Metal ions biology

Metal ion in the vicinity of biomolecular system

Stability: Interaction, binding and thermodynamic stability of the ion-biomolecular complex formed

Close proximity of the metal ion center can be visualized as a coordination complex that we generally treat in inorganic chemistry

Follows coordination principles

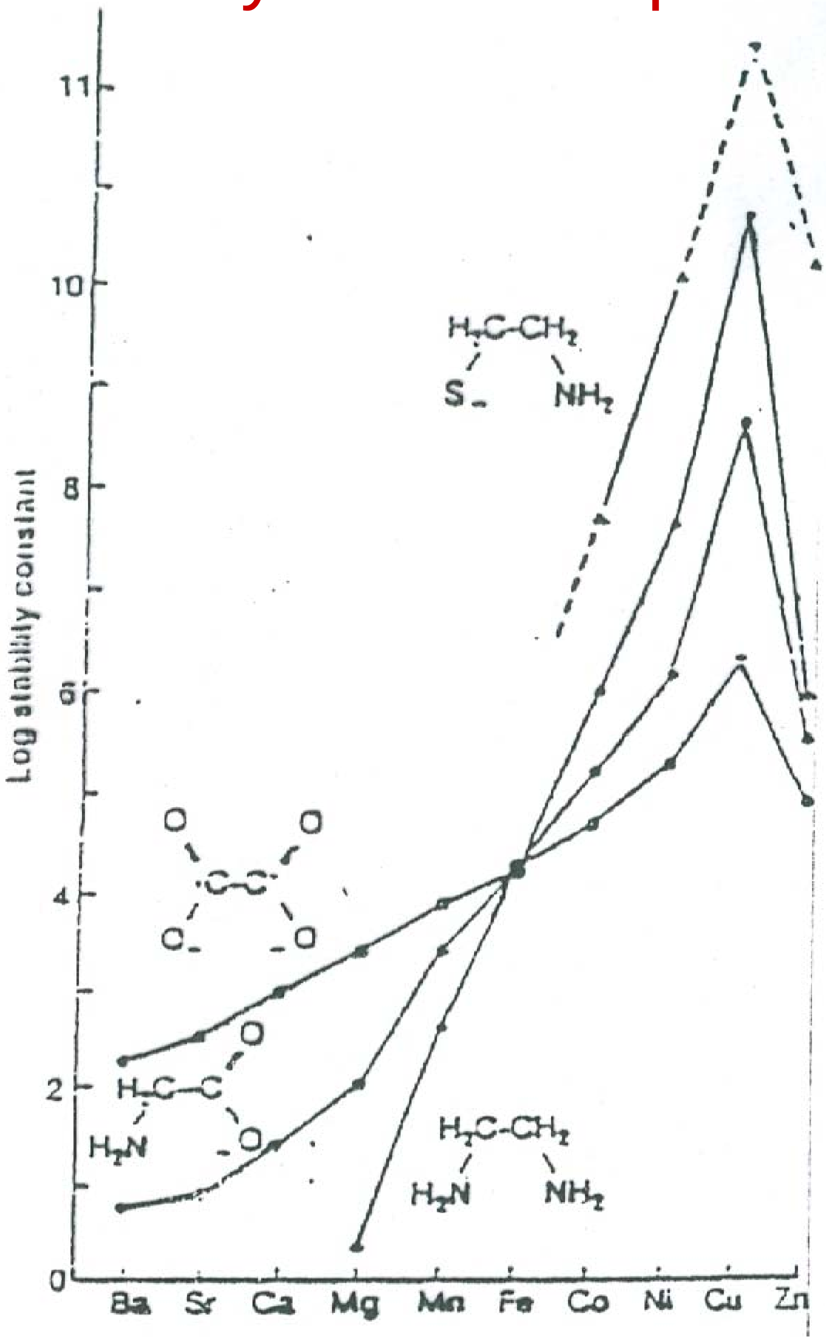
Lability: Reactivity at these metal ion centers present in biomolecular systems

Depends on the rate of exchange of one or more coordination sites

Their readiness to undergo facile redox

Their capability to act as Lewis acid as well as their capability to activate the organic/protein moiety or ligand to which they are bound

Stability of the complexes



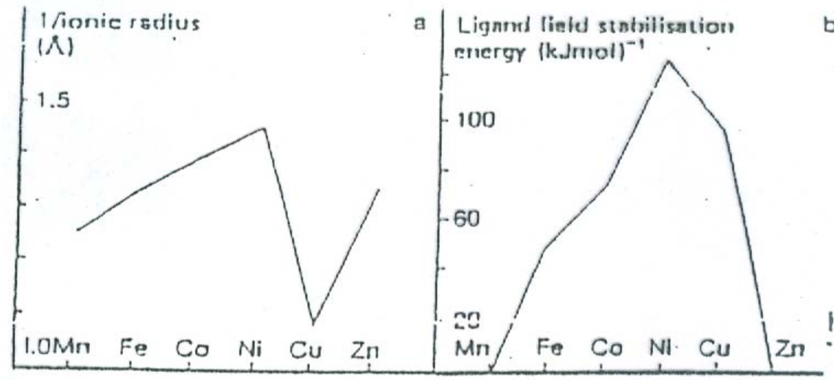


Fig. 1.3 – Factors leading to the Irving-Williams series. From reference [10
reproduced by permission of the Chemical Society, London.

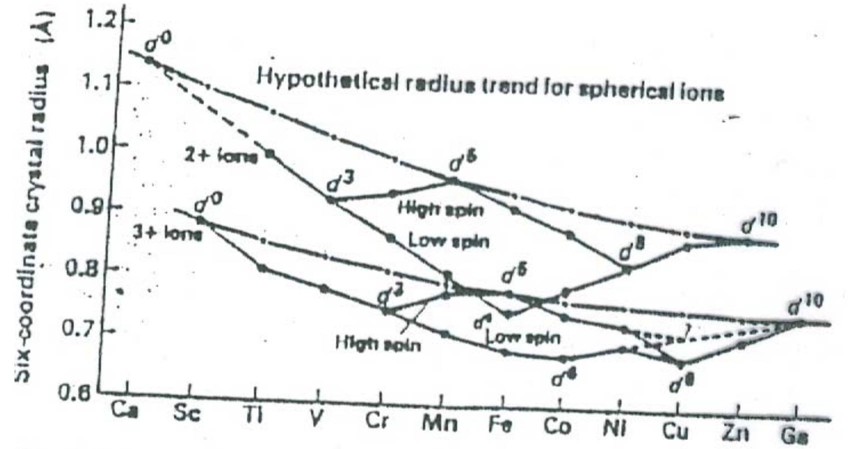
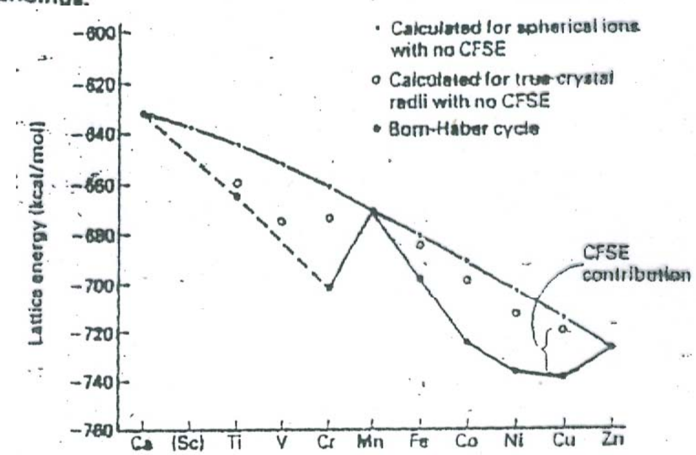


Figure 9.12 Crystal radii for transition-metal ions in octahedral
urroundings.



