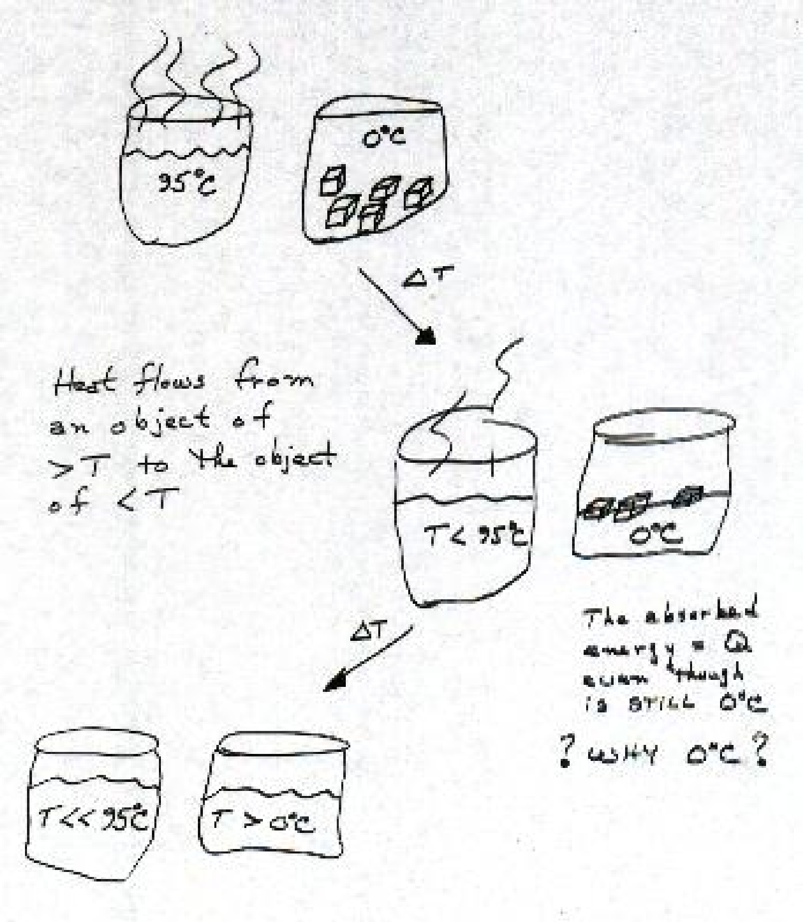
Thermodynamics

The Original Pink Bunny

Heat

- Heat flows from an object of hotter temperature to an object of cooler temperature. The absorbed energy we represent by "Q".



Heat flows from an object of >T to the object of <T

The absorbed energy = Q even though is still 0°C

? why 0°C ?

When talking about heat, it would be helpful to have some terms defined that will allow us to quantitatively determine just how much heat has been transferred between objects or between systems.
The first term for discussion is heat capacity (C).
Heat capacity is defined as the amount of energy transferred per change in absolute temperature or:

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

C is in units of Joules per mole per Kelvin.

- This term (heat capacity) is all fine and dandy -- it doesn't, though, give us a measure in terms of mass and/or amount.
- To that end we use the term specific heat capacity (c).
- Specific heat capacity is equal to the heat capacity divided by the molecular weight and is in units of joules per Kelvin per gram.
- Joules aren't as widely known as are calories.
- One calorie is equal to 4.184 Joules.
- One calorie (cal) is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1° C -- a little less than a perfect definition, yet close enough for our purposes.
- One Calorie (Cal or kcal) is 1000 calories or 1 kilocalorie (kcal).
- The kcal is the unit we use for "food calories".

How could we use this information to determine the amount of heat, Q, that has been transferred between two objects? We use a simple equation:

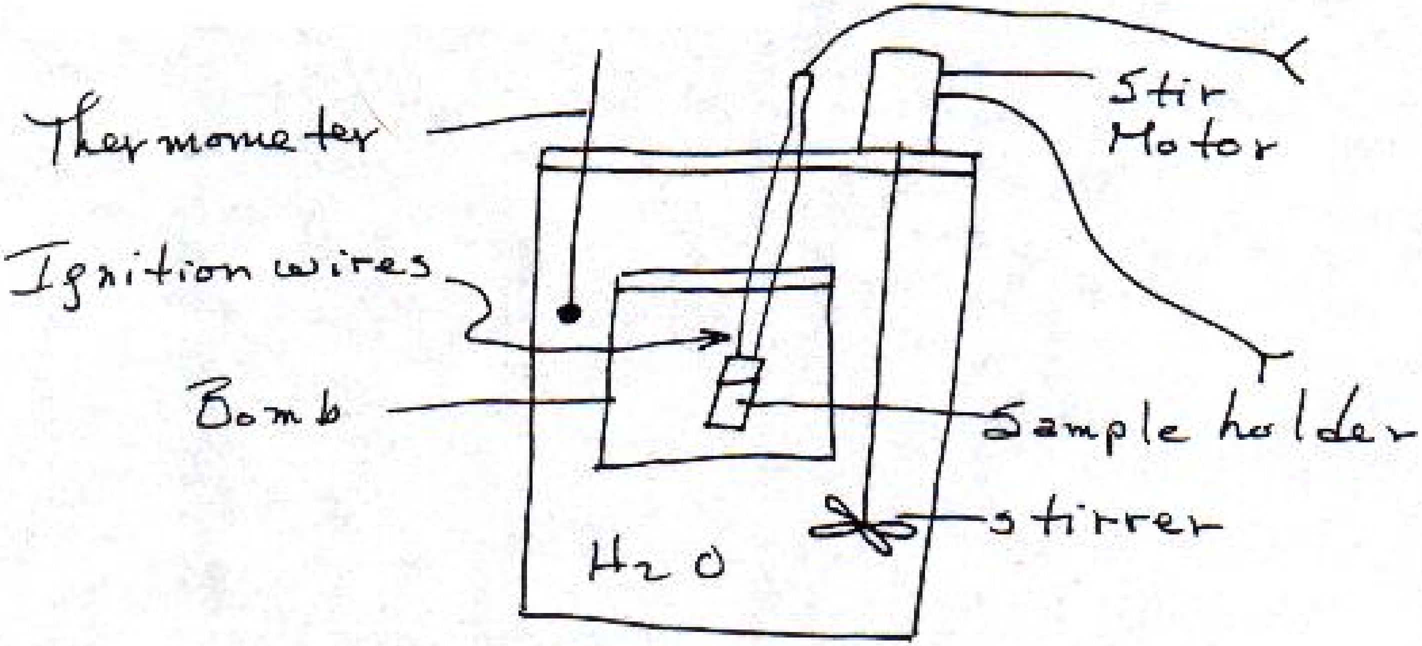
$$Q = m\,c\,\Delta T$$

Where Q = the amount of heat in calories or Joules,
m = the mass in grams,
c = the specific heat in joules per Kelvin per gram OR calories per Kelvin per gram, and
ΔT = the change in temperature in Kelvins (also in °C,
Δsince the difference is numerically equivalent -- remember,
Δthough, to keep your units straight).

The table, below, summarizes the
specific heat capacity of some representative substances:

Substance	Specific Heat Capacity (J/K/g)
Water	4.169
Al	0.898
Diamond	0.518
Fe	0.443
Pb	0.130

- Specific heat capacities are measured in a "bomb calorimeter":
- The way this works is that sample is placed in the sample holder in the 'bomb" and two wires are set in the substance through the water-tight lid.
- The lid is sealed, the wires are attached to a power supply, water is poured around the bomb and the stirrer rotates to mix the water.
- When the temperature of the water is equilibrated, the power is turned on, the sample is ignited and the temperature increase from the sample combustion is measured by an increased water temperature.



Bomb Calorimeter

The challenge is that you have to remember that the calorimeter also absorbs some heat, so we have to take that into account:

$$\Delta Q_c = m_c \, c_c \, \Delta T$$

Where the "c" subscript represents the calorimeter – heat absorbed by it, mass of it, specific heat capacity of it and the change in absolute temperature of the calorimeter. So, when figuring the whole heat transfer, we must write the equation as follows:

$$\Delta Q_{Total} = Q_{Substance} + Q_{Calorimeter}$$

We can then re-write the equation thusly:

$$\Delta Q_{Total} = mc \, \Delta T + m_c \, c_c \, \Delta T$$

The key to this equation and its application is to remember that:

$$\Delta T = T_{final} - T_{initial}$$

Example 1: 50 g of coal are placed in a calorimeter at 20° C. The calorimeter has a mass of 100 g and is made of Fe. 950 J of heat increases the temperature of the calorimeter to 35° C. What is the specific heat capacity of the coal?

We know the specific heat capacity of the Fe from the table above: 0.443 J/g/K.

The change in temperature = 35° C - 20° C = 15° C which is equivalent to 15 K.

Set up the equation:

$$\Delta Q_{Total} = mc\,\Delta T + m_c\,c_c\,\Delta T$$

Manipulate it:

$$\Delta Q_{Total} - m_c\,c_c\,\Delta T = m\,c\,\Delta T$$

Rearrange and isolate "c":

$$\frac{\Delta Q_{total} - m_c\,c_c\,\Delta T}{m\Delta T} = c = \frac{950 - (100)\,(0.443)\,(15)}{(50)\,(15)} = 0.407\,J\,/\,g\,/\,K$$

0.407 J/g/K is equivalent to 0.097 cal/g/K.

Example 2: 100 g tar are placed in a calorimeter at 10° C.
The calorimeter has a mass of 200 g and is made of diamond.
10,000 Joules (J) of heat increases the temperature of the calorimeter to 95° C.
What is the specific heat capacity of the tar?
We already know the specific heat capacity of the diamond from the table, above: 0.518 J/g/K.
The temperature difference is equal to 95° C - 10° C, which equals 85° C -- this is equivalent to 85 K.
Set up the equation as before and solve for "c":

$$\frac{\Delta Q_{total} - m_c\, c_c\, \Delta T}{m \Delta T} = c = \frac{10000 - (200)(0.518)(85)}{(100)(85)} = 0.140\, J / g / K$$

This is equivalent to 0.0336 cal/g/K.

