20.14. We can assume f_{12} to be unity. The redox potential data allows us to calculate K_{12} , since $\varepsilon^{\circ} = [RT/nF]lnK$. The value of ε° can be calculated by subtracting the anodic reduction potential (the Cr^{3+}/Cr^{2+} couple serves as the anode) from the cathodic one.

(a) $k_{11} (Cr^{3+}/Cr^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; k_{22} (Ru^{3+}/Ru^{2+} \text{ for the hexamine complex}) = 6.6 \times 10^3 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; f_{12} = 1; K_{12} = e^{[nF_{\varepsilon}^0/RT]} \text{ where } \varepsilon^0 = 0.07 \text{ V} - (-0.41 \text{ V}) = 0.48 \text{ V}; n = 1; F = 96,485 \text{ C}; R = 8.31 \text{ Jmol}^{-1} \text{K}^{-1} \text{ and } T = 298 \text{ K}.$ Using these values we get $K_{12} = 1.32 \times 10^8$. Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 2.95 \times 10^3 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}.$

(b) $k_{11} (Cr^{3+}/Cr^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; k_{22} (Fe^{3+}/Fe^{2+} \text{ for the aqua complex}) = 1.1 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; f_{12} = 1; K_{12} = e^{[nF\epsilon^0/RT]} \text{ where } \epsilon^\circ = 0.77 \text{ V} - (-0.41 \text{ V}) = 1.18 \text{ V}; n = 1; F = 96,485 \text{ C}; R = 8.31 \text{ Jmol}^{-1} \text{K}^{-1} \text{ and } T = 298 \text{ K}.$ Using these values we get $K_{12} = 9.26 \times 10^{19}$. Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 3.19 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

(c) $k_{11} (Cr^{3+}/Cr^{2+}) = 1 \times 10^{-5} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; k_{22} (Ru^{3+}/Ru^{2+} \text{ for the bipy complex}) = 4 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}; f_{12} = 1; K_{12} = e^{[nF \varepsilon^0/RT]} \text{ where } \varepsilon^0 = 1.26 \text{ V} - (-0.41 \text{ V}) = 1.67 \text{ V}; n = 1; F = 96,485 \text{ C}; R = 8.31 \text{ Jmol}^{-1} \text{K}^{-1} \text{ and } T = 298 \text{ K}.$ Using these values we get $K_{12} = 1.81 \times 10^{28}$. Substitution of these values in the Marcus-Cross relationship gives $k_{12} = 8.51 \times 10^{15} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Note: The assumption that $f_{12} = 1$ is used in all cases; however, a more precise value would be needed for cases (b) and (c) because of higher values of the equilibrium constant.

- 20.1. Suggest a reason why K_{f5} is so different? The value of the stepwise formation constants drop from 1 to 4, as expected on statistical grounds. However the fifth stepwise formation constant is substantially lower, suggesting a change in coordination. In fact, what happens is that the square-planar $[Cu(NH_3)_4]^{2^+}$ ion forms, and further coordination does not occur.
- 20.2 Compare these values with those of ammonia given in exercise 20.1 and suggest why they are different? The salient comparison is of log β_2 (7.65) for the ammonia reaction with log K_{fl} (10.72) for the en reaction. The value for the en reaction is substantially higher, indicating more favourable complex formation, and this can be attributed to the chelate effect. A comparison can also be drawn between the 3rd and 4th stepwise formation constants with ammonia (5.02) and the 2nd one for en (9.31).
- **20.3 Mechanism?** If the mechanism of substitution were to be associative, the nature of incoming ligand should affect the rate of the reaction. This is because the rate-limiting step would require the formation of M—X bonds (X = incoming ligand). In the present however, rate of the reaction does not vary much depending on the nature or size of the incoming ligand. Therefore, the more likely mechanism would be *dissociative*.
- 20.4 If a substitution process is associative, why may it be difficult to characterize an aqua ion as labile or inert? The rate of an associative process depends on the identity of the entering ligand and, therefore, it is not an inherent property of $[M(OH_2)_6]^{n^+}$.
- **20.5** Is the reaction of Ni(CO)₄ with phosphanes and phosphites *d* or *a*? Since the rate of substitution is the same for a variety of different entering ligands L, the activated complex in each case must not include any significant bond making to the entering ligand and the reaction must be *d*. If the rate-determining step included any Ni-L bond making, the rate of substitution would change as the electronic and steric properties of L were changed.
- 20.6 How would you determine if the formation of $[MnX(OH_2)_5]^+$ is d or a? The rate law for this substitution reaction is:

ate =
$$(kK_{\rm E}[{\rm Mn}({\rm OH}_2)_6^+][{\rm X}^-])/(1 + K_{\rm E}[{\rm X}^-])$$

where K_E is the equilibrium constant for the formation of the encounter complex {[Mn(OH₂)₆]²⁺, X⁻}, and k is the first-order rate constant for the reaction:

$$\{[Mn(OH_2)_6^{2^+}], X^-\} \rightarrow [Mn(OH_2)_5X]^+ + H_2O$$

The rate law will be the same regardless of whether the transformation of the encounter complex into products is dissociatively or associatively activated. However, you can distinguish d from a by varying the nature of X^- . If k varies as X^- varies, then the reaction is a. If k is relatively constant as X^- varies, then the reaction is d.

Note that k cannot be measured directly. It can be found using the expression $k_{obs} = kK_E$ and an estimate of K_E , as described in Section 20.6.

- 20.7 The nonlability of octahedral complexes of metals with high oxidation numbers or metals of periods 5 and 6? If ligand substitution takes place by a *d* mechanism, the strength of the metal-leaving group bond is directly related to the substitution rate. Metal centers with high oxidation numbers will have stronger bonds to ligands than metal centers with low oxidation numbers. Furthermore, period 5 and 6 *d*-block metals have stronger metal ligand bonds (see Section 19.1). Therefore, for reactions that are dissociatively activated, complexes of period 5 and 6 metals are less labile than complexes of period 3 metals, and complexes of metals in high oxidation states are less labile than complexes of metals in low oxidation states (all other things remaining equal).
- 20.8 Explain in terms of associative activation the fact that a Pt(II) complex of tetraethyldiethylenetriamine is attacked by Cl⁻ 10⁵ times less rapidly than the diethylenetriamine analog? The two complexes are shown below. The ethyl substituted complex presents a greater degree of steric hindrance to an incoming Cl⁻ ion nucleophile. Since the rate-determining step for associative substitution of X⁻ by Cl⁻ is the formation of a Pt-Cl bond, the more hindred complex will react more slowly.



20.9 Substitution of PhCl in [W(CO)₄L(PhCl)]? Since the rate of loss of chlorobenzene, PhCl, from the tungsten complex becomes faster as the cone angle of L increases, this is a case of dissociative activation (i.e., steric crowding in the transition state accelerates the rate). This is not at odds with the observation that the rate is proportional to the concentration of the entering phosphane at low phosphane concentrations, since K_E for the equilibrium producing the encounter complex, $C + Y \rightarrow \{CY\}$, is inversely proportional to [Y] (C is the tungsten complex, Y is the entering phosphane; see Section 20.6, *Rate laws and their interpretation*). The overall rate is given by:

rate =
$$(kK_{\rm E}[{\rm C}][{\rm Y}])/(1+K_{\rm E}[{\rm Y}])$$

and, in the limit of low [Y], this becomes rate $\sim kK_{\rm E}[C][Y]$.

