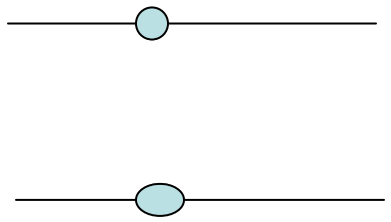
Statistical thermodynamics L1-L3

Lectures 11, 12, 13 of CY101

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



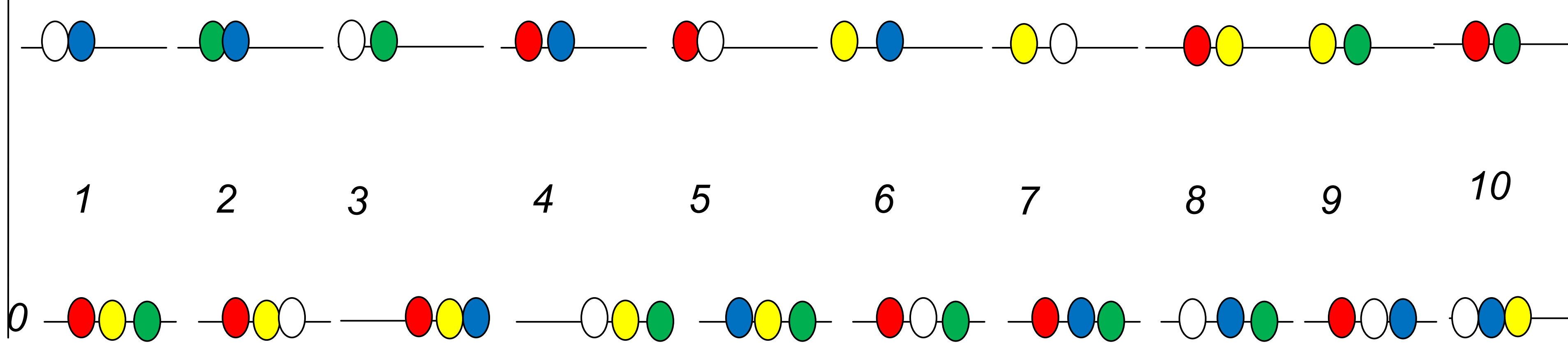
{1,1}, {2,0}, {0,2}
Weight of a configuration = how many times the configuration can be reached.

Various forms of energies.

Configuration - instantaneous
n_1, n_2,…molecules exist in states with energies ε_1, ε_2,…
N is the total number of molecules
{N,0,0,…} and {N-2, 2,0,…} are configurations
Second is more likely than the first

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

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
How about a general case of N molecules?

N! ways of selecting balls
n_0! for the balls in first level, n_1! for the second, etc.

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

W is the weight of the configuration.

How many ways a configuration can be achieved.

Better to use natural logarithm

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

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

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

$$= \ln N! - \Sigma_i \ln n_i!$$

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

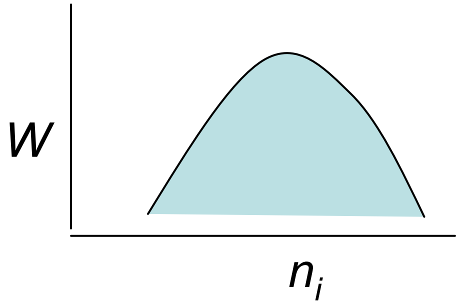
$$\ln W = (N \ln N - N) - \Sigma_i (n_i \ln n_i - n_i) = N \ln N - \Sigma_i n_i \ln n_i$$

Which is the dominating configuration having maximum weight?

Generalised 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. $\Sigma_i n_i = N$



Lagrange, method of undetermined multipliers

A constraint should be multiplied by a constant and then added to the variation equation

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 ∞.

