Chem 431A-Lecture 2 9/24/07
admin:
(1) sign attendance sheet.
(collect blue books)

lecture:

(0) thermo review and mixtures of water and nonpolar molecules:

Be able to explain water phenomena.
Be able to use thermodynamic arguments.

Let's look at some impt thermo equations:

2nd law: $\Delta S_{univ} \geq 0$ for a reaction to occur

From this we get:

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$
for a reaction/process to occur:
$\Delta G \leq 0$ (negative)

either $\Delta S_{sys} > 0$ or $\Delta H_{sys} < 0$ (ie exothermic)

example: oil in water:

here, $\Delta H \approx 0$; so $\Delta S > 0$ (entropy driven)

it's the case with plasma bilayer membrane formation. What determines if micelles form or bilayers form?

Clusters of lipid molecules

Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.

Micelles

All hydrophobic groups are sequestered from water; ordered shell of H_2O molecules is minimized, and entropy is further increased.

(1) Colligative properties:

Colligative properties of solutions:
a) Freezing point depression
  ($\Delta T_f = K_f m$)
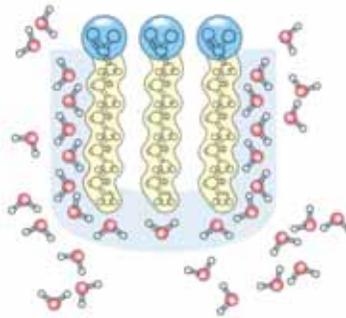b) boiling point elevation
  (ΔT_b) = $K_b m$)
c) vapor pressure depression
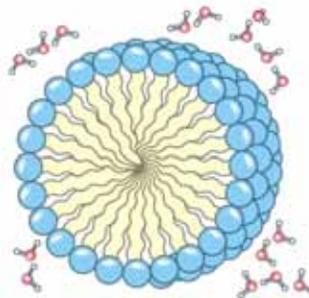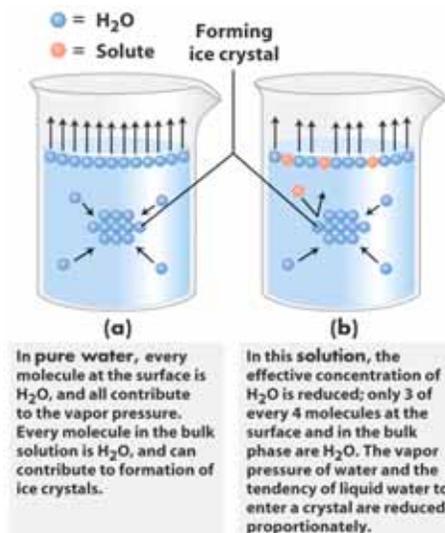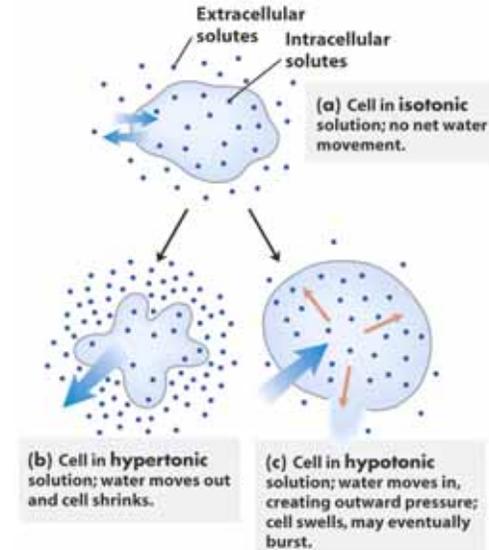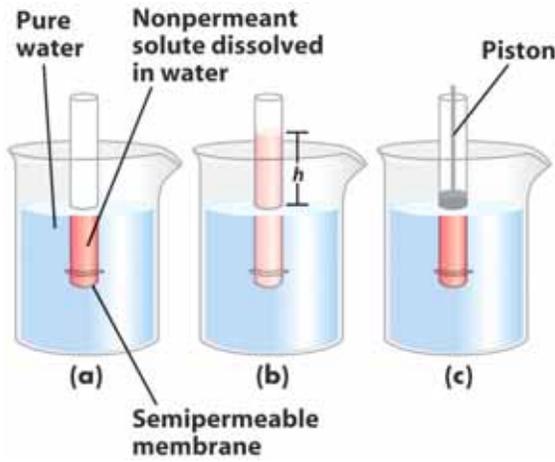(Henry'sLaw: $P_i = X_i P°$)
d) osmotic pressure $\pi V = nRT$
or, $\pi = icRT$; i= van't Hoff factor
c=molarity of solute

= H_2O
= Solute

Forming ice crystal

(a) In pure water, every molecule at the surface is H_2O, and all contribute to the vapor pressure. Every molecule in the bulk solution is H_2O, and can contribute to formation of ice crystals.

