

2106NSC

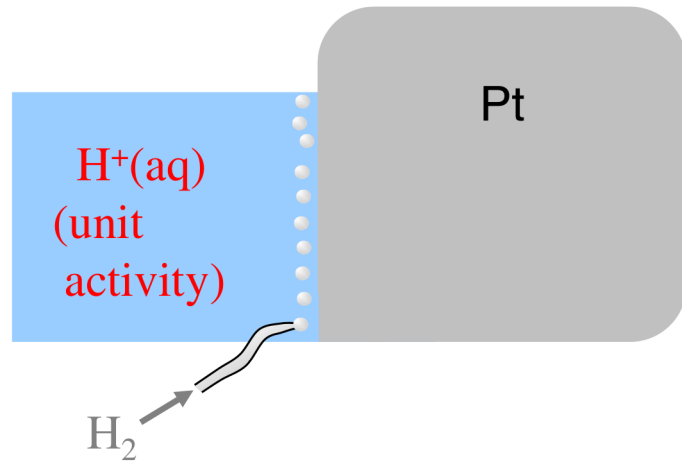
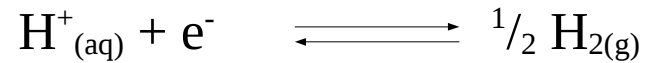
Physical & Analytical Chemistry

Thermodynamics 12

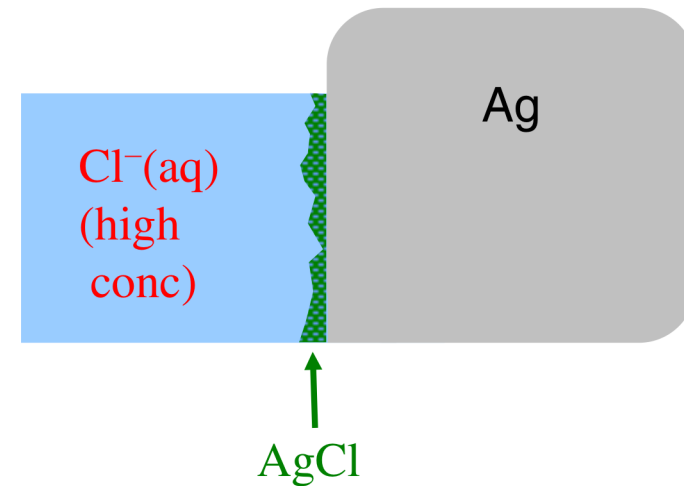
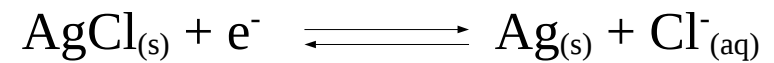
Fundamentals of electrochemistry (cont.)
Solutions of electrolytes

Reference electrodes

Standard hydrogen electrode



Ag_(s) | AgCl_(s) electrode



$$\Delta E^\ominus = E^\ominus_{\text{right}} - E^\ominus_{\text{left}} = E^\ominus_{\text{Ag/AgCl}} - E^\ominus_{\text{SHE}} = 222 \text{ mV} - 0 = 222 \text{ mV}$$

