The Mond Process

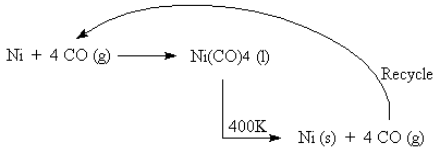
Nickel carbonyl, a gas formed from carbon monoxide and metallic nickel.

Scientific Serendipity

In 1890 Ludwig Mond, was investigating the rapid corrosion of nickel valves used in apparatus for the **Solvay process***, and discovered $Ni(CO)_4$.

In contrast to many nickel compounds which are usually green solids, $Ni(CO)_4$ is a colourless, volatile, toxic liquid with a very "organic character".

He used it as the basis of a method to purify nickel, called the **"Mond process".**

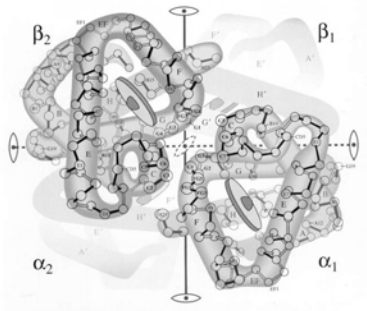


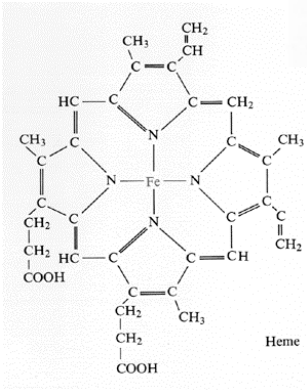
Ni reacts with CO (leaving the impurities behind), to form $Ni(CO)_4$.

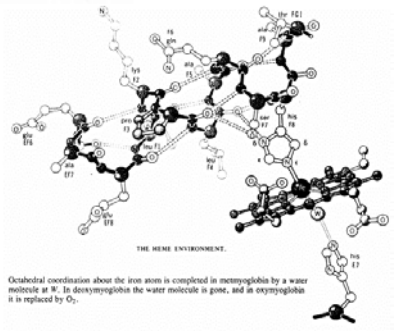
The $Ni(CO)_4$ is passed through a tower filled with nickel pellets at a high velocity and 400 K. Pure Ni plates out on the pellets.

* A commercial process for the manufacture of Na_2CO_3. NH_3 and CO_2 are passed into a sat'd $NaCl_{(aq)}$ solution to form soluble $(NH_4)(HCO_3)$, which reacts with the NaCl to form soluble NH_4Cl and solid $NaHCO_3$ if the reactor temperature is maintained below 15°C. The $NaHCO_3$ is filtered off and heated to produce Na_2CO_3.

Hemoglobin and Heme







Course Outline

I. Introduction to Transition Metal Complexes.
Classical complexes (Jorgenson and Werner)
Survey of ligand coordination numbers, geometries and types of ligands
Nomenclature
Isomerism

II. Bonding in Transition Metal Complexes.
Electron configuration of transition metals
Crystal field theory
Valence bond theory
Simple Molecular Orbital Theory
Electronic Spectra and Magnetism

III. Kinetics and Mechanisms of Inorganic Reactions.
Stability and lability
Substitution reactions
Electron transfer reactions

IV. Descriptive Chemistry of TMs.

V. Organometallic Chemistry
18 e^- rule, σ, and π bonding ligands (synergistic bonding)
Metal carbonyls, synthesis, structure, reactions
Compounds with delocalized π-conjugated organic ligands.
Reactions and catalysis

Formation and Reactions of TM Complexes

Very brief discussion in R-C pages 449-451.

What have we done so far?

1. What is the structure of these compounds?
   (Coordination Number, Geometry, Isomerization)

2. What holds these complexes together and how do we study them?
   (CFT d-orbital splitting, electronic spectroscopy, MO theory)

But….you can't study them if you can't get them…..

How are they made?

Where do we start?

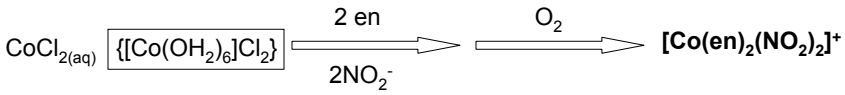
How about with a Co and Pt complex? **$[Co(en)_2(NO_2)_2]^+$,** and **cis/trans platin.**

This is an interesting case:

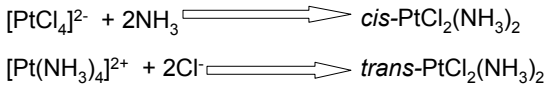
We start with a Co^{2+} salt….**what is the oxidation state of Co in the product?**

Why do we use the Co^{2+}?

