# Modern Physics - Topics in Medical Physics 

## Topics Covered

- Mechanics
- Buoyancy
- Compressibility
- Viscosity
- Human Circulatory System
- Systems of Large Particles
- Scaling Laws
- Gibbs Free Energy
- Chemical Potential


## Forces in Achilles Tendon

$$
\begin{aligned}
& F_{T} \cos \left(7^{\circ}\right)+W-F_{B} \cos \theta=0 \\
& F_{T} \sin \left(7^{\circ}\right)-F_{B} \sin \theta=0
\end{aligned}
$$



Fig. 1.9 Simplified anatomy of the foot

$10 W-5.6 F_{T} \cos \left(7^{\circ}\right)=0$
$F_{T}=\frac{10 W}{5.6 \cos \left(7^{\circ}\right)}=1.8 \mathrm{~W}$
Gives the tension in the tendon.
$2.8 W=F_{B} \cos \theta$ and $0.22 W=F_{B} \sin \theta$

$$
\tan \theta=\frac{0.22}{2.8}=0.079 \text { so } \theta=4.5^{\circ}
$$

Fig. 1.10 Forces on the foot, neglecting its own weight

- All the forces have to be balanced.


## Forces on the Hip



$$
\begin{aligned}
& \rightarrow \text { cols } \\
& \text { F: net force of the abductor muscles, acting on } \\
& \text { the greater trochanter. Muscles primarily the } \\
& \text { gluteus medius and gluteus minimus. } \\
& R \text { : force of the acetabulum (the socket of the } \\
& \text { pelvis) on the head of the femur. } \\
& \mathrm{N} \text { : upward force of floor on the bottom of foot } \\
& \text { (equal to weight). } \\
& \mathrm{W}_{\mathrm{L}} \text { : weight of leg, acting vertically downward at } \\
& \text { the center of gravity of the leg. Some sources } \\
& \text { indicate } \mathrm{W}_{\mathrm{L}} \sim \mathrm{~W} / 7 \text {. } \\
& \sum F_{y}=F \sin \left(70^{\circ}\right)-R_{y}-\frac{W}{7}+W=0 \\
& \sum F_{x}=F \cos \left(70^{\circ}\right)-R_{x}=0 \\
& \sum \tau=-F \sin \left(70^{\circ}\right)(7)-\left(\frac{W}{7}\right)(10-7)+W(18-7)=0 \\
& F=1.6 W \text { and } R_{x}=0.55 W \text { and } R_{y}=2.36 \mathrm{~W} \\
& \tan \phi=\frac{R_{x}}{R_{y}}=0.23 \text { or } \phi=13^{\circ}
\end{aligned}
$$



## Buoyancy

$$
F=\left(-\frac{d p}{d z}-\rho g\right) d x d y d z
$$

- Buoyancy is the tendency for objects in "fluids" to resist the fluid itself, and depends on the density of objects in play.
- The total buoyant force experienced by an object with density $\rho$ can be described by

$$
F=\left(\rho_{\text {fluid }}-\rho\right) g V
$$

- Mammals are typically made of mostly water and some air.
- For humans, average densities are $500-950 \mathrm{~kg} / \mathrm{m}^{3}$. Considering surface seawater densities, we can see why human bodies typically float in the ocean (positive force pushes upwards in $z$ direction).


- Salinity of the ocean water (image from Welcome1To1The1Jungle on Wikipedia), as measured in practical salinity units
- At the surface, seawater ranges from 1020 to $1029 \mathrm{~kg} / \mathrm{m}^{3}$, dependent on temperature and salinity and geographical position

