(33) **Today**

Chap 12.4 and 12.5

Next Class (34)

Chap 12.5 and 12.7

(35) **Second Class from Today**

Chap 12.5 and 12.7

Third Class from Today (36)

Test 3

Kinetics

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

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

Thermodynamics

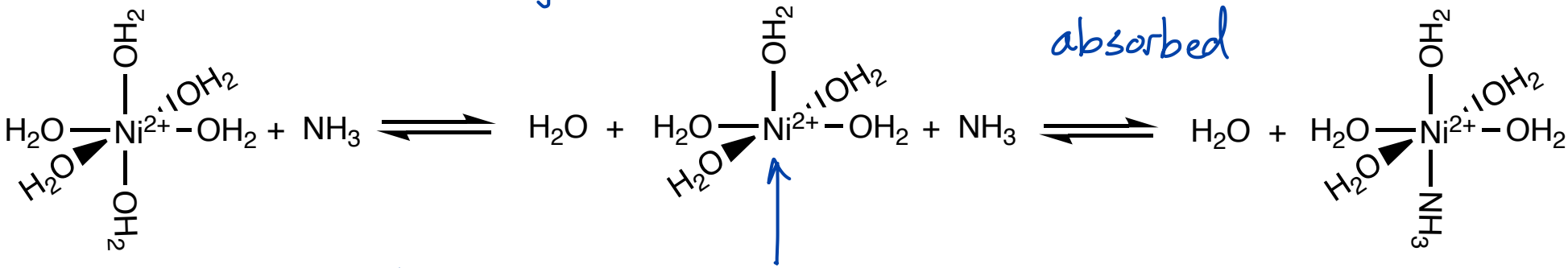
$\Delta G° = \Delta H° - T\Delta S°$ and $\Delta G° = -RT ln K$

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

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



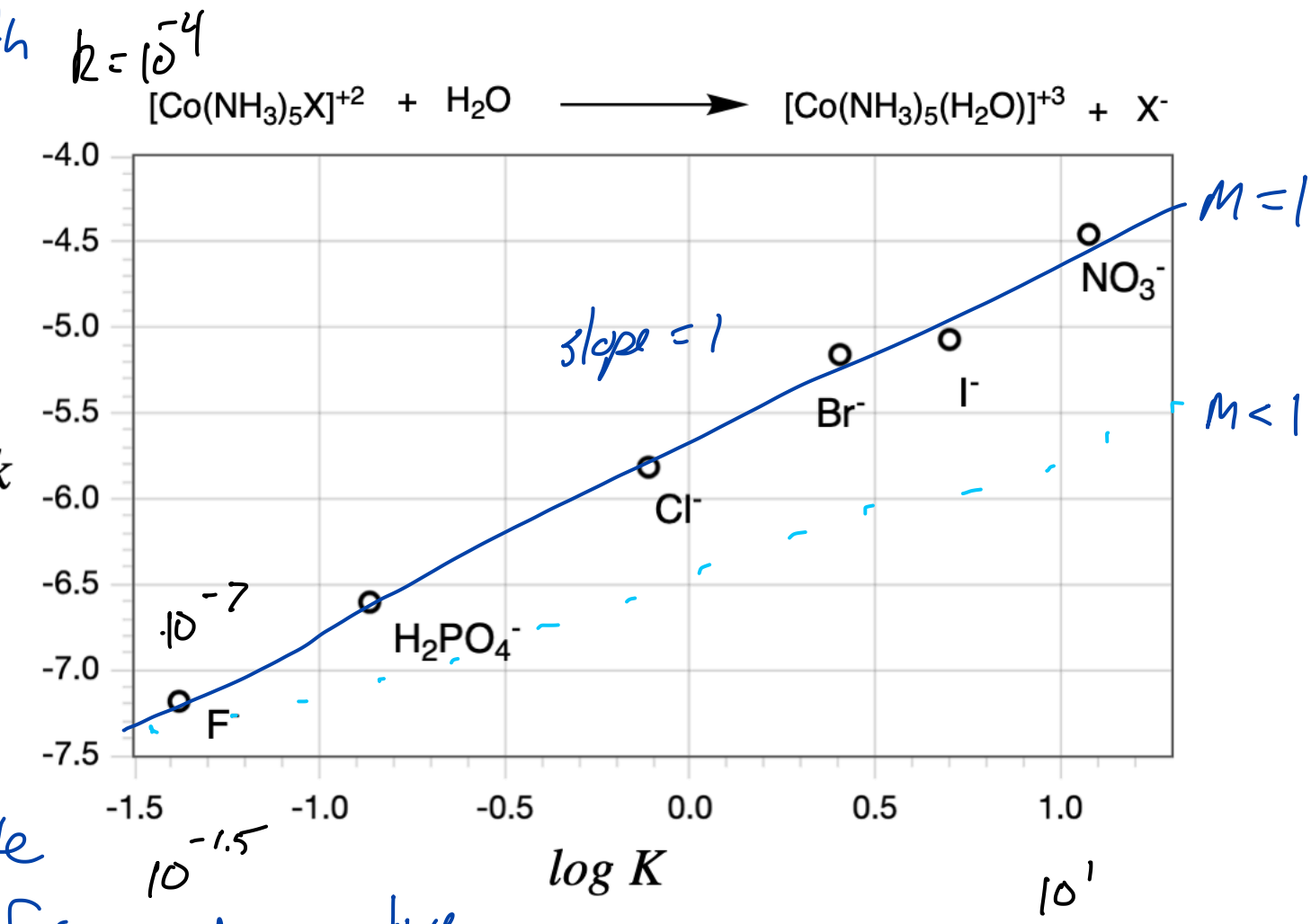
Charge LG slightly Cl^-, Br^-, I^-

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



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

Ligand... incoming ligand

LG ... leaving group

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

H_2O

LG

much slower

only 12% slower

k change dramatically with changing incoming ligand

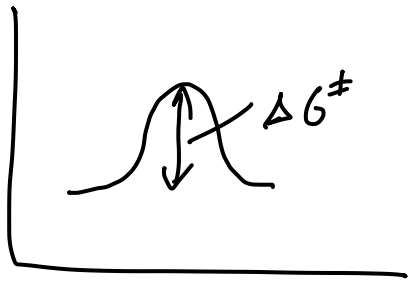
k are similar... within an order of magnitude

