

Today's class:

Physical and chemical properties of water

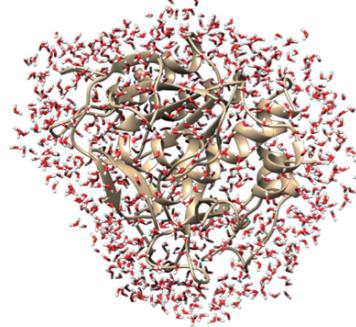
*This lecture follows the parts of chapters 5, 9 and 12 from the book
‘Physical Biology of the Cell’ by Philips, Kondev, Theriot and Garcia , 2nd Ed*

Importance of water in life

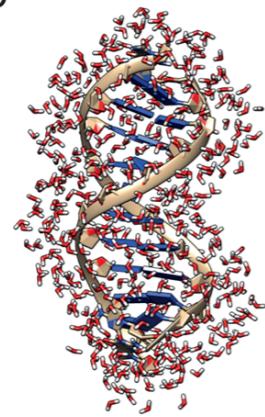
All life on earth depend on water. All the molecules of life inhabit a watery medium.

How does water interact with life?

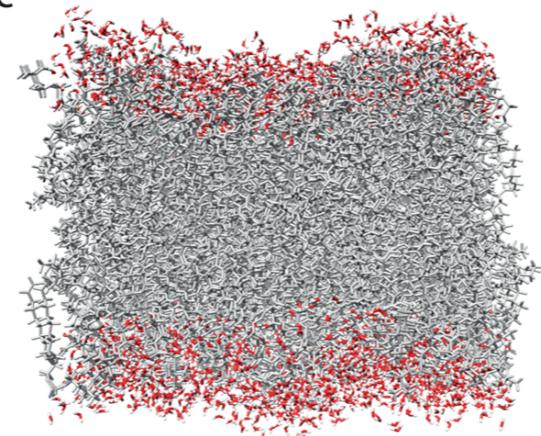
a



b



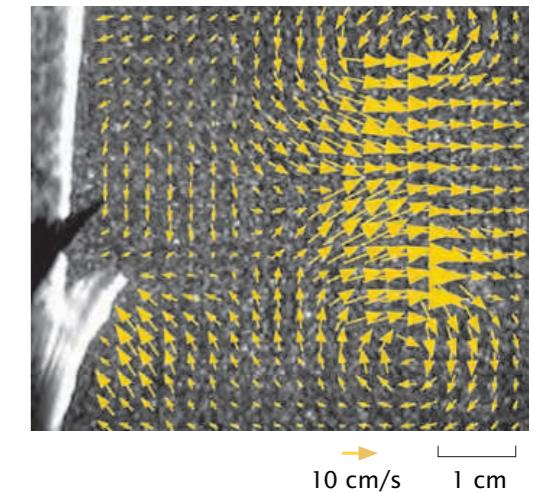
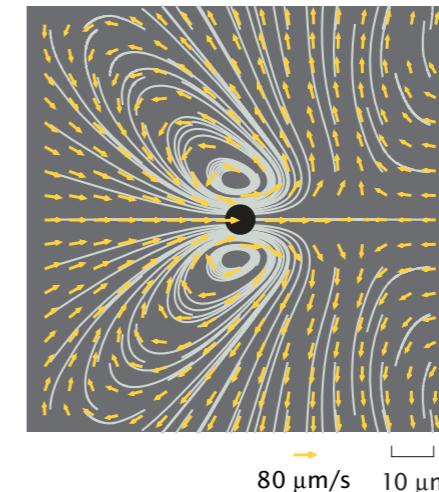
c



(A)