(b) In this solution, the effective concentration of H_2O is reduced; only 3 of every 4 molecules at the surface and in the bulk phase are H_2O. The vapor pressure of water and the tendency of liquid water to enter a crystal are reduced proportionately.

generally:
$\pi = RT(\sum i_j c_j)$ (for several solutes)

(a)   (b)   (c)

Pure water

Nonpermeant solute dissolved in water

Piston

Semipermeable membrane

Behavior of H^+ in solutions:

Proton-hopping leads to rapid net movement of protons in water

(2) Next: Acids and bases: concept of acids and bases are important because they often determine the interactions/mechanism of biochemical reactions...
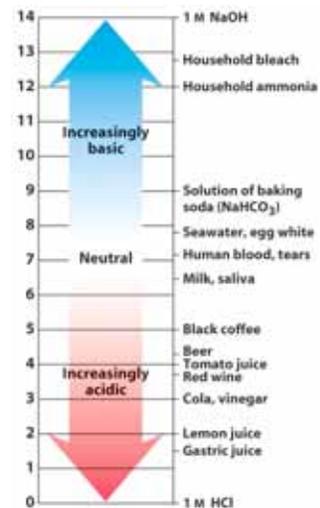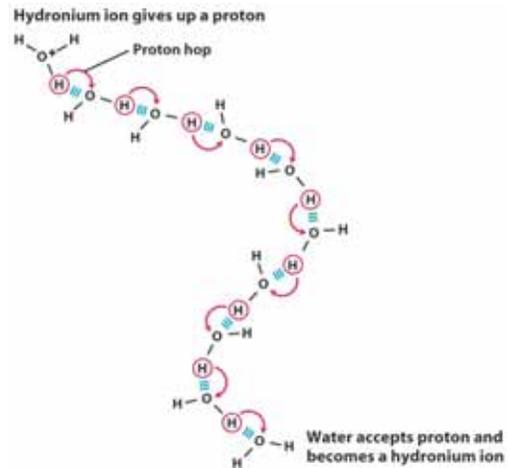
Review acids and bases.

acids = proton donors;
bases = proton acceptors
strong acids dissociate 100% while weak acids only dissociate partially. weak acids have a K_a (acid dissoc constant)

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

$HA <=> H^+ + A^-$, $K_a = [H^+][A^-]/[HA]$

$pK_a = -\log K_a$. A pK_a is a fixed number which characterizes a weak acid. A pK_a of 2 shows a stronger acid than a pK_a of 9. water has a self-ionization constant, $K_w = 10^{-14}$. so

(a) Cell in isotonic solution; no net water movement.

(b) Cell in hypertonic solution; water moves out and cell shrinks.

(c) Cell in hypotonic solution; water moves in, creating outward pressure; cell swells, may eventually burst.

Hydronium ion gives up a proton

Proton hop

Water accepts proton and becomes a hydronium ion

if we have A⁻, $A^- + H_2O \Leftrightarrow HA + OH^-$
K_b where $K_aK_b=K_w$
or $pK_a+pK_b=pK_w=14$

$pH = -\log[H^+]$ is a measure of acidity. low pH acidic soln, high pH basic soln.

we note that pH + pOH = 14; so for a soln, we can always get pOH if we know pH and viceversa.

pH of pure water is 7 (an ideal situation). In the cell, this is also close to the physiological pH. For example in human blood plasma, pH is 7.40 ideally.

but to keep it at that pH, it needs a <u>buffer</u>. Human blood can fluctuate only from 7.35 (acidotic) to 7.45 (alkalotic). beyond those limits, we would pass out and die.Most drinks are acidic in pH.

buffer = soln which tends to stabilize the pH by absorbing or releasing H^+ as needed. It is made up of a weak acid and its conjugate base.

