Solid sodium chloride

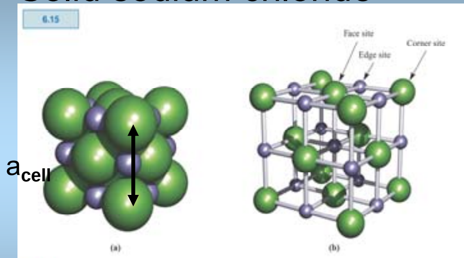
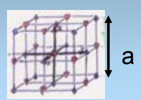


Fig. 6.15 Two representations of the unit cell of NaCl: (a) shows a space-filling representation and (b) shows a 'ball-and-stick' representation which reveals the coordination environments of the ions. The Cl^- ions are shown in green and the Na^+ ions in purple; since both types of ion are in equivalent environments, a unit cell with Na^+ ions in the corner sites is also valid. There are four types of site in the unit cell: central (not labelled), face, edge and corner positions.

Sodium chloride cell constant

- d_{NaCl}= 2.165 g·cm^{-3}



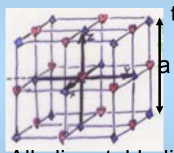
$$a_{calc}{}^3 = \frac{58.44\,\frac{\mathbf{g}}{\mathbf{mol}}\cdot 10^{24}\,\frac{\mathbf{Å^3}}{\mathbf{cm^3}}\cdot 4\,\frac{\mathbf{NaCl-units}}{\mathbf{unit-cell}}}{2.165\,\frac{\mathbf{g}}{\mathbf{cm^3}}\cdot 6.022\cdot 10^{23}\,\frac{\mathbf{NaCl-units}}{\mathbf{mol}}} = 179.3\ \text{Å}^3\text{/unit cell}$$

a_{calc} = 5.639 Å

a_{cryst} = 5.627 Å

The cell constant

Sodium chloride structure



for many salts

Alkali metal halides and several MO, MS, and MSe from group 2

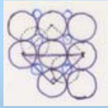
	F	Cl	Br	I
Li	4.01	5.14	5.49	6.00
Na	4.63	5.63	5.96	6.45
K	5.33	6.28	6.58	7.04
Rb	5.63	6.57	6.87	7.33
Cs	-	7.02*	-	-
Ag	4.92	5.55	5.76	

*T>445 ºC

Ionic size?

$a_{KX} - a_{NaX}$	.70	.65	.62	.59
X	F	Cl	Br	I

Landé: LiI



a=6.00 Å= $2r(I^-)+2r(Li^+)$

$4r(I^-)=6.00\cdot\sqrt{2}$ ⇨ $r(I^-) = 2.12$; $r(Li^+) = 0.88$

Ionic size?

Pauling: A and B have same electron configuration ⇨

$Z(A)^{eff}/ Z(B)^{eff} = r(B)/r(A)$

For KCl (a = 6.28 Å) : 18 electrons in K^+ and Cl^-

Cl^-: $Z^{eff} = 17-2\cdot1 -8\cdot0.85 -7\cdot0.35 = 5.75$

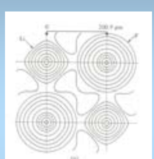
K^+: $Z^{eff} = 19-2\cdot1 -8\cdot0.85 -7\cdot0.35 = 7.75$

$r(K^+)$=1.34Å ; $r(Cl^-)$=1.80Å

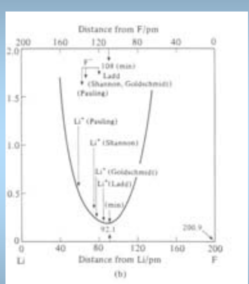
$a_{KX} - a_{NaX}$	.70	.65	.62	.59
X	F	Cl	Br	I

$r(K^+)-r(Na^+)$= .29-.35Å ⇨ r(Na+)=.99-1.05Å

Lithium fluoride



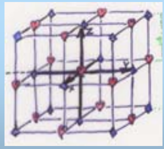
r_{min} ?

