Last section of the course!

- Thus far we have learned a lot about the symmetry of metal complexes and how that relates to the properties and bonding of these complexes
- Further, we have learned about how different types of ligands can influence the properties of these metal complexes

- Now we will look into on what metal complexes can do!
    - ligand subsitution reactions, redox reactions, catalytic cycles (organometallic chemistry), biological functions

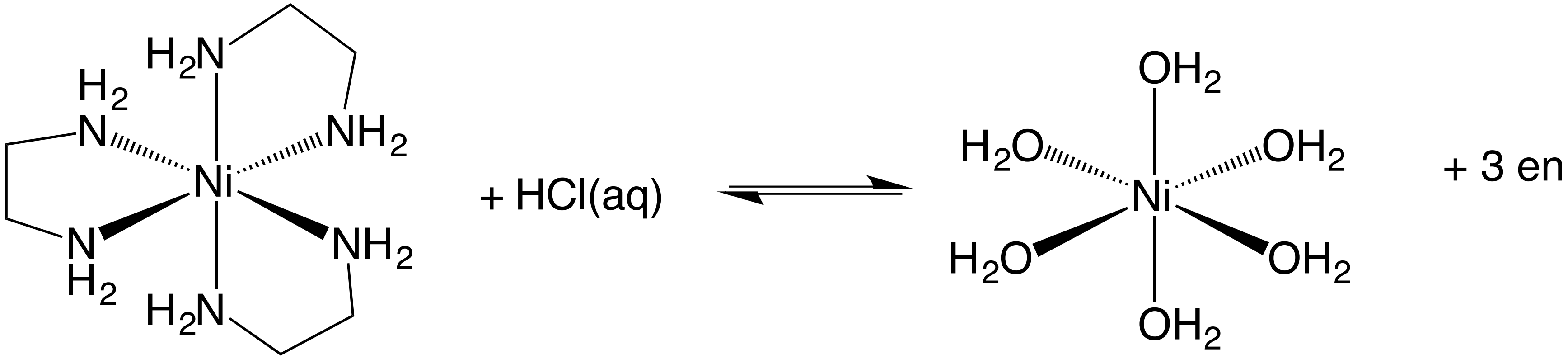
LIGAND SUBSTITUTION REACTIONS IN COORDINATION COMPOUNDS

CH431

MFT Ch 12

Ligand substitution reactions

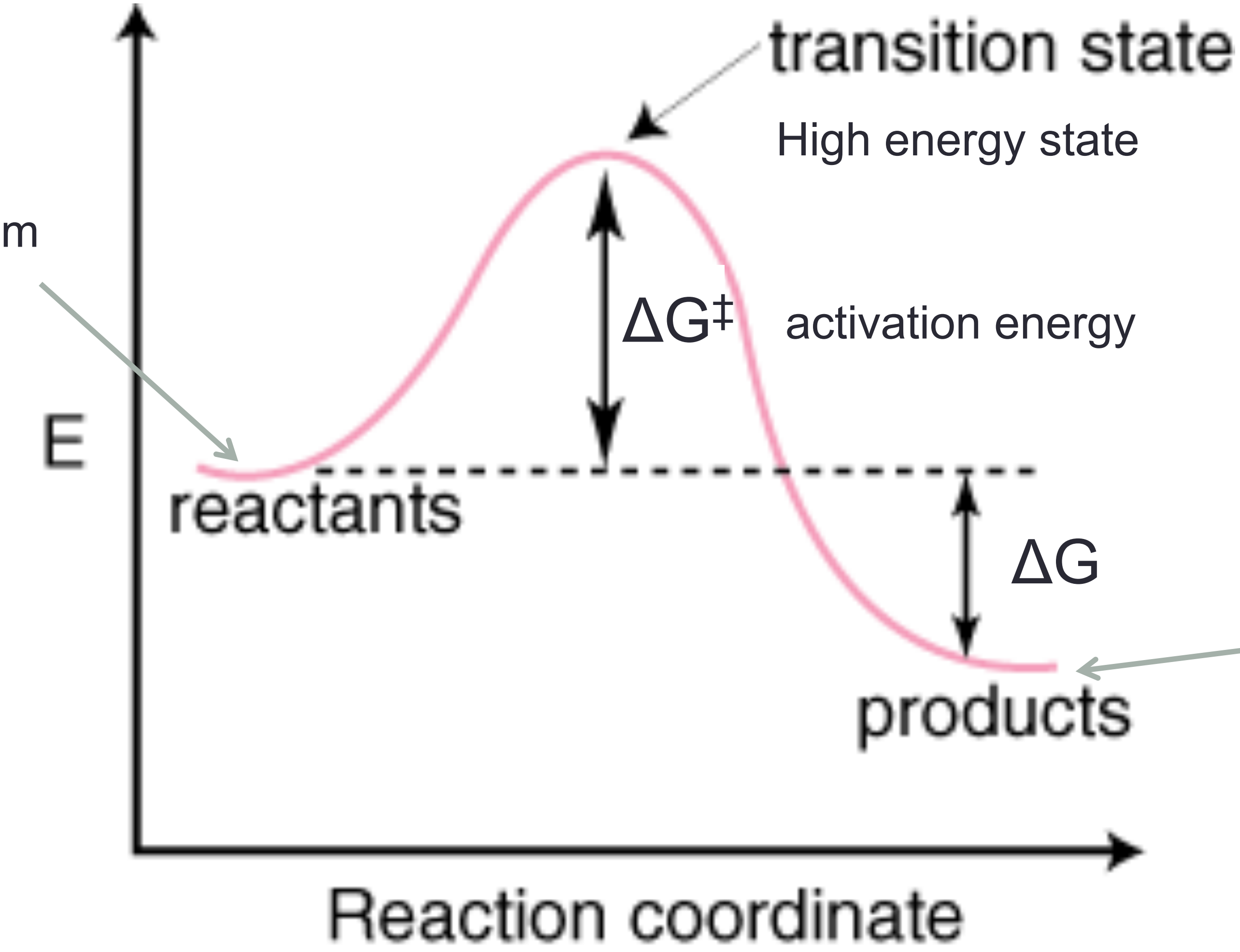
- Ligand substitution is an important step in many reactions of coordination complexes
- Case Study 1: exchange of ethylene diamine (en) and water ligands on Ni^{2+}



https://www.youtube.com/watch?v=HXWkQOh5rZQ

Note: Ni^{2+} complex reacts quickly, but corresponding Co^{3+} complex reacts very slowly!