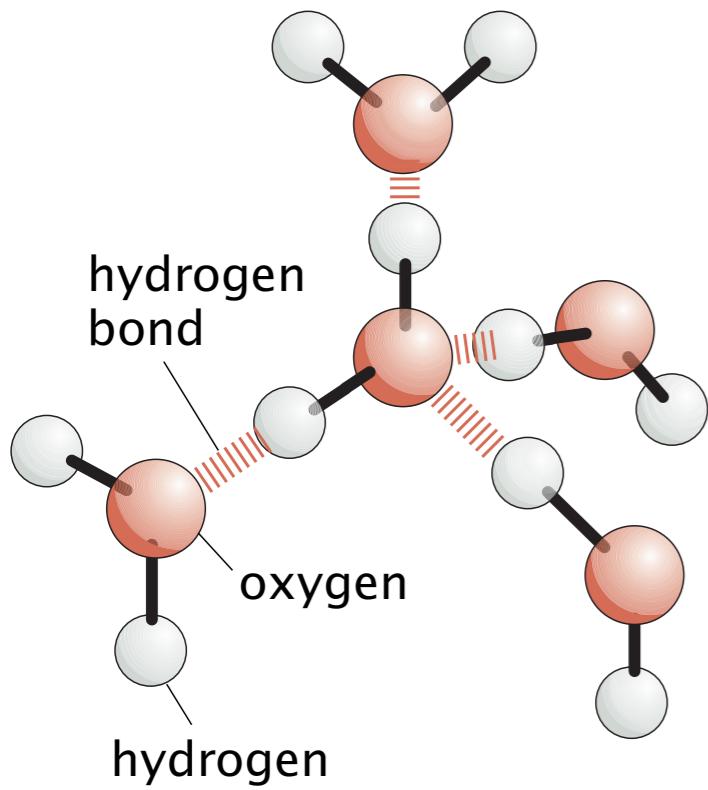
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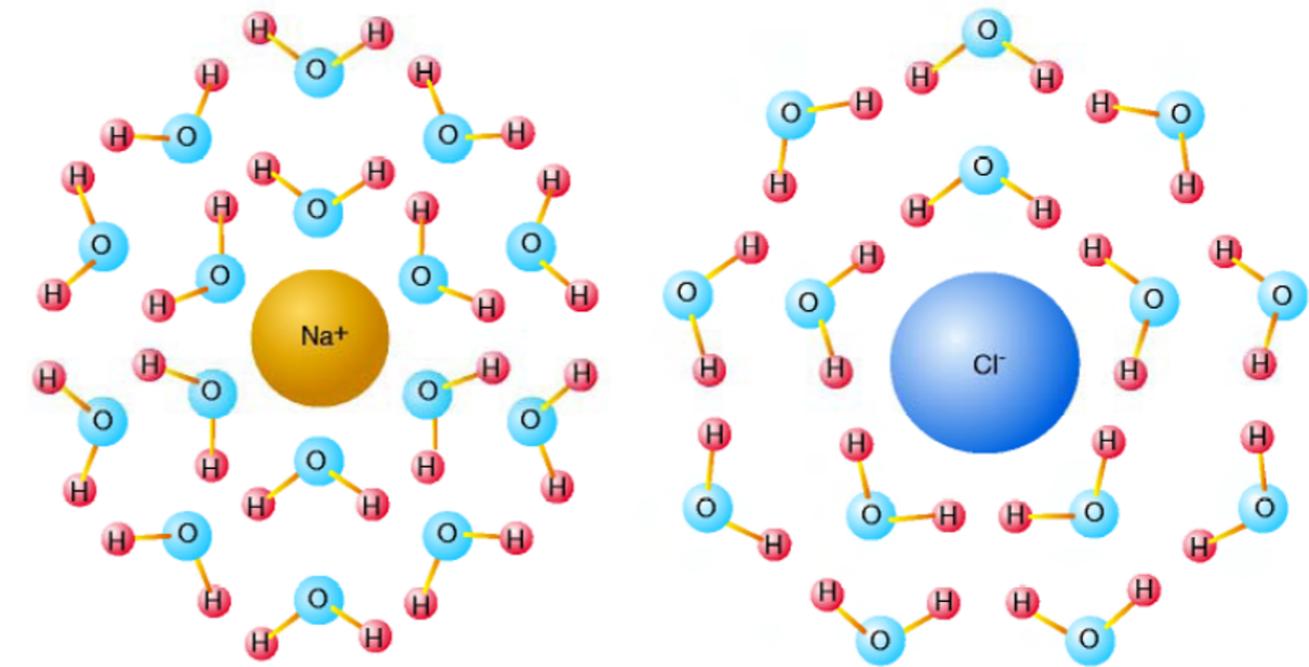
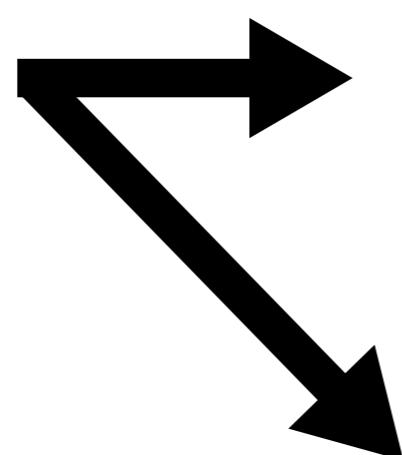
- Manipulation of the charge state of molecules of life
- Unfavorable interactions with water act as a driving force of organization

Swimming of organisms across scales depend on mechanical interaction with water

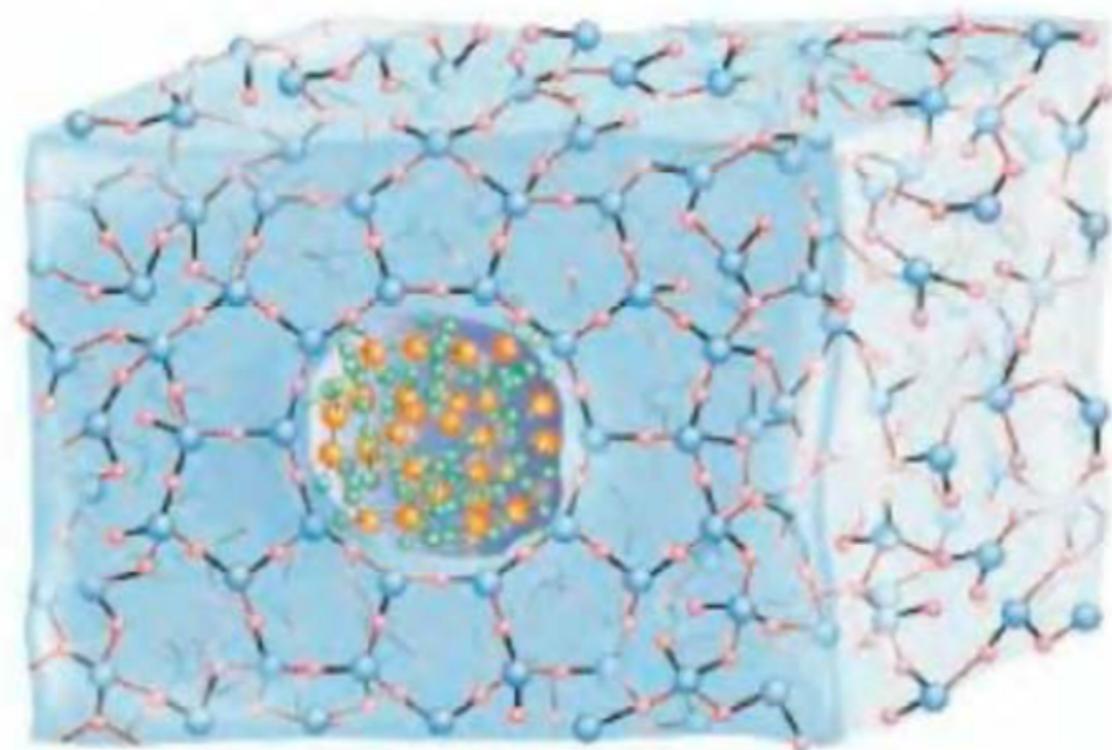
Structure of water is modified around other molecules



