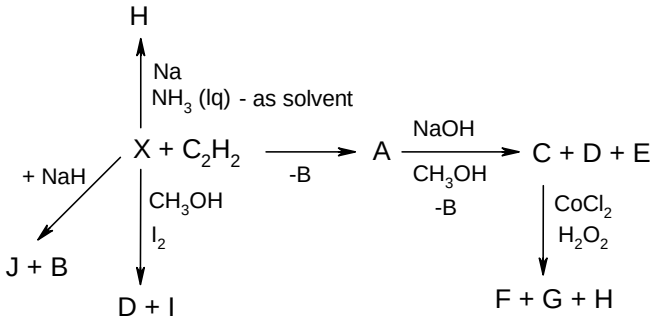
Inorganic Chemistry

I1. One of the most stable hydride (**X**) of an element **Z** with the fundamental spectral term $\mathbf{2^2P_{1/2}}$ has the atomic ratio, Z : H=1:1.4

a) Establish the chemical formula and the structure of hydride **X.**

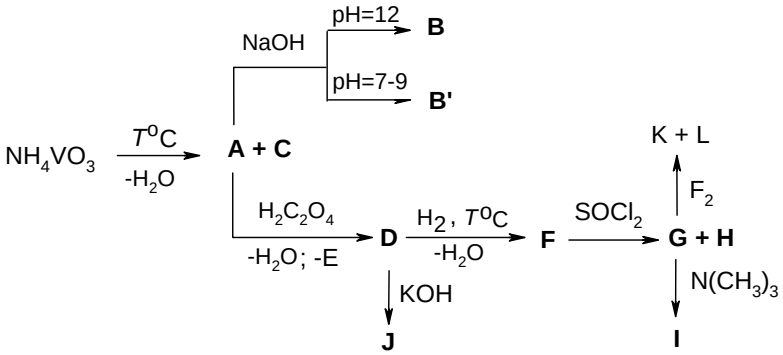
b) Establish the chemical formula of the compounds **A-H** in the following scheme and write the corresponding chemical reactions:



c) Compare the reactivity of the element **Z** with those of silicon and aluminum towards water, NaOH and HNO_3.

d) Determine the structure of the compound **A** and its isomers.

I2. a) Establish the chemical formula of the compounds **A-L** in the following scheme and write the chemical reactions. It is known that **A**, **B**, **B'**, **D**, **F**, **G**, **I**, **J** and **K** are vanadium compounds (**A** is a binary compound).



b) Draw the structures of **B**, **B'**, **I** and **K** vanadium compounds.

c) Compare the structure of **K** vanadium compound with the similar one of niobium.

Answers:

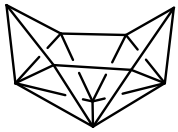
I1.- 10p

a)4p $2^2P_{1/2}$; period 2; 2S+1=2 ⇒ S=1/2; L=1; J=1/2; ⇒ J=L-S (before half filling with electrons) ⇒ [He]$2s^2 2p^1$; Z=B

H:Z=1.4 ⇒ B_nH_{n+4} – boranes and B_nH_{n+6} – hydroboranes

$B_{10}H_{14}$ – decaborane or $B_{15}H_{21}$ – quindeca hydroborane, $B_{10}H_{14}$ is the stable hydride

X= $B_{10}H_{14}$



Structure is determined by applying the Wade's rules.

3x10 (B) + 1x14 (H)=44 electrons ⇒ 22 electron pairs (ep)

10 ep for normal B-H bonds ⇒ 12 ep for the cluster ⇒ (n+2) nido (nest) structure

b) 0p

$$B_{10}H_{14} + C_2H_2 \xrightarrow[-\,2H_2]{} C_2B_{10}H_{12} \xrightarrow[3\,CH_3OH]{2\,NaOH} Na_2(C_2B_9H_{11}) + B(OCH_3)_3 + 2H_2O + H_2$$

decaborane ortho-carborane

A=$C_2B_{10}H_{12}$; B=H_2; C=$Na_2(C_2B_9H_{11})$; D=$B(OCH_3)_3$; E=H_2O

$$2\,Na_2(C_2B_9H_{11}) + CoCl_2 + 1/2\,H_2O_2 \longrightarrow Na[Co(C_2B_9H_{11})_2] + 2\,NaCl + NaOH$$

