# Reactivity of Transition Metal Complexes
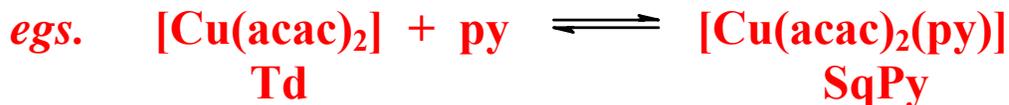
## (H&S 3$^{rd}$ Ed., Chpt. 26)

*Four main types of reactivity:*
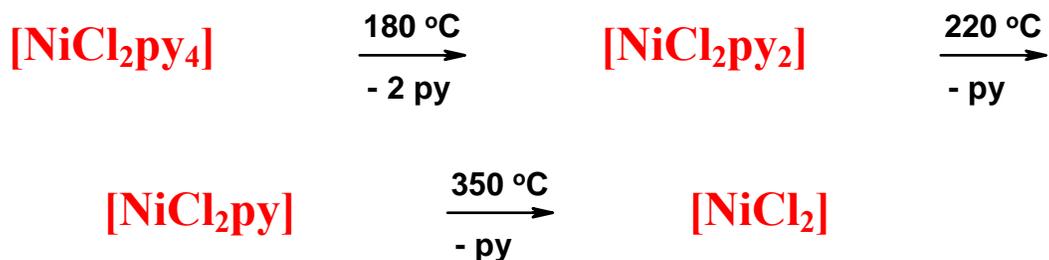
1) **Substitution reactions:** $ML_n + L' \rightarrow ML_{n-1}L' + L$

   *egs.*   $[Fe(H_2O)_6]^{3+} + 3\ acac^- \rightarrow Fe(acac)_3 + 6\ H_2O$

   $[Cu(H_2O)_6]SO_4 + 4\ NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]SO_4$

2) **Addition (dissociation) reactions:** $ML_n + L' \rightarrow ML_nL'$

   *egs.*   $[Cu(acac)_2] + py \rightleftharpoons [Cu(acac)_2(py)]$
   
            Td                               SqPy

   **dissociation (the reverse reaction) usually requires heat or light to occur:**

   $$[NiCl_2py_4] \xrightarrow[-\ 2\ py]{180\ ^oC} [NiCl_2py_2] \xrightarrow[-\ py]{220\ ^oC}$$

   $$[NiCl_2py] \xrightarrow[-\ py]{350\ ^oC} [NiCl_2]$$

**3) Redox (e⁻ transfer) reactions:** $ML_n^{x+} \rightarrow ML_n^{(x+1)+} + e^-$

*eg.* $[Ru(NH_3)_6]^{2+} \rightarrow [Run(NH_3)_6]^{3+} + e^-$

**also includes *oxidative-addition* (and its reverse: *reductive-elimination*), especially of SqP complexes**

L—M⋯L + X-Y ⇌ L—M⋯X (with Y and L axial)

L = PPh₃

Wilkinson's catalyst

L—Rh—Cl + H-H ⇌ L—Rh⋯H (with H and Cl axial)
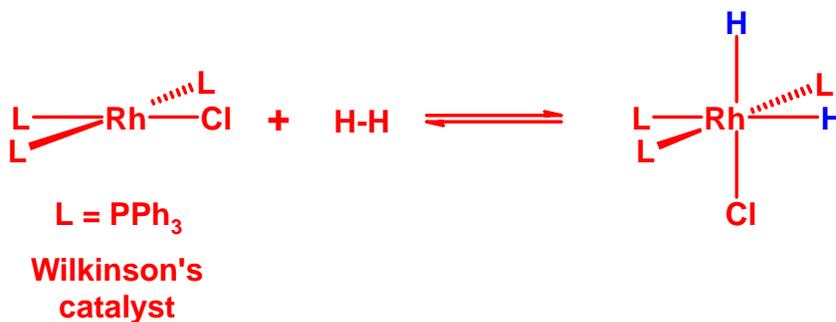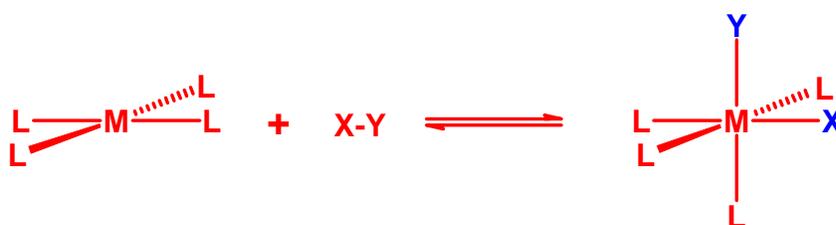
**4) Reactions at coordinated ligands (many variants here)**