20.10 Why substitution reactions of $[Ni(CN)_4]^{2-}$ are very fast? The fact that the five-coordinate complex $[Ni(CN)_5]^{3-}$ can be detected does indeed explain why substitution reactions of the four-coordinate complex $[Ni(CN)_4]^{2-}$ are fast. The reason is that, for a detectable amount of $[Ni(CN)_5]^{3-}$ to build up in solution, the forward rate constant k_f must be numerically close to or greater than the reverse rate constant k_f :

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow [Ni(CN)_5]^{3-}$$

If k_f were much smaller than k_r , the equilibrium constant $K = k_f / k_r$ would be small and the concentration of $[Ni(CN)_5]^{3-}$ would be too small to detect. Therefore, since k_f is relatively large, you can infer that rate constants for the association of other nucleophiles are also large, with the result that substitution reactions of $[Ni(CN)_4]^{2-}$ are very fast.

20.11 A two-step synthesis for cis- and trans-[PtCl₂(NO₂) (NH₃)]^{-?} Starting with [PtCl₄]²⁻, you need to perform two separate ligand substitution reactions. In one, NH₃ will replace Cl⁻ ion. In the other, NO₂⁻ ion will replace Cl⁻ ion. The question is, which substitution to perform first? According to the trans effect series shown in Section 20.5, the strength of the trans effect on Pt(II) for the three ligands in question is NH₃ < Cl⁻ < NO₂⁻. This means that a Cl⁻ ion trans to another Cl⁻ will be substituted faster than a Cl⁻ ion trans to NH₃, while a Cl⁻ ion trans to NO₂⁻ will be substituted faster than a Cl⁻ ion. If you first add NH₃ to [PtCl₄]²⁻, you will produce [PtCl₃(NH₃)]⁻. Now if you add NO₂⁻, one of the mutually trans Cl⁻ ligands will be substituted faster than the cl⁻ ligand trans to NH₃, and the cis isomer will be the result. If you first add NO₂⁻

to $[PtCl_4]^2$, you will produce $[PtCl_3(NO_2)]^2$. Now if you add NH₃, the Cl⁻ ligand *trans* to NO₂⁻ will be substituted faster than one of the mutually *trans* Cl⁻ ligands, and the *trans* isomer will be the result. These two-step syntheses are shown below:



20.12 How does each of the following affect the rate of square-planar substitution reactions? (a) Changing a *trans* ligand from H to Cl? Hydride ion lies higher in the *trans* effect series than does chloride ion. Thus if the ligand *trans* to H or Cl is the leaving group, its rate of substitution will be decreased if H is changed to Cl. The change in rate can be as large as a factor of 10⁴ (see Table 20.6).

(b) Changing the leaving group from CI^{\circ} to I[?]. The rate at which a ligand is substituted in a square-planar complex is related to its position in the *trans* effect series. If a ligand is high in the series, it is a *good* entering group (i.e., a good nucleophile) and a *poor* leaving group. Since iodide ion is higher in the *trans* effect series than chloride ion, it is a poorer leaving group than chloride ion. Therefore, the *iodo* complex will undergo I^{\circ} substitution more slowly than the *chloro* complex will undergo CI^{\circ} substitution.

(c) Adding a bulky substituent to a *cis* ligand? This change will hinder the approach of the entering group and will slow the formation of the five-coordinate activated complex. The rate of substitution of a square-planar complex with bulky ligands will be slower than that of a comparable complex with sterically smaller ligands.

(d) Increasing the positive charge on the complex? If all other things are kept equal, increasing the positive charge on a square-planar complex will increase the rate of substitution. This is because the entering ligands are either anions or have the negative ends of their dipoles pointing at the metal ion. As explained in Section 20.3, if the charge density of the complex decreases in the activated complex, as would happen when an anionic ligand adds to a cationic complex, the solvent molecules will be *less* ordered around the complex (the opposite of the process called electrostriction). The increased disorder of the solvent makes $\delta^{\ddagger}S$ less negative (compare the values of $\delta^{\ddagger}S$ for the Pt(II) and Au(III) complexes in Table 20.7).

20.13 Why is the rate of attack on Co(III) nearly independent of the entering group with the exception of OH? The general trend is easy to explain: octahedral Co(III) complexes undergo dissociatively activated ligand substitution. The rate of substitution depends on the nature of the bond between the metal and the leaving group, since this bond is partially broken in the activated complex. The rate is independent of the nature of the bond to the entering group, since this bond is formed in a step subsequent to the rate determining

activated complex. Therefore, this change, from NH₃ to the less basic ligand H₂O, will result in a decreased rate.

