4. Entropy Changes accompanying specific processes, the Third Law of Thermodynamics

4.1 Entropy Changes in Isothermal Transformations, Trouton's rule

From the definition

$$d\boldsymbol{S} \equiv \eth q_{rev} / T$$

For an isothermal reversible process,

$$\Delta \boldsymbol{S} = q_{rev} / T$$

EXAMPLE:

For an isothermal expansion of *n* moles of an ideal gas, $\Delta \boldsymbol{U} = 0$

so that $q = -W$ whether the process is carried out reversibly or not.

If carried out reversibly, $p_{op} = p_{gas}$

$-W = nRT \ln (V_f/V_i) = q_{rev}$

$\Delta \boldsymbol{S} = q_{rev}/T = nR \ln(V_f/V_i) = nR \ln (p_i/p_f)$

EXAMPLE:

For reversible heating and cooling,

$$\Delta \boldsymbol{S} = \int \eth q_{rev}/T = \int C_{rev}dT/T$$

Generally $C = a + bT + cT^2 + \ldots$

If constant volume, use C_V. If constant pressure use C_p.

EXAMPLE:

For a reversible transition at temperature T, at constant pressure,

$$\Delta_{trans}\boldsymbol{S} = \Delta_{trans}\boldsymbol{H}/T_{trans}$$

for example, $\Delta_{vap}\boldsymbol{S} = \Delta_{vap}\boldsymbol{H}/T_b$

For many liquids, the entropy of vaporization has approximately the same value (Trouton's rule) :

$\Delta_{vap}\boldsymbol{S} \approx 85\ \mathrm{J\ mol^{-1}\ K^{-1}}$ or $21\ \mathrm{cal\ mol^{-1}\ K^{-1}}$

This empirical observation permits

estimation of $\Delta_{vap}\boldsymbol{H}^{\ominus}$ from boiling points.

4.2 Entropy as a Function of Temperature and Volume

In a reversible transformation, $p_{op} = p_{gas}$, so that $d\boldsymbol{U} = \text{đ}q_{\mathrm{rev}} - p\,dV = T\,d\boldsymbol{S} - p\,dV$

or $d\boldsymbol{S} = (1/T)\,d\boldsymbol{U} + (p/T)\,dV$

$$d\boldsymbol{U} = C_V\,dT + (\partial \boldsymbol{U}/\partial V)_T\,dV$$

$$d\boldsymbol{S} = (1/T)\{C_V\,dT + (\partial \boldsymbol{U}/\partial V)_T\,dV\} + (p/T)\,dV$$

$$d\boldsymbol{S} = (1/T)C_V\,dT + (1/T)\{p + (\partial \boldsymbol{U}/\partial V)_T\}\,dV$$

$$d\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_V\,dT + (\partial \boldsymbol{S}/\partial V)_T\,dV$$

Thus we identify

$$(\partial \boldsymbol{S}/\partial T)_V = (1/T)C_V$$

$$(\partial \boldsymbol{S}/\partial V)_T = (1/T)\{p + (\partial \boldsymbol{U}/\partial V)_T\} = (\partial p/\partial T)_V$$

Thus,

$$d\boldsymbol{S} = (1/T)C_V\,dT + (\partial p/\partial T)_V\,dV$$

Since C_V/T is always positive, the above expresses the important fact that *at constant volume the entropy increases with increase in temperature.*

EXAMPLE:

Changes in entropy for an ideal gas:

$d\boldsymbol{S} = (1/T)C_V\, dT + (\partial p/\partial T)_V\, dV$ *general*

For an ideal gas $(\partial p/\partial T)_V = R/V$

$\Delta \boldsymbol{S} = \int C_V dT/T + \int R dV/V$

EXAMPLE:

At constant volume, for any substance

$\Delta \boldsymbol{S} = \int C_V dT/T$

Aside: More properties of exact differentials

The total differential of a function of two variables $f(x,y)$ is written in the form

