

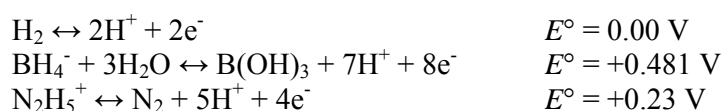


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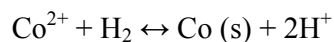
## EXERCISE 6 - SOLUTION

### PROBLEM 1

The reduction reactions for the reducing agents should be reversed as the reducing agents are themselves oxidized:



As an example, the reduction of  $\text{Co}^{2+}$  with  $\text{H}_2$  would be:



with the corresponding reaction potential:

$$E^\circ_{\text{tot}} = E^\circ_{\text{Co}^{2+}/\text{Co}} + E^\circ_{\text{H}_2/\text{H}^+} = -0.28 \text{ V} + 0.00 \text{ V} = -0.28 \text{ V}$$

As  $E^\circ_{\text{tot}}$  is negative, the reaction is not thermodynamically favorable and will not proceed (remember  $\Delta G = -nFE$ ). However,  $\text{BH}_4^-$  can reduce  $\text{Co}^{2+}$ , and all three reagents can reduce  $\text{Au}^+$ . The results are summarized below (No = no reduction possible, Yes = reduction possible).

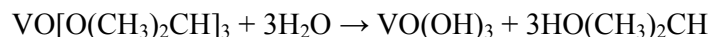
	$\text{H}_2$	$\text{N}_2\text{H}_5^+$	$\text{BH}_4^-$
$\text{Co}^{2+}$	No	No	Yes
$\text{Au}^+$	Yes	Yes	Yes

### PROBLEM 2

- a) Hydrolysis of vanadium tri-iso-propoxide oxide, in which a hydroxyl ion becomes attached to the metal atom, is the first step of the sol-gel synthesis, and it can be described by the following reaction:



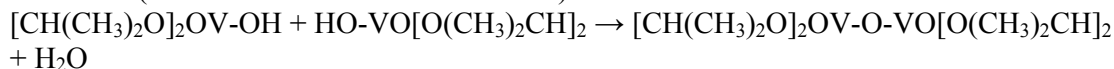
Depending on the amount of water added, the hydrolysis may go to completion so that all the iso-propoxy groups are replaced by hydroxyl groups:



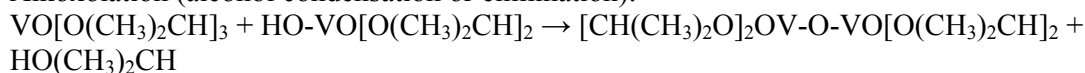
- b) The second step in the sol-gel synthesis is the condensation/polymerization reaction in which two partially hydrolyzed molecules can be linked together. Condensation can occur

by two different reactions, either by oxolation or by alkoxolation. Both reactions are condensation reactions in which an oxobridge (-O-) is formed between two vanadium atoms, and they can be described as follows:

Oxolation (water condensation or elimination):

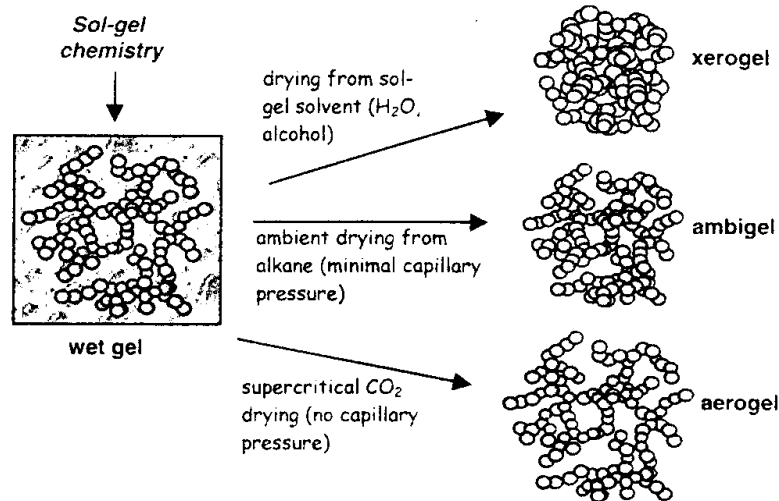


Alkoxolation (alcohol condensation or elimination):