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

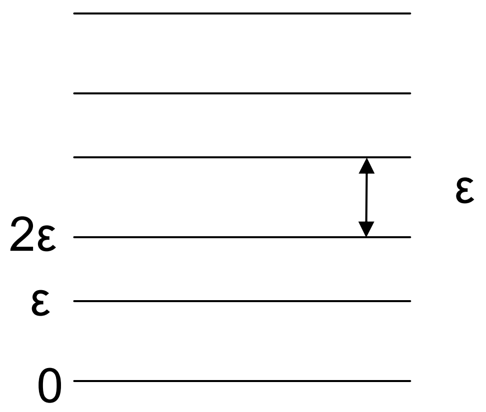
All terms will reduce to 1.
e^{-x} is 1 when x is 0

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



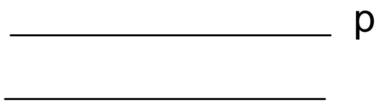
$1 + x + x^2 + x^3 + \ldots = 1/(1-x)$

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

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

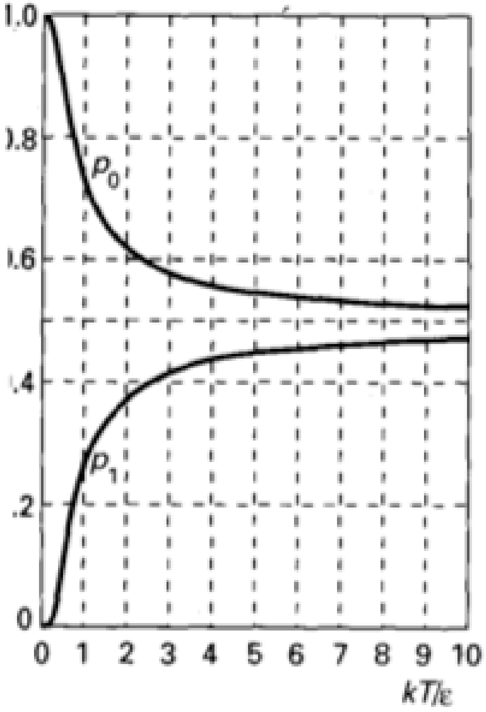
For a two level system,

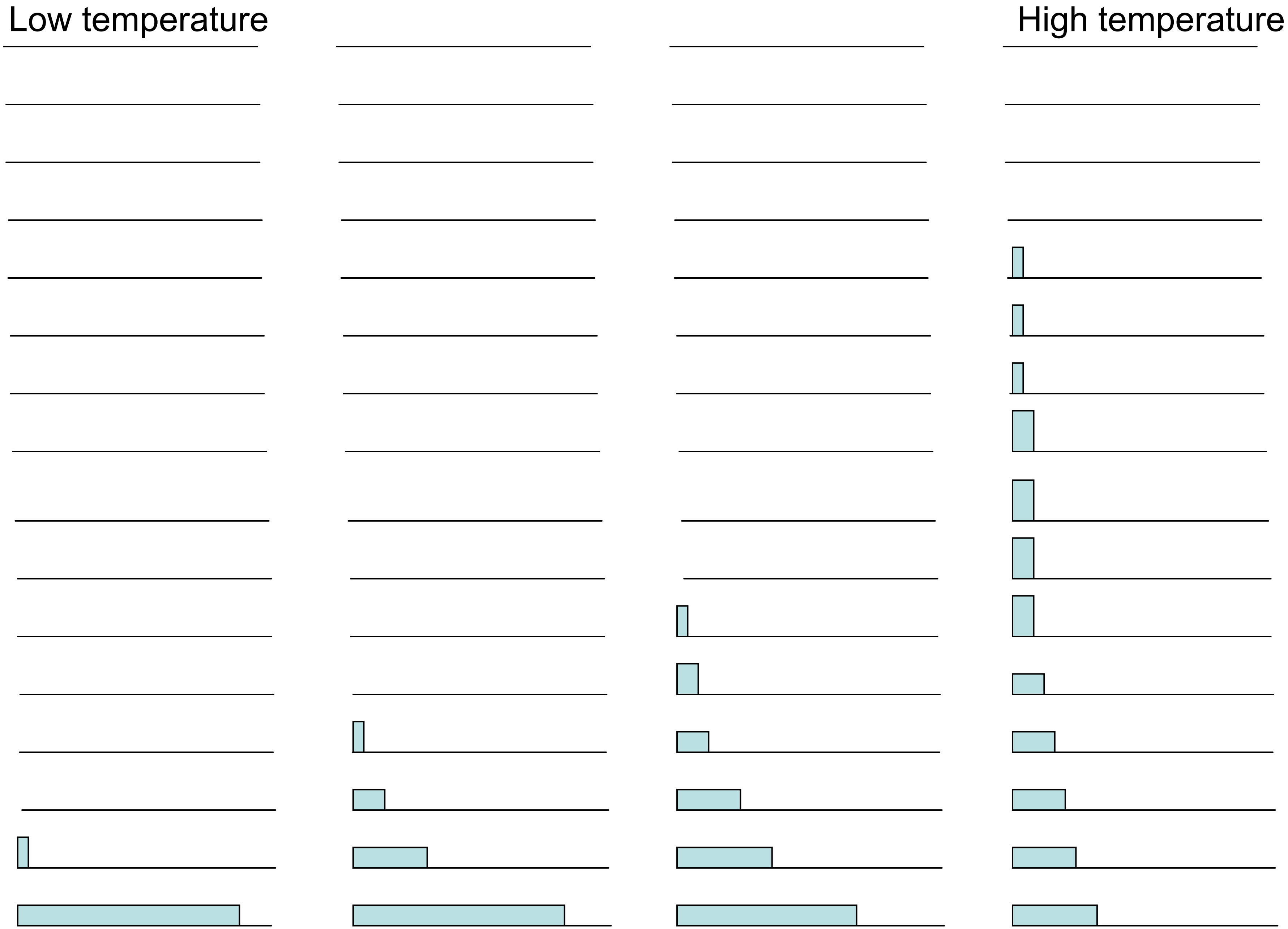


$p_o = 1/(1 + e^{-\beta\varepsilon})$
$p_1 = e^{-\beta\varepsilon}/q = e^{-\beta\varepsilon}/(1 + e^{-\beta\varepsilon})$

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

$$\boxed{\begin{aligned} q &= \Sigma_{\text{all } n}\, e^{-\beta\varepsilon(X)_{n1}\, -\beta\varepsilon(Y)_{n2}\, -\beta\varepsilon(Z)_{n3}} \\ &= \left[\Sigma_{n1}\, e^{-\beta\varepsilon(X)_{n1}}\right]\left[\Sigma_{n2}\, e^{-\beta\varepsilon(Y)_{n2}}\right]\left[\Sigma_{n3} e^{-\beta\varepsilon(Z)_{n3}}\right] \\ &= q_x q_y q_z \end{aligned}}$$

