Thermal Equilibrium

\[ E = E_1 + E_2 \]
\[ S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \]

...impossible, impermeable, 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.
\[ E = E_1 + E_2 \text{ fixed} \Rightarrow dE = dB_1 + dB_2 = 0 \]

so \( dB_2 = -dB_1 \)

Change in entropy \( S = S_1 + S_2 \) as system equilibrates is then

\[
ds = \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1N_1} dB_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2N_2} dB_2
\]

\[
= \frac{1}{T_1} dB_1 + \frac{1}{T_2} dB_2
\]

\[
= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dB_1 \quad \text{as} \quad dB_2 = -dB_1
\]

Equilibrium is when \( S \) becomes maximum.

At the maximum, \( dS = 0 \), so \( S \) will not change for small changes in \( dB_1 \),

\[
ds = 0 \Rightarrow \boxed{ T_1 = T_2 }
\]

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

Note: \( dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dB \Rightarrow \text{If } T_1 > T_2 \text{ then since system evolves so that } dS > 0 \text{ always (entropy increases as one approaches equilibrium),}
\]

\( dB_1 < 0 \). So energy flows from (1) to (2) i.e. from higher \( T_1 \) to lower \( T_2 \). Agrees with our intuition about temperature 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 $V = V_1 + V_2$ fixed \Rightarrow dV_2 = -dV_1$

We have

$E = E_1 + E_2$ fixed \Rightarrow dE_2 = -dE_1$

$V = V_1 + V_2$ fixed \Rightarrow 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

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

\[ = \frac{T_1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 + \frac{T_2}{T_2} dE_2 + \frac{P_2}{T_2} dV_2 \]

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

\[ dS = 0 \text{ at equilibrium so } \Rightarrow T_1 = T_2, \quad P_1 = P_2 \]

When volume can change, equilibrium reached when pressure of separate subsystems are equal.

Chemical equilibrium.

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

\[ E = E_1 + E_2 \Rightarrow dE_1 = -dE_2 \]

\[ V = V_1 + V_2 \Rightarrow dV_1 = -dV_2 \]

\[ N = N_1 + N_2 \Rightarrow dN_1 = -dN_2 \]

Let number \( N \) fixed, but \( N_1 \) and \( N_2 = N-N_1 \) vary

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

\[ + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_{N_2}} dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_{N_2}} dV_2 + \left( \frac{\partial S_2}{\partial N_2} \right)_{E_{N_2}} dN_2 \]
\[(\frac{1}{T_1} - \frac{1}{T_2})dE_1 + (\frac{P_1}{\mu_1} - \frac{P_2}{\mu_2})dV_1 - (\frac{N_1}{\mu_1} - \frac{N_2}{\mu_2})dN_1\]

dS = 0 \Rightarrow T_1 = T_2, \ p_1 = p_2, \ \mu_1 = \mu_2

When particles can be exchanged, equilibrium 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 1, 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 is conceptually split in half (no physical wall in reality), \(\Delta E = 0\), as the two halves must have equal energy. But consider how the entropy changes if \(\Delta E\) is allowed to vary.
Concavity of the Entropy

Consider a container of gas conceptually divided 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

\[
S_{\text{total}} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)
\]

Consider how \( S \) depends on \( E \). If \( S \) were not a convex function of \( E \) (i.e., if \( \frac{d^2S}{dE^2} \geq 0 \)) then the system would be unstable as follows:

\[
S = \frac{1}{2} [S(E_0 + \Delta E) + S(E_0 - \Delta E)]
\]

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

\[
S_{\text{total}} = 2S(E_0) \leq S(E_0 + \Delta E) + S(E_0 - \Delta E)
\]

Therefore, the total system would increase 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 system acts so as to maximize its entropy, we see that the system will be unstable if $S(E)$ is not concave.

If $S(E)$ is concave, i.e. $\frac{d^2S}{dE^2} < 0$, this does not happen.

$$\frac{1}{2} [S(E_0 + \Delta E) + S(E_0 - \Delta E)]$$

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

The maximum total entropy $S_{\text{total}}$ will be when both halves have equal energy $E_0$.

