Counting distinguishable arrangements

Notes on General Chemistry

http://quantum.bu.edu/notes/GeneralChemistry/CountingDistinguishableArrangements.pdf
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Spontaneous change proceeds in the direction that increases the number of distinguishable arrangements. We consider two different kinds of arrangements. The first is the ways molecules can be distributed in space. The second is the ways energy can be distributed among molecules.

■ Molecules distributed in space

The number of distinguishable ways to distribute n molecules of one type and m molecules of another type is

$$W_{\text{molecules}}(n, m) = \frac{(n+m)!}{n!\,m!}.$$

For example, the number of ways of arranging 3 ink molecules and 3 water molecules is

$$\frac{(3+3)!}{3!\,3!} = \frac{6\times5\times4\times3!}{3!\,(3\times2\times1)} = \frac{6\times5\times4}{3\times2\times1} = 2\times5\times2 = 20.$$

Here is a way to derive $W_{\text{molecules}}(n, m)$. The number of arrangements of $n + m$ molecules, ignoring whether the arrangements are distinguishable is $(n+m)!$, since the first molecule can be in any of $n + m$ places, the second can be in any of the remaining $n + m - 1$ places, and so on to the last molecule which can be in the single remaining space. Now, the number of arrangements $(n+m)!$ must be the product of (1) the number of unique arrangements, (2) the number of ways $n!$ that a particular arrangement of the n molecules can arise, and (3) the number of ways $m!$ that a particular arrangement of the m molecules can arise:

$$W_{\text{molecules}}(n, m)\times n!\times m\,! = (n+m)!.$$

Solving this expression for $W_{\text{molecules}}(n, m)$, we get the expression above. Note that in this expression $n!\times m!$ is the number of ways that a particular one of the $W_{\text{molecules}}(n, m)$ distinguishable arrangements can occur.

Questions

How many distinguishable ways can n different objects be arranged: n, n^2, n^n or $n!$?

Answer: $n!$

How many indistinguishable ways can w identical objects be arranged: w, w^2, w^n or $w!$?

Answer: $w!$

How many ways can w different objects and i different objects (a total of $w + i$ different objects) be arranged: $w + i$, $(w + i)^2$, $(w + i)^{w+i}$, or $(w + i)!$?

Answer: $(w + i)!$

What is true about the number, $W_p(w, i)$, of distinquishable ways can w identical objects on one kind and i identical objects of another kind (a total of $w + i$ different objects) be arranged: $W_p(w, i)\, w!\, i! = (w + i)!$, $W_p(w, i) = w!\, i!$, or $W_p(w, i) = (w + i)$?

Answer: $W_p(w, i)\, w!\, i! = (w + i)!$

How many distinguishable ways can w water molecules and i ink molecules be arranged: $w!\, i!$, $(w + i)! / (w!\, i!)$, $(w + i)!$, or none of the these?

Answer: $(w + i)! / (w!\, i!)$

How many distinguishable ways can 2 water molecules and 2 ink molecules be arranged: 4, 6, 24, or none of these?

Answer: 6

How many distinguishable ways can 3 water molecules and 2 ink molecules be arranged: 10, 12, 120, or none of these?

Answer: 10

How many distinguishable ways can 4 water molecules and 2 ink molecules be arranged: 15, 48, 720, or none of these?

Answer: 15

How many distinguishable ways can 5 water molecules and 2 ink molecules be arranged: 21, 240, 5040, or none of these?

Answer: 21

How many distinguishable ways can 3 ink molecules be arranged in the top two layers of a column of water three molecules wide: 20, 36, 720, or none of these?