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

Since the differential coefficients $\frac{\partial f}{\partial x}$ $\frac{\partial f}{\partial y}$ are functions of x and y, we may write

$$M(x,y) = \frac{\partial f}{\partial x} \qquad N(x,y) = \frac{\partial f}{\partial y}$$

and we get

$df = M(x,y)dx + N(x,y)dy$

We can form second derivatives of the function $f(x,y)$: $\frac{\partial^2 f}{\partial x^2}$ $\frac{\partial^2 f}{\partial y^2}$ $\frac{\partial^2 f}{\partial x \partial y}$ $\frac{\partial^2 f}{\partial y \partial x}$

Of these four, only three are distinct. The order of differentiation with respect to two variables such as x and y does not matter and the mixed derivatives are equal

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

Let us differentiate $M(x,y) = \dfrac{\partial f}{\partial x}$ with respect to y,

$$(\partial M/\partial y) = \frac{\partial^2 f}{\partial y \partial x} \qquad \text{and}$$

differentiate $N(x,y) = \dfrac{\partial f}{\partial y}$ with respect to x,

$$(\partial N/\partial x) = \frac{\partial^2 f}{\partial x \partial y}$$

But since the order of differentiation does not matter, $(\partial M/\partial y) = (\partial N/\partial x)$. These are sometimes called "cross derivatives" because of their relation to the total differential $df = M(x,y)dx + N(x,y)dy$.

In summary,
for $df = M(x,y)dx + N(x,y)dy$.
$(\partial M/\partial y) = (\partial N/\partial x)$ *holds.*

On the other hand,
$R(x,y)dx + Q(x,y)dy$
is an exact differential if and only if
$(\partial R/\partial y) = (\partial Q/\partial x)$. If this is true then there must exist some function $g(x,y)$ such that $dg = Rdx + Qdy$.

When we apply the cross derivative rule to fundamental equations, we obtain additional fundamental relations called ***the Maxwell relations***.

4.2 Entropy as a Function of Temperature and Volume

What is $(\partial \boldsymbol{U}/\partial \boldsymbol{V})_T$?

First law $\mathrm{d}\boldsymbol{U} = \eth q + \eth W$, $\eth W = -p_{op}\mathrm{d}V$

Second law $\mathrm{d}\boldsymbol{S} = \eth q_{rev}/T$

In a reversible transformation, $p_{op} = p_{gas}$

so that $\mathrm{d}\boldsymbol{U} = \eth q_{rev} - p\mathrm{d}V$

$$\boxed{\mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V}$$

or $\mathrm{d}\boldsymbol{S} = (1/T)\mathrm{d}\boldsymbol{U} + (p/T)\mathrm{d}V$

$\boldsymbol{U}$ is a function of T and V,

$\mathrm{d}\boldsymbol{U} = C_V\mathrm{d}T + (\partial \boldsymbol{U}/\partial V)_T\mathrm{d}V$

Cross derivatives give us

$$(\partial C_V/\partial V)_T = (\partial^2 \boldsymbol{U}/\partial T\partial V)$$

Substitute $\mathrm{d}\boldsymbol{U}$

$\mathrm{d}\boldsymbol{S} = (1/T)\{C_V\mathrm{d}T + (\partial \boldsymbol{U}/\partial V)_T\mathrm{d}V\} + (p/T)\mathrm{d}V$

$\mathrm{d}\boldsymbol{S} = (1/T)C_V\mathrm{d}T + (1/T)\{p + (\partial \boldsymbol{U}/\partial V)_T\}\mathrm{d}V$

