Spontaneity: Second law of thermodynamics

CH102 General Chemistry, Spring 2012, Boston University

> "… three or four forces and, as capstone, a minimalist cosmic constitution to legislate their use:
> Article I, the laws of conservation and symmetry; Article II, the laws of blind chance and dumb luck.
> There, I think, is the surprise and irony of the universe and also its incomparable beauty:
> that all complexity is an illusion; that nature's rich texture emerges from such a small bag of tricks;
> that things happen simply because they *can* happen and because they are statistically *most* likely to happen."
> Michael Munowitz, "Principles of Chemistry," W. W. Norton, 2000

[Related material is Mahaffy et al., sections 17.2–17.5]

■ Things happen because of dispersal of energy

When all is said and done, the first law of thermodynamics allows us to track the energy flow. For example, we know that, in an expansion of a gas, the gas is doing work *on* the surroundings ($w < 0$), and so a corresponding amount of energy must be supplied.

If the gas expands *isothermally* ($\Delta U = 0$), then the energy must come from the surroundings in the form of heat flow *into* the gas ($q > 0$). The temperature of the gas does not change because all of the heat energy drawn into the gas goes right back out of the gas in the form of work done on the surroundings.

If instead the gas expands *adiabatically* ($q = 0$), then the energy must come from the gas itself in the form of lowered kinetic energy of the gas particles ($\Delta U < 0$). The temperature of the gas *drops* in proportion to the energy lost by the gas in the form of work done *on* the surroundings.

In either case, something peculiar happens: The spontaneous expansion of the gas is able either to cool the surroundings (isothermal case) or to cool itself (adiabatic case). Now, isn't it remarkable that a gas is able to *spontaneously* draw heat from the surroundings or from the motion of its particle, to use it to do work?

I certainly think so, for the following reason: This means that the essentially *disorganized motion* of the particles of the surroundings (isothermal case) or of the gas itself (adiabatic case) is being channeled into the *coordinated motion* of the gas piston to do work on the surroundings. Imagine trying to herd cats!

Why is it that this happens? Evidently it is the *natural tendency* of a gas to expand, to fill the volume available to it uniformly. But what is the source of this natural tendency? The answer is one of the most fundamental aspects of the physical world:

Spontaneity in any aspect of the universe *always* is accounted for by one thing, and one thing only: *energy dispersal mediated by blind chance*.

In the case of expansion of a gas, the spontaneity is due to the simple fact that there are *more ways (greater chance) in which the gas can exist in a large volume than in a small volume*. This means the energy of the gas is more dispersed in a large volume than in a small volume. We will call this dispersal a measure of the *entropy* of the gas and we will see than that

In any *spontaneous process* there is a *net dispersal of energy*, that is, the *entropy of the universe increases*.

Entropy and the second law

The quantitative definition of entropy proceeds from the interpretation that it is a measure of energy dispersal. For example, energy is more dispersed—there are more ways of storing the energy—when a given amount of gas at a given temperature occupies a larger volume than a smaller volume.

For example, when we neaten up our rooms, by putting things in their places, we are taking advantage of the fact that, for a given gravitational potential energy (say), there are fewer ways things can be where they belong (say, socks paired and collected in the sock drawer) then elsewhere (say, one sock of a pair behind the door and the other in the drier). Cleaning up is equivalent to making energy less dispersed, to lowering the entropy. We all know that (absent a sorcerer's apprentice) rooms do not clean themselves; cleaning a room is a non-spontaneous process. We all also know, however, that rooms certainly seem to get into disarray by themselves; *increased dispersal of energy is evidently a spontaneous process*.

There are two approaches to quantifying the energy dispersal associated with spontaneous processes. The first is to analyze the change in the number of equal energy arrangements in which the system can exist in going from the initial to the final state; this is known as the *microscopic, statistical approach*. The second is based on the idea that when a system is heated it becomes more disorganized, due to the increase in thermal motion, and so the increased dispersal of energy should be proportional to heat flow; this is known as the *macroscopic, thermodynamic approach*.

The results of the two approaches are the same. We will begin with the microscopic, statistical approach. We will then see how to relate this approach to the macroscopic, thermodynamic approach.