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## Seawater elemental composition at salinity 3.5\% on Earth

| Element | Percent by mass |
| :--- | :--- |
| Oxygen | 85.84 |
| Hydrogen | 10.82 |
| Chlorine | 1.94 |
| Sodium | 1.08 |
| Magnesium | 0.1292 |
| Sulfur | 0.091 |
| Calcium | 0.04 |
| Potassium | 0.04 |
| Bromine | 0.0067 |
| Carbon | 0.0028 |
| Vanadium | $1.5^{* 10-11}$ to $3.3 * 10^{-11}$ |


| Liquid | Compressibility |  |
| :--- | :--- | :--- |
|  | Pa-1 $\times 10^{-11}$ | Atm-1 $\times 1^{-6}$ |
| Carbon disulfide | 93 | 94 |
| Ethyl alcohol | 110 | 111 |
| Glycerine | 21 | 21 |
| Mercury | 3.7 | 3.8 |
| Water | 45.8 | 46.4 |
| Loose sand | 10,000 to 5200 <br> $\left(1^{*} 10^{-7}\right.$ to $\left.5.2^{*} 10^{-8}\right)$ |  |
| Dense sand | 2000 to 1300 <br> $\left(2 * 10^{-8}\right.$ to $\left.1.3^{*} 10^{-8}\right)$ |  |

Some data from Sears, Zemansky, Young, and Freedman, University Physics, 10th Ed., Section 11-6.

## Compressibility of Oils Versus Gases

For example, let's consider the compressibility of some oils under isothermal conditions:
rewrite the equation above as.
The oil expands in a cell volume by reducing pressure (?!) and concomitant oil volume increase and oil pressure decrease are monitored. At the bubble-point pressure, free gas accumulates in the cell.

$$
c_{0}=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T}
$$



- Compressibility of Oil

- Compressibility of Gas


## Viscosity

- Viscosity of a material arises from sheared stress, a force that is in directions perpendicular to the original movement.

$$
\frac{F}{S}=\eta \frac{d v_{x}}{d y}=\eta \frac{d \epsilon_{s}}{d t}
$$

- The second term describes the force gradient as a function of the rate of change of the shear strain.



## Water

- That ever most valuable resource, water, is a Newtonian fluid.


Rate of shearing strain, $\frac{d u}{d y}$

Measurement from Anton Paar, https://wiki.anton-paar.com/en/water/


## Common Viscosities of Glass and Materials



| Substance | Viscosity <br> (mPa s) | Tempreature <br> (Celsius) |
| :--- | :--- | :--- |
| Benzene | 0.604 | 25 |
| Water | 1.0016 | 20 |
| Mercury | 1.526 | 25 |
| Whole Milk | 2.12 | 20 |
| Olive Oil | 56.2 | 26 |
| Honey | $2000-10000$ | 20 |
| Ketchup | $5000-20000$ | 25 |
| Peanut Butter | $1^{*} 10^{4}$ to | $1^{*} 10^{6}$ |

## Human Circulatory System

- Sphygmomanometer measures blood pressure, systolic/ diastolic (maximum pressure during cardiac cycle/ minimum pressure during cardiac cycle). A typical reading gives 110/70 torr.
- $R=\frac{\Delta p}{8 \eta \dot{\Delta} x}$ in torr $\mathrm{ml}^{-1} \mathrm{~min}$ or Pa
- $=\frac{8 \eta \Delta x}{\pi R^{4}}$ (if Poiseuille) $\mathrm{m}^{-3} \mathrm{~s}(\mathrm{SI})$. The vascular resistan'te (as measured globally) is the pressure difference in the "pipes" measured from the contributing current (blood) flow in that pipe region.
- The mathematical manipulation of vascular resistance is similar to electrical resistance:
- $R_{\text {tot }}=R_{1}+R_{2}+R_{3} \ldots$ For vessels in series
- $\frac{1}{R_{\text {tot }}}=\frac{1}{R_{1}}+\frac{1}{R_{2}}+\frac{1}{R_{3}} \ldots$ For vessels in parallel



## Velocity Profile in a Pipe

- Consider laminar viscous flow of fluid through a pipe of constant radius Rp. Force balance gives

$$
\begin{gathered}
\frac{d v}{d r}=\frac{r}{2 \eta}\left(\frac{p(x+\Delta x)-p(x)}{\Delta x}\right)=\frac{d p}{d x} \frac{r}{2 \eta} \\
v(r)=\frac{1}{4 \eta} \frac{\Delta p}{\Delta x}\left(R_{p}^{2}-r^{2}\right)
\end{gathered}
$$