a template reaction

-2 H₂O
+ RNH₂

RNH₂ H₂NR
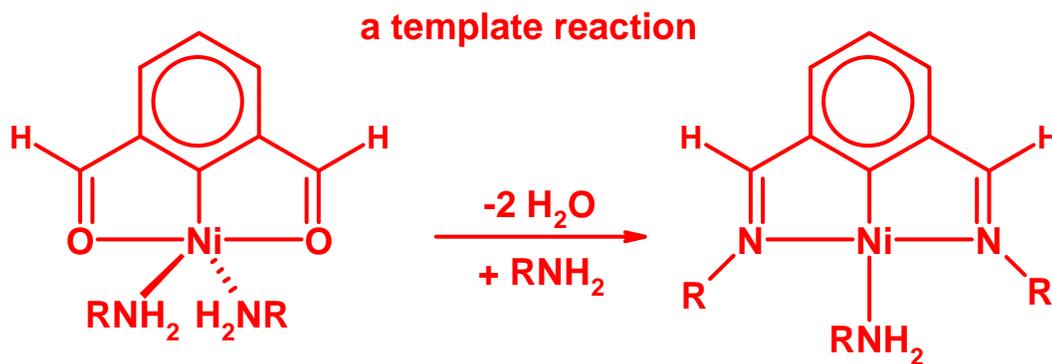
# Substitution Reactions

*General mechanistic considerations*

Four recognized mechanisms for ligand substitution in inorganic chemistry:

1) Associative (**A**)
2) Dissociative (**D**)
3) Associative Interchange (**I$_A$**)
4) Dissociative Interchange (**I$_D$**)

**A**ssociative and **D**issociative differ from **I$_A$** and **I$_D$** respectively in that there is a discrete ***intermediate*** of higher or lower coordination number:
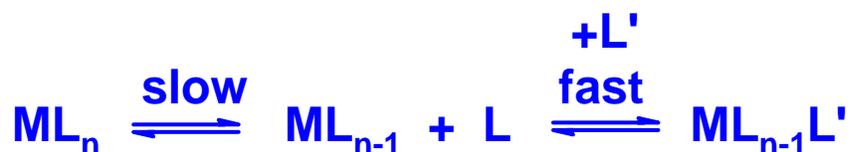


**Associative mechanism:**

$$ML_n + L' \overset{slow}{\rightleftharpoons} ML_nL' \overset{fast}{\rightleftharpoons} ML_{n-1}L' + L$$
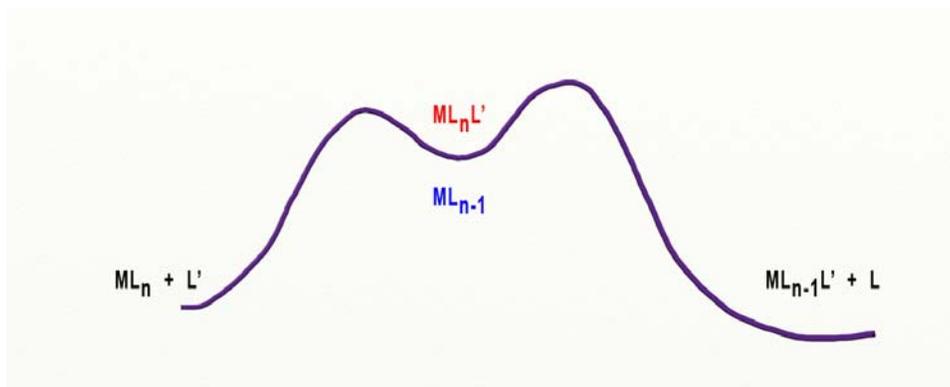
**A mechanism** (cont.):

