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Estrutura e reatividade de complexos metálicos



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Estável ou inerte?

26.1

Average residence time for H₂O molecule in first hydration shell / s

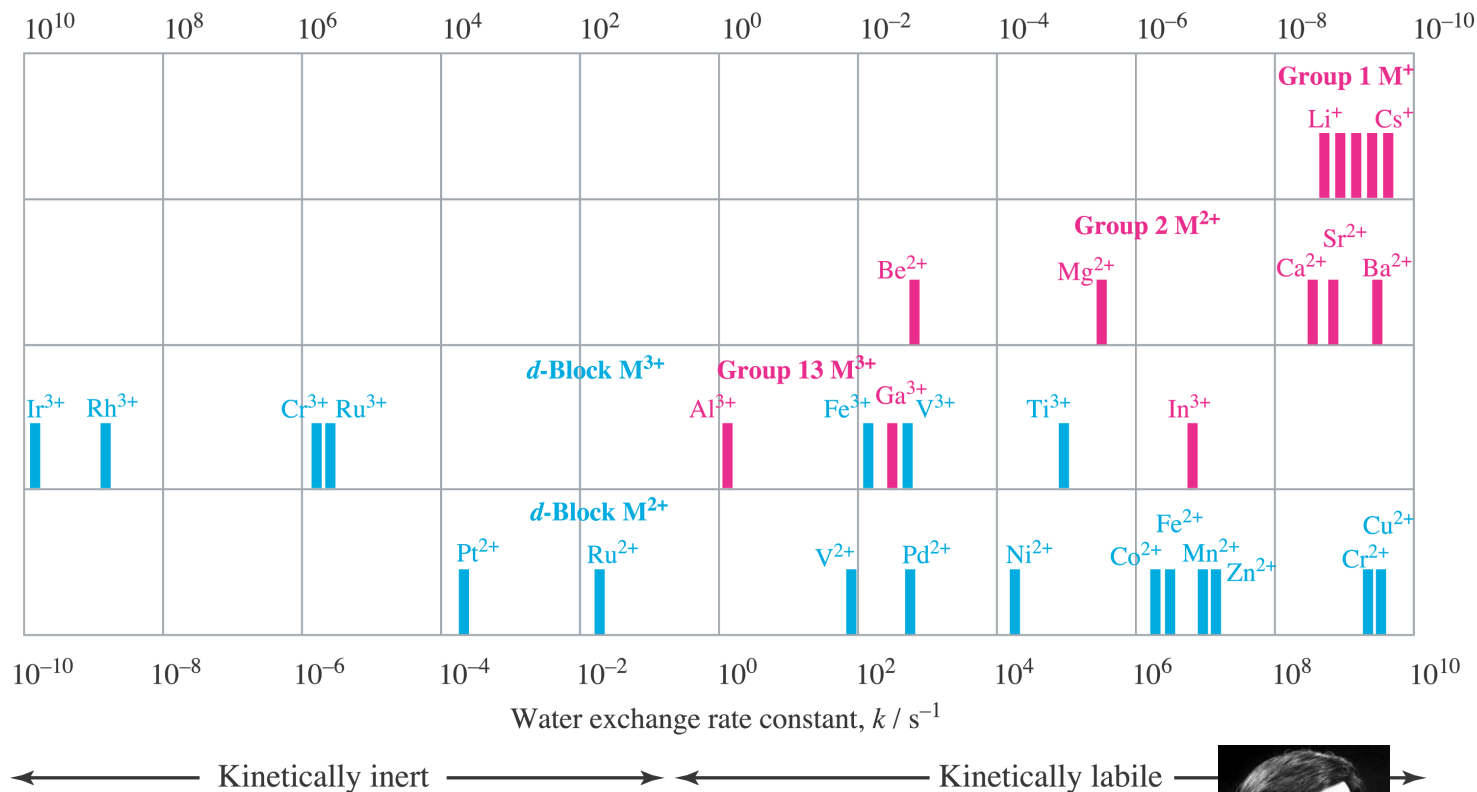
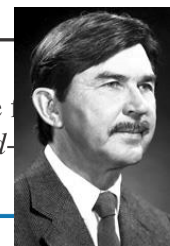