- In units of $\mathrm{m}^{3} \mathrm{~s}^{-1}$. Note that $\mathrm{r}^{*} \mathrm{dp} / \mathrm{dx}$ is the force to area ratio, with viscosity in units $\mathrm{Ns} \mathrm{m}^{-2}$ or $\mathrm{kg} \mathrm{m}^{-1} \mathrm{~s}^{-1}$ or Pa s. An older unit is the dyn $\mathrm{cm}^{-2}$ or poise ( 1 poise $=0.1 \mathrm{~Pa} \mathrm{~s}$ ).


## Human Circulatory System

- As a modle, consider an incompressible fluid during time $\Delta t$ with velocity v , the volume fluence is

$$
j_{v}=\frac{(\text { volume transported })}{(\text { area })(\text { time })}=\frac{S v \Delta t}{S \Delta t}=v
$$



- The volume current is $i$, integrated over the cross sectional area of the pipe, for Poiseuille flow.

$$
i=\int_{0}^{R_{p}} j_{v}(r) 2 \pi r d r=\frac{2 \pi}{4 \eta} \frac{\Delta p}{\Delta x} \int_{0}^{R_{p}}\left(R_{p}^{2}-r^{2}\right) r d r=\frac{\pi R_{p}^{4}}{8 \eta} \frac{\Delta p}{\Delta \mathrm{x}}
$$

Note the compressibility is defined as $\frac{\Delta V}{V}=-\kappa \Delta p$ with units $\mathrm{Pa}^{-1}$ or $\mathrm{N}^{-1} \mathrm{~m}^{2}$. Compressibility of water is $5 \times 10^{-10} \mathrm{~Pa}^{-1}$.

Integration by parts

$$
u \int d v=u v-v \int d u
$$

## Human Circulatory System: Examples

- As an example, consider a pore with certain size that might be found in the basement membrane of the glomerulus of the kidney.
- $R p=5 \mathrm{~nm}, \Delta \mathrm{p}=15.4$ torr $=\rho \mathrm{g} \Delta \mathrm{z}=2.04 * 10^{3} \mathrm{~Pa}$ ( $\sim 15$ torr, Hg density $\left.13.55^{*} 10^{3} \mathrm{kgm}^{-3}\right), \eta=1.4^{*} 10^{-3} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}, \Delta \mathrm{x}=50 \mathrm{~nm}$. This gives $\mathrm{i}=$ $7.2 \times 10^{-21} \mathrm{~m}^{3} \mathrm{~s}^{-1}$.


$$
i=\frac{\pi R_{p}^{4}}{8 \eta} \frac{\Delta p}{\Delta \mathrm{x}}
$$

Is this tiny $i$ what is felt what a stone is passed?! Velocity ~2* ${ }^{\sim} 0^{\wedge}-11$ to even smaller?!

## Human Circulatory System



Stroke volume 100-35 = 65 mL .

## Human Circulatory System

Table 1.4 Typical values for the average pressure at the entrance to each generation of the major branches of the cardiovascular tree, the average blood volume in certain branches, and typical dimensions of the vessels