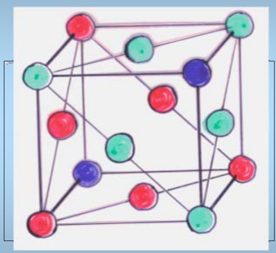


Goldschmith, Shannon…
Data analysed for best sets of r's to reproduce a's in crystals

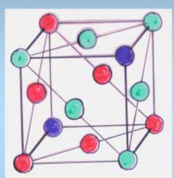
NaCl-structure revisited

CCP of blue diamond's:
4 layers shown :
blue, green, red, blue

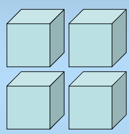




Number of spheres for CCP



- 6 on faces of cube:
  each counts one half
  i.e. 3

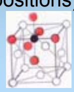


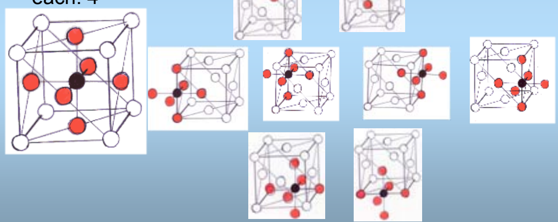
- 8 in corners:
  each counts one eights
  i.e. 1

4 spheres in CCP-cell

Octahedral holes

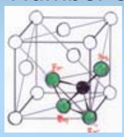
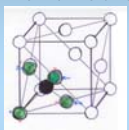
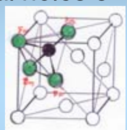
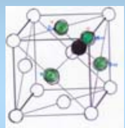
Number of spheres in the CCP structure:8/8 + 6/2 = 4
Number of octahedral holes (black positions)
1 in center + 12 on edges which count ¼
each: 4

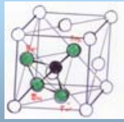




Tetrahedral holes

Number of tetrahedral holes 8

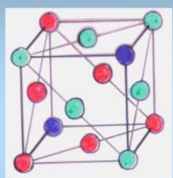





back  back back

23/03/2017 IC 10 group 1 JJ 10

CCP-cell

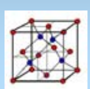
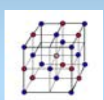
- 4 spheres
- 4 octahedral holes
- 8 tetrahedral holes

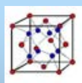
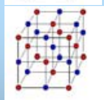


23/03/2017 IC 10 group 1 JJ 11

Many crystal structures

Cf “Notes” p. 30

 ZnS:½ t-holes  Al_2O_3:2/3 o-holes

 CaF_2 t-holes  NaCl: o-holes

23/03/2017 IC 10 group 1 JJ 12

Alkali metals

	Li	Na	K	Rb	Cs
Occurence %	0.007	2.8	2.6	0.03	0.0007
Ionisation energy 1 / $kJxmol^{-1}$	520	496	419	403	376
2	7298	4542	3052	2633	2234
Hydration enthalpy	-519	-404	-321	-296	-271
Eo/V	-3.04	-2.71	-2.93	-2.98	-3.03
Ionic radius (r/Å)	0.76	1.02	1.38	1.49	1.70
Ionic potential (q/r)	1.67	1.05	0.75	0.68	0.57
Ionic mobility/$10^8 m^2 s^{-1} V^{-1}$	4.0	5.2	7.6	8.1	8.1
Melting point/^{0}C metal	180	98	63	39	29
Density /$g{\cdot}ml^{-1}$	0.534	0.968	0.856	1.532	1.87
Atomic radius /Å	1.52	1.86	2.27	2.48	2.65
Metal	BCC	BCC	BCC	BCC	BCC
Flame colour	crimson	yellow	blue-violet	red-violet	blue
Lewis acid M^+	hard	hard	hard	hard	hard
C(plasma) /mM		160	10		
C(erythrocyte)/mM		11	92		

Simple reactions

- $M + O_2 \rightarrow Li_2O$
  Na_2O_2
  KO_2
- $M + H_2O \rightarrow MOH + ½H_2$
- M + ROH → ?

