

CAPVT III

IONI

Monoatomni ioni

- Gubitak ili primanje elektrona u neutralni atom
- Postoje samo u plinovitoj fazi

Kationi u otopini

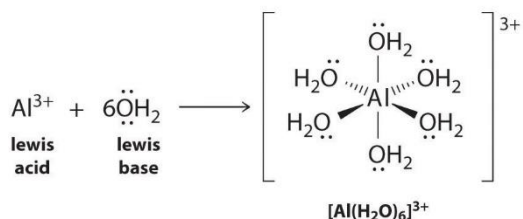
- Solvatacija
- Za neelektronegativne ione ovisna o naboju i radijusu – Latimer/hidratacija

$$\Delta H_{\text{hid}} \approx -60900 Z^2 / [(r + 50) / \text{pm}] \text{ kJ mol}^{-1}$$

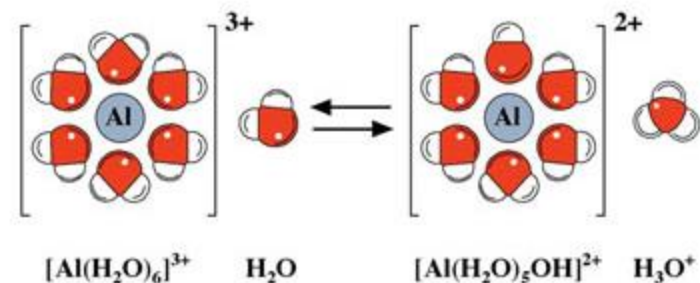
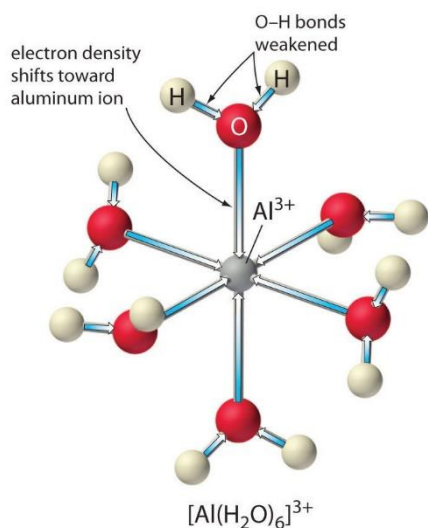
- Ako je $\chi > 1,5$ hidratacijska entalpija raste
– kemijska veza između atoma i molekule otapala

Akvatizirani kationi

- Molekule vode vezane ne centralni ion
- Raste kiselost (pada pK_a) takvih molekula vode – “hidroliza”



(a)

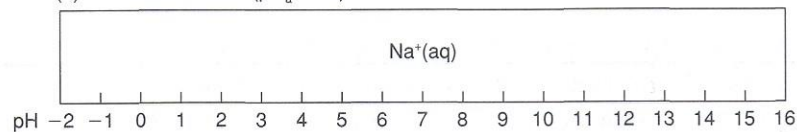


$$K_a = 1,1 \cdot 10^{-5}$$

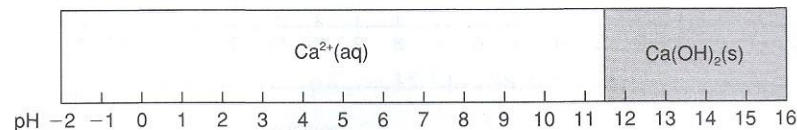
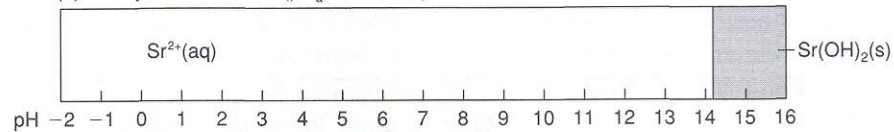
Kategorije kiselosti iona

- $pK_a > 14$ nekiseli kationi (Cs^+ , Rb^+)
- $11,5 < pK_a < 14$ slabašno kiseli (*feebly acidic*; Li^+ , Ba^{2+})
- $6 < pK_a < 11,5$ slabo kiseli (Mg^{2+})
- $1 < pK_a < 6$ srednje kiseli (Al^{3+})
- $-4 < pK_a < 1$ jako kiseli (Ti^{4+})
- $pK_a < -4$ vrlo jako kiseli – kvantitativno reagiraju s vodom, postoje samo formalno (Mn^{7+} , Cr^{6+})

