Chemistry
Education Research
and Practice

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/cerp

The Significance of the Origin of Physical Chemistry for Physical Chemistry Education: The case of Electrolyte Solution Chemistry

Physical Chemistry's birth was fraught with controversy, a controversy about electrolyte solution chemistry which has much to say about how scientific knowledge originates, matures, and responds to challenges. This has direct implications for the way our students are educated in physical chemistry in particular and science in general. The incursion of physical measurement and mathematics into a discipline which had been largely defined within a laboratory of smells, bangs, and colours was equivalent to the admission into chemistry of the worship of false gods according to one chemist. The controversy can be classified as a battle between *dissociationists* on the one hand and *associationists* on the other; between the *Europeans* on the one hand and the *British* on the other; between the *ionists* on the one hand and the *hydrationists* on the other. Such strong contrasts set the ideal atmosphere for the development of argumentation skills. The fact that a compromise position, first elaborated in the late 19th century, has recently enhanced the explanatory capacity for electrolyte solution chemistry is challenging but one in which students can participate to their benefit.

Introduction

Modern physical chemistry tends to be dominated by topics in Atomic and Molecular Structure, Quantum Chemistry, and Spectroscopy, but this was not the case at the birth of physical chemistry, taken to be around 1887, the year associated with the publication of the first physical chemistry journal, *Zeitschrift fur Physicalische Chemie.* In 1887 the electron, proton and neutron had not been discovered and some physical chemists of this early period, such as Wilhelm Ostwald, even doubted whether atoms really existed. The preparation of new elements and compounds and the determination of the elemental composition of the compounds, including the determination of the atomic weights of the elements, dominated the chemistry landscape up until the end of the 19th century. It was aqueous solution chemistry that nourished the birth of physical chemistry and like most births it was associated with pain, albeit in this case, the pain of controversy.

The controversy raged between the European school of Svante Arrhenius [1859-1927], Wilhelm Ostwald [1853-1932], and Jacobus van't Hoff [1852-1911] who believed that salts partially dissociated when dissolved in water, and the British school of Henry Armstrong [1848-1937], Spencer Pickering [1858-1920], and George Fitzgerald [1851-1901] who regarded the dissociation hypothesis as unthinkable and lacking in firm laboratory evidence. By the beginning of the 20th century the controversy had spread to the United States with local proponents of the dissociation hypothesis such as Gilbert Lewis [1875-1946] and opponents of the hypothesis such as Louis Kahlenberg [1870-1941]. Accounts of the controversy have been written by Dolby (1976) and de Berg (2003).

In this paper we focus on some aspects of the controversy that have important applications for physical chemistry education. A variety of experimental data was used by the European school to promote the idea of the dissociation of salts in aqueous solution. Measurements of electrical conductivity, boiling point elevation, freezing point depression, vapour pressure lowering, osmotic pressure, and heats of neutralization were among the techniques of interest. In this paper we will confine ourselves predominantly to the data on osmotic pressure since this is pertinent to our discussion of an equation of state for aqueous solutions. As a brief background it should be recalled that if, in a U-tube, an aqueous solution of sucrose in the left hand arm of the tube is separated from pure water in the right hand arm by a membrane permeable only to water and placed at the base of the U-tube, the solution in the left hand arm will rise and the solution in the right hand arm will fall over time due to osmosis. Osmotic pressure is the pressure needed to be applied to the left hand arm to prevent osmosis occurring. It should be noted that the first Nobel Prize in Chemistry was awarded to Van't Hoff in 1901 for his work on osmosis and osmotic pressure, central concepts in the emerging physical chemistry.

Consequently, we examine (a) the controversial emergent character of the new chemistry and its implications for nature of science (NOS) study; (b) the dual interpretations of the data and how this can be used as a rich resource for chemistry education; and (c) the significance of mathematics for physical chemistry with a particular focus on osmotic pressure and the equation of state for aqueous electrolyte solutions.

Controversial Emergent Character of the New Chemistry

Chemistry had its roots in alchemical tradition and so was always associated with laboratories containing apparatus for preparing new substances and analysing known substances. It was this kind of context that Armstrong (1896, p. 78) had in mind when he referred to that "chemical feeling, an indefinable instinct which, however, has very real existence". The new chemistry, according to Armstrong, was destitute of this *chemical feeling* because of its increasing reliance on *physical measurement* and *mathematical formulas* derived from the numerical results of experiment. Armstrong (1928, p. 51) quotes Sir Oliver Lodge as saying in 1889 that, "chemists have permitted themselves to be run away with by a smattering of quasi mathematics and an overpressing of empirical formulae", and says himself that, "the physical chemist has been neither chemist nor physicist at heart. The mutation from chemist to physical chemist certainly seems to have involved the loss of the primary factor in chemistry: chemical feeling".

The ionists, as we shall call the European school, insisted that the measurement of the osmotic pressure of a range of aqueous salt solutions was best interpreted in terms of the partial dissociation of the dissolved substance. A list of osmotic pressure data taken from De Vries (1888, 1889) is shown in Table 1.

Table 1 Isotonic coefficients for different solutions with potassium nitrate taken as 3 for comparison (after De Vries 1888, 1889)

Substance	*Isotonic Coefficient*
Glycerol	1.78
Glucose	1.88
Cane sugar	1.81
Malic acid	1.98
Tartaric acid	2.02
Citric acid	2.02
Magnesium sulphate	1.96
Potassium nitrate	3.00
Potassium chloride	3.00
Sodium chloride	3.00
Potassium iodide	3.04
Sodium nitrate	3.00
Sodium iodide	2.90
Sodium bromide	3.05
Potassium acetate	2.85
Potassium bromide	3.05
Potassium sulphate	3.90
Calcium chloride	4.05
Potassium citrate	4.74

The isotonic coefficients in Table 1 represent the relative concentrations of solution required for equal osmotic pressures based on a value of 3 for potassium nitrate. A solution which contains 3 mol/L of glycerol would have the same osmotic pressure as a potassium nitrate solution containing 1.78 mol/L. Mole for mole, therefore, a potassium nitrate solution would have an osmotic pressure about 1.7 times that of glycerol. If potassium nitrate completely dissociated into its ions one would expect it to have an osmotic pressure double that of glycerol. If potassium nitrate did not dissociate at all one would expect it to have an osmotic pressure similar to that of glycerol. A value of 1.78 indicated to the ionist that potassium nitrate was about 68.5% dissociated into its ions.

