relationship between M to LG bond strength + rate

Kinetics

$k = Ae^{-E_a/RT}$

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

Thermodynamics

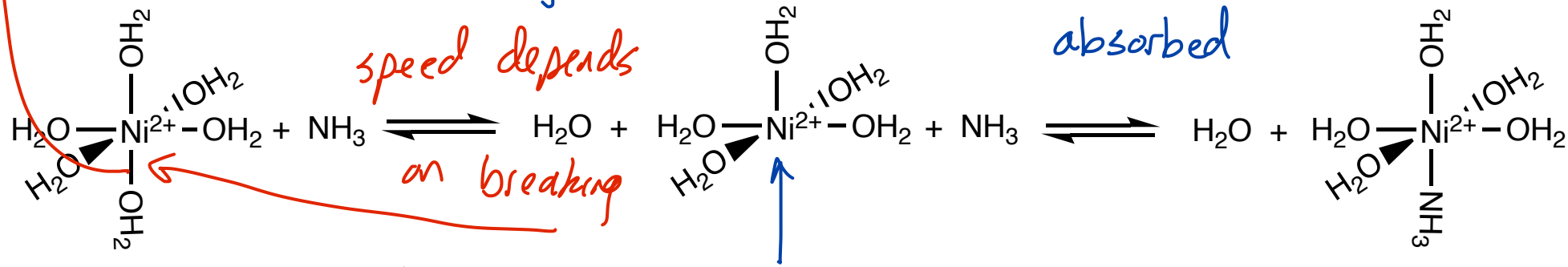
$\Delta G° = \Delta H° - T\Delta S°$ and $\Delta G° = -RT ln K$

and $ln K = -\Delta H°/(RT) + \Delta S°/R$

If A and $\Delta S°$ are nearly constant, and E_a depends on $\Delta H°$ then a plot of ln k vs ln K should be linear

change in entropy

heat released or absorbed



Charge LG slightly

Cl^-, Br^-, I^-

lost the ligand to metal bond

the strong the bond the harder it is for the reaction to proceed which means the slower it will go