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

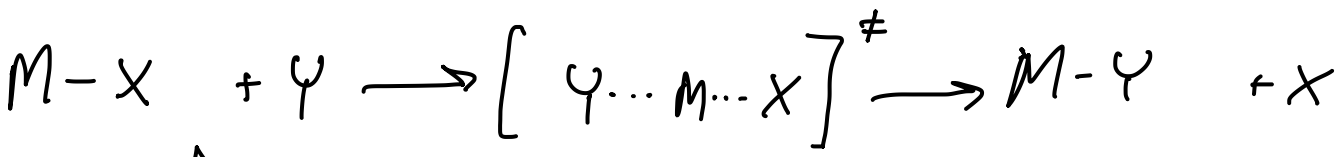
constant with a dissociative mechanism

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

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



‡ means transition state



more ordered

or

less ordered

than

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

S of transition state is lower than S of reactions

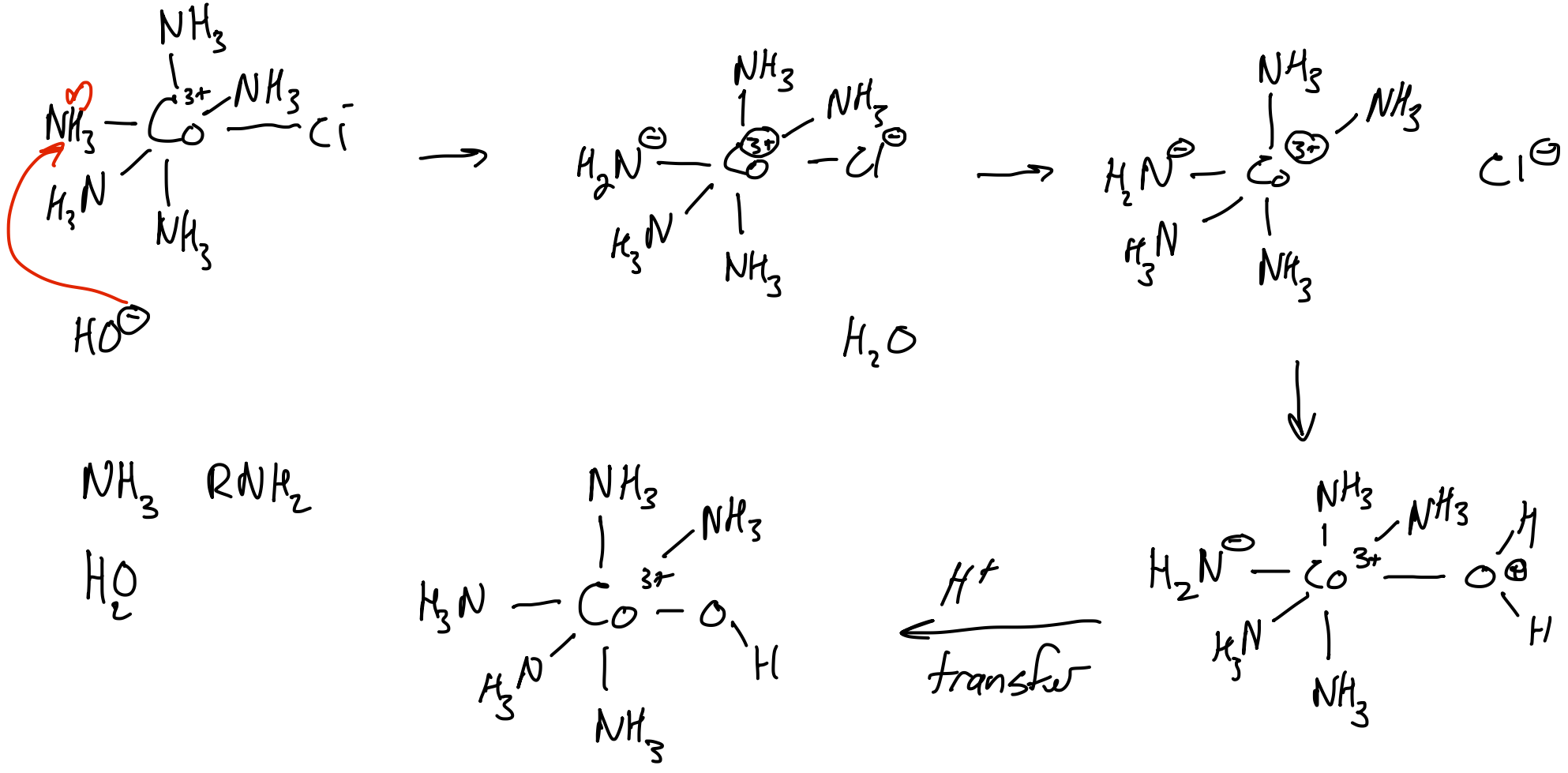
$\Delta V^{\ddagger}$ associative $2 \rightarrow 1$ $\Delta V^{\ddagger} < 0$

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

aqueous

rate = k [M][OH]

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



NH_3 RNH_2

H_2O

S_N1CB conjugate base

Support for an S_N1CB Mechanism