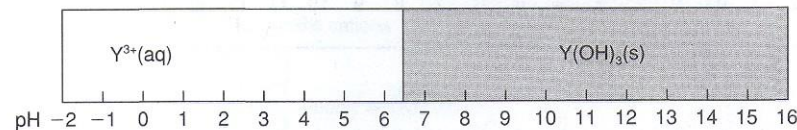
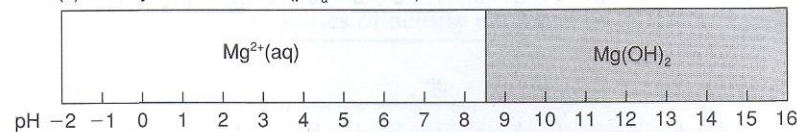
(a) Nonacidic Cations ($pK_a > 14$)



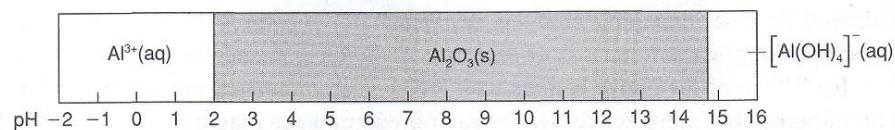
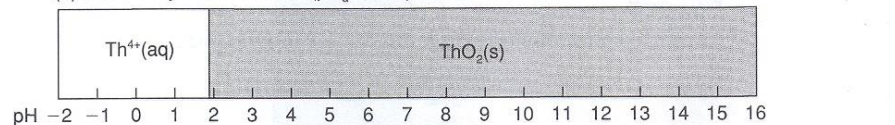
(b) Feebly Acidic Cations ($pK_a = 11.5\text{--}14$)



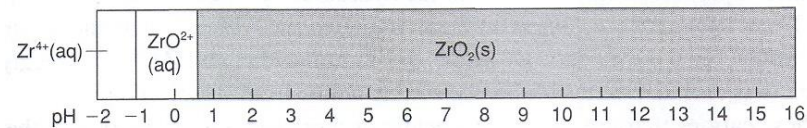
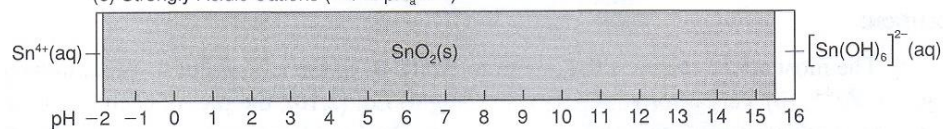
(c) Weakly Acidic Cations ($pK_a = 6\text{--}11.5$)



(d) Moderately Acidic Cations ($pK_a = 1\text{--}6$)



(e) Strongly Acidic Cations ($-4 \leq pK_a \leq 1$)



