CAPVT III

IONI

Monoatomni ioni

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

Kationi u otopini

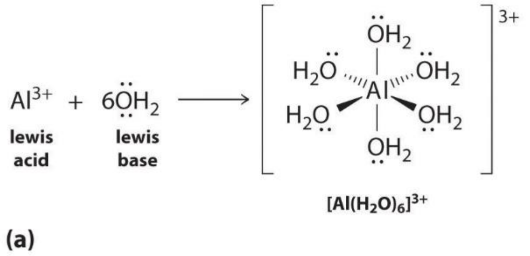
- Solvatacija
- Za neelektronegativne ione ovisna o naboju i radijusu – Latimer/hidratacija

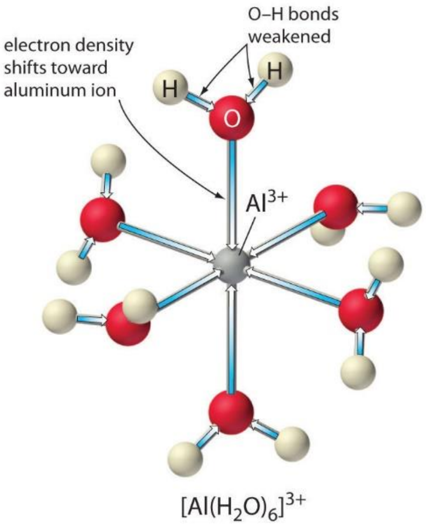
$$\Delta H_{\mathrm{hid}} \approx -60900\ Z^2/[(r + 50)/\mathrm{pm}]\ \mathrm{kJ\ mol^{-1}}$$

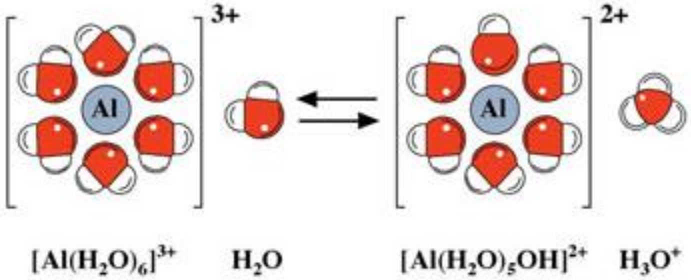
- Ako je $\chi > 1{,}5$ hidratacijska entalpija raste – kemijska veza između atoma i molekule otapala

Akvatizirani kationi

- Molekule vode vezane ne centralni ion
- Raste kiselost (pada p*K*$_a$)takvih molekula vode – “hidroliza”





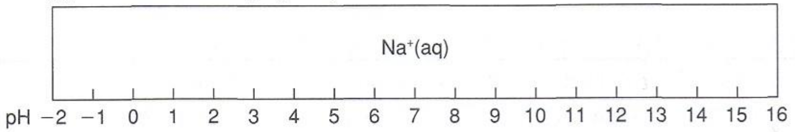


Ka = 1,1 . 10^{-5}

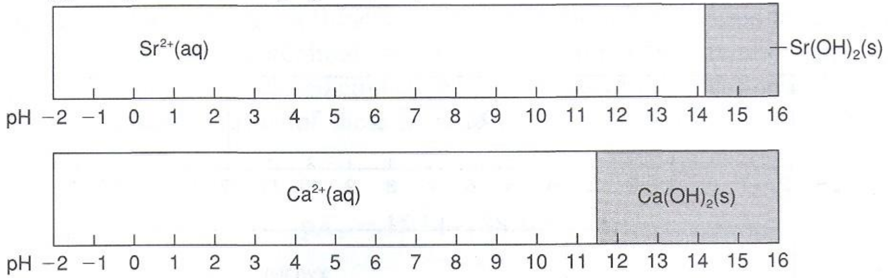
Kategorije kiselosti iona

- $pK_a > 14$ 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+})

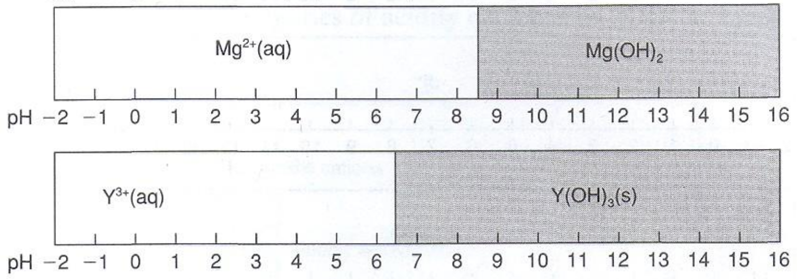
(*a*) Nonacidic Cations (p$K_a > 14$)



