

## Thermodynamics - Callen Chpt 1 and 2

- system with  $10^{23}$  degrees of freedom
- we are not interested in the microscopic details, but only in average macroscopic properties.
- assume that there exists a set of macroscopic variables, in terms of which the macroscopic behavior is completely described

for example: for a gas of particles one has

$E$	total <sup>internal</sup> energy	} <u>extensive variables</u> - grows proportional to size of system
$V$	volume	
$N$	total number of particles	

for another system there might be additional variables

ex: ferromagnets:  $E, V, N, \vec{M}$   $\vec{M}$  total magnetization

ferroelectrics:  $E, V, N, \vec{P}$   $\vec{P}$  total polarization

The first step is always to identify the relevant macroscopic variables.

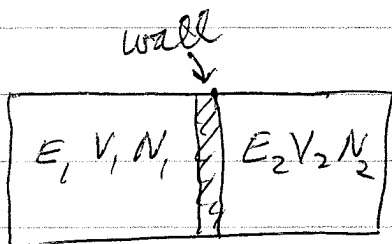
Thermodynamics can be reduced to a set of postulates, from which all other results can be derived. (just like Newton's laws determine the results for classical mechanics)

## Postulate I

there exist equilibrium states characterized completely by  $E, V, N$

criteria for equilibrium: time independent  
does not depend on history

we are interested here only in equilibrium states



## Basic question of thermodynamics

two systems in equilibrium,  
separated by a wall (a constraint)  
what happens if the wall is  
removed (constraint relaxed)?

## Postulate II

There exists a function of the extensive macroscopic variables, called the entropy  $S$ .  
The value of  $S$  is maximized when a constraint is removed.

## Postulate III

The entropy  $S$  is additive over subsystems.  
 $S$  is a continuous and differentiable and increasing function of the total internal energy  $E$ .



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

$$S = S_1 + S_2$$

$$\left(\frac{\partial S}{\partial E}\right)_{V, N} > 0$$

monotonic  
increasing  
in  $E$

(alternatively, additivity of entropy is only strictly valid in the limit of large system sizes)

Note: additivity of subsystems is only valid when one has short range interactions, so that

$$E = E_1 + E_2$$

more generally,  $E = E_1 + E_2 + E_{12}$  ← interaction energy between subsystem 1 and 2

$E_1$	$E_2$
$V_1$	$V_2$

but  $E_1 \sim V_1$ ,  $E_2 \sim V_2$

if interaction is short range then

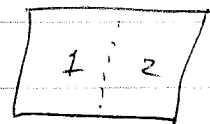
$E_{12} \sim A$  area of wall separating subsystems

as  $V \rightarrow \infty$ ,  $\frac{A}{V} \rightarrow 0$ , so energy is additive

when this assumption of additivity fails, the limit  $V \rightarrow \infty$  [called the thermodynamic limit] may depend on the shape of the system.

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

If we view the subsystems as only conceptually the two halves of a single system (rather than physically distinct subsystems) then



$$S(E, V, N) = 2 S(E/2, V/2, N/2)$$

or more generally

( $\lambda = 1/2$  in above ex)

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

⇒ In thermodynamic limit, the entropy is homogeneous 1<sup>st</sup> order function of the extensive vars

$$\text{or } S(E, V, N) = N S\left(\frac{E}{N}, \frac{V}{N}, 1\right) \equiv N \alpha(u, v)$$

where  $u = \frac{E}{N}$  energy per particle  $\alpha(u, v) = S\left(\frac{E}{N}, \frac{V}{N}, 1\right)$   
 $v = \frac{V}{N}$  volume per particle  
 $\alpha = \frac{S}{N}$  entropy per particle

$S, E, N, V$  are extensive - grow prop to volume  
 $u, v$  are intensive - become constant as  $N \rightarrow \infty$   
 take thermodynamic limit

$S$  is monotonic increasing function of  $E$   
 $\Rightarrow$  we can invert the function to get