Cross derivatives give us

$$\underline{(1/T)(\partial C_V/\partial V)_T} = -(1/T^2)\{p + (\partial \boldsymbol{U}/\partial V)_T\} + \underline{(1/T)}\{(\partial p/\partial T)_V + \underline{(\partial^2 \boldsymbol{U}/\partial T\partial V)}\}$$

leading to

$$(1/T^2)\{p + (\partial \mathbf{U}/\partial V)_T\} = (1/T)(\partial p/\partial T)_V$$

$$(1/T)\{p + (\partial \mathbf{U}/\partial V)_T\} = (\partial p/\partial T)_V$$

which lead to two important results:

$$\boxed{(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p}$$

$$\mathrm{d}\boldsymbol{S} = (1/T)C_V\,\mathrm{d}T + (1/T)\{p + (\partial \mathbf{U}/\partial V)_T\}\,\mathrm{d}V$$

compare directly with

$$\mathrm{d}\boldsymbol{S} = (\partial \mathbf{S}/\partial T)_V\,\mathrm{d}T + (\partial \mathbf{S}/\partial V)_T\,\mathrm{d}V$$

Thus we identify

$$(\partial \mathbf{S}/\partial T)_V = (1/T)C_V$$

$$(\partial \mathbf{S}/\partial V)_T = (1/T)\{p + (\partial \mathbf{U}/\partial V)_T\} = (\partial p/\partial T)_V$$

$$\boxed{(\partial \mathbf{S}/\partial V)_T = (\partial p/\partial T)_V}$$

Thus,

$$\mathrm{d}\boldsymbol{S} = (1/T)C_V\,\mathrm{d}T + (\partial p/\partial T)_V\,\mathrm{d}V$$

$$dS = (1/T)C_V\,dT + (\partial p/\partial T)_V\,dV$$

Since C_V/T is always positive, the above expresses the important fact that *at constant volume the entropy increases with increase in temperature.*

EXAMPLE:

Changes in entropy for an ideal gas:

$dS = (1/T)C_V\,dT + (\partial p/\partial T)_V\,dV$ *general*

For an ideal gas $(\partial p/\partial T)_V = R/V$

$$\Delta S = \int C_V dT/T + \int R dV/V$$

EXAMPLE:

At constant volume, for any substance

$$\Delta S = \int C_V dT/T$$

4.3 Entropy as a Function of Temperature and pressure

What is $(\partial \boldsymbol{H}/\partial \boldsymbol{p})_T$?

First law $\mathrm{d}\boldsymbol{U} = \eth q + \eth W,\ \eth W = -\,p_{op}\mathrm{d}V$

Second law $\mathrm{d}\boldsymbol{S} = \eth q_{rev}/T$

In a reversible transformation, $p_{op} = p_{gas}$

so that $\mathrm{d}\boldsymbol{U} = \eth q_{rev} - p\mathrm{d}V$

$$\boxed{\mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V}$$

or $\mathrm{d}\boldsymbol{S} = (1/T)\mathrm{d}\boldsymbol{U} + (p/T)\mathrm{d}V$

$\boldsymbol{H} = \boldsymbol{U} + pV$

$\mathrm{d}\boldsymbol{H} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p$

$\mathrm{d}\boldsymbol{U} = \mathrm{d}\boldsymbol{H} - p\mathrm{d}V - V\mathrm{d}p$

$\mathrm{d}\boldsymbol{S} = (1/T)\{\mathrm{d}\boldsymbol{H} - p\mathrm{d}V - V\mathrm{d}p\} + (p/T)\mathrm{d}V$

$\mathrm{d}\boldsymbol{S} = (1/T)\{\mathrm{d}\boldsymbol{H} - V\mathrm{d}p\}$

$\boldsymbol{H}$ is a function of T and p,

$\mathrm{d}\boldsymbol{H} = C_p\,\mathrm{d}T + (\partial \boldsymbol{H}/\partial p)_T\,\mathrm{d}p$

Cross derivatives give us

$(\partial C_p/\partial p)_T \quad = (\partial^2 \boldsymbol{H}/\partial T\partial p)$

Substitute $\mathrm{d}\boldsymbol{H}$

$$\mathrm{d}\boldsymbol{S} = (1/T)\{\, C_p\,\mathrm{d}T + (\partial \mathbf{H}/\partial p)_T\,\mathrm{d}p - V\mathrm{d}p \,\}$$

