# THERMAL & STATISTICAL PHYSICS
# SSP3133

# THERMAL INTERACTION

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- Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

# AXIOM or Postulate

is a proposition that is not proved or demonstrated but considered to be either self-evident, or subject to necessary decision.

Therefore its truth is taken for granted and serves as a starting point for deducing and inferring other truths theory (dependent).

# AXIOM 1 /Postulate 1

There exist special states of macroscopic physical system, called equilibrium states, which can be fully described by the internal energy, U, and a set of extensive parameters, $X_0$, $X_1$, $X_2$,….$X_c$

# AXIOM 2/Postulate 2

For all system in equilibrium there exists a function of the extensive parameters, called the **entropy, S**. If there are no internal constraints on the system, the extensive parameters can take the values that **maximize S** over the possible states with internal constraints.

Macroscopic property
(physical system) → **Equilibrium State (ES)**

fully described by

microscopic properties
(extensive thermodynamic
properties) → U , V , N , S , …..

= S maximised

Intensive thermodynamic properties → Independent of the size of the thermodynamic system : P, T, ρ

Extensive thermodynamic properties → Dependent : V , S, U, H, N, …..

The functional relation between S and the extensive parameters

$$S = S\,(U, X_0, X_1, \ldots\ldots X_C)$$

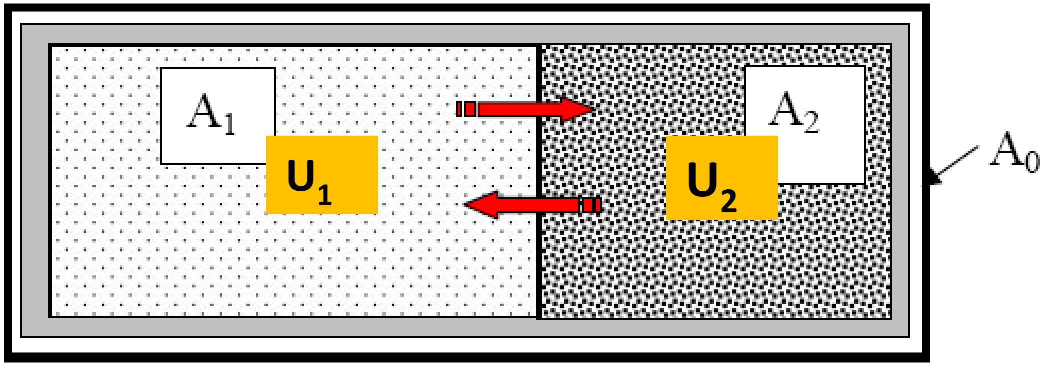
Note: $X_0$ can be V; $X_1$ can be N,….

2 systems interacting thermally

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

no mechanical interactions

no exchange of particle



$A_0 = A_1 + A_2$

$\partial U_1 + \partial U_2 = \partial U_0$

*same temperature,*

$\Rightarrow \ \partial U_0 = 0$

$$\boxed{\therefore \ \partial U_1 = -\partial U_2}$$

When $A_1$ and $A_2$ are in equilibrium;

$\boxed{\text{The entropy } S_0 \text{ is at it maximum value}}$

If $S_0 = f(U_1)$ $\boxed{\left(\frac{\partial S_0}{\partial U_1}\right)_{V,N} = 0}$

$\boxed{\text{Using } S_0 = S_1 + S_2}$

$$\boxed{\left(\frac{\partial S_0}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} + \left(\frac{\partial S_2}{\partial U_1}\right)_{V,N}}$$

$$\boxed{substituting\ \partial U_1 = -\partial U_2}$$

$$\boxed{\left(\frac{\partial S_0}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N} = 0}$$

$$(*) \quad \boxed{\left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N}}$$

For 2 systems in thermal equilibrium,

$$\boxed{\text{The property } \left(\frac{\partial S}{\partial U}\right)_{V,N} \text{ is the same— Temperature, T}}$$

Temperature is defined as $\left(\frac{\partial S}{\partial U}\right)_{V,N} \equiv \frac{1}{T}$

$$\text{From } (*) \left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N} \Rightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

Note: when 2 systems are in equilibrium, their temperatures are equal.

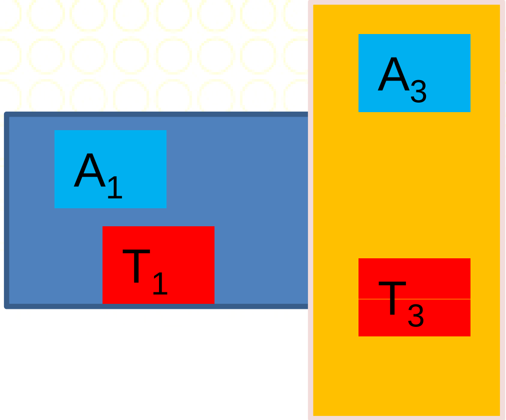
Therefore, for 2 systems of the same temperature in thermal contact,

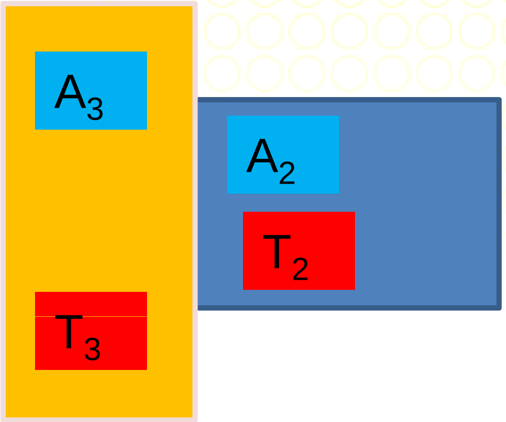
$$0 = \frac{1}{T_1} - \frac{1}{T_2} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V,N} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V,N}$$
$$= \left(\frac{\partial (S_1 + S_2)}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_0}{\partial U_1}\right)_{V,N}$$

Entropy of combined system is maximum at equilibrium

Let $A_1$ in thermal equilibrium with $A_3$

$A_2$ in thermal equilibrium with $A_3$





$$\boxed{T_1 = T_3}$$

$$\boxed{T_2 = T_3}$$

$$\boxed{\text{Therefore } T_1 = T_2}$$

# Zeroth Law:

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

Note:

i. Temperature is the indicator of thermal equilibrium
ii. All parts of a system must be in thermal equilibrium if the system is to have a definable single temperature.

