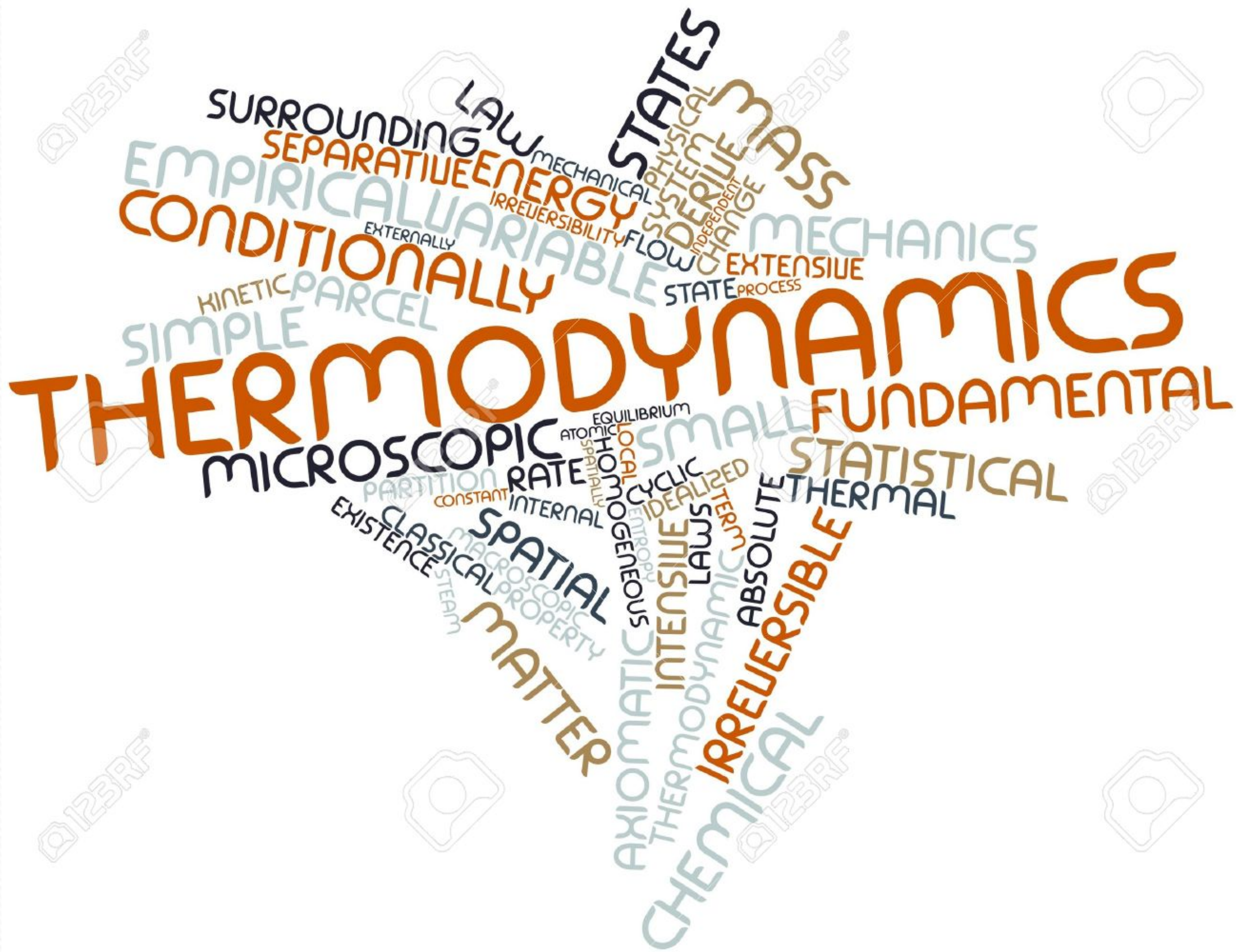
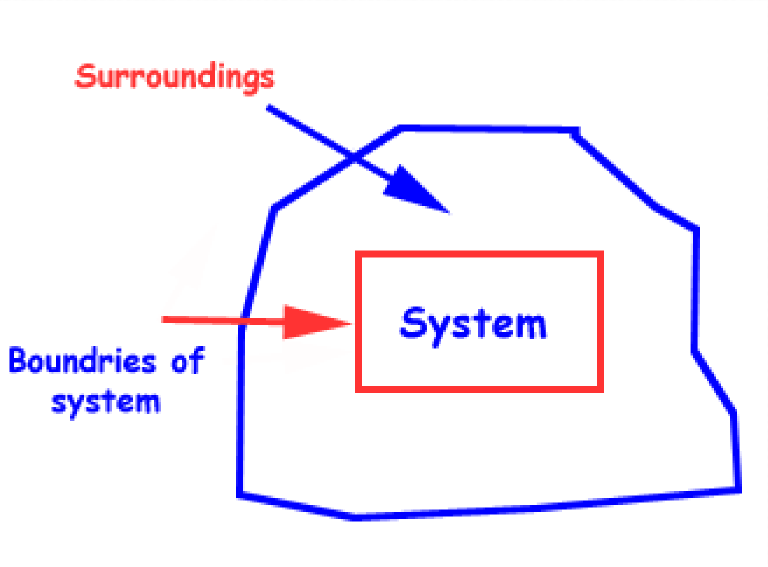


The underlying prerequisite to the application of thermodynamic principles to natural systems is that the system under consideration should be at equilibrium.

http://eps.mcgill.ca/~courses/c220/

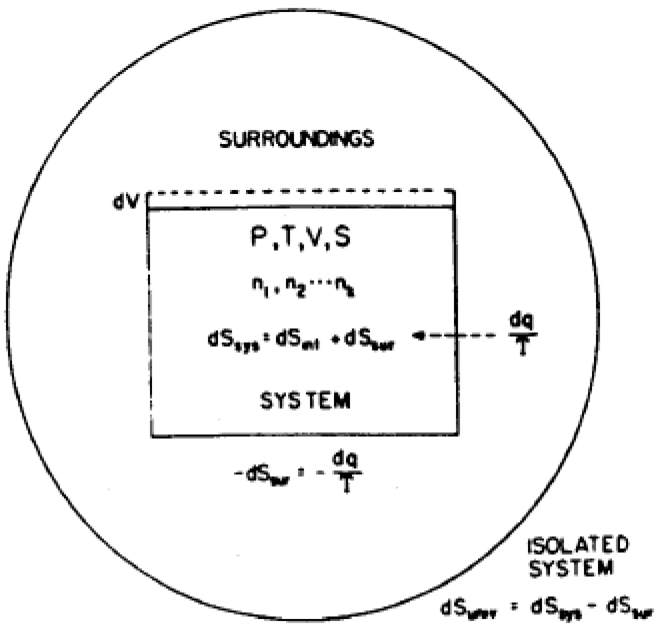
Thermodynamics: Definitions and concepts

A thermodynamic system is a portion of matter (assemblage of atoms, minerals, rocks, gases, solutions, etc.) in a defined volume of space with boundaries that are defined to one's convenience and to which the laws of thermodynamics are applied. …
There are various types of systems. These are defined on the basis of whether or not they are permitted to exchange matter, heat, and work with their surroundings.