| Location | Average pressure (torr) | Blood volume ${ }^{\text {a }}$ (ml) | $\begin{aligned} & \text { Diameter }^{\text {b }} \\ & (\mathrm{mm}) \end{aligned}$ | Length ${ }^{\text {b }}$ (mm) | Wall thickness ${ }^{\text {b }}$ (mm) | Avg. velocity ${ }^{\text {b }}$ $\left(\mathrm{m} \mathrm{~s}^{-1}\right)$ | Reynolds <br> number <br> at maximum <br> flow ${ }^{\text {c }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Systemic circulation |  |  |  |  |  |  |  |
| Left atrium | 5 |  |  |  |  |  |  |
| Left ventricle | 100 |  |  |  |  |  |  |
| Aorta | 100 | 156 | 20 | 500 | 2 | 0.48 | 9400 |
| Arteries | 95 | 608 | 4 | 500 | , | 0.45 | 1300 |
| Arterioles | 86 | 94 | 0.05 | 10 | 0.2 | 0.05 |  |
| Capillaries | 30 | 260 | 0.008 | 1 | 0.001 | 0.001 |  |
| Venules | 10 | 470 | 0.02 | 2 | 0.002 | 0.002 |  |
| Veins | 4 | 2682 | 5 | 25 | 0.5 | 0.01 |  |
| Vena cava | 3 | 125 | 30 | 500 | 1.5 | 0.38 | 3000 |
| Right atrium | 3 |  |  |  |  |  |  |
| Pulmonary circulation |  |  |  |  |  |  |  |
| Right atrium | 3 |  |  |  |  |  |  |
| Right ventricle | 25 |  |  |  |  |  |  |
| Pulmonary artery | 25 | 52 |  |  |  |  |  |
| Arteries | 20 | 91 |  |  |  |  | 7800 |
| Arterioles | 15 | 6 |  |  |  |  |  |
| Capillaries | 10 | 104 |  |  |  |  |  |
| Veins | 5 | 215 |  |  |  |  | 2200 |
| Left atrium | 5 |  |  |  |  |  |  |

## Bernoulli Equation

- Valid for nonuniform viscous flow that may be laminar or turbulent.
$p_{1}-p_{2}=\Delta p=\rho \int_{s_{1}}^{s_{2}} \frac{\partial v}{\partial t} d s+\int_{s_{1}}^{s_{2}}-\frac{d p_{v i s c}}{d s} d s+\int_{s_{1}}^{s_{2}}-\rho v\left(\frac{d v}{d s}\right)+\int_{x_{1}}^{x_{2}} \frac{d p_{\text {grav }}}{d z} d z=\rho \int_{s_{1}}^{s_{2}} \frac{\partial v}{\partial t} d s+\int_{s_{1}}^{s_{2}}-\frac{d p_{v i s c}}{d s} d s+\frac{\rho v_{2}^{2}}{2}-\frac{\rho v_{1}^{2}}{2}+\rho g\left(z_{2}-z_{1}\right)$


A flow of air through a Venturi meter, showing the columns connected in a manometer and partially filled with water. The meter is "read" as a differential pressure head in cm or inches of water.

## Scaling Laws Applied to Organisms



Taking $\mathrm{H}^{\sim} \mathrm{M} \times$.

- Children's (up to > 6 yrs) growth via consumption versus body mass. This model assumes that the mass is proportional to height.


Fig. 2.20 Plot of resting metabolic rate vs. body mass for many different organisms. (Graph is from R. H. Peters 1983. Modified from A. M. Hemmingsen 1960). Used with permission

Plot for different unicellular and sea based organisms at 20 C And homeotherms with body temperature at 39 C.

## Energy loss from breathing

- Assuming each breath intakes 0.5 L of air.
- $\mathrm{Q}=\mathrm{c} \rho \mathrm{V}\left(\mathrm{T}_{\text {body }}-\mathrm{T}_{\text {surround }}\right)=1000 \mathrm{~J} / \mathrm{K}^{*} \mathrm{~kg} * 1.3 \mathrm{~kg} / \mathrm{m}^{3}$ * 0.5 L * $(37 \mathrm{C}-$ 20 C ) $=11 \mathrm{~J}$ with average power lost to air of 2.2 W (assuming breath every 5 s ). For comparison, a typical basal metabolic rate is 100 W .
- $\rho_{\text {water }}=1000 \mathrm{~kg} / \mathrm{m}^{3}, \rho_{\text {air }}=1.3 \mathrm{~kg} / \mathrm{m}^{3}, \mathrm{c}_{\text {air }}=1000 \mathrm{~J} / \mathrm{K}^{*} \mathrm{~kg}, \mathrm{c}_{\text {water }}=4200 \mathrm{~J} / \mathrm{K}^{*} \mathrm{~kg}$. Note assuming no metabolism.
- Note heat capacity is $\mathrm{C}=\mathrm{Q} / \Delta \mathrm{T}$ with units $\mathrm{J} / \mathrm{K}$. Specific heat capacity is $\mathrm{J} / \mathrm{K}^{*} \mathrm{~kg}$ or J/K*mol.