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

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

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 distinguishable 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

■ Understanding spontaneity in terms of increased spatial arrangements

Here are some examples showing how spontaneous changes we are familiar with trace to an increase in the number of arrangements of particles. To analyze the examples, we use the generalized counting expression,

$$W = \frac{(i + j + k)!}{i!\, j!\, k!}$$

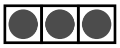
to get the number of unique ways i objects of one kind, j objects of another kind, and k objects of a third kind can be arranged. If there are only two different kinds of objects, this expression reduces to

$$W = \frac{(i+j)!}{i!\,j!}.$$

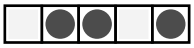
If there are more than three different kinds of objects, the expression can be extended by adding the additional terms in the numerator and additional factorials in the denominator.

A gas evenly fills its container

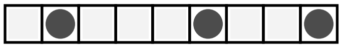
Here is a model of $j = 3$ particles confined in successively more possible positions. The maximum number of arrangements corresponds the particles spread out over the greatest number of possible positions.



$$W = \frac{(j+\ell)!}{j!\,\ell!} = \frac{(3+0)!}{3!\quad 0!} = 1.$$



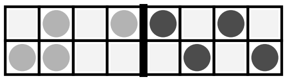
$$W = \frac{(j+\ell)!}{j!\,\ell!} = \frac{(3+2)!}{3!\quad 2!} = 10.$$



$$W = \frac{(j+\ell)!}{j!\,\ell!} = \frac{(3+6)!}{3!\quad 6!} = 84.$$

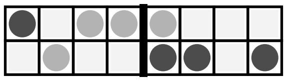
Two gases evenly mix

Here is a model of 4 particles of one kind (light circles) and 4 particles of another kind (dark circles) confined in a lattice of 16 possible positions. The lattice is separated into halves by a fixed membrane that is permeable to both kinds of particles. The maximum number of arrangements corresponds to each kind of particle evenly spread out over the two halves of the whole lattice.



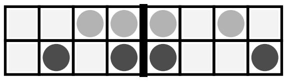
In this arrangement, the particles are segregated in the different sides of the container.

$$W = W_{\mathrm{left}}\, W_{\mathrm{right}} = \frac{(4+4)!}{4!\quad 4!}\,\frac{(4+4)!}{4!\quad 4!} = 70 \times 70 = 4900.$$



In this arrangement, the one particle of each type has moved to the other side of the container, and the result is a large increase in the number of possible arrangements,

$$W = W_{\mathrm{left}}\, W_{\mathrm{right}} = \frac{(1+3+4)!}{1!\quad 3!\quad 4!}\,\frac{(3+1+4)!}{3!\quad 1!\quad 4!} = 280 \times 280 = 78\,400.$$



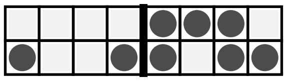
In this arrangement, the particles of each type are evenly distributed on both sides if the container, and the result is the maximum number of possible arrangements,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+2+4)!}{2!\;\;2!\;\;4!}\,\frac{(2+2+4)!}{2!\;\;2!\;\;4!} = 420\times 420 = 176\,400.$$

Two regions of a gas come to a common pressure

Here is a model of 2 particles confined in one region and 6 particles of confined in another region. The two regions are separated by an impermeable barrier that is free to move, thereby changing the volume (the number possible positions) of the two regions. The maximum number of arrangements corresponds to the same pressure (number of particles per possible positions) in each region.

In this initial configuration



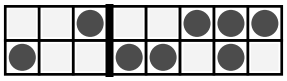
the number of arrangements is

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+6)!}{2!\;\;6!}\,\frac{(6+2)!}{6!\;\;2!} = 28\times 28 = 784,$$

and the pressure on the left is too low,

$$\Delta p = p_{\text{left}} - p_{\text{right}} = 2/8\,R\,T - 6/8\,R\;\,T = -1/2\,R\,T = -0.50\,R\,T.$$

Moving the barrier left decreases the volume on the left and increases the volume on the right.



