

MEASURING CHANGES IN ENTROPY

Stat Mech Relation $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$

↳ Connect changes in Entropy S
to MEASURABLE MACROSCOPIC quantities

$\Omega(N, V, U) \rightarrow$ not macroscopically measurable
↳ # of μ states

write about in terms of VERY SMALL changes

$$\left(\frac{\Delta S}{\Delta U}\right) \Big|_{N, V \text{ const}} = \frac{1}{T}$$

$$\Delta S \Big|_{N, V \text{ const}} = \frac{\Delta U}{T}$$

↳ Change in entropy of system

with $N, V \text{ const} \rightarrow$ ONLY HEAT EXCHANGED
 \rightarrow NO WORK DONE.

In this case (no work) $\Delta U = Q$

$Q \rightarrow$ amount of HEAT absorbed / given up by system \rightarrow infinitesimal

$$\left. \frac{\Delta S}{N, V} \right|_{N, V} = \frac{\Delta U}{T} = \frac{Q}{T}$$

\hookrightarrow As a system absorbs a small amount of HEAT, without changing N, V (no work done), the ENTROPY of the system will change

$\Delta S = \frac{Q}{T}$ \leftarrow CLAUSIUS Defn of Entropy 19th C
Small enough that T constant

S is something that always increases.

εντροπία εντροπία in transformation

1865 the Energy of the Universe is Constant
the Entropy of the Universe is Maximum

S → mysterious "substance" for Clausius

Today $S = Nk \ln(\text{multiplicity})$

$\Delta S = \text{increase of } k \ln(\text{multiplicity})$

$\Delta S \geq 0 \rightarrow 2^{\text{ND}} \text{ Law}$



postulate of STAT MECH
for closed system.

this Definition of Entropy

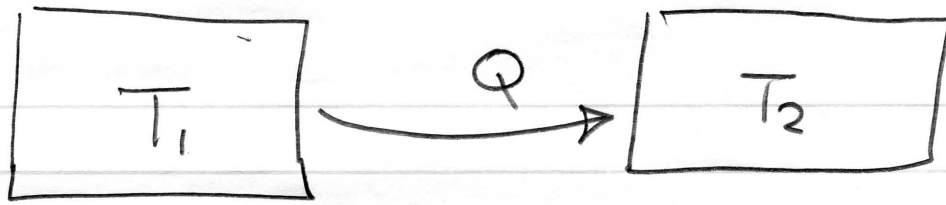
$$\Delta S \Big|_{\substack{\text{no} \\ \text{work}}} = \frac{Q}{T} + \Delta S \Big|_{\text{CLOSED}} \geq 0$$

explains direction of HEAT FLOW.

Suppose we have two systems

↳ spontaneously exchange

some amount of HEAT = Q



1 gives up heat

2 Absorbs heat.

$$\Delta S_1 = -\frac{Q}{T_1}, \quad \Delta S_2 = +\frac{Q}{T_2}$$

TOTAL CHANGE IN ENTROPY

$$\Delta S_{\text{TOT}} = \Delta(S_1 + S_2)$$

$$= Q \left(-\frac{1}{T_1} + \frac{1}{T_2} \right) \geq 0$$

• $T_1 = T_2$, $\Delta S = 0 \rightarrow$ no exchange of Heat.
 $\hookrightarrow S$ already maximized

• $\Delta S > 0$ if $T_1 > T_2 \rightarrow \frac{1}{T_2} - \frac{1}{T_1} > 0$

HEAT FLOWS HOT \rightarrow COLD

$\Delta S|_{N,V} = \frac{Q}{T} \rightarrow$ way to measure changes in entropy

Fixed V, N - change U by ΔU

$\Delta U = C_V \Delta T$ } $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$ }
 ↳ changes T by ΔT

So $\Delta S|_{N,V} = \frac{Q}{T} = \frac{\Delta U}{T} = C_V \frac{\Delta T}{T}$

$Q = \Delta U$ ← no work done

Suppose MEASURE C_V for some system as a fn of T (Generally C_V depends on T)

↳ for some small ΔT $T_i \rightarrow T_f$

$S(T_f) - S(T_i) = \int_{T_i}^{T_f} C_V \frac{dT}{T}$

↳ measure as fn of T .

Example: ideal classical monoatomic gas

$$C_V = \frac{3}{2} Nk.$$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{3}{2} Nk \frac{dT}{T}$$

$$= \frac{3}{2} Nk \ln\left(\frac{T_2}{T_1}\right)$$

→ Sakur Tetrode gives this
↳ OBVIOUSLY

In general $\Delta S = C_V \frac{\Delta T}{T}$

↳ insight on T dependance of C_V .

Consider very small $T \rightarrow$ approaching Absolute 0.

