NH_3	**H_2O**	**HF**
-46	-242	-271
10^{-23}	$1{,}8 \cdot 10^{-16}$	$6{,}6 \cdot 10^{-4}$
PH_3	**H_2S**	**HCl**
5,4	-21	-92
	$8{,}7 \cdot 10^{-8}$	10^{3}
AsH_3	**H_2Se**	**HBr**
66	33	-34
	$1{,}3 \cdot 10^{-4}$	10^{9}
	H_2Te	**HI**
	$2{,}3 \cdot 10^{-3}$	26
		$1{,}6 \cdot 10^{11}$
K_A/mol l $^{-1}$		**ΔH_f/ kJmol^{-1}**

IONSKI MF_x MCl_x MBr_x Mi_x

TOPLJIVOST

$\longrightarrow$

TALIŠTE

$\longleftarrow$

$\longleftarrow$

Energ. krist. reš.

Energ. hidrat.

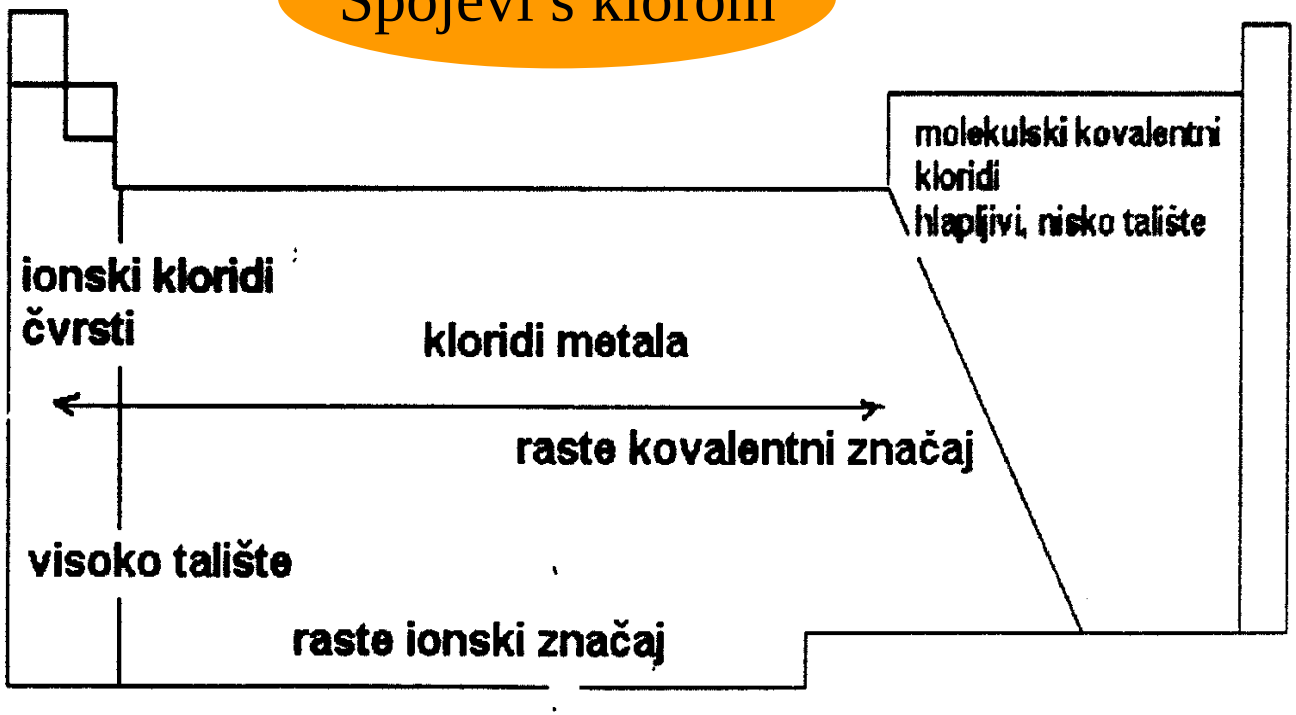
KOVALENTNI TALIŠTE

$\longrightarrow$

$\longrightarrow$

Polarizibilnost

Spojevi s klorom



SPOJEVI: *OKSIDACIJSKI BROJ* -I

- **HALOGENIDI**
- **-SOLNOG KARAKTERA** **s, f (II, III)**
- **-MAKROMOLEKULARNI** **p, d (I, II, III)**
- **-MOLEKULARNI** **p, d (> III)**

