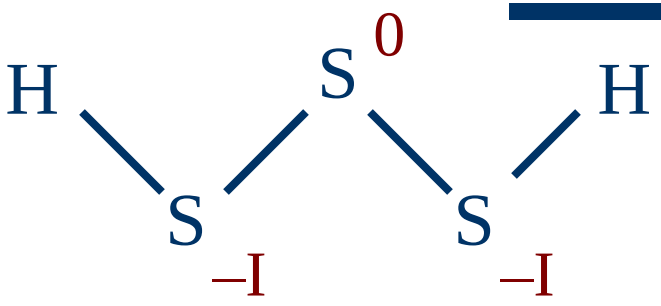
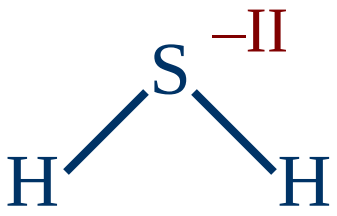
OLTINGUGURTNING O’ZIGA XOSLIGI.

VODORODLI VA KISLORODLI BIRIKMALARI

Sulfanlar H_2S_x ($x = 1 \div 8$)





- Vodorod sul'fid – rangsiz, yoqimsiz hidli(aynigan tuxum), juda zaharli gaz, suyuqlanish harorati –85,54 °C, qaynash harorati – 60,35 °C.
- H_2S molekulasi diamagnitli, qutbli (dipol momenti - 0,93 D ga teng).
- Suyuq vodorod sulfidda avtoprotoliz

$H_2S + H_2S \leftrightarrows HS^- + H_3S^+$; $K_S \approx 10^{-33}$

H_2S ning suvli eritmasi (0,1 mol/l)

1. $H_2S + H_2O \leftrightarrows HS^- + H_3O^+$; $K_{K1} = 1{,}05 \cdot 10^{-7}$
2. $HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+$; $K_{K2} = 1{,}23 \cdot 10^{-13}$

- $[H_3O^+] = [HS^-] = \sqrt{K_{K1} \cdot c_0}$
- $[S^{2-}] \approx 1{,}23 \cdot 10^{-13}$ mol/l
- HCl qo'shilganda (1 mol/l) $[S^{2-}]$ konsentratsiyasi vodorod sul'fidli suvda $\approx 1 \cdot 10^{-21}$ mol/l. Gacha kamayadi.

Sul’fidlar

1. Suvda eriydigan (ishqoriy va ishqoriy-yer metallari va ammoniy kationlari):

$Na_2S = 2Na^+ + S^{2-}$; $S^{2-} + H_2O \leftrightarrows HS^- + OH^-$

2. Binar (kovalent) birikmalari:

$Al_2S_3 + 6H_2O = 2Al(OH)_3\downarrow + 3H_2S\uparrow$

$SiS_2 + 4H_2O = H_4SiO_4\downarrow + 2H_2S\uparrow$

3. Kam eriydigan (keyingilarini qarang)

Qiyin eriydigan sul’fidlari

Suyultirilgan HCl eriydigan	Konsentrlangan HCl da eriydigan	Oksidlovchimas-kislotaarda erimaydigan
MnS (EK $\approx 10^{-13}$) FeS (EK $\approx 10^{-17}$)	CdS (EK $\approx 10^{-28}$) CuS (EK $\approx 10^{-36}$) SnS (EK $\approx 10^{-28}$) PbS (EK $\approx 10^{-28}$)	HgS (EK $\approx 10^{-45}$) Bi_2S_3(EK$\approx 10^{-105}$)

H_2S (0,1 mol/l) eritmasida sul'fid – ionlarini konsentratsiyasini hisoblash

1. $H_2S + H_2O \leftrightarrows HS^- + H_3O^+$ $\quad K_{K1} = 1{,}05 \cdot 10^{-7}$

[...]: $C_0 - x$ $\quad x$ $\quad x$

2. $HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+$ $\quad K_{K2} = 1{,}23 \cdot 10^{-13}$

[...]: $x - y$ $\quad y$ $\quad y + x$

$$K_{K2} = \frac{[S^{2-}] \times [H_3O^+]}{[HS^-]} = \frac{y \times (y + x)}{(x - y)} \approx \frac{y \times x}{x} = y$$

$x >> y$

$y = [S^{2-}] \approx K_{K2} = 1{,}23 \cdot 10^{-13}$ моль/л

Eritmadagi $[S^{2-}]$ ni topamiz: H_2S (0,1 mol/l) + HCl (1 mol/l)

1. $H_2S + H_2O \leftrightarrows HS^- + H_3O^+$ $\quad K_{K1} = 1{,}05 \cdot 10^{-7}$

[...]: $C_0 - x \quad x \quad x + C_1$

2. $HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+$ $\quad K_{K2} = 1{,}23 \cdot 10^{-13}$

