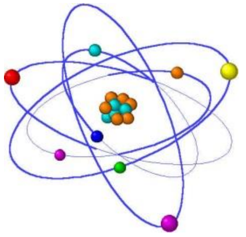
Lecture 1



Life, the Universe, and Everything

Chapters 1-3

Where Biochemistry Fits In

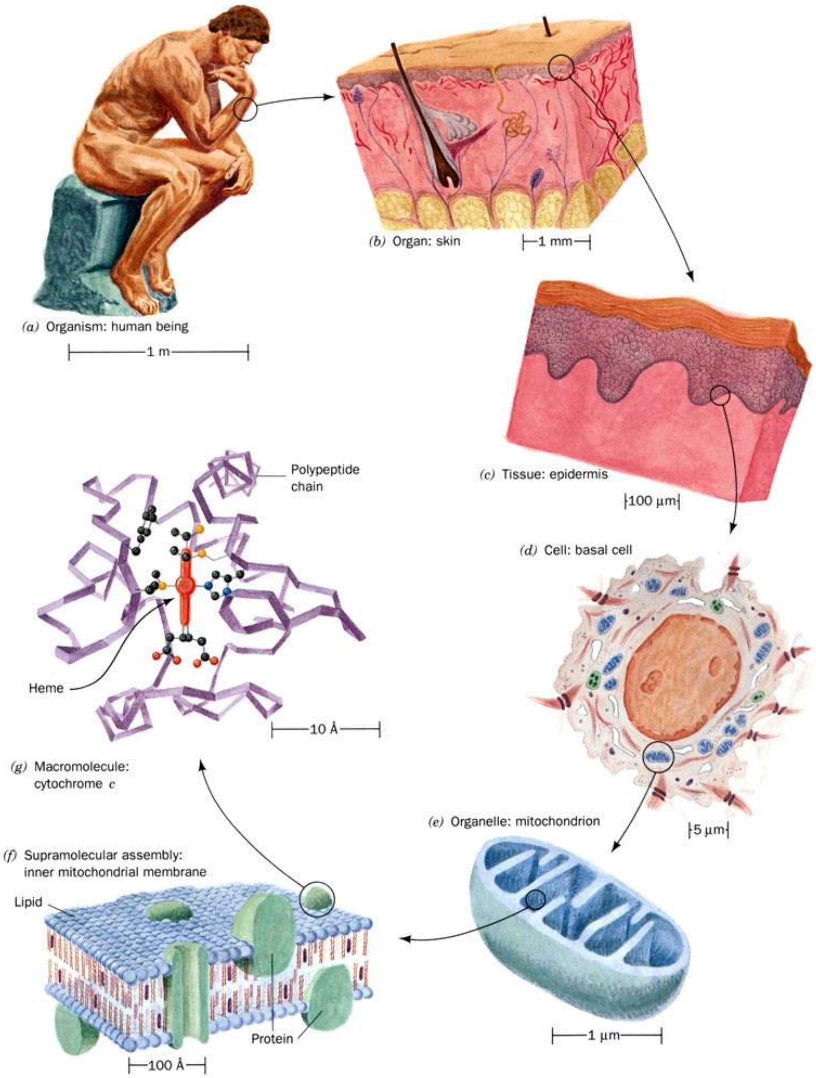
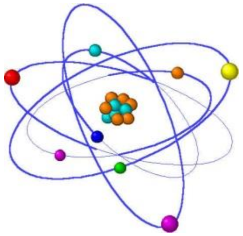


Figure 1-14

The Basics



What exactly is Biochemistry?

Study of life on the molecular level

Life - ?

Capacity for growth, reproduction, functional activity, and continual change preceding death.

Smallest Unit of Life?