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

Postulate IV

States for which  $\left(\frac{\partial E}{\partial S}\right)_{N, V} = 0$

(this will turn out to correspond to  $T=0$ )  $\uparrow$  constant  $N$  and  $V$

have  $S=0$  zero entropy

(Planck's extension of Nernst's 3<sup>rd</sup> law of thermo)

## Conditions for Equilibrium

Considering  $E(S, V, N)$  as the basic thermodynamic function, we can define (i.e. name) its partial derivatives as:

$$\left(\frac{\partial E}{\partial S}\right)_{V, N} \equiv T \quad \text{temperature}$$

subscripts mean derivative is taken keeping these variables held constant

$$-\left(\frac{\partial E}{\partial V}\right)_{S, N} \equiv p \quad \text{pressure}$$

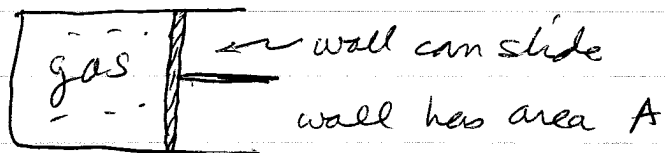
$$\left(\frac{\partial E}{\partial N}\right)_{S, V} \equiv \mu \quad \text{chemical potential}$$

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

$$\Rightarrow \boxed{dE = T dS - p dV + \mu dN}$$

$T, p, \mu$  are intensive parameters since they are derivatives with respect to extensive parameters

The definition of pressure above agrees with the mechanical notion that pressure is force per unit area. Consider a gas confined in the chamber of a piston.



If the chamber is thermally insulating so no heat is added or taken out, and the gas is allowed to expand by moving the piston wall a distance  $\Delta x$ , then the work done by the gas on the wall is  $F^{\text{total}} \Delta x = p A \Delta x = p \Delta V$  where  $\Delta V = A \Delta x$  is the change in volume.

Since the gas is not heated (chamber thermally insulating) and it does mechanical work, the energy of the gas must decrease by the work done

$$\Rightarrow \Delta E = -p \Delta V$$

$$\Rightarrow \left( \frac{\partial E}{\partial V} \right)_{S, N} = -p \quad \text{as defined above}$$

↑  
constant  $S$  means no heat is exchanged with gas and outside world.

When  $dN=0$ , as is the case for a gas confined to a box,

$$dE = T dS - p dV$$

Since we just showed that  $p dV$  is the mechanical work done by the gas, then  $T dS = dQ$  is the heat absorbed by the gas

heat absorbed  $\Rightarrow$  entropy increases

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

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

$$\Rightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

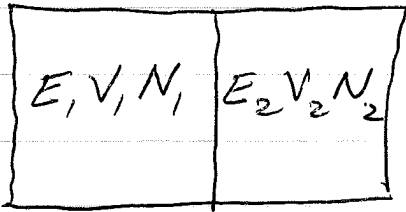
from which we have

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

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

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

## Thermal Equilibrium



↑  
immoveable, impermeable,  
insulating wall

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

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,



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

$$\text{so } dE_2 = -dE_1$$

Change in entropy  $S = S_1 + S_2$  as system equilibrates is then

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

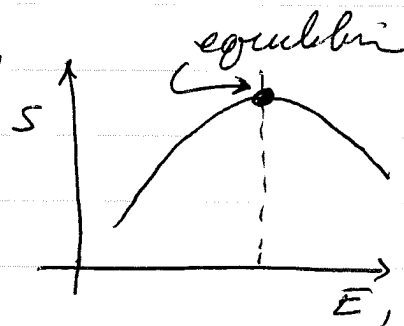
$$= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2$$

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

equilibrium is when S becomes maximum

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

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



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

Note:  $dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \Rightarrow$  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) i.e. from higher  $T_1$  to lower  $T_2$ . Agrees with our intuition about temperature that heat flows from hot to cold.