THERMODYNAMICS

The Nature of Energy

-What is energy? How does it move and can it be stored?

-The industrial revolution spawned the birth of a branch of chemistry called thermodynamics. This translates as the study of "the movement of heat"

-Henry Watt's steam engine was the fundamental machine that was studied to learn about the nature of energy. It required two essential pieces: a heat source and a fluid to carry the heat.

-Heat is carried by steam in order to produce work. This means that energy can be defined as "the capacity to do work or to produce heat."

energy = the ability to resist a force or to do work/produce heat

-The Stirling Engine demonstrates that the amount of energy transferred between bodies is directly proportional to the difference in temperature of the bodies.

T (temperature) $\equiv$K (Kelvins)
Q = quantity of heat/energy
J (joules) = Nm (newton meter)
ΔT directly proportional to ΔQ

Storage
gravitational, potential, chemical

Conversion
into work as mass
is moved

Friction

Absorption

Transfer
(conduction, convection, radiation)

-Convection: heat transfer through a fluid medium
-Conduction: direct touching
-Radiation: heat being carried by light (infrared waves)

Temperature and Energies

-heat = energy

-temperature is the property of a body or space that determines whether of not heat energy will flow into or out of it from its neighbors

$$KE = \frac{1}{2} MV^2$$

-Temperature is closely related to the internal motions of a given amount of any substance. This can be thought of as an expression of the average amount of kinetic energy of particles in the substance.

$$KE \approx T$$

-Temperature is measured on scales, which use specific events as fixed points on their scales. E.G. the freezing point and boiling point of water are 0 and 100 Celsius.

-Heat is kinetic energy

-The Kelvin Scale is absolute and relies on the idea that a substance must have a point at which it contains no heat and heat cannot flow out of the body, but must at all times flow into it. Consider the following:

delta Q is directly proportional to delta T, the Q is proportional to T
or Q/T is a constant
$Q_1/T_1 = Q_2/T_2$

-temperature can be defined thermodynamically as a function of the heat content of a body.

-The 2 fixed points for the Kelvin scale are absolute 0 (0K) and the triple point of water (273.15K). Water freezes at 273.15K and boils at 272.15K respectively

-Heat can be defined as the quantity of energy that is transferred between bodies of different temperatures.

-The kinetic energy of any body is made up of specific energies that together make up the Internal Energy (U) of the substance. The 4 together are:

electronic energy	
vibrational energy (symmetric, asymmetric, bending)(bonds)	solid, liquid, gas
rotational energy	liquid, gas
translational energy	gas

Type	**Cause**	**Type of body**
Electronic	The quantum mechanical nature of the atom. Electrons move in electronic levels about nucleus.	All
Vibrational	The "shivering" of molecules. Asymmetric stretch, symmetric stretch, bend.	All with chemical bonds. 2 or more atoms; solids, liquids, gases.
Rotational	Tumbling. 3 dimensions and around the molecules common center of mass.	All bodies with chemical bonds 2 or more atoms. Liquid/gas.
Translational	Movement of whole particles in 3 dimensions.	Only gas.

-Change in U is calculated as the change in heat of the body minus any work done by the system.

$\Delta U = \Delta Q - w$, ΔU= change in U (J), ΔQ = quantity of heat transferred (J)
w=any work performed by the system and surroundings
$w = P \times \Delta V$, pressures times change in volume

-Pascal = N/m^2, = 101325 Pa

-Monotonic gases have 2 energy pockets, electronic and translational.

0th Law of Thermodynamics

-a=b, and b=c, then a=c, time is not considered

Heat Death of the Universe

1. Inevitable
2. Space will reach thermal equilibrium, about 5 K

-1 liter = .01 m^3

Specific Heat Capacity/Heat Capacity

-When an object receives heat, its temperature rises. The actual rise in temp depends on the heat capacity of the object.

-*Heat capactiy*: the amount of heat required to raise the temperature by 1K

$\Delta Q = C\Delta T$, C=heat capacity

-Heat capacity is "C" (units are J/K) are unique to the chemical nature of all substances. They are calculated through empiracle investigation. Predictions can be made but no theory produces accurate values.

-Heat capacity is a unit of a mass, 1g, of a substance, is the *specific heat capacity*.