# Entropy - a measure of the number of accessible states Ω

$\frac{1}{T}$ – *measures the* $\Omega$ *which varies with the internal energy* $U$.

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\partial}{\partial U}\left(k \ln \Omega(U)\right)_{V,N}}$$

$$\boxed{\text{But} \quad \Omega(U) = (const)U^{\frac{R}{2}}}$$

Therefore

$$\boxed{\begin{aligned} \frac{1}{T} &= \frac{\partial}{\partial U}\left(k \ln \Omega(U)\right)_{V,N} = \frac{\partial}{\partial U}\left(k \ln(const)U^{\frac{R}{2}}\right) \\ &= \frac{kR}{2}\frac{\partial}{\partial U}\left(\ln(const) + \ln U\right) = \frac{kR}{2}\left(\frac{1}{U}\right) \end{aligned}}$$

$$\boxed{\frac{1}{T} = \frac{kR}{2U} \quad or \; U = \frac{1}{2}kRT = U_{thermal}}$$

U is measured to the zero-energy reference level, Nμ

$$U_{thermal} = U_{total} - N\mu$$

$$U_{total} = U_{thermal} + N\mu$$

$$= \frac{1}{2} kRT \quad + \ \mu N$$

*If each particle has υ degrees of freedom,*

*hence* $R = \upsilon N$

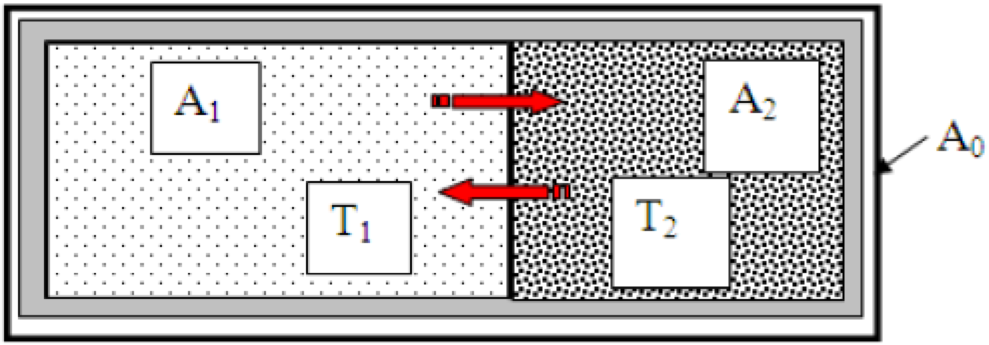
$$U_{total} = \frac{\upsilon}{2} NkT + N\mu = N\left(\frac{\upsilon}{2} kT + \mu\right)$$

Many common process, μ does not change or very little

$$\boxed{\Delta U \approx \frac{\nu}{2} Nk(\Delta T)}$$

$\Rightarrow$ Internal energy changes with temperature.

## Heat Flow



$A_1$ and $A_2$ -- not yet in thermal equilibrium

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

$$\Delta S_0 = \Delta S_1 + \Delta S_2 = \frac{\Delta U_1}{T_1} + \frac{\Delta U_2}{T_2} > 0$$

1st Law $\Delta U_1 = -\Delta U_2$

If $T_2 > T_1$, then $\Delta U_1 > 0$

$$\Delta S_0 = \Delta U_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0$$

If $T_1 > T_2$, then $\Delta U_1 < 0$

Note: if 2 interacting systems are not yet in thermal equilibrium, then the 2nd law demands that the energy must flow from the hotter system to the cooler one, and not vice versa.

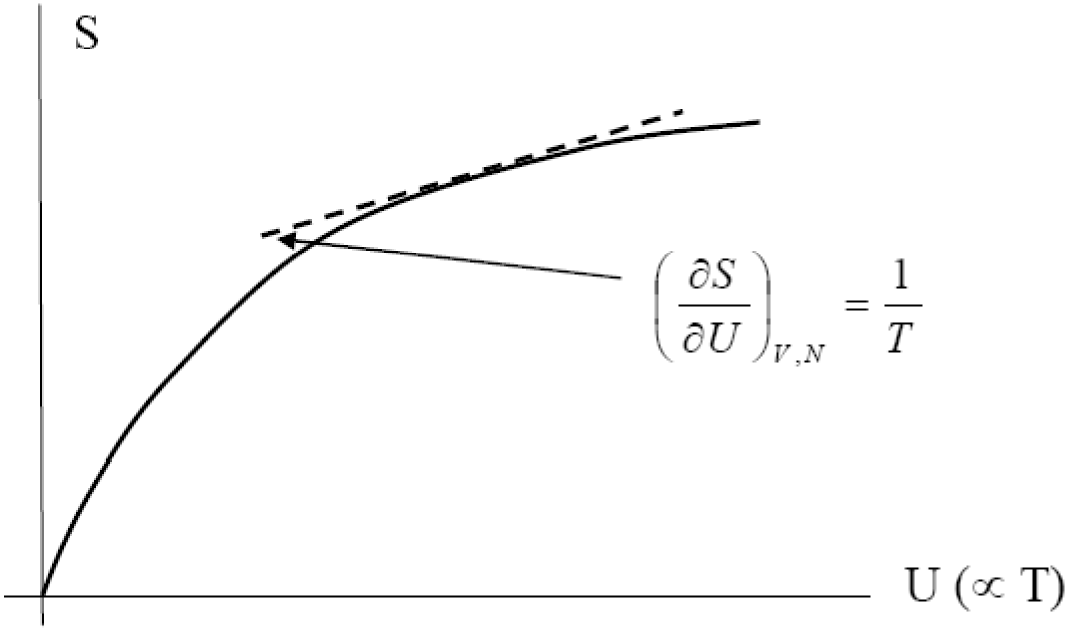
# Phase Transition (add heat, T unchanged)

$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ at higher T, the $\left(\frac{\partial S}{\partial U}\right)_{V,N}$ is smaller

From $S = k \ln \Omega(U)$

Where $\Omega(U) = (\text{const})U^{R/2}$

$S = \frac{1}{2} Rk \ln U$ & $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{Rk}{2}\left(\frac{1}{U}\right) = \frac{1}{T}$