Fig. 26.1 Water exchange rate constants and average residence times for water molecules in the first hydration shell of aquated metal ions at 298 K. Group 1, 2 and 13 metal ions are shown in pink, and d-block metal ions in blue. [Based on S.F. Lincoln (2005) *Helv. Chim. Acta*, vol. 88, p. 523 (Figure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



ion sphere
ons in blue

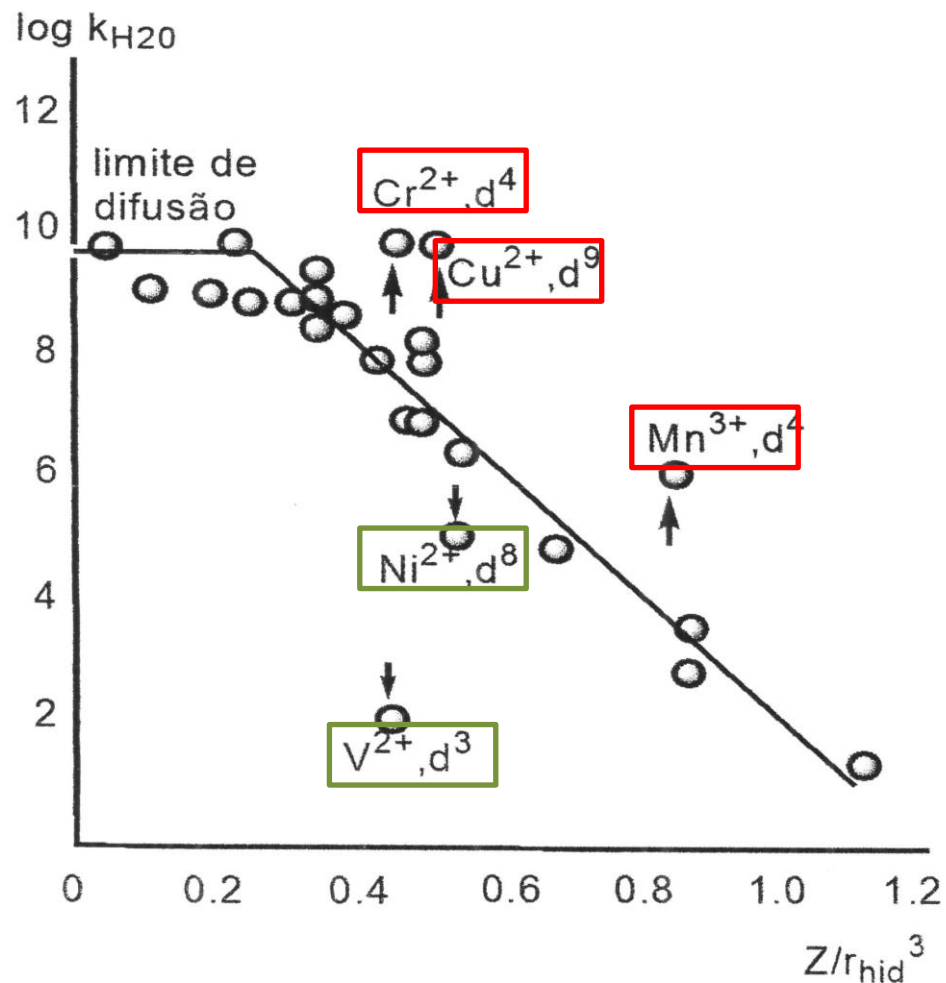
H. Taube - 1983



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Labilidade e inércia

- Está relacionada com a relação carga/raio do íon



➤ Aumento da relação Carga/raio → força da ligação metal-ligante → diminui k

➤ Íons d^4 e d^9 tem distorção Jahn-Teller → mais lábeis

➤ Íons d^3 , d^8 , d^5 e d^6 (spin baixo) → grande EECL → mais inertes



Gráfico de Eyring

26.2

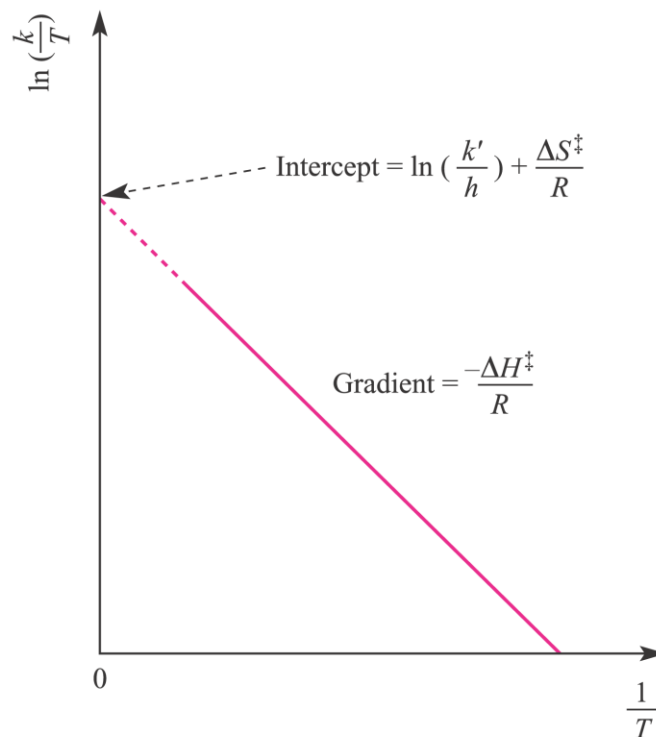


