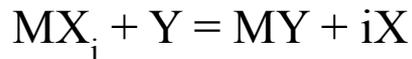


# Влияние растворителя на процесс комплексообразования

Гёрни – шкала мольных долей вместо молярной (моляльной).

Если раствор не концентрированный, считается, что в 1 л раствора содержится такое же число молей, что и в 1 л чистого растворителя.

$N_A \approx [A]/[H_2O]$ ,  $[H_2O]$  – как в чистом растворителе



$$K(N) = \frac{([MY]/[H_2O])([X]/[H_2O])^i}{([MX_i]/[H_2O])([Y]/[H_2O])} = K(c)[H_2O]^{-(i-1)} \quad K(c) = \frac{[MY][X]^i}{[MX_i][Y]}$$

$$K(N) = K(c) \cdot [Sl]^{-\Delta n}$$

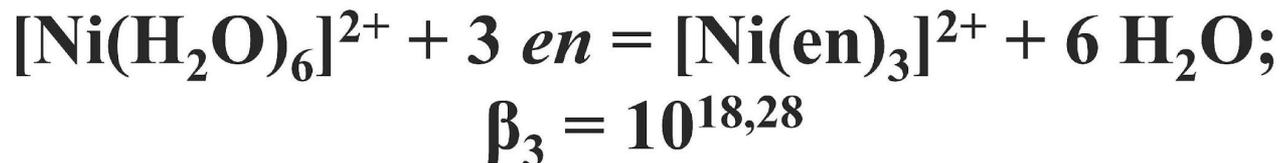
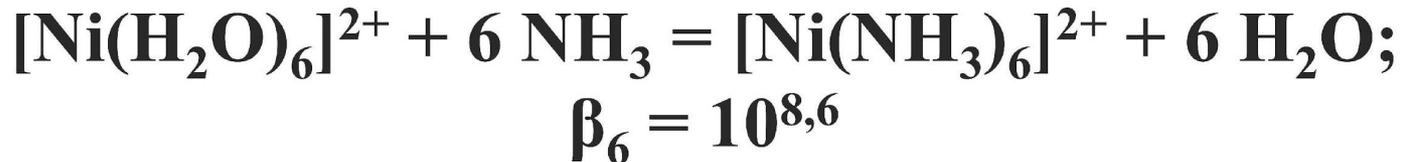
$$\lg K(N) = \lg K(c) - \Delta n \lg[Sl] = -\frac{\Delta G^0}{2.3RT} - \Delta n \lg[Sl] = -\frac{\Delta H^0}{2.3RT} + \frac{\Delta S^{0'}}{2.3R} - \Delta n \lg[Sl]$$

$$\Delta G^0 = \Delta G^{0'} - 2.3RT \Delta n \lg[Sl]$$

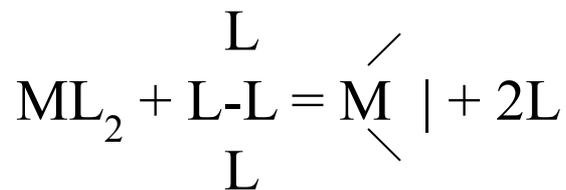
$$\Delta H^0 = \Delta H^{0'} \quad \Delta S^{0'} = \Delta S^0 - 2.3 \Delta n \lg[55.5] = \Delta S^0 - 33 \Delta n$$

Энтропия: унитарная составляющая, кратическая составляющая

## Хелатный эффект



	$\lg \beta$	$\Delta G^\circ$ , кДж/моль
1 $\text{NH}_3$	2.8	-16
2 $\text{NH}_3$ (1 <i>en</i> )	5.0 (7.51)	-28.5 (-42.8)
3 $\text{NH}_3$	6.6	-37.7
4 $\text{NH}_3$ (2 <i>en</i> )	7.87 (13.86)	-44.9 (-79.1)
5 $\text{NH}_3$	8.6	-49.1
6 $\text{NH}_3$ (3 <i>en</i> )	8.61 (18.28)	-49.2 (-104.4)



$$\Delta H^\circ = H^\circ \text{M} \begin{array}{c} \diagup \text{L} \\ | \\ \diagdown \text{L} \end{array} - H^\circ_{\text{ML}_2} - H^\circ_{\text{L-L}} + 2H^\circ_{\text{L}} = 0$$

$$\Delta S^\circ = S^\circ \text{M} \begin{array}{c} \diagup \text{L} \\ | \\ \diagdown \text{L} \end{array} - S^\circ_{\text{ML}_2} - S^\circ_{\text{L-L}} + 2S^\circ_{\text{L}}$$

$$\Delta S^0 = R \cdot \ln 55.5 = 33$$

$$\text{Дж} \cdot \text{моль}^{-1} \cdot \text{К}^{-1}$$

$$\Delta S^0 = 33 \cdot n \text{ Дж} \cdot \text{моль}^{-1} \cdot \text{К}^{-1}$$

A.E. Martell, R.D. Hancock, R.J. Motekaitis. Factors affecting stabilities of chelate, macrocyclic and macrobicyclic complexes in solution. Coordination Chemistry Reviews, Volume 133, 1994, Pages 39–65

Термодинамический вклад в хелатный эффект при образовании комплексов этилендиамина с Ni(II) ( $\Delta G^0$  и  $\Delta H^0$  в кДж·моль<sup>-1</sup>,  $\Delta S^0$  в Дж·моль<sup>-1</sup>·К<sup>-1</sup>)

	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$	33n
Монодентатный к-кс				
$[\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$	-29.0	-32.6	-13	
$[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	-46.3	-65.3	-63	
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	-51.8	-100	-163	
Хелатный аналог				
$[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$	-43.1	-38	17	
$[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	-79.9	-76.6	13	
$[\text{Ni}(\text{en})_3]^{2+}$	-105	-117	-42	
Хелатный эффект				
Ni(en)	-14.1	-5.4	30	33
Ni(en) <sub>2</sub>	-33.6	-11.3	76	66
Ni(en) <sub>3</sub>	-53.2	-17	121	99

