

CEM 882

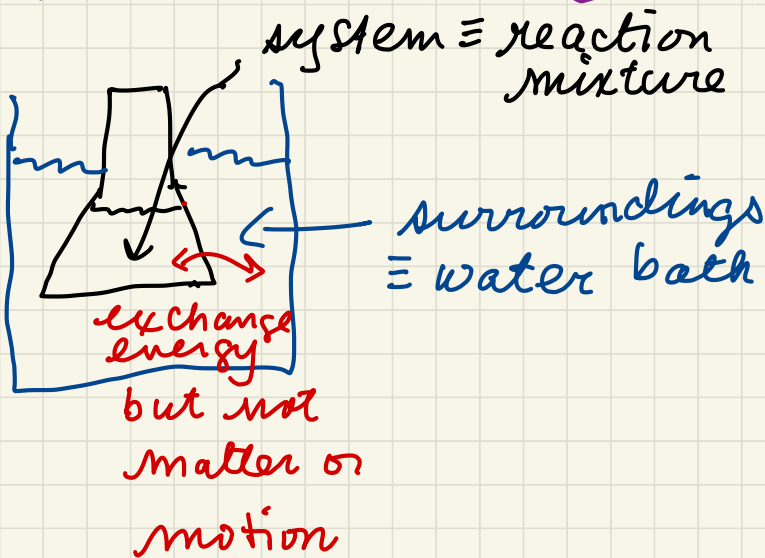
Lecture Notes 4

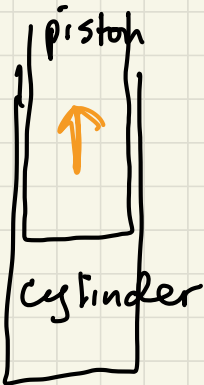
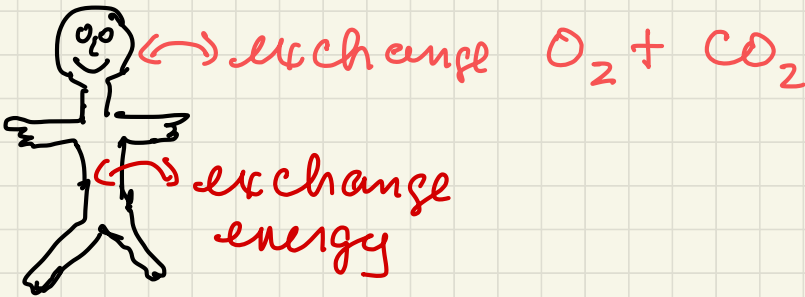
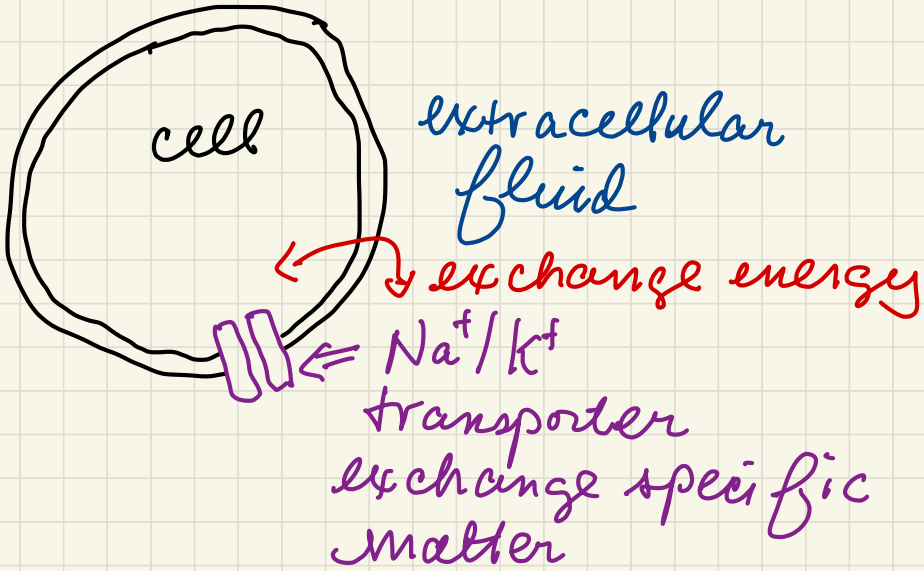
Weliky



