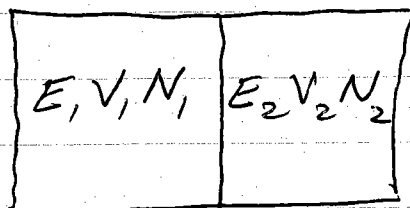## Thermal Equilibrium

$$E = E_1 + E_2$$
$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

↑ immoveable, unpermeable, insulating wall

thermally insulating wall is often called an "adiabatic" wall — no heat can flow across it. (A "diathermal" wall is a wall that can conduct heat.) As long as the wall is in place, the two subsystems cannot exchange energy, volume, or particles.

1) Suppose now that the wall is changed to a thermally conducting one, so the systems can exchange energy? What will be the new E_1 and E_2 after the system equilibrates?

$E = E_1 + E_2$ is a fixed constant by conservation of energy

But E_1 and $E_2 = E - E_1$ can change

$E = E_1 + E_2$ fixed $\Rightarrow dE = dE_1 + dE_2 = 0$

$\qquad\qquad\qquad$ so $\quad dE_2 = -dE_1$

change in entropy $\quad S = S_1 + S_2$ as system equilibrates is then

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2$$

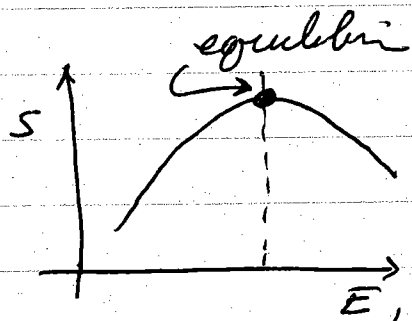$$= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 \qquad\qquad \text{as} \quad dE_2 = -dE_1$$

equilibrium is when $\underline{S \text{ becomes maximum}}$

At the maximum, $dS = 0$, ie S will not change for small changes in dE_1

$$dS = 0 \Rightarrow \boxed{T_1 = T_2}$$

equilibrium

System is in equilibrium when the two subsystems have the same temperature.

<u>Note</u>: $\quad dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE \Rightarrow$ If $T_1 > T_2$ then since system evolves so that $dS > 0$ always (entropy increases as one approaches equilibrium) $\Rightarrow dE_1 < 0$. So energy flows from (1) to (2) ie from higher T_1 to lower T_2. Agrees with our intuition about temperature that heat flows from hot to cold.

Mechanical Equilibrium

2) Now suppose the wall is thermally conducting **AND** it is allowed to slide so that volumes V_1 and V_2 can change.

Still the total volume $V = V_1 + V_2$ is fixed so $V_2 = V - V_1$ and $dV_2 = -dV_1$

We have

$$E = E_1 + E_2 \text{ fixed} \implies dE_2 = -dE_1$$
$$V = V_1 + V_2 \text{ fixed} \implies dV_2 = -dV_1$$

We will also assume that the wall moves **slowly** so that no energy is dissipated in friction of the moving wall

as system equilibrates the change in entropy is

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2$$

$$= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_2$$

$dS = 0$ at equilib so $\Rightarrow$ $T_1 = T_2$
$$P_1 = P_2$$

when volume can change, equilib is reached when pressure of ~~lighter~~ subsystems are equal.

Chemical Equilibrium

3) Now suppose wall becomes conducting, can slide, and is permeable to particles?

$$E = E_1 + E_2 \quad \Rightarrow \quad dE_1 = -dE_2$$
$$V = V_1 + V_2 \quad \Rightarrow \quad dV_1 = -dV_2$$
$$N = N_1 + N_2 \quad \Rightarrow \quad dN_1 = -dN_2$$

tot number N fixed, but N_1 and $N_2 = N - N_1$ vary

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1 V_1} dN_1$$

$$+ \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2 V_2} dN_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1$$

$$dS = 0 \implies T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2$$

when particles can be exchanged, equilib is reached when the subsystems have equal chemical potential.

The role of statistical mechanics is to calculate the entropy from the microscopic details of the system. Once the entropy is known, all thermodynamic properties follow.

Convexity of the Entropy

From postulate II we know S will be maximized whenever a constraint is removed. We can use this to show that S is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall
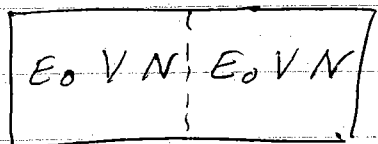
$\frac{E}{2} + \Delta E$	$\frac{E}{2} - \Delta E$
$\frac{N}{2}$ $\frac{V}{2}$	$\frac{N}{2}$ $\frac{V}{2}$

in equilib, $\Delta E = 0$, as the two halfs must have equal energy. But consider how the entropy changes if ΔE is allowed to vary.