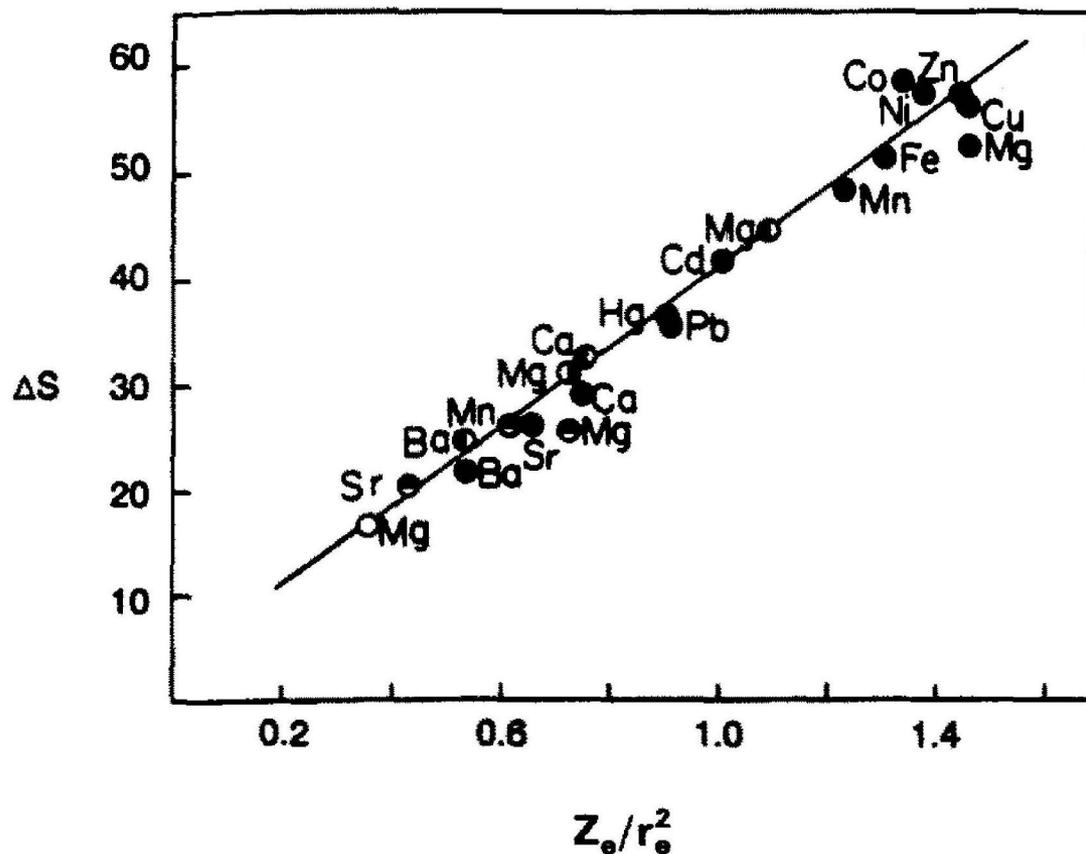
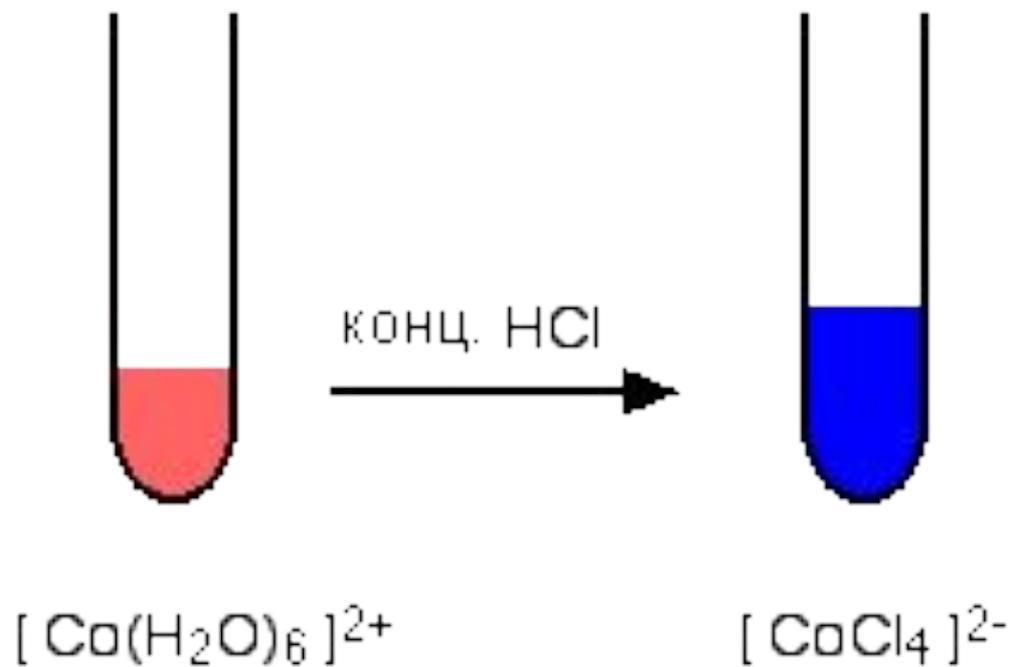
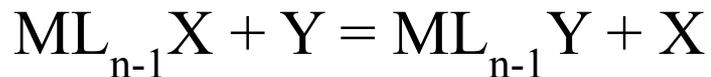


Fig. 1. Correlation of entropies of formation of aminopolycarboxylic acid chelates in aqueous solution with effective radius of the metal ion,  $r_e$ , and number of negative carboxylate groups of the ligand,  $Z_e$ , that become coordinated with the metal ion;  $r_e$  = crystal (Pauling) radius + 1.0 Å; ●, EDTA = ethylenediaminetetraacetic acid; ⦿, NTA = nitrilotriacetic acid; ◐, MIMDA = *N*-methyliminodiacetic acid; ◑, DMEDDA = *N,N'*-di-methylethylenediaminediacetic acid; ○, DMG = *N,N*-dimethylglycine.

