RECIPROCAL SOLUBILITY INFLUENCE IN SALT MIXTURES. THE CONTRIBUTIONS OF WALTHER NERNST AND OF ARTHUR NOYES

John T. Stock, University of Connecticut

In 1887, Walther Hermann Nernst (1864-1941; Nobel Laureate 1920) began his highly successful career as an assistant to Wilhelm Ostwald (1853-1932; Nobel Laureate 1909) at the University of Leipzig. Ostwald strongly supported the ionic theory and had extended it, especially to the dissociation of weak electrolytes. By 1889, Nernst had established the principles of electrode potential, familiarized in the textbook "Nernst equation," and hence of the emf of a reversible cell. That the solubility of a salt is diminished by the addition of another salt having an ion in common with the first was well known. While briefly at the University of Heidelberg, Nernst developed a quantitative theory of this common ion effect, supported by experiments with uni-univalent strong electrolytes (1).

Nernst's simplest case assumes that the salts are completely dissociated in solution. If to the saturated solution of MX (molar concentration m_0) MY or NX is added to concentration x, then the now smaller solubility m is given by

$$m\,(\,m + x\,) = m_0^2 \qquad (1)$$

The symbols are those used by Nernst. The quantity m_0^2 became known as the *solubility product* of MX. (Nowadays, K_{sp} is the usual symbol for a solubility product). Unless the solubility of MX is very small, equation (1) must be modified to allow for incomplete dissociation:

$$ma\,(\,ma + xa\text{¢}\,) = m_0^2 a_0^2 \qquad (2)$$

Here a_0 is the degree of dissociation of MX when saturated in water and a the value after the addition of, e.g., NX, which is dissociated to the extent a¢. Svante Arrhenius (1859-1927) had pointed out that the mixing of two solutions with one ion in common does not alter the degree of dissociation of the salts (2). For example, a mixture of equivalent solutions of a pair of alkaline halides has a conductivity equal to that of the mean of the conductivities of the individuals (3). Therefore when solving equation (2) with respect to m, Nernst felt justified in making the assumption that a and a¢ were equal, so that m is given by:

$$m = -\frac{x}{2} + \sqrt{\frac{m_0^2 a_0^2}{a^2} + \frac{x^2}{4}} \qquad (3)$$

Then, with CH_3COOAg (solubility 0.0603M at 16° C) as MX and known concentrations of $AgNO_3$ or CH_3COONa as additive, Nernst found that the measured and the calculated solubilities were similar. The largest concentration of additive was 0.230 M, when the solubility of CH_3COOAg fell to approximately one-third of its solubility in water.

Nernst commented that solubility measurements might throw light on the existence in solution of both M^+ and MX^-. He also theorized that, when two common-ion salts form a single saturated solution, their solubilities, m_1 and m_2, must be less than their m_0 values.

Nernst provided no experimental support for these ideas. Before his move to the University of Göttingen in 1890, Nernst was able to place the verification and extension of mutual solubility problems in the hands of Arthur Amos Noyes (1866-1936).

Noyes graduated from the Massachusetts Institute of Technology (MIT) in 1886 and continued research in organic chemistry to obtain his M.S. and an assistantship in 1887 (4). By the summer of 1888, Noyes had planned to study under Johann Friedrich Wilhelm Adolf von Baeyer (1835- 1917) in Munich, but there was no laboratory space for him. Instead, he went to Leipzig, aiming to study organic chemistry under Johannes Wislicenus (1835-1902). However, having heard Ostwald's lectures on physical chemistry, Noyes decided to work in his laboratory. Eventually, Noyes became the first American to obtain a Ph.D. under Ostwald's guidance.

Noyes began his studies with a survey of the principles of mutual salt solubilities (5). He pointed out that a consideration of the undissociated portion of MX leads to a very simple alternate expression for *m* :

Walther Nernst

$$m = m_0 (1 - a_0) / (1 - a) \qquad (4)$$

However, this simplicity is offset by a greater sensitivity to any error in *a*. A positive error obviously yields a value of *m* that is too large; Noyes commented that if the same value of *a* is inserted in equation (3), *m* is found to be too small.

