

WARNING NOTICE:

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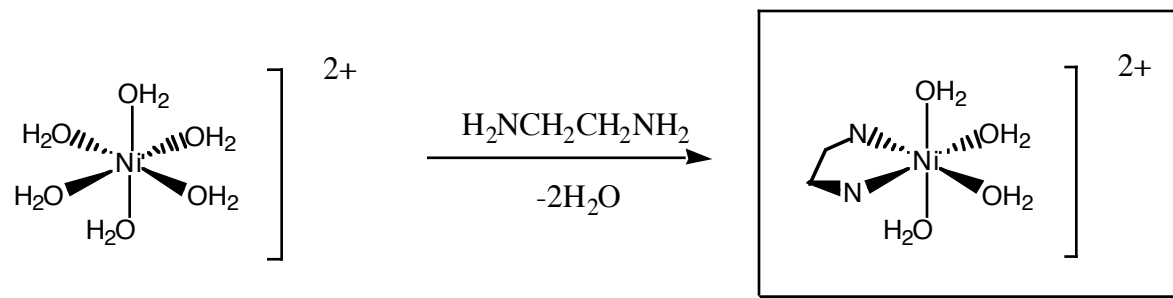
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I. Chemical Equilibrium

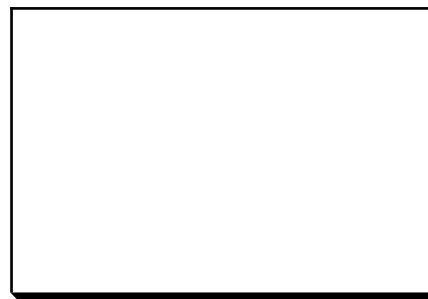
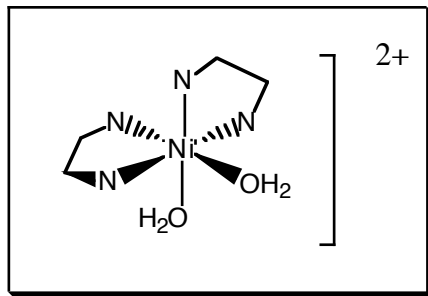
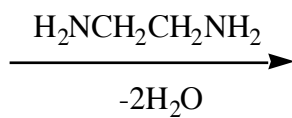
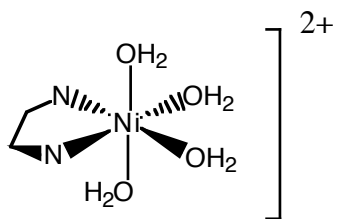
I.1- Coordination Chemistry: Nickel Complexes