# Кинетика и механизм замещения внутрисферных лигандов





Инертные комплексы:  $t_{1/2} \geq 10$  с

Лабильные комплексы:  $t_{1/2} < 10$  с

$d^3$ :  $V^{2+}$ ,  $Cr^{3+}$ ,  $Mo^{3+}$ ,  $W^{3+}$ ,  $Mn^{4+}$ ,  $Re^{4+}$

$d^0$ :  $Sc^{3+}$ ,  $P3\Theta^{3+}$ ,  $Ti^{4+}$ ,  $Ce^{4+}$ ,  $Th^{4+}$ ,  $Mo^{6+}$

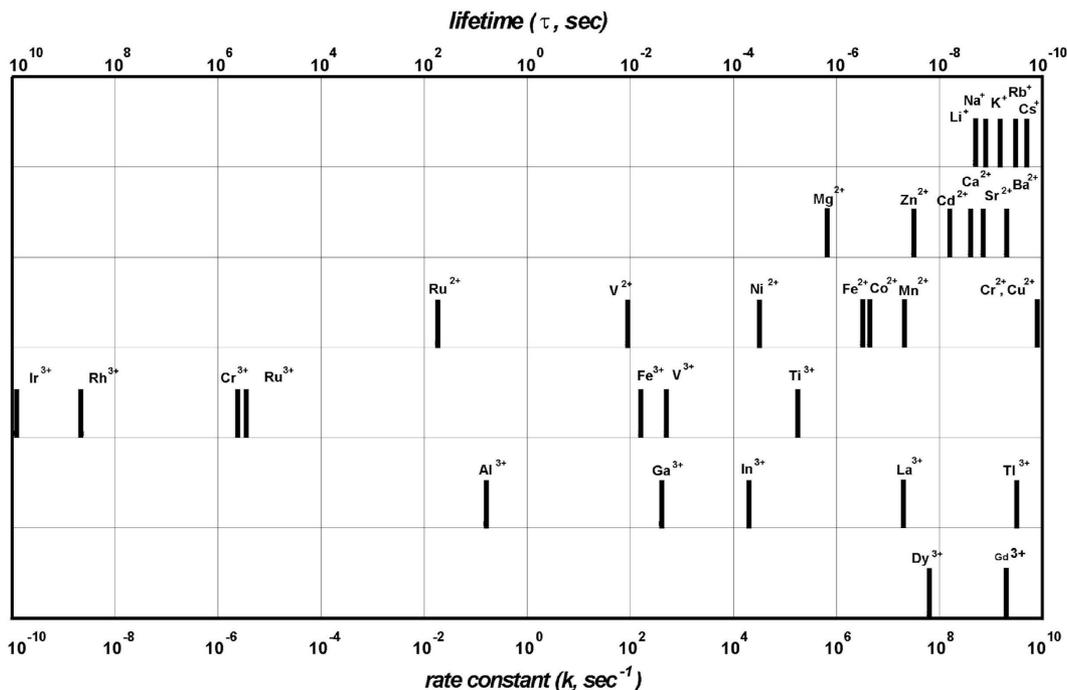
$d^4$ :  $(Cr^{2+})$ ,  $Mn^{3+}$ ,  $Re^{3+}$ ,  $Ru^{4+}$ ,  $Os^{5+}$

$d^1$ :  $Ti^{3+}$ ,  $V^{4+}$ ,  $Mo^{5+}$ ,  $W^{5+}$ ,  $Re^{6+}$

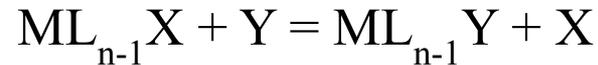
$d^5$ :  $(Fe^{3+})$ ,  $Ru^{3+}$ ,  $Os^{3+}$ ,  $Ir^{4+}$

$d^2$ :  $Ti^{2+}$ ,  $V^{3+}$ ,  $Mo^{4+}$ ,  $W^{4+}$ ,  $Re^{5+}$

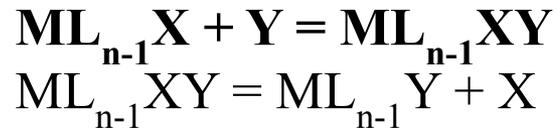
$d^6$ :  $(Fe^{2+})$ ,  $Ru^{2+}$ ,  $Os^{2+}$ ,  $Co^{3+}$ ,  $Ir^{3+}$ ,  $Pd^{4+}$ ,  $Pt^{4+}$  ( $d^{10}$ ):  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Al^{3+}$ ,  $Ga^{3+}$ ,  $In^{3+}$ ,  $Tl^{3+}$



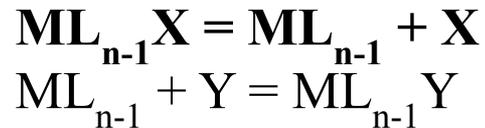
# Механизмы обмена лигандов



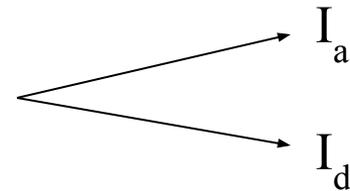
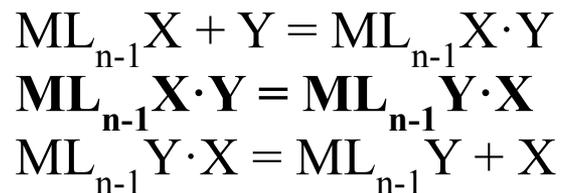
1) Ассоциативный механизм (A)