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

Undergoing phase transition—

Add Heat, temperature remains constant

$$\frac{Rk}{2}\left(\frac{1}{U}\right) = \frac{1}{T} \quad \text{--- why??}$$

2 reasons;

i) As heat is added, R increases, R/U constant

ii) The added heat – releases particles from potential wells (the zero-energy reference is higher)

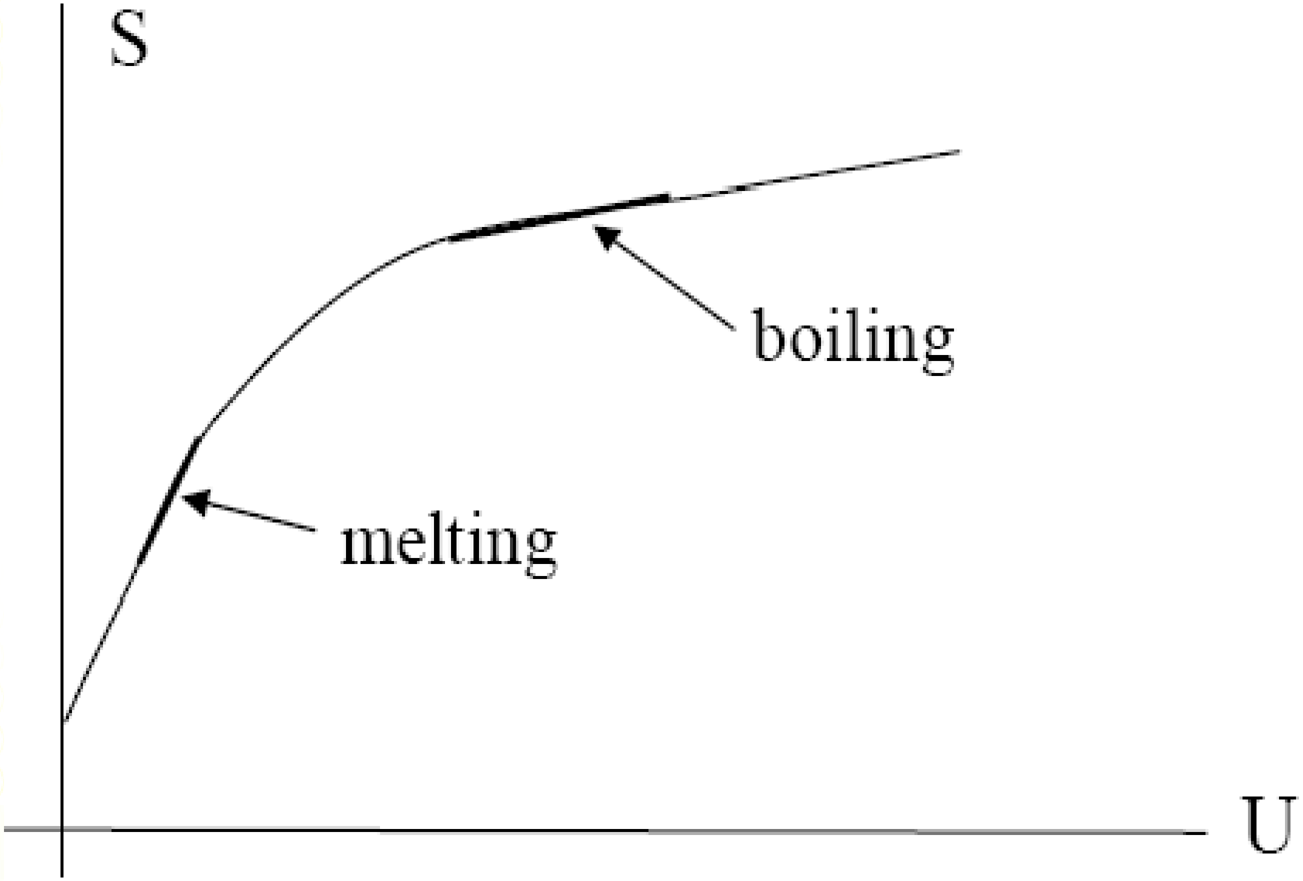
$U_{thermal} = U_{total} - N\mu$

$$\boxed{\frac{\partial S}{\partial U} = \frac{Rk}{2(U - N\mu)} = \frac{1}{T}}$$

from $\Omega(U) = (\text{const})U^{R/2}$ , $\Omega(U) = (\text{const})(U-N\mu)^{R/2}$

$$\boxed{S = \tfrac{1}{2} Rk \ln (U - N\mu)}$$

2 phase region $\frac{\partial S}{\partial U}$ constant



# Heat Reservoirs (add heat, T unchanged)

Heat reservoirs – sufficiently large systems that their temperatures do not change when a small amount of heat is added to or removed from them.

$\Delta$Q – small amount of heat.
Taylor series expansion

$$S(U+\Delta Q)=S(U)+\left(\frac{\partial S}{\partial U}\right)_{V,N}(\Delta Q)+\frac{1}{2}\left(\frac{\partial^2}{\partial U^2}\right)_{V,N}(\Delta Q)^2+\ldots.$$

Ignoring $(\Delta Q)^2$ and higher

$$S(U+\delta Q)=S(U)+\left(\frac{\partial S}{\partial U}\right)_{V,N}(\delta Q)$$

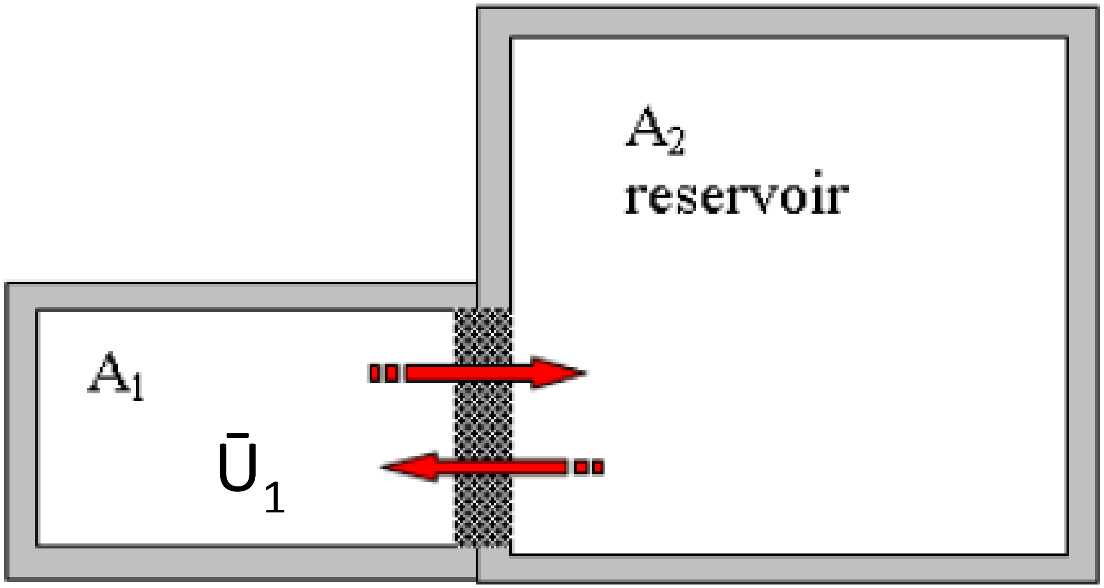
$$\boxed{S(U+\delta Q)=S(U)+\left(\frac{\partial S}{\partial U}\right)_{V,N}(\delta Q)}$$