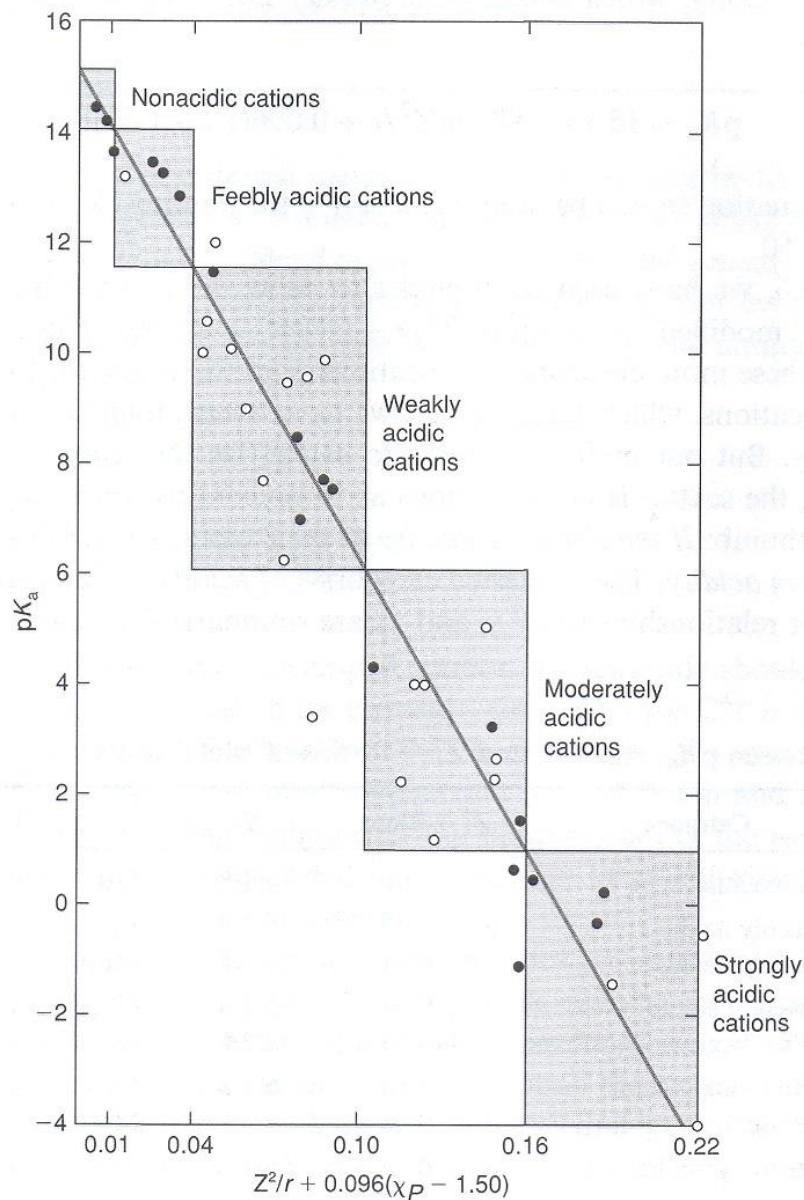
Kiselost i svojstva iona

- Kiselost je funkcija naboja, radijusa (i elektronegativnosti, i drugih stvari koje se u prvu ruku mogu zanemariti...)

$$\text{p}K_{\text{a}} \approx 15,14 - 88,16 \text{ pm} * [Z^2/r]$$

za elektronegativnije elemente ($\chi_{\text{P}} > 1,50$), potrebno je uvesti i korekciju na elektronegativnost:

$$\text{p}K_{\text{a}} \approx 15,14 - 88,16 \text{ pm} * [Z^2/r + 0,096 \text{ pm}^{-1} (\chi_{\text{P}} - 1,50)]$$



Korelacija mjerenih pK_a i
(korigiranog) omjera kvadrata
naboja i radijusa

$[Z^2/r + 0,096 \text{ pm}^{-1} (\chi_P - 1,50)]$
za monoatomne katione

Anioni

- Također solvatirani
- Latimer/hidratacija

$$\Delta H_{\text{hid}} \approx -57 \cdot 10^3 Z^2 / r \text{ pm kJ mol}^{-1}$$

- Ponašaju se kao baze

- $pK_b > 14$ nebazni anioni (Cl^- , Br^- , I^-)
- $11,5 < pK_b < 14$ slabašno bazni
- $6 < pK_b < 11,5$ slabo bazni (F^-)
- $1 < pK_a < 6$ srednje bazni (Te^{2-})
- $-4 < pK_a < 1$ jako bazni (Se^{2-} , S^{2-})
- $pK_a < -4$ vrlo jako bazni (O^{2-})