Cross derivatives give us

$$\underline{(1/T)(\partial C_p/\partial p)_T} \;= -\,(1/T^2)\{\, (\partial \mathbf{H}/\partial p)_T - V \,\}$$
$$+\underline{(1/T)}\{-(\partial V/\partial T)_p + \underline{(\partial^2 \mathbf{H}/\partial T\,\partial p)}\}$$

leading to

$$(1/T^2)\{\, (\partial \mathbf{H}/\partial p)_T - V \,\} = -(1/T)(\partial V/\partial T)_p$$
$$(1/T)\,\{\, (\partial \mathbf{H}/\partial p)_T - V \,\} = -\,(\partial V/\partial T)_p$$

which lead to two important results:

$$\boxed{(\partial \mathbf{H}/\partial p)_T = -T(\partial V/\partial T)_p + V}$$

$$\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T + \{(\partial \mathbf{H}/\partial p)_T - V\,\}\,\mathrm{d}p$$

compare directly with

$$\mathrm{d}\boldsymbol{S} = (\partial \mathbf{S}/\partial T)_p\,\mathrm{d}T + (\partial \mathbf{S}/\partial p)_T\,\mathrm{d}p$$

Thus we identify

$(\partial \mathbf{S}/\partial T)_p \;= (1/T)C_p$ and

$$(\partial \mathbf{S}/\partial p)_T \;= (1/T)\{(\partial \mathbf{H}/\partial p)_T - V\,\} = \;-\partial V/\partial T)_p$$

$$\boxed{(\partial \mathbf{S}/\partial p)_T \;=\; -(\partial V/\partial T)_p}$$

Thus, $\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T \;-\, (\partial V/\partial T)_p\,\mathrm{d}p$

$$dS = (1/T)C_p\,dT - (\partial V/\partial T)_p\,dp$$

Since C_p/T is always positive, the above expresses the important fact that *at constant pressure the entropy increases with increase in temperature.*

EXAMPLE:

Changes in entropy for an ideal gas:

$dS = (1/T)C_p\,dT - (\partial V/\partial T)_p\,dp$ *general*

For an ideal gas $(\partial V/\partial T)_p = R/p$

$$\Delta S = \int C_p\,dT/T - \int R\,dp/p$$

EXAMPLE:

At constant pressure, for any substance

$$\Delta S = \int C_p\,dT/T$$

To summarize, we have derived:

$(\partial \mathbf{U}/\partial V)_T$ **and** $(\partial \mathbf{H}/\partial p)_T$ **from the equation of state**

$$\boxed{\begin{gathered}(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p \\ (\partial \mathbf{H}/\partial p)_T = -T(\partial V/\partial T)_p + V\end{gathered}}$$

