Lecture 17

Thermodynamics
and
Biophysics

Thermodynamics

- Thermodynamics is a science about equilibrium and systems exchanging matter and energy between each other

- Thermodynamic parameters – volume, temperature, pressure, concentration, viscosity are defined for sufficiently large homogeneous phases

- Equilibrium Thermodynamics:
- Considers equilibrium and close to equilibrium states, assumes linear relations between forces and rates

- Non-Equilibrium Thermodynamics:
- Non-equilibrium states (dissipative structures) and non-linear processes,

Thermodynamic system

- **Thermodynamic system** is a system consisting of a great number of continuously interacting particles (atoms, molecules, chemical substances)
- System is defined accordingly to the problem under consideration
- (i.e. cell compartment, cell, organ, whole organism)

- **Isolated system** is system, which cannot exchange both matter and energy with the environment

- **Closed system** cannot exchange matter, but can exchange energy with the environment

- **Open system** – exchanges both matter and energy with the environment

Living cells are thermodynamically open systems

- Cells exchange matter and energy with each other and with environment
- Cells in order to survive and maintain themselves work constantly and transform chemical energy of food into energy of chemical bonds, and mechanical energy of muscular contraction, into electrical energy of nerve impulses
- Transformation of energy and matter in cells can be described by thermodynamics laws
- Living cell is non-equilibrium system it can be:
- far from equilibrium or near equilibrium
- Evolution, self-replication – non-equilibrium processes
- Many slow processes are close-to-equilibrium processes – can be described by thermodynamics laws

Thermodynamics State Functions

- Define the state of the system,
- Change in state function does not depend on the path, only on initial and final state of the system

- U Gibbs Free Energy (Internal Energy)
- F Helmholtz Free Energy
- S Entropy
- H Enthalpy

Internal energy U.

Does a glass of water sitting on a table have any energy?

No apparent energy of the glass of water on a macroscopic scale.

Microscopic kinetic energy is part of internal energy.

Molecular attractive forces are associated with potential energy

Internal energy is defined as the energy associated with the random, disordered motion of molecules. It is separated in scale from the macroscopic ordered energy associated with moving objects; it refers to the invisible microscopic energy on the atomic and molecular scale.

First Law of Thermodynamics

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

| Change in Internal energy | Heat added to the system | Work done by the system |

ΔU only depends on initial and final state of the system and not on the path,

$\Delta U = U_f - U_i$,   Q and W depend on the path.

Heat

- Heat may be defined as energy transferred from a high temperature object to a lower temperature object.

- An object does not possess "heat"; the appropriate term for the microscopic energy in an object is internal energy. The internal energy may be increased by transferring energy to the object from a higher temperature (hotter) object - this is called heating.

- in living systems heat Q is the energy transfer due to temperature difference between the system and its environment or between the systems

- Heat flow and work are both ways of transferring energy. The temperature of a gas can be raised either by heating it, by doing work on it, or a combination of the two.

System Work

Work done W is due to the exchange of any other energy but heat,

When work is done by a thermodynamic system, it is usually a gas that is doing the work. The work done by a gas at constant pressure is: W=PΔV
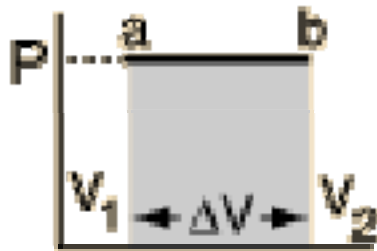
The line from a to b represents an expansion of a gas at constant pressure. The work done is the area under the curve.

in general work can be expressed:

$$W = X \Delta \theta$$

The work W is done because the force X produces displacement Δθ

$$\Delta U = Q - P\Delta V - W'$$

Universal type of work, pressure-volume (W=P Δ V) work, is uncommon in living systems, they do not change their volume under external pressure, we need to exclude this work for living systems

In living systems work W' can be mechanical, osmotic, electrical or chemical

Equilibrium is a state when all thermodynamic parameters remain constant in time (like P, V, T)

In equilibrium the system does not exchange energy or matter with its surroundings

Application of first law.

- If the temperature of the system changes the energy changes too.
- There are two cases:

- **1. at constant volume: the change in energy = heat**

$$\Delta U = Q_v \qquad \Delta U = c_v m \Delta T$$

Specific heat at const V

- **2. at constant pressure: the change in energy = heat - work**

$$W = -p\Delta V \qquad \Delta U = Q_p - p\Delta V$$

For solid not a big difference

For gases
Cp/Cv=1.2-1.7

$$\Delta U = c_p m \Delta T - p\Delta V$$

Specific heat at const P

Enthalpy

- In practice many physical and chemical processes take place at constant pressure, this is valid for living systems too.
- At constant pressure for a system in equilibrium at temperature T and volume V, we introduce new state function enthalpy, H:

$$\Delta U = Q_p - p\Delta V \longrightarrow \boxed{H = U + pV}$$

$$\Delta H = Q_p$$

At constant pressure the exchanged heat is equal to change in enthalpy

$$\Delta U = Q_v$$

At constant volume, where there is no work, the exchanged heat is equal to change in internal energy