To extend Nernst's studies, Noyes chose the systems listed in Table 1. The substrates were chosen to have qualitatively similar low solubilities. Experiments with TlBr were made at 68.5° C because the solubility of this salt was unacceptably low at ambient temperatures. The solutions used were thermostatted, usually at 25° C. Classical gravimetric and volumetric methods were used for the analyses. Equation (3) or its modifications was used to calculate the expected solubilities.

Noyes tabulated the results obtained with the various pairs of electrolytes. In all cases, the observed solubility was greater than the calculated value. Noyes noted that the difference between the two values became greater as the concentration of additive was increased. This is, of course, an expected result of a greater total ionic strength. Noyes felt that the differences might be caused by the use of conductivity measurement to find degrees of dissociation. Certainly the "zero concentration" equivalent conductivity values were at that time the best estimates. The Kohlrausch square root rule for finding such values by linear extrapolation from measurements made at finite concentrations did not appear until 1900 (6).

Noyes chose the pair TlCl and TlSCN for a quantitative examination of Nernst's conclusions concerning the solubilities of two common-ion salts in a single saturated solution. He found decreases in solubility of approximately 26% for the more soluble TlCl and 28% for TlSCN.

Nernst had indicated that solubility measurements might throw light upon the state of dissociation of ternary salts. For example, is $AgSO_4^-$ present in a saturated solution of Ag_2SO_4? To find an indirect answer to this kind of problem, Noyes added equivalent amounts of $TlNO_3$, $BaCl_2$, and Tl_2SO_4 to saturated solutions of TlCl. He found that the solubility of the latter salt was lowered by the same extent with each of the additives. Because Tl^+ and Cl^-, but not $TlSO_4^-$ and $BaCl^+$, control the solubility of TlCl, he concluded that there were no significant amounts of the double ions. Otherwise, less Cl^- or Tl^+ would be available from the additives.

Table 1. Common-ion Systems

Substrate	Solubility, m_0	Additive
PhCH:CBr.COOH[a]	0.0176	PhNH.CO.COOH
$AgBrO_3$[b]	0.00810	$KBrO_3$or $AgNO_3$
TlBr[c]	0.00869	$TlNO_3$
TlSCN	0.0149	$TlNO_3$ or KSCN
TlCl	0.0161	$TlNO_3$ or HCl

[a] Common ion, H^+ [b]24.5° C [c]68.5° C

Noyes turned to systems that have no ions in common. He examined the effect of KNO_3 and of CH_3COONa on the solubility of TlCl and found that these increased the solubility, as we would expect from the present-day concept of ionic strength. However, Noyes attributed the increase to the formation of some undissociated KCl by an exchange reaction with TlCl, thereby increasing the solubility of the latter. At additive concentrations greater than about 0.03M, the solubility was less than expected from his mode of calculation. He could not explain this but suggested that it might be due to inaccurate dissociation values, or to the assumption that all of the salts had equal dissociation constants.

Having examined the common-ion effects in solutions of sparingly soluble salts, Noyes considered such effects in solutions containing only freely soluble salts. He critically surveyed the solubility results obtained by numerous earlier workers, pointing out certain peculiarities such as the formation of double salts. He concluded that the mutual solubility principles were also obeyed in the necessarily more concentrated solutions, although the results might lack quantitative exactitude. Noyes considered that the application of solubility measurements to the determination of degrees of dissociation was one of the most important results of his work. With the elimination of m_0 by combining equations (3) and (4) he obtained the relationship:

$$a = [\,(m_0 - m)/x\,][\,1 + (1 + x/m)^{1/2}\,] \qquad (5)$$

At this point he stressed that a is the dissociation of each salt in the presence of the other and is equal to the dissociation undergone by each salt at concentration ($m + x$). For a single salt, the application of the law of mass action leads to the relationship $(1 - a).n = k.a^2.n^2$, where n is the normality of the solution and k is the factor that Noyes termed the "dissociation constant " of the salt. This relationship, a form of the Ostwald "dilution law," is applicable to solutions of weak electrolytes. When, as was usual, the degree of dissociation a was obtained from conductivity measurements, attempts to apply the above relationship to solutions of strong electrolytes resulted in failure. Noyes illustrated this by the results obtained with solutions of $TlNO_3$. These results, along with those found when a was calculated from solubility measurements, are listed in Table 2.