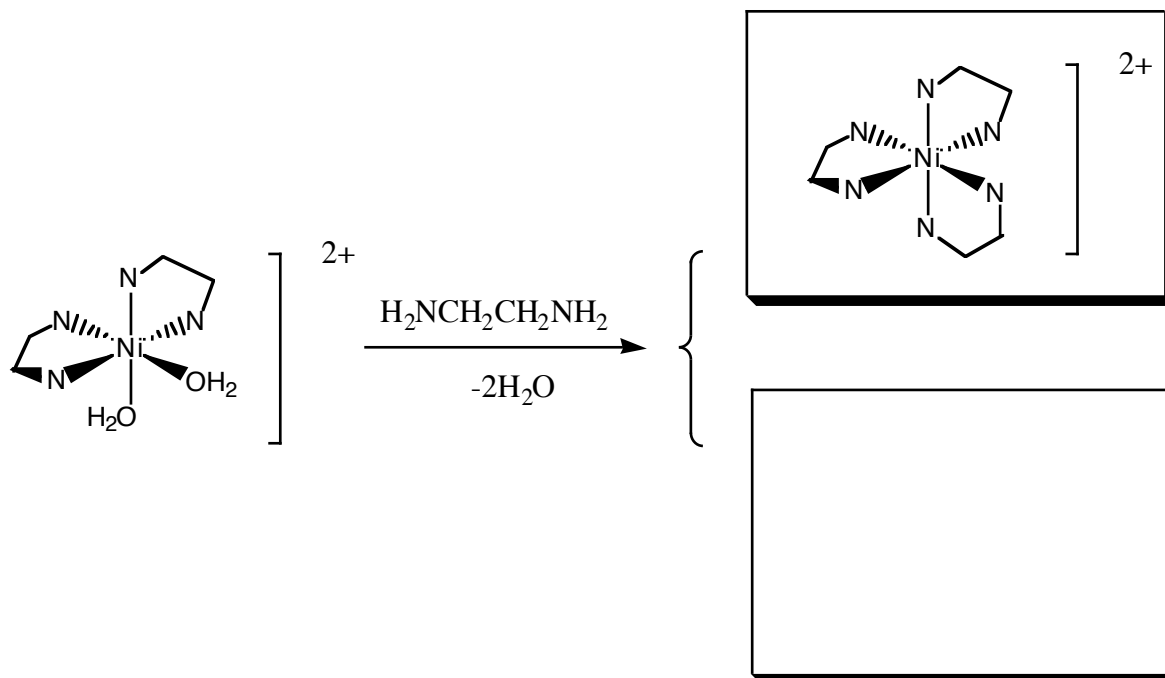
Background

Ni^{2+} in aqueous solution exists as the octahedral complex ion hexaaquanickel (II), $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. When the bidentate ethylenediamine ligand (*en*) is added to the solution in a 1:1 concentration ratio, it replaces two water ligands of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ to form $[\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$:



Further additions of ethylenediamine form the di- and tri- ethylenediamine complex, which have geometric and/or optical isomers.





Materials:

- 2 mL of 1.0 M Nickel sulfate (NiSO_4) solution
- 3 mL of 2.0 M Ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) solution
- 125 mL Erlenmeyer flask
- Four small test tubes (and a small beaker to hold them)

Safety: Ethylenediamine is a caustic, flammable liquid with an irritating vapor similar to ammonia. Nickel sulfate is a suspected carcinogen.

Procedure:

- Add 2 mL of nickel sulfate solution to the 125 mL Erlenmeyer flask . Bring up to 30 mL with water. Calculate the final concentration of nickel (II) ion. Transfer about 1 mL into a test tube.
- Add to the Erlenmeyer flask 1.0 mL of ethylenediamine solution. Record your observations. Transfer about 1 mL into a clean test tube.
- Add another 1.0 mL aliquot* of ethylenediamine solution to the Erlenmeyer flask. Record your observations. Transfer about 1 mL into a clean test tube. (aliquot = a volume of a solution)
- Add another 1.0 mL of ethylenediamine into the Erlenmeyer flask. Record your observations. Transfer about 1 mL into a clean test tube.
- Group test tubes together to contrast the four colors.
- Optional: Work in teams to obtain the spectrum of each solution by UV-VIS spectroscopy.

Clean Up: Collect all waste in the designated container.

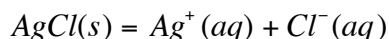
Discussion:

- Draw the missing isomers in the Background section and describe in each case the type of isomerism.
- At approximately what wavelengths of the electromagnetic spectrum do these complexes, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$, $[\text{Ni}(\text{en})_3]^{2+}$, absorb light?
- Use your understanding of the splitting of d orbitals and the spectrochemical series to explain your results.

I.2- Solubility Equilibrium: Precipitates and Complexes of Silver(I)

Background

The solubility of a substance in a solvent is defined as the greatest amount that will dissolve in equilibrium in a specified volume of solvent at a particular temperature. When an ionic solid such as silver chloride (AgCl) dissolves in water, it breaks up into ions that move apart from each other and become solvated by water molecules, and the following equilibrium is established:



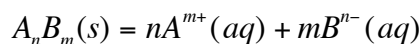
The equilibrium constant for this reaction, or *solubility product*, K_{sp} , is given by:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-].$$

A simple relation exists between the solubility of an ionic compound (S) and its solubility product:

$$K_{sp} = S^2$$

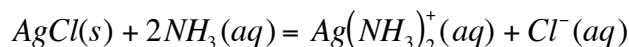
It can be easily shown that for the general solubility equilibrium



the relation between the solubility and the solubility product is given by

$$K_{sp} = n^n m^m S^{n+m}$$

The formation of coordination complexes can have a large effect on the solubility of a compound in water. Silver chloride is only very weakly soluble in water, but addition of ammonia (NH₃) to the solution allows the complex ion Ag(NH₃)₂⁺ to form:



This greatly increases the solubility of the silver chloride.