In the oxolation reaction two partially hydrolyzed vanadium alkoxide molecules react to form an oxygen bond while releasing a water molecule. Alkoxolation is a reaction between one vanadium alkoxide molecule and one partially hydrolyzed vanadium alkoxide molecule. These two molecules are linked together through an oxobridge while an alcohol molecule is released. The remaining positions around the vanadium atoms are in both reactions occupied by isopropoxy groups.

- c) Both steps of the sol-gel synthesis are carried out in an inert solvent, such as acetone, providing the water and alkoxide precursor a soluble medium in which to hydrolyze and polymerize. With large amounts of acetone present the oligomers will be spread farther apart, which retards the condensation reactions and increases the gelation time. This allows for a more controlled polymerization process. However, as the amount of solvent is increased a point is reached where the gel will not form. With these compositions no aerogels, xerogels or ambigels can be successfully synthesized. Also, the aerogels produced from sol-gels with extremely high water content tend to be deformed.
- d) Drying of a sol-gel can be performed by several different methods. Two of these include drying at ambient conditions (APD) and supercritical drying (CPD). Both methods are based on the removal of the pore solvent from the bulk wet gel, leaving a solid metal oxide network. When the wet gel is dried at ambient temperature and pressure the solvent evaporates to the air, resulting in the formation of either a xerogel or an ambigel. A xerogel results from drying the gel from the sol-gel solvent (f.ex. water and acetone), whereas an ambigel is obtained when drying from a solvent with minimal surface tension such as hexane. The figure below gives a simplified picture of the structure of these gels compared to the original wet gel.



APD is a quick and effective way of removing the pore solvent. It can be applied to both bulk wet gel and thin film samples, and the resulting material can be fairly porous. However, APD gives rise to high capillary pressure that causes shrinkage of the gel network, which causes the xerogels to have extremely low pore volume and hence be very dense. Most of the porous network has collapsed and the specific surface area is usually less than  $10 \text{ m}^2/\text{g}$ . Ambigels experience somewhat lower capillary pressures and will have a higher total pore volume and lower density. Specific surface areas of several hundred  $\text{m}^2/\text{g}$  can be achieved.

CPD is the process of removing the pore solvent from the gel above the critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) of the solvent. Under supercritical conditions the densities become equal and there is no interface between liquid and vapor. In this process the wet gel is placed into an autoclave and pressure and temperature are increased in such a way that the phase boundary is not crossed. When  $T_c$  and  $P_c$  are reached the pressure is slowly released at constant temperature ( $>T_c$ ). The resulting material has extremely low density and high porosity, and the volume is similar to that of the original wet gel. This product is mostly air, and volume fractions of solid may be as low as  $\sim 1\%$ . An aerogel retains most of its porous network when the solvent is removed. Shrinkage is normally less than  $10\%$  and specific surface area for some metal oxides such as  $\text{SiO}_2$  can reach up to  $1000 \text{ m}^2/\text{g}$ .

- e) The Pechini process is a modified sol-gel process for metals that are not suitable for traditional sol-gel type reactions due to their unfavorable hydrolysis equilibria.

In the Pechini process, complexes are formed from alkali metals, alkaline earths, transition metals, or even nonmetals with bi- and tridentate organic chelating agents. A polyalcohol such is added to establish linkages between the chelates by a polyesterification reaction, resulting in gelation of the reaction mixture. After drying, the gel is heated to initiate pyrolysis of the organic species, resulting in agglomerated submicron oxide particles.

In the production of  $\text{BaTiO}_3$ ,  $\text{BaCO}_3$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  are the precursors providing the transition metal cations. Citric acid is the chelating agent used to complex the metal cations in order to stabilize the ions in solution. Ethylene glycol is the polymerization agent providing the linkages between the chelated cations which results in the formation of a gel.