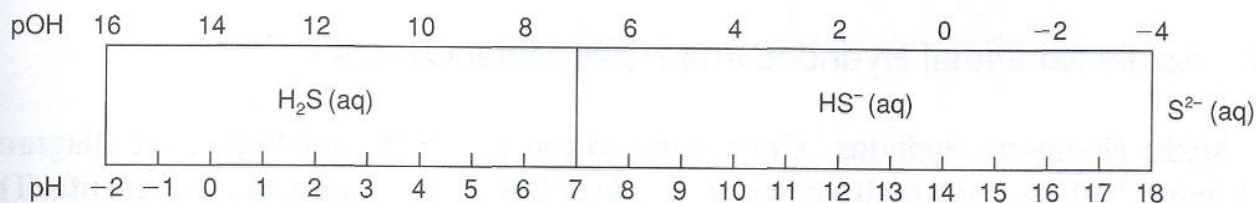
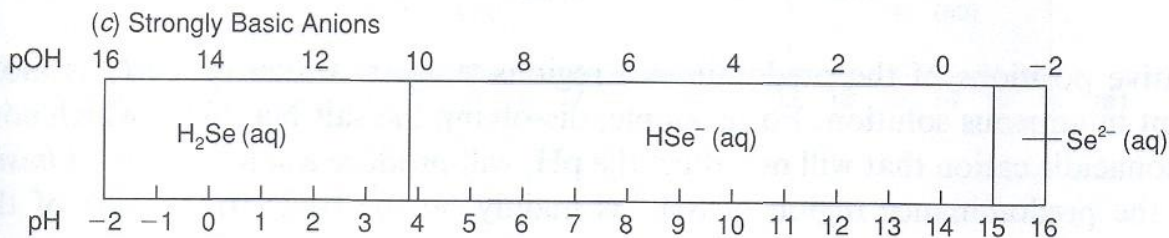
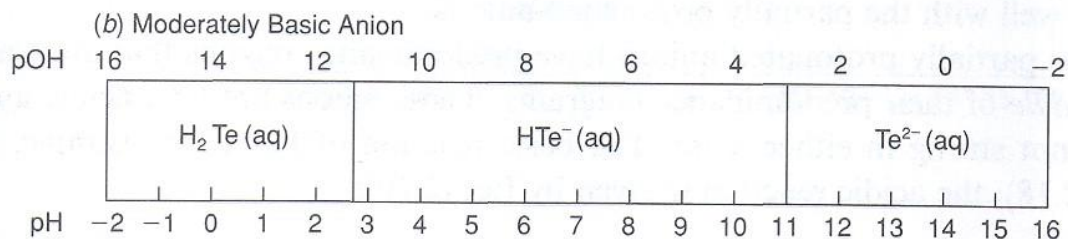
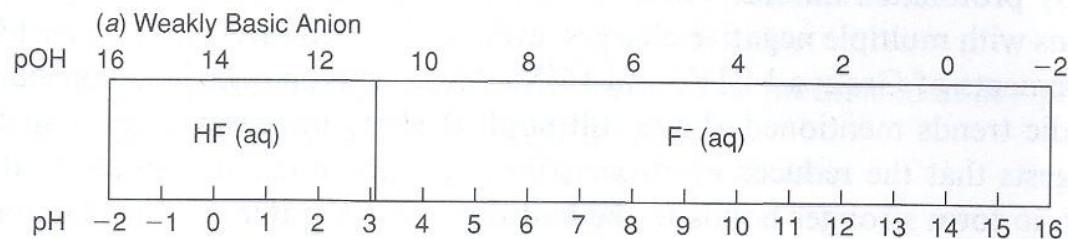


Figure 2.10

Acid–base predominance diagrams for (1 M total concentrations of) nonmetal monoatomic anions and their partially protonated and fully protonated forms.