Concavity

~~Convexity~~ of the Entropy   Callen Chpt 3 + 5
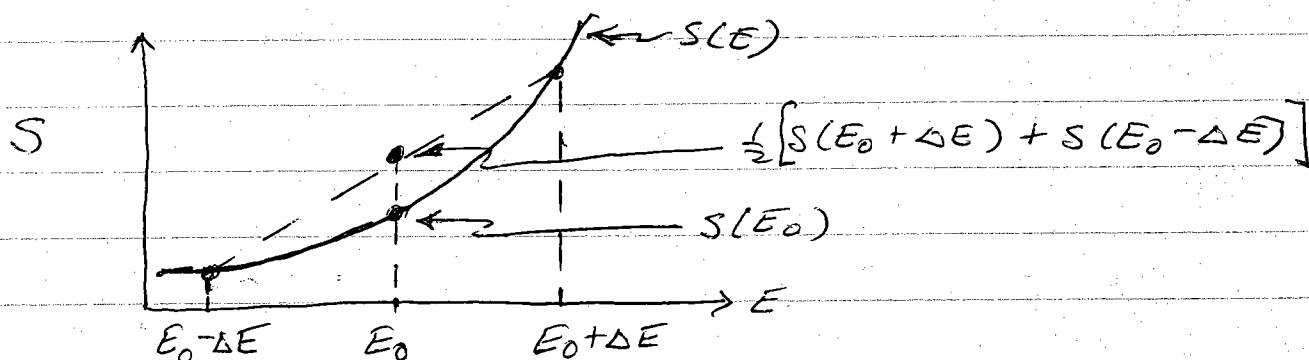
| $E_0 \; V \; N$ | $E_0 \; V \; N$ |

consider a container of gas
conceptually divide into two
equal halves (no physical wall)

If N and V are fixed to be the same on both sides,
we expect the energy will be equal on both sides

$$S^{total} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)$$

Consider how S depends on E. If S were <u>not</u>
a ~~convex~~ concave function of E (ie if $\partial^2 S / \partial E^2 > 0$) then
the system would be unstable as follows:

If S(E) is not ~~convex~~ concave, then we have from above

$$S^{total} = 2S(E_0) < S(E_0 + \Delta E) + S(E_0 - \Delta E)$$

therefore, the total system would <u>increase</u> its
entropy by having the LHS with $E_0 - \Delta E$, and
the RHS with $E_0 + \Delta E$ — the system would
not be stable with equal energies on both sides.

Since, by Postulate II, the systems acts so as to maximize its entropy, we see that the system will be unstable if $S(E)$ is not ~~convex~~ concave.

If $S(E)$ is ~~convex~~ concave, ie $\frac{\partial^2 S}{\partial E^2} < 0$, this does not happen
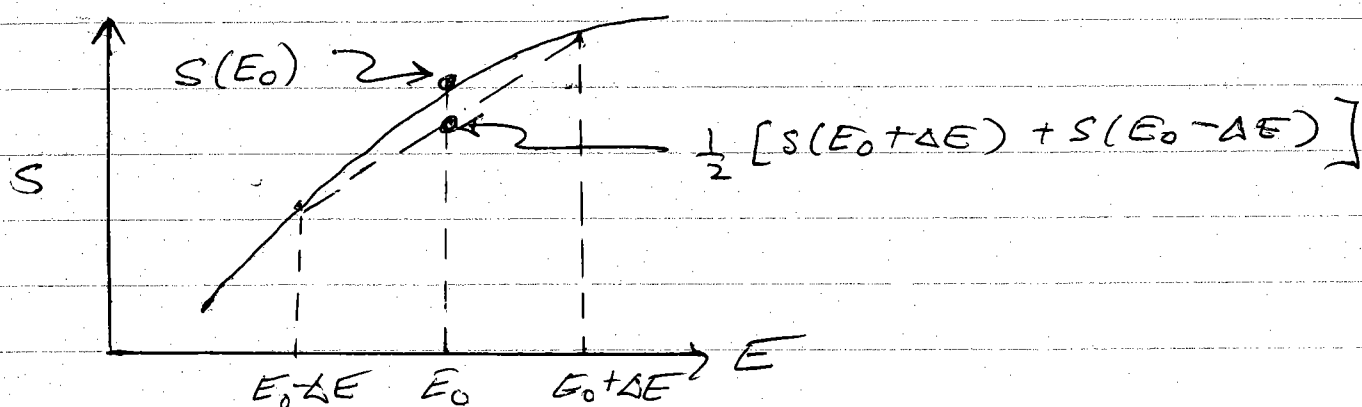
$$S(E_0) \searrow \qquad \frac{1}{2}\left[S(E_0 + \Delta E) + S(E_0 - \Delta E)\right]$$