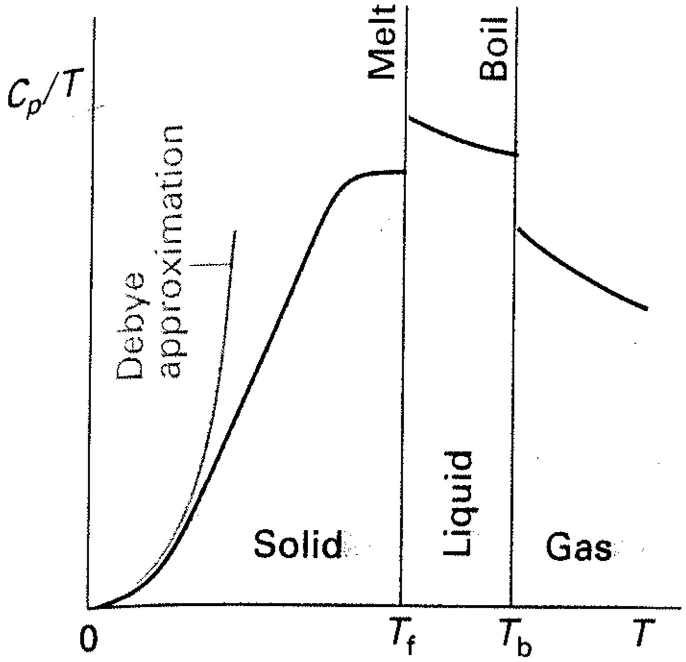
and

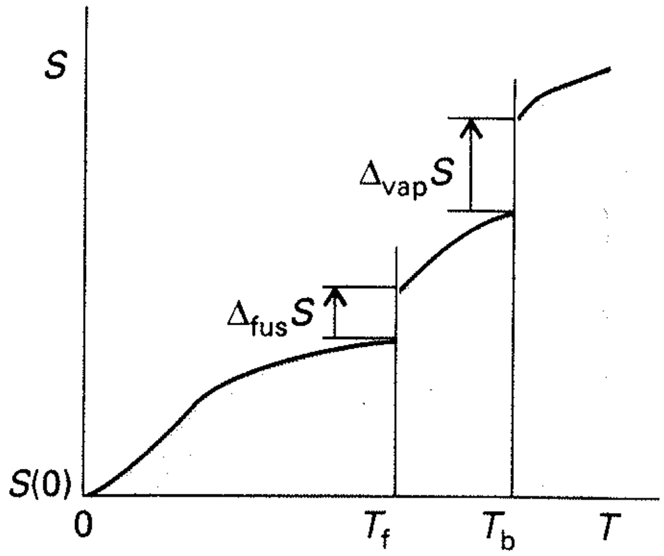
$$d\boldsymbol{S} = (1/T)C_V\, dT + (\partial p/\partial T)_V\, dV$$

$$d\boldsymbol{S} = (1/T)C_p\, dT - (\partial V/\partial T)_p\, dp$$

EXAMPLE:

The entropy of a system at a temperature *T* is related to its entropy at $T = 0$ by means of the calculable changes in entropy that accompany the temperature and phase changes in taking the system from 0 K to temperature *T*.





$$\boxed{\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T - (\partial V/\partial T)_p\,\mathrm{d}p}$$

(at p = 1 bar)

Standard entropy of a substance $\boldsymbol{S}^{\ominus}_{T}$

$$\boldsymbol{S}^{\ominus}_{T} = \boldsymbol{S}_{0\,\mathrm{K}} + \int_{0}^{T} C_p\,dT/T + \ldots$$

At zero K the entropy has its smallest algebraic value, $\boldsymbol{S}_{0\,\mathrm{K}}$. The entropy at any higher temperature is greater than $\boldsymbol{S}_{0\,\mathrm{K}}$

The Third Law of Thermodynamics defines the value of $\boldsymbol{S}_{0\,\mathrm{K}}$:

All perfectly pure, perfectly crystalline materials have the same entropy at absolute zero.

The entropy of a pure, perfectly crystalline substance is <u>zero</u> at the absolute zero of temperature.

Standard entropy of a solid $S^{\ominus}_T$
is sometimes called third law entropy because the value is based on $S_{0\ \mathrm{K}} = 0$.

Since a change in the state of aggregation (melting, vaporization, change in crystalline form) involves a change in entropy, these contributions must be included in computation of the entropy of a substance at temperature *T*.

EXAMPLE:

Solids at very low temperatures
How to do the integral?

$$\int_0^T C_p \ dT/T$$

C_p behaves asymptotically as aT^3 (Debye T-cubed law) at very very low temperatures, so that the integral has a finite value $(1/3)aT^3$.

EXAMPLE:

Calculate the standard molar entropy of nitrogen gas at 25°C.

