Colligative Properties of Solutions

Yanovska Anna Olexandrivna

PhD physical chemistry

Senior teacher of General chemistry department

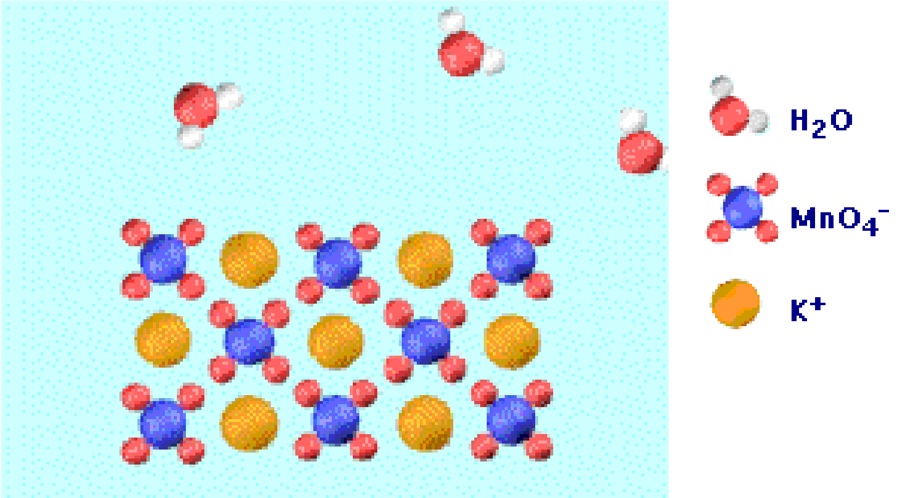
IONIC COMPOUNDS

Compounds in Aqueous Solution

Many reactions involve ionic compounds, especially reactions in water — aqueous solutions.

$KMnO_4$ in water

$K^+(aq) + MnO_4^-(aq)$

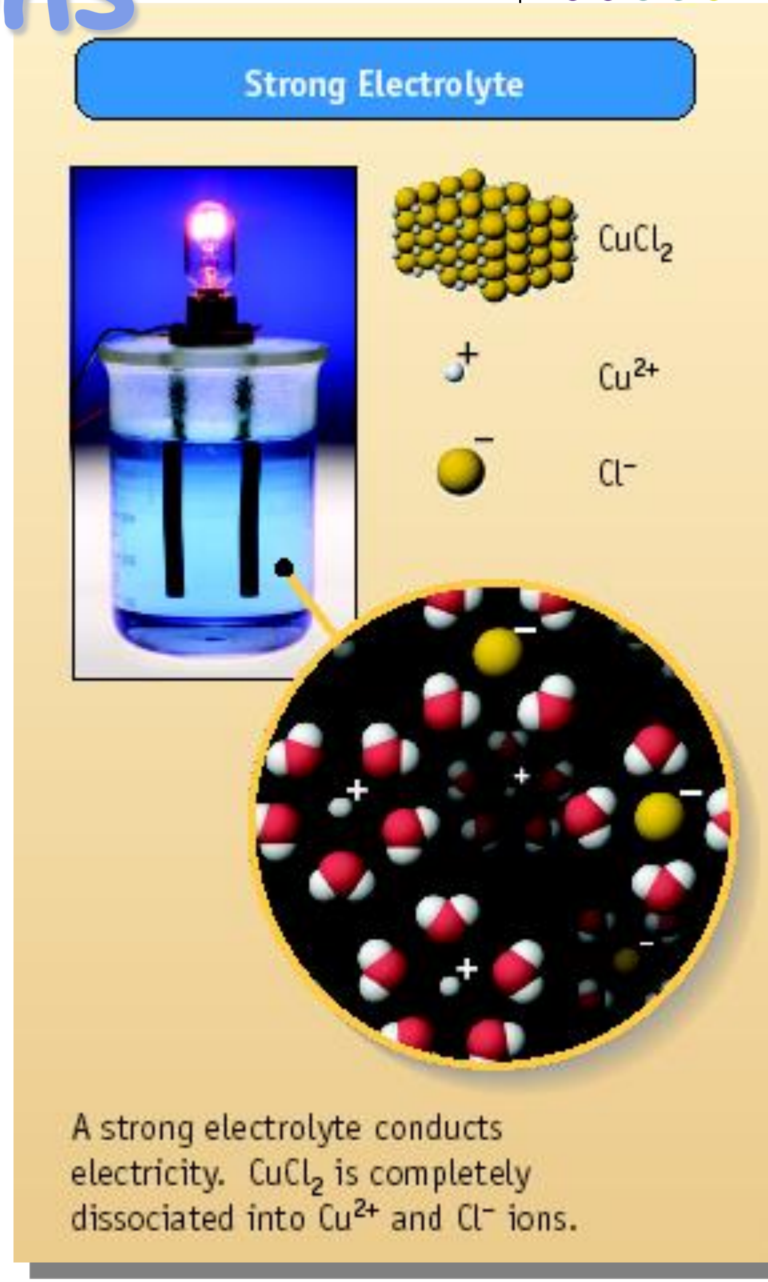


Aqueous Solutions

If compounds completely dissociates on ions they are called ELECTROLYTES

HCl, $MgCl_2$, and $NaCl$ are strong electrolytes.

Degree of dissociation α for such electrolytes is 1 or nearly 100%.



Strong Electrolyte

A strong electrolyte conducts electricity. $CuCl_2$ is completely dissociated into Cu^{2+} and Cl^- ions.

Electrolytes in the Body

- Carry messages to and from the brain as electrical signals
- Maintain cellular function with the correct concentrations electrolytes

Make your own

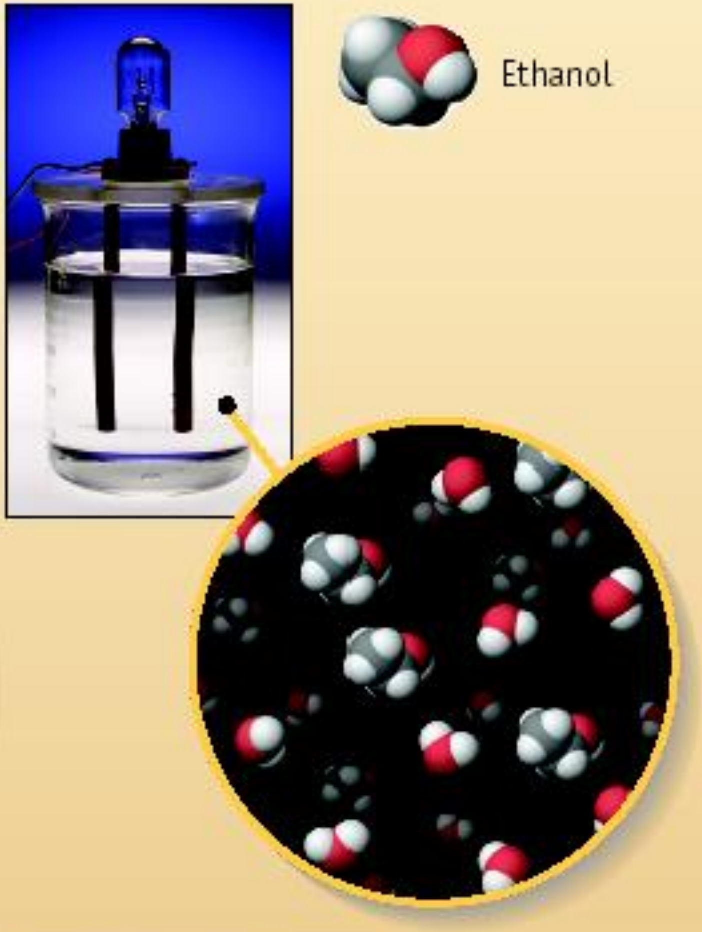
50-70 g sugar
One liter of warm water
Pinch of salt
200ml of sugar free fruit squash
Mix, cool and drink

Aqueous Solutions

Some compounds dissolve in water but do not conduct electricity. They are called nonelectrolytes.

Examples include:
- sugar
- ethanol
- ethylene glycol

Nonelectrolyte



A nonelectrolyte does not conduct electricity because no ions are present in solution.

Constant of dissociation for weak electrolytes

$$Kt_xAn_y \Leftrightarrow xKt^{y+} + yAn^{x-}.$$

$$K = \frac{[Kt^{y+}]^x \cdot [An^{x-}]^y}{[Kt_xAn_y]},$$

$$[Kt^+] = [An^-] = \alpha C,$$

$$[KtAn] = C - \alpha C = C(1 - \alpha).$$

$$Kd = \frac{[Kt^+]\,[An^-]}{[KtAn]} = \frac{\alpha C \cdot \alpha C}{C(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha}.$$

$$K = \alpha^2 C,$$

$$\alpha = \sqrt{K / C}\,.$$

- In our life we can see decreasing of freezing point by adding salt on the road. Due to this road is free of snow and ice.

Colligative properties

- Properties of ideal solutions don’t depend on nature of the solute they only depend on its concentration.
- So properties that depend only on the number of solute particles and not on their identity named – ***colligative properties:***
- Vapor pressure lowering
- Boiling point elevation
- Freezing Point depression

Colligative Properties

On adding a solute to a solvent, the properties of the solvent are modified.

- Vapor pressure decreases
- Melting point decreases
- Boiling point increases
- Osmosis is possible (osmotic pressure)

These changes are called COLLIGATIVE PROPERTIES.

They depend only on the NUMBER of solute particles relative to solvent particles, not on the KIND of solute particles.