DOBIVANJA:

- *SUHI POSTUPAK*

DIREKTNA SINTEZA

- $\overset{0}{Sn} + 2\,\overset{0}{Cl_2} \rightarrow \overset{IV\ -I}{SnCl_4}\ (g)$
- **-HALOGENIRANJE OKSIDA**
- $\overset{IV}{SiO_2} + 2\overset{0}{C} + 2\,\overset{0}{Cl_2} \rightarrow \overset{IV\ -I}{SiCl_4}\ (g) + 2\,\overset{II\ -II}{CO}$
- **-REAKCIJE S HALOGENOVODIKOM**
- $\overset{0}{Cr} + 2\,HCl\ (g) \xrightarrow{900\,^{o}C} \overset{II}{CrCl_2}\ (s) + \overset{0}{H_2}$

- OSTALI POSTUPCI

- **MOKRI POSTUPAK**

- ***-REAKCIJE*** **-METALA**
- **-OKSIDA**
- **-HIDROKSIDA**
- **-KARBONATA**
- **I KISELINE**

-TALOŽNE REAKCIJE

$$Pb^{2+} + 2I^- \rightarrow PbI_2\ (s)$$

-REDOKS REAKCIJE

$$\overset{II}{Cu}Cl_2 + \overset{o}{Cu} \rightarrow \overset{I}{Cu_2}Cl_2$$

$$3\ \overset{o}{Cl_2} + 6\ OH^- \xrightarrow{topl.} 5\ \overset{-I}{Cl^-} + \overset{V}{Cl}O_3^- + 3\ H_2O$$

redukcija

SPOJEVI S POZITIVNIM STUPNJEVIMA OKSIDACIJE

	F	Cl	Br	I
^{+1}HXO	—	+	—	—
$^{+3}HXO_2$	—	+	—	—
$^{+5}HXO_3$	—	+	+	$(H_2I_2O_6)$
$^{+7}HXO_4$	—	+	+	H_5IO_6
$^{+1}XO^-$	—	+	+	+
$^{+3}XO_2^-$	—	+	—	—
$^{+5}XO_3^-$	—	+	+	+
$^{+7}XO_4^-$	—	+	+	10_6^{5-}

Imena kiselina i soli elemenata 17. skupine

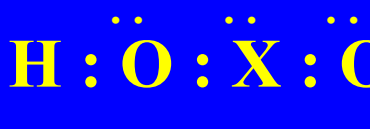
Formula	*Tradicijsko ime*	*soli*
HCl	**klorovodična**	**klorid**
HClO	**hipoklorasta**	**hipoklorit**
$HClO_2$	**klorasta**	**klorit**
$HClO_3$	**klorna**	**klorat**
$HClO_4$	**perklorna**	**perklorat**

kiselinska nomenklatura

- **HCl** **klorovodična kiselina**
- **$HClO$** **monooksoklorna kiselina**
- **$HClO_2$** **dioksoklorna kiselina**
- **$HClO_3$** **trioksoklorna kiselina**
- **$HClO_4$** **tetraoksoklorna kiselina**

vodikova nomenklatura

-
- **HCl** **vodikov klorid**
- **$HClO$** **vodikov monooksoklorat**
- **$HClO_2$** **vodikov dioksoklorat**
- **$HClO_3$** **vodikov trioksoklorat**
- **$HClO_4$** **vodikov tetraoksoklorat**



$(HO)_nXO_m$

$\chi_x = 1{,}7$

$K_1 : K_2 : K_3 \approx 1 : 10^{-5} : 10^{-10}$

m	K_A/mol L^{-1}	n	
0	$= 10^{-7}$	1	HClO
		3	H_3BO_3
1	$\sim 10^{-2}$	1	HPH_2O_2
		2	H_2PHO_3
		3	H_3PO_4
2	$\sim 10^{3}$	2	H_2SO_4
3	$\sim 10^{8}$	1	$HClO_4$

