



10.4 氮族元素及其主要化合物

氮族(VA): N、P、As、Sb、Bi
nitrogen, phosphorus, arsenic, antimony, bismuth

- ▶ 10.4.1 通性
- ▶ 10.4.2 氮
- ▶ 10.4.3 磷
- ▶ 10.4.4 砷、锑、铋

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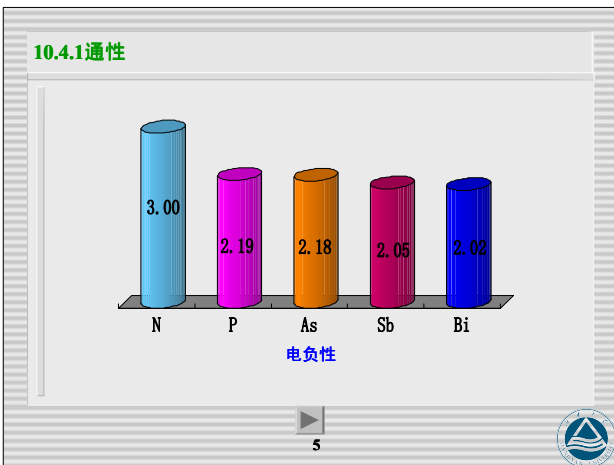
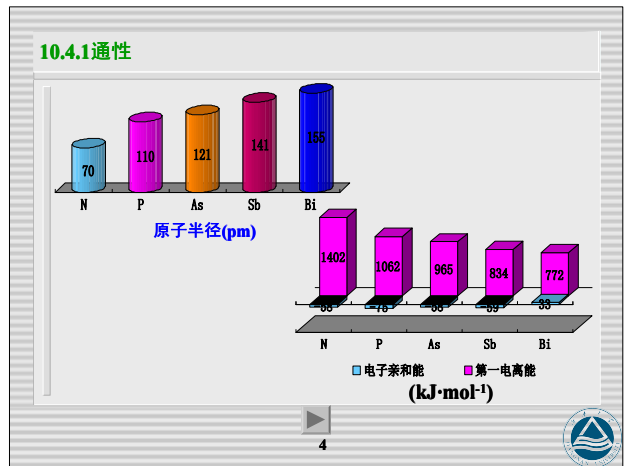
10.4.1 通性

1. characteristics of the nitrogen group:

(1) 形成正氧化值趋势较明显;
价电子构型: ns^2np^3 ;
金属性递增.

(2) 与电负性较大的元素化合, 氧化值主要为 +3, +5.
rule:
从上到下, 氧化值为+3的化合物稳定性增加, 而氧化值为+5的物质稳定性降低.
惰性电子对效应:
自上而下低氧化值物质比高氧化值物质稳定的现象.

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10.4.1 通性

氮族(VA)	N	P	As	Sb	Bi
单质性质	nonmetal		quasi-metal	metal	

如Sb:

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10.4.1 通性

(3) 多数化合物为共价型。

2. compare of properties of some compounds:

氮族(V)	N	P	As	Sb	Bi
M ₂ O ₃ 酸性	酸性	酸性	两性	两性	碱性
MH ₃ 碱性	强	→			弱
MH ₃ 稳定性	高	→			低

MH₃除NH₃外,都是毒性较大或剧毒的物质。

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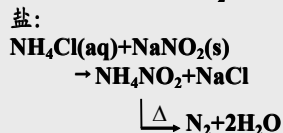
10.4.2 氮

1. N₂:

氮气沸点-195.8℃,微溶于水.常温下化学性质极不活泼。

当反应系统需惰性气氛时常用氮气。

实验室制少量N₂或除去铵



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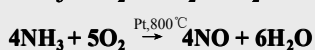
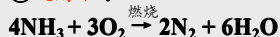
10.4.2 氮

2. NH₃及铵盐(ammonia & ammonium salt):

(1) ammonia:

① 碱性: 一元弱碱。

② 还原性:



2NH₃ + 3Cl₂ $\xrightarrow{\text{常温}}$ N₂ + 6HCl, 用于Cl₂管道的检漏;
“折点加氯法”除氨氮。

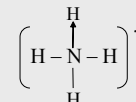
③ 加合反应:

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10.4.2 氮

如,能加合H⁺。



还能与一些金属离子加合,如[Cu(NH₃)₄]²⁺等。

④ 取代反应:



NH₂OH称为羟胺,既有氧化性,又有还原性。



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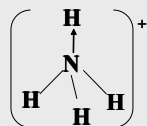


10.4.2 氮

(2) ammonium salt:

r_{NH₄⁺}(537pm)与r_{K⁺}(530pm)很接近,故铵盐性质与钾盐相似。

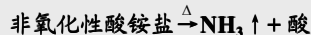
NH₄⁺结构:



性质:

① 与碱的作用:

② 热稳定性:



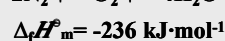
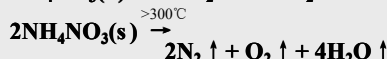
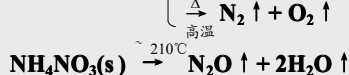
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10.4.2 氮