[...]: $x - y \quad y \quad y + x + C_1$

3. $HCl + H_2O = Cl^- + H_3O^+$ $\quad x >> y;\ C_1 >> x;\ C_0 >> x$

$C_1 \quad C_1 \quad C_1$

$$K_{K2} = \frac{[S^{2-}] \times [H_3O^+]}{[HS^-]} = \frac{y \times (y + x + C_1)}{(x - y)} \approx \frac{y \times C_1}{x}$$

$$K_{K1} = \frac{[HS^-] \times [H_3O^+]}{[H_2S]} = \frac{x \times (x + C_1)}{(C_0 - x)} \approx \frac{x \times C_1}{C_0}$$

$$K_{K2} = \frac{y \times C_1}{x}$$

$$y = [S^{2-}] \approx \frac{K_{K1} \times K_{K2} \times C_0}{C_1^{\,2}}$$

$$[HS^-] = x \approx \frac{K_{K1} \times C_0}{C_1}$$

$$y = [S^{2-}] \approx 1{,}29 \cdot 10^{-21} \text{ mol/l}$$

Cho’ktirish sharoiti: $C(M^{2+}) \times C(S^{2-}) \geq EK\,(MS)$

- Kislotali sharoitdaя MnS ($EK \approx 10^{-13}$), FeS ($EK \approx 10^{-17}$) cho’kmaydi;
- Kislotali sharoitda CdS ($EK \approx 10^{-28}$), CuS ($EK \approx 10^{-36}$), SnS ($EK \approx 10^{-28}$), PbS ($EK \approx 10^{-28}$) va boshqalar cho’kadi.

Qaytaruchlik xossasi

- $H_2S - 2e^- = S + 2H^+$; $\varphi^\circ = +0{,}14$ V (pH < 7)
- $HS^- + OH^- - 2e^- = S + H_2O$; $\varphi^\circ = -0{,}48$ V

  $S^{2-} - 2e^- = S$; $\varphi^\circ = -0{,}44$ V (pH > 7)
- $H_2S + I_2 = 2HI + S$

  $H_2S + 4Cl_2 + 4H_2O = 8HCl + H_2SO_4$
- $2H_2S$ (ortiqcha) $+ O_2 = 2H_2O + 2S$

  $2H_2S + 3\ O_2$ (ortiqcha) $= 2H_2O + 2SO_2$

Olinishi

- Sanoatda: $H_2 + S \leftrightarrows H_2S$
- Laboratoriyada: $FeS + 2HCl = FeCl_2 + H_2S\uparrow$

Polisul'fidlar:

$Na_2S + (x–1)S = Na_2S_x$

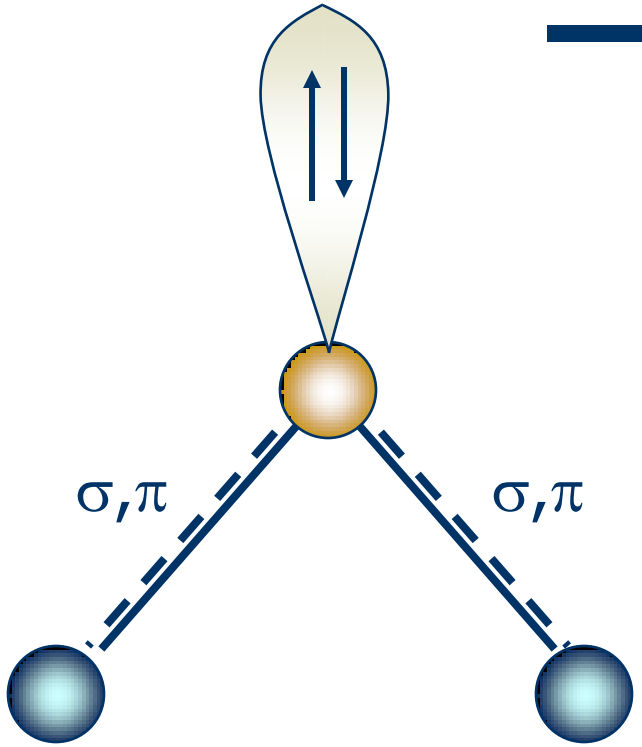
$Na_2S_x + 2HCl = H_2S_x + 2NaCl$ (sovutilganda)

$Na_2S_n + 2HCl = 2NaCl + H_2S\uparrow + (n–1)S\downarrow$ (xona haroratida)

Polisul'fidlarni oksidlovchilik xossasi:

$Na_2S_2^{-I} + Sn^{+II}S_{(т)} = Na_2[Sn^{+IV}S_3^{-II}]$

Kislorodli birikmalari - SO_2



sp ^{2} –gibridlanish

μ = 1,63 D

- SO_2 – o'tkir hidli, rangsiz gaz, termik barqaror, suyuqlanish harorati = –75,5 °C, qaynash harorati = –10,1 °C.
- Olinishi: piritni kuydirib

$$4FeS_2 + 11\ O_2 = 2Fe_2O_3 + 8SO_2$$

- Laboratoriyada:

$$M_2SO_3 + 2H_2SO_4\ (kons.) = 2MHSO_4 + SO_2\uparrow + H_2O$$

Suvli eritmada:

- $SO_2 + nH_2O \leftrightarrows SO_2 \cdot nH_2O$ ($n = 1 \div 7$)

$SO_2 \cdot nH_2O + H_2O \leftrightarrows HSO_3^- + H_3O^+ + (n-1)H_2O;$

$K_K = 1{,}66 \cdot 10^{-2}$

$HSO_3^- + H_2O \leftrightarrows SO_3^{2-} + H_3O^+ ; K_K = 6{,}31 \cdot 10^{-8}$