Buffer eq'n: Henderson-Hasselbalch eqn:

$pH = pK_a + \log[base]/[acid]$

we can calculate the pH of a solution of weak acid or weak base or a buffer which is a mixture of weak acid and its conjugate base.
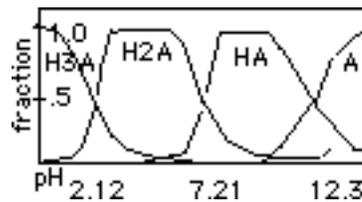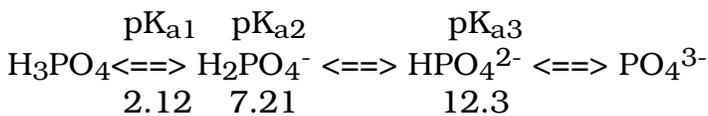
To illustrate buffering, suppose we have a 1.0 L solution with concs:1.0M HA and 1.0M A⁻. Then the pH= 4.76. Suppose then we add 0.2 mol HCl, the resulting pH can be calculated to be: 4.58.
(pH=4.76+log(1.0-.2/1.0+.2) = 4.58

Adding that much HCl to 1 L of pure water would drop it's pH from 7.0 to 0.70. This is the power of the buffer solution: it tends to stabilize the pH of a solution. Obviously, the higher
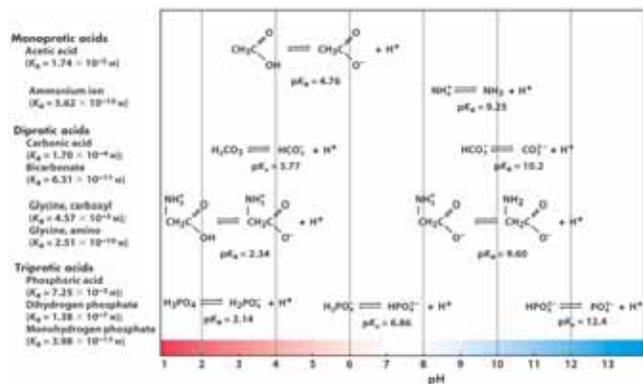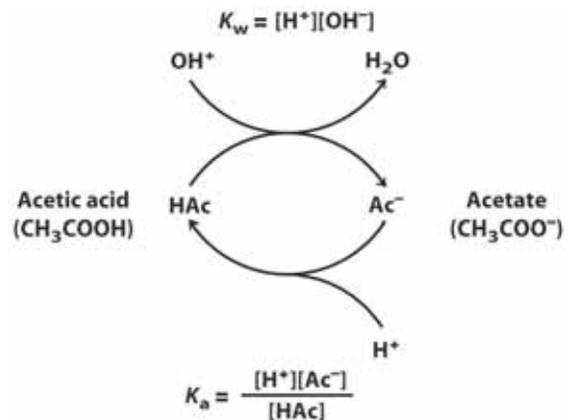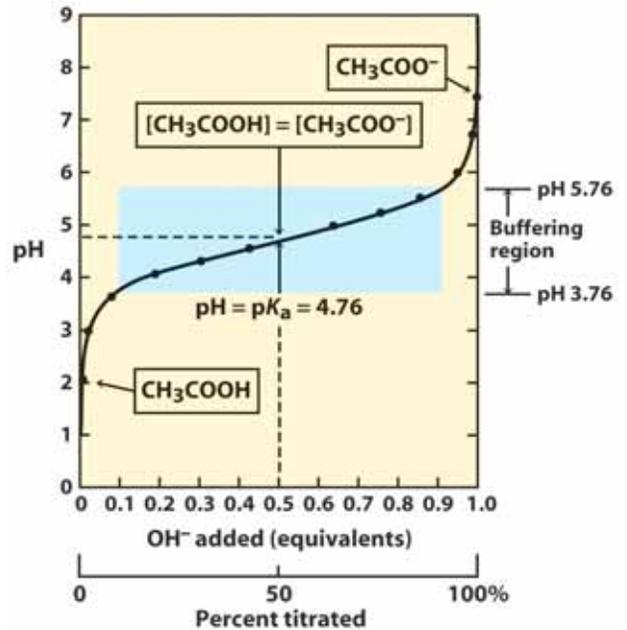
the total conc of the buffering species, the greater the buffering capacity. If we had used 0.1 M acetate buffer and added .2 mol HCl, the H+ ions would have caused the pH to drop drastically. As a practical rule of thumb, buffering action is good up to 1 pH unit above and below the pK_a.