Answer: 20

■ Energy distributed among molecules

The number of distinguishable ways to distribute q quanta of energy among m molecules is

$$W_{\text{energy}}(q, m) = \frac{(q + m - 1)!}{q!\,(m - 1)!}.$$

For example, the number of ways of arranging 3 quanta among 3 molecules

$$\frac{(3+3-1)!}{3!\,(3-1)!} = \frac{5\times 4\times 3!}{3!\,(2\times 1)} = \frac{5\times 4}{2\times 1} = 5\times 2 = 10.$$

Here is a way to derive $W_{\text{energy}}(q, m)$, using as example $q = 8$ quanta distributed over $m = 4$ molecules. We can represent a particular arrangement pictorially as

$$\times\times | \times | \times\times\times\times | \times,$$

where the $\times$'s are the quanta and the three vertical lines separate the quanta into the four groups. Different arrangements correspond to different partitioning of the eight quanta into four groups. For example, another arrangement is

$$\times\times | \times || \times\times\times\times\times,$$

corresponding to two quanta in the first molecule, one quantum in the second molecule, no quanta in the third molecule, and five quanta in the last molecule. If we ignore whether an arrangement is distinguishable, then the total number of arrangements is the number of way of assigning the eight $\times$'s and the three |'s, that is, $(8 + 3)\,! = (q + m - 1)!$. Now, the number of arrangements $(q + m - 1)!$ must be the product of (1) the number of unique arrangements, (2) the number of ways $q!$ that a particular arrangement of the q quanta can arise, and (3) the number of ways $(m - 1)!$ that a particular arrangement of the $m - 1$ |'s can arise:

$$W_{\text{energy}}(q, m)\times q!\times(m-1)! = (q+m-1)!.$$

Solving this expression for $W_{\text{energy}}(q, m)$, we get the expression above. Note that in this expression $q!\times(m-1)!$ is the number of ways that a particular one of the $W_{\text{energy}}(q, m)$ distinguishable arrangements can occur.

Questions

Here is a representation of four quanta of energy, q, distributed among three molecules: $q \mid q \mid q\, q$. How many ways can the four units of energy end up with one in first molecule, one in the second molecule, and two in the third molecule:1, $q = 4$, or $q = 4 = 4 \times 3 \times 2 \times 1 = 24$.

Answer: 24

Here is a representation of four units of energy, q, distributed among three molecules: $q \mid q \mid q\;\; q$. How many different ways can the two partitions, |, be assigned to achieve the arrangement $q \mid q \mid q\, q$: 1, $(m - 1) = (3 - 1) = 2 \times 1 = 2$, or $m = 3 = 3 \times 2 \times 2 \times 1 = 6$?

Answer: 2

Here is a representation of four units of energy, q, distributed among three molecules: $q \mid q \mid q\, q$. How many different arrangements of the six objects in the diagram are there, ignoring that q and | are different: $m + q = 7$, $(m - 1)\, q = 2 \times 3 = 6$, or $(q + m - 1)! = 6! = 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$?

Answer: 720

How many ways can the arrangement $q \mid q \mid q\, q$ of four quanta among three molecules be made: $q!\, m! = 2! \times 2! = 4.$, $q!\, (m - 1)! = 4!\, (3 - 1)! = 24 \times 2 = 48$, or $(q + m)! = (4 + 3)! = 7! = 5040$?

Answer: 48

Two arrangements of 4 quanta among three molecules are $q \mid q \mid q\, q$ and $q\, q\, q \mid\mid q$. Which relation is true about the number of unique ways, $W_e(q, m)$, that four quanta can be distributed among three molecules: $W_e(q, m) = q!\, m!$, $W_e(q, m) = (q + m - 1)!$, or $W_e(q, m)\, q!\, (m - 1)! = (q + m - 1)!$?

Answer: $W_e(q, m)\, q!\, (m - 1)! = (q + m - 1)!$

$W_e(q, m) = (q + m - 1)! / [q!\, (m - 1)!]$ is the number of unique ways that q quanta can be distributed among m molecules. How many ways can two quanta be distributed among three molecules: 3, 6, or 9?

Answer: 6

$W_e(q, m) = (q + m - 1)! / [q!\, (m - 1)!]$ is the number of unique ways that q quanta can be distributed among m molecules. How many ways can three quanta be distributed among three molecules: 10, 16, or 20?