The results in Table 1 suggested to the ionist school that substances from glycerol to magnesium sulphate had similar osmotic pressures; those from potassium nitrate to potassium bromide similar osmotic pressures but higher than the glycerol group due to partial dissociation into two ions; potassium sulphate and calcium chloride similar osmotic pressures but higher than the potassium nitrate group due to partial dissociation into three ions. The result for potassium citrate indicated partial dissociation into four ions. The British school considered this kind of reasoning to be akin to the juggling of numbers to support a ridiculous hypothesis. If the dissociation model applied particularly to soluble metal salts why was the result for magnesium sulphate not equivalent to that of salts partially dissociating into two ions? As late as 1928 Armstrong (1928, p. 50) was saying that “Ostwald’s contentions were chemically absurd and the function of water in solution has to be considered and properly evaluated”. The fact that laboratory experience confirmed the production of hydrated compounds from solution was evidence, according to Armstrong (1896) and Pickering (1897), that solution was an *association with water* phenomenon rather than a *dissociation in water* phenomenon. So while the European school was classified as the *ionist* or *dissociationist* school, the British school was classified as the *hydrationist* or *associationist* school.

When Arrhenius (1887) first proposed the dissociation hypothesis he called the part that conducted electricity the *active part* and the part that did not conduct electricity the *inactive part*. Later the active part was identified with the presence of positive and negative charges or what became known as ions and the inactive part with the neutral undissociated compound. The hydrationists could not understand how a neutral compound could take on a charged form simply when coming into contact with water. At the 1890 meeting of the British Association in Leeds, Fitzgerald is quoted by Tilden as saying in relation to dissociation, “I can’t see where the energy comes from” (Tilden, 1918, pp. 117-118). The dissociation issue was double-headed: How could a stable neutral compound get the energy to dissociate in the first place? And secondly, How could the dissociated part get the energy to be charged? However, the development of the physical technique of X-ray diffraction of crystals in the early 20th century helped to partially resolve this issue, at least to the satisfaction of the ionists, by showing that ions were present in the solid state already so water didn’t need energy to produce them.

When W.L.Bragg published the results of his X-ray study of sodium chloride and concluded that no molecules of sodium chloride, NaCl, existed as such but rather sodium and chloride ions were distributed in a chessboard fashion in a three-dimensional lattice, Armstrong (1927, p. 478) protested that this model “is repugnant to common sense, absurd to the nth 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 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 highlights the difficulty that some chemists faced in accepting the new chemistry, physical chemistry. By the 1920's the ionist school of dissociation was well established within the new discipline of physical chemistry. Even at this time Armstrong used colourful language to continue his opposition to the now popular physical chemistry by lamenting the fact that so many of his chemistry colleagues were falling "victim to the modern disease, physical measurement….like measles" (Armstrong, 1928, p. 51). He proposed that many chemists were the victims of fashion: "After all, we scientific workers….like women, are the victims of fashion: at one time we wear dissociated ions, at another electrons; and we are always loth to don rational clothing" (Armstrong, 1909, p. 643). Physical chemists received the brunt of his criticism: "The fact is that physical chemists never use their eyes and are most lamentably lacking in chemical culture. It is essential to caste out from our midst, root and branch, this physical element and return to our laboratories" (Armstrong, 1936, p. 917).

Aside from his criticism of physical chemistry, Armstrong was instrumental in being one of the first to promote laboratory chemistry and the heuristic method in chemistry education (Brock, 1973). He had an abiding interest in helping prepare young chemists for a laboratory-based profession and tirelessly worked to protect them from the incursion of physical techniques and measurement in chemistry as we have seen. He also worked to protect them from what he considered to be the blatant use of empirical mathematical formulae like that introduced by van't Hoff for interpreting osmotic pressure data. The relationship, $\pi_{os}V = iRT$, where π_{os} is the osmotic pressure, V is the volume of solution per mole of solute dissolved, R is the gas constant, T is the absolute temperature, and i is an empirical factor designed to match theory with experiment, was first proposed by van't Hoff in 1886. The van't Hoff factor, i, was usually a number between 1 and 2 for 1:1 electrolytes; between 2 and 3 for 1:2 and 2:1 electrolytes and so on. The hydrationists regarded a reliance on such empirical factors as lacking the precision demanded by chemists and mathematicians. We will say more about this equation later.

Issues in the Nature of Science

The kind of historical chemistry narrative portrayed here is not a common feature of chemistry curricula. When Niaz and Rodriguez (2000) examined fifty-three general chemistry tertiary level textbooks, published over the period (1929-1992), for their treatment of atomic structure, they concluded that chemistry was being presented as a 'rhetoric of conclusions' with practically little discussion of the historical context. Atomic structure was also the focus of a study of twelve secondary school textbooks by Justi and Gilbert (2000) who found that the models of atomic structure presented were commonly hybrids of different historical models. When hybrids are used, "the gaps of validity between attributes of a given model cannot readily be addressed, no questions requiring different ways of thinking about a phenomenon can be raised, and no different approaches to the interpretation of a phenomenon are possible" (Justi and Gilbert 2000, p. 1006). This is a little like teaching the solution process as a combination of hydration and dissociation without realizing or identifying that there is a rich historical context of controversy behind the phenomenon of solution, and it is this rich historical context that tells us something of what the practice of science is like.

The tendency to hybridize models is probably a symptom of a universal tendency in education to give priority to the conceptual over the epistemic, that is, to the finished product over how one got to the finished product and justified it. Osborne (2005, p. 369) further observes that, "Such an emphasis is not so much a consequence of teachers' choice but more a product of an assessment system which prioritizes ontology at the expense of epistemology". Some emphasis on the kind of arguments and counter-arguments that populate the emergence of a new science like physical chemistry is meant to restore some balance to a physical chemistry curriculum which is traditionally heavily focussed on the conceptual.

The brief analysis given here of an emerging discipline has major implications for Nature of Science (NOS) research in chemistry education. The dissociation story illustrates how idiosyncratic it is and thus how difficult it is to form a generalised picture of science across the concepts of a discipline and, in fact, across disciplines of science. In a study of twenty-four practising research scientists, Schwartz and Lederman (2008, p. 762) concluded that, "the variations described here provide evidence that these scientists do not all hold to the same view of the NOS". In spite of this they propose (p. 764) that "with the numerous distinctions and nuances associated with authentic science practices, there is a danger of losing the 'forest through the trees' if these nuances are the focus of science instruction rather than the broader, overarching commonalities among the contexts. A focus on differences may muddle the broader concepts. Instructional objectives for NOS are probably more attainable and relevant to the goals of scientific literacy when kept at levels of generality shown here to apply across science disciplines and approaches".

But is a generalised broad picture of NOS any different to that broad generalised notion of the 'scientific method' which has received significant criticism from historians and philosophers of science? Could the so-called myth of the scientific method be replaced with an equally spurious NOS? This is a challenging issue. As far as K-12 science education is concerned, Schwartz and Lederman (2008, p. 764) suggest that the "impracticality of introducing all the finer perspectives of authentic science practice into school-based science leads(s) to the conclusion that the generalised treatment of NOS across science disciplines is appropriate…". While one can understand the authors' concerns about introducing 'all the finer perspectives' into school-based science, might not a small selection of the finer perspectives be more instructive than nebulous generalised perspectives often divorced from science content. As far as tertiary level science education is concerned, there are some distinct advantages (one of which is authenticity) in uncovering NOS issues in specific science content. This view is consistent with that expressed by Clough (2005). Because of the multi-dimensional issues associated with NOS, there is a strong case for being less ambitious in what one hopes to achieve in all levels of education in relation to the NOS. Observing science through its stories may be more effective in exposing our students to the wonders of science than in generalising science and, in the process, killing off its substance.

From what has been said one should not think that a generalised approach to NOS has not been of some benefit to science education. For example, Boujaoude *et al*. (2005) studied a drama presentation by high school students of the development of the concept of light using the contributions of Archimedes, Al-Haran Ibn Al-Hartham, Newton, and Edison as the historical setting. They focused on how the drama group and a control group scored on the generalised NOS concepts of *tentative but durable, empirical,* and *theory-laden.* The drama group showed larger gains than the control group in the *tentative but durable* and the *theory-laden* NOS concepts. The use of the historical context for a specific science topic was a feature of this study, and is a case where productive use has been made of generalised NOS concepts. Nevertheless, it is a contention of this paper that there are gains to be had at the tertiary level at least for exposing our students to some of the finer aspects of the chemistry story over a more stereotypical approach that generalises the nature of chemistry.

A study on the nature of scientific knowledge by KolstØ and Mestad (2005) used an open-ended approach to examine the social processes that accompany the development of scientific knowledge. Human beings in a social context bring a particular kind of flavour to knowledge not always recognized. Henry Armstrong had a passionate vision for chemistry which he regarded as sacrosanct. His language betrays a commitment to chemistry akin to a commitment to religious faith and fair play in a game of cricket. The impact that such a commitment had for the developing physical chemistry is an important one to consider. Chemistry itself was undergoing a transition from an exclusively laboratory-observational science to a science which also increasingly engaged with the disciplines of physics and mathematics. Generalised views of the NOS fail to capture such transitions in science itself. While Gratzer (1996, p. 123) described Armstrong as a "hot-air balloon who hovered over the scientific scene in England for about seventy years", his example serves to remind us that chemistry is a human enterprise with both positive and negative consequences.

Dual Interpretations as a Resource for Chemistry Education

A major focus in science education research over the last decade has been on the role of scientific argument in the establishment of scientific knowledge (Osborne *et al.*, 2013). Since we know that students learn more effectively in active and cooperative learning environments (Bransford *et al.*, 1999), it seems appropriate to sketch the arguments and counter-arguments used by the Dissociationists (or Ionists) and the Associationists (or Hydrationists) to understand solution chemistry around the turn of the 20th century. The arguments and counter-arguments listed in Table 2 are very distinct and suitable for forming the skeleton of a vigorous class debate or incisive class assignment.

The first criticism of dissociation shown in Table 2 was advanced before one knew about the existence of electrons or ions. The hydrationists had argued that there was no evidence of the presence of the white metal, sodium, or yellow chlorine gas when sodium chloride was dissolved in water. Arrhenius (1912) countered this argument by suggesting that sodium must exist in at least two forms, natural sodium not charged with electricity, and another form of sodium which was charged with electricity. This seemed a reasonable suggestion given the knowledge that some elements like phosphorous and carbon have different elemental forms like red and yellow phosphorous and diamond and graphite respectively. Subsequently, of course, the 'sodium charged with electricity' became the sodium cation, Na^+, and the 'natural sodium not charged with electricity' became the sodium atom, Na. This is a pertinent point since we know that students have difficulty distinguishing between an element's atoms and its ions in properties and atomic structure (Croft, 2010; Taber, 1993). Precision in scientific language becomes critical when referring, for example, to the element sodium. Are we referring to the neutral sodium atom or the positively charged sodium cation?

The data in Table 2 illustrates how important the solvent, water, was to both sides of the argument. Its dielectric behaviour allowed ions to exist independently of each other in solutions giving credibility to the idea of partial dissociation of salts into ions in aqueous environments. Its capacity to act as a hydrating material gave credibility to the role of the solvent in the solution process. So, while the ionists focused on solute behaviour and the hydrationists focused on solvent behaviour in the solution process, a small number of chemists were suggesting a compromise position which allowed for both dissociation and hydration when a salt dissolved in water. Whetham was convinced of the ionic dissociation theory because of the simple way it was able to explain chemical properties in terms of the properties of the individual ions but he was also convinced that water could also play a crucial role. He (1897, p. 606) proposed that "Dissociation of the ions from each other does not forbid the assumption that the ions are linked with one or more solvent molecules". While Armstrong refused to accept such a compromise position, the idea of partial dissociation and hydration has proved to be of great value in electrolyte chemistry as we shall see.

According to Osborne (2005), argumentation is a key ingredient of the way scientific knowledge develops and the information in Table 2 bears witness to this fact. If argumentation is to be encouraged, then, "students need a resource for arguing…… For in the context of science, critical evaluation of evidence can only take place if there is evidence to evaluate…" (Osborne 2005, p. 370). There was a numerous range of scientific evidence to evaluate in electrolyte solution chemistry as already alluded to. In this paper we have focussed, however, on the osmotic pressure data for reasons earlier explained and this data has proved crucial in the scheme of things. In addition, the analytical framework used by Osborne (2005) for assessing the quality of argumentation involves five levels ranging from an argument involving no rebuttals at the lowest level through to an argument containing more than one rebuttal at the highest level. The content of Table 2 thus provides the potential for high quality argumentation due to the number of counter-arguments or rebuttals involved.

Table 2 A summary of the criticisms and counter-criticisms of the Dissociation and Association models of solution of a salt (NaCl) 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 osmotic pressure 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.

How might one practically use the argumentation flow in Table 2 in a teaching-learning situation? One possibility is the use of Interactive Historical Vignettes which are "a series of lively, carefully crafted, brief (approximately fifteen minutes), interactive" (Wandersee and Boudoin-Griffard 2002, p. 34) stories tailored towards the topic currently under study. The Vignettes could be guaranteed to be lively if students were chosen to represent Svante Arrhenius and Henry Armstrong, the two historical characters of strong differing opinions and with colourful personalities. Scientific stories by their very nature will address conceptual issues but if human and social factors can also feature there is likely to be more effective engagement with the plot and the concepts (Klassen 2007). Arrhenius is described as stocky with a ruddy complexion, blonde hair, blue eyes and a love for controversy. In fact, he enjoyed debate, argument and counter-argument so much that he sought every opportunity to engage in such repartee (Crawford 1996). Put Arrhenius with Armstrong, the hot-air traditionalist from England whose colourful language we have already witnessed, and you have the ideal setting for a lively encounter. Each fifteen minute story could revolve around each of the criticisms and counter-criticisms shown in Table 2, but emboldened with interesting human factors. Imagine the drama which could unfold between a dyed-in-the-wool laboratory chemist and an upstart foreigner who fancied himself more as a physicist than a chemist.

Mathematics in Physical Chemistry: An Equation of State for Solutions

Van't Hoff (1887) was the first to observe that the osmotic pressure of dilute aqueous solutions of sucrose appeared to obey an equation analogous to the gas law; $\pi_{\mathrm{os}}V = RT$, where π_{os} is the osmotic pressure, V is the solution volume per mole of solute dissolved, R is the gas constant, and T is the absolute temperature. One of the pervading problems in physical chemistry education relates to the question of why the gas constant, R , should appear in equations purporting to describe solution behaviour. This was one of the reasons why the hydrationists could not accept that the use of such empirical equations was going to be of any use to the chemist, even though the relationship might fit mathematically. Aqueous solutions were obviously different to gases. However, thermodynamically, it turns out that the *entropy* increase with volume is the same (R/V) for the expansion of a gas against a vacuum and the expansion of a solution against pure solvent. So, R, is really a universal constant. This is why thermodynamics has become a central organizing theme in physical chemistry since it has the capacity to unify obviously disparate systems like gases and aqueous solutions. However, the use of thermodynamics in chemistry was regarded by the hydrationists as nothing more than a cloak for the mathematically-minded. Using colourful language once again, Armstrong (1906, p. 79) comments, "As a chemist and a friend of the poor molecules, I feel that the aspersion of immorality should not be allowed to rest upon them forever unless the evidence be really condemnatory beyond question. In any case, it is important that we should discover the true nature of the crime committed in solution; to cloak the inquiry by restricting it to thermodynamic reasoning-a favourite manoeuvre of the mathematically minded- is akin to using court influence in abrogation of a full and complete investigation; such a course may satisfy the physicist but is repulsive to the chemist". The significance of a gas constant, R, appearing in an equation describing aqueous solution behaviour and the significance of mathematical analogies for science education are discussed in detail by de Berg (2006). Our focus in this paper is to trace how the compromise idea of dissociation and hydration came to play a role in establishing an equation of state for aqueous strong electrolyte solutions.

Aqueous solutions of common salt, sodium chloride, NaCl, gave osmotic pressures nearly double that for sucrose on a mole to mole basis so van't Hoff incorporated the coefficient, i, in his equation to accommodate this, thus, $\pi_{\mathrm{os}}V = iRT$. At about the same time Ostwald (1888) was able to show that some electrolytes like acetic acid obeyed the equilibrium law known as Ostwald's Dilution Law. That is, for, $\mathrm{AB} \leftrightarrow \mathrm{A}^+ + \mathrm{B}^-$, $\propto^2 c/(1-\propto)$, where ∝ is the degree of dissociation, was constant for different concentrations, c, of electrolyte. However, the relationship did not appear to work for electrolytes like NaCl where ∝, the degree of dissociation, was close to the value of 1. Thus solutions like acetic acid became known as weak electrolytes since $\propto \ll 1$, and solutions like NaCl (aq) became known as strong electrolytes since ∝ was close to 1.

From about 1920 chemists dealt with the problem of strong electrolytes by assuming they were completely dissociated and allowing for departure from ideal behaviour by incorporating coefficients which allowed for such interactions as interionic attractions and repulsions. This meant that new concepts had to be developed. Lewis and Randall (1921) developed the concepts of *activity*, *activity coefficient*, and *ionic strength* to deal with such phenomena and Debye and Huckel (1923) theoretically derived a relationship between the activity coefficient and the ionic strength of a dilute solution. The Debye-Huckel law was extended for more concentrated solutions and Pitzer (1995) was responsible for establishing equations with a large number of empirical coefficients for activity and osmotic coefficients over a large range of concentrations for strong electrolytes.

Assuming '*m*' molal of NaCl dissociates completely into its ions, $NaCl \rightarrow Na^+ + Cl^-$, the equation of state for an aqueous solution of NaCl is:

$$\pi_{\mathrm{os}} V_A = 2m\varphi RT \text{ (Equation 1)}$$

where V_A is the volume of the solvent and φ is the osmotic coefficient of the solution accounting for deviations from ideal behaviour. The extensive empirical expression developed for φ is as follows (Heyrovska, 2006):

$$\varphi = 1\text{-}Z_M Z_X A_\varphi\, I^{1/2}/(1+bI^{1/2}) + m(2\nu_M\nu_X/\nu)(\beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(1)}\exp(-aI^{1/2}) + m^2(4\nu_M{}^2\nu_X Z_M/\nu)C_{MX}$$

where Z_M, Z_X are the charges on M and X respectively, A_φ is a constant characteristic of the solvent medium, I is the ionic strength, a and b are constants for a particular solute and solvent, and $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$, and C_{MX} are empirical constants defined in Pitzer (1995). Values of φ for a variety of electrolytes are listed in Robinson and Stokes (2002) and Hamer and Wu (1972). Table 3 contains a set of calculated values of π_{os} for 1 molal solutions of the alkali metal chlorides at 25^0C using Equation 1 and values of φ taken from Hamer and Wu (1972).

Table 3 Calculated values of π_{os} for 1 molal alkali metal chloride aqueous solutions at 25^0C using Equation 1

Alkali Metal Chloride	$\boldsymbol{\varphi}$	$\boldsymbol{\pi_{\mathrm{os}}}$ **/atmospheres**
LiCl	1.02	49.7
NaCl	0.936	45.6
KCl	0.898	43.8
RbCl	0.886	43.2
CsCl	0.861	42.0

The use of extended empirical equations for activity and osmotic coefficients was severely criticised in 1991 because of an increasing reliance on coefficients lacking any physical or chemical significance (Darvell and Leung, 1991). Heyrovska (1996) answered the challenge by reformulating the chemistry of strong electrolytes in terms of partial dissociation and hydration, that is, using ideas which originally constituted the compromise position of the late 19th century. Heyrovska uses the published values of the osmotic coefficient, φ, and determines hydration numbers at the surface and within the bulk of the solution, n_s and n_b respectively; the molalities of free water at the surface and within the bulk of the solution, n_{Afs} and n_{Afb} respectively; the volume of free water per mole of solute particles in the bulk, V_f ; and the extent of dissociation of the solute, α. This is accomplished through the use of five equations shown in Box 1. The technique is described by Heyrovska (1996, 1997, 2011).

What is interesting is that by distinguishing between free water and bound water and allowing the strong electrolyte to be only partially dissociated as originally proposed by Arrhenius, the equation of state for the electrolyte is immensely simplified as:

$$\pi_{\mathrm{os}} V_f = RT \quad \text{(Equation 2)}$$

which applies up to saturation for most electrolytes (Heyrovska, 2004).

$$a_A = \exp(-2m\varphi/55.51) \qquad \textbf{(1)}$$

$$-a_A \ln a_A/(1-a_A) = n_{Afs}/n_{Afb} = R_{Af} \qquad \textbf{(2)}$$

$$n_{Afs} = (55.51 - mn_s) \qquad \textbf{(3)}$$

$$n_{Afb} = (55.51 - mn_b) \qquad \textbf{(4)}$$

$$i = 2\varphi\, n_{Afb}/55.51 \qquad \textbf{(5)}$$

where a_A = activity of water
m = molality of the NaCl solution
φ = osmotic coefficient
n_{Afb}, n_{Afs} = molalities of free water in the bulk and at the surface respectively
55.51 = moles of water in 1 kg
n_b, n_s = hydration numbers in the bulk and at the surface respectively
$i = (1 + \alpha)$ where α is the degree of dissociation
= number of NaCl ion pairs, Na^+ and Cl^- ions, per molal of NaCl dissolved

Box 1 The five Heyrovska equations used to describe the properties of electrolytes.

Values for n_b, α, V_f, and π_{os} for 1 molal alkali metal chlorides at 25^0C are given in Table 4. This kind of data is a rich resource for enhancing physical chemistry students' understanding of thermodynamic processes in electrolyte solutions.

Table 4 Values of n_b, α, V_f, and π_{os} (calculated from Equation 2) for 1 molal alkali metal chlorides at 25^0C. The density of free water at 25^0C is taken as 0.997 g cm^{-3} (Aylward and Findlay, 2008)

Alkali Metal Chloride	n_b	α	V_f / L	π_{os} /atmospheres
LiCl	5.17	0.8489	0.492	49.7
NaCl	2.47	0.7890	0.536	45.6
KCl	1.19	0.7598	0.558	43.8
RbCl	1.03	0.7436	0.565	43.2
CsCl	0.93	0.6947	0.582	42.0

The calculated osmotic pressure values in Table 4 are identical to those calculated in Table 3 but the data used in Table 4 is much more explanatory than that in Table 3. The hydration number, n_b, is a measure of the average number of water molecules attracted and bound to an alkali metal ion and a chloride ion in the bulk of the solution. From this value one can calculate the mass of water in 1000 grams of water that is in a state of hydration and therefore the mass of water that is free. Using the density of free water one can calculate the volume of free water. Since the number of moles of solute particles (ions and ion pairs) per mole of solute dissolved is $(1+\alpha)$, V_f can be easily calculated, and consequently π_{os}. Equation 2 as an equation of state is now widely applicable. Even though such an approach to an equation of state does not yet appear in physical chemistry textbooks, it has great explanatory power over and above anything currently available. The approach serves to enhance the centrality of an equation of state for solutions, a centrality noted by Atkins (2008, p. 54) in the case of gases. What is of great worth here is that physical chemistry students can explore and participate in the enhanced explanatory power of the new equation of state. The following tasks are designed to enhance a student's data processing skills using EXCEL as well as their reasoning skills particularly in relation to data trends.

An Advanced Physical Chemistry Exercise for students

The following is a set of tasks that draw upon ideas present at the birth of physical chemistry and those that also represent some recent developments in the field of electrolyte solution chemistry. One of the challenges faced by physical chemistry educators is how to meaningfully engage students in the mathematics now central to much of physical chemistry. One approach might be to derive the equations in Box 1 from first principles. This would obviously increase the mathematical load a student would have to bear but would give some insight, potentially, into the origin of the equations. Another approach is to think of the equations in Box 1 as a set of tools, but a set of tools demystified by qualitative descriptions of the variables and what the equations are designed to accomplish. Qualitative reasoning over and above simple algorithmic substitution is an approach strongly recommended by Carson and Watson (2002). The following tasks assume that such a qualitative approach might have already taken place.

Stenhouse (1985, p. 21) argues that, "What is inculcated in a great deal of science education is, all too often, not understanding, but rather a sort of recipe book acquaintance with a number of mathematical techniques which tend often to be used on an ad-hoc basis without any proper understanding either of the mathematical theory and assumptions on which the techniques are based, or of the subject matter to which they are applied". Several of the tasks that follow certainly involve mathematical technique but the tools in Box 1 have embedded in them the rich history behind *dissociation*, α, and *association* or *hydration*, n_b and n_s. Placing the tools in their historical context reduces the chance that the mathematical techniques will just become a mindless manipulation of symbols. In addition, tasks 4, 5, and 6 demand of the student the capacity to interpret their calculated values in a broader thermodynamic context and also according to the original historical arguments of the *ionist* and the *hydrationist*. So the tasks that follow combine the development of mathematical skill with the development of a deepening appreciation of the chemical significance of the results.

TASK 1: Use the Heyrovska equations (in Box 1 here) and the published osmotic coefficient data, φ, to set up formulae in an EXCEL spreadsheet to determine n_b and α for the alkali metal chlorides at 25^0C.
Note: An example of the technique is given in de Berg (2011, p. 18) for NaCl following the processes described by Heyrovska (1996, 1997, 2006, 2011). The instructor may wish to break up this task into a number of smaller steps if deemed to be more manageable. The steps can be summarised as follows.

<u>Step 1:</u> Calculate the activity of water, a_A, using equation (1) in Box 1 from the published φ data.

<u>Step 2:</u> Calculate R_{Af} from a_A using equation (2) in Box 1.

<u>Step 3:</u> It follows from equations (2), (3), and (4) in Box 1 that $(55.51\text{-}mn_s)/R_{Af}$ should

equal (55.51 – mn_b), the equation of straight line. So (55.51-mn_s)/R_{Af} is plotted against m and the value of n_s changed until a straight line with the highest correlation coefficient is obtained. The slope of the line will yield n_b.

Step 4: Use the n_b value determined in Step 3 to calculate i using equation (5) and consequently the value of 'α', the degree of dissociation.

TASK 2: Use the n_b values determined in TASK 1 to determine the mass of bound and free water in 1000 grams of water for 1 molal solutions of the alkali metal chlorides and, using the density of free water at 25^{0}C, determine the volume of free water for each alkali metal chloride solution. Since the number of moles of ions and ion pairs per mole of salt dissolved is given by (1+α), determine the value of V_f , the volume of free water per mole of solute particles dissolved.

TASK 3: Use the Heyrovska equation of state for solutions (Equation 2 here) to determine the osmotic pressure, π_{os}, for each alkali metal chloride solution. Tabulate the values of n_b, α, V_f, and π_{os} for each solution in order from LiCl to CsCl.
Note: At this stage a table of values like that shown in Table 4 should be constructed.

TASK 4: Describe and explain the trend in n_b , α, and V_f from CsCl to LiCl. As a hint, you may wish to consider the size of the alkali metal ion in the hydrated and dehydrated form and the impact this might have on the magnitude of the electric field around the ion.

TASK 5: (a) Consider the enthalpy change for the process, $M^+(g) \rightarrow M^+(aq)$. Would you expect the process to be accompanied by a positive or negative enthalpy change and how would the magnitude of the change vary from Li^+ to Cs^+ ?
(b) Consider the entropy values, S^0, for $M^+(aq)$ compared to [$S^0(H^+) = 0$]. Would you expect S^0 ($M^+(aq)$) to be positive or negative and how would the magnitude of $S^0(M^+(aq))$ vary from $Li^+(aq)$ to $Cs^+(aq)$?

TASK 6: Study the trend in π_{os} values from CsCl to LiCl. In the late 19th century ionists explained osmotic pressure by focusing on the solute whereas hydrationists explained osmotic pressure by focusing on the solvent.

(a) Hydrationists said that an increase in osmotic pressure was caused by an increase in the number of free water molecules that become bound to the salt. Does your data agree with this proposition? Explicitly illustrate using the data.
(b) Ionists said that an increase in osmotic pressure was caused by enhanced dissociation of the salt in water. Does your data agree with this proposition? Explicitly illustrate using the data.
(c) What do you conclude about the hydrationist and ionist positions on osmotic pressure increase?

Note: There are other ways of constructing the tasks. One could, for example, focus on a particular alkali metal halide over a range of concentrations up to saturation and ask students to demonstrate that, $\pi_{os}V_f = RT$, applies over the range of concentration.

Conclusion

Electrolyte solution chemistry gave birth to physical chemistry and has a rich controversial history which has had a distinct bearing on recent developments in the field and how one might relate to the nature of science. The recent developments have drawn on the strengths of both the ionists' and the hydrationists' arguments and illustrate how important mathematics has proved to be for physical chemistry. The hydrationists' insistence on the importance of the solvent in the solution process has proved correct but their suspicion relating to the incursion of mathematics into chemistry has not proved productive. The challenge for physical chemistry educators is how to link the mathematics more intimately with the chemistry so that a student doesn't think of physical chemistry as just a fancy form of mathematical problem solving. The suggested tasks outlined here are one way in which this might be accomplished.

This paper has shown that rich historical data on solution chemistry is available for constructing a class debate between an aspiring Armstrong's team and a daring Arrhenius' team, or alternatively, the construction of a critical assignment or a sample of Interactive Historical Vignettes. It has also been demonstrated that recent developments in physical chemistry have been drawing upon some of the historical elements of the electrolyte solution debate to construct a more explanatory model of solution behaviour than that relying on empirical coefficients based on a model of complete dissociation for strong electrolytes. At this stage it is not clear as to whether the physical chemistry of electrolytes will be reconfigured along the lines suggested by Heyrovska or whether the empirical coefficient approach of Pitzer using activities, activity coefficients, osmotic coefficients and ionic strength will prevail. It is likely that both approaches will sit side by side for some time with the Heyrovska approach being of great value for physical chemistry education and the Pitzer approach retaining some role for chemistry research associated with complex solution mixtures.

References

Armstrong H.E., (1896), Letters to the Editor, *Nature*, **55**(1413), 78.

Armstrong H.E., (1906), Osmotic Pressure, *Nature*, **74**(1908), 79.

Armstrong H.E., (1909), The Thirst of Salted Water or the Ions Overboard, *Sci. Prog.*, **3**, 643.

Armstrong H.E., (1927), Poor Common Salt, *Nature*, **120**, 478.

Armstrong H.E., (1928), The Nature of Solutions, *Nature*, **121**(3037), 48-51.

Armstrong H.E., (1936), Ionomania in Extremis, *Chem. & Indust.*, **14**, 917.

Arrhenius S., (1887), Uber die Dissociation der in Wasser gelosten Stoffe, *Z. Phys. Chem.*, **i,** 631-648.

Arrhenius S., (1912), Electrolytic Dissociation, *J. Am. Chem. Soc.*, **34**(4), 353-364.

Atkins P., (2008), The Evolution of Physical Chemistry Courses. In M.D. Ellison and T.A. Schoolcraft (eds.), *Advances in Teaching Physical Chemistry*, Washington, DC: American Chemical Society.

Aylward G. and Findlay T., (2008), *SI Chemical Data* (6th ed.), Brisbane: John Wiley & Sons.

Boujaoude, S., Sowwan, S. and Abd-El-Khalick, F., (2005), The Effect of using Drama in Science Teaching on Students' Conceptions of the Nature of Science. In K. Boersma, M. Goedhart, O. De Jong and H. Eijkelhof (eds.), *Research and the Quality of Science Education*, Dordrecht: Springer, 259-267.

Bransford J.D., Brown A.L. and Cocking R.R., (1999), *How people learn*: *Brain, mind, experience and school*, Washington DC: National Academy Press.

Brock W.H., (1973), *Introduction to H.E. Armstrong and the Teaching of Science*, London: Cambridge University Press.

Carson E.M. and Watson J.R., (2002), Undergraduate Students' Understandings of Entropy and Gibbs Free Energy, *Univ. Chem. Educ.*, **6**(1), 4-12.

Clough M., (2005), Learners' Responses to the demands of Conceptual Change: Considerations for effective NOS Instruction, Paper presented at the 8th IHPST Conference, July, University of Leeds, England.

Crawford, E., (1996), *Arrhenius: from Ionic Theory to the Greenhouse Effect,* Canton, MA: Science History Publications.

Croft M., (2010), Towards the development of a Pedagogical History for a key chemical idea: Chemical Bonding, Unpublished MEd(Hons) thesis, Avondale College of Higher Education.

Darvell B.W. and Leung V.W-H., (1991), RIP ionic strength 1921-1991, *Chem. Brit.*, Jan., 29-30.

De Berg K.C., (2003), The Development of the Theory of Electrolytic Dissociation: A Case Study of a Scientific Controversy and the changing Nature of Chemistry, *Sci. & Educ.*, **12**, 397-419.