Reference electrodes



Standard hydrogen electrode



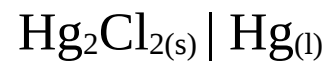
$$E^\ominus = 0$$

Ag/AgCl electrode



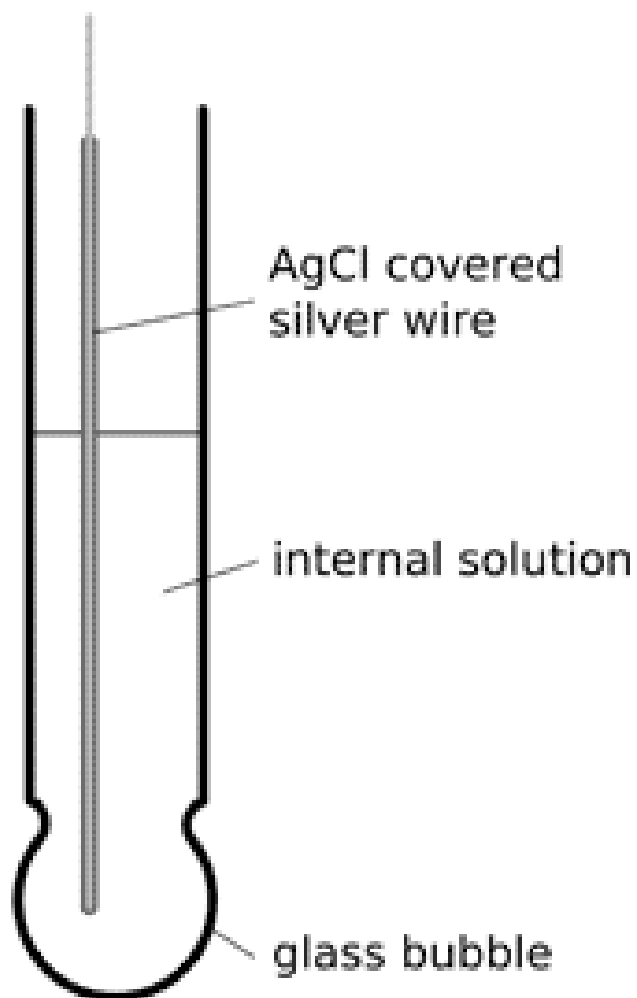
$$E^\ominus = 0.22 \text{ V}$$

Calomel electrode



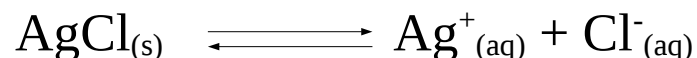
$$E^\ominus = 0.26 \text{ V}$$

Solubility product



Glass electrode

Silver chloride is rather insoluble in water (0.002 g l^{-1}). A saturated aqueous AgCl solution contains only $13 \mu\text{M}$ Ag^+ (and $13 \mu\text{M}$ Cl^-) ions. Dissolution reaction:



The equilibrium constant is $K_c = \frac{c(\text{Ag}^+)}{c^\ominus} \cdot \frac{c(\text{Cl}^-)}{c^\ominus}$

Note: $[X] = \frac{c(X)}{c^\ominus}$; and also remember that H_2O is omitted since it is neither consumed nor produced.

Since $\text{AgCl}_{(s)}$ is a solid, $c(\text{AgCl}_{(s)})$ is a constant, it is not included in the above equilibrium constant expression.

The solubility product is the equilibrium constant for the above dissolution reaction:

$$K_{\text{sp}}(\text{AgCl}) = K_c = 2 \cdot 10^{-10}$$

[Solubility product at Purdue University](#)

Solutions: Colligative properties

Colligative properties result from the reduction of the chemical potential μ of the liquid solvent, as a result of the presence of the solute.

For the ideal solution:

$$\mu_{\text{solvent}} = \mu^* \rightarrow \mu_{\text{solvent}} = \mu^* + R \cdot T \cdot \ln x_{\text{solute}} \quad (x < 1 \Rightarrow \ln x < 0)$$

The lowering of the chemical potential of the liquid solvent is an entropic effect.

Molality: $b_{\text{solute}} = n_{\text{solute}} / m_{\text{solvent}}$

Melting point depression: $\Delta T_f = K_f \cdot b$ with K_f cryoscopic constant

Boiling point elevation: $\Delta T_b = K_b \cdot b$ with K_b ebullioscopic constant

Osmosis: $\Pi = c \cdot R \cdot T$

Solutions of electrolytes

The osmotic pressure of non-electrolytes is given by the van't Hoff equation:

$$\Pi = c \cdot R \cdot T$$

For electrolytes, a variation of this equation needs to be used that includes the correction factor i :