## Large System of Particles

- Considering the forces on all particles in a large system is a very complex problem (although this helps to push efforts in computing science)
- Instead of solving the force on each molecule or particle, traditionally consider the state of the entire system and the statistics of these ensembles of particles $\rightarrow$
- With for example, entropy $\mathrm{S}=\mathrm{S}(\mathrm{U}, \mathrm{N}, \mathrm{V}, \mathrm{x})$

$$
\begin{gathered}
d S=\left(\frac{\partial S}{\partial U}\right)_{N, V, x} d U+\left(\frac{\partial S}{\partial N}\right)_{U, V, x} d N+\left(\frac{\partial S}{\partial V}\right)_{U, N, x} d V+\left(\frac{\partial S}{\partial x}\right)_{U, N, V} d x \\
d S=\left(\frac{1}{T}\right) d U+\left(\frac{a}{T}\right) d N+\left(\frac{p}{T}\right) d V+\left(\frac{X}{T}\right) d x
\end{gathered}
$$

- Let's talk about some additional important concepts, such as the Boltzmann factor, Principle of Equipartition of Energy, Chemical Potential and the Gibbs free energy.

Let me emphasize that we do care where particles might be. The problem is just very complex computationally.

## Statistical Mechanics: Gas Molecules in a Box

- For a large system, consider the average behavior of the system, such as pressure, temperature, particle concentration and probability distributions (for example of the velocity).

$$
P(n)=\frac{(\text { number of systems in the ensemble in which } n \text { is found })}{(\text { total number of systems })}
$$



Suppose we would like to know how often a particle is in the left half of
An ensemble of boxes divided into halfs each box. If one particle is in the box, $N=1$, then there are two possible states, $L$ or $R$. If the particle is in the left, then we denote for state $L$ that $n$ $=1$ and for $\mathrm{R}, \mathrm{n}=0$.

The probability $\mathrm{P}(\mathrm{n})$ for n in $\mathrm{L} \rightarrow \mathrm{P}(0)=0.5$ and $\mathrm{P}(1)=0.5$, with total summing to 1 (necessary condition).

## Gas Molecules in a Box

| Molecule 1 | Molecule 2 (etc.) | n | $P(n ; 2$ in this case) |
| :--- | :--- | :--- | :--- |
| R | R | 0 | $1 / 4$ |
| R | L | 1 | $1 / 2$ |
| L | R | 1 | $1 / 2$ |
| L | L | 2 | $1 / 4$ |

Let's formazlie the discussion: each box has two volumes $v$ and v ' so that total volume $\mathrm{V}=\mathrm{v}+\mathrm{v}$.
The probability that a single particle is in volume $v\left(v^{\prime}\right)$ is called $p(q)$. Necessarily $p+q=1$. From these two equations we find that $\mathrm{p}=\mathrm{v} / \mathrm{V}$ and $\mathrm{q}=\mathrm{v}^{\prime} / \mathrm{V}$. The total number N of particles can be distributed so that n is in v and $\mathrm{n}^{\prime}=\mathrm{N}-\mathrm{n}$ is in $\mathrm{v}^{\prime}$.

$$
P(n ; N)=P(n ; N, p)=\frac{N!}{n!(N-n)!} p^{n}(1-p)^{N-n}
$$

$\ln [22]:=\operatorname{DiscretePlot}[$ Table [PDF [BinomialDistribution [12, p], $k],\{p,\{0.1,0.5,0.7\}\}] / /$ Evaluate,
$\{k, 20\}$, PlotRange $\rightarrow$ All, PlotMarkers $\rightarrow$ Automatic $]$