An isolated system cannot exchange heat, matter or work with its surroundings. It has a constant mass and energy content.

An isolated system cannot exchange heat, matter or work with its surroundings. It has a constant mass and energy content.



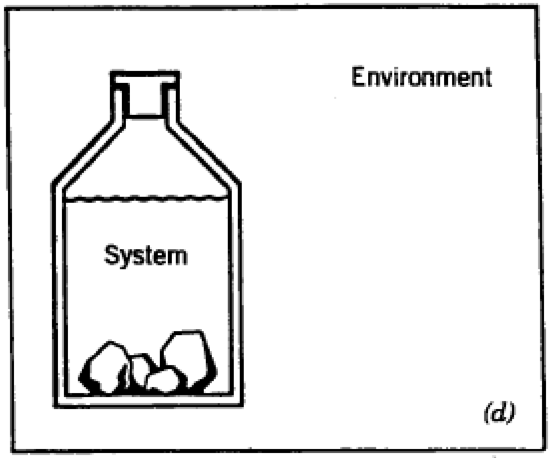
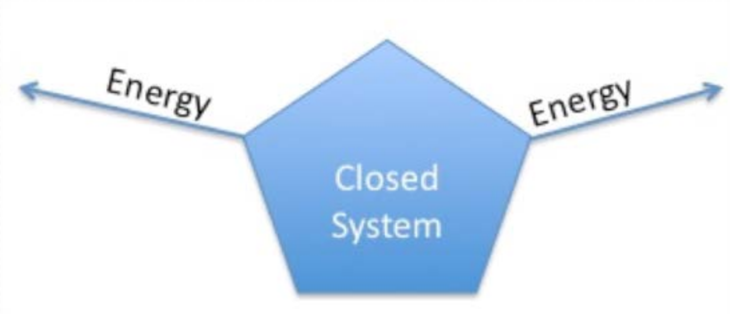
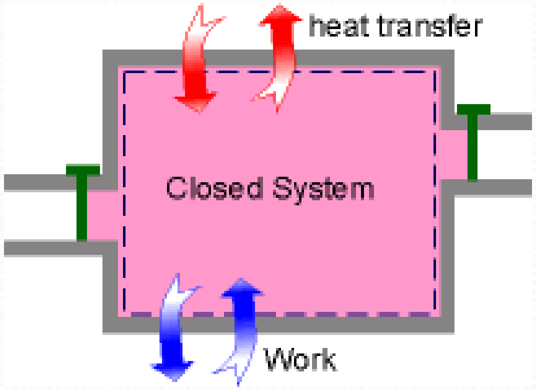


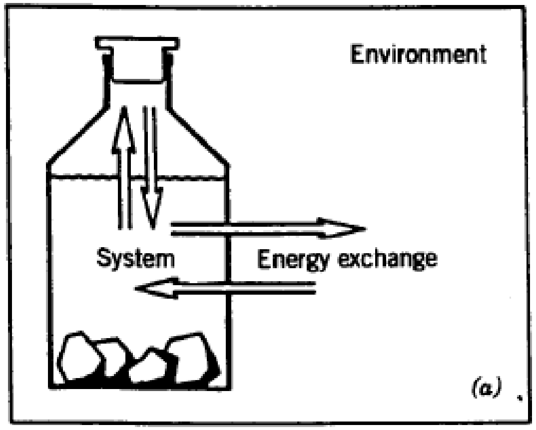
Figure 2.3. Illustration of a closed system, surroundings, and an isolated system or "universe" of a system plus surroundings. Heat transferred to the system, q, is positive, and that lost from the surroundings is $-q$. The entropy change of the system, dS_{sys}, is the *sum* of an internal change dS_{int} and a flow from the surroundings dS_{sur}.

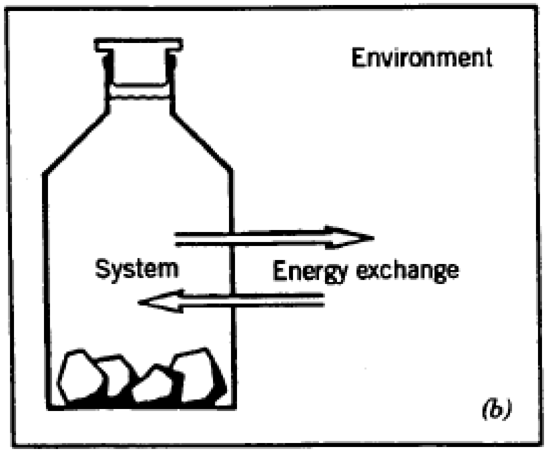
A closed system can exchange energy, but not matter, with its surrounding. It has a constant mass and composition but variable energy.



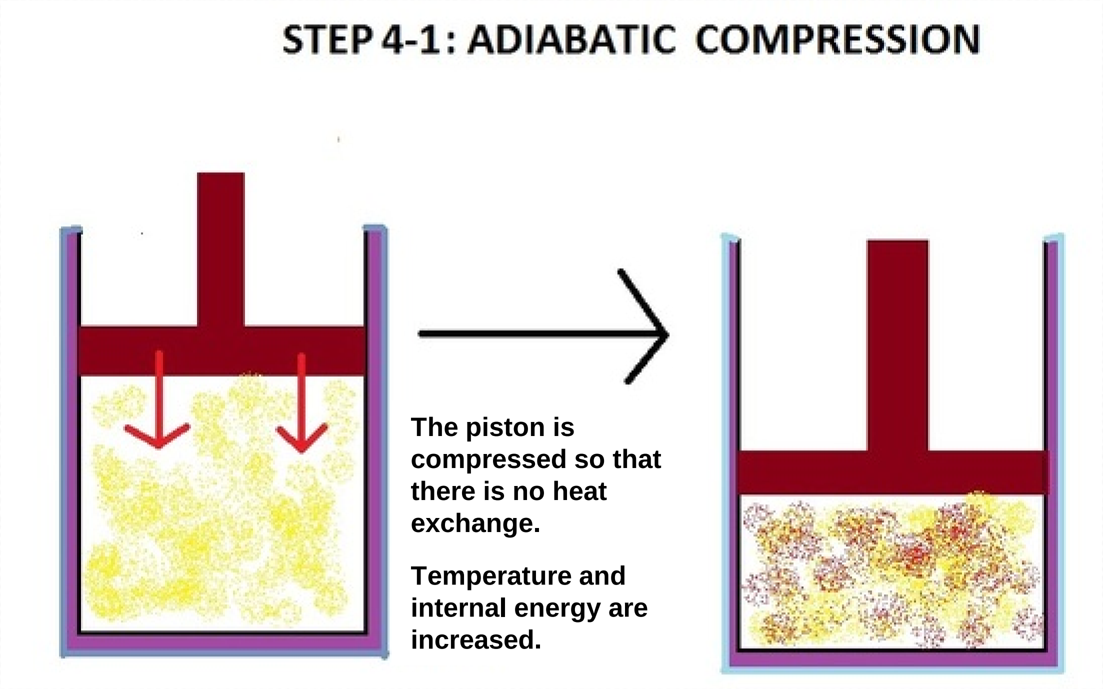


A closed system can exchange energy, but not matter, with its surrounding. It has a constant mass and composition but variable energy.

