Coordination equilibria

Stability and competition

$M^{n+} + :L \leftrightarrow M:L^{n+}$

Wilson's disease

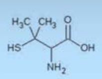
A recessive genetic disorder resulting in copper accumulation in liver and brain:

Liver problems and
neurological and psychiatric symptoms

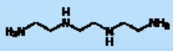
Treatment: chelation therapy

Chelation therapy

To decrease copper levels in liver:
penicillamine (orally)



or triethylenetetramine



Why these ligands?

What about zinc-levels?

Selectivity ? (relies on relative stabilities)

Stepwise complex formation

$[M(H_2O)_{N-n+1}L_{n-1}] + L \leftrightarrow [M(H_2O)_{N-n}L_n] + H_2O$

Consecutive stability constant K_n

$$[ML_n] = K_n \cdot [ML_{n-1}] \cdot [L]$$

$[M(H_2O)_N] + nL \leftrightarrow [M(H_2O)_{N-n}L_n] + nH_2O$

Overall stability constant β_n

$$[ML_n] = \beta_n \cdot [M] \cdot [L]^n$$

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An example

Cd^{2+} - CN^-

$Cd^{2+} + CN^- \leftrightarrow CdCN^+$ K_1

$CdCN^+ + CN^- \leftrightarrow Cd(CN)_2$ K_2

$Cd(CN)_2 + CN^- \leftrightarrow Cd(CN)_3^-$ K_3

$Cd(CN)_3^- + CN^- \leftrightarrow Cd(CN)_4^{2-}$ K_4

$Cd^{2+} + 4CN^- \leftrightarrow Cd(CN)_4^{2-}$ β_4

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The Cd^{2+} - CN^- system

$Cd^{2+} + nCN^- \leftrightarrow Cd(CN)_n^{(n-2)-}$ β_n

n	$\log K_n$	$\log \beta_n$
1	5.62	5.62
2	5.18	10.8
3	4.9	15.7
4	3.5	19.2

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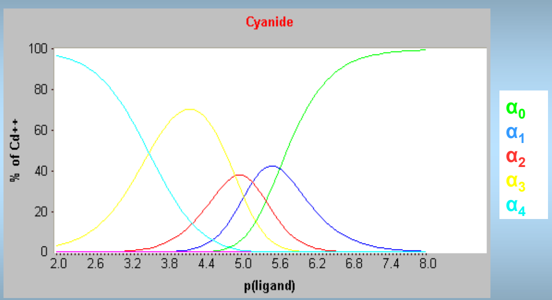
Distribution of central atom

Degree of formation of ML_n

$$\alpha_n = [ML_n]/C_M \; < 1$$

$$\Sigma\, \alpha_n = 1 \quad C_M = C_M \cdot \Sigma\, \alpha_n$$

The Cd^{2+} - CN^{-} system



Distribution of central atom

Degree of formation α_n of ML_n

$$\alpha_n = [ML_n]/C_M$$

$$\Sigma\, \alpha_n = 1$$

$C_M = [M] + [ML] + [ML_2] + \ldots\ldots + [ML_N]$ use $[ML_n] = \beta_n \cdot [M] \cdot [L]^n$

$$C_M = \beta_0[M] + \beta_1[M]\cdot[L] + \beta_2[M]\cdot[L]^2 + \ldots\ldots + \beta_N[M]\cdot[L]^N$$

$$C_M = [M]\sum_{n=0}^{N} \beta_n \cdot [L]^n$$

Distribution of ligand

$$C_L = [L] + [ML] + 2[ML_2] + ... + N[ML_N]$$

use $[ML_n] = \beta_n \cdot [M] \cdot [L]^n$

$$C_L = [L] + \beta_1[M]\cdot[L] + 2\beta_2[M]\cdot[L]^2 + ... + N\beta_N[M]\cdot[L]^N$$

$$C_L = [L] + [M]\sum_{n=0}^{N} n\beta_n \cdot [L]^n$$

$$C_L - [L] = C_M \Sigma n\alpha_n$$

Degree of formation of the system = mean (average) ligand number

$$\bar{n} = \frac{C_L - [L]}{C_M}$$

$$\bar{n} = \frac{\sum n\beta_n \cdot [L]^n}{\sum \beta_n \cdot [L]^n} = \frac{\Sigma \mathbf{n} \cdot \alpha_n}{\Sigma \alpha_n}$$