- $2NaOH$ (ortiqcha) + $SO_2 = Na_2SO_3 + H_2O$
- $2NaOH + 2SO_2$ (ortiqcha) = $2NaHSO_3$

Oksidlanish- qaytarilish xossasi

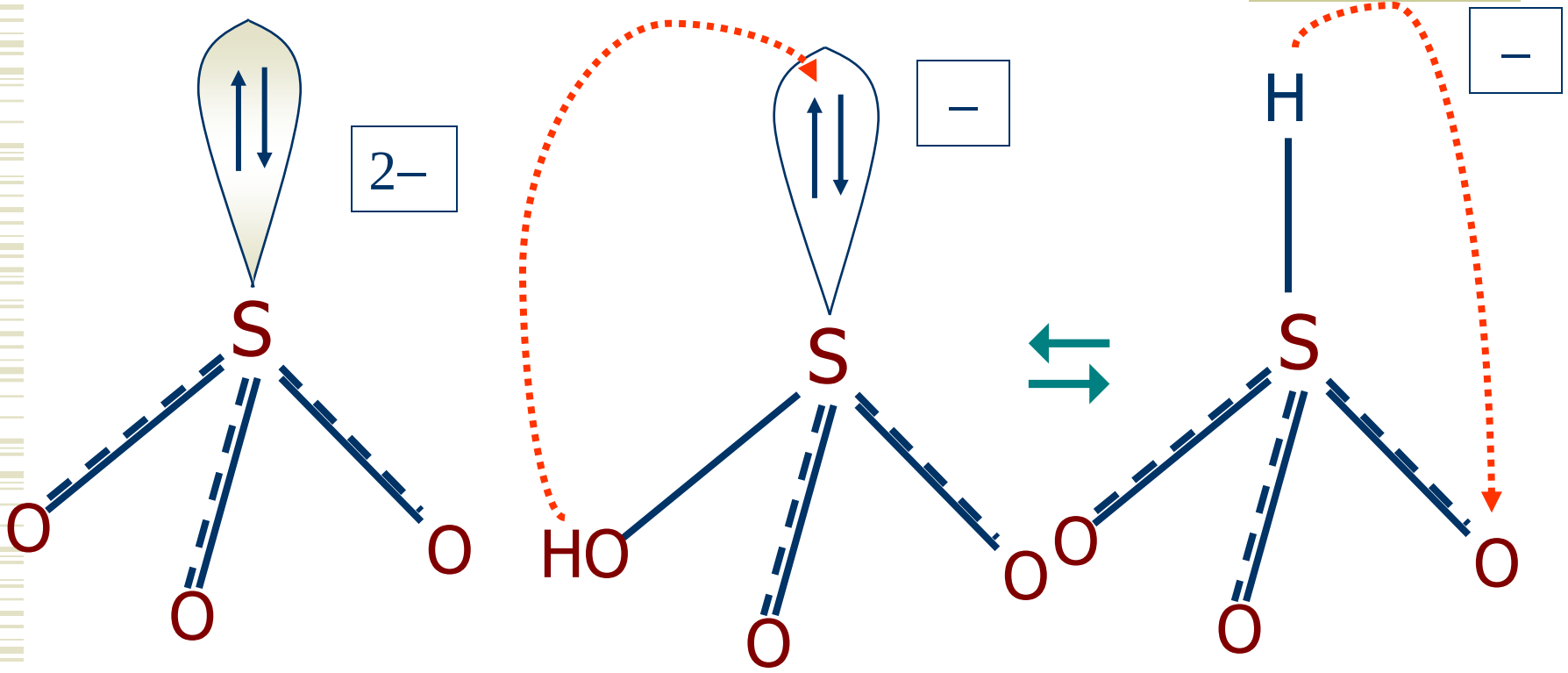
- $SO_2 + 2H_2S = 3S + 2H_2O$

$SO_2 + 2H_2O + 4e^- = S + 4OH^-$; $\varphi° = -0,7$ V

- $SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$

$SO_2 + 2H_2O - 2e^- = SO_4^{2-} + 4H^+$; $\varphi° = +0,17$ V

SO_3^{2-} va HSO_3^- anionlarining tuzilishi



Sul’fit-ion

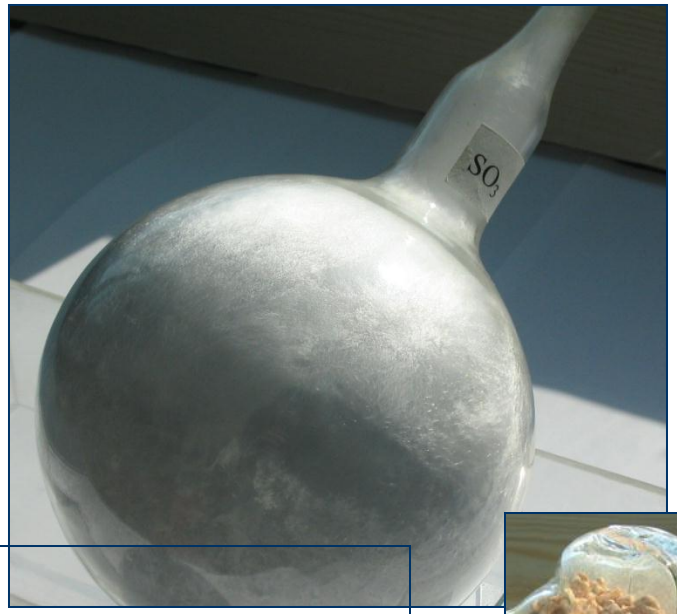
Gidrosul’fit-ion: **tautumeriya**

Oltingugurt (VI) - oksid $(SO_3)_x$

- Polimorf modifikatsiyalari α, β va γ (suyuqlanish harorati 16,8 °C, 32,0 °C va 62,2 °C)