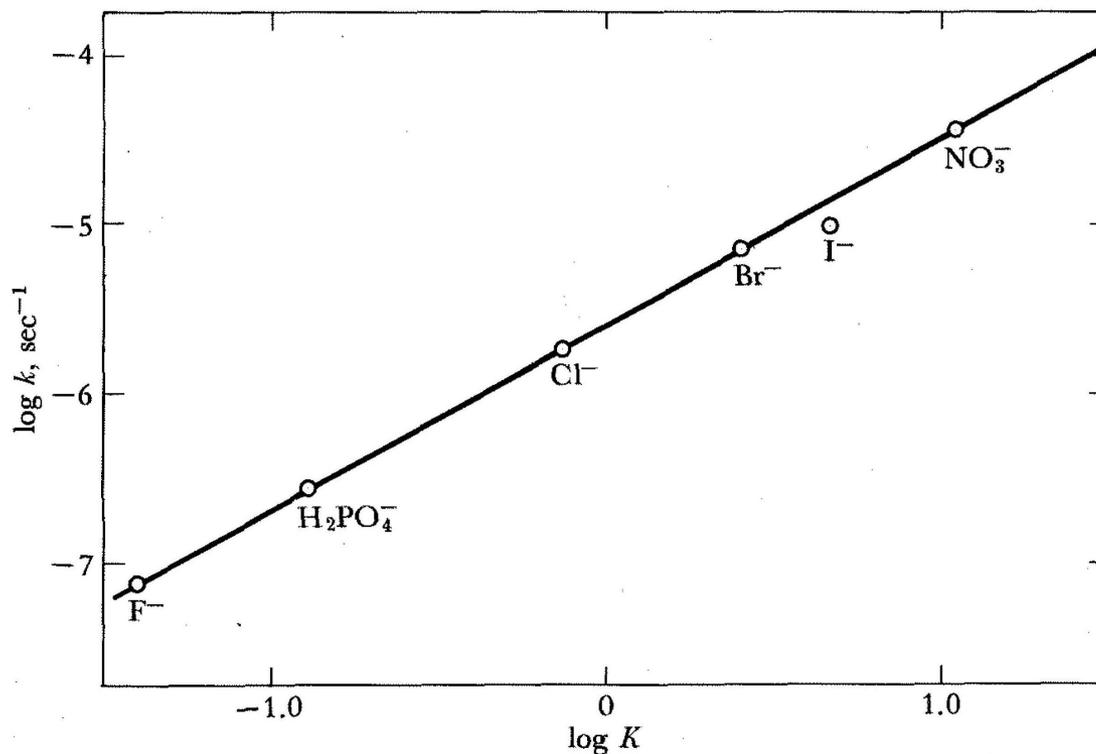
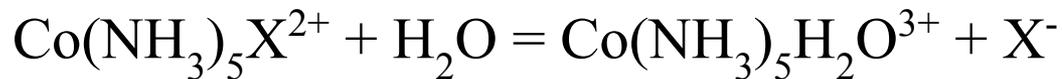
2) Диссоциативный механизм (D)



3) Механизм взаимного обмена (I)

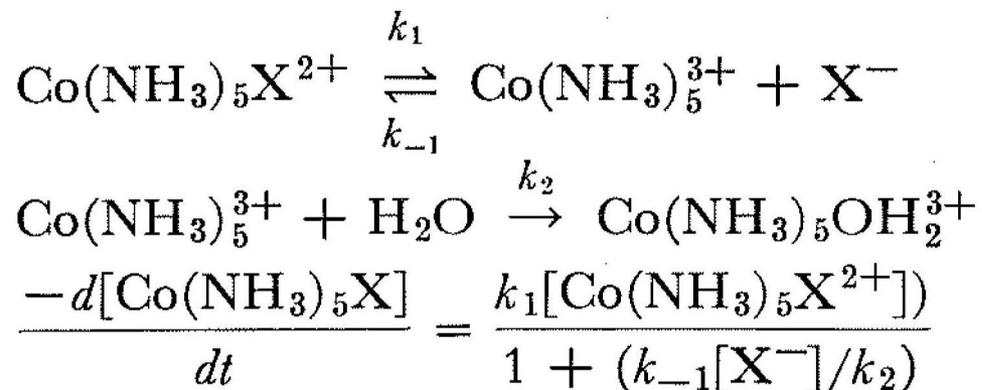


## Реакция аквазации (октаэдрические комплексы)



Влияние ассоциации (протоны, ионы металлов:  $\text{Hg}^{2+}$ ,  $\text{Tl}^{3+}$ ,  $\text{Ag}^+$ )

Редокс-катализ замещения ( $\text{Cr}^{3+} - \text{Cr}^{2+}$ )