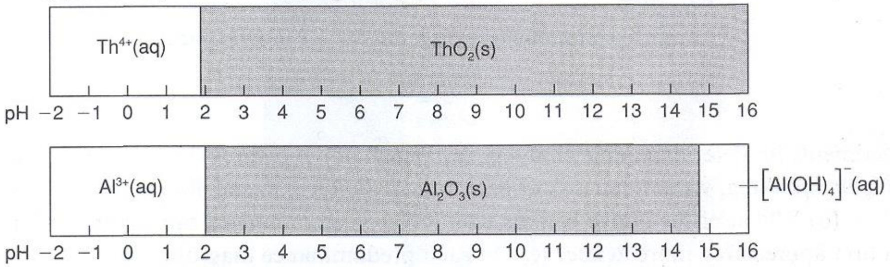
(*b*) Feebly Acidic Cations (pK_a = 11.5–14)



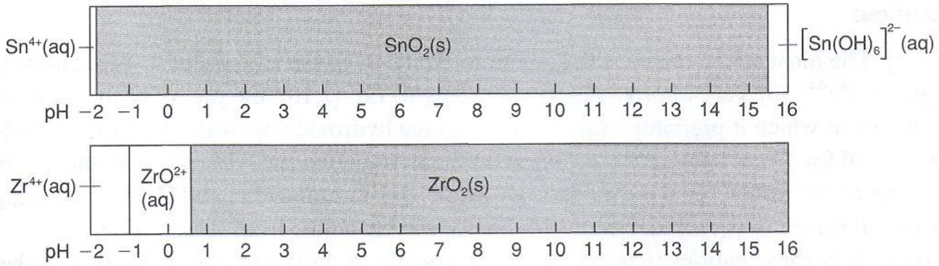
(*c*) Weakly Acidic Cations (pK_a = 6–11.5)



(*d*) Moderately Acidic Cations (pK_a = 1–6)



(*e*) Strongly Acidic Cations (−4 ≤ pK_a ≤ 1)



