Thermodynamics

The idea of this first part is to give a very brief overview of thermodynamics, introducing some concepts that will be important in the later development of this class

Let us then define a generic system comprised of N particles (that interact with each other)

a) We will disregard any potential energy

b) We will ignore (for now) interaction with an Electromagnetic Field } just to make things simpler

Hamiltonian for the system

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j)$$

both classical and quantum mechanical

If we were able to "solve" the problem by either calculating

$\{ \vec{r}(t), \vec{p}(t) \}$ → classical mechanics

Solving Newton's, or Hamilton's or Lagrange's equation of motion

or

$|\Psi(\vec{r}_1, \ldots \vec{r}_N)(t)\rangle$ → quantum mechanics

Solving Schroedinger's equation

We would find the so-called microstate ≡ the microscopic configuration of the system

Let's however suppose that we have very large number of particles (say of the order of Avogadro's number $\sim 10^{23}$)

Then, besides it's energy, the number of particles, we can also define the volume V that encloses all the particles

If the number of particles is large and we define a small unit of volume ΔV that is small compared with V, but at a given time t contains a large number of particles, we can calculate averages of a number of microstates

We thus define global macroscopic variables that describe the so-called macrostate

Obs: the microstates will not be ignored in our macroscopic approach, we will instead assume a probabilistic approach to treat them in order to build the macrostate (if the sample is "large enough")

Going back to our Hamiltonian we consider that a system is isolated if its energy is conserved → this means it is independent of time

But we go further and define the concept of thermodynamic equilibrium

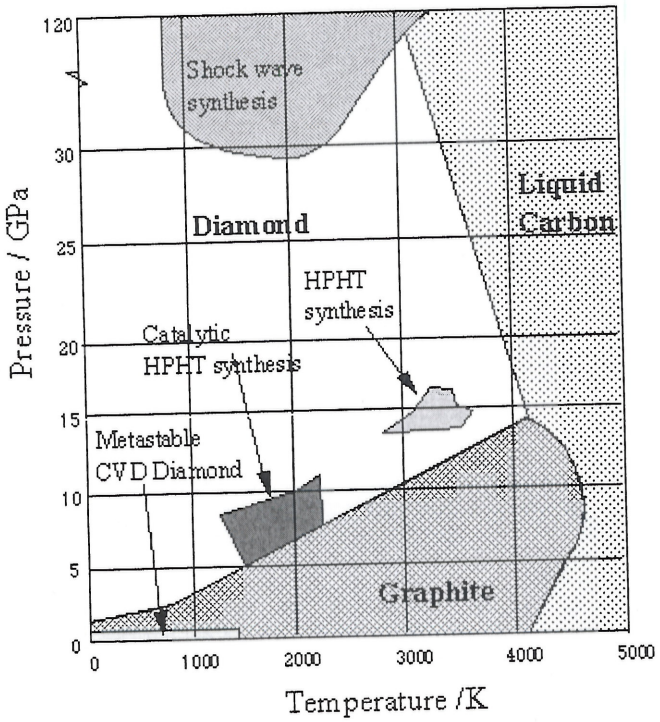
Postulate I [Callen]: There exist states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by internal energy U, the volume V and the mole numbers $N_1, \ldots, N_r$

What this means is that they do not depend on the past history of the system (a previously applied external influence, for example) and are, by definition, time independent

Obs: the number of parameters required to describe equilibrium increases as we allow for more complicated mechanical and electrical properties.

These equilibrium states are hard to determine experimentally because the ammount of time it takes for the system to go to these equilibrium states can be very long

Diamonds are not forever!!!

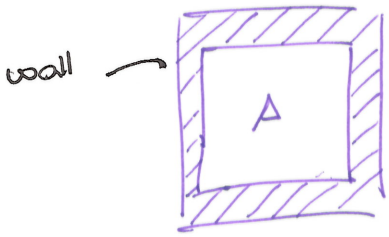


equilibrium in practice: a system is said to be in equilibrium if its properties can be described by thermodynamic theory

Circular argument - practical! We assume that the theory is correct. If it is not described by the theory, something is missing from the model, not the theory.

Let's now go back to the concept of an isolated system. How can we isolate the system from the rest of the environment?

