Examples of spontaneity in terms of increased spatial arrangements

Notes on General Chemistry

http://quantum.bu.edu/notes/GeneralChemistry/SpontaneityInTermsOfIncreasedSpatialArrangements.pdf
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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,

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

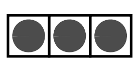
to get the number of unique ways i objects of one kind, j objects of another kind, and k objects of a third kind can be arranged. If there are only two different kinds of objects, this expression reduces to

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

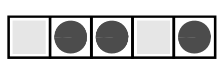
If there are more than three different kinds of objects, the expression can be extended by adding the additional terms in the numerator and additional factorials in the denominator.

■ A gas evenly fills its container

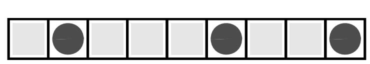
Here is a model of $j = 3$ particles confined in successively more possible positions. The maximum number of arrangements corresponds the particles spread out over the greatest number of possible positions.



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



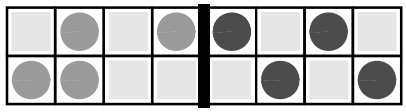
$$W = \frac{(j + \ell)!}{j!\, \ell!} = \frac{(3 + 2)!}{3!\, 2!} = 10.$$



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

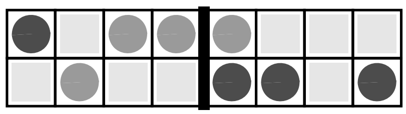
■ Two gases evenly mix

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.



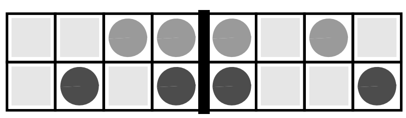
In this arrangement, the particles are segregated in the different sides of the container.

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



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,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(1+3+4)!}{1!\,3!\,4!}\,\frac{(3+1+4)!}{3!\,1!\,4!} = 280 \times 280 = 78400.$$



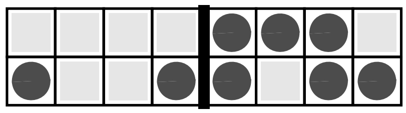
In this arrangement, the particles of each type are evenly distributed on both sides if the container, and the result is the maximum number of possible arrangements,

$$W = W_{\text{left}}\, W_{\text{right}} = \frac{(2+2+4)!}{2!\,2!\,4!}\,\frac{(2+2+4)!}{2!\,2!\,4!} = 420 \times 420 = 176400.$$

■ 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



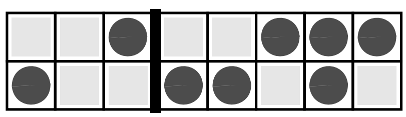
the number of arrangements is

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

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.



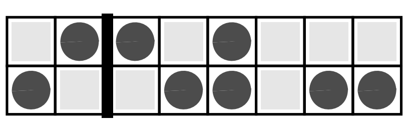
This results in an increase in the number of arrangements,

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

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,



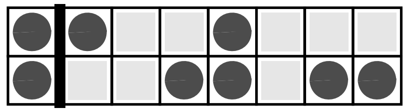
results in an additional increase in the number of arrangements,

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

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,

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

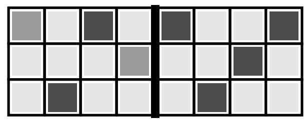
and reappearance of a pressure difference,

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

■ A pressure difference develops across a semipermeable membrane

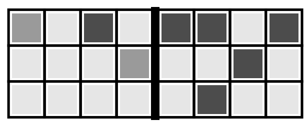
Here is a model of 2 particles of one kind (light squares) and 6 particles of another kind (dark squares). The membrane is impermeable to the light colored particles but permeable to the dark colored particles.

Here is an initial arrangement.



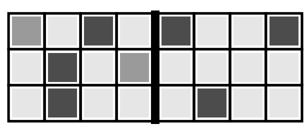
$$W = W_{\text{left}}\,W_{\text{right}} = \frac{(2+2+8)!}{2!\,2!\,8!}\,\frac{(4+8)!}{4!\,8!} = 2970\times 495 = 1470150.$$

If one solvent particle moves to the right, there is a decrease in the number of arrangements.



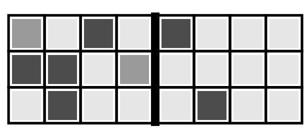
$$W = W_{\text{left}}\,W_{\text{right}} = \frac{(2+1+9)!}{2!\,1!\,9!}\,\frac{(5+7)!}{5!\,7!} = 660\times 792 = 522720.$$

If instead one solvent particle moves to the left, there is an increase in the number of arrangements.



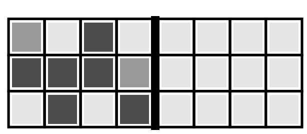
$$W = W_{\text{left}}\,W_{\text{right}} = \frac{(2+3+7)!}{2!\,3!\,7!}\,\frac{(3+9)!}{3!\,9!} = 7920\times 220 = 1742400.$$

If a second solvent particle moves to the left, there is a decrease in the number of arrangements.



$$W = W_{\text{left}}\,W_{\text{right}} = \frac{(2+4+6)!}{2!\,4!\,6!}\,\frac{(2+10)!}{2!\,10!} = 13860\times 66 = 914760.$$

If all of the solvent particle move to the left, there is a large decrease in the number of arrangements.



$$W = W_{\text{left}}\,W_{\text{right}} = \frac{(2+6+4)!}{2!\,6!\,4!}\,\frac{(0+12)!}{0!\,12!} = 13860\times 1 = 13860.$$

The maximum number of arrangements corresponds to equal numbers of the dark particles on either side of the membrane, $n_{\text{dark,left}} = n_{\text{dark,right}}$. Since the light particles cannot pass through the membrane, there is a pressure difference when the number of arrangements is a maximum,

$$\Pi = p_{\text{left}} - p_{\text{right}} = \frac{n_{\text{light}} + n_{\text{dark,left}}}{V} R\,T - \frac{n_{\text{dark,right}}}{V} R\,T = \frac{n_{\text{light}}}{V} R\,T.$$

This pressure difference—the osmotic pressure Π—depends only on the concentration of the particles that cannot pass through the membrane.