$\ln [24]=\operatorname{DiscretePlot}[T a b l e[P D F[N o r m a l D i s t r i b u t i o n[12, ~ p], k],\{p,\{0.1,0.5,0.7\}\}] / / E v a l u a t e$, $\{k, 20\}$, PlotRange $\rightarrow$ All, PlotMarkers $\rightarrow$ Automatic $\}$
… General: Exp[-6050.] is too small to represent as a normalized machine number; precision may be lost.
... General: Exp[-5000.] is too small to represent as a normalized machine number; precision may be lost.
… General: Exp[-4050.] is too small to represent as a normalized machine number; precision may be lost.

- General: Further output of General::munfl will be suppressed during this calculation.

Out $[24]=25$

- Binomial distribution for $\mathrm{n}=12$, with probabilities of $0.1,0.5$ or 0.7 for example.
- Comparison to a Gaussian disbribution
- Converted to a number, for example
- $P(n=0, N=10)=0.001$
- $P(n=5, N=10)=0.246$
- For our case of 12 boxes, the probability that all particles are in the left half is $(1 / 2)^{12}=0.000244$.
- Sampling at 1 million times a second gives a measurement that is 244 seconds long.
- Hence as the number of boxes increases the calculation time increases exponentially!


# The Energy of a System: First Law of Thermodynamics <br> - What we just saw was how to consider the 

 energy state of a system of particles, for example particles in 12 boxes.- Classically we consider two ways the total energy of a system can change. Work W can be done on the system by the surroundings and heat Q can flow from the surroundings to the system. If no work is done, then $\Delta U=Q$. The work done by the system on surroundings is $\Delta U=-W$.

$$
\Delta U=Q-W \quad \text { First Law of Thermodynamics }
$$

Fig. 3.6 No work is done on the system, but heat is added. The positions of the levels do not change; their average population does change


Fig. 3.7 Work is done on the system, but no heat flows. Each level has been shifted to a higher energy

(a)


Fig. 3.8 Symbols used to indicate various types of isolation in a system. a This system is completely isolated. b There is no heat flow through the double wall, but work can be done (symbolized by a piston). c No work can be done, but there can be heat flow through the single wall

## Ensembles and the Basic Postulates

- The microstate of a system is determined by specifying the quantum numbers of each particle in the system. The total number of quantum numbers is the number of degrees of freedom.
- The microstate of a system is determined by all of the external parameters, such as volume, fields, on which the positions of the energy levels depend, and the total energy of the system, U .

$$
P(\text { of being in microstate } i)=\frac{\text { number of systems in microstate } i}{\text { total number of systems in the ensemble }}
$$

Postulates:

- If an isolated system (really, an ensemble of isolated systems) is found with equal probability in each one of its accessible microstates, it is in equilibrium. Conversely, if it is in equilibrium, it is found with equal probability in each one of its accessible microstates.
- If it is not in equilibrium, it tends to change with time until it is in equilibrium. Therefore, equilibrium state is the most random, most probable state.


## Thermal Equilibrium

| $A$ | $A^{\prime}$ |
| :---: | :---: |
| $N$ |  |
| $V$, | $N^{\prime}$ |
| $U$ | $V^{\prime}, U^{\prime}$ |

- Consider an isolated system (from the universe) that can exchange heat Q , work W , particles N within itself with a total energy $U^{*}$ (each of these terms is the sum of the components in the prime and unprimed system). The total number of microstates accessible to the total system is $\Omega^{*}=\Omega^{*}$ tot. Make a partition so that the total system comprises of $A$ and $A^{\prime}$ sub-systems with the condition that particles cannot be exchanged. Then the total number of microstates in each partition depends on the energetics in the partition, $\Omega^{*}(\mathrm{U})$.
- The probability of finding sytem A with energy $U$ is