Vapour pressure depression

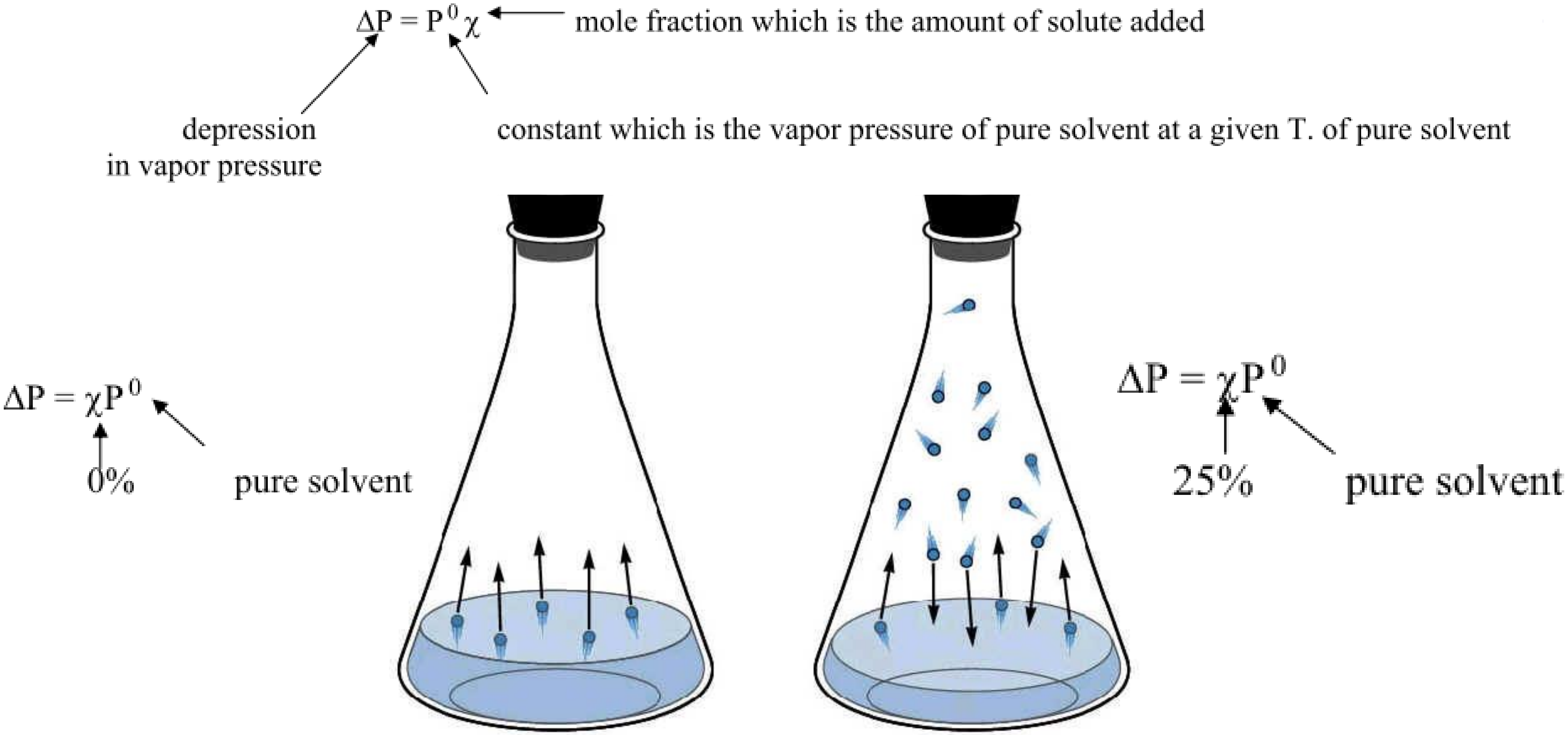
The Raoult's law: The relative depression of the saturated vapour pressure of a solvent over a solution equals the mole fraction of the solute.

The mathematical expression of the first Raoult's law is:

$$\frac{P_o - P_s}{P^o} = \frac{n_2}{n_1 + n_2},$$

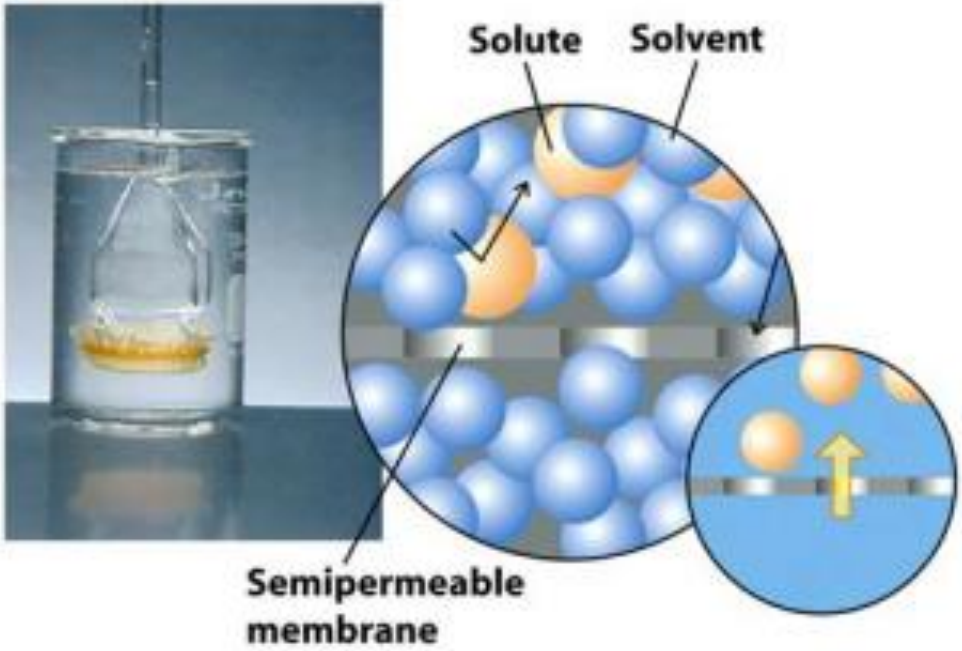
where p^o – vapour pressure of the solvent,
P_s – vapour pressure of the solution,
n_2 – number of moles of the solute,
n_1 – number of moles of the solvent,

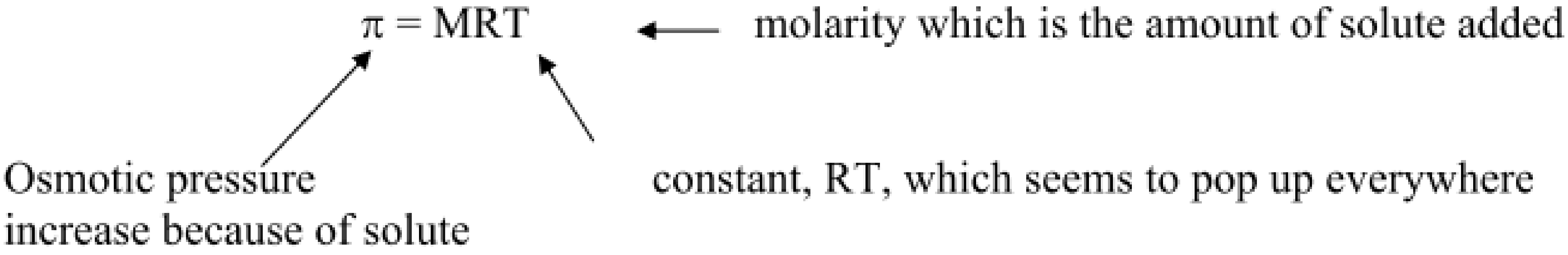
Vapour pressure depression



- The particles of solute are surrounded by and attracted to particles of solvent.
- Now the solvent particles have less kinetic energy and tend less to escape into the space above the liquid.
- So the vapor pressure is less.

P osmotic= C_MRT





$\pi = MRT$

molarity which is the amount of solute added

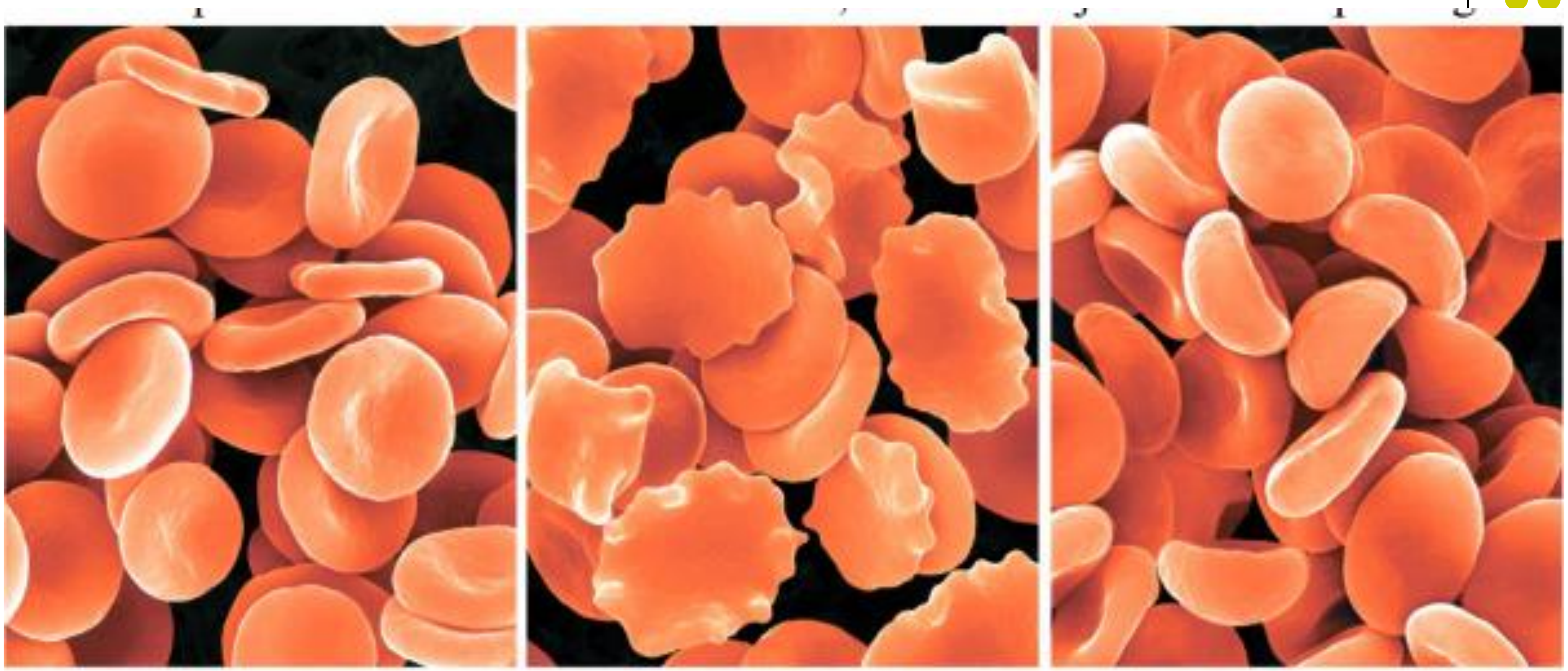
Osmotic pressure increase because of solute

constant, RT, which seems to pop up everywhere

The constants R and T are the ideal gas law constant and the system temperature

So the osmotic pressure change is $\pi = MRT = (1.17\ M)(0.082)(298\ K) =$ **28.6 atm**

Isotonic, hypotonic and hypertonic solutions



The solution around the cells has the same concentrations like inside of them (first picture), too high concentration in which case the water flows out of the cell and they shrivel up (second picture), or too low concentration in which case water flows into the cells and they lyse or rupture (third picture.)