Reaction coordinate diagram



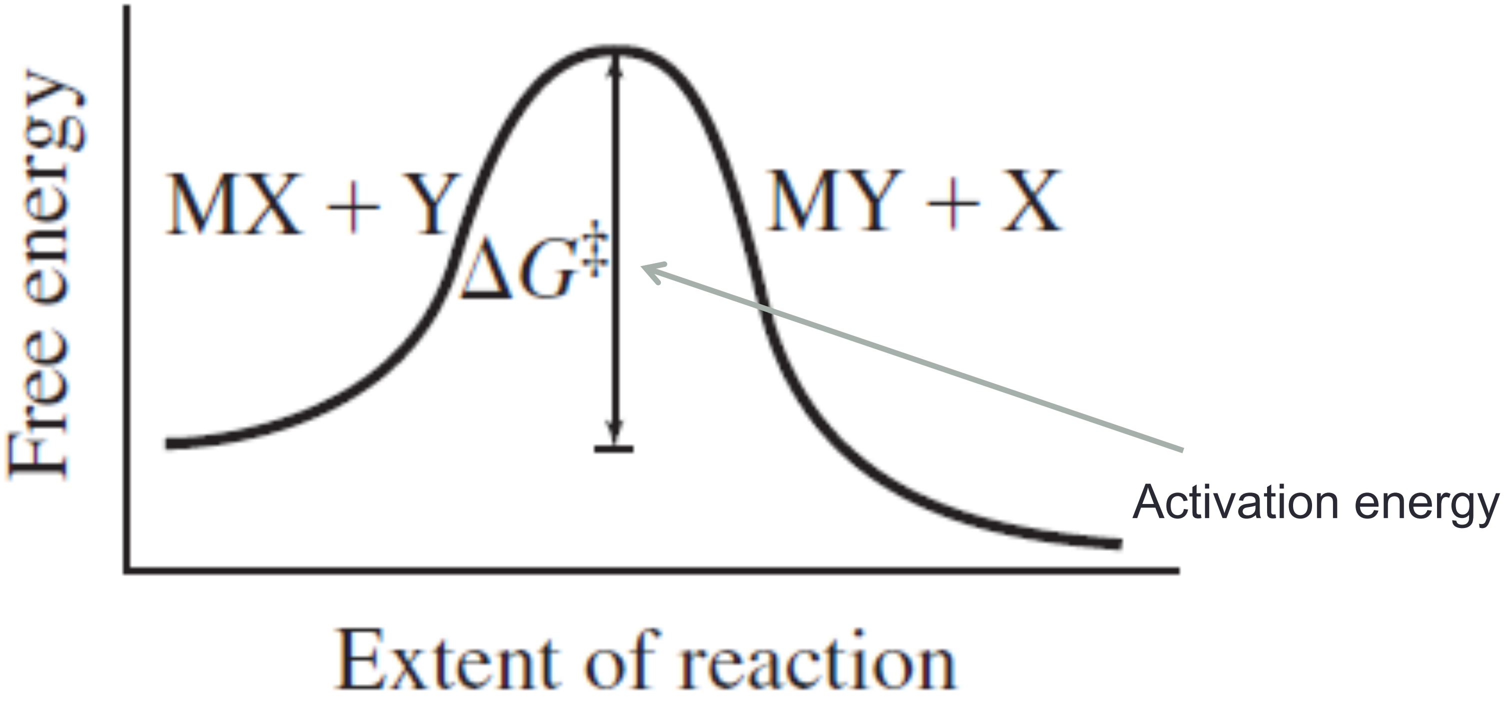
Energy minimum

High energy state

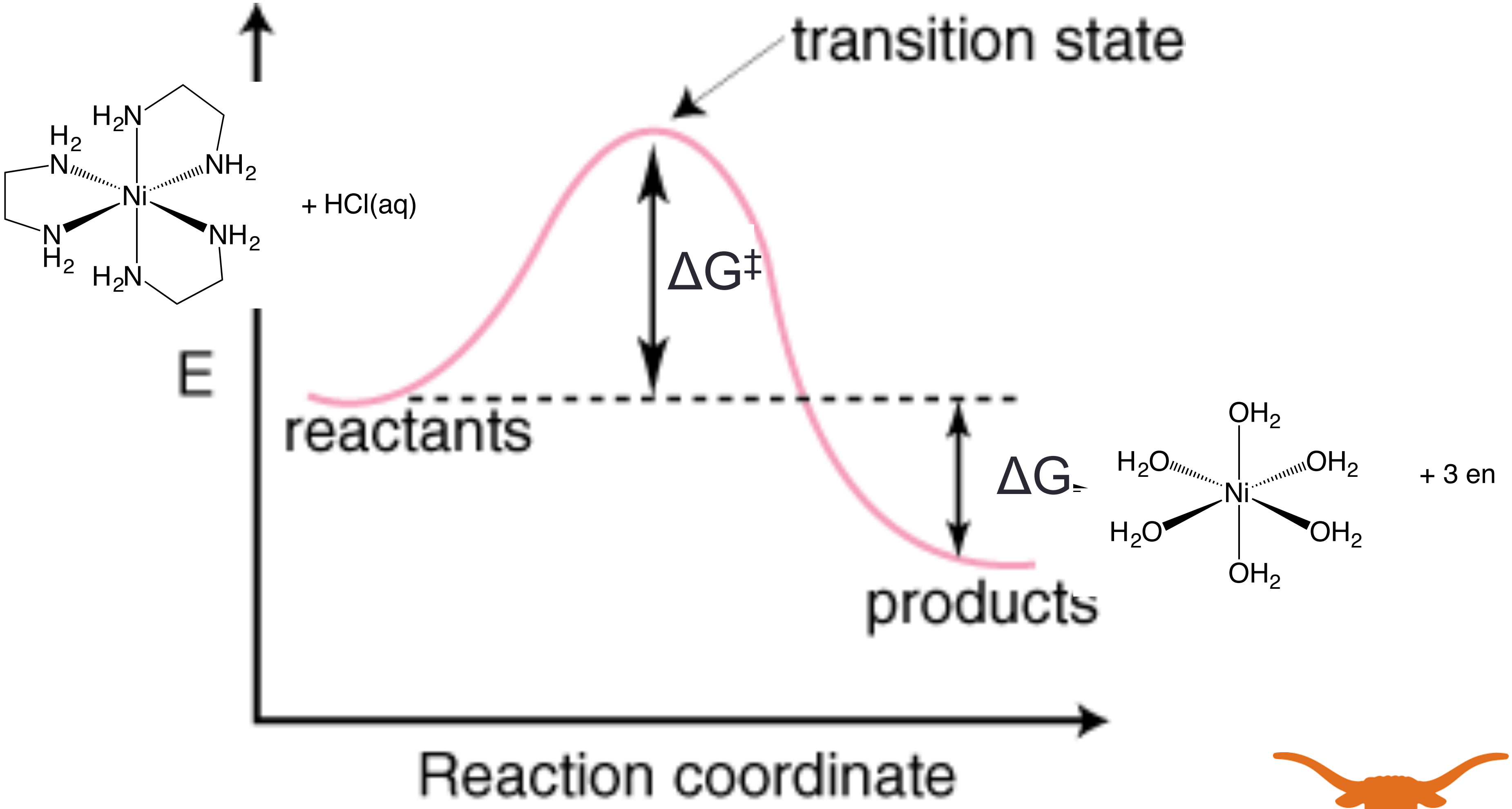
activation energy

Energy minimum

Reaction coordinate for ligand substitution



Reaction coordinate diagram

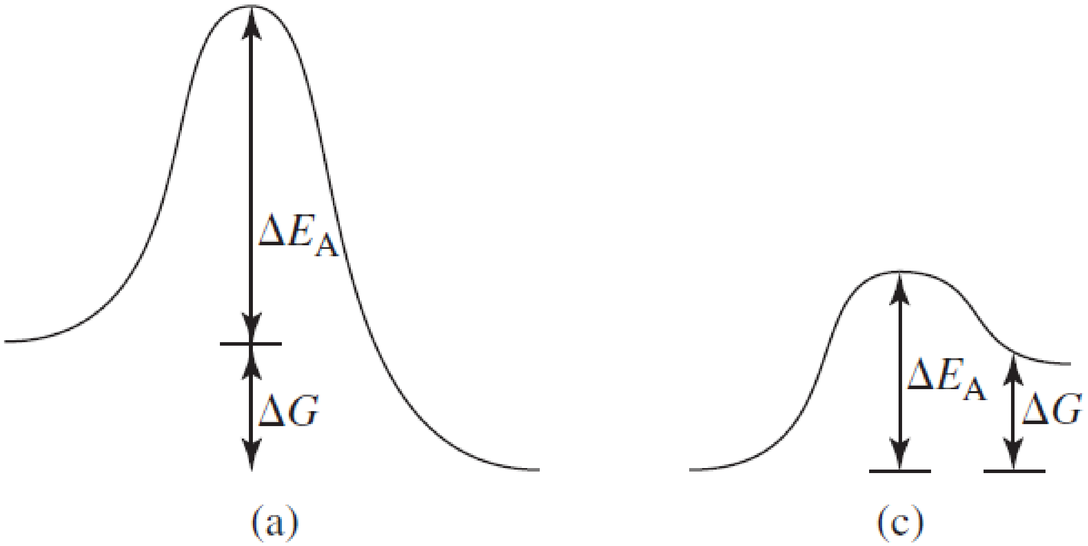


Vocabulary for reaction kinetics

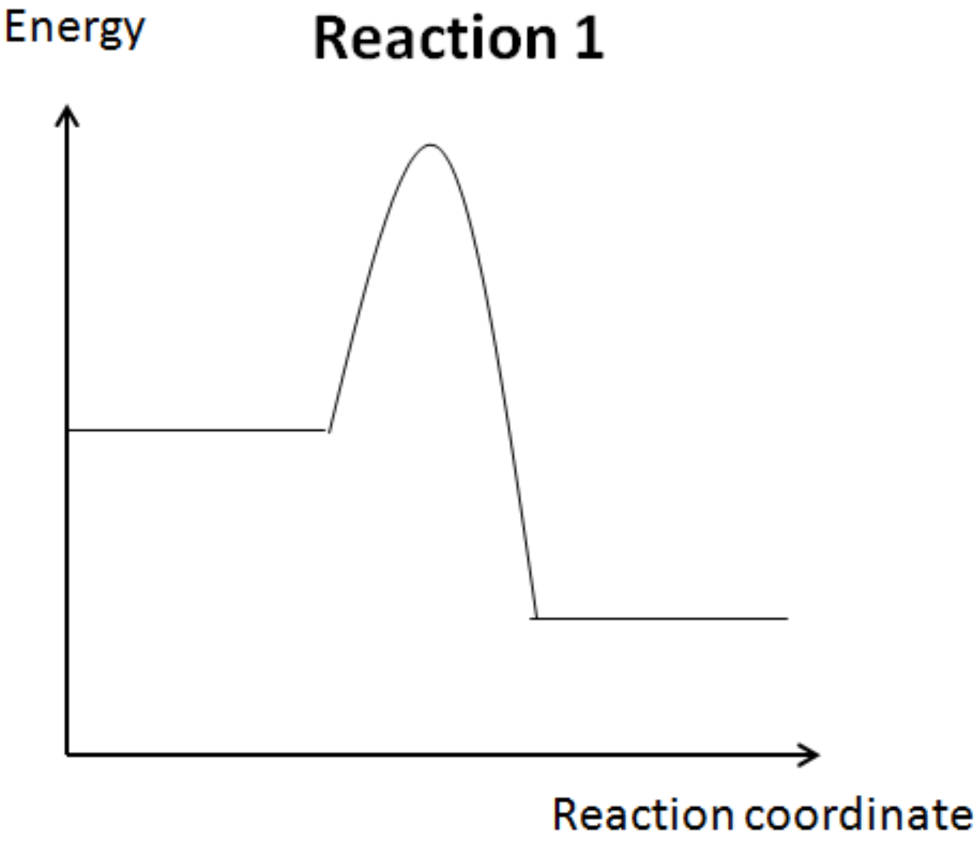
- **ΔG**: overall free energy change of a reaction (difference in free energy of reactants and products)
  - Thermodynamically favorable reactions: **$\Delta G < 0$**
  - Thermodynamically unfavorable reactions: **$\Delta G > 0$**