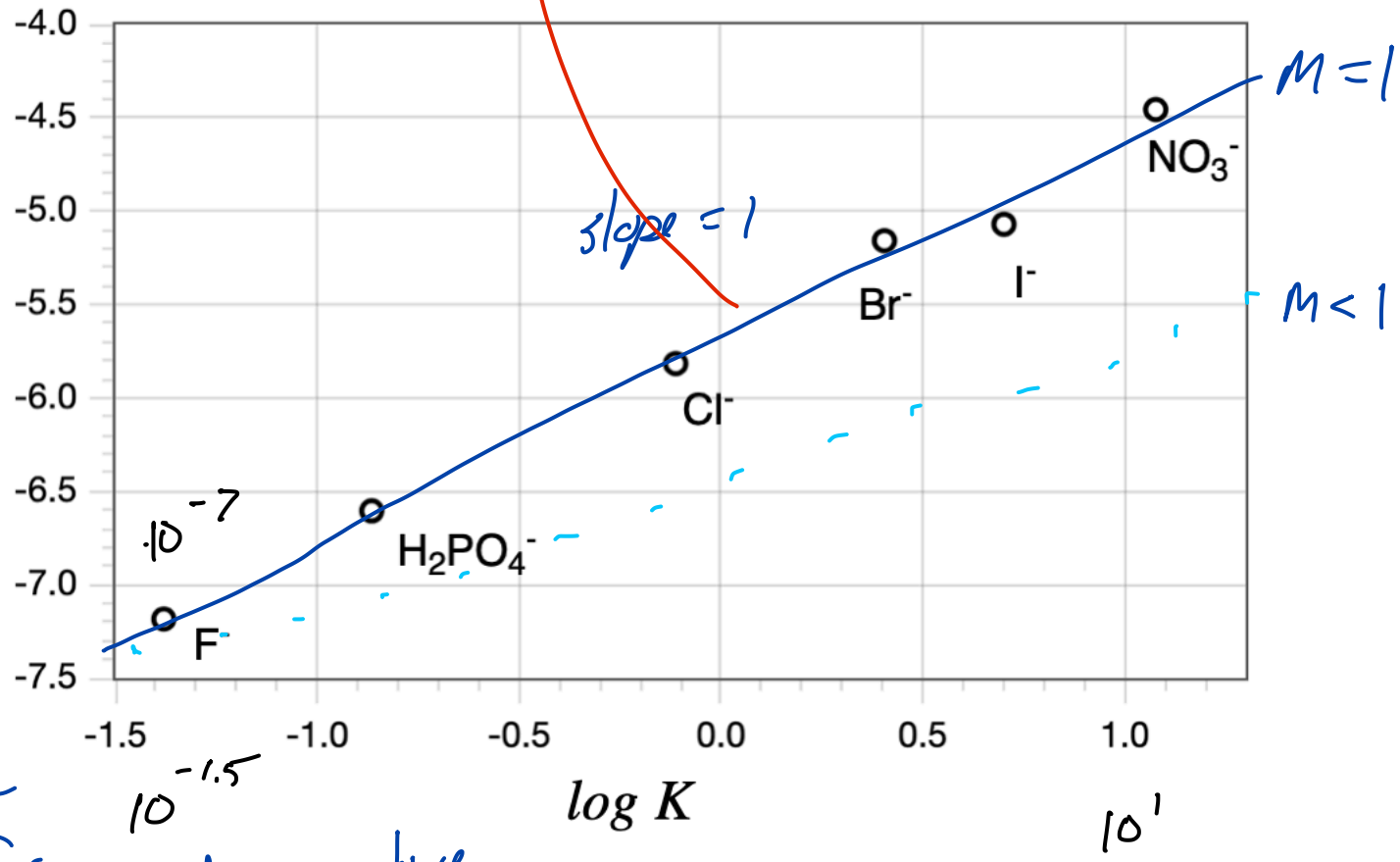
As K gets larger k becomes smaller

straight line with a slope of 1... then this is a strong relationship between the strength of the bond & the rate and evidence for a dissociative rxn

a slope of 1 ... strong correlation between strength of LG bond & rate

$k = 10^{-4}$

$[Co(NH_3)_5X]^{+2} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{+3} + X^-$



10^{-7}

$10^{-1.5}$

10^{1}

Kathryn Hass, https://chem.libretexts.org/@api/deki/files/411156/clipboard_eef3275a6c324cc18958d9f3fb43136a1.png?revision=1&size=bestfit&width=666&height=468 accessed 11/2025.

evidence

Ligand... incoming ligand

LG ... leaving group

Associative Mechanisms

H_2O

LG

Incoming Ligand	Rate Constants for Reactions with indicated Metal Complex[1]	
	$[Cr(H_2O)_6]^{3+}$ k (10^{-8} M^{-1} s^{-1})	$[Cr(NH_3)_5(H_2O)]^{3+}$ k (10^{-4} M^{-1} s^{-1})
NCS^-	180	4.2
NO_3^-	73	no data
Cl^-	2.9	0.7
Br^-	1.0	3.7
I^-	0.08	no data
CF_3COO^-	no data	1.4

much slower

only 12% slower

k change dramatically with changing incoming ligand

k are similar... within an order of magnitude

* Incoming ligand is participating in the formation of the transition state because we see a large change in rate with change in incoming ligand

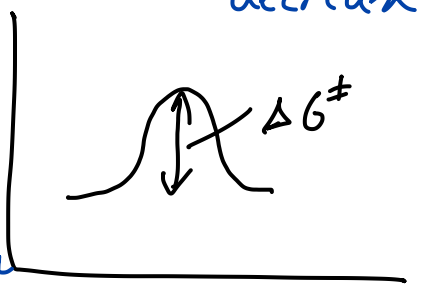
constant with a dissociative mechanism

[1]Data from Miessler and Tarr, Inorganic Chemistry 4th Ed, page 455

how does entropy relate to associative & decrease

$\Delta S^{\circ\ddagger}$?

dissociative mechanisms ↑ increase



‡ means transition state

$$M-X + Y \longrightarrow [\,Y\cdots M\cdots X\,]^{\ddagger} \longrightarrow M-Y + X$$