Classical Thermodynamics

Divide relevant space into "system"
(where measurements are made)
and "surroundings" (nearby
space \Rightarrow sometimes also called
"reservoir" or "bath"). System can
sometimes exchange energy and/or
matter (often specific molecules)
and/or move relative to surroundings





piston moves in response to increased pressure in cylinder with combustion

For a system (large number of molecules), there are mathematical functions that relate the

"state" properties of the system \Rightarrow

i.e. it doesn't matter by what path the system got to the

properties \Rightarrow mathematical relationships

are always the same

total energy \Rightarrow $U = U(S, V, N)$ \Rightarrow most easily controlled for gases

associated with $\frac{1}{2}mv^2$ magnitude of molecular motion or ability to cause motion (potential energy)

$$S = S(U, V, N)$$

Ideal Gas Law

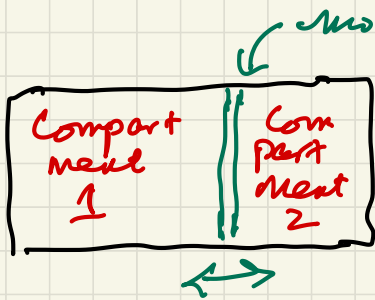
$$pV = nRT$$

Typically changes in energy and entropy measured

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N} dV + \left(\frac{\partial U}{\partial N} \right)_{S, V} dN$$

T
 $-p \equiv \text{pressure}$
 $\mu \equiv \text{chemical potential}$

Reasoning for pressure



movable barrier

Barrier moves until

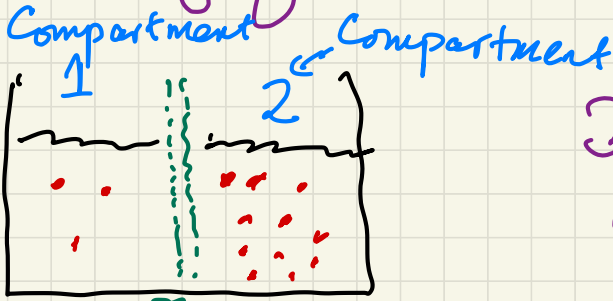
$$\left(\frac{\partial S_1}{\partial V} \right) = \left(\frac{\partial S_2}{\partial V} \right)$$

like energy flow and $T_1 = T_2$

Experimental observation?

Unit analysis

Reasoning for chemical potential



Diffusion occurs until $\left(\frac{\partial S_1}{\partial N}\right) = \left(\frac{\partial S_2}{\partial N}\right)$

What is experimental observation for solute diffusion?

