

# Thermodynamics

Step back (in time): Thermodynamics = phenomenological macroscopic theory

- can't explain  $PV = NK_B T$ ,  $E = \frac{3}{2} NK_B T$  ← from experiments
- widely applicable: physics, chemistry, biology, engineering, black holes, ...

## (A) Temperature and the 0<sup>th</sup> Law

Def.: isolated system: no exchange from outside, enclosed in adiabatic walls

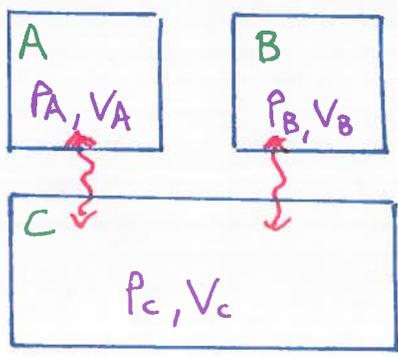
• diathermal system: in thermal contact with environment, can exchange heat

• Equilibrium: state of an isolated system after a very long time, no change in macroscopic properties.

Macroscopic variables: focus on gas  $\left\{ \begin{array}{l} \text{pressure } P \\ \text{volume } V \end{array} \right\}$  enough to specify a (macro) state

(Sometimes more: magnetization, magnetic field, etc ...)

0<sup>th</sup> Law: If two systems A, B are in equilibrium with a third system C, then A and B are in equilibrium with each other. (Equilibrium is a transitive property)



• Equilibrium between A, C:  $F_{AC}(p_A, V_A; p_C, V_C) = 0$   
(constant)

solve  $\Rightarrow V_C = \beta_{AC}(p_A, V_A; p_C)$

• Equilibrium between B, C:  $V_C = \beta_{BC}(p_B, V_B; p_C)$

$\Rightarrow \beta_{AC}(p_A, V_A; p_C) = \beta_{BC}(p_B, V_B; p_C) \quad (*)$

Other Law: A, B in equilibrium:  $F_{AB}(p_A, V_A; p_B, V_B)$   
implied by (\*) but  $p_C$  vanished (can be cancelled out)

$\Rightarrow \mathcal{O}_A(p_A, V_A) = \mathcal{O}_B(p_B, V_B)$

Temperature  $\nearrow$   $T = \mathcal{O}(p, V)$  Equation of state

Remark: doesn't fix T uniquely (could choose  $T = \sqrt{\mathcal{O}(p, V)}$ ) but implies its existence as a function of state. Ideal gas:  $T = \frac{pV}{Nk_B}$

(B) The 1<sup>st</sup> Law

Observation: Energy of isolated system is conserved

1<sup>st</sup> Law: The amount of work required to change the state of an otherwise isolated system depends only on the initial and final states, and is independent of how the work is done.

$\Rightarrow$  There exists a function  $E(p, V)$  such that  $\Delta E = E_f - E_i = W$   
 $\uparrow$  energy

Heat: If the system is not otherwise isolated,  $\Delta E \neq W$

$\Rightarrow \exists$  another mode of transfer of energy:  $Q = \Delta E - W$

(Ex: two systems with  $T_A \neq T_B$  placed in thermal contact  $\Rightarrow$  E change)

1st Law

$\Delta E = W + Q$

↑ work ↑ heat



Arrows: convention  
 $W, Q \geq 0$ : work done on the system  
heat absorbed by S

Note: Can't write  $E = W + Q$  or  $\Delta W, \Delta Q$ :  $Q, W$  not functions of state

$dE = \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial P} dP$  Total derivative, not possible for  $Q, W$   
(exact differential)

$\Rightarrow$  we write  $dE = \delta W + \delta Q$  for an infinitesimal process

$\int_i^B dE = \Delta E = E_B - E_i$  while  $\int_i^B \delta W$  and  $\int_i^B \delta Q$  depend on path (details of process)