Cell

Classification

Prokaryotes

Eukaryotes

Prokaryotes

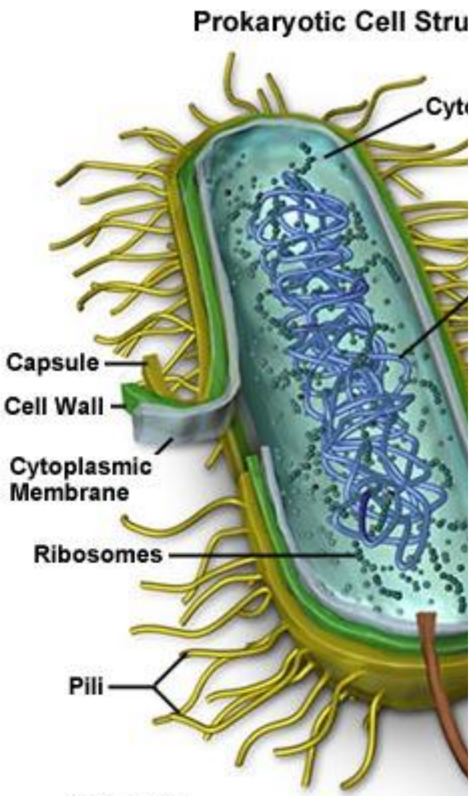


Figure 1

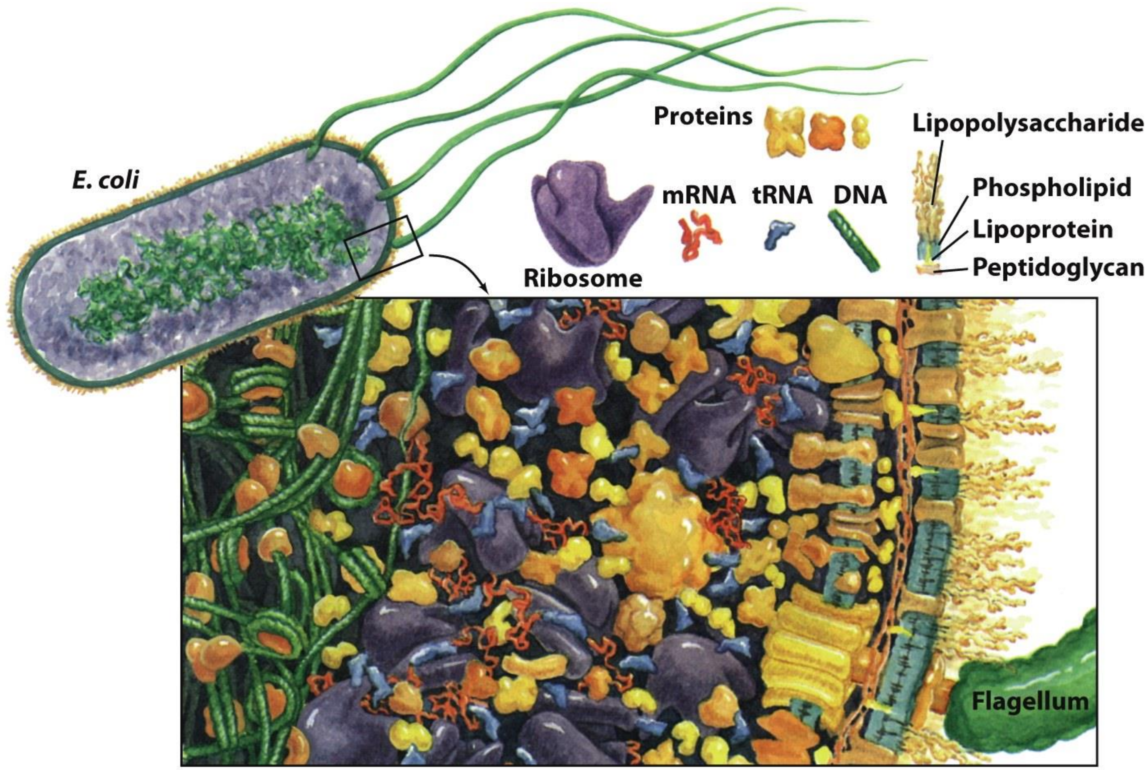
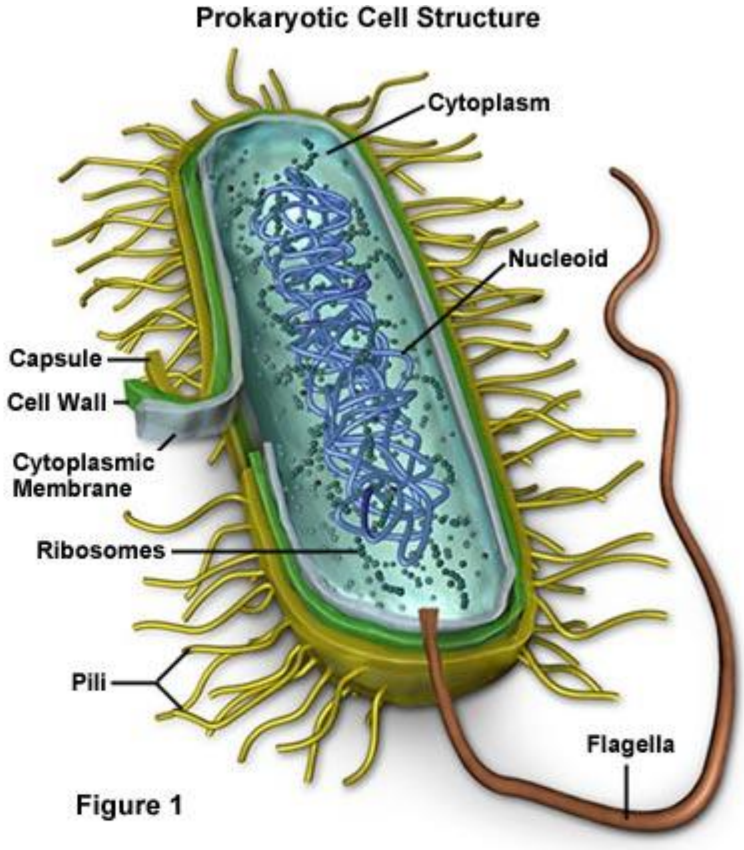