Standard enthalpy

- The enthalpy (internal energy) is fixed so that the enthalpy of chemical element at 25C and 101 kPa (in the state in which they are considered stable) are considered to be zero

- The enthalpy of a chemical compound at 25C and 101 kPa is equal to its heat of formation (per mole) at constant T and P and is called standard heat of formation or standard enthalpy H^0 or ΔH^0)

- Because enthalpy does not depend on the path, the changes can be calculated from the enthalpies of initial and final states (chemical reactions – reagents and products)

Standard enthalpies of some compounds

Element or compound	state	H^0 kJ/mol
H_2	Gas	0.0
O_2	Gas	0.0
C (graphite)	Solid	0.0
H_2O	Liquid	-286.0
H_2O	Gas	-242.0
CO_2	Gas	-394.0
Acetic acid	Liquid	-487.4
Lactic acid	Liquid	-677.0
Ethyl alchohol	Liquid	-278.0
Glycerine	Liquid	-666.6
Glucose	Solid	-1280.1

Second Law of Thermodynamics (reversible process)

Second law defines a state function entropy S:

$$(\Delta S)_{sys} = \frac{Q_r}{T}$$

Heat exchange, reversible process

(reversible process)

$$(\Delta S)_{env} = -(\Delta S)_{sys}$$

$$\Delta S_{total} = 0$$

The process A $\longrightarrow$ B is called reversible if time reversed process
B $\longrightarrow$ A is also possible and there is no changes in Entropy

A reversible process is an idealization

It means that when cyclic process   A $\longrightarrow$ B $\longrightarrow$ A
complete, there will be no indication that such process took place,
all thermodynamic parameters return to their original values, the
process goes very slowly and only through equilibrium states

All natural phenomena are really irreversible, but in many cases
can be approximated as reversible if changes are small and
processes are slow

Entropy

- Like internal energy, entropy is a state function:

  $\Delta S = S_{final} - S_{initial}$

- Second Law of Thermodynamics: In any cyclic process the entropy will either increase or remain the same.

- Entropy: a state variable whose change is defined for a reversible process at T where Q is the heat absorbed.

- Entropy: a measure of the amount of energy which is unavailable to do work.

- Entropy: a measure of the disorder of a system.

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Entropy on the Molecular Scale

- Temperature is a measure of the average kinetic energy of the molecules in a sample.

- Molecules exhibit several types of motion:

  – Translational: Movement of the entire molecule from one place to another.

  – Vibrational: Periodic motion of atoms within a molecule.

  – Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.

Vibrations   Rotation
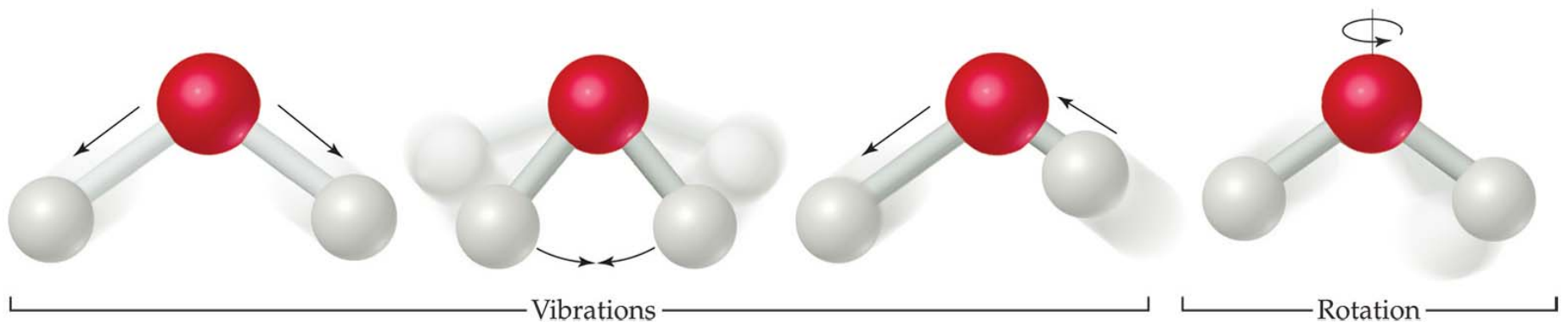
- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
  - This would be equivalent to taking a snapshot of all the molecules.
- He referred to this sampling as a microstate of the thermodynamic system.

- Each thermodynamic state has a specific number of microstates, W, associated with it.
- Entropy is $$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.

Entropy on the Molecular Scale

Implications:

• more particles

     -> more states   -> more entropy

• higher T

     -> more energy states -> more entropy

• less structure (gas vs solid)

     -> more states   -> more entropy

In general, more disorder -

     -> more states   -> more entropy

Second Law of Thermodynamics, irreversible process

- Thermodynamic processes progress simultaneously towards the most probable state
- In other words: the heat always flows spontaneously form warmer to cooler body.
- Thermodynamic equilibrium statistically means state of most probable distribution.
- The most probable state has highest degree of disorder
- When the isolated system with higher order (non-equilibrium state) is left free to itself, it will come to most probable (disordered) and equilibrium state
- Entropy can be thought of as a measure of disorder of a system.