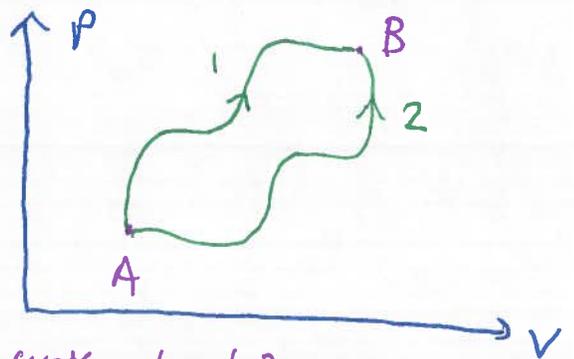
Ex:  $\delta W = -p dV$  if we squeeze the gas  
 $\rightarrow$  no function  $W(p, V)$  s.t.  $dW = -p dV$

Def: Quasistatic process = slow change so that the system is always effectively in equilibrium.

$\Rightarrow$  vary system quasistatically from A to B

$\Delta E = \int_A^B dE = E(P_B, V_B) - E(P_A, V_A)$

but  $W = - \int_A^B P dV$  depends on path



well defined at all steps of the path

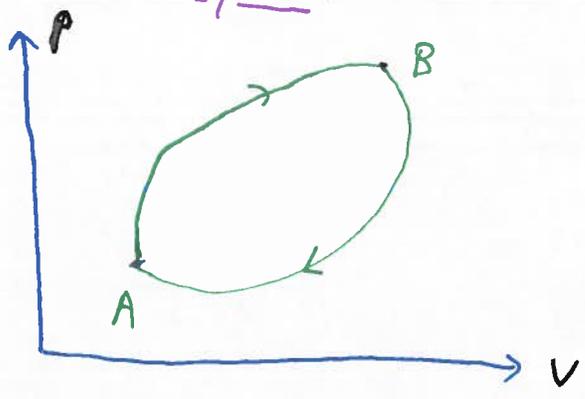
$\hookrightarrow$  area under the curves 1 and 2

C) The 2<sup>nd</sup> Law

Def: **reversible process** = quasi-static process that can be run backwards. (no "friction")

**irreversible process** = "can't un-scramble an egg"

Consider cycles:



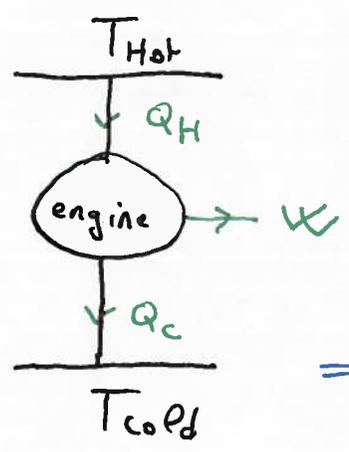
$\oint dE = 0$  for a round trip

but  $\oint p dV \neq 0$

1<sup>st</sup> law:  $\oint \delta Q = \oint p dV$

reversible: can run cycle both ways  
 $\Rightarrow$  100% conversion between work and heat?

Heat engine:



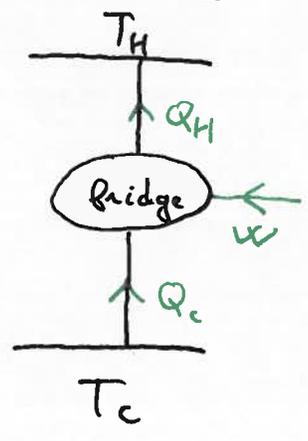
$\eta = \frac{W}{Q_H}$  (efficiency)

and

$\Delta E = 0 = Q_H - W - Q_C$

$\Rightarrow \eta = 1 - \frac{Q_C}{Q_H} \leq 1$

Refrigerator:



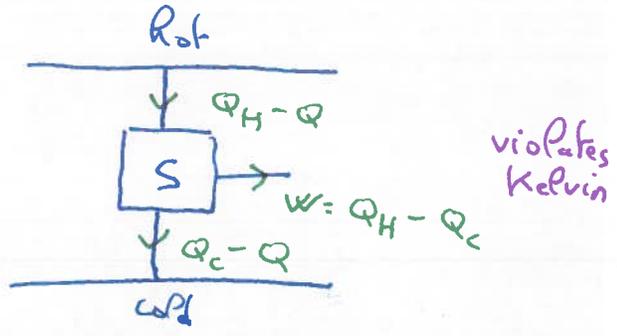
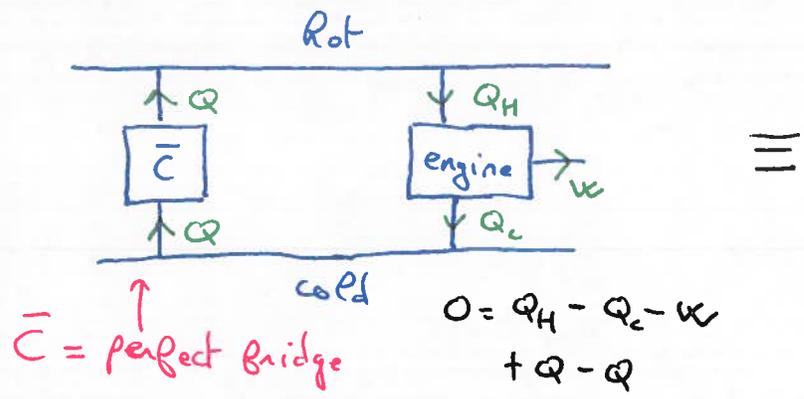
$\eta = \frac{Q_C}{W}$   
 $= \frac{Q_C}{Q_H - Q_C}$

2<sup>nd</sup> Law:

- Kelvin: No process is possible whose sole effect is to extract heat and convert it entirely into work. (can't have engine with  $Q_C = 0$ )
- Clausius: No process is possible whose sole effect is the transfer of heat from a colder to a hotter body (need W for bridge!)

Remark: Kelvin  $\iff$  Clausius

Proof: not Clausius  $\implies$  not Kelvin:

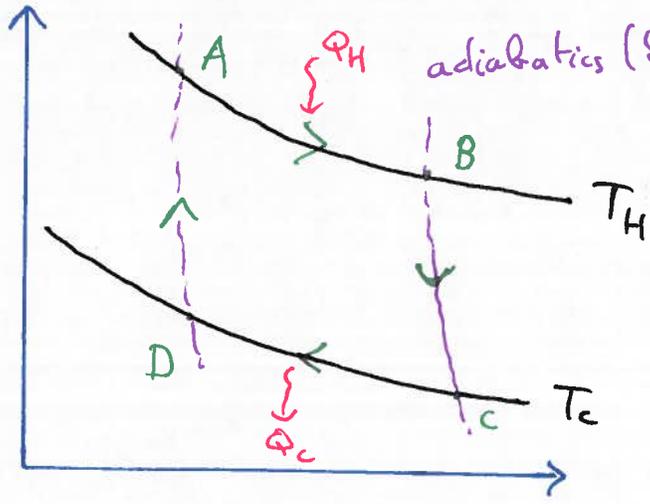


$\implies$  choose  $Q = Q_C \implies$  perfect engine with  $\eta = 1$

not Kelvin  $\implies$  not Clausius: similarly, if we had a perfect engine at our disposal, we could use it to get a perfect refrigerator.