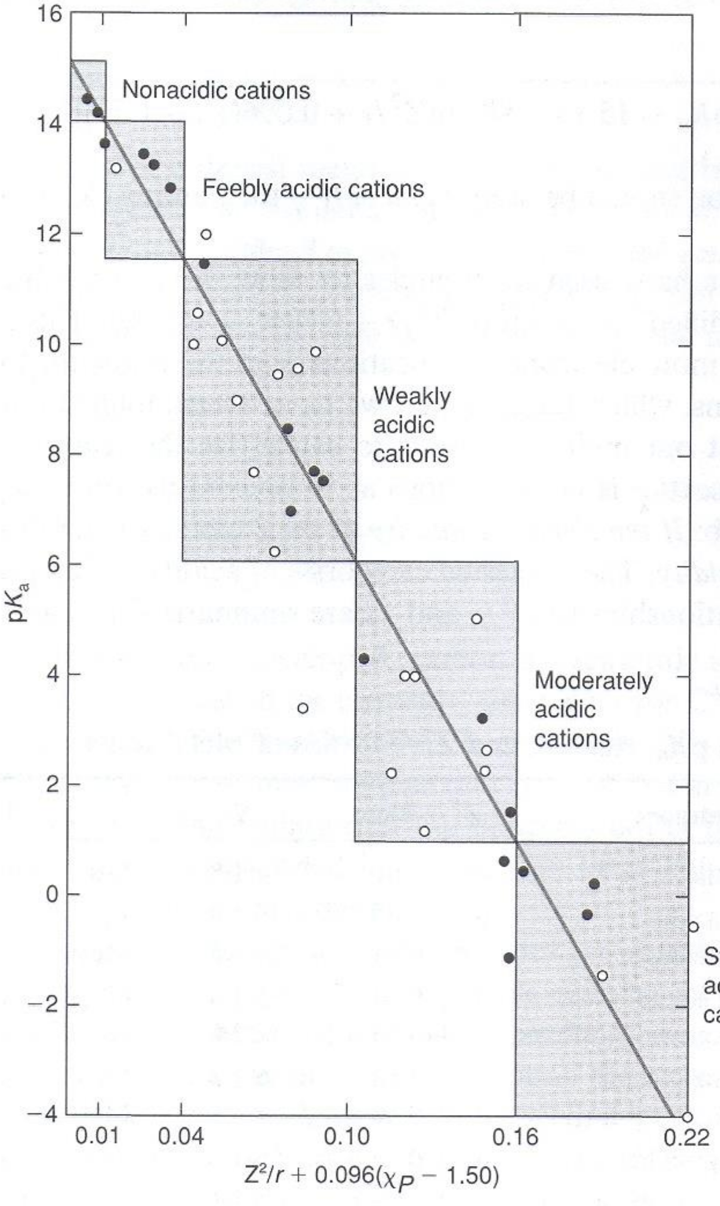
Kiselost i svojstva iona

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

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

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

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



Korelacija mjerenih pK_a i (korigiranog) omjera kvadrata naboja i radijusa [Z^2/r + 0,096 pm^{-1} (χ_P – 1,50)] za monoatomne katione

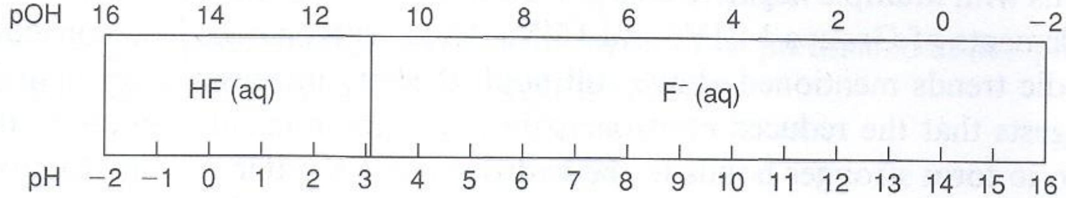
Anioni

- Takojer solvatirani
- Latimer/hidratacija

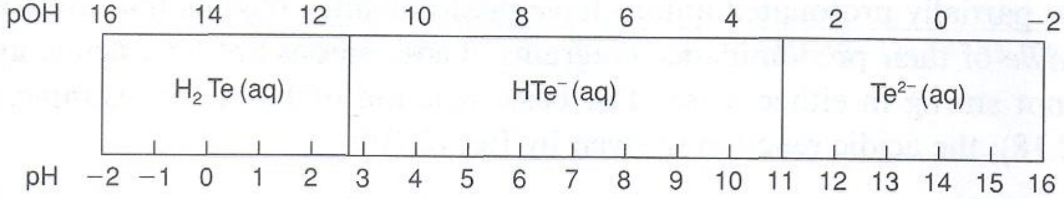
  $\Delta H_{\mathrm{hid}} \approx -57 \cdot 10^3\, Z^2/r$ pm kJ mol^{-1}
- Ponašaju se kao baze

- 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-})