	$\mathrm{J\ K^{-1}\ mol^{-1}}$
Debye extrapolation 0 to 10 K	1.92
Integration, 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration, 35.61 K to 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration, 63.14 K to 77.32 K	11.41
Vaporization at 77.32 K	72.13
Integration, 77.32 K to 298.15 K	41.12
	192.06

using $\Delta_{trans}\boldsymbol{S} = \Delta_{trans}\boldsymbol{H} / T_{trans}$

and $\int_{T''}^{T'} C_p\ dT/T$

General trends in the values of standard molar entropies:

1. Entropies of gases are larger than those of liquids, which are larger than those of solids.
2. The entropy of a series of gases increases logarithmically with the mass.
3. Comparing gases having the same mass, Ne, HF, H2O for example, entropy is greater for greater number of degrees of freedom.(translation, +2, +3 rotations)
4. Solids built structurally with single simple unit: higher cohesive energy, lower entropy
5. Solids built structurally of a single complex unit: lower cohesive energy (van der Waals forces), higher entropy.
6. Where complex units occur in the crystal, the entropy is greater due to additional degrees of freedom

The molecular interpretation of entropy

The entropy of a system in a definite state can be related to what is called the *probability of that state* of the system. For this we need a structural model.

If we consider the system as made up of particles (for example rare gas atoms):

The entropy of a system in a specified state can be defined in terms of the *number of possible arrangements of the particles composing the system which are consonant with the state of the system*. Boltzmann defined (statistical mechanical) entropy by the equation:

$$\boldsymbol{S} = k_B \ln \Omega$$

When the constraints are simple and the system is sufficently small, it is possible to look at each way of arriving at a physical state, that is it is possible to count out each of the "arrangements" in the total number of arrangements Ω.

EXAMPLE

Consider a pair of dice. Question: What is the most probable sum? Answer: That sum which corresponds to the largest number of distinguishable ways Ω of getting it.

The "physical state" in this example is defined by having a specific value of the property called "sum".

Ω , the number of possible arrangements which are consonant with the physical state of the system, is the number of distinguishable ways of ending up with a given value for the property called "sum".

∑	#1	#2	Ω
2	1	1	**1**
3	1	2	**2**
	2	1	
4	1	3	**3**
	2	2	
	3	1	
5	1	4	**4**
	2	3	
	3	2	
	4	1	
6	1	5	**5**
	2	4	
	3	3	
	4	2	
	5	1	
11	5	6	**2**
	5	5	
12	6	6	**1**

∑	#1	#2	Ω
7	1	6	**6**
	2	5	
	3	4	
	4	3	
	5	2	
	6	1	
8	2	6	**5**
	3	5	
	4	4	
	5	3	
	6	2	
9	3	6	**4**
	4	5	
	5	4	
	6	3	
10	4	6	**3**
	5	5	
	6	4	

①②③④⑤⑥⑦⑧...

N particles into 3 levels

𝔄	𝔅	ℭ

Consider level 𝔄. Suppose 3 particles are to be in level 𝔄:

There are N choices for picking the first particle, there are (N-1) choices for picking the second one, and (N-2) choices for picking the third. That is, there are N(N-1)(N-2) ways of selecting three particles from N particles.

So suppose we happened to pick the particles ①②③ :

The same occupancy (three particles in level 𝔄) results whether we picked them in the order ①first, ② second, ③ last

or in the order ②③①

or in the order ②①③, etc. 3! ways in all

read this as “3 factorial”, $3! = 3\times2\times1$

To get the *number of distinguishable ways* of picking, we have to divide $N(N-1)(N-2)$ by 3!

Now consider level $\mathfrak{B}$. Suppose 2 particles are to be in level $\mathfrak{B}$:
There are $(N-3)$ choices for picking the first particle, there are $(N-4)$ choices for picking the second one. Then the *number of distinguishable ways* of picking particles to go into level $\mathfrak{B}$ is

$$(N-3)(N-4)/2!$$

Consider level $\mathfrak{C}$. Suppose 3 particles are to be in level $\mathfrak{C}$:
There are $(N-5)$ choices for picking the first particle, there are $(N-6)$ choices for picking the second one, ... Then the number of distinguishable ways of picking particles to go into level $\mathfrak{C}$ is

$$(N-5)(N-6)(N-7)/3!$$

Altogether, the number of distinguishable ways of picking particles to go into level $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{C}$ such that the occupancies are 3, 2, and 3 respectively is