Ligand substitution occurs more readily than with Co^{3+}… but why?



If we change our starting material we can control stereochemistry…. but why?



Why do these reactions occur the way they do?
We are going to look at influencing factors and mechanisms.

Stable vs. Unstable
Inert vs. Labile

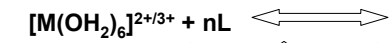
When TM ions are dissolved in water the ions form aqua complexes.

UV-Vis, NMR indicate a six-coordinate octahedral species for 1st row TMs.

$[M(OH_2)_6]^{2+/3+}$

(neutron diffraction of these species was first reported in 1984)

Given that the ions are not "free" in solution, formation of TM complexes involves the replacement (substitution) of one ligand with another.



That these reactions occur in aqueous solution is VERY important to numerous disciplines including Inorganic Chemistry, Biochemistry, Analytical Chemistry, Environmental Chemistry and other applications.

TM Aqua Complexes

An IMPORTANT point about TM-aqua complexes.

The amount of time (residence time) the H_2O ligands spends attached to the TM can vary significantly from metal to metal.

$[Cr(OH_2)_6]^{3+}$ and $[Co(OH_2)_6]^{3+}$ fail to exchange with $^{18}OH_2/^{17}OH_2$ after several hours.

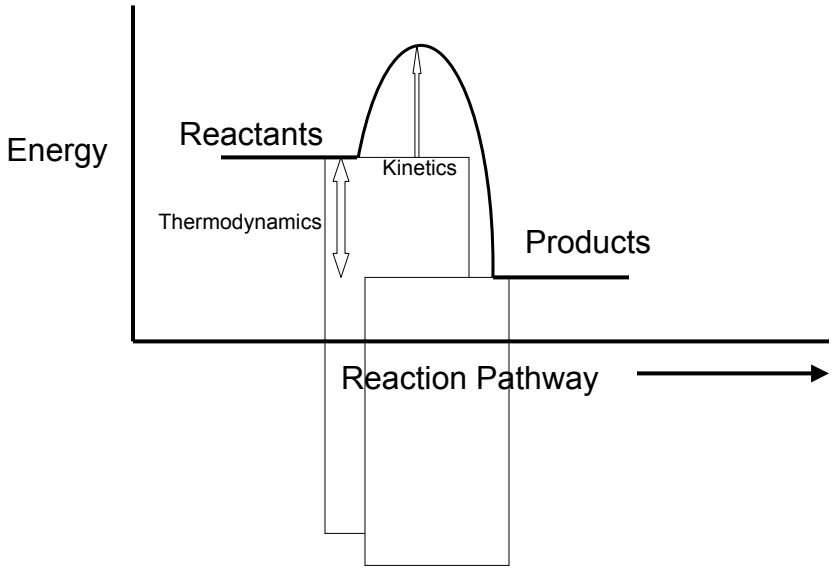
$$[Cr/Co^{16}(OH_2)_6]^{3+} + \text{large XS } {}^{18}OH_2/{}^{17}OH_2 \xleftrightarrow{\text{hours}} [Cr/Co^{18/17}(OH_2)_6]^{3+}$$

Most other TMs exchange water rapidly.

What does this tell us about formation of TM complexes and what we need to consider?

1. **Thermodynamics**: When examining thermodynamics of a reaction we are entirely interested in the start and finish of a reaction. **What is the extent of reaction? Where does the equilibrium lie? How do we investigate this?**
   $\Delta G^o_{rxn} = \Delta G^o_{f,prod} - \Delta G^o_{f,reacts}$
2. **Kinetics:** How fast does a reaction reach equilibrium? This relates directly to the mechanism.

Look at the reaction coordinate diagram…



Kinetics vs. Thermodynamics

We use terms to describe the Thermodynamic and Kinetic aspects of reactivity.

Thermodynamic. <u>Stable</u> or <u>Unstable</u>

Kinetic. <u>Inert</u> or <u>Labile</u>

An inert compound is not "inert" in the usual sense that no reaction will occur. Rather, the reaction takes place slower than for labile compounds.

There is <u>NO</u> connection between Thermodynamic Stability/Instability of a complex and its Lability/Inertness toward substitution.