M – liquid NH_3

- $M_{am} \leftrightarrows M^+_{am} + e^-_{am}$ logK~ -2
- $M_{am} + e^- \leftrightarrows M^-_{am}$ logK~ 3
- $2M_{am} \leftrightarrows M_{2am}$ logK~ 3.7

Low concentration: blue paramagnetic
0.04 M: low conductivity, diamagnetic
Sat. solutions: bronze, metallic conductivity

- Slow $\rightarrow MNH_2 + ½H_2$

M^+ - salts

- Generally highly soluble in water.

Exceptions: Li_3PO_4 , $NaSb(OH)_6$,KClO4 ….

- Solubility in alcohols: MCl differences

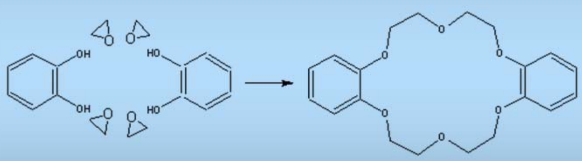
Coordination chemistry

- Alkali metal ions:
  - hard lewis acids and small charge

Weak interactions – low stability.

How then, can single cell organisms concentrate K^+ and expel Na^+ against concentration gradients?

Ligands: Crown ethers



dibenzoe-18-crown-6

Crown ether – alkali metal ions

Polyether	Hole size/Å	logK (K^+)	Relative affinity Na^+(D=1.9)	K^+ (D=2.26)	Cs^+(D=3.38)
Dicyclohexyl 14-crown 4	**1.5**	**1.3**	**7.6**	**1**	**0.16**
Dicyclohexyl 15-crown 5	**2.2**	**2.18**	**1.3**	**1**	**0.16**
Dicyclohexyl 18-crown 6	**3.2**	**6.01**	**0.016**	**1**	**0.04**
Dibenzoe 18-crown 6	**3.2**	**5.0**	**0.23**	**1**	**0.36**
Dibenzoe 21-crown 7	**4.3**	**4.30**	**.012**	**1**	**0.8**
18-crown 6	**3.2**	**6.1**	**0.021**	**1**	**0.033**
21-crown 7	**4.3**	**4.1**	**-**	**1**	**4.0**

Methanol

11.8

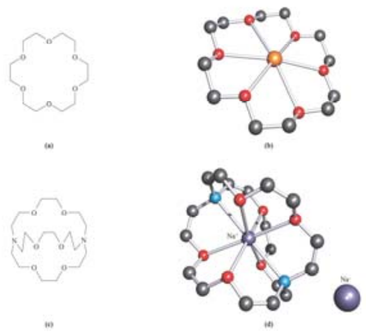
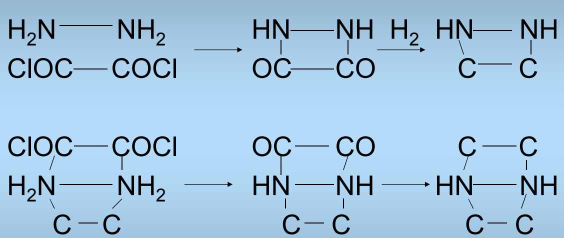


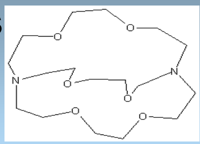
Fig. 11.8 The structures of (a) the macrocyclic polyether 18-crown-6, (b) the $[K(18\text{-crown-}6)]^+$ cation for the $[Ph_3Sn]^-$ salt (X-ray diffraction) [T. Birchall *et al.* (1988) *J. Chem. Soc., Chem. Commun.*, p. 877], (c) the cryptand ligand crypt-[222], and (d) $[Na(crypt\text{-}[222])]^+Na^-$ (X-ray diffraction) [F.J. Tehan *et al.* (1974) *J. Am. Chem. Soc.*, vol. 96, p. 7203]. Colour code: K, orange; Na, purple; C, grey; N, blue; O, red.