Some molecs have more than one pK_a. PO_4^{3-} has 3. Note that PO_4^{3-} is an important buffer in vivo: $pK_{a1}=2.12$, $pK_{a2} = 7.21$, $pK_{a3} = 12.3$

$$pK_{a1} \quad pK_{a2} \qquad\qquad pK_{a3}$$
$$H_3PO_4 <==> H_2PO_4^- <==> HPO_4^{2-} <==> PO_4^{3-}$$
$$2.12 \quad 7.21 \qquad\qquad 12.3$$

In what form is the phosphate ion in the cell (which is close to neutral pH?), at pH 7.0, more in the form of $H_2PO_4^-$, and less but substantial amounts also of HPO_4^{2-}. The other forms are virtually negligible.

The bicarbonate-carbonic acid has two values: $pK_{a1}=3.8$, $pK_{a2} = 6.1$.
$$pK_{a2} = 6.1$$
Note that
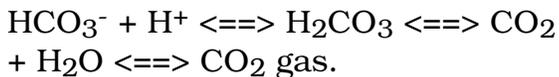
$$HCO_3^- + H^+ <==> H_2CO_3 <==> CO_2 + H_2O <==> CO_2 \text{ gas.}$$
This system maintains the pH of the blood at pH = 7.40±0.05. Human blood can fluctuate only from 7.35 (acidotic) to 7.45 (alkalotic). beyond those limits, we would pass out and die. Under normal conditions, that is more concentrated, HCO_3^- or H_2CO_3?

$[HCO_3^-]$ is regulated by the kidneys for long term control. But there is a quick control via the lungs (ventilation controls the $[CO_2]$ and hence $[H_2CO_3]$ in the blood. It is estimated that the equivalent of 10-40 liters of 1 N carbonic acid is
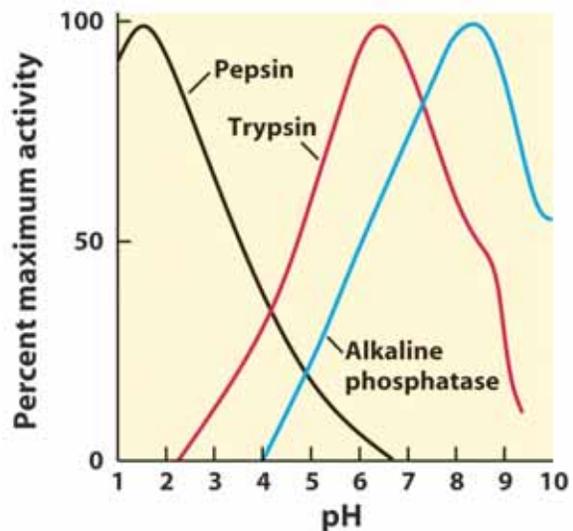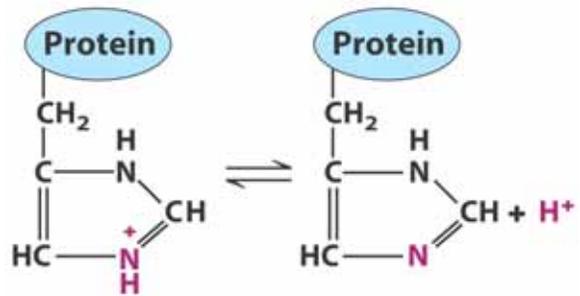
removed by the lungs of an adult
each day.

In the cell, biomolecules are much
larger than the ions discussed
above, but having essentially the
same type of property: that of
ionizable H donors and acceptors.
One can distinguish the different
biological molecules present in a
mixture by means of the
electrophoretic characteristics of the
various molecules. (electrophoresis
is a technique in which an electric
field is applied to a solution mixture,
causing various charged
components to migrate with a
characteristic pattern).

The molecules move according to
their charge. If we were to look at
the ions discussed above: we note
for the phoshate ion that practically
all pH values of the phosphate ion
will migrate toward the positive
electrode (ie all its forms except
H_3PO_4 which is neutral). But we
note that other molecules act as
both an acid and as a base.

$H^+ + HCO_3^-$

reaction 1

Aqueous phase
(blood in capillaries)

H_2CO_3

reaction 2

H_2O ⟶ ⟶ H_2O

$CO_2(d)$

reaction 3

Gas phase
(lung air space)

$CO_2(g)$