

*The Arrhenius Story:
More than a Legend from the Past*

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ABSTRACT: Svante Arrhenius (1859-1927) was known for his love of speculation, theory, discussion, and controversy. Famous for the electrolytic dissociation theory, his career had a number of ironic twists to it. His research dissertation on the electrical conductivity of aqueous organic acids and inorganic salts received such a cool reception by the examiners that a future research and teaching career at university level was considered to be out of the question. Yet he ultimately became a central figure in the development of physical chemistry research. Arrhenius always considered himself to be a physicist but it was the area of chemistry which yielded him the Nobel Prize in 1903. His belief that all electrolytes are completely dissociated only at infinite dilution was accepted in the case of the organic acids, the so-called weak electrolytes, but rejected in the case of the inorganic salts, the so-called strong electrolytes which were considered to be completely dissociated even at finite dilutions. In this case the assumption of complete dissociation led to the development of correction factors for strong electrolytes to account for non-ideal behavior. However, recent developments in 1:1 strong electrolyte chemistry suggest that Arrhenius' original idea of partial dissociation at all concentrations other than infinite dilution is a better explanation of the behavior of 1:1 strong electrolytes than that assuming complete dissociation. This paper attempts to explore this irony and colorful history in a way that is instructive for tertiary level chemistry students in both the content and processes of scientific investigation.

KEYWORDS: Arrhenius, chemistry.

Introduction

Svante August Arrhenius (1859-1927) was born just outside the city of Uppsala in Sweden and is credited with the theory that acids, bases, and salts spontaneously dissociate into positive and negative

ions when present in aqueous solution, such dissociation increasing with the extent of dilution. As elaborated in a previous paper (de Berg 2003), this view led to one of the most significant scientific controversies in the history of chemistry. Elsewhere (de Berg 2004; 2006) it has been shown how such a controversy has the potential to enhance students' understanding of chemical epistemology and some aspects of the nature of science. This is purported to be one of the advantages of the 'story' approach, or 'narrative' approach, or 'contextual' approach to the teaching and learning of science over and against the traditional 'catalogue of facts' approach (Metz et al 2007). 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 affective 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). One of his major antagonists, Henry Armstrong (1848-1937), was described by Gratzner (1996, p.123) as a "hot-air balloon who hovered over the scientific scene in England for about seventy years". With two such individuals in alternative corners of the controversy one can imagine how vigorous the debate was at times.

What is interesting is that the controversy over the nature of solutions did not cease with the death of Arrhenius or Armstrong. The key elements of a story described by Scholes (1981) and elaborated by Milne (1998) as *events*, *text*, and *interpretation* are still thus in a state of flux as far as the Arrhenius story is concerned. The *events* are still unfolding, the *text* is still being written, and the *interpretation* is still being fine-tuned. When students are granted access to this controversy they experience science in action. This paper is primarily concerned with the Arrhenius story as it has unfolded from the beginning of the 20th century to the present, particularly in relation to the chemistry of strong 1:1 electrolytes. Suggestions are made as to how this unfolding story, not yet a part of the modern physical chemistry textbook, can become a part of the curriculum of the tertiary-level chemistry student.

The Early Controversy in Review

It is important to remember that very little was known about atomic and molecular structure in the 1880's. The electron had not been discovered; the small dense positively charged nucleus had not been identified; and the neutron would not be discovered for another 50

years. In fact there were some chemists such as Wilhelm Ostwald who considered the concepts of atom and molecule as no more than convenient models to help explain certain chemical facts. However, important discoveries in electricity such as Faraday's laws of electrolysis had been made and it is not surprising that Arrhenius chose a topic related to the electrical conductivity of solutions for his dissertation. Arrhenius always considered himself to be primarily a physicist, not a chemist, but the problem for Arrhenius was that the physics professor, Robert Thalen, considered his topic to lie outside the domain of physics. Likewise, Cleve, the chemistry professor, considered the topic outside the domain of chemistry and it is thus not surprising that a subdiscipline of physics and chemistry, physical chemistry, was soon to emerge. The irony, of course, is that it was in the field of chemistry, not physics, that Arrhenius was recognized in 1903 with the Nobel Prize after having defended a dissertation in 1884 which was considered by his examiners as not worthy of an academic posting in either physics or chemistry.. This ironic situation has made the Arrhenius story "particularly prone to a kind of distorting mythmaking" according to Crawford (1996, p.21). There appears to have been a genuine and substantive criticism of Arrhenius' experimental procedure by an examiner appointed by Arrhenius himself but this is not to discount the progress made from 1884 to 1887 in outlining what was to become the theory of electrolytic dissociation. The personal setback in 1884 remained a sensitive issue for Arrhenius for the rest of his life as noted by Crawford (1996, p.43) in these words: "Two years before his death he could still accuse Cleve and Thalen of having decided to sacrifice him because they considered theories and hypotheses worthless, inventorying was the only work worth doing".

In 1884 Arrhenius had called the dissociated part of a salt in water the *active* part and the undissociated molecules the *inactive* part. By 1887 (Arrhenius 1887) the *active* part was called positive and negative ions which formed spontaneously when a salt was dissolved in water. What concerned chemists of the time was the cause of such a process. What would make a tightly bound molecule suddenly disintegrate into positive and negative parts at the sight of a few water molecules? And why would not the positive and negative parts attract each other with powerful forces to produce the neutral molecule again? As far as electrical conductivity experiments were concerned it was thought that the disintegration and production of ions might be caused by the external electrical field. But when van't Hoff's osmotic pressure results and Raoult's vapour pressure lowering

results, results not dependent on the application of an external electric field, could also be interpreted in terms of spontaneous dissociation into ions this lent great support to Arrhenius' idea. The puzzle relating to the origin of the charges on the dissociated parts was clarified when X-ray diffraction studies of salts was published in the early 20th century. The X-ray photographs were best interpreted in terms of charged ions already existing in the solid lattice and so water molecules were simply responsible for separating the already existent ions, not charging them as some were accusing the Ionists (Arrhenius, van't Hoff, Ostwald) of suggesting.