Determine [L], calculate $\bar{n}$ and do that for N different solutions

Solve N equations with N unknown β's

The ligand method

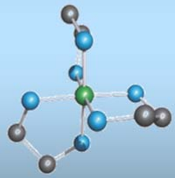
- Find [L] using $[L] = K_{HL^+} \cdot \frac{[LH^+]}{[H^+]}$

Measure pH in solutions of a high (constant) concentration of an LH^+ salt e.g. $LHNO_3$

The acidity constant of LH^+ should therefore be determined.

Case study 1

- 1,2-ethanediamine as a ligand
- Abbreviation : en



Acidity constants

questions1,2,3

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The central ion

- Potentiometry: M^{n+}/M reversible electrode

$E = E^0_M + (RT\ln 10/nF)\cdot \log[M^{n+}]$

$$\alpha_0 \cdot C_M = 10^{\frac{(E_M - E^0_M)\cdot n}{0.0592}}$$

$M \mid C_L , C_M \parallel C_M \mid M$

$\Delta E = (RT\ln 10/nF)\cdot \log(C_M/[M^{n+}])$

$= - (0.0592/n)\cdot \log\alpha_0$

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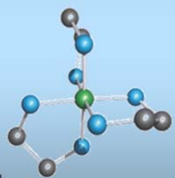
Case study 1

Ligand: 1,2-ethanediamine

Central atom: Cd^{2+}



Question 7

- Acidity constants, pH = 6.43:
  consider distribution of ligand
- ΔE = 25.6 mV
  consider distribution of metal ion

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Q7

pH=6.43:

- [en] ~0 => $[enH_2^{2+}] = [enH^+]\cdot 10^{-6.43+7.49}$

25.6 mV = (59.2/2)· $\log(\alpha_0 \cdot 0.0990/0.00990)$

- $\alpha_0=0.735$ => $\alpha_1=0.265$
- => $[Cden^{2+}]$ = .0990·0.265 = 0.0262 M

C_{en} =0.0787 M = $[enH_2^{2+}] + [enH^+] + [Cden^{2+}]$ ([en]~0)

0.0525 = $[enH_2^{2+}] + [enH^+]$

- => $[enH^+] = 4.21\cdot 10^{-3}$ M
- $[en]=[enH^+]\cdot 10^{6.43-10.20} = 10^{-6.14}$ M

$$\log K_1 = \log(\alpha_1/\alpha_0) + 6.14 = 5.70$$

Coloured compounds

$A_\lambda = \varepsilon_\lambda \cdot C_M \cdot l$

$A_\lambda = \varepsilon_\lambda(M)\cdot[M]\cdot l + \varepsilon_\lambda(ML)\cdot[ML]\cdot l + \varepsilon_\lambda(ML_2)\cdot[ML_2]\cdot l + \varepsilon_\lambda(ML_3)\cdot[ML_3]\cdot l + \ldots\ldots + \varepsilon_\lambda(ML_N)\cdot[ML_N]\cdot l$

$\varepsilon_\lambda = \varepsilon_\lambda(M)\cdot\alpha_0 + \varepsilon_\lambda(ML)\cdot\alpha_1 + \varepsilon_\lambda(ML_2)\cdot\alpha_2 + \ldots + \varepsilon_\lambda(ML_N)\cdot\alpha_N$

Measure spectra of solutions with different C_M and C_L

Approach experiment to solutions having identical ε_λ

- Then solutions are said to be "corresponding" : $\alpha_n(1) = \alpha_n(2)$

Corresponding solutions

All α_n's are identical in different corresponding solutions. It can be shown that also the free ligand concentration [L] is identical in the two solutions :

$$\bar{n}_a = \frac{C^a_L - [L]}{C^a_M} = \bar{n}_b = \frac{C^b_L - [L]}{C^b_M} \quad \text{i.e.}$$

$$[L] = \frac{C^a_L \cdot C^b_M - C^b_L \cdot C^a_M}{C^b_M - C^a_M}$$

from which $\bar{n}$ can be found

Corresponding solutions

In corresponding solutions the values of $\overline{n}$ (the degree of formation of the system or the mean ligand number) are the same. The degree of formation of each single species (and all the α's) are the same.