- **rates depends on starting complex and incoming ligand concentration**
- **sensitive to nature of L' (but solvent effects can sometimes mask this)**
- **more likely for low coordination number complexes**

**Dissociative mechanism:**

$$ML_n \quad \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \quad ML_{n-1} + L \quad \underset{}{\overset{\substack{\text{+L'} \\ \text{fast}}}{\rightleftharpoons}} \quad ML_{n-1}L'$$
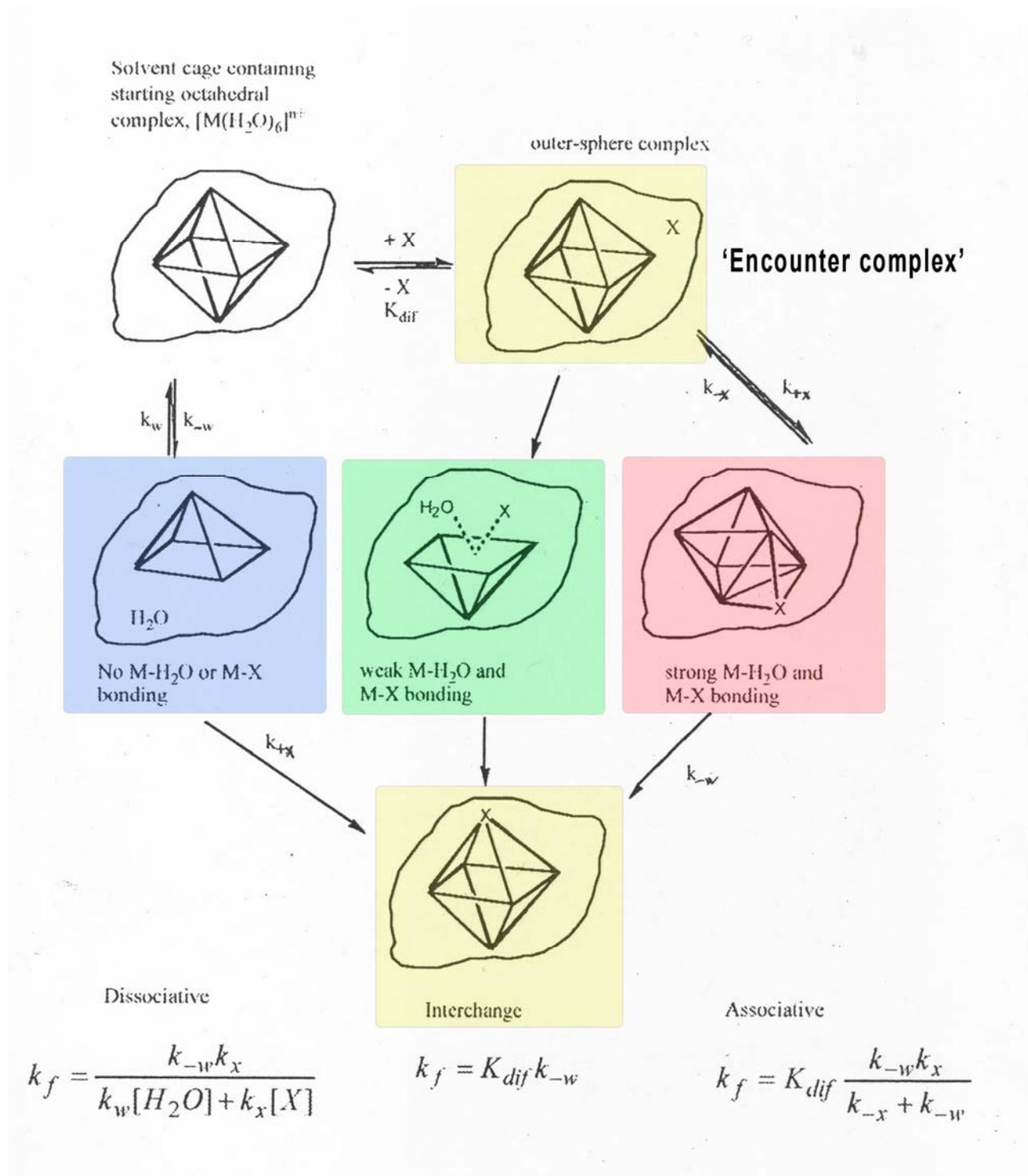
- **equivalent to a $S_N1$ reaction in organic chemistry**
- **rates depend only on concentration of starting complex $ML_n$**
- **insensitive to nature of incoming ligand L'**
- **more common for high coordination number complexes and those containing very bulky ligands L**