$$\boxed{S(U+\delta Q)-S(U)=\left(\frac{1}{T}\right)(\delta Q)}$$

$$\boxed{dS=\frac{\delta Q}{T}}$$

----- for any system, large or small

# Thermal interaction with reservoir



Let $\overline{U}_1$ : average Internal Energy for $A_1$
$S_0$: entropy of the combined system ($A_1$+$A_2$)
$\Omega_o$: accessible states for the combined system

From fundamental postulate,

$$P(U_1) = (\text{const})\,\Omega_o(U_1)$$

And $S_0 = k \ln \Omega_o$ or $\Omega_0 = e^{\frac{S_0}{k}}$

$$P(U_1) = (const)\,e^{\frac{S_0(U_1)}{k}}$$

Entropy of the combined system

$$S_0\,(U_1 = \overline{U}_1 + \Delta U_1)$$

Using Taylor series expansion

$$S_0(U_1 = \overline{U}_1 + \Delta U_1) = S_0(U_1 = \overline{U}_1) + \left(\frac{\partial S_0}{\partial U_1}\right)_{\overline{U}_1}(\Delta U_1) + \frac{1}{2}\left(\frac{\partial^2 S_0}{\partial {U_1}^2}\right)_{\overline{U}_1}(\Delta U_1)^2 + \ldots$$

at equilibrium, $S_0$ is maximum

$$\left(\frac{\partial S_0}{\partial U_1}\right)_{\overline{U_1}} = 0$$

And

$$\left(\frac{\partial^2 S_0}{\partial {U_1}^2}\right) = \frac{\partial^2}{\partial U_1}(S_1 + S_2) = \frac{\partial}{\partial U_1}\left(\frac{\partial S_1}{\partial U_1} + \frac{\partial S_2}{\partial U_1}\right)$$

$$= \frac{\partial}{\partial U_1}\left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right) = \frac{\partial}{\partial U_1}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$T_2$, reservoir temperature, -- constant

$$\frac{\partial}{\partial U_1}\left(\frac{1}{T_2}\right) = 0$$

And since $$U = \frac{Rk}{2} T$$

$$\frac{\partial}{\partial U_1}\left(\frac{1}{T_1}\right) = \frac{\partial}{\partial U_1}\left(\frac{Rk}{2U_1}\right) = -\frac{Rk}{2U_1^{\,2}}$$

Therefore $$\left(\frac{\partial^2 S_0}{\partial U_1^{\,2}}\right)_{\bar{U}_1} = -\frac{Rk}{2U_1^{\,2}}$$

And,

$$S_0(U_1 = \overline{U}_1 + \Delta U_1) = S_0(U_1 = \overline{U}_1) - \frac{Rk}{4U_1^{\,2}}(\Delta U_1)^2$$

Put this into the probability equation

$$P(U_1) = (const)\,e^{\frac{S_0(\overline{U}_1) - (Rk/4U_i^2)(\Delta U_1)^2}{k}}$$

$$= \left[(const)\,e^{\frac{S_0(\overline{U}_1)}{k}}\right] e^{\frac{R}{4U_1^2}(\Delta U_1)^2}$$

$$= (const)\,e^{-(\Delta U_1)^2/2\sigma^2}$$

With $$\sigma = \sqrt{\frac{2}{R}}\;\overline{U}_1$$

The probability the system has energy in the range $U_1$ and $U_1+dU_1$ is proportional to the size of the range $dU_1$

$$P(U_1)dU_1 = (const)e^{-(\Delta U_1)^2/2\sigma^2}dU_1$$

$$\int_{U_1} P(U_1)dU_1 = 1$$

$$(const)\int_{U_1} e^{-(\Delta U_1)^2/2\sigma^2}dU_1 = (const)\int_{U_1} e^{-a\Delta U_1}dU_1$$