Figure 1-13

Prokaryotes



Cytoplasm –

Ribosome –

Nucleoid –

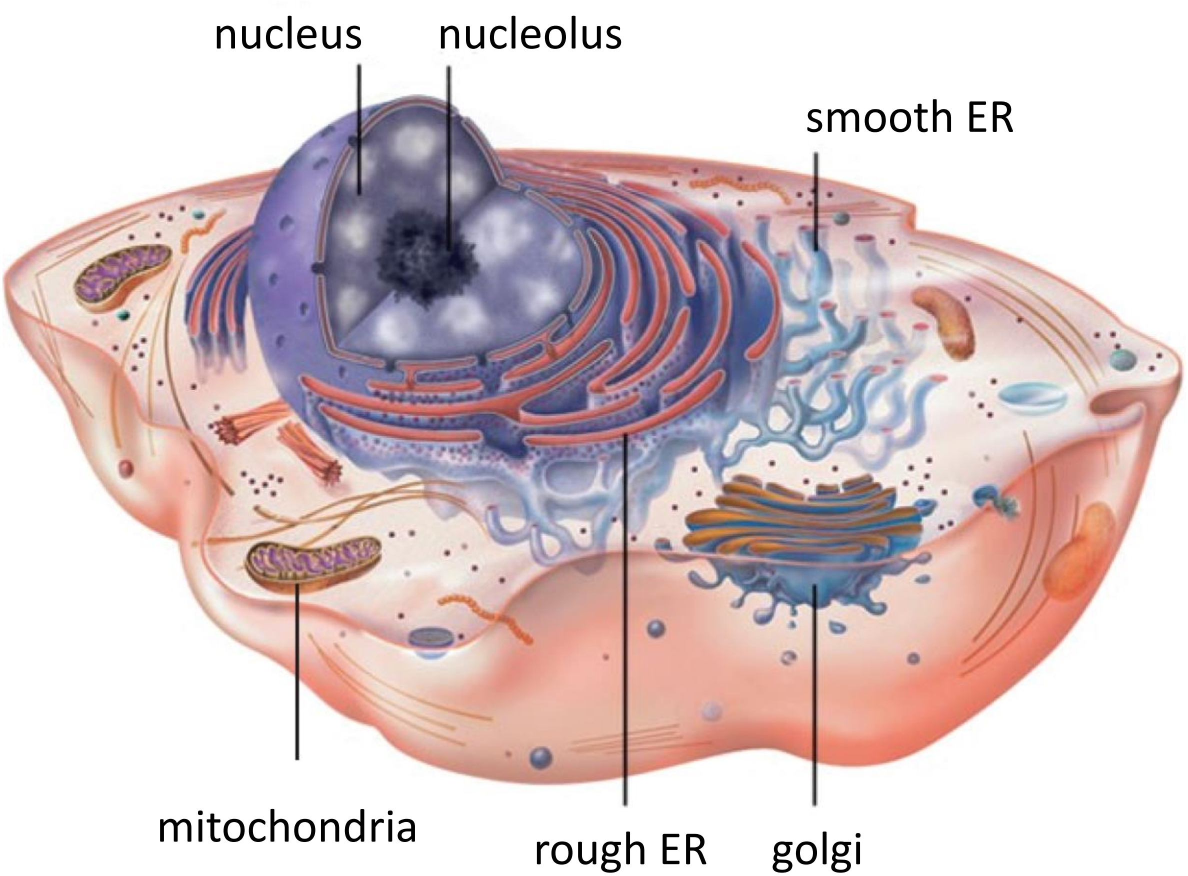
Flagella

Cell Wall –

Plasma Membrane –

Pili –

Eukaryotes



Components of the Cell

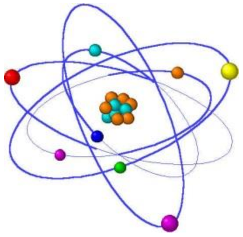


Table 1-3 **Elemental Composition of the Human Body**

Element	Dry Weight (%)[a]	Elements Present in Trace Amounts
C	61.7	B
N	11.0	F
O	9.3	Si
H	5.7	V
Ca	5.0	Cr
P	3.3	Mn
K	1.3	Fe
S	1.0	Co
Cl	0.7	Ni
Na	0.7	Cu
Mg	0.3	Zn
		Se
		Mo
		Sn
		I

[a]Calculated from Frieden, E., *Sci. Am.* **227**(1), 54–55 (1972).

Table 1-3

Components of the Cell

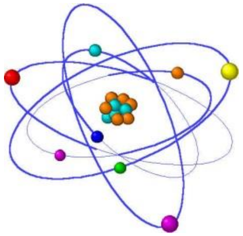


Table 1-1 **Molecular Composition of *E. coli***

Component	Percentage by Weight
H_2O	70
Protein	15
Nucleic acids:	
DNA	1
RNA	6
Polysaccharides and precursors	3
Lipids and precursors	2
Other small organic molecules	1
Inorganic ions	1

Source: **Watson, J.D., *Molecular Biology of the Gene* (3rd ed.), *p.* 69, Benjamin (1976).**

Table 1-1

Water – the solvent of life

What makes water ideal for living systems?

Water – the solvent of life

What makes water ideal for living sysems?