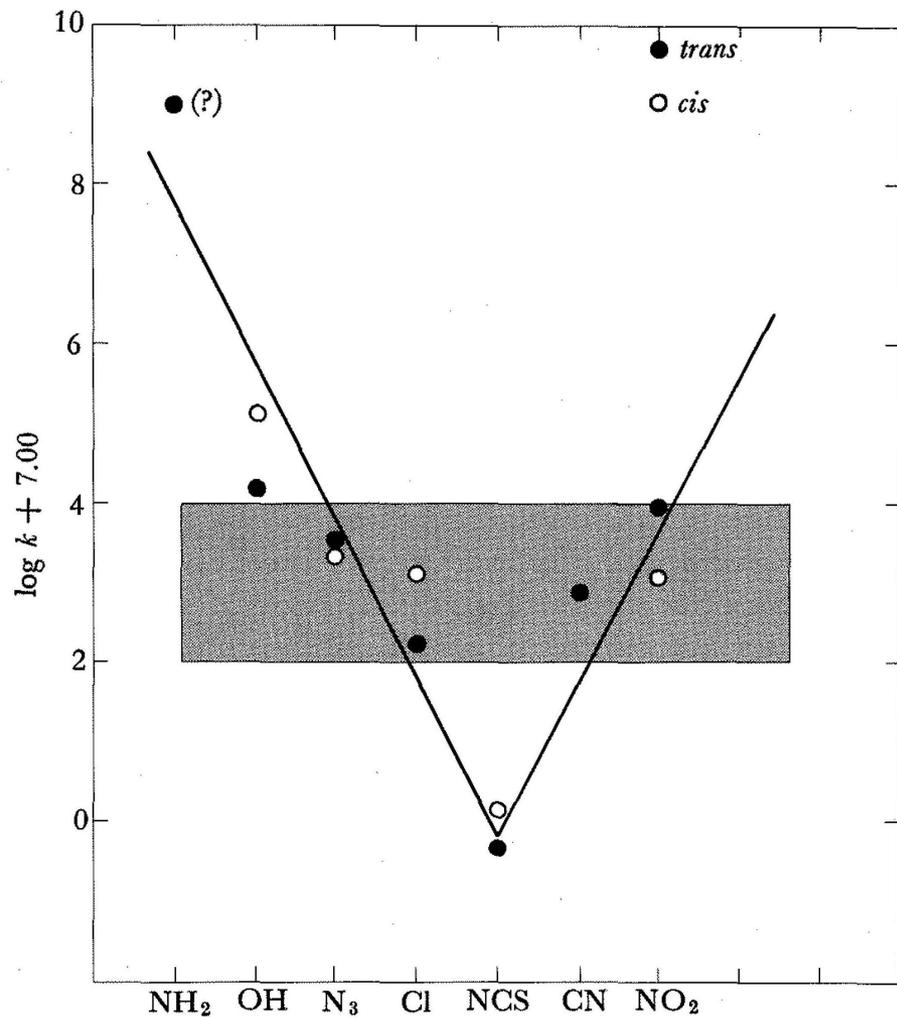
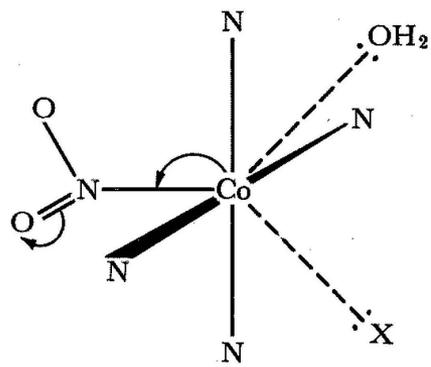
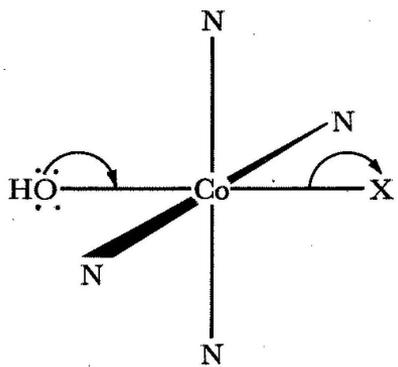
**Table 3-1** Rates of first acid hydrolysis of *trans*-Co(AA)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> at 25°C

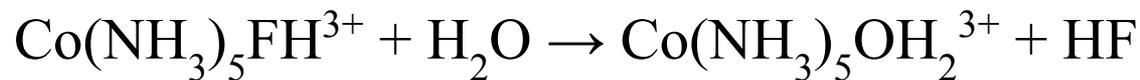
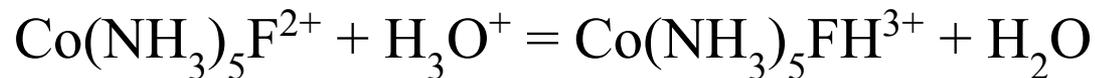
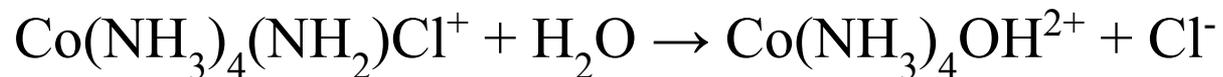
AA	$k \times 10^4, \text{sec}^{-1}$
H <sub>2</sub> N—CH <sub>2</sub> CH <sub>2</sub> —NH <sub>2</sub> (en)	0.32
H <sub>2</sub> N—CH <sub>2</sub> —CH(CH <sub>3</sub> )—NH <sub>2</sub> (pn)	0.62
<i>d,l</i> -H <sub>2</sub> N—CH(CH <sub>3</sub> )—CH(CH <sub>3</sub> )—NH <sub>2</sub> ( <i>d,l</i> -bn)	1.5
<i>meso</i> -H <sub>2</sub> N—CH(CH <sub>3</sub> )—CH(CH <sub>3</sub> )—NH <sub>2</sub> ( <i>meso</i> -bn)	42
H <sub>2</sub> N—C(CH <sub>3</sub> ) <sub>2</sub> —C(CH <sub>3</sub> ) <sub>2</sub> —NH <sub>2</sub> (tetrameen)	330

Langford C.H., Gray H.B. Ligand Substitution Processes. W. A. Benjamin, Inc., New York. 1965

Complex	Ligand replaced	Rate constant, sec <sup>-1</sup>	t, °C
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	Cl <sup>-</sup>	6.7 × 10 <sup>-6</sup>	25
<i>trans</i> -Co(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> )Cl <sup>2+</sup>	Cl <sup>-</sup>	2.2 × 10 <sup>-6</sup>	20
<i>cis</i> -Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	"very fast"	25
<i>trans</i> -Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	1.8 × 10 <sup>-3</sup>	25
<i>cis</i> -Co(en) <sub>2</sub> (NH <sub>3</sub> )Cl <sup>2+</sup>	Cl <sup>-</sup>	1.4 × 10 <sup>-6</sup>	35
<i>trans</i> -Co(en) <sub>2</sub> (NH <sub>3</sub> )Cl <sup>2+</sup>	Cl <sup>-</sup>	4.0 × 10 <sup>-7</sup>	24
<i>cis</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	2.5 × 10 <sup>-4</sup>	25
<i>trans</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	3.2 × 10 <sup>-5</sup>	25
<i>trans</i> -Co(en) <sub>2</sub> (N <sub>3</sub> )Cl <sup>+</sup>	Cl <sup>-</sup>	2.5 × 10 <sup>-4</sup>	25
<i>cis</i> -Co(en) <sub>2</sub> (NO <sub>2</sub> )Cl <sup>+</sup>	Cl <sup>-</sup>	1.1 × 10 <sup>-4</sup>	25
Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	Br <sup>-</sup>	6.3 × 10 <sup>-6</sup>	25
<i>trans</i> -Co(en) <sub>2</sub> (NH <sub>3</sub> )Br <sup>2+</sup>	Br <sup>-</sup>	1.2 × 10 <sup>-6</sup>	25
<i>trans</i> -Co(en) <sub>2</sub> Br <sub>2</sub> <sup>+</sup>	Br <sup>-</sup>	1.4 × 10 <sup>-4</sup>	25
<i>trans</i> -Co(en) <sub>2</sub> (NO <sub>2</sub> )Br <sup>+</sup>	Br <sup>-</sup>	4.0 × 10 <sup>-3</sup>	25

