The wonders of table salt

Table salt is a seemingly mundane compound, not offering much except a slight addition of flavour to your chips. Most people will learn about table salt as a bunch of sodium, reacted with a bunch of chlorine in a simple ratio and be satisfied with this knowledge. I however, would like to present to you the case why you should come to be as interested in salt as I have become whilst diving into its inner complexities.

Opposites attract

It is common knowledge that when two oppositely charged ions interact, they exert a pulling force on each other. This is known as the electrostatic force. What is less well known is how immense the relative strength of such attractive (or repulsive) forces are.

Let's start with gravity:

The gravitational attraction between any two particles is given by the formula:

$$F_g = G\frac{m_1 \times m_2}{r^2}$$

Where G is the gravitational constant ($6.67\text{x}10^{-11}$ $m^3kg^{-1}s^{-2)}$, m_1 and m_2 are the masses of the two particles and r is the distance between the two particles. In order to apply this formula to find the attractive force between a sodium and a chloride ion we must first know their masses. The relative atomic masses of sodium and chlorine are 22.99gmol^{-1} and 35.453gmol^{-1} respectively. We can divide these values through by Avogadro's constant ($6.02\text{x}10^{-23}$) and convert from g to kg to find mass of a singular atom. It is safe to assume mass of atoms is the same as for an ion as the transfer of a singular electron would have negligible impact because the mass of the single electron lost by one sodium atom to form a sodium ion is only 0.002% of the whole atom.

Next, we need to determine the distance between ion's nuclei as this is where the majority of the mass is found. Assuming that the ions in the lattice are as tightly packed as possible, the distance r would equal the sum of the radii of the two ions:

Radius of Na^+: 1.00 Å

Radius of Cl^-: 1.82 Å

Distance R = 2.82 Å

If you are wondering what this seemingly bizarre unit Å is, it is the Angstrom and is equivalent to 1x10^{-10}m; so this means that 2.82 Å is 282pm.
Let's substitute these values into the above equation:

$$F = 6.6743 \times 10^{-11} \times \frac{\frac{22.9898}{6.02 \times 10^{26}} \times \frac{35.453}{6.02 \times 10^{26}}}{(2.82 \times 10^{-10})^2} = 1.89 \times 10^{-42} N$$

N.B. in the above equation, relative atomic mass is being divided by 6.02x10^{26} kgmol^{-1} as opposed to 6.02x10^{-23}gmol^{-1}.

The formula for electrostatic force bears great resemblance to that for gravity

$$F_e = k_e \frac{|q_1 \times q_2|}{r^2}$$

Where q_1 and q_2 are the absolute charges of the two particles and k_e is coulomb's constant, the value of which will be explored with more depth later.
K_e = 8.99x10^9

We know the charge of the two ions have magnitude e where e is the elementary charge as the ionic bonding of sodium chloride only involves the transfer of one electron. e = 1.602x10^{-19}C.

$$F_e = 8.99 \times 10^9 \frac{(1.602 \times 10^{-19})^2}{(2.82 \times 10^{-10})^2} = 2.901 \times 10^{-9}\text{N}$$

By dividing electrostatic force by gravitational force, we can gauge the vastly different strengths of these two forces:

$$\frac{F_e}{F_g} = 1.5 \times 10^{33}$$

Lattices

So far, we have only been concerned with the magnitude of forces, however in any ionic lattice there are both repulsive and attractive forces due to like and oppositely charged ions. So why is it that a rigid lattice structure is favourable if there is also significant repulsion alongside the attraction. This can be shown through the equation for electrostatic potential energy:

$$E_e = k_e \frac{q_1 \times q_2}{r}$$

In these lattices, charged ions are formed by gaining or losing an electron hence we can denote q_1 as q_+ and q_2 as q_-.

$$q_1 = z_+ e$$
$$q_2 = -z_- e$$

Where z is the magnitude of the relative charge of the ion. And e is the elementary charge (charge of an electron). This allows us to rewrite the equation for E_e as:

$$E_e = -k_e \frac{z_- z_+ e^2}{r}$$

It is clear that the value for electrostatic potential energy of a lattice is negative and as such it is a more favourable and stable state for the ions to exist in when in a vacuum and also air.