A: a container

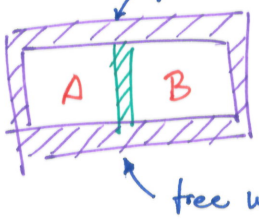


But this container must have special properties that will isolate it from the outside world

We then define a "wall" that separates our system from its surroundings

Manipulations of these walls will allow for the redistribution of some quantity associated with the system

Example: Suppose two systems A and B isolated from the rest of the environment and separated from each other by a wall with specific properties



fixed wall → prevents redistribution of volume ⇒ restrictive with respect to volume

free wall → redistribution of volume is permitted → irrestrictive with respect to volume

Some special kinds of walls

diathermal: permits the flow of energy (that we will later call heat), but not the flow of molecules/particles

adiabatic: impermeable to the flow of heat

The importance of walls then is that they will allow the control of internal energy in some form

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With that in mind we can define the concept of thermal equilibrium

Zeroth law of thermodynamics: If bodies A and B are each in equilibrium with a third body C, then they are in thermal equilibrium with each other

This means we can define a quantity associated with thermal equilibrium ⇒ the temperature

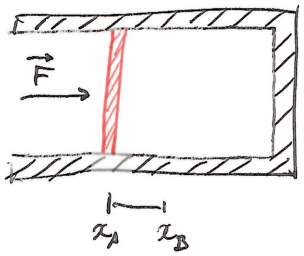
and temperature can be measured by using a - calibrated - measuring apparatus that is in thermal equilibrium with the object you want to measure the temperature from.

Thermodynamic equilibrium → (true) thermal equilibrium

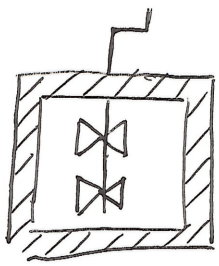
thermal equilibrium → (not necessarily true) Thermodynamic equilibrium

Now let's look at a few examples where we might have some energy exchange between the system and its surroundings

case I



case II



In the first case, if we consider that the force acts "slow enough" we can calculate the work done by the force on the piston

$$\delta W = F(x)\,dx$$

$$W_{A\to B} = \int_{x_A}^{x_B} F(\vec{x})\,dx$$

In both cases some external parameter is altered

- ↳ volume (case I)
- ↳ rotation of the paddles (case II)

case III

"hot" coffee cup cools down!

no change in external parameters ⟶ ⇒ another form of energy transfer (heat)

Two types of energy transfer [Le Bellac]

Work → one or more external parameters are altered (controlled by the experimentalist)

Heat → characterized by the fact that neither the external parameter of the system, nor the configuration of the external medium are modified

Now let's suppose we two systems with equal mole numbers

We pose the following question

Is it possible to figure out a solely mechanical process (thus adiabatic → with no heat transfer) that takes me from A to B ?

Answer: It is possible that this process does not exist

But Joule noted that there exists a solely mechanical process that takes us from either A to B or B to A

[We will later see that this concept of irreversibility is associated with this asymmetry]

Conclusion: using adiabatic walls and by measuring only mechanical work, the energy of any thermodynamic system relative to an appropriate reference can be measured

The internal energy of a system in thermodynamical equilibrium does not depend on history (it only depends on the configuration of A and B)

We are now in a position to make a quantitative definition of heat

The heat flux to a system in any process (at constant mole numbers) is the difference in internal energy between final and initial states minus the work done in that process

In differential form

$$đQ = dU - đW$$

imperfect differential → depends on the process

「First law of thermodynamics」

Example

a) Work is done in the form of a change in volume (e.g. piston)

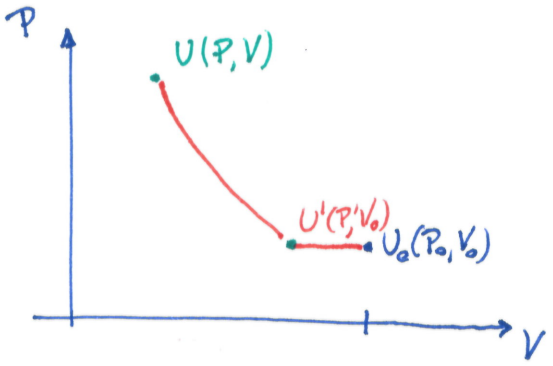
b) A transformation with constant volume from P_0 to P'

$$Q' = A(P' - P_0)$$

c) The adiabats in the system follow $PV^\gamma = \text{constant}$

Solution: In a P-V diagram

Question: find $U(P,V)$ $\forall P,V$



When only changes in volume provide work, a transformation for fixed volume $W = 0$

