

features

What happens when salt dissolves in water?

An introduction to scientific argument and counter argument drawn from the history of science

by Kevin de Berg

There is an increasing demand being placed on teachers to use episodes from the history of science in their teaching/learning activities in science classes but there is a dearth of material available to teachers that are suitable for such activities. This paper outlines two models of salt dissolution drawn from late 19th and early 20th century chemistry and some of the arguments advanced for each model at the time that are suitable for the senior chemistry classroom. It suggests that teachers create a fifteen-minute Interactive Historical Vignette using the content of the solution controversy to teach students how scientific knowledge is formed. Chemistry is thus not just exposition and explanation but can be seen as a dynamic process of knowledge construction so important in helping our students understand something of the nature of science.

Introduction

Chemistry education has been described as consisting of expository and explanatory statements of concepts and applications of concepts (Hutchinson, 2000); of laboratory exercises designed to confirm or discover an already familiar law (Duschl, 1988); and of problem-solving exercises that are algorithmic in nature (de Berg, 1989, Nakhleh & Mitchell, 1993). While all these elements are endemic to any chemistry curriculum it is the predominance of these elements that has been of concern to chemistry educators. In addition to what has been common practice in chemistry education it is considered important that students should be given the opportunity to learn how chemical ideas originated, how chemists

go about justifying knowledge, and how problems involving qualitative information can enrich concepts if something of the nature of science is to be communicated to students. In fact, the NSW Board of Studies HSC Chemistry Syllabus (2000) requires students to engage with the historical context of a number of chemistry concepts. Such an engagement helps students to realise that, although some chemical ideas might appear today to be non-controversial, this was certainly not the case at the time of their origin. This is certainly the case with the *ionic dissociation* model for salts in water that proved to be one of the most controversial in chemistry about 110 years ago. In fact, the history of the nature of solutions provides students with two contrasting models of the

solution process, both of which were vigorously debated at the time (de Berg, 2003). Since it has been considered important for students to be exposed to the role of scientific argumentation in the establishment of scientific knowledge (Osborne, Erduran, Simon & Monk, 2001), and since we know that students learn more effectively in active and cooperative learning environments (Bransford, Brown & Cocking, 1999), it seems appropriate to sketch the arguments and counter arguments used for the two models of solution in the late 19th and early 20th centuries in a format that could promote an active learning environment at the Senior Chemistry level. Students are not presented with just the dry facts of chemistry but are introduced to the stimulating features of scientific argument so important to the

In this paper, we will outline the format of the two models of solution and the nature of the controversy in a style suitable for the use of teachers and students at the Senior Chemistry Level and will suggest one way in which this data can be used to promote interest and an active learning environment for the students.

The two models

The two models of salt dissolution in water can be described as the *dissociation* and *association* models. *Dissociation* implies that a salt breaks up into ions when dissolved in water and *Association* implies that a salt, instead of breaking apart, actually stays intact and combines with water in the dissolving process. Three major proponents of the dissociation model were Svante Arrhenius, Wilhelm Ostwald, and Jacobius van't Hoff who became known as the *ionists*. The major proponents of the association model were Henry Armstrong, S. Pickering, G. Fitzgerald, and E. Herroun (Dolby, 1976). Thus the controversy was between a European or Ionist understanding of dissolution and a British establishment view respectively.

(a) The dissociation model

Typically a form of this model is presented as the accepted and non-controversial one in our secondary school classrooms. As Arrhenius, Ostwald, and van't Hoff understood it, the model can be described as follows.



One of the objections to this model raised at the time was that if this was true one would expect to see yellow pungent chlorine gas coming off the solution and, even more dramatically, sodium metal forming with its immediate violent reaction with water, but this was simply not the case. The European contingent countered this argument by claiming that a sodium ion, Na^+ , is a different chemical species to a sodium atom, Na, and that a chloride ion, Cl^- , is a different chemical species to a chlorine atom, Cl, or chlorine molecule, Cl_2 . While we would agree with this argument today given our knowledge of the role of electron structure in chemical behaviour this was by no means as clear an argument in the late 19th century. There was a belief that atoms charged with electricity would still exhibit the same chemical behaviour as their uncharged counterparts. In fact, their chemical behaviour might become even more obvious when charged

with electricity. This argument touches on a delicate issue as far as student conceptions are concerned. Students often do not discriminate between a sodium atom and a sodium ion and might even ascribe similar chemical behaviour to both. They think of both species as simply *sodium* (Taber, 2002, pp.90-94). The same is true in the case of chlorine. This happens to be a perfect opportunity to deal with and highlight this phenomenon in a historical context.