Now $\qquad 2S(E_0) > S(E_0 + \Delta E) + S(E_0 - \Delta E)$

The maximum total entropy s^{total} will be when both halves have equal energy E_0

$\Rightarrow S(E)$ is ~~convex~~ concave

By similar arguement, S must be a ~~convex~~ concave function of all its variables

$$d^2 S < 0 \qquad\qquad \underline{\text{~~convex~~ concave}}$$

Further consequences of S being a 1st order homogeneous function

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

$$\Rightarrow \quad \lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N) \qquad E \text{ is also a 1st order homogeneous function}$$

differentiate with respect to S.

$$\Rightarrow \quad \lambda \left(\frac{\partial E(S,V,N)}{\partial S} \right)_{V,N} = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial S} \right)$$

$$\Rightarrow \quad \lambda \, T(S,V,N) = T(\lambda S, \lambda V, \lambda N) \, \lambda$$

$$T(S,V,N) = T(\lambda S, \lambda V, \lambda N)$$

similarly from $p = -\left(\frac{\partial E}{\partial V} \right)_{S,N}$ and $\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V}$
we conclude

$$\left. \begin{array}{l} T(S,V,N) = T(\lambda S, \lambda V, \lambda N) \\ p(S,V,N) = p(\lambda S, \lambda V, \lambda N) \\ \mu(S,V,N) = \mu(\lambda S, \lambda V, \lambda N) \end{array} \right\}$$

T, p, μ are homogeneous functions of zeroth order

let $\lambda = \frac{1}{N}$, then

$$\left. \begin{array}{l} T(S,V,N) = T\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = T(s, v) \\ P(S,V,N) = P\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = P(s, v) \\ \mu(S,V,N) = \mu\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = \mu(s, v) \end{array} \right\} \begin{array}{l} \text{"equation} \\ \text{of state} \end{array}$$

T, p, μ are really functions of only <u>two</u> intensive variables $s = S/N$ and $v = V/N$

Since the three variables T, p, μ are all functions of the two variables u, v, there must exist a relation among them — T, p, μ are <u>not independent</u>.

For example, one could imagine taking the two equations $T = T(s, v)$ and $p = p(s, v)$ and solving for s and v in terms of T and p. One could then take this result and substitute it into the third equation $\mu = \mu(s, v)$ to get a relation $\mu = \mu(T, p)$.

The differential form for this constraint on T, p, μ is known as the <u>Gibbs-Duhem</u> relation. We derive it as follows:

<u>Consider:</u>

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

differentiate with respect to λ

$$E(S, V, N) = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial \lambda} \right)$$

$$+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \right)_{\lambda S, \lambda N} \left(\frac{\partial(\lambda V)}{\partial \lambda} \right)$$

$$+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \right)_{\lambda S, \lambda V} \left(\frac{\partial(\lambda N)}{\partial \lambda} \right)$$

$$\Rightarrow \quad E(s,v,N) = T(\lambda s, \lambda v, \lambda N) \, S$$
$$- p(\lambda s, \lambda v, \lambda N) \, V$$
$$+ \mu(\lambda s, \lambda v, \lambda N) \, N$$

Now take $\lambda = 1$,

$$E(s,v,N) = T(s,v,N) \, S - p(s,v,N) \, V + \mu(s,v,N) \, N$$

$(*)$ $\boxed{E = TS - pV + \mu N}$ $\qquad$ Euler relation

or dividing by N

$$u = Ts - pv + \mu$$

Now from the fundamental definitions of T, p, μ we can write

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

$$\Rightarrow dE = TdS - pdV + \mu dN$$

But from $(*)$ above we can write

$$dE = TdS + SdT - pdV - Vdp + \mu dN - Nd\mu$$

Subtracting these two differential relations gives

$$\boxed{\begin{array}{l} SdT - Vdp + Nd\mu = 0 \\[2mm] \text{or} \quad d\mu = -s\,dT + v\,dp \end{array}}$$ $\qquad$ $\underline{\text{Gibbs - Duhem}}$ $\underline{\text{relation}}$

one cannot vary $T, P,$ and μ <u>independently</u>.
The Gibbs - Duhem relation gives the variation of
one in terms of the variation in the other two.