Second law:

For irreversible processes:

$$\Delta S_{sys} > \frac{Q_r}{T}$$

Isolated system

Changes in entropy in the system undergoing irreversible process can be divided into two components:

The entropy production within the system $\Delta_i S$

The entropy exchange between the system and environment $\Delta_e S$

- An isolated system neither exchanges matter nor energy with the environment. Isolated system=adiabatic (heat ΔQ=0).
- The entropy law for isolated system:

$$\Delta_i S \geq 0, \ \ \Delta_e S = 0$$

All real spontaneous processes within an isolated system increase its entropy. As the system tends towards equilibrium, its entropy approaches maximum

Thermodynamic Equilibrium is a state of maximum entropy

Increasing the entropy means spontaneous evolution of system

Open system

An open system is non-equilibrium system

Entropy changes for open system:

$$\Delta S_{sys} = \Delta_i S + \Delta_e S$$

For entropy change due to irreversible process:

$$\Delta S_{total} \geq 0$$

Equilibrium state of an open system is not a state of max entropy, because open system always exchanges entropy with surrounding

Open system can be in steady or stationary state defined by:

$$\Delta_i S = \Delta_e S$$

In stationary state the entropy produced by a system is given to the environment, so that net entropy change is 0. Entropy remains constant, though its never maximum

$$T \Delta S_{total} = 0$$

Second Law of Thermodynamics

If we consider (system +surrounding) as one big isolated system (called Universe) then second law states that total entropy of the Universe increases:

The entropy of the universe does not change for reversible processes,

and increases for spontaneous (irreversible) processes.
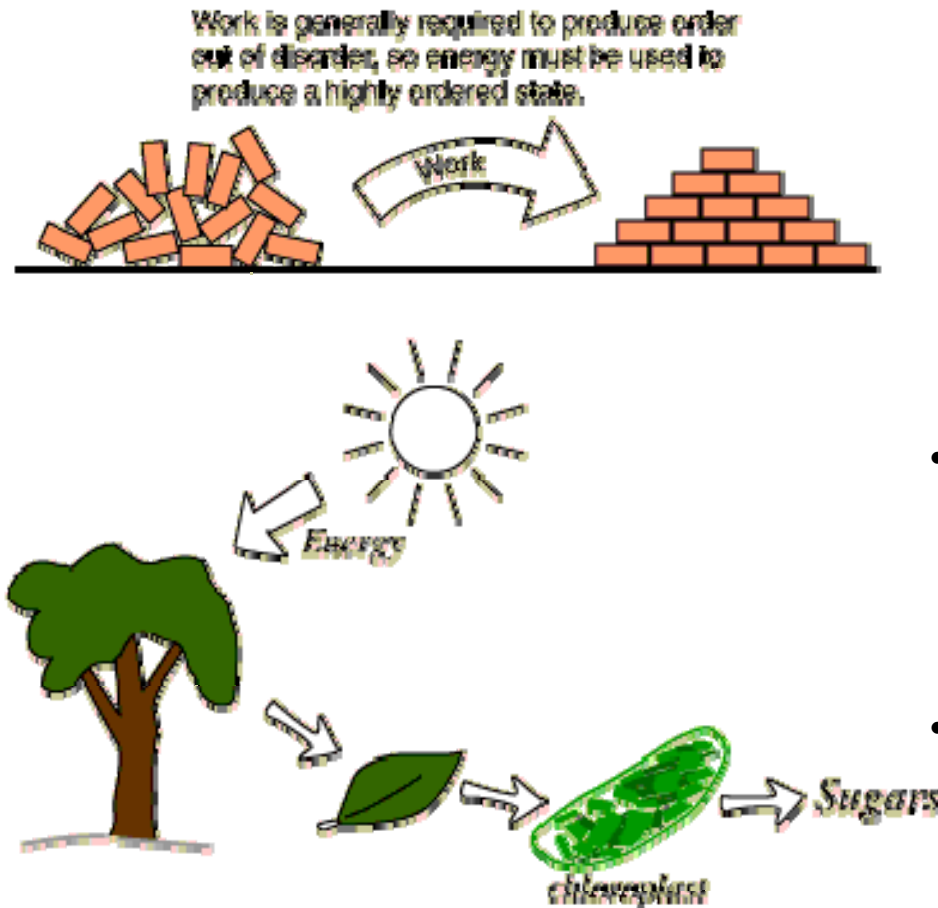
Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

- Since entropy gives information about the evolution of an isolated system with time, it is said to give us the direction of "time's arrow" . If snapshots of a system at two different times shows one state which is more disordered, then it could be implied that this state came later in time. For an isolated system, the natural course of events takes the system to a more disordered (higher entropy) state.

Energy and Order in Biological Systems

Work is generally required to produce order out of disorder, so energy must be used to produce a highly ordered state.

Work

Energy

Sugars

chloroplast

- The concept of entropy and the second law of thermodynamics suggests that systems naturally progress from order to disorder. If so, how do biological systems develop and maintain such a high degree of order? Is this a violation of the second law of thermodynamics?

- Order can be produced when energy is supplied, and the order associated with life on the earth is produced with the aid of energy from the sun.