- Baznost kao funkcija naboja i radijusa

$$pK_b \approx 29 - 1200 Z^2 / r$$

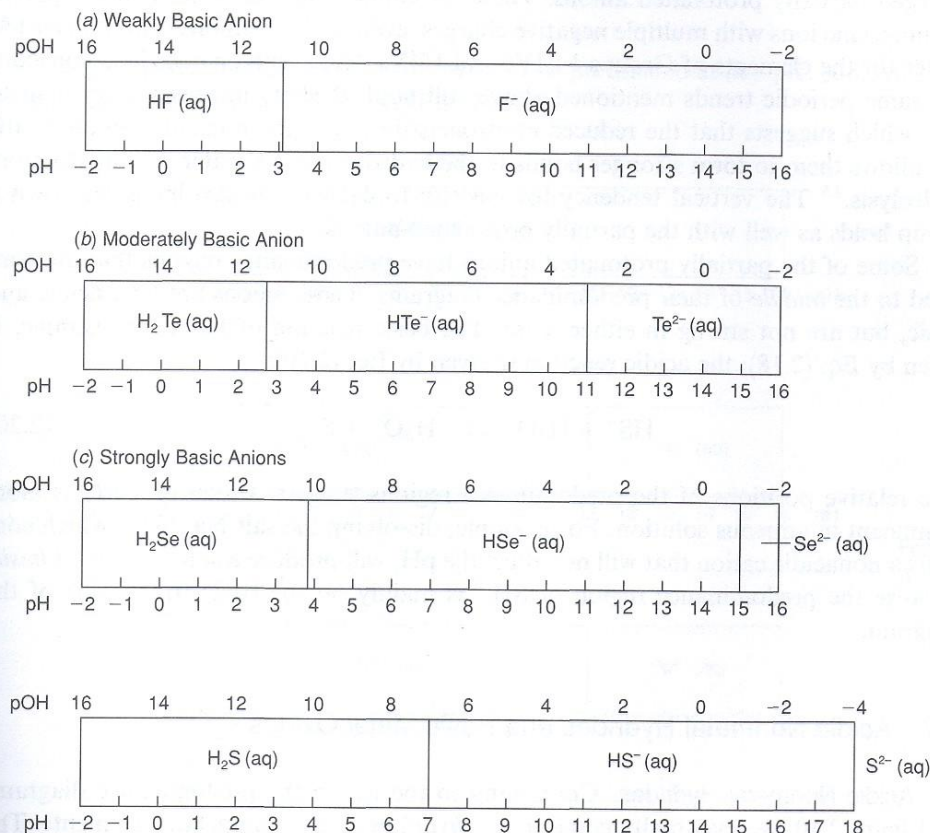


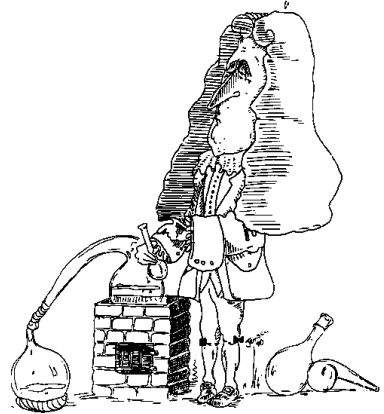
Figure 2.10

Acid-base predominance diagrams for (1 M total concentrations of) nonmetal monoatomic anions and their partially protonated and fully protonated forms.

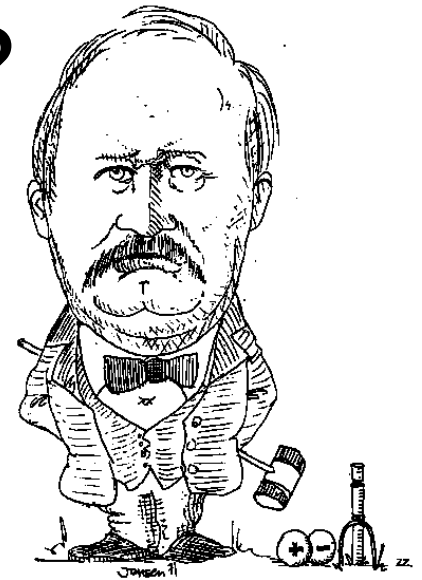
Što je kiselina?



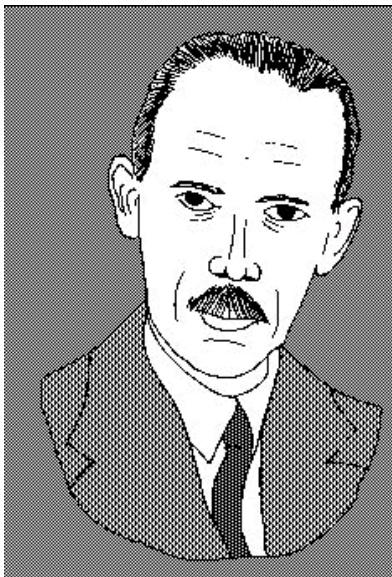
Ono što je kiselo



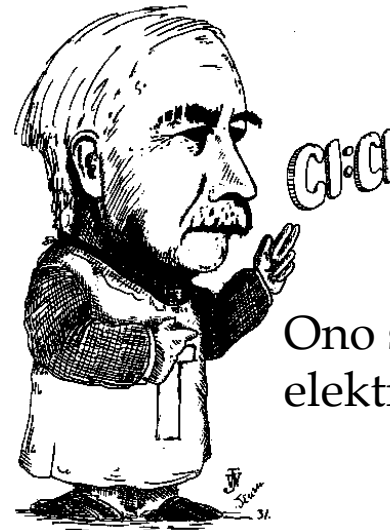
Ono od čega ekstrakt
ljubičice pocrveni



Ono što u vodenoj otopini
poveća koncentraciju
vodikovih kationa



Ono što otpušta
protone (hidrone)



Ono što prima
elektronski par

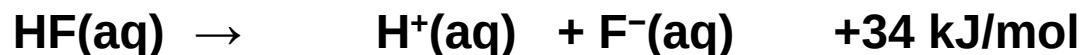
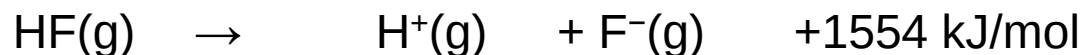
afinitet prema protonu (PA, E_{pa})

$$E_{\text{pa}}(A) = -\Delta_r H$$

za $A(\text{g}) + \text{H}^+ \rightarrow \text{HA}^+$

- Mjera za kiselost/baznost neovisna o otapalu
- Bazičnost aniona ovisi o otapalu: jako solvatirani anion slabija baza od slabo solvatiranog:

(npr, za OH^- , $E_{\text{pa}} = 1635 \text{ kJ/mol}$; $\text{p}K_{\text{a}}(\text{u vodi}) = 14$; $\text{p}K_{\text{a}}(\text{u dmso}) \approx 32$)



