Define Reservoir:

1st Law says cant contain P.T. which does work without supplying energy & can create energy. QUANTITY
No direction in which process will occur. But nature says there is something else. Ex: 1. Hot phase to cold
2. Matter, bleed & white, mix dont commute limitation on heat to work. No limit on work to heat = direction. P.T. 2nd law

Based on this experience of a natural direction of process, postulate second law, QUALITY

It is impossible to devise an engine which, working in a cycle, will produce no other effect other than the transfer of heat from a colder to a hotter body [Clausius]

A non-cyclic process can transfer heat from cold to hot

1. Expand gas to extract Q from T to C 2. Compress gas (increase to T) 3. Put it in contact with the reservoir, compress further to give heat to reservoir. But state of gas is different now (depress)

It is impossible to devise an engine which, working in a cycle, will produce no other effect other than the extraction of heat from a reservoir and the performance of an equal amount of mechanical work [Kelvin]

(There are other formulations - any of these are just the more obvious)
Kelvin-Heaviside cycle: Isothermal expansion of an ideal gas

Then \( U = U(t) \), \( \Delta U = 0 \) since \( T \) fixed

\[-W = \frac{q}{T}\]

So constant temperature, heat into work, but gas expands, so initial and final states different.
We shall prove the equivalence of Clausius and Kelvin-Unexpected. To do so we will show: not (c) ⇔ not (k)

To show not (k) ⇒ not (c) is easy. Converse requires introduction of a very important theorem, construct the Carnot cycle.

not (k) ⇒ not (c)

Reason: Extract energy from reservoir at T1. Spin gas indefinitely using this work in our system to raise temperature of another body, then T1 > Tc. This implies not (c).

Now we must consider the transformation of heat into work.

The Carnot cycle:

K ⇒ Heat cant convert heat into work, completely, at one tap.

So consider a two tank setup: Two reservoirs at Tc and T1, T1 > Tc.

\[
\begin{align*}
P & \quad A \quad B \\
V & \quad C \quad D \\
\end{align*}
\]

\[(AB), (CD) \text{ isotherms at fixed} \quad (AC), (BD) \text{ adiabatic} \quad \Delta Q = 0\]

Shale follow, say, from ideal gas

Any two variable eg. P, V, T1, Tc can be extended to more variables.
only cylinder base may conduct, rest insulated.

A: Piston equilibrated with reservoir at $t_2$ (reservoir at $t_2$)
B: Piston raised to point B (reservoir at $t_2$)
D: Piston raised further to point D (on insulator now)
C: Piston lowered to C (reservoir at $t_1$)
A': Piston lowered to A (on insulator now)

All done very slowly so reversible.

What happens: AB, system absorbs heat $q_H$ (>0 heat flows into the system is taken to be positive)
DC, system gives heat $q_C$ (so absorbs heat $q_H$ to the reservoir at $t_C$)
BD, CA no heat change (adiabatic). Thus total heat absorbed by system is $q_H + q_C$.

Apply 1st law: Since cycle $\Delta U = 0$, Therefore

\[ D = W + q_B \text{ or } W = (q_H + q_C) \]

($W$ is work done on the system by surroundings)
Then define the efficiency \( e \) as

\[
e = \frac{\text{work output by system}}{\text{energy input}} = \frac{-W}{\Delta H} = \frac{S_f + S_c}{S_f} = 1 + \frac{S_c}{S_f}
\]

\[
e = 1 + \frac{S_c}{S_f} \quad (\text{N.B. } S_c < 0)
\]

\( e \leq 1 \) !

(We define energy input as \( q_r \) since this is what we add to system, from the surroundings - e.g., boiler, for example - to get work.)

The Carnot cycle, run this way, extracts heat from the high temperature reservoir and rejects heat to the low temperature reservoir, and does some work.

We can run it in reverse - path ACDBA, and extract heat from low temperature reservoir, reject to high temperature while system does work. This is a refrigerator.

First application of Carnot cycle: not (C) \( \Rightarrow \) not (K)

Not (C) transfer heat \( q_f \) from \( t_c \) to \( t_h \) reservoir. 

The Carnot cycle. Use \( q_f \) at \( t_f \) to do work \(-W\). This is not result; reservoir at \( t_h \) doesn't change - it gained and gave up \( q_f \). 

The reservoir at \( t_c \) however gave up \( q_f \) and work \(-W\) was done, i.e. not (K). Q.E.D.

delete
How do we know that $g > 0$, if $-w > 0$, i.e., if the system does work, heat extracted from high $T$ reservoir and given to low $T$ reservoir.

Proof:
Assume $g > 0 \Rightarrow$ system absorbs heat from cold reservoir. Place C+H in contact, let C absorb some amount $g_c$ from H. Thus reservoir C doesn't change. The result would be transformation of heat into work without reservoirs at $T_H$, i.e., not Kelvin.

Therefore $g_c > 0$.

From cycle $-w = g + g_c$, where $-w > 0, g < 0$.

$\Rightarrow g > -g_c > 0$. A BONUS.

Therefore, from $K$, $g_c < 0, g_H > 0$. Q.E.D.

Now consider another engine between $T_c$ and $T_H$.

$-w' = g' + g_c'$.

Prove that:

1. If first engine reversible then
\[ \frac{q_c}{q_H} \geq \frac{q'_c}{q'_H} \implies e \geq e' \]

6. If the second engine is also reversible, then

\[ \frac{q_c}{q_H} = \frac{q'_c}{q'_H} \implies e = e' \]

(Note that b implies that a reversible engine is independent of the nature of the working substance, e set by parameters, not by material.)