Lattice energies for transition-metal difluorides MF_2 (all high spin

Hard Soft Acids Bases

HSAB Classification

Cations

Hard: H^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Al^{3+}

Borderline: Zn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Sn^{2+}, Pb^{2+}, R_3C^+

Soft: Cu^+, Ag^+, Au^+, Tl^+, Pd^{2+}, Pt^{2+}, Cd^{2+}, Hg^{2+}, Te^{4+}

Ligands/anions

Hard: H_2O, OH^-, ROH, OR^-, R_2O, NH_3, NCS^-, Cl^-, PO_4^{3-}, SO_4^{2-}, F^-, NO_3^-, CO_3^{2-}, $CH_3CO_2^-$, N_2H_4

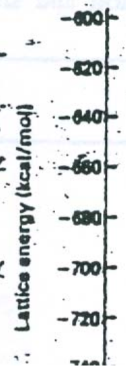
Borderline: Py, RNH_2, N_2, N_3^-, NO_2^-, Br^-

Soft: RSH, RS^-, R_2S, R_3P, R_3As, CO, CN^-, SCN^-, $S_2O_3^{2-}$, H^-, I^-, C_2H_4

Spectrochemical Series

$I^- < Br^- < OCrO_3^{2-} < Cl^- \simeq SCN^- < N_3^- < F^- \simeq SSO_3^{2-} \simeq$ Urea $< OCO_2^{2-} < OCO_2R^- < ONO^- \simeq OH^- < OSO_3^{2-} < O_2CCO_2^{2-} < H_2O < NCS^- <$ gly$^- \simeq EDTA^{4-} <$ Py $\simeq$ en $< SO_3^{2-} <$ dipyridyl $< NO_2^- <$ Cp $< CN^-$

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} \simeq V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} \simeq Ru^{3+} < Pd^{4+} < Ir^{3+} < Re^{4+} < Pt^{4+}$

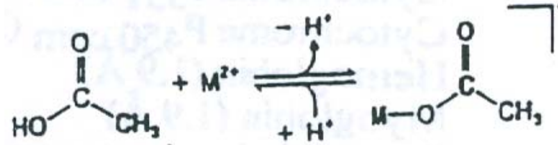
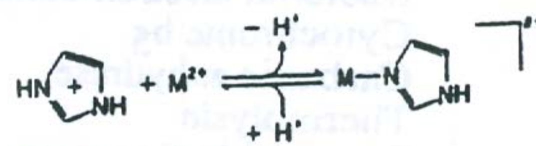


Hydolysis & pKa

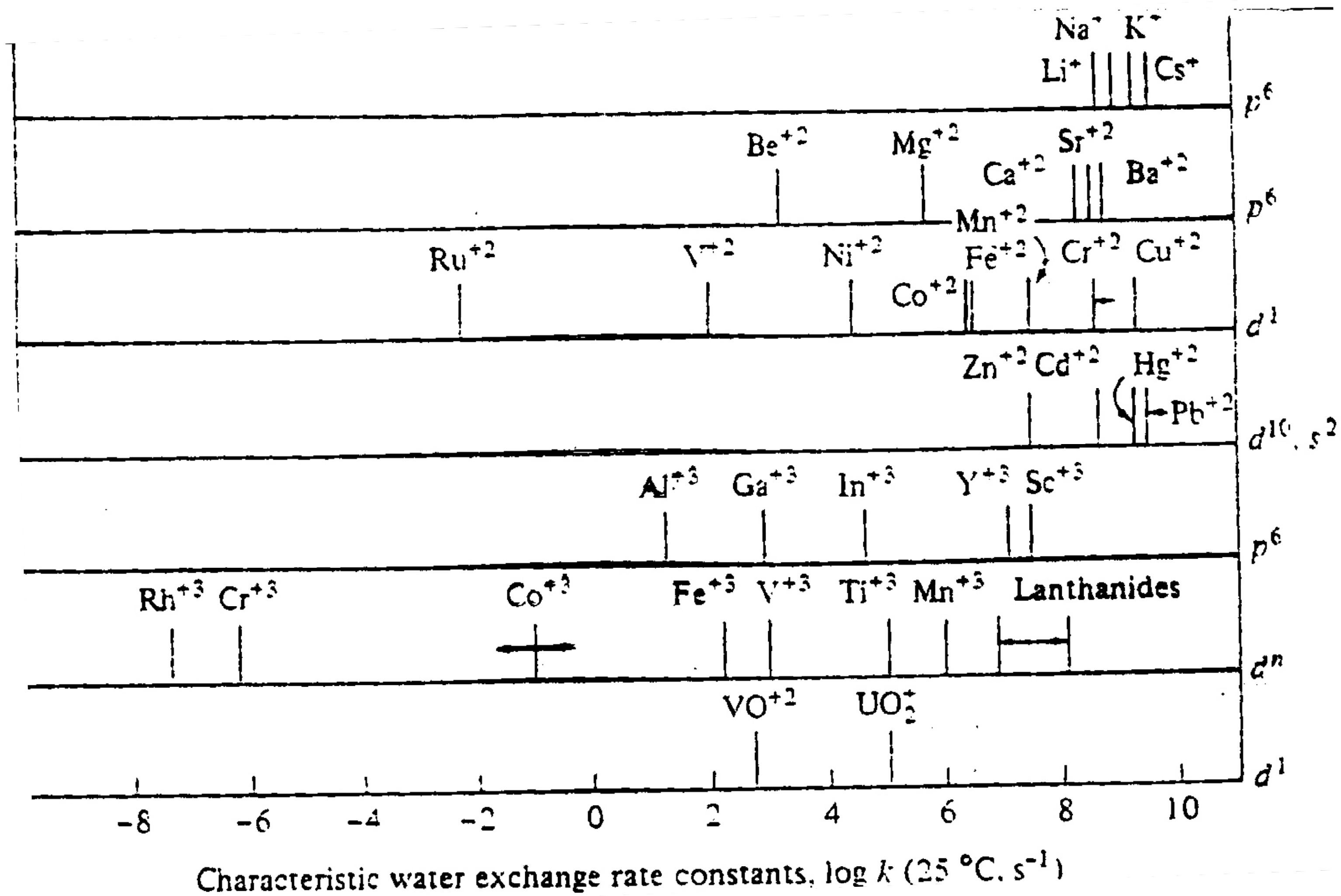
Hydrolysis reactions of Fe(III), 25°[a]

Reaction	P
$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$	
$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+$	
$Fe(OH)^{2+} + H_2O \rightarrow Fe(OH)_2^+ + H^+$	
$Fe(OH)_2^+ + H_2O \rightarrow Fe(OH)_3\downarrow + H^+$	
$Fe(OH)_3 + H_2O \rightarrow Fe(OH)_4^- + H^+$	1(

[a] Additional water molecules coordinated to the iron atoms are shown.

