Statistical thermodynamics
Lectures 7, 8

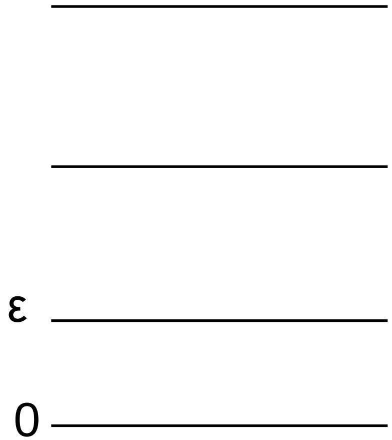
Quantum ↔ classical

Energy levels *Bulk properties*

Various forms of energies.

Everything turns out to be controlled by temperature

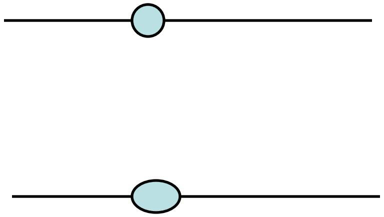
Ref. Atkins 7th or 8th edition
Alberty, Silbey, Bawendi 4th edition



Reference to zero

Need for statistical thermodynamics
Microscopic and macroscopic world
Energy states
Distribution of energy - population
Principle of equal *a priori* probabilities

Configuration - instantaneous
n_1, n_2,…molecules exist in states with energies ε_0, ε_1,…
N is the total number of molecules
{N,0,0,…} and {N-2, 2,0,…} are configurations
Second is more likely than the first

