Steric Numbers and Molecular Geometry

SN = # atoms bonded to central atom + # lone pairs on central atom

Without lone pairs:

<table>
<thead>
<tr>
<th>SN</th>
<th>Geometry</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>109.5</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>120, 90</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>90</td>
</tr>
</tbody>
</table>

With lone pairs:

<table>
<thead>
<tr>
<th>SN</th>
<th>Geometry</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>AX₂E 3 bent</td>
<td>&lt;120</td>
</tr>
<tr>
<td>4</td>
<td>AX₃E 4 trigonal bipyramidal</td>
<td>&lt;109.5</td>
</tr>
<tr>
<td>4</td>
<td>AX₂E₂ 4 bent</td>
<td>&lt;109.5</td>
</tr>
<tr>
<td>5</td>
<td>AX₄E 5 seesaw</td>
<td>&lt;120, &lt;90</td>
</tr>
<tr>
<td>5</td>
<td>AX₃E₂ 5 T-shaped</td>
<td>&lt;90</td>
</tr>
<tr>
<td>6</td>
<td>AX₃E₃ 5 linear</td>
<td>&lt;180</td>
</tr>
<tr>
<td>6</td>
<td>AX₄E₆ square pyramidal</td>
<td>&lt;90</td>
</tr>
<tr>
<td>6</td>
<td>AX₃E₄ 6 T-shaped</td>
<td>&lt;90</td>
</tr>
</tbody>
</table>

Lone pairs occupy more space as one moves down a column.

Coordination Complexes

CN is the number of ligands bonded to the metal ion.
d-count: group number – oxidation number

D-Orbitals

- dyz: on a 45° tilt with the y and z axes
- dxz: on a 45° tilt with the x and z axes
- dxy: on a 45° tilt with the x and y axes
- dz²: max amplitude along z, donut
- dx²-y²: on x and y axes

Crystal Field Theory

For Δ₀:

- dz² and dx²-y² are degenerate and positive (eg)
- dxy, dyz, dxz are degenerate and negative (t₂g)

High spin case: Δ₀ is small. Fill orbitals before pairing. I, Br, Cl

Low spin case: Δ₀ is large. Pair before going to next orbital. NH, CO, CN

Square planar: dx²-y², dxy, dz², (dxz, dyz)

Colors – Δ₀ = hc/λ. Colorless complexes have no d-d transitions. Red has big λ, little ν; purple has little λ, big ν.

For Δₚ:

- dz² and dx²-y² are degenerate and negative
- dxy, dyz, dxz are degenerate and positive


Kinetics

Rate laws: k[A]ⁿ. Actually raise concentration to the power.
The overall expression is the sum of the total exponents.
Units for $k$: mol$^{-(p-1)}$L$^{(p-1)}$s$^{-1}$ where $p$ is the sum of the exponents. But do the figuring so they give you credit.
First order kinetics:
\[ \ln[A] = -kt + \ln[A]_0 \] or \[ [A] = [A]_0 \ e^{kt} \]
half-life: \[ t_{1/2} = \ln 2 / k \]
To apply to radioactive decay: \[ N = Noe^{-kt} \] or, because \( A = kN \), \( A = Noe^{kt} \).
Second order kinetics:
\[ 1/[A] = 2kt + 1/[A]_0 \] and \( t_{1/2} = 1 / 2k[A]_0 \)
Remember molecularity.
Reaction mechanisms:
\[ K = \frac{k_1}{k_{-1}}. \] If $K<1$, then $k_1<k_{-1}$.
Get rid of intermediates by noting fast and slow steps or by steady state approximation.
Steady state approximation: $\Delta[A] = 0$. All steps which form – all steps which use up = 0.
Temperature: \[ \ln k = -E_a/RT + \ln A \]
\[ \Delta \ln k = -(E_a/R)(1/T_2 - 1/T_1) \] (like Van’t Hoff)
Michaelis-Menten Equation: \[ k_2[ES] = k_2[E]_0[S] / ([S] + K_m) \]
ES is bound enzyme, $E_0$ is total enzyme, $S$ is substrate
Maximal rate \( V_{max} = k_2[E]_0 \). $K_m \equiv [S]$ for which rate is $\frac{1}{2} V_{max}$. 