Proof:

1st law to cycles

\[ -W = \frac{q_H}{q_H} + \frac{q_c}{q_H} \]

\[ -W' = \frac{q'_H}{q'_H} + \frac{q'_c}{q'_H} \]

Consider process where 1st is run N times in reverse, second N' times in forward. (\( q_H < 0, q_c > 0 \iff q'_H > 0, q'_c < 0 \)).

Define (1)

\[ \frac{q_H}{q_H} = \frac{N'}{N} \quad N, N' \text{ number of cycles.} \]

Then

\[ -W_{\text{total}} = -NW - N'W' \]

\[ + q_H, \text{total} = Nq_H + N'q'_H \]

\[ q_c, \text{total} = Nq_c + N'q'_c \]
Adding results of both cycles

\[ W_{\text{total}} = W_{\text{fr}} + W_{\text{cr}} \]

Integrate

\[ W_{\text{fr}} = Nq + N'q' = Nq + N = 0 \quad \text{Eq}(1) \]

Thus

\[ W_{\text{total}} = W_{\text{cr}} \]

If \( W_{\text{total}} > 0 \), then system would have done work equal to heat \( q_{c,\text{total}} \) with no other changes. This is not \( K \). Then

\[ W_{\text{total}} \leq 0 \]

\[ q_{c,\text{total}} \leq 0 \]

From \( q_{c,\text{total}} \) expression

\[ Nq + N'q' = q_{c,\text{total}} \leq 0 \]

Then \( Nq' \leq -N'q' \quad \text{recall} \quad q > 0, q' < 0 \)

And using \( -N'/N = 1 + qH/q'H \) we have

\[ \frac{q'}{qH} \leq \frac{q'-q}{q'H} \quad \text{(be careful with inequalities)} \]

\[ \frac{q'}{qH} < 0 \quad \text{(involving negative numbers)} \]

Now consider engine to also be reversible. And intercycle engine. Then will obtain

\[ \frac{q}{qH} \geq \frac{q'}{q'H} \]


\[ \text{Can't have both inequalities. Therefore} \quad \frac{q'}{qH} = \frac{q}{q'H} \quad \text{(rev.)} \]
Therefore \( e = e' \) (reversible engines)

- Efficiency independent of working substance.

Finally, let's get to temperature. Since any reversible engine operating between \( t_1 \) and \( t_2 \) gives the same work, it must be that

\[
\frac{Q_H}{Q_C} = f(t_1, t_2)
\]

where \( f \) is a universal (same for all substances) function of \( t_1 \) and \( t_2 \).

Convention: if \( A \) and \( B \) are two systems which, when in thermal contact, heat flows from \( A \to B \), we have \( T_A > T_B \).

Consider three Carnot cycles, each between \( t_1, t_2, t_3 \) (with \( t_1 < t_2 < t_3 \)), i.e.

\[
\begin{align*}
0 & \rightarrow 1 & \frac{Q_1}{T_1} = f(t_2, t_3) \\
1 & \rightarrow 2 & \frac{Q_2}{T_2} = f(t_3, t_1) \\
2 & \rightarrow 0 & \frac{Q_3}{T_3} = f(t_1, t_2)
\end{align*}
\]

from (1) \( \frac{-Q_1}{T_1} = f(t_2, t_3) \)

while (2) gives \( \frac{-Q_2}{T_2} = f(t_3, t_1) \)

Now, since \( f(t_3, t_1) = f(t_1, t_2) + f(t_2, t_3) \)
This implies that \( f(t_1, t_2) = \frac{f(t_2)}{f(t_1)} \), thus \( t_2 = t_1 \).

Thus \( \frac{-q_1}{q_2} = \frac{f(t_2)}{f(t_1)} \).

The simplest choice of \( f(t) \) is \( f(t) = K \theta \) with \( K \) a constant. Then

\[
-\frac{q_2}{q_1} = \frac{\theta_2}{\theta_1}
\]

Thermodynamic temperature scale (independent of properties of particular substance!) ABSOLUTE.

Take the reference temperature \( f(0, k) \) (fixed) to be triple point.

Write \( \theta_{tk} = 273.16^\circ \).

Then \( \theta = 273.16^\circ \), and use Carnot cycle between \( \theta_{tk} = 0^\circ \) and \( \theta = 0^\circ \).

Now observe, page 74-75 shows that for an ideal gas,

\[
-\frac{q_2}{q_1} = \frac{T_2}{T_1}
\]

Therefore, combining above,

\[
T = \theta
\]

The absolute and perfect gas temperature coincide (numerically identical).
We have shown (cf. eq. 2d)
\[-\frac{2e}{T_e} = \frac{T_e}{T_H}\]  
(reversibly, Adiabatic cycle).

\[\frac{2e}{T_e} + \frac{T_e}{T_H} = 0.\]

Can break up actual cycle into very small adiabatic and isothermal. Take limit of infinitesimal piece to get
\[\oint \frac{dQ_{net}}{T} = 0\]  
(reversible, any cycle).

Therefore, defining a function \( S \) from
\[dS = \frac{dQ_{net}}{T}\]  
Exact differential.

\( S \) is a state function \( \oint dS = 0 \Rightarrow S \) state function.

\[\Delta S = S_2 - S_1 = \int_{S_1}^{S_2} \frac{dQ_{net}}{T}\]  
path independent.

We can use this for irreversible process as long as we can find a reversible path between states 1 and 2.
To get this irreversible case, let $S$ be a state function, then
\[ dS = \frac{dH}{T} - dQ \]

Consider now irreversible cycles (they can't really be represented on PV diagrams). Take two cycles. We showed that
\[ e = e' \quad e = 1 + g' / g' \quad e' = 1 + g / g' \]

If they both do the same amount of work $-W = W'$, what equals $g' + g$ and $g + g'$, respectively, then since $e = e'$
\[ g' + g = g + g' \]

Now, if an extra quantity $2dQ$ should be transferred in one, then can we use the other cycle to draw this cycle in reverse and get result in $dQ$. Since $dQ$ is transferred from $a$ to $b$ in violation of 2nd law, i.e.
\[ q_{a+b} \]

But, if one of these cycles is irreversible, then an extra $dQ$ may flow since can't reverse cycle for our process.
From our previous result
\[ \frac{q_c}{q_H} \geq \frac{q'_c}{q'_H} \]
where \( q_c \) is irreversible cycle, unformed. \( q_H \) is reversible cycle.