Polarity – allows cellular compartmentalization

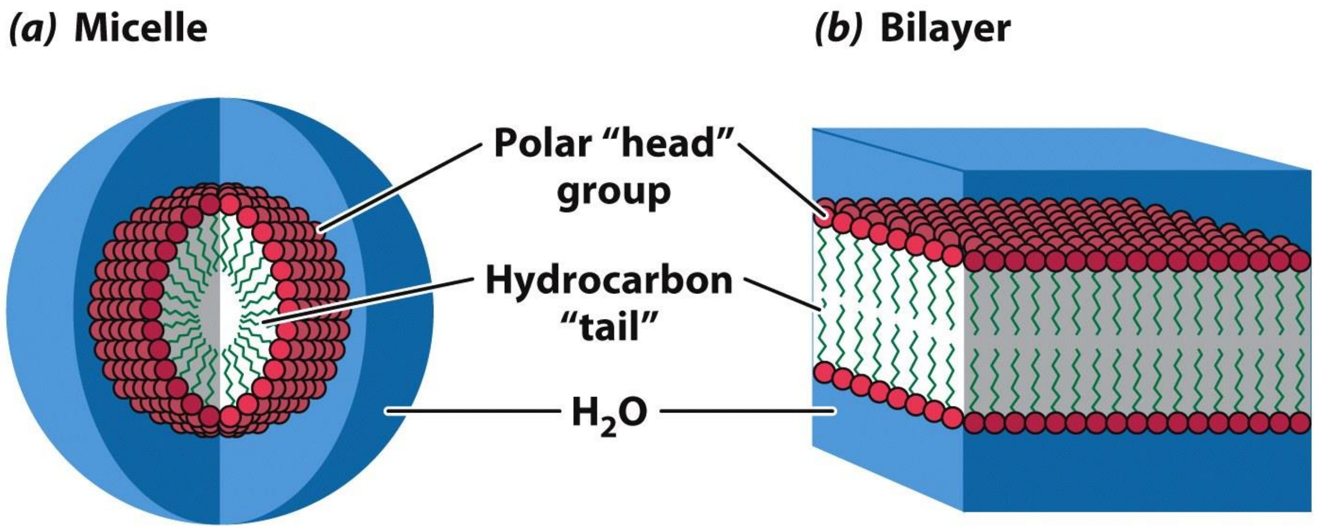


Figure 2-8

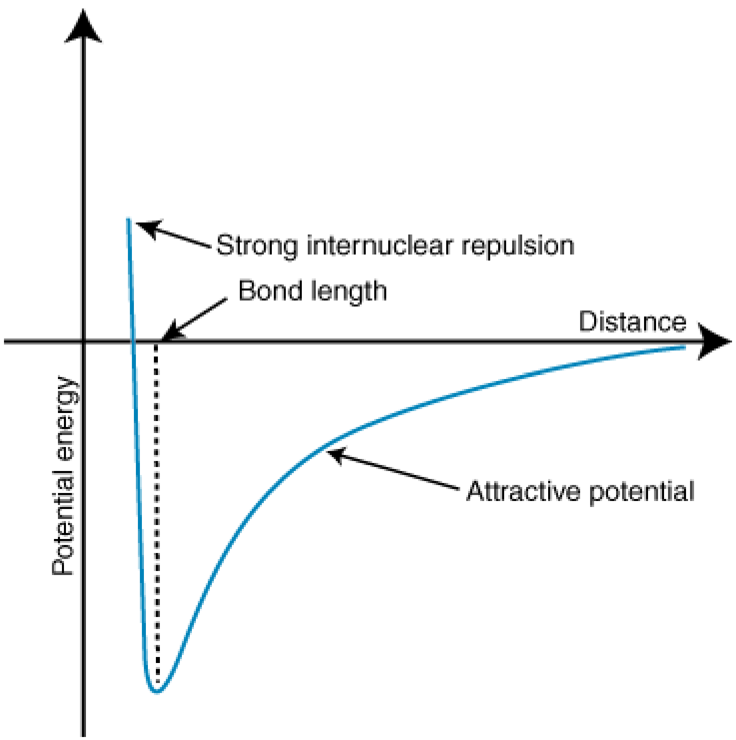
Water – the solvent of life

What makes water ideal for living sysems?

$$F = \frac{kq_1q_2}{r^2}$$

Polarity and dielectric – allows dissolution of ions

Dielectric Constant of the solvent



Substance	Dipole Moment (debye)
Formamide	3.37
Water	1.85
Dimethyl sulfoxide	3.96
Methanol	1.66
Ethanol	1.68
Acetone	2.72
Ammonia	1.47
Chloroform	1.15
Diethyl ether	1.15
Benzene	0.00
Carbon tetrachloride	0.00
Hexane	0.00

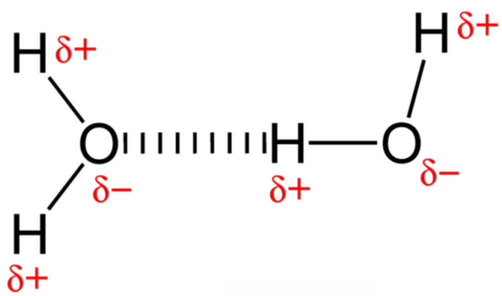
Source: **Brey, W.S., *Physical Chemistry and Its Biological Applications*, *p.* 26, Academic Press (1978).**

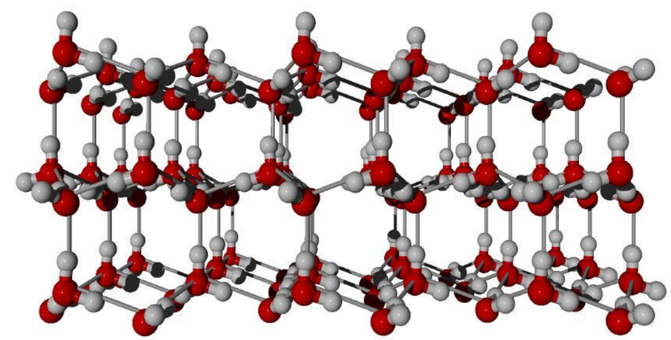
Table 2-1

Water – the solvent of life

What makes water ideal for living sysems?

H-bonding potential

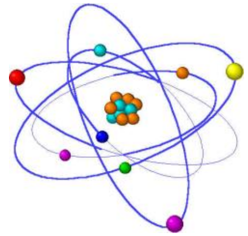




Substance	Specific Heat J/(g·°C)	Molar Heat Capacity J/(mol ·°C)
Air (dry)	1.01	29.1
Aluminum	0.902	24.4
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.450	25.1
Mercury	0.140	28.0
NaCl	0.864	50.5
Water(*s*)*	2.03	36.6
Water(*l*)	4.179	75.3

*At −11°C

Water and Acids-Bases Chemistry



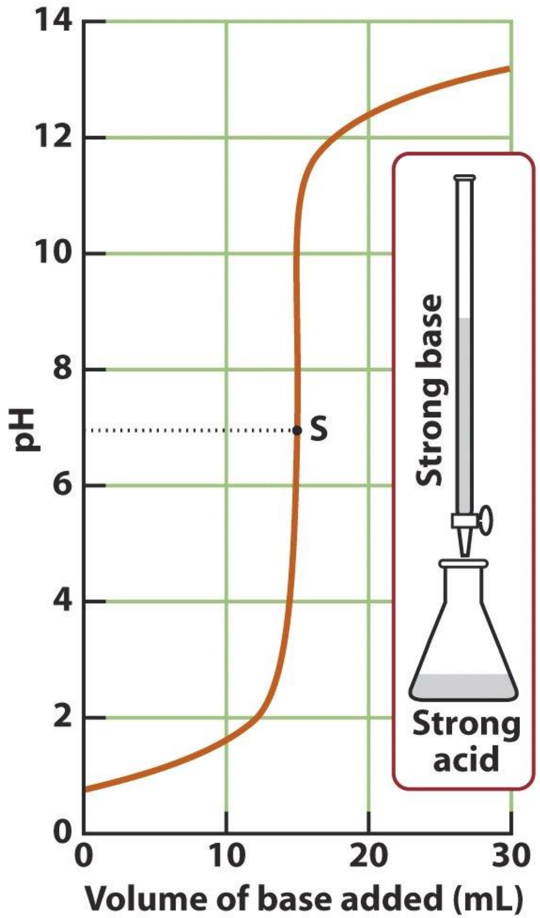
When Bronsted Acid is dissolved in water, something MUST act as a base

