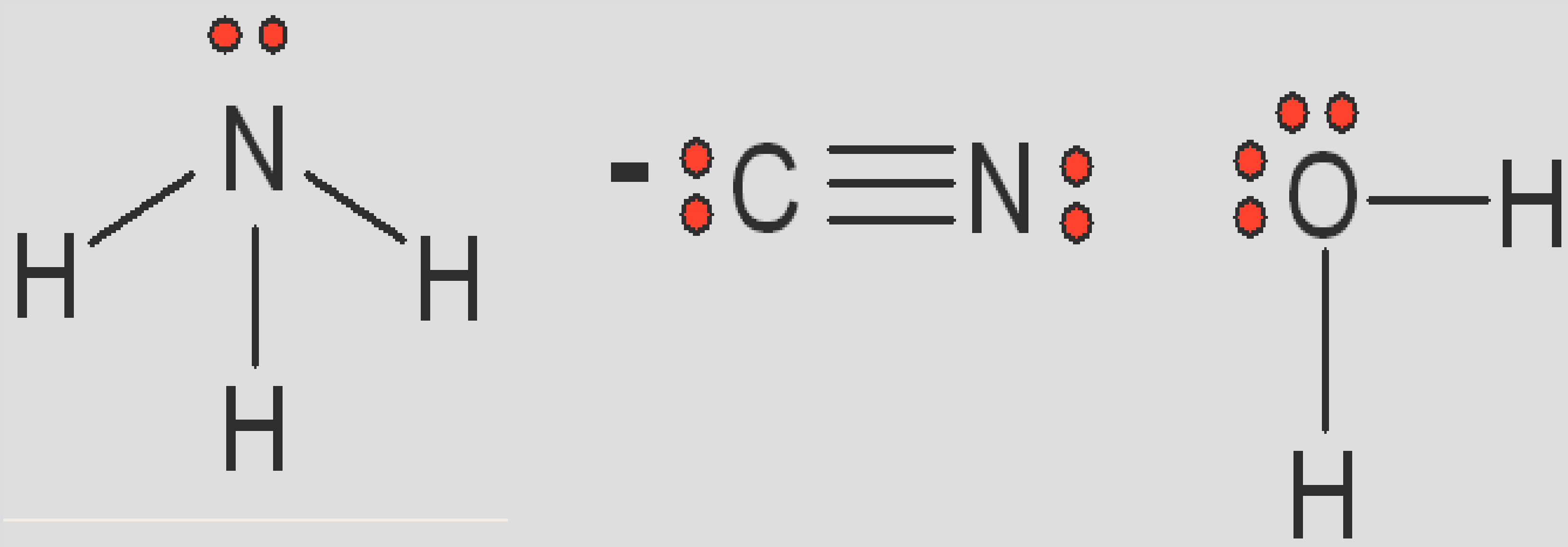
# Complexes and Eqm

- A complex ion is an ion composed of
  - A metal
  - A ***ligand*** : A ligand is a Lewis base (electron pair donor). They have lone pair(s) of electrons that can fill the empty orbital in the metal.
  - Ligands can be neutral or negatively charged as long as they have electrons to donate.

# $NH_3$, $CN^-$, and $H_20$ are common ligands




- Each has at least 1 pair of electrons to donate to the complex

# Coordination Number

- Coordination number is the number of ligands surrounding the central metal ion.
- Remember from VSEPR theory, the number of neighbors controls your geometry.

# Common coordination #s

| Coordination Number | Examples |
|---|---|
| 2 | $Ag(NH_3)_2^-$ |
| 4 | $CoCl_4^{2-}$, $Cu(NH_3)_4^{2+}$ |
| 6 | $Co(H_2O)_6^{2+}$, $Ni(NH_3)_6^{2+}$ |

# Two types problems

- Equilibrium concentrations
- Solubility (This is cool)

# Equilibrium concentrations

- Assumptions: metal concentration is quite low
- Ligand concentration is quite high.
- Complexes are made step-wise
- Complexes have 2 or more K's
- The K's are large numbers
- Complexes like to form, reactions go to **completion**