F=$Na[Co(C_2B_9H_{11})_2]$; G=NaCl; H=NaOH

$$B_{10}H_{14} + 30\,CH_3OH + 22\,I_2 \longrightarrow 10\,B(OCH_3)_3 + 44HI$$

D=$B(OCH_3)_3$; I=HI

$$B_{10}H_{14} + NaH \longrightarrow Na(B_{10}H_{13}) + H_2$$

J=$Na(B_{10}H_{13})$

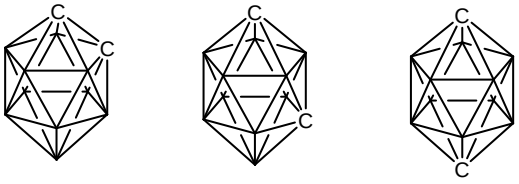
$$B_{10}H_{14} + 2\,Na \xrightarrow{NH_3(lq)} Na_2(B_{10}H_{14})$$

H=$Na_2(B_{10}H_{14})$

c) 6p

$2B + 3H_2O \rightarrow B_2O_3 + 3H_2$ at heating	Silicon reacts with water only as powder, at high temperature. $Si + H_2O \rightarrow SiO_2 + H_2$	Aluminum reacts with water only in the presence of Hg^{2+} salts. $Al(Hg^{2+}) + 3H_2O \rightarrow Al(OH)_3 + 3/2H_2$
$2B + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 3H_2$ boron as powder reacts with molten NaOH	$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$ in molten NaOH or concentrated solution	$Al + NaOH + 5H_2O \rightarrow Na[Al(OH)_4(H_2O)_2] + 3/2H_2$
$B + 3HNO_3(aq) \rightarrow H_3BO_3 + 3NO_2$ at heating	Nitric acid attacks silicone only on surface. $Si + HNO_3$conc. $\rightarrow SiO_2 + NO_2 + H_2O$	Concentrated HNO_3 forms a metal oxide layer Al_2O_3 that protects the metal from further oxidation. Only diluted nitric acid reacts with Al. $Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + H_2O$

d) 0p Carborane has three isomers: *ortho*, *meta* and *para*



ortho meta para

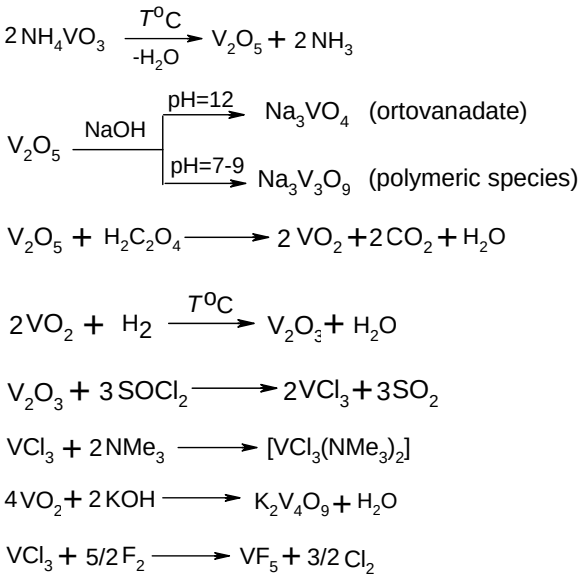
$C_2B_{10}H_{12}$ 4x2+3x10+12=50 $\Rightarrow$ 25 ep

12 ep for normal bonds $\Rightarrow$ 13 ep $\Rightarrow$ (n+1) *closo* (cage) structure

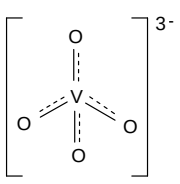
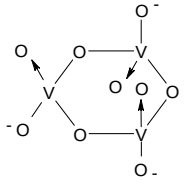
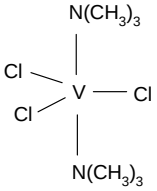
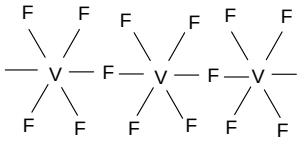
I2.-20p

a)15p

A=V_2O_5; B=Na_3VO_4, B'=$Na_3V_3O_9$; C=NH_3; D=VO_2; E=CO_2; F=V_2O_3; G=VCl_3; H=SO_2; I=$[VCl_3(NMe_3)_2]$; J=$K_2V_4O_9$; K=VF_5; L=Cl_2



b) 4p (each structure 1p)

			
Tetrahedral structure	Cyclic structure	Trigonal bipyramide structure	Polymeric structure

c) 1p VF_5 has polymeric structure, unlike niobium pentafluoride that has tetrameric structure, but both compounds have fluoride ions in bridge.