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

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

□ has dimensions of length, thermal wavelength

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

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.

Statistical entropy

Partition function is the number of thermally accessible states.
Entropy is the distribution of energy
The two must be related

$S = k \ln W$ ←

W is the most probable configuration of the system.

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

$N = \Sigma_i n_i$

$$
\begin{aligned}
S &= k\, \Sigma_i (n_i \ln N - \Sigma_i n_i \ln n_i) \\
&= -k\, \Sigma_i n_i \ln n_i / N \\
&= -Nk\, \Sigma_i p_i \ln p_i
\end{aligned}
$$

$p_i = n_i/N$

$\ln p_i = -\beta\varepsilon_i - \ln q$ *[definition of p_i]*

$S = -Nk(-\beta\, \Sigma_i p_i \varepsilon_i - \Sigma_i p_i \ln q) = -k\beta\, [U - U(0)] + Nk \ln q$

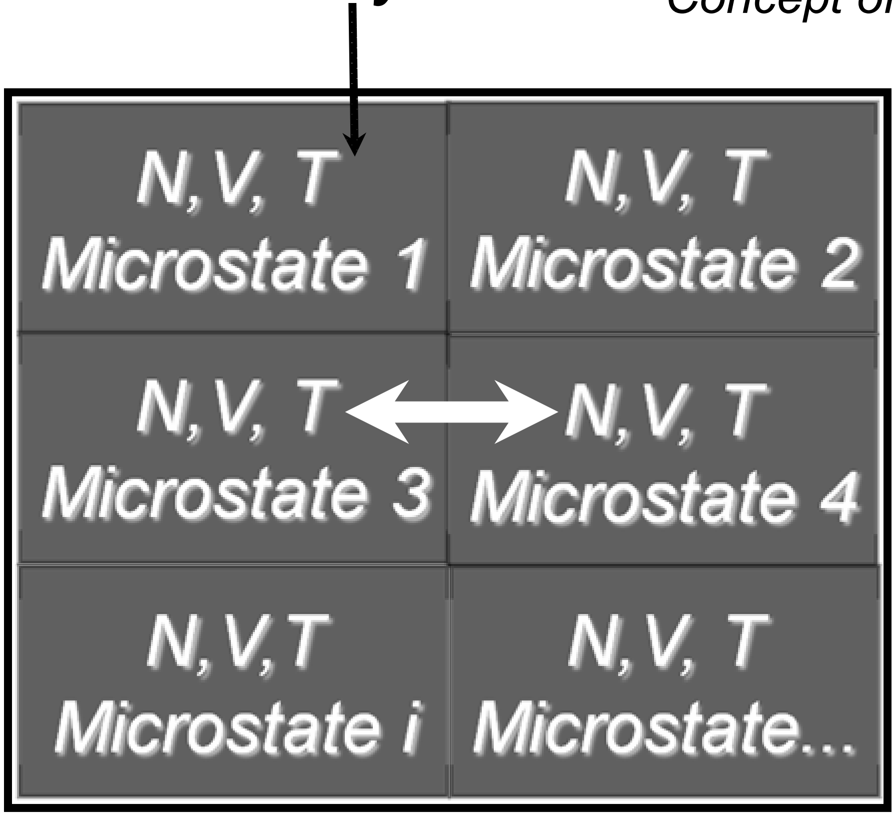
We used, $\Sigma_i p_i = 1$ and $N\Sigma_i p_i \varepsilon_i = \Sigma_i N p_i \varepsilon_i = \Sigma_i n_i \varepsilon_i = E$