The H-bond network of water

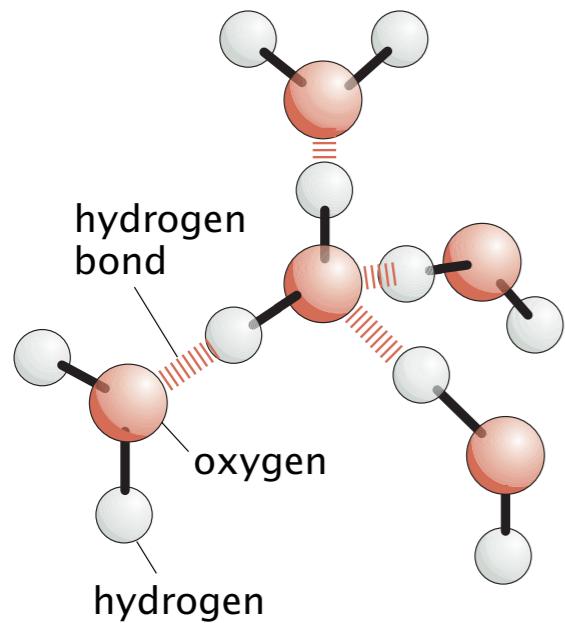


solvation of ions in water: **hydrophilic effect**



solvation of non-polar molecules in water: **hydrophobic effect**

Estimation of the hydrophobic effect

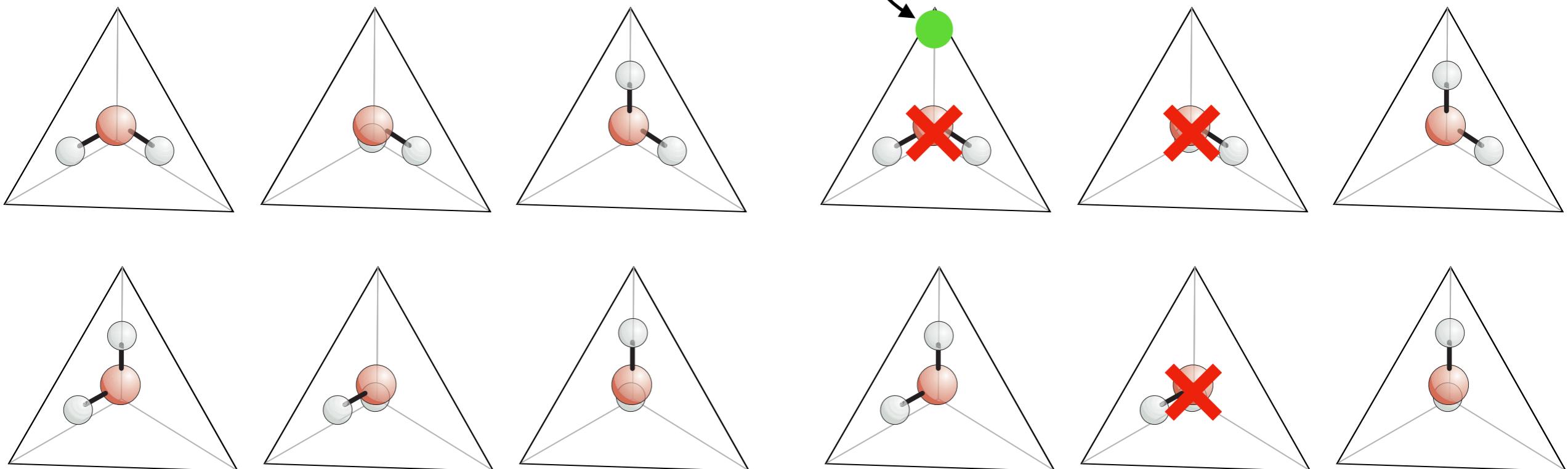


Key observations to make:

- Oxygen atoms from neighboring water molecules form a tetrahedral network
- Each O-atom forms H-bonds with two of the four neighboring water molecules

Near a non-polar molecule, H-bonding partners of water molecules become limited

Orientations available for a water molecule in a tetrahedral network



Nearby non-polar molecule restricts the set of orientations

Estimation of the hydrophobic effect...*contd*

the presence of the nonpolar molecule deprives each neighboring water molecule of **half** of its possible orientations as a participant in the hydrogen bonding network