$$dU = TdS - pdV + \mu dN$$

integrate

$$U = TS - pV + \mu N$$

hypothesis that is consistent with many data

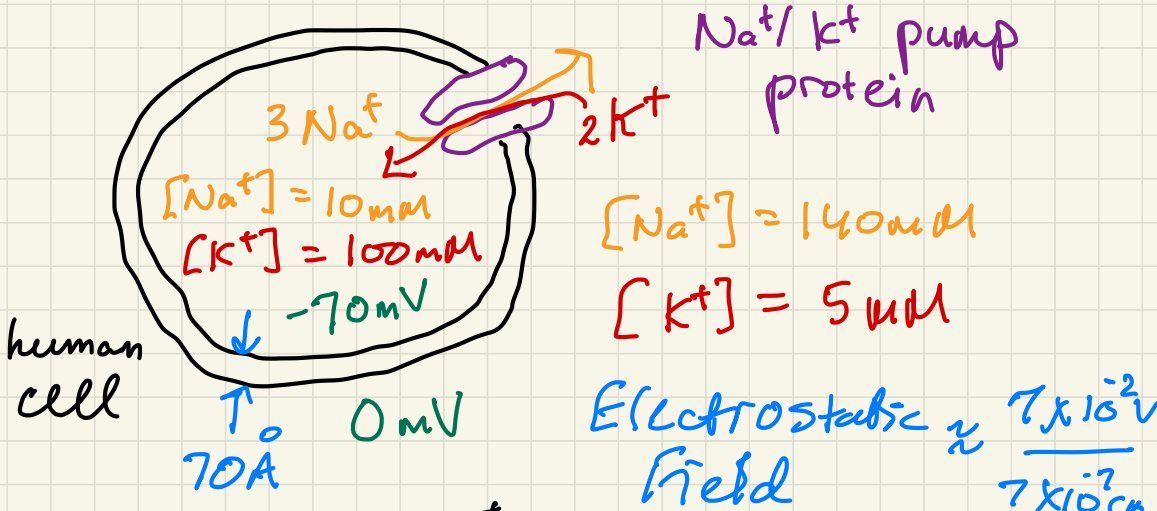
More complete equation

$$dU = TdS - pdV + \sum_{j=1}^t (\mu_j + q_j \Delta \Phi) dN_j$$

sum over all chemical species

μ_j c.p. of species j

$q_j \Delta \Phi$ charge of species j voltage change with process



$$U = TS - pV + \sum_{j=1}^t (\mu_j + q_j \Phi) N_j \approx 1 \times 10^5 \text{ J/cm}^3$$

$$dS = \left(\frac{\partial S}{\partial U} \right)_{N,V} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV + \left(\frac{\partial S}{\partial N} \right)_{U,V} dN$$

$$dS = \left(\frac{1}{T} \right) dU + \left(\frac{p}{T} \right) dV - \frac{\mu}{T} dN$$

energy flows from smaller $\frac{1}{T}$ to larger $\frac{1}{T}$

Do these make sense?

Most measurements on systems are changes in ^{values of} properties rather than measurements of the ^{the} values of properties, i.e. $\Delta U, \Delta S, \Delta V, \Delta N$

Changes in energy are one important

Measurement conserved \equiv constant on a process between two

$$\Delta U = Q + W$$

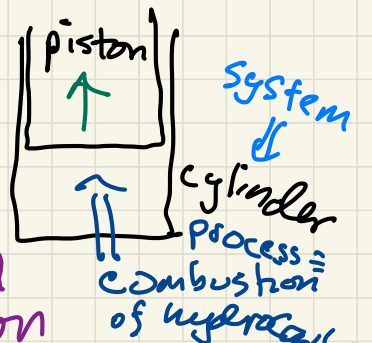
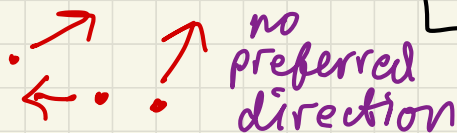
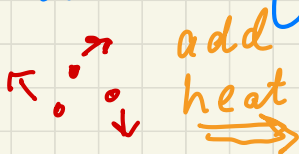
First Law of Thermodynamics

work \equiv motion of molecules

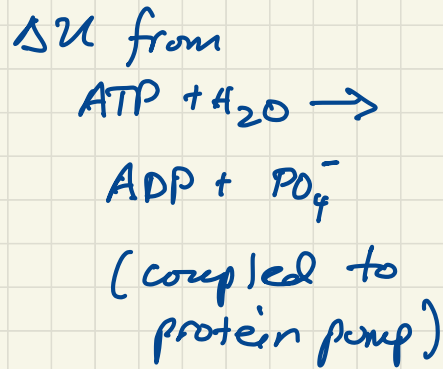
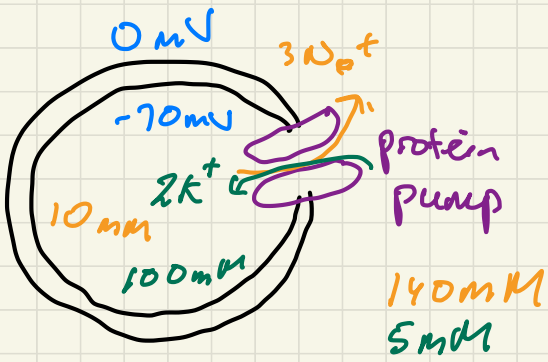
along a defined (non-isotropic) direction

heat \equiv causes change in T of system and surrounding bath

\equiv change in magnitude of random (isotropic) motion of molecules



human cell



$\approx 30\%$ of
 cellular energy
 used for this
 pump

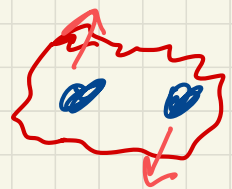
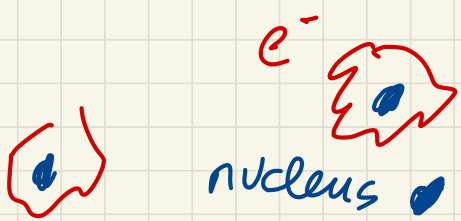
Formation of specific chemical
 bonds (chemical reactions)
 is another important type of