And our result
\[ -\frac{q_c}{q_H} = \frac{T_c}{T_H} \]
we have \[ \frac{T_c}{T_H} \geq \frac{q_c}{q_H} \]

\[ \frac{q'_c}{q'_H} + \frac{T_c}{T_H} \leq 0 \]
\[ \frac{q'_c}{q'_H} + \frac{T_c}{T_H} \leq 0 \]

Hence\( f_ir \leq 0 \) [Clausius inequality]

\( f_{ir} \) is heat transfer of system.
Since \( \Delta q = 0 \) for reversible \( \Rightarrow \Delta q \not> 0 \) for irreversible and

\[ \text{clearly } \Delta q > 0 \] (\( \Delta q \not> 0 \) would again violate 1st law).

The free irreversible cycle requires more heat extracted

from the and dumped to \( T_c \) to obtain same amount of work.

Adding this onto \( \frac{E}{T} \) (\( T \) for new cycle), thermal

\[ \begin{align*}
\frac{\Delta q}{T} &= \frac{\Delta q}{T} + \Delta q \\
&= \Delta q_T - \Delta q_d = \Delta q - \Delta q_d = \Delta q - \Delta q_d < 0
\end{align*} \]

Extending this to general cycle yields

\[ \frac{\Delta q_{irr}}{T} \leq 0 \] (irreversible cycle) \( \text{N.B. } T = \text{reservoir temperature,} \)

\( \text{(Clairaut's inequality)} \)

Now consider the process

\[ \int_A^B \frac{d_\text{s}}{T} = \left( \int_A^B \frac{d_\text{q}}{T} \right)_1 + \left( \int_A^B \frac{d_\text{q}}{T} \right)_R \]

\[ \text{Int } \int_A^B \frac{d_\text{s}}{T} = S(A) - S(B) \quad \Rightarrow \]

\[ \int_A^B \frac{d_\text{s}}{T} \leq S(B) - S(A) \quad \text{unreversible process,} \]

\[ \text{(rev. in equality)} \]
For an adiabatic system \((dS \geq 0)\),

\[ S(B) \geq S(A) \]

Every adiabatic transformation results in a final entropy which is not less than the initial entropy.

If the transformation is reversible, then the entropy doesn't change (in an adiabatic process).

When an isolated system is in a state of maximum \(S\), then it cannot undergo any further transformation. That's all folks!

**The toothpaste doesn't go back in the tube.**

This proves all that is obtained in lecture \(S.3.5\) in a new way, I think.

The energy of the "world" is constant.

The entropy of the "world" tends to a maximum.
\[ e = -\frac{W}{H} = -\frac{8H + 8C}{8H} = 1 + \frac{8C}{8H} = 1 - \frac{1}{H} \]

\((T \text{ in K})\)

**For high pressure steam engines**

\[ T_H \approx 200^\circ C = 473 K \]
\[ T_C \approx 50^\circ C = 323 K \]

\[ e = 1 - \frac{323}{473} \approx 0.329 \]

**For**

\[ T_H = 400^\circ C \approx 750^\circ F = 673 K \]

\[ e \approx 0.529 \]

So, it pays to use large \(T\) input.
1. **Reversible adiabatic** \( \mathcal{Q} = 0 \) Thus
\[
\frac{\Delta S}{\Delta S_0} = 0 \quad \text{new, ad.}
\]

2. **Reversible phase change at fixed** \( T, p \)
\[
\Delta S = \frac{\int_A^B \text{d}q}{T} = \frac{1}{T} \int_A^B \text{d}q = \frac{q_{\text{rev}}}{T}
\]
Since \( p \) constant, \( q_{\text{rev}} = \Delta H \). Thus
\[
\Delta S = \frac{\Delta H}{T} \quad \text{now phase change at fixed.}
\]

Thermodynamic \( \Delta S \text{atb} \sim 85.3 \text{kJ mol}^{-1} \text{~K} \) many liquids - good disorder is "uniform". Extern. 
\( \Delta H \) for solid-liquid is \( \text{LATENT HEAT} \) \( \Delta H \text{fusio} \) and
\( \text{eqw} - \text{eqw} \) is "" " of vap.rolatioin...

Melt: \( \text{sqm} \) ice at \( 0^\circ \text{C, } 1 \text{~atm.} \)
\[
L = \Delta H = 79.7 \text{kJ/gm}
\]
\[
\Delta S = \left( \frac{79.7 \text{kJ}}{273 \text{K}} \right) \Delta H = 0.76 \text{kJ/K} = 6.1 \text{J/K}.
\]

3. **Reversible chemical process, \( T \) fixed,**
\[
\Delta S = \frac{\int A^B \text{d}q_{\text{rev}}}{T} = \frac{1}{T} \text{d}q_{\text{rev}}.
\]
4. Reversible, perfect gas

\[
q = dU - p dV = CV \Delta T + p dV = CV \Delta T + nRT \Delta V/V
\]

\[
\Delta S = \frac{q}{T} = \frac{CV \Delta T}{T} + nR \frac{\Delta V}{V}
\]

\[
\Delta S = CV \ln \left( \frac{TV_f}{TV_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right) \quad \text{assuming } CV \propto T \text{ in } \text{ideal gas}
\]

For an isothermal process

\[
\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \quad \text{for ideal gas, i.e.,}
\]

5. Irreversible, ideal gas

S is state function. Draw up new path.