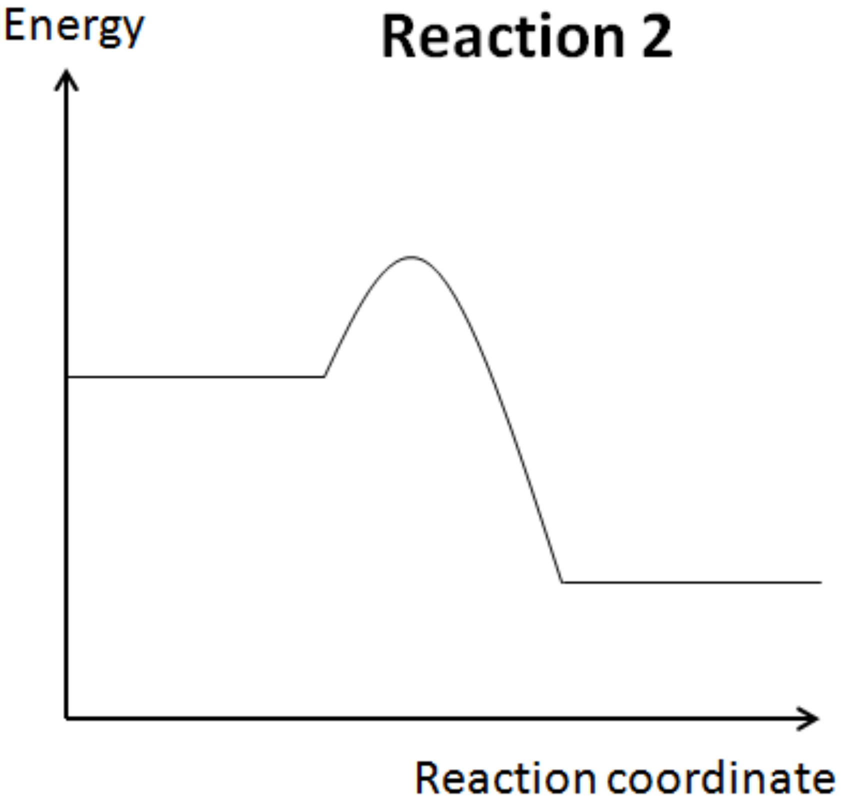
- **Rate constant**: constant that describes how quickly a reaction proceeds
- **$\Delta G^\ddagger$** : free energy of activation, composed of the enthalpy (**$\Delta H^\ddagger$**) and entropy (**$\Delta S^\ddagger$**) of activation.

- Reaction rate (kinetics) depends on **$\Delta G^\ddagger$** and not **ΔG**
- Equilibrium constant (thermodynamics) depends on **ΔG**

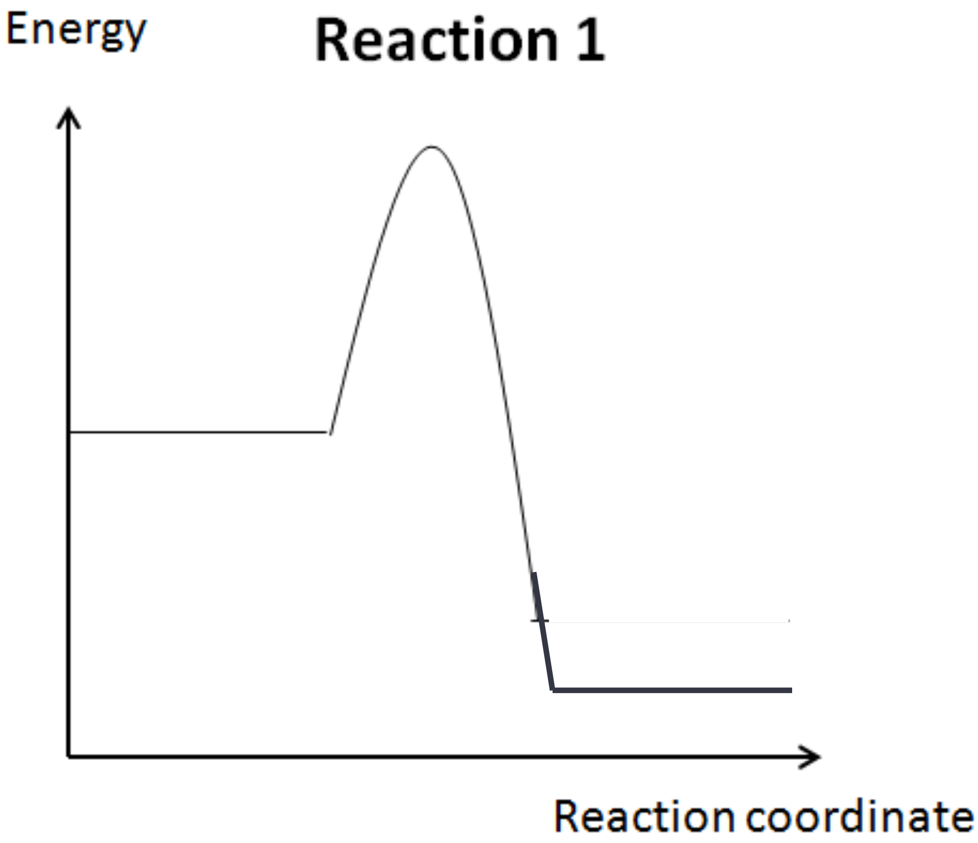


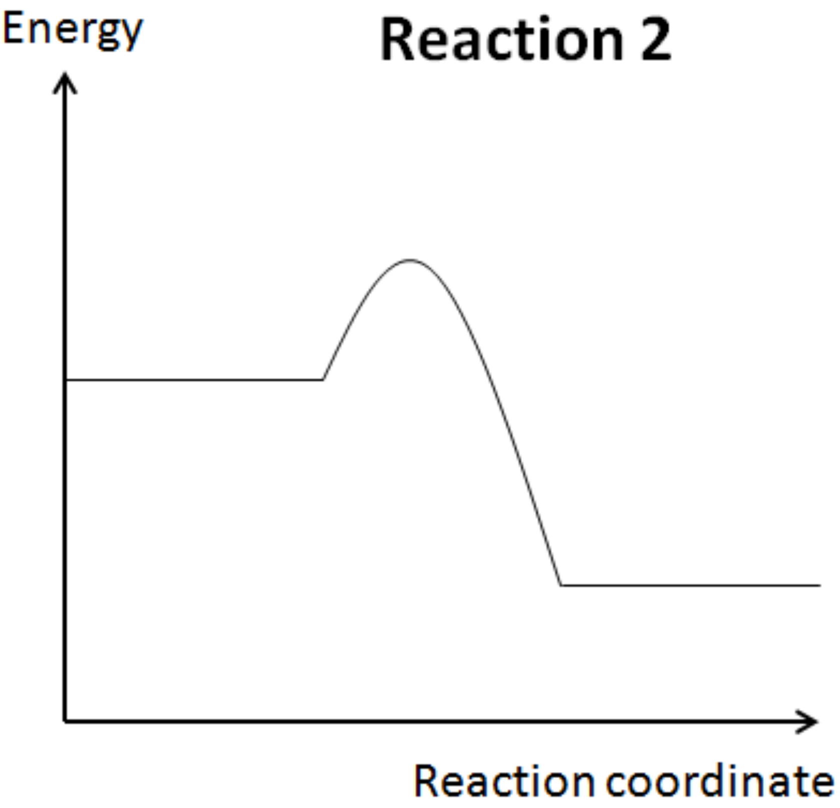
Which of these reactions is thermodynamically favorable?



