

Chapter -2- Dr.Rula Abdul-Ghani

Water

- Physical and chemical properties of water.
- Ionization of water, pH, titration curve, weak acid, weak base.
- Buffering against pH changes.

Polar biomolecules:

dissolve in water, because they can replace water-water interactions with water – solute interactions.

Nonpolar biomolecules:

interfere with water–water interactions but unable to form water – solute interactions.

Nonpolar solutes cluster together.

table 4–1

Melting Point, Boiling Point, and Heat of Vaporization of Some Common Solvents

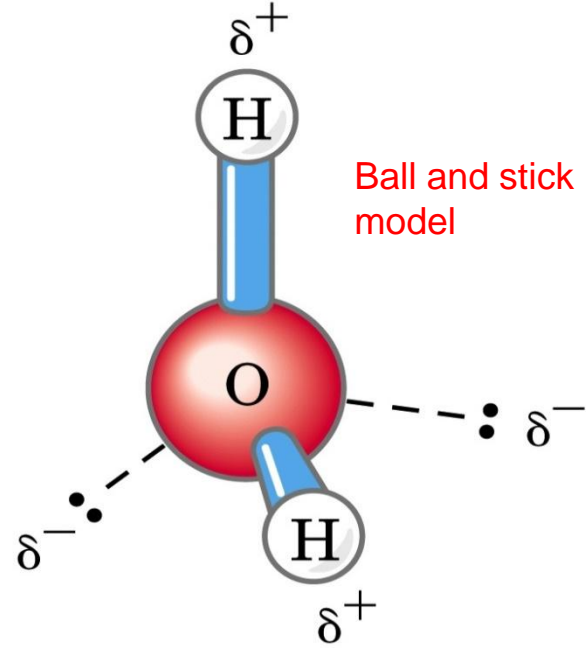
	Melting point (°C)	Boiling point (°C)	Heat of vaporization (J/g)*
Water --- highest ---	0	100	2,260
Methanol (CH ₃ OH)	−98	65	1,100
Ethanol (CH ₃ CH ₂ OH)	−117	78	854
Propanol (CH ₃ CH ₂ CH ₂ OH)	−127	97	687
Butanol (CH ₃ (CH ₂) ₂ CH ₂ OH)	−90	117	590
Acetone (CH ₃ COCH ₃)	−95	56	523
Hexane (CH ₃ (CH ₂) ₄ CH ₃)	−98	69	423
Benzene (C ₆ H ₆)	6	80	394
Butane (CH ₃ (CH ₂) ₂ CH ₃)	−135	−0.5	381
Chloroform (CHCl ₃)	−63	61	247

*The heat energy required to convert 1.0 g of a liquid at its boiling point, at atmospheric pressure, into its gaseous state at the same temperature. It is a direct measure of the energy required to overcome attractive forces between molecules in the liquid phase.

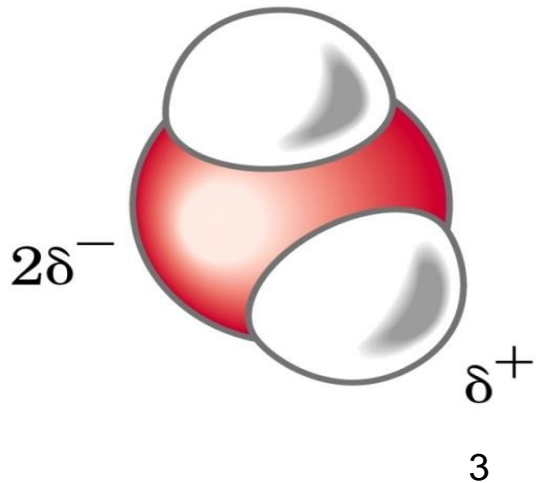
Unusual properties of water are a consequence of attraction bw adjacent water molecules → give liquid water great internal cohesion.

Structure of water molecule:

- Dipolar nature of water.
- Tetrahedral arrangement of electron pairs around the oxygen atom which has partial -ve charge.
- Rough tetrahedron with a hydrogen atom at each of 2 corners and unshared electron pairs at the other 2 corners.
- The tetrahedral arrangement allows each water molecule to form H- bonds with 4 neighboring water molecules.



(a)
Space filling model



(b)

Two water molecules joined together by a H - bond.

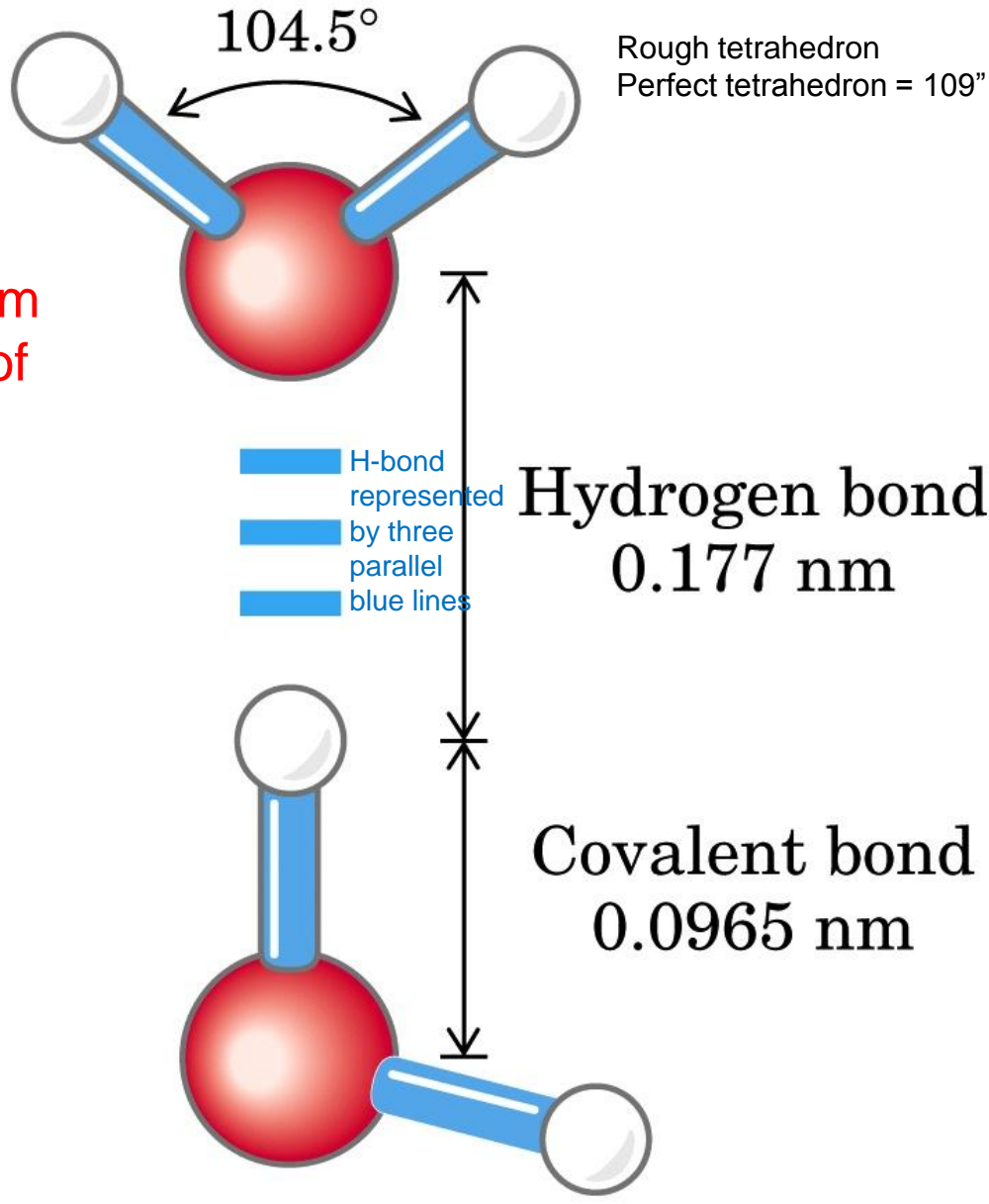
H-bond:
electrostatic attraction bw. oxygen atom of one water molecule and hydrogen of another.

H - bonds longer and weaker than covalent O-H bond.

Hydrogen bonds are relatively weak:

Bond dissociation energy=
Energy required to break a bond

- H-bond= 23kJ/mol
- Covalent O-H = 470kJ/mol
- Covalent C-C = 348kJ/mol



Hydrogen bonding in ice:

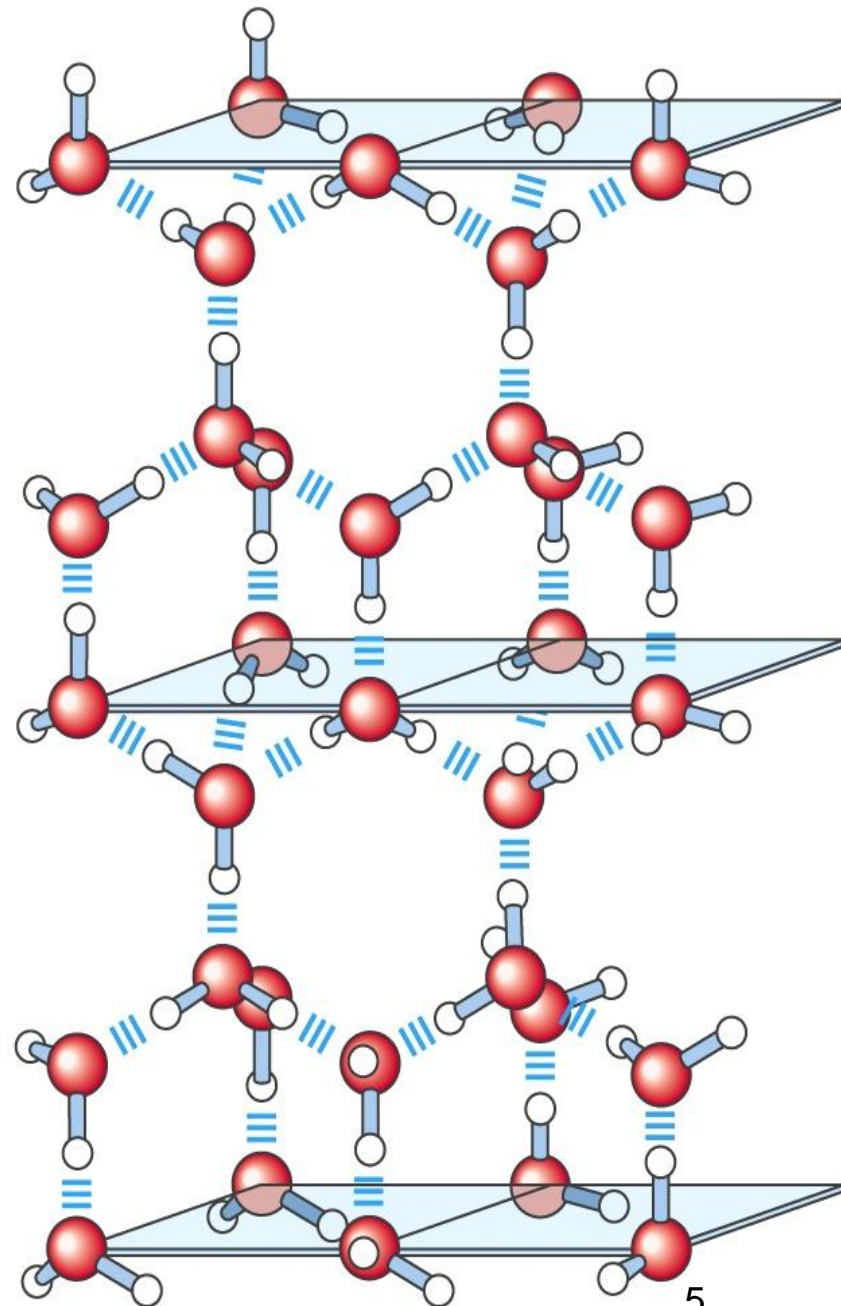
At room temp.

water is liquid, water molecules are disorganized and in continuous motion, each molecule forms H-bond with an av 3.4 molecule.

In ice

water molecules are fixed in space with 4 H-bond with neighboring water molecules forming a crystal structure .

TO break H-bonds and destabilize the crystal → Heat to melt or evaporate.

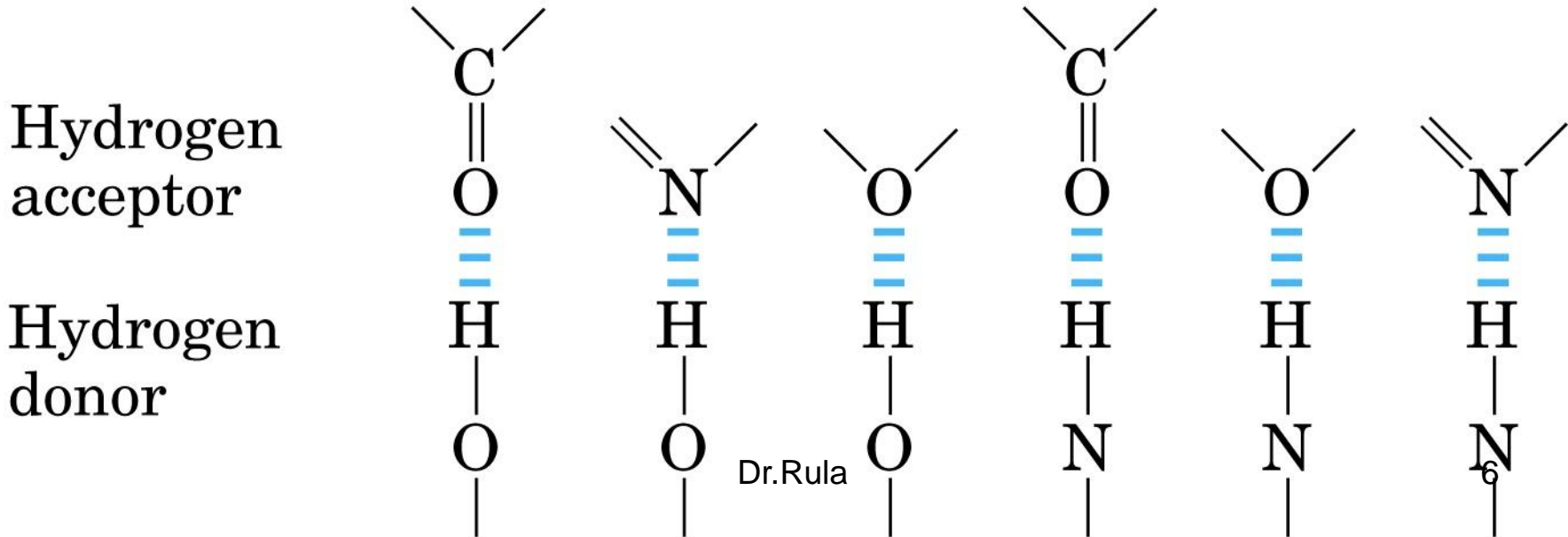


Common H - bonds in biological systems:

H-bonds not unique to water. Sugars, alcohols, aldehydes, ketones, compounds containing N-H bonds are water soluble.