Ligand and reaction	Metal Ion	Log K (25°C, 0.1
$H_2O + M^{2+} \rightleftharpoons [M{-}OH]^+$ ($-H^+$ / $+H^+$)	None	14.0
	Ca^{2+}	13.4
	Mn^{2+}	11.1
	Cu^{2+}	10.7
	Zn^{2+}	10.0
$NH_3 + M^{2+} \rightleftharpoons [M{-}NH_2]^+$ ($-H^+$ / $+H^+$)	None	35.0
	Co^{2+}	32.9
	Cu^{2+}	30.7
	Ni^{2+}	32.2
	None	4.7
	Mg^{2+}	4.2
	Ca^{2+}	4.2
	Ni^{2+}	4.0
	Cu^{2+}	3.0
	None	7.0
	Co^{2+}	4.6
	Ni^{2+}	4.0
	Cu^{2+}	3.8

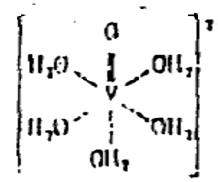
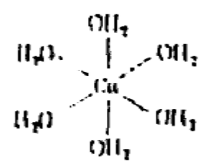
Lability of the complexes



Lability of the complexes

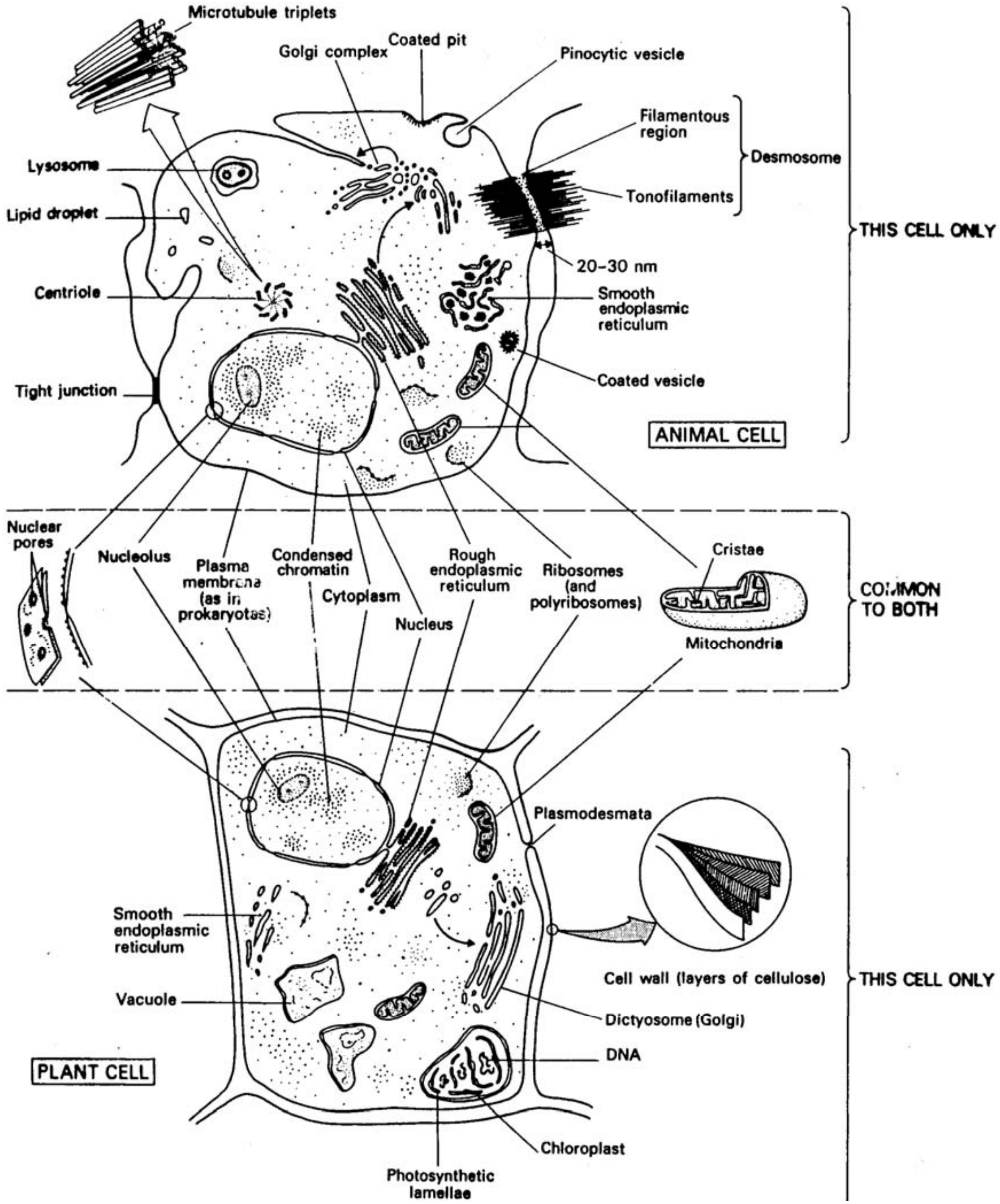
Table 11.1 Change in LFSE (units *Dq*)[c] upon changing a 6-coordinate complex to a 5-coordinate (square pyramidal) or a 7-coordinate (pentagonal bipyramidal) species

	High spin		Low spin	
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7
d^0	0	0	0	0
d^1	+0.57	+1.28	+0.57	+1.28
d^2	+1.14	+2.56	+1.14	+2.56
d^3	−2.00	−4.26	−2.00	−4.26
d^4	+3.14	−1.07	−1.43	−2.98
d^5	0	0	−0.86	−1.70
d^6	+0.57	+1.28	−4.00	−8.52
d^7	+1.14	+2.56	+1.14	−5.34
d^8	−2.00	−4.26	−2.00	−4.26
d^9	+3.14	−1.07	+3.14	−1.07
d^{10}	0	0	0	0