\* We will show below that these practical statements about thermal machines lead to a new state function  $\rightarrow$  entropy

Carnot cycle: Carnot engine = reversible cycle with all heat exchanges between a source with temperature  $T_H$ , and a sink with  $T = T_C$



Assume ideal gas as internal working substance:  
 $E = \frac{3}{2} N k_B T$   
 $PV = N k_B T$  } without stat mech: empirical

**AB** isothermal expansion:  $T = T_H$   
 $\Delta E = 0 = Q_H - \int_A^B P dV \implies Q_H = \int_A^B \frac{N k_B T_H}{V} dV$

$\implies$  system absorbs

$Q_H = N k_B T_H \ln \frac{V_B}{V_A} > 0$

**CD** isothermal contraction: system dumps  $Q_C = -N k_B T_C \ln \frac{V_D}{V_C} > 0$

**BC** adiabatic expansion: first law  $\delta Q = 0 = dE - \delta W$   
 $= d\left(\frac{3}{2} PV\right) + PdV$

$\Rightarrow$  along this path:  $\frac{5}{2} PdV + \frac{3}{2} VdP \Leftrightarrow \frac{dP}{P} + \frac{5}{3} \frac{dV}{V} = 0$

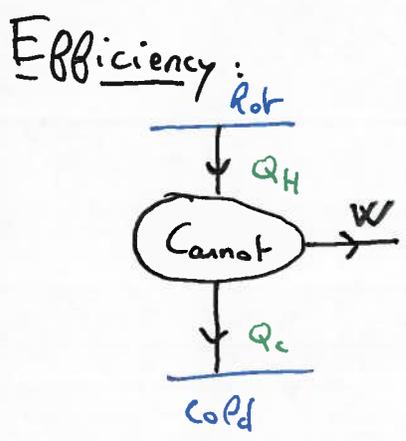
$\Rightarrow$  integrate:  $PV^\gamma = \text{cst}$   
 $TV^{\gamma-1} = \text{cst}$

$P \propto \frac{T}{V}$   
 adiabatic path for ideal gas

$\Rightarrow T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1}$

**DA**  $T_C V_D^{\gamma-1} = T_H V_A^{\gamma-1}$

$\Rightarrow \frac{V_C}{V_D} = \frac{V_B}{V_A}$



$\eta_{\text{Carnot}} = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C \rho_n \cancel{V_C} \frac{V_C}{V_D}}{T_H \rho_n \cancel{V_B} \frac{V_B}{V_A}}$

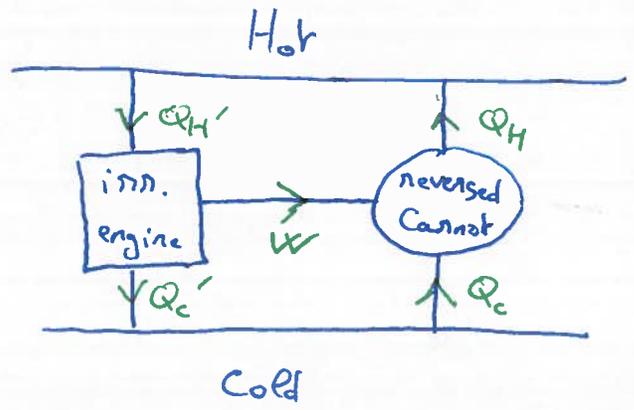
$\Rightarrow \eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$

Efficiency of Carnot engine

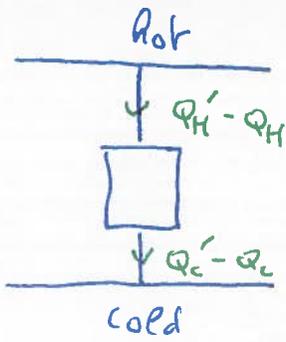
Why is the Carnot engine special?