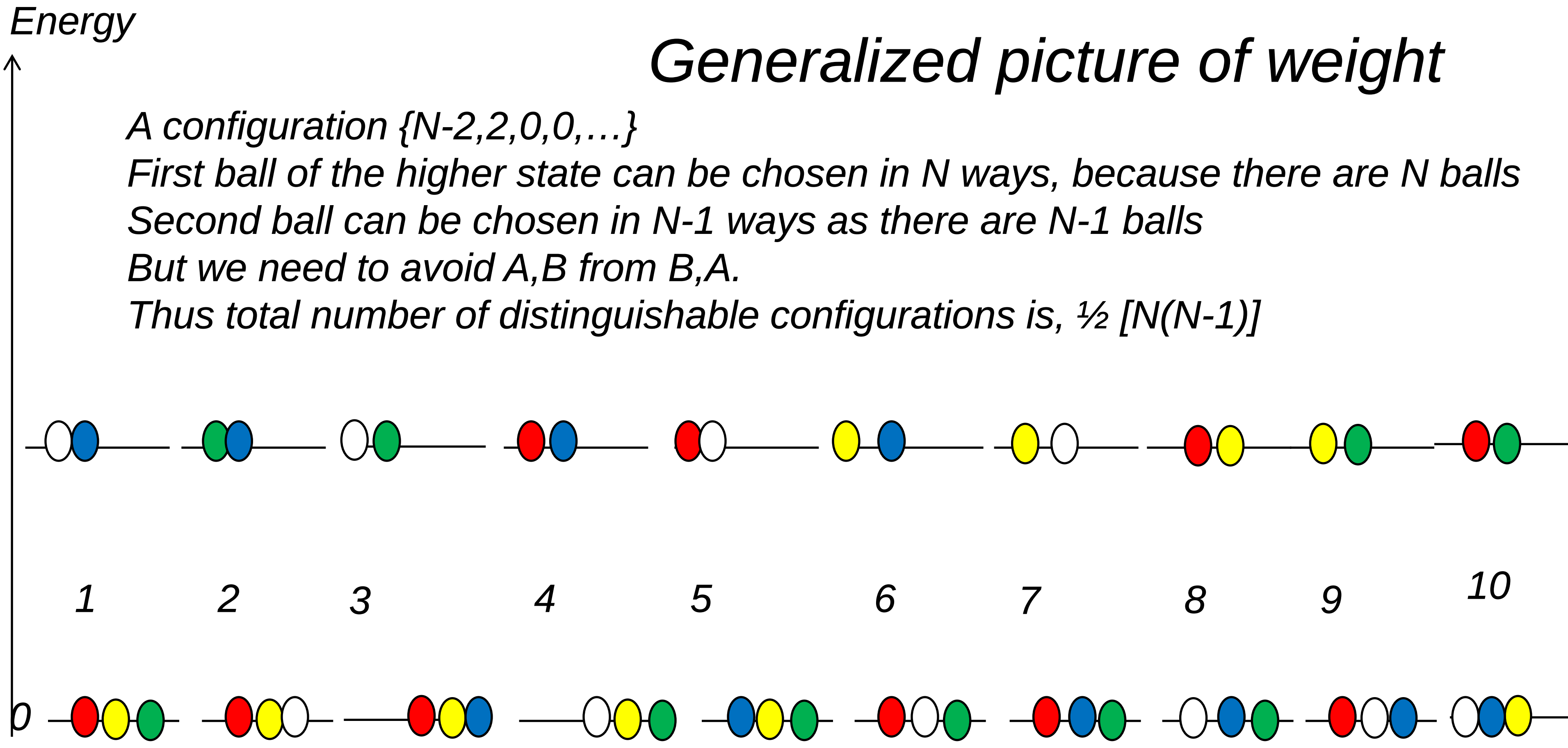


Fluctuations occur

{1,1}, {2,0}, {0,2}
Weight of a configuration = how many times the configuration can be reached.

Generalized picture of weight

A configuration {N-2,2,0,0,…}
First ball of the higher state can be chosen in N ways, because there are N balls
Second ball can be chosen in N-1 ways as there are N-1 balls
But we need to avoid A,B from B,A.
Thus total number of distinguishable configurations is, ½ [N(N-1)]



A configuration {3,2,0,0,..} is chosen in 10 different ways - weight of a configuration
How about a general case of N particles ? {n_0,n_1,…..} configuration of N particles.

Distinct ways,

$$W = \frac{N!}{n_0!n_1!n_2!....}$$

N! ways of selecting balls (first ball N, second (N-1), etc.)
n_0! ways of choosing balls in the first level. n_1! for the second, etc.

W is the weight of the configuration.

How many ways a configuration can be achieved.

Better to use natural logarithm

$$\ln W = \ln \frac{N!}{n_0!\, n_1!\, n_2! \ldots}$$

$$= \ln N! - \ln(n_0!\, n_1!\, n_2! ..)$$

$$= \ln N! - (\ln n_0! + \ln n_1! + \ln n_2! \ldots)$$

$$= \ln N\mathbf{!} - \Sigma_i \ln n_i\mathbf{!}$$

$\ln x! \approx x \ln x - x$ Stirling’s approximation

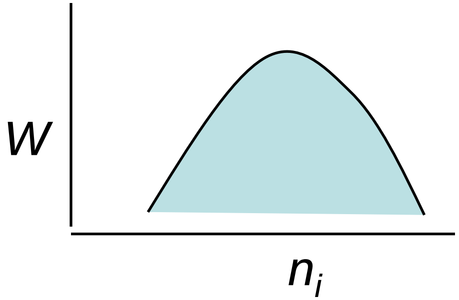
$$\ln W = (N \ln N - N) - \Sigma_i (n_i \ln n_i - n_i) = N \ln N - \Sigma_i n_i \ln n_i$$

Which is the dominating configuration having maximum weight?

Generalized approach is to set dW = 0

There are problems as any configuration is not valid.

1. Energy is constant. $\Sigma_i n_i \varepsilon_i = E$
2. Constant molecules. $\Sigma_i n_i = N$



Populations in the configuration of greatest weight depends on the energy of the state.

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\Sigma_i e^{-\beta\varepsilon_i}}$$

Boltzmann distribution

i is a sum over available states

$$\beta = \frac{1}{kT}$$

Temperature gives the most probable populations

Boltzmann distribution – population, $p_i = \dfrac{e^{-\beta\varepsilon_i}}{q}$

Molecular partition function

$q = \Sigma_i e^{-\beta\varepsilon_i}$

There are several ways of looking at i

Another form of q: $q = \Sigma_{\text{levels } i}\, g_i e^{-\beta\varepsilon_i}$

How to look at partition functions?