Fig. 26.2 An Eyring plot allows the activation parameters ΔH^\ddagger and ΔS^\ddagger to be determined from the temperature dependence of the rate constant; the dotted part of the line represents an extrapolation. See equation 26.9 for definitions of quantities.



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Reactants	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger / \text{cm}^3 \text{mol}^{-1}$
$[\text{Pt}(\text{dien})\text{Cl}]^+ + \text{H}_2\text{O}$	+84	-63	-10
$[\text{Pt}(\text{dien})\text{Cl}]^+ + [\text{N}_3]^-$	+65	-71	-8.5
<i>trans</i> - $[\text{PtCl}_2(\text{PEt}_3)_2] + \text{py}$	+14	-25	-14
<i>trans</i> - $[\text{PtCl}(\text{NO}_2)(\text{py})_2] + \text{py}$	+12	-24	-9

Table 26.1 Activation parameters for substitution in selected square planar complexes.



26.3

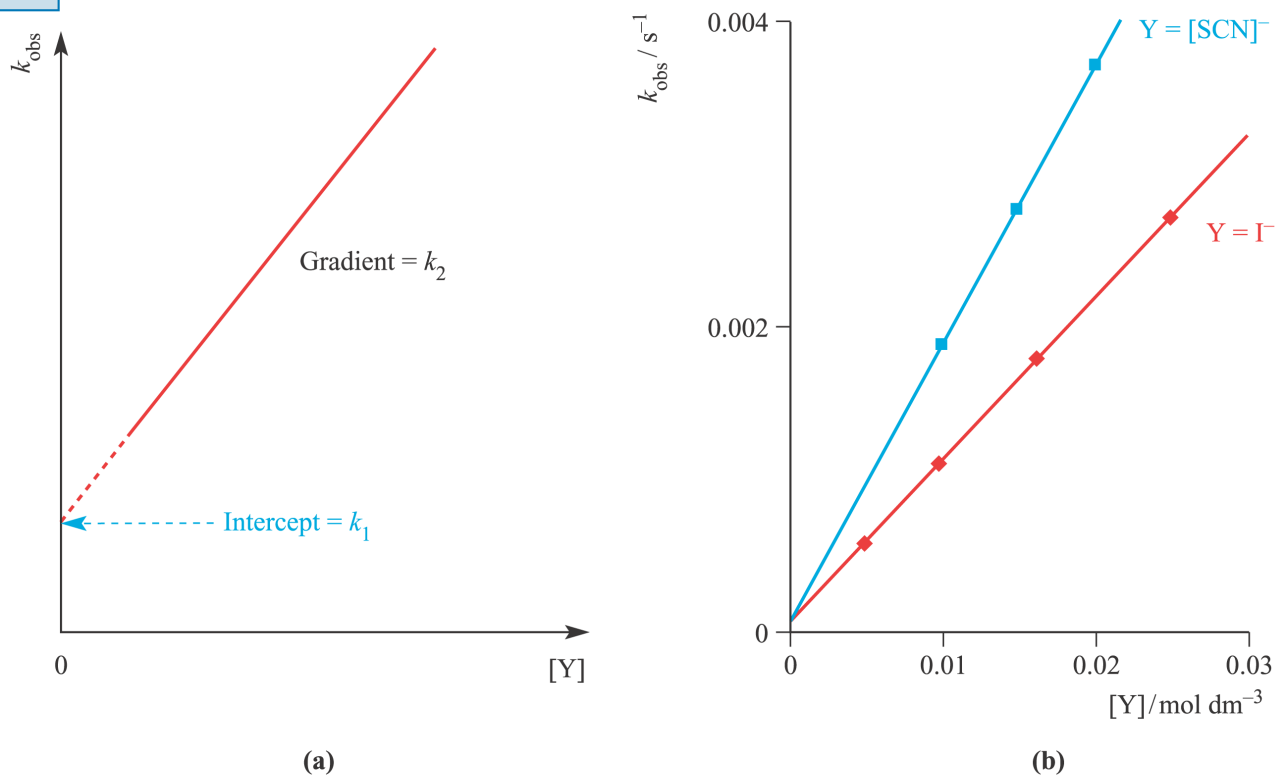
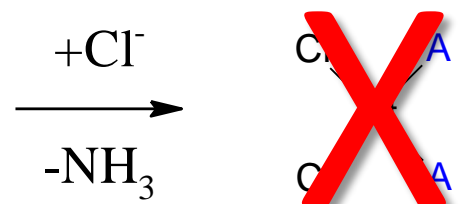
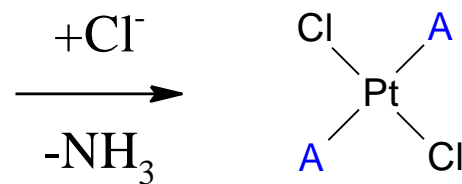
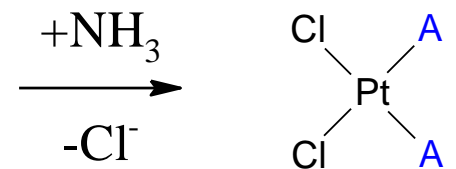
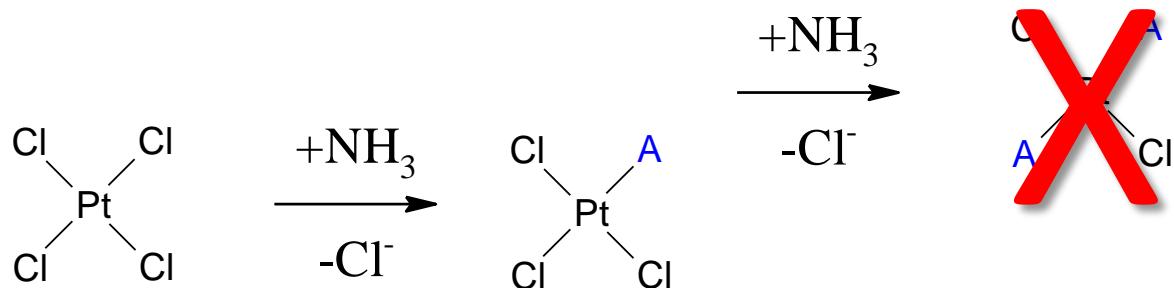