H-bond formed bw an electronegative atom (O/N = hydrogen acceptor) and a hydrogen atom linked to another electronegative atom (hydrogen donor) in the same/another molecule.

Note: hydrogen atom covalently bound to carbon don't participate in H-bonding because C-H bond is weakly polar.

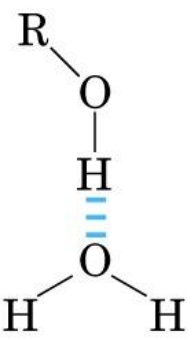


Some Biologically important H bonds:

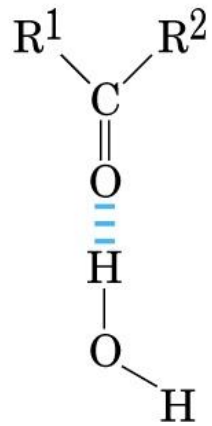
polar biomolecules such as sugars dissolve readily in water.

Because of the stabilizing effect of H-bond bw hydroxyl /carbonyl oxygen of the sugar and the polar water molecules.

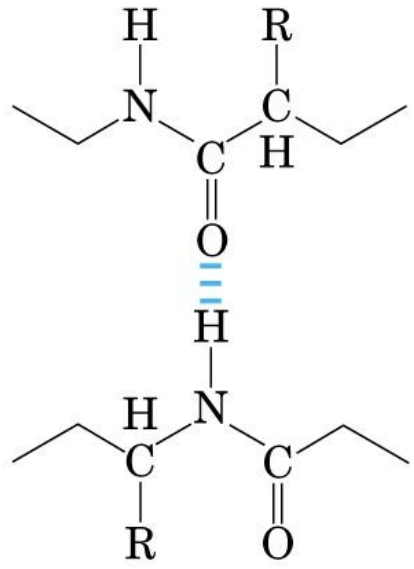
Between the hydroxyl group of an alcohol and water



Between the carbonyl group of a ketone and water

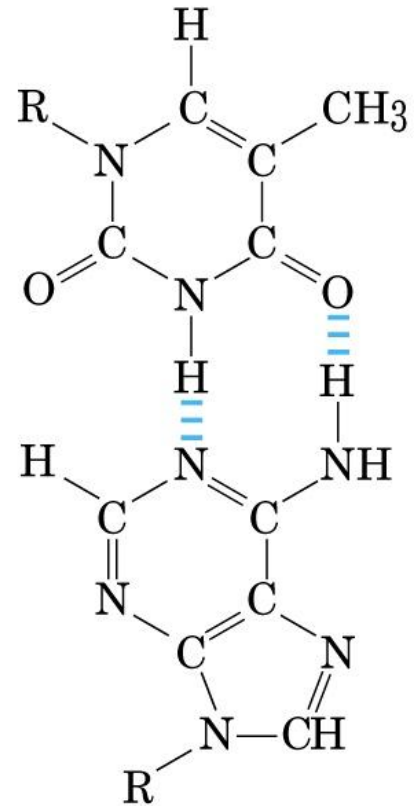


Between peptide groups in polypeptides



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Between complementary bases of DNA



Thymine

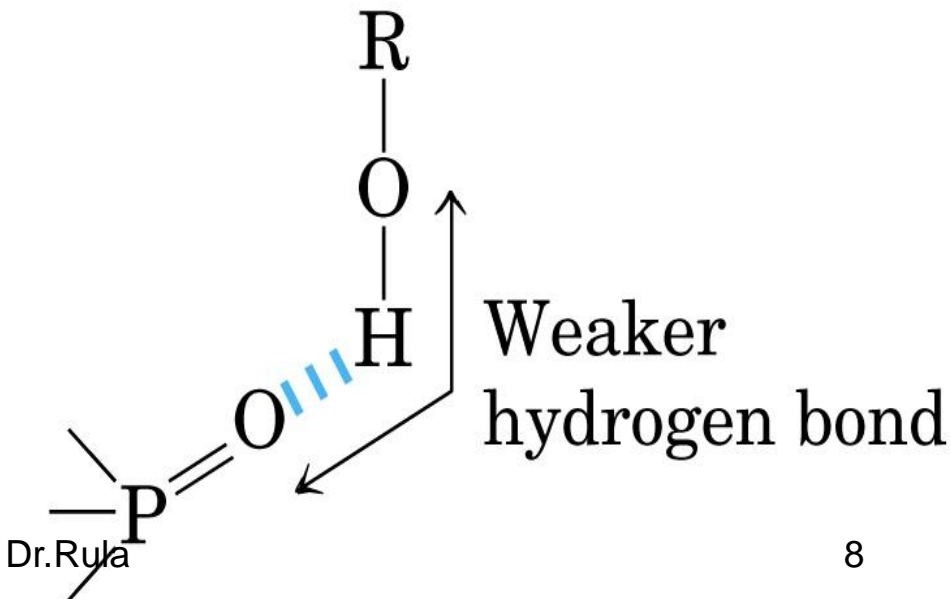
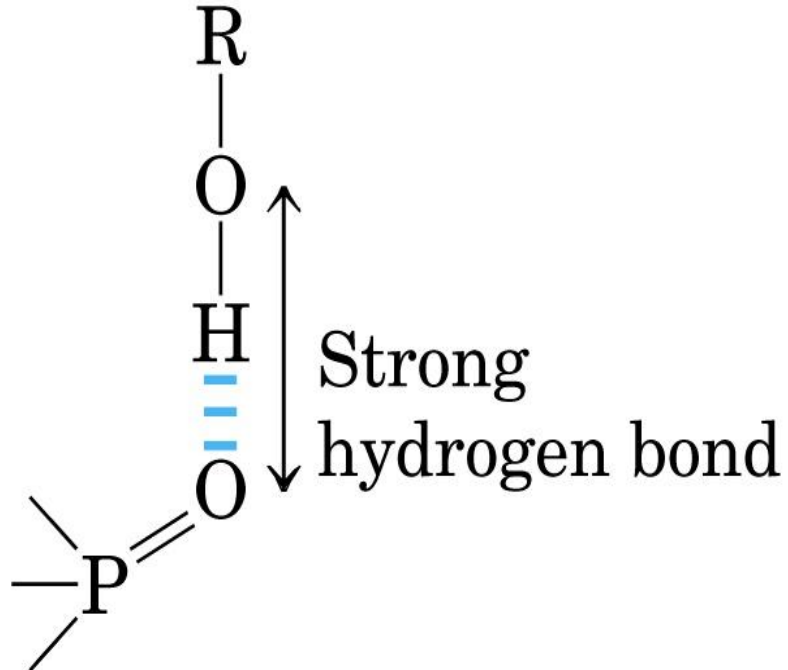
Adenine

Directionality of the H- bond:

The H-bond strongest when the three atoms (O-H-O) lie in a straight line (maximize electrostatic interaction).

H-bond highly directional and capable of holding 2 H- bonded molecules in a specific geometric arrangement.

Ideal geometry not always possible when molecule structurally constrained such as parts of a single protein molecule.



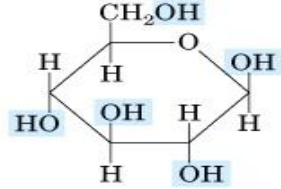
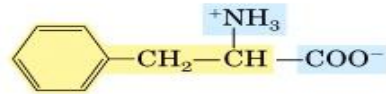
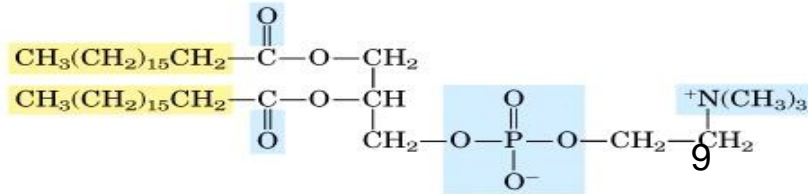
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Hydrophilic, Hydrophobic, Amphipathic

table 4-2

Water a polar solvent
 dissolves biomolecules.
 Compounds dissolve
 easily = **hydrophilic**
 (water - loving)

Nonpolar solvents
 chloroform and benzene
 dissolve nonpolar
 molecules = **hydrophobic**
 (water - fearing).

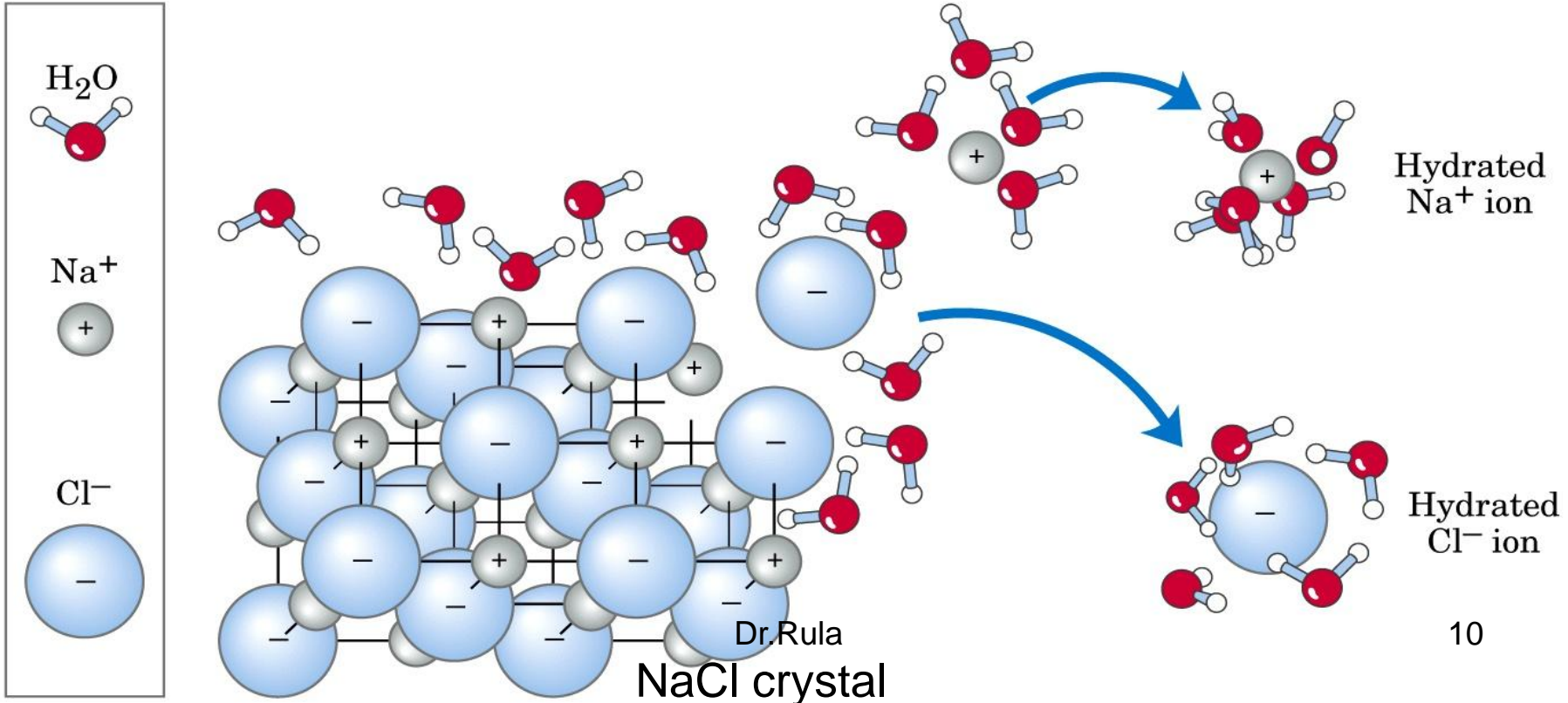
Some Examples of Polar, Nonpolar, and Amphipathic Biomolecules (Shown as Ionic Forms at pH 7)	
Polar Glucose	
Glycine	$^+NH_3-CH_2-COO^-$
Aspartate	$^-OOC-CH_2-CH(^+NH_3)-COO^-$
Lactate	$CH_3-CH(OH)-COO^-$
Glycerol	$HOCH_2-CH(OH)-CH_2OH$
Nonpolar Typical wax	$CH_3(CH_2)_7-CH=CH-(CH_2)_6-CH_2-C(=O)-O-CH_2$ $CH_3(CH_2)_7-CH=CH-(CH_2)_7-CH_2$
Amphipathic Phenylalanine	
Phosphatidylcholine	

 Polar groups
 Nonpolar groups

Water as solvent:

Water dissolves crystalline salts by hydrating + stabilizing their ions. The NaCl crystal is disrupted as water molecules cluster about Na⁺ and Cl⁻ ions. Water weakens electrostatic interactions bw them and counteracting their tendency to associate in a crystal (**replace solute-solute H-bond with solute-water H-bond**). The same applies to biomolecules carboxylic acids (COO⁻) , protonated amines (NH₃⁺) .

The ionic charges are partially neutralized and electrostatic attractions weakened.



Biologically important gases are CO₂, O₂.

In O₂ and N₂ electrons shared equally by the 2 atoms. In CO₂ each C=O bond is polar but the 2 dipoles are oppositely directed and cancel each other.