Ex.: adiabatic, free expansion: \( T, V \rightarrow T_2, V \)

\[
\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \quad \text{ideal gas, \( \text{ad.} \)}
\]

We have focused on system here. Now consider

\( \text{Universe! Note } \Delta S > 0 \text{ for rev. exp. But we find } \Delta S = 0 \text{ new isolated system} \)
System + Surroundings. Surroundings are reservoirs, \[ \text{[No T,V,day]} \]

Combine the two processes. 4) \( \text{p}_1 \), gas, rev. extensions.
\[ \Delta S = R \ln V/V_1 \]

5) \( \text{p}_1 \), gas, \( \text{v}_1 \) free expansion - does not do lone.
\[ \Delta S = R \ln V/V_1 \]

But what about surroundings. They are huge reservoirs.
No volume or temperature changes here.

From first law, \( dU_{\text{sum}} = dQ_{\text{sum}} + dW_{\text{sum}} \)

so \( \Delta Q_{\text{sum}} = dU_{\text{sum}} = \Delta dW_{\text{sum}} \) is state function, so doesn't mix with \( f \) heat come in rev. or ir. Thus,

\[ \Delta S_{\text{sum}} = \frac{dQ_{\text{sum}}}{T} \text{ } \text{ } \text{is state function, so heat through Maxwell} \]

\( T = T_{\text{sum}} = \text{const.} \) \( \text{if} \) \( T_{\text{sum}} = \text{const and t force} \text{ } T^\text{in} = \text{const} \text{, so } \text{so forth}. \)

\[ \Delta S_{\text{sum}} = g \frac{dQ_{\text{sum}}}{T}. \]

Now for rev. expansion, \( \text{re} \), \( dU = 0 \) so
\[ (\text{rev}) \text{ heat } Q_{\text{re}} \]
\[ \Delta S_{\text{rev}} = -nR \ln V/V_1 = -\Delta S_{\text{sp}} \]

\[ \Delta S_{\text{irr}} = \Delta S_{\text{sum}} + \Delta S_{\text{sp}} = 0 \text{ } \text{[rev. heat from reservoirs]} \]
Now for our exp. \( W = 0 \) for exp. \( g = 0 \) etc. \( \Delta U = 0 \)
but \( \Delta \sum \text{sun} = g \sum \text{sun} / T = 0 \) (from \( \Delta \text{sun} = \Delta \text{sun} / T \))
So \( \Delta \sum \text{un} = \Delta \sum \text{sp} + \Delta \sum \text{sun} = \pi \beta K / N > 0 \)
\( \Delta \sum \text{un} \text{(iii)} > 0 \)

We are negative entropy generators— but we are not adiabatic— our life requires coupling to surroundings.
Our entropy decreases at the expense of increased surroundings entropy. To the extent that we carry out processes irreversibly (must otherwise we would live infinitely long) \( \Delta S_{\text{sp}} + \Delta S_{\text{sun}} = \Delta S_{\text{un}} > 0 \)
4. Reversible perfect gas.
\[ dS = \frac{dU}{T} - dW = C_v dT + p dV = C_v dT + nRT dV/V \]

\[ \Delta S = \int C_v \frac{dT}{T} + nR \int \frac{dV}{V} \]

\[ \Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right) \quad \text{Handy formula.} \]

5. Irreversible ideal gas

\[ S \text{ is state function. So draw up new path between same initial and final state.} \]

Ex. Adiabatic free expansion into vacuum.

\[ T_1 V_1 \rightarrow T_2 V_2 \]

But for ideal gas \( T_2 = T_1 \) since \( U = U(T) = f(T) \)

\[ \left( \frac{\partial U}{\partial V} \right)_V = 0. \]

Since adiabatic \( q = 0 \). But \( \Delta S \) is not given (as it is for new, ad. exp.)

\[ \Delta S = nR \ln \left( \frac{V_2}{V_1} \right) \]

6. Irreversible phase change (at fixed P)

\[ \Delta S \text{ for changing supercooled liquid at } T_5 \text{ to solid.}\]

The equi phase change temperature is \( T_6 \) say. This is irreversible since while we can change supercooled liquid to solid by-
\[ \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 \]

1. Recently warm supercooled liquid from \( T_s \rightarrow T_f \)
2. Recently freeze liquid (resemble one that is again temp between \( L + S \))
3. Recently cool solid back to \( T_s \).

\[
\text{Constant pressure heating reversible or irreversible recovered.}
\]
\[
\Delta S = \Delta S_{r}\]
\[
\Delta S = \int \frac{(pV)_{r}}{T} \, dt = \Delta H(T_f, T_s)
\]

But \( S \) state function, so can use this expression for irreversible process too.
The condition that
\[ \Delta S \geq 0 \]
for an isolated system, equality holding for reversible process, is not very useful since most chemical transformations are done at constant \( V \) or \( p \).

Example: Chem. reactions in gas, constant \( V \), in liquids, constant \( p \).

Phase changes in dissolution of crystal, at constant \( p \).

Thus, we would like criteria for material equilibrium in closed systems which are in thermal contact with a reservoir.

\[ \int_{f}^{g} \frac{df}{T} \leq \Delta S \]

Now, if \( T \) the reservoir temperature is a constant, then it can be extracted from the integral to give

\[ \int_{f}^{g} \frac{df}{T} \leq \Delta S \]

\[ T \Delta S \geq Q \]
From the first law, \( \Delta U = Q + W \), we have

\[ \Delta U \leq T \Delta S + W \]

And, let's write this as

\[ \Delta U - T \Delta S \leq W \]

Or, defining a new state function,

\[ \Delta G = U - TS \] (Helmholtz free energy)

we have

\[ A(t) - A(0) = \Delta A \leq W \] (T reservoir)

Now, if the process is reversible then

\[ \Delta A = W \] (Reversible, T reservoir)

What are implications?

