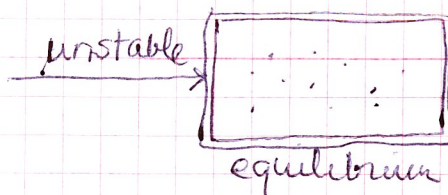
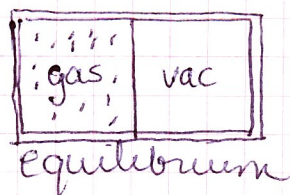


Lecture 2

Second Law of Thermodynamics

The second law says that some processes are impossible,

more order



never =
"wait longer than the
age of the universe"

you never see them return to previous state

Reversibility

macroscopic - something breaks, something from grave again lives
microscopic - very small probability

Heat can flow by itself from cold to hot body
It is easy to convert work into heat

However, a complete conversion of heat to work is
impossible in practice - isothermal process of perfect gas

Two properties of a perfect gas: $E = E(T)$ internal energy
 $PV = NKT$ eq. of state

in isothermal expansion, heat is converted to work

Entropy

Every state has a definite entropy, measure of disorder

Statistical Weight of a Macrostate P, V, T

many microstates correspond to the same macrostate
in QM - can always count the number of microstates
in classical you can't count them

Ω = Statistical Weight = number of microstates
compatible with a given macrostate

$\Omega = \Omega(E, V, N, \alpha)$ function of macro variables

Fundamental Postulate of Statistical Thermodynamics.

All { quantum } of a given state of equally probable, (Axiom)
microstates

Maximum probability is proportional to # of microstates

Reversibility is given in a statistical sense.

How to define entropy in terms of statistical weight Ω ?

Ω_1 = state 1
 Ω_2 = state 2
 $\Omega_1 \cdot \Omega_2$ = combined

Volume, energy and "extensive" variables are added for combined states.
 We want entropy to be extensive

$$\ln(\Omega_1 \cdot \Omega_2) = \ln \Omega_1 + \ln \Omega_2$$

Boltzmann's Definition
 of entropy

$$S \equiv k \ln \Omega$$

2nd Law of Thermodynamics: In any natural process (non-eq to eq state) the entropy always increases

Applications of the 2nd Law

$[E_1, V_1, N_1] [E_2, V_2, N_2]$ energy flows

The combined system is isolated $S_c = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$

$E_c = E_1 + E_2 = \text{constant}$ strictly speaking only one variable

Condition for maximum

$$\frac{\partial S}{\partial E} = 0$$

$$\frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} = 0 = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0 = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} = 0$$

S is inverse temperature

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

Two things

- ① Definition of absolute temperature
- ② Temperature must be the same at equilibrium

$$kT = \left(\frac{1.38 \cdot 10^{-23} \text{ J K}^{-1}}{1.6 \cdot 10^{-19} \text{ J}} \right) (300 \text{ K}) \text{ eV} \approx 40 \text{ eV}$$

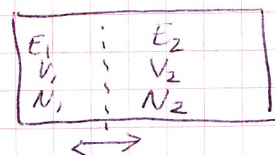
$$k = \frac{1.38 \cdot 10^{-23} \text{ J K}^{-1}}{1.6 \cdot 10^{-19} \text{ J/eV}} = 8.62 \cdot 10^{-5} \frac{\text{eV}}{\text{K}} \quad 1.6 \cdot 10^{-19} \text{ J} = 1 \text{ eV}$$

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

$$E = E_1 + E_2 = \text{constant}$$

$$V = V_1 + V_2 = \text{constant}$$

partition moves



Lecture 2 continued

When is entropy maximized for the moving partition system?

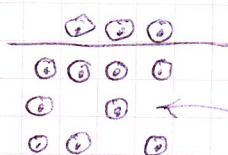
$$\frac{\partial S}{\partial E_1} = 0 \quad \frac{\partial S}{\partial V_1} = 0 \quad \frac{1}{T_1} = \frac{1}{T_2}$$

$$\frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_1} = 0 = \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_2} \frac{\partial V_2}{\partial V_1} = 0 \Rightarrow \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0$$

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

\therefore partition can't move

Schottky Defects of Crystals



some atoms go to the surface of the crystal

What is the energy of an atom on the surface?
of atom at empty lattice site?

\mathcal{E} = energy of each atom on surface

n = number of atoms displaced to the surface

N = total number of atoms AND the total number of lattice sites

$$E = n\mathcal{E} = \text{for some macroscopic state}$$

The number of microstates corresponding to that energy is equal to Ω

$$E = n\mathcal{E} \Rightarrow \Omega(n)$$

How many ways can you choose n objects?

$$\Omega(n) = \frac{N!}{n!(N-n)!}$$

entropy of the Schottky effect

$$S(E, n) = k \ln(\Omega) = k \ln\left(\frac{N!}{n!(N-n)!}\right)$$

Due to vibrations

$$S_{\text{total}} = S(n) + S_{\text{Remainder}}$$

$$E_{\text{total}} = E(n) + E_{\text{Remainder}} = \text{constant}$$

How do you maximize the total entropy?

$$\frac{\partial S_{\text{total}}}{\partial E(n)} = 0 \quad E = E(n)$$

$$\frac{\partial S_S}{\partial E} + \frac{\partial S_R}{\partial E} = 0 \quad \frac{\partial S_S}{\partial E} = \frac{\partial S_R}{\partial E_R} \frac{\partial E_R}{\partial E}^{-1}$$

$$\frac{\partial S}{\partial E} = \frac{\partial S_R}{\partial E_R} = \frac{1}{T}$$

due to vibrations

$$\therefore \frac{\partial S}{\partial E} = \frac{1}{T}$$

$$\frac{\partial S}{\partial E} = \frac{\partial S}{\partial n} \frac{\partial n}{\partial E}$$