

Chapter 1.1: Foundations of thermodynamics

Two points of view:

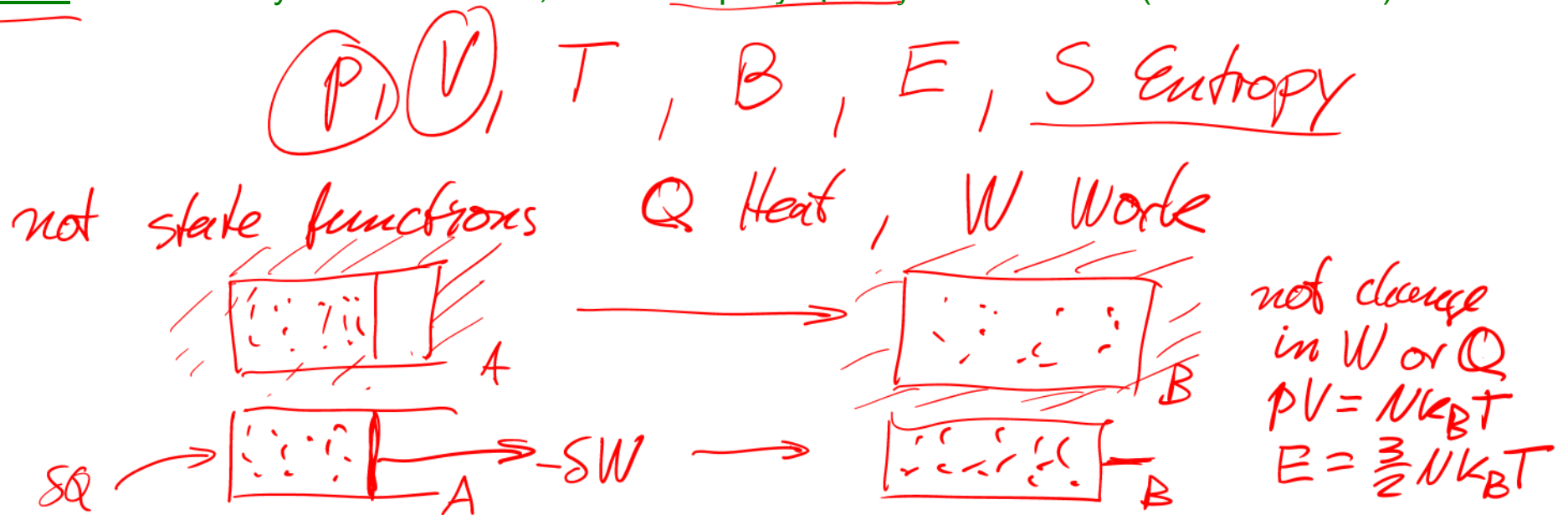
1.) Microscopic view: describe the Microstate by specifying all degrees of freedom

$$\begin{matrix} \vec{r}_1, \vec{r}_2 \dots \vec{r}_N; 3N \\ \vec{p}_1, \vec{p}_2 \dots \vec{p}_N; 3N \end{matrix}$$

2.) Macroscopic view: describe the Macrostate by only few thermodynamic variables

Def. 1.1:

State functions are thermodynamic variables, which uniquely specify a macrostate (and vice versa)



Def. 1.2:

We consider a quantity A which changes infinitesimally as a function of two independent (thermodynamic) variables x and y .

The infinitesimal change $dA = a(x,y) dx + b(x,y) dy$ is called an exact differential, if a function $A(x,y)$ exists, so that

$$dA = A(x+dx, y+dy) - A(x,y) = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy$$

The variables $a(x,y)$ and $b(x,y)$ are therefore also thermodynamic parameters and are given by the partial derivatives

$$a = \left(\frac{\partial A}{\partial x}\right)_y \quad b = \left(\frac{\partial A}{\partial y}\right)_x$$

Other equivalent statements:

$$\left(\frac{\partial^2 A}{\partial x \partial y}\right) = \left(\frac{\partial^2 A}{\partial y \partial x}\right) \Rightarrow \left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \quad \text{Equivalent!}$$

$$\int_a^b dA \text{ independent of path} \quad \text{or} \quad \oint dA = 0$$

State functions always form exact Differentials
in equilibrium

not exact differential ΔQ

Def. 1.3:

A thermodynamic process is called

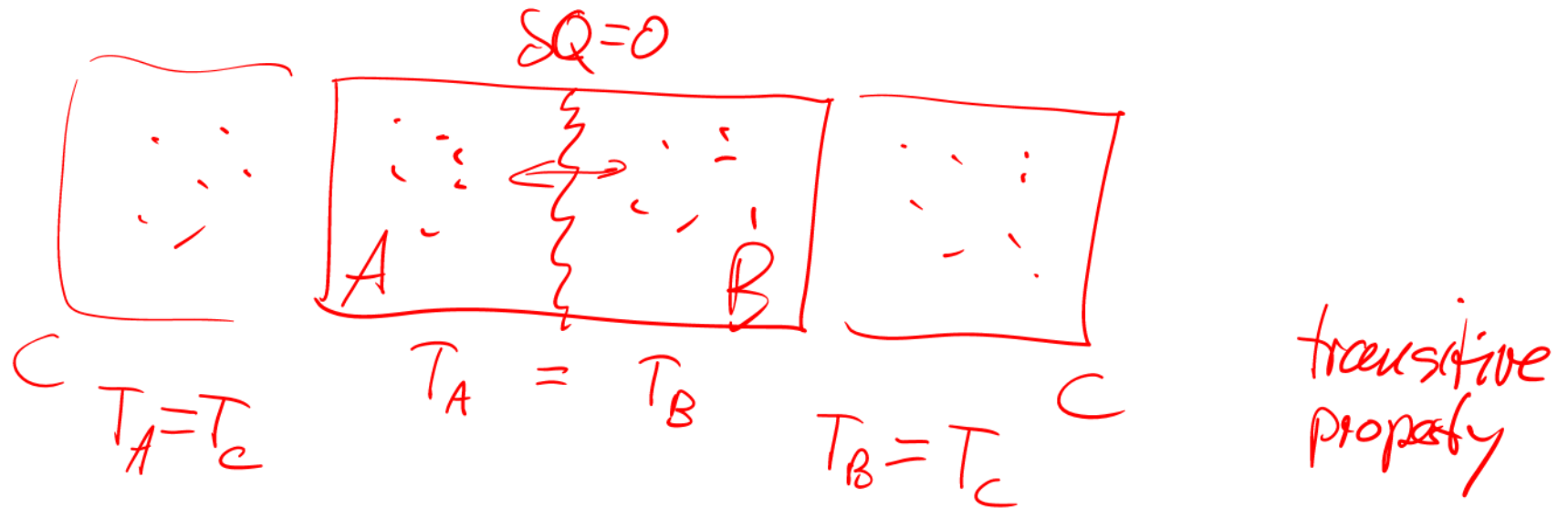
i) reversible, if the system remains in equilibrium at each time.

- ii) isobaric if $dp=0$ ~~X~~
- isochoric if $dV=0$ ~~X~~
- isothermal if $dT=0$ ~~X~~
- isentropic if $dS=0$ ~~X~~
- adiabatic if $\delta Q=0$ ~~X~~

Zerth law of thermodynamics

Two systems are in thermal equilibrium and have the same temperature, if no heat is transferred when they are brought in contact with each other.

If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.



Sorting allows concept of different temperatures

First law of thermodynamics

In a closed isolated system, the sum of the changes of heat and work are conserved. $dE = 0$

$dE = \delta Q + \delta W$ is an exact differential

for reversible processes

\Leftrightarrow for general reversible processes
 dE is an exact differential

$\Leftrightarrow E$ is a state function

δQ and δW are forms of energy

$$\delta W = -pdV$$

$$\delta Q = ? d?$$

$$\oint dE = 0$$

$$\text{but } \oint \delta Q = -\oint \delta W \neq 0$$

\rightarrow cyclic reversible processes at heat engines

Def. 1.4:

The entropy is given by $S = \int \delta Q/T$ for a reversible process.

$dS = \delta Q/T$ an exact differential.

The entropy is a state function

If the multiplication of an infinitesimal change δB becomes an exact differential $dA = g(x,y) \delta B$, then the function $g(x,y)$ is called an integrating factor.

$$\underline{dS} = \frac{\delta Q}{T} \Rightarrow S = \int_a^b \frac{\delta Q}{T}$$

here $\frac{1}{T}$ is integrating factor ^{is state function}

$$dV = -\frac{\delta W}{p} \rightarrow -\frac{1}{p} \text{ is an integrating}$$

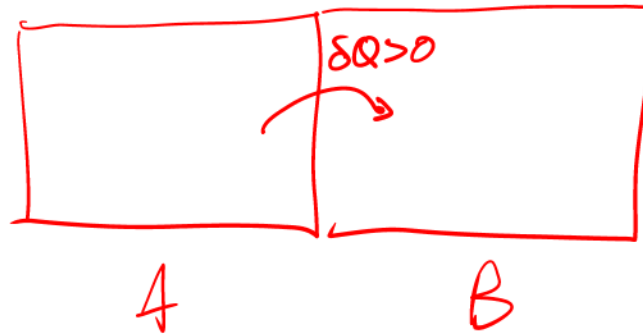
$$\underline{dE} = \delta Q + \delta W = \underline{T dS - p dV} \quad E(S, V) \text{ is a function}$$

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad -p = \left(\frac{\partial E}{\partial V} \right)_S$$

$$\Rightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV \Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V$$

Second law of thermodynamics

Heat may spontaneously be transferred only from higher to lower temperatures. (Clausius 1850).



A and B separately
are in equilibrium
(reversible)

Entropy production:

$$dS_A = - \frac{\delta Q}{T_A}$$

$$dS_B = \frac{\delta Q}{T_B}$$

$$dS = dS_A + dS_B = \delta Q \left(\frac{1}{T_B} - \frac{1}{T_A} \right) > 0$$

Spontaneous irreversible entropy production for system as whole

Tendency to reach equilibrium $\rightarrow S = \text{max in equilibrium}$