- Qizdirilganda haydaladi
- Olinishi:

$2SO_2 + O_2 \leftrightarrows 2\ SO_3$

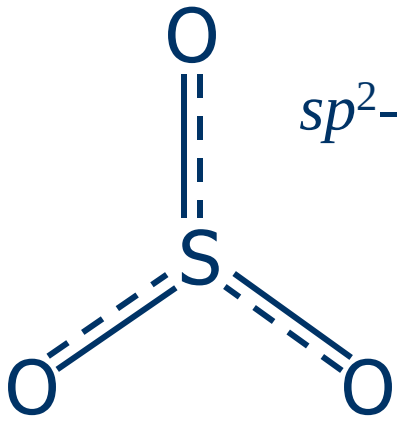
(600 °C, katalizator V_2O_5)



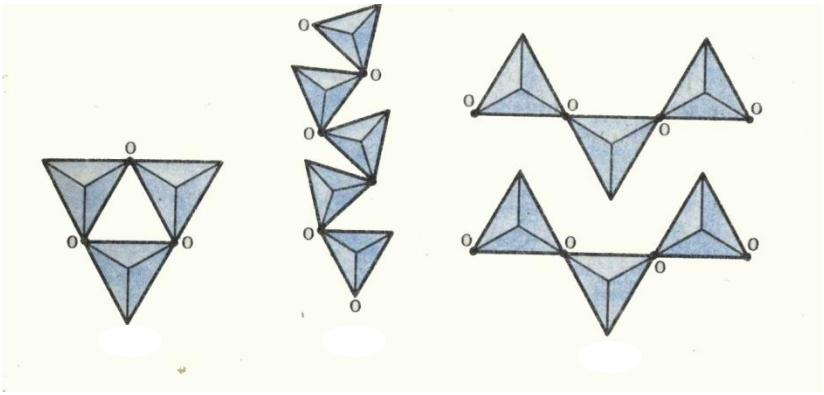
Preparat $(SO_3)_x$

Katalizator V_2O_5

SO_3 molekulasi – qutbsiz va diamagnitli



sp^2-gibridlanish



- α-modifikatsiyasi SO_3 – trimer S_3O_9
- β-modifikatsiyasi – xalqada $[SO_4]$ tetraedrik bo'laklaridan tashkil topgan zig-zaglar hosil bo'ladi
- γ-modifikatsiyasida $[SO_4]$ tetraedri xalqalari to'rsimon qatlamga birlashishadi.

SO_3 – kislotali oksid

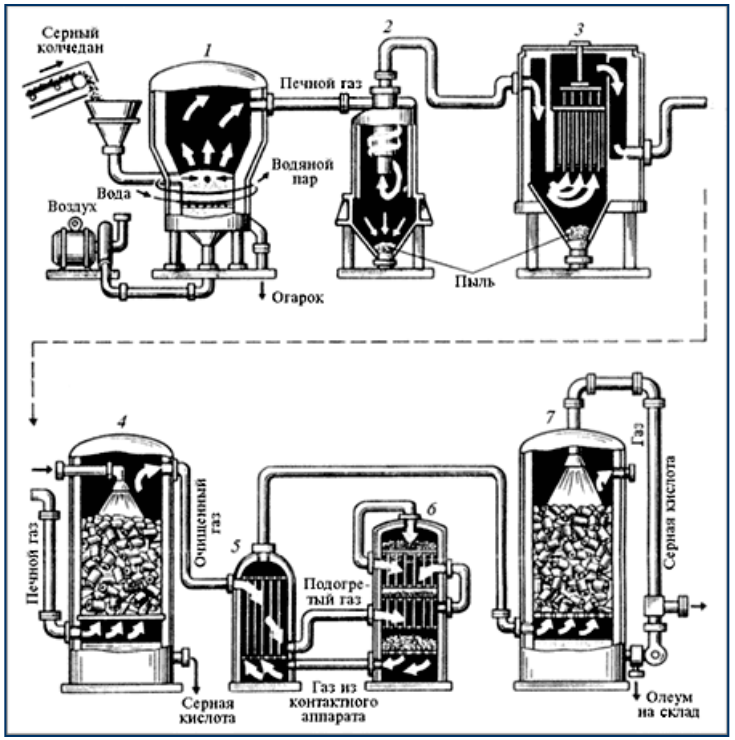
- $SO_3 + H_2O = H_2SO_4$;

$\Delta H° = -130$ kJ/mol

- sanoatda:

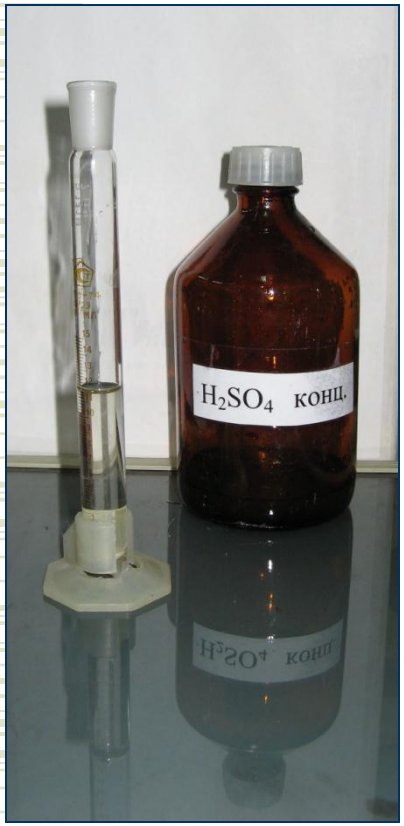
$SO_3 + H_2SO_4 = H_2S_2O_7$

(disulfat kislota, олеум)



Sul’fat kislota ishlab chiqarish

Sul’fat kislota H_2SO_4



- H_2SO_4 – rangsiz qovushqoq suyuqlik, zichligi 1,84 g/sm^3, suyuqlanish harorati 10,4 °C.
- Anomaliya xossalari sababi – vodorodli bog’lar bilan tushuntiriladi:

  $H_2SO_4 \cdots H_2SO_4 \cdots H_2SO_4 \cdots$
- Avtoprotoliz:

$$H_2SO_4 + H_2SO_4 \leftrightarrows HSO_4^- + H_3SO_4^+;$$

$$K_S \approx 10^{-4} \div 10^{-5}$$

H_2SO_4 suvli muhitda

- Suyultirilgan suvli eritmada H_2SO_4 – kuchli ikki asosli kislota:

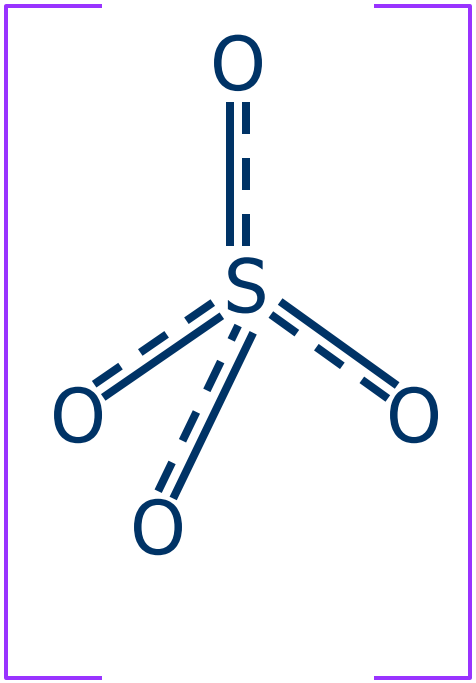
$$H_2SO_4 + 2H_2O = SO_4^{2-} + 2H_3O^+$$

- suvli eritmalarda gidrosul'fatlar – tuzlarida pH < 7 (HSO_4^- ioni protolizi):

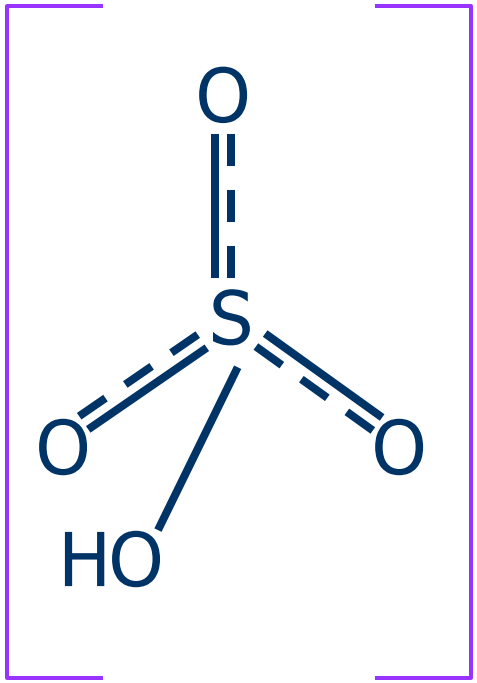
$$NaHSO_4 = Na^+ + HSO_4^-,$$

$$HSO_4^- + H_2O = SO_4^{2-} + H_3O^+$$

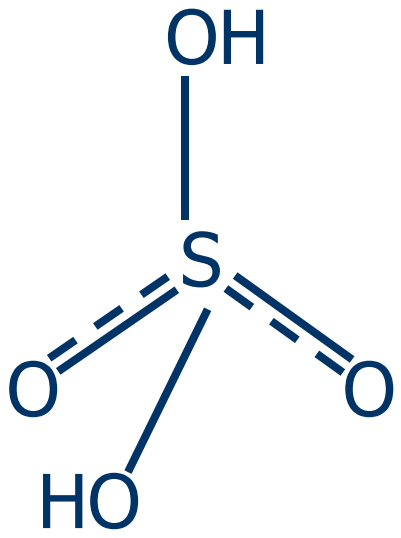
Tuzilishi (sp^3-gibridlanish)



Sul’fat-ion



Gidrosul’fat-ion



Sul’fat kislota

Kuporoslar $MSO_4 \cdot 5(7)H_2O$ (M – Cu, Fe, Ni, Mg …)

Mis kuporosi

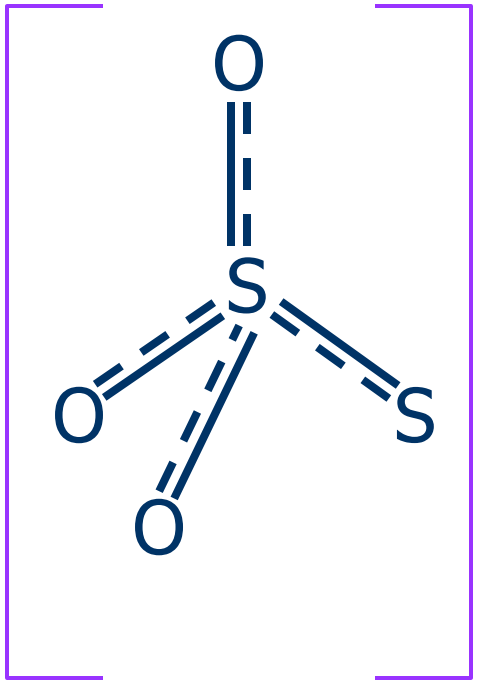
Kvaslar $M^IM^{III}(SO_4)_2 \cdot 12H_2O$ (M^I – Na, K, NH_4…, M^{III} – Al, Ga, Cr…)

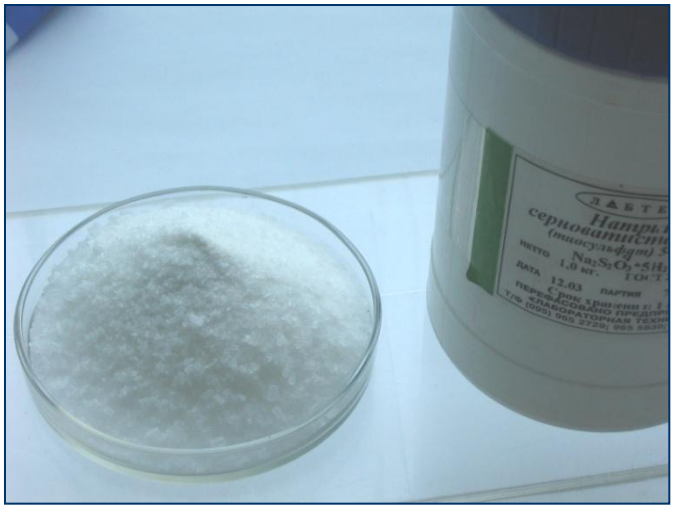
Alyuminiylikaliyli-kvaslar va xromli-kaliyli kvaslar

Shyonitlar $M_2^IM^{II}(SO_4)_2 \cdot 6H_2O$ (M^I – Na, K… , M^{II} – Mg, Zn, Co…)

