



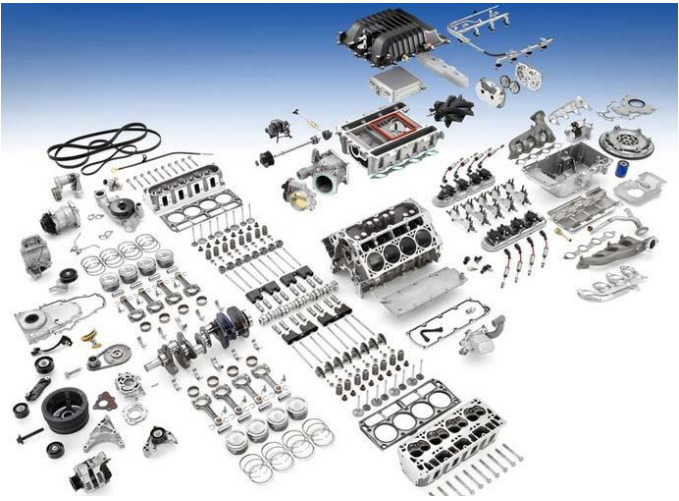
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Termodinâmica de compostos de coordenação

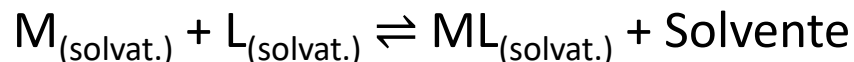


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1. Interação Metal-Ligante



$$\Delta H = \Delta H_{\text{solvatação/dessolvatação}} + \Delta H_{\text{eletrostático}} + \Delta H_{\text{covalente}}$$

$$\Delta H_{\text{eletrostático}} = \frac{Z_M \cdot Z_L \cdot e^2}{r_{ML}}$$

$$\Delta H_{\text{covalente}} = \frac{\sum c_M^2 \cdot c_L^2 \cdot H_{ML}^2}{H_{MM} - H_{LL}}$$