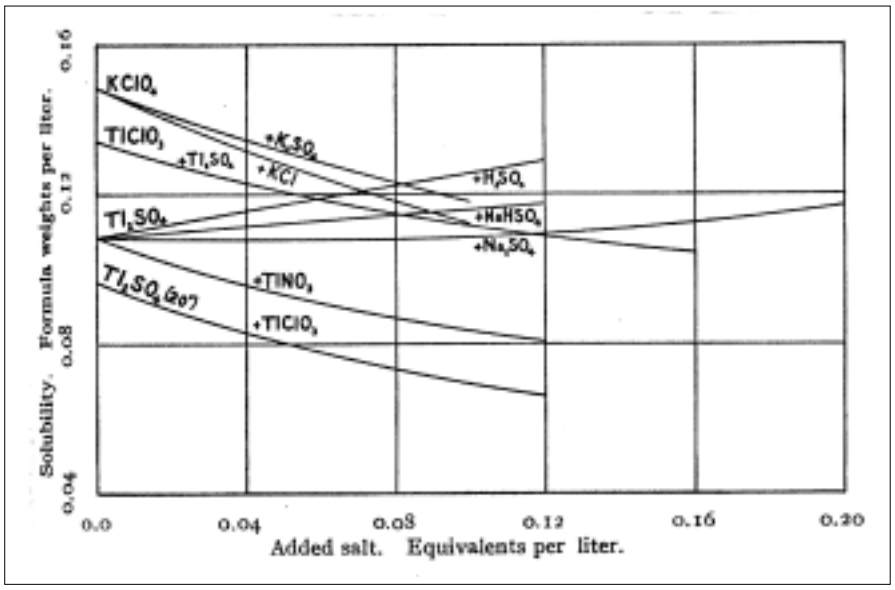
Although not completely independent of concentration, the results in column 2 show a degree of constancy that is completely absent from the results obtained from conductivity data. Noyes concluded that the determination of dissociation from solubility measurements was the most reliable method then known. Solutions of pairs of salts that differ completely, i.e., have no ion in common, such as the pair TlCl and KNO_3, were examined. The results of several experiments showed that the solubility increase agreed approximately with that calculated from known dissociation constants. In validating and extending Nernst's concepts, Noyes produced much valuable solubility data. He showed decisively that the common ion effect was a highly significant phenomenon in quantitative chemistry.

After receipt of his Ph.D. in 1890, Noyes returned to MIT, to become a great teacher of chemistry in its widest sense (4). This activity was accompanied by extensive research, especially on solutions of electrolytes. Noyes' doctoral studies must have led him to suspect that rather more than the law of mass action and the Arrhenius ionic theory were needed to explain some of the phenomena encountered. By 1903 he had begun to consider the possibility that anomalies in electrolytic conductivity might be attributable to electrical charges on the ions and not to specific chemical affinity (7,8).

Table 2. "Dissociation Constant" (k) of $TlNO_3$

Concn.	***k,*** solubility	*K,* conductivity
0.0161	5.45	7.11
0.0366	5.45	4.84
0.0617	5.21	4.03
0.100	5.07	3.32
0.150	4.81	2.90

He retained his interest in the solubilities of electrolytes and the properties of their solutions. This included the effect of salts on the solubility of other salts, an effect that Noyes had investigated in his doctoral studies.