The entropy change of each such water molecule is given by

$$\Delta S_{\text{hydrophobic}} = \frac{k_B \ln 3}{\text{constrained H}_2\text{O}} - \frac{k_B \ln 6}{\text{unconstrained H}_2\text{O}} = -k_B \ln 2.$$

Entropic contribution to the free energy cost for hydrophobicity can be written as

$$\Delta G_{hyd} = -T\Delta S_{hyd} = nk_B T \ln 2$$

This needs to be balanced by the free-energy cost for immersing the hydrophobic molecule

This can be estimated as a free-energy cost per unit area $\Delta G_{surface} = \gamma_{hyd} A_{mol}$

Equating we get, $\gamma_{hyd} = \frac{nk_B T \ln 2}{A_{mol}}$


Area of the non-polar molecule

Area of 10 water molecules is $\sim 1 \text{ nm}^2$, so $\gamma_{hyd} \approx 7 \text{ } k_B T/\text{nm}^2$

Estimation of the hydrophobic effect...*contd*

$$\gamma_{hyd} \approx 7 k_B T/\text{nm}^2$$

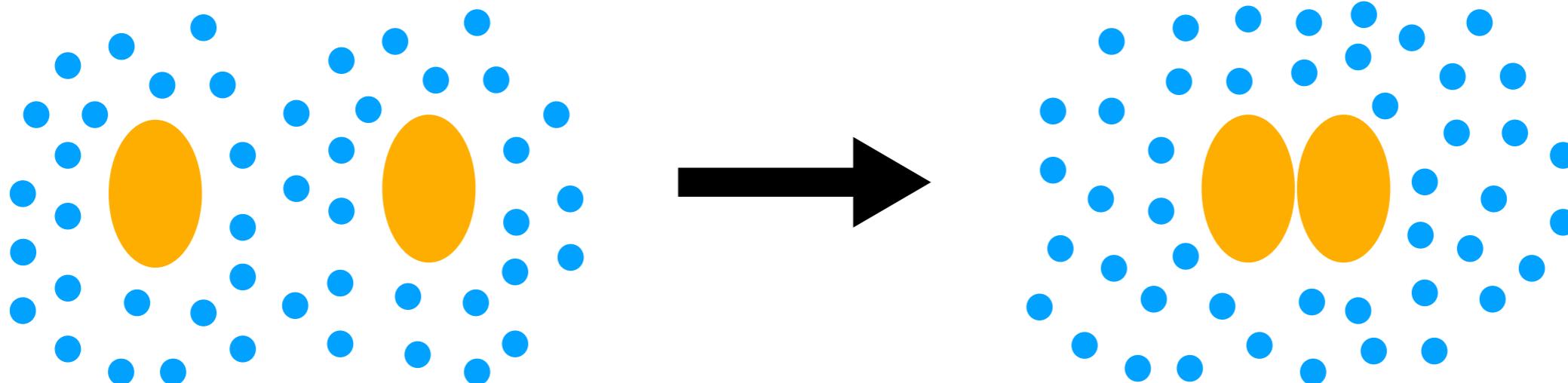
The free energy cost for dissolving an oxygen molecule (area $\sim 0.1 \text{ nm}^2$) $\approx 0.7 k_B T$

Feasible at room temperature!

The free energy cost for dissolving an octane molecule (area $\sim 1.5 \text{ nm}^2$) $\approx 10 k_B T$

Not feasible at room temperature!