Following the adiabat $Q = 0$

For the internal energy, the path is not important so

$$U - U_0 = \underbrace{(U - U')}_{\text{adiabat}} + \underbrace{(U' - U_0)}_{\text{no work}}$$

$$= -\int_{V_0}^{V} P\,dV + A(P' - P_0) = -\int_{V_0}^{V} \frac{C}{V^\gamma}\,dV + A\left[P\left(\frac{V}{V_0}\right)^\gamma - P_0\right]$$

along the adiabat

$PV^\gamma = C$ and $P = \frac{C}{V^\gamma}$

$PV^\gamma = P'V_0^\gamma$

$$U(P,V) - U_0(P_0,V_0) = \frac{C}{(\gamma-1)} V^{-(\gamma-1)} \Big|_{V_0}^{V} + A\left[P\left(\frac{V}{V_0}\right)^{\gamma} - P_0\right]$$

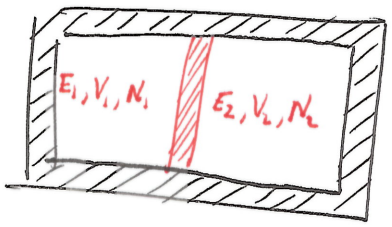
$$- A\left[P\left(\frac{V}{V_0}\right)^{\gamma} - P_0\right] + \frac{P}{\gamma-1}\left[V - V_0\right]$$

$$- A\left[P\left(\frac{V}{V_0}\right)^{\gamma} - P_0\right] + \frac{P}{\gamma-1}\left[\left(\frac{V}{V_0}\right) - 1\right]$$

The central problem in thermodynamics

[Callen]: The single all-encompassing problem of thermodynamics is the determination of the equilibrium state that results after the removal of internal constraints in a closed, composite system

Example:



$E = E_1 + E_2 \qquad V = V_1 + V_2 \qquad N = N_1 + N_2$

Quantities are said to be extensive if we merge two identical systems in equilibrium, the quantities are doubled

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If the piston is fixed

- $W = 0$ no work $\Leftarrow$ fixed
- $Q = 0 \Leftarrow$ adiabatic
- no flow $\Leftarrow$ impermeable of particles

Postulates (equivalent to the second law of thermodynamics)

I) For any system at equilibrium there exists a ~~function that is~~ positive and differentiable entropy function

$$S(E, V, N^{(1)} \dots N^{(r)})$$

In general, it increases as a function of E for fixed V and $N^{(i)}$

II) For a system made of M subsystems, S is additive, or extensive: the total entropy is the sum of the entropies of the individual systems

$$S_{tot} = \sum_{m=1}^{M} S(E_m, V_m, N_m^{(1)}, \dots, N_m^{(r)})$$

III) If we have a global isolated system that is divided into subsystems, each of which at equilibrium. If we lift some or all the constraints, the entropy of the final (and new equilibrium) system must be greater than or equal to the initial entropy

The entropy of an isolated system cannot decrease!

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We now introduce the notion of a quasi-static process

A process is quasi-stati if it is always infinitesimaly close to equilibrium

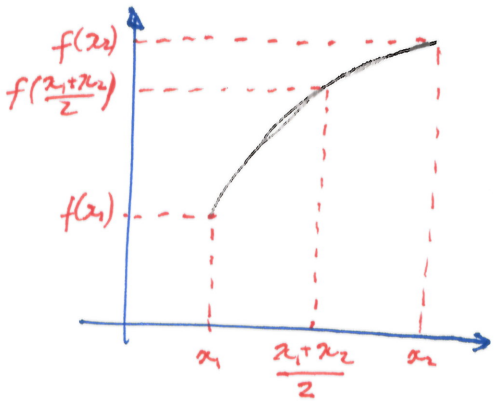
$$\Rightarrow S = S(t)$$

In general, for a non-equilibrium process, one cannot define a unique entropy, but, in many cases the system can be divided into subsystems which are locally in equilibrium, and we deal with the system with the help of postulate (II)

For a homogenous system, the entropy is a concave function of the variables (E, V, N)