$$\boxed{S = 1/T[U - U(0)] + Nk \ln q}$$

Canonical partition function

Particles are interacting.
Concept of ensemble

Closed System



***Canonical Ensemble**: Imaginary replication of the closed system in different microstates corresponding to the same macrostate "N, V, T"*

Microcanonical Ensemble: Imaginary replication of the isolated system in microstates corresponding to the same macrostate "N, V, E"
Grand canonical Ensemble: Imaginary replication of the isolated system in microstates corresponding to the same macrostate "μ, V, T"

N molecules, Ń imaginary replications
Number of members in the state with energy E_i is $\acute{n}_i$. Total energy of all the replications $\dot{E}$

Total energy of the isolated ensemble is constant.

Dominating configuration
$\{ń_{0,}\ ń_{1....}\}$ has a weight, Ẃ

$$Ẃ = \frac{Ń\,!}{ń_0!\ ń_1!\ ń_2!...}$$

Configuration of greatest weight, with conditions of total energy, Ė and number of members, Ń is called ***cannonical distribution****.*

$$\frac{ń_i}{Ń} = \frac{e^{-\beta E_i}}{\Sigma_i\ e^{-\beta E_i}} \qquad Q = \Sigma_i\ e^{-\beta E_i}$$

Q is called cannonical partition function.
Q is more important than q as the former talks about interacting particles.

Total energy of the ensemble is E and there are Ń members. Average energy of a member, E is Ė/ Ń. Let us calculate U when Ń (and therefore Ė) reaches infinity.

$$U = U(0) + E = U\ (0) + Ė/\ Ń \qquad Ń \rightarrow \infty$$

The fraction, $\acute{p}_i$ of members of the ensemble in state i with energy Ei is,

$$\acute{p}_i = \frac{\acute{n}_i}{\acute{N}} = \frac{e^{-\beta Ei}}{Q}$$

Internal energy, $U = U(0) + E = U(0) + \Sigma_i \acute{p}_i E_i = U(0) + 1/Q\, \Sigma_i E_i e^{-\beta Ei}$

$$\boxed{U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_v}$$

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

Entropy

Weight of a configuration, $\acute{W}$ of the ensemble is the product of the average weight W of each member within the ensemble so that, $\acute{W} = W^{\acute{N}}$

$S = k \ln W = k \ln \acute{W}^{1/\acute{N}} = (k/\acute{N}) \ln \acute{W}$

This as in the case of molecular partition function, $S = 1/T[U - U(0)] + k \ln Q$

Molecular partition function and cannonical partition function

When molecules are independent, total energy of state, i is
$Ei = \varepsilon_i(1) + \varepsilon i_(2) + \varepsilon_i(1) + \ldots + \varepsilon i_(N)$
ε_i (1) is the energy of molecule 1 for the system is in state i. Sum is for all the N molecules constituting the state i.

$$Q = \sum_i e^{-\beta\varepsilon i(1) - \beta\varepsilon i(2) - \ldots. - \beta\varepsilon i(N)}$$

Instead of summing over states of the system, we can sum over all the states, i of the molecules 1, 2, 3….