$$\Pi = i \cdot c \cdot R \cdot T$$

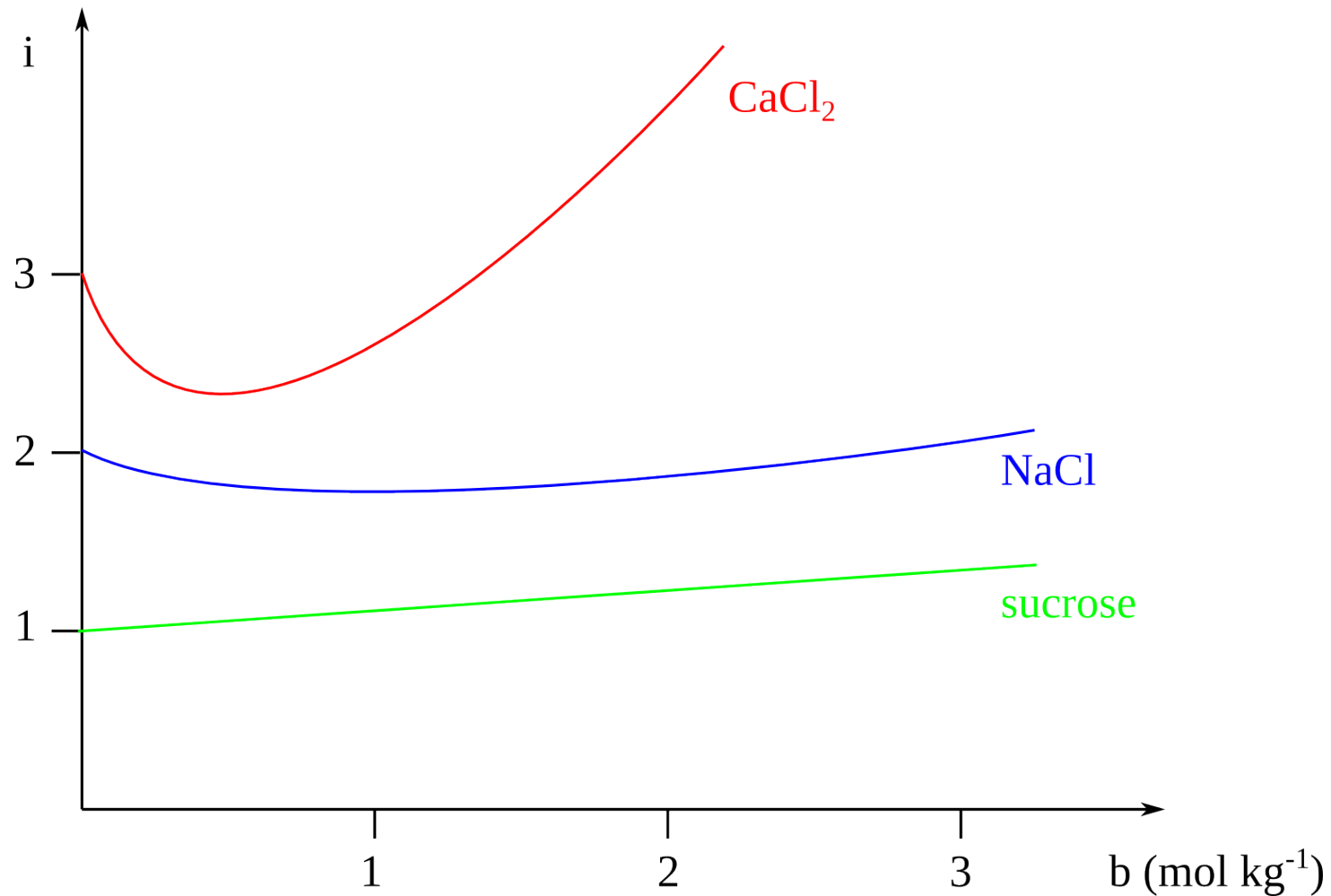
The van't Hoff correction factor i approaches the number (ν) of ions into which the solute molecule dissociates when the solution is increasingly being diluted.

Similarly, for boiling point elevation and melting point depression:

$$\Delta T_b = i \cdot K_b \cdot b$$

$$\Delta T_f = i \cdot K_f \cdot b$$

van't Hoff correction factor



van't Hoff correction factor

Requirement for van't Hoff correction (i.e. why $i \neq v$, with v being the theoretical number of ions yielded per solute molecule):

Electrolytes and non-electrolytes:

- difference in internal pressure of solute and solvent
- polarity
- compound formation or complexation
- association of either solute or solvent

And additionally for electrolytes:

- dissociation of weak/strong electrolytes
- interaction of the ions of strong electrolytes

Degree of dissociation

If the deviation of i from ν is due to dissociation only, the **degree of dissociation α** can be determined as per:

$$\alpha = \frac{i - 1}{\nu - 1}$$

with ν being the theoretical number of ions yielded per solute molecule (e.g. for CaCl_2 : $\nu = 3$).