- Biological systems are open systems and exchange both matter and energy with their environment

- For example, plants use energy from the sun in tiny energy factories called chloroplasts. Using chlorophyll in the process called photosynthesis, they convert the sun's energy into storable form in ordered sugar molecules. In this way, carbon and water in a more disordered state are combined to form the more ordered sugar molecules.

- In animal systems there are also small structures within the cells called mitochondria which use the energy stored in sugar molecules from food to form more highly ordered structures.
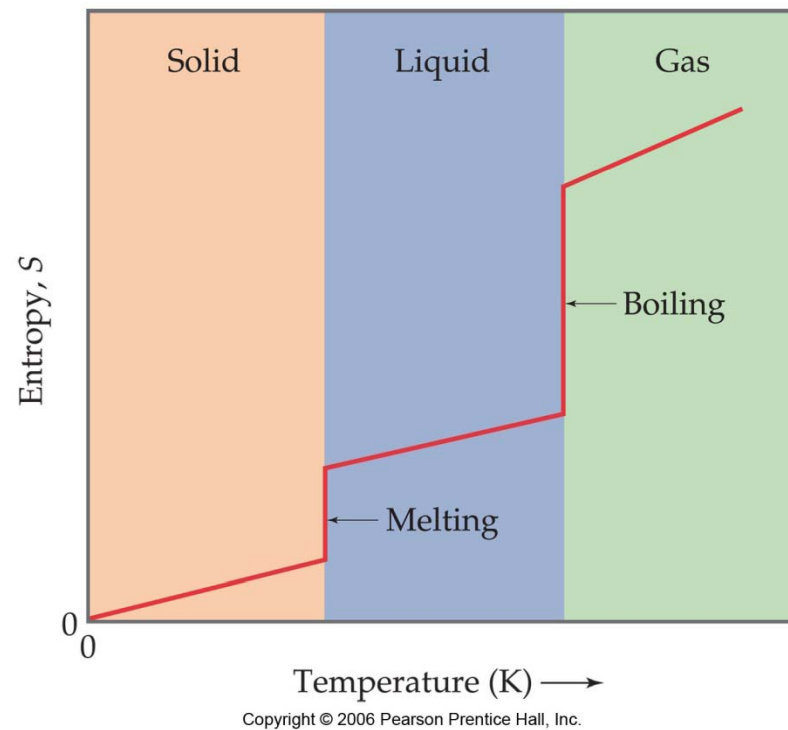
Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero is 0.

$$S = k \, lnW = k \, ln1 = 0$$

0 K
$S = 0$

Increasing temperature

> 0 K
$S > 0$
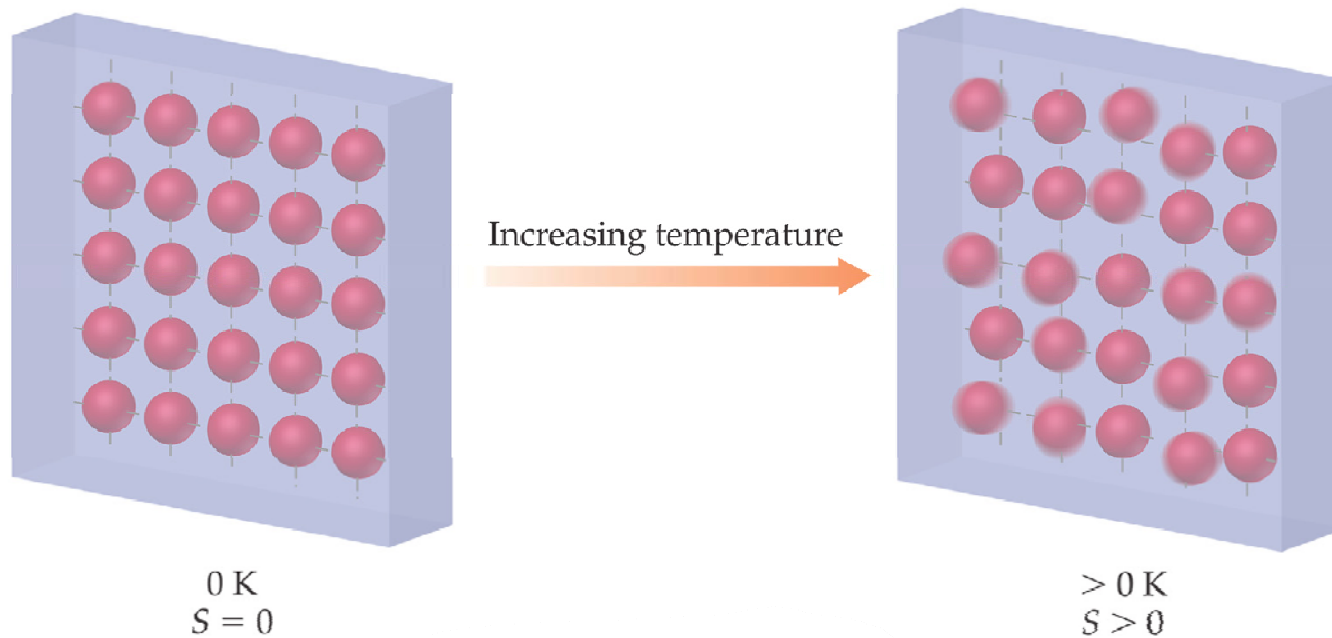
The entropy of a pure crystalline substance at absolute zero is 0.