$\Rightarrow S(E)$ is **concave**

By similar argument, $S$ must be a **concave** function of all its variables.

$\Rightarrow d^2S < 0$ **concave**
Further consequences of $S$ being a 1st order homogeneous function

\[ T(S, V, N) = S(\lambda S, \lambda V, \lambda N) \]

\[ \Rightarrow \lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N) \]

$E$ is also a 1st order homogeneous function

differentiate with respect to $S$.

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

\[ \Rightarrow \lambda T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \lambda \]

\[ T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \]

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

\[ T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \]

\[ p(S, V, N) = p(\lambda S, \lambda V, \lambda N) \]

\[ \mu(S, V, N) = \mu(\lambda S, \lambda V, \lambda N) \]

$T$, $p$, $\mu$ are homogeneous functions of zeroth order

let \( \lambda = \frac{1}{N} \), then

\[ T(S, V, N) = T\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = T(s, v) \]

\[ p(S, V, N) = p\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = p(s, v) \]

\[ \mu(S, V, N) = \mu\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = \mu(s, v) \]
\( T, \ p, \ \mu \) are really functions of only two intensive variables \( s = s(N) \) and \( v = v(N) \).

Since the three variables \( T, p, \mu \) are all functions of the two variables \( u, v \), there must exist a relation among them — \( T, p, \mu \) are not independent.

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 \( T, p, \mu \) is known as the Gibbs—Duhem relation. We derive it as follows:

Consider:

\[
\Delta E(s, v, N) = E(\Delta s, \Delta v, \Delta N)
\]

differentiate with respect to \( \Delta \)

\[
E(s, v, N) = \left( \frac{\partial E(s, v, N)}{\partial s} \right)_{\Delta v, \Delta N} \left( \frac{\partial (s)}{\partial v} \right)_{s, \Delta N} + \left( \frac{\partial E(s, v, N)}{\partial v} \right)_{\Delta s, \Delta N} \left( \frac{\partial (v)}{\partial s} \right)_{s, \Delta v} + \left( \frac{\partial E(s, v, N)}{\partial \Delta N} \right)_{\Delta s, \Delta v} \left( \frac{\partial (\Delta N)}{\partial s} \right)_{s, \Delta v} + \left( \frac{\partial E(s, v, N)}{\partial \Delta s} \right)_{\Delta s, \Delta v} \left( \frac{\partial (\Delta s)}{\partial v} \right)_{s, \Delta v} + \left( \frac{\partial E(s, v, N)}{\partial \Delta v} \right)_{\Delta s, \Delta N} \left( \frac{\partial (\Delta v)}{\partial s} \right)_{s, \Delta N} \]

or

\[
\Delta E(s, v, N) = \left( \frac{\partial E(s, v, N)}{\partial s} \right)_{\Delta v, \Delta N} \Delta s + \left( \frac{\partial E(s, v, N)}{\partial v} \right)_{\Delta s, \Delta N} \Delta v + \left( \frac{\partial E(s, v, N)}{\partial \Delta N} \right)_{\Delta s, \Delta v} \Delta \Delta N
\]
\[ \Rightarrow E(s, v, N) = T(s, v, N) S - p(s, v, N) V + \mu(s, v, N) N \]

Now take \( \lambda = 1 \),

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

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

or dividing by \( N \)

\[ u = T - pV + \mu \]

Now from the fundamental definitions of \( T, p, \mu \) we can write

\[ dE = \left( \frac{\partial E}{\partial s} \right)_{s, N} ds + \left( \frac{\partial E}{\partial v} \right)_{s, N} dv + \left( \frac{\partial E}{\partial N} \right)_{s, V} dN \]

\[ \Rightarrow \quad dE = -TdS - pdV + \mu dN \]

But from \((*)\) above we can write

\[ dE = -TdS + SdT - pdV - Vdp + \mu dN - Ndp \]

Subtracting these two differential relations gives

\[ SdT - Vdp + Ndp = 0 \]

or

\[ d\mu = -SdT + Vdp \]

\boxed{\text{Gibbs-Duhem relation}}
one cannot vary \( T, p, \) and \( \mu \) independently.

The Gibbs-Duhem relation gives the variation of one in terms of the variations in the other two.