1) If a system undergoes a reversible transformation \( 1 \rightarrow 2 \), where \( 1 \rightarrow 2 \) has \( T \) (by ass.) and if the system only exchanges heat with reservoir, the work done on the system equals the increase in free energy (work done by system equals the decrease in free energy of the system).

2) If reversible, then decrease in free energy is an upper limit on the work done by the system. MAX work for REV.

Now consider \( W = -p \Delta V \) and the \( V \) fixed. Then

\[ \Delta A \leq 0 \] (T, V fixed)

\[ A_2 \leq A_1 \]

A closed system in thermal and mechanical equil with...
...reservoir, in a temperature $A$ cannot have its $A$ decrease. Thus, at equilibrium $A$ is a minimum, and if $A$ is a minimum, the system (fixed $T$) is at equilibrium.

We can do the above in terms of differentials, of course. Write $\frac{dA}{dT} < 0$

For fixed $T$, $d_A \leq T ds$

Then $dU - Tds \leq dW$

For $dv = 0$,

$\frac{dU}{dT} ds \leq 0$

$A = U - TS$

$dA = dU - Tds$ (since $T$ fixed)

$\frac{dA}{dT} \leq 0$ (Thus, $T, U$ fixed)

Now consider the circumstances where $T, P$ are fixed. During a transformation at fixed $T, P$, we have $W = - pDV$

But $\Delta A \leq W = - pDV$ thus,

$\Delta A \leq - pDV$ or

$A(2) - A(1) \leq - p(V(2) - V(1))$
\[ A(2) + pV(2) \leq A(1) + pV(1) \]

Define
\[ G = A + pV \] so above read
\[ G(2) \leq G(1) \quad \text{(fixed } T, P) \]

Thus, if \( G \) is a minimum, the system (fixed \( T, P \)) is at equilibrium.

\[ G \text{ is Gibbs free energy.} \]

Since \[ G = A + pV = U + pV-TS = H-TS \]
and the expression

One can do this in differential form to get
\[ dG = 0. \]

Returning to \( \Delta A \leq W \)
\[ W = -p\Delta V + \text{work}, \text{ fuel} \]

\[ \Delta A + p\Delta V \leq \text{work} \]

and at fixed \( p \) (and \( T \))
\[ \Delta G \leq \text{work} \quad \text{(fixed } T, P \text{ fixed).} \]

\[ \Delta G \leq -W \text{ by other} \]

Thus system free from Gibbs free energy decreases by amount which is an upper limit on work done by system. At equil. get max other work.
Thermodynamics. Combine 1st and 2nd Law, with derivatives stored in.

1st Law: \[ dU = dq + dw \]

for reversible change

\[ dq = Tds - pdV \]

2nd Law: \[ dU = Tds - pdV \text{ rel. } 1st + 2nd \]

But \( STpV \) are state functions. Therefore \( dU \) is path independent and \( \Delta U = U(2) - U(1) \) must be path independent. So \( \Delta U \) must refer close to reversible limit. Be sure that \( dq \neq Tds \) \( dw 
eq -pdV \)

Then \[ dU = Tds - pdV \text{ rel. to revers.} \]

The way the above is written, it looks natural to consider \( U = U(S, V) \)

Then take

\[ dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \]

Contrary \[ T = \left( \frac{\partial U}{\partial S} \right)_V \]

\[ p = -\left( \frac{\partial U}{\partial V} \right)_S \]
Note: The first find \( F \) in terms of \( S \) of 1st law quantity \( U \) and 2nd law quantity \( S \).

Experimentally, these derivatives aren't very convenient. Let's relate them to measurable derivatives. (How do you keep \( S \) constant in most experiments?)

Let's go further and differentiate \( 37.5e + 37.5s \) again.

\[
\frac{\partial F}{\partial V} = -\frac{2}{3} \left( \frac{\partial U}{\partial S} \right)_V
\]

\[
\frac{\partial P}{\partial S} = -\frac{2}{3} \left( \frac{\partial U}{\partial V} \right)_S
\]

But order of taking a second derivative is immaterial, i.e.,

\[
\frac{2}{3} \left( \frac{\partial U}{\partial S} \right)_V = \frac{2}{3} \left( \frac{\partial U}{\partial V} \right)_S
\]

Therefore,

\[
\frac{\partial F}{\partial V} = -\frac{\partial P}{\partial S}
\]

Maxwell relation.
Consider the enthalpy now. Legendre Transformation

\[ dH = d(U + PV) = dU + p dV + V dP = T dS - p dV + p dV + V dP \]

Then \[ dH = T dS + V dP \]

Similarly \[ dU = T dS - p dV \]

\[ \begin{cases} dH = T dS + V dP \\ dU = T dS - p dV \\ dA = -S dT + P dV \\ dG = -S dT + V dP \end{cases} \] Gibbs' duffentiale

Natural to write, then, \( U = U(S, V) \); \( H = H(S, P) \); \( A = A(T, V) \); \( G = G(T, P) \)

Clearly \( G \) is very important since most (or some) experiments are carried out at fixed \( T \) and \( P \).