Example 3: 75 g aspirin are placed in a calorimeter at 20° C.
The calorimeter has a mass of 125 g and is made of lead (Pb).
850 J of heat increases the temperature of the calorimeter to 22° C.
What is the specific heat capacity of aspirin?
We know the specific heat capacity of Pb from the table: 0.130 J/g/K.
The change in temperature is 2K.
Set up the equation, isolate and solve for "c", as before:

$$\frac{\Delta Q_{total} - m_c\, c_c\, \Delta T}{m \Delta T} = c = \frac{850 - (125)(0.130)(2)}{(75)(2)} = 5.45\, J/g/K$$

This is equivalent to 1.303 cal/g/K.

We saw that the combination of both the substance and the calorimeter contributed to the ΔQ. What about the ΔQ BETWEEN 2 different containers or systems? In that case,

$$\Delta Q_1 = \Delta Q_2$$

Since one is absorbing heat, the other must be losing heat. We can use this set up to determine the final temperature of 2 systems mixing.

Example 1: a Pb pipe of 300 g is at 25° C.
If the ends of the pipe are plugged after 300 g water at 90° C
are poured into it, what is the final temperature of the new system?
Key to this is that the lead pipe is going heat up and
the water is going to cool down.
The 2 equations, then for the temperature differential are as follow:
$\Delta T_{Pb} = T_f - 25$ and $\Delta T_{H2O} = 90 - T_f$
The heat capacities of Pb and water are as follow,
respectively: 0.130 J/K/g and 4.169 J/K/g
Set up the formula and solve for T_f:

$$Q_{Pb} = Q_{H2O}$$

$$(300)(0.130)(T_f - 25) = (300)(4.163)(90 - T_f)$$

$$39T_f - 975 = 112563 - 1251T_f$$

$$1290T_f = 113538$$

$$T_f = 88^o C\, or\, 361K$$

In other words, as we discussed before,
lead heats up and water cools down.

Example #2: A gold container at 30° C has 400 g water
at 100° C poured into it. The gold container has a mass of 500 g.
What is the T_f? (the specific heat capacity (c) of Au is 0.130 J/g/K).
Key to this is that the gold container is going heat up
and the water is going to cool down.
The 2 equations, then, for the temperature differential are as follow:
$\Delta T_{Au} = T_f - 30$and $\Delta T_{H2O} = 100-T_f$
The heat capacities of Au and water are as follow, respectively:
0.130 J/K/g and 4.169 J/K/g
Set up the formula and solve for T_f:

$$Q_{Au} = Q_{H2O}$$

$$(500)(0.130)(T_f - 30) = (400)(4.163)(100 - T_f)$$

$$65T_f - 1950 = 166760 - 1668T_f$$

$$1733T_f = 168710$$

$$T_f = 97.35^o C\ or\ 370K$$

Problem Set 12

1. 454 g of paper are placed in a calorimeter at 25°C. The calorimeter has a mass of 3 kg and is made of iron. 500 kJ are added to the system. If the specific heat capacity of paper is 5 J/K/g, what is the final temperature of the system?

2. An aluminum pipe of 150 g is at 5°C. If the ends of this pipe are plugged after 400 g of Pb at 400°C are poured into it, what is the final temperature of the system?

3. A diamond container at 10°C has 150 g water at 75°C poured into it. The diamond container has a mass of 30 g. What is the final temperature of this system?

While we are discussing heat, it's always nice to have a handle on how heat leaves "bodies". It does this by at least three mechanisms -- or at least the mechanisms that are of the greatest significance to those heading into [allied] health care as a profession.

The three mechanisms and their definitions are summarized in the table, below:

Mechanism	Definition
Conduction	Heat removal by touching the objects that leads to temperature equilibration between the objects.
Convection	Heat is carried by the medium, e.g., air movement, water moving as it's heating.
Radiation	Heat leaving as "waves of energy" being emitted from the warm object.

An Arithmetic Approach to Temperature Regulation in Humans

- When discussing heat regulation, the unit "watt" is fairly common.
- We are familiar with the term "kilowatt" from our electrical bills at home.
- What though does it mean in terms of something we have either studied or can easily relate to?
- A watt is 1 J/sec or 0.24 calories/second.
- One watt is also equal to $1.44 \text{ X } 10^{-2}$ kcal/minute.

Let's put some perspective on this in terms of exercise activities by men and women:

Perspective			
	Light Exercise	**Heavy Exercise**	**Very Heavy Exercise**
Examples	**Walking, fishing, golfing**	**Ice skating, jogging**	**Running fast, racquet ball**
Male	**2-5 Cal/min**	**7.5-10 Cal/min**	**≥ 12.5 Cal/min**
Female	**1.5-3.4 Cal/min**	**5.5-7.4 Cal/min**	**≥ 9.5 Cal/min**

Examples:

Heavy Exercise:

$$\frac{10\,Cal}{\min\ ute} * \frac{\min\ ute - Watt}{1.4 \times 10^{-2}\ Cal} = 694\,watts$$

Or about 0.694 kW.

Very Heavy Exercise:

$$\frac{12.5\,Cal}{\min\ ute} * \frac{\min\ ute - Watt}{1.44 \times 10^{-2}\ Cal} = 868\,Watts$$

Or about 0.868 kW.

Since 1 kW is about 1.34 horsepower,
heavy exercise is about 0.92 horsepower and
very heavy exercise is about 1.2 horsepower.

Humans and Heat

In humans, as in other mammals, heat is both generated and lost.

The table, below, summarizes the sources of heat generated and heat lost:

Heat	
Generated	**Lost**
Q_m = heat generated from metabolism; 80-1600 W depending on the circumstances	************************************
	Q_c = convective heat loss
	Q_R = radiative heat loss
	Q_s = heat loss from the evaporation of sweat
	Q_l = heat loss via lung water loss; a constant: 10.5 W

Of all the terms above, the heat lost by convective, radiative and sweat evaporation mechanisms are calculable:

$$Q_c = \frac{7.1W}{m^2\,K} * (SA) * (\Delta T)$$

$$Q_R = \frac{6.5W}{m^2\,K} * (SA) * (\Delta T)$$

$$Q_s = \frac{674\,W\,h}{kg} * \frac{kg\,sweat\ produced}{hour}$$

At a constant temperature,
$Q_m = Q_c + Q_r + Q_s + Q_l$
And "SA" is the surface area of the person in square meters.
ΔT is equal to the temperature of the skin minus the temperature of the air -- ALWAYS.

Application

Example 1: The "average" person" at rest emits 100 W of heat. If the surface area of the person is 1.975 m^2 and the skin temperature is 37° C and the air temperature is 14.4° C, how much sweat will be produced by this person?

1) the temperature difference is 22.6 K

2) the SA is 1.975 m^2

3) Q_m = 100 W

4) Q_c = (7.1)(1.975)(22.6) = 316.9 W

5) Q_R = (6.5)(1.975)(22.6) = 290.1 Watts

6) Q_s = (674)X

7) Q_l = 10.5 W

8) $Q_m = Q_c + Q_R + Q_s + Q_l$

rearrange step 8 and solve for Q_s:

$Q_m - Q_c - Q_R - Q_l = Q_s$

100 - 316.9 - 290.1 - 10.5 = -517.5 W = Q_s

674X = -517.5

X = -0.768 kg sweat produced per hour

Note that the answer is a negative number! This means that the person does not produce sweat and is cold and requires heat.

Example 2: The "average" person" at rest emits 100 W of heat. If the surface area of the person is 1.975 m^2 and the skin temperature is 37° C and the air temperature is 38° C, how much sweat will be produced by this person?

1) the temperature difference is -1 K

2) the SA is 1.975 m^2

3) $Q_m = 100$ W

4) $Q_c = -14$ W

5) $Q_R = -13$ Watts

6) $Q_s = ?$

7) $Q_l = 10.5$ W

8) $Q_m = Q_c + Q_R + Q_s + Q_l$

rearrange step 8 and solve for Q_s:

$Q_m - Q_c - Q_R - Q_l = Q_s$

$100 - (-14) - (-13) - 10.5 = 116.5$ W $= Q_s$

$674X = 116.5$

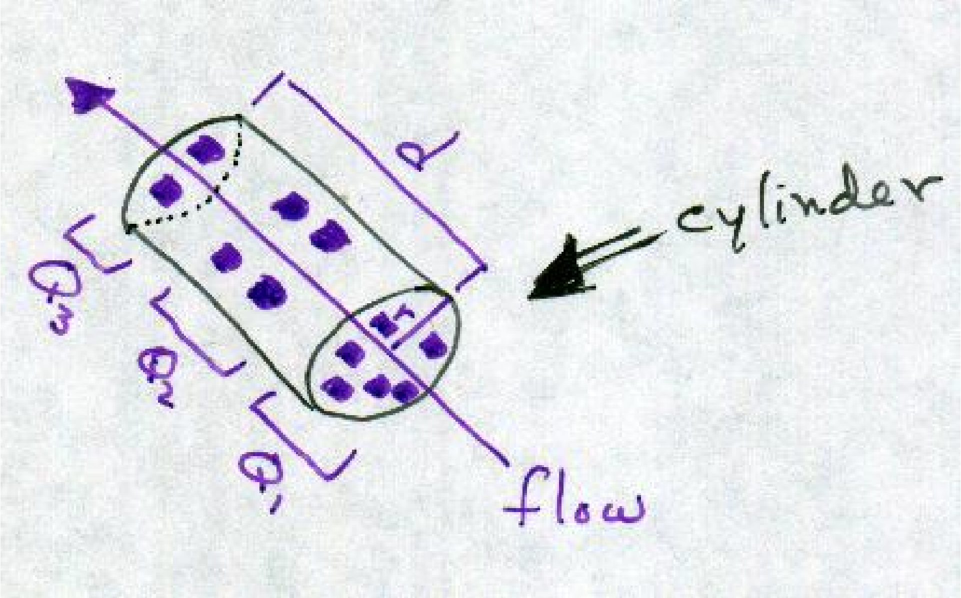
X = 0.173 kg sweat produced per hour. This is about 173 mL/hour. At about 30 oz per mL, this is about 5.8 oz/hour.