Tvrde i meke kiseline i baze

- Za potpun opis ponašanja dane Lewisove kiseline nedovoljan je podatak o jakosti
- Pearson – tvrde i meke kiseline i baze
- Tvrde:
 - Malen radijus, velik naboj, mala polarizabilnost
- Meke:
 - Velik radijus, malen naboj, velika polarizabilnost

Kiseline

tvrde	meke
H^+	$\text{CH}_3\text{Hg}^+, \text{Hg}^{2+}, \text{Hg}_2^{2+}$
$\text{Li}^+, \text{Na}^+, \text{K}^+$	Pt^{2+}
Ti^{4+}	Pd^{2+}
$\text{Cr}^{3+}, \text{Cr}^{6+}$	Ag^+
BF_3	BH_3
R_3C^+	M^0
	Au^+

Baze

tvrde	meke
OH^-	H^-
RO^-	RS^-
F^-, Cl^-	I^-
NH_3	PR_3
CH_3COO^-	SCN^-
CO_3^{2-}	CO
N_2H_4	C_6H_6

Apsolutna tvrdoća

Kiseline

H ⁺	-
Al ³⁺	45.8
Li ⁺	35.1
Sc ³⁺	24.6
Na ⁺	21.1
La ³⁺	15.4
Zn ²⁺	10.8
CO ₂	10.8
SO ₂	5.6
I ₂	3.4

Baze

F ⁻	7
NH ₃	6.8
H ⁻	6.8
CO	6.0
OH ⁻	5.6
CN ⁻	5.3
PH ₃	5.0
NO ₂ ⁻	4.5
SH ⁻	4.1
CH ₃ ⁻	4.0

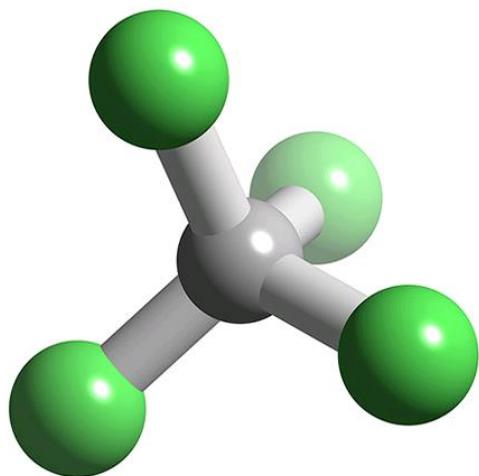
$$\eta = \frac{1}{2} \left[\frac{\partial^2 E}{\partial^2 N} \right]_Z$$

$$\eta \approx -\frac{1}{2} (E_i + E_a) = -\frac{1}{2} \chi_M$$

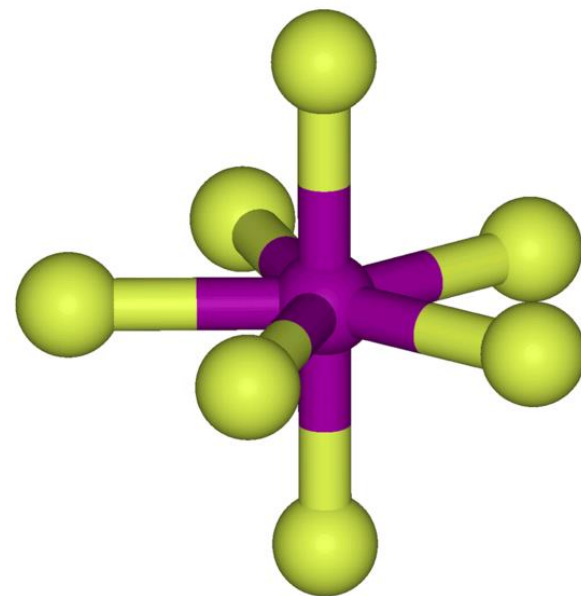
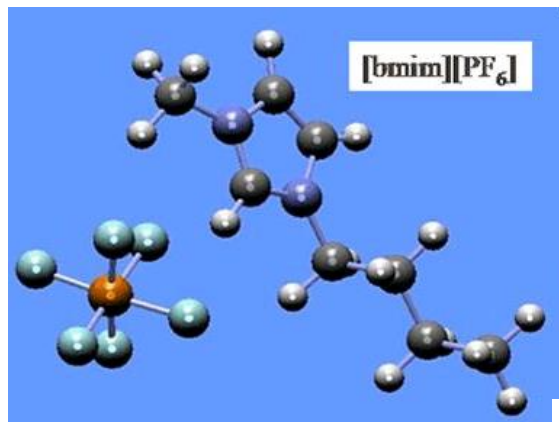
Višeatomni ioni