work

Two atoms

molecule



$$\Delta U = q + w$$

always the same for a given initial and final state of system

vary depending on how system goes from initial to final state

$$q_1 + w_1 = q_2 + w_2$$

$$q_1 = q_2 + w_2 \quad (2)$$

burn fuel

$$\Delta U = q$$

$$\Delta U < 0$$

$$q < 0$$

negative heat is given off by system

T of system and surroundings ↑

burn fuel in an engine

$$\Delta U = q + w$$

vehicle motion ↑



$$V = \frac{nRT}{P}$$

$$q_1 < q_2$$

$$0 = w_1 > w_2$$

④
^ 3 ^

Mitochondrion organelle

Cytoplasm

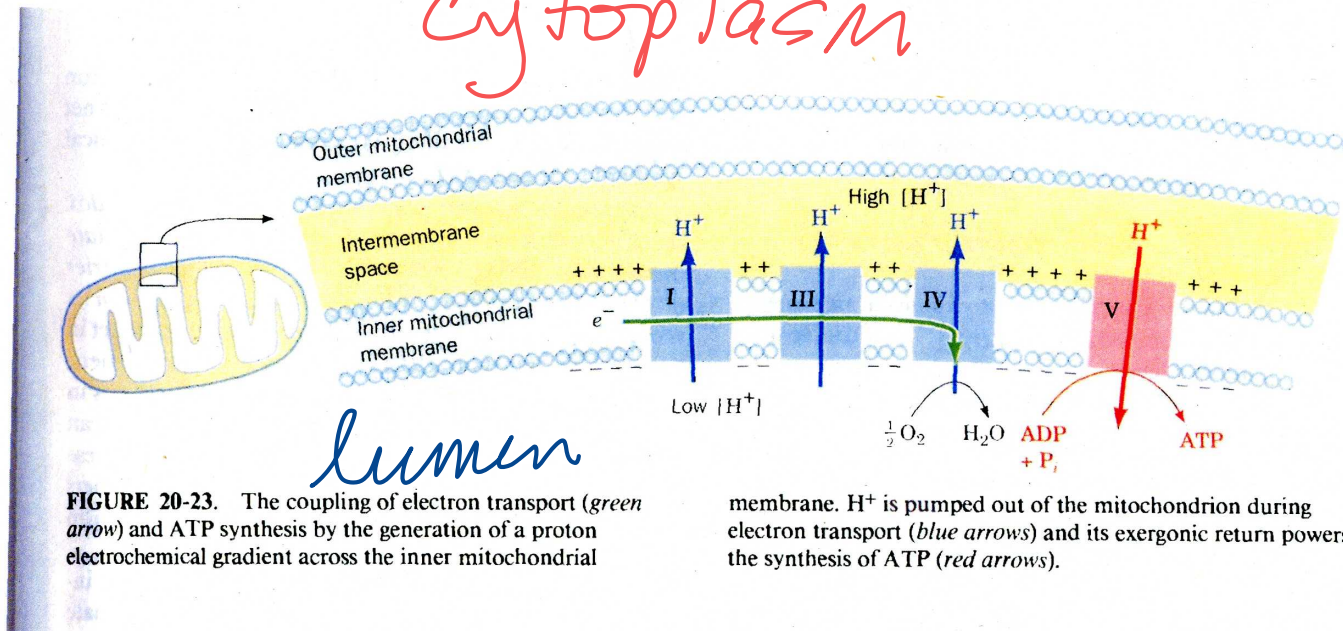
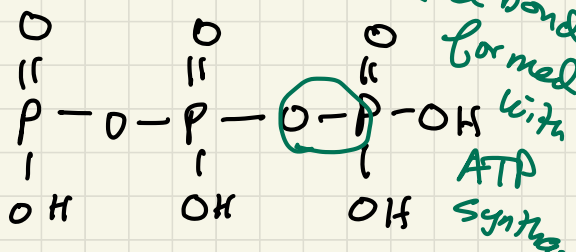
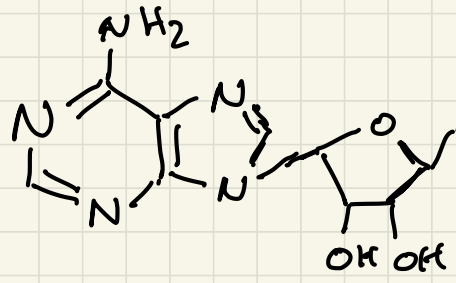
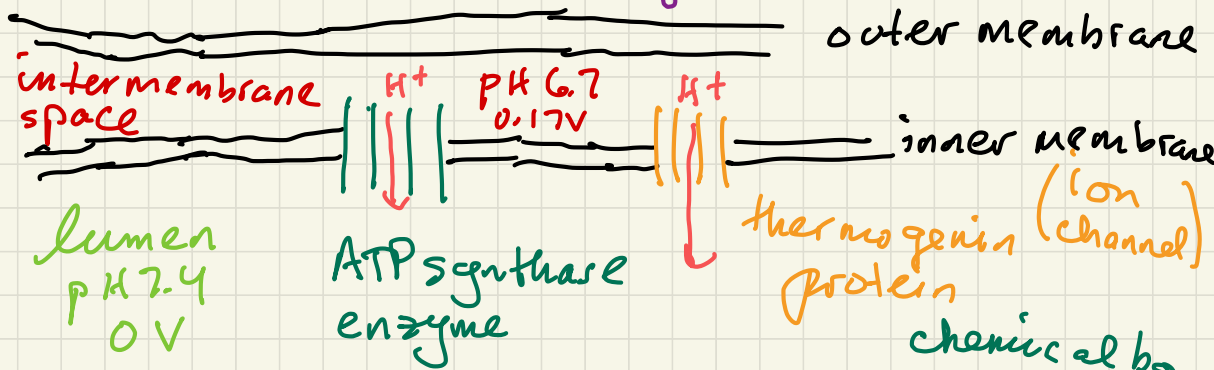