$X(OH)_n$	pK_A	$(HO)_nXO$	pK_A
$Cl(OH)$	7,5	$HONO$	3,3
$Br(OH)$	8,7	$HOClO$	2,0
$B(OH)_3$	9,2	$(HO)_2CO$	3,9
$Si(OH)_4$	10	$(HO)_2SO$	1,8
$Te(OH)_6$	6,2	$(HO)_3PO$	1,8
		$(HO)_5IO$	3,3

$(HO)_nXO_2$		$(HO)_nXO_3$	
$HONO_2$	-1,6	$HOClO_3$	-10
$HOClO_2$	-1		
$(HO)_2SO_2$	-3		

I		III		V		VII
$HClO$	<	$HClO_2$	<	$HClO_3$	<	$HClO_4$
$3 \cdot 10^{-8}$		10^{-2}		10		10^{10}

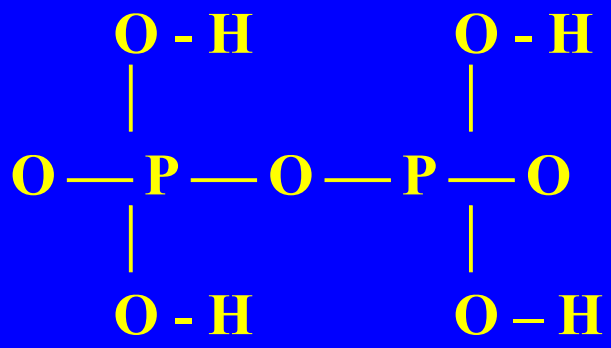
$\frac{K_A}{mol L^{-1}}$

I		III		V
HPH_2O_2	~	H_2PHO_3	~	H_3PO_4
10^{-2}		$1.6 \cdot 10^{-2}$		$1,1 \cdot 10^{-2}$