REMEMBER:

These are approximations and do NOT take into account other biological processes.

Flow of Heat

- When discussing heat, it's important to actually comprehend how heat flows.
- Among other reasons, we can eventually fold a discussion on the flow of heat into a discussion of how gases traverse membranes in the body to provide oxygen to the cells and CO_2 transport out of the body.
- To begin the discussion, let's examine Fick's Law.
- Fick's Law says that **the rate of diffusion of heat per unit area through a cylinder in a direction perpendicular to the area is proportional to the heat gradient through the cylinder in that direction**



The heat gradient is defined as:

$$\frac{\Delta Q}{volume \times d} \Leftrightarrow \frac{H}{d}$$

And the area of the face of the cylinder is $\underline{\pi\ r^2}$.
If we combine these two equations with one more:

$$\frac{Q}{t} = Flow\ of\ heat$$

We get the following:

$$\frac{Q}{t} = D\,A\,\frac{H}{d}$$

Where Q is the amount of heat,
t is time,
D is a constant,
A = $\pi\ r^2$,
H is the heat per unit volume
d is distance or thickness of the cylinder.

This cylinder for heat diffusion may be likened to a semipermeable membrane, therefore, the heat flow is analogous to diffusion of a solute. The rate of diffusion of a solute per unit area in a direction perpendicular to the area is proportional to the concentration gradient in that direction. By substituting mass (m) for amount of heat (Q) and concentration gradient (∆ [C]) for H, then, the mass of solute diffusing per unit time may be expressed as below:

$$\frac{m}{t} = D\,A\,\frac{\Delta[\,C\,]}{d}$$

Again, "m" is mass diffusing,
"t" is the time in which diffusion is occurring,
and ∆ [C] is the concentration gradient.
The remainder of the terms are as defined before.

Diffusion is analagous to the flow of gas through semipermeable membranes:

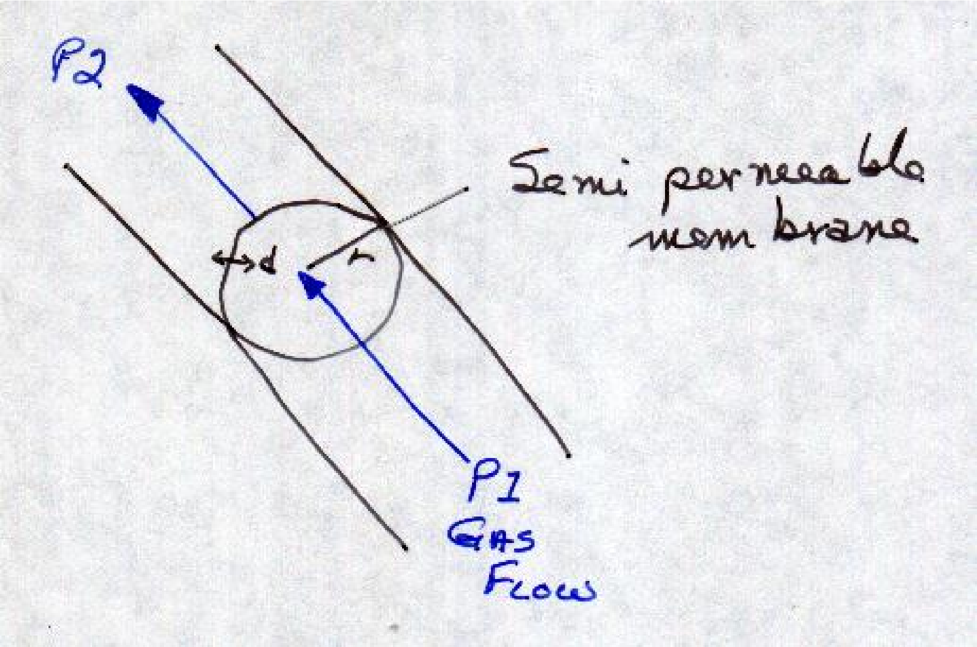
$$\frac{\Delta d}{\Delta t} \alpha \frac{A \Delta P}{d}$$

or

$$\frac{\Delta d}{\Delta t} = D \frac{A \Delta P}{d}$$

Where Δ d is the difference in thickness of the membrane,
Δ t is the time it takes to cross the membrane (time difference) and
Δ P is the pressure gradient or pressure difference across the membrane.

- This last equation tells us that the speed of a gas through a semi-permeable membrane is directly proportional to the cross sectional area of that membrane and the pressure gradient between the two sides of the membrane.
- It also tells us that flow is inversely proportional to the thickness of the membrane.
- This is illustrated below.
- Where a semi-permeable membrane is placed in a tube with gas flowing in one direction through the membrane.



From our previous equation, note that that the distance difference per time difference is simply velocity. We can re-write the equation, now, as follows:

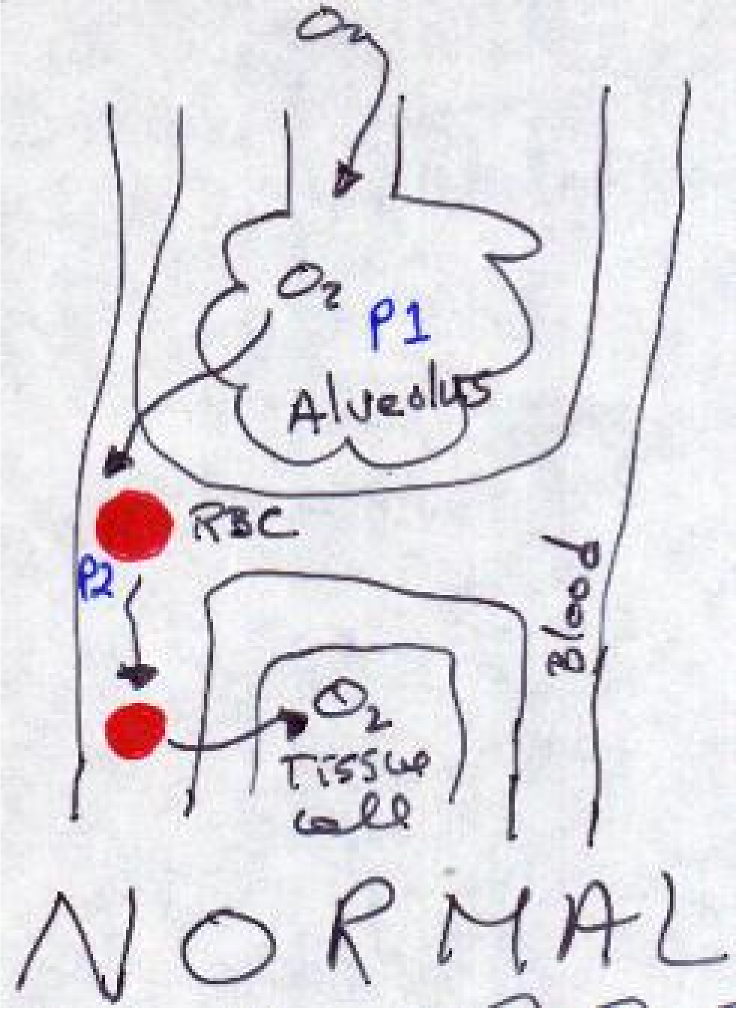
$$\frac{\Delta d}{\Delta t} = v = D\frac{A\,\Delta P}{d}$$

Where the only new variable is "v": velocity (or speed). We may, thus, write the equation as follows:

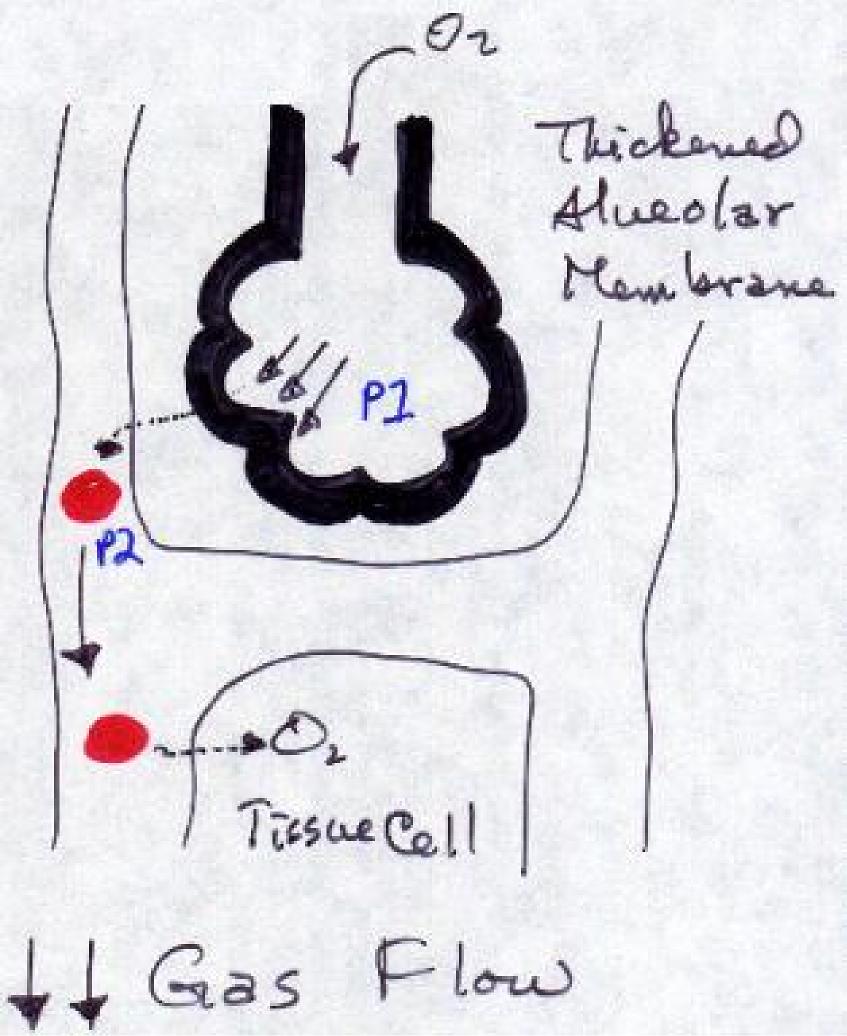
$$v = D\frac{A\,\Delta P}{d}$$

If d reduces by half, v increases by two-fold. If d increases its thickness by 3 fold, then v reduces to one third its original value. Hence, the thicker the membrane, the slower the diffusion of the gas. Can we apply this in a clinical perspective? Yes, we can.

Normal Gas Exchange Across Normal Alveolar Membranes



- If, though, one develops pulmonary edema through heart failure, chemical inhalation, mountain sickness or pulmonary frostbite, then the alveolar membranes thicken as in the figure, right, that makes it very difficult to get gases across the membranes and cause the cells to begin to consider the possibility of their death without treatment as long as the body can function (have you seen "Vertical Limit"?) .
- **REFERENCE**: MacDonald, S. and Burns, D. : Physics for Life and Health Sciences. (Addison-Wesley: London) Ó 1975.



Problem Set 13

1. Describe Ficke's Law as it applies to the diffusion of gases across a semipermeable membrane.

2. Roughly speaking, determine the change in flow velocity with the following alterations in membrane thickness:

A) Increase 3-fold B) Increase 2-fold

C) Decrease to 0.125 thickness

D) Decrease to 0.2 thickness E) Decrease to 0.1 thickness F) Increase 10-fold

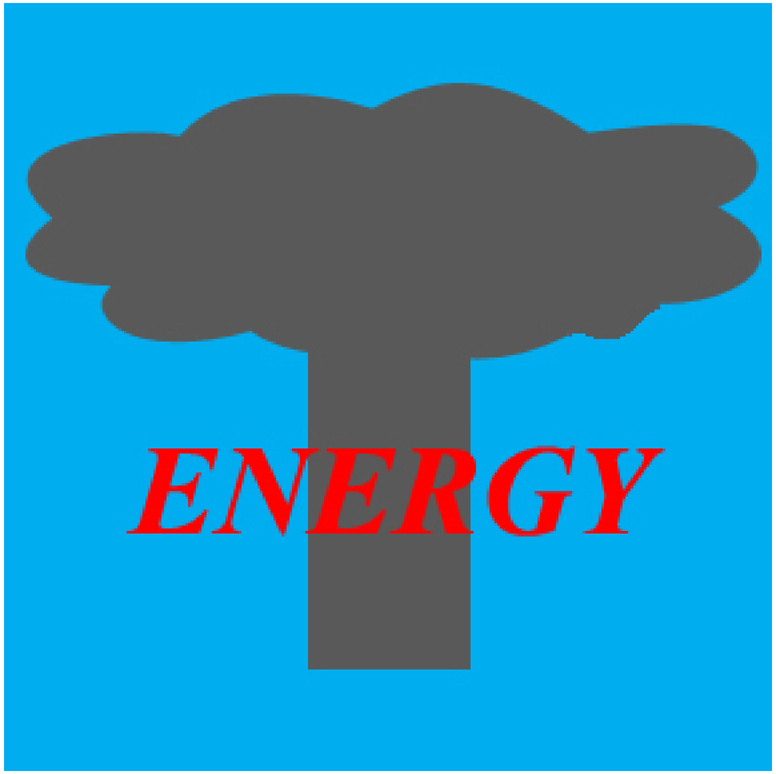
G) Decrease to 0.24 thickness

H) Increase 100-fold

3. Describe pulmonary edema.

4. What are four causes of pulmonary edema?

Introduction to The Laws of Thermodynamics


ENERGY

- Thermodynamics is the study of the change of energy from one form to another.
- Energy is the ability to do work.
- Work is the change in kinetic energy of the object.
- Kinetic energy is the energy of motion.

Potential Energy

- Stored energy
- Energy of position
- If object is above the ground

= gravitational potential energy

- Since Wt = m g, then,

$$PE_{grav} = m\, g\, h,$$

where m = mass, g = gravity, h = height above ground

Kinetic Energy

- Energy of motion:

$$KE = \frac{1}{2} m v^2$$

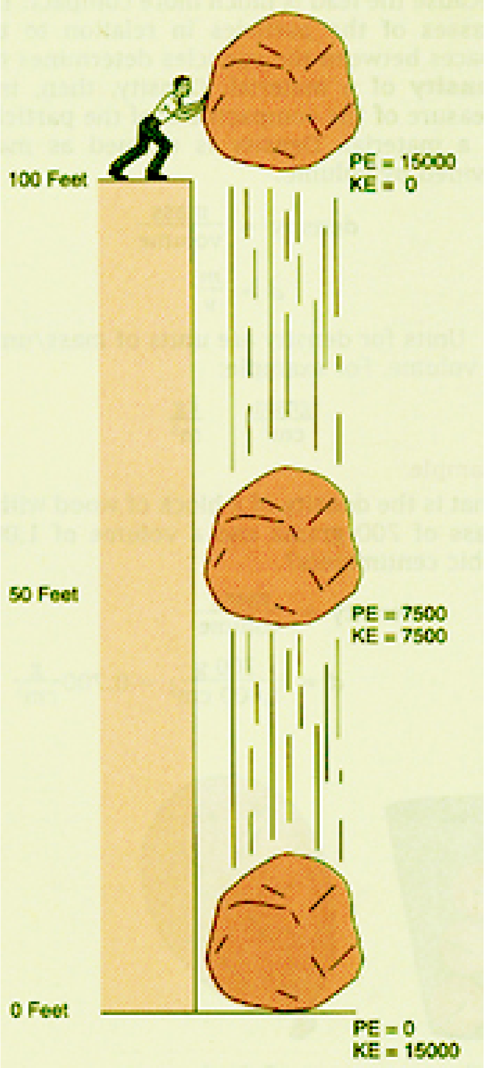
Law of Conservation of Energy

- Is the relationship between PE and KE:

- The total energy is always conserved

or

- Energy is neither created nor destroyed – merely transformed


100 Feet
PE = 15000
KE = 0
50 Feet
PE = 7500
KE = 7500
0 Feet
PE = 0
KE = 15000

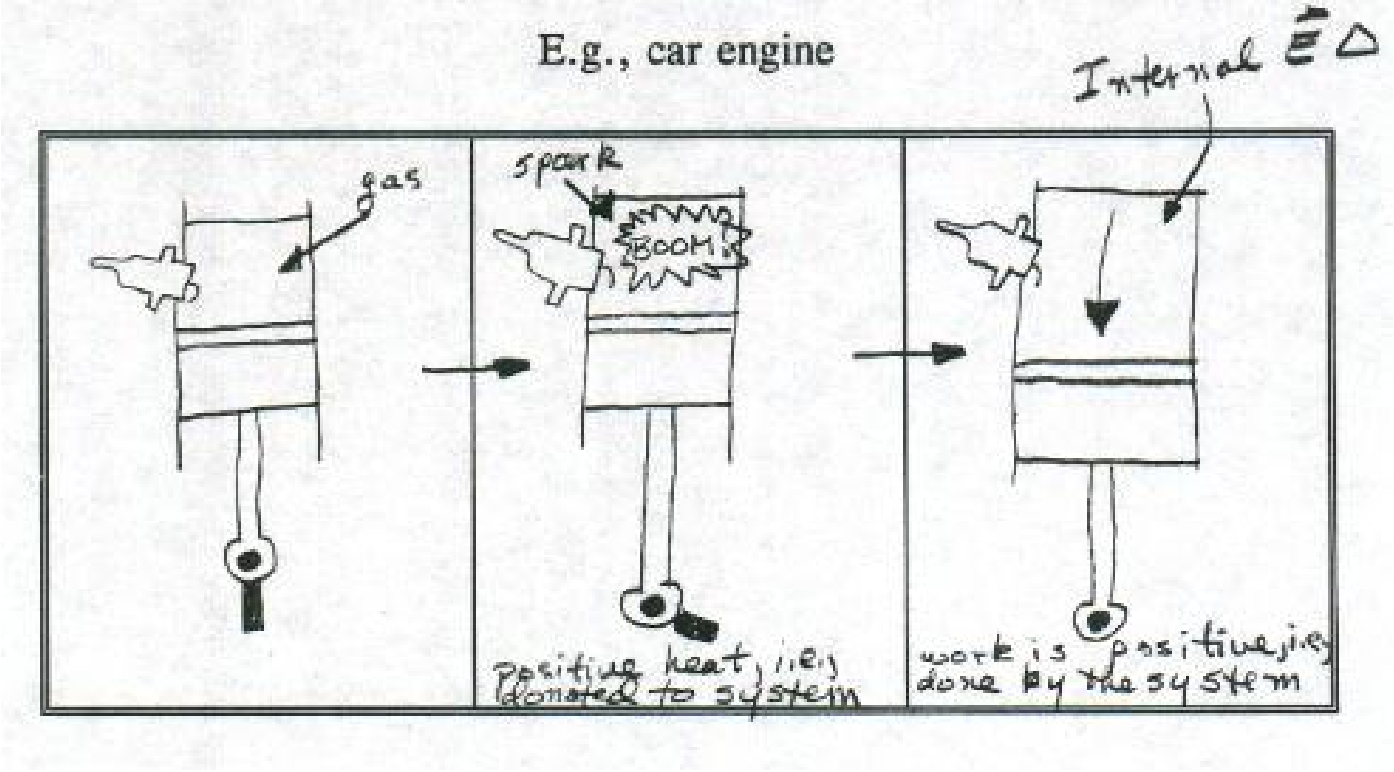
The First Law of thermodynamics says that when heat is added to a system at rest, the system will perform work due to the change in internal energy of the system.