Water soluble carrier proteins (hemoglobin, myoglobin)

CO₂ → HCO₃⁻ – (highly soluble)

table 4-3

Solubilities of Some Gases in Water

Gas	Structure*	Polarity	Solubility in water (g/L) [†]
Nitrogen	N≡N	Nonpolar	0.018 (40 °C)
Oxygen	O=O	Nonpolar	0.035 (50 °C)
Carbon dioxide	$\begin{array}{c} \delta^- \quad \delta^- \\ \longleftarrow \quad \longrightarrow \\ \text{O}=\text{C}=\text{O} \end{array}$	Nonpolar	0.97 (45 °C)
Ammonia	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \diagdown \quad \quad / \\ \text{N} \\ \downarrow \delta^- \end{array}$	Polar	900 (10 °C)
Hydrogen sulfide	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{S} \\ \downarrow \delta^- \end{array}$	Polar	1,860 (40 °C)

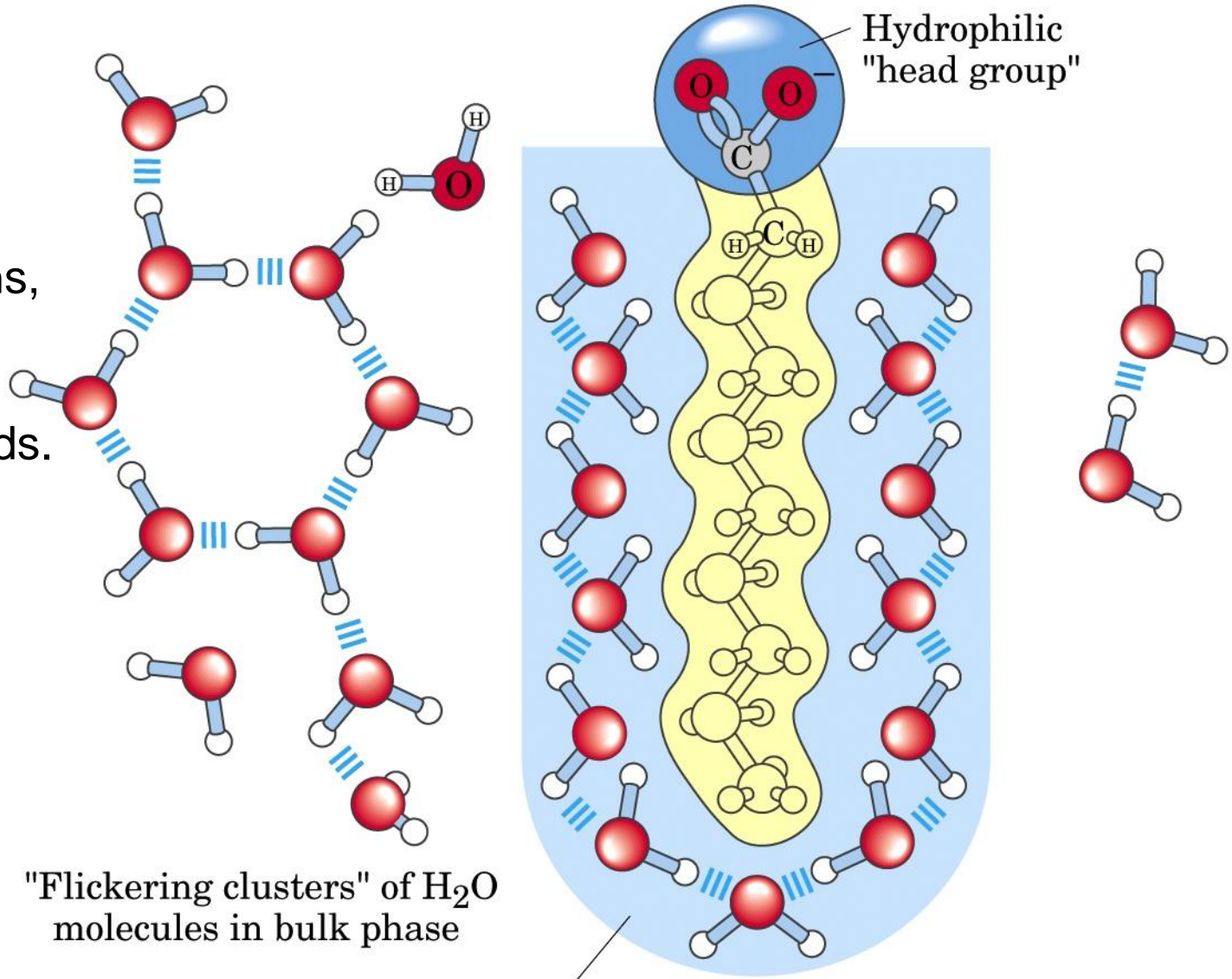
Very poorly
Soluble in
water

*The arrows represent electric dipoles; there is a partial negative charge (δ^-) at the head of the arrow, a partial positive charge (δ^+ ; not shown here) at the tail.

[†]Note that polar molecules dissolve far better even at low temperatures than do nonpolar molecules at relatively high temperatures.

Amphipathic compounds in aqueous solution:

Many biomolecules
are amphipathic
Phospholipids,
membranes, proteins,
vitamins.
Long chain fatty acids.



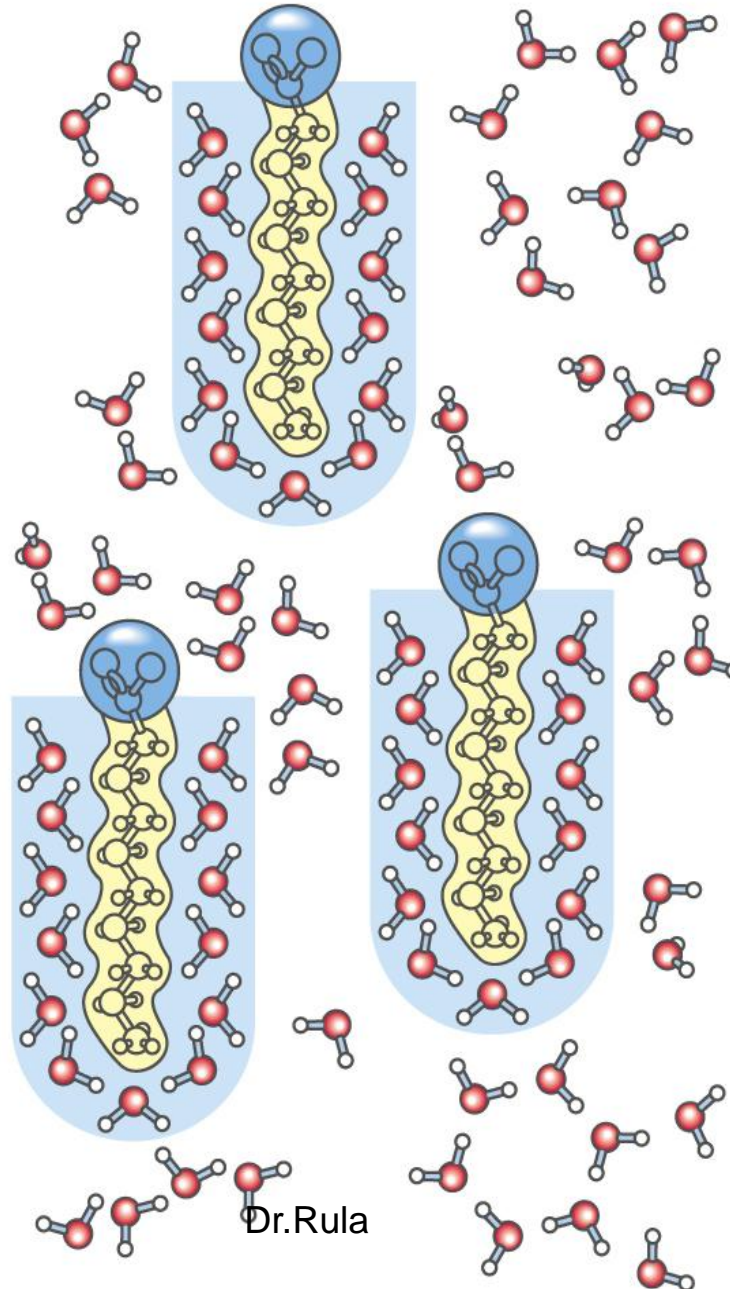
"Flickering clusters" of H₂O molecules in bulk phase

Dr. Rupa Highly ordered H₂O molecules form¹² "cages" around the hydrophobic alkyl chains

(a)

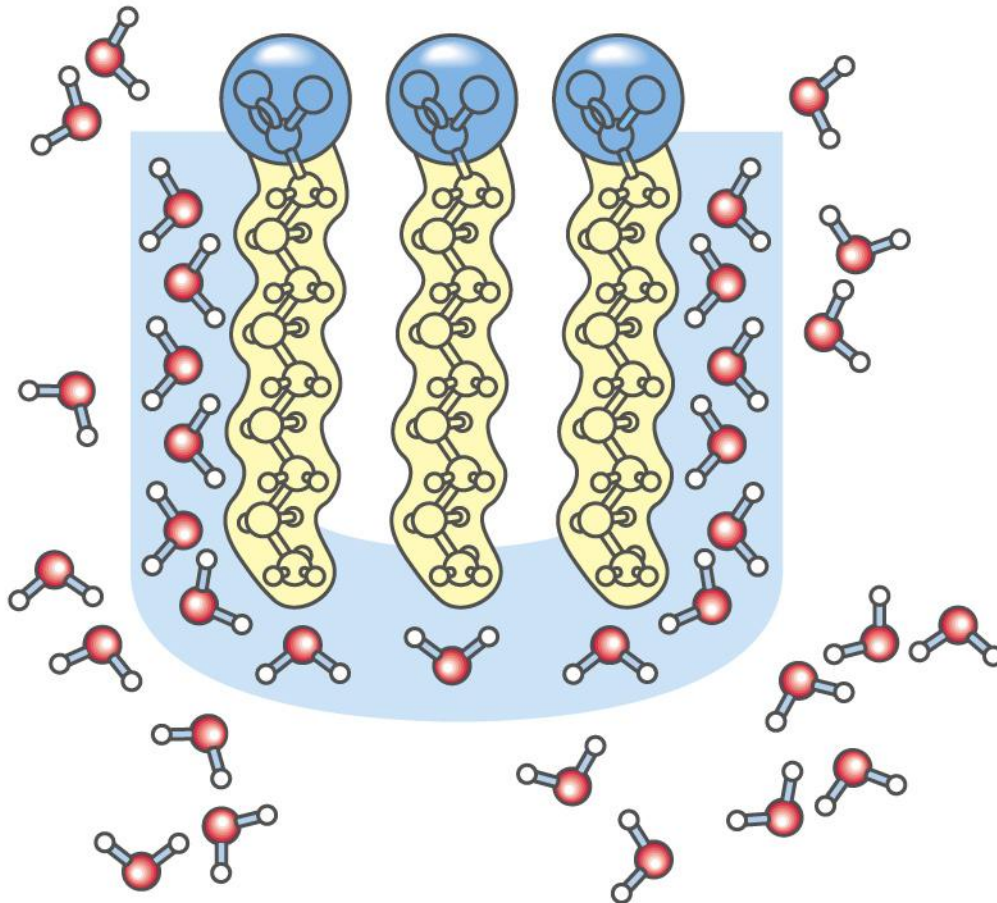
Micelle formation:

Stable structures of
amphipathic compounds
in water.



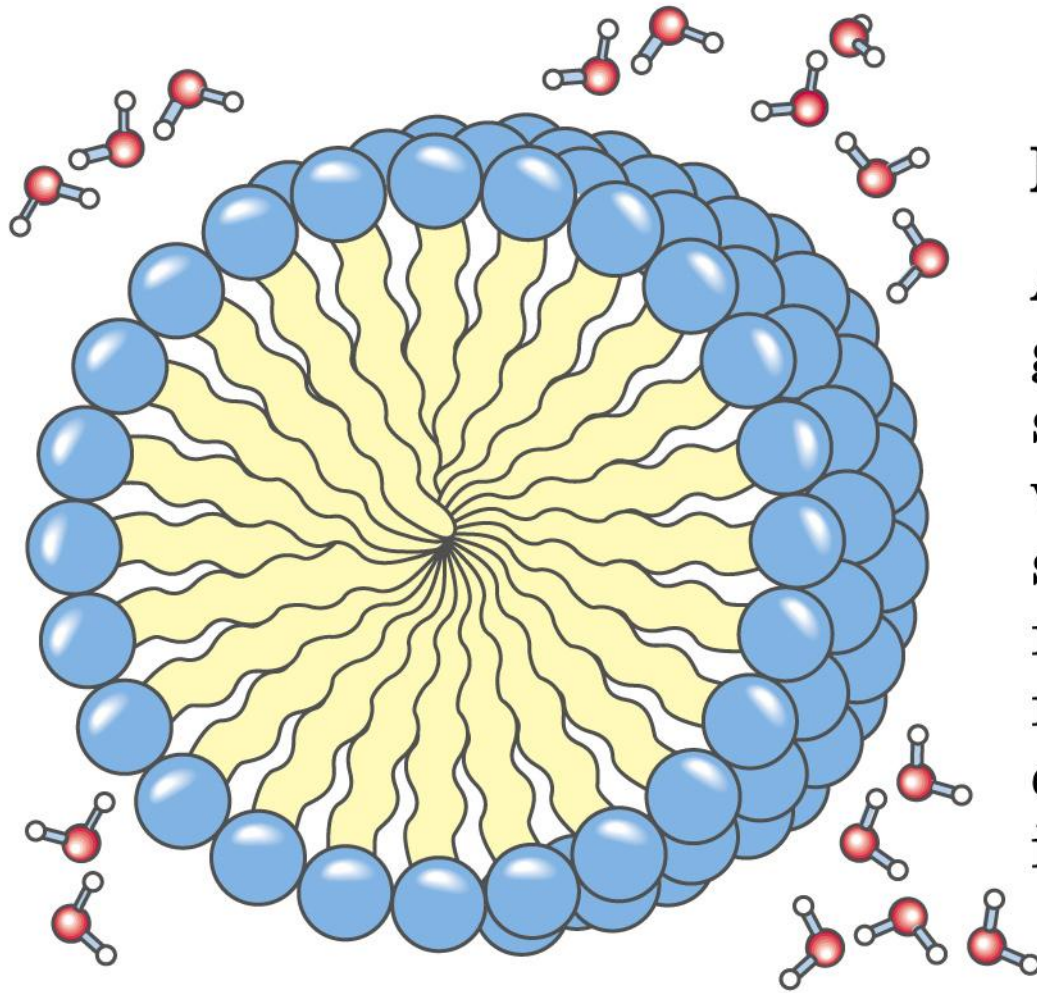
Dispersion of lipids in H₂O

Each lipid
molecule forces
surrounding H₂O
molecules to become
highly ordered.