Carnot's Theorem: No engine operating between two reservoirs is more efficient than a Carnot engine operating between them

Proof: Carnot engine is reversible: run it backwards as a refrigerator and use an irreversible, non-Carnot, engine to run it.



equivalent  
= machine



$$Q_C' - Q_C = Q_H' - Q_H \geq 0 \Rightarrow Q_H' \geq Q_H$$

↑ 1st Law      ↑ Clausius

Efficiency irr. engine:  $\eta = \frac{Q_H' - Q_C'}{Q_H'} = \frac{Q_H - Q_C}{Q_H'} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{Carnot}$

$\Rightarrow \eta \leq \eta_{Carnot}$

→ Less efficient than Carnot engine

Corollary: All reversible engines have the same efficiency  $\eta = \eta_{Carnot}$

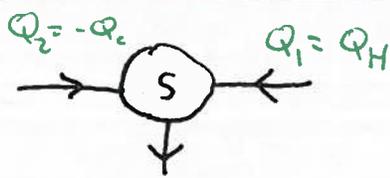
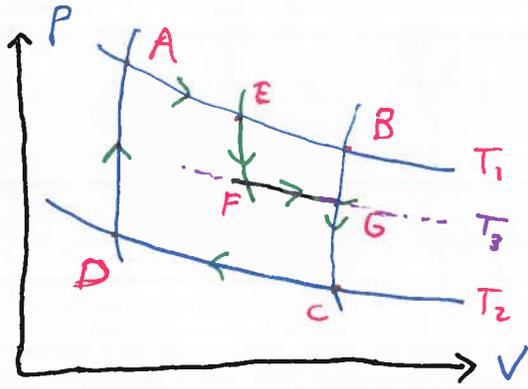
Proof: if engine reversible after all, run everything backwards:  $\eta \geq \eta_{Carnot}$   
 $\Rightarrow \eta = \eta_{Carnot}$

Remark: This maximum theoretical efficiency  $\eta = 1 - \frac{T_C}{T_H}$  can be used to define a temperature scale (cf. Kelvin)

Entropy We need one more theorem to finally construct S (entropy)

Clausius's Theorem: For any cyclic transformation,  $\oint \frac{\delta Q}{T} \leq 0$  where  $\delta Q$  is the heat increment supplied to the system at temperature T. = for reversible transfo.

Proof: Change convention



Carnot cycle:  $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$   
 $\Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \sum_{i=1}^2 \frac{Q_i}{T_i} = 0$

idea: subdivide Carnot cycle

ABCD:  $\frac{Q_{AB}}{T_1} + \frac{Q_{CD}}{T_2} = 0$

EBGF:  $\frac{Q_{GF}}{T_2} + \frac{Q_{EB}}{T_1} = 0 \rightarrow$  "mini" Carnot cycle

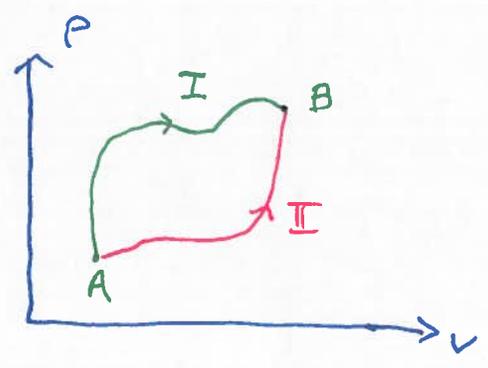
We have:  $Q_{AB} = Q_{AE} + Q_{EB} \Rightarrow \frac{Q_{AE}}{T_1} + \frac{Q_{FG}}{T_3} + \frac{Q_{CD}}{T_2} = \frac{Q_{AB} - Q_{EB}}{T_1} - \frac{Q_{GF}}{T_3} + \frac{Q_{CD}}{T_2}$   
 $Q_{FG} = -Q_{GF}$

we can approximate any reversible cycle using such subdivisions:  $\sum_i \frac{Q_i}{T_i} = 0$

$\Rightarrow$  for a reversible cycle:  $\oint \frac{\delta Q_{rev}}{T} = 0$

if cycle not reversible:  $\eta_{inn} = \frac{W}{Q_1'} \leq \frac{W}{Q_1} = \eta_{carnot}$  for 2 reservoirs  $\Rightarrow Q_1' \geq Q_1$   
 $W = Q_1 + Q_2 = Q_1' + Q_2'$  (consider a reversible and an irreversible machines doing the same work)