From \( dH \), we have

\[ dH = \frac{\partial H}{\partial S} dS + \frac{\partial H}{\partial P} dP \]

and then

\[ T = \frac{\partial H}{\partial S} \quad V = \frac{\partial H}{\partial P} \]

and Maxwell relation

\[ \frac{\partial T}{\partial P} = \frac{\partial V}{\partial S} \]
\[ \frac{dA}{dT} + \frac{dA}{dV} \frac{dV}{dT} = 0 \]

and Gibbs' eqs. we have

\[ S = -\frac{dA}{dT}|_V \quad p = -\frac{dA}{dV}|_T \]

Maxwell:

\[ \frac{dS}{dV}|_T = \frac{dp}{dT}|_V \]

From:

\[ dG = \frac{dG}{dT}|_p \frac{dT}{dA} + \frac{dG}{dp}|_T d\rho \]

and Gibbs' eqs. we have

\[ S = -\frac{dG}{dT}|_p \quad V = \frac{dG}{dp}|_T \]

Maxwell:

\[ \frac{dS}{dp}|_T = -\frac{dV}{dT}|_p \]

The experimentally measured quantities are: \( C_V, C_p, \)
\( \alpha \) and \( \kappa \). The quantities we want are
\( U, S \) and then \( H, A, G \). Equation of state
\( \text{theory or empirical very helpful, too} \)
Maxwell give relations to pVT expressions.

The six PVT derivatives

\[ \theta \Delta T(p, \theta V/\theta p) + \theta \Delta T(p, \theta V/\theta T) + \theta \Delta T(\theta p/\theta V) + \theta \Delta T(\theta T/\theta V) + \theta \Delta T(\theta p/\theta T) \]

\( \theta \Delta T \) are independent. (3 reciprocs + Euler chain)

Define \( \lambda(T, p, \theta V/\theta T) \) elemental expansion

\[ \lambda(T, p) = -\frac{1}{\theta}(\theta V/\theta p) \] partial elemental expansion \( \lambda \geq 0 \)

\[
\begin{array}{c|c|c|c}
g & \lambda & s \\
\hline
10^{-1} & 10^{-2} & 10^{-1} & K^{-1} \\
-10^{-1} & 10^{-3} & 10^{-2} & 10^{-1} \\
\end{array}
\]

Recall \( d\theta = dU + pdV = dU + V d\theta \) \( \theta \) fixed

\[ CV = \frac{\partial \theta}{\partial T} \] \( CV = TAS \)

\[ CP = \frac{\partial H}{\partial T} \] \( CP = TAS \)

Equation of state \( p = p(\theta T) \)
General procedure: \( dJ = \left( \frac{\partial J}{\partial X_1} \right)_x X_1 \, dx_1 + \left( \frac{\partial J}{\partial X_2} \right)_x X_2 \, dx_2 \)

where \( X_1, X_2 \) are independent variables (simple system is assumed). \( J \) is quantity whose change we want (for \( A \rightarrow B \)).

Then express partial \( \frac{\partial J}{\partial X_1} X_1 \) or \( \frac{\partial J}{\partial X_2} X_2 \) in terms of experimentally measured quantities and of their derivatives which are accessible - i.e., \( \frac{\partial J}{\partial V}, \frac{\partial J}{\partial T}, \frac{\partial J}{\partial S} \) (not \( \partial J/\partial S \)).

Call these \( a(x, x_1), b(x, x_2) \).

Then \( dJ = a(x, x_1) \, dx_1 + b(x, x_2) \, dx_2 \)

Then \( \Delta J = J(B) - J(A) = \int_A^B dJ \)

\[ = \int_A^B a(x, x_1) \, dx_1 + b(x, x_2) \, dx_2 \]

These are path integrals. To specify state \( A \rightarrow B \), it is clear that it is best to have chosen \( X_1, X_2 \) to correspond to state specifications, i.e. \( A \) is defined by \( X_1^A, X_2^A \)

\( B \) specified by \( X_1^B, X_2^B \). If not, we have

\[ A \text{ specified by } Y_1^A, Y_2^A, \text{ etc. Then must relate } X_1, X_2 \text{ to } Y_1, Y_2. \]

Simpler path to choose (and since \( \Delta J \) is path independent, this is legitimate) is where in

- \( dy \) integral \( X_1 \) is constant
  - and then in \( dx_2 \) integral

\( X_2 \) constant.

If no, then
\[ X^A X_2 \rightarrow X^B X_2 \rightarrow X^B X_1 \]
and for \( X^A X_2 \rightarrow X^B X_1 \) we have

\[ \int \text{a} \left( \frac{X_1}{X_2} \right) \text{d}X_1 + 0 \left( \text{d}X_2 = 0 \right) \]

\[ \int \text{b} \left( \frac{X_1}{X_2} \right) \text{d}X_1 + 0 \left( \text{d}X_2 = 0 \right) \]

\[ = \Delta J. \]

And both are ordinary integrals.

Let us now illustrate this procedure with an example. Bartschetz

For a van der Waals gas, we have \( \text{bars} \) indicate \( n \) taken into \( V \) and all coeff. written this way.

\[ p = \frac{RT}{V-b} - \frac{a}{TV^2} \quad \text{with} \quad \bar{C}_v = A + BT + \frac{2a}{T^2V} \]

\[ V_m = \frac{\bar{V}}{n} \]

where \( a, b, A, B \) constants. (Note \( \bar{C}_v \) involves \( a \),

so eq. of state and \( \bar{C}_v \) are connected - we will come back to this point shortly.)

Find \( \Delta S \) for process where \( T_1V_1 \rightarrow T_2V_2 \)

\[ \left( p + \frac{a}{TV^2} \right) (V-b) = RT \]

\[ \epsilon_6 \] repulsion; \( (p + \frac{a}{TV^2}) \) attraction; \( \epsilon_6 \) constant.
First step, write \( S = S(T,V) \)
\[
    dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV
\]

Now, relate derivatives to measurable.

First \( \left( \frac{\partial S}{\partial T} \right)_V \): Recall that \( C_V \equiv \frac{\partial Q}{\partial T} \) \( V \) fixed.

But \( dQ = T dS \) \( \Rightarrow \) \( C_V = T dS \), \( V \) fixed.

Thus, \( \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \).