O- va S - analoglari

Tiosul’fat-ion
SO_3S^{2-}

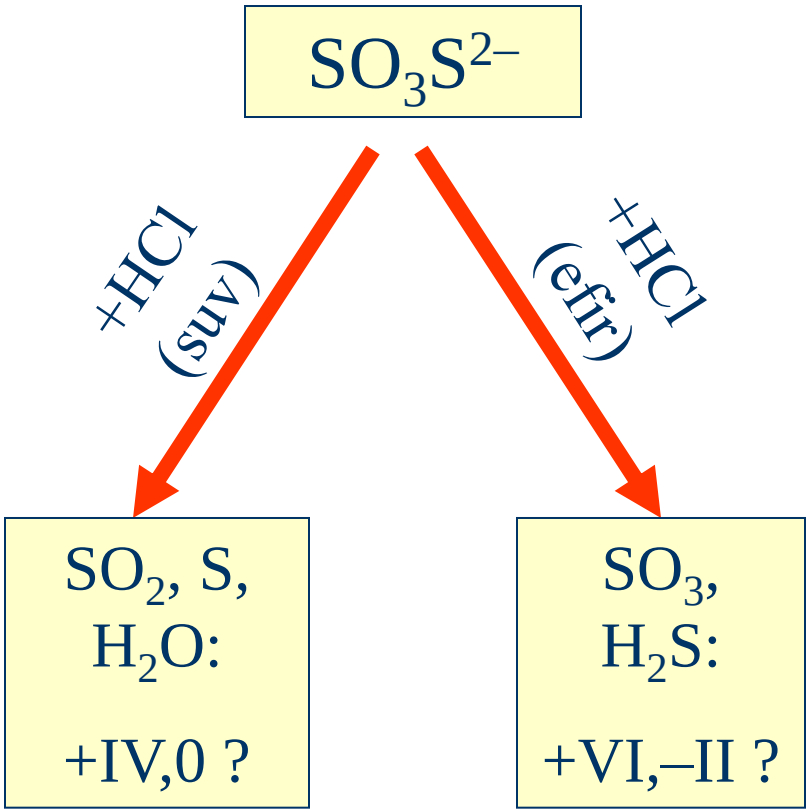


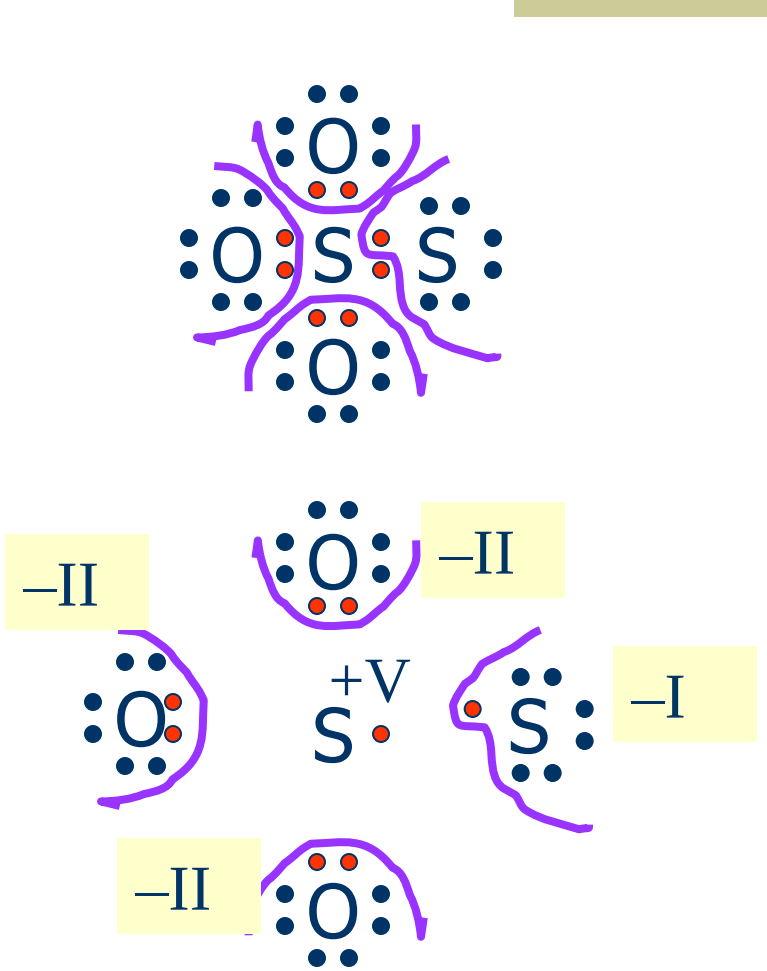


Natriy tiosul’fat

Olinishi: $Na_2SO_3 + S = Na_2SO_3S$
(+t, suvli eritma)

Tiosul’fat-ion: oltingugurtning oksidlanish darajasi





Kimyoviy xossalari

- $Na_2SO_3S + 2HCl = 2NaCl + H_2O + SO_2\uparrow + S\downarrow$

  $SO_3S^{2-} + H_2O - 4e^- = 2SO_2 + 2H^+$

  $SO_3S^{2-} + 6H^+ + 4e^- = 2S + 3H_2O$
- $Na_2SO_3S + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl$

  $SO_3S^{2-} + 5H_2O - 8e^- = 2SO_4^{2-} + 10H^+$, $\varphi° = +0{,}275$ V

  $Cl_2 + 2e^- = 2Cl^-$
- $Na_2SO_3S + I_2 = 2NaI + Na_2S_4O_6$ (tetrationat)

  $2SO_3S^{2-} - 2e^- = S_4O_6^{2-}$, $\varphi° = +0{,}015$V

  $I_2 + 2e^- = 2I^-$

Analitik kimyoda qo’llanilishi: iodametriya

- $Cu + 4HNO_3 =$

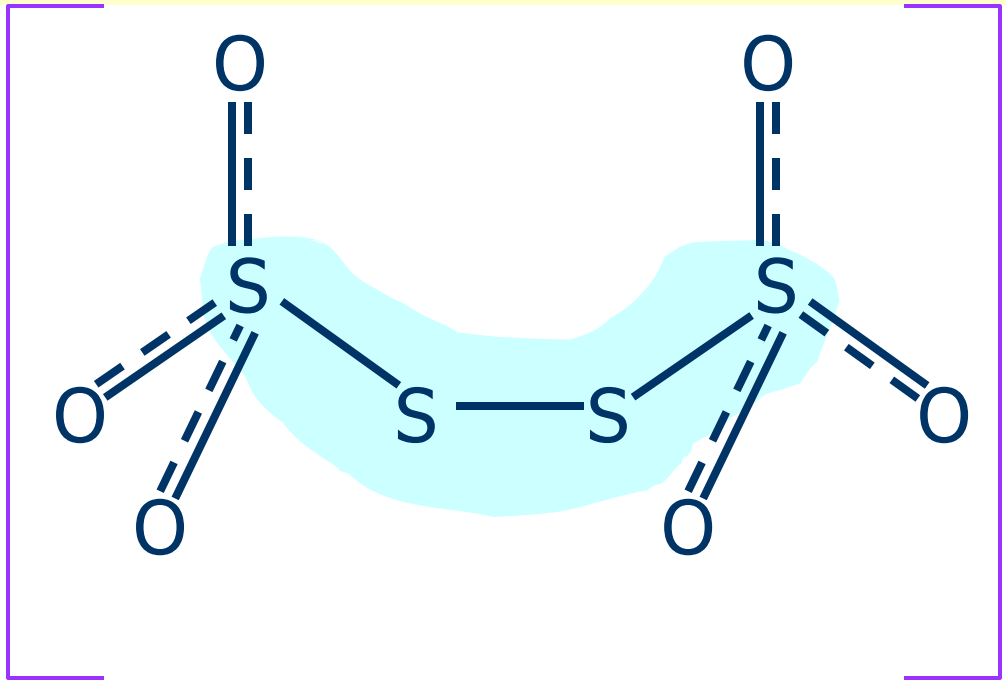
  $= Cu(NO_3)_2 + 2NO_2\uparrow + H_2O$
- $2Cu(NO_3)_2 + 4KI =$