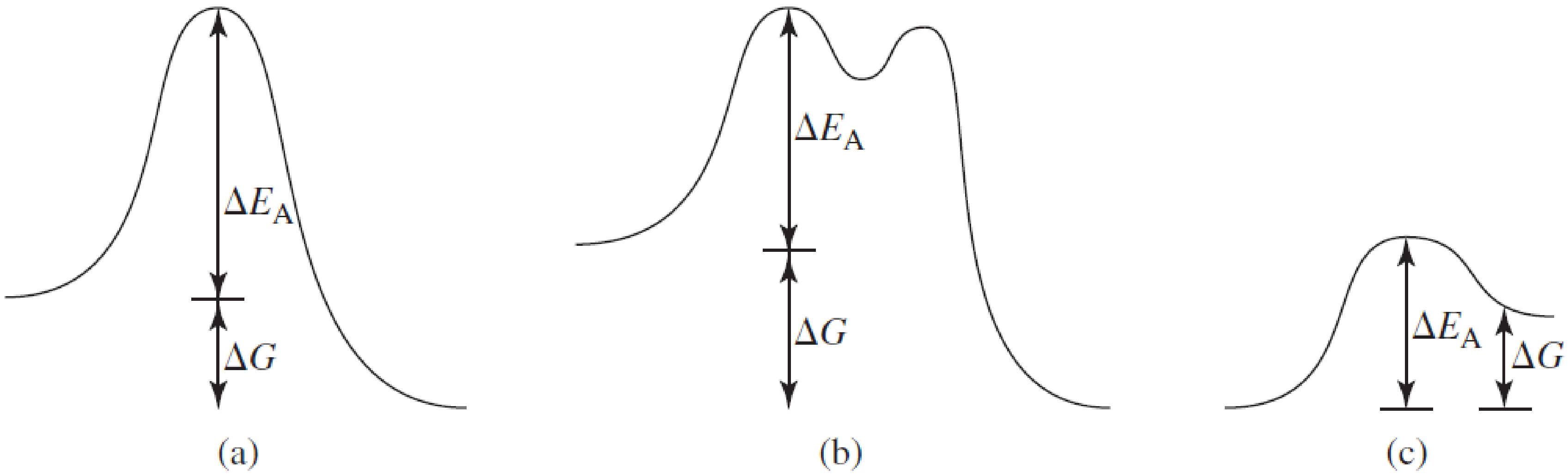


Which of these reactions is faster?





Which of these reactions is faster?
Which of these reactions is more thermodynamically favorable?

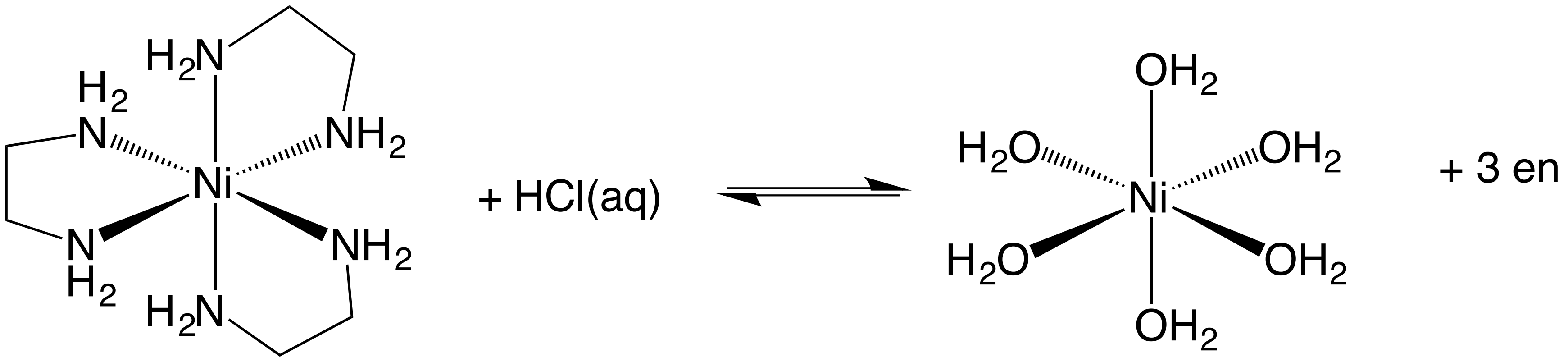


A. Large equilibrium constant (ΔG < 0). Reaction is slow (kinetics slow) due to large $\Delta G^\ddagger$

B. Large, positive equilibrium constant (ΔG < 0). Reaction is slow due to large $\Delta G^\ddagger$. Reaction has an intermediate.

C. Small equilibrium constant (ΔG > 0). Reaction is fast because $\Delta G^\ddagger$ is small

Ligand substitution reactions



- Both the Ni^{2+} and the Co^{3+} reactions are thermodynamically favorable, but the Ni^{2+} reaction happens instantaneously whereas the Co^{3+} reaction requires weeks to complete

- What do the reaction coordinate diagrams look like for the Ni^{2+} and Co^{2+} reactions?