Second \( \left( \frac{\partial S}{\partial V} \right)_T \): From Maxwell relations for A,

\[
    \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V
\]

So,
\[
    dS = \left( \frac{C_V}{T} \right) dT + \left( \frac{\partial P}{\partial T} \right)_V dV
\]

We have \( C_V \) given. And, from eq. (a) above,

\[
    \left( \frac{\partial P}{\partial T} \right)_V = \frac{2}{\partial T} \left\{ \frac{RT}{V-b} - \frac{\alpha A}{TV^2} \right\} = \frac{R}{V-b} + \frac{\alpha}{TV^2}
\]

Thus,
\[
    dS = \left[ \frac{A}{T} + B + \frac{2 \alpha}{T^2 V} \right] dT + \left[ \frac{R}{V-b} + \frac{\alpha}{TV^2} \right] dV.
\]
Now, $\Delta S = \int \frac{T_2 V_2}{T_1 V_1} dS$ along any path.

Choose $T_1 V_1 \xrightarrow{\text{1}} T_2 V_2 \xrightarrow{\text{2}} T_3 V_3$.

1. $\Delta S = \int \frac{T_2 V_2}{T_1 V_1} \left[ \frac{A}{T} + B + \frac{2a}{T^3 V_1} \right] dT$

2. $\int \frac{T_2 V_2}{T_3 V_3} \left[ \frac{R}{V - b} + \frac{a}{T_2^2 V_2} \right] dV$

Now, these are ordinary integrals. All variable limits correspond to those of $\bar{V}$, so integrate:

$\Delta S = A \ln \left( \frac{T_2}{T_1} \right) + B \left( T_2 - T_1 \right) - \frac{2a}{T_1 V_1} \left( \frac{1}{T_2^2} - \frac{1}{T_1^2} \right) + R \ln \left( \frac{V_2 - b}{V_1 - b} \right) - \frac{a}{T_2^2} \left[ \frac{1}{V_3} - \frac{1}{V_1} \right]$

$\Delta S = A \ln \left( \frac{T_2}{T_1} \right) + B \left( T_2 - T_1 \right) - a \left[ \frac{1}{T_2^2 V_2} - \frac{1}{T_1^2 V_1} \right] + R \ln \left[ \frac{V_3}{V_1 - b} \right]
Entropy of Mixing (at fixed $T, P$) \( S_{\text{mix}} \)

\[
P = n_1 V_1 T + n_2 V_2 T
\]

\[
\Delta S_{\text{mix}} = \frac{R}{T} \ln \frac{V}{V_1}
\]

Since \( U = U(T) \) at fixed $T$

\[
\Delta U = 0 \Rightarrow \Delta W = 0
\]

\[
W = -\int P \, dV = -\int V \frac{dT}{T} = -n_1 R \ln (V/V_1) + n_2 R \ln (V/V_2)
\]

So

\[
\Delta S = -w = \frac{Q}{T} = \eta R \ln (V/V_1)
\]

\[
\Delta S = n_2 R \ln (V/V_2)
\]

\[
\Delta S = \Delta S_1 + \Delta S_2 = R \left[ n_1 \ln (V/V_1) + n_2 \ln (V/V_2) \right]
\]

\[
= -n_1 R \ln x_1 - n_2 R \ln x_2
\]

where \( x_i = n_i / (n_1 + n_2) \)

General:

\[
\Delta S = -R \sum_{c=1}^{N} n_c \ln x_c \quad N \text{ different gas}
\]

\( \Delta S > 0 \) Comes from expansion, 

\[
\Delta S > 0 \Rightarrow \frac{dU}{T} \ln (V/V_0) \Rightarrow \Delta S > 0 \text{ for expansion}
\]

What if we derive for some other variable? \( \Delta S > 0 \text{ for } \Delta E \text{ too!} \)

But must be \( \Delta S = 0 \). From figure. In @ $T$ QN, equation Gibbs.
1. Ideal gas expands reversibly and adiabatically. How does $T$ change with $p$?

Now, $dU = TdS - pdV$

If $q = 0$, then $\int TdS = 0 \Rightarrow dS = 0$

So $S = \text{constant}$. Thus, we use $\int TdS$ for our work.

\[
\frac{dT}{dS} = \frac{2p}{3S} = \frac{2}{S} = \frac{\partial S}{\partial T}
\]

Now, this is difficult, so let us use the Hesse identity of Euler chain:

\[
\frac{\partial T}{\partial p} \frac{\partial p}{\partial S} \frac{\partial S}{\partial T} = -1
\]

To write, with reference to Maxwell's (G):

\[
\frac{\partial T}{\partial p} = -\frac{dS/dp}{dS/dT} = \frac{2V/p}{C_v/T} = \frac{V}{C_v T} \frac{\partial V}{\partial T}
\]

Then, if we have equation of state, R.H.S. is easy to calculate.

\[pV = RT \quad V = \frac{RT}{p} \quad \frac{\partial V}{\partial T} = R/p \quad \text{for} \] ideal gas

\[
\frac{dT}{dS} = \frac{RT}{pC_v}
\]

Thus for isentropic process, we have
\[
\frac{dT}{T} = \frac{R}{C_p} \frac{dp}{p}
\]

\[
\ln(T_2/T_1) = \frac{R}{C_p} \ln(p_2/p_1)
\]

\[
\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{R/C_p}
\]

This can be checked against our earlier derivation.

\(p \neq p_f\), so for expansions, then \(T \leq T_f\), Thermo in 6th exp. (Liquids).

Because internal energy depends on work done.