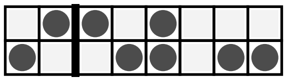
This results in an increase in the number of arrangements,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+4)!}{2!\;\;4!}\,\frac{(6+4)!}{6!\;\;4!} = 15\times 210 = 3150,$$

and a reduction in the pressure difference,

$$\Delta p = p_{\text{left}} - p_{\text{right}} = 2/6\,R\,T - 6/10\,R\;\,T = -4/15\,R\,T = -0.27\,R\,T.$$

Further decreasing the volume on the left side and increasing the volume on the right side,



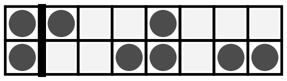
results in an additional increase in the number of arrangements,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+2)!}{2!\;\;2!}\,\frac{(6+6)!}{6!\;\;6!} = 6 \times 924 = 5544,$$

and now the pressure is the same on both sides,

$$\Delta p = p_{\text{left}} - p_{\text{right}} = 2/4\,R\,T - 6/12\,R\;\,T = 0.$$

Further decreasing the volume of the left side and increasing the volume of the right side,



results in a decrease in the number of arrangements,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+0)!}{2!\;\;0!}\,\frac{(6+8)!}{6!\;\;8!} = 1 \times 3003 = 3003,$$

and reappearance of a pressure difference,

$$\Delta p = p_{\text{left}} - p_{\text{right}} = 2/2\,R\,T - 6/14\,R\;\,T = +4/7\,R\,T = +0.57\,R\,T.$$

■ Energy distributed among molecules

Let’s consider the total energy to consist of equal sized quanta of energy. Then, distributing energy among molecules amounts to dividing up the quanta into groups.

For example, say we have $q = 8$ quanta distributed among four molecules. A pictorial representation of one way of doing this is

$$\times\times \mid \times \mid \times\times\times\times \mid \times,$$

where the ×'s are the quanta; this arrangement corresponds to two quanta in the first molecule, one quantum in the second molecule, four quanta in the third molecule, and one quantum in the last molecule. Another, different arrangement is

$$\times\times \mid \times \mid\mid \times\times\times\times\times,$$

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. As we will now learn how to determine, there are 163 additional different arrangements of 8 quanta distributed among four molecules.

These two examples show that enumeration of the number of different groupings amounts to counting the different possible placements of the dividers. To make the role of the placement of the dividers explicit, let’s call the number of dividers d, equal to one less than the number of molecules. $d = m - 1$.

For the example of eight ×’s and three dividers, if we ignore whether an arrangement is distinguishable, then the total number of arrangements is the number of ways of assigning the eight ×'s and the three dividers, that is, $(8+3)! = (q+d)!$. Now, this total number of arrangements, $(q+d)!$, must be the product of

(1) the number of unique arrangements, W,
(2) the number of ways $q!$ that a particular arrangement of the ×'s can arise, and
(3) the number of ways $d!$ that a particular arrangement of the d dividers can arise,

that is

$$(q + d)\,! = W\, q\,!\, d\,!.$$

Solving this expression for W, we get

$$W = \frac{(q + d)\,!}{q\,!\, d\,!}.$$

Note that in this expression $q\,!\, d\,!$ is the number of ways that a particular one of the W distinguishable arrangements can occur.

Now that we see how to count the ways of dividing up the q quanta with the d dividers, let’s shift attention from the number of dividers, d, to the number of molecules, m. We do this by replacing d with $m - 1$ to rewrite the number of arrangements as

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

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

With this expression we can verify that for 8 quanta distributed among four molecules, there are 165 different ways of dividing up the quanta,

$$W_{\text{energy}}(q,\, m) = W_{\text{energy}}(8,\, 4) = \frac{(8 + 4 - 1)\,!}{8\,!\, (4 - 1)\,!} = \frac{11 \times 10 \times 9 \times 8\,!}{8\,!\, (3 \times 2)} = \frac{11 \times 10 \times 9}{3 \times 2} = \frac{11 \times 5 \times 3}{3 \times 2} = 165$$

As another example, there are 6 different ways the number of ways of arranging 2 quanta and among three molecules,

$$\frac{(2 + 2)\,!}{2\,!\, (3 - 1)\,!} = \frac{4 \times 3 \times 2\,!}{2\,!\, (2 \times 1)} = \frac{4 \times 3}{2} = 6,$$

and these six arrangements are

$$\times \times ||,\ \ \times | \times |,\ \ \times || \times,\ \ | \times \times |,\ \ | \times | \times,\ \ \text{and} \,|| \times \times.$$