氧化性酸铵盐 $\begin{cases} \xrightarrow{\Delta, \text{低温}} \text{N}_2 \text{ 或 氮的化合物;} \\ \xrightarrow{\Delta, \text{高温}} \text{N}_2 \uparrow + \text{O}_2 \uparrow \end{cases}$



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10.4.2氮

3.一氧化氮(NO)、二氧化氮(NO₂):

N₂O: 笑气, 甜, 牙科麻醉剂。

NO(nitrogen monoxide): 奇分子。

奇分子(odd molecule): 奇数价电子的分子。

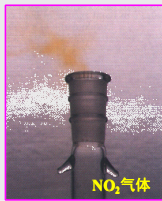
N: 2s²2p³, O: 2s²2p⁴。

有一个σ键, 一个双电子π键和一个3电子π键组成, 共11个电子。

NO气体常温下极易氧化。

NO₂(nitrogen dioxide)结构:

N: 不等性sp²杂化



10.4.2氮



4.亚硝酸及其盐(nitrous acid, nitrite):

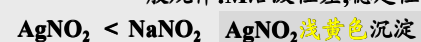
①酸性与稳定性:

HNO₂: 很不稳定的弱酸(K_a^o = 7.2 × 10⁻⁴).



亚硝酸盐: 相对稳定。

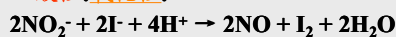
一般规律: M活性差, 稳定性也差:



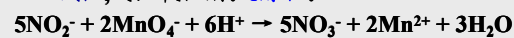
10.4.2氮

②氧化还原性:

酸性: 氧化性。



碱性, 或强氧化剂: 还原性。



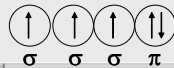
5.硝酸及其盐(nitric acid, nitrate):

一般浓硝酸: 68%;

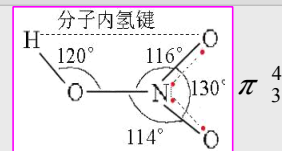
> 86%: 发烟硝酸。

(1) structure of nitric acid:

N: 不等性sp²杂化。



10.4.2氮



(2) property of nitric acid:

热稳定性差:



HNO₃强氧化性:

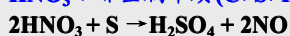
其中N呈最高氧化值, 分子又不稳定。



10.4.2氮

①与非金属单质:

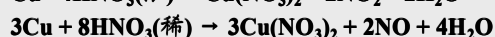
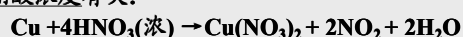
HNO₃ + 非金属单质(C, S, P) → 相应的高价酸 + NO



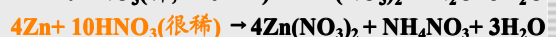
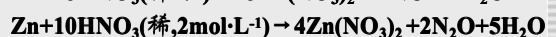
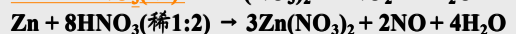
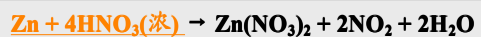
②与金属单质:

冷、浓硝酸能使Fe、Al、Cr钝化。

与金属作用, 硝酸被还原的程度与金属活泼性和硝酸浓度有关。

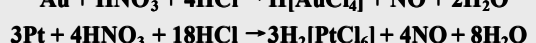
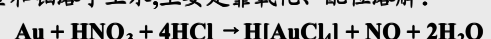


10.4.2氮



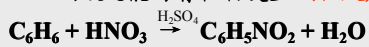
rule:

浓度越稀, M越活泼, HNO₃被还原的氧化值越低。金和铂溶于王水, 主要是靠氧化、配位溶解:



10.4.2氮

硝酸还能与有机物发生硝化反应:



(3) structure & properties of nitrate:

structure: π^6_4

property:

①氧化性:

aq: 酸性条件.

s: 高温(焰火).

②稳定性:

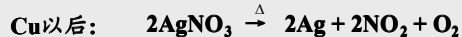
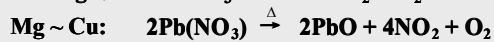
热稳定性差.



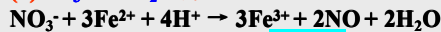
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10.4.2氮



(4) NO_3^- 与 NO_2^- 的鉴定:



(5) 亚硝酸、硝酸及其盐的性质对比:

酸性:

氧化性: $E^\circ(\text{NO}_3^-/\text{NO}) = +0.96\text{V}$; $E^\circ(\text{HNO}_2/\text{NO}) = +1.0\text{V}$

热稳定性: 活泼金属 $\text{MNO}_3 > \text{MNO}_2$



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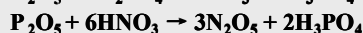
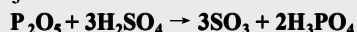


10.4.3磷

1. P_2O_5 (phosphorous pentoxide):

P_2O_5 (P_4O_{10}) 又称磷酸酐.

P_2O_5 具强吸水性.