FIGURE 20-23. The coupling of electron transport (green arrow) and ATP synthesis by the generation of a proton electrochemical gradient across the inner mitochondrial

membrane. H^+ is pumped out of the mitochondrion during electron transport (blue arrows) and its exergonic return powers the synthesis of ATP (red arrows).

cytoplasm

Mitochondrion organelle



adenosine triphosphate (ATP)

thermogenin

$$\Delta U_{H^+} = q$$

P-O bond formation energy

$$\Delta U_{H^+} = q + w$$

ATP synthase

$$\Delta U_{H^+} = \Delta U_{H^+}$$

U is a state function
 ≡ only depends on initial + final conditions ⇒ no dependence on path

S is a state function because

$S = k \ln W$ multiplicity always the same for a specific set of conditions

ΔS fixed (conserved)

$$dU = \delta q + \delta w \quad \text{path-dependent}$$

slow process \equiv reversible

fast process \equiv irreversible

differential calculus is approximately correct

directional change

$$\delta q_{\text{rev}} = T dS$$

$$\delta w_{\text{rev}} = -pdV + (\Delta \mu + q \Delta \Phi) dN$$

$$\int dS = \int \frac{\delta q_{\text{rev}}}{T}$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

often approximately measurable by calorimetry

often approximately constant

Most chemical and biochemical reactions occur under conditions of approximately constant T & p

Other state energy functions are useful for these conditions

enthalpy energy (derived from physics-based forces)

$$H = U + pV$$

all system (not surroundings)

$$dH = dU + pdV + Vdp =$$

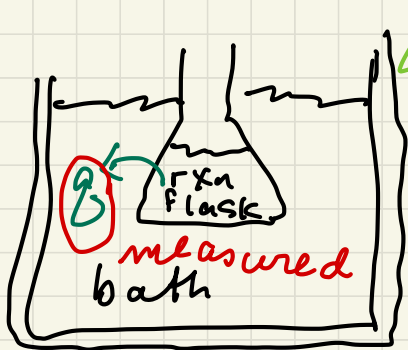
$$= TdS - pdV + \mu dN + pdV + Vdp$$

haven't included electrostatic energy

$$= TdS + Vdp + \mu dN$$

$$\left(\frac{\partial H}{\partial S}\right)_{p,N} = T \quad \left(\frac{\partial H}{\partial p}\right)_{S,N} = V \quad \left(\frac{\partial H}{\partial N}\right)_{S,p} = \mu$$