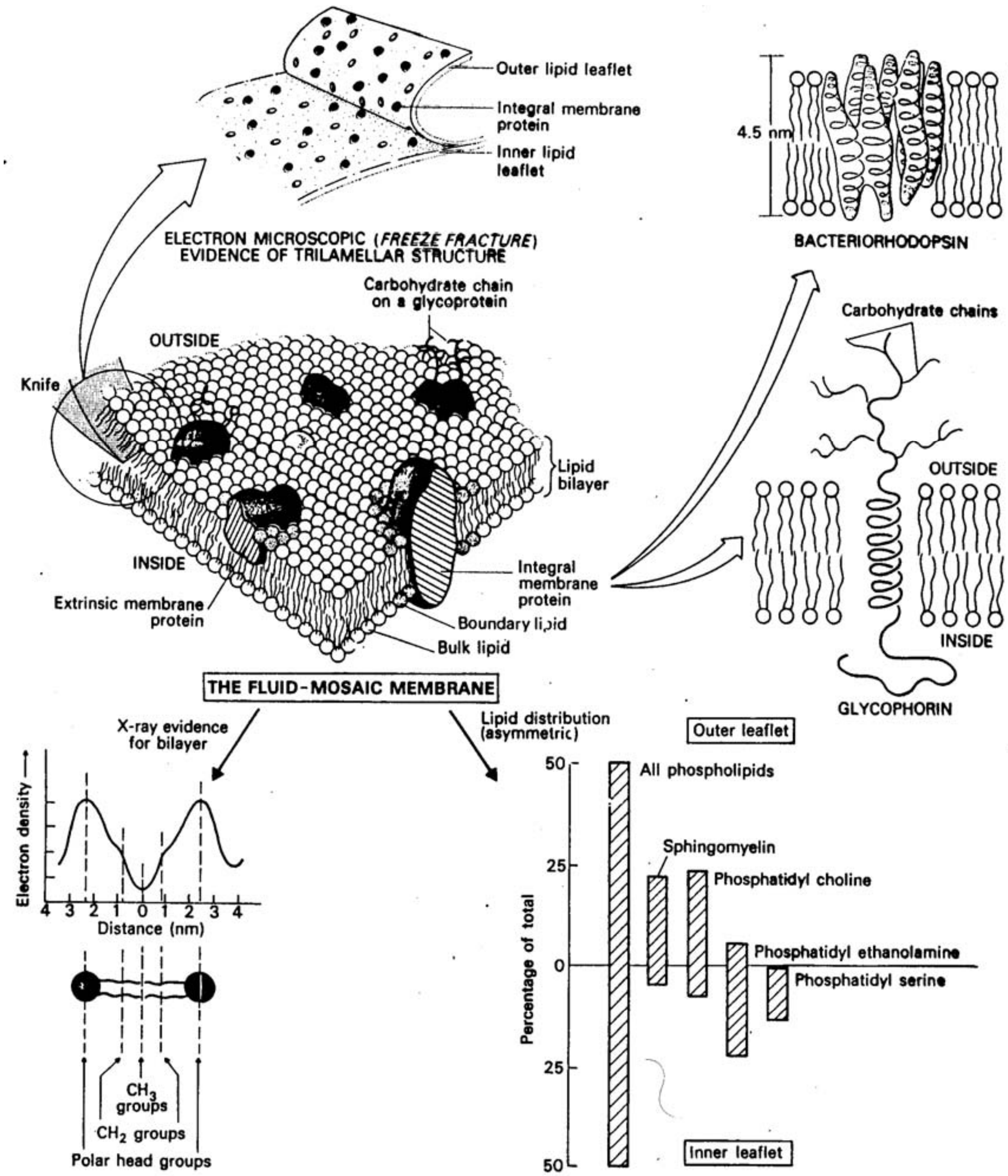
V(IV) (d^1)	labile	
	k (double bonded oxygen)	$< 20\ s^{-1}$
	k (equatorial water)	$5 \times 10^2\ s^{-1}$
	k (axial water)	$5 \times 10^9\ s^{-1}$
Cr(III) (d^3)	inert	$[Cr(H_2O)_6]^{3+}$
Co(II) (d^7)	labile	$[Co(H_2O)_6]^{2+}$
Co(III) (d^6, LS)	inert	$[Co(H_2O)_6]^{3+}$
Cu(II) (d^9)*	labile	

*Rapid exchange of axial water ligands due to Jahn–Teller distortion.