c_M = Coeficiente das funções de onda do metal

c_L = Coeficiente das funções de onda do ligante

H_{ML} = Integral de ressonância

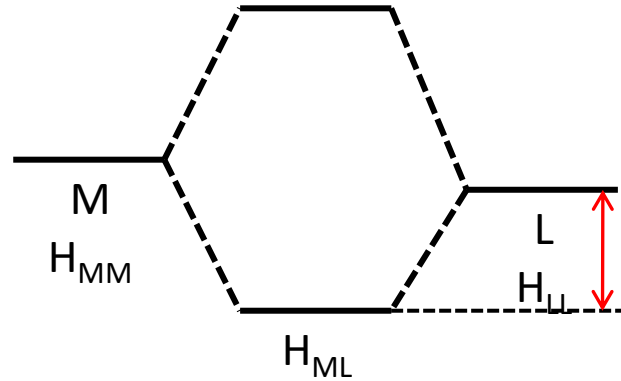
H_{MM} = Orbitais de fronteira do metal

H_{LL} = Orbitais de fronteira do ligante



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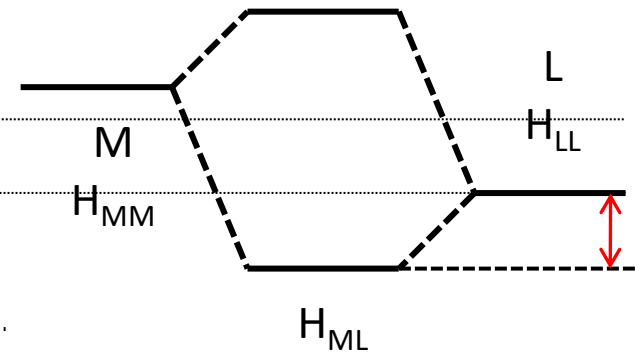
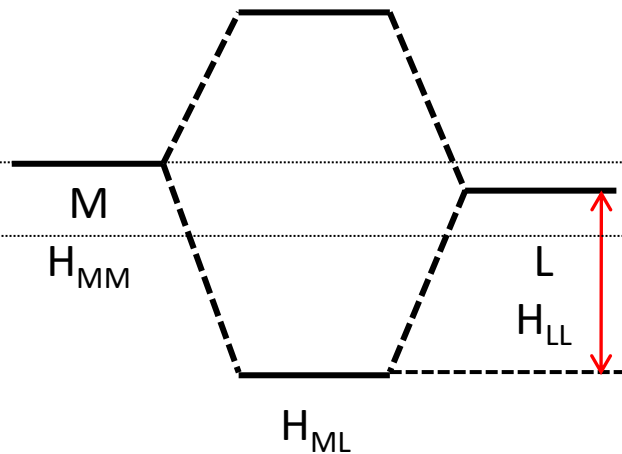
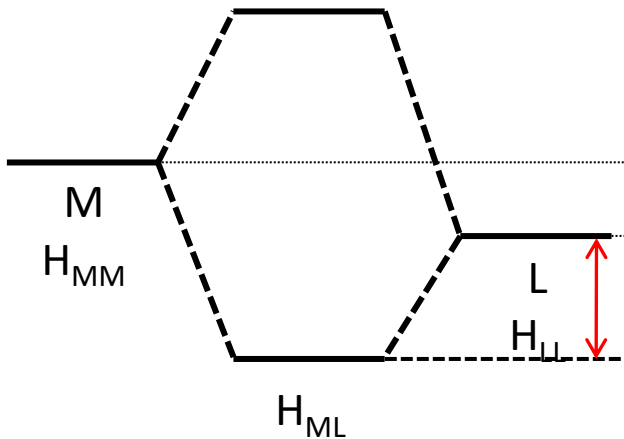
Variação entálpica e entrópica



Caráter covalente da ligação

Caso 1: Aumento do Ligante

Caso 2: Aumento do Metal





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Ácidos e bases

Classificação duro-mole

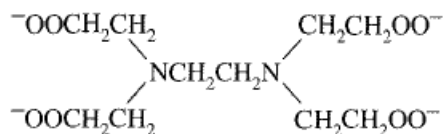
	ÁCIDOS	BASES
DUROS:	Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} Sc^{3+} , La^{3+} , Lu^{3+} , Cr^{3+} , Fe^{3+} (s.a.), Al^{3+} , In^{3+} Ce^{4+} , Th^{4+} , U^{4+} , Ti^{4+} , Zr^{4+} , Hf^{4+}	H_2O , OH^- , O_2^- , ROH , RO^- , R_2O CH_3COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} SO_4^{2-} , ClO_4^- R-SO_3^- , Cl^- , F^-
INTERMEDIÁRIOS:	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} Rh^{3+} , Ir^{3+} , Ru^{3+} , Os^{3+} , Sb^{3+} , Bi^{3+}	N_3^- , N_2 , py , NO_2^- , SO_3^{2-} , Br^- , <u>NCS^-</u>
MOLES	Cu^+ , Ag^+ , Au^+ , Hg^+ , Tl^+ , Cd^{2+} , Hg^{2+} , CH_3Hg^+ $[\text{Co}(\text{CN})_5]^{3-}$, $[\text{Fe}(\text{CN})_5]^{3-}$, Pd^{2+} , Pt^{2+} , Pt^{4+} , Ru^{2+} , Os^{2+}	H^- , R^- , RS^- , I^- , NO^+ , CO , RNC , CN^- , C_2H_4 , R_3P , $(\text{RO}_3)\text{P}$, R_3As R_2S , R_2SO



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Variações entálpicas e entrópicas para reações de formação de compostos de coordenação

