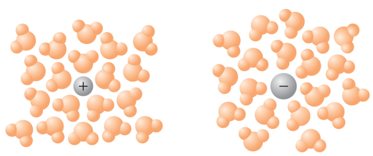
Electrolyte Solutions and biochemical applications

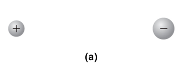
Chapter 5, Sections 5.7-5.10
(We already did most of 5.8.)

Ions in solution, hydration process



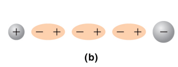
- Charge-dipole interaction causes ordering of water around ions
- Number of waters surrounding an ion is hydration number
- Hydration effects greater for small ions and highly charged ions

Forces between ions



$$F = \frac{q_{Na^+} q_{Cl^-}}{4\pi\epsilon_o r^2}$$

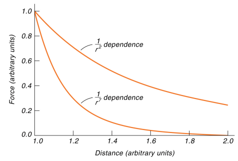
- q = charge
- ϵ_o = "permittivity of the vacuum" = 8.854×10^{-12} C^2 N^{-1} m^{-2}
- F is proportional to $1/r^2$



$$F = \frac{q_{Na^+} q_{Cl^-}}{4\pi\epsilon_o \epsilon r^2}$$

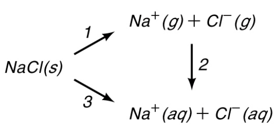
- ϵ = dielectric constant
- Effective interaction between ions reduced
- ϵ depends on solvent

Charge-Charge vs Van der Waals Interactions



- Interactions between ions are much stronger than interactions between neutral molecules
- Although not shown charge-dipole interactions are also stronger than interactions between neutrals, although weaker than charge-charge interactions

Hydration vs Solvation



1 => separate ions:
gives lattice energy (U_o)
2 => hydrate ions ($\Delta_{hydr}H$)
3 => solvate NaCl(s) = 1 + 2 ($\Delta_{soln}H$)

Often, and U_o and $\Delta_{hydr}H$ nearly balance, e.g. for NaCl:
U_o = 787 kJ/mol
$\Delta_{hydr}H$ = - 783 kJ/mol
$\Delta_{soln}H = U_o + \Delta_{hydr}H$ = 3.8 kJ/mol

Table 5.4
Thermodynamic Values for the Hydration of Gaseous Ions at 298 K

Ion	$-\Delta_{hydr}H°$ kJ · mol^{-1}	$-\Delta_{hydr}S°$ J · K^{-1} · mol^{-1}	Ionic Radius/Å
H^+	1089[a]	132[a]	—
Li^+	520	119	0.60
Na^+	405	89	0.95
K^+	314	51	1.33
Ag^+	468	94	1.26
Mg^{2+}	1926	268	0.65
Ca^{2+}	1579	209	0.99
Ba^{2+}	1309	159	1.35
Mn^{2+}	1832	243	0.80
Fe^{2+}	1950	272	0.76
Cu^{2+}	2092	259	0.72
Fe^{3+}	4355	460	0.64
F^-	506	151	1.36
Cl^-	378	96	1.81
Br^-	348	80	1.95
I^-	308	60	2.16

[a] This is a theoretical estimate.

Note trends with respect to charge and ionic radius

Enthalpy, Entropy, Gibbs Energy of Ions

Not directly measurable for an individual ion because ions come in pairs/groups, e.g.

$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$

Therefore we DEFINE:

$\Delta_f H^o[H^+(aq)] = 0$ kJ/mol

$S^o[H^+(aq)] = 0$ J K^{-1} mol^{-1}

$\Delta_f G^o[H^+(aq)] = 0$ kJ/mol

Values for other ions can be obtained by "bootstrapping" from measurements, e.g.

$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$ $\quad \Delta_r H^o = -167.2$ kJ/mol

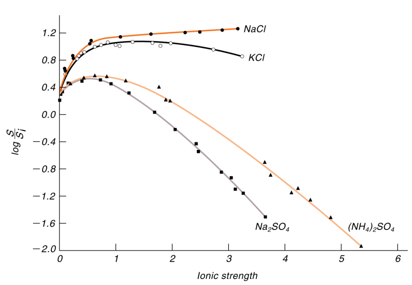
$\rightarrow \Delta_f H^o[Cl^-] = -167.2$ kJ/mol