Entropy increases when disorder increases

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Helmholtz Free Energy

- Four quantities called "thermodynamic potentials" are useful in the chemical thermodynamics of reactions and non-cyclic processes. They are **internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy**.

- The **Helmholtz free energy F** is defined by

•The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume. But if the system is created in an environment of temperature T, then some of the energy can be obtained by spontaneous heat transfer from the environment to the system. The amount of this spontaneous energy transfer is TS where S is the final entropy of the system.

Absolute
temperature

$$F = U - TS$$

Helmholtz
free energy

Internal
energy

Final
entropy

Energy you can
get from the
system's
environment
by heating

•In that case, you don't have to put in as much energy. Note that if a more disordered (higher entropy) final state is created, less work is required to create the system. The Helmholtz free energy is then a measure of the amount of energy you have to put in to create a system once the spontaneous energy transfer to the system from the environment is accounted for.

Gibbs Free Energy

- Biological systems are open systems and are in equilibrium with the environment, which maintains constant T_0 and constant P_0

- The pressure and T can change during the processes, but initial and final T and P are constant:

- $$\Delta P=0, \text{ and } \Delta T=0$$

- Non-equilibrium processes at const T and P are described by state function G – Gibbs Energy or Free Energy:

$$G = U + PV - TS_{sys} \quad \text{or} \quad G = H - TS_{sys}$$

$$\Delta G = \Delta U + P_0 \Delta V - T_0 \Delta S_{sys}$$

Gibbs Energy

- The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume. But an additional amount of work PV must be done if the system is created from a very small volume in order to "create room" for the system. As discussed in defining the Helmholtz free energy, an environment at constant temperature T will contribute an amount TS to the system, reducing the overall investment necessary for creating the system. This net energy contribution for a system created in environment temperature T from a negligible initial volume is the Gibbs free energy.

- The change in Gibbs free energy, ΔG, in a reaction is a very useful parameter. It can be thought of as the maximum amount of work obtainable from a reaction. For example, in the oxidation of glucose, the change in Gibbs free energy is ΔG = 686 kcal = 2870 kJ. This reaction is the main energy reaction in living cells.

The four thermodynamic potentials are related by offsets of the "energy from the environment" term TS and the "expansion work" term PV. A mnemonic diagram suggested by Schroeder can help you keep track of the relationships between the four thermodynamic potentials.
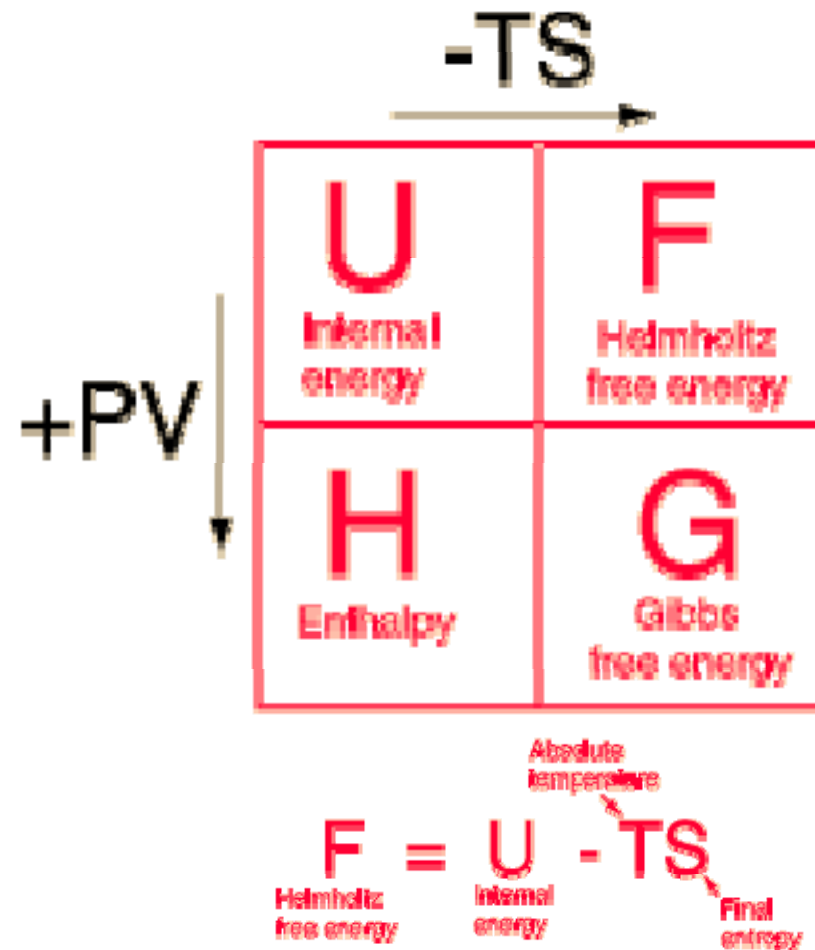
Gibbs Free Energy