Look at limiting cases

$\lim_{T\to 0} q = g_0$

Because, $\varepsilon_0 = 0$
For all higher levels ε is finite.
$e^{-\beta\varepsilon} = 1$. e^{-x} is 0 when x is ∞.

$\lim_{T\to\infty} = \infty$

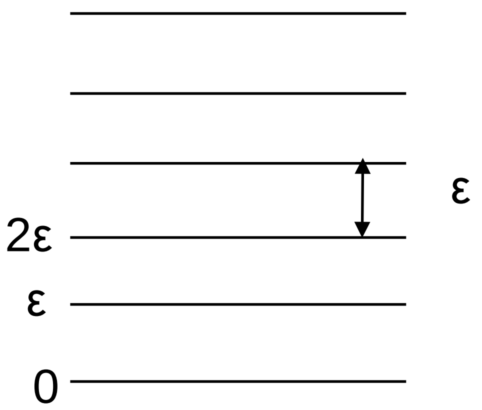
All terms will reduce to 1.
e^{-x} is 1 when x is 0

When number of states is finite,
we will not get ∞.

1. Partition function is the number of available states.
2. Partition function is the number of thermally accessible states.
3. How molecules are ‘partitioned’ into available states.

How to look at thermodynamic properties?

Evaluation of molecular partition function



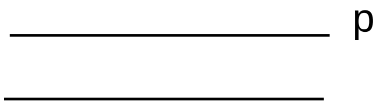
$1 + x + x^2 + x^3 + \ldots. = 1/(1-x)$

$q = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + \ldots = 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + (e^{-\beta\varepsilon})^2 + \ldots = 1/(1- e^{-\beta\varepsilon})$

Fraction of molecules in energy levels is,
$p_i = e^{-\beta\varepsilon_i}/q = (1- e^{-\beta\varepsilon})\, e^{-\beta\varepsilon_i}$