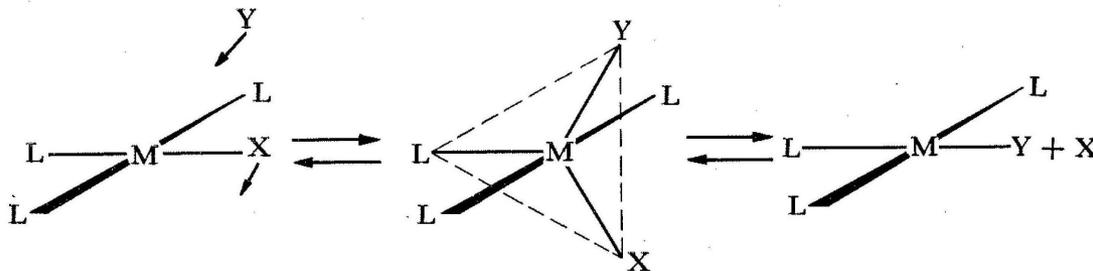
цис- и транс-  
 $\text{Co(en)}_2(\text{A})\text{Cl}^+$



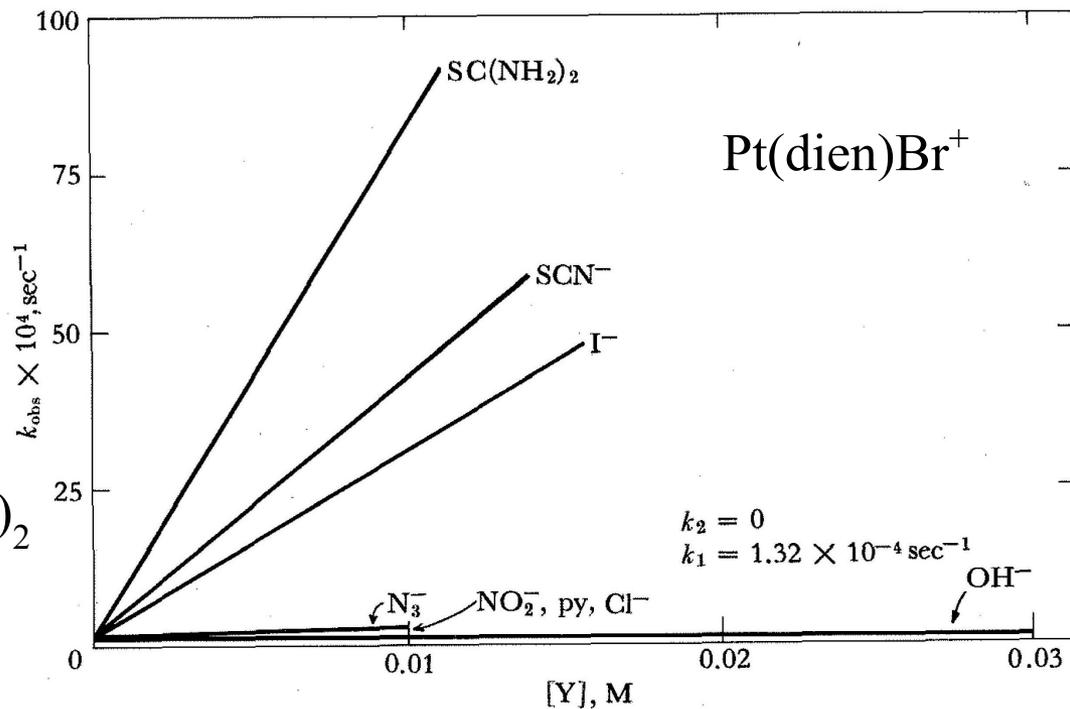
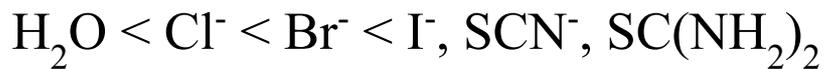
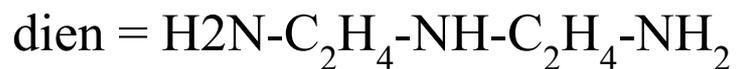
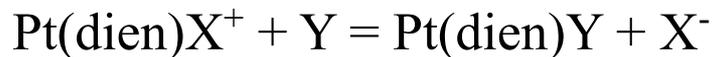