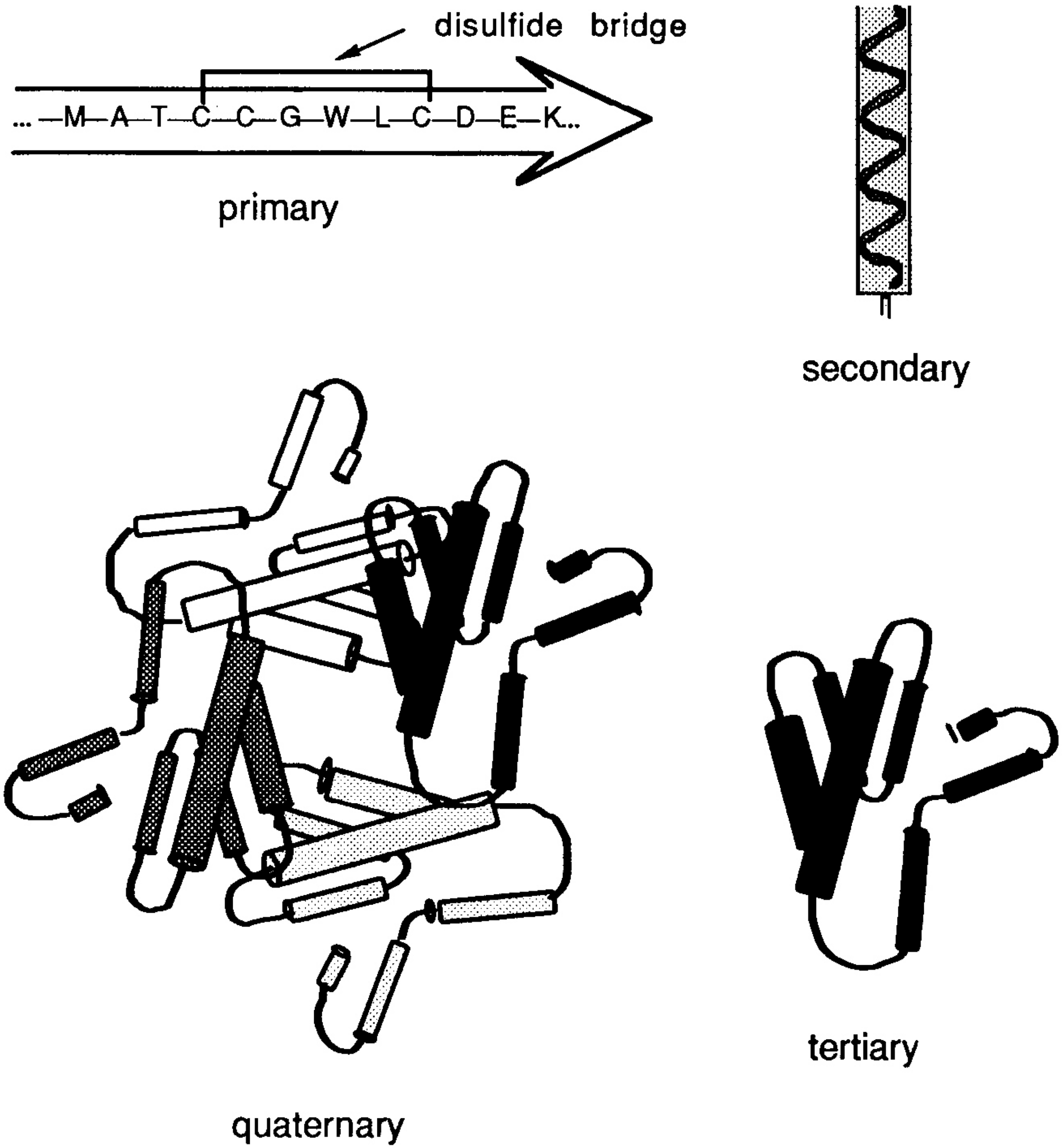
Eukaryotic cells



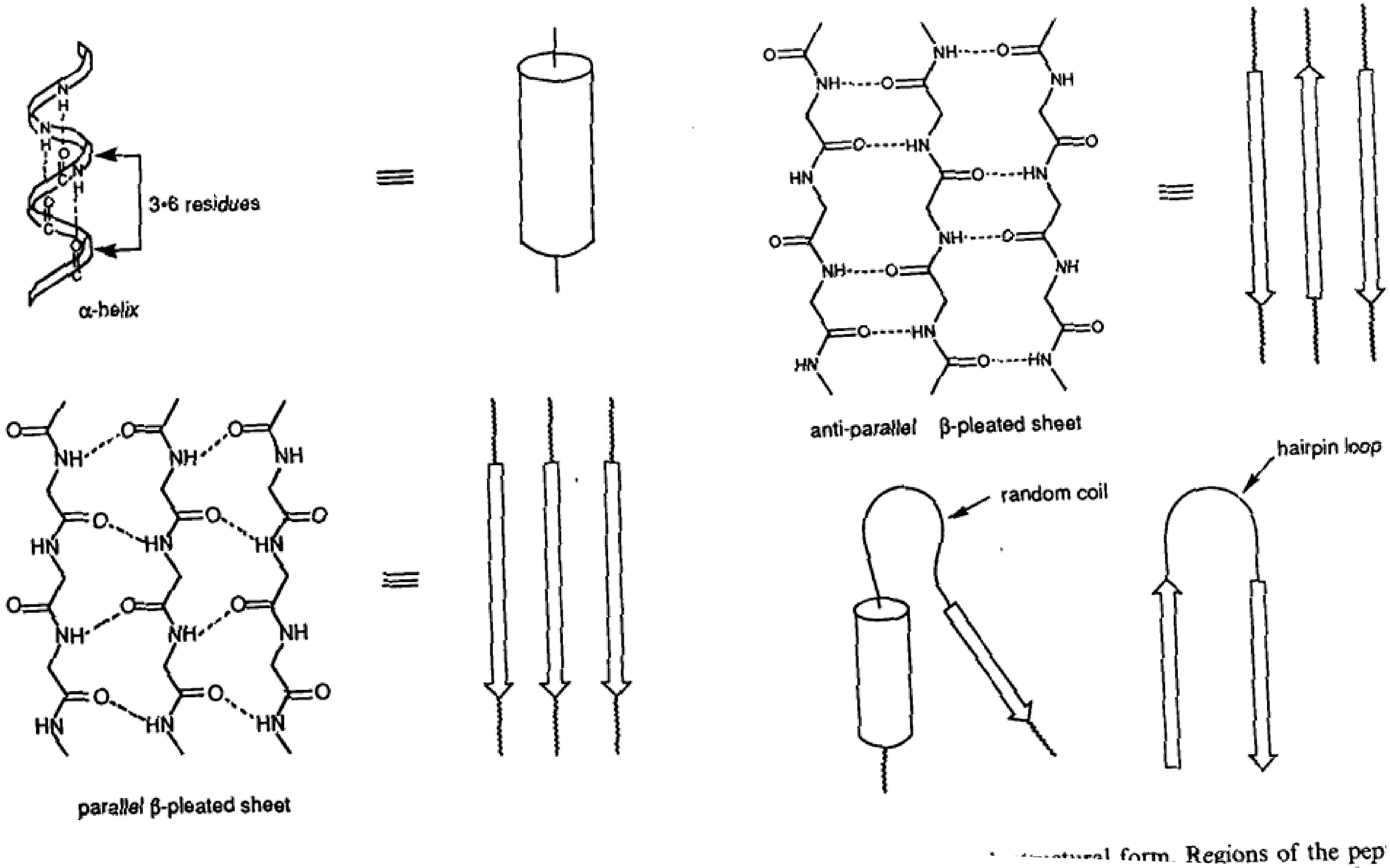
Lipids


Outer lipid leaflet
Integral membrane protein
Inner lipid leaflet
ELECTRON MICROSCOPIC (FREEZE FRACTURE) EVIDENCE OF TRILAMELLAR STRUCTURE
4.5 nm
BACTERIORHODOPSIN
Carbohydrate chain on a glycoprotein
OUTSIDE
Knife
Lipid bilayer
INSIDE
Extrinsic membrane protein
Integral membrane protein
Boundary lipid
Bulk lipid
Carbohydrate chains
OUTSIDE
INSIDE
GLYCOPHORIN
THE FLUID-MOSAIC MEMBRANE
X-ray evidence for bilayer
Electron density
4 3 2 1 0 1 2 3 4
Distance (nm)
CH3 groups
CH2 groups
Polar head groups
Lipid distribution (asymmetric)
Outer leaflet
50
25
0
25
50
Percentage of total
All phospholipids
Sphingomyelin
Phosphatidyl choline
Phosphatidyl ethanolamine
Phosphatidyl serine
Inner leaflet
34.1