A car engine is a good example of this.

When gas fills the cylinder and the spark jumps across the plug, the gasoline ignites and explodes, forcing the piston down.

This is positive heat, i.e., it is donated to the system.

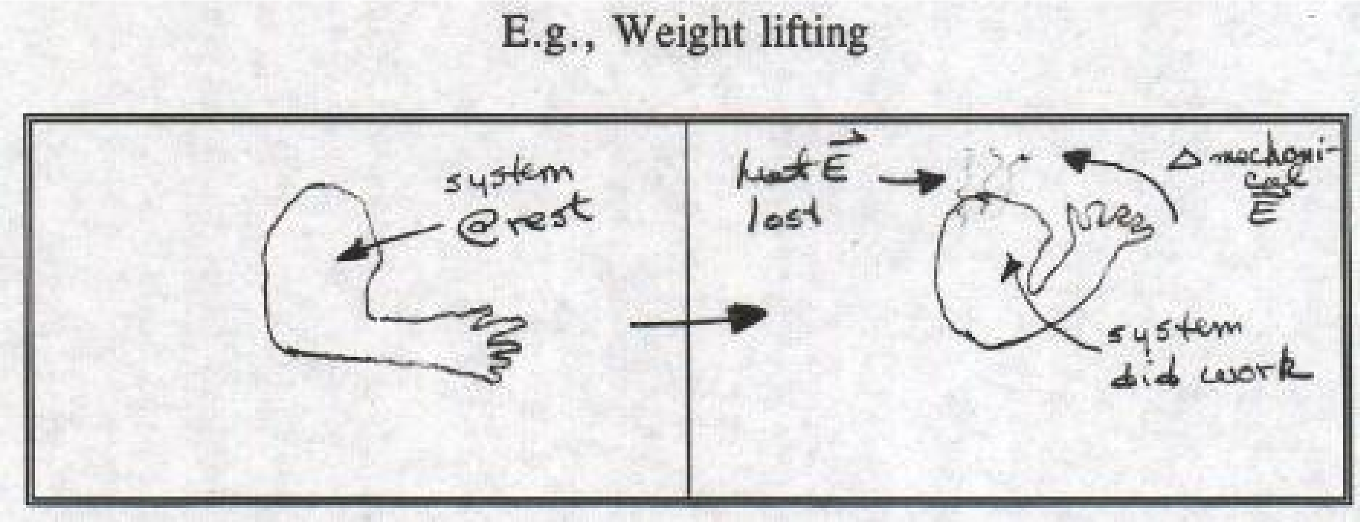
There are internal energy changes and work is positive, i.e., work is done by the system -- the car moves when in gear.



Alternatively, the First Law may be stated as follows: work done BY a system is equal to the change in mechanical energy PLUS the energy that LEAVES the system.

Weight lifting is a good example of that.

When a system is at rest (e.g., the biceps brachii), nothing happens. When the biceps contracts, the system did work, heat energy is lost and there is a change in mechanical energy.



E.g., Weight lifting

Another perspective on the First Law is that energy is neither created nor destroyed, but changed from one form to another.

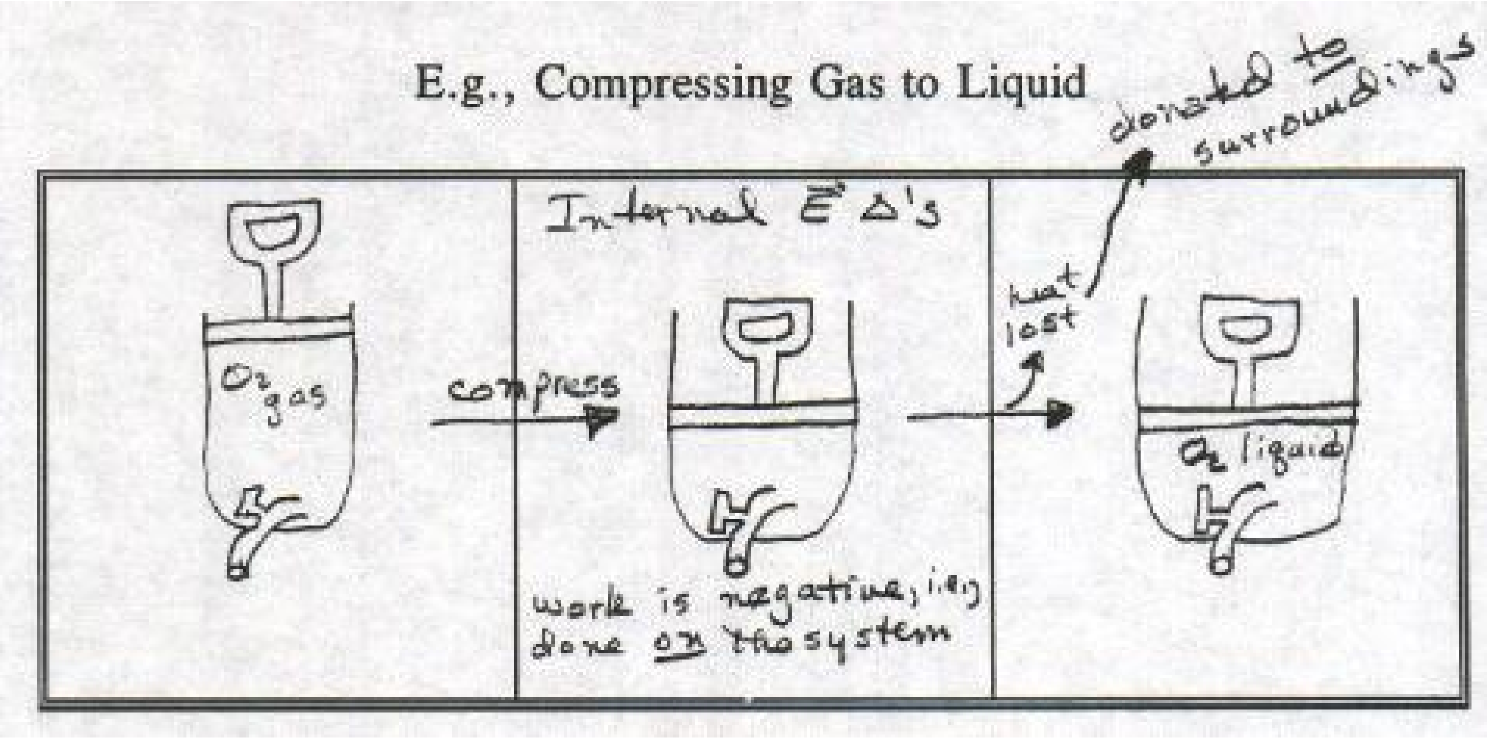
The converse First Law says that work done on a system is equal to the change in mechanical energy PLUS the energy that is absorbed BY the system.

A good example of this is compressing a gas to a liquid.

When a gas that is compressible is placed inside a cylinder with a piston and the piston is compressed, the work is negative.

In other words, work is done ON the system.