With $a = \dfrac{1}{2\sigma^2}$

$$(const)\int_{U_1} e^{-a\Delta U_1}\, dU_1 = (const)\sqrt{\frac{\pi}{a}}$$

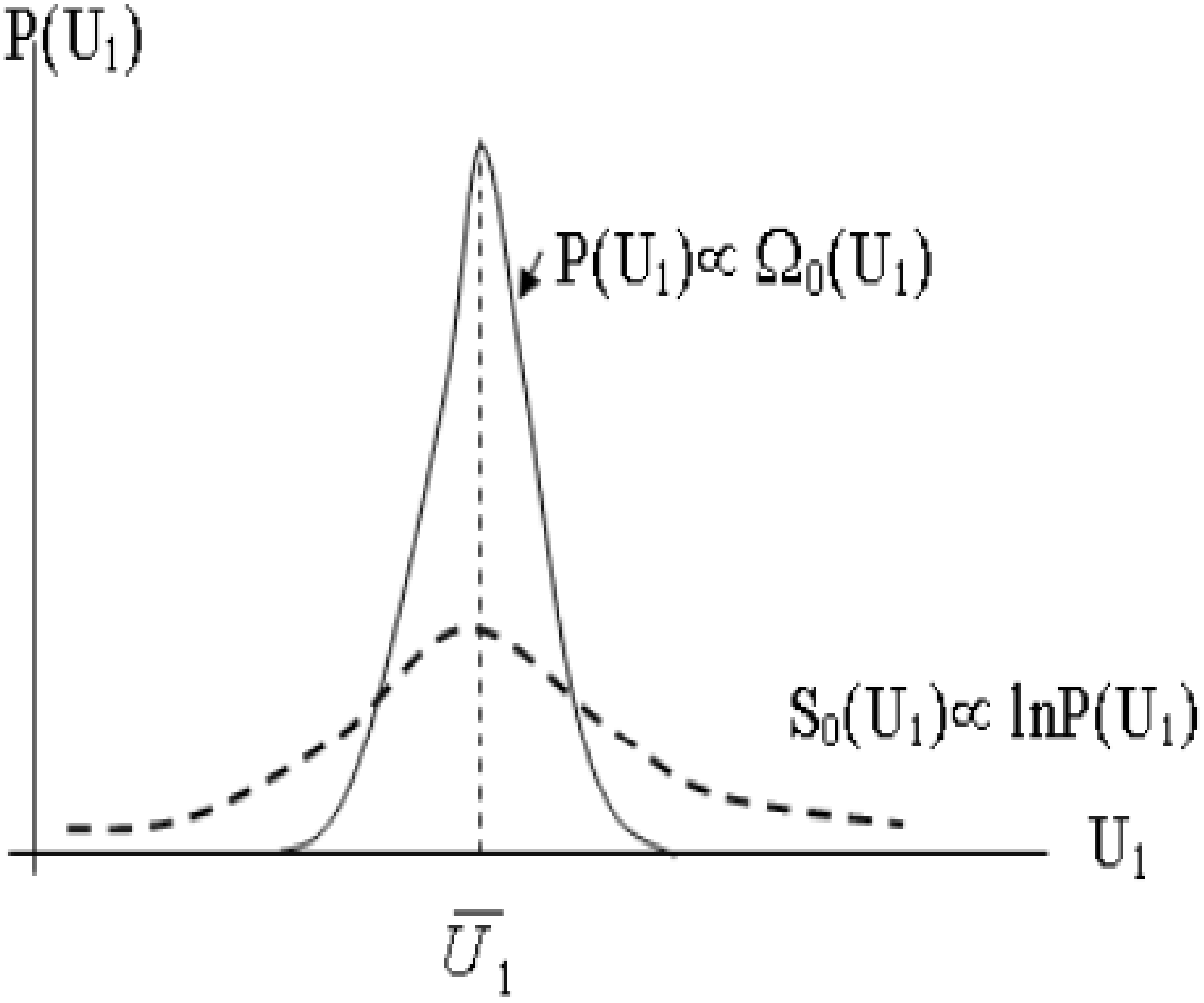
$$(const)\sqrt{\frac{\pi}{a}} = 1$$

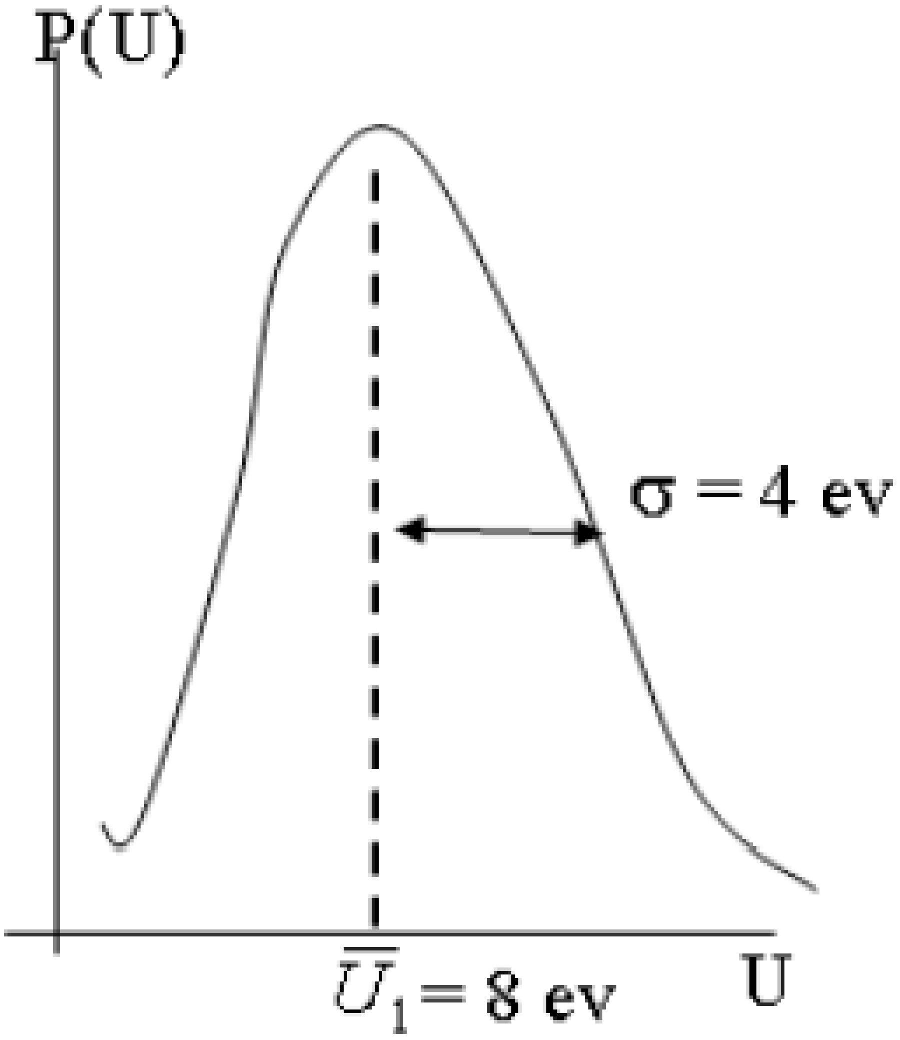
Therfore $(const) = \sqrt{\dfrac{a}{\pi}} = \sqrt{\dfrac{1}{2\pi\sigma^2}}$