For example:

Stable …but labile

$[Ni(CN)_4]^{2-} + 4{}^{13}CN^- \rightleftharpoons [Ni({}^{13}CN)_4]^{2-} + 4CN^-$ $\quad t_{1/2}$ ~ 30sec.

$[Ni(CN)_4]^{2-} \rightleftharpoons Ni^{2+}_{(aq)} + 4CN^-_{(aq)}$ $\quad K_{eq} = 1 \times 10^{-30}$

Unstable but inert

$[Co(NH_3)_6]^{3+} + 6H_2O \rightleftharpoons [Co(OH_2)_6]^{3+} + 6NH_4^+$ $\quad t_{1/2}$ ~ days.

$K_{eq} = 1 \times 10^{25}$

Conclusions from these examples.

Stable complexes have a large POSITIVE ΔG^o_{RXN} for ligand substitution and Inert complexes have a large POSITIVE $\Delta G^{\ddagger}$ (activation).

Stability and Coordination Complexes ($[ML_n]^{x+}$)

Typically expressed in terms of an overall formation or stability constant.
(This is K_{st} on the Chemistry Data sheet you receive with exams)

$$[M]^{x+} + nL \rightleftharpoons [ML_n]^{x+} \qquad K_{st} = \frac{[ML_n]^{x+}}{[M^{x+}_{(aq)}][L]^n}$$

BUT, this does not occur in one fell swoop!!
Water molecules do not just all fly off and are immediately replaced by nL ligands.

$$[M]^{x+}_{(aq)} + L \rightleftharpoons [ML]^{x+} \qquad K_1$$

$$[ML_{(n-1)}]^{x+} + L \rightleftharpoons [ML_n]^{x+} \qquad K_n$$

K_s are the stepwise formation constants and provide insight into the solution species present as a function of [L].

Stepwise formation constants

These formation constants provide valuable information given that different species may have VERY DIFFERENT properties…including environmental impact. Such information provides selective isolation of metal ions from solution through reaction with ligands.

For formation of divalent alkaline earth and 3d M^{2+} TM ions the **Irving-Williams Series** holds true.

Ba<Sr<Ca<Mg<Mn<Fe<Co<Ni<Cu>Zn

⇧

What is contributing to this trend?

1. Charge to radius ratio.
2. CFSE (beyond Mn^{2+})
   Jahn-Teller Distortion
3. Hard-Soft Acids/Bases

See R-C p 450-451.

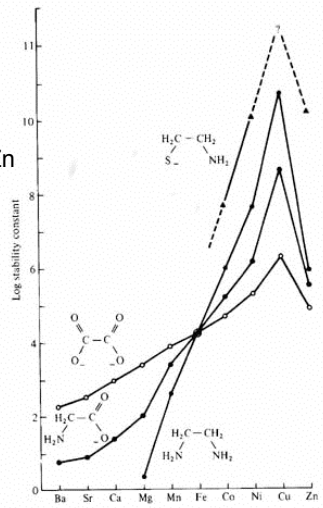


Fig. 9.5 The Irving–Williams effect: The stability increases in the series Ba–Cu, decreases with Zn. [From Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201. Reproduced with permission.]

The Pearson LA/LB "Hard"/"Soft" Approach

Hard Lewis Bases: high EN, low polarizability, hard to oxidize: O, N, F^- donors (Cl^- is borderline).

Soft Lewis Bases: low EN, highly polarizable, easy to oxidize: S, P, I^-, Br^-, R^-, H^- donors.

Hard Lewis Acids: small, highly charged (high ox. State): H^+, alkali metal (M^+) and alkaline earth (M^{2+}) cations, Al^{3+}, Cr^{3+}, BF_3.

Soft Lewis Acids: large, low oxidation state: Cu^+, Ag^+, Au^+, Tl^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, BH_3

In this model, hard acids "like" hard bases and soft acids "like" soft bases.

Chelate Effect

$[Ni]^{2+} + 6\ NH_3 \Longleftrightarrow [Ni\ (NH_3)_6]^{2+}$ $\log K_{st} = 8.61$

$[Ni]^{2+} + 3\ en \Longleftrightarrow [Ni\ (en)_3]^{2+}$ $\log K_{st} = 18.28$

Both ligands have a N-donor, yet the en complex is 10 orders of magnitude more stable than the NH_3.

This is a general effect that a complex with one (or more) 5 or 5-membered rings has a greatly enhanced stability relative to the similar complex lacking rings.

Why is this happening? What's missing from our equation?