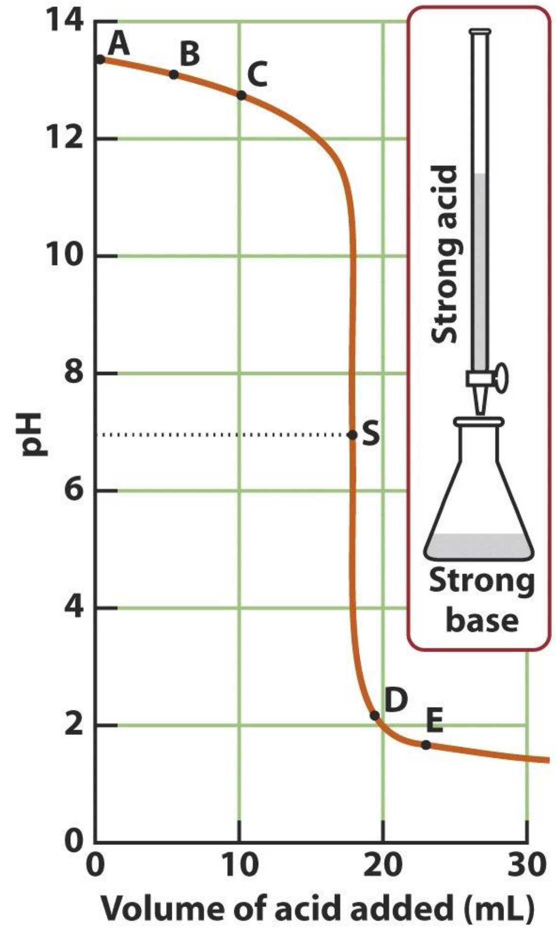
$$HA_{aq} + H_2O \rightleftharpoons H_3O^{+}{}_{aq} + A^{-}{}_{aq} \qquad K_a = \frac{[H^{+}][A^{-}]}{[HA]}$$

$$H_2O_{(l)} + A^{-}{}_{aq} \rightleftharpoons OH^{-}{}_{aq} + HA_{aq} \qquad K_b = \frac{[OH^{-}][HA]}{[A^{-}]}$$

What are the equilibrium constants?

Titration Curves





Weak Acids and Bases

Calculate the pH of 465 μM Acetic Acid ($pK_a = 4.75$)

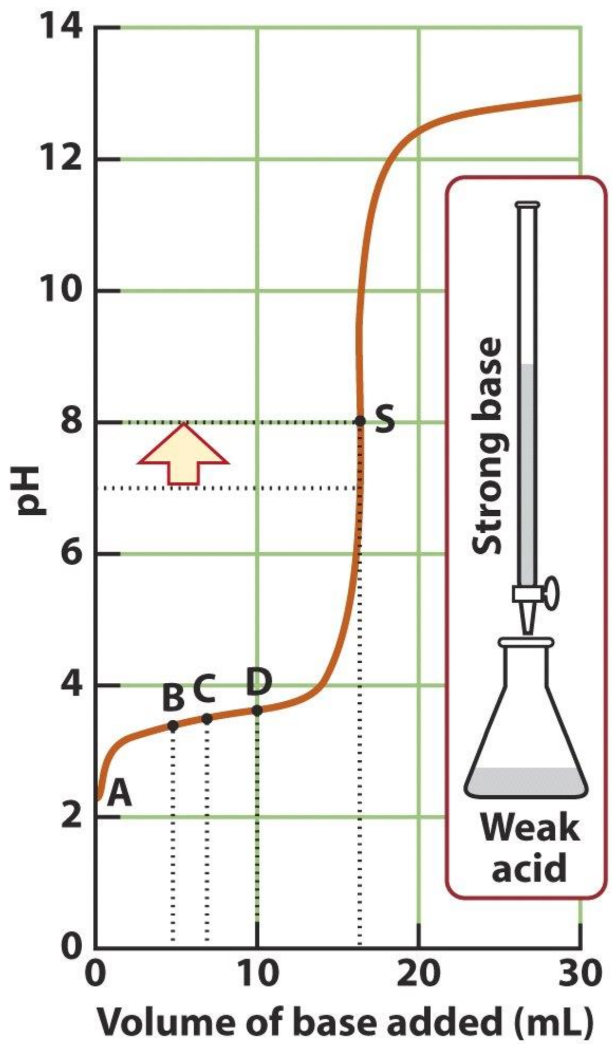
$$HX_{aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{aq} + X^-_{aq}$$

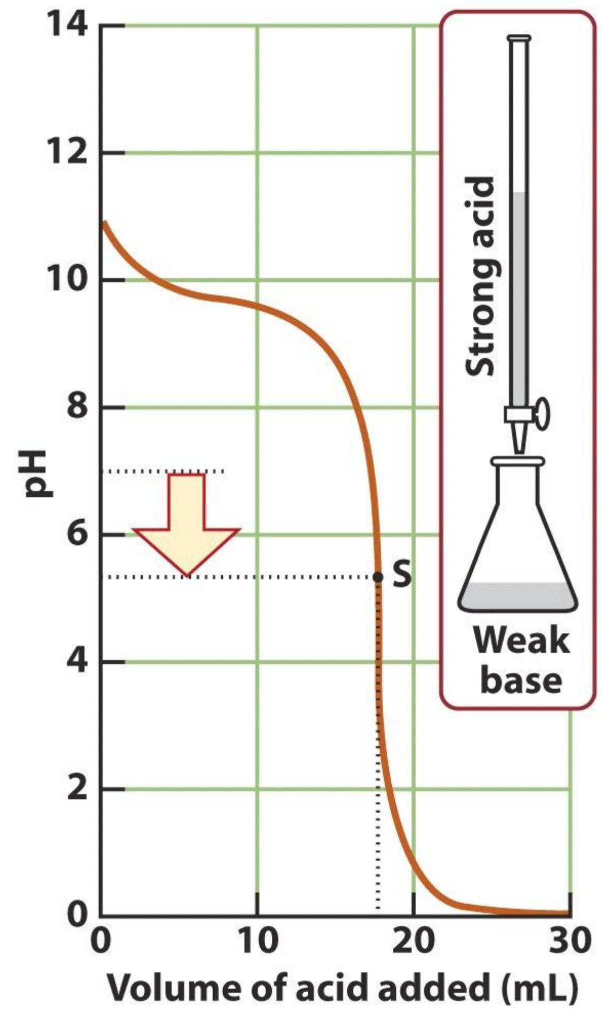
Weak Acids and Bases

Calculate the pH of 465 μM pyridine (pK_a = 5.25)

$$X_{aq} + H_2O_{(l)} \rightleftharpoons OH^-_{aq} + HX^+_{aq}$$

Titrations of Weak Acids with a Strong Base





Mathematical simplification of Acid-Base Chemistry

Derive a mathematical expression that relates the pH and pK_a with the ratio of conjugate acid to conjugate base.