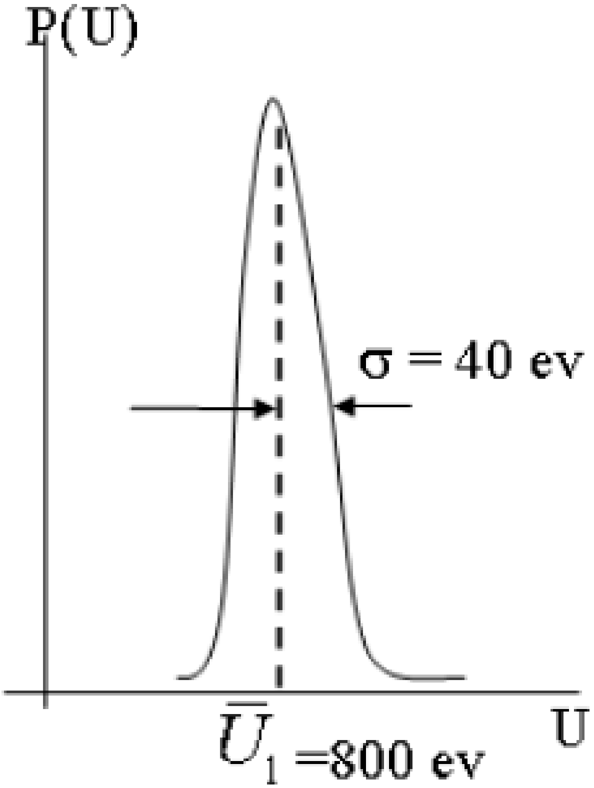
For system in equilibrium with reservoir, the probability that the system has energy in the range U and U+dU is

$$P(U)dU = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\Delta U)^2/2\sigma^2} dU$$

With $\sigma = \sqrt{\frac{2}{R}}\,\overline{U}$ and $\Delta U = (U - \overline{U})$


$P(U_1)$
$P(U_1) \propto \Omega_0(U_1)$
$S_0(U_1) \propto \ln P(U_1)$
$U_1$
$\overline{U}_1$


P(U)
σ = 4 ev
$\overline{U}_1 = 8$ ev
U



e.g: 2 systems & let $\bar{\varepsilon} = 1\,\text{ev}$ for degree of freedom
R = 8 and R = 800

# Heat Capacity (The Storage of Thermal Energy)

-a measure of how much heat energy must be added in order to raise its temperature by one standard unit.

## General Definition

- If $C_T$ = Total Amount of Heat Energy required to raise the temperature of some System by 1 °C, therefore $Q = C_T \Delta T$ ; where $C_T$ is heat capacity (SI: J/ °C)

## SPECIFIC HEAT CAPACITY

If c = Amount of Heat Energy per kilogram that is required to raise the temperature of one kilogram of the substance 1 °C, therefore $q = m\,c\,\Delta T$ ; where c is specific heat capacity (SI: J/kg.°C)

## MOLAR HEAT CAPACITY

If c = Amount of Heat Energy per mole that is required to raise the temperature of $6.022 \times 10^{23}$ molecules of the substance 1 °C, therefore $Q = n\,c\,\Delta T$; where c molar heat capacity (SI: J/mole/°C)

## VOLUMETRIC HEAT CAPACITY of a SUBSTANCE

If $c_v$ = Amount of Heat Energy per unit volume that is required to raise the temperature of one cubic meter of the substance 1 °C, therefore $Q = V\,c_v\,\Delta T$, where cv is volumetric heat capacity (SI: $J/m^3.°C$ )

$c_v$

Definition

$$C_X = \left(\frac{\partial Q}{\partial T}\right)_X$$ : heat capacity at constant X

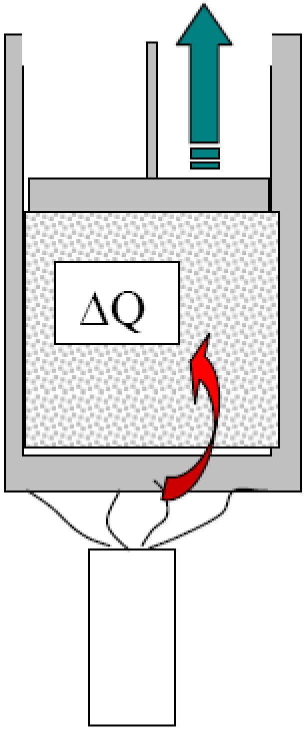
Two types of heat capacity

Heat capacity at constant pressure,

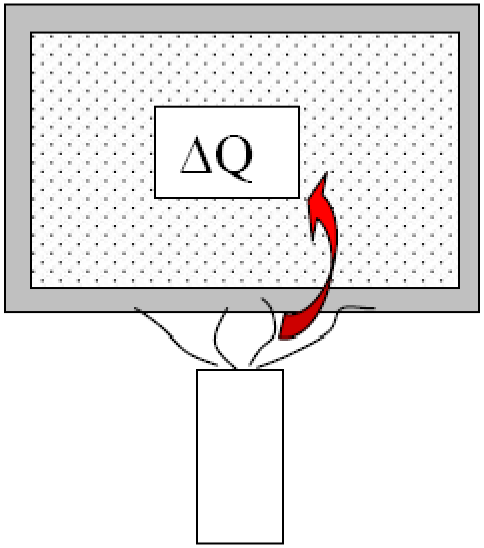
$$C_P = \left(\frac{\Delta Q}{\Delta T}\right)_P$$