For a concave function $f(x)$

$$f''(x) \leq 0$$



$x_2 > x_1$

$$f'\left(\frac{x_1+x_2}{2}\right) \approx \frac{f\left(\frac{x_1+x_2}{2}\right) - f(x_1)}{\frac{x_1+x_2}{2} - x_1} -$$

$$f'(x_2) \approx \frac{f(x_2) - f\left(\frac{x_1+x_2}{2}\right)}{x_2 - \frac{x_1+x_2}{2}}$$

$$f''(x_2) \approx \frac{\frac{f(x_2) - f\left(\frac{x_1+x_2}{2}\right)}{\frac{x_2-x_1}{2}} - \frac{f\left(\frac{x_1+x_2}{2}\right) - f_1(x_1)}{\frac{x_2-x_1}{2}}}{\frac{x_2-x_1}{2}}$$

$$= \frac{f(x_2) + f(x_1) - 2f\left(\frac{x_1+x_2}{2}\right)}{\left(\frac{x_2-x_1}{2}\right)^2} \leq 0$$

≥ 0

$$\Rightarrow \quad f(x_2) + f(x_1) - 2f\left(\frac{x_1+x_2}{2}\right) \leq 0$$

$$\Rightarrow \quad f\left(\frac{x_1+x_2}{2}\right) \geq \frac{f(x_2) + f(x_1)}{2}$$

Let's however assume that it is actually convex on the energy (around $\{E-\Delta E, E+\Delta E\}$)

$$\Rightarrow \quad S\left(\frac{E-\Delta E + E+\Delta E}{2}\right) < \frac{S(E-\Delta E) + S(E+\Delta E)}{2}$$

$$2S(E) < S(E-\Delta E) + S(E+\Delta E)$$

additivity of S

$$S(2E) < S(E-\Delta E) + S(E+\Delta E)$$

$\Rightarrow$ an entropy increase would be possible if we applied a constraint on the energy

$\Rightarrow$ two systems with different energies

$\Rightarrow$ inhomogeous $\rightarrow$ contradicts our initial hypothesis

$\Downarrow$

phase transition

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Since $S(U, V, N_1 \dots N_r)$ is continuous, differentiable and monotonic we can find the inverse function (with respect to U)

$$U(S, V, N_1, \dots N_r)$$

In differential form

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1 \dots N_r} dV + \sum_{j=1}^{r} \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_1 \dots N_{j-1}, N_{j+1}, N_r} \quad (1)$$

I then define the intensive parameters

$$\left(\frac{\partial U}{\partial S}\right)_{S,N_1,\dots N_r} \equiv T$$ the temperature

$$\left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots N_r} \equiv P$$ the pressure

$$\left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_1,\dots N_{j-1},N_{j+1},\dots N_r} \equiv \mu_j$$ the electrochemical potential of the j-th component

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We can do something similar for S

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N_1,\dots N_r}}_{\frac{1}{T}} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N_1,\dots N_r} dV + \sum_{j=1}^{r}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_1,\dots N_{j-1},N_{j+1},\dots N_r} dN_j \qquad (2)$$

reorganizing everything

$$dU = \frac{1}{\left(\frac{\partial S}{\partial U}\right)_{V,N_1,\dots N_r}}\left[dS - \left(\frac{\partial S}{\partial V}\right)_{U,N_1,\dots N_r} dV - \sum_{j=1}^{r}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_1,\dots N_{j-1},N_{j+1},\dots N_r} dN_j \right]$$

By comparison with eq. (1)

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_1,\dots N_r} = \frac{1}{T}$$

$$-\frac{\left(\partial S/\partial V\right)_{U,N_1,\dots N_r}}{\left(\partial S/\partial U\right)_{V,N_1,\dots N_r}} = +\left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots N_r} = -P$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N_1,\dots N_r} = \frac{P}{T}$$

$$\frac{-\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_1,\dots N_{j-1},N_{j+1},\dots N_r}}{1/T} = \mu_j \quad \forall j$$

$$\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_1,\dots N_{j-1},N_{j+1},\dots N_r} = -\frac{\mu_j}{T}$$

Thermal equilibrium

Let's go back to our two systems separated by a piston. Let's make each system initially in equilibrium

$$\Rightarrow \quad S_1(E_1, V_1) = S(E_1, V_1, N_1)$$
$$S_2(E_2, V_2) = S(E_2, V_2, N_2)$$