$$Q = \left(\sum_{i(1)} e^{-\beta\varepsilon i}\right)\left(\sum_{i(2)} e^{-\beta\varepsilon i}\right)\cdots\left(\sum_{i(N)} e^{-\beta\varepsilon i}\right)$$

$$q = \sum e^{-\beta\varepsilon\, i}$$

$$Q = q^N$$

Limitations

This discussion was for molecules which are distinguishable. Every possible state of individual molecule is counted in determining Q. But this is not the case when molecules are alike. In such cases, several states are counted in excess. The correction factor is N!, the number of permutations possible for a N member system to create a state.

$$Q_{distinguishable} = q^N$$

$$Q_{indistinguishable} = q^N / N!$$

$$Q = \frac{1}{N!} q^N$$

Single species, ideal gas

What is distinguishable: Similar molecules in the lattice as each one can be assigned a coordinate
Indistinguishable: Even when they are similar as in rare gases

Sackur-Tetrode equation

$S = 1/T[U - U(0)]\ k \ln Q$ distinguishable molecules

$Q = q^N/N!$ indistinquishable molecules

$S = 1/T[U - U(0)] + Nk \ln q - k \ln N!$

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

$$U = U(0) + 3/2\ nRT$$

Number of molecules is large, $N = nN_A$ as well as Sterling approximation

$S = 1/T[U - U(0)] + nR \ln q - nR \ln N + nR$

$S = 3/2nR + nR [\ln V/\Lambda^3 - \ln nN_A + 1] = nR [\ln e^{3/2} + \ln V/\Lambda^3 - \ln nN_A + \ln e]$

$$\boxed{S = nR \ln [e^{5/2}V/nN_A\Lambda^3]}$$

Gas is perfect. $V = nRT/p$

Equation can be expressed in terms of pressure.

Implications: Higher molar mass – higher entropy

Expansion of gas leads to grater entropy. $\Delta S = nR \ln aV_f - nR \ln aV_i = nR \ln V_f/V_i$

Same as classical. *a is a collection of terms*

Relations for various thermodynamic quantities

$$U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V \qquad S = \frac{U - U(0)}{T} + k \ln Q$$

Substitute Q = q^N or $q^N/N!$ as in the case may be.

U and S relate to other functions.

1. Helmholtz function

A = U – TS which means A(0) = U(0)

A - A(0) = -kTlnQ

$A = U - TS$
$dA = dU - TdS - SdT$
$dU = TdS - pdV + \Sigma \mu_i dn_i$
$dA = -SdT - pdV + \Sigma \mu i\, dni$
$p = -(\partial A/ \partial V)_{T,ni}$

2. Pressure

$p = -(\partial A/ \partial V)_T$ $\longrightarrow$ $$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

Valid for all substances.
This is a relation between p, V, T amount of substance. An equation of state.

Equation of state for independent particles:

$p = kT\ (\partial \ln Q/\partial V)_T = kT\ (\partial \ln(q^N/N!)/\partial V)_T = NkT/q\ (\partial q/\partial V)_T$ (1)

$= (NkT\Lambda^3/V)\ (1/\Lambda^3) = NkT/V = nRT/V$ (2)

For (1) we have used, $Q = q^N/N!$
For (2) $(\partial q/\partial V)_T = (\partial(V/\Lambda^3)/\partial V)_T = 1/\Lambda^3$ and $NkT = nN_AkT = nRT$

3. Enthalpy

$H = U + pV$

$$H - H(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_v + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$U - U(0) = \frac{3}{2} nRT$$

$$pV = nRT$$

$$H - H(0) = \frac{5}{2} nRT$$

4. Gibbs free energy

G = H – TS = A + pV = A + nRT

$$G - G(0) = -kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$G - G(0) = -kT \ln Q + nRT$$

$Q = q^N/N!$ $\quad \ln Q = N \ln q - \ln N! = N \ln q - (N \ln N - N)$

$$G - G(0) = -NkT \ln q + kT \ln N! + nRT$$

$$= -nRT \ln q + kT(N \ln N - N) + nRT$$

$$= -nRT \ln\left(\frac{q}{N}\right)$$

Gibbs free energy is proportional to the logarithm of the average number of thermally accessible states.