We can also derive a Gibbs - Duhem relation in
the entropy formulation:

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N \qquad \text{from Euler relation}$$

$$\Rightarrow dS = E\,d\left(\frac{1}{T}\right) + \frac{1}{T}dE + V\,d\left(\frac{P}{T}\right) + \frac{P}{T}dV - N\,d\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN$$

but from definitions $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}, \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}, \left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{-\mu}{T}$
we get
$$dS = \left(\frac{1}{T}\right)dE + \left(\frac{P}{T}\right)dV - \left(\frac{\mu}{T}\right)dN$$

combining with the above we get

$$E\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - N\,d\left(\frac{\mu}{T}\right) = 0$$

$$\text{or} \quad d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{P}{T}\right)$$

The fundamental thermodynamic function, which determines all thermodynamic behavior, is the _entropy_

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

as function of the extensive variables E, V, N

or equivalently the total _internal energy_

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

as function of the extensive variable S, V, N

The partial derivatives

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

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

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

give the three "equations of state"

If one knows the three equations of state, then it is equivalent to knowing the fundamental thermodynamic function since by Euler's relation

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

If one knows any two of the equations of state one can find the third by using the Gibbs-Duhem relation

example: The ideal monatomic gas

From expt: $PV = Nk_BT$ $\Rightarrow \frac{P}{T} = \frac{N}{V}k_B = \frac{k_B}{v}$

$E = \frac{3}{2}Nk_BT$ $\Rightarrow \frac{1}{T} = \frac{3}{2}k_B\frac{N}{E} = \frac{3}{2}\frac{k_B}{u}$

if we can find μ, then we have entropy S via

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N$$

From Gibbs-Duhem relation in entropy representation

$$d\left(\frac{\mu}{T}\right) = u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right)$$

$$= u\,\frac{3}{2}k_B\, d\left(\frac{1}{u}\right) + v\, k_B\, d\left(\frac{1}{v}\right)$$

$$d\left(\frac{\mu}{T}\right) = -\frac{3}{2}\frac{k_B}{u}\,du - \frac{k_B}{v}\,dv$$

integrate to get

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2}k_B\ln\left(\frac{u}{u_0}\right) - k_B\ln\left(\frac{v}{v_0}\right)$$

where u_0 at v_0 are some reference state, and $\left(\frac{\mu}{T}\right)_0$ is an unknown constant of integration. Then one gets

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N = \frac{3}{2}\frac{k_B E}{(E/N)} + \frac{k_B V}{(V/N)}$$

$$+ \frac{3}{2}Nk_B\ln\left(\frac{u}{u_0}\right) + k_B N\ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N$$

$$S = \frac{3}{2}k_B N + k_B N - \left(\frac{\mu}{T}\right)_0 N + Nk_B\ln\left[\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right]$$

use $E = uN$, $E_0 \equiv u_0 N_0$, $V = vN$, $V_0 \equiv v_0 N_0$

$$\Rightarrow \quad \boxed{S(E,V,N) = \frac{N}{N_0} S_0 + N k_B \ln\left[\left(\frac{E}{E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right]}$$

where $S_0 = \frac{5}{2} k_B N_0 + \left(\frac{\mu}{T}\right)_0 N_0$ is a constant

So from experimental knowledge of two of the equations of state $\frac{1}{T}$ and $\frac{P}{T}$ as functions of E, N, V, we have derived the entropy $S(E,V,N)$. All behaviors of the ideal gas can now be deduced from knowledge of S.

Alternatively, we could derive $s = \frac{S}{N}$ as follows:

$$E = TS - pV + \mu N \quad \Rightarrow \quad S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N$$

$$\Rightarrow \quad s = \frac{u}{T} + \frac{P}{T}v - \frac{\mu}{T} \qquad \text{where } u = \frac{E}{N}, \ v = \frac{V}{N}$$

$$ds = \frac{1}{T}du + \frac{P}{T}dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right) - d\left(\frac{\mu}{T}\right)}$$

these cancell due to the Gibbs-Duhem relation as expressed in the entropy formulation

So

$$\Rightarrow \quad \boxed{ds = \frac{1}{T}du + \frac{P}{T}dv}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

$$= \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv \qquad \text{since} \begin{cases} \frac{1}{T} = \frac{3}{2} \frac{k_B}{u} \\ \frac{P}{T} = \frac{k_B}{v} \end{cases}$$

integrate

$$s - s_0 = \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

$$\boxed{s = s_0 + k_B \ln \left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right) \right]}$$

substitute in $S = Ns$, $\quad E = Nu$, $\quad V = Nv$

$$S_0 = N_0 s_0 \;,\quad E_0 = N_0 u_0 \;,\quad V_0 = N_0 v_0$$

and we recover the earlier result for $S(E, V, N)$