Case Study 2: Water exchange in metal hexaqua complexes

$$[M(H_2O)_6]^{n+} + H_2O \rightleftharpoons [M(H_2O)_5(H_2O)]^{n+} + H_2O$$

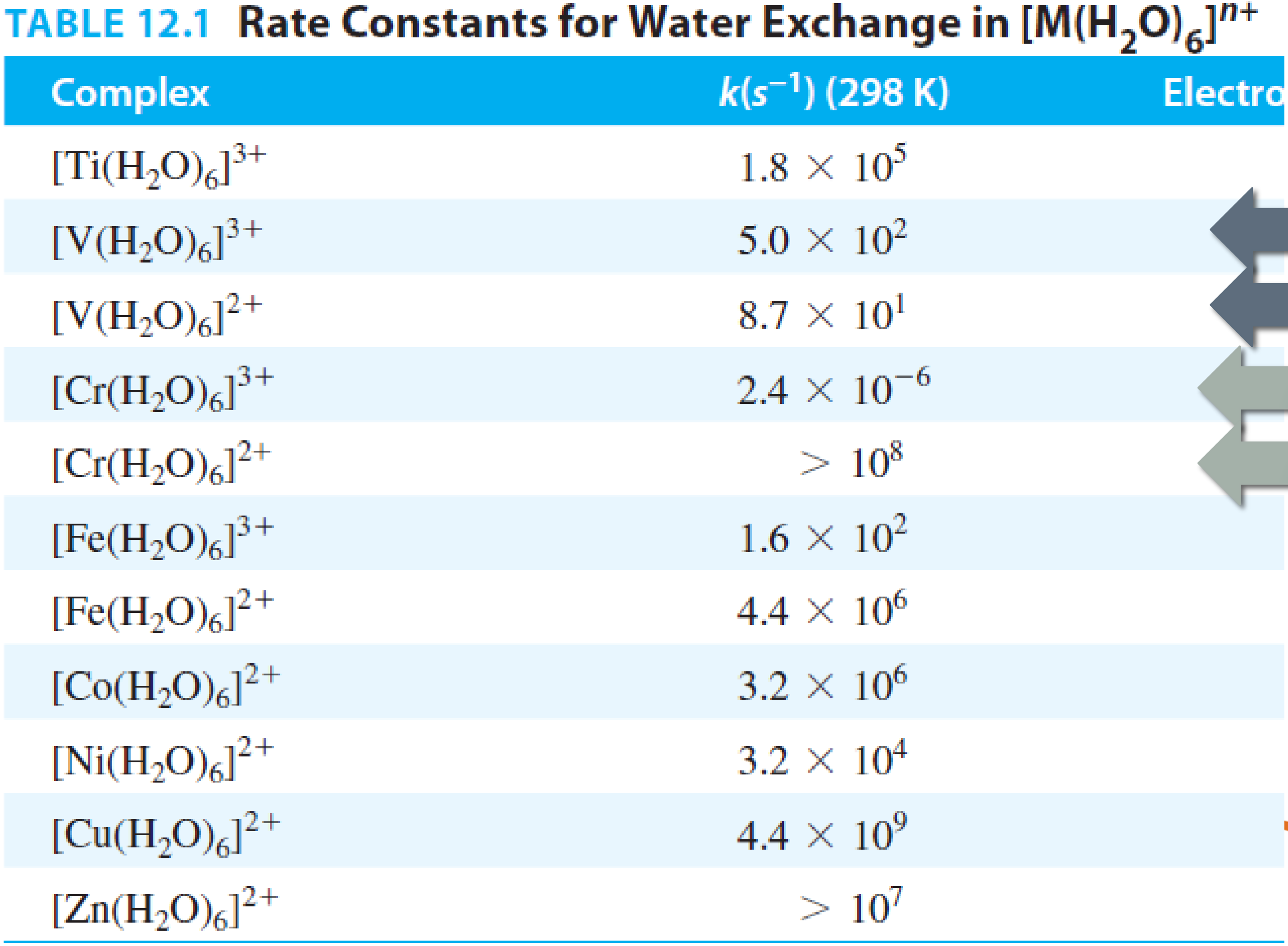


TABLE 12.1 Rate Constants for Water Exchange in $[M(H_2O)_6]^{n+}$

Complex	$k(s^{-1})$ (298 K)	Electro
$[Ti(H_2O)_6]^{3+}$	1.8×10^5	
$[V(H_2O)_6]^{3+}$	5.0×10^2	
$[V(H_2O)_6]^{2+}$	8.7×10^1	
$[Cr(H_2O)_6]^{3+}$	2.4×10^{-6}	
$[Cr(H_2O)_6]^{2+}$	$> 10^8$	
$[Fe(H_2O)_6]^{3+}$	1.6×10^2	
$[Fe(H_2O)_6]^{2+}$	4.4×10^6	
$[Co(H_2O)_6]^{2+}$	3.2×10^6	
$[Ni(H_2O)_6]^{2+}$	3.2×10^4	
$[Cu(H_2O)_6]^{2+}$	4.4×10^9	
$[Zn(H_2O)_6]^{2+}$	$> 10^7$	

faster

slower

slow

fast

What contributes to the rate of ligand exchange reactions?

- $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{2+}$ reaction rates differ by 13 orders of magnitude!

- $[Cr(H_2O)_6]^{3+}$ rate is very slow ($\sim 10^{-6}$ s^{-1}): this complex is **kinetically inert** (slow exchange rate)

- $[Cr(H_2O)_6]^{2+}$ rate is very fast($> 10^{8}$ s^{-1}): this complex is **kinetically labile** (fast exchange rate)

- **Inert and labile** are kinetic terms.
- Should not be confused with **stable** and **unstable**: these terms refer to the thermodynamic stability of a complex

What's the difference between octahedral Cr^{2+} and Cr^{3+}?

- Electronic configuration!
- Cr^{2+}: $t_{2g}^{3}\ e_{g}^{1}$
- Cr^{3+}: $t_{2g}^{3}\ e_{g}^{0}$

- Cr^{3+} has no d electrons in e_g orbitals, LFSE is large, perturbations in coordination environment result in less negative LSFE, making ligand substitution reactions slow.

- Generally, complexes with very negative LFSE are **inert**, complexes with less negative LFSE are **labile**

$$[M(H_2O)_6]^{n+} + H_2O \rightleftharpoons [M(H_2O)_5(H_2O)]^{n+} + H_2O$$

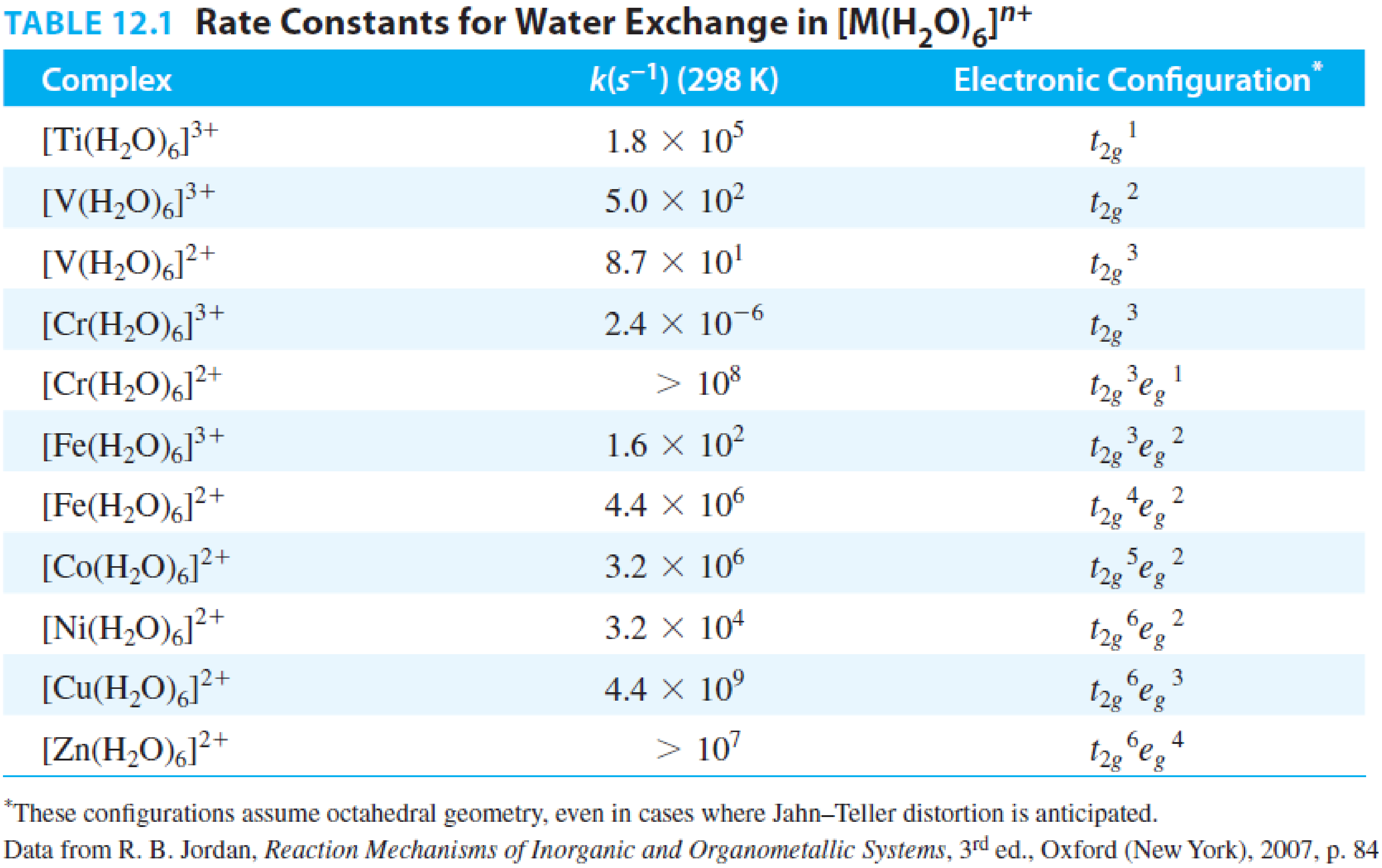


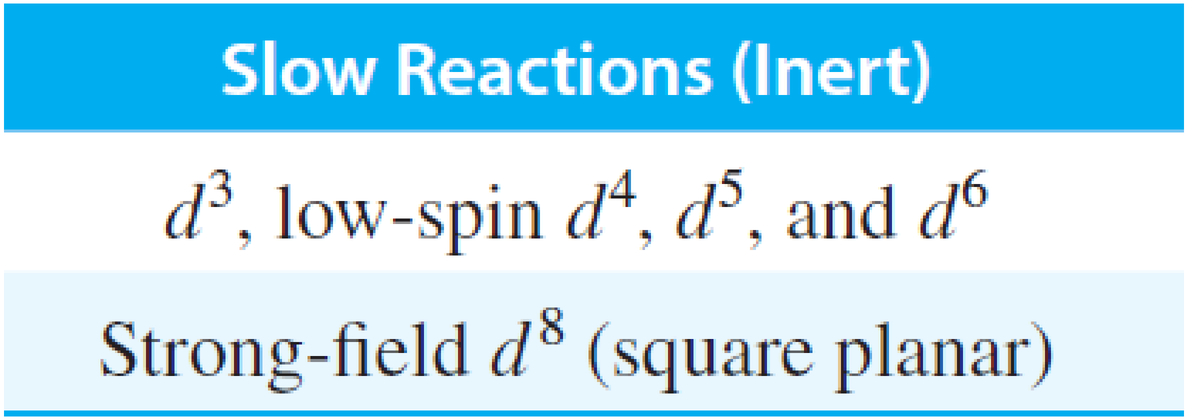
TABLE 12.1 Rate Constants for Water Exchange in $[M(H_2O)_6]^{n+}$