- Načelni pristup: centralni atom (“kation”) na koji su vezani drugi
- Koordinacijski broj – broj atoma vezanih na centralni atom
- Totalni koordinacijski broj – koordinacijski broj + broj elektronskih parova
- Maksimalni totalni koordinacijski broj – funkcija veličine centralnog atoma: 2. perioda – 4; 3. i 4. – 6; 5. i 6. – više od 6

Fluoro-anioni



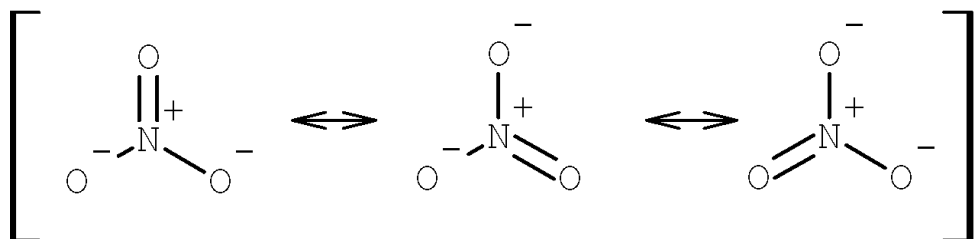
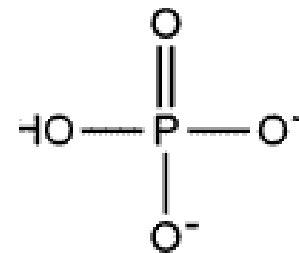
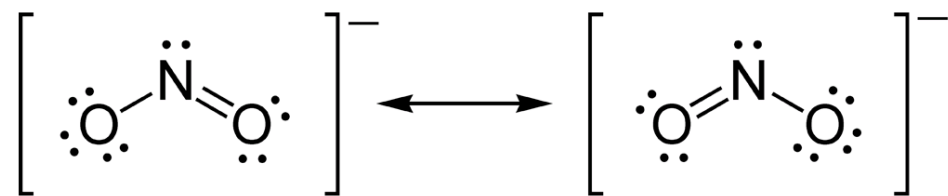
BF_4^-



IF_7^-

Okso-anioni

- Totalni koordinacijski broj u pravilu za 1 manji od maksimalnog – elektronski a ne sterički razlozi



klasifikacija

Classification	Type	Calculated pK_{b1}	Examples with Known pK_{b1} Values
Nonbasic anions	MO_4^-	22.6	M = Cl, Br, Mn, Tc, Re
	MO_3^-	16.9	M = N, Cl, Br, I(13.2)
Feebly basic anions	MO_4^{2-}	12.4	M = S(12.1), Se(12.0), Xe, Cr(7.5), Mo(9.9), W(9.4), Fe(6.2), Ru, Os
	MO_2^-	11.2	M = N(10.7), Cl(12.1)
Moderately basic anions	MO_6^{4-}	3.4	M = Xe, Os
	MO_4^{3-}	2.2	M = P(2.0), As(1.5), V(1.0)
	MO_3^{2-}	6.7	M = C, S(6.8), Se(7.4), Te(6.3)
	MO^-	5.5	M = Cl(6.5), Br(5.3), I(3.4)
Very strongly basic anions (Exist as hydroxo anions in solution)	MO_6^{5-}	-6.8	M = I, Np
	MO_4^{4-}	-8.0	M = Si, Ge
	MO_3^{3-}	-3.5	M = As, Sb
	MO_6^{6-}	-17.0	M = Te
	MO_4^{5-}	-18.2	M = B, Al, Ga
	MO_3^{4-}	-14.7	M = Sn

SOURCES: Known pK_{b1} values are calculated from the appropriate pK_a values given in F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 5th ed., Wiley-Interscience, New York; 1988, p. 105; R. C. Weast, Ed., *Handbook of Physics and Chemistry*, 50th ed., Chemical Rubber Publishing Co., Cleveland, 1969; J. A. Dean, Ed., *Lange's Handbook of Chemistry*, 13th ed., New York, McGraw-Hill, 1985; and B. H. J. Bielski, *Free Radical Res. Commun.*, **12-13**, 469 (1991).