While Arrhenius was proposing simple spontaneous dissociation into ions, the extent of dissociation depending on dilution with water, Armstrong (1896, 1928) was insisting that water must be playing a greater part in the dissolving process than just encouraging ion separation. The existence of hydrates was evidence, according to Armstrong, that dissolution was a phenomenon involving an *association* of the salt with water rather than a *dissociation* of the salt in water. How the dissociation model finally predominated has been elaborated elsewhere (de Berg 2003). But was there a need to reject Armstrong's ideas completely?

The Later Controversy in Progress

The fact that Arrhenius' work is not a relic of the past has been supported by Crawford's (1996, p.xii) observation that between 20 and 30 citations appeared each year in the Science Citation Index (1980-1992) and more recently the research activities of Raji Heyrovská (2006) have highlighted the importance of Arrhenius' work. What has produced such consistent interest in his work?

When Arrhenius left Sweden for Germany some time after his great disappointment in 1884 he found the laboratories of Wilhelm Ostwald (1853-1932) a welcome reprieve from what he considered to be the indifference of his homeland. Ostwald was an avid experimenter who was greatly interested in Arrhenius' work. He showed that dissociation of organic acids obeyed Guldberg and Waag's law [$K = \alpha^2 m / (1 - \alpha)$] for different concentrations of the acid. In this equation, K is the equilibrium constant and α is the fraction of acid dissociated taken as the ratio of the molar conductivity at molality m divided by the molar conductivity at infinite dilution (Λ / Λ_0). However, when it came to salts like the alkali halides the ratio, $\alpha^2 m / (1 - \alpha)$, was not constant for different values of m . This is illustrated in Table 1 for acetic acid (CH₃COOH) and sodium chloride (NaCl). Consequently salts like sodium chloride came to be regarded

Substance	$c/\text{mol L}^{-1}$	$\Lambda/\text{mS m}^2 \text{mol}^{-1}$	$\Lambda_o/\text{mS m}^2 \text{mol}^{-1}$	$\alpha = (\Lambda/\Lambda_o)$	$\alpha^2 c/(1-\alpha)$
CH ₃ COOH	0.1	0.52	39.1	0.0133	1.79×10^{-5}
CH ₃ COOH	0.01	1.6	39.1	0.0409	1.75×10^{-5}
CH ₃ COOH	0.001	4.8	39.1	0.1228	1.72×10^{-5}
NaCl	0.1	10.67	12.65	0.8435	0.4545
NaCl	0.01	11.85	12.65	0.9368	0.1388
NaCl	0.001	12.37	12.65	0.9779	0.0432

Table 1: Molar conductivities and values for, $\alpha^2 c/(1-\alpha)$, for CH₃COOH and NaCl over a range of concentrations.

as completely dissociated (strong electrolytes), since (Λ/Λ_o) values were close to 1 and the idea of K appeared to be meaningless, while organic acids like acetic acid for which the Ostwald dilution law held were classified as weak electrolytes (partially dissociated) since (Λ/Λ_o) values were much less than 1. Thus Arrhenius' idea of partial dissociation was applied only to weak electrolytes. We will now confine our discussion to the case of strong electrolytes and to the property of electrical conductivity as this was the property most closely associated with Arrhenius' work.

As far as we know Kohlrausch was the first to observe the linear relationship of the molar conductivity of NaCl (Λ_m) as a function of the square root of the concentration. This was an empirical relationship and applied only to dilute solutions. Figure 1 shows the data for NaCl up to a concentration of 0.01 M. Beyond this concentration there is a significant departure from a linear relationship as shown in Figure 2.

Chemists now attempted to explain the linear relationship for dilute solutions in terms of the molecular properties of the solution and also attempted what proved to be a most difficult task; a molecular explanation for the behavior over the whole concentration range. In the early 1920's Debye, Huckel, and Onsager (D-H-O) were able to reproduce the Kohlrausch empirical law by considering the concept of an ionic atmosphere around the positive and negative ions and the impact this had on the mobility of the ions. This approach depended very much on the basic ideas of *activity* and *ionic strength* introduced by Lewis and Randall in 1921. The Debye-Huckel-Onsager equation is shown by Bockris and Reddy (1998, pp.518-519) to fit the general form:

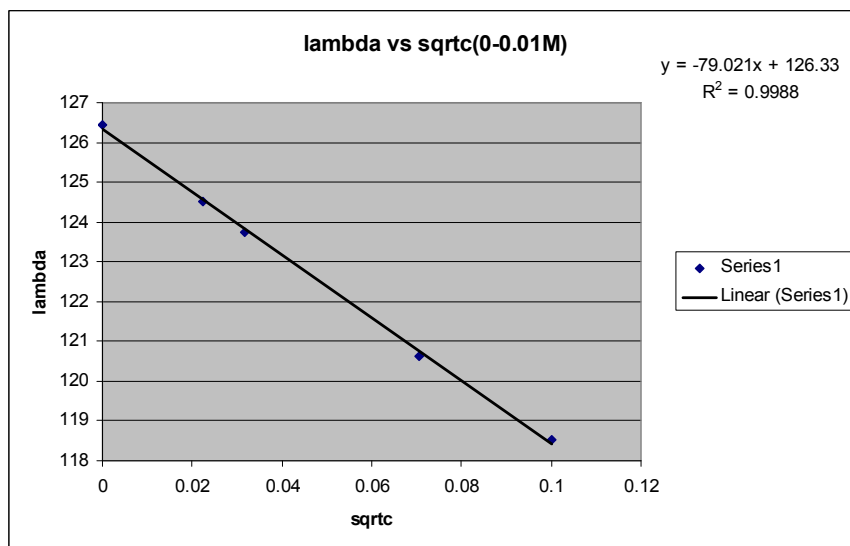


Figure 1: The plot of molar conductivity (λ -S cm² mol⁻¹) against the square root of the concentration of NaCl up to 0.01 M.

$$\Lambda = \Lambda_o - (A + B \Lambda_o) c^{1/2} \quad (\text{A})$$

where, $A = 60.20$ and $B = 0.229$ for aqueous NaCl solutions for which the molar conductivity values are expressed in the units, S cm² mol⁻¹ and c is expressed in the units, mol L⁻¹. It can be seen in Figure 3 that the D-H-O equation matches the experimental data reasonably well for very dilute solutions but departs markedly from the experimental values at higher concentrations.