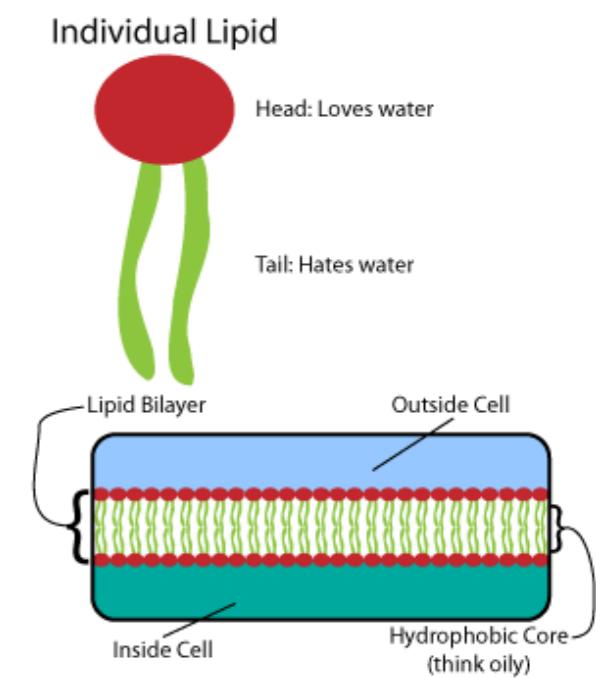
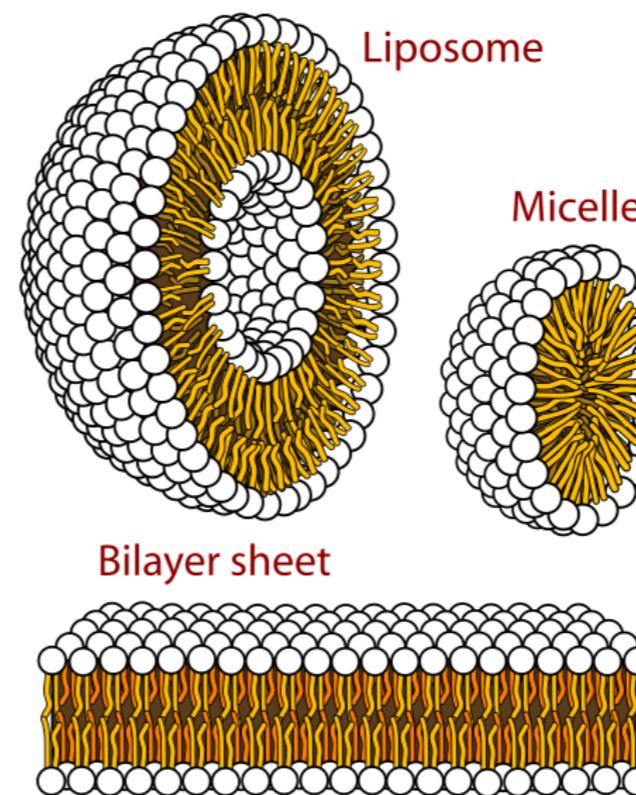
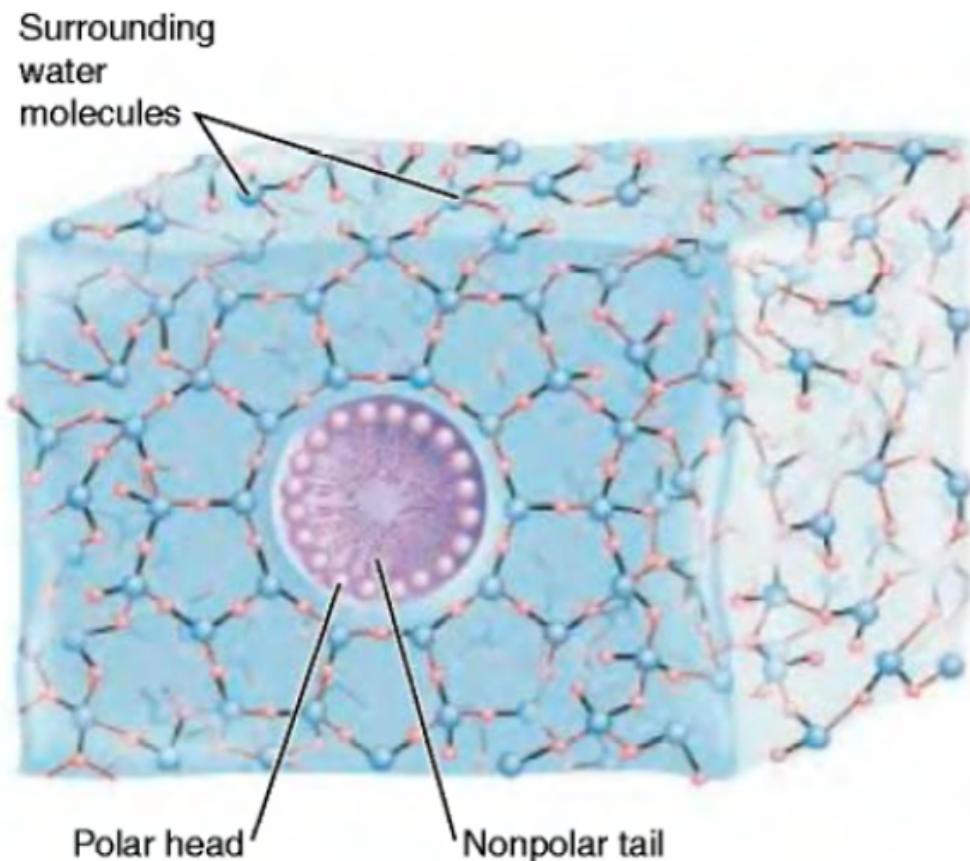
This is how this energy penalty is avoided