1. If ΔG is negative, the forward reaction is spontaneous.

2. If ΔG is 0, the system is at equilibrium.

3. If ΔG is positive, the reaction is spontaneous in the reverse direction.
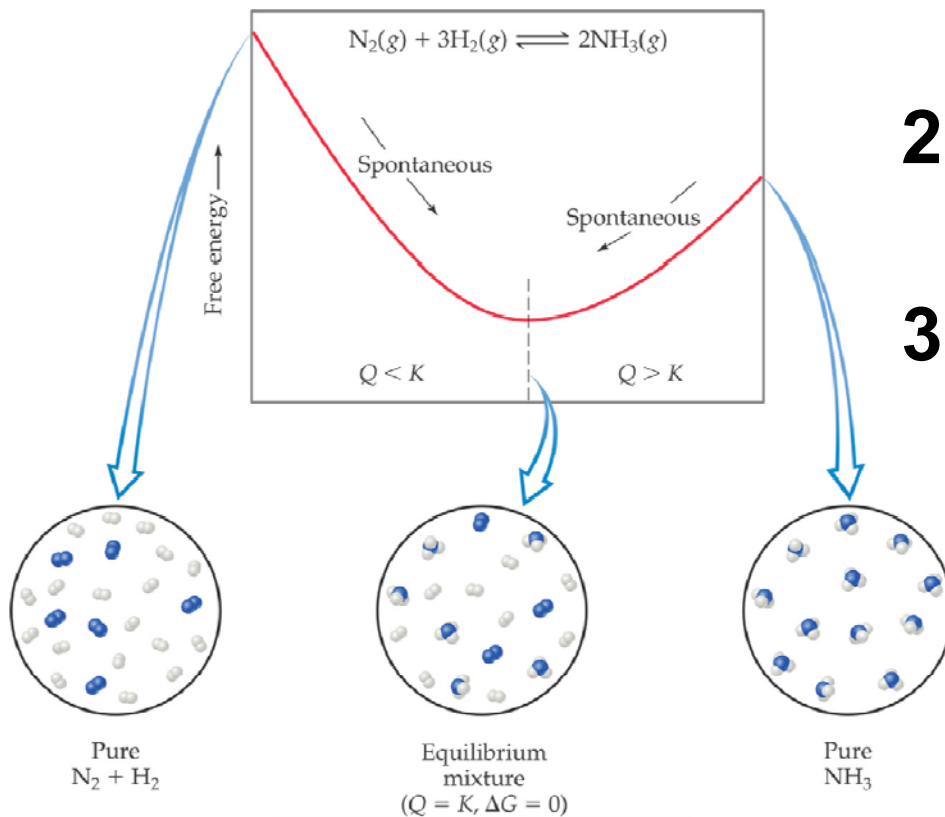
Free Energy and Equilibrium

Remember from above:

If ΔG is 0, the system is at equilibrium.

So ΔG must be related to the equilibrium constant, K.

The **standard** free energy, $\Delta G°$, is directly linked to K_{eq} by:

$$\Delta G° = -RT \ln K$$

$$A + B \rightleftharpoons C + D \qquad \Delta G = \Delta G^{\circ} + RT \ln \frac{[C][D]}{[A][B]}$$

$$\Delta G^{\circ} = -RT \ln \frac{[C][D]}{[A][B]} = -RT \ln K_{eq} = -2.3RT \log K_{eq}$$

$$K_{eq} = \frac{[C][D]}{[A][B]} \qquad K_{eq} = 10^{-\frac{\Delta G^{\circ}}{2.3RT}} = 10^{-\frac{\Delta G^{\circ}}{1.36}}$$

at 25C

Whether reaction is spontaneous or not is decided by ΔG and not ΔG^0

The steady state

$$\frac{\Delta S_{sys}}{\Delta t} = \min$$

$$\frac{\Delta S}{\Delta t} = \frac{\Delta G}{\Delta t} = \frac{\Delta T}{\Delta t} = \min$$

- Steady state is a non-equilibrium state at which the change of entropy is minimum

- If the system can not achieve an equilibrium state it tends to a steady state with min change of entropy

Chemical Potential

$$\mu_i = \left(\frac{\Delta G}{\Delta n_i} \right)_{T,P,j \neq i}$$

- the "chemical potential **μ**" is a measure of how much the free energy of a system changes if you add or remove a number moles **Δnᵢ** particles of the particle species **i** while keeping the number of the other particles (and the temperature **T** and the pressure **p**) constant

For a single component system at constant P and T:

$$\Delta G = \mu \Delta n$$

$$G = \mu n$$

- Thus for one component system, the chemical potential is a free energy per mole

Chemical Potential

- the particles considered in the context of general thermodynamics do not have to be only atoms or molecules (i.e. the objects of chemistry). They can be electrons, holes, or anything else that can be identified and numbered. In considering e.g., the equilibrium between electrons and holes in semiconductors. Moreover, since electrons and holes are Fermions, chemical potential usually is called "**Fermi energy**" in solid state physics.