Baznost okso-aniona

- Raste s nabojem (pK_b pada za oko 10,2 za svaki dodatni negativni naboj)
- Pada s brojem kisikovih atoma (pK_b raste za oko 5,7 za svaki dodatni (okso) kisikov atom)
- Pada s porastom elektronegativnosti centralnog atoma

za ion MO_x^{y-}

$$pK_b = 10 + 5,7x - 10,2y \pm 1,0$$

Protoniranje okso-aniona



$$\Delta \text{p}K_b = -5,7 + 10,2 = 4,5$$

Nastavljajući se do kiseline $[\text{MO}_{(x-y)}(\text{OH})_y]$

$$\text{p}K_a = 14 - \text{p}K_b = 8,5 - 5,7(x-y)$$

$x - y$ = broj okso-liganada u kiselini – nužno poznavanje strukture (H_3PO_3 i H_3PO_2 ; $\text{p}K_a \approx 2$)

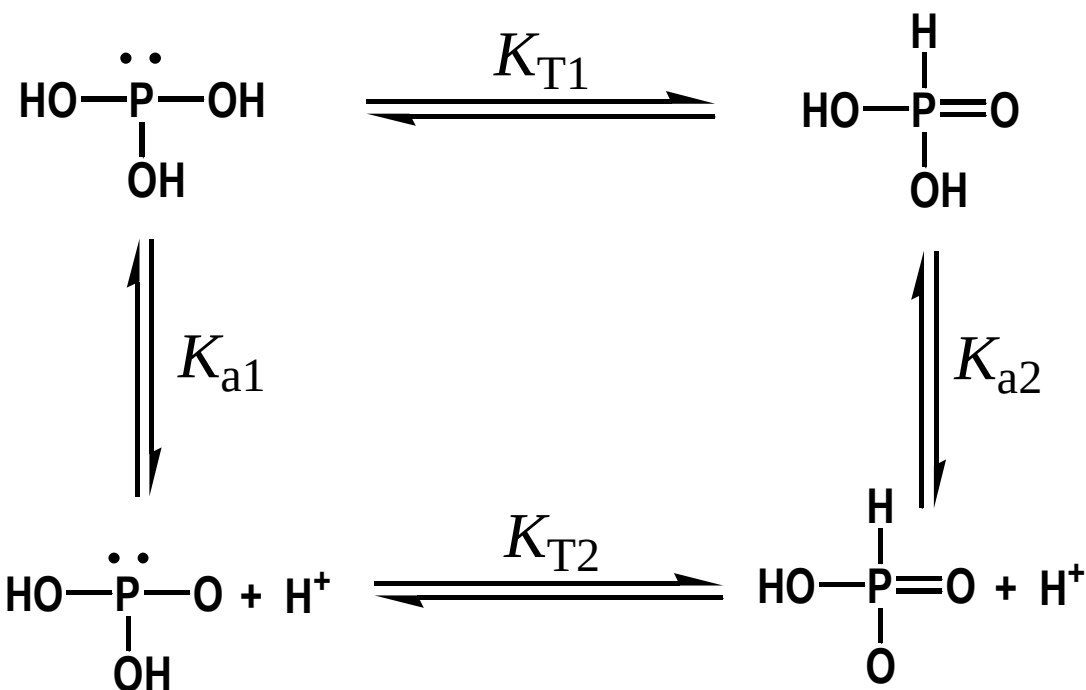
Tautomerija okso-kiselina i aniona

Kod kiselina koje mogu postojati u više tautomernih formi, pojedini tautomeri imaju različite vrijednosti pK_a tvore anione istog naboja (y), ali različitog broja okso- liganada (x)

$$\Delta pK_a = - \Delta pK_b \approx -5,7\Delta x$$

tj, K_a se povećava oko pola milijuna ($10^{5,7}$) puta za svaki okso-kisik razlike.

Za fosforastu kiselinu:



iz ciklusa lijevo proizlazi:

$$K_{a1} K_{T2} = K_{T1} K_{a2}$$

$$\text{p}K_{a2} \approx \text{p}K_{a1} - 5,7\Delta x$$

$$\rightarrow K_{a2} \approx K_{a1} \cdot 10^{5,7} \approx 5 \cdot 10^5 K_{a1}$$

$$\rightarrow K_{T2} \approx 5 \cdot 10^5 K_{T1}$$

Općenito, konstante tautomerije za anione (K_{T2}) i za kiseline (K_{T1}) odnositi kao

$$K_{T2} \approx 5 \cdot 10^5 \Delta x K_{T1}$$

Posljedično, anion oblika s većim brojem okso liganada će biti stabilniji (isto vrijedi i za kiseline s više oblika koji se razlikuju u sadržaju vode, usp H_5IO_6 vs. HIO_4)