(a) Weakly Basic Anion



(b) Moderately Basic Anion



(c) Strongly Basic Anions

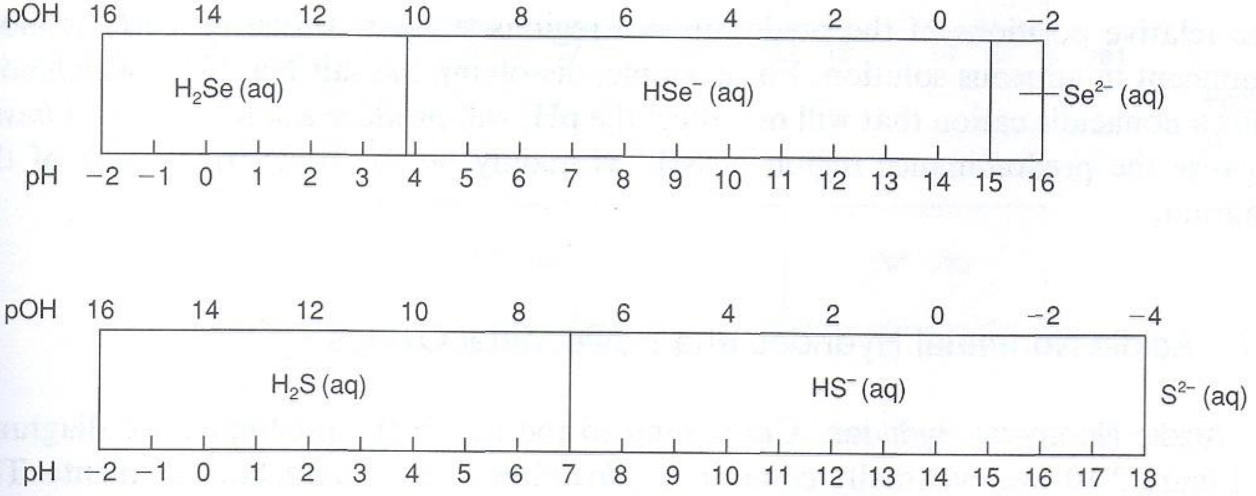


Figure 2.10

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

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

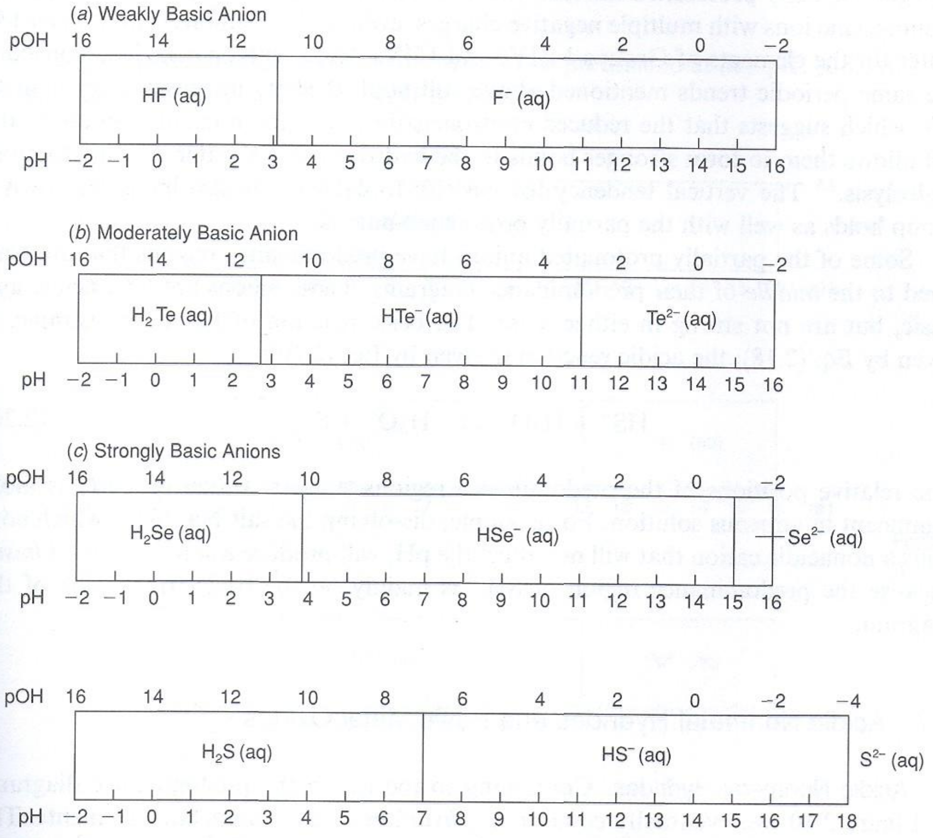
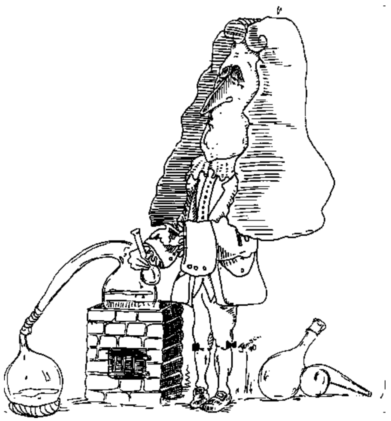