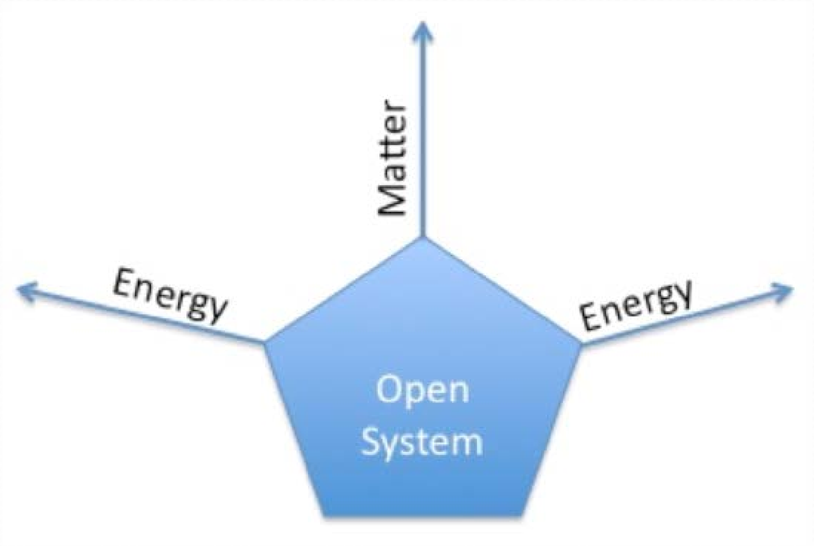




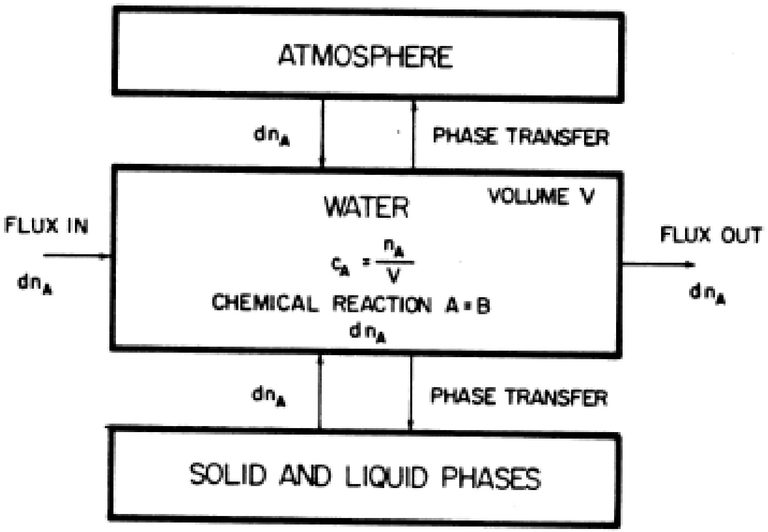
An adiabatic system is a closed system in which the boundaries are thermally insulated, but upon which work can be done.



An open system may exchange both matter and energy across its boundaries.



An open system may exchange both matter and energy across its boundaries.



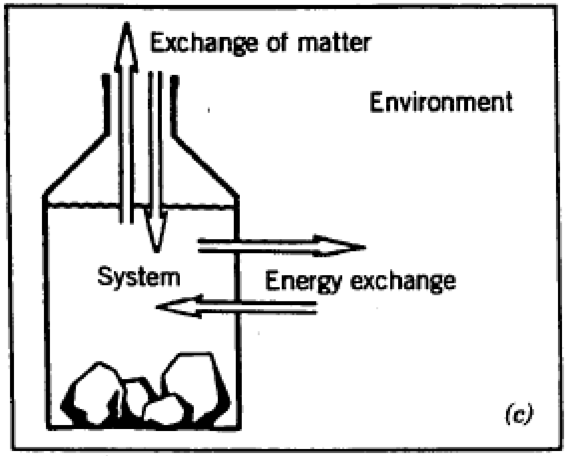


Figure 2.2. General representation of a natural water system treated as a continuous, open system. The system receives fluxes of matter from the surroundings and undergoes chemical changes, symbolized by the reaction A = B. The time-invariant condition is represented by $dC_A/dt = 0$.

An open system may exchange both matter and energy across its boundaries.

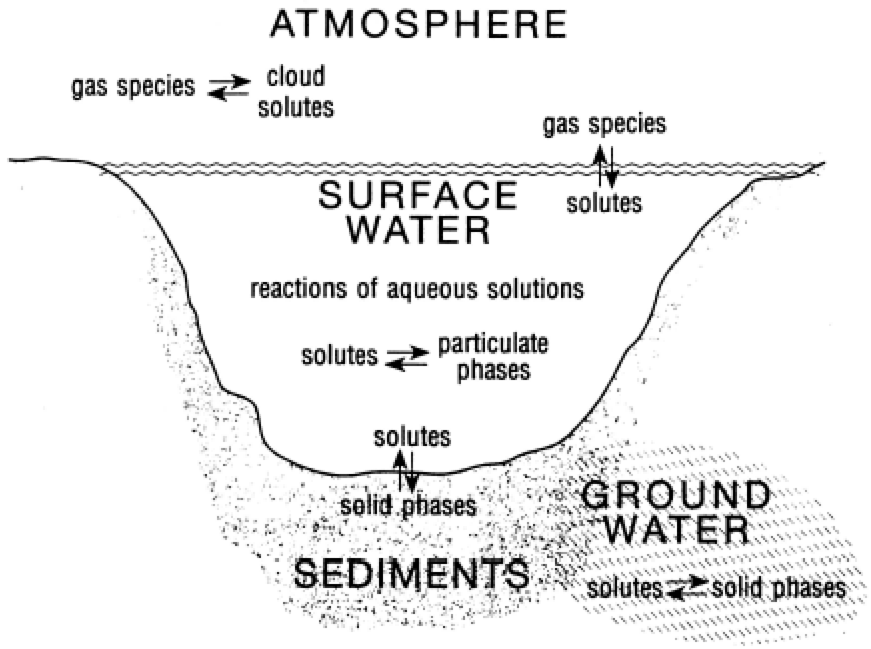
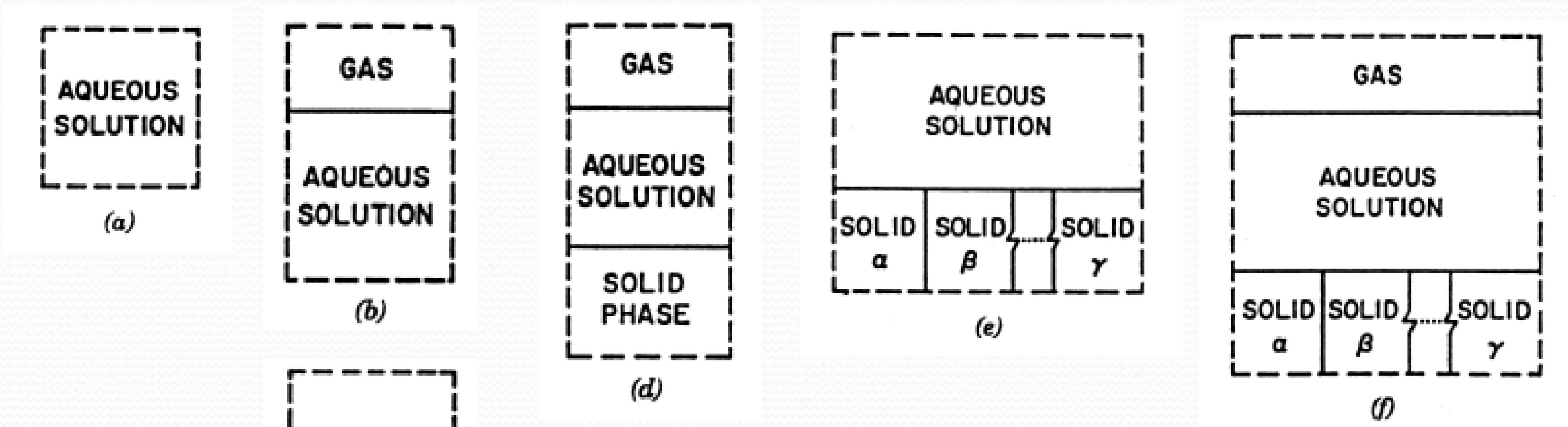