$[Ni(OH_2)_6]^{2+} + 6\ NH_3 \Longleftrightarrow [Ni\ (NH_3)_6]^{2+} + 6H_2O$ $\log K_{st} = 8.61$

$[Ni\ (OH_2)_6]^{2+} + 3\ en \Longleftrightarrow [Ni\ (en)_3]^{2+} + 6H_2O$ $\log K_{st} = 18.28$

In the GAS PHASE there is no difference in K_{st}

Reactions of Coordination Complexes

The reactions of Coordination Complexes may be divided into three classes:

i) Substitution at the metal center
ii) Reactions of the coordinated ligands
iii) Oxidation and Reduction reactions at the metal center.

For the purposes of our discussion we will confine our discussion to (i) for substitution reactions on **Octahedral** and **Square Planar** complexes.

We will only briefly discuss one specific reaction involving a coordinated ligand.

Rxns of Octahedral Complexes

Consider ML_5X : In this complex there are 5 inert ligands (L) and one labile ligand (X).

For our purposes we will consider the replacement of X with an incoming ligand Y.

$$ML_5X + Y \longrightarrow ML_5Y + X$$

How might this happen?

We need to look at the molecular components.

What elemental steps will result in this process….

In more technical terms: What is the mechanism of this reaction?

There are Two Extreme Cases

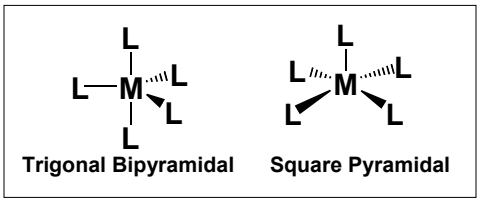
Dissociative Mechanism (D) Associative Mechanism (A)

Dissociative Mechanism

$$ML_5X + Y \longrightarrow ML_5Y + X$$

Step 1. Dissociation of X to yield a 5 coordinate intermediate.

$$ML_5X \xrightarrow{K_1} ML_5 + X$$



M-X bond is broken

Slow and *rate determining*

The rate of D is only depends on the conc. of ML_5X

Step 2. Coordination of Y to the ML_5 intermediate.

$$ML_5 + Y \xrightarrow[\text{fast}]{K_2} ML_5Y$$

This mechanism is independent of [Y]

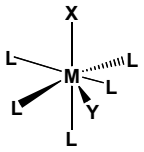
The rate law for this process is rate = $K_1[ML_5X]$ (the units of K_1 are sec^{-1})
If we find a reaction follows this rate law we conclude it is dissociative.

Associative Mechanism

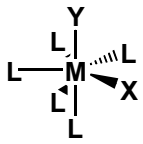
$ML_5X + Y \longrightarrow ML_5Y + X$

Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$ML_5X + Y \xrightarrow{K_1} ML_5XY$ (slow, rate determining)



Capped Octahedron



Pentagonal Bipyramid

Step 2. Cleavage of the M-X bond. (fast)

$ML_5XY \longrightarrow ML_5Y + X$ (fast)

The rate law for this process is rate = $K_1[ML_5X][Y]$ (the units of K_1 are $sec^{-1}Mole^{-1}$)
If we find a reaction follows this rate law we conclude it is associative.

Telling the difference…

By determining the rate law (uni- vs. bi- molecular) we can determine the mechanism of the reaction in question.

rate = $K_1[ML_5X]$ **or** **rate = $K_1[ML_5X][Y]$**

This is achieved via monitoring the disappearance reactant(s) and the appearance of product(s) using spectroscopic methods and variations in reactant concentrations.

This is not always as simple as we see here….

We will discuss one complication.

Solvents and Water!!

Often experimental conditions "mask" the dependence upon [Y].

When a reaction is carried out in a solvent….the solvent is in HUGE excess and it is not necessarily "innocent" (it can take a role in the rxn)

What is the concentration of water?

Effectively constant at 55.5M.
Be sure you can determine this!!

Given the excess of water, its concentration remains seemingly constant. As a result, the influence of the water on the mechanism is "masked". This results in a pseudo-first order rate law.

Solvent and Associative Processes

$$ML_5X + Y \xrightarrow{H_2O} ML_5Y + X$$

Step 1. Collision of ML_5X with Y or H_2O to yield a 7-coordinate intermediate.