Clusters of lipid molecules

Only lipid portions at the edge of the cluster force the ordering of water. Fewer H₂O molecules are ordered, and entropy is increased.



Micelles

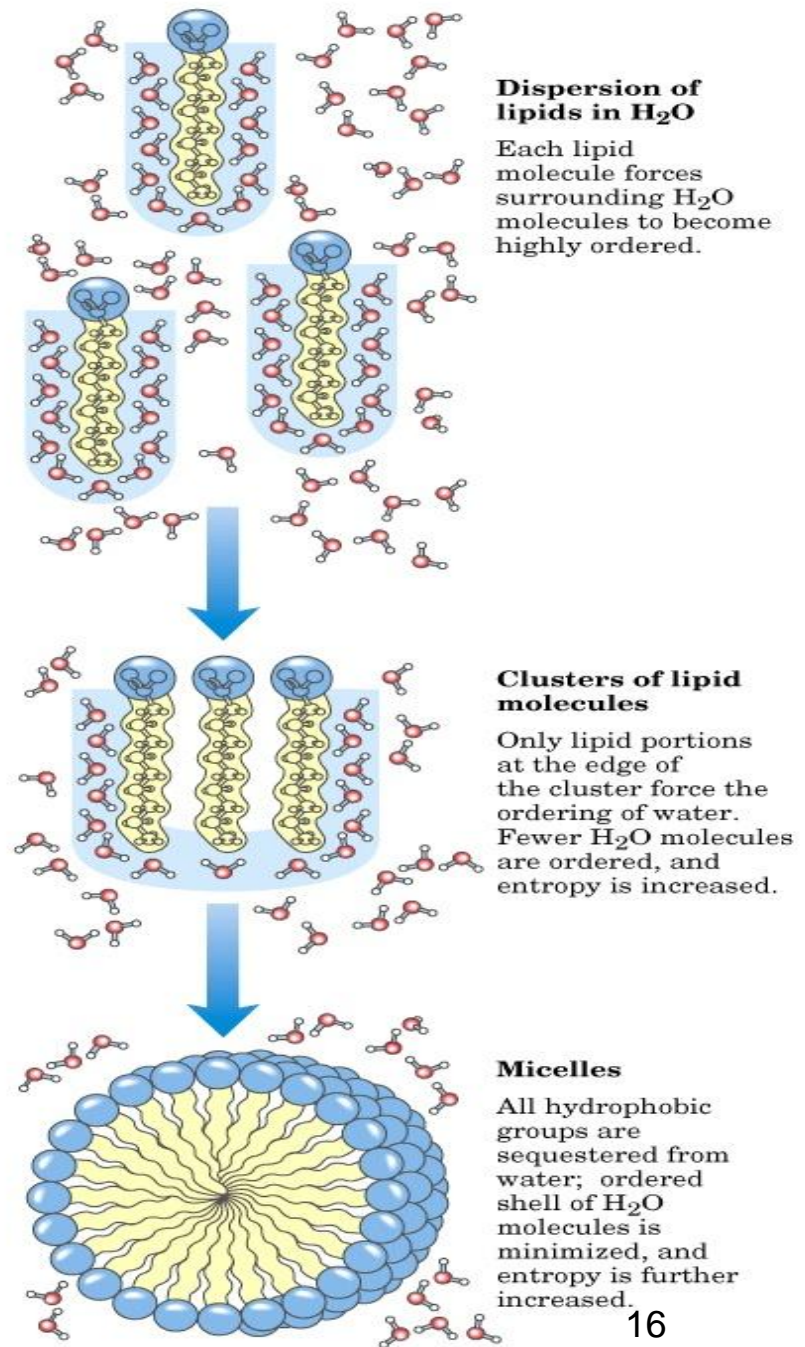
All hydrophobic groups are sequestered from water; ordered shell of H₂O molecules is minimized, and entropy is further increased.

Hundreds/ thousands of molecules.

By clustering together in micelle the f.a molecules expose the smallest possible hydrophobic surface areas to water.

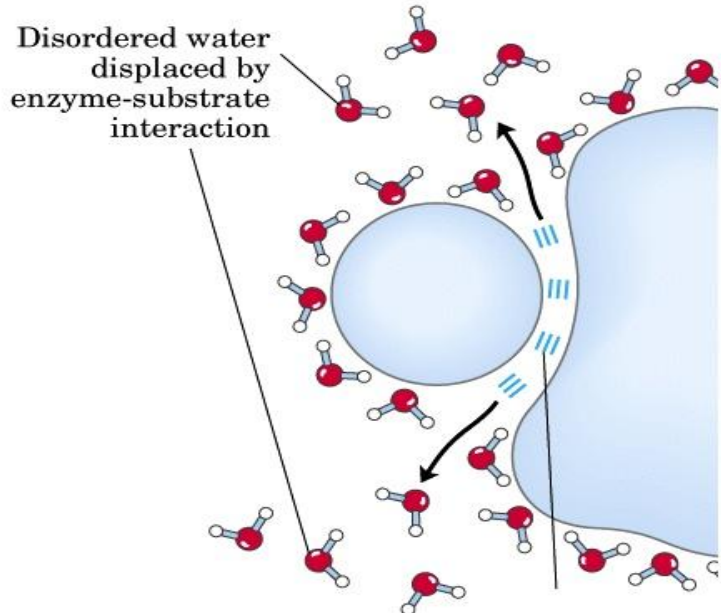
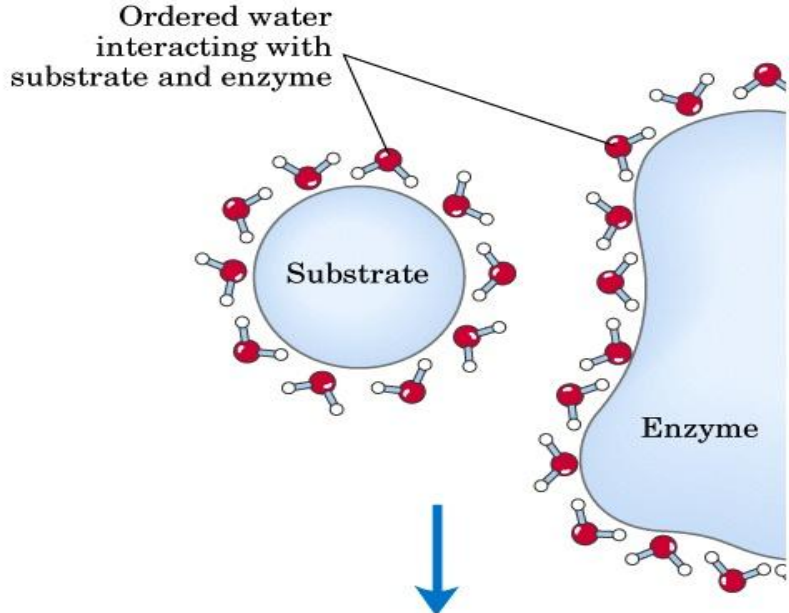
Hydrophobic interactions:

Forces that hold nonpolar regions of the molecule together.



While separate , both E and S force neighboring water molecules into an ordered shell.

Binding of S to E releases some of the ordered water. The resulting increase in entropy provides a push to the E-S complex.



Van der Waals interaction:

Weak interactions when two uncharged atoms are brought very close together.

Van der Waal raddi :

a measure of how close one atom will allow another to approach.

In space filling models atoms are in sizes proportional to their van der Waal radii.

table 4-4

Four Types of Noncovalent ("Weak") Interactions among Biomolecules in Aqueous Solvent

Hydrogen bonds

Between neutral groups



Between peptide bonds



Ionic interactions

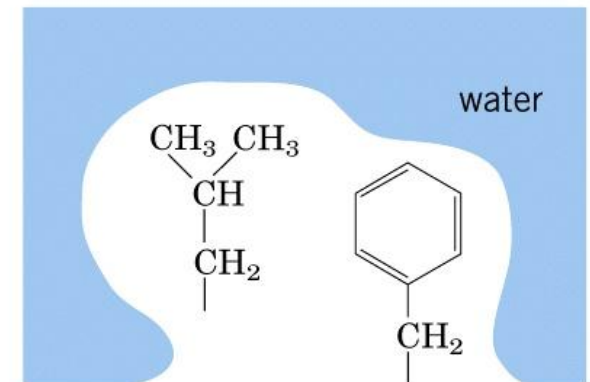
Attraction



Repulsion



Hydrophobic interactions



Van der Waals interactions
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Any two atoms in
close proximity 19

Noncovalent interactions:

Weaker than covalent.

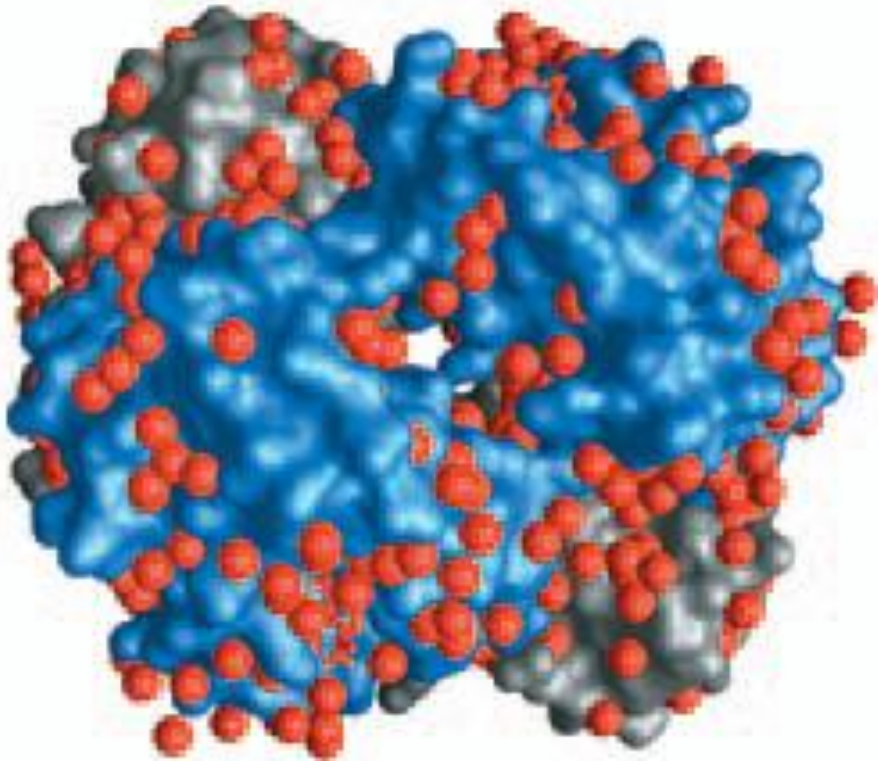
Although all 4 are weak:

The cumulative effect of all is very significant e.g. noncovalent binding of E to S involve several H bond + ionic interactions hydrophobic, Van der Waals. Macromolecules proteins, DNA, RNA, contains many sites for H-bond, Van der Waals, or hydrophobic interactions.

Water binding in hemoglobin:

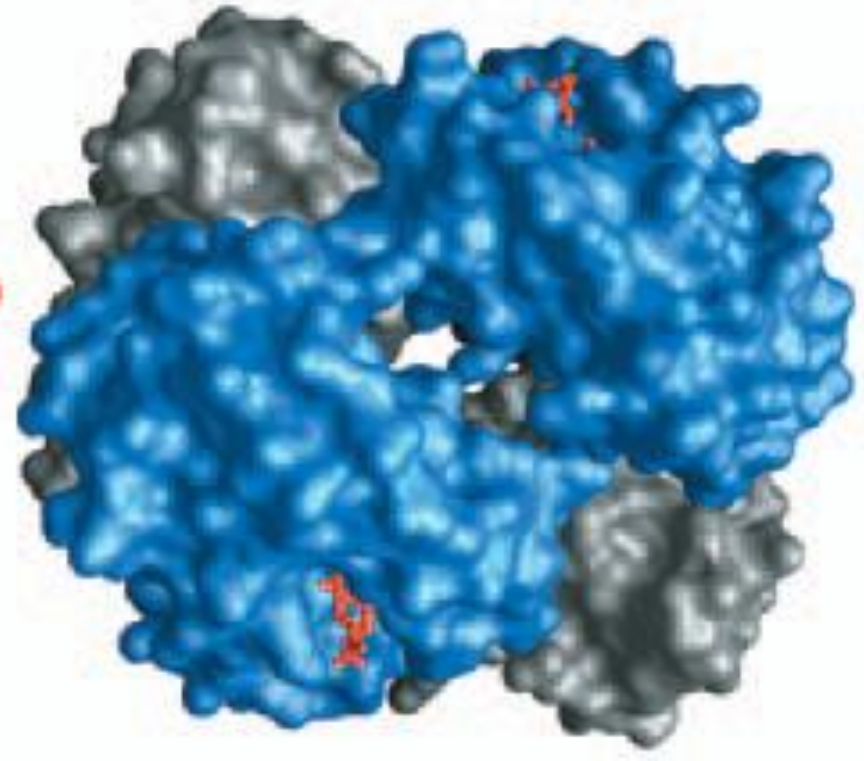
Water molecules bound tightly so firmly as part of the crystal structure, they affect the x-ray diffraction pattern as if they were fixed parts of the crystal.

The same for RNA and DNA.



a) Hemoglobin with bound water molecules

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b) Without water molecules

20

Solutes affect Colligative property of aqueous soln:

- Colligative properties = Tied together properties.
- Solutes alter the characteristics of the solvent (boiling point, Melting/ freezing , and osmotic pressure...etc).
- The same basis= water conc. lower than in pure water.
- The effect is independent on solute chemical properties only no. of solute.
A compound such as NaCl which dissociates in water has twice the effect on osmotic pressure than glucose.

Osmosis:

- Movement of water molecules from a region of higher conc with water to the lower.