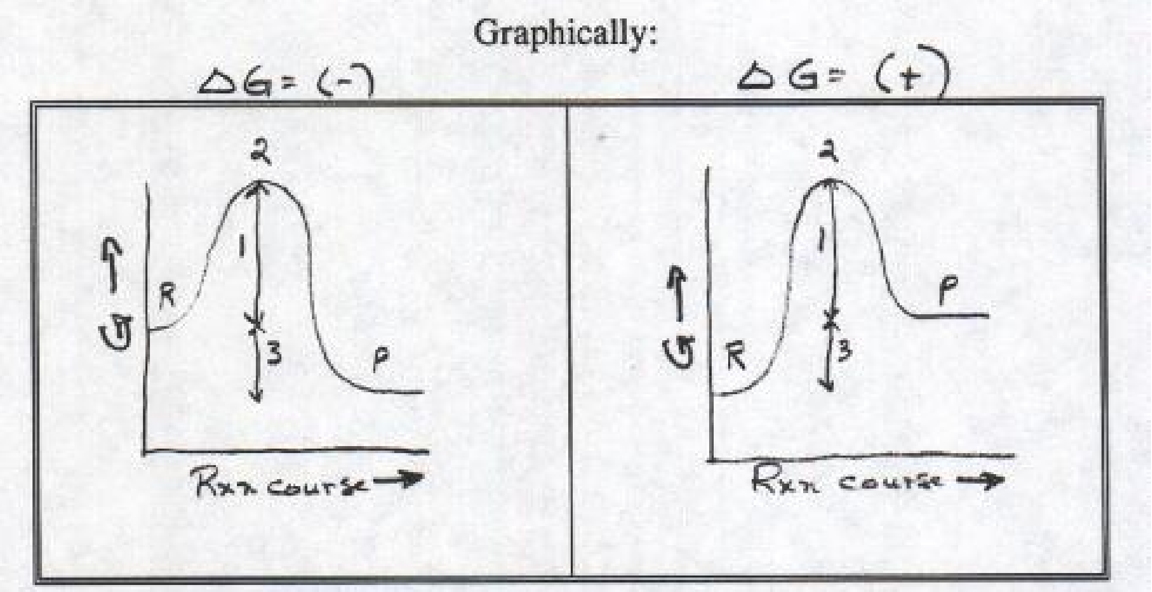
Heat is lost and donated to the surroundings.



- The Second Law of thermodynamics says that systems prefer a sense of chaos (entropy), i.e., chaos is more probable than an ordered system.
- For example, in poker, there are only a few hands, e.g., royal flush, with high points.
- This says, then, that there are MORE hands with NO value.
- This is entropy.
- Another example of entropy comes to us from family structure and dynamics: in dysfunctional families there is a high degree of entropy and a low degree of order.
- In functional families, there is some entropy and more order.
- Entropy is ALWAYS increasing -- or at least equals zero.
- In processes that are reversible, the change in entropy equals zero and chaos equals a constant.
- In processes that are IRreversible, which includes most natural processes, the change in entropy is greater than or equal to zero always and chaos increases.

- Thermodynamics predicts whether a reaction will go as written or not.
- Thermodynamics does NOT predict how fast the reaction will go -- that's the function of kinetics.
- How is it possible to predict whether or not a reaction will go?
- By studying Gibbs Free Energy (G).
- In general,
  - When the change in Gibbs Free energy (ΔG) is NEGATIVE, the reaction GOES as written.
  - When the ΔG is POSITIVE, the reaction does NOT go as written.

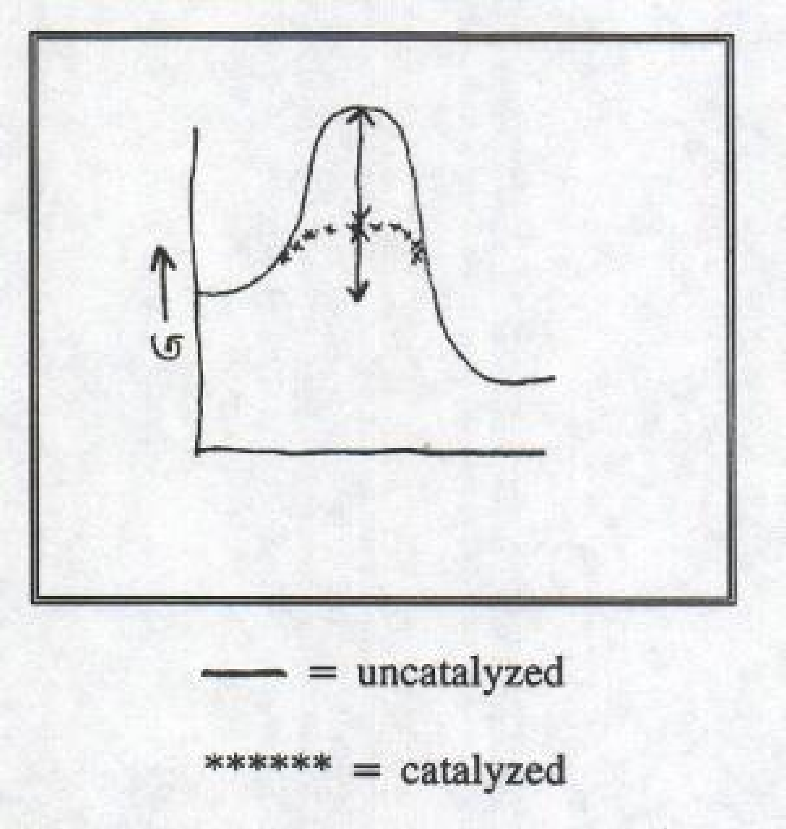
- The following graphic illustrates this concept.
- Each graphic has ΔG on the vertical axis and the reaction course (reactant [R] to product [P]) on the horizontal axis.
- Note that in an exergonic reaction that the energy level for the reactants is higher than for the products.
- Note that for an endergonic reaction that the energy level for the reactants is lower than for the products.
- The region labeled #1 in each plot is the energy of activation, sometimes labeled ΔG' or E_a; #2 is the transition state -- where the energy is so high the bonds make-n-break -- if this energy is not reached, no bonds make-n-break; #3 is the free energy difference (ΔG).



$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
Exergonic rxn

α-D-glucose → β-D-glucose
Endergonic rxn

Is it possible to decrease the energy of activation? Yes! With a catalyst.
A catalyst is something that speeds up the rate of the reaction without being consumed during the course of the reaction.
Note in the graphic that the difference between the solid line ("regular" reaction) and the asterisked line (catalyzed reaction) is the decrease in E_a. This decrease in E_a is caused by the catalyst.



- **There is a relationship between 1st law, 2d law and Gibbs free energy:**

$$\Delta G = \Delta \text{1st law} - T\Delta \text{2d law}$$

- **or the change in free energy (Δ G) is equal to the change in the first law (enthalpy or Δ H) minus the absolute temperature (T) times the change in the 2d law (entropy or Δ S). This, then, may be re-written as**

$$\Delta G = \Delta H - T \Delta S$$

- **In other words, the change in free energy is equal to the change in enthalpy less the change in entropy at some absolute temperature, T. The difference in this equation is sometimes called the Third Law of thermodynamics and may be stated as follows: as the energy of a reaction is changed from one form to another, entropy changes -- if the difference at a fixed absolute temperature is negative, the reaction goes spontaneously as written; if it is positive, it does NOT go spontaneously as written.**

Hess' Law

The Serious Thermodynamics Part

- A state function is defined as a property of a system that does not depend on how the system gets to the state that shows that property, i.e., it's not dependent on the previous history of the system.

Enthalpy (ΔH), entropy (ΔS) and free energy (ΔHG) are state functions.

- NON-chemical example: the change in potential energy of a bowling ball as it's moved from a 4th floor fire escape landing to a 6th floor fire escape landing.
- Remember that the potential energy is the measure of how hard the ball would hit the ground **if** it fell off the landing.
- The change in potential energy of the ball from the 4th to 6th floor is identical to the change in potential energy of the ball if it went from the 4th floor to the penthouse then to the 6th floor.
- The PATH [how a system (bowling ball) goes from the initial state (4th floor) to a final state (6th floor)] is irrelevant to the system in its final state and makes no difference on how hard the ball hits the ground when it falls off the 6th floor landing.

CHEMICAL example: the condensation of 1 mol of steam to 1 mol of water at 100° C and 1 atmosphere:

DIRECT PATH:

$$H_2O(g) \rightarrow H_2O(l)$$

change in energy (ΔE) = -37.6 kJ)

INDIRECT PATH:

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

$$\underline{O_2(g) + H_2(g) \rightarrow H_2O(l)}$$

$$H_2O(g) \rightarrow H_2O(l)$$

Products and Reactants in RED cancel as the equations are added together.

change in energy (ΔE) = -37.6 kJ)

The path doesn't matter! It's a lot like climbing Mt. Everest: it don't matter HOW you git there, as long as you git to the top!

Review of the First Law of Thermodynamics

The total energy in the universe is a constant, i.e., it is neither created not destroyed.:

i	+ q	+ W	→	u
System with E_1	**Plus heat**	**Plus work done ON the system**		**System with E_2**

It follows, then, that:

$$E_2 = E_1 + q + W$$

and

$$E_2 - E_1 = q + W$$

$$\therefore \Delta E = q + W \text{ for the system}$$

and

$$\Delta E_{sur} = \Delta E \text{ for the surroundings}$$

Hence,

$$\Delta E + \Delta E_{sur} = 0 \leftarrow \text{First Law in a nutshell}$$

When q is negative (-), heat leaves the system.
When q is positive (+), heat is gained by the system.
When W (work)is negative (-), work is done on the surroundings by the system.
When W is positive (+), work is done on the system by the surroundings.

ΔH = ENTHALPY = q = amount of heat exchanged when the ONLY work done by the system is expansion work ($P\Delta V$ work). At a constant pressure, the volume increases, hence,

$$W = -P(V_2 - V_1) = -P\Delta V$$

At constant pressure and constant volume, $-P\Delta V = 0$ and $\Delta H = \Delta E = q + \underline{0}$

When ΔH is negative (-), the reaction is exothermic.

When ΔH is positive (+), the reaction is endothermic.

Enthalpy example: Calculate ΔH for the reaction below at 25° C and 1 atm (STP = 298 K, 1 atm and 1 M solutions): $S(s) + 1.5\ O_2(g) \rightarrow SO_3(g)$ from the enthalpy of formation of $SO_2(g)$ ($\Delta H^\circ_{298\ \text{formation}}$; -296.8 kJ/mol) and the $\Delta H^\circ_{298\ \text{formation}}$ for the following reaction: $SO_2(g) + 0.5\ O_2(g) \rightarrow SO_3(g)$; $\Delta H^\circ_{298\ \text{formation}}$ = -98.9 kJ. The "° " means the enthalpy change has been determined at STP.