**Interchange mechanisms:** concerted reaction with no discrete intermediate of higher or lower coordination number

$$L'-----[ML_{n-1}]-----L$$

$$ML_n + L'$$

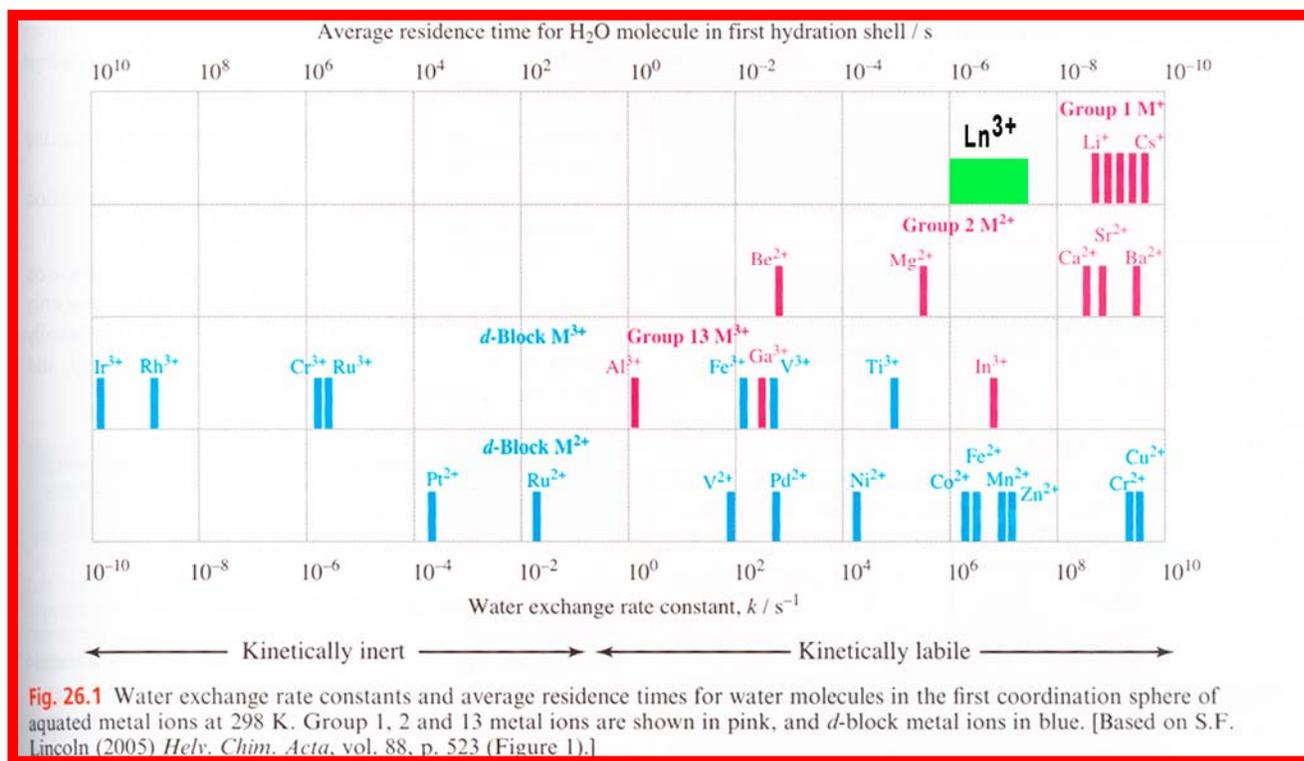$$ML_{n-1}L' + L$$
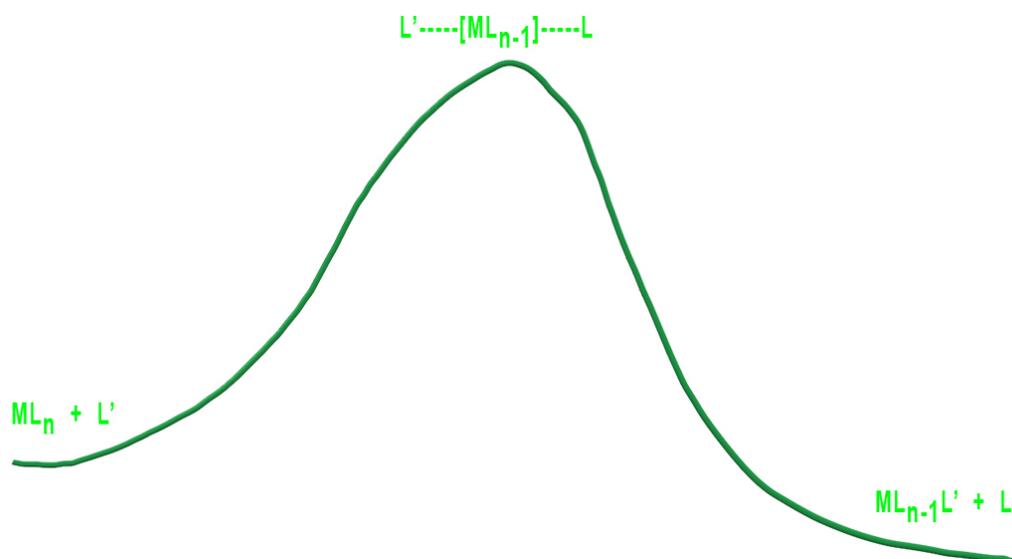
- **more common than true A or D mechanisms**