# Процессы обмена лигандов в плоско-квадратных комплексах

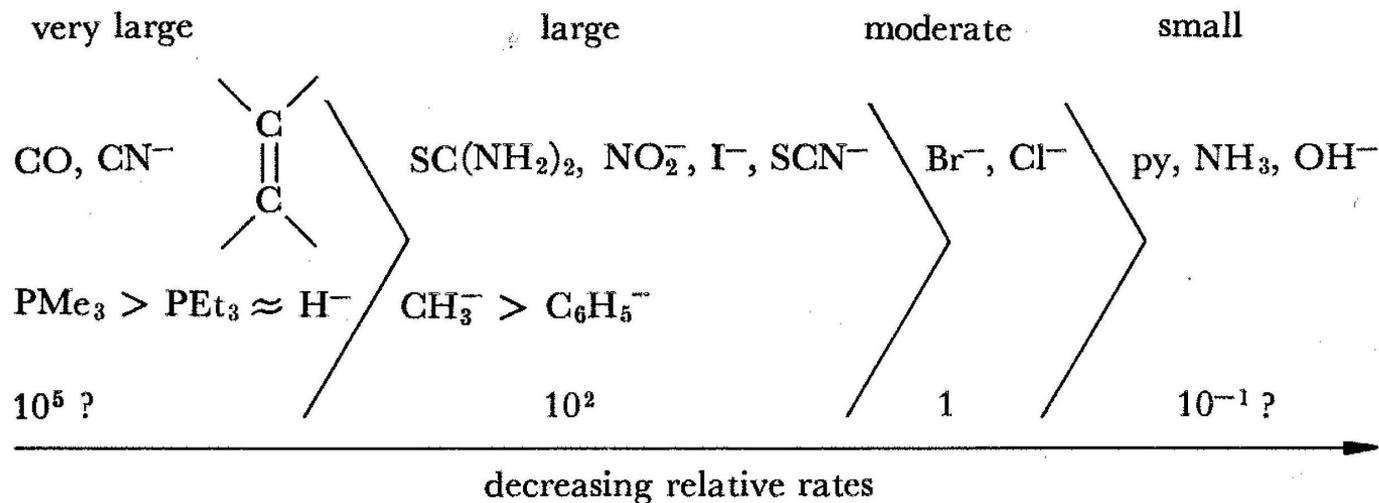
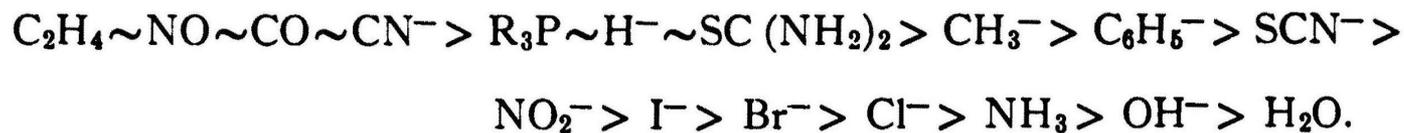
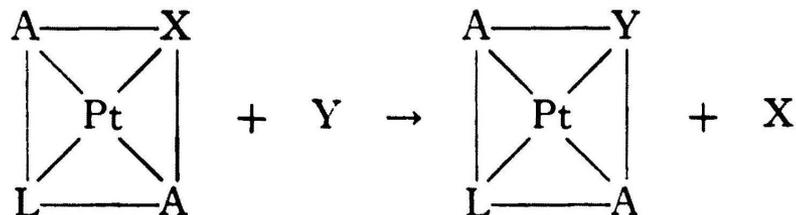
Ni(II), Rh(I), Pd(II), Ir(I), Pt(II), Au(III), конфигурация d8



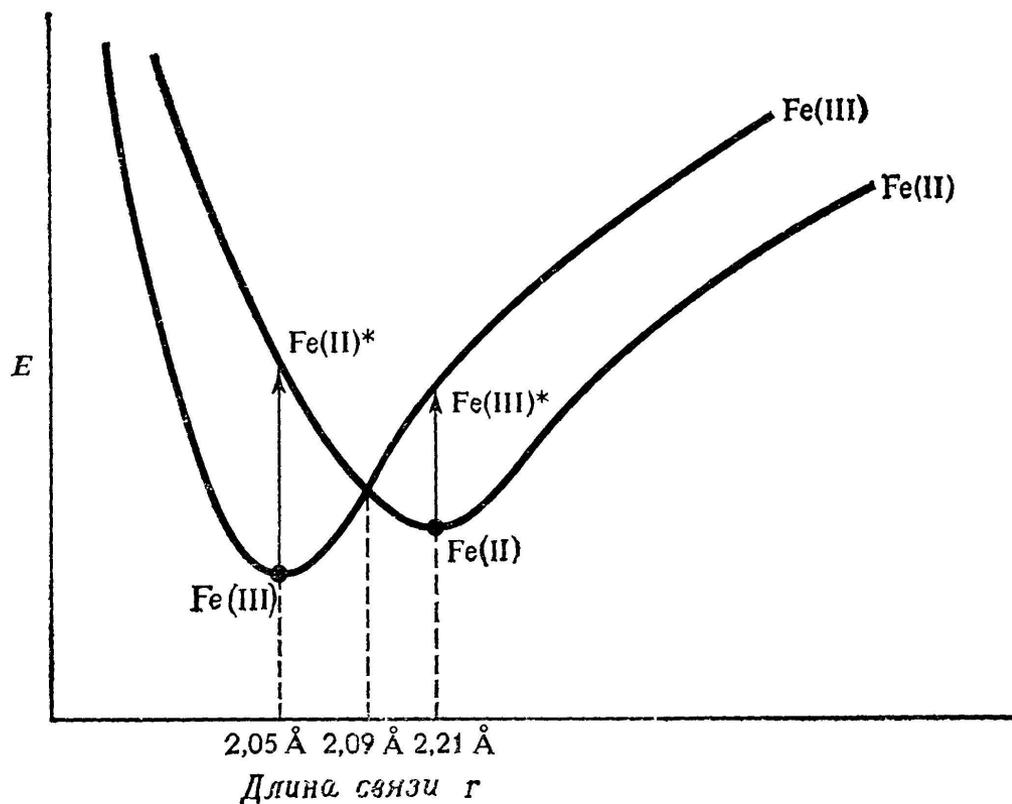
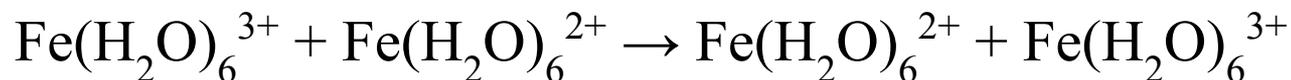
$$\text{скорость} = \frac{-d[\text{комплекс}]}{dt} = (k_1 + k_2[Y]) \cdot [\text{комплекс}]$$