From the early 1920's it became increasingly difficult to explain the chemistry of strong electrolytes up to saturation without introducing empirical correction factors. Debye, Huckel, and Onsager, for example, attempted to extend their law to higher concentrations by introducing a correction factor for activity coefficients and using an additional correction term in the expression for molar conductivity. Their extended law can be written in the form:

$$\Lambda = \Lambda_o - \left(\frac{A\Lambda_o + B_2}{1 + B_1 a c^{1/2}} \right) c^{1/2} + \frac{AB_2 c}{(1 + B_1 a c^{1/2})^2} \quad (\text{B})$$

where, for NaCl aqueous solutions, $A = 0.2300$, $B_1 = 3.291 \times 10^9$, a (the distance of closest approach of the ions) = 4×10^{-8} cm, $B_2 = 60.65$ for conductivity values expressed in the units S cm² mol⁻¹ (Robinson and

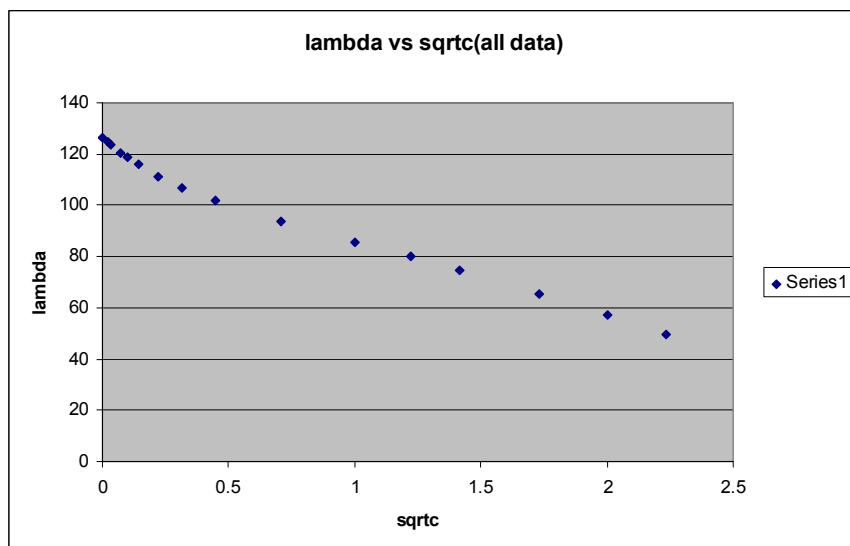


Figure 2: The plot of molar conductivity (λ -S cm² mol⁻¹) against the square root of the concentration of NaCl up to 5 M.

Stokes 2002, p. 468). It can be seen in Figure 4 that this gives an improved match to the experimental values but still not an adequate match at higher concentrations.

Further improvements have been attempted but as Bockris and Reddy (1998, p.523) observe, "These empirical modifications of the Debye-Huckel-Onsager theory of electrolytes do not yet give much physical insight into what changes in the elderly (but still famous) theory might improve the theory of ionic conductance". The use of equations with a large number of empirical correction factors has been of concern to a number of chemists because correction factors often lack chemical or molecular significance. Heyrovská (1998, 1996, 1997, 2006) has shown how the published data for 1:1 strong electrolytes is better interpreted in terms of Arrhenius' original idea of partial dissociation and the use of hydration numbers rather than on a theory that depends on concepts like ionic strength and activity coefficients. The idea of hydration of course ironically contains some of the ideas of Henry Armstrong. How Heyrovská's idea might work for the case of sodium chloride is now discussed.

The attempt to give a more chemical or molecular interpretation to the relationship between electrical conductivity and concentration

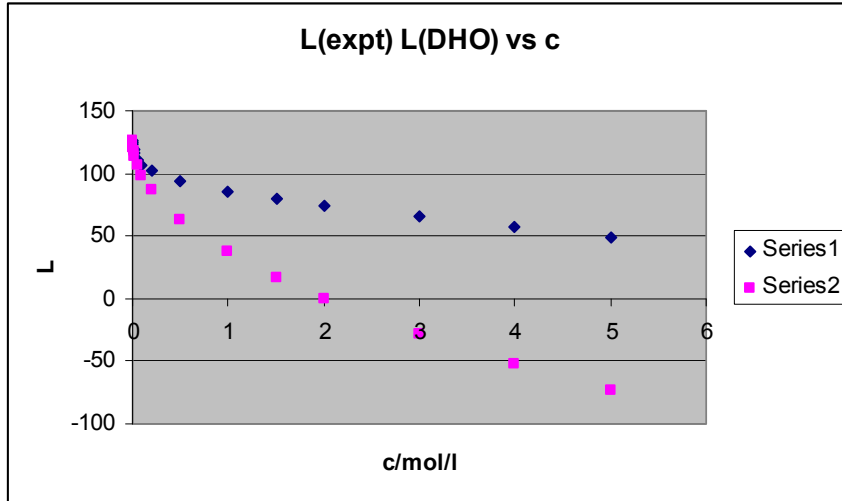


Figure 3: Molar conductivity, L , ($\text{S cm}^2 \text{ mol}^{-1}$) of NaCl solutions against concentration. A comparison of experimental (Series 1) and D-H-O values (Series 2).

revolves around distinguishing free water molecules from bound water molecules or molecules of hydration in the bulk of solution and at the surface (Heyrovská, 2006). The relevant equations involving free and bound water molecules are as follows.

$$\alpha_A = N_{Afs} = n_{Afs} / (n_{Afs} + im) = \exp(-2m\varphi/55.51) \quad (1)$$

$$-\alpha_A \ln \alpha_A / (1 - \alpha_A) = n_{Afs} / n_{Afb} = R_{Af} \quad (2)$$

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

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

$$\Pi_{os} = iRT(55.51m / n_{Afb})d_{Afb} = 2RTm\varphi d_{Afb} \quad (5)$$

where

α_A = activity of water

N_{Afs} = mole fraction of free water molecules at the surface

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

$i = (1 + a)$ where a is the degree of dissociation

= number of NaCl ion pairs, Na^+ and Cl^- ions, per molal of NaCl dissolved

d_{Afb} = density of free water in the bulk

Π_{os} = osmotic pressure

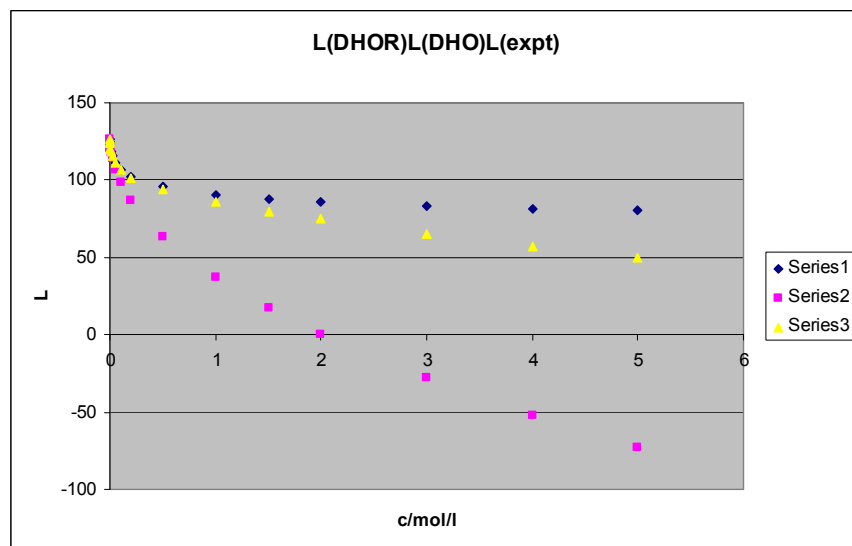


Figure 4: Molar conductivities, L , ($\text{S cm}^2 \text{ mol}^{-1}$) against c for NaCl solutions. Series 3 are experimental values, Series 2 are D-H-O values (equation (A)), and Series 1 are extended D-H-O values (equation (B)).

Robinson and Stokes (2002, p.476) provide tables of water activities for molalities of NaCl up to saturation and these are reproduced in Table 2. This data can be used with the equations above to determine the hydration numbers on the surface (n_s) and in the bulk (n_b); the degree of dissociation (α); and the osmotic pressure of the solutions (π_{os}).

(i) *Determination of n_s and n_b (hydration numbers)*

The water activities in Table 2 can be used to determine the osmotic coefficients for each solution using equation (1) above. These are shown in Table 2 along with the water activities. Rearranging the five equations above, the following equation can be derived which enables a determination of n_s and n_b .

$$[55.51/m - 2\phi\alpha_A/(1-\alpha_A)] = n_s - [2m\phi\alpha_A/55.51(1-\alpha_A)]n_b$$

A plot of $[55.51/m - 2\phi\alpha_A/(1-\alpha_A)]$ against $[2m\phi\alpha_A/55.51(1-\alpha_A)]$ should give a straight line of slope $-n_b$ and intercept n_s . The plot is shown in Figure 5 for the NaCl data. One can see that the plot is linear except for values of α_A approaching one when the plotted fraction becomes undefined. The intercept, n_s , obtained from the

m	a_A	$\phi(\varphi)$	i	$\alpha(\alpha)$
0.1	0.996646	0.9324	1.85643	0.85643
0.2	0.99336	0.9245	1.832402	0.832402
0.3	0.99009	0.9215	1.818184	0.818184
0.4	0.98682	0.9203	1.807555	0.807555
0.5	0.98355	0.9209	1.800467	0.800467
0.6	0.98025	0.923	1.796287	0.796287
0.7	0.97692	0.9257	1.793231	0.793231
0.8	0.97359	0.9288	1.790899	0.790899
0.9	0.97023	0.932	1.788703	0.788703
1	0.96686	0.9355	1.787022	0.787022
1.2	0.9601	0.9428	1.784041	0.784041
1.4	0.9532	0.9513	1.783046	0.783046
1.6	0.9461	0.9616	1.785087	0.785087
1.8	0.9389	0.9723	1.787494	0.787494
2	0.9316	0.9833	1.790063	0.790063
2.2	0.9242	0.9948	1.793138	0.793138
2.4	0.9166	1.0068	1.796693	0.796693
2.6	0.9089	1.0192	1.800523	0.800523
2.8	0.9011	1.0321	1.804782	0.804782
3	0.8932	1.0453	1.809098	0.809098
3.2	0.8851	1.0587	1.813282	0.813282
3.4	0.8769	1.0725	1.817662	0.817662
3.6	0.8686	1.0867	1.822218	0.822218
3.8	0.86	1.1013	1.826928	0.826928
4	0.8515	1.1158	1.830949	0.830949
4.2	0.8428	1.1306	1.834937	0.834937
4.4	0.8339	1.1456	1.838714	0.838714
4.6	0.825	1.1608	1.84227	0.84227
4.8	0.816	1.1761	1.845437	0.845437
5	0.8068	1.1916	1.848365	0.848365
5.2	0.7976	1.2072	1.850889	0.850889
5.4	0.7883	1.2229	1.853005	0.853005
5.6	0.7788	1.2389	1.855007	0.855007
5.8	0.7693	1.2548	1.856286	0.856286
6	0.7598	1.2706	1.856848	0.856848

Table 2. Water activities (a_A), osmotic coefficients (ϕ), i and α , for NaCl aqueous solutions of different molalities, m .(Robinson & Stokes 2002, p.476)

linear portion of the graph in Figure 5, can be used to find a refined value of n_b using equations 2, 3, and 4 which yield,

$$(55.51 - mn_s)/R_{Af} = 55.51 - mn_b$$

Therefore a plot of $(55.51 - mn_s)/R_{Af}$ against m should give a line of slope $-n_b$. The results are excellent and shown in Figure 6. Values

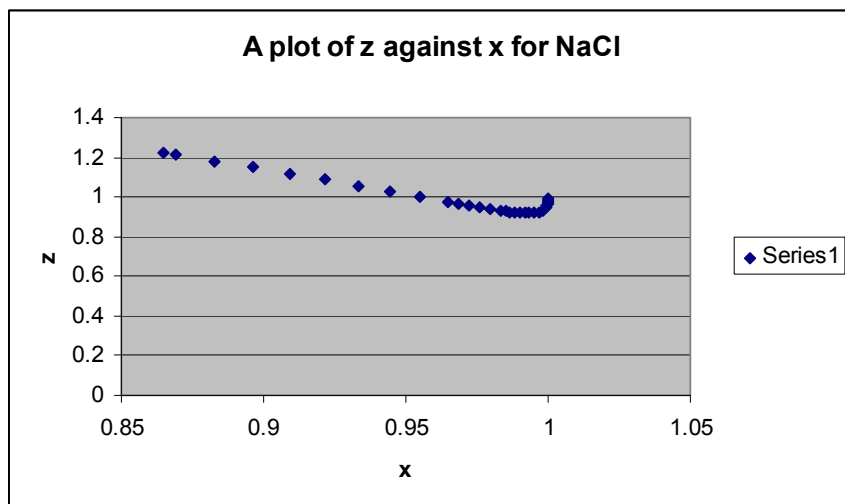


Figure 5: The plot of z ($=[55.51/m - 2\phi aA/(1-aA)]$) against x ($=[2m\phi aA/55.51(1-aA)]$) for NaCl solutions.

of n_b and n_s for NaCl of 2.49 and 3.38 respectively, using EXCEL, are in good agreement with those listed by Heyrovska (2006), 2.47 and 3.36 respectively.

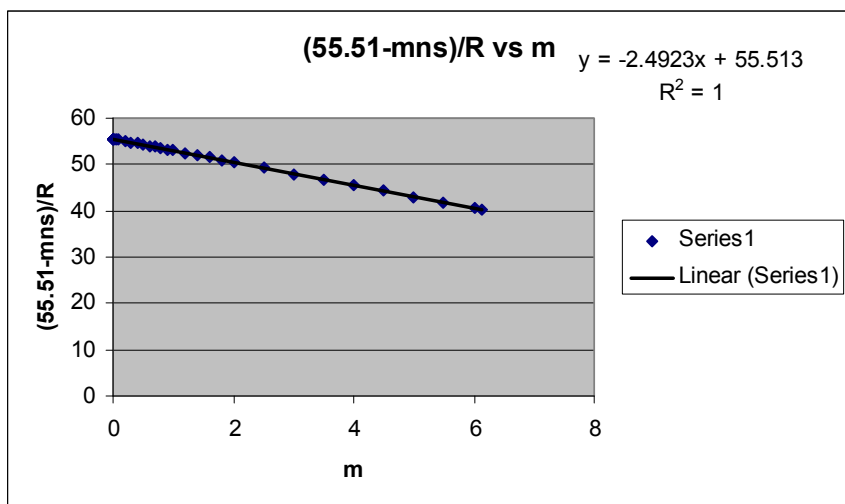


Figure 6: The plot of $(55.51 - mns)/RAf$ against m (mol kg⁻¹) for NaCl solutions.

m	phi(ϕ)	pi(π)(atm)	i	alpha(α)	lambda(Λ)
0	1	0	2	1	126.45
0.000495	0.993	0.023931	1.985956	0.985956	124.51
0.000989	0.99	0.047717	1.979912	0.979912	123.74
0.004947	0.978	0.235741	1.955566	0.955566	120.64
0.009895	0.969	0.467191	1.937139	0.937139	118.53
0.0198	0.9592	0.9254	1.916695	0.916695	115.76
0.0495	0.944	2.27684	1.883805	0.883805	111.06
0.0992	0.9324	4.50681	1.856497	0.856497	106.74
0.1989	0.9245	8.959772	1.832493	0.832493	101.71
0.5011	0.9209	22.48496	1.800376	0.800376	93.62
1.015	0.9382	46.39987	1.790917	0.790917	85.76
1.5419	0.9586	72.0193	1.784518	0.784518	79.86
2.0816	0.9859	99.99664	1.787574	0.787574	74.71
3.1998	1.058	164.9543	1.812102	0.812102	65.57
4.3696	1.145	243.7825	1.840875	0.840875	57.23
5.591	1.2389	337.5056	1.856008	0.856008	49.46

Table 3: Osmotic pressures and molar conductivities ($\text{S cm}^2\text{mol}^{-1}$) for NaCl solutions.

(ii) Determination of α (degree of dissociation)

Once n_s and n_b have been determined, the coefficient 'i' can be calculated using equations 1 and 3. This automatically leads to the degree of dissociation, α , through, $i = (1+\alpha)$. These values are shown in Table 2. The significance of this formula can be seen in Figure 7, based on partial dissociation of NaCl.

(iii) Determination of π_{os} (osmotic pressure) and Λ (molar conductivity)

Using values of i , and taking the density of free water in the bulk as 0.997 g cm^{-3} , osmotic pressures (π_{os})(in atmospheres) can be calculated using equations 4 and 5. Molar conductivity values are given in Robinson and Stokes (2002, p.466). The molar conductivity at infinite dilution, Λ_0 , is given by Robinson and Stokes (2002, p.466) as $126.45 \text{ S cm}^2 \text{ mol}^{-1}$. Osmotic pressures and molar conductivities appear in Table 3. If $(\Lambda_0 - \Lambda)/\pi_{os}$ is plotted against $(1-\alpha)/\pi_{os}$, a straight line is obtained as shown in Figure 8. The equation for the line is:

$$(\Lambda_0 - \Lambda)/\pi_{os} = 131.71(1-\alpha)/\pi_{os} + 0.2369$$

	$\text{NaCl} \leftrightarrow \text{Na}^+ + \text{Cl}^-$		
I_c	m	0	0
Δ_c	αm	αm	αm
E_c	$m(1-\alpha)$	αm	αm
Total particle number	$= m(1-\alpha) + 2 \alpha m$ $= m(1+\alpha)$ $= im \text{ where } i = (1+\alpha)$		

Figure 7: An equilibrium diagram showing the dissociation of αm moles of NaCl starting with an initial molality m , (I_c) of NaCl leading to equilibrium concentrations (E_c) and the total particle number im .

