

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 11.6

Electrolyte Solutes

ELECTROLYTES



Svante Arrhenius

“Salts of strong acids and bases separate into their constituent ions in solution.”

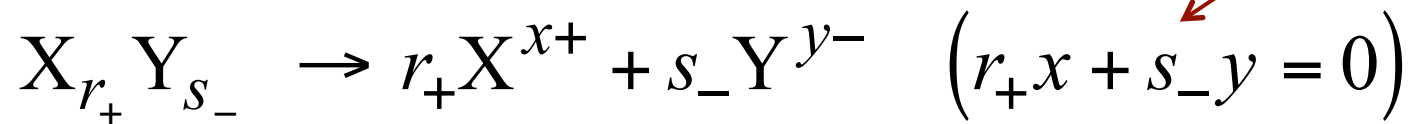
The fact is, there has been a split of chemistry into two schools since the intrusion of the Arrhenic faith, rather it should be said, the addition of a new class of worker into our profession—people without knowledge of the laboratory arts and with sufficient mathematics at their command to be led astray by curvilinear agreements; without the ability to criticise, still less of giving any chemical interpretation. The fact is, the physical chemists never use their eyes and are most lamentably lacking in chemical culture. It is essential to cast out from our midst, root and branch, this physical element and return to our laboratories.

H. Armstrong, 1936

DISSOCIATING SALTS

Defining a generic m - n electrolyte as:

charge neutrality



The chemical potential of the salt, μ_2 , is the sum of the (unknowable) chemical potentials of constituent ions:

$$\mu_2 = r_+ \mu_{X^{x+}} + s_- \mu_{Y^{y-}}$$

$$\mu_2^\circ(T) + RT \ln a_2 = r_+ \mu_{X^{x+}}^\circ(T) + r_+ RT \ln a_{X^{x+}} + s_- \mu_{Y^{y-}}^\circ(T) + s_- RT \ln a_{Y^{y-}}$$

This implies, in terms of activities: $\ln a_2 = r_+ \ln a_{X^{x+}} + s_- \ln a_{Y^{y-}}$

or, using properties of logarithms: $a_2 = a_{X^{x+}}^{r_+} a_{Y^{y-}}^{s_-} = a_{\pm}^{(r_+ + s_-)}$

mean ionic activity

MEAN IONIC QUANTITIES

$$a_2 = a_{\text{X}^{x+}}^{r_+} a_{\text{Y}^{y-}}^{s_-} = a_{\pm}^{(r_+ + s_-)}$$

By analogy, we define mean ionic molality and mean ionic activity coefficient, so that

$$a_2 = (m_{\pm} \gamma_{\pm})^{(r_+ + s_-)}$$

where

$$m_{\text{X}^{x+}}^{r_+} m_{\text{Y}^{y-}}^{s_-} = m_{\pm}^{(r_+ + s_-)}$$

$$\gamma_{\text{X}^{x+}}^{r_+} \gamma_{\text{Y}^{y-}}^{s_-} = \gamma_{\pm}^{(r_+ + s_-)}$$

From starting *compound* molality m : $a_2 = m^{(r_+ + s_-)} \left(r_+^{r_+} \right) \left(s_-^{s_-} \right) \gamma_{\pm}^{(r_+ + s_-)}$

Self-assessment

Given the definition: $m_{X^{x+}}^{r_+} m_{Y^{y-}}^{s_-} = m_{\pm}^{(r_+ + s_-)}$

Verify that: $m_{\pm}^{(r_+ + s_-)} = m^{(r_+ + s_-)} \left(r_+^{r_+} \right) \left(s_-^{s_-} \right)$

Then, determine the value of every variable in the above equations for the case of 1 mole of $\text{Al}_2(\text{SO}_4)_3$ (assuming that salt to be a strong electrolyte) added to 1 kg of water.