- Osmotic pressure Π = force necessary to resist water movement.

$$\Pi = RT \sum c_i, \text{ for } n \text{ solutes } \Pi = RT (i_1c_1 + i_2c_2 + i_3c_3 + \dots + i_nc_n)$$

R = gas constant, T = temp, c_i = osmolarity, c = solute conc, i = van't Hoff factor = no. of solute particles. (for NaCl $i=2$)

- A measure of the extent to which the solutes dissociates to one or more ionic species.

Solutes alter colligative

properties of aqueous soln. :

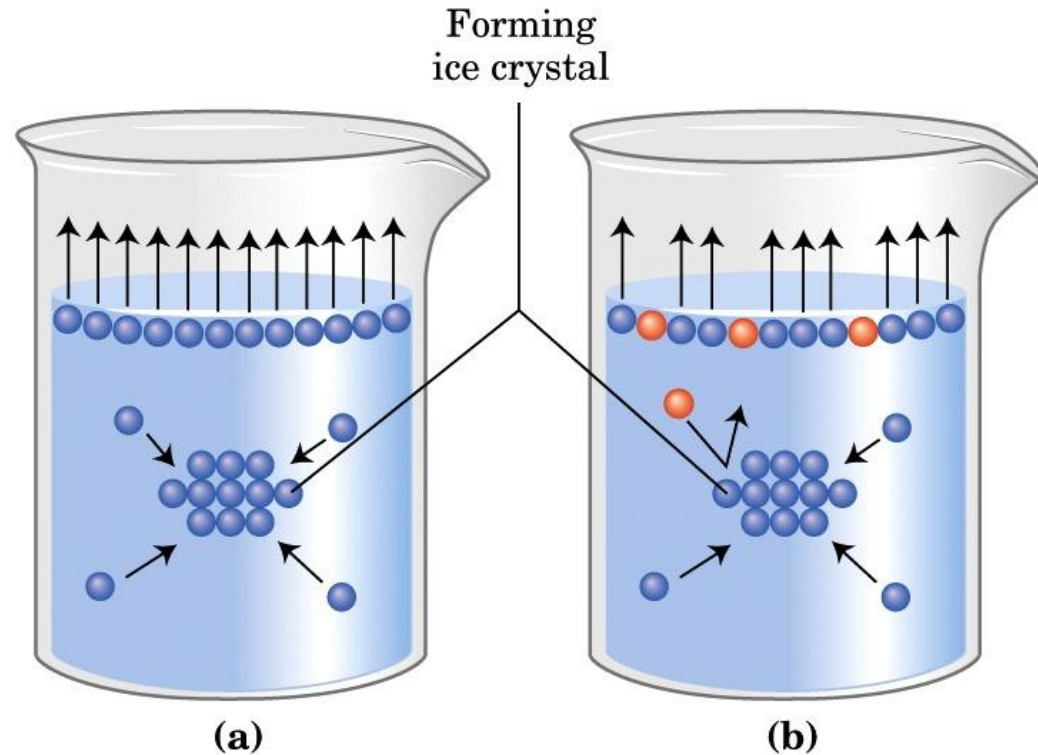
At 1 atm pure water boils at 100C
freezes at 0C.

In presence of solute, the
probability of water molecules
leaving reduced.

boiling temp increased, freezing
point decreased.

● = H₂O

● = Solute



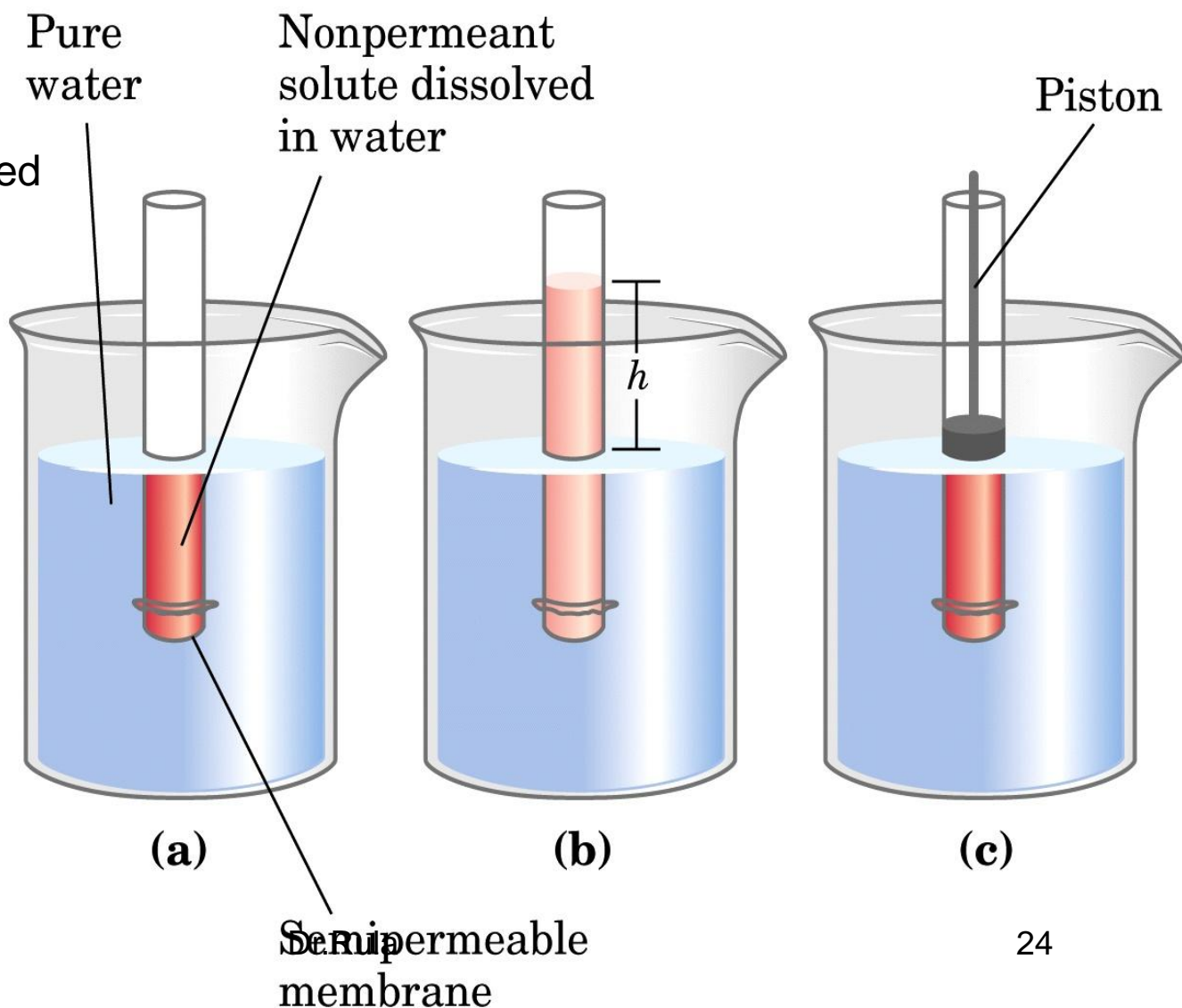
In **pure water**, every molecule at the surface is H₂O, and all contribute to the vapor pressure. Every molecule in the bulk solution is H₂O, and can contribute to formation of ice crystals.
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In this **solution**, the effective concentration of H₂O is reduced; only 3 of every 4 molecules at the surface and in the bulk phase are H₂O. The vapor pressure of water and the tendency of liquid water to enter a crystal are reduced proportionately.

Osmosis: water movement across a semipermeable mb driven by differences in osmotic pressure.

Measurement of osmotic pressure:

Osmotic pressure measured as the force needed to return the soln. in the tube to the level of that in the beaker, proportional to height h of column b .



Isotonic:

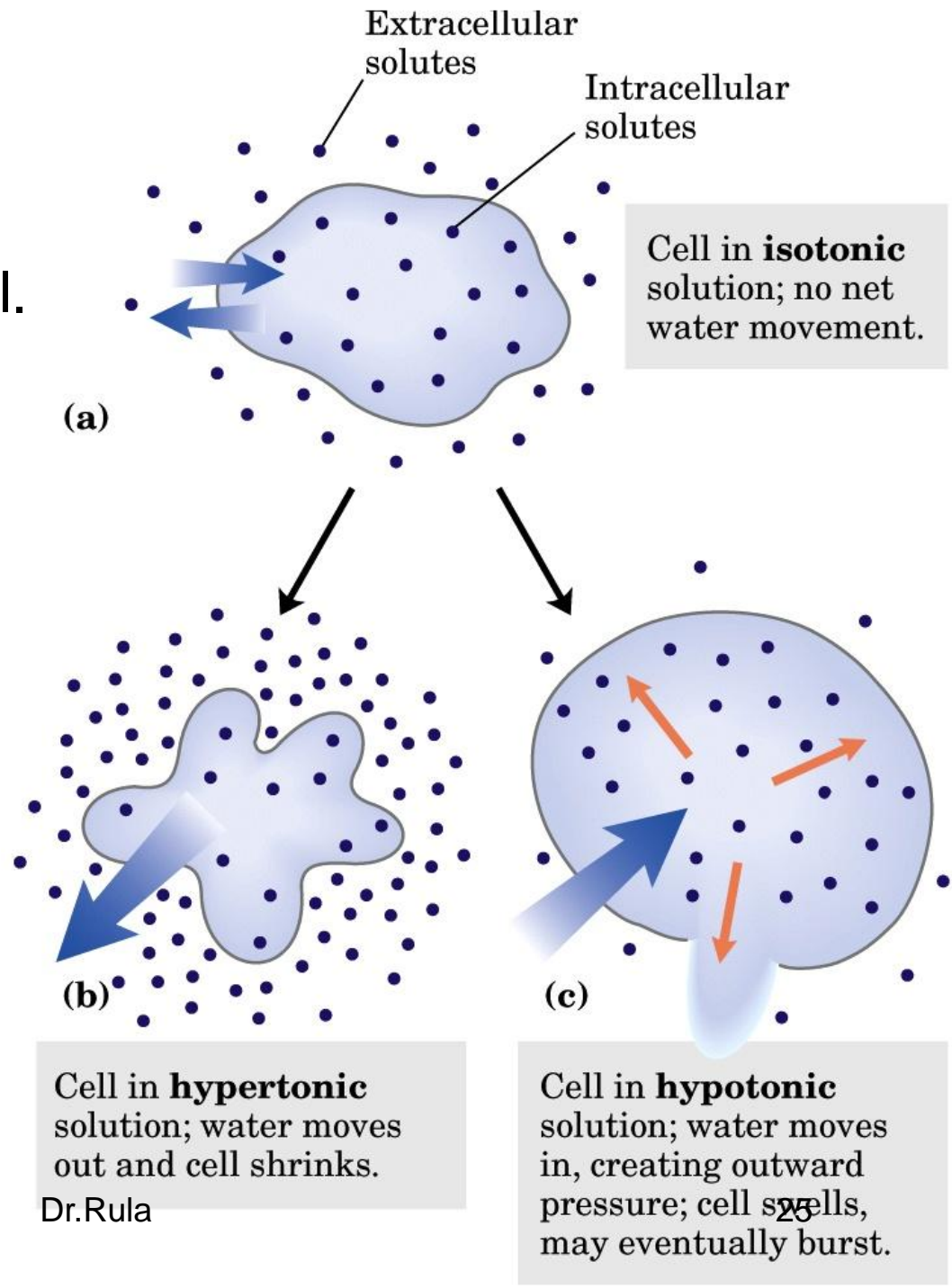
no gain or loss of water.

Hypertonic:

higher osmolarity than cytosol.

Hypotonic:

lower osmolarity than cytosol.



Osmotic Lysis a catastrophe that has been overcome by:

In bacteria + plants:

Rigid strong nonexpandable cell wall that resist osmotic pressure.

Organisms that live in fresh water:

Contractile vacuole = tiny pumps excel water out of the cell.

In multicellular Animals:

Excess water removed by kidney, sweat glands, lungs.

Blood plasma + interstitial tissue (extracellular fluid of tissues) similar osmolarity to cytosol. Due to blood proteins e.g. albumin + cells pump out ions such as Na^+ to stay in osmotic balance with the surroundings.

Osmolarity depend on number of solutes not mass:

Macromolecules (proteins, polysaccharides, nucleic acids) has less effect on osmolarity than an equal mass of their monomers.

One effect of storage of sugar by polysaccharides (starch /glycogen) than glucose is prevention of high osmotic pressure within the storage cell.

-In lab protocols osmosis taken into consideration, buffers in cellular fractionation contain 0.2 M sucrose to protect organelles from osmotic lysis.

Touch response in Venus flytrap:

The specialized leaves fold together in response to a light touch by an insect.

Trapping the insect for further digestion.

Change within
0.5 sec .
Achieved by K^+
release from cells.



(a)



(b)

Ionization of water, weak acids and weak bases:

Water undergo reversible ionization



Free protons don't exist in solution, hydrated to form $\rightarrow \text{H}_3\text{O}^+$
hydronium ion

Water ionization measured by electrical conductivity:

H^+ migrates to \rightarrow cathode.

OH^- migrates to \rightarrow anode.