The solution is equal to the sums of the enthalpy changes of two reactions:

$$S(s) \rightarrow SO_2(g)$$
$$SO_2(g) \rightarrow SO_3(g)$$

$S(s) + O_2(g) \rightarrow SO_2(g)$	$\Delta H^\circ_{298\ \text{formation}} = -296.8\ \text{kJ}$
$SO_2(g) + 0.5\ O_2(g) \rightarrow SO_3(g)$	$\Delta H^\circ_{298\ \text{formation}} = -98.9\ \text{kJ}$
$S(s) + 1.5\ O_2(g) \rightarrow SO_3(g)$	$\Delta H^\circ_{298\ \text{rxn}} = -395.7\ \text{kJ}$

Reactants and products in RED are cancelled out as we add the reactions together.

Units of enthalpy change, unless otherwise proscribed, are in units of kJ/mol.

The next example is to calculate the heat of formation of $OsO_4(g)$ from the heat of formation of $OsO_4(s)$ (-391 kJ/mol) and the heat of formation of $OsO_4(g)$ (56.4 kJ/mol) from the following reaction:

$Os(s) + 2\,O_2(g) \rightarrow OsO_4(g)$

$Os(s) + 2\,O_2(g) \rightarrow OsO_4(s)$ $OsO_4(s) \rightarrow OsO_4(g)$	$\Delta H^\circ_{298\ \text{formation}} = -391\ \text{kJ}$ $\Delta H^\circ_{298\ \text{formation}} = 56.4\ \text{kJ}$
$Os(s) + 2\,O_2(g) \rightarrow OsO_4(g)$	$\Delta H^\circ_{298\ \text{rxn}} = -334.6\ \text{kJ}$

The next example is to calculate the heat of formation at STP for the following reaction:

$\mathrm{Cd(s) + S(s) + 2\ O_2(g) \rightarrow CdSO_4(s)}$

Using:

The heat of formation is -162 kJ/mol for $\mathrm{Cd(s) + S(s) \rightarrow CdS(s)}$ and the heat of formation of $\mathrm{CdS(s) + 2\ O_2(g) \rightarrow CdSO_4(s)}$ is -933.28 kJ/mol:

$\mathrm{Cd(s) + S(s) \rightarrow CdS(s)}$ $\mathrm{CdS(s) + 2\ O_2(g) \rightarrow CdSO_4(s)}$	$\Delta\ H^\circ_{\mathrm{298\ formation}} = -162\ \mathrm{kJ}$ $\Delta\ H^\circ_{\mathrm{298\ formation}} = -933.28\ \mathrm{kJ}$
$\mathrm{Cd(s) + S(s) + 2\ O_2(g) \rightarrow CdSO_4(s)}$	$\Delta\ H^\circ_{\mathrm{298\ rxn}} = -1095.28\ \mathrm{kJ}$

Next example: calculate the heat of formation for the formation of copper sulfate from copper, sulfur and oxygen:

$Cu(s) + S(s) \rightarrow CuS(s)$ $CuS(s) + 2\ O_2(g) \rightarrow CuSO_4(s)$	$\Delta H^\circ_{298\ \text{formation}} = -531\ \text{kJ}$ $\Delta H^\circ_{298\ \text{formation}} = -771.36\ \text{kJ}$
$Cu(s) + S(s) + 2\ O_2(g) \rightarrow CuSO_4(s)$	$\Delta H^\circ_{298\ \text{rxn}} = -1302.36\ \text{kJ}$

- The next examples are slightly different and are proportional to the heats of formation of the reactants and the products.

- BTW: All the “numbers” we’ve been using are accessible in the CRC or traditional textbooks (appendices).

Calculate the heat of formation for the reaction of sodium with chlorine to form sodium chloride. This problem is set up a bit differently:

1) Write the balanced reaction: $2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl$

2) The $\Delta H°_{298\ formation}$ is equal to the sums of the heats of formation of the products less the sums of the heats of formation of the reactants. As the arithmetic expression is written out, one needs to remember that each heat of formation MUST be multiplied by the number of moles from the balanced reaction:

$$\Delta H°_{298\ rxn} = [\Sigma n \Delta H°_{298\ products}] - [\Sigma n \Delta H°_{298\ reactants}]$$

where "n" is equal to the coefficient from the balanced reaction

$$\Delta H°_{298\ rxn} = [2 \bullet \Delta H°_{298\ NaCl(s)}] - [2 \bullet \Delta H°_{298\ Na(s)} + \Delta H°_{298\ Cl2(g)}]$$

$$= (2 \bullet -411) - (2 \bullet 0 + 0) = -822\ kJ$$

The next example is to determine the heat of reaction at 298 K for the formation of carbon tetrachloride and hydrogen from methane and chlorine.

1) Write the balanced reaction: $CH_4(g) + 2\ Cl_2(g) \rightarrow CCl_4(l) + 2\ H_2(g)$

2) The $\Delta H°_{298\ formation}$ is equal to the sums of the heats of formation of the products less the sums of the heats of formation of the reactants. As the arithmetic expression is written out, one needs to remember that each heat of formation MUST be multiplied by the number of moles from the balanced reaction:

$$\Delta H°_{298\ rxn} = [\Sigma n\Delta H°_{298\ products}] - [\Sigma n\Delta H°_{298\ reactants}]$$

where "n" is equal to the coefficient from the balanced reaction

$$\Delta H°_{298\ rxn} = [\Delta H°_{298\ CCl4(l)} + 2 * \Delta H°_{298\ H2(g)}] - [2 * \Delta H°_{298\ Cl2(g)} + \Delta H°_{298\ CH4(g)}]$$

$$= (-165.4 + 0) - (-74.81 + 0) = -90.59\ kJ$$

- An additional application of enthalpy changes is used in Hess' Law: if a chemical reaction may be written as the sum of multiple reaction steps, the ΔH of the final reaction is equal to the sum of the individual enthalpy changes of the various reaction steps.
- Another definition of Hess' Law is that the $\Delta H°$ is a constant for a reaction, whether carried out in one reaction or through a series of reactions.
- The following three examples illustrate this Law:

Example 1: Calculate the $\Delta H^\circ_{298\ rxn}$ for $N_2O_5(g) + H_2O(g) \rightarrow 2HNO_3(l)$ from the following information:

Reaction	ΔH°_{298}
$N_2(g) + 2.5\ O_2(g) \rightarrow N_2O_5(g)$	11 kJ/mol
$H_2(g) + 0.5\ O_2(g) \rightarrow H_2O(l)$	-285.83 kJ/mol
$H_2(g) + 3O_2(g) + N_2(g) \rightarrow 2HNO_3(l)$	-348.2 kJ/mol

We want to have N_2O_5 and H_2O as the reactants and HNO_3 as the product. Some of these reactions will need to be re-written in the reverse. When we do that, the signs on the enthalpy changes will need to be reversed, as well:

$N_2O_5(g) \rightarrow N_2(g) + 2.5\ O_2(g)$ $H_2O(l) \rightarrow H_2(g) + 0.5\ O_2(g)$ $H_2(g) + 3O_2(g) + N_2(g) \rightarrow 2HNO_3(l)$	-11 kJ 285.83 kJ -348.2 kJ
$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(l)$	-73.37 kJ

Calculate the $\Delta H^\circ_{298\ \mathrm{rxn}}$ for $2C(\text{graphite}) + O_2(g) \rightarrow 2CO(g)$ from the following information:

Reaction	$\boldsymbol{\Delta H^\circ_{298}}$
$\mathbf{C(graphite) + O_2(g) \rightarrow CO_2(g)}$	**-393.5 kJ/mol**
$\mathbf{2CO(g) + O_2(g) \rightarrow 2CO_2(g)}$	**-566 kJ/mol**

Do this the same way we did the previous example:

$\mathbf{2C(graphite) + 2O_2(g) \rightarrow 2CO_2(g)}$ $\mathbf{2CO_2(g) \rightarrow 2CO(g) + O_2(g)}$	**-787 kJ** **566 kJ**
$\mathbf{2C\ (graphite) + O_2 \rightarrow 2CO(g)}$	**-221 kJ**

Calculate the enthalpy change for the reaction of hydrazine with hydrogen peroxide to form gaseous nitrogen and liquid water from the following information:

Reaction	ΔH°_{298}
$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$	-622.2 kJ/mol
$H_2(g) + 0.5\ O_2(g) \rightarrow H_2O(l)$	-285.83 kJ/mol
$H_2(g) + O_2(g) \rightarrow H_2O_2(l)$	-187.8 kJ/mol

Again, do this the same way we did the previous example:

$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$ $2H_2O_2(l) \rightarrow 2H_2(g) + 2O_2(g)$ $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$	-622.2 kJ 375.6 kJ -571.6 kJ
$N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$	-818.2 kJ

Note that whenever we change the coefficients in front of a reaction, we must also change the standard enthalpy of formation by multiplying it by the same coefficient.

We can also use the enthalpies of combustion to determine standard enthalpies of formation

The $\Delta H°_{combustion}$ for $2(CH_3)_2CHOH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8\ H_2O(l)$ is -4011 kJ.
From this, calculate the enthalpy of formation of $(CH_3)_2CHOH$ at STP.
Each individual reactant and product has its own standard enthalpy of formation.
ALL enthalpies of formation may be either calculated or may be found in tables in traditional chemistry texts or in the CRC Handbook of Chemistry and Physics.