Self-assessment Explained

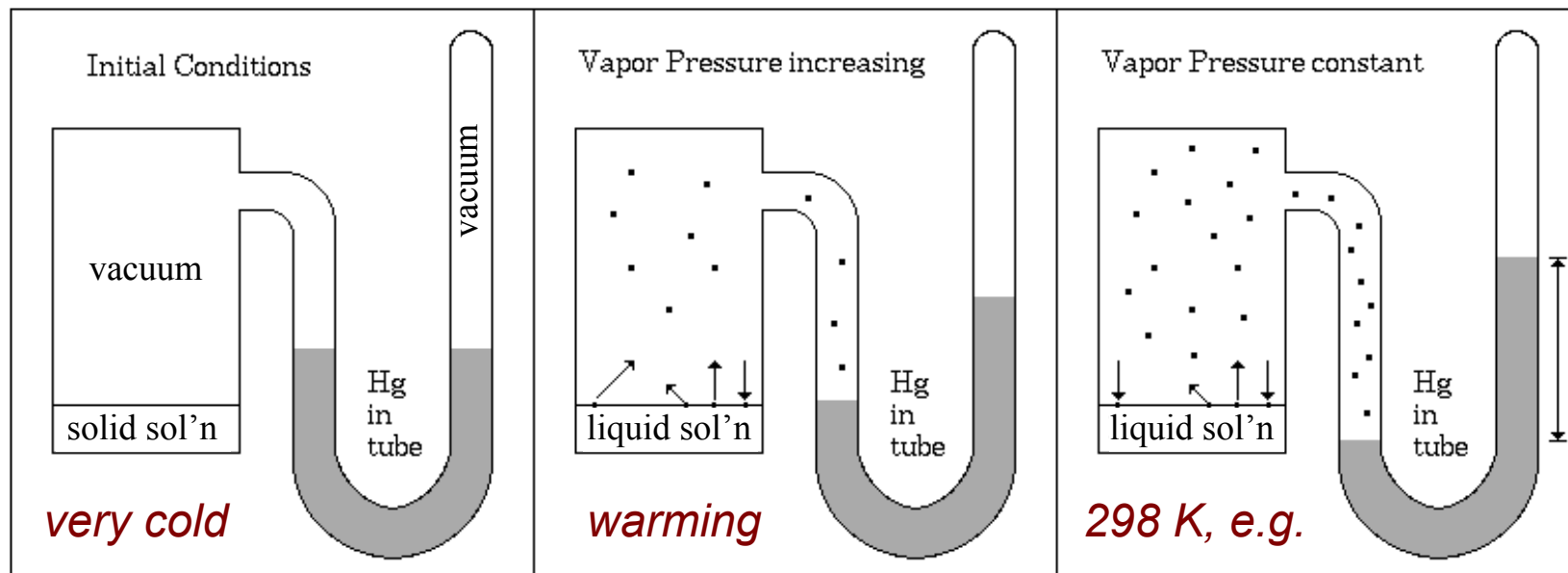
$$\begin{aligned} m_{\pm}^{(r_+ + s_-)} &= m_{X^{x+}}^{r_+} m_{Y^{y-}}^{s_-} \\ &= (r_+ m)^{r_+} (s_- m)^{s_-} \\ &= m^{(r_+ + s_-)} (r_+)^{r_+} (s_-)^{s_-} \quad \text{Q.E.D.} \end{aligned}$$

For the case of 1 mole of $\text{Al}_2(\text{SO}_4)_3$ (assuming that salt to be a strong electrolyte) added to 1 kg of water:

$$X = \text{Al} \quad Y = \text{SO}_4 \quad r_+ = 2 \quad s_- = 3 \quad x = 3 \quad y = 2$$

$$m = 1 \quad m_{X^{x+}} = 2 \quad m_{Y^{y-}} = 3 \quad m_{\pm} = (108)^{1/5}$$

DETERMINING ELECTROLYTE ACTIVITY



$$\ln a_1 \approx \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{(r_+ + s_-)m}{55.51 \text{ mol kg}^{-1} \text{ water}}$$

Colligative Properties

$$\Delta T_{\text{fus}} = (r_+ + s_-)K_f m$$

$$\Delta T_{\text{vap}} = (r_+ + s_-)K_b m$$

$$\Pi = (r_+ + s_-)cRT$$

Define ϕ , whose deviation from unity quantifies non-ideality of solution

$$\ln a_1 = -\frac{(r_+ + s_-)m\phi}{55.51 \text{ mol kg}^{-1} \text{ water}}$$

$$dU = \delta q + \delta w$$



Next: Debye-Hückel Theory