Figure 1.1. Natural water environments of interest in aquatic chemistry. Water links elemental cycles of the atmosphere with those of the sediments. Atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are needed.

Systems consist of one or more parts that are called **phases**.
Each phase is a region of the system with distinct boundaries. It is physically and chemically homogeneous, or, in other words, spatially uniform in its properties. Individual minerals, well-mixed gases and liquids qualify, but …



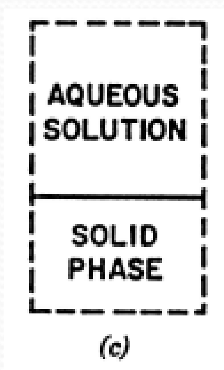


Figure 1.2. Models of various parts comprising overall natural water systems: (a) aqueous solution phase model; (b) aqueous solution and gas phase model; (c) aqueous solution and solid phase model; (d) three-phase aqueous, gas, and solid phase model; (e) aqueous solution plus several solid phases model; and (f) multiphase model for solids, aqueous solution, and a gas phase.

Phases are made up of one or more **components**.
Components are chemical entities that combine to describe the composition of the species and substances in the system.
Species are molecular or ionic entities that exist in solution and are themselves made up of one or a combination of components.

Ex: Pure H_2O has three species in solution, H^+, OH^-, and H_2O (and there may be more) but only two components are required to describe them.

1. H_2O and H^+, with $OH^- = H_2O - H^+$
($H_3O^+ = H_2O + H^+$; $H_9O_4^+ = 4H_2O + H^+$)

2. H_2O and OH^-, with $H^+ = H_2O - OH^-$

3. OH^- and H^+, with $H_2O = H^+ + OH^-$

Selecting the smallest number of components (or master species) required to describe the system is one of the fundamental decisions that one has to make in setting up geochemical computer models.

Gibbs Phase Rule

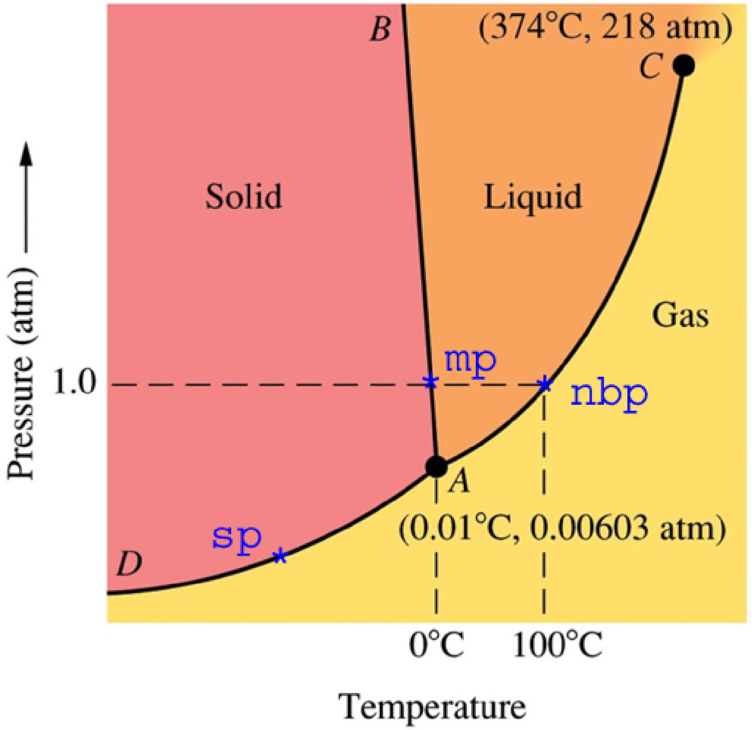
The Gibbs phase rule relates the number of components (C) and phases (P) that can exist in a system at equilibrium. The rule is:

$$F = C - P + 2$$

where F is the number of independent variables or degree of freedom.
The Gibbs phase rule tells us how many stable phases co-exist at equilibrium.

The simplest and perhaps the most familiar phase rule example deals with the triple point of water, for which the equilibrium reaction is:

H_2O (ice) = H_2O (liquid) = H_2O (vapor)



Gibbs Phase Rule

The Gibbs phase rule relates the number of components (C) and phases (P) that can exist in a system at equilibrium. The rule is:

$$F = C - P + 2,$$

but can also be re-written as:

$$F = C' + 2 - P - R$$

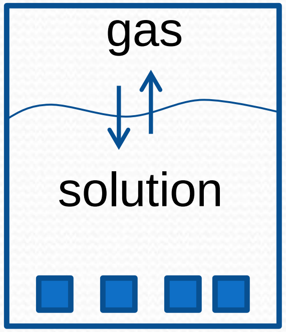
where F is the number of independent variables or degree of freedom, C' is the number of different chemical species in the system and R equals the number of auxiliary restrictions (i.e., the various chemical equilibria or mass-action laws that describe the species, plus the charge and mass balance equations).

Gibbs Phase Rule

The H_2O-CO_2-$CaCO_3$ system

-Three phases: solid, solution, gas → P = 3
-Nine chemical species: $CaCO_{3(s)}$, $CO_{2(g)}$, H_2O, H^+, OH^-, Ca^{2+}, $H_2CO_3^o$, HCO_3^- CO_3^{2-}
C' is therefore equal to 9.
- Five mass-action equations:

1) $CaCO_3$ (calcite) = $Ca^{2+} + CO_3^{2-}$
2) $CO_2(g) + H_2O = H_2CO_3^o$
3) $H_2CO_3^o = H^+ + HCO_3^-$
4) $HCO_3^- = H^+ + CO_3^{2-}$
5) $H_2O = H^+ + OH^-$



and the charge balance equation makes up the sixth restriction:
$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

Thus, R = 6 and C' – R = C = 3. Only three components are necessary to describe the system and F = 9 + 2 - 3 - 6 = 2.
Two degrees of freedom indicate that, at equilibrium, the concentrations of the nine species will be fixed but different for every combination of temperature and pressure. … Numerous solutions, one for each set of P, T conditions.