$N = nN_A$

We can also define a molar partition function, $q_m = q/n$

$$G - G(0) = -nRT \ln\left(\frac{q_m}{N_A}\right)$$

Molecular partition function

$$\varepsilon_i = \varepsilon_i{}^T + \varepsilon_i{}^R + \varepsilon_i{}^V + \varepsilon_i{}^E$$

$$q=\Sigma_i e^{-\beta\varepsilon i}=\Sigma_{i\ (all\ states)} e^{-\beta\varepsilon_i T-\beta\varepsilon_i R-\beta\varepsilon_i V-\beta\varepsilon_i E}$$

$$=\underbrace{(\Sigma_i e^{-\beta\varepsilon iT})}_{Trans}\ \underbrace{(\Sigma_i e^{-\beta\varepsilon iR})}_{Rot}\ \underbrace{(\Sigma_i e^{-\beta\varepsilon iV})}_{Vib}\ \underbrace{(\Sigma_i e^{-\beta\varepsilon iE})}_{Elec}\ =q^T q^R q^V q^E$$

1. Translational

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

2. Rotational

$$q^R = \Sigma_J (2J+1) e^{-\beta hcBJ(J+1)}$$

For linear rotors (A-B),

$$q^R = \frac{kT}{hcB} = \frac{T}{\Theta_R}$$

Characteristic rotational temperature
$T >> \Theta_R$

$$q^R = \frac{kT}{2\ hcB} = \frac{T}{2\ \Theta_R}$$

Linear, symmetric molecules
A-A, counting states twice
$CH \equiv CH$

$$q^R = \frac{kT}{\sigma hcB}$$

σ Symmetry number

$q^R = \int_0^\infty (2J+1)e^{-\beta hcBJ(J+1)}dJ$

We can simplify

$d/dJ\,[e^{aJ(J+1)}] = d/dJ\,[aJ(J+1)]\,e^{aJ(J+1)} = a(2J+1)e^{aJ(J+1)}$

$q^R = (1/\beta hcB) \int_0^\infty d/dJ\,[e^{-\beta hcBJ(J+1)}]\,dJ$

$q^R = -\,(1/\beta hcB)\,[e^{-\beta hcBJ(J+1)}]^\infty_0 = 1/\beta hcB$

$= kT/\,hcB$

3. Vibrational

$$E_v = \left(v+\frac{1}{2}\right)hc\tilde{v}$$

$$q^v=\sum_v e^{-\beta v hc\tilde{v}} = \sum_v (e^{-\beta hc\tilde{v}})^v = 1/(1-e^{-\beta hc\tilde{v}})$$

$$q^v = \frac{1}{1-e^{-\beta hcv}}$$

4. Electronic

$q^E = g_{ground} = 1$

NO → …π^1
Gives ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$
Each state is doubly degenerate
Gap is small between these two

$q^E = \Sigma_{levels}\, g^E\, e^{-\beta\varepsilon}{}_i = 2 + 2e^{-\beta\varepsilon}$

Leads to occupancy in all the states.

Overall partition function

$$q = g^E \left(\frac{V}{\Lambda^3} \right) \left(\frac{T}{\sigma\Theta_R} \right) \left(\frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \right)$$

$$q = g^E \left(\frac{V}{\Lambda^3} \right) \left(\frac{T}{\sigma\Theta_R} \right) \left(\frac{1}{1 - e^{-T/\Theta_\nu}} \right)$$

Using statistical theromodynamics

Mean energies

Mean energy for each mode, M

$$\langle \varepsilon^{\mathrm{M}} \rangle = -\frac{1}{q^{\mathrm{M}}}\left(\frac{\partial q^{\mathrm{M}}}{\partial \beta}\right)_V$$

Rest of the material in this file is as in Atkins.

$$\langle \varepsilon^{\mathrm{M}} \rangle = -\frac{1}{q^{\mathrm{M}}}\left(\frac{\partial q^{\mathrm{M}}}{\partial \beta}\right)_{\mathrm{V}}$$

(a) The mean translational energy

One-dimensional system of length X, for which $q^T = X/\Lambda$, *with* $\Lambda = h(\beta/2\pi m)^{1/2}$. Λ *is a constant times* $\beta^{1/2}$

$$\langle \varepsilon^{\mathrm{T}} \rangle = -\frac{\Lambda}{X}\left(\frac{\partial}{\partial \beta}\frac{X}{\Lambda}\right)_{V} = -\beta^{1/2}\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{1}{\beta^{1/2}}\right) = \frac{1}{2\beta} = \tfrac{1}{2}kT$$