more ordered

or

less ordered than

$\Delta S^{\ddagger} < 0$ neg

S of transition state is lower than S of reactions

$\Delta V^{\ddagger}$ associative $2 \rightarrow 1$ $\Delta V^{\ddagger} < 0$

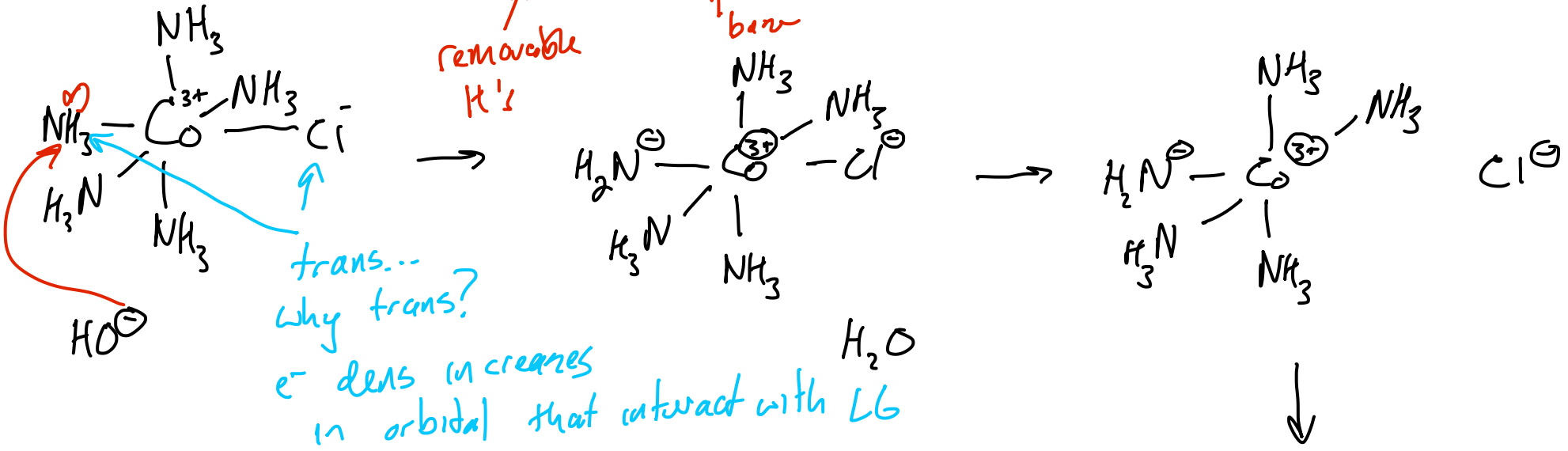
$\Delta V^{\ddagger}$ dissociative $2 \rightarrow 3$ $\Delta V > 0$

similarity to associative

aqueous

rate = k [M][OH]

$[Co(NH_3)_5Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH] + Cl^-$

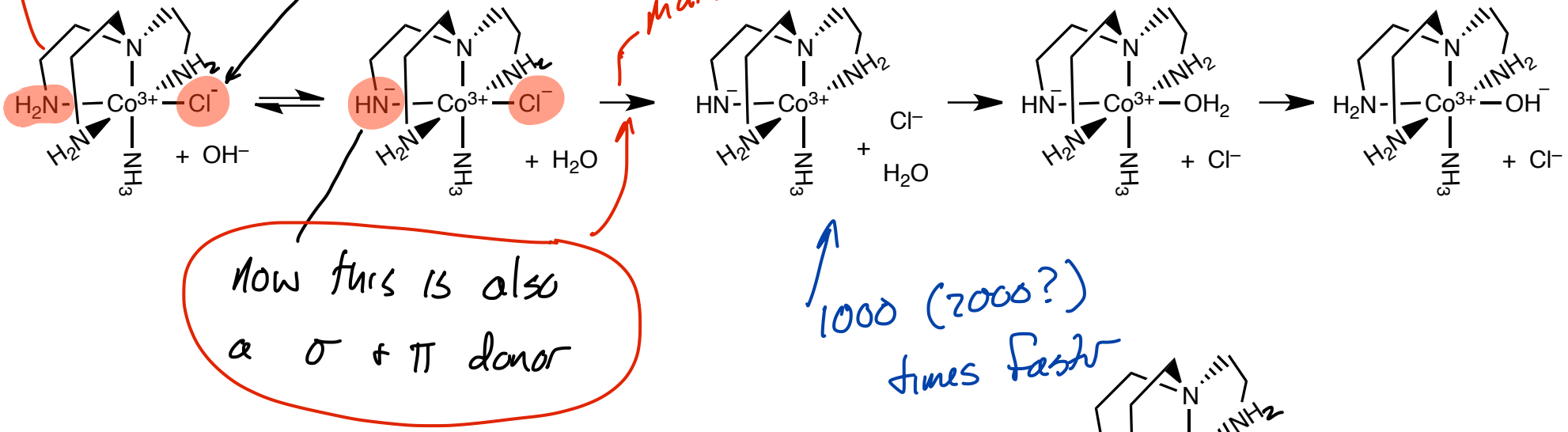


S_N1CB conjugate base

removable H's trans to LG

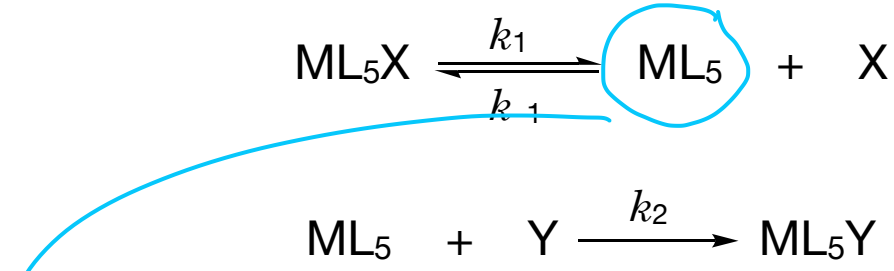
Support for an S_N1CB Mechanism

Section 12.4



no removable H trans to LG

new gets the speed boost



intermediate forms and is consumed

(must be able to see or trap the intermediate)

assuption is that ML_5 forms as quickly as it is consumed

Mechanisms make predictions ...