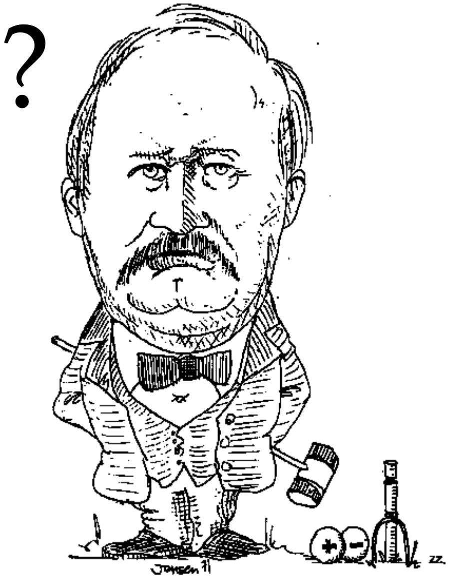
Figure 2.10
Acid–base predominance diagrams for (1 *M* total concentrations of) nonmetal monoatomic anions and their partially protonated and fully protonated forms.

Što je kiselina?

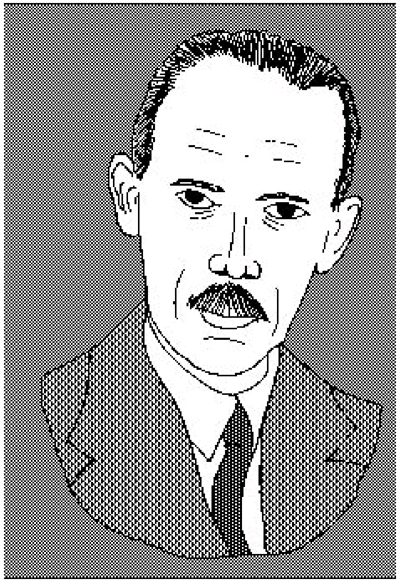
Ono što je kiselo



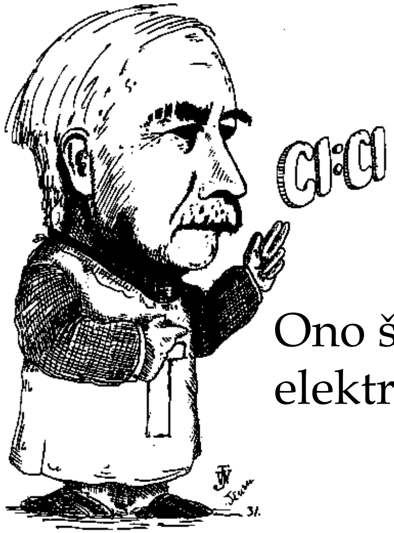
Ono od čega ekstrakt ljubičice pocrveni



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})

$$E_{\mathrm{pa}}(\mathrm{A}) = -\Delta_{\mathrm{r}}H$$

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

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

(npr, za $\mathrm{OH^-}$, E_{pa} = 1635 kJ/mol; pK_{a}(u vodi) = 14; pK_{a} (u dmso) ≈ 32)

$\mathrm{HF(g)}$	→	$\mathrm{H^+(g)}$	+ $\mathrm{F^-(g)}$	+1554 kJ/mol
$\mathrm{HF(aq)}$	→	$\mathrm{HF(g)}$		+23 kJ/mol
$\mathrm{H^+(g)}$	→	$\mathrm{H^+(aq)}$		−1530 kJ/mol
$\mathrm{F^-(g)}$	→	$\mathrm{F^-(aq)}$		−13 kJ/mol
$\mathrm{HF(aq)}$	**→**	**$\mathrm{H^+(aq)}$**	**+ $\mathrm{F^-(aq)}$**	**+34 kJ/mol**

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		**Baze**	
tvrde	**meke**	**tvrde**	**meke**
H^+	CH_3Hg^+, Hg^{2+}, Hg_2^{2+}	OH^-	H^-
Li^+,Na^+,K^+	Pt^{2+}	RO^-	RS^-
Ti^{4+}	Pd^{2+}	F^-,Cl^-	I^-
Cr^{3+},Cr^{6+}	Ag^+	NH_3	PR_3
BF_3	BH_3	CH_3COO^-	SCN^-
R_3C^+	M^0	CO_3^{2-}	CO
	Au^+	N_2H_4	C_6H_6