# Кинетический транс-эффект

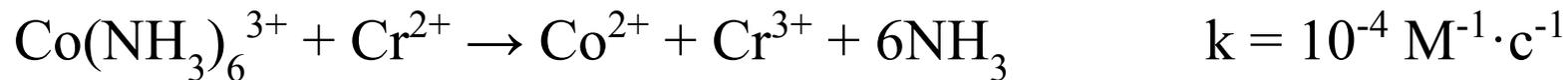


# Кинетика и механизм гомогенных окислительно-восстановительных реакций комплексов металлов



Константы скорости некоторых окислительно-восстановительных реакций второго порядка, идущих по внешнесферному механизму (растворитель — вода, температура 25°C)

Реагенты	Электронная конфигурация	$k_2$ , (моль/л) <sup>-1</sup> ·с <sup>-1</sup>
а. Свободная энергия не изменяется		
$\text{Fe}(\text{phen})_3^{2+} + \text{Fe}(\text{phen})_3^{3+}$	$t_{2g}^6 + t_{2g}^5$	10 <sup>5</sup>
$\text{Os}(\text{bipy})_3^{2+} + \text{Os}(\text{bipy})_3^{3+}$	$t_{2g}^6 + t_{2g}^5$	5·10 <sup>4</sup>
$\text{Fe}(\text{CN})_6^{4-} + \text{Fe}(\text{CN})_6^{3-}$	$t_{2g}^6 + t_{2g}^5$	7,4·10 <sup>2</sup>
$\text{IrCl}_6^{3-} + \text{IrCl}_6^{2-}$	$t_{2g}^6 + t_{2g}^5$	10 <sup>3</sup>
$\text{Co}(\text{phen})_3^{2+} + \text{Co}(\text{phen})_3^{3+}$	$t_{2g}^6 e_g + t_{2g}^6$	1,1
б. Приращение свободной энергии		
$\text{Fe}(\text{CN})_6^{4-} + \text{Fe}(\text{phen})_3^{3+}$	$t_{2g}^6 + t_{2g}^5$	10 <sup>8</sup>
$\text{Fe}(\text{CN})_6^{4-} + \text{IrCl}_6^{2-}$	$t_{2g}^6 + t_{2g}^5$	3,8·10 <sup>5</sup>
$\text{Ru}(\text{phen})_3^{2+} + \text{RuCl}_6^{2-}$	$t_{2g}^6 + t_{2g}^5$	2,5·10 <sup>9</sup>



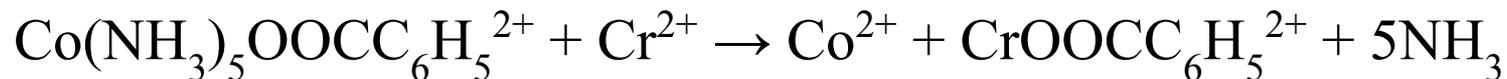
внешнесферный механизм



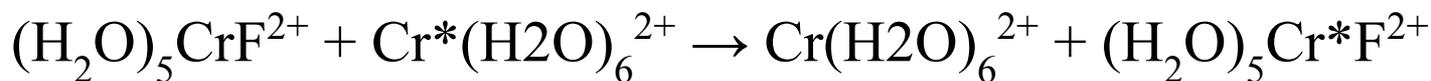
внутрисферный механизм

$[(\text{NH}_3)_5\text{Co-X-Cr}]^{4+}$  - активированный комплекс

$(\text{NH}_3) < (\text{py}) < \text{H}_2\text{O} < \text{Cl}^- < \text{Br}^-$



$k = 0.15 \text{ M}^{-1} \cdot \text{c}^{-1}$

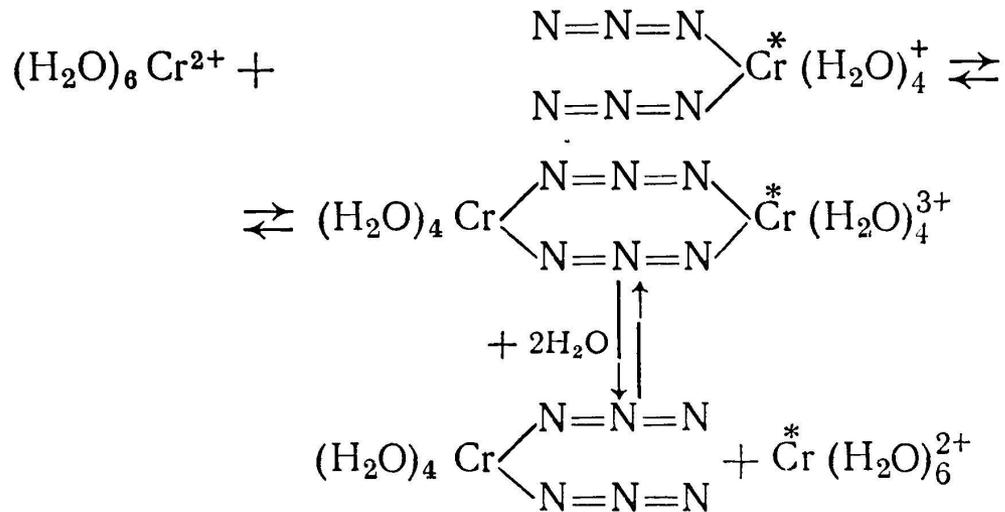


$$k = 2.2 \cdot 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$$



RELATIVE RATES OF REACTION OF  $\text{Cr}^{++}$  WITH  $\text{Fe}(\text{III})$  SPECIES, AND OF ELECTRON EXCHANGE BETWEEN  $\text{Fe}^{++}$  AND  $\text{Fe}(\text{III})$  SPECIES

	Relative rates	
	For $\text{Cr}^{++}$ (at $2^\circ$ , $\mu = 2.2$ )	For $\text{Fe}^{++}$ (at $0^\circ$ , $\mu = 0.5$ )
$\text{Fe}^{+++}$	1	1
$\text{FeF}^{++}$	3	11.1
$\text{FeCl}^{++}$	18	11.1
$\text{FeBr}^{++a}$	>100	..
$\text{FeOH}^{++}$	$2.8 \times 10^3$	$1.16 \times 10^3$



Влияние присутствующего противоиона:

