RSC | Advancing the Chemical Sciences

Reckitt Benckiser

Why passive diffusion happens – entropy considerations

Spontaneous movement

Experimentally, it can be shown that if equal volumes of water and an aqueous solution are separated by a partially permeable membrane, solute particles (molecules or ions) move through the membrane until their concentration is the same either side of it. This happens spontaneously. No energy is required.

It is a dynamic process. Solute particles move from the solution into the water. Some move back. Particles move to and fro until there are solutions of equal concentrations on both sides. A position of dynamic equilibrium is reached. This represents the greatest disorder and, therefore, the highest entropy that the system can have.

Click here to see an animation:

http://www.presentingscience.com/quantumcasino/simulations/entropyanddisorder.html

The description of this spontaneous movement lies in the concept of entropy and the Second Law of Thermodynamics.

Entropy and disorder

Some things are more ordered than others. People standing in a queue to get tickets for a concert are more ordered than people wandering around a supermarket doing their shopping.

Entropy is a mathematical way of measuring order. It is related to the number of arrangements of particles that lead to a particular state.

Entropy has the symbol S and is defined by the equation:

$S = k\ln W$

where,

W is the number of ways of arranging the particles in a given state of the system;

k is a constant called Boltzmann's constant which has the value 1.38×10^{-23} J K^{-1}.

Without going into the maths further it is enough to know that:

- well ordered systems have low entropy – the more order, the lower a system's entropy;
- disordered systems have high entropy – the more disorder, the higher system's entropy.

Change in entropy is shown by ΔS. It is the difference between the entropy before (S_{before}) and after a change (S_{after}).

$\Delta S = S_{before} - S_{after}$

Thinking about the three states of matter (solid, liquid and gas) the particles of a given substance are most ordered in the solid state, less in the liquid state and much less in the gas state. So,

$$S_{ice} < S_{water} < S_{steam}$$

The units for entropy are J K^{-1}.

The following entropies are for 18 g (1mole of H_2O molecules) of the three states of water:

ice	solid	48 J K^{-1} mol^{-1}
water	liquid	70 J K^{-1} mol^{-1}
steam	gas	189 J K^{-1} mol^{-1}

Values are for standard conditions (273 K and 1.01×10^{5} Pa).

See the animation comparing the arrangement and movement of particles in a solid, liquid and gas at http://www.presentingscience.com/quantumcasino/tutorial/entropy.html. There is also more about entropy.

Second Law of Thermodynamics

The Second Law of Thermodynamics says that changes leading to greater disorder are favoured over changes that produce greater order. So if there are no other influences in any spontaneous change, entropy increases.

Therefore, ΔS is positive for a spontaneous change.

This does not mean that ice spontaneously changes to water and then steam, but it does tell us that the change is feasible. It does not, however, tell us how fast the change will occur.

See: http://www.presentingscience.com/quantumcasino/tutorial/secondlaw.html for more detail about the Second Law.

Passive diffusion and entropy change

Imagine two compartments separated by a partially permeable membrane. Each has a solution in it. This is an observable state. The entropy of this state is related to the number of ways solute particles can be arranged.

Diffusion of solute particles from a compartment of higher concentration to one of lower concentration leads to an increase in the entropy of the system. This is the driver for change.

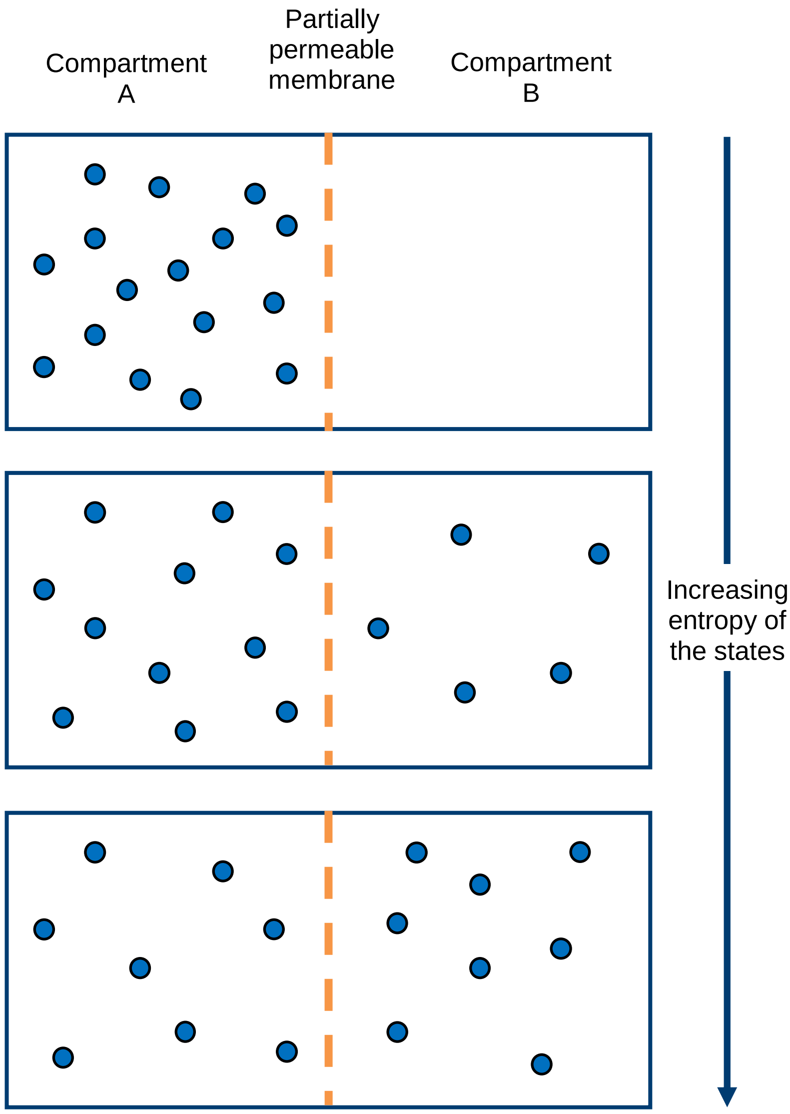

Figure Three different distributions of solute particles between two compartments.

Finding out

When diffusion happens in a closed system, such as that shown in the figure, a position of dynamic equilibrium is reached. What does this mean in terms of the movement of particles when the position of equilibrium has been established?