Answer: 10

■ ACS *Chemistry*, 8.14 Consider This: Effect of temperature on entropy change

Since entropy is proportional to the natural logarithm of the number of distinguishable configurations, the entropy change associated with a change in the number of configurations depends on the ratio of the number of configurations, as

$$\Delta S = S(\text{after}) - S(\text{before}) = k_B \ln(W_{\text{after}}) - k_B \ln(W_{\text{before}}) = k_B \ln(W_{\text{after}} / W_{\text{before}})$$

Let's apply this expression to the entropy change when one quantum of energy is added to a system consisting of *m* molecules which contain *q* quanta of energy. We have

$$\frac{W_{\text{after}}}{W_{\text{before}}} = \frac{W_{\text{energy}}(q+1,\, m)}{W_{\text{energy}}(q,\, m)}$$

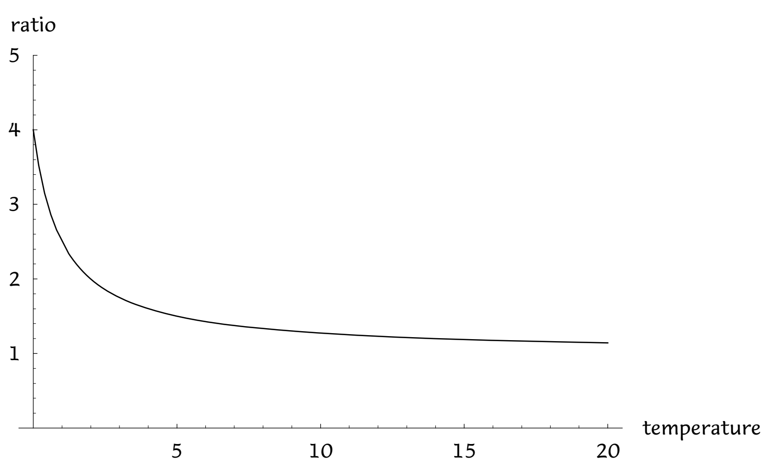
Using the counting formula

$$W_{\text{energy}}(q,\, m) = \frac{(q+m-1)!}{q!\,(m-1)!}.$$

we can simplify the ratio to

$$\begin{aligned}\frac{W_{\text{energy}}(q+1,\, m)}{W_{\text{energy}}(q,\, m)} &= \frac{(q+m)!}{(q+1)!\,(m-1)!} \Big/ \frac{(q+m-1)!}{q!\,(m-1)!}\\ &= \frac{q!\,(m-1)!\,(q+m)!}{(q+1)!\,(m-1)!\,(q+m-1)!}\\ &= \frac{(q+m)}{(q+1)}.\end{aligned}$$

This ratio always greater than 1 (provided there are at least two molecules, $m > 1$). It is largest when the number of quanta is smallest, while when the number of quanta, *q*, becomes very large compared to the number of molecules, *m*, the ratio is nearly 1. This variation is shown in the figure, for the example of $m = 4$ molecules.



Ratio $W_{\text{energy}}(q+1,\, m)/W_{\text{energy}}(q,\, m)$ for $m = 4$ molecules versus the number of quanta *q* originally present.

This means that the entropy change, proportional to the natural logarithm of the ratio $W_{\text{energy}}(q+1,\, m)/W_{\text{energy}}(q,\, m)$, is *greater* the *smaller* the number of quanta originally present. We can interpret the number of quanta present as a measure of the temperature, and so this means the entropy change per unit of heat (quantum of energy) added is inversely proportional to the temperature.