- **Example** 1.2 L of solution contains 20.5 mg of sucrose ($C_{12}H_{22}O_{11}$). Calculate the osmotic pressure of the solution at 22ºC.
- **Solution**

$$M(C_{12}H_{22}O_{11}) = 342\,g/mol$$

$$C_M = \frac{n(C_{12}H_{22}O_{11})}{V(solution)} = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11})\cdot V(solution)} = \frac{20.5\cdot 10^{-2}\,g}{342\,g/mol\cdot 1.2\,L} = 5.0\cdot 10^{-5}\,mol/L$$

$$P_{osmotic} = \mathrm{C_M RT} = 5.0\cdot 10^{-5}\,\mathrm{mol/L}\cdot 8.314\,\mathrm{J/mol}\cdot\mathrm{K}\cdot 295\,\mathrm{K} = 0.123\ \mathrm{kPa} = 123\,\mathrm{Pa.}$$

Answer: $P_{osmotic}$=123 Pa.

Ionic vs Molecular Solutes
Electrolytes vs Non electrolytes

- Ionic solutes produce two or more ion particles in solution.
- They affect the colligative properties proportionately more than molecular solutes (that do not ionize).
- The effect is proportional to the **number of particles of the solute in the solution.**

$$Kt_xAn_y \Leftrightarrow xKt^{y+} + yAn^{x-}.$$

$$nAl_2(SO_4)_3 \rightarrow 2nAl^{3+} + 3nSO_4^{2-}$$

Freezing Point Depression and Boiling Point Elevation

Boiling Point Elevation

- **$\Delta T_b = k_b \, Cm$** (for water k_b=0.51 $^oC/m$)

- Freezing Point Depression
- **$\Delta T_f = k_f \, Cm$** (for water k_f=1.86 $^oC/m$)

- **Note**: C**m is the molality of the particles**, so if the solute is ionic, multiply by the ***i -Vant Hoff coefficient*** of particles it dissociates to (ν).
- **$i=1+\alpha(\nu-1)$**

Boiling Point Elevation and Freezing Point Depression

$$\Delta T = K \cdot Cm \cdot i$$

i = van’t Hoff factor = number of particles produced per molecule/formula unit. For covalent compounds, i = 1. For ionic compounds, i = the number of ions present (both + and -)

Compound	Theoretical Value of **i**
glycol	1
NaCl	2
$CaCl_2$	3
$Ca_3(PO_4)_2$	5

Boiling Point Elevation and Freezing Point Depression

$$\Delta T = K \cdot Cm \cdot i$$

Cm = molality

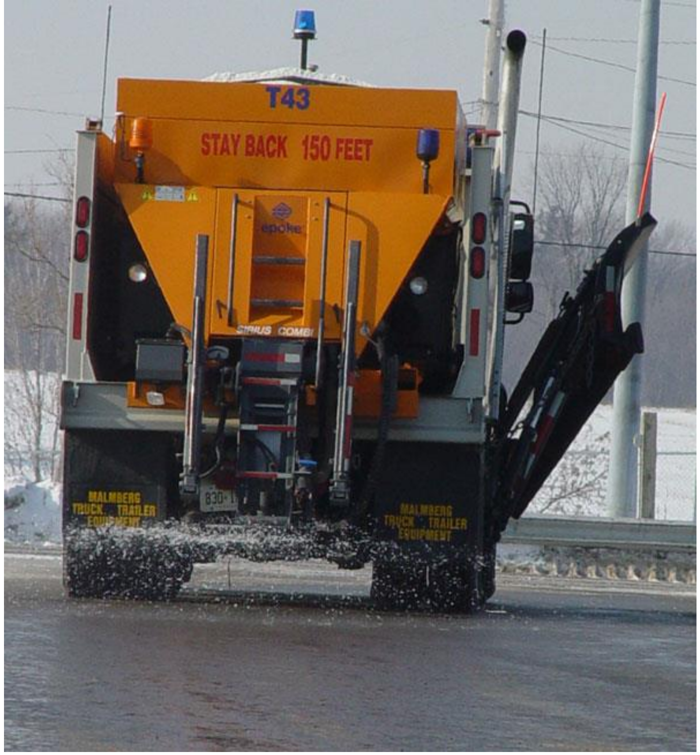
K = molal freezing point/boiling point constant

Substance	K_f
benzene	5.12
camphor	40.
carbon tetrachloride	30.
ethyl ether	1.79
water	1.86

Substance	K_b
benzene	2.53
camphor	5.95
carbon tetrachloride	5.03
ethyl ether	2.02
water	0.52

How many particles do each of the following give upon solvation?

- NaCl
- $CaCl_2$
- Glucose



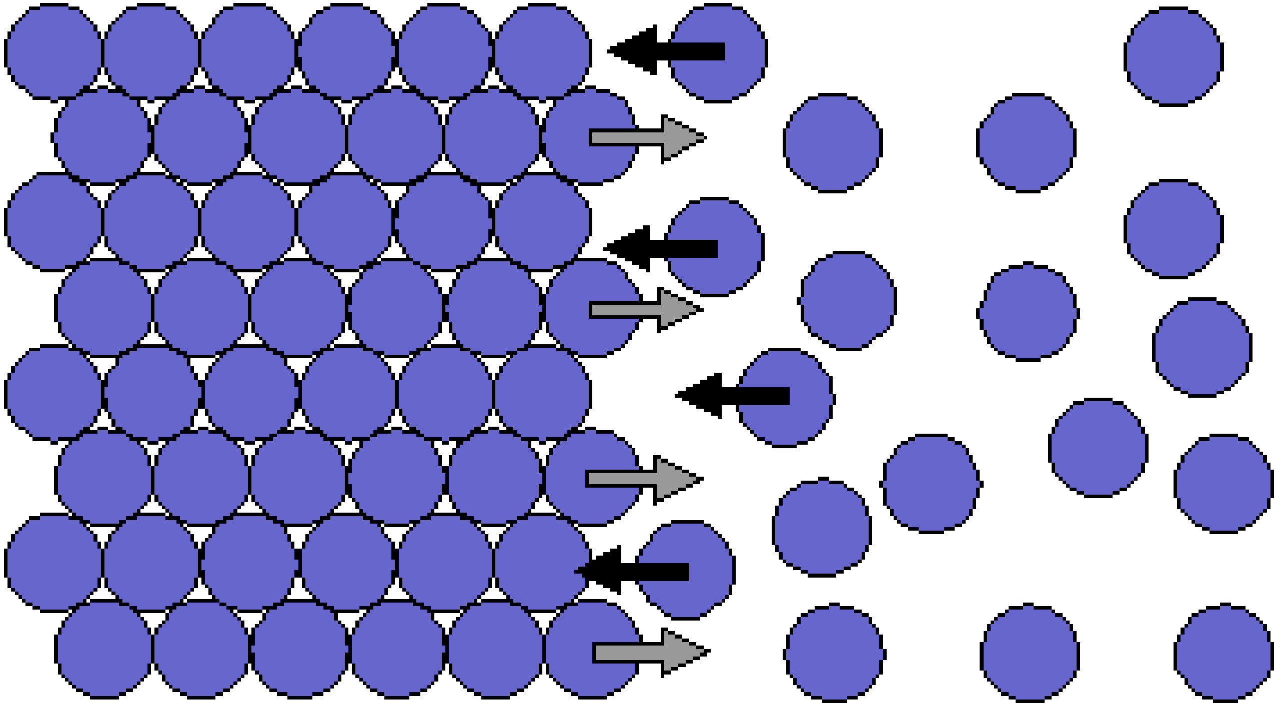
Which is more effective for lowering the freezing point of water? NaCl, $CaCl_2$ or Glucose

$$\Delta T_f = K\mathit{f}\ \mathrm{K \cdot kg/mol} \cdot \frac{\mathrm{m\,(solute)g \cdot 1000}}{\mathrm{M(solute)g/mol \cdot m(H_2O)g}}$$

$$\Delta T_b = K_b\ \mathrm{K \cdot kg/mol} \cdot \frac{\mathrm{m\,(solute)g \cdot 1000}}{\mathrm{M(solute)g/mol \cdot m(H_2O)g}}$$

Freezing Point Depression

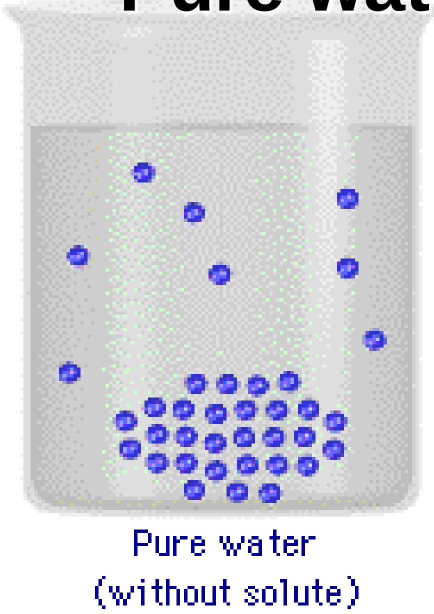
$$\Delta T_f = Kf \cdot Cm \qquad \Delta T_f = i \cdot Kf \cdot Cm$$