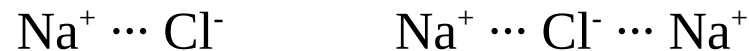
α can be estimated reliably for weak electrolytes, as there are only few ions at all concentrations.

The equation does not work well for strong electrolytes at moderate or strong concentrations, due to interactions between ions.

Strong electrolytes

In case of strong electrolytes, the attractive interactions become important.

In particular, it is possible that ion pairs or triplets form:



The van't Hoff correction factor i can thus be smaller than expected, since some ions are 'taken out of play'.

We therefore have to use an 'effective concentration': **activity a**.

For strong electrolytes and weak electrolytes in presence of salts (e.g. buffer systems), one should generally use **activities** rather than concentrations.

Strong electrolytes

Definition of activity (cf. **Thermodynamics 6**):

$a = \gamma_x \cdot x$ activity in terms of the mole fraction (**Thermodynamics 6**)

$a = p / p^*$ activity for a volatile solvent (Raoult's law: $p = x \cdot p^*$)

$a = \gamma_b \cdot b$ activity in terms of molality

$a = \gamma_c \cdot c$ activity in terms of molar concentration

The activity is usually less than the molar concentration, but it becomes equal to the molar concentration at high dilution.

The activity may be different for cations and anions of a salt.

For an ideal solvent, the activity coefficient $\gamma = 1$.

Ionic strength

The comparison of activity of electrolytes should be made at constant ionic strength.

The **ionic strength** μ is defined as:

$$\mu = \frac{1}{2} \cdot \sum_{i=1}^N c_i \cdot z_i^2$$

where c_i is the molar concentration and z_i is the charge of the i -th ion; N is the number of different ions in the solution.

The ionic strength is important in biochemistry, e.g. when investigating the effect of pH on an enzymatic reaction, the effect of the salt concentration in the buffer may obscure the results unless the buffer is adjusted to ionic strength in each experiment.

Buffers

Buffers are compounds or mixtures of compounds that withstand a change in pH upon addition/generation of acid or base (in a reasonable window).

Buffer compounds are typically weak acids with their conjugate bases, or weak bases and their conjugate acids.

Example: on addition of a strong acid to a solution containing equal quantities of acetic acid and sodium acetate, the hydrogen ions react with the acetate according to



The pH-buffering region of buffers



$$K_a = \frac{\frac{c(\text{H}_3\text{O}^+)}{c^\ominus} \cdot \frac{c(\text{Ac}^-)}{c^\ominus}}{\frac{c(\text{HAc})}{c^\ominus}}$$

$$K_a = \frac{[\text{H}_3\text{O}^+] \cdot [\text{base}]}{[\text{acid}]}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = K_a \cdot \frac{[\text{acid}]}{[\text{base}]}$$

$$\Rightarrow -\lg[\text{H}_3\text{O}^+] = -\lg K_a \cdot \frac{c(\text{acid})}{c(\text{base})} = -\lg K_a - \lg \frac{[\text{acid}]}{[\text{base}]}$$

$$\Rightarrow \text{pH} = \text{p}K_a + \lg \frac{c(\text{base})}{c(\text{acid})} \quad \text{Henderson-Hasselbalch equation}$$

The pH-buffering region of buffers

... with activities instead of molar concentrations

For real (non-ideal) situations, we set up the equilibrium constant with activities instead of concentrations:

$$K_a = \frac{a(\text{H}_3\text{O}^+) \cdot a(\text{Ac}^-)}{a(\text{HAc})} = \frac{a(\text{H}_3\text{O}^+) \cdot [\gamma(\text{Ac}^-) \cdot \frac{c(\text{Ac}^-)}{c^\ominus}]}{\gamma(\text{HAc}) \cdot \frac{c(\text{HAc})}{c^\ominus}}$$

$\gamma(\text{HAc}) \approx 1$ Here, HAc is the solvent; for all solvents $\gamma \rightarrow 1$ as $x \rightarrow 1$.