Buffers

$$X^-_{aq} + H_2O_{(l)} \rightleftharpoons OH^-_{aq} + HX_{aq}$$

$$HA_{aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{aq} + A^-_{aq}$$

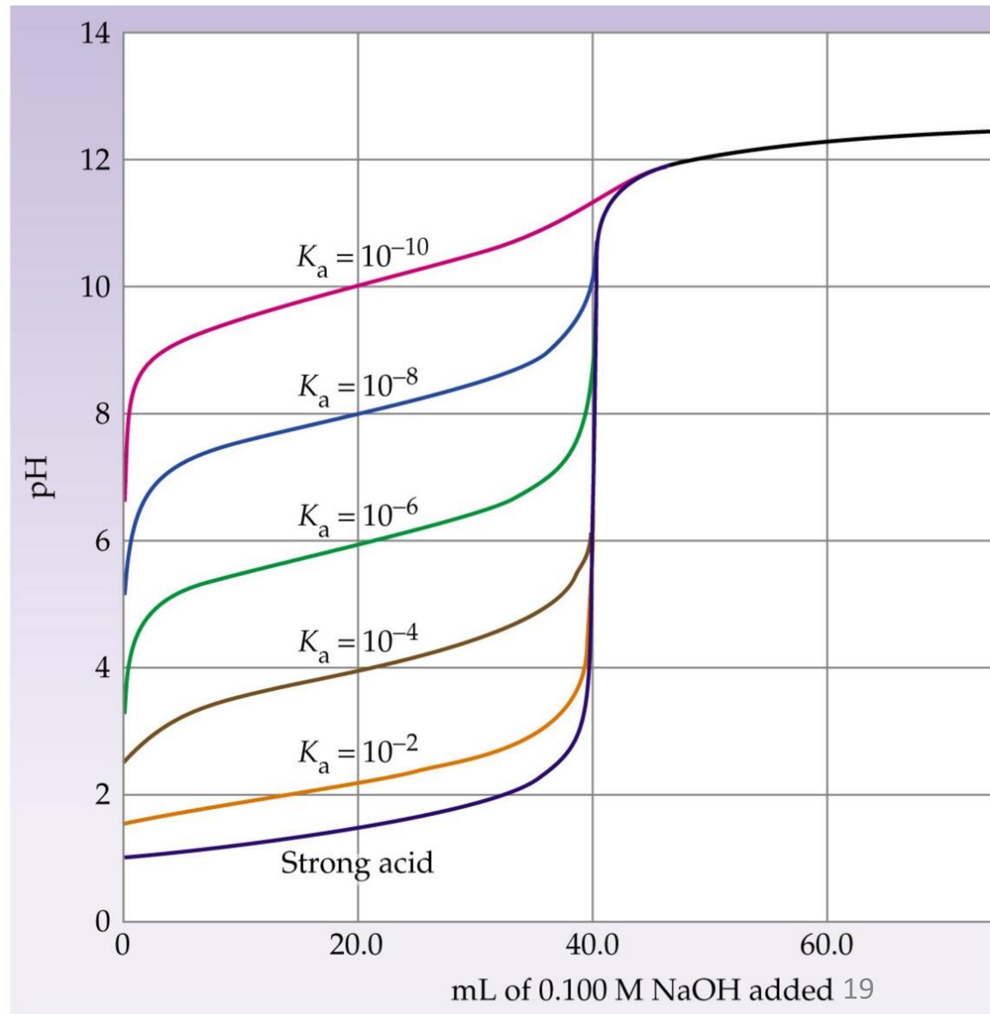
$$pK_a + \log\frac{[A^-]}{[HA]} = pH$$

TABLE 10.1 Acidity Constants at 25°C*

Acid	K_a	pK_a
formic acid, HCOOH	1.8×10^{-4}	3.75
benzoic acid, C_6H_5COOH	6.5×10^{-5}	4.19
acetic acid, CH_3COOH	1.8×10^{-5}	4.75
carbonic acid, H_2CO_3	4.3×10^{-7}	6.37
hypochlorous acid, HClO	3.0×10^{-8}	7.53
hypobromous acid, HBrO	2.0×10^{-9}	8.69
boric acid, $B(OH)_3$†	7.2×10^{-10}	9.14
hydrocyanic acid, HCN	4.9×10^{-10}	9.31
phenol, C_6H_5OH	1.3×10^{-10}	9.89
hypoiodous acid, HIO	2.3×10^{-11}	10.64

*The values for K_a listed here have been calculated from pK_a values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

†The proton transfer equilibrium is $B(OH)_3(aq) + 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.



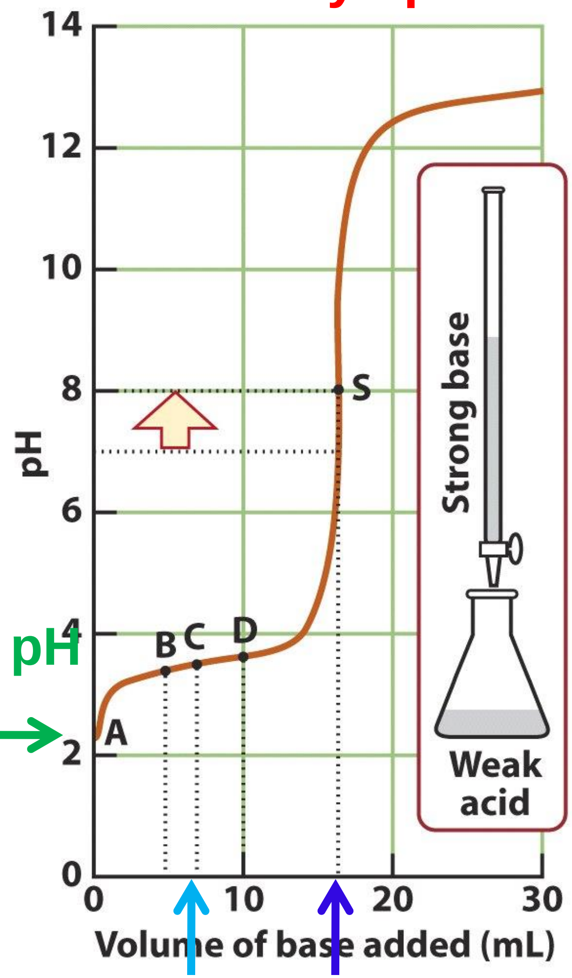
Buffers

What is the pH of a buffer containing 0.04 M NaAcetate and 0.1 M Acetic Acid? pKa = 4.75

