"We should use the activity, that is more correct"

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Chemical activity is what happens, we try to approximate this with models

$$K = \frac{a_c^c a_d^d}{a_a^a a_b^b} \Rightarrow$$
$$K = \frac{([c]\gamma)^c ([d]\gamma)^d}{([a]\gamma)^a ([b]\gamma)^b}$$

The activity coefficients are approximated to 1 and we get



$$K = \frac{[c]^c [d]^d}{[a]^a [b]^b}$$

Why is activity seldom used?



What I plan to learn during this presentation:

Will the ions affect the solvent?



Is concentration effect additive?



Should we always use activity coefficients?



How will these questions be answered?



For the first question we will have to look at ions in solvent



change in concentration

The Second question we will discuss by looking at some concentrations

$$\ln \gamma_{\pm} = \frac{Az^2 \sqrt{I}}{1 + Ba_j \sqrt{I}}$$

The third question will be answered by looking at some equations and graphs

Ideal liquids, do they exist?



So what happens to water as ion concentration is increased

C (mol/l)	0.001	0.01	0.1	1.0	10.0
Separation (Å)	94	44	20	9.4	4.4



7

So what happens to water as ion concentration is increased



(1) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solution of Simple Electrolytes*: London Butterworths Scientific Publications, 1959

The charge of a ion will affect more than just it's surrounding water molecules



The size of the ion is dependent on the charge and on the dielectrics of the solute.

The dielectric of the solute will change as ions are added and with increasing temperature.

Malmberg, C. G.; Maryott, A. A. Dielectric Constant of Water from 0 to 100 °C. *Journal of Research of the National Bureau of Standards* 1956, 56 (1), 1.
 Hasted, J. B.; Riston, D. M.; Collie, C. H. Dielectric Properties of Aqueous Ionic Solutions Parts I and II. *The Journal of Chemical Physics* 1948, 16 (1), 1.
 Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in*

9 Solution of Simple Electrolytes: London Butterworths Scientific Publications, 1959.

Different ions will need more or less water to be solvate, Mg²⁺ will need 12 while K⁺ is satisfied with 4



The solvation dependes on the size and the charge of the ion, but it is an important property when the interaction between the solute and the solvent are to be described.

Robinson, R. A.; Stokes, R. H. Electrolyte Solutions

(1)

10 *The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solution of Simple Electrolytes*: London Butterworths Scientific Publications, 1959.

High concentrations of ions in water will then alter the structure of the solvent drastically



Adding ions to water will then change it from an ideal liquid into something that is more difficult to explain



Hasted, J. B.; Riston, D. M.; Collie, C. H. Dielectric Properties of Aqueous Ionic Solutions Parts I and II. *The Journal of Chemical Physics* 1948, 16 (1), 1.
 Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *The Journal of Physical Chemistry* 1974, 77 (2), 268.

(1) (1), 1.

So how can these effects be predicted?

Debye and Hückel thought that the interaction between ions and water could be described combining Boltzmann distribution. To describe concentration of ions around an ion.

C (mol/l)	0.001	0.01	0.1	1.0	10.0
Separation (Å)	94	44	20	9.4	4.4

And the Poisson equation to explain the force interaction between charged bodies



(1) Debye, P.; Hückel, E. De La Theorie des Electrolytes. I. Abaissement du Point de Congelation et Phenomenes Associes.
 13 *Physickalische Zeitschrift* **1923**, *24* (9), 185.

We then end up with the Debye-Hückel formula



(1) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *The Journal of Physical Chemistry* 1974, 77 (2), 268.
 (1) Manov, G. G.; Bates, R. G.; Hamer, W. J.; Acree, S. F. Values of the constants in the Debye-Hückel Equation for Activity Coefficients. *Journal of the American Chemical Society* 1943, 65 (9), 1765.

The activity coefficient of chloride will also change drastically as concentrations increase



[CI]

We need to introduce the concept lonic strength, concentration of charge in the solution

change in concentration

It is possible to make concentration effect additive by using an inert salt in excess

[CI]

It turns out liquids are difficult to predict and empirical data has to be added

Pitzer equations

20

Solutions are complex and there are more interactions than purely electrostatic.

Several different models have been proposed for this Pitzer equations will be discussed.

All models based on Debye and Hückel assume that ions are equal in size.

$$\log \gamma = -f^{\gamma} + m \frac{2v_n v_x}{v} B_{nx}^{\gamma} + m^2 \frac{2(v_n v_x)^{\frac{3}{2}}}{v} C_{nx}^{\gamma}$$
$$f^{\gamma} = A(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I}))$$
$$B_{nx}^{\gamma} = 2\beta_{nx}^{o} + \frac{2\beta_{nx}^{1}}{\alpha^{2}I}(1 - e^{-\alpha\sqrt{I}}(1 + \alpha\sqrt{I} - 0.5 \alpha I))$$

1) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolyts. IV. Activity and Osmotic Coefficient for Mixed Electrolytes. *Journal of American Chemical Society* **1974**, *96* (18), 5701.