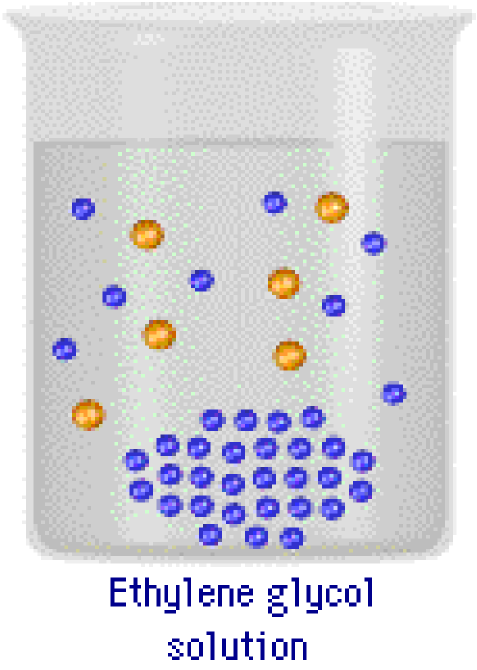


Change in Freezing Point

Ethylene glycol/water solution

Pure water





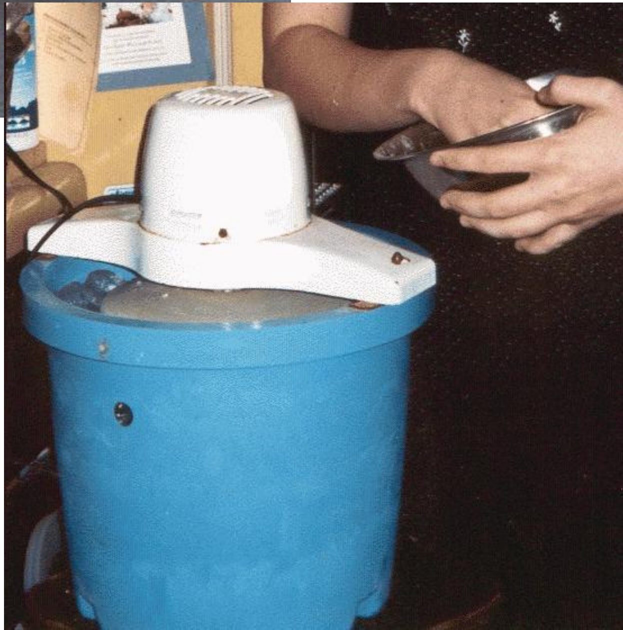
The freezing point of a solution is LOWER than that of the pure solvent

Change in Freezing Point

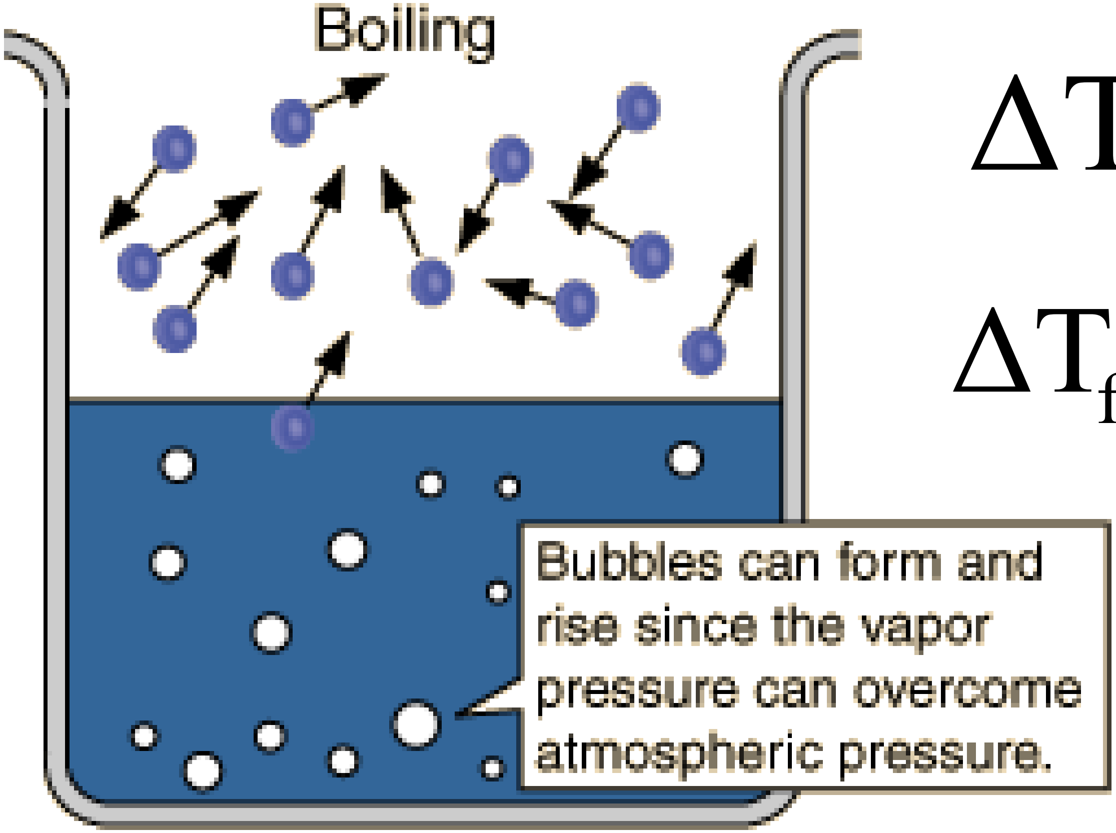
Common Applications of Freezing Point Depression

Propylene glycol

Ethylene glycol – deadly to small animals



Boiling Point Elevation



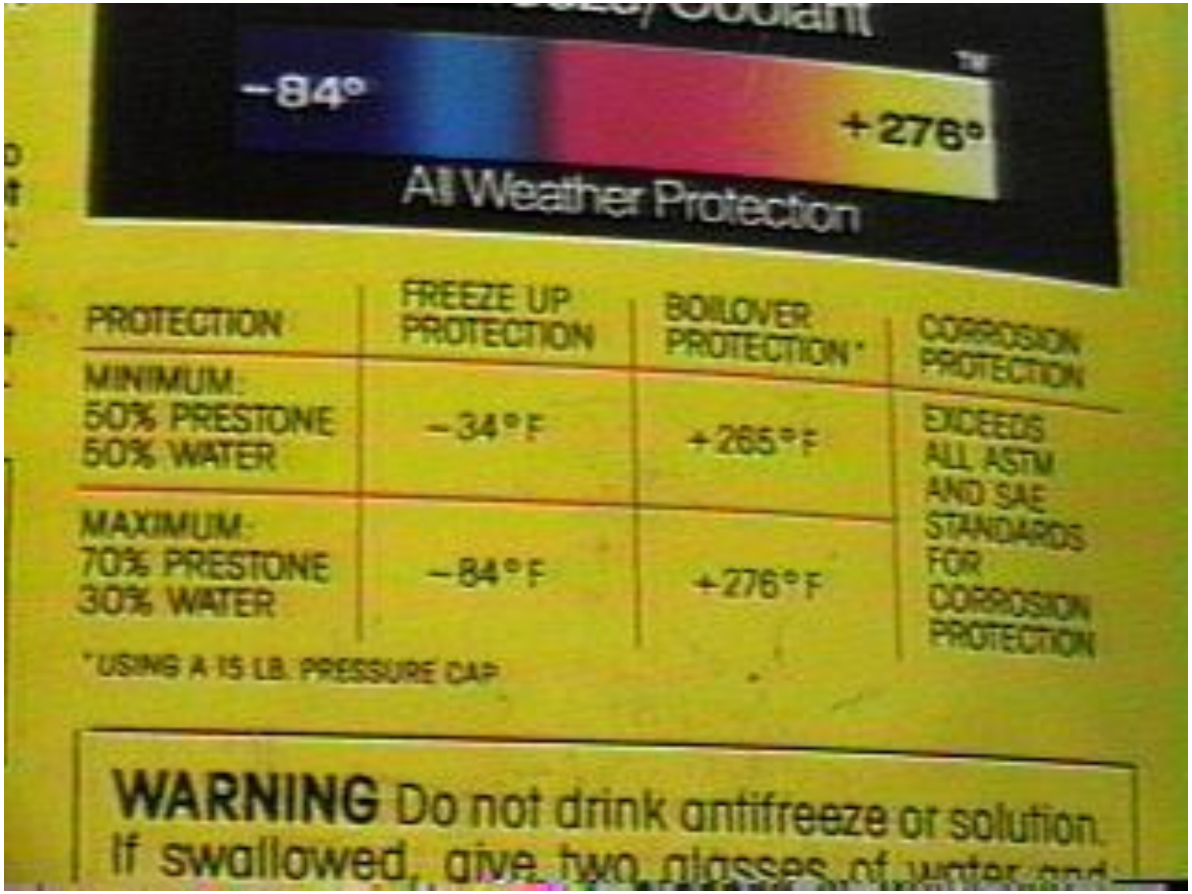
Bubbles can form and rise since the vapor pressure can overcome atmospheric pressure.

$$\Delta T_f = Kf \cdot Cm$$

$$\Delta T_f = i \cdot Kf \cdot Cm$$

Change in Boiling Point

Common Applications of Boiling Point Elevation



-84°

+276°

All Weather Protection

PROTECTION	FREEZE UP PROTECTION	BOILOVER PROTECTION*	CORROSION PROTECTION
MINIMUM: 50% PRESTONE 50% WATER	-34°F	+265°F	EXCEEDS ALL ASTM AND SAE STANDARDS FOR CORROSION PROTECTION
MAXIMUM: 70% PRESTONE 30% WATER	-84°F	+276°F	

*USING A 15 LB. PRESSURE CAP

WARNING Do not drink antifreeze or solution. If swallowed, give two glasses of water and

Change in Boiling Point

Dissolve 62.1 g of glycol (1.00 mol) in 250. g of water. What is the boiling point of the solution?