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: $q \Big| q \Big| q \;\; q$. 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 $q \,|\, q \,|\, q\, q$ and $q\, q\, q \,||\, q$. Which relation is true about the number of unique ways, $W_\mathrm{e}(q, m)$, that four quanta can be distributed among three molecules: $W_\mathrm{e}(q, m) = q!\,m!$, $W_\mathrm{e}(q, m) = (q+m-1)!$, or $W_\mathrm{e}(q, m)\, q!\,(m-1)! = (q+m-1)!$?
>
> Answer: $W_\mathrm{e}(q, m)\, q!\,(m-1)! = (q+m-1)!$

> $W_\mathrm{e}(q, m) = (q+m-1)!/[q!\,(m-1)!]$ 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

> $W_\mathrm{e}(q, m) = (q+m-1)!/[q!\,(m-1)!]$ 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: Temperature and 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

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

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

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

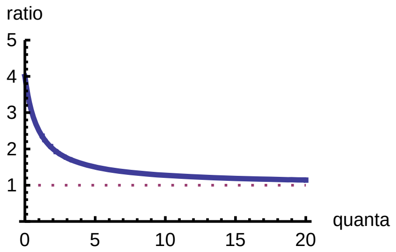
Using the counting formula

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

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 $W_\text{energy}(q+1,\, m)\big/W_\text{energy}(q,\, m)$, 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.

A more detailed analysis confirms this finding: Whenever there is a transfer of heat energy at temperature T, the entropy change is

$$\Delta S = \text{heat}/T$$

Here is a macroscopic way of looking at this result. Adding heat to a system increases its energy content and this energy is more dispersed, because the added energy increases the motion of the particles of the system. The more heat we add, the greater this increase, and so we expect the increase in dispersal to be *proportional* to the heat added.

If a system is initially very cool, then its particles are not moving very much. If a given amount of heat is added to such a cool system, the relative increase in motion will be large compared to what it would be if the system were initially hotter and so its particles moving faster. (Sneezing in a crowded church is more disruptive than sneezing in a crowded subway). This means that the lower the temperature at which we add heat to the system, the larger the increase in energy dispersal; that is, that we expect the increase in energy dispersal to be *inversely proportional* to the temperature at which the heat is added.

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 $W_e(5, 4)/W_e(4, 4)$?

■ Entropy change when a gas expands at constant temperature

We know that an ideal gas spontaneously expands it is allowed to do so, for example, by reducing the pressure exerted on the gas. This in turn means that there is an increase in entropy when an ideal gas expands spontaneously. We now have the tools to calculate the entropy change for such a process, both in terms of the microscopic picture of changes in the number of arrangements W and in terms of the macroscopic analysis of the heat that flows during the expansion. By comparing the microscopic and macroscopic calculations, we will see that the results are the same, and so will establish that the microscopic and macroscopic picture of entropy change are equivalent.

Macroscopic approach

Let’s begin with the macroscopic approach to entropy change, by calculating

$$\Delta S = q/T$$

in terms of the heat, q, that flows when the gas expands at constant temperature (isothermally).

The first step is to recall (1) that since the energy of an ideal gas is due entirely to the kinetic energy of its particles and, from the kinetic molecular theory, (2) that each mole of gas has energy

$$\overline{\text{KE}} = \frac{1}{2} M\, {u_{\text{rms}}}^2 = \frac{3}{2} R\, T,$$

and so that molar *energy of an ideal gas depends only on it temperature*. This in turn means that if we keep the temperature of the gas constant (isothermal) during its expansion, then from the first law

$$\Delta U = 0 = q + w$$

and so $q = -w$. This means that we can determine q in terms of the work, w, done *on* the gas during the expansion.