$\Delta H°_{298\ O2(g)}$	$\Delta H°_{298\ CO2(g)}$	$\Delta H°_{298\ H2O(l)}$	$\Delta H°_{298\ (CH3)2CHOH}$
0 kJ/mol	-393.5 kJ/mol	-285.8 kJ/mol	????????????

$$\Delta H° = (\Sigma n\Delta H°_{products}) - (\Sigma n\Delta H°_{reactants})$$

Where "n" is the number of moles of reactant or product from the balanced reaction.

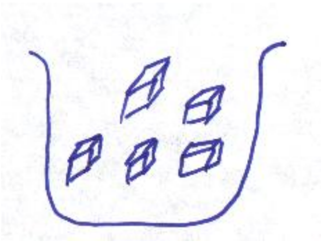
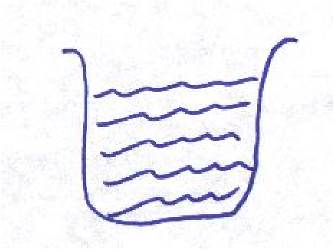
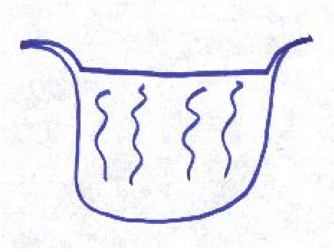
$$-4011\text{ kJ} = [(6 * -393.5) + (8 * -285.8)] - [(2 * \Delta H°_{298\ (CH3)2CHOH}) + (9 * 0)]$$

$$-4011\text{ kJ} = (-2361-2286) - 2 * \Delta H°_{298\ (CH3)2CHOH}$$

$$2 * \Delta H°_{298\ (CH3)2CHOH} = 4011 - 2361 - 2286 = -636\text{ kJ}$$

$$\Delta H°_{298\ (CH3)2CHOH} = (-636\text{ kJ}/2\text{ mol}) = -318\text{ kJ/mol}$$

ΔS = ENTROPY = the amount of disorder, chaos, randomness of a system

	$\Delta S>0$ → $\Delta S<0$ ←		$\Delta S>0$ → $\Delta S<0$ ←	
Solid ice: highest order and least entropy		Liquid Water		Water vapor (gas): most disorder and highest entropy

An entropy increase corresponding to any increase in chaos is the major driving force in many chemical and physical processes. The entropy change for a reaction is equal to:

$$\Delta S° = (\Sigma n\Delta S°_{products}) - (\Sigma n\Delta S°_{reactants})$$

E.g.,

For the reaction, $pQ + rS \rightarrow tU + vW$

$\Delta S° = [(t * S_U) + (v * S_W)] -[(p * S_Q) + (r * S_S)]$, where S_U = the entropy for U, etc.

When $\Delta S>0$, chaos is high; when $\Delta S<0$, chaos is low or order is high.

- The Second Law of Thermodynamics says that spontaneous changes in the universe are accompanied by increasing entropy in the universe, i.e., chaos is always increasing.
- $\Delta S°_{298}$ values are known just like the standard heats of reaction ($\Delta H°_{298}$).
- From that information, we can calculate entropy changes for reactions.
- Note the similarities of these calculations to those of enthalpy determinations.

Calculate $\Delta S°_{298}$ for the vaporization of water to steam at STP:

$$\Delta S°_{298} = S°_{H2O(g)} - S°_{H2O(l)}$$

Since 1 mol of each is present, $\Delta S°_{298} = 188.71 - 69.91 = 118.80$ J/K; $\Delta S°$ is positive.

This reaction is spontaneous. Note the units of $\Delta S°$: J/mol/K. This unit is smaller than the unit for enthalpy.

Calculate ΔS°_{298} for the condensation of methanol vapor (CH_3OH) to liquid methanol.

$\Delta S^\circ_{298} = S^\circ_{CH3OH(l)} - S^\circ_{CH3OH(g)}$

$\Delta S^\circ_{298} = 239.7 - 127 = 112.7$ J/K

Calculate ΔS°_{298} for the formation of carbon tetrachloride and hydrogen from methane and chlorine. Note that in the balanced reaction, 2 mols of chlorine and 2 mols of hydrogen are required and produced, respectively.

$\Delta S^\circ_{298} = [S^\circ_{CCl4(l)} + 2$ ´ $S^\circ_{H2(g)}] - [S^\circ_{CH4(g)} + S^\circ_{Cl2(g)}]$

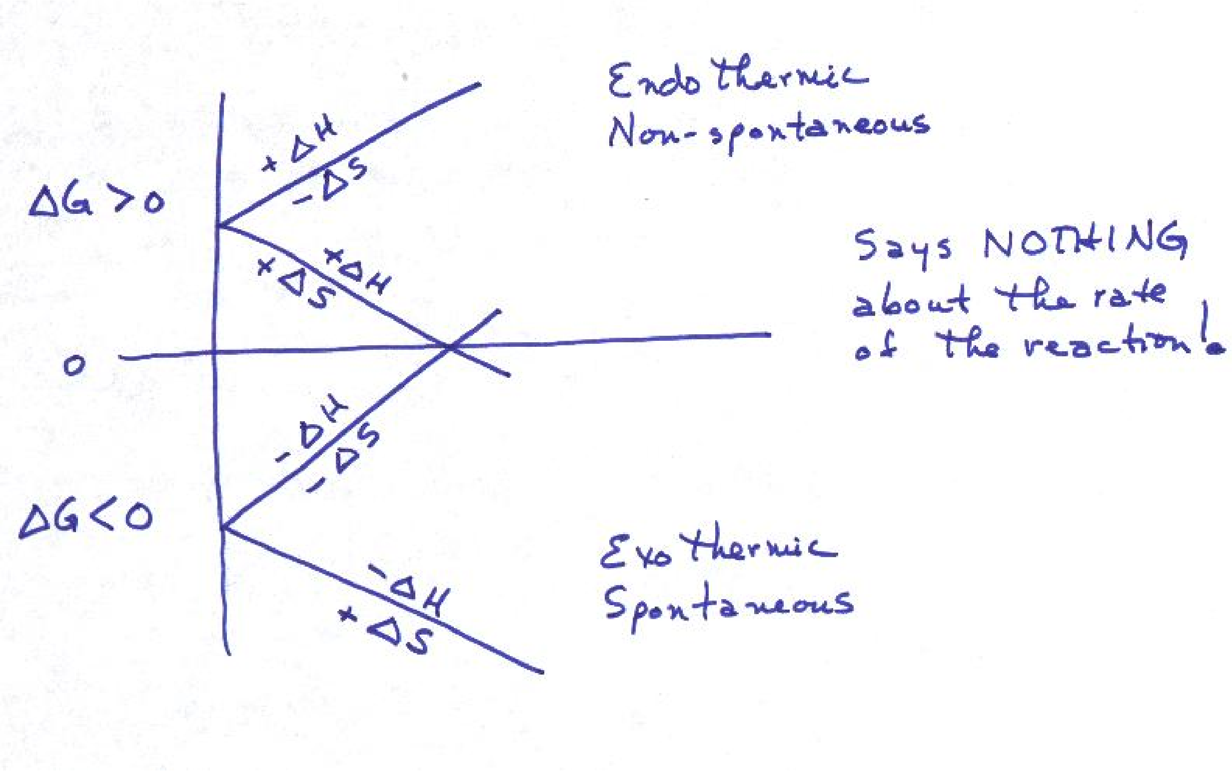
$\Delta S^\circ_{298} = [216.4 + (2$ ´ $0)] - [186.15 - (2$ ´ $0)]$

$= 216.4 - 186.15 = 30.25$ J/K

Another state function is the free energy change, aka GIBB'S FREE ENERGY = ΔG.
This free energy change is equivalent to expressing arithmetically the difference between a state of minimum energy (-ΔH) and maximum chaos (+ΔS) that occurs when possible for a chemical reaction to proceed spontaneously, i.e., as written.
The arithmetic expression is: $\Delta G = \Delta H - T\Delta S$, where the "T" is the absolute temperature of the system.

When $\Delta G<0$, the reaction goes as written.

When $\Delta G>0$, the reaction does NOT go as written, see graphic below:



$\Delta G°_{298}$ values are also known, so $\Delta G°$ values for reactions may be calculated just as enthalpy and entropy values were.

E.g., calculate $\Delta G°_{298}$ for the formation of sulfuric acid(l) from sulfur trioxide gas and liquid water:

$$\Delta G°_{298} = [\Delta G°_{H2SO4(l)}] - [\Delta G°_{SO3(g)} + \Delta G°_{H2O(l)}]$$

$$= 690.1 - [-371.1 + -237.18] = 690.1 - (-608.28)$$

$$\Delta G°_{298} = 1298.38 \text{ kJ}$$

Units, again, for reactants and products are in kJ/mol as with enthalpy.

Calculate the $\Delta G°_{298}$ for $2Al(g) + 3F_2(g) \rightarrow 2AlF_3(s)$:

$$\Delta G°_{298} = [2 * \Delta G°_{AlF3(s)}] - [2 * \Delta G°_{Al(g)} + 3 * \Delta G°_{F2(g)}]$$

$$2(66.44) - [(2*286) + (3 * 0)] = -439.12 \text{ kJ}$$

- The Third Law of Thermodynamics says that the entropy of ANY pure, perfect crystalline element or compound at 0 K is ZERO: there is NO molecular movement.
- Impure substances also have NO molecular movement at 0 K, but since the impurity is not equally distributed, this causes an increasing entropy, i.e., entropy does not equal zero in impure substances at 0 K.