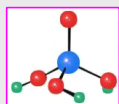


2. H_3PO_4 (phosphoric acid):

structure:

properties: ①酸性;

②形成多酸:



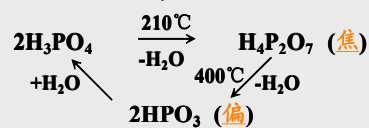
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10.4.3磷

polyacid:

几个单酸经过脱水, 通过氧原子连起来的酸.



3. 多酸酸性变化的一般规律:

① 缩合度增加, 酸性增强;

② 同一元素不同氧化态, 高价偏酸, 但磷酸的含氧酸例外.

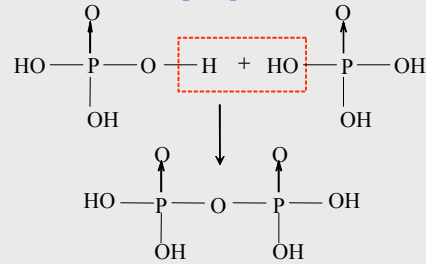


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10.4.3磷

$\text{H}_4\text{P}_2\text{O}_7$ 焦磷酸 (diphosphoric acid):

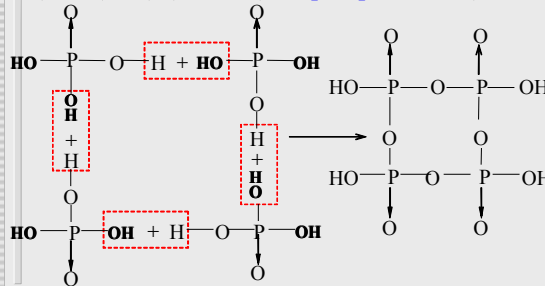


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10.4.3磷

$(\text{HPO}_3)_4$ 四(聚)偏磷酸 (metaphosphoric acid):

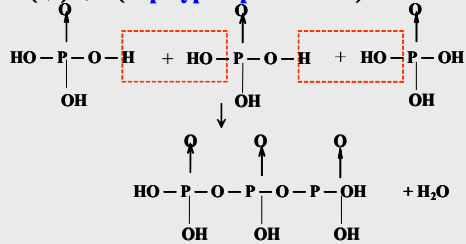


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10.4.3磷

三(聚)磷酸(tripolyphosphoric acid):

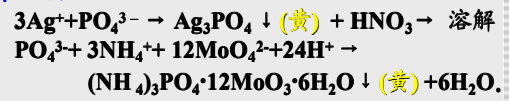


$\text{H}_5\text{P}_3\text{O}_{10}$ 形成的钠盐俗称“五钠”: $\text{Na}_5\text{P}_3\text{O}_{10}$.



10.4.3磷

PO_4^{3-} 的鉴定:

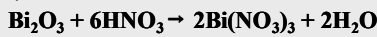


10.4.4砷、锑、铋

1.氧化物(oxides)及其水合物(hydrates):

① 酸性:

As_2O_3 和 H_2AsO_3 均为两性偏酸性;而 Bi_2O_3 则是弱碱性.

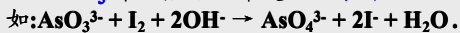


② 氧化还原性:

惰性电子对效应:

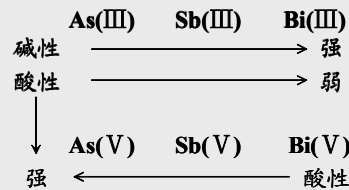
还原能力: $\text{As}(\text{III}) > \text{Sb}(\text{III}) > \text{Bi}(\text{III})$

AsO_3^{3-} 在碱性溶液中是强还原剂.



10.4.4砷、锑、铋

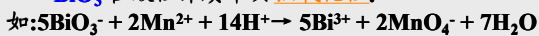
砷、锑、铋oxide及其hydrate酸碱性变化规律:



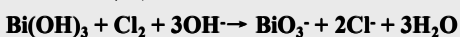
10.4.4砷、锑、铋

氧化能力: $\text{Bi}(\text{V}) > \text{Sb}(\text{V}) > \text{As}(\text{V})$

BiO_3^- 在酸性介质中具强氧化性.



因 BiO_3^- 强氧化性,只能在强碱性介质中使用强氧化剂才能得到它.



另外, As_2O_3 俗称“砒霜”,是剧毒物质.

2.sulfides:

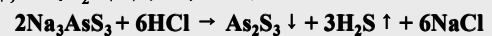
主要性质表现在溶解性、酸碱性以及颜色.



10.4.4砷、锑、铋

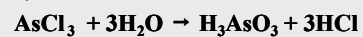
As_2S_3 除能溶于酸、 NaOH 外,还溶于 Na_2S ,甚至 $(\text{NH}_4)_2\text{S}$ 溶液中,形成硫代亚砷酸盐.

砷和锑的硫代亚砷酸盐和硫代酸盐,遇强酸都会分解,生成 H_2S 和相应的硫化物沉淀.



3.氯化物(chlorides):

① 水解性:



② 配位能力(有空d轨道):