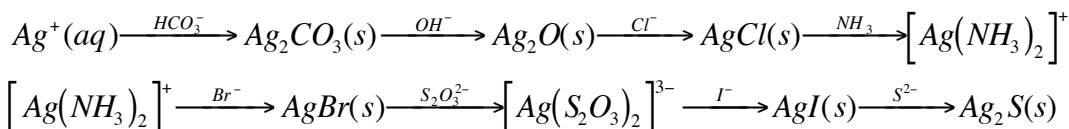
Materials:

- 1.0 mL of 0.1M silver nitrate (AgNO₃)
- 0.1M sodium bicarbonate (NaHCO₃)
- 0.1M sodium hydroxide (NaOH)
- 0.1M sodium chloride (NaCl)
- 5.0M ammonia (NH₃) (ammonium hydroxide, NH₄OH)
- 0.1M sodium bromide (NaBr)
- 0.1M sodium thiosulfate (Na₂S₂O₃)
- 0.1M potassium iodide (KI)
- 0.1M sodium sulfide (Na₂S)
- 50mL beaker
- magnetic stirrer with stirring bar

Safety: Sulfide salts, their solutions and hydrogen sulfide gas, which smells like rotten eggs at low concentration and is produced by reaction of sulfides with acids, are all poisonous. Avoid adding any acid to a solution containing sulfide salts. Silver nitrate solutions are light sensitive, irritating and oxidizing. Ammonium hydroxide is corrosive and highly irritating upon inhalation.

Procedure:

- Place a 50mL beaker containing 20 mL of distilled water and a magnetic stirring bar on the magnetic stirrer, and adjust the rate of stirring so it is vigorous but not turbulent.
- Add about 1 mL of AgNO₃ solution and allow time for complete mixing.
- Add dropwise in sequence the following solutions until a change is clearly observed. This will generally be 0.5-1.0 mL (10-20 drops): NaHCO₃, NaOH, NaCl, NH₃, NaBr, Na₂S₂O₃, KI, and Na₂S.
- Write down your observations (color, state, etc.).



Clean Up: Precipitate any silver still in solution by adding excess sodium sulfide.

Discussion: Silver forms a series of precipitates and complex ions with different solubilities and formation constants, respectively.

Interpret your results in terms of solubility constants, complex formation constants, and relative concentrations of reactants. How could you explain the different solubilities of the silver halides?

Compound	K_{sp}	K_f
Ag_2CO_3	6.2×10^{-12}	
AgOH	1.5×10^{-8}	
AgCl	1.6×10^{-10}	
AgBr	7.7×10^{-13}	
AgI	1.5×10^{-16}	
Ag_2S	6.3×10^{-51}	
$[Ag(NH_3)_2]^+$		1.7×10^7
$[Ag(S_2O_3)_2]^{3-}$		2.9×10^{13}

I.3- Equilibrium and temperature: Complexes of Cobalt (II)

Background

Chemical reactions are either *endothermic* (taking heat from the surroundings) or *exothermic* (giving off heat). The effects of temperature in chemical equilibrium can be predicted in terms of Le Châtelier's principle. If the reaction is endothermic, a raise in the temperature will shift the equilibrium to the right. In an exothermic reaction, the shift occurs in the opposite direction. The dependence of the equilibrium constant on the temperature is given by the *van't Hoff equation*:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

where ΔH° is the change in enthalpy of the reaction, R the universal gas constant ($8.31 \text{ J K}^{-1}\text{mol}^{-1}$), and K_1 and K_2 , the equilibrium constants at temperatures T_1 and T_2 , respectively.

Materials:

- 0.5g cobalt(II) chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
- 12 mL 2-propanol, $\text{C}_3\text{H}_7\text{OH}$
- distilled water
- Test tube with stopper
- Hot water bath
- ice-salt bath

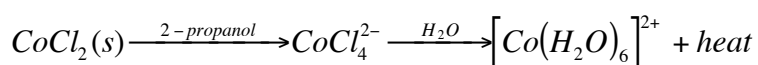
Safety: Cobalt chloride is a suspected carcinogen in animals. The dust is a respiratory tract irritant. Isopropanol is a flammable liquid and vapor (may cause a flash fire). REMOVE stopper before heating (never heat a closed system). When heating the testtube be sure it is not pointed towards yourself or colleagues.