K_b = 0.52 °C/molal for water (see K_b table).

Solution $\Delta T_{BP} = K_b \cdot Cm \cdot i$

1. Calculate solution molality = 4.00 m
2. $\Delta T_{BP} = K_b \cdot Cm \cdot i$

   $\Delta T_{BP} = 0.52\ ^{o}C/molal\ (4.00\ molal)\ (1)$

   $\Delta T_{BP} = 2.08\ ^{o}C$

   BP = 100 + 2.08 = 102.08 °C

   (water normally boils at 100)

Freezing Point Depression

At what temperature will a 5.4 molal solution of NaCl freeze?

Solution

$$\Delta T_{FP} = K_f \cdot Cm \cdot i$$

$$\Delta T_{FP} = (1.86\ {}^{o}C/molal) \cdot 5.4\ mol/kg \cdot 2$$

$$\Delta T_{FP} = 20.1\ {}^{o}C$$

$FP = 0 – 20.1 = -20.1\ {}^{o}C$

pH of Solutions. Buffers. Hydrolysis

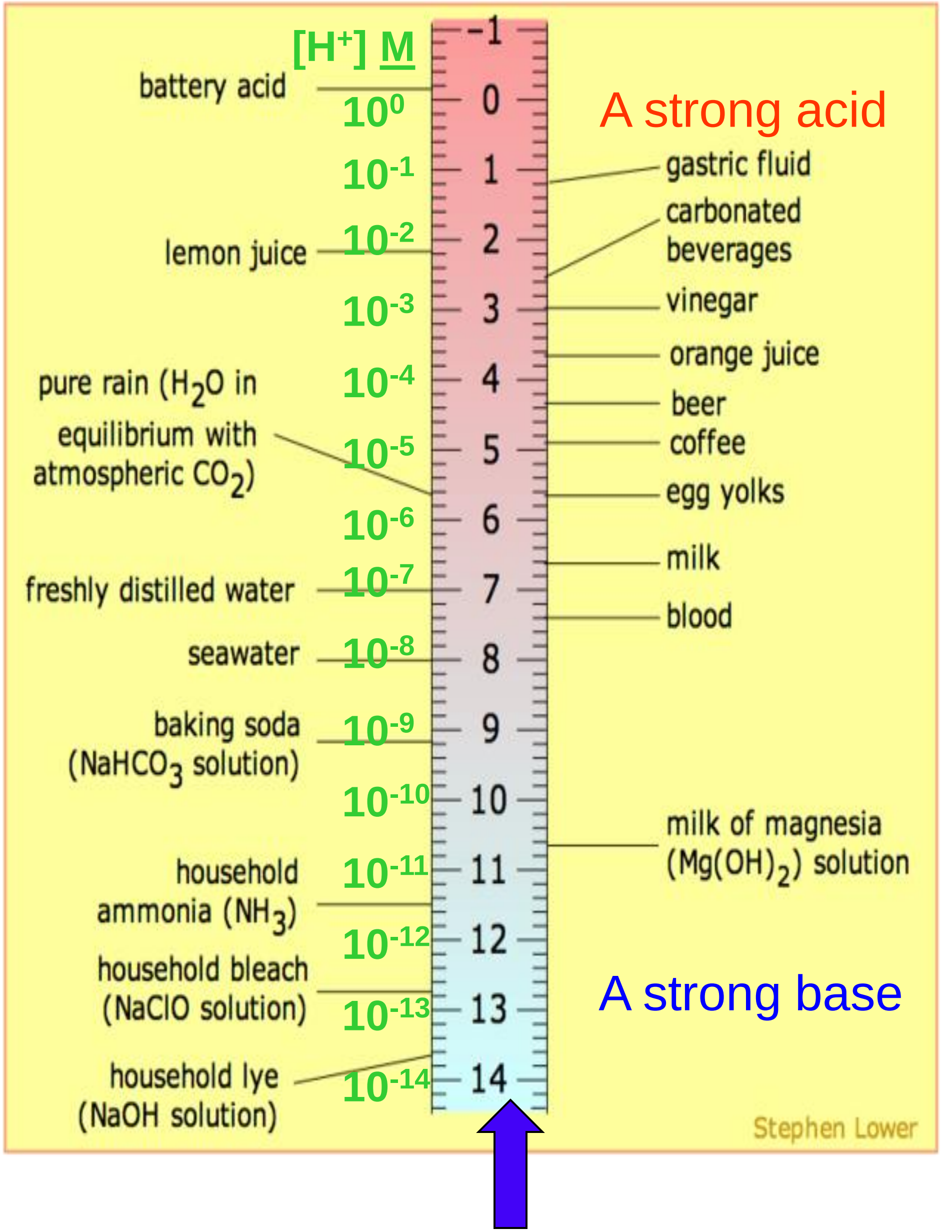
What is an Acid?

- An acid is a substance which, when dissolved in water, releases protons.
- The extent of dissociation, that is, the amount of protons released compared to the total amount of compound, is a measure of the strength of the acid.
- For example, HCl (hydrochloric acid) is a strong acid, because it dissociates completely in water, generating free $[H^+]$ and $[Cl^-]$.
- Acidity can be measured on a scale called pH (more scarily, “the negative logarithm of the hydrogen ion concentration”).

$$pH = -\log [H^+]$$

pH

SOURCE: http://en.wikipedia.org/wiki/Image:PH_scale.png#file



- Most living cells have a *very* narrow range of tolerance for pH, i.e. $[H^+]$.
- The $[H^+]$ concentration will be important (either explicitly or implicitly) for many other topics in biology.
- $[H^+]$ is controlled in all biological organisms, and in virtually all biochemical experiments.
- Each pH unit represents a factor of 10 difference in $[H^+]$.

The pH scale goes from 0 to 14—because $[H^+][OH^-] = 10^{-14}$

Question: In an aqueous solution where the H^+ concentration is 1×10^{-6} M, the OH^- concentration must be:

A. 14×10^{-6} M
B. 1×10^{-6} M
C. 1×10^{-7} M
D. 1×10^{-8} M
E. 14×10^{-8} M

How Can You Actually Determine the pH of a Solution?

- Use a pH meter—read the number.
- Use pH paper (color patterns indicate pH).
- Titrate the solution with precise amounts of base or acid in conjunction with a soluble dye, like phenolphthalein, whose color changes when a specific pH is reached.

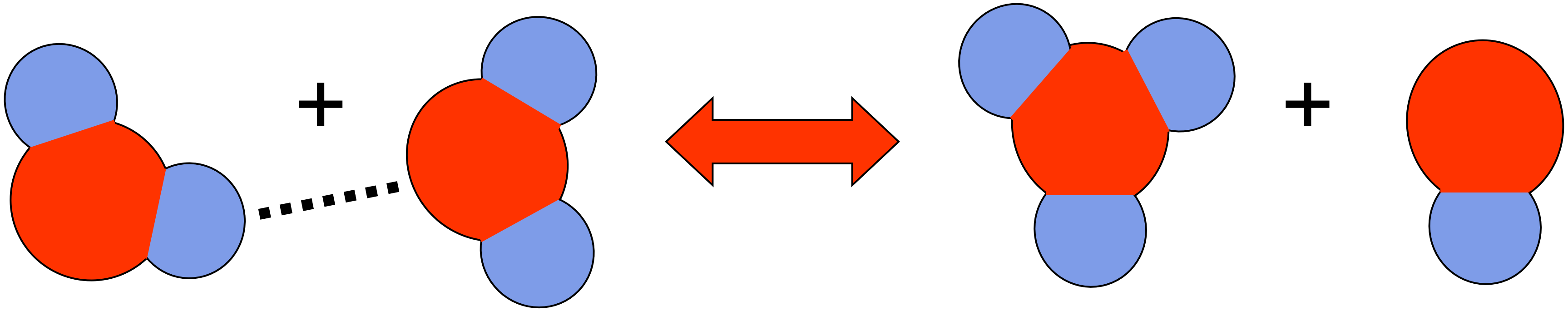
Weak acids thus are in equilibrium with their ionized species:

Governed by the Law of Mass Action, and characterized by an ***equilibrium constant***:

$$HA \longleftrightarrow H^+ + A^-$$

$$K_{eq} = \frac{[H^+][A^-]}{[HA]}$$

Water: A Very Weak Acid



$2\,H_2O$

hydronium ion
H_3O^+
(an acid)

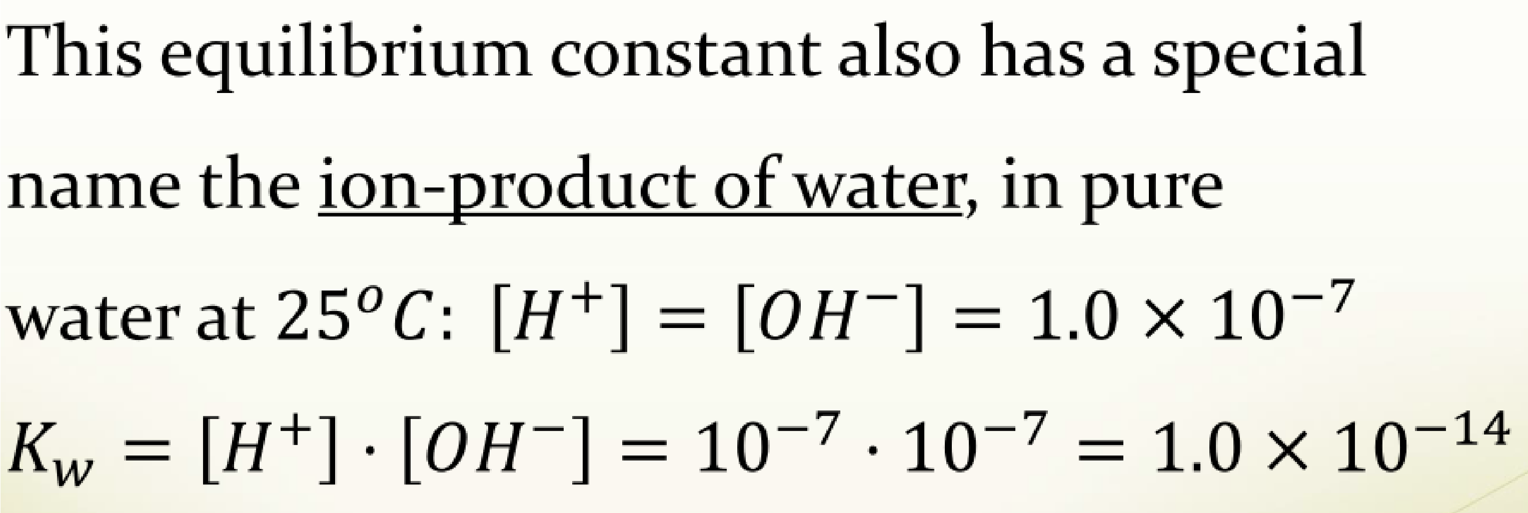
+

hydroxide ion
OH^-
(a base)

