







- For transition metal ions the electronic configurations are important because the CFSE will affect the rates of exchange here. For these metal ions the rate of exchange is partially related to the size of the cations and partly to the CFSE. (see handout).
- Remember this plot from lecture 10. This shows that the highest OSPE is for low spin d<sup>6</sup> and d<sup>3</sup> octahedral complexes, d<sup>4</sup> and d<sup>7</sup> configs also have some OSPE. d<sup>0</sup> and d<sup>10</sup> have none.



- It is important to be able to rationalize what effect the CSFE has on increasing the activation energy for the formation of a 5- or 7-coordinate intermediate.
- You need to be able to rationalize why six coordinate hexaaquo complexes of transition metal ions with d<sup>3</sup> or d<sup>6</sup> configuration are kinetically inert with respect to substitution reactions.























## TABLE 5.1Rate Constants for SubstitutionReactions of [Ni(H20)6]2+

$[\mathrm{Ni}(\mathrm{H}_{2}\mathrm{O})_{6}]^{2+} + L \xrightarrow{k} [\mathrm{Ni}(\mathrm{H}_{2}\mathrm{O})_{5}L]^{n+} + \mathrm{H}_{2}\mathrm{O}$			
L	k, s <sup>-1</sup>	log k	
-	2	1.000	

F -	$8 \times 10^{3}$	3.9
SCN <sup>-</sup>	$6 \times 10^{3}$	3.8
CH <sub>3</sub> COO <sup>-</sup>	$30 \times 10^{3}$	4.3
NH <sub>3</sub>	$3 \times 10^{3}$	3.5
H <sub>2</sub> O	$25 \times 10^{3}$	4.4

Source: Data from R. G. Wilkins, Acc. Chem. Res. 3 (1970): 408.

So the conclusion is that the rate doesn't depend on the incoming ligand significantly which is consistent with the loss of water being rate determining and a dissociative rate determining step which a water molecule breaks away from the Ni(II) and in a succeeding fast step is replaced by L.

## ii. Effects of Leaving Group

Table 5.2 shows how the rate of the reaction measured by (k,  $s^{\mbox{-}1})$  now depends on the strength of the metal-ligand bond.

The rate constants k refer to the following reactions:

$$[Co(NH_3)_5L]^{2+} + H_2O \xrightarrow{k} [Co(NH_3)_5(H_2O)]^{3+} + L^{-1}$$

The equilibrium constants  $K_a$  refer to the following anation reactions:

$$[Co(NH_3)_5(H_2O)]^{3+} + L^- \xrightarrow{K_a} [Co(NH_3)_3L]^{2+} + H_2O$$

The stronger the M-L bond the larger the equilibrium constant  $K_{\alpha}$ , the slower the reaction (k, s<sup>-1</sup>).