Questions

> Which expression is the value of $W_e(10\text{ quanta}, 4\text{ molecules})$: $13 \times 12 \times 11 = 1716$, $12 \times 11 = 132$, $13 \times 2 \times 11 = 286$, or none of these?
>
> Answer: 286

> Which expression is the value of $W_e(9\text{ quanta}, 4\text{ molecules})$: $11 \times 10 = 110$, $10 \times 22 = 220$, $13 \times 11 = 143$, or none of these?
>
> Answer: 220

> $W_e(10\text{ quanta}, 4\text{ molecules})$ has $286 - 220 = 66$ more arrangements than $W_e(9\text{ quanta}, 4\text{ molecules})$. What is true for the increase going from $W_e(4\text{ quanta}, 4\text{ molecules})$ to $W_e(5\text{ quanta}, 4\text{ molecules})$: greater than 66, 66, or less than 66?
>
> Answer: Less than 66

> The change $W_e(9, 4) \to W_e(10, 4)$ is 66, and the change $W_e(4, 4) \to W_e(5, 4)$ is 21. *Without doing any numerical estimates*, for which change to you expect the entropy increase to be greater: $W_e(9, 4) \to W_e(10, 4)$ or $W_e(4, 4) \to W_e(5, 4)$?

> The general expression for the entropy change when a 4 molecule system with q quanta gains one quantum is: $W_e(q+1, 4) - W_e(q, 4)$, $\ln(W_e(q+1, 4)) - \ln(W_e(q, 4))$, $\ln(W_e(q+1, 4) / W_e(q, 4))$, or both of the previous two?
>
> Answer: both of the previous two

> Which is larger: $W_e(10, 4) / W_e(9, 4)$ or $W_e(5, 4) / W_e(4, 4)$?

■ Stirling's approximation for $n!$ when n is very large

Stirling's approximation is

$$n! \approx \sqrt{2 \pi n}\, (n / e)^n.$$

In computing entropy changes we need the logarithm of W, and so we are interested in the logarithm of Stirling's approximationto $n!$,

$$\ln(n!) \approx \ln\left(\sqrt{2 \pi n}\right) + \ln[(n / e)^n] = \frac{1}{2} \ln(2 \pi n) + n \ln(n) - n.$$

When n is on the order of the number of particles in a macroscopic sample (typically at least 10^{20}), then the first term in this expression is tiny compared to the other two, and so we can use

$$\ln(n!) \approx n \ln(n) - n.$$

Taking the exponential of this expression, the corresponding approximation to $n!$ for the number of particles in macroscopic samples is

$$e^{\ln(n!)} = n! \approx (n / e)^n.$$

This expression is useful for estimate relative sizes of factorials. For example we can quickly see that $10^6!$ is on the order of 10^7, since $(10^6)^{10^6} \approx 10^7$.

Derivation of Stirling's approximation

A derivation of Stirling's approximation is

Eric W. Weisstein. "Stirling's Approximation." From MathWorld--A Wolfram Web Resource. http://mathworld.wolfram.com/StirlingsApproximation.html.

The derivation starts with the integral representation of $n!$,

$$n! = \int_0^\infty e^{-x} x^n \, dx.$$

A way to verify this integral representation is to integrate by parts,

$$\int_0^\infty f \, dg = [f \, g]_0^\infty - \int_0^\infty g \, df,$$

repeatedly. The first integration by parts, with $f = x^n$, $df = n \, x^{n-1} \, dx$, $dg = e^{-x} \, dx$, and $g = -e^{-x}$, gives

$$\int_0^\infty e^{-x} x^n \, dx = [-x^n \, e^{-x}]_0^\infty + n \int_0^\infty e^{-x} x^{n-1} \, dx = n \int_0^\infty e^{-x} x^{n-1} \, dx$$

since $[-x^n \, e^{-x}]_0^\infty = -\infty^n \, e^{-\infty} + 0^n \, e^0 = 0$. The next integration by parts gives in a similar way

$$\int_0^\infty e^{-x} x^n \, dx = n(n-1) \int_0^\infty e^{-x} x^{n-2} \, dx.$$

The n-th integration by parts gives

$$\int_0^\infty e^{-x} x^n \, dx = n! \int_0^\infty e^{-x} \, dx = n!$$

since $\int_0^\infty e^{-x} \, dx = [-e^{-x}]_0^\infty = 0 + 1 = 1$.