Table 5.5
Thermodynamic Data for Aqueous Ions at 1 bar and 298 K

	$\Delta_f \overline{H}^\circ$/kJ · mol^{-1}	$\Delta_f \overline{G}^\circ$/kJ · mol^{-1}	$\overline{S}^\circ$/J · K^{-1} · mol^{-1}
H^+	0	0	0
Li^+	−278.5	−293.8	14.23
Na^+	−239.7	−261.9	60.25
K^+	−251.2	−282.3	102.5
Mg^{2+}	−462.0	−456.0	−138.1
Ca^{2+}	−543.0	−553.0	−55.23
Fe^{2+}	−87.9	−84.9	−137.7
Zn^{2+}	−152.4	−147.2	−112.1
Fe^{3+}	−47.7	−4.7	−293.3
OH^-	−229.9	−157.3	−10.54
F^-	−329.1	−276.5	−13.8
Cl^-	−167.2	−131.2	56.5
Br^-	−120.9	−102.8	80.71
I^-	−55.9	−51.7	109.37
CO_3^{2-}	−676.3	−528.1	−53.14
NO_3^-	−206.6	−110.5	146.4
PO_4^{3-}	−1284.1	−1025.6	−217.6

So for an aqueous ion can be negative! Just a consequence of arbitrarily defining $S^o[H^+(aq)] = 0$ J K^{-1} mol^{-1}. Does NOT contradict 3[rd] Law.

Salting-In and Salting-Out



Definitions

AgCl → Ag^+(aq) + Cl^-(aq)

$K_{sp}^o = a_{Ag^+}a_{Cl^-}$ thermodynamic solubility product

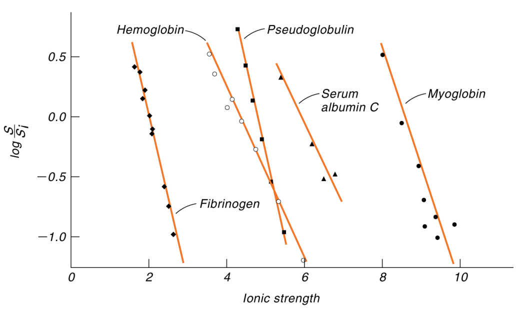
$K_{sp} = m_{Ag^+}m_{Cl^-}$ apparent solubility product

$a_+ = \gamma_+ m_+ \quad a_- = \gamma_- m_-$

$S^o = (K_{sp}^o)^{1/2}$ thermodynamic solubility

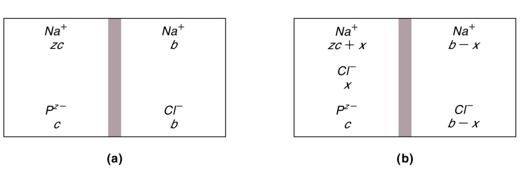
$S = (K_{sp})^{1/2}$ apparent solubility

From theory: $log_{10}\frac{S}{S^o} = 0.509|z_+z_-|\sqrt{I} - K'I$

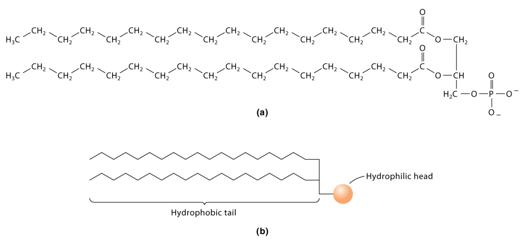


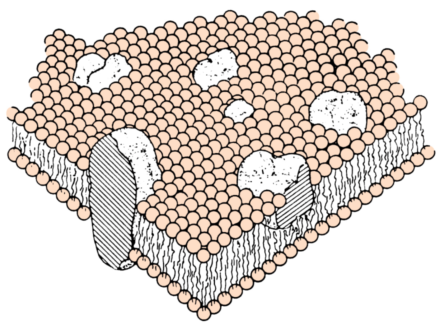
Different proteins precipitate at different ionic strengths
→Separation method

Donnan Effect



Biological Membranes

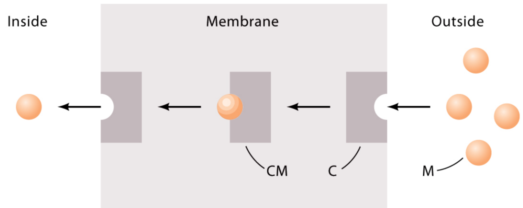




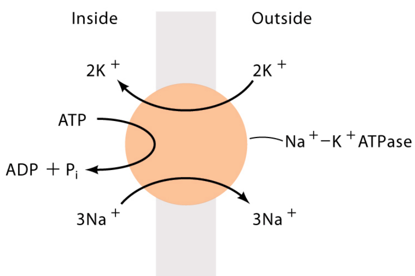
Membrane Transport

- Simple diffusion
- Facilitated diffusion
- Active transport

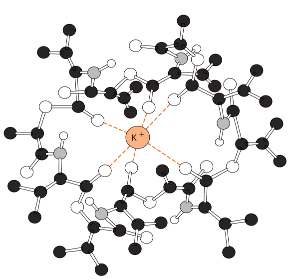
Facilitate diffusion



Sodium-potassium ATP-ase



Valinomycin



Protein forming transmembrane pore
(e.g. Gramicidin A)