But this hardly happens at all: In fact, at equilibrium,
$[H^+] = [OH^-] = 0.0000001\ M = 10^{-7}\ M = pH\ 7$

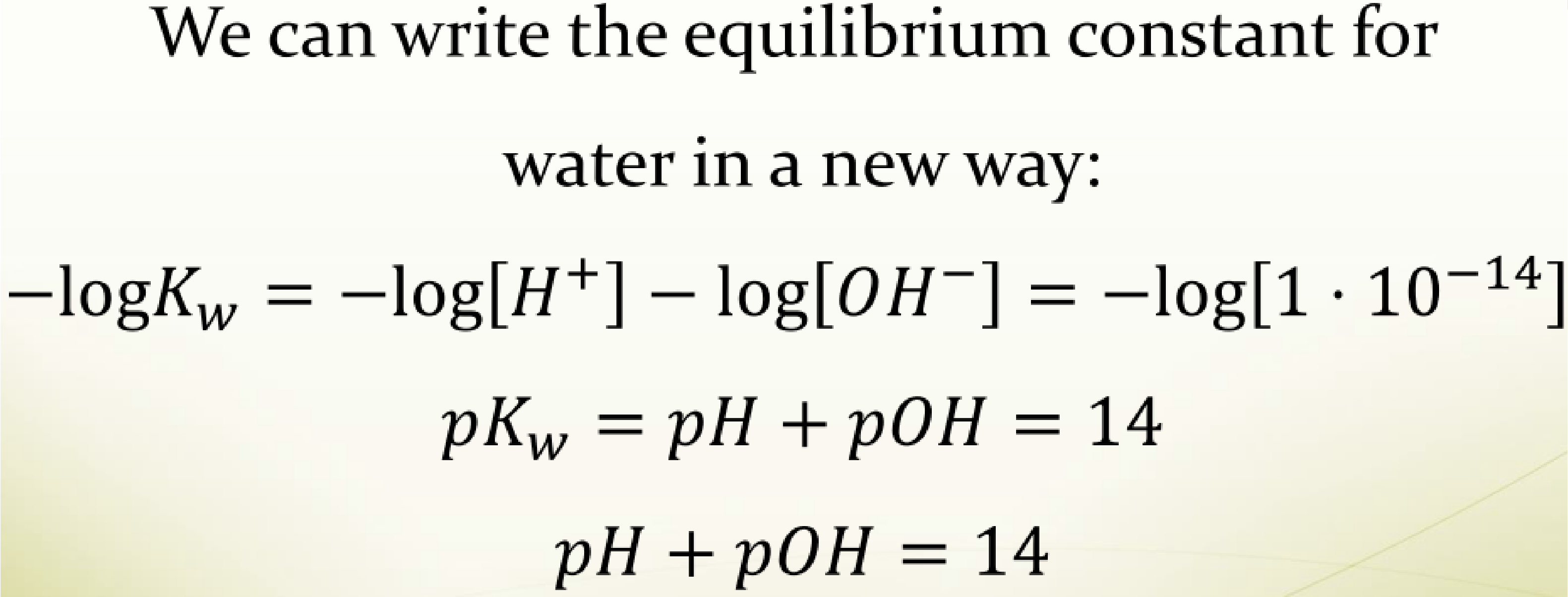
Indeed, only two of every 10^9 (1 billion) molecules in pure water are ionized at any instant - ***Can you confirm this?***

Equilibrium constant for water



This equilibrium constant also has a special name the ion-product of water, in pure water at 25°C: $[H^+] = [OH^-] = 1.0 \times 10^{-7}$

$$K_w = [H^+] \cdot [OH^-] = 10^{-7} \cdot 10^{-7} = 1.0 \times 10^{-14}$$



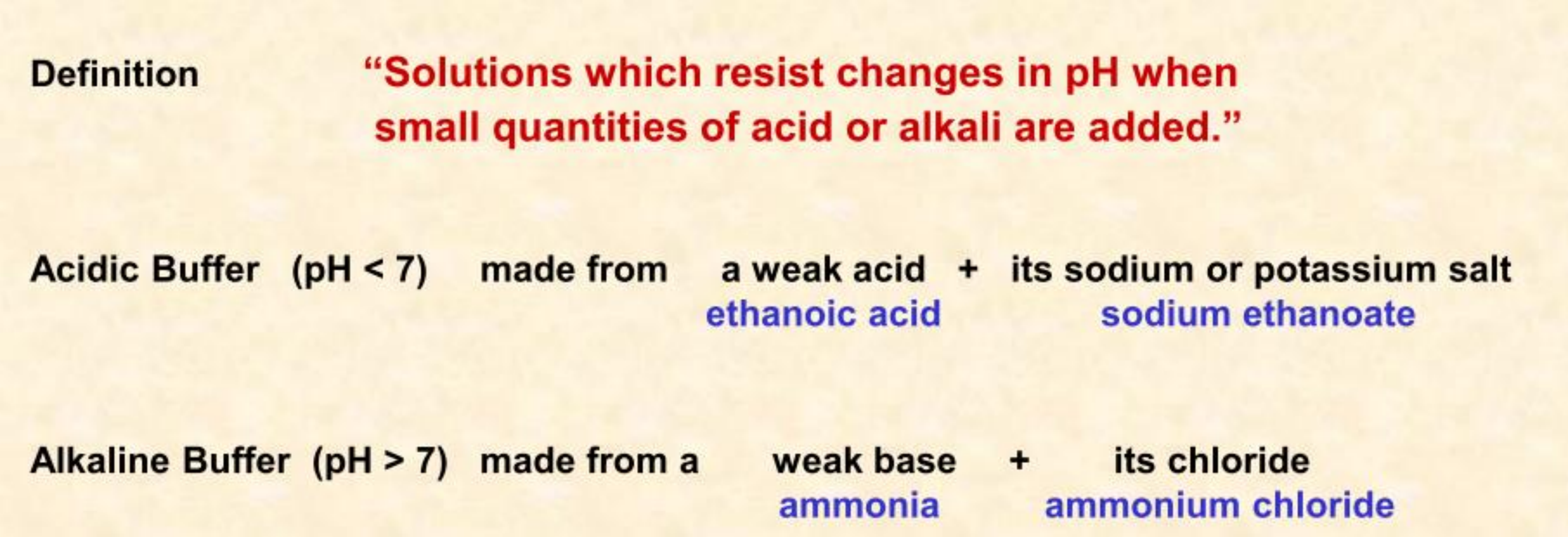
We can write the equilibrium constant for water in a new way:

$$-\log K_w = -\log[H^+] - \log[OH^-] = -\log[1 \cdot 10^{-14}]$$

$$pK_w = pH + pOH = 14$$

$$pH + pOH = 14$$

Buffer solutions



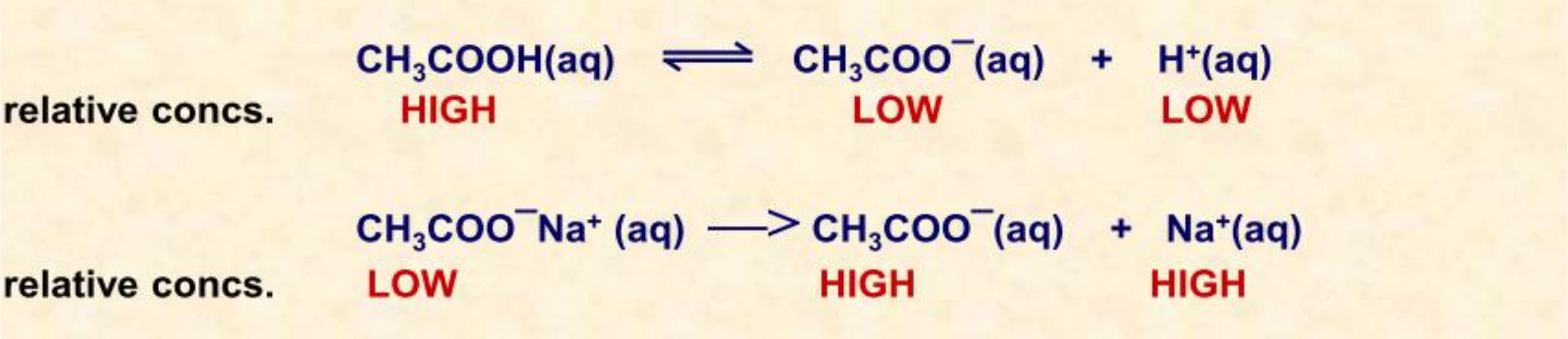
Definition "Solutions which resist changes in pH when small quantities of acid or alkali are added."