This converts to: $(\Lambda_0 - \Lambda) = 131.71(1-\alpha) + 0.2369 \Pi_{os}$; which is of the general form found by Heyrovská (2006);

$$(\Lambda_0 - \Lambda) = \lambda_{+} (1-\alpha) + K \Pi_{os} \quad (\text{C})$$

found valid for all concentrations up to about 3 molal.

Equation (C) is very instructive in that it identifies two molecular properties responsible for the deviation of the molar conductivity from its value at infinite dilution. The term, $\lambda_{+} (1-\alpha)$, is due to the formation of ion pairs (see Figure 7) and the term, $K \Pi_{os}$, is due to, what Heyrovská (2006) calls, the molecular or ionic crowding effect.

Karel Mysels (1978, 1997) explains osmotic pressure in terms of the kinetic-molecular principle of solvent tension. The thermal motion of the solute molecules exerts a distending pressure on the confining solvent molecules putting the solvent molecules under tension somewhat like putting a spring under tension. Barton (1971) shows that the dominant forces operating under solvent tension are intermolecular attractive ones leading to an increase in what he calls the internal pressure. This pressure is different to that due to thermal motion. Further discussion of the kinetic-molecular approach to osmosis is given elsewhere (de Berg 2006). What is clear is that as the internal pressure of the solvent increases, the mobility of the solute's ions is decreased leading to a reduction in molar conductivity. Equation (C), using the principles of partial dissociation and hydration, undoubtedly provides a clearer explanation of how molar conductivity changes with concentration than does equation (A) or

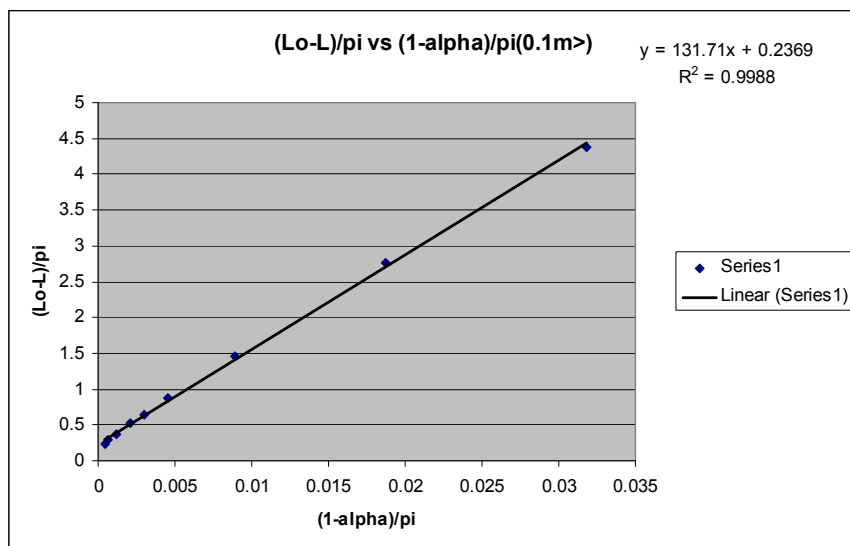


Figure 8: The plot of $(\Lambda_0 - \Lambda)/\pi_{os}$ against $(1-\alpha)/\pi_{os}$ for NaCl solutions up to 5.591 molal.

equation **(B)** which relies on correction coefficients. This is confirmed in Table 4 where Λ values predicted from equations **(A)**, **(B)**, and **(C)** are compared to the experimental values up to about 3 molal.

According to Heyrovská (2006) the analysis given here for NaCl has been shown to hold for over 100 1:1 so called strong electrolytes. This is one of the most promising analyses of solution chemistry given in the last 20 years. It has been controversial, at least in the early stages of its development (see Darvell & Leung 1991, Franks 1991, Wright 1991, Heyrovská 1991) but it is difficult not to concur with the more powerful molecular explanations given for strong electrolyte chemistry. To what extent 2:2 electrolytes (and 2:1 and 1:2) can be similarly analyzed awaits further research.

Nature of Science Issues

The story of electrolyte solution chemistry demonstrates how complex the weave of knowledge generation is in science. Our current best model of 1:1 strong electrolytes combines the partial dissociation model of Arrhenius with the hydration model of Armstrong. It would appear, then, that both the Ionists and the Hydrationists, bitter enemies of the late 19th and early 20th centuries, have both made

their contribution to our knowledge of solutions. Arrhenius was accused by the Hydrationists of ignoring the contribution of water to the solution process and the Hydrationists were accused by the Ionists of ignoring the simplicity and explanatory power of the dissociation model. In the early stages of solution theory when Lowry proposed a compromise position, a position which allowed for both dissociation and hydration in the solution process, he was strongly remanded by Armstrong (1928, p.51) for diluting the hydrationist cause. It is ironic that it would appear that just such a compromise position has led to an enhanced understanding in our day of 1:1 electrolytes.

But can such a circuitous path of knowledge generation as outlined in this paper be generalizable across all scientific concepts? No one with a reasonable knowledge of the history of science would hardly venture such a proposition. This is why it is difficult, despite some very valiant efforts, to arrive at definitions for what constitutes science that are widely applicable, but specific enough to make sense. It is almost as if each concept in science has its own developmental story which needs telling at some length to understand what might be called "the nature of science".