$\Rightarrow \frac{Q_1'}{T_1} + \frac{Q_2'}{T_2} = \frac{Q_1'}{T_1} + \frac{Q_2 + Q_1 - Q_1'}{T_2} + \frac{Q_1}{T_1} - \frac{Q_1}{T_1} = \underbrace{(Q_1' - Q_1)}_{\geq 0} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \leq 0$  ( $T_1 > T_2$ )  
 $\Rightarrow \frac{Q_1'}{T_1} + \frac{Q_2'}{T_2} \leq 0 \Rightarrow$  subdivide  $\oint \frac{\delta Q}{T} \leq 0$  for any cycle Q.E.D.



paths I and II reversible:  $\oint \frac{\delta Q_{rev}}{T} = \int_I \frac{\delta Q_{rev}}{T} - \int_{II} \frac{\delta Q_{rev}}{T} = 0$   
 $\Rightarrow \int_A^B \frac{\delta Q_{rev}}{T}$  path independent!  
 (for a reversible process)

Def: For some fixed reference state 0, we define the **entropy** of a state A with  $P_A, V_A$  as  $S(A) = \int_0^A \frac{\delta Q_{rev}}{T}$  for a reversible path

Clausius'  $\rightarrow$  Theorem: Function of state  $S(P, V)$ , independent from path we choose

Consider:  $I = \text{irreversible}$   
 $II = \text{reversible}$  }  $\Rightarrow \oint \frac{\delta Q}{T} = \int_I \frac{\delta Q}{T} - \int_{II} \frac{\delta Q_{rev}}{T} \leq 0$

$\Rightarrow \int_I \frac{\delta Q}{T} \leq \int_{II} \frac{\delta Q_{rev}}{T} = \Delta S = S_B - S_A$

For a general process:

$\Delta S = \int_A^B \frac{\delta Q}{T} + S_c$  with  $S_c \geq 0$   
 $dS = \frac{\delta Q}{T} + \delta S_c$  with  $\delta S_c \geq 0$

"Modern" formulation of the 2<sup>nd</sup> Law

entropy exchanged with environment

created entropy (= 0 if reversible)

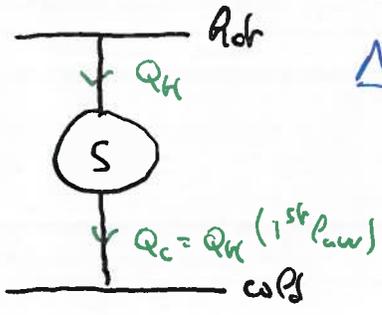
Notes: (a) For a adiabatically isolated system,  $\delta Q = 0 \Rightarrow \Delta S \geq 0$   
 "The entropy of the universe always increases"  $\rightarrow$  time arrow!

(b) Consider reversible infinitesimal process  $dE = \delta W + \delta Q$  (1<sup>st</sup> Law)  
 and  $dS = \frac{\delta Q}{T} \Rightarrow dE = T dS - p dV$   
 $\hookrightarrow -p dV$

true for any path b.c. E state function

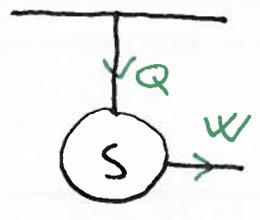
$\rightarrow$  this entropy is the same as that defined through  $S = k_B \ln \Omega$ !