If α_n in one solution is the same as α_n in another solution then the two solutions are corresponding.

Electrochemical (α_0) or spectroscopic (ε) methods.

Corresponding solutions

”Problems ..” on Moodle

The determination of stability constants – a simple example

$$M^+ + 2L \leftrightarrow ML_2^+$$

$C_M = 0.01$; $C_L = 0.02$ $C_M = 0.03$; $C_L = 0.04$

36=60log(C_M/[M^+]) : α_0=.25

[L] = 0.01 ň = 1

$K_1 = 200$ $K_2 = 50$

Relative magnitude of consecutive constants

n	pK_1	pK_2	dpK
0	1.28	4.19	2.96
1	2.87	5.70	2.83
2	4.22	5.70	1.48
3	4.35	5.40	1.05
4	4.44	5.44	1.00
5	4.51	5.51	1.00
6	4.52	5.52	.99
7	4.56	5.53	.97
8	4.58	5.54	.96

Acidity constants for dicarboxylic acids and for α,ω-diamonium ions (25 °C) - n is the number of carbon atoms in the chain connecting the two acid groups

Consider probabilities

n	pK_1	pK_2	dpK
2	7.17	9.98	2.83
3	8.71	10.31	1.60
4	9.49	10.67	1.19
5	9.92	10.77	.85
6	10.12	10.80	.68
7	10.16	10.85	.69
8	10.27	10.88	.61
10	10.35	10.94	.59

$$\frac{K_1}{K_2} = \frac{[HBB^-]\cdot[H^+]}{[HBBH]}\cdot\frac{[HBB^-]}{[H^+]\cdot[^-BB^-]} = \frac{2}{1}\cdot\frac{2}{1}$$ dpK=0.6

Cd^{2+} - NH_3

n	$\log K_n$	$\log(K_n/K_{n+1})$
1	2.66	0.57
2	2.09	0.66
3	1.43	0.5
4	0.93	

Probability of forming ML_n

- Relative probabilities are found:

There are N sites to occupy with equal probability – but some have already been occupied

$$\frac{K_n}{K_{n+1}} = \frac{[ML_n]}{[ML_{n-1}]\cdot[L]} \cdot \frac{[L]\cdot[ML_n]}{[ML_{n+1}]} = \frac{N-n+1}{n} \cdot \frac{n+1}{N-n}$$

Cd^{2+} - NH_3

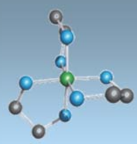
$\log K_{max}$	$\log K_{max}$	n	$\log K_n$	$\log(K_n/K_{n+1})_{min-calc}$		
N = 4	N = 6			exp	N = 4	N = 6
		1	2.66	0.57		
		2	2.09	0.66		
		3	1.43	0.5		
		4	0.93			

Nickel(II)-ammonia

experimental and predicted

n	$\log\beta_n$ (stat)	$\log\beta_n$ (exp)	K_n/K_{n+1}
1	-	2.78	12/5
2	5.18	5.05	15/8
3	7.05	6.70	16/9
4	8.10	8.01	15/8
5	9.05	8.66	12/5
6	8.93	8.74	

Case study 1

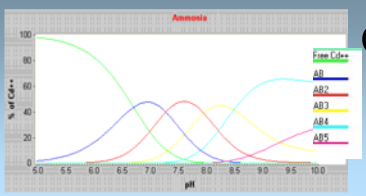


- 1,2-ethanediamine as a ligand

Abbreviation : en

M^{2+}	$\log K_1$	$\log K_2$	$\log K_3$
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	See question 6	4.59	2.09

Cd^{2+} - NH_3



C_M=1mM; C_L=1M

$mM^{n+} + hH^+ + lL^{y-} \leftrightarrow M_mH_hL_l^{(mn-ly+h)+}$ β_{mhl}

m, h, l	1, 0, 1	1, 0, 2	1, 0, 3	1, 0, 4	1, 0, 5	1, 0, 6	0, 1, 1
$\log\beta_{mhl}$	2.66	4.75	6.18	7.11	6.84	4.4	9.38
$\log K_n$	2.66	2.09	1.43	0.93	-0.27	-2.24	