$\frac{K_A}{mol L^{-1}}$

Polinuklearne kiseline

$H_4P_2O_7$



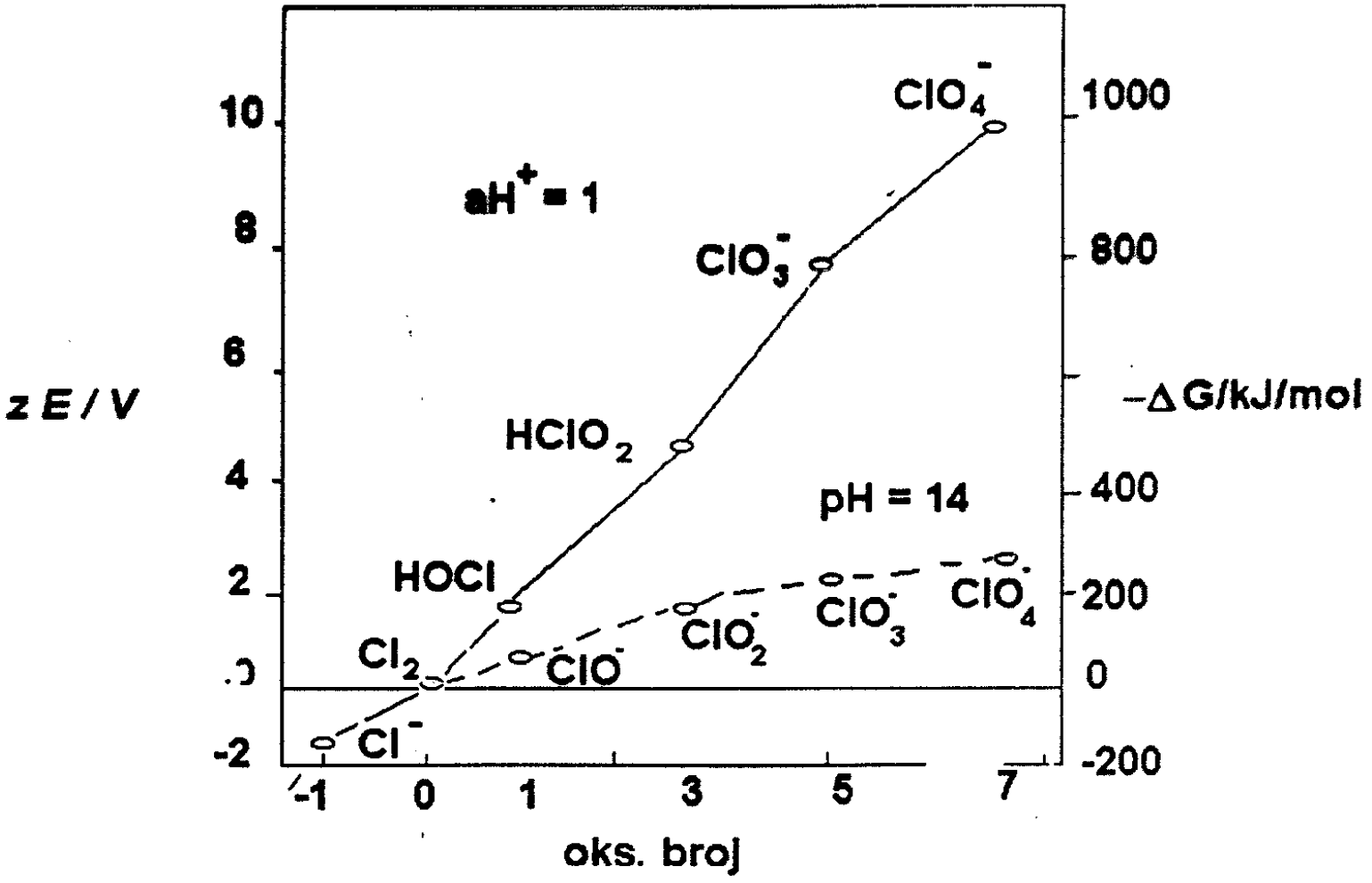
- $K_1 = 3{,}2 \cdot 10^{-2}$ mol l^{-1} ⎫ 10
- $K_2 = 4 \cdot 10^{-3}$ mol l^{-1} ⎭
- $K_3 = 2{,}5 \cdot 10^{-7}$ mol l^{-1} ⎫ 10^4
- $K_4 = 6{,}3 \cdot 10^{-10}$ mol l^{-1} ⎭

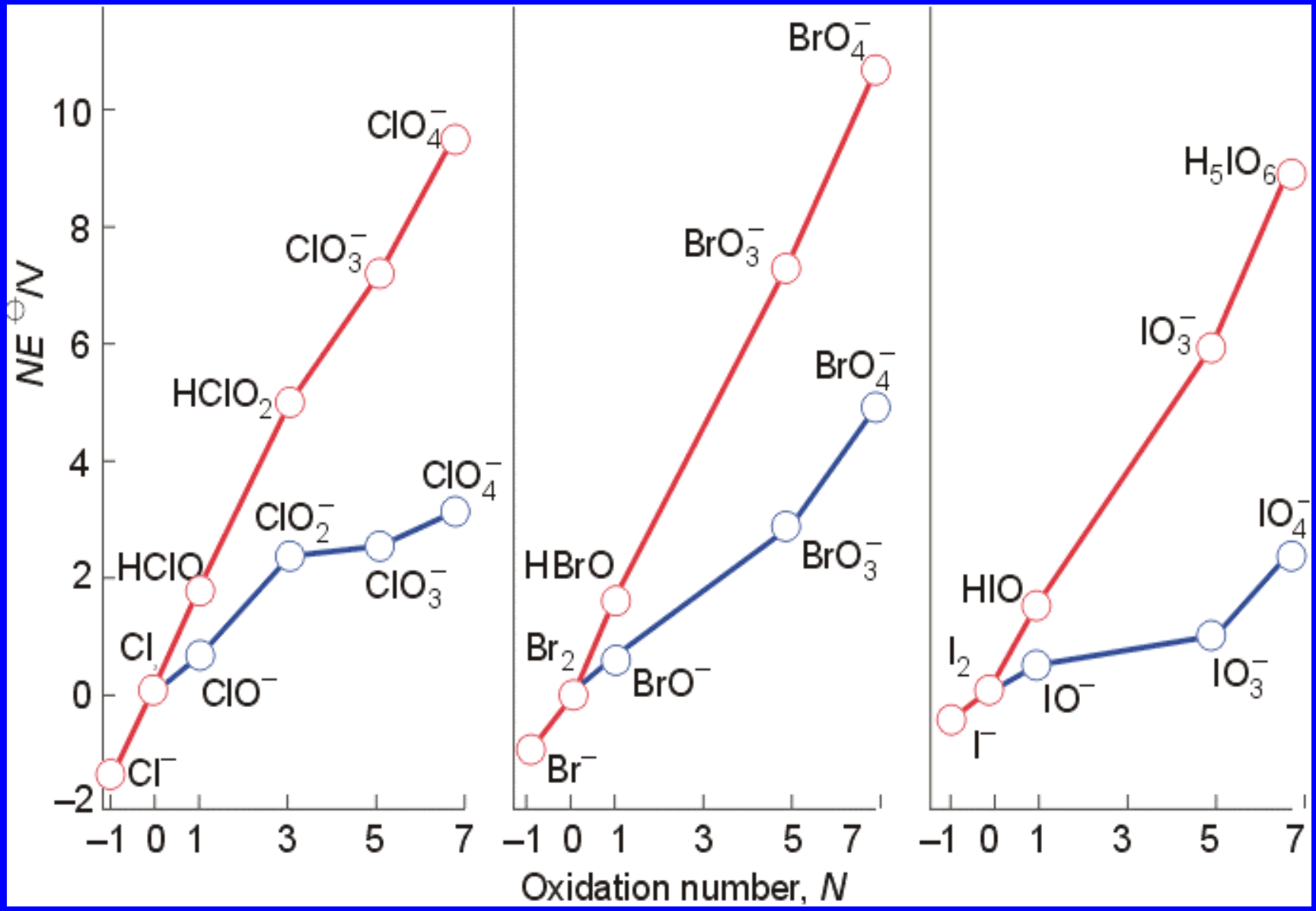
$E^o_{O/R}$ / V

$-\Delta G^o = z\, E^o \cdot F$

E^o ClO_3^-/1/2 Cl_2 = (1,61 V + 2 · 1,65 V + 2 · 1,21 V) /5 = 7,33 V/5 = 1,47 V

E^o ClO_3^-/1/2 Cl_2 = (3 · 1,64 V + 2 · 1,21 V)/5 = 7,33 V/5 = 1,47 V


z E / V
10
8
6
4
2
0
-2
aH+ = 1
ClO4-
ClO3-
HClO2
HOCl
Cl2
ClO-
ClO2-
pH = 14
ClO3-
ClO4-
Cl-
-1
0
1
3
5
7
oks. broj
1000
800
400
200
0
-200
-ΔG/kJ/mol


$NE^\ominus/V$
10
8
6
4
2
0
−2
ClO_4^-
ClO_3^-
$HClO_2$
ClO_2^-
HClO
Cl
Cl^-
ClO^-
−1 0 1 3 5 7
BrO_4^-
BrO_3^-
BrO_4^-
HBrO
BrO_3^-
Br_2
BrO^-
Br^-
−1 0 1 3 5 7
H_5IO_6
IO_3^-
IO_4^-
HIO
I_2
IO^-
IO_3^-
I^-
−1 0 1 3 5 7
Oxidation number, N