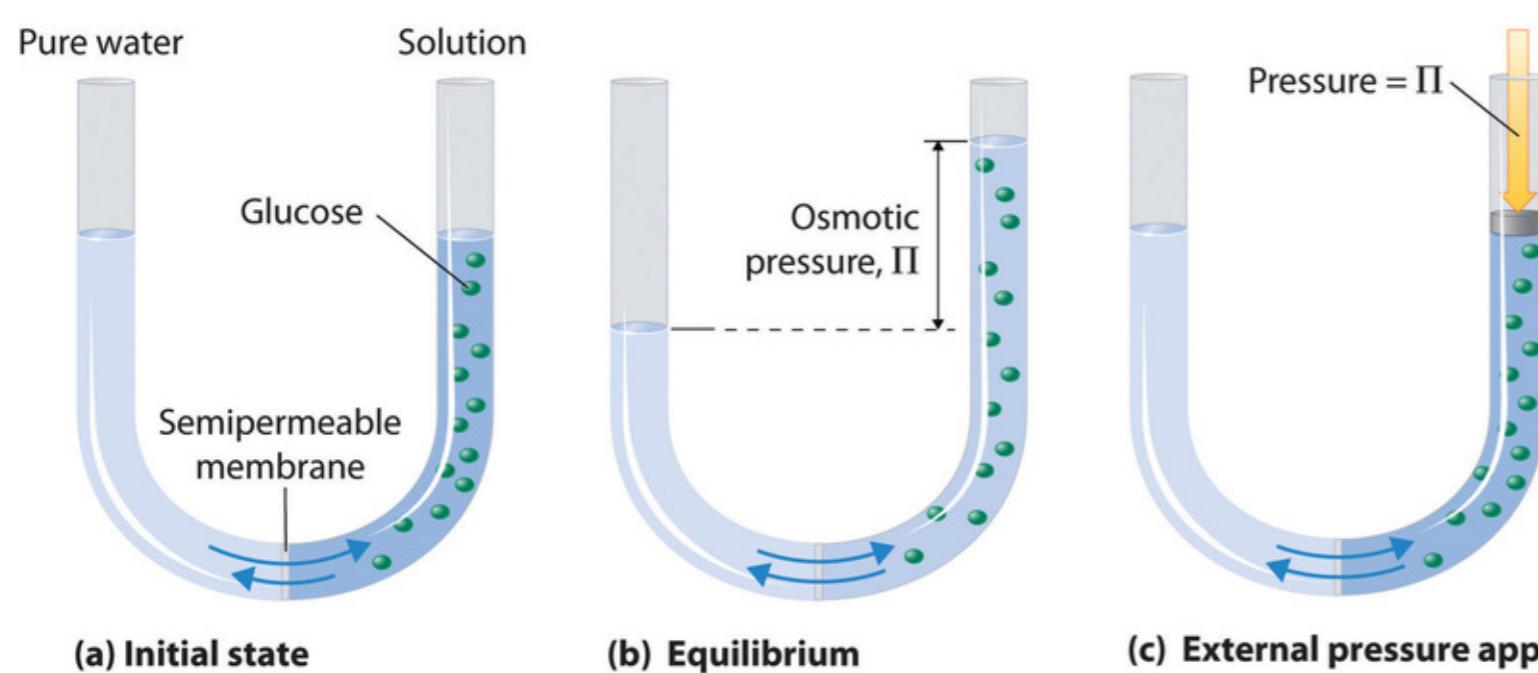
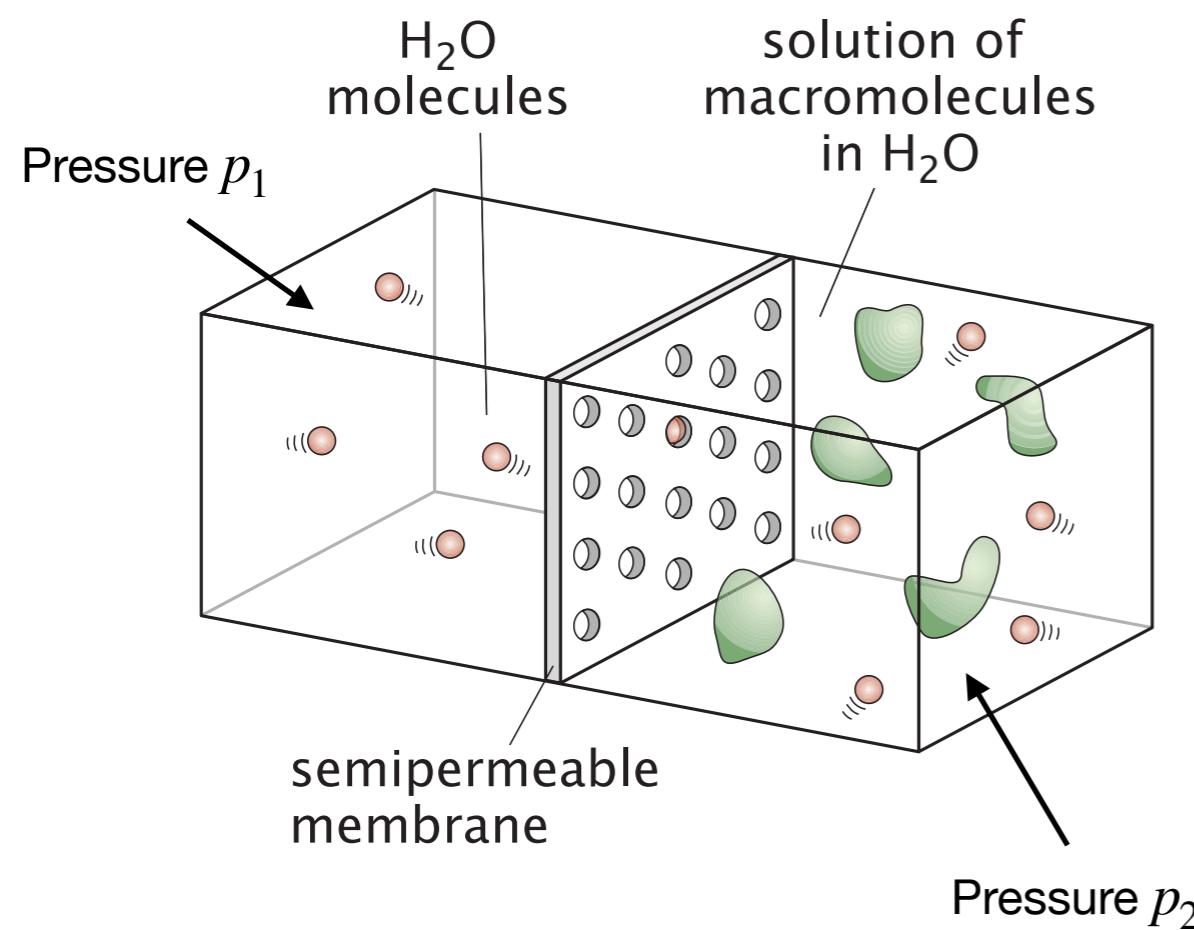
Amphipathic molecules