(for simplicity I'll use just one type of particle → easy to generalize)

diathermic piston (no change of volume, no flow of particles ⇒ exchange of energy)

from Postulate II

$$dS = \left.\frac{\partial S_1}{\partial E_1}\right|_{V_1} dE_1 + \left.\frac{\partial S_2}{\partial E_2}\right|_{V_2} dE_2$$

the new equilibrium will be reached when we reach maximum entropy i.e. $dS = 0$

conservation of energy ⇒ $E = E_1 + E_2 = \text{constant}$
⇒ $dE = 0$ and $dE_1 = -dE_2$

$$\Rightarrow \left[\underbrace{\left.\frac{\partial S_1}{\partial E_1}\right|_{V_1}}_{\frac{1}{T_1}} - \underbrace{\left.\frac{\partial S_2}{\partial E_2}\right|_{V_2}}_{\frac{1}{T_2}}\right] dE_1 = 0$$

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \Rightarrow \quad \boxed{T_1 = T_2}$$

flow of heat leads to equal temperatures ⇓ thermal equilibrium

(i) Let's suppose the initial temperatures are T_1' and T_2' in such a way that $T_2' > T_1'$

(ii) Let's also suppose that $E_1' > E_1 \Rightarrow T_1' > T_1$

from energy conservation

$$E_2 > E_2'$$
$$\Rightarrow T_2 > T_2'$$

consequently

$$T_2 > T_2' > T_1' > T_1 \Rightarrow T_2 > T_1 \Rightarrow$$ there can be no thermal equilibrium

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Thus we require

$E_1 > E_1'$ and $E_2 < E_2'$

energy (heat) flows from the ~~colder~~ hotter to the ~~hotter~~ colder system

Note: what happens when/if $\frac{\partial^2 S}{\partial E^2} = 0$ → this means the energy does not change the temperature

↓

phase transition

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Mechanical equilibrium

piston is diathermal and mobile

$$dS = \left.\frac{\partial S_1}{\partial E_1}\right|_{V_1} dE_1 + \left.\frac{\partial S_2}{\partial E_2}\right|_{V_2} dE_2 + \left.\frac{\partial S_1}{\partial V_1}\right|_{E_1} dV_1 + \left.\frac{\partial S_2}{\partial V_2}\right|_{E_2} dV_2 = 0$$

$E = E_1 + E_2 = \text{const} \Rightarrow dE = 0$ and $dE_1 = -dE_2$

$V = V_1 + V_2 = \text{constant} \Rightarrow dV = 0$ and $dV_1 = -dV_2$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 = 0$$

independent variables

$$\Rightarrow \quad \frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \text{and} \quad \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0$$

$$T_1 = T_2 \Rightarrow P_1 = P_2$$

the compartment with the higher pressure increases the volume

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Chemical potential

piston is diathermic, fixed and permeable

$$dS = \left(\left.\frac{\partial S}{\partial E_1}\right|_{V_1, N_1^{(i)}} dE_1 + \left.\frac{\partial S}{\partial E_2}\right|_{V_2, N_2^{(i)}} dE_2 \right) +$$

$$\sum_i \left(\left.\frac{\partial S}{\partial N_1^{(i)}}\right|_{E_1, V_1, N_1^{(j\neq i)}} dN_1^{(i)} + \left.\frac{\partial S}{\partial N_2^{(i)}}\right|_{E_2, V_2, N_2^{(j\neq i)}} dN_2^{(i)} \right) = 0$$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 - \left(\frac{\mu_1^{(i)}}{T_1} - \frac{\mu_2^{(i)}}{T_2}\right) dN_1^{(i)} = 0$$

independent variables

$$T_1 = T_2 \qquad \mu_1^{(i)} = \mu_2^{(i)} \quad \forall i$$

We can then rewrite the first law for the case of quasi-static processes

$$dE = TdS + dW$$

From the principle of maximal entropy

$$S_{final} \geq S_{initial}$$

This means that

$A \rightleftharpoons B$ only exists if $S_{final} = S_{initial}$

i.e. $dS = 0$

and from

$$dQ = TdS \Rightarrow dQ = 0$$

We now go back to our definition

$$\left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T} \quad \Rightarrow \quad \frac{1}{T} = f_T(E,V)$$

for fixed number of particles

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T} = f_P(E,V)$$

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We have also noted that $E = E(T,V)$

$$\Rightarrow P = T f_P(E(T,V),V) = h(T,V) \rightarrow \text{equation of state}$$

—//—

Going back to equation (2)

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

for a single type of particle

$$\Rightarrow TdS = dU + PdV - \mu dN$$

Using equation (1)

$$dE = TdS - PdV + \mu dN$$

For a quasi-static process with N and V fixed

$$dE = TdS = dQ$$

↑ no work is done