Classical Thermodynamics

The theory of chemical thermodynamics can be represented in terms of five fundamental variables, two modes of energy transfer and one characteristic state function, whereas the theory is developed on the basis of three principles or laws (of thermodynamics).

The five fundamental variables of a system are:

T, absolute temperature, an intensive property
S, entropy, an extensive property
P. pressure, an intensive property
V, volume, an extensive property
n_i, number of moles of a component *i*, an extensive property

Extensive properties/variables are internal to the system and are additive. They vary with the mass of the system (e.g., # moles, mass, E, V)

Intensive properties/variables are independent of mass and are not additive (e.g., P, T, μ, ρ, etc.). They are external and act on a system.

Classical Thermodynamics

The two modes of energy transfer for a system:

q, heat transferred to a system from its surroundings
w, work done on a system by its surroundings
(there are a number of ways in which work can be applied to or done by a system: expansion (PV), electrical (charge), gravitational (mg), chemical (μ), surficial (γ).

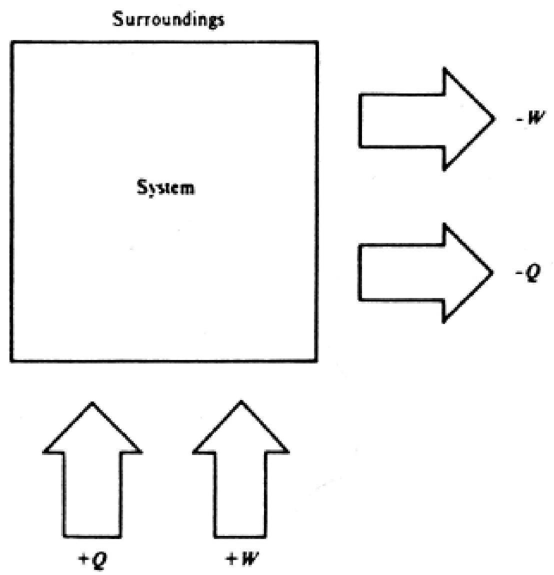


Figure 3-1. Sign conventions for heat and work.

Energy lost by the system is a negative quantity, similarly heat given off by the system is also negative by convention. The same convention applies to work; a system that does work on its surroundings or environment "loses work" so work done by the system carries a negative sign.

Classical Thermodynamics

The characteristic state function (i.e., a property that depends only on the initial and final states of a system) is:

E, the internal energy of a system, an extensive property
or $\Delta E = E_{final} - E_{initial}$ (irrespective of how you get there)

ex: A → C or A → B → C
(in the case of a chemical system = sum of the kinetic and potential energies of its constituent atoms)

Other state functions can also be derived:

H, the enthalpy, an extensive property
(heat released or absorbed by a system at constant pressure, …)
A, the Helmhotz free energy, an extensive property
(energy available for work)
G, the Gibbs free energy, an extensive property
(energy of a chemical system)

Law of Thermodynamics

The first law relates the two modes of energy transfer for a system, heat and work:

$$\Delta E = q + w_{on} = E_{final} - E_{initial}$$

Or, in other words, the internal energy of a system, ΔE, is the sum of the heat transferred to the system, q, and the work done on the system, w. For infinite variations:

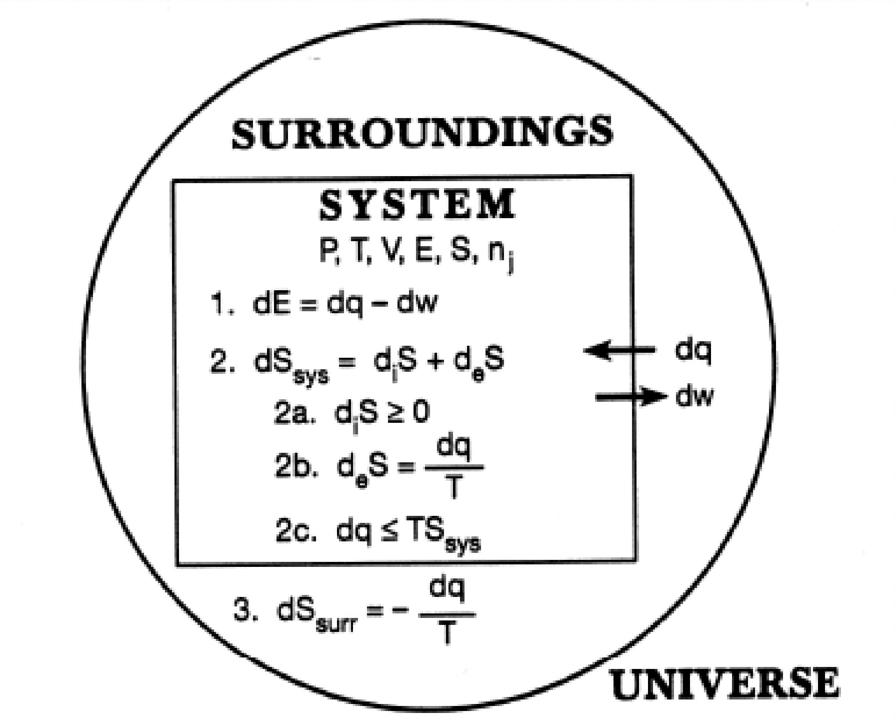
$$dE = dq + dw$$

Implicit in the first law but often stated separately (as **the zeroeth law**) is the law of conservation of energy. It states that a system may gain or lose energy, but its surroundings must change energy in equal and opposite way such that:

$$E\ (system) + E(surroundings) = constant = E(Universe)$$

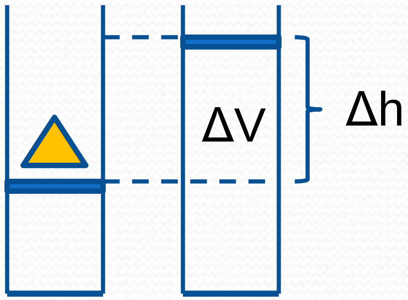
Law of Conservation of Energy

E (system) + E(surroundings) = constant = E(Universe)



Laws of Thermodynamics

If a system is set up so that work is done by expansion against an external pressure, such as a system confined in a vertical cylinder, and that expansion results in raising a mass m at the top of the cylinder against the force of gravity:



For PV work done by the system:

$E = q + w_{on} = q + PV = q – mg\,\Delta h$

Since $P = mg/area = mg/L^2$, and $\Delta V = L^2 \times \Delta h$, then $mg\,\Delta h = P\,\Delta V$