That contain both polar and non-polar groups, eg ionized fatty acids

Spontaneously rearrange to form micelles



Osmotic pressure



Osmotic pressure is defined as

$$p_2 - p_1 = \frac{N_s}{V} k_B T \quad \text{Van't Hoff formula}$$

N_s = number of solute molecules

V = volume of the solution

Can be rewritten as

$$\Pi = CRT$$

$$C = \frac{N_s}{N_A V}, \text{ molar conc of solute}$$

$$R = k_B N_A = \text{universal gas constant}$$

Essentially, osmotic pressure is the pressure required to stop the flow

Osmotic pressure for electrolytes

Van't Hoff formula: $\Pi = CRT$

This is only valid for solutions of non-electrolytes

For electrolytes, one molecule dissociates into several ions which change the effective concentration

General form of the Van't Hoff formula is: $\Pi = iCRT$

Where, i = Van't Hoff factor, a measure of the extent of ionization in solution

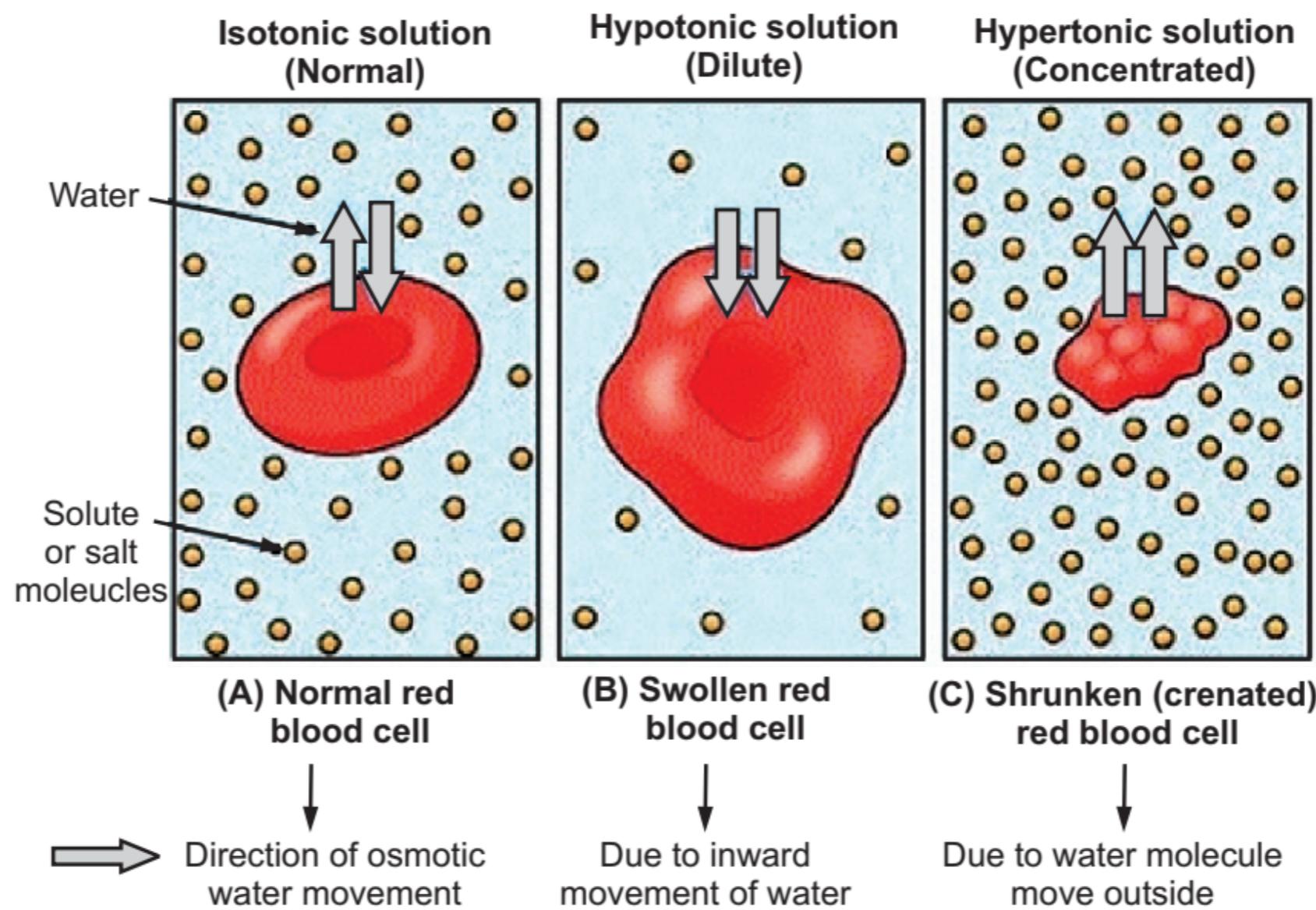
Definition: $i = 1 + \alpha(n - 1)$, where α = fraction of dissociation, zero for non-electrolytes