$$\{N(N-1)(N-2)/3!\} \times \{(N-3)(N-4)/2!\} \times \{(N-5)(N-6)(N-7)/3!\}$$

or

$$\frac{N(N-1)(N-2)(N-3)(N-4)(N-5)(N-6)(N-7)}{3!\;2!\;3!}$$

Now suppose we have a large number of levels and we want to distribute <u>all</u> the N particles among the levels, such that there are $n_{\mathfrak{A}}$ particles in level $\mathfrak{A}$, $n_{\mathfrak{B}}$ particles in level $\mathfrak{B}$ etc. then the number of distinguishable ways of doing this is

$$\Omega = \frac{N!}{n_{\mathfrak{A}}!\; n_{\mathfrak{B}}!\; n_{\mathfrak{C}}!\; n_{\mathfrak{D}}!\; \ldots\ldots}$$

When N particles are indistinguishable from one another, the number of possible arrangements, Ω, of distributing these particles among states having energies ε_1, ε_2, ... is the number

$$\Omega = N! / \{n_1!\, n_2!\, n_3!\, n_4! \ldots\}$$

where n_1 particles are in ε_1 etc.

If each has 1 or zero occupation, then this would give the largest possible value of Ω and would correspond to the largest possible value of entropy.

On the other hand if all were crowded together into the first level, then Ω would be very much smaller than that of a broad distribution.

To achieve a high entropy then, the particles would have to be spread out into as broad an energy distribution as possible.

The internal energy of the system would be ***U*** = $n_1\varepsilon_1 + \varepsilon_2 n_2 + \varepsilon_2 n_3 + \varepsilon_4 n_4 + \ldots$ When ***U*** is small this greatly limits the occupancies of higher values of ε_i , thus limits severely the number Ω. If the internal energy of the system is increased the distribution can be broader, the number Ω and ***S*** of the system goes up. *This is the statistical interpretation of the fact illustrated by the fundamental equation* $d\boldsymbol{S} = (1/T)d\boldsymbol{U} + (p/T)dV$.

Now consider the spatial distribution also. Imagine space being divided up into tiny voxels, and the N particles being distributed into voxels such that there are n_1 in voxel 1, ... etc. By increasing the volume, the spatial distribution broadens.

The broader distribution in energy or space is the more probable one since it can be made up in greater number of ways.

In a pure crystal the atoms are located in an exact periodic pattern. There are N! ways of arranging the atoms but since the atoms are identical these arrangements differ only in the order of choosing the atoms. Since the arrangements are not unique we must divide by N! and so we obtain

$\Omega = N!/N! = 1$ for the perfect crystal

$\boldsymbol{S} \equiv k_B \ln \Omega$

$\boldsymbol{S} = k_B \ln(1) = 0$ for the perfect crystal

This is the statistical interpretation of the Third Law.

Entropy of mixing

Suppose we arrange two kinds of atoms A and B on the N sites of a crystal.

$$N_A + N_B = N$$

$$\Omega = N! / N_A ! N_B!$$

$$\boldsymbol{S} = k_B \ln \Omega = k_B \ln\{ N! / N_A ! N_B! \}$$

$\ln N! \approx N \ln N - N$ for very large N

$$\boldsymbol{S} = k_B \{ N\ln N - N_A \ln N_A - N_B \ln N_B - N + N_A + N_B \}$$

In terms of mole fractions

$$N_A = x_A N, \quad N_B = x_B N$$

$$\boldsymbol{S} = - k_B \{ N_A \ln N_A + N_B \ln N_B - N\ln N \}$$

$$\boldsymbol{S} = - k_B \{ x_A N \ln x_A N + x_B N \ln x_B N - N\ln N \}$$

$$\boldsymbol{S} = - k_B N \{ x_A \ln x_A N + x_B \ln x_B N - \ln N \}$$

$$\boxed{\boldsymbol{S} = - k_B N \{ x_A \ln x_A + x_B \ln x_B \}}$$

is positive