Acids and bases

•Brønsted :
•H^+ donor and acceptor
$HA + B \rightarrow HB^+ + A^-$

•Lewis :
electron pair acceptor and donor
$A + :B \rightarrow A:B$

Brønsted acids HA

HA in aqueous solution:

Hydration and hydrogen bonding

H_3O^+ $H_9O_4^+$

$HA_{aq} \rightarrow H^+_{aq} + A^-_{aq}$

Bond strength

H-A

Figures from textbook

- 7.3
- 7.4

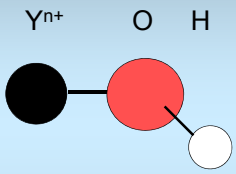
Ionic potential

- Charge density on surface of ion

Increases when
- charge increases
- size decreases

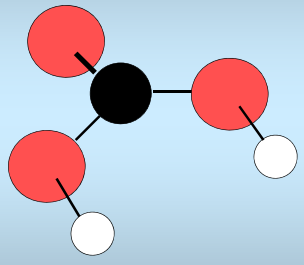
Small ions with high charge:
high Ionic potential

Weak acids YOH



Relative bond strength
- Increase in size of Y^{n+}: weaker Y-O bond
- Increase in charge (n) : stronger Y-O bond

Acids: $XO_n(OH)_m \rightarrow XO_n(OH)_m^- + H^+$



pK~8-5n (Bell's rule)

n=3 : very strong -7
n=2 : strong -2
n=1 : weak 3
n=0 : weak 8

Oxy acids acidity
$XO_n(OH)_m$: pK ≈8-5n

Very weak pK ~ 8	Weak pK ~ 3	Strong pK ~ -2	Very strong (pK ~ -7)
ClOH 7.2	NOOH 3.3	NO_2OH -1.4	ClO_3OH (-10)
BrOH 8.7	ClOOH 2.0	ClO_2OH -1	MnO_3OH (-a lot)
IOH 10.0	$CO(OH)_2$ 3.9	IO_2OH 0.8	
$As(OH)_3$ 9.2	$SO(OH)_2$ 1.9	$SO_2(OH)_2$ <0	
$Sb(OH)_3$ 11.0	$SeO(OH)_2$ 2.6	$SeO_2(OH)_2$<0	
$B(OH)_3$ 9.2	$TeO(OH)_2$ 2.7		
$Si(OH)_4$ 10.0	$PO(OH)_3$ 2.1		
$Ge(OH)_4$ 8.6	$AsO(OH)_3$ 2.3		
$Te(OH)_4$ 8.8	$IO(OH)_5$ 1.6		
	$HPO(OH)_2$ 1.8		
	$H_2PO(OH)$ 2.0		

Predict the pK of the acid corresponding to

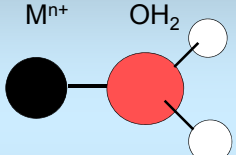
arsenate(V) — arsenic(V) acid

antimonate(V) — antimonic(V) acid

germanate(IV) — germanic(IV) acid

Aqua ions as acids

M^{n+} OH_2 in $M(H_2O)_x^{n+}$



$\rightarrow M(OH)(H_2O)_{x-1}^{(n-1)+} + H^+$

n = 2 pK > 7

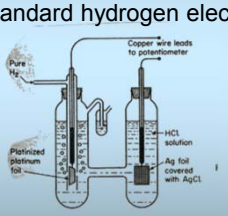
n = 3 pK < 7

pH

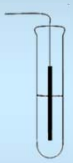
S.P.L.Sørensen
1909

$pH \equiv -\log(H^+) \sim -\log [H^+]$

Standard hydrogen electrode



Glass electrode



- Copper wire
- Silver wire covered with AgCl-paste in hydrochloric acid
- Special glass bulb susceptible to protons (more or less selectively)
- $E = E^o - k \cdot pH + E_{diffusion}$
- To be standardised with buffers

Standard buffers

Composition	pH
Potassium hydrogentartrate, saturated at 25 °C	3.557
0.050 m potassium hydrogenphthalate	4.008
0.025 m KH_2PO_4 + 0.025 m Na_2HPO_4	6.865
0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4	7.413
0.010 m borax	9.180

Acids and bases

Lewis :

electron pair acceptor and donor

$A + :B \rightarrow A:B$

acid-base chemistry

$H^+ + :B \rightarrow H:B^+$

complex formation

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

Hard and soft acids and bases

- Polarisability of electron cloud
- Ion potential

Hard: low polarisability , high ion potential

Soft: high polarisability, low ion potential

Stable:

Hard-hard interactions (electrostatic)

Soft-soft interactions (covalent)

Unstable :hard-soft and soft-hard

Tables from textbook

- 7.8
- 7.9a
- 7.9b