Apsolutna tvrdoća

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

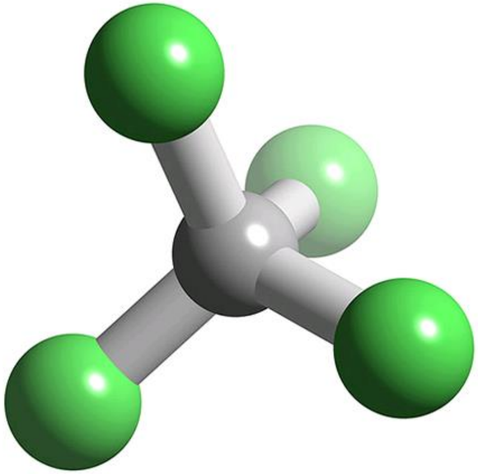
$$\eta \approx -\frac{1}{2}(E_i + E_a) = -\frac{1}{2}\chi_{\mathrm{M}}$$

Kiseline		**Baze**	
H^+	-	F^-	7
Al^{3+}	45.8	NH_3	6.8
Li^+	35.1	H^-	6.8
Sc^{3+}	24.6	CO	6.0
Na^+	21.1	OH^-	5.6
La^{3+}	15.4	CN^-	5.3
Zn^{2+}	10.8	PH_3	5.0
CO_2	10.8	NO_2^-	4.5
SO_2	5.6	SH^-	4.1
I_2	3.4	CH_3^-	4.0

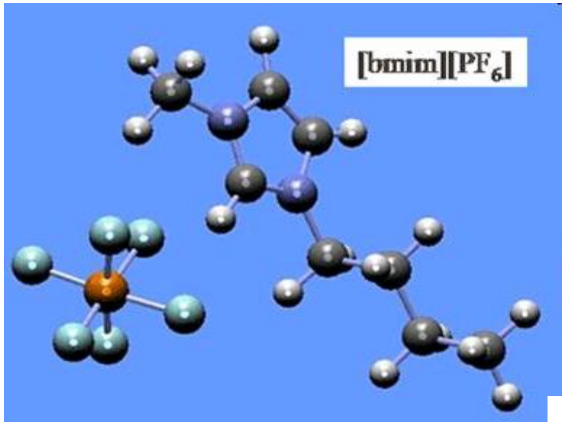
Višeatomni ioni

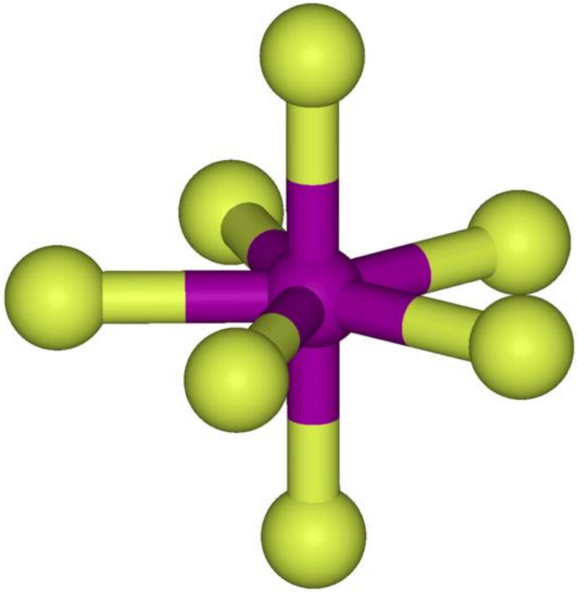
- Načelni pristup: centralni atom (“kation”) na koji su vezani drugi
- Koordinacijski broj – broj atoma vezanih na centralni atom
- Totalni koordinacijski broj – koordinacijski broj + broj elektronskih parova
- Maksimalni totalni koordinacijski broj – funkcija veličine centralnod atoma: 2 perioda – 4;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