-*Specific Heat Capacity* is "c" (units J/(Kg)), is the amount of energy required to raise 1g of the substances by 1K. This value multiplied by the mass of the substance in question is "C", the heat capacity.

-Specific heat capacities are typically low for metals (less than 1). However, liquid water has a staggeringly high specific heat capaicty of 4.186 J/(Kg). This is the definition of the calorie! To convert from calories to Joules, multiply by 4.1868.

-The signs connected to delta values now become very important. Positive changes reflect endothermic processes, where energy increases. Negative values are exothermic, meaning the heat in the system decreases.

$+\Delta Q$ = endothermic = $+\Delta T$

$-\Delta Q$ = exothermic = $-\Delta T$

Heat of Reaction, Enthalpy, and the First Law (514-518)

-The total sum of all kinetic energies in a sample is called the internal energy (U), but this does into take into account any potential chemical energy. This is energy stored not in the vibrations or rotations of chemical bonds, but in the potential of the very bonds themselves.

-*The combined sum of all energy in any sample of matter is called* ***enthalpy.*** Enthalpy tells us why a match can exothermically burn and release energy to the surroundings that was not present as kinetic energy.

-Enthalpy is related mathematically to work and internal energy as the sum of <u>all</u> energy change in a system.

$\Delta H = \Delta U + w$

-The concept of enthalpy of reaction ($\Delta H_{reaction}$) relates to the change during the course of a chemical reaction. Positive values of ΔH mean endothermic reactions, whereas negative values mean exothermic reactions.

-In order to preserve the correct sign (+/-) for ΔH, it follows the same mathematical principle of $H_f - H_i$. This means that enthalpy changes are calculated as

$\Delta H_{reaction} = H_{products} = H_{reactants}$

-However, hope lies in the idea that in a constant pressure environment, any enthalpy change is equal to a change in heat for the system, thus

$\Delta H = \Delta U + w$, where $\Delta U = \Delta Q - w$,

$\therefore \Delta H = \Delta Q$ (at standard pressure)

-Exothermic reactions release energy to the surroundings, and in so doing there must be a decrease in the enthalpy of the system. This in turn correlates to a typical increase in stability of products. The opposite is true of endothermic reactions.

-From this flows the concept of the conservation of energy, or the first law of thermodynamics. The enthalpy of a system may decrease (exothermic), but it is matched by an exact increase (endothermic) in the enthalpy of the universe.

-The First Law can be stated thus: *"Energy can neither be created nor destroyed, it simply changes from one form to another."* Mathematically:

$\sum \Delta H_{universe} = 0$.

-The first law, like the 0th, can never be broken. The universe contains a finite, definite amount of energy that is in three places: motion, location, or chemical potential. Even the "Heat death" allows for this stating that without different temperatures, the energy simply will not flow, preventing work to be done!

Heat of Reaction, Formation, Combustion, and Hess's Law (514-524)

-As discussed earlier, the enthalpy change during the course of a chemical reaction can be dtected through calorimetry and characterized as exothermic ($-\Delta H$) or endothermic ($+\Delta H$). This also corresponds to a change in the stability of the chemicals and the system, and is equal to the change in heat content (ΔQ) at constant pressure.

-On the whole, it is fair to say that chemical reactions move in a direction of increasing stability, and lowering enthalpy. The enthalpy profiles for this process should be well understood.

-It's also fair to state that a chemical reaction can be written indicating the change in enthalpy and the location and direction of the energy change.

-Enthalpy changes for specific chemical reactions have specific names, however, according to the type of chemical reaction involved. Here are the major types and the definitions with examples:

Heat of Formation

-the enthalpy change that occurs when one mole of product is formed from the constituent elements in their standard states

Heat of Combustion

-The enthalpy change that occurs when one mole of reactant in its standard state is "burned" wiht oxygen to form simple oxides.

Heat of Solution

-The enthalpy change that occurs when one mole of reactant is dissolved into a solution (typically aqueous) from its standard state.

-Calculation enthalpy changes for these various reactions can be tedious and predicting energy changes of reactions impossible. However, Hess's Law can be used as a shortcut for calculating the heat of <u>any</u> reaction.