The ironic nature of the Arrhenius story continues when one considers the role of empirical equations in chemistry. Crawford (1996, p.6) recounts James Walker's (a colleague of Arrhenius) description of how Arrhenius "might begin a new line of work by the consideration of tables of numerical data.....He would frame a formula to fit them-an exercise at which he was uncannily expert-and then evolve a physical hypothesis to account for the formula. Or he might start with a bold speculation as to how two entities were related, formulate this relation, and check the formula by means of data of observation or experiment. There was a constant interplay between the speculative and the quantitative sides of his mind". When van't Hoff interpreted osmotic pressure data in 1887 in terms of the dissociation model of Arrhenius and introduced an empirical coefficient, i , in the relationship, $\pi V = iRT$, to enhance the correlation between theory and experiment, he was accused by the Hydrationists of playing with numbers for his own purpose rather carelessly and inappropriately. 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". What is ironic about this situation now is that the use of elaborate empirical equations for strong electrolytes has been criticized by those espousing a return to the simple partial dissociation model of Arrhenius. In any event it would seem that the development of empirical equations has been an important stepping-stone in the development of useful theories in science, although there is probably a case for some caution when it comes to a dependence on elaborate empirical equations that will potentially always lack *physical* insight. Cushing (1991, pp.337-338) has suggested that scientific theories function at three levels: *empirical adequacy* which often involves the development of an algorithm or formula which can reproduce the observed data; *explanation* which might involve a formal derivation of the empirical equation; and *understanding* which might involve a physical interpretation of the formalism used in the explanation. All three of these levels function in the Arrhenius story.

The relationship between experiment and theory is an important one in science. Arrhenius' theory of electrolytic dissociation has been and continues to be an important factor in explaining solution properties such as electrical conductivity and osmotic pressure. Is there any direct experimental evidence, however, for the existence of ion pairs in a sodium chloride solution? In 1992 Ohtaki and Fukushima (1992) published the results of an X-ray diffraction study of a saturated aqueous sodium chloride solution and reported that about 30% of the ions formed ion-pairs at saturation. The Na⁺-Cl⁻ distance was calculated to be 282 pm which is almost identical to the sum of the crystal radii (283 pm). This finding has lent great support to the idea of partial dissociation in strong electrolytes. Thus the Arrhenius story illustrates the delicate interplay that exists between experiment and theory. The theoretical speculations of Arrhenius drew heavily upon the experimental data of Kohlrausch and the X-Ray diffraction work on electrolytic solutions drew upon the speculation of the existence of ion pairs in electrolyte solutions prominent since the time of Bjerrum (Bockris & Reddy 1998, pp.304-314).

Teaching / Learning Issues

The analysis of the Arrhenius story given in this paper illustrates how idiosyncratic it is and thus how difficult it is to form a generalized picture of science across the concepts of a discipline and, in fact, across disciplines of science. In a study of twenty-four practicing research scientists Schwartz and Lederman (2008, p.762)

c/mol/l	mol/kg	Λ (expt)	Λ (A)	Λ (B)	Λ (C)
0	0	126.45	126.45	126.45	126.45
0.0005	0.000495	124.51	124.4563	124.5075	124.5946
0.001	0.000989	123.74	123.6305	123.7386	123.7929
0.005	0.004947	120.64	120.1454	120.7036	120.5417
0.01	0.009895	118.53	117.534	118.6294	118.0599
0.02	0.0198	115.76	113.8409	115.9498	115.2587
0.05	0.0495	111.06	106.5132	111.3644	110.6066
0.1	0.0992	106.74	98.25513	107.1097	106.4816
0.2	0.1989	101.71	86.57644	102.2959	102.2651
0.5	0.5011	93.62	63.40436	95.45882	94.83078
1	1.015	85.76	37.29	90.31141	87.91951
1.5	1.5419	79.86	17.25175	87.44514	81.00744
2	2.0816	74.71	0.358719	85.51128	74.78223
3	3.1998	65.57	-27.9797	82.95563	62.62424

Table 4: A comparison of molar conductivities ($\text{S cm}^2\text{mol}^{-1}$) calculated using the D-H-O equation (A), the extended D-H-O equation (B), and the Heyrovská equation (C) with experimental values from Robinson and Stokes (2002, p.466)

concluded that, “the variations described here provide evidence that these scientists do not all hold to the same view of “the” NOS (nature of science)”. 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 generalized broad picture of NOS any different to that broad generalized 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 lead(s) to the conclusion

that the generalized treatment of NOS across science disciplines is appropriate...” While one can understand the authors’ concern about introducing “all the finer perspectives” into school-based science, might not a small selection of the finer perspectives be more instructive than nebulous generalized perspectives often divorced from science content. As far as tertiary level science education is concerned I think 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 I think 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 generalizing science and, in the process, killing off its substance.

In support of a less ambitious approach to NOS, apart from the problems already mentioned in relation to generalizability, I would nominate how central mathematical skill is to appreciating the NOS and the fact of the reduction in the number of students doing advanced-level mathematics in year 12 and also the reduction in the number of pre-service teachers electing mathematics as a teaching field. Preliminary results of giving first-year chemistry students a written pedagogical history of the theory of ions in solution with questions to complete (de Berg, 2004), the earlier part of the Arrhenius story, demonstrate how difficult students find the concept of proportion, for example. This pedagogical history dealt only with the Arrhenius story up until the acceptance of the partial dissociation hypothesis for weak electrolytes. Translating the Arrhenius story since that time, the subject of this paper for 1:1 strong electrolytes, into a teaching/learning device has not yet been composed as the details of the story have only just been emerging. The question is how best to translate it for the tertiary-level student.