Calorimeter



thermal insulation
so $\Delta U_{\text{sys}} + \Delta U_{\text{bath}} = 0$
 $\Delta U_{\text{sys}} = -\Delta U_{\text{bath}}$
 $= -q_{\text{bath}}$

For reaction flask system at constant P

$$\Delta H = \Delta U + P\Delta V + \underbrace{V\Delta P}_{=0}$$

typically small in condensed phase
typically no work is done in bath

Known, e.g. if water $q_{\text{sys}} = -q_{\text{bath}}$

$$\Delta H \approx -q_{\text{bath}} \approx C_{p, \text{bath}} \Delta T$$

measured in calorimeter by small temperature increase in bath

Gibbs Free Energy

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= TdS + Vdp + \mu dN - TdS - SdT$$

$$= -SdT + Vdp + \mu dN$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu$$

An important idea in thermodynamics is that everything that happens in the universe increases S (multiplicity) of universe (Second Law of Thermodynamics)

A more useful formulation of the 2nd Law is in terms of the free energy of the system of interest under conditions of constant T & P

For all processes that happen

$$dS_{tot} = dS_{sys} + dS_{bath} \geq 0$$

$$TdS_{tot} = TdS_{sys} + TdS_{bath} \geq 0$$

relevant part of universe is near

$$-TdS_{bath} - TdS_{sys} \leq 0$$

system like thermal bath of a reaction

$$TdS_{bath} = \delta Q_{bath} = -dH_{sys}$$

from previous slide

no work on bath, bath is large enough

that all processes are slow and

reversible

insulated system + bath

for constant p

$$-dU_{sys} = dU_{bath} = \delta Q_{bath} = TdS_{bath} \text{ at constant } P$$

$$-dU_{sys} = -dH_{sys} = PdV - Vdp$$

small for liquid system

Note that although $TdS_{bath} = \delta Q_{bath}$,

TdS_{sys} is often not δQ_{sys} (system processes are often not reversible)

$dH - TdS = dG \leq 0$ ^{all system} at constant T

$\Delta H - T\Delta S = \Delta G \leq 0$

condition for a system process to happen under constant T, p system (conserved)

Processes require $\Delta H < 0, \Delta S > 0, \text{ or both}$

system (conserved)

$dU = \delta q + \delta w$

$-\delta q_{bath} - \delta q_{rev} \leq 0$

$\delta q - \delta q_{rev} \leq 0$

A system process giving up heat has $\delta q < 0$, so reversible (slow) process gives up the least heat and allows for the most work

$\delta w - \delta w_{rev} \geq 0$

$\delta w = dU - \delta q \geq dU - \delta q_{rev} = dU - TdS$

$\delta w \geq d(G + TS - pV) - TdS$

$\geq dG + SdT - pdV - Vdp$

0 at constant T, p

$\delta w - \delta w_{rev, pV} \geq dG$

$w - w_{rev, pV} \geq \Delta G$

ΔG represents the most negative (useful) non-pV work

similar arguments for processes that happen for a system at constant T, V (gases typically)

Helmholtz Free Energy

$$F = U - TS$$

$$dF = -SdT - pdV + \mu dN$$

$$\left(\frac{\partial F}{\partial T}\right)_{V, N} = -S$$

$$\left(\frac{\partial F}{\partial V}\right)_{T, N} = -p$$

$$\left(\frac{\partial F}{\partial N}\right)_{T, V} = \mu$$

system at
For constant T, V , $dF \leq 0$ defines the direction process will happen

$\Delta F \equiv$ maximum non- pV work possible from process

Mathematical Functions have the property that the order of differentiation doesn't matter

$$\left\{ \frac{\partial \left(\frac{\partial G}{\partial T} \right)_{P,N}}{\partial P} \right\}_{T,N} = \left\{ \frac{\partial \left(\frac{\partial G}{\partial P} \right)_{T,N}}{\partial T} \right\}_{P,N}$$

$$-\left(\frac{\partial S}{\partial P} \right)_{T,N} = \left(\frac{\partial V}{\partial T} \right)_{P,N} \quad \text{Maxwell Relations}$$

Allows one to relate properties for a process