Hess's Law is simply stated: "that the enthalpy for any reaction is independent of the route take." This means that the sum of the energies of any and all steps in a reaction is equal to the overall enthalpy change in a system. This can be written as:

$$\Delta H_{reaction} = \sum \Delta H_{products} - \sum_{\Delta hreactants}$$

-Hess's Law means that the reverse of an endothermic reaction is an exothermic reaction one, and vice versa. Also, that the quantity of energy released or absorbed is also identical (by the first law), and independent of direction.

-By balancing known equations with $H_{reaction}$, and the quantity of moles, it is possible to accurately determine enthalpy changes of reactions not yet carried out.

Entropy, 2nd and 3rd Laws (526-528)

-as discussed earlier in the 0th law, the universe is moving in a direction where heat is equal with everything

-Why should energy move at all during chemical reactions??? Why is it that 2 substances at thermal equilibrium should react chemically? Rudolf Clausius asked this, as well as Sadi Carnot. -Entropy (S): is a measure of disorder (wasted work) or chaos in a system, or more accurately, defined by Boltzmann as the probability distribution within matter:

$S = k \ln W$, with S= entropy, k=boltzmann constant, w = probability

-amount, temperature, and phase affect probability

-hot = disorganized, cold = organized (solid)

-work out < work in

-phase change = entropy change.

-Entropy is an energy term and as such is measured in Joules, but is also temperature dependent and is combined with a K measurements.

-Entropy is measured in J/K

-2nd Law observed during processes of nature, reason that energy flows, spontaneously flows in a direction that makes entropy increase

-Entropy is one of the most potent concepts in the universe. It is responsible for the aging of life forms, crime, weather, and evolution.

-2nd Law shows us that in a closed system, $\Delta S > 0$, or in a closed system, entropy always increases.

-However, the 0th law has shown us there is no such closed system. , so the $\Delta s_{universe} > 0$

-for every increase in S, there is a decrease somewhere else.

-Unlike enthalpy, entropy has an absolute value. The **3rd Law of Thermodynamics** is "the entropy of a perfect crystal at absolute 0 is 0" or mathematically,

$S = k \ln W$, at absolute 0, w=1, so $S = k \ln 1, = 0$

-Entropy increases as the number of particles in a system increases (more combinations)

-Temperature increases as entropy increases

-exothermic processes ($-\Delta H$) are typically endotropic processes ($+\Delta S$), and endothermic processes ($+\Delta H$) are typically exotropic processes ($-\Delta S$).

-As substances change phase, the entropy of the substance changes.

-Entropy increases in the following series, solid > liquid > gas

-for gases under standard conditions, entropy increases with mass:

-noble gases have unordinary low standard entropies

-diamond has the lowest standard entropy per mole

Free Energy and the Gibbs Function (528 - 530)

-impossible to predict whether energy will move and reactions take place

-entropy = "where heat dies", or "fixed energy."

-for a reaction, you need free energy

-For both the 1st and 2nd laws to be satisfied, amount of free energy in the universe always decreases. Just as the amount of fixed energy (entropy) most always increase. Energy spontaneously moves in a direction in which the amount of free energy decreases ($-\Delta G$). This also complies with the Heat Death (No $+\Delta G$).

-As the ΔG relies upon the 1st law (how much energy available), the 2nd law (how much becomes fixed) and that entropy increases with temperature, the change in Gibbs free energy is

$\Delta G = \Delta H - T\Delta S$ (only at constant temp.)

-ΔG has a negative value (irrespective of magnitude); a thermodynamic process (chemical reaction) will occur. If a reaction is observed, free energy is consumed and $|G|$ decreases.

Chemical reaction = unexpected color
unexpected temp change
solid precipitate

gas

-3 immediate conclusions:
  -at abs 0, the free energy in a system is the potential energy associated with chem. bonds
  -when $\Delta G = 0$, the system comes to equilibrium, chemical and thermodynamical
  -when ΔG is negative, the reaction is feasible.
-important: low temps effect of S is reduced and ΔH of system dominant, system favors lower H

-Kinetic control prevents spontaneous reactions. Reactants don't move fast enough, so a successful collision can occur.
-Kinetic control is not having successful collisions to start a chain reaction
-reaction flux under kinetic control is less than 1
  KC<1
  KC>1 = chain reaction
  KC = 1, for every one that occurs, one occurs after, no chain reaction though.