Protein Structures



α-helix, β-sheet & random coil



Protein Translation

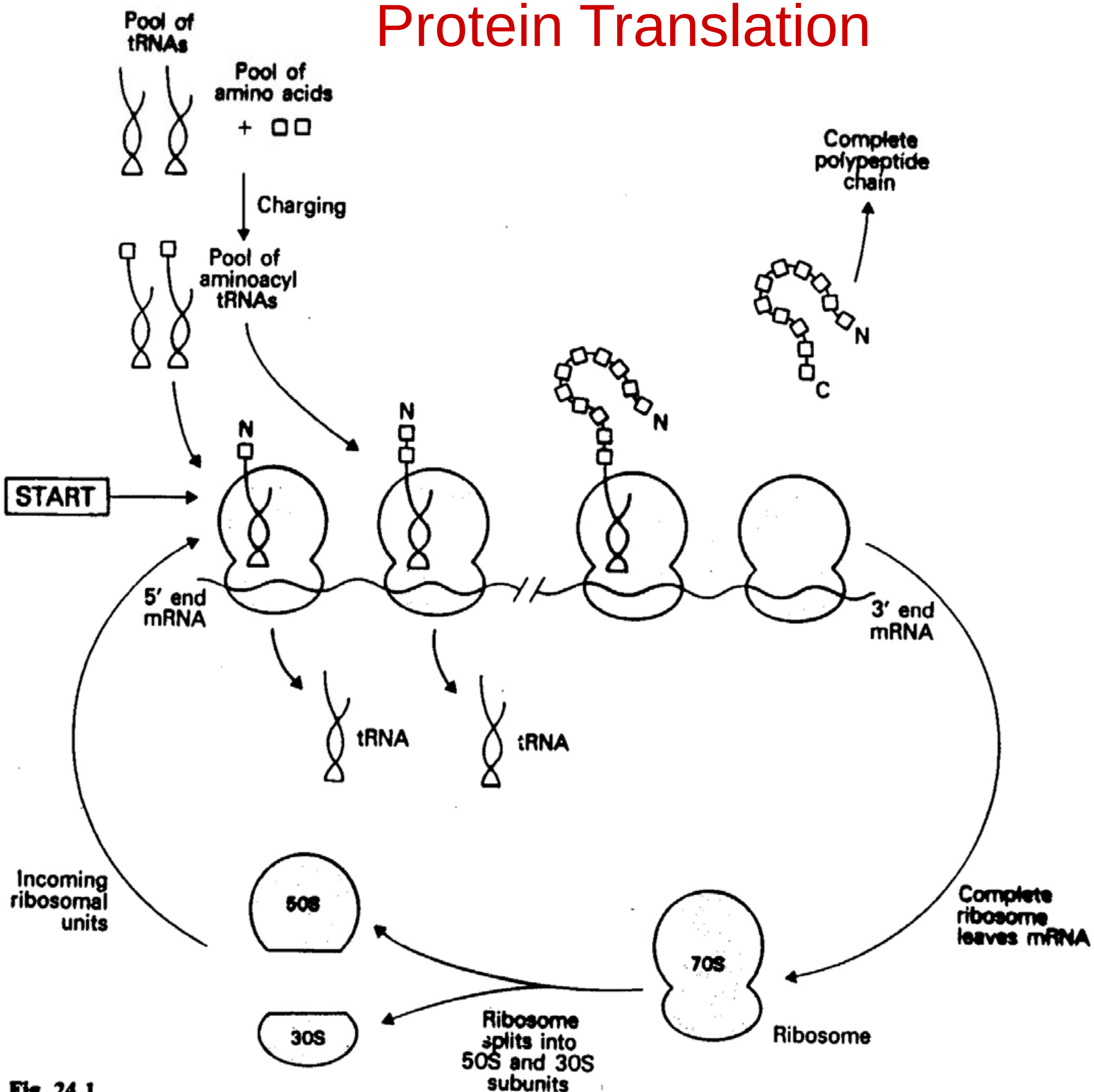
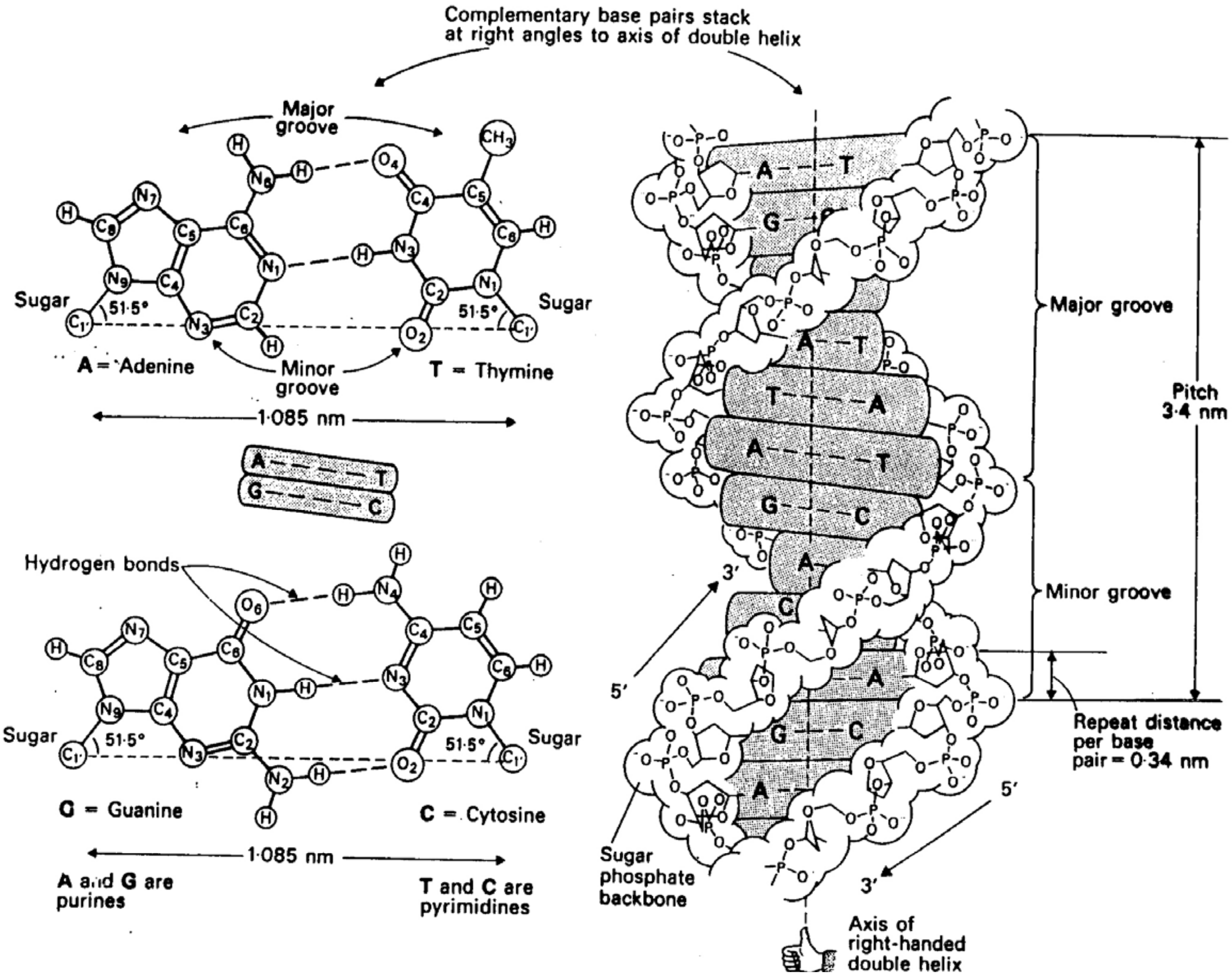
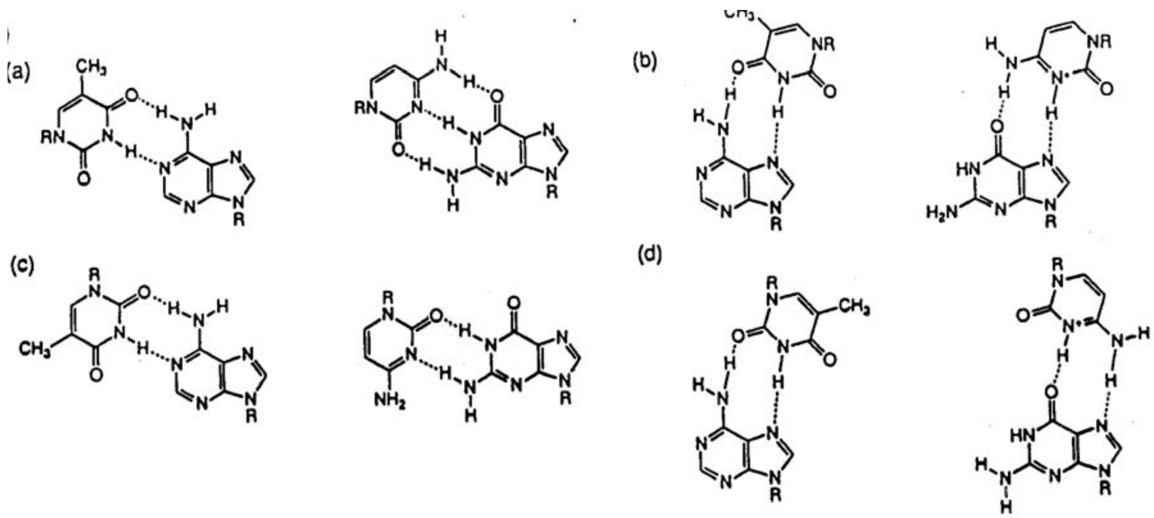