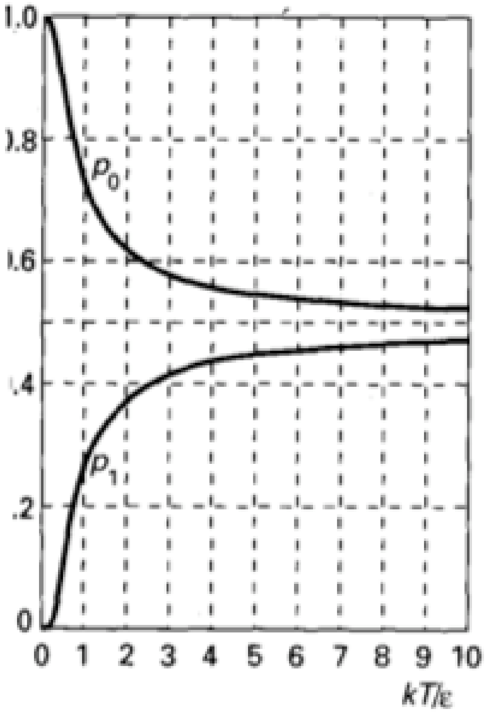
Discussion of figure, next slide

For a two level system,

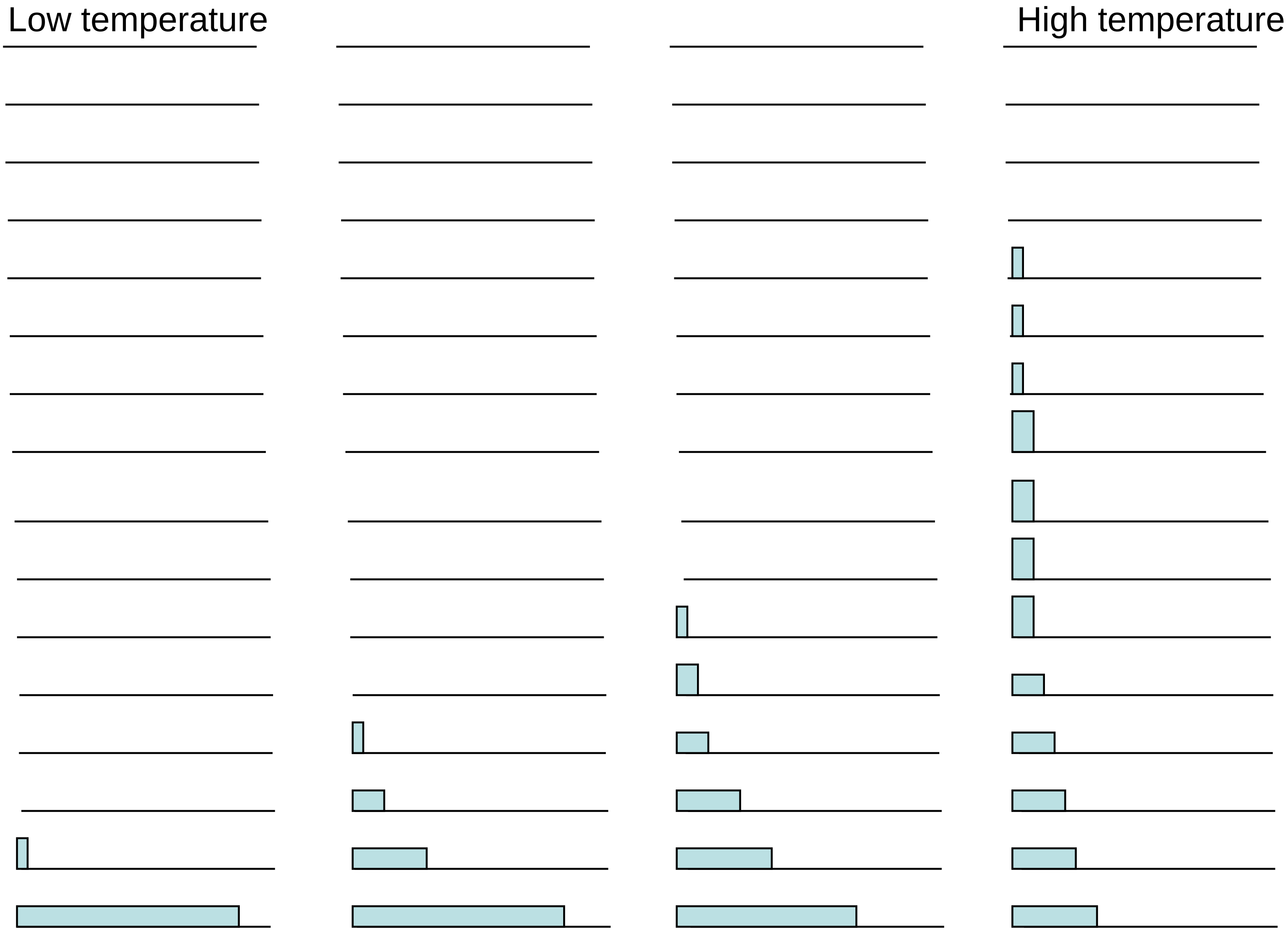


$p_o = 1/(1 + e^{-\beta\varepsilon})$
$p_1 = e^{-\beta\varepsilon}/q = e^{-\beta\varepsilon}/ (1+ e^{-\beta\varepsilon})$

As T → ∞, both p_o and p_1 go to ½.



Consequences?


Low temperature
High temperature

Approximations:

Partition functions are often complex. Analytical expressions cannot be obtained in several cases. Approximations become very useful.

For example, partition function for one dimensional motion

$$E_n = \frac{n^2h^2}{8\ mX^2} \qquad n = 1,2\ldots.$$

$$\varepsilon_n = (n^2-1)\varepsilon \qquad \varepsilon = \frac{h^2}{8mX^2}$$

$$q_x = \Sigma^{\infty}_{n=1}\ e^{-(n^2-1)\beta\varepsilon}$$

$$q_x = \int^{\infty}_{1} e^{-(n^2-1)\beta\varepsilon}\ dn$$ energy levels are close, sum becomes an integral

No big difference, if we take the lower limit to 0 and replace n^2-1 to n^2.

$$q_x = \left[\frac{1}{\beta\varepsilon}\right]^{1/2} \int_0^{\infty} e^{-x^2} dx = \left[\frac{1}{\beta\varepsilon}\right]^{1/2} \left[\frac{\pi}{2}\right]^{1/2} = \left[\frac{2\pi m}{h^2\beta}\right]^{1/2} X$$