For a molecule free to move in three dimensions:

$$\langle \varepsilon^{\mathrm{T}} \rangle = \tfrac{3}{2}kT$$

Classical equiparition theorem

1. *Mean energy of each quadratic contribution to the energy is 1/2kT*
2. *Mean energy is independent of the size of the container*
3. *Consistent with the thermodynamic result that the internal energy of a perfect gas is independent of its volume*

(b) The mean rotational energy

When the temperature is low ($T < \theta_R$), we get:

$$q^{\mathrm{R}} = 1 + 3\mathrm{e}^{-2\beta hcB} + 5\mathrm{e}^{-6\beta hcB} + \cdots$$

Hence

$$\langle \varepsilon^{\mathrm{R}} \rangle = \frac{hcB(6\mathrm{e}^{-2\beta hcB} + 30\mathrm{e}^{-6\beta hcB} + \cdots)}{1 + 3\mathrm{e}^{-2\beta hcB} + 5\mathrm{e}^{-6\beta hcB} + \cdots}$$

At high temperature ($T >> \theta_R$), q^R is given by $q^R = T/2\theta_R$

$$\langle \varepsilon^{\mathrm{R}} \rangle = -\frac{1}{q^{\mathrm{R}}}\frac{\mathrm{d}q^{\mathrm{R}}}{\mathrm{d}\beta} = -\sigma hc\beta B \frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{\sigma hc\beta B} = \frac{1}{\beta} = kT$$

(q^R is independent of V, so the partical derivatives have been replaced by complete derivatives).

The high-Temperature result is also in agreement with the equipartition theorem, for the classical expression for the energy of a linear rotor is $E_K = 1/2I\omega_a^2 + 1/2I\omega_b^2 = 2 \times ½\, kT = kT$

(c) The mean vibrational energy

$$\frac{\mathrm{d}q^{\mathrm{V}}}{\mathrm{d}\beta}=\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{1}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}\right)=-\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{(1-\mathrm{e}^{-\beta hc\tilde{\nu}})^{2}}$$

and hence from

$$\langle\varepsilon^{\mathrm{V}}\rangle=-\frac{1}{q^{\mathrm{V}}}\frac{\mathrm{d}q^{\mathrm{V}}}{\mathrm{d}\beta}=-(1-\mathrm{e}^{-\beta hc\tilde{\nu}})\left\{-\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{(1-\mathrm{e}^{-\beta hc\tilde{\nu}})^{2}}\right\}=\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}$$

$$\langle \varepsilon^{\mathrm{V}} \rangle = \frac{hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}} - 1}$$

At high temperatures, when $T \gg \theta_v$, or $\beta hcv \ll 1$, the exponential function can be expanded ($e^x = 1 + x + \ldots.$) and all but the leading terms are discarded.

$$\langle \varepsilon^{\mathrm{V}} \rangle = \frac{hc\tilde{\nu}}{(1 + \beta hc\tilde{\nu} + \cdots) - 1} \approx \frac{1}{\beta} = kT$$

This result is in agreement with the value predicted by the classical equipartition theorem, because the energy of a one – dimensional oscillator is $E = 1/2mv^2_x + 1/2kx^2$ and the mean energy of each quadratic term is $1/2kT$.

Heat capacities

The constant-volume heat capacity is defined as $C_v = (\partial U/\partial T)v$. The derivative with respect to T is converted into a derivative with respect to β by using:

$$\frac{d}{dT} = \frac{d\beta}{dT}\frac{d}{d\beta} = -\frac{1}{kT^2}\frac{d}{d\beta} = -k\beta^2\frac{d}{d\beta}$$

$$C_V = -k\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_V$$

Because the internal energy of a perfect gas is a sum of contributions, the heat capacity is also a sum of contribution from each mode. The contribution of mode M is,

$$C_V^{\mathrm{M}} = N \left(\frac{\partial \langle \varepsilon^{\mathrm{M}} \rangle}{\partial T} \right)_V = -Nk\beta^2 \left(\frac{\partial \langle \varepsilon^{\mathrm{M}} \rangle}{\partial \beta} \right)_V$$

The individual contributions

The temperature is always high enough (provided the gas is above its condensation temperature) for the mean translational energy to be 3/2 kT, the equipartition value. Therefore, the molar constant-volume heat capacity is:

$$C_{V,\mathrm{m}}^{\mathrm{T}} = N_{\mathrm{A}} \frac{\mathrm{d}(\frac{3}{2}kT)}{\mathrm{d}T} = \frac{3}{2}R$$

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$$

$C_P - C_V = R$