Acidic Buffer (pH < 7) made from a weak acid + its sodium or potassium salt

ethanoic acid sodium ethanoate

Alkaline Buffer (pH > 7) made from a weak base + its chloride

ammonia ammonium chloride

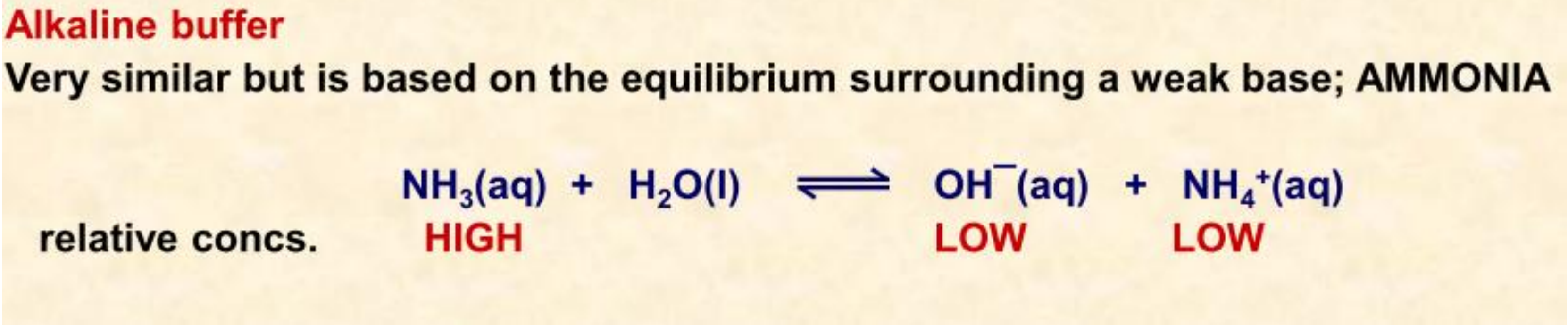


$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

relative concs. HIGH LOW LOW

$CH_3COO^-Na^+(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$

relative concs. LOW HIGH HIGH



Alkaline buffer

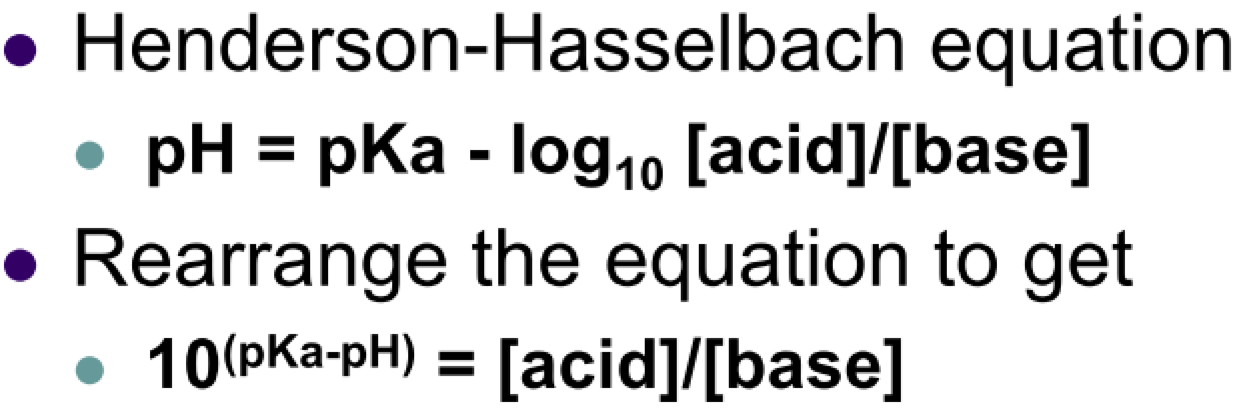
Very similar but is based on the equilibrium surrounding a weak base; AMMONIA

$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

relative concs. HIGH LOW LOW

Weak acids, their conjugate bases, and buffers…

- Weak acids have only a modest tendency to shed their protons (definition of an acid).
- When they do, the corresponding negatively charged anion becomes a willing proton acceptor, and is called the *conjugate base.*
- The properties of a *buffer* rely on a balance between a weak acid and its conjugate base.



- Henderson-Hasselbach equation
  - **$pH = pKa - \log_{10} [acid]/[base]$**
- Rearrange the equation to get
  - **$10^{(pKa-pH)} = [acid]/[base]$**

Example

- You want to make about 500 mL of 0.2 M acetate buffer (acetic acid + sodium acetate), pH 4.0.
- Look up pKa and find it is 4.8.
- **$10^{(4.8 - 4.0)} = 10^{0.8} = 6.3 =$ [acid]/[base]**
- If you use 70 mL of base, you will need 6.3X that amount of acid, or 441 mL. Mix those together and you have 511 mL (close enough).

Buffer solutions

- Definition: a solution that resists change in pH
  - Typically a mixture of the acid and base form of a chemical
  - Can be adjusted to a particular pH value