$$K_a = \frac{a(\text{H}_3\text{O}^+) \cdot [\gamma(\text{Ac}^-) \cdot c(\text{Ac}^-)]}{c(\text{HAc})}$$

$$a(\text{H}_3\text{O}^+) = K_a \cdot \frac{c(\text{HAc})}{\gamma(\text{Ac}^-) \cdot c(\text{Ac}^-)}$$

$$-\lg a(\text{H}_3\text{O}^+) = -\lg \left[K_a \cdot \frac{c(\text{HAc})}{\gamma(\text{Ac}^-) \cdot c(\text{Ac}^-)} \right] = -\lg K_a - \lg \frac{c(\text{HAc})}{\gamma(\text{Ac}^-) \cdot c(\text{Ac}^-)}$$

$$\text{pH} = \text{p}K_a + \lg \frac{c(\text{Ac}^-)}{c(\text{HAc})} + \lg \gamma(\text{Ac}^-)$$

The Debye-Hückel theory

The Debye-Hückel theory of ionic solutions provides a relationship between the activity coefficient and the ionic strength of the solution (Debye-Hückel limiting law):

$$\lg \gamma = -|z_+ \cdot z_-| \cdot A \cdot \sqrt{I}$$

where z_+, z_- are the charge numbers of the ions of the electrolyte
 A is a constant for the solvent of interest ($\approx 0.5 \text{ l}^{3/2} \text{ mol}^{-1/2}$ for H_2O)
 I is the ionic strength

Therefore:

$$\lg \gamma(\text{Ac}^-) = -|-1| \cdot 0.5 \cdot \text{l}^{3/2} \text{ mol}^{-1/2} \cdot \sqrt{I} = -0.5 \cdot \text{l}^{3/2} \text{ mol}^{-1/2} \cdot \sqrt{I}$$

which yields for the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \lg \frac{c(\text{Ac}^-)}{c(\text{HAc})} - 0.5 \cdot \text{l}^{3/2} \text{ mol}^{-1/2} \sqrt{I}$$

The pH of solutions

The pH of solutions can be affected by:

- neutral salts, which may modify the ionic strength
- water addition, which may either change activity coefficients or act as a weak acid or base
- temperature, which changes K_a and K_w

pH buffers are therefore important in many (bio-)chemical formulations:

- in drug preparation
- preparation of creams
- buffers in blood keep pH at about 7.4 (blood outside the range 6.9 and 7.8 puts life in danger)
- tears

Isotonic solutions

As well as controlling the pH of a solution, it is often necessary to control the osmotic pressure Π of the solution; especially when membranes are involved.

If the solution on one side of a membrane has a different osmotic pressure than the other, the pressure difference will cause swelling or contraction.

Example: isotonic NaCl solution is used to wash the eye.

Tonicity describes the measurement of the osmotic pressure, but can also be defined for any other colligative property (melting point, boiling point).

Isotonic solutions: solutions that possess the same colligative properties.

Isotonic solutions: Example

The freezing point of human blood and tears is -0.52°C . Determine the mass ratio w of an isotonic NaCl solution in water ($K_f = 1.86 \text{ K kg mol}^{-1}$).

$$\Delta T_f = i \cdot K_f \cdot b$$
$$b(\text{NaCl}) = \frac{n(\text{NaCl})}{m(\text{H}_2\text{O})} \qquad w(\text{NaCl}) = \frac{m(\text{NaCl})}{m(\text{H}_2\text{O})}$$
$$b(\text{NaCl}) = \frac{n(\text{NaCl})}{m(\text{H}_2\text{O})} = \frac{m(\text{NaCl})}{m(\text{H}_2\text{O}) \cdot M(\text{NaCl})} = \frac{w(\text{NaCl})}{M(\text{NaCl})}$$

$$i(\text{NaCl}) \approx 2$$

$$\Rightarrow w(\text{NaCl}) = b(\text{NaCl}) \cdot M(\text{NaCl}) = \frac{\Delta T_f}{i \cdot K_f} \cdot M(\text{NaCl})$$

$$w(\text{NaCl}) = \frac{0.52 \text{ K}}{2 \cdot 1.86 \text{ K kg mol}^{-1}} \cdot 58 \text{ g mol}^{-1} = \frac{0.52 \cdot 58 \cdot 10^{-3}}{2 \cdot 1.86} \cdot \frac{\text{K} \cdot \text{kg} \cdot \text{mol}}{\text{mol} \cdot \text{K} \cdot \text{kg}}$$

$$w(\text{NaCl}) = 0.008 = 0.8\%$$

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections IV.3.1-IV.3.8

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Section 5.5 (pp. 169-176)
Sections 5.10 – 5.13 (pp. 190-198)