(c) From this modern formulation, one can easily recover all the results of this section:



$\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} + S_c = 0$   
 $\Rightarrow \leq 0$   
 $\Rightarrow Q_H \left( \frac{1}{T_H} - \frac{1}{T_C} \right) \leq 0$

$\Rightarrow Q_H \geq 0$  (Clausius)



$\Delta E = 0 = Q - W$   
 $\Delta S = \frac{Q}{T} + S_c$

$\Rightarrow \frac{Q}{T} \leq 0 \Rightarrow W \leq 0$

(Kelvin)

### D) The 3<sup>rd</sup> Law

up to now, entropy only defined up to a constant:  $\Delta S = \int \frac{\delta Q_{rev}}{T}$

**3<sup>rd</sup> Law:**  $\lim_{T \rightarrow 0} S(T) = 0$  (Nernst's postulate)

can be relaxed to  $s = \frac{S}{N} \rightarrow 0$  as  $T \rightarrow 0$  and  $N \rightarrow 0$

Not as fundamental as other laws: property of QM: groundstate not exponentially degenerate!

Comment:  $\Delta S = \int \frac{C_V}{T} dT \Rightarrow C_V \sim T^\alpha$  as  $T \rightarrow 0$  for integral to converge  $\alpha > 0$

Ideal gas:  $C_V \approx \frac{3}{2} N k_B$  violates 3<sup>rd</sup> Law  $\Rightarrow$  QM needed at low T

### E) Thermodynamic potentials

Many variables:  $p, V, T, S, E, N, \mu, \dots$

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

$$dE = T dS - p dV + \mu dN$$

Enthalpy:  $H = E + pV$

"Legendre transform"

$$dH = T dS + V dp$$

$$H = H(S, p)$$

$p = \text{const}$ :  $\Delta H = Q$  (1<sup>st</sup> Law)  
 $w = -p \Delta V$

useful if  $p = \text{const}$

$$C_V = \left( \frac{\delta Q}{dT} \right)_V = \left( \frac{\partial E}{\partial T} \right)_V, \quad C_P = \left( \frac{\delta Q}{dT} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P$$

ideal gas:  $H = \frac{5}{2} N k_B T$

$$C_P - C_V = N k_B$$

Free Energy:  $F = E - TS$

$$dF = -S dT - p dV$$

$$F = F(T, V)$$

$$\left( \frac{\partial F}{\partial T} \right)_V = -S, \quad \left( \frac{\partial F}{\partial V} \right)_T = -p$$

useful if  $T = \text{const}$

$$dE = -\delta w + \delta Q = -\delta w + T dS - T \delta S_c$$

$\uparrow$  take  $w =$  work performed by the system

$\delta Q$  (2<sup>nd</sup> Law)

$$\Leftrightarrow \delta S_c = - \frac{(dE - T dS + \delta w)}{T} \geq 0 \Leftrightarrow dF \leq -\delta w \quad (T = \text{const})$$

$W \leq -\Delta F$  maximum extractable work at  $T = \text{const}$ .

if  $W=0$  and  $T=const$ :  $\Delta F \leq 0$  (Free energy decreases)

Gibbs Free Energy:  $G = H - TS$  especially useful in chemistry  
 $T$  and  $P$  fixed

$$dG = -SdT + VdP + \mu dN$$

$\uparrow$  reintroduce  $N$  here

extensivity:  $G(T, P, \lambda N) = \lambda G(T, P, N)$  (take  $\frac{d}{d\lambda}(\dots)|_{\lambda=1}$ )  
 $\Rightarrow G = \left(\frac{\partial G}{\partial N}\right)_{T,P} N \Leftrightarrow G = \mu(T, P) N$

$$dG = \cancel{\mu dN} + N d\mu = -SdT + VdP + \cancel{\mu dN}$$

$$\Rightarrow N d\mu = -SdT + VdP$$

Gibbs-Duhem relation

Maxwell's relations:  $dE = TdS - PdV \Rightarrow T = \left(\frac{\partial E}{\partial S}\right)_V$   $P = -\left(\frac{\partial E}{\partial V}\right)_S$

Second derivatives commute:  $\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Physically non-trivial!

$\Rightarrow$  play the same game with  $H, F, G \Rightarrow 4$  relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(no need to remember these relations! very easy to recover them from  $dE = TdS - PdV, F = E - TS, H = E + PV, G = E + PV - TS$ )