M	L	K	$\Delta G(\text{kcal/mol})$	$\Delta H(\text{kcal/mol})$	$\Delta S(\text{cal/mol.K})$
Mg ²⁺	SO ₄ ²⁻	1,8x10 ²	-3,07	4,8	26
Mg ²⁺	EDTA ⁴⁻	3,5x10 ⁸	-11,5	3,14	50,5
La ³⁺	SO ₄ ²⁻	6,4x10 ³	-5,2	2,5	26
La ³⁺	CH ₃ COO ⁻	3,8x10 ⁸	-2,16	2,18	14,6
La ³⁺	EDTA ⁴⁻	1,5x10 ¹⁵	-20,7	-0,8	66,8
Ni ²⁺	SO ₄ ²⁻	2,1x10 ²	-3,16	3,3	22
Ni ²⁺	NH ₃	6,8x10 ²	-3,86	-4,01	-0,5
Ni ²⁺	NH ₂ C ₂ H ₄ NH ₂	5,0x10 ⁸	-10,5	-8,90	5,5
Ni ²⁺	NH ₂ CH ₂ CO ₂ ⁻	1,5x10 ⁶	-8,43	-4,14	14,4
Ni ²⁺	EDTA ⁴⁻	2,0x10 ¹⁸	-25,0	-8,35	56,7
Zn ²⁺	SO ₄ ²⁻	2,1x10 ²	-3,16	4,4	22
Zn ²⁺	CH ₃ COO ⁻	8,8	-1,29	2,04	11,2
Zn ²⁺	NH ₂ C ₂ H ₄ NH ₂	8,0x10 ⁵	-8,05	-7,0	3,5
Zn ²⁺	EDTA ⁴⁻	1.7x10 ¹⁶	-22.1	-5.61	56.3
CH ₃ Hg ⁺	-SCH ₂ CH ₂ OH	7,0x10 ¹⁵	-21,6	-19,8	6,2



EDTA

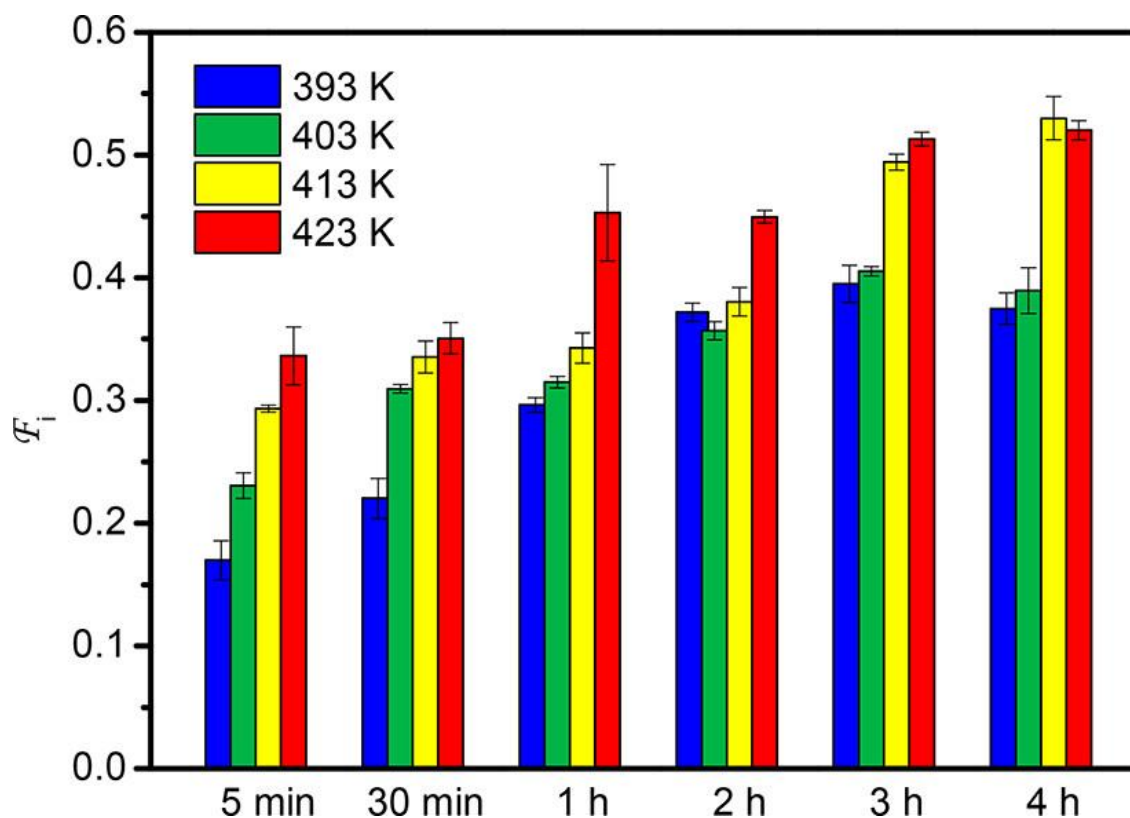
Metal duro prefere ligante duro (controle entrópico)
Metal mole prefere ligante mole (controle entálpico – por covalência)