A second common objection related to the fact that opposite charges attract and it was inferred that a Na^+ ion and a Cl^- ion would powerfully attract each other and re-form the undissociated species, $\text{NaCl}_{(s)}$. In Pickering's words (1897, p.223): '(Can these atoms), so strongly charged with electricity of opposite signs, meander about in the liquid with a supreme disdain for their former associates and the attractive charges which they carry'. Arrhenius understood that if the solution was concentrated enough one might expect these powerful attractive forces to operate and produce the neutral, NaCl , but in the case of dilute solutions the oppositely charged ions would be kept sufficiently distant from each other by water molecules and forces of attraction would be rendered ineffective thus allowing the independent existence of oppositely charged ions. A related objection concerned the type of forces that would lead to a molecule simply falling apart in water and adopting charges in the process. Armstrong (1896, p.78) called the theory the 'nonsensical hypothesis of ionic dissociation ... It asserts that (sodium) chloride and a few other compounds are so loosely strung together that they fall to pieces when dissolved in water. No valid motive is suggested for such self-sacrifice'. Herroun (1896, p.152) questioned the origin of the charges in this dissociation: 'where did they get these charges from in the first place'. This remained a fairly powerful criticism of the model up until the time W. L. Bragg published the results of his X-ray diffraction study of crystalline sodium chloride which suggested that the ions were already present in the solid distributed throughout space in the shape of a cube (Figure 1).

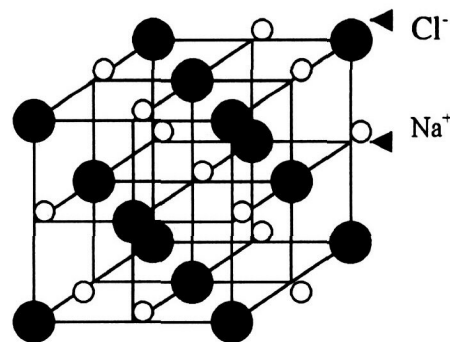


Figure 1. Crystalline lattice of sodium chloride

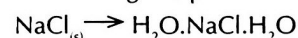
On dissolution in water, water molecules penetrated the interstices and separated the ions from each other. So the ions were not created in the dissolution process. They were already present. Armstrong (1927, p.478) responded to Bragg's announcement of the sodium chloride structure in one of the most colourful responses recorded in the letters to *Nature*.

'(This) is repugnant to common sense, absurd to the n^{th} degree, not chemical cricket. Chemistry is neither chess nor geometry whatever X-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged. A little study of the Apostle Paul may be recommended to Professor Bragg as a necessary preliminary even to X-ray work, that science is the pursuit of truth. It were (*sic*) time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods: at least taught them to ask for something more than chessboard evidence'.

This statement reflects the difficulty some chemists had in accepting physical evidence into a subject like chemistry. Since it is the electrons that diffract X-rays, X-ray diffraction can distinguish between a sodium atom and a sodium ion. This, of course, was not immediately obvious when the X-ray technique was first developed so one might sympathise a little with Armstrong, although he was regarded by Gratzer (1996, p.123) as a 'hot-air balloon who hovered over the scientific scene in England for about seventy years'.

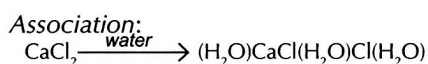
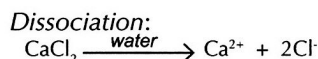
(b) The association model

The associationists believed that water had to play a significant part in the solution process and suggested that the solution process involved a combination of the salt with water. The simplest way of illustrating this process is as follows.



According to the ionists this model could not explain the conductivity of salt solutions because no charged species like ions, necessary for conduction in solution, were present to conduct the electricity. The associationists countered this argument by suggesting that it was the action of the external electric field on the solution that resulted in charged species that could transport the current rather than the spontaneous production of ions in the dissolving process. This was a difficult argument to refute until it was found that the ions were already present in the solid state and were simply released on dissolution.

One of the experimental evidences that had to be accounted for at the height of the solution controversy was the effect of a salt and a sugar on the depression of the freezing point for water. For example, it was known that a 0.1 M solution of sodium chloride produced about twice the freezing point depression as a 0.1 M solution of glucose. This was interpreted by the ionists as due to a doubling of the number of solute particles in solution due to the dissociation of NaCl into Na⁺ and Cl⁻. On the other hand, the doubling of the freezing point depression was interpreted by the associationists as due to a doubling of the number of free water molecules bound by a salt particle as shown by the above equation for NaCl. The almost tripling of the freezing point depression for a 0.1 M calcium chloride solution compared to that for a 0.1 M glucose solution was likewise explained by both models in terms of either a tripling of the number of solute particles produced on dissociation or the tripling of the number of free water molecules bound by the salt. This can be illustrated as follows.

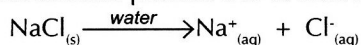


So both models appeared to have a consistent method for explaining freezing point depression. However, there was some data such as the enthalpy of solution data that did not seem to be consistent with either model and a compromise solution was suggested.