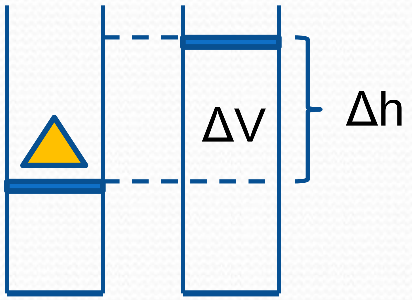
or for an infinitesimal expansion, $dE = dq - PdV - VdP$

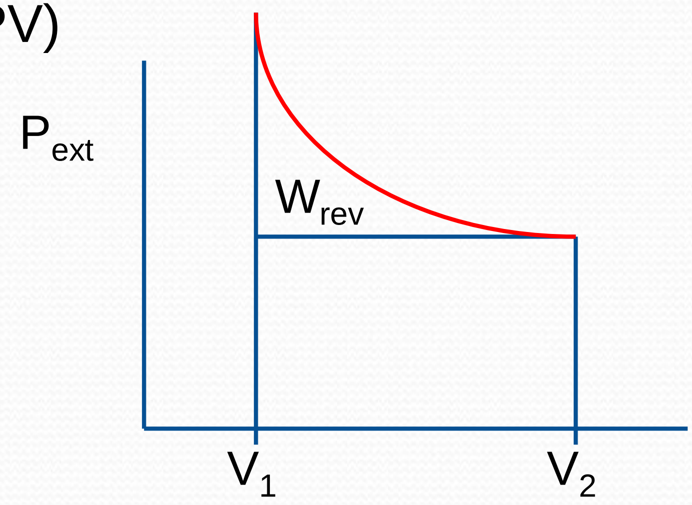
Laws of Thermodynamics

At constant pressure $dE = dq - PdV$

from which comes the definition of enthalpy, heat at constant pressure,

$dq_p = dH = dE + PdV \quad (H = E + PV)$





for an adiabatic system, $dq_p = 0$ and so:

$$dE = dW = -P\,dV \text{ or } -\int_{v1}^{V2} P_{ext}\,dV \text{ if } P_{int} > P_{ext}$$

Laws of Thermodynamics

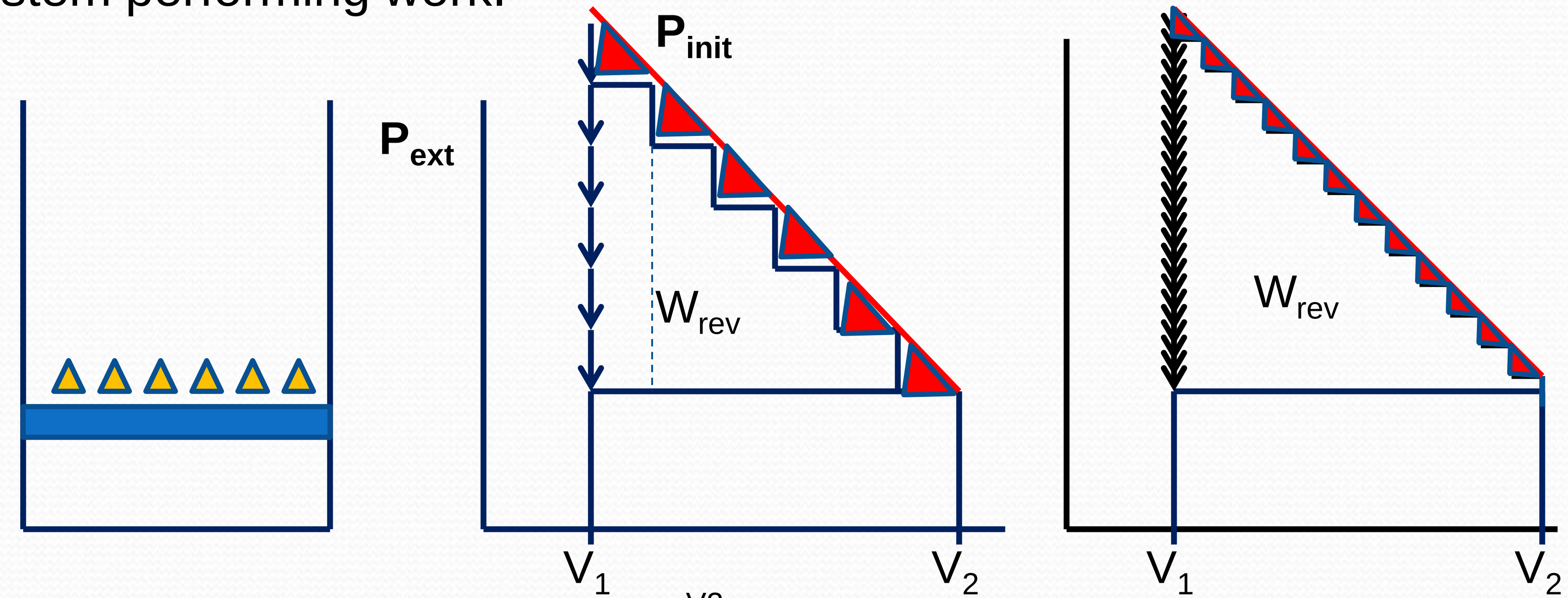
The second law of thermodynamics deals with **entropy**.
In any reversible process, the change in entropy, ΔS, of a system, or parts of it, is equal to the heat it absorbs or is transferred to it (q), divided by the absolute temperature:

$$\Delta S = q_{rev}/T \text{ or } dS = dq_{rev}/T$$

Historically, the second law of thermodynamics arose (was developed) from the search for a state function that describes the tendency for all processes to change in a certain direction.
For example, water always flows from a high hydraulic to a low hydraulic head, dissolved salts always diffuse from a more concentrated solution to less concentrated ones, and heat always flows from high temperatures to lower temperatures. In other words, all natural processes are unidirectional if allowed to proceed spontaneously, but there is nothing in the first law that prevents the reverse from happening.

Laws of Thermodynamics

The greatest amount of work that can be achieved in a real system is reversible work, but reversibility cannot be fully attained in any real system performing work.



Each time a weight is removed, $\int_{V1}^{V2} P\,dV = -w_{rev}$

Thus, work (as heat) is not a state function because it is path dependent. It approaches reversible work by taking infinitesimal steps.

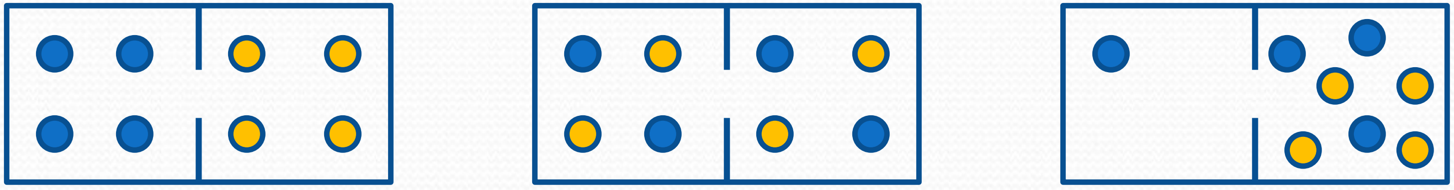
$dS \geq dq_{rev}/T$ where q_{rev} is reversible heat.