Mechanisms predict the kinetics ... the rate law

$ML_5X + Y \rightarrow ML_5Y + X$

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

assuming $k_2 >> k_{-2}$

change in conc of ML_5Y

change in time

$$\text{reaction rate} = \frac{d[ML_5Y]}{dt} = k_2[ML_5][Y]$$

actual exponent must be determined experimentally

the rate at which ML_5 forms = rate at which it is consumed

rate formation

$$k_1[ML_5X] = k_{-1}[ML_5][X] + k_2[ML_5][Y]$$

rate of formation = rate of consumption

$$k_1[ML_5X] = k_{-1}[ML_5][X] + k_2[ML_5][Y]$$

rate of formation = rate of consumption

$$k_1[ML_5X] = \left(k_{-1}[X] + k_2[Y]\right)[ML_5]$$

$$\frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]} = [ML_5]$$

$$\text{rate} = \frac{k_2 \, k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]} = \frac{d[ML_5Y]}{dt}$$

initial rate $[X] = 0$ $\quad \text{rate} = \dfrac{k_2 k_1[ML_5X][Y]}{k_2[Y]}$ $\quad 1[Y]^0$

rate forward / rate backward = equilibrium

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y{\bullet}ML_5X$$

$$YML_5{\bullet}X \xrightarrow{k_2} ML_5Y$$

$$\frac{d[ML_5Y]}{dt} = \frac{k_1K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

where $[M]_0$ is the total amount of metal complex present and initially

$[M]_0 = [ML_5X] + [Y{\bullet}ML_5X]$

$[Y]_0$ is approximately = $[Y]$

and $K_1 = k_1/k_{-1}$

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Y \cdots ML_5 \cdots X]^{\ddagger} \xrightarrow{k_2} YML_5 + X$$

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} YML_5X$$

$$YML_5X \xrightarrow{k_2} ML_5Y + X$$

intermediate forms must be observed or trap it. otherwise it could be I_a

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1} + k_2}$$

dependence on different species

Associative Reaction

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1} + k_2}$$

always 1st order with respect to [Y]

Interchange

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 K_1 [M]_0 [Y]_0}{1 + K_1[Y]_0}$$

as [Y] goes from dilute to concentrated order with respect to [Y] goes from 1 to less than 1

$1 + 0.001$

$1 + 1$

intermediate between 1st and 0 order in $[Y]_0$

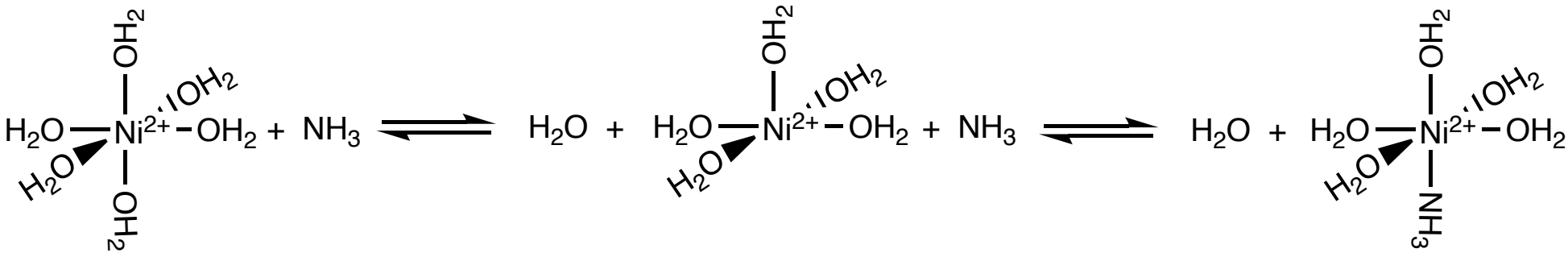
Dissociative

$$\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

↑ [X] (LG) slows rate

initial rate is zero order with respect to [X] and [Y]

adding X to the reaction will slow the initial rate



Oh

square pyramidal

LFSE ↑ ligand field stabilization energy

LFSE = activation energy

Oxidation state

High oxidation state — slower

+3 attracts ligand more strongly

LG has a harder time leaving

Low Oxidation State — faster

+1 attracts ligand less strongly

Size of Ion

Smaller Ion — slower

+2 strong attraction

Larger Ion

+2 less attraction

1. Rate of reaction changes only slightly with changes in incoming ligand
2. Making metal reactant charge more positive slows rate
3. Bulky ligands increase rate
4. Rate of reaction correlates with metal to leaving group bond strength
5. Activation entropies are favorable

for example

$:PMe_3$ vs $:PEt_3$ vs $:P\phi_3$

or

$:NH_3$ vs $:NH_2CH_3$ vs $:NH_2CH_2CH_3$