Fig. 26.3 (a) Determination of the k_1 and k_2 rate constants (equation 26.14) from the observed rate data for ligand substitution in a square planar complex; Y is the entering ligand. The dotted part of the line represents an extrapolation. (b) Plots of k_{obs} against concentration of the entering group for the reactions of $\text{trans}[\text{PtCl}_2(\text{py})_2]$ with $[\text{SCN}]^-$ or with I^- ; both reactions were carried out in MeOH and so there is a common intercept. [Data from: U. Belluco *et al.* (1965) *J. Am. Chem. Soc.*, vol. 87, p. 241.]



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Compostos de platina

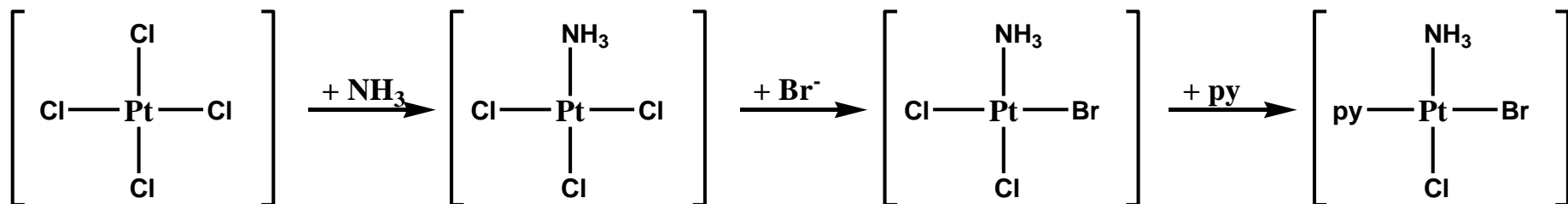




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Efeito trans

- Favorecimento da labilização de ligantes *trans* a outros ligantes
- Investigação de diversos sistemas
 - Série do efeito *trans*: $\mathbf{CN^-}$, \mathbf{CO} , $\mathbf{C_2H_4}$ > $\mathbf{PR_3}$, $\mathbf{H^-}$ > $\mathbf{CH_3^-}$ >> $\mathbf{C_6H_5^-}$,
 $\mathbf{NO_2^-}$, $\mathbf{I^-}$, $\mathbf{SCN^-}$ > \mathbf{Br} > $\mathbf{Cl^-}$ > \mathbf{py} > $\mathbf{NH_3}$ > $\mathbf{H_2O}$ >> $\mathbf{OH^-}$