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

\[
S = \frac{E}{T} + \frac{F}{T} V - \frac{\mu}{T} N \quad \text{from Euler relation}
\]

\[
\Rightarrow \; dS = E \frac{d(1/T)}{} + \frac{1}{T} dE + V \frac{d(\frac{F}{T})}{T} + \frac{F}{T} dV - \frac{\mu}{T} dN
\]

But from definitions \( \frac{dS}{dE}_{V,N} = \frac{1}{T} \), \( \frac{dS}{dV}_{E,N} = \frac{F}{T} \), \( \frac{dS}{dN}_{E,V} = -\frac{\mu}{T} \)

we get

\[
dS = \left( \frac{1}{T} \right) dE + \left( \frac{F}{T} \right) dV - \left( \frac{\mu}{T} \right) dN
\]

Combining with the above we get

\[
E \frac{d(1/T)}{} + V \frac{d(\frac{F}{T})}{T} - N \frac{d(\frac{\mu}{T})}{T} = 0
\]

or

\[
\frac{d(\frac{\mu}{T})}{} = \nu \frac{d(\frac{1}{T})}{T} + \omega \frac{d(\frac{F}{T})}{T}
\]
Summary

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

\[ S(E,V,N) \]

as a function of the extensive variables

\[ E, V, N \]

or equivalently the total internal energy

\[ E(S,V,N) \]

as a function of the extensive variables

\[ S, V, N \]

The partial derivatives

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

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

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

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 exp.: \( PV = Nk_B T \) \( \Rightarrow \frac{P}{T} = \frac{N}{V} k_B = \frac{k_B}{\frac{V}{N}} \)

\( E = \frac{3}{2} Nk_B T \) \( \Rightarrow \frac{1}{T} = \frac{3}{2} k_B N \frac{E}{E} = \frac{3}{2} \frac{k_B}{\frac{V}{N}} \)

If we can find \( \mu \), 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

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

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

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

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

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

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

\[ S = \frac{3}{2} k_B N + k_B N - \left( \frac{\mu}{T} \right)_0 + Nk_B \ln \left[ \left( \frac{u}{u_0} \right)^{3/2} \left( \frac{v}{v_0} \right) \right] \]
\[ E = uN, \quad E_0 = u_0 N_0, \quad V = vN, \quad V_0 = v_0 N_0 \]

\[ S(E,V,N) = \frac{N}{N_0} S_0 + N k_b \ln \left[ \left( \frac{E}{E_0} \right)^{\frac{3}{2}} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-\frac{5}{2}} \right] \]

where \( S_0 = \frac{5}{2} k_b N_0 + \frac{(\mu T)}{N_0} N_0 \) is a constant.

So from experimental knowledge of two of the

equations of state \( P = \frac{E}{V} \) 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 \( a = \frac{s}{N} \) as follows:

\[ E = TS - PV + \mu N \implies S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N \]

\[ \implies a = \frac{\mu}{T} + \frac{P}{T} V - \frac{\mu}{T} \quad \text{where} \quad u = \frac{E}{N}, \quad v = \frac{V}{N} \]

\[ da = \frac{1}{T} du + \frac{P}{T} dv + ud(\frac{1}{T}) + vd(\frac{P}{T}) - d(\frac{\mu}{T}) \]

These cancel due to the

Gibbs-Duhem relation as

expressed in the entropy

formulation.

\[ \implies da = \frac{1}{T} du + \frac{P}{T} dv \]
\[ ds = \frac{1}{T} \, du + \frac{P}{T} \, dv \]

\[ = \frac{3}{2} \frac{k_B}{u} \, du + \frac{k_B}{u} \, dv \quad \text{since} \quad \frac{1}{T} = \frac{3}{2} \frac{k_B}{u} \]

\[ \frac{P}{T} = \frac{k_B}{u} \]

Integrate

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

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

Substitute \( S = N A, \) \( E = N u, \) \( V = N v \)

\[ s_0 = N_0 A_0, \] \( E_0 = N_0 u_0, \) \( V_0 = N_0 v_0 \)

Then we recover the earlier result for \( S(E, V, N) \)