<u>Why dissolve?</u>

If sodium chloride exists favourably as a lattice when in air, why does it appear to disappear when added to water. It's disappearing trick is as a result of the salt dissolving meaning the strong ionic lattice has broken down now that the salt is in water. But why? The secret lies in coulomb's constant K_e.

Up to this point we have accepted the value of k_e to be 8.99×10^9, where does this originate from?

$$k_e = \frac{1}{4\pi\varepsilon_0}$$

This equation demonstrates that the coulomb constant is inversely proportional to the permittivity of the surroundings of the salt. The permittivity of water is approximately 80 times greater than that for air. As a result the value of k_e for water is much lower meaning the resulting electrostatic energy between ions in the lattice is significantly less negative. This makes it possible for the dipoles (partial charges) on the water molecules to overcome the ionic bonding in the lattice so the salt dissolves. This is because the dissolved state of sodium chloride is more favourable than for it to remain solid in water (i.e. when dissolved it has more negative electrostatic potential energy).

The reason for the aqueous phase to be more favourable is explained by the second law of thermodynamics which is expressed in terms of entropy which simply put is the degree of disorder in a system:

In a spontaneous process, the entropy of the universe increases

We can separate the entropy of the universe into two distinct components: that of the system and of the surroundings, hence:

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

We also know that

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}}$$

Where q is energy and T is temperature in kelvin.

From this we can derive that:

$$\Delta S_{univ} = \frac{q_{surr}}{T_{surr}} + \Delta S_{sys}$$

Then with the knowledge that energy absorbed by the surroundings is equal to the energy given out by the system and with the assumption that temperature of the surroundings and system are the same:

$$\Delta S_{univ} = \frac{-q_{sys}}{T_{sys}} + \Delta S_{sys}$$

Under constant pressure and temperature, the energy of the system is the same as the enthalpy change (ΔH_{sys}). The final step is to define a new composite term called the Gibbs energy:

$$\Delta G_{sys} = \Delta H_{sys} - T_{sys}\Delta S_{sys}$$

Now substituting in the Gibbs energy to the prior equations generates the equation:

$$\Delta S_{univ} = \frac{-G_{sys}}{T_{sys}}$$

Therefore it is evident that as temperature is always positive in kelvin, it is the Gibbs energy of the system which determines if the salt can dissolve – a negative Gibbs energy value would mean a positive value for change in entropy of the universe so the dissolving of the salt would be favourable. E.g. at 20^{o}c:

$$\Delta G_{sys} \approx 3900 - (293 \times 27) \approx 4011 Jmol^{-1}$$

As Gibbs energy is positive, the entropy of the universe will increase so the process is favourable and the salt dissolves. As temperature decreases there will be a temperature when $T_{sys}\Delta S_{sys} < \Delta H_{sys}$ at which point the salt will no longer be able to dissolve by itself as the value for ΔS_{univ} will be negative.

Arranging ions

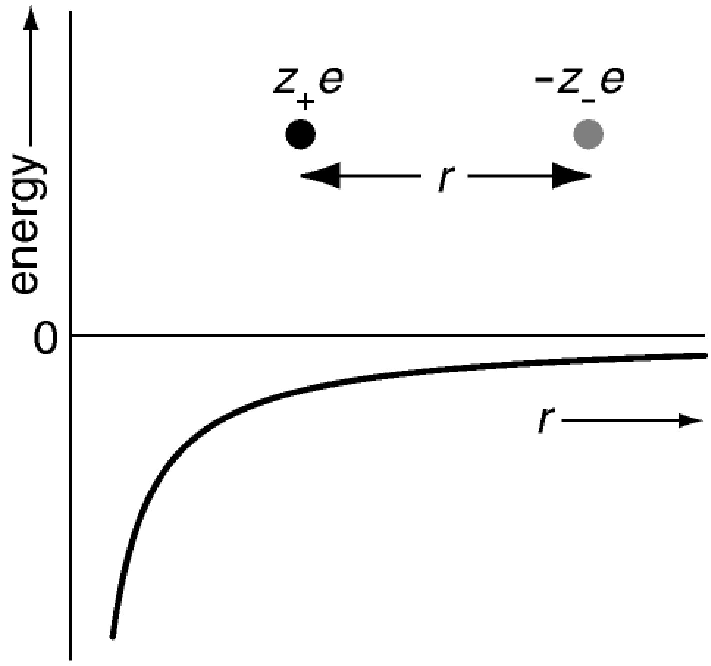
As is seen in the equation:

$$E_e = -k_e \frac{z_- z_+ e^2}{r}$$

The distance r between two oppositely charged nuclei, r, and the electrostatic potential energy are inversely proportional:

$$E_e \propto -\frac{1}{r}$$

The graph (**G1**) of this relationship can be seen below



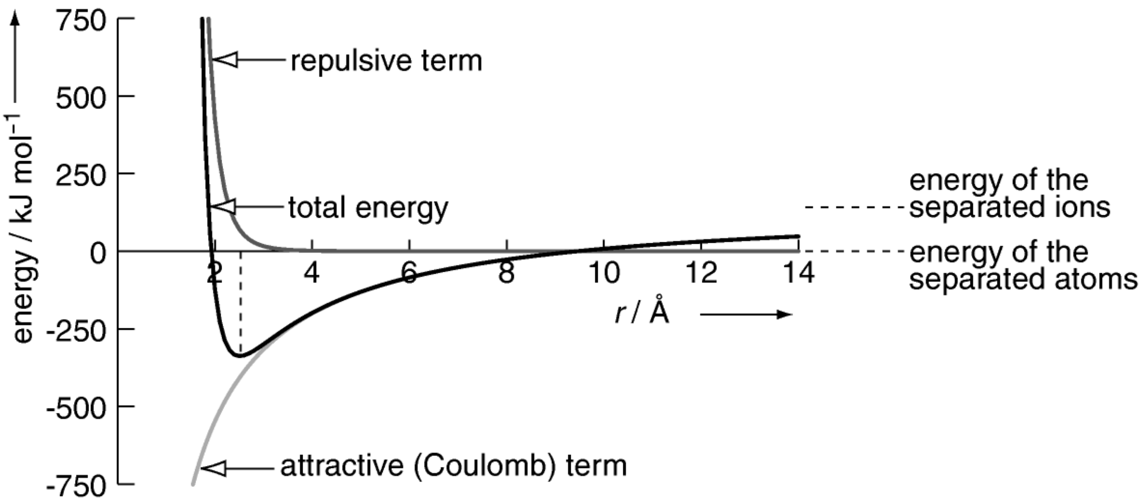
As is clear above, the further two oppositely charged ions are moved from each other, the weaker and hence less negative the electrostatic energy that occurs due to their interacting. This can be better expressed as:

$$\lim_{r \to \infty} -\frac{1}{r} = 0$$

It would be sensible to suggest that as r tends to 0, i.e. as the ions get closer and closer, that the electrostatic energy will become more and more negative. However this is not the case as we have to introduce a second function to the graph which accounts for the impact of the repulsion of the like charged nuclei of the ions which becomes the dominant factor in determining electrostatic potential energy when the ions are very close together. The relationship can be expressed as:

$$E_e \propto \frac{1}{r^n}$$

Where n is a value between 5 and 12 depending on the ions involved in the lattice. For sodium chloride it approximately equals eight. Note the relationship is no longer involving a negative sign as the repulsion is positive as it makes the overall electrostatic potential much less negative as seen in **G2**:

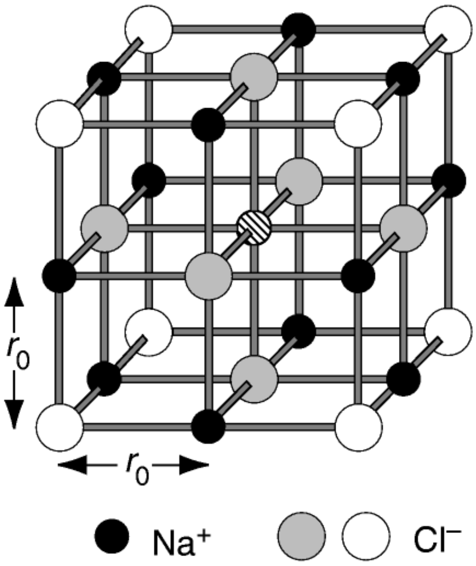


The fact that the r term for repulsion is raised to the power n means that it reaches greater values much faster as r tends to 0 and reaches smaller values much faster as r tends to infinity. As such the effect of nuclear repulsion is extremely significant in close proximity but much less important as the ions move further apart and the $-\frac{1}{r}$ function becomes more significant. There is therefore an optimum distance between nuclei of the ions as can be seen on the graph where there is a minimum point at approximately 2.5 Å.

Extending the lattice

Thus far, only the interactions of a single oppositely charged pair of ions has been considered. To tackle this problem, lets first rewrite our equation for electrostatic potential energy using our substitution for k_e:

$$E_e = -\frac{z_- z_+ e^2}{4\pi \varepsilon_0 r}$$



Suppose we take a central, positively charged sodium ion in this cubic lattice and draw a 2x2x2 cube around it. The nearest six ions will all be oppositely charged chloride ions, one lying in the centre of each face of our imagined cube at a distance of 1 from the centre and will be attracting the sodium ion. Following this would be 12 sodium ions, one lying on the midpoint of each side of our 2x2x2 cube, from which we can gather that they are a relative distance of $\sqrt{2}$ from the central sodium ion, like charges repel so each will be exerting a repulsive force. Finally in the simple 2x2 cube, there will be 8 chloride ions, one on each vertex of the cube at a relative distance of $\sqrt{3}$ from the original sodium ion. Each chloride ion will be attracting the central sodium ion. From this we can generate a simplified equation for the electrostatic potential energy of a 2rx2rx2r lattice:

$$E_e = -6\frac{z_- z_+ e^2}{4\pi \varepsilon_0 r} + 12\frac{z_- z_+ e^2}{4\pi \varepsilon_0 \sqrt{2} r} - 8\frac{z_- z_+ e^2}{4\pi \varepsilon_0 \sqrt{3} r}$$

We can take out the common factor to rewrite as:

$$E_e = -\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}}\right)\frac{z_- z_+ e^2}{4\pi \varepsilon_0 r} = -1.75 \times 10^{-18} J$$

As we continue to expand the cube, we can generate a series of positive and negative terms which continues infinitely as the lattice grows:

$$-\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{2}+\frac{24}{\sqrt{5}}-\frac{24}{\sqrt{6}}\dots\right)$$

Many methods have been used to attempt to converge this series of alternating terms. Only few have been successful such as a method known as expanding cubes which is a very tedious approach but does reach an accurate value for the constant term. This constant is named the Madelung constant, M, and is unique for all ionic lattices, for sodium chloride, M = 1.748. Having this constant value allows us to form the equation for the molar lattice energy after adding in a term to account for repulsion due to nuclei being in close proximity:

$$E_e=-\frac{MN_Az_-z_+e^2}{4\pi\varepsilon_0 r}+\frac{C}{r^n}$$

Where C is some unknown constant and n is also unknown. However the equation does not particularly hinge on either of these two values and as such we can rewrite and slightly simplify the expression to be:

$$E_e=-\frac{MN_Az_-z_+e^2}{4\pi\varepsilon_0 r}+\frac{1}{n}$$

This equation provides the molar electrostatic potential energy within the lattice when the ions are separated at exactly the right distance for the most negative electrostatic potential at the minimum point on Figure **G2** above.

Conclusion

The complexities of such simple compounds like sodium chloride have firm roots in mathematics of many branches. From limits of functions and derivation of formulae through to sums of series, the applications of pure techniques maths in in a less theoretical environment are far and wide and even if the science of salt isn’t to your taste I hope that an appreciation has been gained for how much further it is possible to take maths outside of the classroom.

References:

1. Graphs from ‘Why Chemical reactions happen’ by James Keeler and Peter Wothers https://global.oup.com/uk/orc/chemistry/keelerwhy/freelecturer/figures/ch03/
2. Figures for all constants used in the calculations are taken from their respective Wikipedia pages.