Substitute, $X^2 = n^2\beta\varepsilon$, $dn = dx/(\beta\varepsilon)^{1/2}$

$$\boxed{q_x = \left[\frac{2\pi\, m}{h^2\beta}\right]^{1/2} X}$$

Substitute for ε

Independent motion in three dimensions

$\varepsilon_{n1n2n3} = \varepsilon_{n1}{}^{(X)} + \varepsilon_{n2}{}^{(Y)} + \varepsilon_{n3}{}^{(Z)}$ Energy is a sum of independent terms

$$q = \Sigma_{\text{all } n}\, e^{-\beta\varepsilon(X)_{n1} - \beta\varepsilon(Y)_{n2} - \beta\varepsilon(Z)_{n3}}$$

$$= \left[\Sigma_{n1}\, e^{-\beta\varepsilon(X)_{n1}}\right]\left[\Sigma_{n2}\, e^{-\beta\varepsilon(Y)_{n2}}\right]\left[\Sigma_{n3}\, e^{-\beta\varepsilon(Z)_{n3}}\right]$$

$$= q_x q_y q_z$$

$$q = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} XYZ$$

$$q = \frac{V}{\Box^3} \qquad \Box = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \frac{h}{(2\pi mkT)^{1/2}}$$

□ has dimensions of length, thermal wavelength

$J = kg\ m^{-2}\ s^{-2}$

Question: How many more quantum states will be accessible for $^{18}O_2$ compared to $^{16}O_2$, if it were to be confined in a box of 1 cm^3?

How to get thermodynamics?

All information about the thermodynamic properties of the system is contained in the partition function. Thermal wavefunction.

Total energy

$$E = \Sigma_i n_i \varepsilon_i$$

$$E = \frac{N}{q} \Sigma_i \varepsilon_i \, e^{-\beta\varepsilon i}$$

Most probable configuration is dominating.
We use Boltzmann distribution.

We know, $\varepsilon_i e^{-\beta\varepsilon i} = -\frac{d}{d\beta} e^{-\beta\varepsilon i}$

$$E = -\frac{N}{q} \Sigma_i \frac{d}{d\beta} e^{-\beta\varepsilon i} = -\frac{N}{q} \frac{d}{d\beta} \Sigma_i e^{-\beta\varepsilon i} = -\frac{N}{q} \frac{dq}{d\beta}$$

$$\boxed{U = U(0) + E}$$

1. *All E's are relative*
   E is the value of U relative to T = 0.

$$\boxed{U = U(0) - \frac{N}{q} \left(\frac{\partial q}{\partial \beta}\right)_V}$$

$$\boxed{U = U(0) - N \left(\frac{\partial \ln q}{\partial \beta}\right)_V}$$

2. *Derivative w.r.t.* β is partial as there are other parameters (such as V) on which energy depends on.

Partition function gives internal energy of the system.

How to get entropy?

For a process, change in internal energy, $U = U(0) + E$

$$U = U(0) + \Sigma_i \, n_i \varepsilon_i$$

Internal energy changes occur due to change in populations ($n_i + dn_i$) *or energy states* ($\varepsilon_i + d\varepsilon_i$). Consider a general case:

$$dU = dU(0) + \Sigma_i \, n_i \, d\varepsilon_i + \Sigma_i \, \varepsilon_i \, dn_i$$

For constant volume changes, $dU = \Sigma_i \, \varepsilon_i \, dn_i$

$dU = dq_{rev} = TdS$ $\qquad$ $dS = dU/T = k \beta \, \Sigma_i \varepsilon_i \, dn_i$

$$\boxed{\beta \, \varepsilon_i = (\partial \ln W / \partial \, n_i \,) + \alpha}$$

$$dS = k \, \Sigma_i (\partial \ln W / \partial \, n_i \,) \, dn_i + k\alpha \Sigma_i \, dn_i$$

Number of molecules do not change. Second term is zero.

$$dS = k \, \Sigma_i (\partial \ln W / \partial \, n_i \,) \, dn_i = k \, (d\ln W)$$

$$S = k\ln W$$