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Blood: pH = 7.35-7.45

$$[H+] = K_a \times [acid]/[base]$$

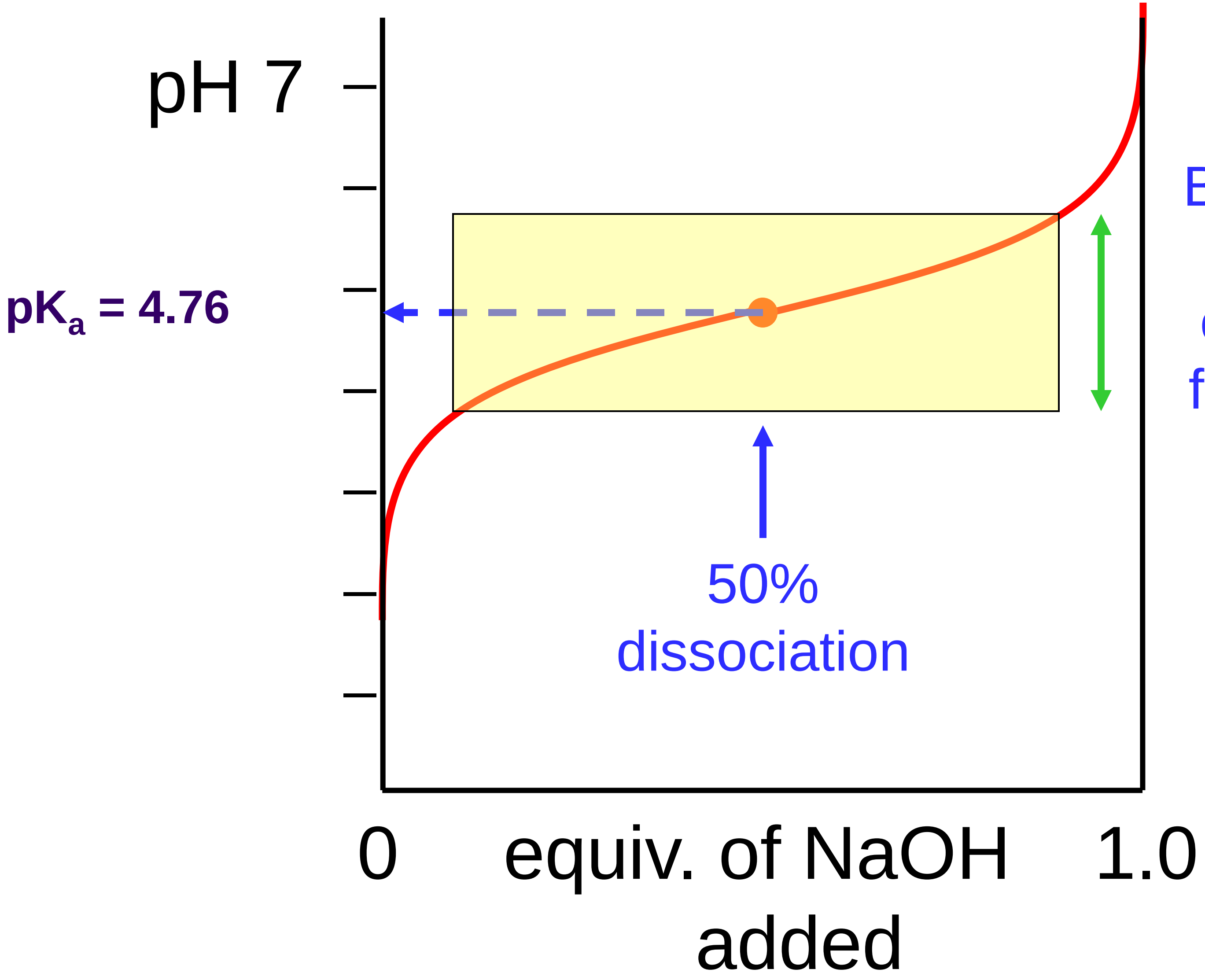
Then take the log of both sides

- $\log_{10}[H+] = \log_{10}K_a + \log_{10} [acid]/[base]$

Henderson-Hasselbach equation

- **$pH = pKa - \log_{10} [acid]/[base]$**

Titration of acetic acid with sodium hydroxide



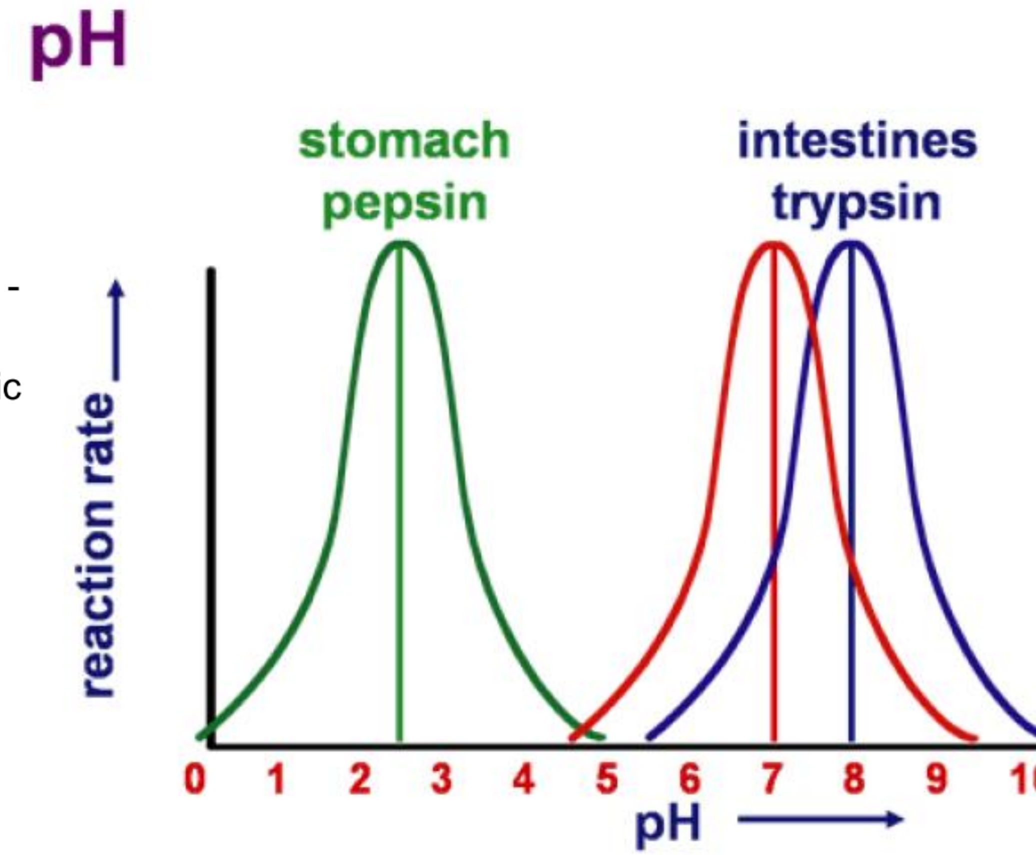
Buffering range: only small pH changes result from addition of base or acid

Ways to measure pH

- Indicator dyes and test strips
  - Less precise
  - Each indicator is only good for a small pH range (1-2 pH units)
  - But may be good for field usage, or measuring small volumes, or dealing with noxious samples.

Why is pH important in biology?

- pH affects solubility of many substances.
- pH affects structure and function of most proteins - including enzymes.



- pH affects solubility of many substances.
- pH affects structure and function of most proteins - including enzymes.
- Many cells and organisms (esp. plants and aquatic animals) can only survive in a specific pH environment.

Hydrolysis

This reaction, in which water reacts with an ionic species in solution, is called hydrolysis.

Salts of strong acids and strong bases (for example, NaCl) do not hydrolyze: PH=7

$$NaCl + H_2O = no\ reaction$$

Salts of weak acids and strong bases (for example CH_3COONa) hydrolyze, producing a basic solution: pH>7.

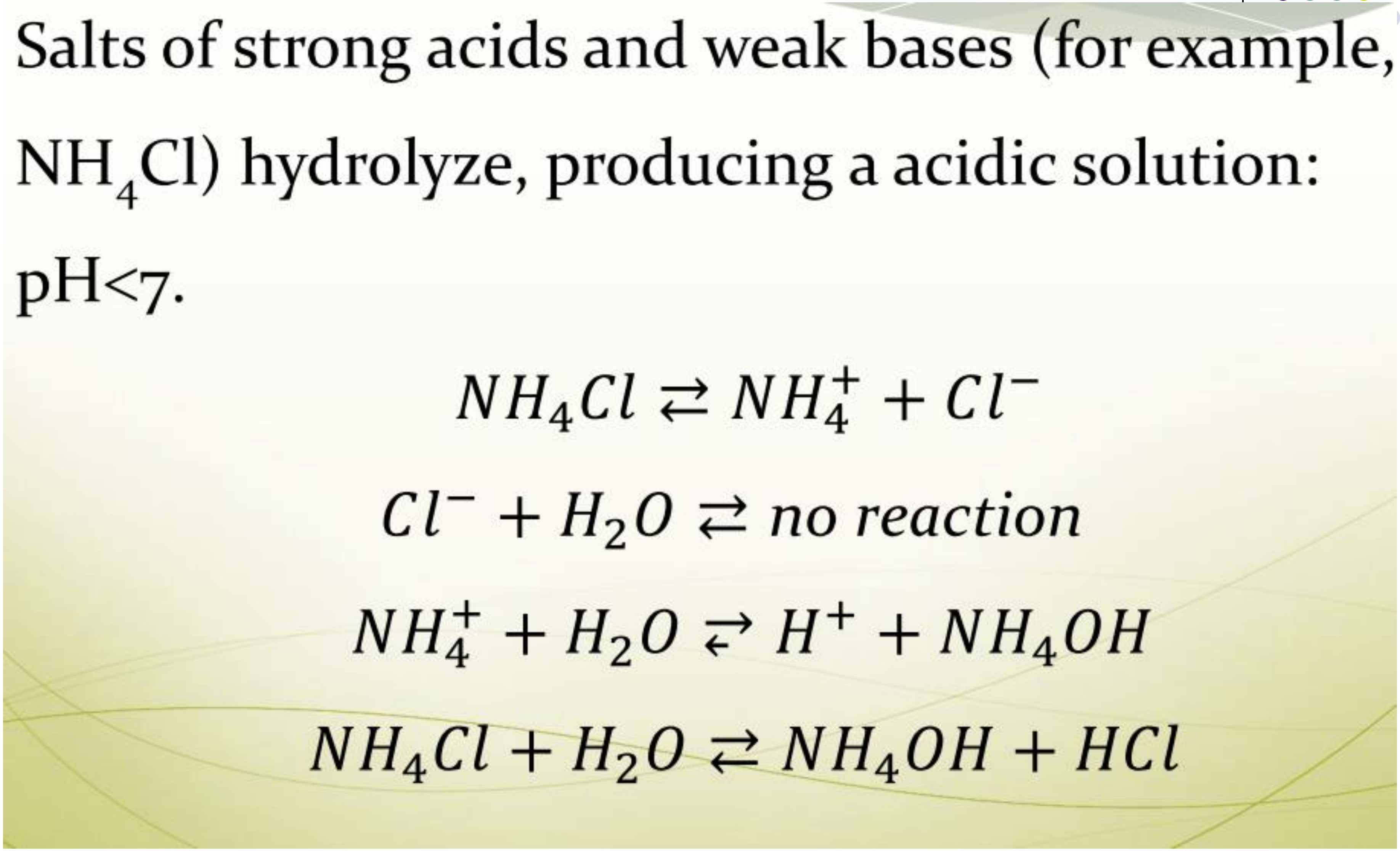
$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH$$

$$CH_3COO^- + Na^+ + HOH \rightleftarrows CH_3COOH + Na^+ + OH^-$$

$$Na^+ + HOH = no\ reaction$$

Water reacts with a CH_3COO^- to produce OH^-.

A solution of CH_3COONa has a pH>7.



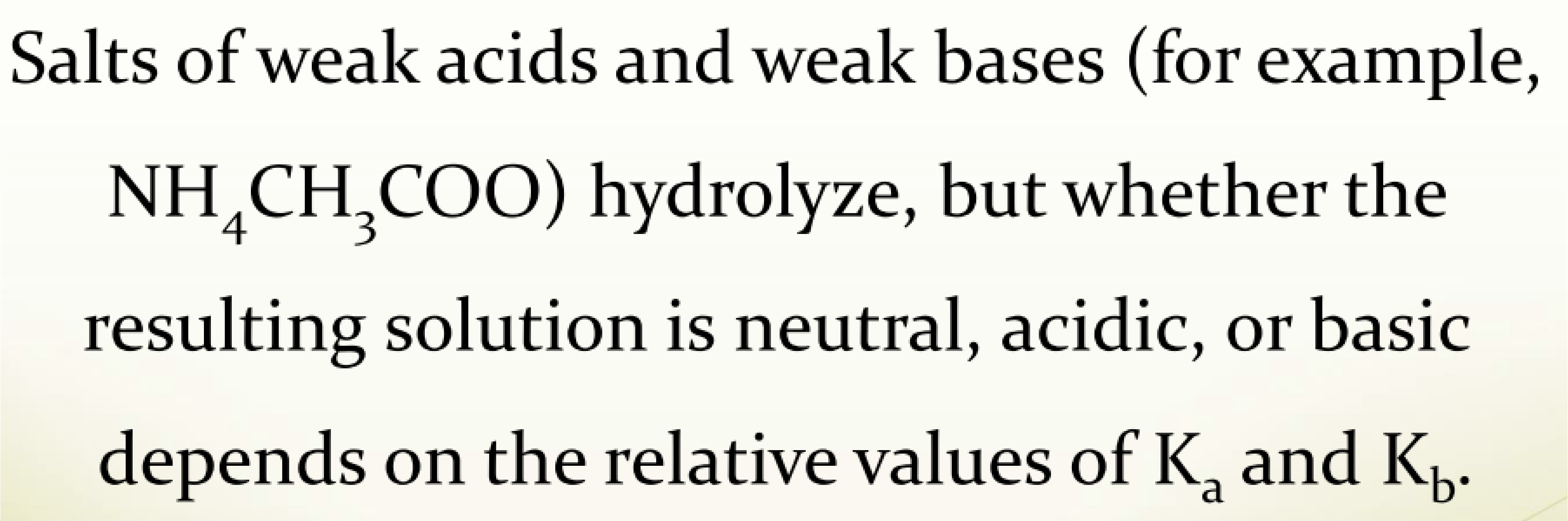
Salts of strong acids and weak bases (for example, NH_4Cl) hydrolyze, producing a acidic solution: pH<7.

$$NH_4Cl \rightleftarrows NH_4^+ + Cl^-$$

$$Cl^- + H_2O \rightleftarrows \textit{no reaction}$$

$$NH_4^+ + H_2O \rightleftarrows H^+ + NH_4OH$$

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl$$



Salts of weak acids and weak bases (for example, NH_4CH_3COO) hydrolyze, but whether the resulting solution is neutral, acidic, or basic depends on the relative values of K_a and K_b.

Find more: http://www.chem.teset.sumdu.edu.ua

Thank you for your attention!