Proton / ionic hopping:

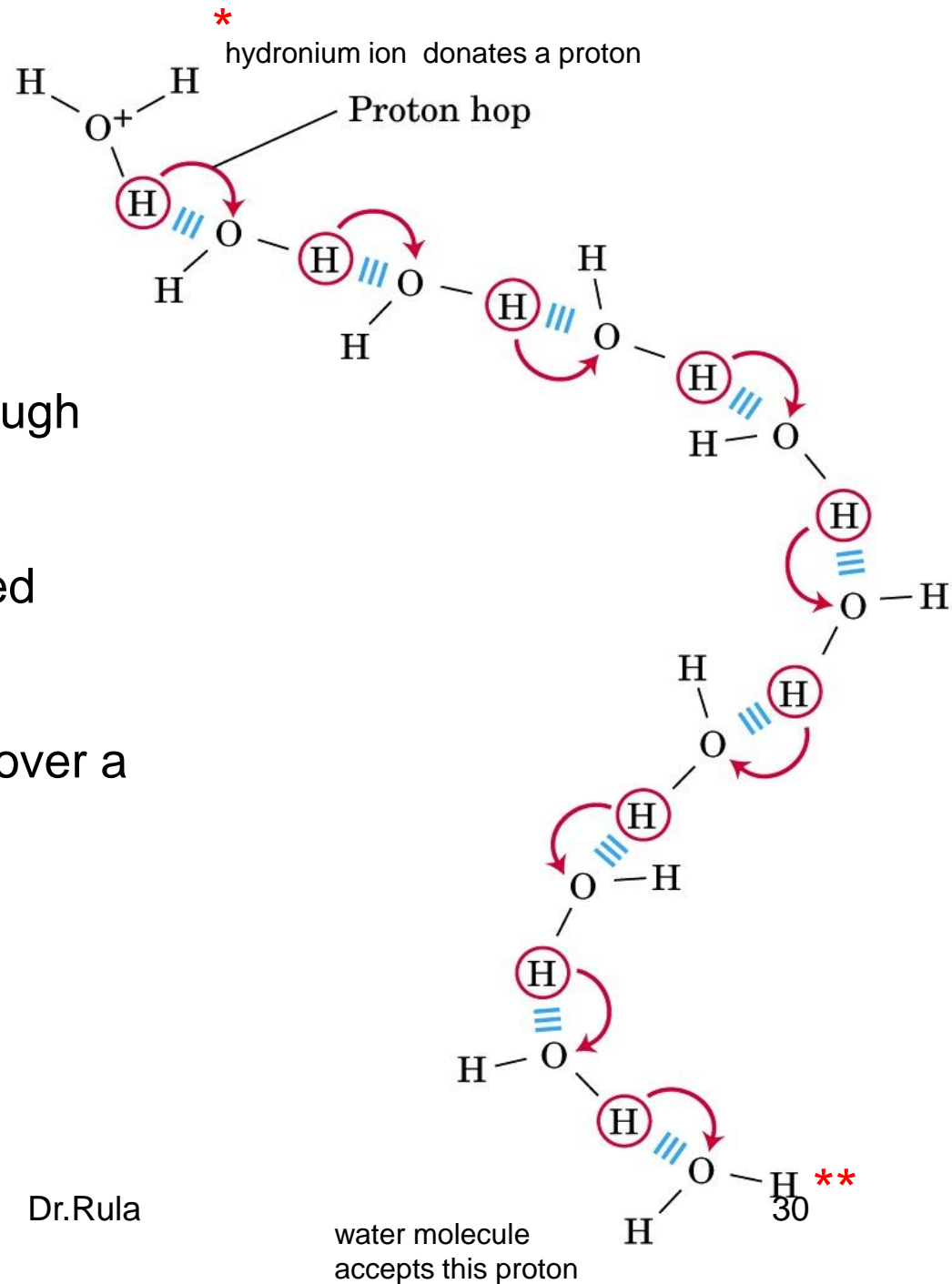
faster than diffusion

High + fast ionic mobility =

-Individual protons don't move through the bulk solution.

-Series of protons hop bw H-bonded water molecules.

- result in net movement of proton over a long distance in a short time.



The position of any rxn given by equilibrium constant = K eq.



$$K \text{ eq} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

In pure water at 25°C,

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

p = “ negative logarithm of ”

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log 10^{-7}$$

$$= 7 = \text{neutral pH}$$

pH = 7 neutral
 pH < 7 acidic
 pH > 7 basic / alkaline.

A differ in 1 pH unit
 Means 10 times more H+ conc.

pH measured by pH indicator,
 litmus paper, pH meter.

pH meter =
 Glass electrode selectively
 sensitive to [H+] not to Na+ or K+

table 4-5

The pH Scale			
[H ⁺] (M)	pH	[OH ⁻] (M)	pOH*
10 ⁰ (1)	0	10 ⁻¹⁴	14
10 ⁻¹	1	10 ⁻¹³	13
10 ⁻²	2	10 ⁻¹²	12
10 ⁻³	3	10 ⁻¹¹	11
10 ⁻⁴	4	10 ⁻¹⁰	10
10 ⁻⁵	5	10 ⁻⁹	9
10 ⁻⁶	6	10 ⁻⁸	8
10 ⁻⁷	7	10 ⁻⁷	7
10 ⁻⁸	8	10 ⁻⁶	6
10 ⁻⁹	9	10 ⁻⁵	5
10 ⁻¹⁰	10	10 ⁻⁴	4
10 ⁻¹¹	11	10 ⁻³	3
10 ⁻¹²	12	10 ⁻²	2
10 ⁻¹³	13	10 ⁻¹	1
10 ⁻¹⁴	14	10 ⁰ (1)	0

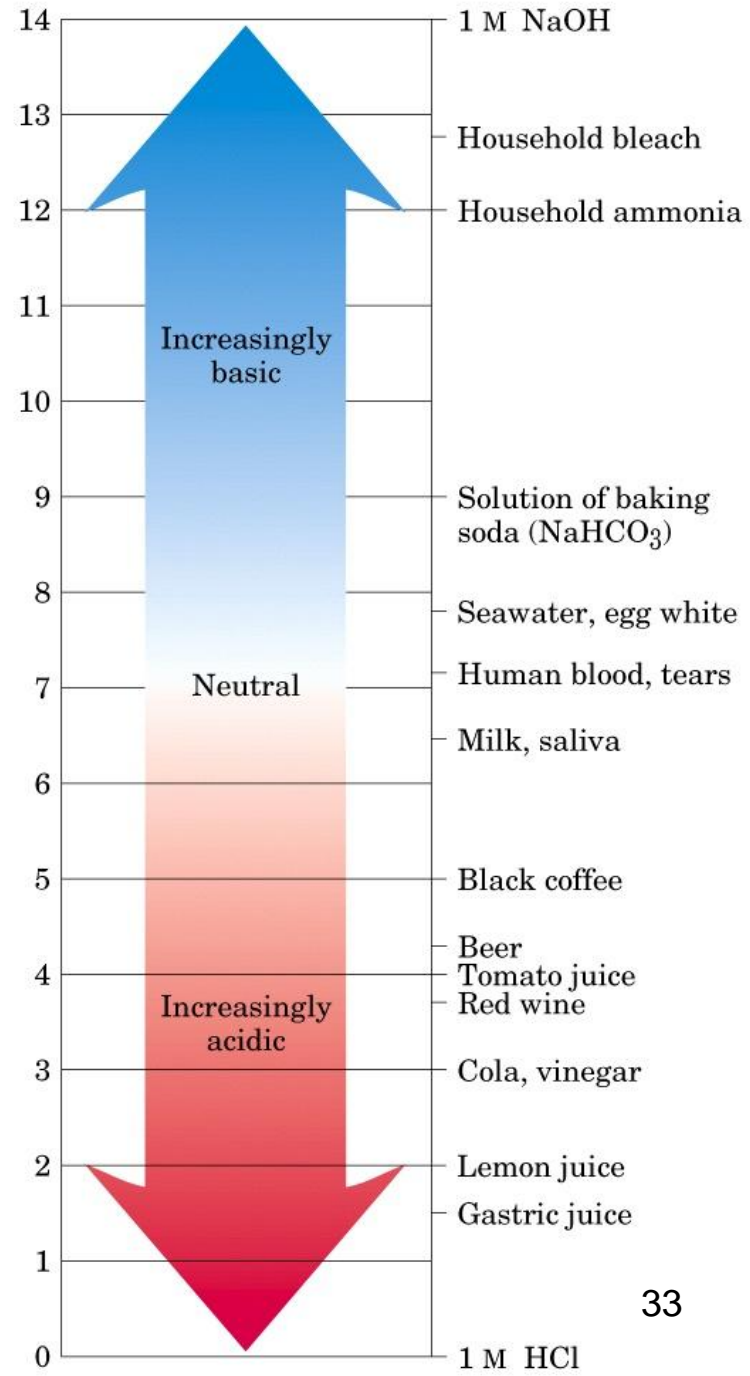
*The expression pOH is sometimes used to describe the basicity, or OH⁻ concentration, of a solution; pOH is defined by the expression pOH = -log [OH⁻], which is analogous to the expression for pH. Note that in all cases, pH + pOH = 14.

pH affects structure + activity of Biological Macromolecules:

- Enzyme catalytic activity dependent on pH
- pH of blood and urine for medical diagnosis.

pH in uncontrolled diabetes is < 7.4
= acidosis. Higher pH > 7.4 alkalosis.

Strong acids/ bases completely ionized in dilute aqueous soln. e.g. Hydrochloric acid, Nitric acid, NaOH and KOH.



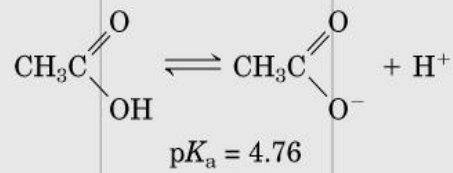
Conjugate acid-base pairs consist of a proton donor and a proton acceptor.

Acids = proton donors, Bases = proton acceptors.

The stronger the acid the greater its tendency to lose proton.

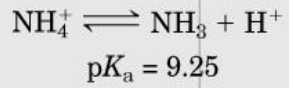
Monoprotic acids

Acetic acid
 $(K_a = 1.74 \times 10^{-5} \text{ M})$



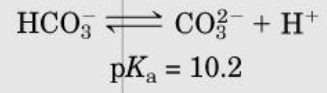
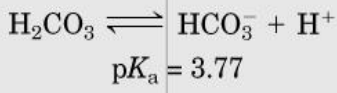
Conjugate acid-base pair
 acetic acid and acetate anion

Ammonium
 $(K_a = 5.62 \times 10^{-10} \text{ M})$

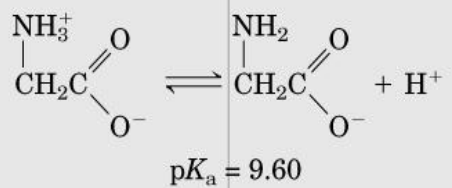
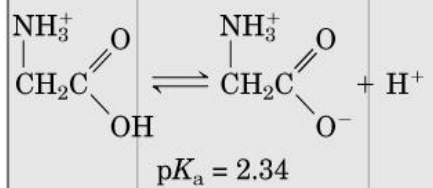


Diprotic acids

Carbonic acid
 $(K_a = 1.70 \times 10^{-4} \text{ M});$
 Bicarbonate
 $(K_a = 6.31 \times 10^{-11} \text{ M})$

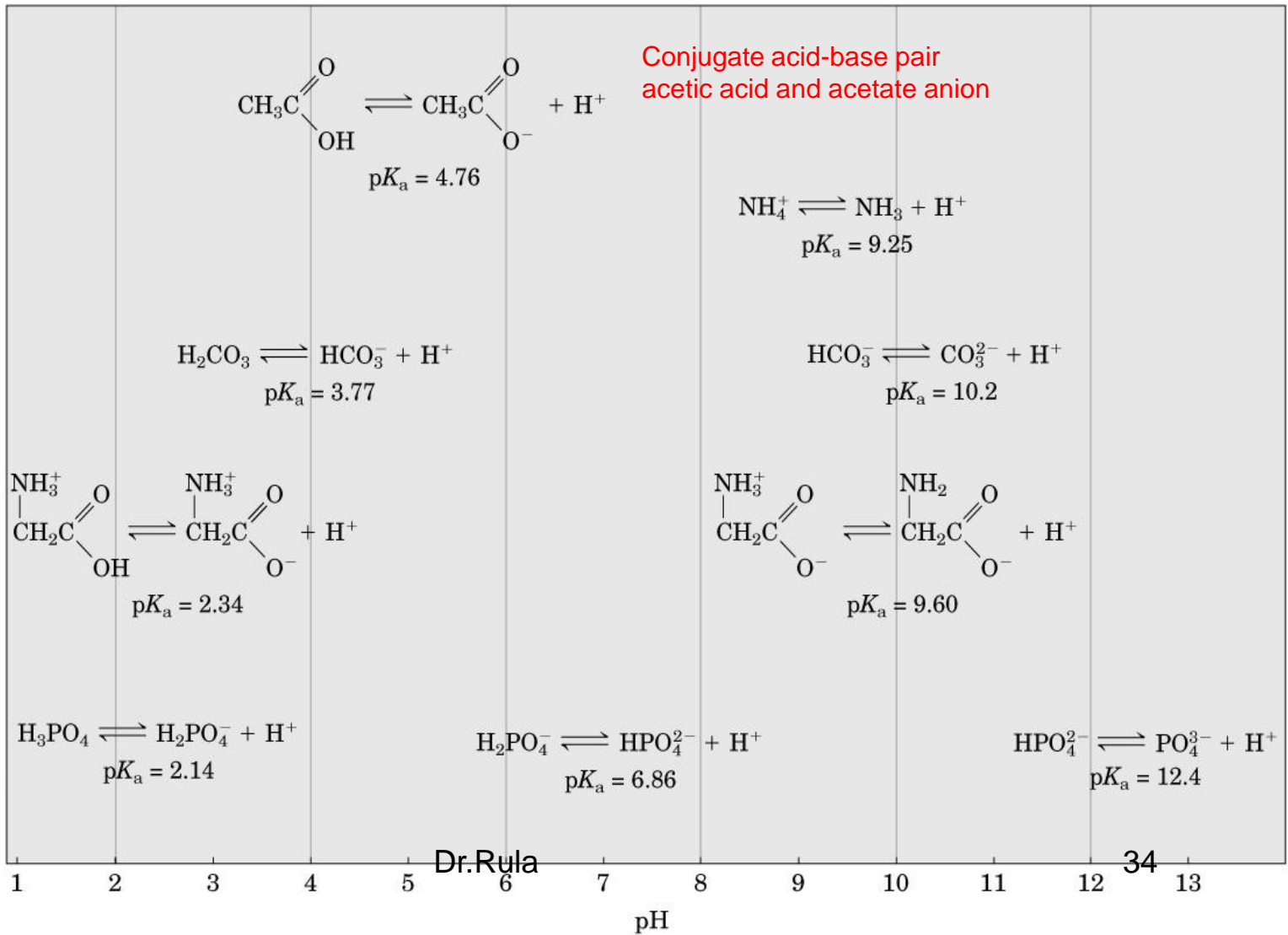
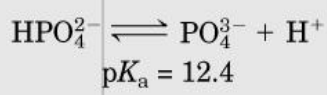
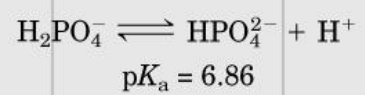
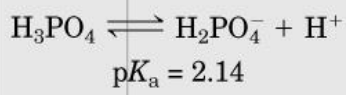