$$pK_a + \log \frac{[A^-]}{[HA]} = pH$$

Drawing a Titration Curve - Summary

Asymptotic final pH



Starting pH

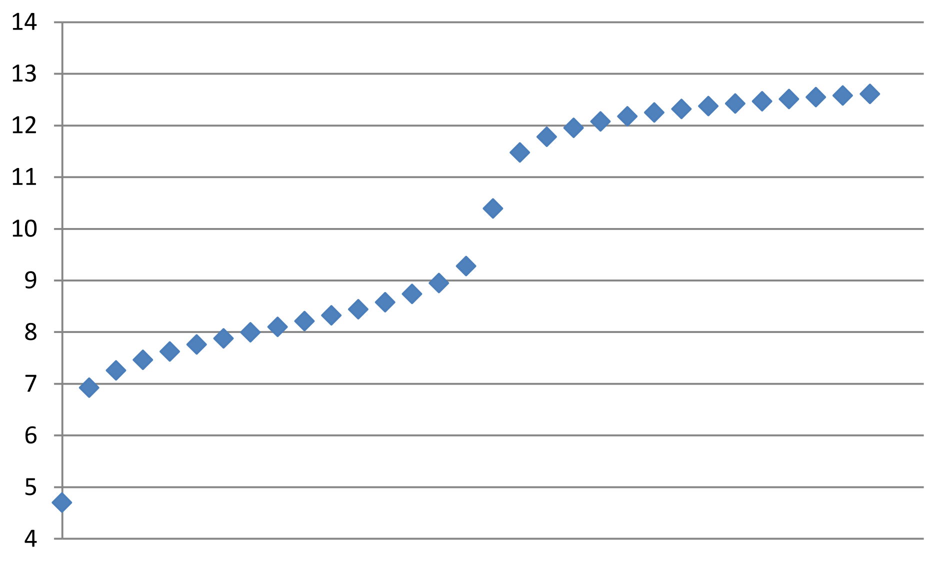
Volume when pH=pKa
½ volume @ Eq. Pt

Equivalence Pt. Volume (this is NOT pH 7)

Let’s Practice

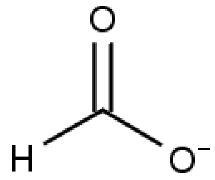
Draw the pH vs. volume plot that would result from titrating 1.25 M NaOH into a 100 mL solution of 50 mM of a weak acid that has a pK_a of 8.1.

1. Starting pH
2. ½ Eq. Pt.
3. Eq. Pt.
4. Final pH



pKa and Structure

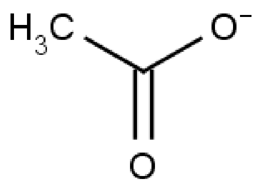
What influences the pKa of an acid?



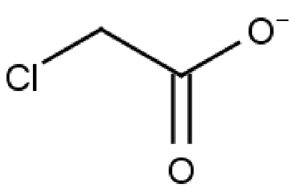
Formic Acid
pKa = 3.75

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

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



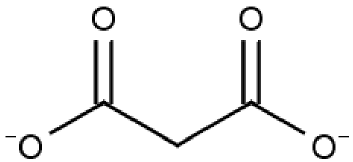
Acetic Acid
pKa = 4.76



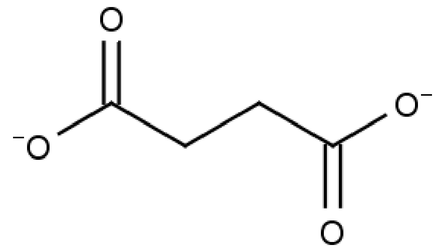
Monochloroacetic Acid
pKa = 2.85

pKa and Structure

What influences the pKa of an acid?