Complex	$k(s^{-1})$ (298 K)	Electronic Configuration*
$[Ti(H_2O)_6]^{3+}$	1.8×10^5	$t_{2g}{}^1$
$[V(H_2O)_6]^{3+}$	5.0×10^2	$t_{2g}{}^2$
$[V(H_2O)_6]^{2+}$	8.7×10^1	$t_{2g}{}^3$
$[Cr(H_2O)_6]^{3+}$	2.4×10^{-6}	$t_{2g}{}^3$
$[Cr(H_2O)_6]^{2+}$	$> 10^8$	$t_{2g}{}^3 e_g{}^1$
$[Fe(H_2O)_6]^{3+}$	1.6×10^2	$t_{2g}{}^3 e_g{}^2$
$[Fe(H_2O)_6]^{2+}$	4.4×10^6	$t_{2g}{}^4 e_g{}^2$
$[Co(H_2O)_6]^{2+}$	3.2×10^6	$t_{2g}{}^5 e_g{}^2$
$[Ni(H_2O)_6]^{2+}$	3.2×10^4	$t_{2g}{}^6 e_g{}^2$
$[Cu(H_2O)_6]^{2+}$	4.4×10^9	$t_{2g}{}^6 e_g{}^3$
$[Zn(H_2O)_6]^{2+}$	$> 10^7$	$t_{2g}{}^6 e_g{}^4$

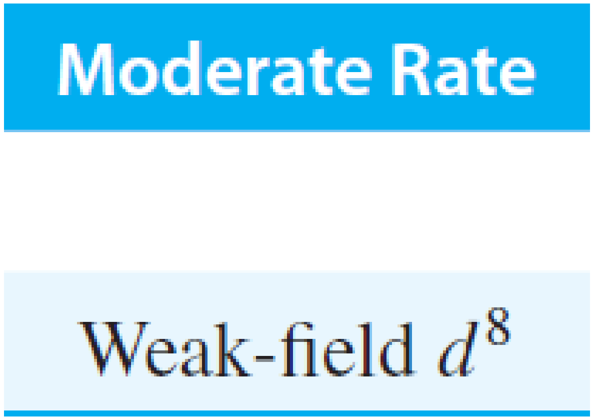
*These configurations assume octahedral geometry, even in cases where Jahn–Teller distortion is anticipated.

Data from R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, 3rd ed., Oxford (New York), 2007, p. 84

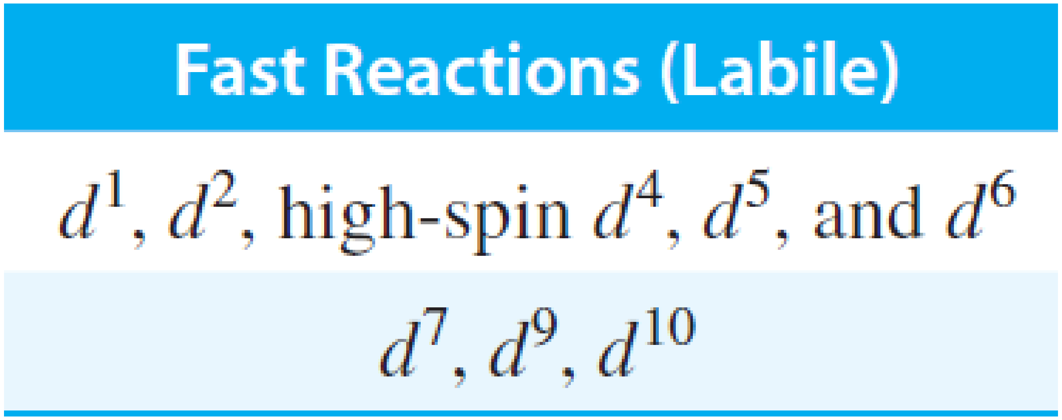
Labile and inert electronic configurations



Slow Reactions (Inert)
d^3, low-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)



Moderate Rate
Weak-field d^8



Fast Reactions (Labile)
d^1, d^2, high-spin d^4, d^5, and d^6
d^7, d^9, d^{10}

Mechanisms of Ligand Substitution

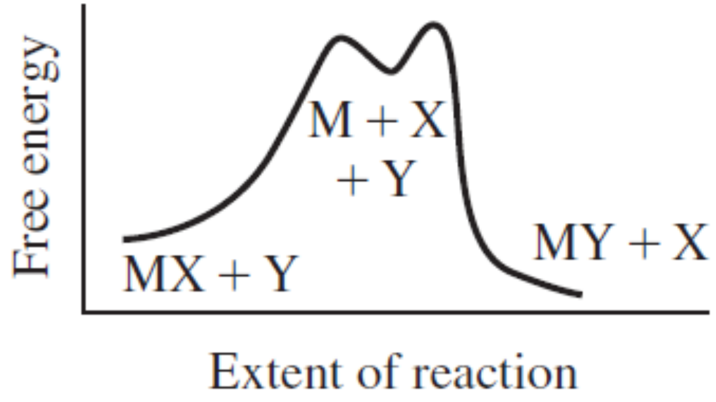
- **Dissociative mechanism (D)**: one ligand leaves, an intermediate with lower coordination number forms, then another ligand binds to metal. Most common for octahedral complexes!

- **Associative mechanism (A)**: incoming ligand adds to complex, an intermediate with higher coordination number forms, then outgoing ligand comes off metal

- **Interchange (I)**: mechanism that is in between **D** and **A**: incoming ligand assists in reaction, but no detectable intermediates are observed (we will not focus on this mechanism)

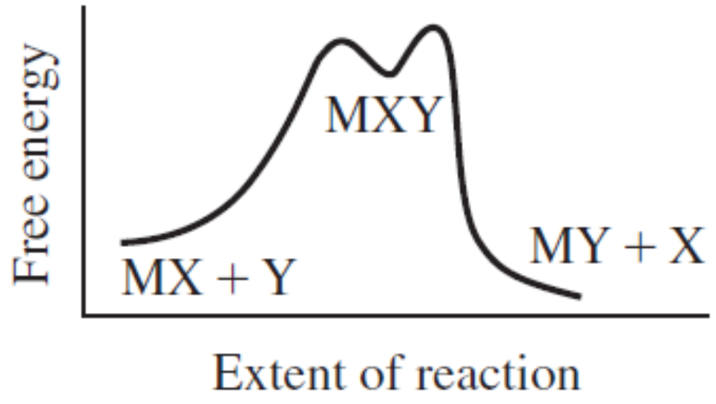
Reaction coordinates

Dissociative mechanism



(a)

Associative mechanism



(b)