2. Express \(C_p - C_V\) in terms of \(p, V, T, \alpha, x\).

\[C_p = T \left(\frac{\partial s}{\partial T}\right)_p\]

\[C_V = T \left(\frac{\partial s}{\partial T}\right)_V\]

\[\frac{\partial s}{\partial T} = \left(\frac{\partial s}{\partial T}\right)_p + \left(\frac{\partial s}{\partial p}\right)_T \frac{\partial p}{\partial T}\]

Dye 2.14

\[\frac{\partial s}{\partial T} = \frac{\partial s}{\partial p} \frac{\partial p}{\partial T}\]

Maxwell (6)

\[\frac{\partial s}{\partial T} = -\frac{\partial V}{\partial T}\frac{\partial p}{\partial T} = -\frac{\alpha}{\kappa} \frac{\partial V}{\partial T}\]

Thus:

\[C_V - C_p = -\frac{T V \alpha^2}{\kappa}\]

\[C_p - C_V = \frac{T V \alpha^2}{\kappa}\]

\(\text{For H}_2\text{O at } 3.5^\circ\text{C} \quad \partial V / \partial p = 0\), so \(C_V = C_p\). \(C_V - C_p\) at close \(T's\).
More generally
\[ dU = Tds - pdV \]
\[ CV \Delta T = Tds - pdV \]

so
\[ \frac{CV}{T} \Delta T = ds - \frac{pdV}{V} \]

\[ C_v \text{ conv} \]

\[ C_v \ln \frac{T_2}{T_1} = S_2 - S_1 = \frac{R}{c_v} \ln \frac{V_2}{V_1} \]

Thus
\[ p_1 V_1^\gamma = S_1 k V_1 = p_2 V_2^\gamma = S_2 / c_v \]

where \( \gamma = c_p / c_v \) to cap, with convex curve. \[ p_1 V_1^\gamma = p_2 V_2^\gamma \]
(1) Volume dependence of $U$ at fixed $T$ (corresponding to constant density).

\[ \frac{\partial U}{\partial V} = \frac{3}{3V} \left( T \frac{\partial S}{\partial T} - p \frac{\partial V}{\partial T} \right) = T \frac{\partial S}{\partial T} - p \]  

Maxwell (a) is $\frac{\partial S}{\partial V} = \frac{\partial p}{\partial T} V$.

\[ \frac{dU}{dT} = T \frac{\partial S}{\partial T} - p \frac{\partial V}{\partial T} \]

\[ \frac{dU}{dV} = T \frac{\partial S}{\partial T} - p \frac{\partial V}{\partial T} \]

From 46.7

For ideal gas, $\frac{\partial p}{\partial T} = \frac{nR}{V}$

\[ \frac{dU}{dT} = T \frac{\partial S}{\partial T} - p \frac{\partial V}{\partial T} = T \frac{nR}{V} - p = p - p = 0 \]

$U = U(T)$. Need 1st and 2nd law to obtain this.

(2) Pressure dependence of $S$.

\[ \frac{\partial S}{\partial p} = \frac{\partial H}{\partial T} + V \]

Maxwell (a)

\[ \frac{\partial H}{\partial T} = -T \frac{\partial V}{\partial T} + V = -TV \alpha + V \]

\[ \frac{\partial S}{\partial p} = \frac{\partial H}{\partial T} \frac{\partial T}{\partial p} \]

\[ \frac{\partial H}{\partial p} \frac{\partial T}{\partial p} \]
Thus \( \mu_{JT} = \frac{qT}{\delta p/\delta T} = -C_p \frac{dT}{dT} \)

and only 49.5

\[ \mu_{JT} = +C_p \left[ \frac{dT}{dT} - 1 \right] \]

ideal gas, \( T(\frac{dV}{dT}/p) = \frac{V}{p} \frac{dP}{dT} \Rightarrow T \frac{dP}{dT} = \frac{P}{V} \)

\( \mu_{JT} = 0. \)

now, if \( \Delta T > 1 \) then compression warms gas.

Another type of problem involves calculating how far along a path a given process will go.

Example: Gas at \( T_1 \) which is \( V_1 \) \( W \) gas expands adiabatically from \( V_1 \) to \( V_2 \) against constant external pressure \( p_e \). Assume \( C_V \) constant.

Find the final temp \( T_2 \)

\[ p = \frac{R T}{V^\gamma} - \frac{a}{V^\gamma} \]

We are given \( V_1, V_2, T_1, p_e \) and \( \gamma \) of state.

We can find \( p_e \) from \( \gamma \) of state

\( \gamma = 1.4 \) some adiabatic

\[ W = -\int V_1 \ p_e \ \delta V = -p_e (V_2 - V_1) \]
\[ \Delta U = Q + W = -p \Delta V \quad \text{(1)} \]

To involve \( T_2 \) we write eq. 1, state for \( T_2 \) \( pV \).

\[ RT_2 = (P_2 + \frac{\alpha}{V^2}) (V - b) \quad \text{(2)} \]

But here we need \( P_2 \). So let's find some eq. that involves \( T_2 \). Since we know \( \Delta U \), let us,

\[ dU = \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial T} dT \]

So, \( \Delta U = -\Delta V \left[ \frac{1}{V_2} - \frac{1}{V_1} \right] + C_V (T_2 - T_1) \quad \text{(3)} \]

We can equate (3) and (1) to get \( V = V_1 \)

\[ -\Delta V \left[ \frac{1}{V_2} - \frac{1}{V_1} \right] + C_V (T_2 - T_1) = -p_{\text{ext}} \Delta V \]

Thus, solve for \( T_2 \)

\[ T_2 = T_1 - \frac{P_{\text{ext}} \Delta V}{C_V} \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \quad \text{(4)} \]

Thus we find \( T_2 \) in terms of known quantity.

\[ \frac{\partial U}{\partial V} = T \frac{\partial S}{\partial T} - p = T \frac{\partial p}{\partial T} - p \quad \text{(47.1)} \]

\[ = T \left( \frac{\partial P}{\partial P} \right) - p = \frac{\alpha}{V^2} \]