Procedure:

- Place 0.5g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in a large test tube
- Add 12 mL of 2-propanol
- Stopper and shake to dissolve solid. Note the color of the solution.
- Carefully add water dropwise, with mixing, until a color change is observed.
- Place the unstoppered test tube in a boiling water bath. Observed any color change.
- Transfer the test tube to an ice bath. Record your observations.

Clean up: Discard the cobalt solution in the designated containers.

Discussion: Identify the colored species. Interpret your results in terms of Le Chatelier's principle.



I.4- Application of Solubility (K_{sp}) and Formation (K_f) Equilibria: Preparation of a Black and White Polaroid Negative.

Background

In early photographic processes salted papers were prepared by first floating the paper on a solution of KCl (or other halide) and then in the dark on a solution of AgNO_3 . AgCl is precipitated into the paper fiber structure. Today the silver halide is usually prepared in a gelatin layer. The silver halide is then exposed to light to capture an image. The image is obtained through the photochemical reduction of Ag^+ to Ag metal. The image can either be obtained through very long exposure times or a "latent" image can be further developed through the use of developing agents. To remove excess, unreacted silver halide from the paper or gelatin layer it must be made soluble. This has been accomplished since the beginning of photography through use of a "fixer" sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$).

This process relies heavily on solubility and precipitation processes governed by **solubility equilibria** (with equilibrium constants known as K_{sp} .) as well as **complex formation equilibria** (with equilibrium constants represented by K_f or β).

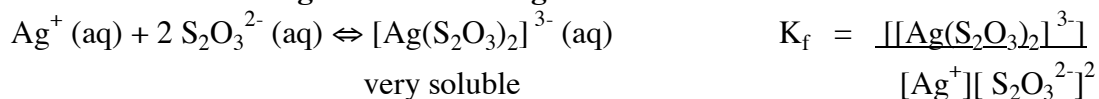
Consider the solubility of AgCl . What is the concentration of Ag^+ in a saturated solution (i.e., there is solid present)?

	AgCl (s)	\rightleftharpoons	$\text{Ag}^+ \text{ (aq)}$	$+$	$\text{Cl}^- \text{ (aq)}$
initial	solid		0		0
change			+x		+x
equilibrium			+x		+x

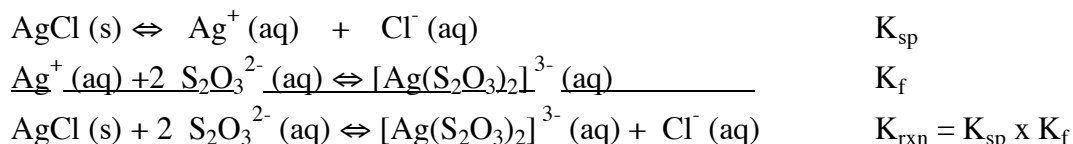
$$K_{sp} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.6 \times 10^{-10} \quad x = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$

The concentrations of the ions are very low in aqueous solution and whenever the concentrations of the ions exceeds $1.3 \times 10^{-5} \text{ M}$ precipitation occurs and consequently unreacted silver halide is not readily removed by simple washing.

How to remove unwanted AgCl from the image?



Combine reactions:



Coupling of two reactions permits pulling AgCl solid into solution and with sufficient washing in water to remove the products, the light sensitive silver halide is removed from the photographic image. In reality there is a variety of soluble silver thiosulfate complexes formed.

To prepare a negative to be used for obtaining a cyanotype print later in the course a Polaroid Land camera and Polaroid Polapan 665P/N will be used. The chief advantage of this route to obtaining a negative is no darkroom is required to obtain a printable negative.

Materials:

Polaroid 220 Land Camera

Polapan 665P/N (Polaroid Black and White Positive/Negative Instant Pack Film)

Sodium sulfite solution

Safety: Wear gloves when separating the film pack as the proprietary chemical mixture is caustic.

Procedure:

You will be given instruction on use of the camera to obtain an image and on the procedure for developing the instant pack film. The negatives are washed in a sodium sulfite solution and rinsed in water. A final rinse in a proprietary surfactant solution is used to minimize water spotting on the negative prior to hanging the negative to dry. To protect the positive image, the black and white print must be coated with the coater provided with the film.