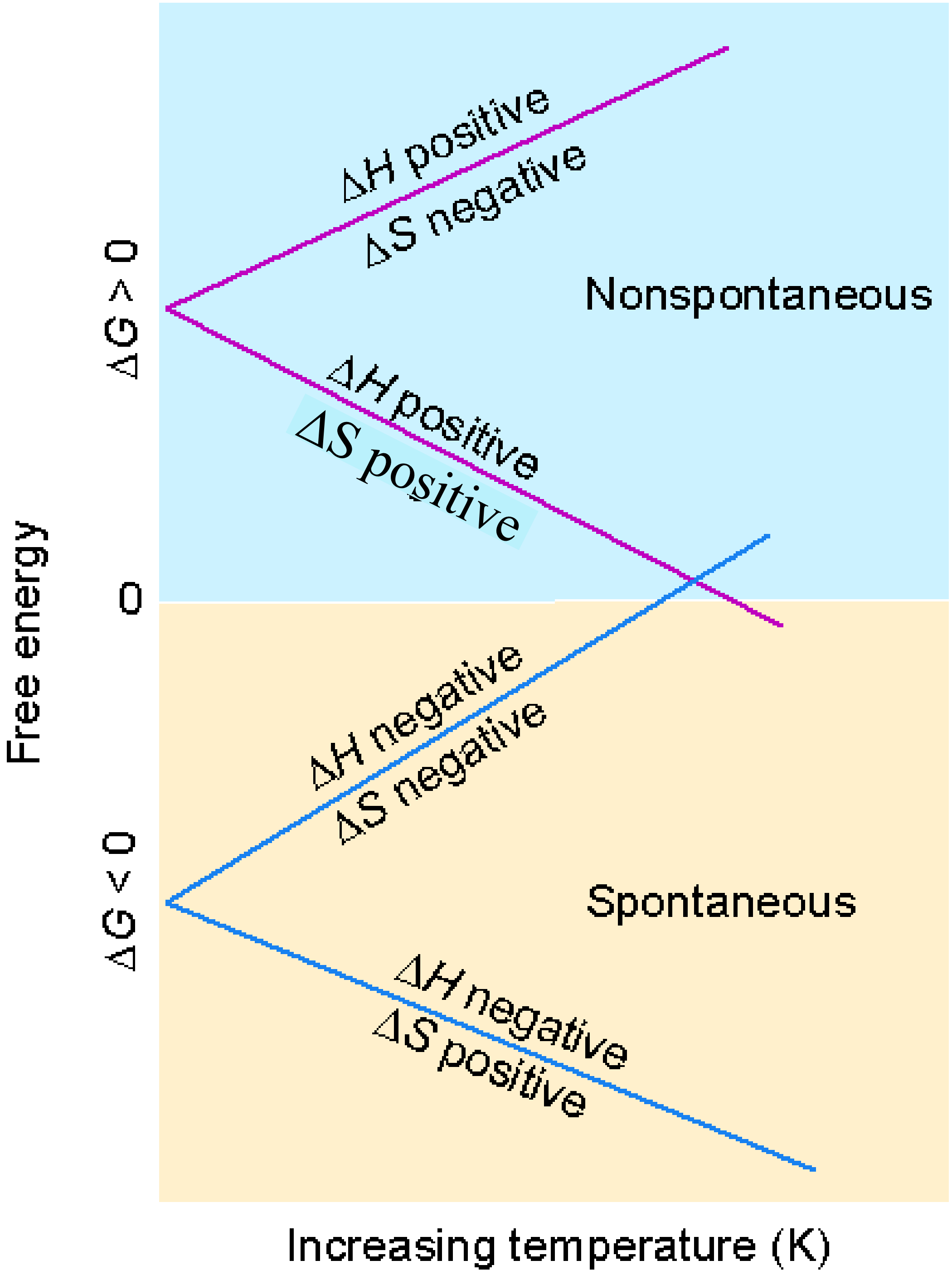
- Entropy reflects the degree of disorder in a system.
- Therefore,
- $S_{solid} < S_{liquid} << S_{gas}$

The Third Law of Thermodynamics

- . . . the entropy of a perfect crystal at 0 K is zero.
- Because *S is explicitly known (= 0) at 0 K, S values at other temps can be calculated.*

Free Energy

- $\Delta G = \Delta H - T\Delta S$ *(from the standpoint of the system)*
- A process (at constant *T*, *P*) *is spontaneous in the direction in which free energy decreases:*
- $-\Delta G$ *means* $+\Delta S_{univ}$


ΔH positive
ΔS negative
Nonspontaneous
ΔH positive
ΔS positive
ΔH negative
ΔS negative
Spontaneous
ΔH negative
ΔS positive
ΔG > 0
0
ΔG < 0
Free energy
Increasing temperature (K)

Effect of ΔH and ΔS on Spontaneity

ΔH	ΔS	Result
–	+	spontaneous at all temps
+	+	spontaneous at high temps
–	–	spontaneous at low temps
+	–	not spontaneous at any temp

The Second Law of Thermodynamics

- . . .   in any spontaneous process there is always an increase in the entropy of the universe.
- $\Delta S_{univ} > 0$
  - for a spontaneous process.

Fossil Fuels

Heats of Combustion

The most useful chemical reaction for the production of heat

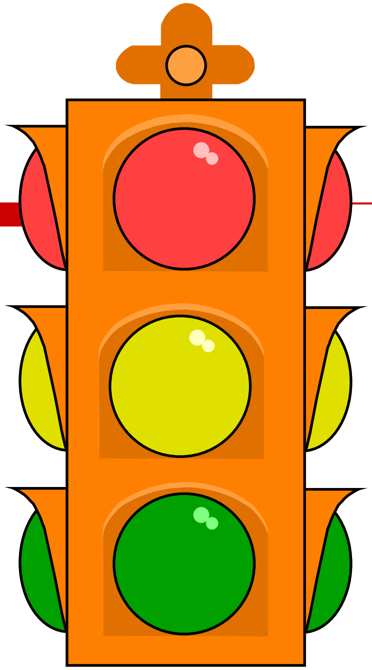
- Requires oxygen
- Produces water and carbon dioxide
- Releases large amounts of energy

Fossil Fuels

- Hydrocarbons
  - Natural gas
    - CH_4
    - C_2H_6
    - C_3H_8
    - C_4H_{10}
    - H_2S
      - contaminant
      - must be removed

- Petroleum
  - Used for the production of various oils and gases
  - A liquid of variable composition

- Coal
  - Variable sulfur content
  - Major source of energy for the production of electricity



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