Example: For 1 M NaCl solution if $\alpha = 90\%$ estimate i



iC = osmolarity or osmotic concentration, used in measurement of osmotic pressure

Osmotic pressure can influence cell morphology



Living organisms constantly face large osmotic pressure

Let's calculate the osmotic pressure for 100 mM concentration difference

$$\Pi = \Delta CRT$$

$$\Pi \approx 2.4 \text{ atm}$$

In some salt lakes this conc difference is realized and cells have devised mechanisms to live in this environment. e.g. ion channels

The chemistry of water

Consider the ionization of water molecules:



We can write the equilibrium constant as:

$$K_{eq} = \frac{C_{\text{H}^+} C_{\text{OH}^-}}{C_{\text{H}_2\text{O}}}$$

Equilibrium constant for the reversible ionization of water is $1.8 \times 10^{-16} \text{ M}$ at 25°C

How do we get $C_{\text{H}_2\text{O}}$?

Density of water = 1000 g L^{-1}

Mol wt of water = 18 g/mol

$$C_{\text{H}_2\text{O}} = \frac{1000 \text{ g L}^{-1}}{18 \text{ g mol}^{-1}} \approx 55 \text{ M}$$

Assuming presence of ions strictly from dissociation of water

$$C_{\text{H}^+} = C_{\text{OH}^-}$$

$$C_{\text{H}^+} = \sqrt{K_{eq} \times C_{\text{H}_2\text{O}}}$$

$$C_{\text{H}^+} = 10^{-7} \text{ M}$$

Recalling definition of $pH = -\log_{10} C_{\text{H}^+}$,
we get pH of neutral water = 7

Charge state of biopolymers depend on pH of the solution

To investigate the way that this charge state is tuned, we consider the generic reaction



Dissociation constant: $K_d = \frac{C_{H^+} C_{M^-}}{C_{HM}}$

We define a quantity called: $pK = -\log_{10} K_d$

Taking log on both sides of K_d we get,

$$-\log_{10} K_d = -\log_{10} C_{H^+} - \log_{10} C_{M^-} + \log_{10} C_{HM}$$

$$\Rightarrow pH = pK + \log_{10} \frac{C_{M^-}}{C_{HM}}$$

Henderson-Hasselbalch equation

Significance: $C_{M^-} = C_{HM} \Rightarrow pK = pH$ So, pK is the pH at which exactly half dissociation takes place!

DNA has $pK \approx 1$ means at normal pH all the phosphate groups will be dissociated!
Thus, DNA behaves as a strong acid

Buffer solutions

Regulation of pH is very important for the cell because specific charge states are needed for biomolecules to function

A buffer is an aqueous solution of a weak acid and its conjugate base or a weak base and its conjugate acid that resists any change of pH



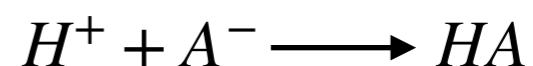
The buffering capacity depends on the robustness of this equilibrium

Le Chatelier's principle is the key! 

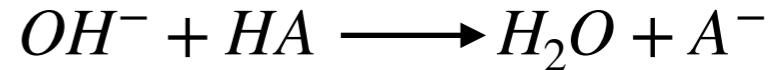
if stress is applied to a reaction in equilibrium, the equilibrium will be displaced in the direction that relieves the stress.

Buffer zone: $pH = pK \pm 1$

addition of H^+



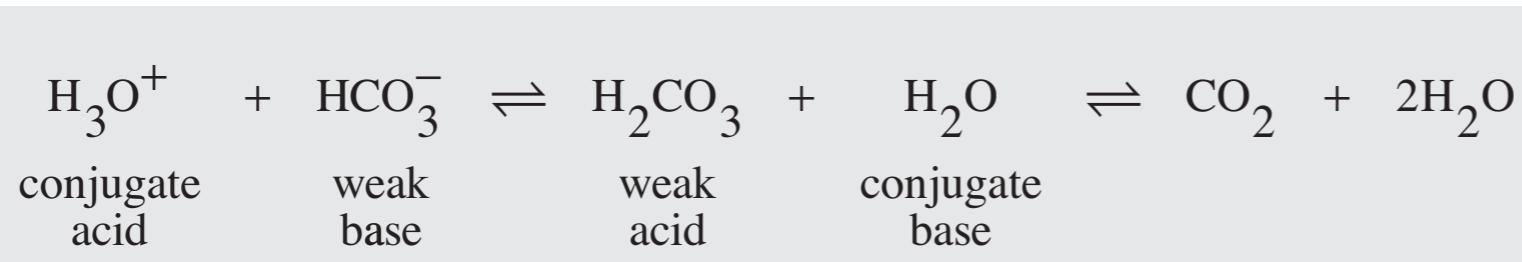
addition of OH^-



Buffer systems in human body

Bicarbonate buffer

carbonic acid/hydrogencarbonate buffering system.



pK is 6.37, looks not effective way to control blood pH of ~ 7.4! But efficiently done by controlling the conc of CO_2 by respiration and bicarbonate concentration in kidney

Phosphate buffer



pK is 7.2, looks like an ideal buffer for blood but found very little in blood, more intracellular and in urine

Plasma protein buffer

Blood plasma is a solution of proteins that also act as weak acids with several ionizable groups and hence show buffering activity. Hemoglobin and albumins effectively regulate blood pH