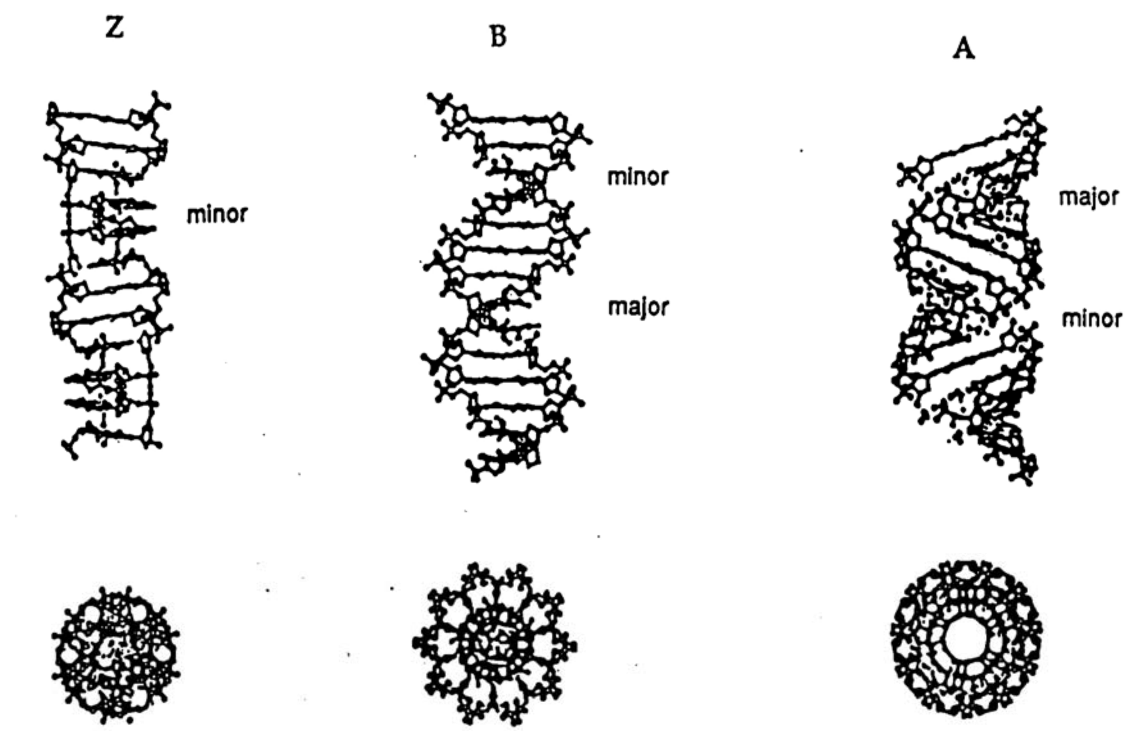
Fig. 24.1

DNA Structures

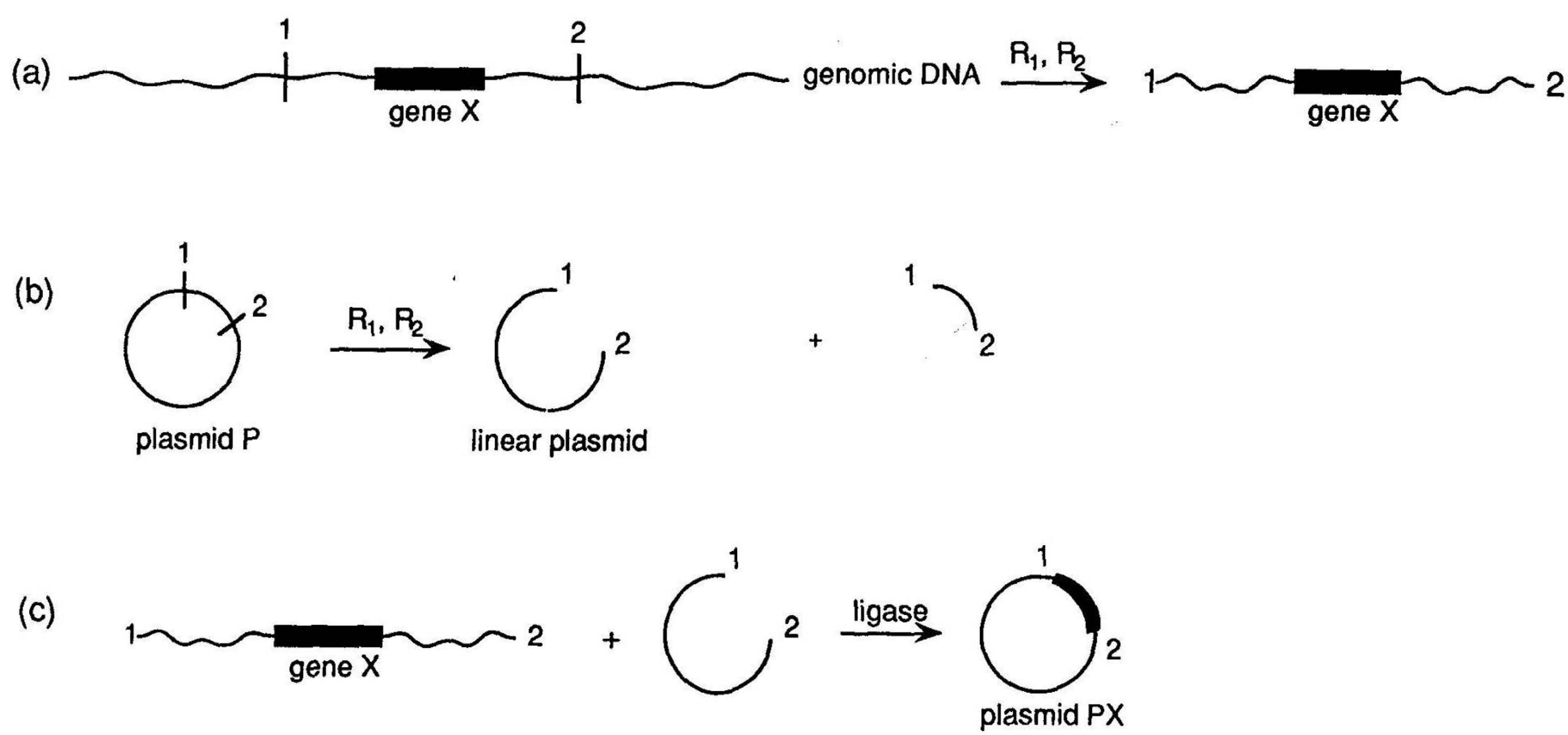


A-,B- & Z- DNA Structures

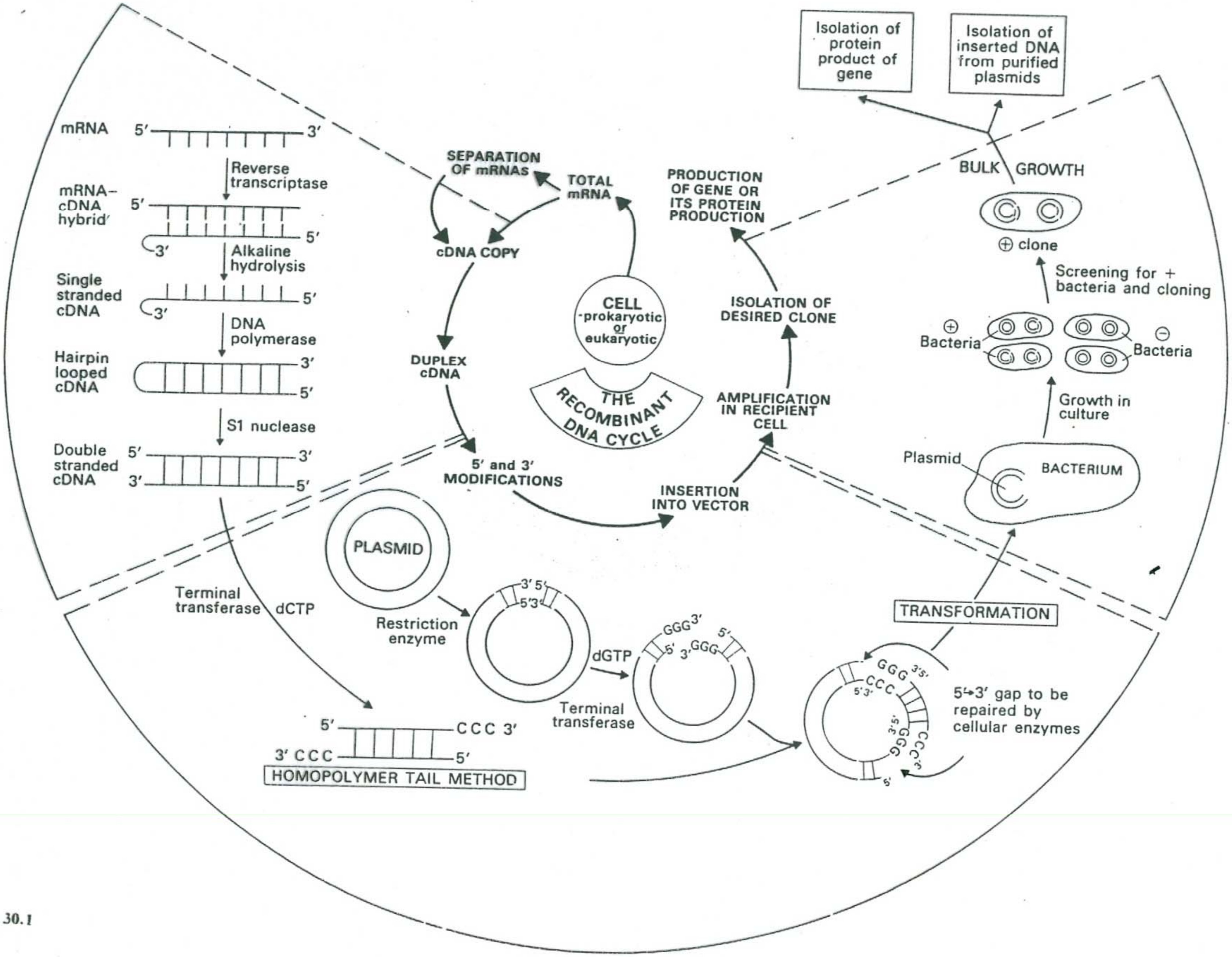




Site targeted mutagenesis



The Recombinant DNA cycle: Protein expression



g. 30.1

Books where you may find SOME relevant material

S. No	*Name of the book*	*Author(s)*	*Year of Publi-cation*	*Publisher*
1	Bioinorganic Chemistry: a short course	Rosette M. Roat-Malone	2007	John Wiley & sons, Inc.
2	Bioinorganic Chemistry- an inorganic perspective of life	Dimitris P. Kessissoglou	1995	Kluwer Academic Publishers
3	Principles of Bioinorganic Chemistry	Stephen J. Lippard, Jeremy Mark Berg	1994	University Science Books
4.	Inorganic Biochemistry: An Introduction	James A Cowan	1993	VCH
5	Bioinorganic Chemistry	Eckhard Bill	1991	Springer-Verlag
6	Bioinorganic Chemistry	Ivano Bertini	1994	University Science Books
7	Bioinorganic Chemistry: The Biological Chemistry of Transition Metals	Michael Watkinson	2009	John Wiley & Sons, Limited
8	Physical methods in bioinorganic chemistry: spectroscopy and magnetism	Lawrence Que	2000	University Science Books
9	Handbook on metalloproteins	Ivano Bertini, Astrid Sigel, Helmut Sigel	2001	CRC Press
10	Bioinorganic chemistry: transition metals in biology and their coordination chemistry	Alfred Trautwein, Deutsche Forschungsgemeinschaft	1997	Deutsche Forschungsgemeinschaft