Mechanisms of Ligand Substitution

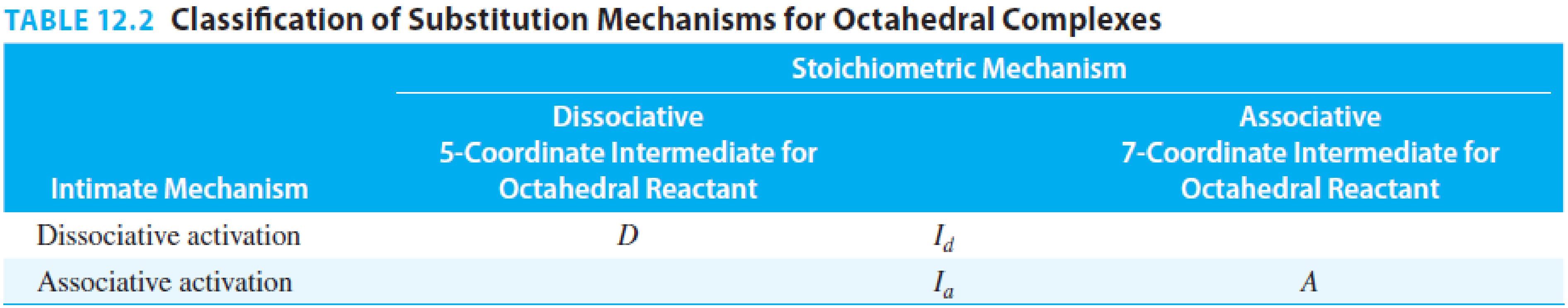
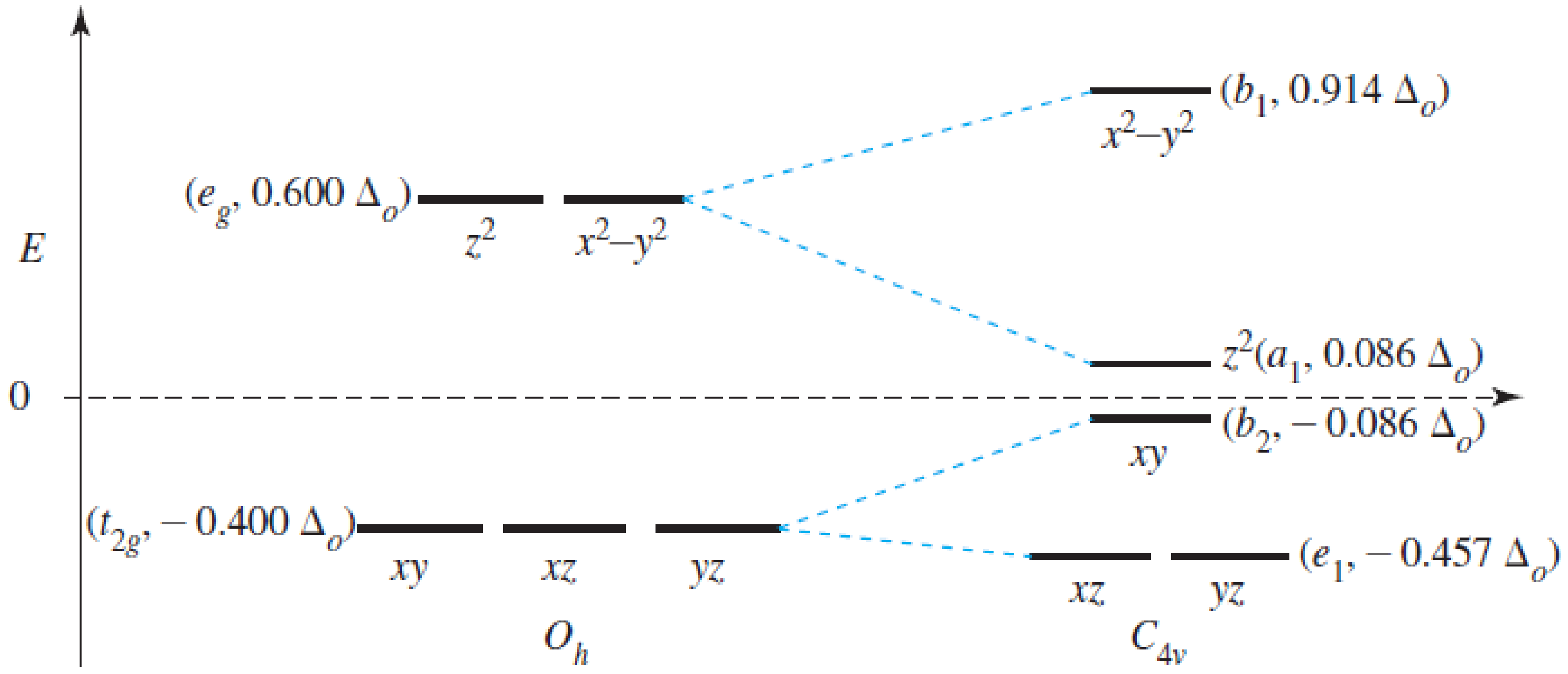


TABLE 12.2 **Classification of Substitution Mechanisms for Octahedral Complexes**

	Stoichiometric Mechanism		
Intimate Mechanism	Dissociative 5-Coordinate Intermediate for Octahedral Reactant		Associative 7-Coordinate Intermediate for Octahedral Reactant
Dissociative activation	D	I_d	
Associative activation		I_a	A

Ligand field activation energy in dissociative mechanism for octahedral complexes



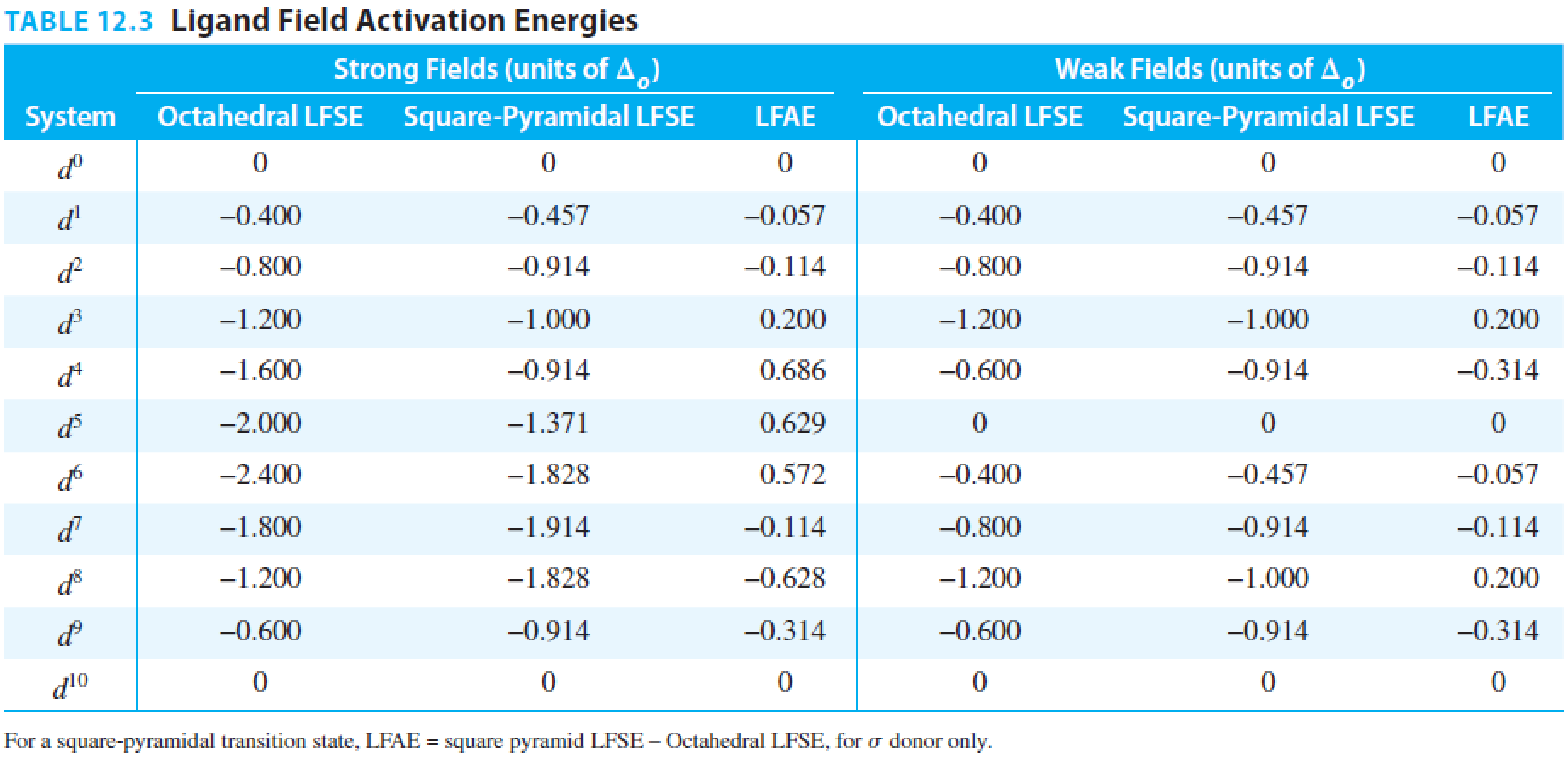


TABLE 12.3 **Ligand Field Activation Energies**

	Strong Fields (units of Δ_o)			Weak Fields (units of Δ_o)		
System	Octahedral LFSE	Square-Pyramidal LFSE	LFAE	Octahedral LFSE	Square-Pyramidal LFSE	LFAE
d^0	0	0	0	0	0	0
d^1	–0.400	–0.457	–0.057	–0.400	–0.457	–0.057
d^2	–0.800	–0.914	–0.114	–0.800	–0.914	–0.114
d^3	–1.200	–1.000	0.200	–1.200	–1.000	0.200
d^4	–1.600	–0.914	0.686	–0.600	–0.914	–0.314
d^5	–2.000	–1.371	0.629	0	0	0
d^6	–2.400	–1.828	0.572	–0.400	–0.457	–0.057
d^7	–1.800	–1.914	–0.114	–0.800	–0.914	–0.114
d^8	–1.200	–1.828	–0.628	–1.200	–1.000	0.200
d^9	–0.600	–0.914	–0.314	–0.600	–0.914	–0.314
d^{10}	0	0	0	0	0	0

For a square-pyramidal transition state, LFAE = square pyramid LFSE – Octahedral LFSE, for σ donor only.