To calculate the work, we need to carry out the expansion reversibly: in many small steps such the outside pressure, P_{ext}, is always just slightly less than the gas pressure, P. At each step, the work *by* the gas is $-w = F\, dh = P\, dV$, since $F = P\, A$ and $dh = A\, dV$. Starting at an initial volume V_1 and ending at a final volume V_2, letting each step along the way become infinitesimally small and then adding up all of the steps, the result is

$$q = -w = \int_{V_1}^{V_2} P\, dV = n\, R\, T \int_{V_1}^{V_2} \frac{1}{V}\, dV = n\, R\, T\, \ln(V_2/V_1).$$

and so

$$\Delta S = q/T = n\, R \ln(V_2/V_1).$$

We see that the entropy change depends only the on volume change, and that for each doubling of volume

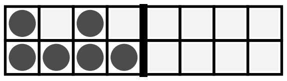
$$\Delta S = n\, R \ln(2).$$

> Calculate the entropy change when exactly 1 mol of ideal gas at 25 °C expands reversibly from exactly 13 L to exactly 14 L. Answer: 0.616169 J/K.

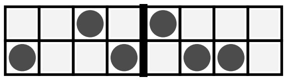
> Calculate the entropy change when exactly 1 mol of ideal gas at 38 °C doubles in volume. Answer: 5.76315 J/K.

Microscopic approach

Let's apply the microscopic approach to the doubling of the volume of a gas of $N = n\, N_0$ particles. Initially the particles are confined to one half of the container, as illustrated for 6 particles below, where the heavy vertical line separates the two halves of the container.



At the end of the expansion, the particles are distributed over the total volume. A particular arrangement of 6 particles spread over the total volume is shown below.



To evaluate the entropy change

$$\Delta S = k_B \ln(W_2 / W_1)$$

we need the ratio, W_2 / W_1, of the number of arrangements after and before the expansion to twice the volume. As a result of the expansion, each of the particle may be in twice as many positions, and therefore in the limit of a very large number of particles, say N,

$$W_2 / W_1 = 2 \times 2 \times 2 \ldots 2 \times 2 = 2^N$$

This means that

$$\Delta S = k_B \ln\left(2^N\right) = N\, k_B\, \ln(2) = 2\, n\, N_0\, k_B \ln(2) = R \ln(2)$$

where the number of particles is expressed in terms of the numbers of moles as $N = n\, N_0$. This is the same result as for the macroscopic analysis.

■ Direction of heat flow

We know from experience that hot objects spontaneously cool and cold objects spontaneously warm to the temperature of their surroundings. We can analyze this process quantitatively using the first and second laws of thermodynamics, to see that this such heat flow from hot to cold is required by the second law of thermodynamics.

Macroscopic approach

To keep things simple, let's assume we have hot and cold objects of the same mass, m, and the same specific, c_s. Let's further assume that the two objects are allowed to exchange energy with one another in the form of heat, but that they do not exchange energy with the surroundings.

Then, from the first law of thermodynamics, the energy gained (or lost) by one object is equal to the energy lost (or gained) by the other object. We can express this as

$$đ q_{\text{hot}} = -đ q_{\text{cold}}$$

From the definition of specific heat c_s, we can write

$$đ q_{\text{hot}} = m\, c_s\, đ T_{\text{hot}},$$

$$đ q_{\text{cold}} = m\, c_s\, đ T_{\text{cold}}.$$

Since the mass and specific heat are the same for the two objects, these first law relations mean that the change in temperature of the hot body and the cold body are the same magnitude but opposite in sign,

$$đ T_{\text{hot}} = -đ T_{\text{cold}};$$

That is, on object becomes hotter and the other becomes correspondingly colder. There are two ways this equality can hold. Either the hot object warms up and the cold object cools down,

$$đ T_{\text{hot}} = T_{\text{hotter}} - T_{\text{hot}} > 0,$$

$$đ T_{\text{cold}} = T_{\text{colder}} - T_{\text{cold}} < 0;$$

or the hot object cools down and the warm object warms up,

$$đ T_{\text{hot}} = T_{\text{colder}} - T_{\text{hot}} < 0,$$

$$đT_{\text{cold}} = T_{\text{hotter}} - T_{\text{cold}} > 0;$$

In this latter case, the cooling of the hot body and the warming of the cold body will continue until a common temperature, $T = T_{\text{colder}} = T_{\text{hotter}}$, is reached,