Effect of salts on the solubility of other salts

In 1911, Noyes collaborated with Research Associate (later, Assistant Professor) William Crowell Bray (1879-1946) to produce a set of papers that critically examined and greatly extended his earlier work (5). The first of these papers showed that the solubility principles initially adopted by Noyes are subject to considerable deviations (9). Additional studies since 1890 had shown that, in a solution saturated at 40°C with both TlCl and TlSCN, the concentration of nonionized TlCl is about 15% less, and the ionic product $[Tl^+][Cl^-]$ about 5% greater than in a solution of TlCl alone. Further, the solubility-product principle failed badly when a salt with a common bivalent ion was added. For example, although the solubility of $PbCl_2$ was decreased slightly by a small addition of $Pb(NO_3)_2$, further additions caused the solubility to become greater than in water. The authors proposed to make use of the thermodynamically related concept of *activity*, A, introduced by Gilbert Newton Lewis (1875-1946) in 1907 (10). In a solution in equilibrium with solid salt BA, the relationships $A_B \times A_A$ = constant and A_{BA} = constant are strictly true. The *activity coefficient*, *i.e.*, the ratio of activity to concentration, A/C, is assumed to be unity at infinite dilution.

The experimental work described in the second paper was shared by Noyes's three coauthors (11). Great care was taken to ensure the purity of the various salts and the temperature was maintained at 25 ± 0.02°C (or 20°C, where indicated). The results of the numerous solubility determinations are summarized as in Fig. 3. The lowered solubility of Tl_2SO_4 by the presence of $TlNO_3$, a salt with a univalent common ion, agreed qualitatively with the ionic product principle. However, with the bivalent common ion salt Na_2SO_4, the solubility, reduced by only 0.3% in 0.1 N Na_2SO_4, was actually increased in higher concentrations of this additive.

Arthur Amos Noyes

Research in the third paper, which dealt with the effect of other salts on the solubility of TlCl, was directed by Bray (12). The solubility of TlCl itself, found to be 16.07 mM per liter, was only 0.13% lower than the original value found by Noyes (5). The increased solubility caused by the presence of KNO_3 or of K_2SO_4, salts without a common ion, was attributed to the formation by metathesis of nonionized $TlNO_3$ or Tl_2SO_4. At comparable concentrations, the

Table 3
Effect of Added Salts on the Dissociation of TlCl

Added salt	Log 10^3 x [Â i]	Log 10^4 x [TlCl]	Log 10^5 x $[Tl^+][Cl^-]$
None	1.1559	1.2443	1.3115
Tl_2SO_4	1.3703	1.6158	1.3183
	1.5911	1.0931	1.3339
	1.8090	1.0362	1.3642
$TlNO_3$	1.4649	1.1446	1.3345
	1.6709	1.0962	1.3690
	1.9141	1.0386	1.4096
K_2SO_4	1.4819	1.1265	1.3243
	1.7157	1.0492	1.3401
	1.9296	0.9850	1.3612
	2.3030	0.8854	1.4126

latter salt is less highly ionized than $TlNO_3$, so that Tl_2SO_4 has the greater effect. The decrease in solubility caused by the addition of salts with a common ion is in accord with that expected from the ionic product principle.

Bray undertook the discussion of the results described in the three foregoing papers (13). Included in the various tables is a listing of the degrees of ionization, at concentrations from 0.01 to 0.25 N, of the seven salts that were used in the studies. The values were obtained by precise conductometric measurements.

The composition of the various solutions saturated with TlCl was calculated on the assumption that, for each salt, the values in mixtures depend only on the equivalent ion concentration (Σi). To show the relationships in dilute solutions more clearly, Σi, the corresponding concentrations of nonionized TlCl, and the values of the ionic product $[Tl^+][Cl^-]$, were expressed logarithmically. Examples are given in Table 3; the effects of the additives $BaCl_2$, KNO_3 and KCl were also examined.

In all cases, an increase in Σi caused a decrease in the concentration of nonionized TlCl and an increase in the ionic product $[Tl^+][Cl^-]$. Although the experiments involved univalent and bivalent salts, with and without a common ion, the results were remarkably similar. This supported the assumption that the total ionic strength in a mixture primarily determines the ionization of uni-univalent salts. In the case of less soluble salts, it was concluded that their solubility products would be practically constant in the presence of small amounts of other salts.