A compromise

In the dissociation model one would expect the process to require energy if particles were to be separated from a lattice and so one would expect all

dissolution reactions to be endothermic. In the association model one would expect energy to be released as the salt became hydrated and so one would expect all dissolution reactions to be exothermic. Some dissolution reactions such as that for ammonium chloride are noticeably endothermic and some such as that for sodium hydroxide are noticeably exothermic. So, how can this fact be explained? Whetham (1897, p.606) proposed a compromise position as follows. 'Dissociation of the ions from each other does not forbid the assumption that the ions are linked with one or more solvent molecules'. This meant that two energies, lattice energy (always endothermic) and hydration energy of ions (always exothermic), had to be considered in determining whether a dissolution process was to be exothermic or endothermic. If lattice energy was greater than hydration energy, then the dissolution process would be endothermic and if the lattice energy was less than the hydration energy the dissolving process would be exothermic. This then explained the energy anomaly. The compromise model suggested that a better way of describing the solution process was as follows.



The aqueous subscripts, (aq), are to indicate hydration of the ions. Some of the associationists were eventually convinced of the value of this compromise model but others such as Henry Armstrong remained bitterly opposed to any compromise.

Using the controversy in the classroom

Wandersee and Baudoin Griffard (2002, p.33) summarise many chemistry classroom experiences as follows. 'We think that the "rush to abstraction" and the "final form science"... evident in chemical education today actually "short-circuits" deep understanding by "cutting-off" all human and epistemological contexts, and by failing to develop a student's need to understand a given concept, principle, theory, or problem-solving algorithm'. The brief outline of the solution chemistry controversy given in this paper provides a good opportunity to restore a "human and epistemological" context to the teaching of chemistry in a way that can involve students. We suggest the use of an Interactive *Historical Vignette* along the lines described by Wandersee (1990) but emphasising a chemistry controversy

rather than a biography although some biographical details could feature as supportive to the controversy. The idea is to construct a 15-minute segment of a normal lesson that can be devoted to elements of the controversy outlined here. The vignette can be in the form of a short dialogue between two students, one representing say Svante Arrhenius and the other representing, say, Henry Armstrong. The arguments for and against each model as discussed in this paper are summarised in Table 1 and these, along with some of the interesting quotations given, can form the substance of the dialogue.

There is an opportunity for the students to be a little creative in their presentation by way of dress code and language accent used. A third person could appear on the scene towards the conclusion of the dialogue to propose the compromise position. It should be noted that Armstrong never accepted the compromise position although the ionists eventually did accept it. The role of human personality in the construction of scientific knowledge is rather prominent in this historical episode. The reasons why one solution model became more acceptable than another is an important question that can also be addressed. As Wandersee and Baudoin Griffard (2002, p.34) suggest, this exercise would 'put people back into chemistry after contemporary textbook authors had come to consider them peripheral to rigorous learning of chemistry and had either marginalised them in "boxed essays" or purged them entirely'.

We would be very interested in getting feedback from high school teachers who try enacting this controversy in their own classrooms. Teachers may like to use the core of the arguments discussed in this paper to write their own dialogues or alternatively may like to work with students to help them construct their own dialogues. While this process allows for some creativity by teachers and students, the vignette should be faithful to the substance of the controversy summarised in Table 1. We would be interested in seeing and hearing of examples of this kind. Further elements of the controversy can be found in de Berg (2003) and an application at the tertiary level is given in de Berg (2004). Teachers will need to be selective here as not all elements will be suitable for a secondary classroom. For this paper we have abstracted what we think are the major elements most suitable for the senior chemistry level. This paper is also

Table 1. A summary of the criticisms and counter-criticisms of the dissociation and association models of solution of a salt in water.

Criticisms of dissociation	Response to the criticisms
1. Expect yellow pungent chlorine gas and reactive sodium, which would react violently with water. None of these are formed.	1. Chlorine gas, Cl ₂ , is a different chemical species to a chloride ion, Cl ⁻ , or a chlorine atom, Cl. Sodium metal, Na, is a different chemical species to a sodium ion, Na ⁺ .
2. Opposite charges attract. Wouldn't the attractive forces between a Na ⁺ ion and a Cl ⁻ ion be so strong that they would combine again to produce the neutral salt?	2. The presence of water helps to reduce this force of attraction. So, as long as the solution is dilute one might expect these ions to exist independently.
3. How does water produce these powerful ionic charges in the first place?	3. Water doesn't produce the charges. The charges already exist in the solid salt. Water just allows the charges to separate.
Criticisms of association	Response to the criticisms
1. A salt solution conducts electricity, which suggests that (+) and (-) charges must be present in solution. The Association model shows no charges to explain this conductivity.	1. The charges are produced by the effect of the external battery on the solution and not by spontaneous dissociation of the salt.
2. Dissociation can explain a higher freezing point depression for salt solutions in terms of an increase in the number of solute particles. How can Association explain this enhanced depression effect for salts?	2. Association can explain this enhanced effect in terms of an increase in the number of free water molecules that become bound to the salt.
Criticism of dissociation and association	Response to the criticism
1. Dissociation suggests an endothermic solution process and Association suggests an exothermic solution process. How can either model explain the fact that some salts dissolve exothermically and some endothermically?	1. Solution of a salt in water involves both dissociation into ions and association of those ions with water.

designed to help teachers with some of the content of the history of science that is not readily available in a useable form for instruction and learning at the high school level.

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