↳ Measure $C_V \rightarrow$ measure.

$$S_2(T_2 \rightarrow 0) - S(T_1)$$

IF C_V constant as $T \rightarrow 0$

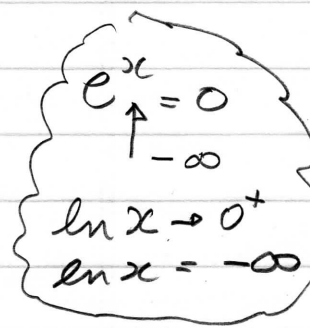
$$\hookrightarrow S(T_2) - S(T_1) = C_V \ln \frac{T_2}{T_1}$$

ALWAYS FINITE
 # OF μ STATES
 FINITE

RHS $\rightarrow \infty$ as $T_2 \rightarrow 0$



SO Assumption of C_V CONSTANT
 IS INCONSISTENT



\rightarrow To produce FINITE AS $T \rightarrow 0$ sufficiently

low T , $C_V(T) \rightarrow 0$ as $T \rightarrow 0$

(could also have $C_V(T) = \text{const } T^\alpha$)
 \uparrow
 > 0

In metals $C_V \sim C_1 T + C_2 T^3$

electrons \nearrow

\nwarrow phonons



this is in the text
 somewhere.

Strange metals $C_V \sim T \ln \frac{\epsilon}{T}$, $T \rightarrow 0$

(21)

So Sakur - Tetrode must BREAK DOWN

↳ finiteness of ΔS at low Temp

↳ $C_V(\tau) = 0$, as $T \rightarrow 0$

→ takes very small amount of ENERGY

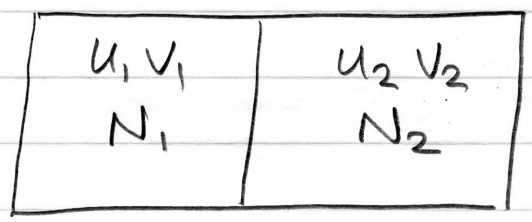
to raise TEMP, at very low T.

Review + look ahead to CHEMICAL Equilibrium.

So far → treated thermodynamic Equilibrium between two systems exchanging

Volume → Pressure
ENERGY → Temperature

①



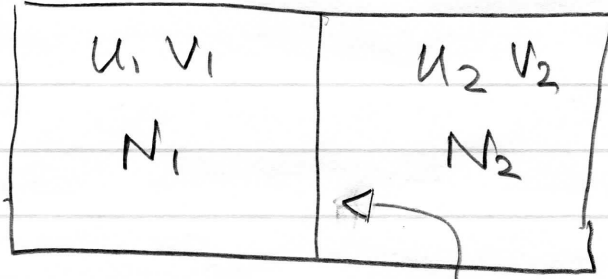
↑ Fixed PARTITION $U_1 + U_2 = U$

$$T_1 = T_2 \rightarrow \left(\frac{\partial S_1}{\partial U_1} \right)_{N_1, V_1} = \left(\frac{\partial S_2}{\partial U_2} \right)_{N_2, V_2}$$



STATISTICAL DEFINITION
of
TEMPERATURE

2



$$U_1 + U_2 = \text{const}$$

moving PARTITION.

$$V_1 + V_2 = \text{const}$$

$$N_1 = \text{const}$$

$$N_2 = \text{const}$$

$$\left. \begin{matrix} T_1 = T_2 \\ P_1 = P_2 \end{matrix} \right\} \text{At Thermodynamic Equilibrium.}$$

$$\left(\frac{\partial S_1}{\partial U_1} \right)_{N_1, V_1} = \left(\frac{\partial S_2}{\partial U_2} \right)_{N_2, V_2}$$

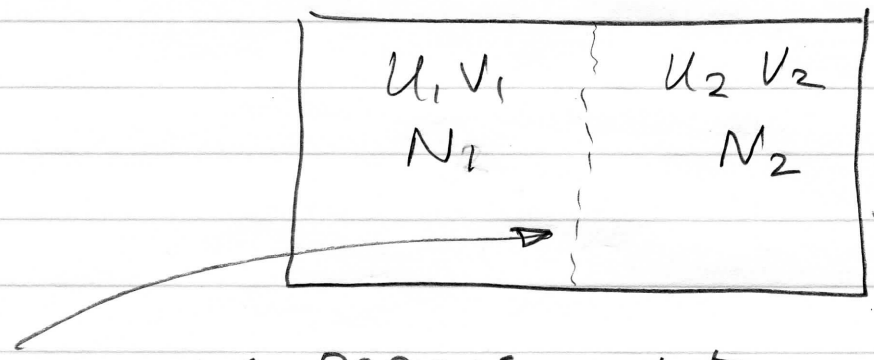
and

$$\left(\frac{\partial S_1}{\partial V_1} \right)_{N_1, U_1} = \left(\frac{\partial S_2}{\partial V_2} \right)_{N_2, U_2}$$

STATISTICAL DEFINITION OF PRESSURE

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

③ CHEMICAL POTENTIAL



movable porous partition.

↳ systems can exchange PARTICLES

N_1 AND N_2 NOT FIXED

$N_1 + N_2$ ← FIXED