$$đT_{\text{hot}} = T - T_{\text{hot}} < 0,$$

$$đT_{\text{cold}} = T - T_{\text{cold}} > 0;$$

We can use the second law of thermodynamics to show that only this second case is possible. The entropy change of the hot and cold bodies is

$$đS_{\text{hot}} = \frac{đq_{\text{hot}}}{T_{\text{hot}}}$$

$$đS_{\text{cold}} = \frac{đq_{\text{cold}}}{T_{\text{cold}}}$$

and so the total entropy change is

$$đS = đS_{\text{hot}} + đS_{\text{cold}} = \frac{đq_{\text{hot}}}{T_{\text{hot}}} + \frac{đq_{\text{cold}}}{T_{\text{cold}}}$$
$$= \frac{đq_{\text{hot}}}{T_{\text{hot}}} - \frac{đq_{\text{cold}}}{T_{\text{cold}}} = đq_{\text{hot}}\left(\frac{1}{T_{\text{hot}}} - \frac{1}{T_{\text{cold}}}\right)$$

Now, since T_{cold} is less than T_{hot}, $1/T_{\text{cold}}$ is greater than $1/T_{\text{hot}}$, and so the difference $1/T_{\text{hot}} - 1/T_{\text{cold}}$ is negative. This means that if $đq_{\text{hot}} > 0$, that is, if heat flows *into the hot object from the cold object*, then

$$đS < 0.$$

But this is impossible according to the second law. The only way out of this problem is for $đq_{\text{hot}}$ to be negative, that is, for heat to flow *from hot objects to cold objects*.

Microscopic approach

At the microscopic level, two objects of the same mass and heat capacity but one hot and one cold, corresponds to each object consisting of the same number of molecules but with their being more quanta of energy in the hot object than in the cold object.

Transfer of a quantum from the hot object to the cold object corresponds to a decrease in their temperature difference, while transfer from the cold object to the hot object corresponds to an increase in their temperature difference. By analyzing the change in the number of arrangements of the quanta among the two blocks, we can account for the observed behavior that transfer from the hot to the cold object results in increased energy dispersal.

To keep things simple, let’s assume that each block consists of four molecules, that 6 quanta are in the hot block and 4 quanta in the cold block. The number of arrangements of the combined system is

$$W_{\text{hot}}(q = 6,\ m = 3)\ W_{\text{cold}}(q = 4,\ m = 3).$$

If one quantum moves from the hot block to the cold block, the number of arrangements is

$$W_{\text{hot}}(q = 5,\ m = 3)\ W_{\text{cold}}(q = 5,\ m = 3).$$

If instead one quantum moves from the cold block to the hot block, the number of arrangements is

$$W_{\text{hot}}(q = 7,\ m = 3)\ W_{\text{cold}}(q = 3,\ m = 3).$$

To see which transfer increases the energy dispersal, we need to compare the ratios of the final and initial number of arrangements. For heat transfer from the hold block to the cold block, the ratio is

$$\text{hot} \rightarrow \text{cold} : (W_{\text{hot}}(q = 5,\ m = 3)\ W_{\text{cold}}(q = 5,\ m = 3)) / (W_{\text{hot}}(q = 6,\ m = 3)\ W_{\text{cold}}(q = 4,\ m = 3)) = 21/20$$

> Without using a calculator, use cancellation to verify this numerical value.

Because the ratio is *greater* than 1, the transfer hot → cold *increases* the energy dispersal and so corresponds to a *positive* entropy change.

For heat transfer to the hot block from the cold block, the ratio is

$$\text{hot} \leftarrow \text{cold} : (W_{\text{hot}}(q = 7,\ m = 3)\ W_{\text{cold}}(q = 3,\ m = 3)) / (W_{\text{hot}}(q = 6,\ m = 3)\ W_{\text{cold}}(q = 4,\ m = 3)) = 6/7$$

> Again, without using a calculator, use cancellation to verify this numerical value.

Because the ratio is *less than* 1, the transfer hot ← cold *decreases* the energy dispersal and so corresponds to a *negative* entropy change.

This is the microscopic basis for the fact that the spontaneous direction of heat transfer is from a hot object to a cold object.