Cryptands



Cryptands

Cryptand [2,2,2]



O's in chains	Hole size/Å	LogK Li$^+$	Na$^+$	K$^+$	Rb$^+$
2,1,1	1.6	5.3	2.8	>2	>2
2,2,1	2.2	2.5	5.4	3.9	2.55
2,2,2	2.8	>2	3.9	5.4	4.35
3,2,2	3.6	>2	1.65	2.2	2.05
3,3,2	4.2	>2	>2	>2	>0.7
3,3,3	4.8	>2	>2	>2	>0.5

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11.10

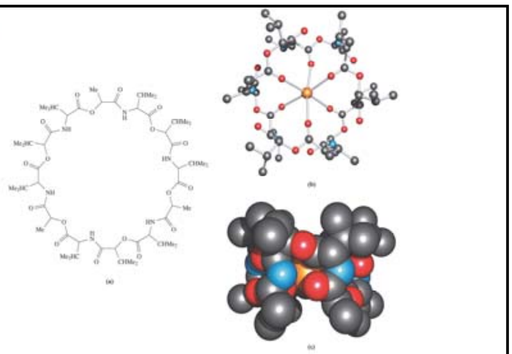
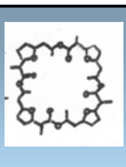
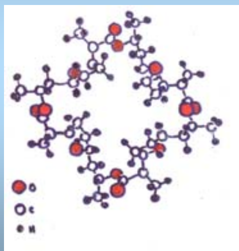


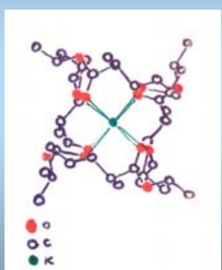
Fig. 11.10 (a) The structure of valinomycin and (b) the structure (X-ray diffraction) of [K(valinomycin)]$^+$ showing the octahedral coordination sphere of the K$^+$ ion. The structure was determined for the salt [K(valinomycin)]$_2$[I$_3$][I$_5$]; H atoms are omitted for clarity [K. Neupert-Laves *et al.* (1975) *Helv. Chim. Acta*, vol. 58, p. 432]. (c) A space-filling representation of the [K(valinomycin)]$^+$ ion which illustrates the hydrophobic exterior. Colour code: O, red; N, blue; C, grey; K$^+$ ion, orange.

Nonactine





+ K$^+$ →



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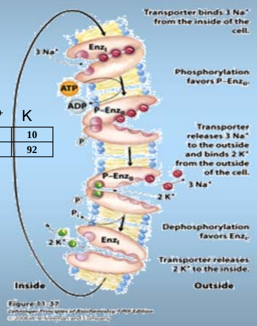
Na^+ K^+ transport

	Na^+	K
C(plasma) /mM	160	10
C(erythrocyte)/mM	11	92



End of Chapter problem 11.23

$KOH + H_2SO_4$
$NaOH + SO_2$
$KOH + C_2H_5OH$
$Na + (CH_3)_2CHOH$
$NaOH + CO_2$
$NaOH + CO$ (450º)
$CsOH + H_2C_2O_4$
$NaH + BCl_3$

End of Chapter problem 11.25

a) $Li_3N + H_2O$

b) $M + O_2 \rightarrow A$
$A + H_2O \rightarrow MOH$
$M + H_2O \rightarrow A + B$ (controlled)

End of Chapter problem 11.27

a) Comments to Stability data of $M(18\text{-crown-}6)^+$

M	Li	Na	K	Rb	Cs
logK	1.5	4.6	6.0	5.23	4.6

b) Solubility of $NaNO_3$, $RbNO_3$, Cs_2CO_3, Na_2SO_4, Li_2CO_3, LiF, LiCl.

c) Which factors affect solubility ? Illustrate using LiF, LiCl as examples

End of Chapter problem 11.28

Li_3N	1 Reacts explosively with water, liberating H_2
NaOH	2 Sparingly soluble in water
Cs	3 Basic compound with antifluorite structure
Cs_7O	4 Possesses the highest ionisation energy of group 1 metals
Li_2CO_3	5 Formed by the direct combination of the elements, layer structure
$NaBH_4$	6 Neutralises aqueous HNO_3 with no evolution of gas
Rb_2O	7 Used as a reducing agent
Li	8 A suboxide