$$
P(U)=\frac{\Omega^{*}(U)}{\Omega_{\text {tot }}^{*}}=C \Omega^{*}(U)
$$

- Now recall that when thinking of probabilities for example for isolated events, we can multiply each isolated event probability to obtain the total probability.
- That means the number of microstates for the total system is the product of the number for each subsystem:

$$
\Omega^{*}(U)=\Omega(U) \Omega^{\prime}\left(U^{\prime}\right)
$$

## A concrete example

$$
U^{*}=10 u .
$$

| $A$ | $A^{\prime}$ |
| :--- | :--- |
| $N$ |  |
| $V$, | $N^{\prime}$ |
| $U$ | $V^{\prime}, U^{\prime}$ |


| System $A$ |  |  | System $A^{\prime}$ |  |
| :--- | :--- | :--- | :--- | :--- |
| $U$ | $\Omega$ | $U^{\prime}$ | $\Omega^{\prime}$ | $\Omega^{*}$ |
| $2 u$ | 1 | $8 u$ | 7 | 7 |
| $3 u$ | 2 | $7 u$ | 6 | 12 |
| $4 u$ | 3 | $6 u$ | 5 | 15 |
| $5 u$ | 4 | $5 u$ | 4 | 16 |
| $6 u$ | 5 | $4 u$ | 3 | 15 |
| $7 u$ | 6 | $3 u$ | 2 | 12 |
| $8 u$ | 7 | $2 u$ | 1 | 7 |
|  |  |  |  | $\Omega^{*}{ }_{\text {tot }}=84$ |

## A concrete example

Omega


- unprimed - primed

Omega*


- Omega*

$$
\frac{d}{d U}\left[\Omega^{*}(U)\right]=0
$$

$$
\Omega^{*}(U)=\Omega(U) \Omega^{\prime}\left(U^{*}-U\right) \text { with } \frac{d \Omega^{*}}{d U}=\Omega \Omega^{\prime}\left(\frac{1}{\Omega} \frac{d \Omega}{d U}-\frac{1}{\Omega^{\prime}} \frac{d \Omega^{\prime}}{d U^{\prime}}\right)
$$

- The two terms are equal in equilibrium. Defining $\frac{1}{\tau} \equiv \frac{1}{\Omega} \frac{d \Omega}{d U}$.
- Notably, the constant parameter is defined so that $\tau=\mathrm{k}_{\mathrm{B}} \mathrm{T}$ with units and value $1.380^{*} 10^{-23} \mathrm{~J} / \mathrm{K}$ or $0.861^{*} 10^{-4} \mathrm{eV} / \mathrm{K}$. This is the Boltzmann's constant.


## Nernst Equation

- See handwritten notes, for the Nernst Equation, the potential difference depends on the concentration ratio on either side of the membrane. This form is an example of the Boltzmann factor.
- Depends on Faraday constant $=96485.32 \mathrm{C} / \mathrm{mol}$, temperature T , gas constant $\mathrm{R}=8.314 / \mathrm{mol}^{*} \mathrm{~K}$

$$
v_{2}-v_{1}=\frac{R T}{z F} \ln \left(\frac{C_{1}}{C_{2}}\right)
$$

## Chemical Potential

- Consider two systems that exchange heat

| $A$ | $A^{\prime}$ |
| :---: | :---: |
| $N$ | $N^{\prime}$ |
| $V$, | $V^{\prime}, U^{\prime}$ |
| $U$ |  |

When a system out of equilibrium exchanges with a system in equilibrium

$$
\Delta S^{*}=\left(\frac{\partial S^{*}}{\partial N}\right) \Delta N=\left(\frac{\partial S}{\partial N}\right) \Delta N+\left(\frac{\partial S^{\prime}}{\partial N^{\prime}}\right) \Delta N^{\prime}
$$

This can be rewritten to

$$
\Delta S^{*}=\left(\frac{\mu^{\prime}-\mu}{T}\right) \Delta N
$$

If particles move from a system of higher chemical potential to one of lower chemical potential, the entropy of the total system increases.