- **based on the Eigen-Wilkins *'encounter complex'* model**

- **$I_A$ has both leaving and entering ligands strongly bound in the TS and shows sensitivity to the nature and concentration of L'**

- **$I_D$ has both leaving and entering ligands weakly bound in the TS and shows little sensitivity to the identity or concentration of L'**

# Eigen-Wilkins '*encounter complex*'



Solvent cage containing starting octahedral complex, $[M(H_2O)_6]^{n}$

outer-sphere complex

$+ X$
$- X$
$K_{dif}$

'Encounter complex'

$k_w \quad k_{-w}$

$k_{-x} \quad k_{+x}$

No M-H$_2$O or M-X bonding

weak M-H$_2$O and M-X bonding

strong M-H$_2$O and M-X bonding

$k_{+x}$

$k_{-w}$

Dissociative

$$k_f = \frac{k_{-w}k_x}{k_w[H_2O] + k_x[X]}$$

Interchange

$$k_f = K_{dif}k_{-w}$$

Associative

$$k_f = K_{dif}\frac{k_{-w}k_x}{k_{-x} + k_{-w}}$$

# Substitution in Octahedral Complexes

- **mechanism generally found to be $I_D$ (there are of course exceptions); true D mechanism is rare**

- **water exchange rates vary enormously across the d-block:**



**Fig. 26.1** Water exchange rate constants and average residence times for water molecules in the first coordination sphere of aquated metal ions at 298 K. Group 1, 2 and 13 metal ions are shown in pink, and d-block metal ions in blue. [Based on S.F. Lincoln (2005) *Helv. Chim. Acta*, vol. 88, p. 523 (Figure 1).]

