

5.111 Study Sheet – Final Exam, 12-18-02

Steric Numbers and Molecular Geometry

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

Without lone pairs:

2	linear	180
3	trigonal planar	120
4	tetrahedral	109.5
5	trigonal bipyramidal	120, 90
6	octahedral	90

With lone pairs:

AX ₂ E	3	bent	<120
AX ₃ E	4	trigonal bipyramidal	<109.5
AX ₂ E ₂	4	bent	<109.5
AX ₄ E	5	seesaw	<120, <90
AX ₃ E ₂	5	T-shaped	<90
AX ₂ E ₃	5	linear	<180
AX ₅ E	6	square pyramidal	<90
AX ₄ E ₂	6	square planar	90
AX ₃ E ₃	6	T-shaped	<90
AX ₂ E ₄	6	linear	180

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	Note: shade negative
dxy	on a 45° tilt with the x and y axes	
dz ²	max amplitude along z, donut	
dx ² -y ²	on x and y axes	

Crystal Field Theory

For Δ_o : dz² and dx²-y² are degenerate and positive (eg)
dxy, dyz, dxz are degenerate and negative (t_{2g})

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

Low spin case: Δ_o is large. Pair before going to next orbital. NH₃, CO, CN⁻

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

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

For Δ_T : dz² and dx²-y² are degenerate and negative
dxy, dyz, dxz are degenerate and positive *high spin

Unpaired electrons: paramagnetic. Very counterintuitive.

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 : $\text{mol}^{-(p-1)}\text{L}^{(p-1)}\text{s}^{-1}$ where p is the sum of the exponents. But do the figuring so they give you credit.

First order kinetics:

$$\ln[A] = -kt + \ln[A]_0 \text{ or } [A] = [A]_0 e^{-kt}$$

$$\text{half-life: } t_{1/2} = \ln 2 / k$$

To apply to radioactive decay: $N = N_0 e^{-kt}$ or, because $A = kN$, $A = A_0 e^{-kt}$.

Second order kinetics:

$$1/[A] = 2kt + 1/[A]_0 \text{ and } t_{1/2} = 1 / 2k[A]_0$$

Remember molecularity.

Reaction mechanisms:

$$K = k_1/k_{-1}. \text{ If } K > 1, \text{ then } k_1 > k_{-1}.$$

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: $\ln k = -E_a/RT + \ln A$

$$\Delta \ln k = -(E_a/R)(1/T_2 - 1/T_1) \text{ (like Van t'Hoff)}$$

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 $1/2 V_{\max}$.