Given the $[H_2O]$ >>>>[Y] it is much more likely that a collision with H2O will occur.

$$[ML_5X] + H_2O \xrightarrow{K_1} [ML_5X(O\,H_2)] \quad \text{(slow, rate determining)}$$

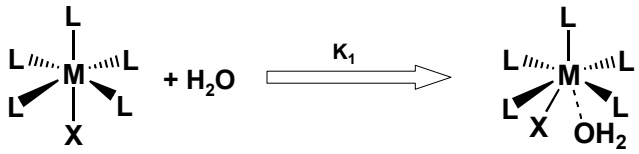
Step 2. Cleavage of the M-X bond.

$$[ML_5X(OH_2)] \xrightarrow{K_2} [ML_5OH_2] + X \quad \text{(fast)}$$

Step 3 Formation of the M-Y bond.

$$[ML_5X(OH_2)] + Y \xrightarrow{K_3} [ML_5OH_2] + X \quad \text{(fast)}$$

Looking at the structures…



Rate Law

Rate = [overall rate] = $k_1[ML_5X][H_2O]$
= $\{k_1[H_2O]\}\ [ML_5X]$
= $K\ [ML_5X]$

Given the $[H_2O]$ is constant the rate appears to follow a pseudo-1st order rate law.

To determine if the process follows A or D mechanism we need to do other exps.

ML_6 Preferred Mechanism

Octahedral complexes tend to favor a *D* mechanism through a 5 -coordinate intermediate.

$$[M(OH_2)_6]^{X+} + {}^{17}OH_2 \Longleftrightarrow [M(OH_2)_5\ {}^{17}(OH_2)]^{X+}$$

We already discussed that the residence time of H_2O varies a lot.
$1x10^{10}\ s^{-1}$ to $1x10^{-8}s^{-1}$

M^{X+}	$K_1\ (s^{-1})$
Cs^+	$5x10^9$
Li^+	$5x10^8$
Ba^{2+}	$2x10^9$
Be^{2+}	$2x10^2$

As the charge/radius ratio increases the rate of water exchange decreases.

What obs. of M^{2+} and M^+ can be made?

Charge/Radius Ratio

Given the M-OH_2 bond strength increases as the charge/radius ratio increases, data are consistent with a mechanism where the intermediate was obtained from the cleavage of the M-OH_2 bond and a new M-*OH_2 bond is formed quickly.

This is Characteristic of a Dissociative Mechanism

Exceptions to the charge/ratio rule exist:

Ni^{2+}(0.83Å), Cr^{2+}(0.94Å), Cu^{2+}(0.87Å) very similar size

Ni^{2+}(K_1= 1x$10^4$$s^{-1}$), Cr^{2+}/Cu^{2+}(K_1= 1x$10^9$$s^{-1}$) very different rates.

Some inert TM ions that exchange H_2O very slowly:

Cr^{3+}, LS Co^{3+} and sqr. planar Pt^{2+}

The inert nature of these complexes made it possible for Werner to work out his theory.

Inert/Labile d-electron configurations

Generally, INERT *oct.* complexes have large CFSE*, specifically

d^3, and L.S. d^4-d^6

Other compounds tend to be labile.

(dividing line labile vs. inert is t1/2 of 1 min. at 25°C)

	Inert Complexes	Labile Complexes
Octahedral	d3 and LS d^4,d^5,d^6	d^1,d^2,d^7, d^8,d^9,d^{10} HS d^4,d^5,d^6
Sqr. Planar	d^8 Pt^{2+}	Ni^{2+}

Pd^{2+}
(intermediate)

This summary applies best for 3d TMs.

If you consider 4d and 5d metals it is found that these metals have greater CFSE and achieve sigma bonds with better overlap than 3d metals.Hence, such systems tend to be inert on the above time scale.

Why look at water exchange?

The study of simple water exchange reactions is important and valuable given the rate at which $M(OH_2)_6^{X+}$ aqua ions combine with other ligands (L) to form other complexes…..

Shows little or no dependence on L

Rates for each metal ion are practically the same as the rate of exchange for H_2O on the same metal ion.

We can use exchange reactions to provide insight into other substitution reactions.

Anation Reactions

$$[M(OH_2)_6]^{X+} + X^- \Longrightarrow [M(OH_2)_5\,X]^{(X-1)+} + H_2O$$

This type of reaction is important as its behavior indicates not only how new complexes are formed but also where coordinated water is replaced by X^-.

$$[L_5M(OH_2)]^{X+} + X^- \Longrightarrow [L_5M\,X]^{(X-1)+} + H_2O$$

Generally two observations can be drawn:

1. For a given aqua ion, the rate of anation show little dependence on the nature of L.
2. The rate constant for anation of a given aqua complex is almost the same as for H_2O exchange.

These are consistent with a dissociative mechanism…..WHY?