# Example

- Calculate the concentrations of $Ag^+$, $Ag(S_2O_3)^-$, $Ag(S_2O_3)_2^{3-}$ in a solution containing 2.86 M $S_2O_3^{2-}$ and $4.29 \times 10^{-4}$ M $Ag^+$ (after mixing)
- $Ag^+ + S_2O_3^{2-} \Longleftrightarrow Ag(S_2O_3)^-$ $K_1 = 7.4 \times 10^8$
- $Ag(S_2O_3)^- + S_2O_3^{2-} \Longleftrightarrow Ag(S_2O_3)_2^{3-}$ $K_2 = 3.9 \times 10^4$

# Example continued

- Work backwards
- $$K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag(S_2O_3)^-][S_2O_3^{2}]}$$
- $$3.9 \times 10^4 = \frac{4.29 \times 10^{-4}}{[Ag(S_2O_3)^-](2.86)}$$
- $[Ag(S_2O_3)^-] = 3.8 \times 10^{-9}$ plug this into $K_1$

# Example pg 3

- $K_1 = \dfrac{[Ag(S_2O_3)^-]}{[Ag^+][S_2O_3^{2-}]} = 7.4 \times 10^8$
- $7.4 \times 10^8 = \dfrac{3.8 \times 10^{-9}}{[Ag+](2.86)}$
- $[Ag+] = 1.8 \times 10^{-18}$ M

# In summary

- $[Ag^+] = 1.8 \times 10^{-18}$ M
- $[Ag(S_2O_3)^-] = 3.8 \times 10^{-9}$
- $[Ag(S_2O_3)_2^{3-}] = 4.29 \times 10^{-4}$
- $[S_2O_3^{2-}] = 2.86$ M
- Within rounding $[S_2O_3^{2-}]$ is unchanged, and all silver has been converted to $Ag(S_2O_3)_2^{3-}$

# Solubility problems

- Recall in Qual, Unknown 1 the first procedure is to add HCl. This is a source of Cl- ions. If you get a precipitate, $Pb^{2+}$, $Ag^{+}$, and/or $Hg^{+}$ must be present.
- We dissolve the $PbCl_2$ by heating. It has the highest Ksp and is most sensitive to heating.
- How then to we dissolve the insoluble AgCl?

# Solubility Rxn and Complexes

- How can you dissolve an insoluble salt?
- Add a ligand (Lewis Base) that the metal likes as much as it likes the current (insoluble anion).
- AgCl <==> $Ag^{+}$ + $Cl^{-}$ $K_{sp} = 1 \times 10^{-10}$
- By LeChatelier's AgCl <==> $Ag^{+}$ + $Cl^{-}$
- Making a complex decreases the Ag+ and the reaction dissolves to replace missing Ag+

# So, For the math

- 1) Balanced chemical equations for all steps. Use Hess' Law and cancel.

$$AgCl(s) <==> Ag^{+} + Cl^{-} \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$Ag^{+} + NH_3 <==> Ag(NH_3)^{+} \qquad K_1 = 2.1 \times 10^{3}$$

$$Ag(NH_3)^{+}\ NH_3 <==> Ag(NH_3)_2^{+} \qquad K_2 = 8.2 \times 10^{3}$$

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$$AgCl + 2NH_3 <==> Ag(NH_3)_2^{+} + Cl^{-} \qquad K = K_{sp} \cdot K_1 \cdot K_2$$

# Solubility cont.

- What is the solubility of AgCl in a strong excess of ammonia, say 10.0 M?
- [Cl-] = x
- $[Ag(NH_3)_2]$= x also
- $[NH_3]$ = 10 – 2x  (review equation)
- $K = 2.8 \times 10^{-3} = \frac{[Ag(NH_3)_2]\,[Cl^-]}{[NH_3]^2}$

# Substitute and Solve

- $$2.8 \times 10^{-3} = \frac{x^2}{(10.0 - 2x)^2}$$
- Sqrt both sides
- $$5.29 \times 10^{-1} = \frac{x}{(10.0 - 2x)}$$
- x = 0.48 M !!!! So we got it to dissolve. Great when theory agrees with real life