Heat capacity at constant volume

$$C_V = \left(\frac{\Delta Q}{\Delta T}\right)_V$$



$c_p$



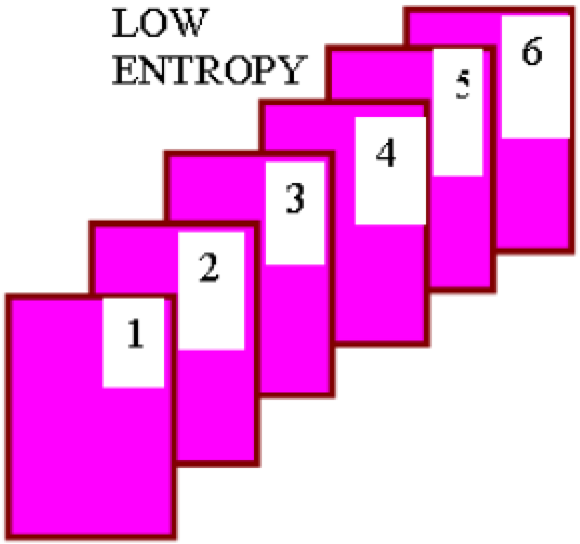
$c_v$

$$c_p = \left(\frac{dQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

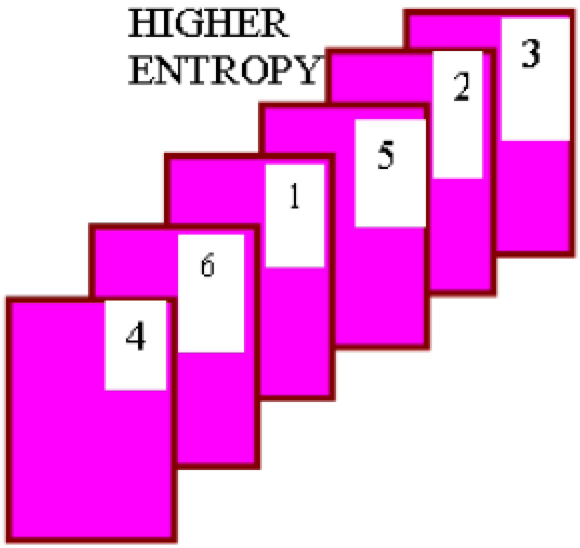
$$c_v = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

# Third law of thermodynamics (Nernst's theorem)

Order & Disorder

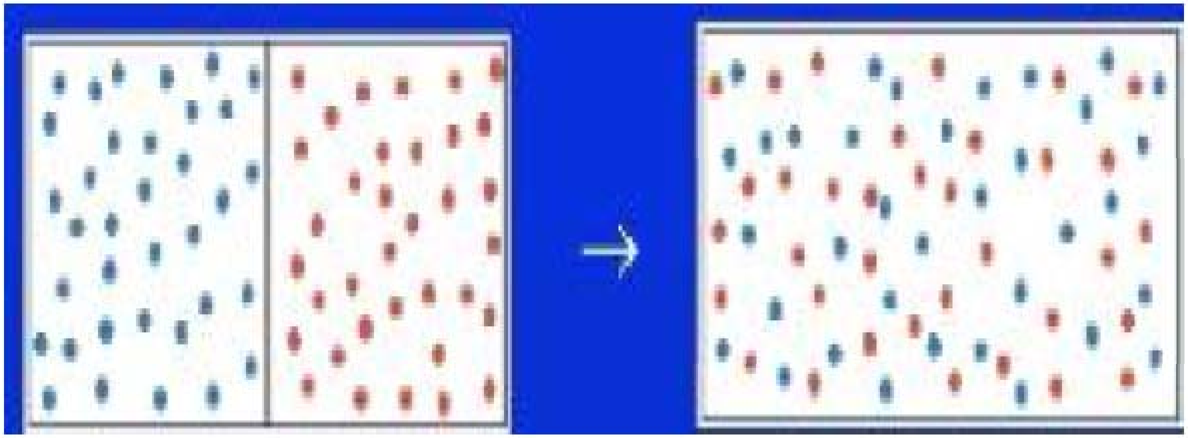


Only 1 way to make
this arrangement



Many ways to randomly arrange
the cards – higher probability

two different gasses separated by a partition will mix when the partition is removed, increasing system disorder.

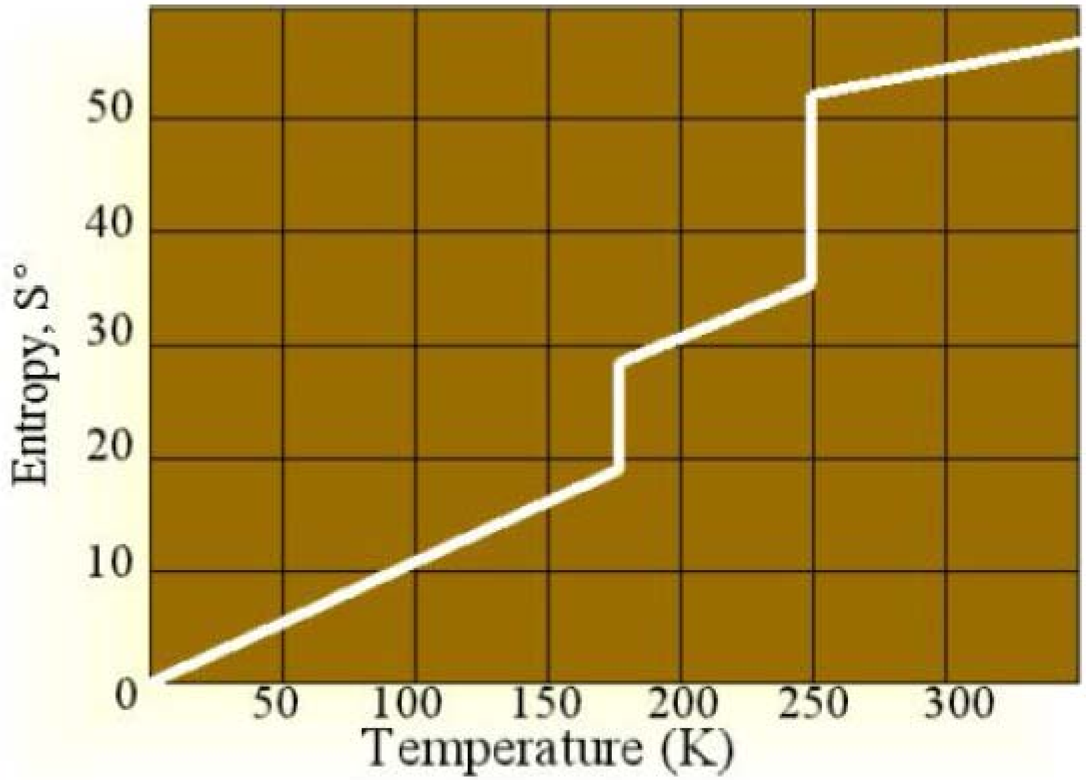


Entropy (S) is the thermodynamic state function that describe the amount of disorder, -- a large value for entropy means high degree of disorder