Other factors that influence octahedral dissociative substitution rates

- Oxidation state of the central ion: central atoms with higher oxidation states have slower ligand exchange
  - Note: as we just discussed, must factor in d electron configuration when transition metals are the central atom
- Ionic radius: smaller ions have slower exchange rates

- Why?
  - Higher electrostatic attraction between central atom and ligands
  - This means stronger M-L bonds
  - Rate determining step in dissociative mechanism is initial breaking of M-L bond
  - The stronger the bond, the slower the rate

Evidence that suggests a substitution reaction might be dissociative

- The rate of the reaction changes only slightly with changes in the incoming ligand (two rates differ by less than a factor of 10)
- Making the charge of the reactive complex more positive decreases the rate of substitution
- Steric crowding of the reactant complex increases the rate of reaction

Associative mechanism for ligand substitution

- Less common than dissociative mechanism for octahedral complexes
- If rate depends on incoming ligand, likely associative

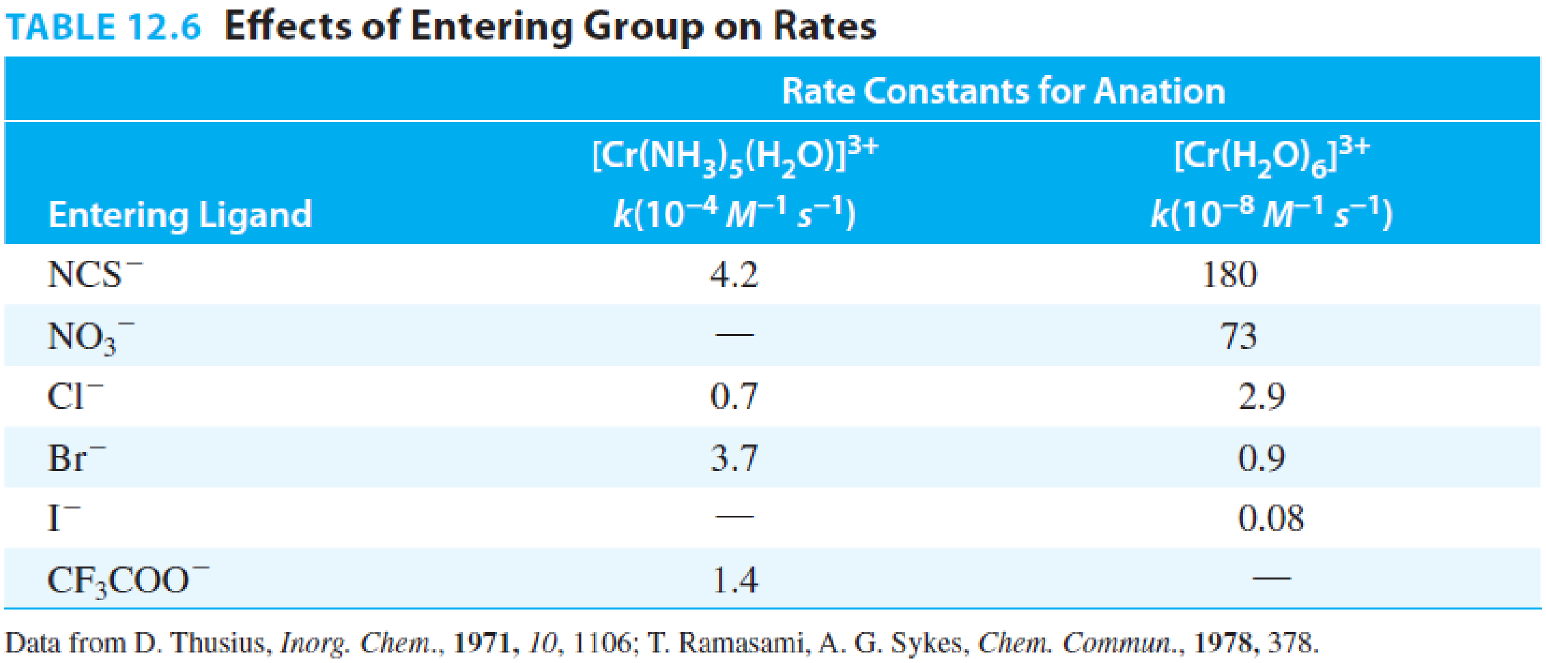


TABLE 12.6 **Effects of Entering Group on Rates**

	Rate Constants for Anation	
Entering Ligand	$[Cr(NH_3)_5(H_2O)]^{3+}$ $k(10^{-4}\ M^{-1}\ s^{-1})$	$[Cr(H_2O)_6]^{3+}$ $k(10^{-8}\ M^{-1}\ s^{-1})$
NCS^-	4.2	180
NO_3^-	—	73
Cl^-	0.7	2.9
Br^-	3.7	0.9
I^-	—	0.08
CF_3COO^-	1.4	—

Data from D. Thusius, *Inorg. Chem.*, 1971, *10*, 1106; T. Ramasami, A. G. Sykes, *Chem. Commun.*, 1978, 378.

Dissociative

Associative

The kinetic chelate effect

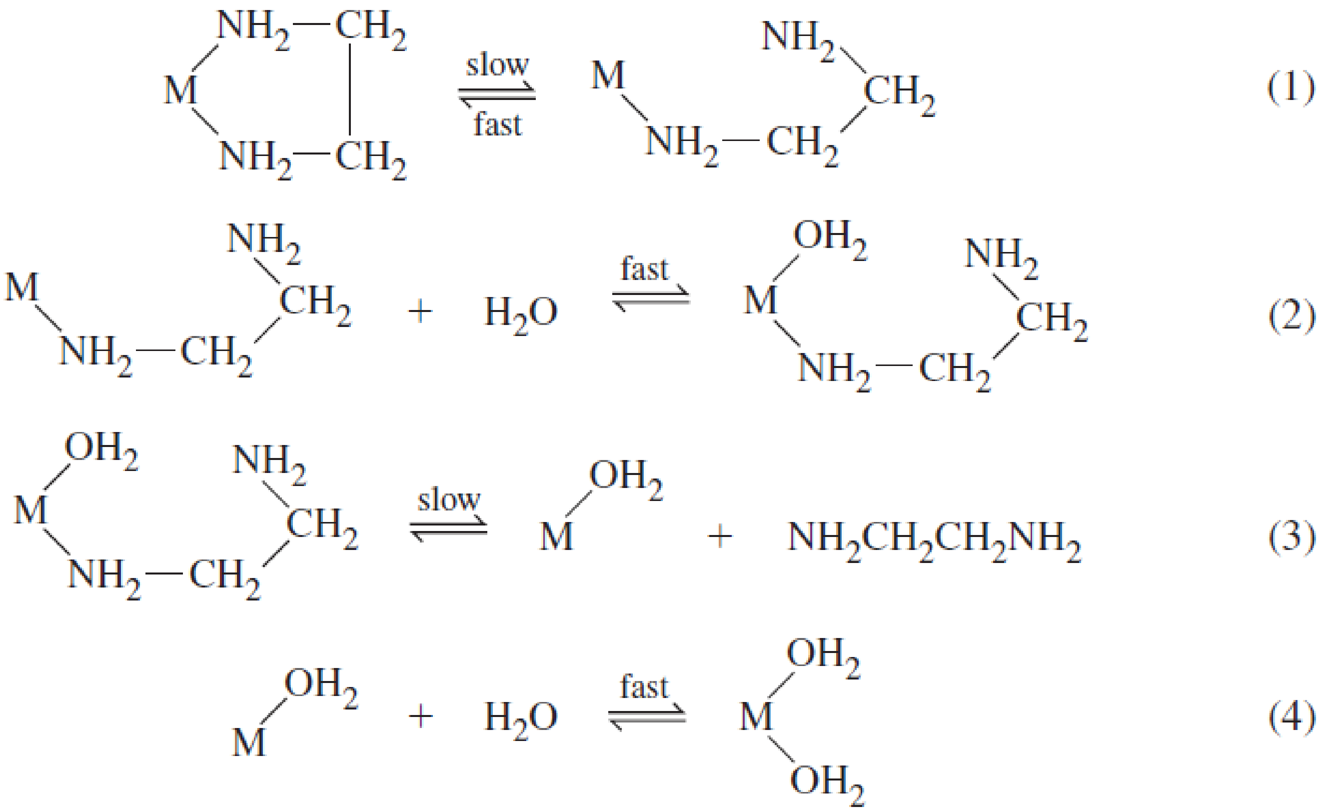
- The chelate effect makes a complex with a multidentate ligand more thermodynamically stable than an analagous monodentate ligand metal complex

- Similarly, ligand substitution rates are slower for multidentate ligand metal complexes

- One reason for this is that ΔH is larger for detachment of the first atom of a multidentate ligand than for a monodentate lidgand to detach

The kinetic chelate effect

- In addition, once first atom detaches from metal center, kinetic barrier for reattachment is lower (rate faster) than for an additional atom to detach from the metal



Take-away messages

- Metal oxidation state and ligands bound to it will affect the rates of ligand substitution reactions

- Electronic configuration (LFSE), ligand sterics, metal-ligand bond strengths (electrostatics) can influence reaction rates

- Substitution can occur via a dissociative mechanism, an associative mechanism, or something in between