Laws of Thermodynamics

By using a molecular rather than a macroscopic view of systems, Boltzmann and others (including Planck) showed that there is a relationship between the spontaneous direction of natural processes and probability theory.

$$S = k \ln \Omega$$

where k = Boltzmann's constant = R/N_A, Ω = # of ways of achieving a given state, R is the gas constant and N_A is Avogadro's number.



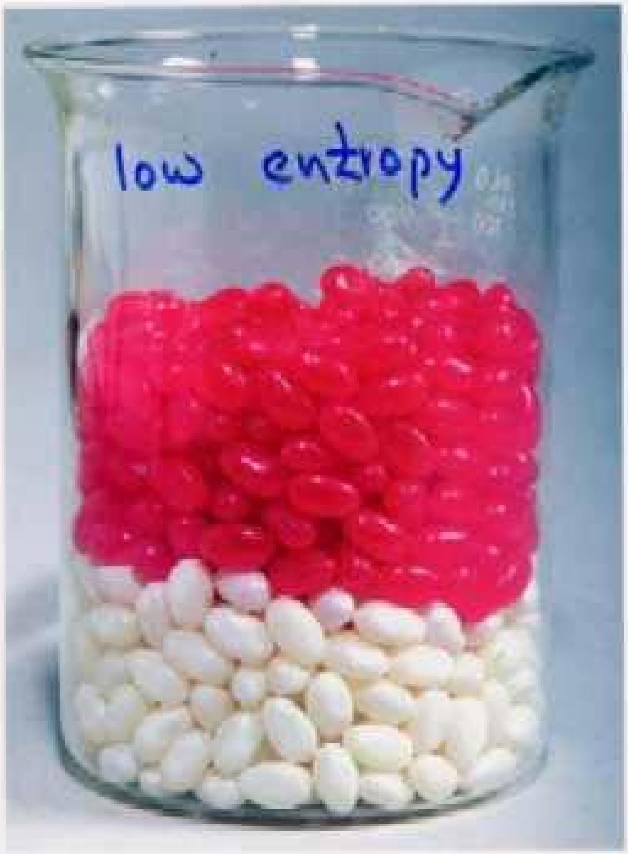
Indicating that every system left to itself will change toward a state of maximum probability.

Laws of Thermodynamics

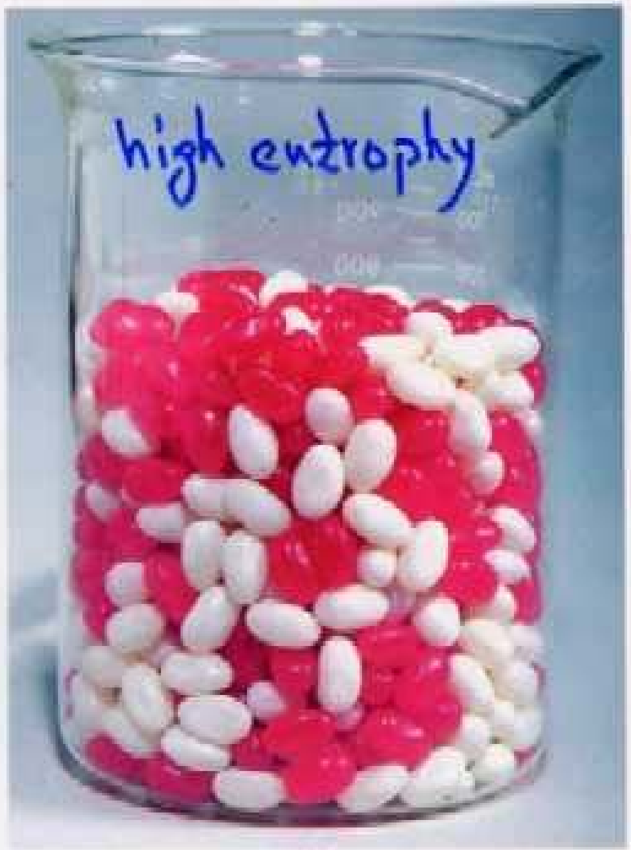
Poker Entropy

n	Hand	W_n	$S = R \ln \Omega$
1	Royal Flush (AKQJ10, one suit)	4	2.76
2	Straight flush (sequence, one suit)	36	7.13
3	Four of a kind (XXXXo)	624	12.81
4	Full house (XXYYY)	3744	16.40
5	Flush (all same suit)	5108	17.02
6	Straight (5 card sequence)	10200	18.40
7	Three of a kind	54912	21.72
8	Two pairs (XXYYo)	123,552	23.20
9	One pair (XXooo)	1,098,240	27.60
10	Bust hand	1,302,540	28.10

ENTROPY IS AN INDICATOR OF RANDOMNESS



8.2a



8.2b

Laws of Thermodynamics

Substituting the second law into the first, we get, for a closed system:

$dE = dq + dw = TdS – PdV \ (+ \Sigma dw')$

This expression shows that the internal energy of a closed system is a function of entropy and volume (if no other type of work is being carried out).
As we did for enthalpy earlier, we can derive other state functions for a combination of independent variables. The one we are most interested in is the **Gibbs free energy**, which is a state function used to describe chemical systems. In other words, a measure of available non-PV work at constant T and P.

$G = H – TS = E + PV – TS$, since $H = E + PV$
$dG = dH – TdS = dE + PdV + VdP – TdS – SdT$
$dG = TdS – PdV + PdV + VdP – TdS – SdT$
$dG = VdP – SdT + (\Sigma dw')$ which, at constant T and P, is equal to $\Sigma dw'$, i.e., non-PV work

Laws of Thermodynamics

T**he third law** of thermodynamics states that the entropy of a perfectly ordered solid approaches zero as T nears 0K.

Since $dS = dq_{rev}/T$ and $dq_p = dH$ at constant P, $dS = dH/T$

A direct result of applying heat to a given mass of a substance is that the temperature rises. If the heat applied and the temperature rise are measured, it will be found that these quantities are proportional.

$$Q \propto \Delta T \text{ or } q = \text{constant} * \Delta T$$

The proportionality constant is known as the heat capacity. The heat capacity itself is a function of temperature and is more accurately defined as the differential change in heat with respect to T:

$$C = dq/dT$$

Laws of Thermodynamics

The value of the heat capacity also depends on the conditions under which the heat is transferred. If P is held constant:

$$Cp = (dH/dT)_p \text{ since } dH = dq_p \text{ and, thus, } dH = Cp\, dT$$

If the volume is held constant, $Cv = (dE/dT)_v$ since $dE = dq - PdV$

$S(T_1) = S(T_0) + S(T_1 - T_0)$ so that,

$$S = \int_0^{Tm} CpdT/T + \Delta H_f/T_m + \int_{Tm}^{Tb} Cp\, dT/T + \Delta H_v/T_b + \int_{Tb}^{T} Cp\, dT/T$$

for a substance (solid) undergoing phase changes.

The laws of thermodynamics only apply to equilibrium conditions and require that the reactions be reversible.