Further analysis of the results led to the conclusion that, in the case of TlCl, deviations of the ionization from the law of mass action are due more to the abnormal behavior of the nonionized salt than to that of the ions. In more concentrated solutions of a single salt, the activity coefficient, A/C, decreased more rapidly with further increase in concentration. Available measurements of the emf of Tl^+-ion concentration cells supported this conclusion.

Theories and equations that were based upon the concept of the complete dissociation of strong electrolytes in solution were eventually developed by others (14). Then Noyes was able to use his acquired experimental results to check these developments.

In 1913, Noyes began a part-time association with Throop College, which became the California Institute of Technology (Cal Tech). This association became full-time in 1919, when Noyes moved from MIT, with the intention of making Cal Tech a great center for education and research. This he certainly achieved. Troubled by ill health during the latter part of his life, Noyes died on June 3, 1936. He had never married; his estate was bequeathed to Cal Tech for support of research in chemistry.

ACKNOWLEDGMENT

This work was partially carried out under the Research Fellowship Program of the Science Museum, London

REFERENCES AND NOTES

1. W. Nernst, "Ueber gegenseitige Beeinflussung der Löslichkeit von Salzen," *Z. Phys. Chem.*, **1889**, *4*, 372-383.
2. S. Arrhenius, "Theorie der isohydrischen Lösungen," *Z. Phys. Chem*., **1888**, *2*, 284-295..
3. P. Chroustchoff and V. Pachkoff, "Sur la Conductibilité Électrique des Dissolutions Salines Contenant des Mélanges de Sels Neutres," *C. R. Hebd. Séances Acad. Sci, Ser. C*, **1889**, *108*, 1162-1164.
4. L. Pauling, "Arthur Amos Noyes," *Biog. Mem. Natl. Acad. Sci. USA*, **1958**, *31*, 322-346.
5. A. A. Noyes, "Ueber die gegenseitige Beeinflussung der Löslichkeit von dissociierten Körpern," *Z. Phys. Chem.*, **1890**, *6*, 241-267.
6. F. Kohlrausch and M. E. Maltby, "Das elektrische Leitvermögen wässringer Lösungen von Alkalichloriden und Nitraten," *Wiss, Abhl. D. Phys. Techn. Reichanstalt*, **1900**, *3*, 156-227.
7. A. A. Noyes and W. D. Coolidge, "The Electrical Conductivity of Aqueous Solutions at High Temperature," *Proc. Am. Acad. Arts Sci.*, **1903**, *39*, 163-219.
8. A. A. Noyes, "The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory," Science, **1904**, *20*, 577-587.
9. A. A. Noyes and W. C. Bray, "The Effect of Salts on the Solubility of Other Salts. I," *J Am. Chem. Soc.*, **1911**, *33*, 1643-1649.
10. G. N. Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Am. Acad. Arts Sci.*, **1907**, *43*, 259-293.
11. A. A. Noyes, C.R. Boggs, F. S. Farrell, and M. A. Stewart, "The Effect of Salts on the Solubility of Other Salts. II," *J. Am. Chem. Soc.*, **1911**, *33*, 1650- 1663.
12. W. C. Bray and W. J. Winninghoff, "The Effect of Salts on the Solubility of Other Salts. III," *J. Am. Chem. Soc.*, **1911**, *33*, 1663-1672.
13. W.C. Bray, "The Effect of Salts on the Solubility of Other Salts. IV," *J. Am. Chem. Soc.*, **1911**, *33*, 1673-1686.
14. P. Debye and E. Hückel, "Zur Theorie der Elektrolyte," *Phys. Z.*, **1923**, *24*, 185-206; 305-325.

ABOUT THE AUTHOR

John T. Stock, recipient of the HIST Dexter Award in 1992, is Professor Emeritus of Chemistry, University of Connecticut, Storrs, CT 06269-4060.