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Efeito trans

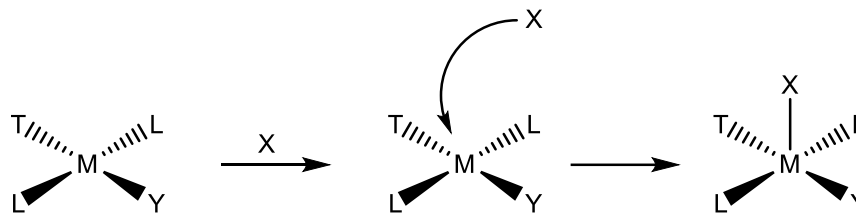
- O quanto um ligante afeta a ligação *trans* a si em um complexo quadrado planar é denominado **efeito trans**
 - Pode ser avaliado através de comprimentos de ligação, constantes de acoplamento e frequências de estiramento
- Está relacionado ao intermediário de reação – *Efeito cinético*





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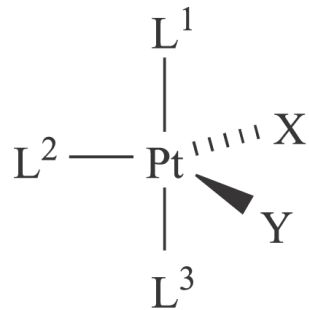
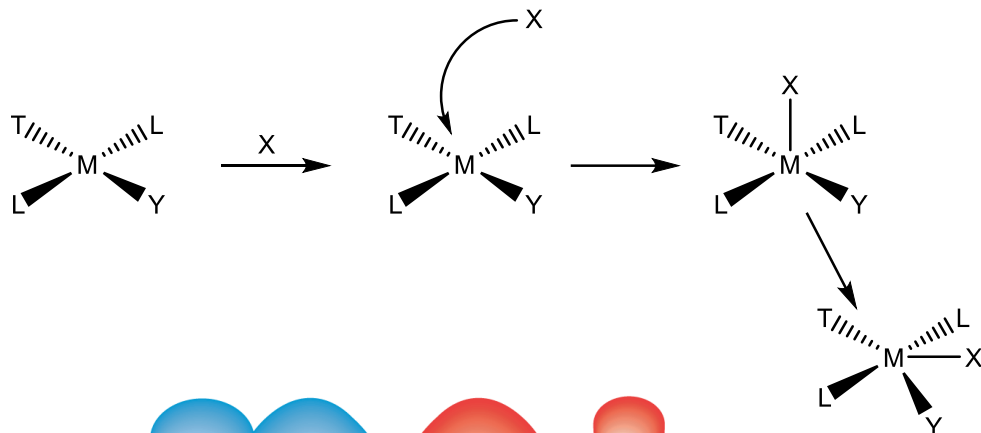
Compostos quadrados planares



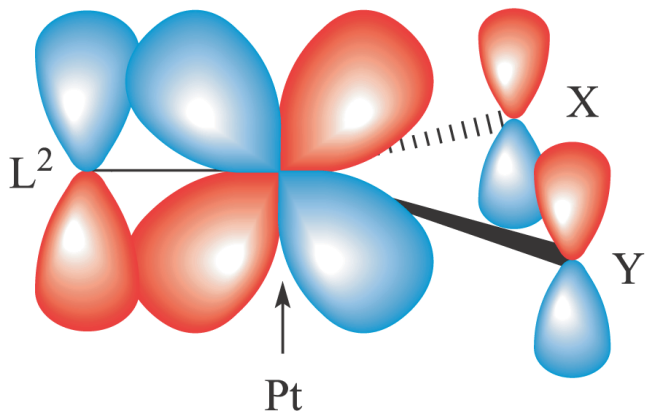


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Compostos quadrados planares



Trigonal bipyramidal
transition state or
intermediate



π -Bonding in the trigonal plane



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