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Produto termodinâmico vs Produto cinético

$$F_i = \frac{SCN^-}{NCS^-}$$

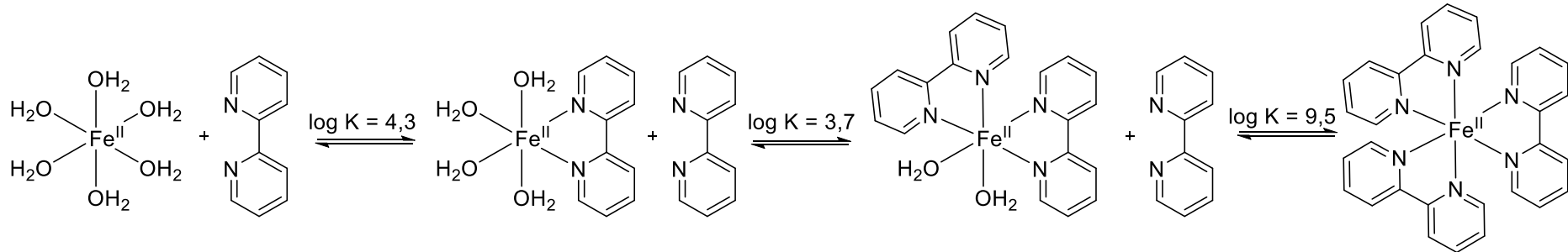


Relative abundance F_i of the $-SCN$ isomers of cis -[Ru(phen)(dcbH₂)(NCS)₂] for different reaction times and temperatures.

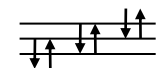
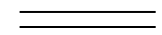
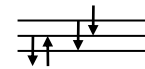
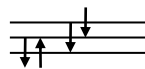
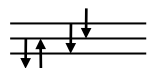
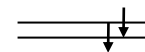
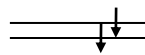
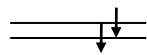
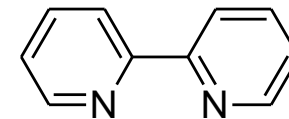


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Efeito de configuração eletrônica



O ligante 2,2'-bipiridina, bpy, é de campo intermediário



EECL = 4Dq-P

EECL = 24Dq-2P



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Estado de oxidação

	E_0 / V
$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + e^- \longrightarrow [\text{Co}(\text{H}_2\text{O})_6]^{2+}$	+1.83
$[\text{Co}(\text{NH}_3)_6]^{3+} + e^- \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$	+0.11
$[\text{Co}(\text{ox})_3]^{3-} + e^- \longrightarrow [\text{Co}(\text{ox})_3]^{4-}$	+0.57
$[\text{Co}(\text{phen})_3]^{3+} + e^- \longrightarrow [\text{Co}(\text{phen})_3]^{2+}$	+0.42

$\text{phen} > \text{NH}_3 > \text{H}_2\text{O} > \text{ox}^{2-}$