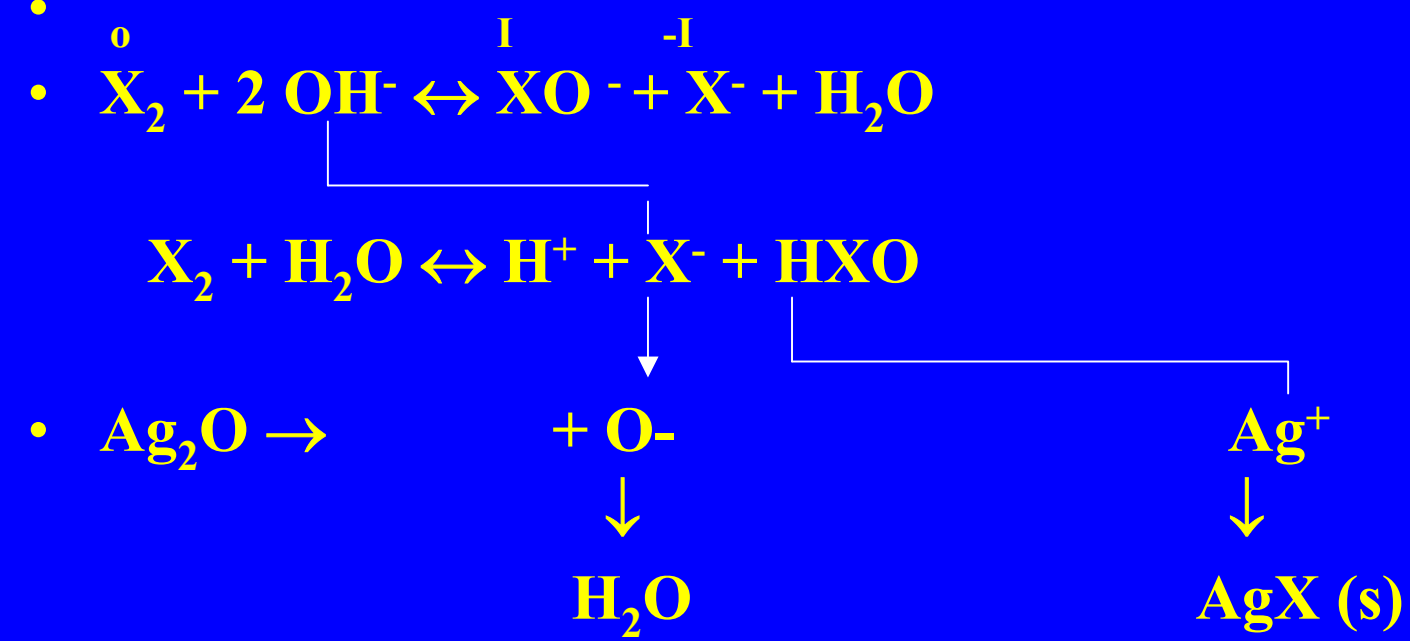
STUPANJ OKSIDACIJE I

- **HXO,** **X = Cl, Br, I**

←

JAKOST I STABILNOST RASTE

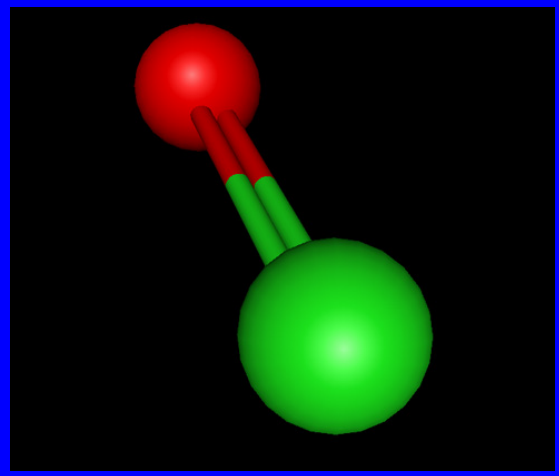
-



- **SLABE KISELINE**
  SOLI HIDROLIZIRAJU
- $XO^- + H_2O \rightarrow HXO + OH^-$

SNAŽAN OKSIDANS
OKSIDIRA VLASTITU SOL

- **HIPOKLORITI:**
- $NaClO$, $Ca(OCl)_2$, $CaCl(OCl)$
- $ClO^- + H^+ \rightarrow HClO$



- $HClO + Cl^- + H^+ \rightarrow Cl_2 + H_2O$
-

- **DISPROPORCIONIRANJE ClO^-**
- **MEHANIZAM**

$$OCl^- + OCl^- \xrightarrow{\text{sporo}} ClO_2^- + Cl^-$$

$$ClO_2^- + OCl^- \xrightarrow{\text{brzo}} ClO_3^- + Cl^-$$

- **Disprop. OBr^- i OI^- katalizira nastali X^-**
- **HXO SE DISPRPORCIONIRAJU BRŽE**
- **HIO SE RASPADA**
- $2HIO \rightarrow 2H^+ + 2I^- + O_2$