- The units are in $\mathrm{J} / \mathrm{K}$


## The Chemical Potential of a Solution

- Consider a binary solution of solute and solvent and what changes to chemical potential occur.
- $S_{\text {solution }}-S_{\text {purewater,puresolute }}=k_{B} \ln \left(\Omega_{\text {solution }} / \Omega_{\text {purewater,puresolute }}\right)=k_{B} \ln \left(\left(N_{w}+N_{s}\right)!/ N_{w}!N_{s}!\right)=k_{B}\left[\ln \left(N_{w}+N_{s}\right)!-\ln \left(N_{w}!\right)-\ln \left(N_{s}!\right)\right]$
- Stirling's approximation gives

$$
S_{\text {solution }}-S_{\text {purewater,puresolute }}=k_{B}\left[\left(N_{w}+N_{s}\right) \ln \left(N_{w}+N_{s}\right)-N_{w} \ln N_{w}-N_{s} \ln N_{s}\right]
$$

- In terms of Gibbs free energy,

$$
\Delta G=-T \Delta S=k_{B} T\left[N_{w} \ln \left(\frac{N_{w}}{N_{w}+N_{s}}+N_{s} \ln \frac{N_{s}}{N_{w}+N_{s}}\right)\right]
$$

- The terms in the natural log are the molecular fractions.


## The Chemical Potential of a Solution

- For two molecular species, the energy (a fundamental equation) is
$T d S=d U-\mu_{w} d N_{w}-\mu_{s} d N_{s}+p d V$
- $\Delta \mu_{s}=k_{B} T \ln \left(C_{2} / C_{1}\right) ; \Delta \mu_{w}=-k_{B} T \Delta C_{s} / C_{w}$


## Gibbs Free Energy



- Consider glucose $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{8}+6 \mathrm{O}_{2} \rightarrow 6 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{aA}+\mathrm{bB} \rightarrow \quad \mathrm{cC}+\mathrm{dD})$
- With U, V, $\mathrm{N}_{\mathrm{A}}, \mathrm{N}_{\mathrm{B}}, \mathrm{N}_{\mathrm{C}}, \mathrm{N}_{\mathrm{D}}$.

$$
d G=d U-T d S-S d T+p d V+V d p
$$

$$
\begin{gathered}
T d S=d U-\mu_{A} d N_{A}-\mu_{B} d N_{B}-\mu_{C} d N_{C}-\mu_{D} d N_{D}+p d V \\
d G=\mu_{A} d N_{A}+\mu_{B} d N_{B}+\mu_{C} d N_{C}+\mu_{D} d N_{D}
\end{gathered}
$$

taking

$$
\mu_{A}=\mu_{A 0}+k_{B} T \ln \frac{C_{A}}{C_{0}}
$$

$$
\mathrm{dG}=\left[c \mu_{C 0}+d \mu_{D 0}+a \mu_{A 0}+b \mu_{B 0}+k_{B} T \ln \left(\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}\right)-k_{B} T \ln \left(\frac{\left[C_{0}\right]^{c}\left[C_{0}\right]^{d}}{\left[C_{0}\right]^{a}\left[C_{0}\right]^{b}}\right)\right] \mathrm{dN}
$$

$$
0=\Delta G^{0}+R T \ln \left(\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}\right)=\Delta G^{0}+R T \ln K_{e q}
$$

## McDonald's Foods

| Meal Menu | Energy <br> (Kcal) | Protein (g) | Fat (g) | Saturated <br> Fats (g) | Trans Fats <br> $(\mathrm{g})$ | Carbonates <br> $(\mathrm{g})$ | Sugar (g) | $\mathrm{Na}(\mathrm{mg})$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Hamburger | 267 | 13 | 9 | 4.4 | 0 | 33 | 5 | 340 |
| Ice cream <br> cone | 147 | 3 | 5 | 2.3 | 0 | 24 | 18 | 70 |
| Coca cola | 199 | 0 | 0 | 0 | 0 | 50 | 50 | 10 |