Entropy changes

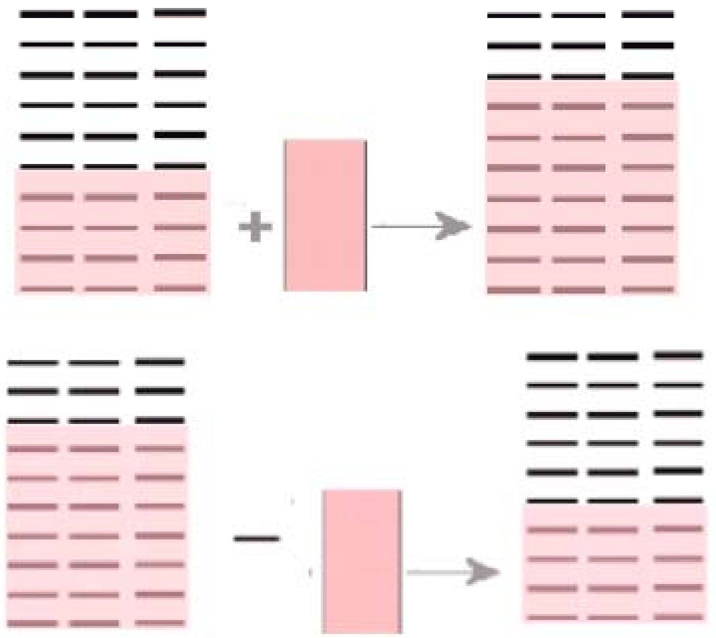
An Increase in disorder results in an increase in entropy.

- S increases when solid – liquid, liquid – gas
- S decreases when gas dissolves in a solvent
- S increases as temperature increases


Entropy, S°
0
10
20
30
40
50
50
100
150
200
250
300
Temperature (K)

Adding heat to the system,

- -increases the number of the accessible states,
- -increases disorder,
- -increases the entropy.



Removing heat from the system,

-decreases the number of accessibles states

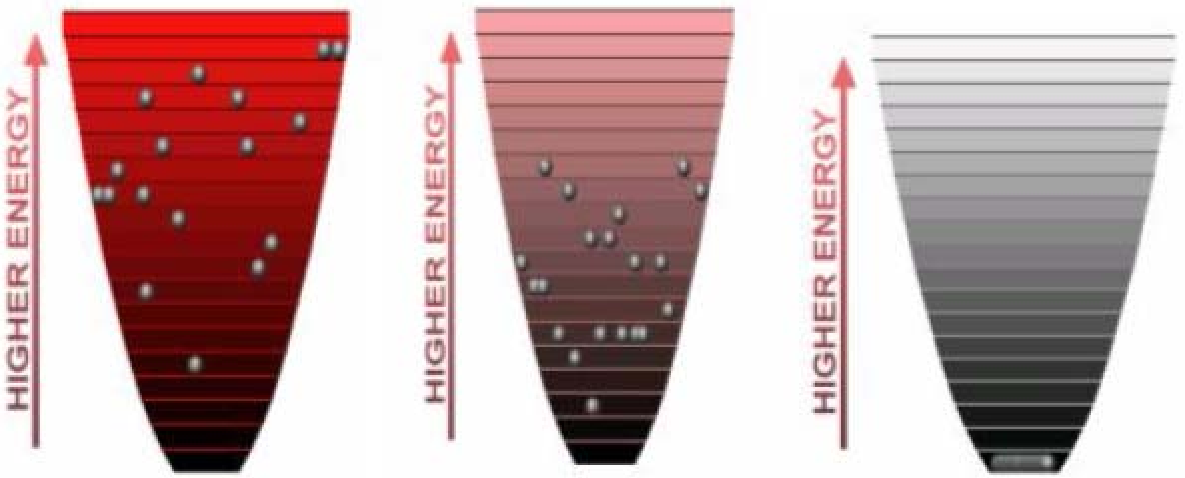
-decreases the disorder

-decreases the entropy

remove the heat until,

The number of accessibles state $\Omega = 1$

From $S = k \ln \Omega = k \ln (1) = 0$



# third law of thermodynamics

the entropy of any pure, perfect crystalline element or compound at absolute zero (0 K) is equal to zero.

-all molecular motion stops at 0K

-represent perfect order

# Absolute zero

**Definition**: *The lowest possible temperature allowed by the laws of thermodynamics.*

At this temperature, molecules would possess the absolute minimum KE allowed by quantum mechanics.

The temperature is equivalent to -273.15°C or 0K (kelvin).

At absolute zero, the entropy of any system vanished.

**Or**

The temperature at which all possible heat has been removed from an object.

Absolute zero **cannot** be reached experimentally, although it can be closely approached.

Cornell and Wieman cooled a small sample of atoms down to only a few *billionths* (0.000,000,001) of a degree above Absolute Zero!

Note: entropy $$dS = \frac{\delta Q}{T}$$

$\delta Q = mC\,dT$ $$dS = \frac{mCdT}{T}$$

$$\Delta S = \int dS = \int \frac{mCdT}{T} = mC \int \frac{dT}{T}$$

if C : constant

heating a sample from absolute zero to finite temperature T, increases the entropy by,

$$\Delta S = \int_0^T dS = \int_0^T \frac{mCdT}{T} = mC \int_0^T \frac{dT}{T}$$

$$= S_T - S_0 = S_T - 0 = S_T$$

Example:

A sample of 1 kg is heated to 300 K from absolute zero. Determine the entropy of the sample at 300 K.

(Take the specific heat of the sample as c = 5T $^{1/2}$ J/kg.K

$$S_{300\ K} = S_{300\ K} - S_0 = \Delta S = \int_0^{300} dS$$

$$= \int_0^T \frac{\delta Q}{T} = \int_0^T \frac{c dT}{T} = \int_0^{300} \frac{5T^{1/2} dT}{T} = 173\ J/K$$

Example:

The reaction A + B → C is carried out at 300 K. How much heat is released (per kg) of C if $c_A = 5T^{1/2}$ J/kg.K, $c_B = 8T^{1/3}$ J/kg.K and $c_C = 15\ T^{1/3}$ J/kg.K.

Ans: $\Delta Q = T\Delta S$ and $\Delta S = S_C - (S_A + S_B)$

$S_A$ (300K) = 173 J/kg.K

$S_B$ (300K) = 161J/kg.K

$S_C$ (300K) = 301 J/kg.K

$\Delta S$ = 173 -161+301= -289 J/kg.K

J/K

$\Delta Q$ = -289 x 300 = - 86.7 kJ/kg (heat is given out by the system)

# THAT'S ALL FOR NOW!!

REFERENCES:

1. REAF, F : “Fundamentals Of Statistical And Thermal Physics”, McGraw-Hill.

2. KITTEL & KROMER: “Thermal Physics”, W.H. Freeman & Company.