*(water exchange rates are simply representative of general exchange kinetics for the d-block metals but they are very useful to know since much chemistry is done in water and they have been extensively studied as a result)*

*How can we rationalize these widely varying rates?*

1) **Non-d-block metals show decreasing k with increasing Q/r**

- **since this is a dissociative mechanism, weakening the $M\text{-}OH_2$ bond should increase rate and the strength of ion-dipole interaction depends on Q/r**

- **no directional (crystal field) effects associated with spherical ions**

2) **Even though there isn't an obvious Q/r trend for the d-block metals, there is some influence of charge**

*egs.*

$Fe^{2+}$ and $Ru^{2+}$ are about $10^4$ x faster in water exchange than $Fe^{3+}$ and $Ru^{3+}$, respectively

BUT $V^{2+}$ is about 10 x SLOWER than $V^{3+}$ so the trend is not perfect

However, within a charge series the Q/r ratio doesn't hold:

$V^{2+}$ has one of the lowest Q/r and yet has one of the slowest rates and $Cr^{2+}$ and $Cu^{2+}$ are very different in size but almost the same in rate

**3) Jahn-Teller ions show exceptional fast water exchange:**

waters in the coordination sphere of $Cr^{2+}$ $(d^4)$ and $Cu^{2+}$ $(d^9)$ have an average residence time of ==*less than a nanosecond!!*==

- **Jahn-Teller ions already show elongation of two (or four) $M-OH_2$ bonds so it is not too surprising that these waters are less tightly bound and more easily lost in an $I_D$ mechanism**

**4) Besides the Jahn-Teller ions, water exchange rates are also significantly influenced by the $d^n$ count for other d-block ions**

- even though the true mechanism is probably $I_D$ not D, it is useful to think about changes in CFSE going from an Oh ground state to a square pyramidal intermediate (or transition state):

  - **a net gain in CFSE is a stabilizing influence on the intermediate, lowering $\Delta G^*$ and increasing the rate**

  - **a net loss in CFSE is a destabilizing influence on the intermediate, increasing $\Delta G^*$ and decreasing the rate**

*Does this actually work? Let's look at the change in CFSE (square pyramidal – octahedral) for various d counts:*

| $d^n$ | $\Delta$CFSE (high spin) | $\Delta$CFSE (low spin) |
|---|---|---|
| 1 | +0.06 | |
| 2 | +0.11 | |
| 3 | -0.20 | |
| 4 | +0.31 | -0.14 |
| 5 | 0 | -0.09 |
| 6 | +0.06 | -0.40 |
| 7 | +0.11 | +0.11 |
| 8 | -0.20 | |
| 9 | +0.31 | |
| 10 | 0 | |

**So, as long as we stay within a particular ionic charge group we do pretty well:**

**For first row 3+ ions:**

**$Cr^{3+}$ ($d^3$) $\Delta$CFSE = -0.20 is in fact substitution inert**

**followed in increasing order of lability by:**

**$Fe^{3+}$ ($d^5$) $\Delta$CFSE = 0**
**$V^{3+}$ ($d^2$) $\Delta$CFSE = +0.11**
**$Ti^{3+}$ ($d^1$) $\Delta$CFSE = +0.06**

**For first row 2+ ions:**

$V^{2+}$ $(d^3)$ $\Delta$CFSE = -0.20 is quite slow (87 $s^{-1}$)

$Ni^{2+}$ $(d^8)$ $\Delta$CFSE = -0.20 is labile but 2$^{nd}$ slowest overall ($10^4$ $s^{-1}$)

$Co^{2+}$ $(d^7)$ $\Delta$CFSE = +0.11; $Fe^{2+}$ $(d^6)$ $\Delta$CFSE = +0.06; $Mn^{2+}$ $(d^5)$ $\Delta$CFSE = 0; $Zn^{2+}$ $(d^{10})$ $\Delta$CFSE = 0 are very close in lability to one another and fast exchanging ($10^7$ $s^{-1}$)

$Cr^{2+}$ $(d^4)$ $\Delta$CFSE = +0.31; $Cu^{2+}$ $(d^9)$ $\Delta$CFSE = +0.31 are both Jahn-Teller distorted ions and have large changes in CFSE as well. There exchange rates are among the fastest known for any ions at >$10^9$ $s^{-1}$

**Second and third row metals**

- generally less labile
- partly due to less favourable $\Delta$CFSE for these low spin metals (remember $\Delta_{oct}$ is larger for these metals so the CFSE corresponds to a greater energy in general)

  - note that the especially unfavourable $\Delta$CFSE of -0.40 for low spin $d^6$ ions leads to substitution inert octahedral $Rh^{3+}$ and $Ir^{3+}$ complexes