Third Law of thermodynamics

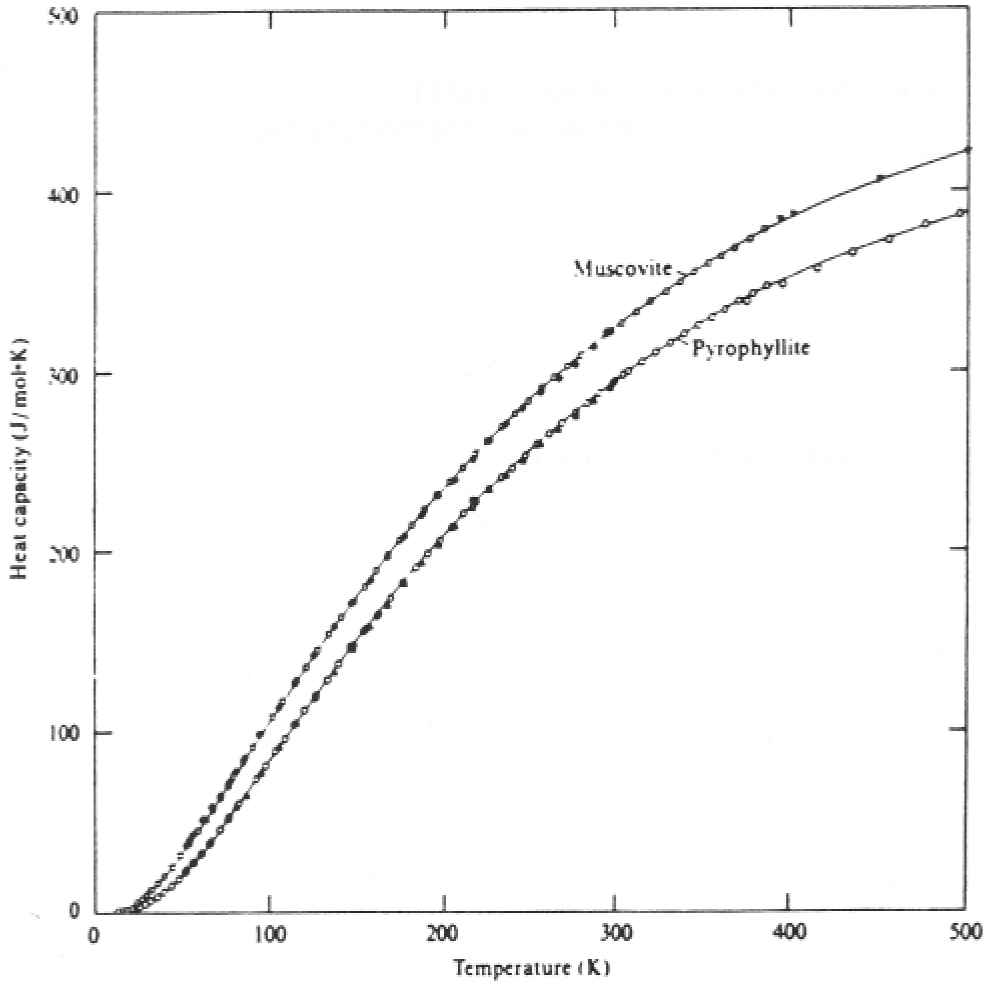
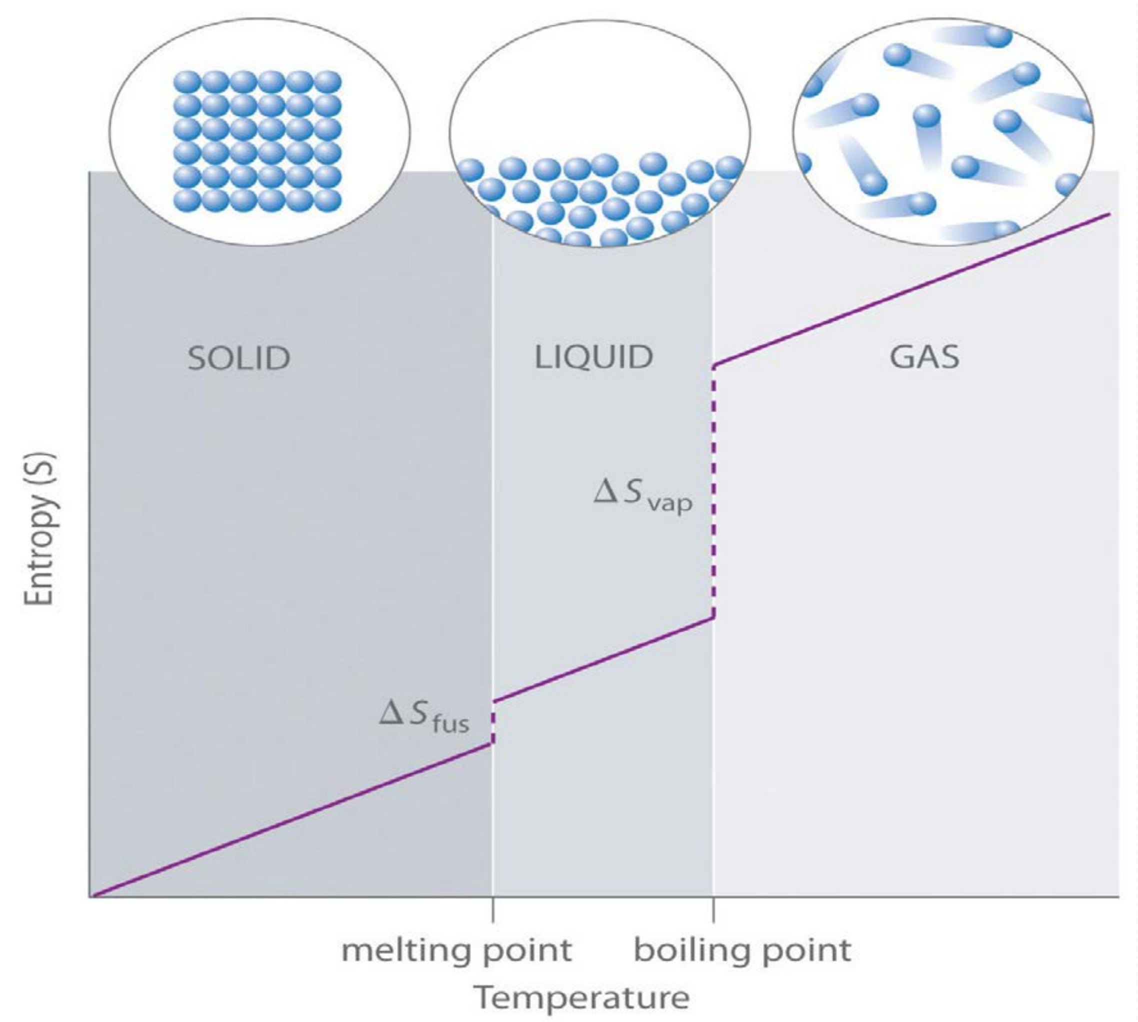


Figure 3-3. Low-temperature heat capacities of muscovite and pyrophyllite (Robie et al., 1976).

Entropy


SOLID
LIQUID
GAS
Entropy (S)
Δ S vap
Δ S fus
melting point
boiling point
Temperature