Fluoro-anioni



BF_4

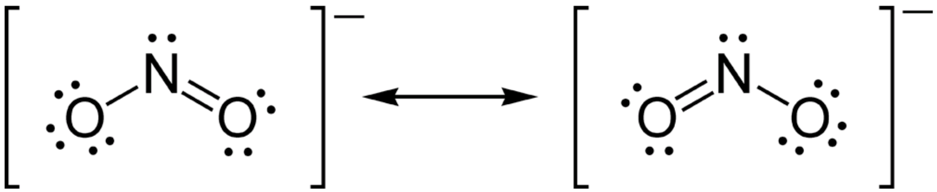


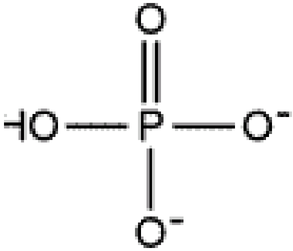


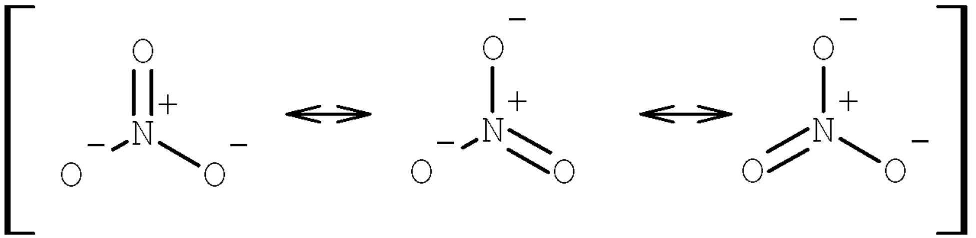
IF_7

Okso-anioni

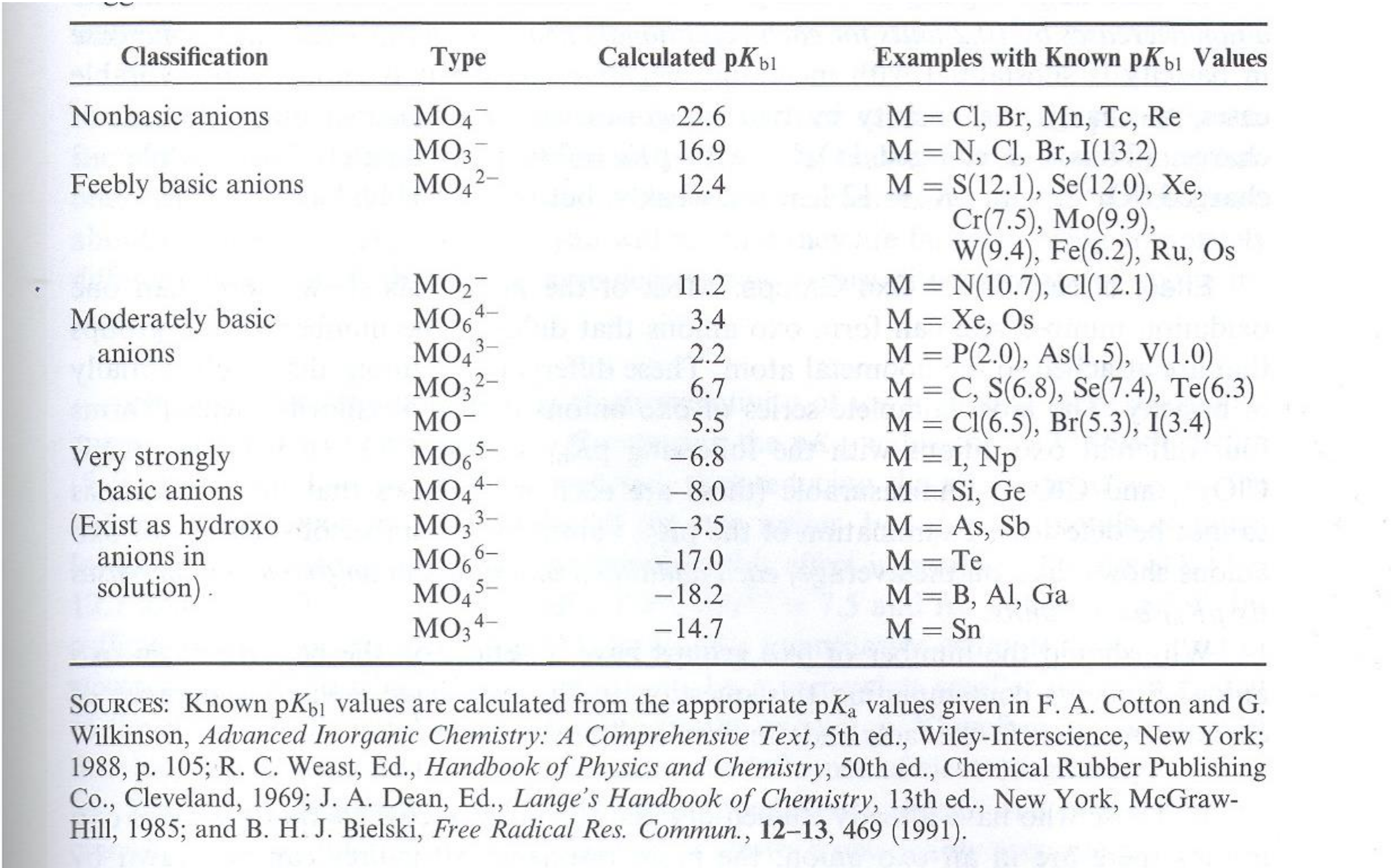
- Totalni koordinacijski broj u pravilu za 1 manji od maksimalnog – elektronski a ne sterički razlozi