Malonic Acid
pKa,1 = 2.83
pKa,2 = 5.69



Succinic Acid
pKa,1 = 4.2
pKa,2 = 5.6

$A^{2-} + H^+ \rightleftharpoons HA^-$

$HA^- + H^+ \rightleftharpoons H_2A$

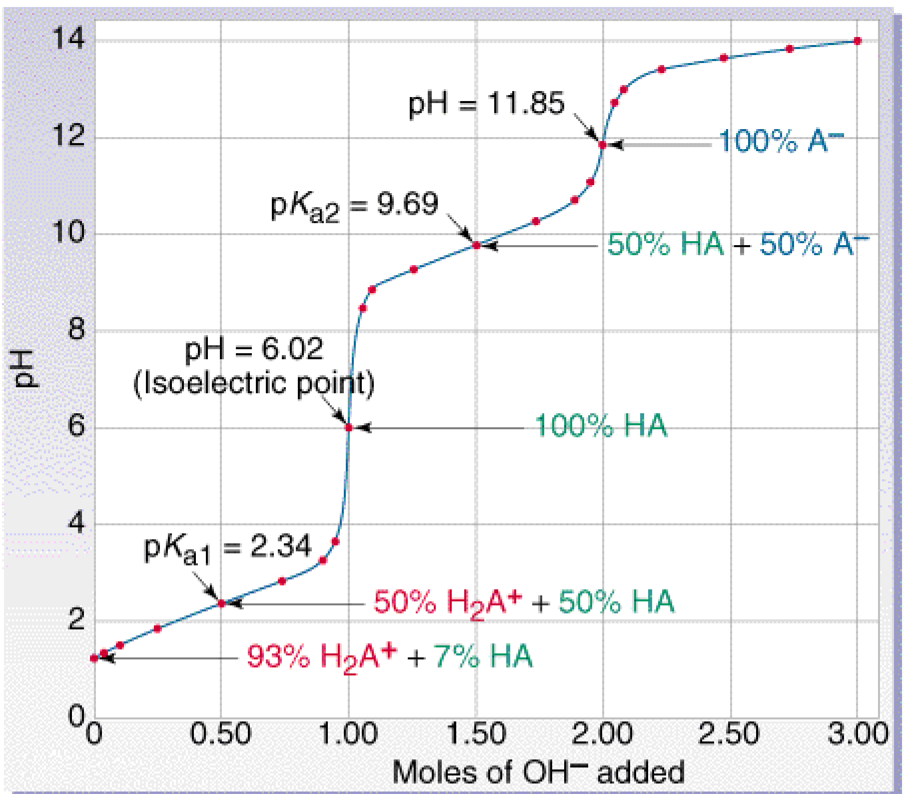
$$K = \frac{[HA^-]}{[H^+][A^{2-}]}$$

$$K = \frac{[H_2A]}{[H^+][HA^-]}$$

Polyprotic Acids and Bases

Polyprotic Acid – an acid that has more than one ionizable proton

Amphiprotic – a molecule that can accept or donate a proton



Important Biological Examples

Phosphoric Acid

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ *pKa = 2.15*

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{-2} + H_3O^+$ *pKa = 7.20*

$HPO_4^{-2} + H_2O \rightleftharpoons PO_4^{-3} + H_3O^+$ *pKa = 12.37*

Carbonic Acid

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$ *pKa = 6.35*

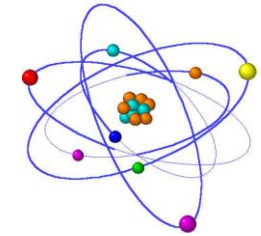
$HCO_3^- + H_2O \rightleftharpoons CO_3^{-2} + H_3O^+$ *pKa = 10.33*

Amino Acids

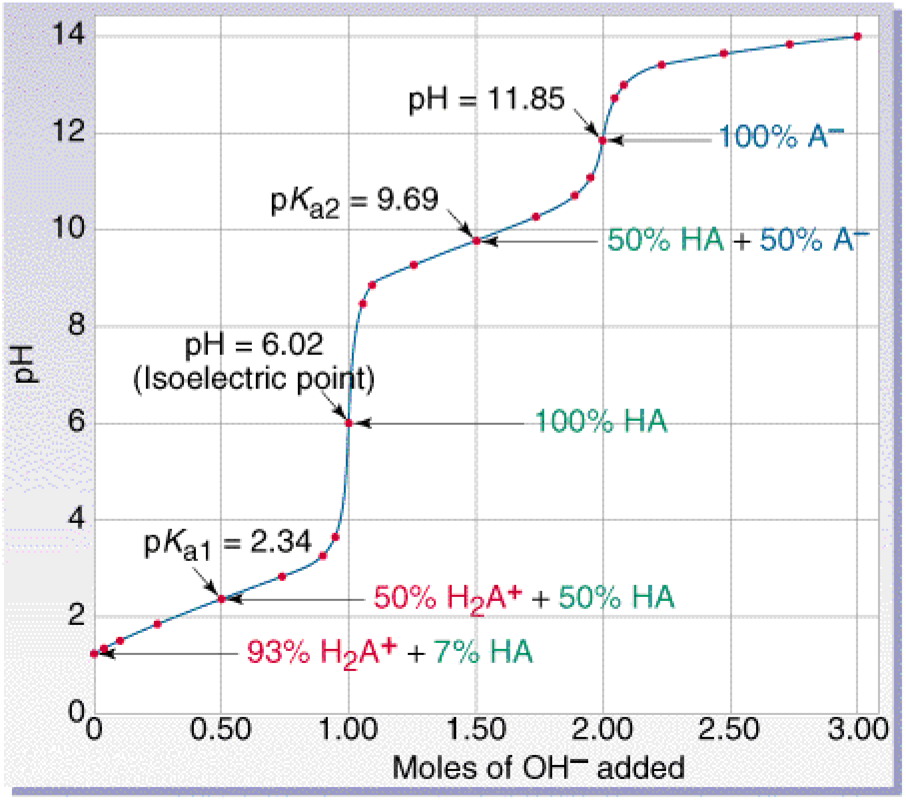
$(NH_3CH_2CO_2H)^+ + H_2O \rightleftharpoons (NH_3CH_2CO_2) + H_3O^+$ *pKa = 2.34*

$(NH_3CH_2CO_2) + H_2O \rightleftharpoons (NH_2CH_2CO_2)^- + H_3O^+$ *pKa = 9.69*

Polyprotic Acids and Bases



Isoelectric Points

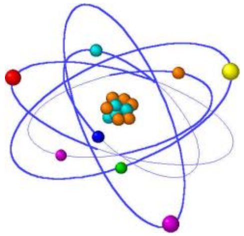


Amino Acids

$(NH_3CH_2CO_2H)^+ + H_2O \rightleftharpoons (NH_3CH_2CO_2) + H_3O^+$ *pKa = 2.34*

$(NH_3CH_2CO_2) + H_2O \rightleftharpoons (NH_2CH_2CO_2)^- + H_3O^+$ *pKa = 9.69*

Thermodynamcis – a review



$$a\text{A} + b\text{B} \rightleftharpoons y\text{Y} + z\text{Z}$$

Write an equilibrium constant expression that describes this equibilibrium.

$$K = \frac{[Z]^z[Y]^y}{[A]^a[B]^b}$$

How do we convert this to a statement of spontaneity (ΔG)

$$\Delta G = -RTlnK$$

What else do we need to know to describe the thermodynamic profile of this reaction?

ΔH → Enthalpy

ΔS → Entropy

$$\Delta G = \Delta H - T\Delta S$$

Thermodynamcis – a review

$$\Delta G = \Delta H - T\Delta S$$

ΔH	ΔS	ΔG	Temperature Dependence of ΔG
-	+		
-	-		
+	+		
+	-		

Thermodynamcis – a review

$$CH_{4(g)} + 2O_{2(g)} \rightleftharpoons 2H_2O_{(l)} + CO_{2(g)} \qquad \Delta H = -890\ kJ$$

Is this reaction endothermic or exothermic?

Will this reaction be entropically favorable?

Is this reaction spontaneous?

Hess's Law

Since ΔH, ΔS, and ΔG are State Functions (path independent), we can determine reaction enthalpies from individual reactions that sum to the desired reaction.