De Berg K.C., (2006), The Kinetic-Molecular and Thermodynamic Approaches to Osmotic Pressure: A Study of dispute in Physical Chemistry and the implications for Chemistry Education, *Sci. & Educ.*, **15**(5), 495-519.

De Berg K.C., (2011), Raoult's Law: A Reinterpretation for Concentrated Strong 1:1 Electrolyte Solutions, *Aus. J. Ed. Chem*., **71**, 15-18.

Debye P. and Huckel, E., (1923), Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen, *Phys. Z.,* **24**, 185–206.

De Vries H., (1888), Osmotische Versuche mit lebenden Membranen, *Z. Phys. Chem.*, **2**, 415.

De Vries H., (1889), Isotonische Koeffizienten einiger Salze, *Z. Phys. Chem.*, **3**, 130.

Dolby R.G.A., (1976), Debates over the Theory of Solution: A Study of Dissent in Physical Chemistry in the English-Speaking World in the late Nineteenth and early Twentieth Centuries. In R. McCormmach (ed.), *Historical Studies in the Physical Sciences*, Princeton NJ: Princeton University Press, 297-404.

Gratzer W., (1996), *A Bedside Nature*, London: Macmillan.

Hamer W.J. and Wu Y., (1972), Osmotic Coefficients and Mean Activity Coefficients of uni-univalent electrolytes in water at 25°C, *J. Phys. Chem. Ref. Data,* **1**(4), 1047-1099.

Heyrovska R., (1996), Physical Electrochemistry of Strong Electrolytes Based on Partial Dissociation and Hydration, *J. Electrochem. Soc.*, **143**(6), 1789-1793.

Heyrovska R., (1997), Equations for Densities and Dissociation Constant of NaCl(aq) at 25°C from "Zero to Saturation" Based on Partial Dissociation, *J. Electrochem. Soc.,* **144**(7), 2380-2384.

Heyrovska R., (2004), A Concise Equation of State for Aqueous Solutions of Electrolytes Incorporating Thermodynamic Laws and Entropy, *Entropy*, **6**, 128-132.

Heyrovska R., (2006), Ionic Concentrations and Hydration Numbers of "Supporting Electrolytes", *Electroanal.*, **18**(4), 351-361.

Heyrovska R., (2011), Arrhenius' theory of partial dissociation and hydration completely replace existing ideas of activity and complete dissociation of electrolytes in solutions, *Curr. Topics Electrochem*., **16**, 47-56.

Justi, R. and Gilbert, J., (2000), History and Philosophy of Science through Models: Some challenges in the case of 'the atom', *Int. J. Sci. Educ.*, **22**(9), 993-1009.

Klassen, S., (2007), The Application of Historical Narrative in Science Learning: The Atlantic Cable Story, *Sci. & Educ.*, **16**(3-5), 335-352.

Kolstø, S.D. and Mestad, I., (2005), Learning about the Nature of Scientific Knowledge: The Imitating-Science Project. In K. Boersma, M. Goedhart, O. De Jong and H. Eijkelhof (eds.), *Research and the Quality of Science Education*, Dordrecht: Springer, 247-257.

Lewis G.N. and Randall M., (1921), The Activity Coefficient of Strong Electrolytes, *J. Am. Chem. Soc.*, **43**(5), 1112-1154.

Niaz, M. and Rodriguez, M., (2000), Teaching Chemistry as Rhetoric of Conclusions or Heuristic Principles-A History and Philosophy of Science Perspective, *Chem. Educ. Res. Pract.* **1**(3), 315-322.

Osborne, J., (2005), The Role of Argument in Science Education. In K. Boersma, M. Goedhart, O. De Jong and H. Eijkelhof (eds.), *Research and the Quality of Science Education*, Dordrecht: Springer, 367-380.

Osborne J., Simon S., Christodoulou, A., Howell-Richardson, C. and Richardson, K., (2013), Learning to argue: A study of four schools and their attempt to develop the use of argumentation as a common instructional practice and its impact on students, *J. Res. Sci. Teach.*, **50**(3), 315-347.

Ostwald W.F., (1888), Stochiometrie und Verwandtschaftslehre., *Z. Phys. Chem.*, **2**, 36-37.

Pickering S., (1897), Letters to the Editor, *Nature*, **55**(1419), 223.

Pitzer K.S., (1995), *Thermodynamics* (3rd ed.), New York: McGraw Hill.

Robinson R.A. and Stokes R.H., (2002), *Electrolyte Solutions* (2nd rev. ed.), Mineola, New York: Dover Publications.

Schwartz R. and Lederman N., (2008), What Scientists Say: Scientists' views of nature of science and relation to science context, *Int. J. Sci. Educ.*, **30**(6), 727-771.

Stenhouse, D., (1985), *Active Philosophy in Education and Science*, London: Allen & Unwin.

Taber K.S., (1993), Student conceptions of chemical bonding: Using interviews to follow the development of A-level students' thinking, Paper presented at the Facets of Education-Dimensions of Research conference, University of Surrey.

Tilden W.A., (1918), *Sir William Ramsay: Memorials of his Life and Work*, London: Macmillan & Co.

Van't Hoff J.H., (1887), Die Rolle des Osmotischen Druckes in der Analogie zwischen Losungen und gasen. In H.C. Jones (ed.), (1899), *The Modern Theory of Solutions*, New York: Harper & Bros., 11-43.

Wandersee, J. and Baudoin-Griffard, P., (2002), The History of Chemistry: Potential and Actual Contributions to Chemical Education. In J.K. Gilbert, O. De Jong, R. Justi, D.F. Treagust and J.H. Driel (eds.), *Chemical Education: Towards Research-Based Practice*, Dordrecht: Kluwer.

Whetham W.C.D., (1897), The Theory of Dissociation into Ions, *Nature*, **55**(1435), 606-607.