- For a mixture of ideal gases or ideal solutions, chemical potential at given T is :

$$\mu_i = \mu_i^o + RT \ln[C]_i$$

Standard reference potential

Molar concentration of i-th component

If a substance exists in two phases A and B the difference in free energy per mole between two phases, arising due to the concentration difference of i-th component is:

$$\Delta\mu_i = \mu_{iA} - \mu_{iB} = RT \ln \frac{[C_{iA}]}{[C_{iB}]}$$

Molar concentration of i-th component in phase A and B

For standard conditions (T = 298.15 K; P = 1 atm) the values of the chemical potential are tabulated

Multi-component system

$$\Delta G = \sum_i \mu_i \Delta n_i$$

Thermodynamic analysis of membrane transport

- Thermodynamics can be applied to describe the transport across membrane

- The cell is an open system and interacts with its surrounding

- Simple diffusion (non-interacting component)

- Facilitated diffusion (substance diffuse with the help of carriers and channels)

Simple diffusion

- Simple model:

- two aqueous phases A and B separated by a semi-permeable membrane

- Several types of particles can move through this membrane

- whole system (A plus B) is closed, no matter exchange between the system and the environment, but the system can exchange heat (energy)

-

- The total entropy change during the membrane transport is the sum of change in two systems A and B:

$$\frac{\Delta S}{\Delta t} = \frac{\Delta S^A}{\Delta t} + \frac{\Delta S^B}{\Delta t}$$

A   B
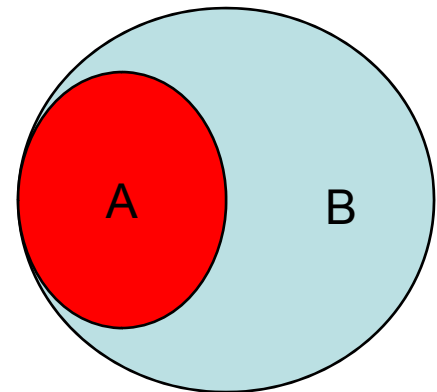
- We assume that the whole system is close to equilibrium, and A and B are also close to equilibrium
- Use equilibrium thermodynamics:

In A:

$$T\Delta S^A = \Delta U^A + P^A \Delta V^A - \sum_i \mu_i^A \Delta n_i^A$$

In B: (1)

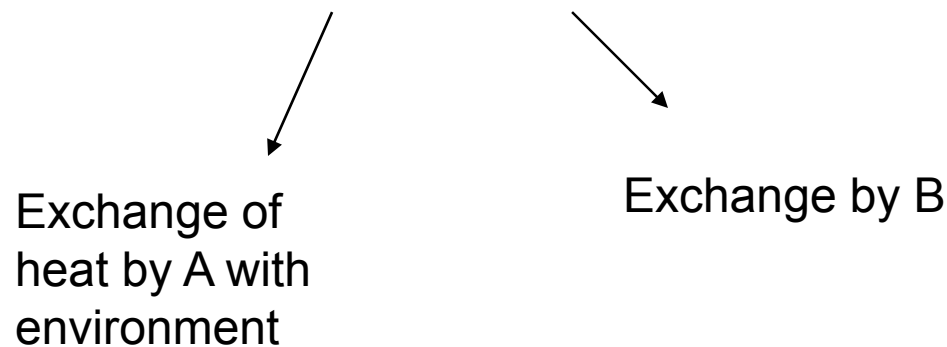$$T\Delta S^B = \Delta U^B + P^B \Delta V^B - \sum_i \mu_i^B \Delta n_i^B$$

Sum over all types of particles

- The net entropy change is a sum of internal entropy change and entropy exchange with the environment:

$$\frac{\Delta S}{\Delta t} = \frac{\Delta_i S}{\Delta t} + \frac{\Delta_e S}{\Delta t}$$

System is closed – only heat exchange with environment:

$$T\Delta_e S = \Delta Q^A + \Delta Q^B \qquad (2)$$

Exchange of
heat by A with
environment

Exchange by B

Total internal energy exchange:

$$\Delta U^A + \Delta U^B = (\Delta Q^A + \Delta Q^B) - (P^A \Delta V^A + P^B \Delta V^B) \quad (3)$$

heat   work

Internal Entropy production = Internal entropy change / time:

$$\frac{\Delta_i S}{\Delta t} = \frac{\Delta S}{\Delta t} - \frac{\Delta_e S}{\Delta t} = \frac{\Delta S^A}{\Delta t} + \frac{\Delta S^B}{\Delta t} - \frac{\Delta_e S}{\Delta t}$$

Using equations 1, 2 and 3

$$\frac{\Delta_i S}{\Delta t} = \frac{1}{T} \sum_i \left(-\mu_i^A \frac{\Delta n_i^A}{\Delta t} - \mu_i^B \frac{\Delta n_i^B}{\Delta t} \right)$$