STUPANJ OKSIDACIJE III , IV

- $\overset{III}{HClO_2}$, $\overset{IV}{ClO_2}$ - nestabilni oksidansi

nestabilnost:

$$5\ \overset{III}{HClO_2} \rightarrow 4\ \overset{IV}{ClO_2} + H^+ + \overset{-I}{Cl^-} + 2\ H_2O$$

$$2\ \overset{IV}{ClO_2} \xrightarrow{h\nu,\ org.tvari} \overset{0}{Cl_2} + 2\ \overset{0}{O_2};\qquad \Delta_r H = -222\ kJ/mol$$

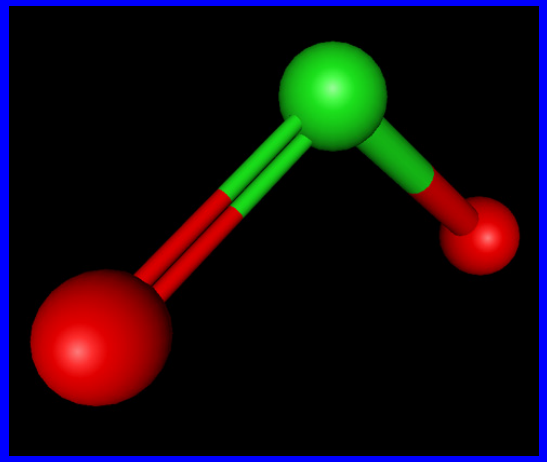
oksidirajuće djelovanje:

- III -I
- $HClO_2 + 3\ H^+ + 4e^- \leftrightarrow Cl^- + 2\ H_2O$
- $E^o = +\ 1{,}57$ V
- III -I
- $ClO_2^- + 2\ H_2O + 4e^- \leftrightarrow Cl^- + 4\ OH^-$
- $E^o = +\ 0{,}76$ V
- IV III
- $ClO_2 + e^- \leftrightarrow ClO_2^-$ (OH^-)
- $E^o = +1{,}15$ V

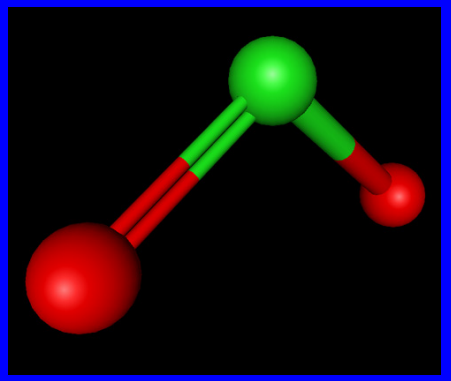
DOBIVANJE SOLI: *SOLI STABILNE*

- ^{IV} $^{+ OH^-}$ ^{III} ^{V}
- $2ClO_2 + H_2O \leftrightarrow HClO_2 + HClO_3$
- $^-$ OH^-

- ClO_2^- RED. s H_2O_2



DOB. ClO_2: - iz klorata



- $(ClO_3^- + H^+)$
-
- $HClO_3 + HClO_2 \rightarrow 2\ ClO_2 + H_2O$
  - $+H^+$
- RED s SO_2
-
- $\rightarrow$ $3\ HClO_3 \rightarrow 2\ ClO_2 + HClO_4 + H_2O$
- H_2SO_4 konc.

iz klorita

- III I IV
- $2\ ClO_2^- + ClO^- + H_2O \rightarrow 2\ ClO_2 + Cl^- + 2\ OH^-$
- (Cl_2)

STUPANJ OKSIDACIJE V

- $HBrO_3$, $HClO_3$, HIO_3 → $H_2I_2O_6$
-
- ← RASTE OKSID DJELOVANJA
- RELATIVNO STABILNE

Dobivanje soli:

-
- $3\ X_2 + 6\ OH^- \rightarrow 3\ XO^- + 3\ X^- + 3\ H_2O$
- $3\ XO^- \rightarrow XO_3^- + 2X^-$
-
- Odnos brzina ClO^- 1
- disproporc. BrO^- 100
- IO^- 30000

+2e⁻

I I V -I

$2\,HClO + ClO^- \rightarrow ClO_3^- + 2\,Cl^- + 2\,H^+$

-4e-

$ClO^- + H_2O \rightarrow HClO + OH^-$

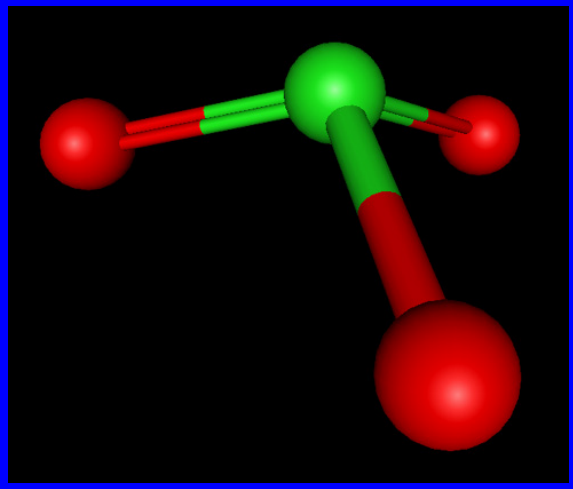
INDUSTRIJSKI POSTUPAK

(H_2O)

KATODA -Fe - H_2 $OH^- \rightarrow ClO^-$

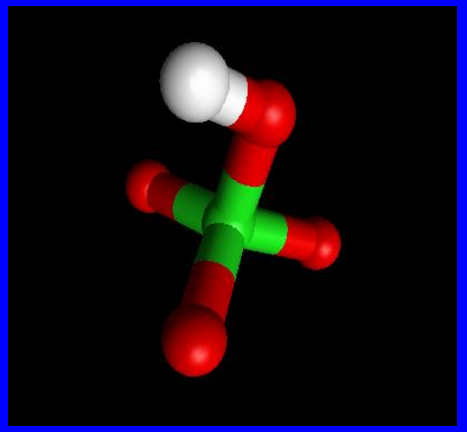
ANODA - GRAFIT - Cl_2

(Cl^-)



STUPANJ OKSIDACIJE VII

- $HClO_4$ $HBrO_4$ HIO_4 H_5IO_6
-
- **DOBIVANJE KISELINA:**
-
- $KClO_4 + H_2SO_4 \rightarrow HClO_4 + KHSO_4$
- (HCl) (KCl)
-
- $H_3O^+ ClO_4^-$ $t_t = 50^oc$
-
- **vrlo jako oksidacijsko sredstvo je bezvodna $HClO_4$**



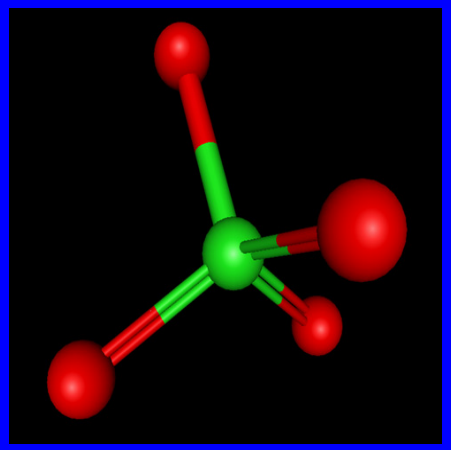
Dobivanje soli:

$$4KClO_3 \rightarrow 3\ KClO_4 + KCl$$

$$KClO_4 \rightarrow KCl + 2O_2$$

- NH_4ClO_4 STAB < 200°C
-
- $Mg(ClO_4)_2 + 6\ H_2O \overset{250\ °C}{\leftrightarrow} Mg(ClO_4)_2 \cdot 6\ H_2O$

- **INDUSTRIJSKI POSTUPAK:**
- A: $ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$
- $\downarrow$
- $NaClO_4$



THE END