Glycine, carboxyl
 $(K_a = 4.57 \times 10^{-3} \text{ M});$
 Glycine, amino
 $(K_a = 2.51 \times 10^{-10} \text{ M})$

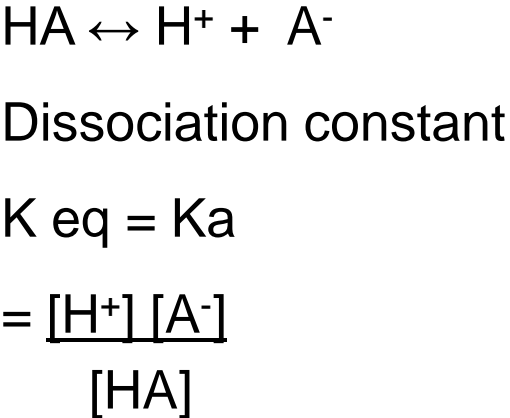


Triprotic acids

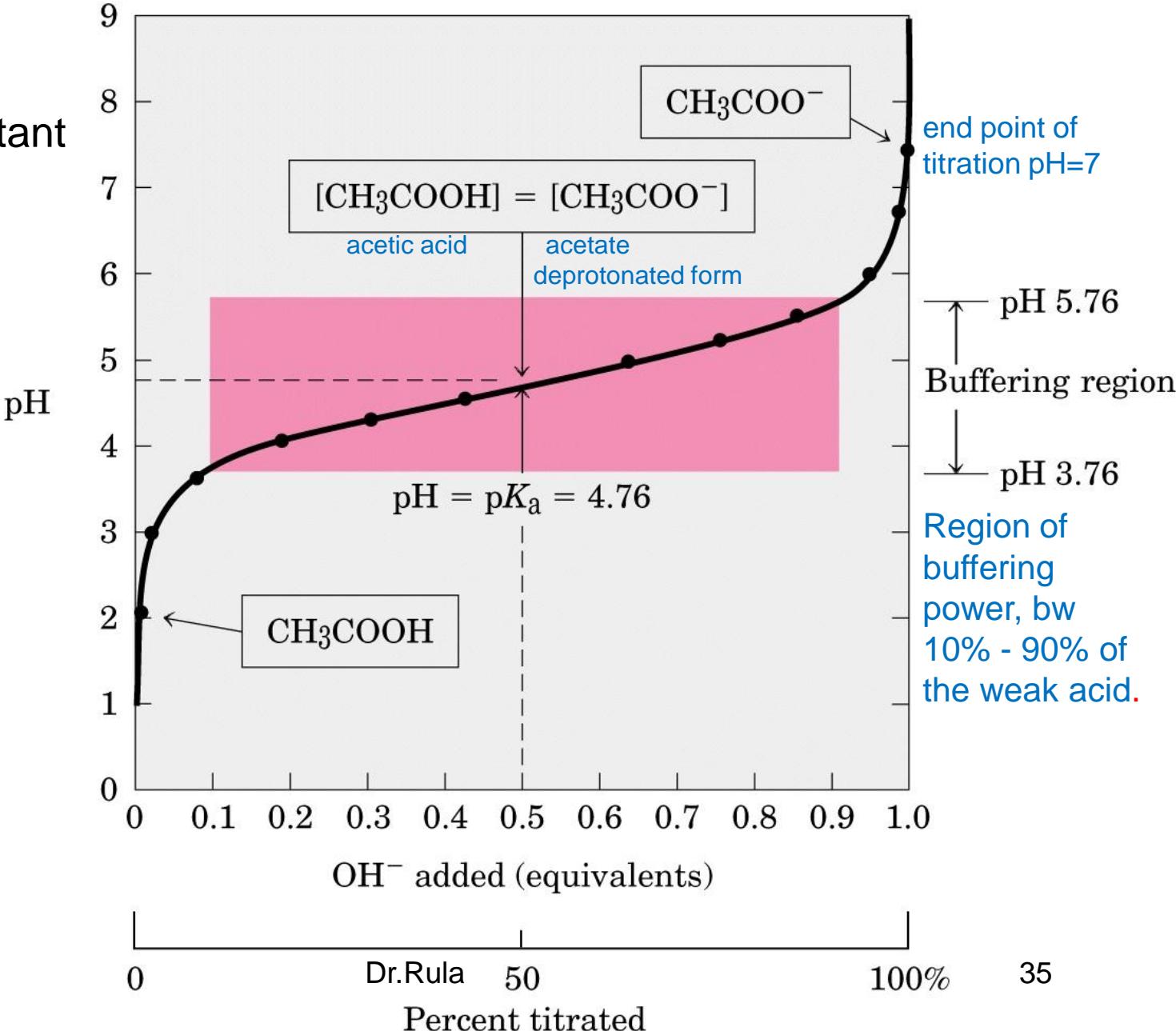
Phosphoric acid
 $(K_a = 7.25 \times 10^{-3} \text{ M});$
 Dihydrogen phosphate
 $(K_a = 1.38 \times 10^{-7} \text{ M});$
 Monohydrogen phosphate
 $(K_a = 3.98 \times 10^{-13} \text{ M})$



Titration curves used to determine the amount of an acid in a soln. :



Midpoint of titration
 [proton donor] =
 [proton acceptor].



Titration curves of 3 weak acids:

$pK_a = -\log K_a$

$pK_a = pH$ at midpoint

of the titration curve.

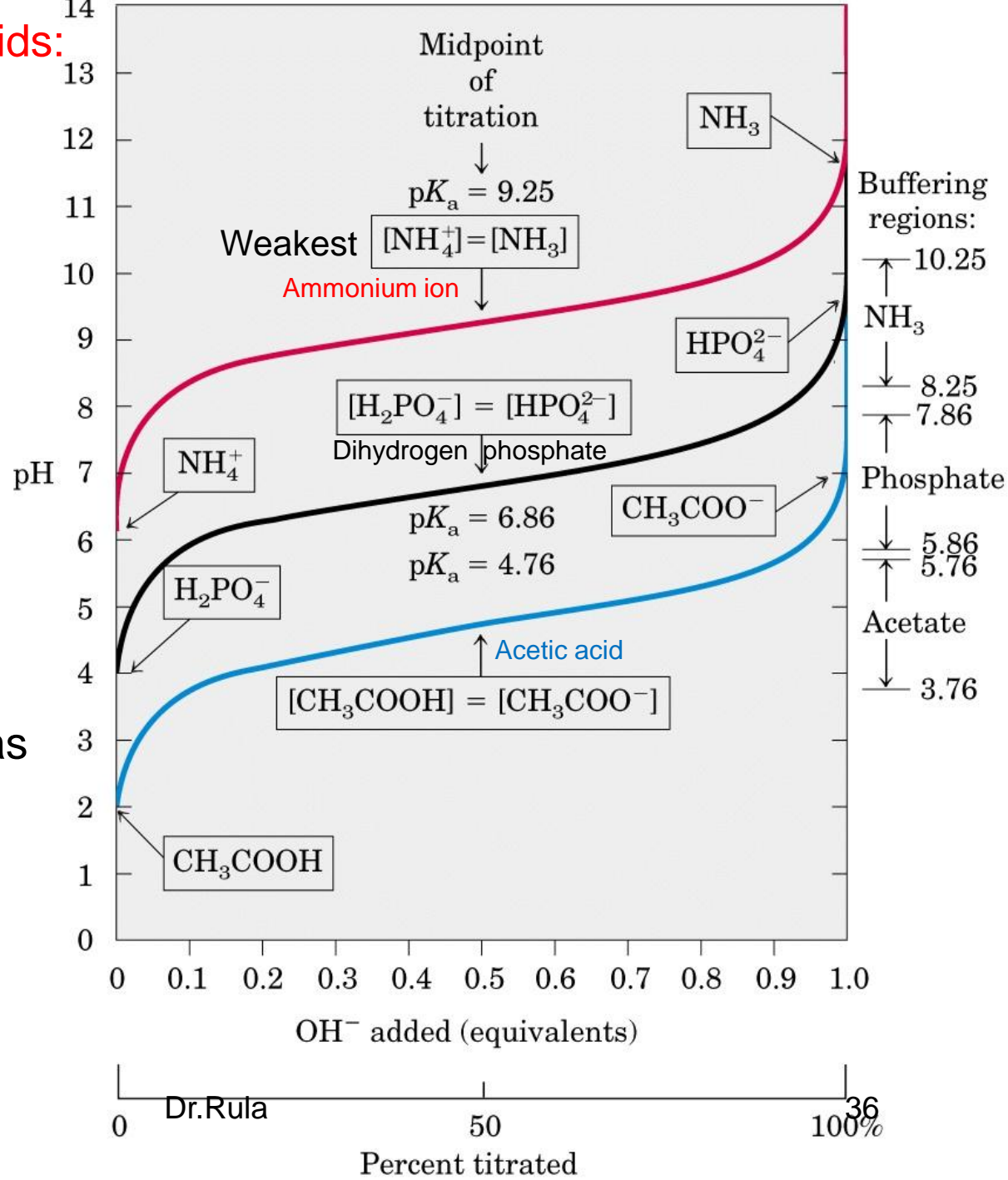
The stronger the acid \rightarrow

the lower its pK_a

The stronger the base \rightarrow

the higher its pK_a

Each conjugate acid-base has a characteristic pH zone in which it is an effective buffer.

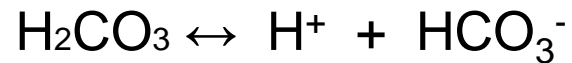
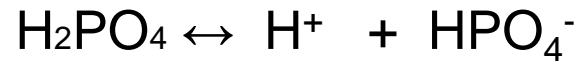


Biological processes are pH dependent :

Cells and organisms maintain a specific and constant cytosolic pH near pH 7

This maintained by **biological buffers**:

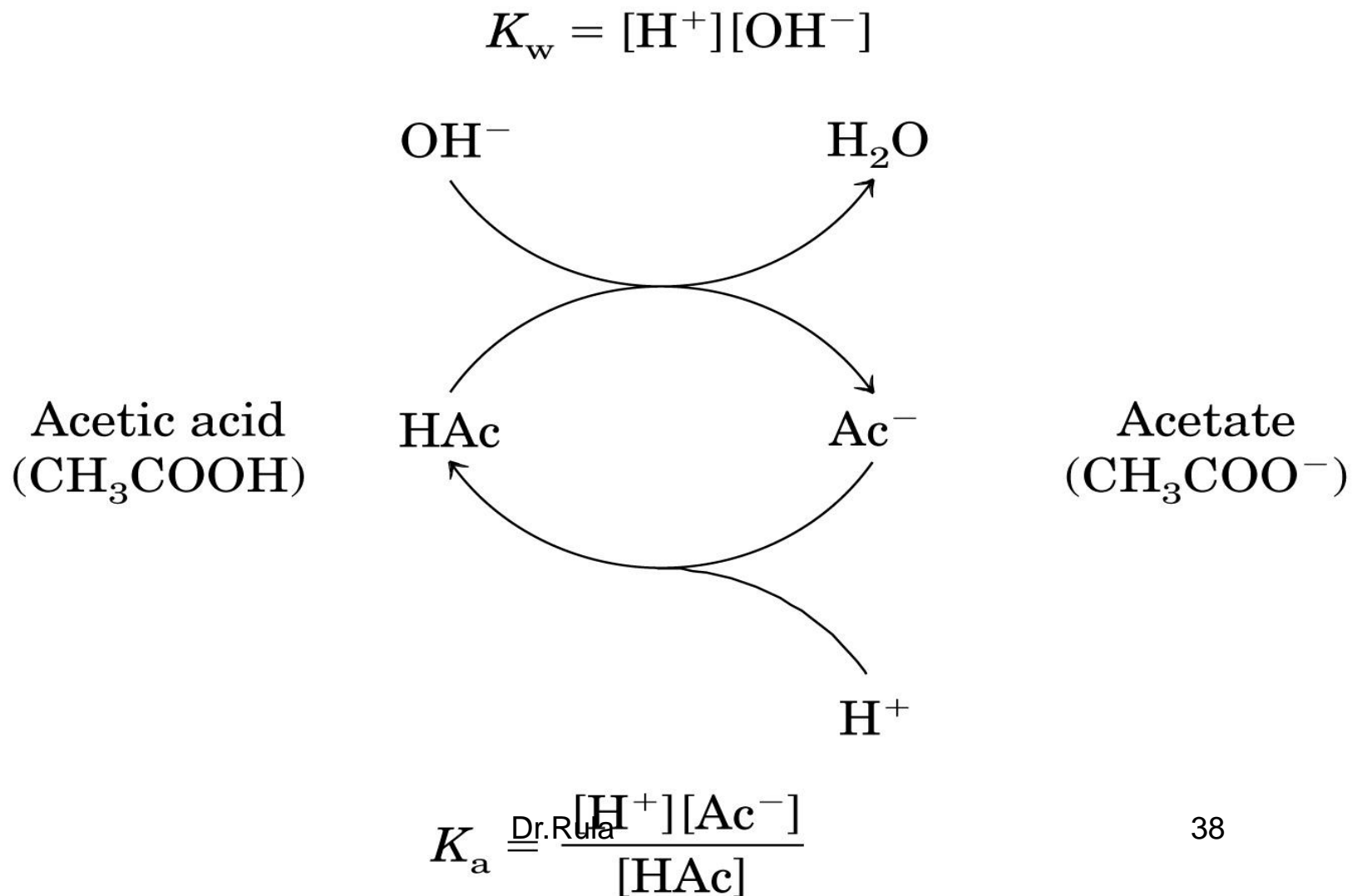
Phosphate and carbonate buffering systems.



Buffer = aqueous system that tend to resist changes in pH when small amounts of acid (H^+) or base (OH^-) are added.

The acetic acid –acetate pair as a buffer system:

Two reversible rxn equilibria , [H+] or [OH-] added to a buffer a slight change in pH occurs . Not comparable to when [H+] or [OH-] are added to pure water, or a soln. with NaCl which has no buffering power.