I would suggest that the on-going Arrhenius story for 1:1 strong electrolytes as presented in this paper is most suitable for second or third year chemistry students. The story deals with the unifying central ideas of partial dissociation and hydration and so fits what Klassen (2007, p.319) calls the ‘storyline’ or ‘thematic’ approach. My chemistry students typically are required to do five or six written assignments during the course of a semester and it is planned that one of these assignments will deal with the 1:1 strong electrolyte issue. The thrust of the assignment would be the analysis of the numerical data as detailed in this paper with ‘interrupted’ historical

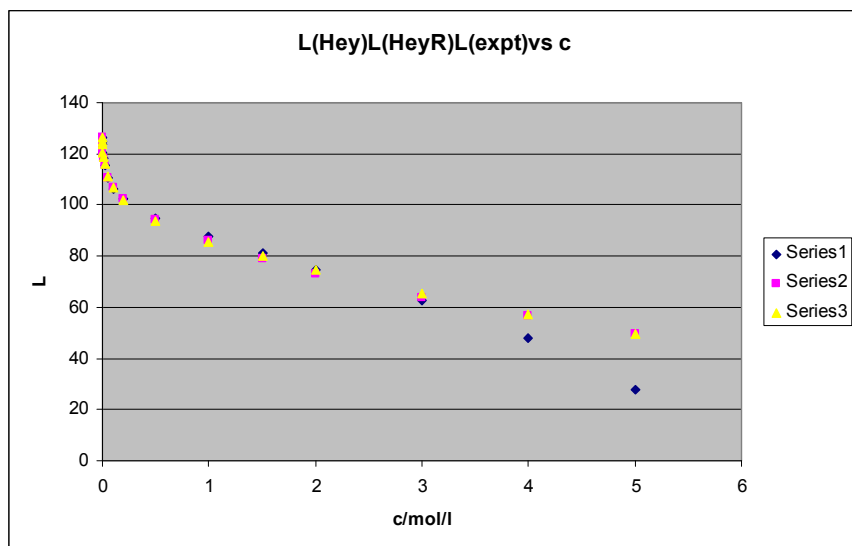


Figure 9: Comparison with experimental values (Series 2) of molar conductivities ($\text{S cm}^2 \text{ mol}^{-1}$) for NaCl calculated from equation (C) (Series 1) and equation (C) using a density correction (Series 3).

segments looking at epistemological issues raised here in the NOS section. The construction of such an assignment is intended to constitute the next phase of the project.

There is an interesting postlude to the Arrhenius story which has great teaching/learning potential in relation to *empirical* law and *physical* insight. The question relates to the relevance of equation (C) at concentrations greater than 3 molal. It can be seen in Figure 9 that the molar conductivity predicted from equation (C) for concentrations of 4 and 5 M (near saturation) is lower than the experimental values, the deviation increasing with concentration. In the calculation of osmotic pressure a value for d_{Afb} (the density of free water in the bulk) was taken to be 0.997 g cm^{-3} for all concentrations. This is the density of water at 25°C . As the concentration of NaCl increases one could expect that the use of this value could introduce an error, which could become more noticeable as the salt concentration increases. Could one introduce a correction factor for the density that would have a more noticeable effect on the data for 4 and 5 M than for the earlier concentrations? And what does this say about the density of free water as the salt concentration increases? If one multiplies the density 0.997 g cm^{-3} by the factor $(1-0.08m)$, the match between

$c/\text{mol/l}$	Λ (expt)	Λ (C)	Λ (C)- density correction
0	126.45	126.45	126.45
0.0005	124.51	124.5946	124.6355
0.001	123.74	123.7929	123.8504
0.005	120.64	120.5417	120.6592
0.01	118.53	118.0599	118.2162
0.02	115.76	115.2587	115.4431
0.05	111.06	110.6066	110.7921
0.1	106.74	106.4816	106.5914
0.2	101.71	102.2651	102.1477
0.5	93.62	94.83078	94.03456
1	85.76	87.91951	86.25454
1.5	79.86	81.00744	79.03821
2	74.71	74.78223	73.13042
3	65.57	62.62424	64.00633
4	57.23	47.73964	56.53521
5	49.46	27.52968	49.75742

Table 5: Comparison of molar conductivities ($\text{S cm}^2 \text{ mol}^{-1}$) for NaCl using equation (C) and a correction term for density in equation (C) with experimental values.

equation (C) and experiment is excellent. This is shown in Table 5 and Figure 9. One is left here with an interesting conundrum. Is one in the process of generating new knowledge by using the factor (1-0.08m) or is one just playing with numbers to force a match between theory and experiment?

Conclusion

The health industry will often, rightly or wrongly, employ scientific terms to enhance the acceptability of its products. Recently I received an advertisement for “The Ionic Bracelet” which could “Re-claim my Life”. Part of the advertisement read: “If you suffer from rheumatism or feel generally unwell and want to improve your vitality, energy and tone, then ionotherapy is undoubtedly the solution you need ... Ionotherapy is a really effective remedy for a great number of illnesses caused by a lack of negative ions in the body. Ions are present in nature, primarily in places benefiting from abundant

vegetation. These ions inevitably disappear in time and are only partially renewed, particularly for those living in city areas. This loss causes problems to our equilibrium with regard to appetite, vitality, sleep, sexual potency and blood circulation". As evidence to support the benefits of ionotherapy (the wearing of the Ionic Bracelet), favorable anecdotal comments from some people who have supposedly tried the bracelet are provided. What would constitute a proper scientific test for the effectiveness or otherwise of wearing such a bracelet and would such a test be of more value to a customer than anecdotal evidence? How reliable is a scientific test in this case anyway and is it reliable just because it is scientific? Is it being too ambitious to think that exposing students to issues in scientific epistemology might help them to answer questions such as these and to understand when caution might be required in ascertaining the worth or otherwise of products said to enhance our health?

Tremendous progress has been made since the mid 1980's in applying Arrhenius' partial dissociation model and the hydration model to the chemistry of 1:1 strong electrolytes. This material has not yet found its way into physical chemistry textbooks but there are important experiences in epistemological issues awaiting the student. These have been outlined in this paper. What is exciting and challenging is that the story has not yet finished. Does the partial dissociation model and hydration model apply to 2:2, 1:2, 2:1 strong electrolytes? A small number of 1:1 electrolytes (AgNO_3 for example) give negative hydration numbers. How are these best interpreted? Is an understanding of science best communicated through specific examples or is a more generalized approach more suitable? I would argue that while some generalized statements may help guide a student in the study of science, a presentation of some of the rich tapestry of the *story* of science as evidenced in its concepts, individuals, communities, and controversies, will reap far greater rewards for the teacher and the student.

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