(2) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *The Journal of Physical Chemistry* **1974**, 77 .268.

What the different factors in the Pitzer equation adds

$$\log \gamma = -f^{\gamma} + m \frac{2v_{n}v_{x}}{v} B_{nx}^{\gamma} + m^{2} \frac{2(v_{n}v_{x})^{\frac{3}{2}}}{v} C_{nx}^{\gamma}$$

$$f^{\gamma} = A(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I}))$$

A small change to the Debye-Hückel formula. Here b is set to 1.2 but it can be varied to fit

Better with experimental data.

$$B_{nx}^{\gamma} = 2\beta_{nx}^{o} + \frac{2\beta_{nx}^{1}}{\alpha^{2}I}(1 - e^{-\alpha\sqrt{I}}(1 + \alpha\sqrt{I} - 0.5 \alpha I))$$

What the different factors in the Pitzer equation does

$$\log \gamma = -f^{\gamma} + m \frac{2v_n v_x}{v} B_{nx}^{\gamma} + m^2 \frac{2(v_n v_x)^{\frac{3}{2}}}{v} C_{nx}^{\gamma}$$

$$B_{nx}^{\gamma} = 2\beta_{nx}^{o} + \frac{2\beta_{nx}^{1}}{\alpha^{2}I}(1 - e^{-\alpha\sqrt{I}}(1 + \alpha\sqrt{I} - 0.5 \alpha I))$$

The B term takes into account the short range interactions between the ions. This offers only small corrections and are only important at high concentrations.

This functions as a sum of terms and can be expanded as needed when binary or ternary

solutions.

The betas are empirical and a function of salts.

The difference between concentration behavior and activity behavior can be rather huge

(1) Powell, K. J.; Brown, P. L.; Byrne, R. H.; Gajda, T.; Hefter, G.; Leuz, A.; Sjöberg, S.; Wanner, H. Chemical Speciation of Environmentally Significant Metals with Inorganic Ligands. Part 4: The Cd²⁺ + OH⁻, Cl⁻,CO₃²⁻,SO₄²⁻, and PO₄³⁻ Systems (IUPAC Technical Report) *Pure and Applied Chemistry* **2011**, *83* (5), 1163.

23

What happens when we keep an constant ionic strength

Summary: what you should be left with after this presentation

Concentration effect is not strictly additive

Ion concentration will change the physical properties of water- vapour pressure, osmosity, Freezing point and others.

Up to a quite high concentration you can avoid activities

The equations do become more complex the more salt is added

$$ln\gamma_{mx} = z^{2}f^{\gamma} + m((1 - y^{2})B_{mx}^{\gamma} + y(\theta_{mn} + \theta_{xy}) + y(1 - y)(B_{my}^{\phi} + B_{nx}^{\phi} - 2B_{mx}^{\phi} + I\theta_{mn} + I\theta_{xy}) + y^{2}(B_{my}^{\gamma} - B_{my}^{\phi} + B_{nx}^{\gamma} - B_{nx}^{\phi} + 2B_{NY}^{\phi} - B_{ny}^{\gamma})) + m^{2}((1 - y)C_{mx}^{\gamma} + y(1 - y)(\psi_{mnx} + \psi_{mxy} + C_{mx}^{\phi} + C_{nx}^{\phi} + C_{my}^{\phi}) + \frac{1}{2}y^{2}(\psi_{mny} + \psi_{nxy} + C_{my}^{\phi} + C_{nx}^{\phi} + C_{ny}^{\phi}))$$

^{26 (1)} Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficient for Mixed Electrolytes. *Journal of American Chemical Society* **1974**, *96* (18), 5701.

There are several other theories Specific ioni interaction theory is accurate up to 4 m

Also called Guggenheim Scathcard equations

$$\log \gamma = -\frac{Az_j^2 \sqrt{I}}{1 + Ba_j \sqrt{I}} + \sum_k \epsilon_{(j,k)} m_k$$

27

Empirical interaction for each ion added, similar to the Pitzer equations

Meissner is completely empirical and "works" up to 22 m

A different approach where the "reduced activity coefficient" is used

$$\log \Gamma = \gamma^{\frac{1}{Z_1 Z_2}}$$

The reduced activity coefficient is made by plotting the change of the activity vs ionic strength. It is built especially for use with leaching and other hydrometallurgy processes

(1) Kusik, C. L.; Meissner, H. P. Calculating Activity Coefficients in Hydrometallurgy- A review. *International Journal of Mineral Processing* **1975**, *2*, 105.

28