Particle exchange between A and B:

$$\frac{\Delta n_i^A}{\Delta t} = -\frac{\Delta n_i^B}{\Delta t} \qquad \longrightarrow \qquad \frac{\Delta_i S}{\Delta t} = \frac{1}{T}\sum_i J_i \Delta\mu_i$$

flux of ith type particles
$$J_i = \frac{\Delta n_i}{\Delta t}$$

$$\Delta\mu_i = \mu_i^A - \mu_i^B$$

Chemical potential difference between A and B

$$X_i = \Delta\mu_i$$

Thermodynamic force, which moves particles

In general Entropy change depends on force as:

at equilibrium

approaching equilibrium
$$\frac{\Delta_i S}{\Delta t} \geq 0 \qquad \frac{\Delta_i S}{\Delta t} = 0$$

$$T\frac{\Delta_i S}{\Delta t} = \sum X_i J_i$$

$$\Delta\mu_i = 0$$

Therefore
$$J_i = 0 \qquad \text{at equilibrium}$$

Facilitated diffusion

- Facilitated diffusion assumes interaction of a transported substance S with the carrier C , we need to consider chemical reaction
- S+C=SC

- Model cell membrane is divided into
- 3 parallel membranes:
- 1 and 2 are permeable to S, 2 is not,
- 2 is permeable to carrier C and complex SC, with permeability constant P
- Substance S cannot go through membrane 2 by itself, concentration S(O) >S(I) – necessary for passive transport
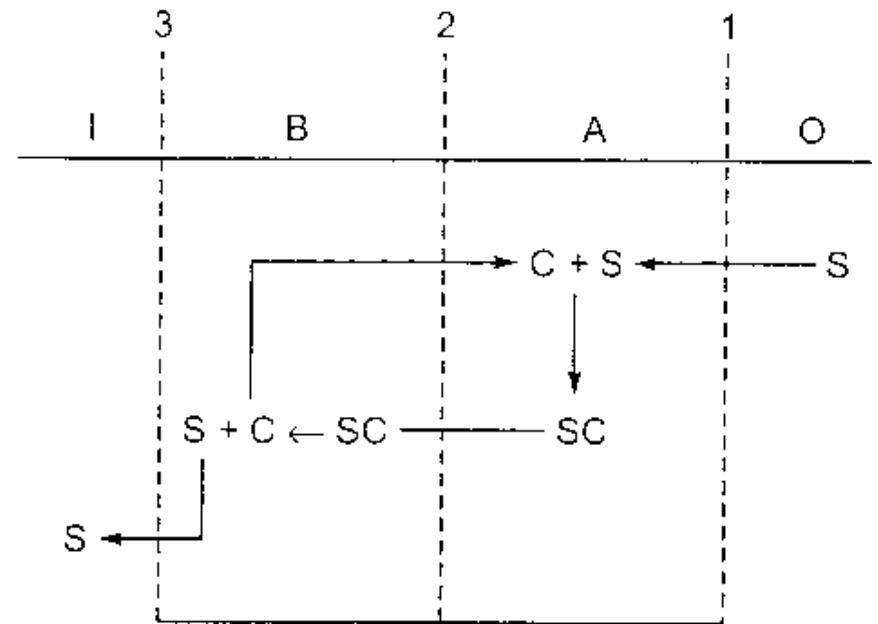
In near equilibrium conditions:

Flux CS from A to B

$$J_{CS} = P\Delta[CS] = -J_C = -P\Delta[C]$$
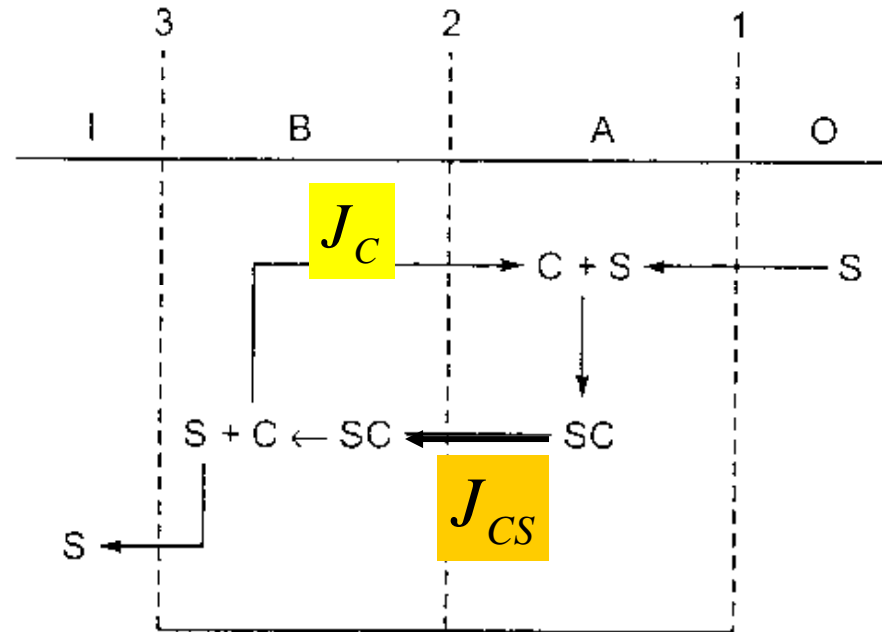
Permeability of
membrane 2 for C
or CS

Flux C from B to A

Flux of S across all 3 membranes:

$$J_S = \frac{PK[C][S]_o - [S]_i}{(K + [S]_o - [S]_i)}$$

$$K = \frac{[C][S]}{[CS]}$$

Equilibrium constant for chemical
coupling C+S=SC

Thermodynamic model of facilitated diffusion