Titration curves have identical shapes →

reflect a fundamental law or relationship described by

Henderson Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-] \text{ Proton acceptor}}{[\text{HA}] \text{ Proton donor}}$$

Note:

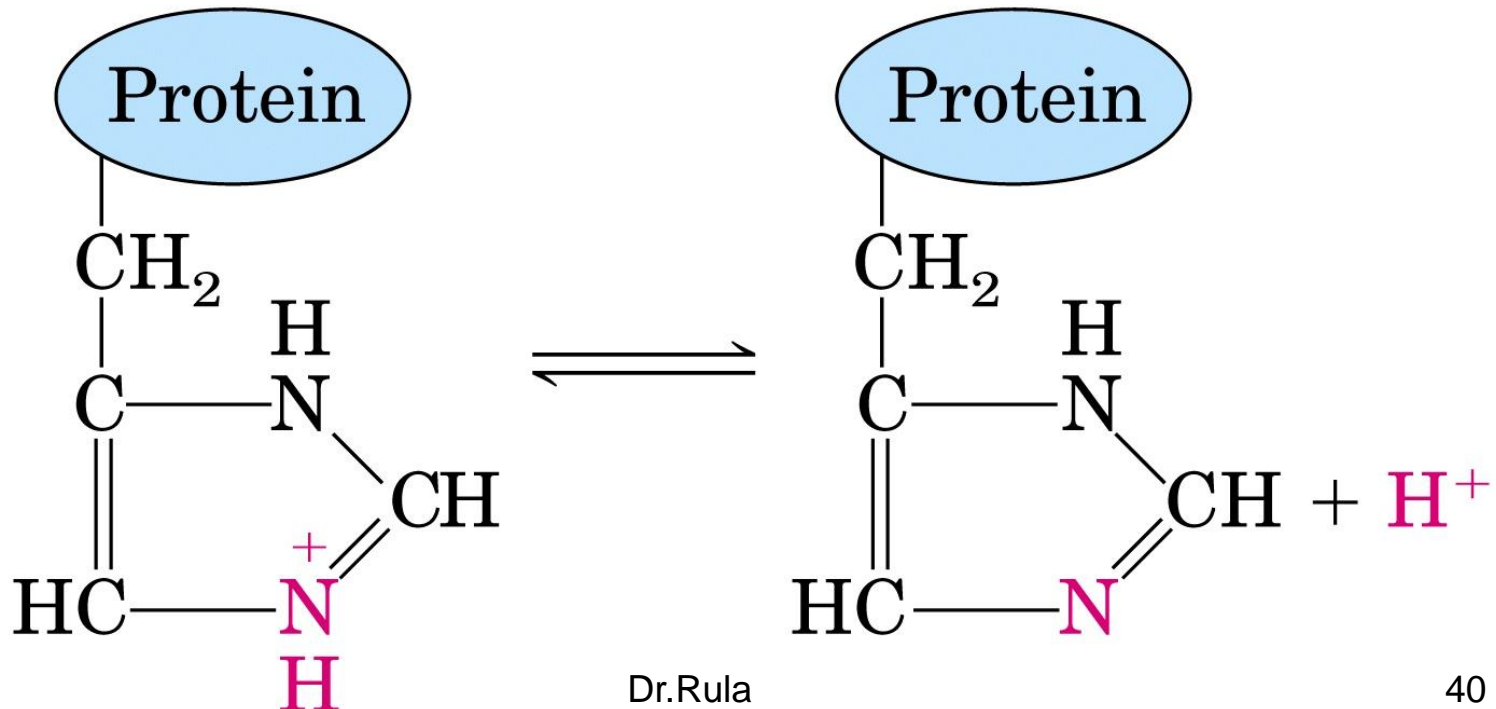
at midpoint $[\text{A}^-] = [\text{HA}] \rightarrow \text{pH} = \text{p}K_a + \log 1 \rightarrow \text{pH} = \text{p}K_a$

Buffers=The organisms 1st line of defense against changes in internal pH

Cytoplasm of most cells contains high conc. of proteins which contain a.a with functional groups that are weak acids or weak bases.

e.g. **histidine** is a weak acid, side chain pKa=6

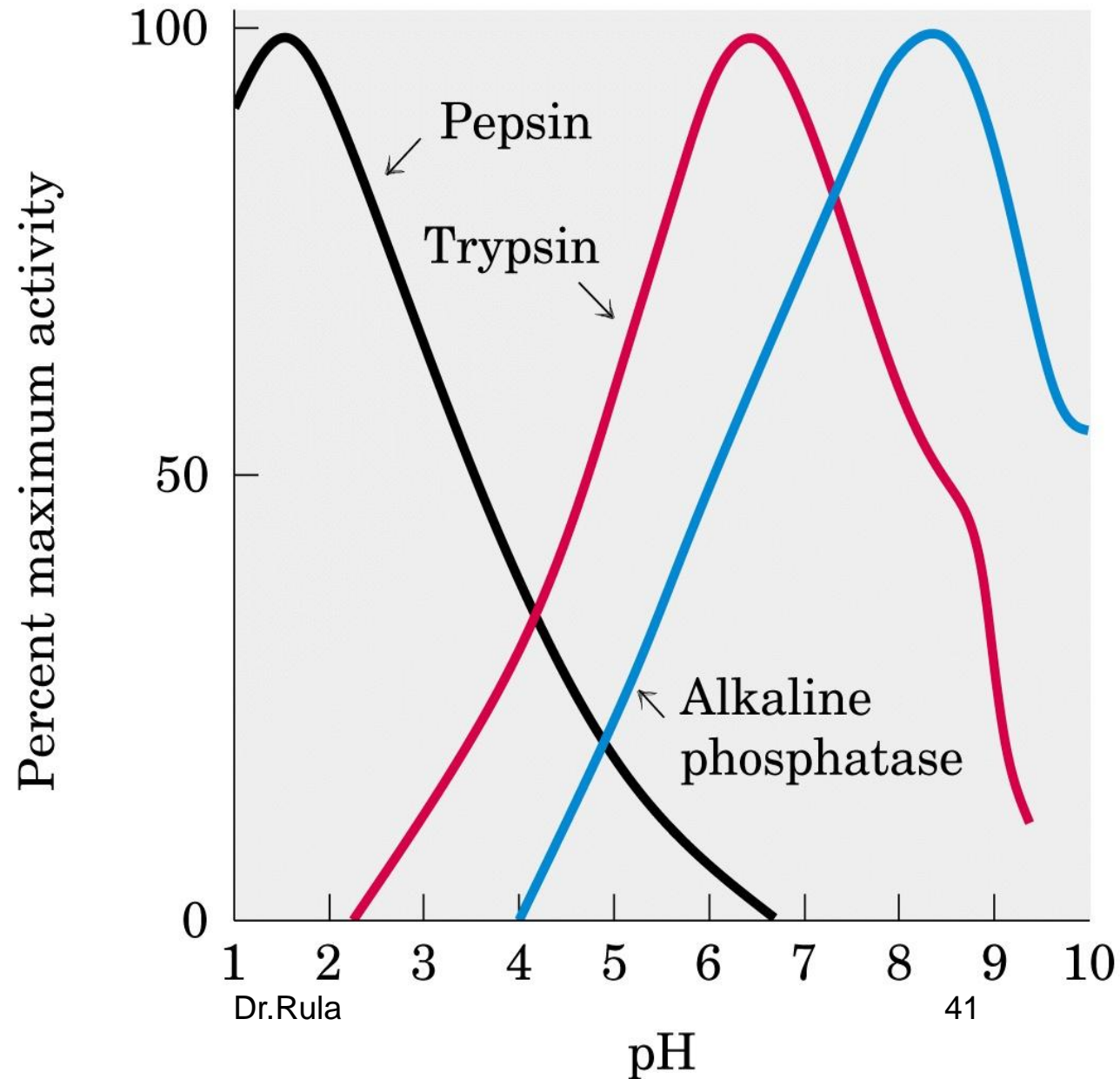
Nucleotides such as ATP contribute to buffering capacity of cytoplasm.



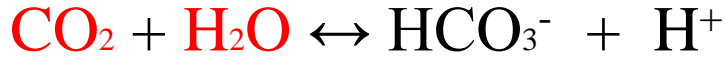
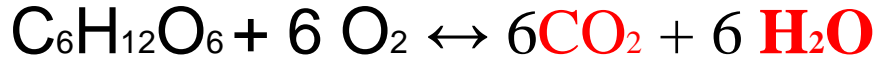
The optimal pH for some enzymes:

The catalytic activity of enzymes require an optimum pH.

Maximal catalytic activity
at a characteristic pH.
pH declines sharply on
both sides of the
optimum pH .

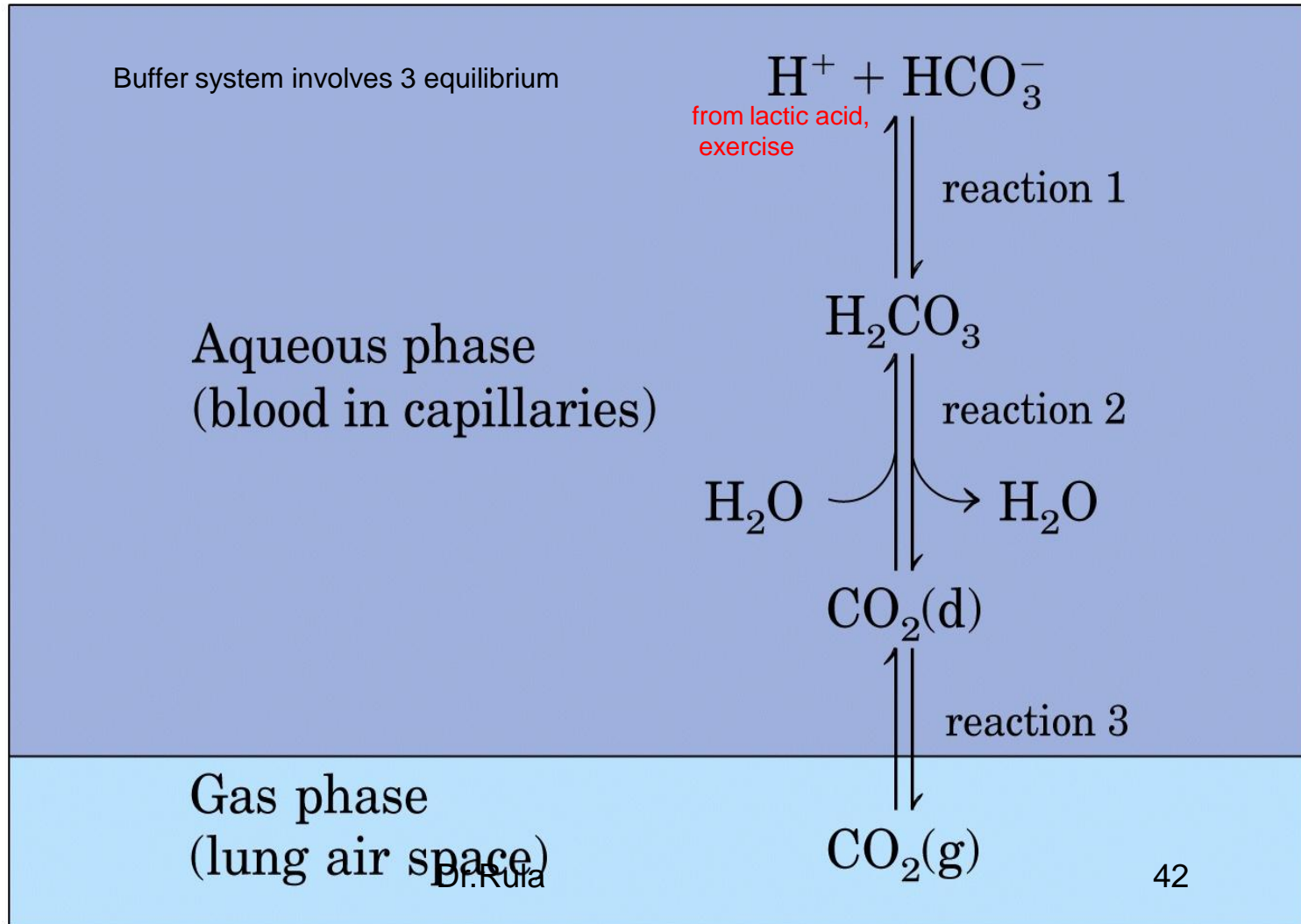


Glucose Oxidation:



CO₂ in lungs in equilibrium with bicarbonate buffer in blood plasma .

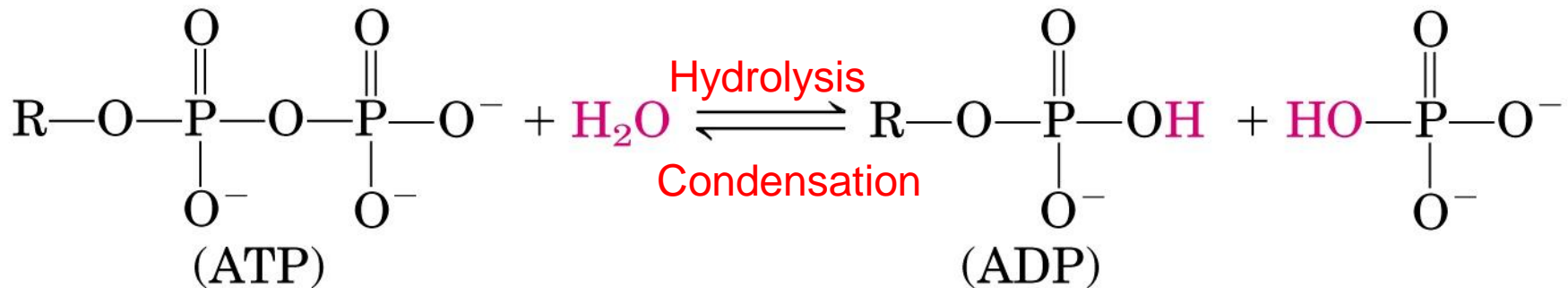
Breathing can quickly adjust blood pH .



Water as a reactant:

Not only a solvent but also a participant in biological rxns:

- Hydrolysis (depolymerization of macromolecules proteins, CHO, nucleic acids)
Exergonic
- Condensation (water molecules eliminated to condense)
Endergonic



Phosphoanhydride

(a)