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

$MO_x^{y-} + H^+ \rightarrow [MO_{(x-1)}OH]^{(y-1)-}$

$\Delta pK_b = -5,7 + 10,2 = 4,5$

Nastavljajući se do kiseline $[MO_{(x-y)}(OH)_y]$

$pK_a = 14 - pK_b = 8,5 - 5,7(x\text{-}y)$

x – y = broj okso-liganada u kiselini – nuždno poznavanje strukture (H_3PO_3 i H_3PO_2 ; $pK_a \approx 2$)

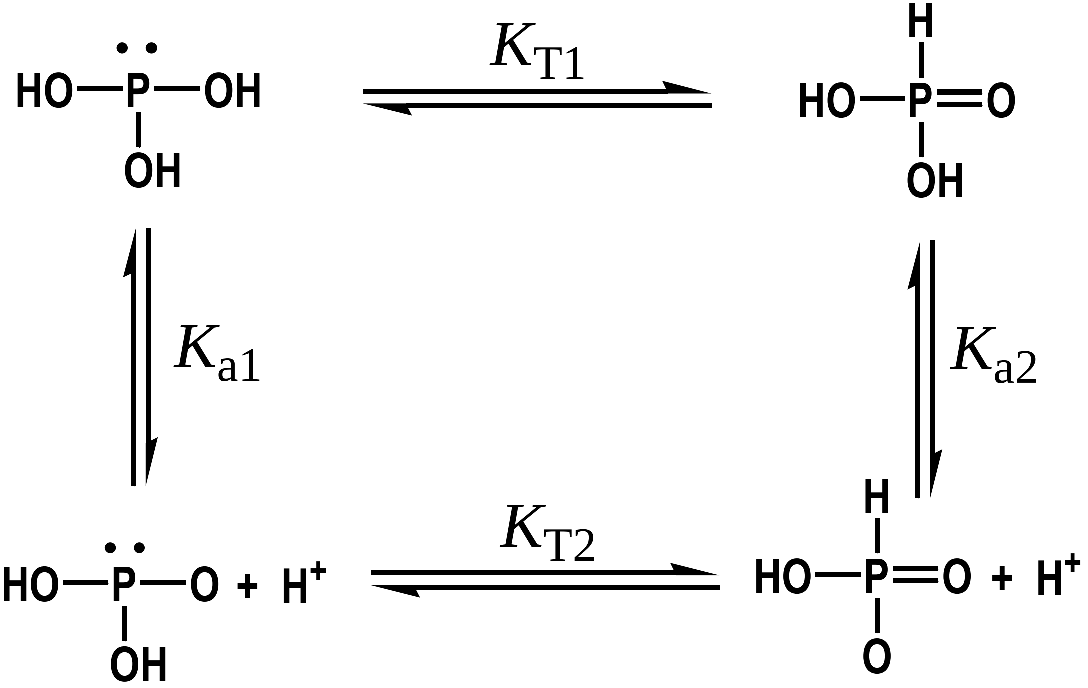
Tautomerija okso-kiselina i aniona

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)

$$\Delta \mathrm{p}K_\mathrm{a} = - \Delta \mathrm{p}K_\mathrm{b} \approx -5{,}7\Delta x$$

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

Za fosforastu kiselinu:



iz ciklusa lijevo proizlazi:
$K_{a1}\,K_{T2} = K_{T1}\,K_{a2}$

$\mathrm{p}K_{a2} \approx \mathrm{p}K_{a1} - 5{,}7\Delta x$
$\rightarrow K_{a2} \approx K_{a1} \cdot 10^{5{,}7} \approx 5 \cdot 10^{5}\,K_{a1}$
$\rightarrow K_{T2} \approx 5 \cdot 10^{5}\,K_{T1}$

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)