  $= 2CuI\downarrow + I_2 + 4KNO_3$
- $KI + I_2 = K[I(I)_2]$
- $K[I(I)_2] + 2Na_2SO_3S =$

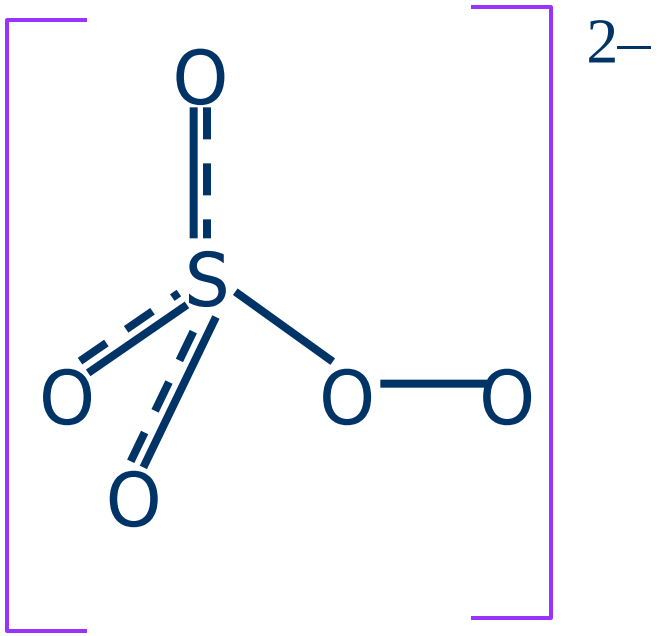
  $=KI + 2NaI + Na_2S_4O_6$

Politionatlar – polition kislotaning tuzlari $H_2S_nO_6$ ($n = 4 \div 6$)

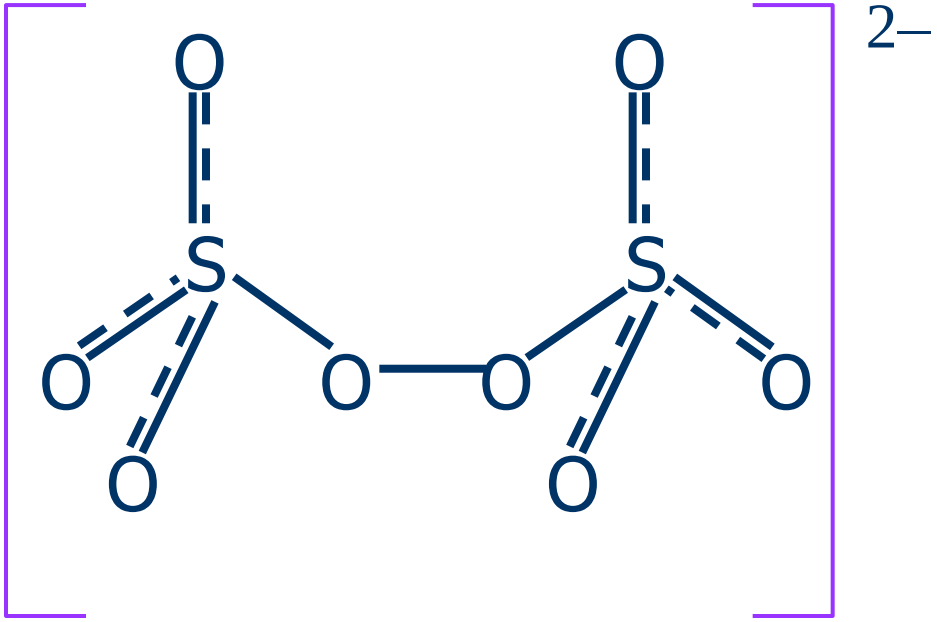
- Tetrationat ionning tuzilishi: 4 ta oltingugurt atomlaridan iborat xalqa hosil bo’ladi:



Пероксосульфаты – сильные окислители



Peroksosul’fat-ion
$SO_3(O_2)^{2-}$



Peroksodisul’fat-ion
$S_2O_6(O_2)^{2-}$