20.17 Pressure dependence of PhCl substitution in [W(CO)₄(PPh₃)(PhCl)]? Since the volume of activation is positive (+11.3 cm³ mol⁻¹), the activated complex takes up more volume in solution than the reactants, as shown in the drawing below. Therefore, the mechanism of substitution must be dissociative. See Section 20.7(d), Associative activation.



20.18 What data might distinguish between an inner- and outer-sphere pathway for reduction of $[Co(N_3) (NH_3)_5]^{2+}$ with $[V(OH_2)_6]^{2+}$? The inner-sphere pathway is shown below (solvent = H₂O):

$$[Co(N_3)(NH_3)_5]^{2^+} + [V(OH_2)_6]^{2^+} \rightarrow [[Co(N_3)(NH_3)_5]^{2^+}, [V(OH_2)_6]^{2^+}\}$$

 $\{ [Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_6]^{2+} \} \rightarrow \{ [Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_5]^{2+}, H_2O \} \}$

 $\{ [Co(N_3)(NH_3)_5]^{2^+}, [V(OH_2)_5]^{2^+}, H_2O \} \rightarrow [(NH_3)_5Co-N=N=N-V(OH_2)_5]^{4^+}$ Co(III) V(II)

 $[(NH_3)_5Co-N=N=N-V(OH_2)_5]^{4+} \rightarrow [(NH_3)_5Co-N=N=N-V(OH_2)_5]^{4+}$ Co(III) V(II) Co(II) V(III)

 $[(NH_3)_5Co-N=N=N-V(OH_2)_5]^{4+} \rightarrow [Co(OH_2)_6]^{2+} + [V(N_3)(OH_2)_5]^{2+}$

Co(II) V(III)

The pathway for outer-sphere electron transfer is shown below:

 $[Co(N_3)(NH_3)_5]^{2+} + [V(OH_2)_6]^{2+} \rightarrow \{[Co(N_3)(NH_3)_5]^{2+} [V(OH_2)_6]^{2+} \}$ $\{[Co(N_3)(NH_3)_5]^{2+}, [V(OH_2)_6]^{2+} \} \rightarrow \{[Co(N_3)(NH_3)_5]^+, [V(OH_2)_6]^{3+} \}$ $\{[Co(N_3)(NH_3)_5]^+, [V(OH_2)_6]^{3+} \} \rightarrow \{[Co(OH_2)_6]^{2+}, [V(OH_2)_6]^{3+} \}$

In both cases, the cobalt-containing product is the aqua complex, since H_2O is present in abundance and highspin d^7 complexes of Co(II) are substitution labile. However, something that distinguishes the two pathways is the composition of the vanadium-containing product. If $[V(N_3)(OH_2)_5]^{2^+}$ is the product, then the reaction has proceeded via an inner-sphere pathway. If $[V(OH_2)_6]^{3^+}$ is the product, then the electron transfer reaction is outer-sphere.

- **20.19** The presence of detectable intermediates in electron transfer reactions? As in exercise 20.18, the direct transfer of a ligand from the coordination sphere of one redox partner (in this case the oxidizing agent, $[Co(NCS)(NH_3)_5]^{2^+}$) to the coordination sphere of the other (in this case the reducing agent, $[Fe(OH_2)_6]^{2^+}$) signals an inner-sphere electron transfer reaction. Even if the first formed product $[Fe(NCS)(OH_2)_5]^{2^+}$ is short lived and undergoes hydrolysis to $[Fe(OH_2)_6]^{3^+}$, its fleeting existence demands that the electron was transfered across a Co–(NCS)–Fe bridge.
- **20.20** Rate constants? We can use the calculations shown in Self-Test 20.6 to calculate the rate constants for the oxidation of $[V(OH_2)_6]^{2^+}$.