

Semester IV

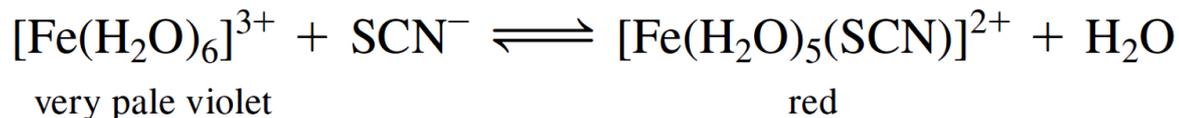
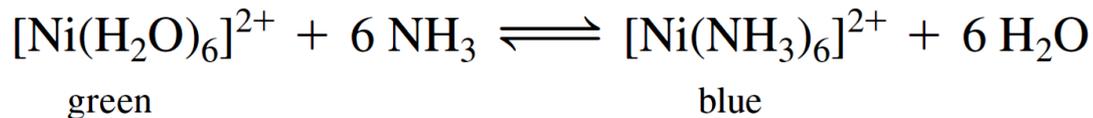
CHE-HC-4014: INORGANIC
CHEMISTRY-III

Topic: Coordination Chemistry

Inert and Labile Complexes

Rates of ligand substitution

- Ligand substitution is an important step in many reactions of coordination complexes.



- The rate at which one complex converts into another is governed by the height of the activation energy barrier that lies between them (**kinetic factor**).
- Complexes that undergoes exchange of one ligand for another within the time of mixing the reactants, are classified as **labile**.
- A **labile complex** has a very **low activation energy** for ligand substitution.
- Taube suggested a reaction half-life of one minute or less as the criterion for lability.
- Complexes that survive for long periods (by convention, at least a minute) are commonly called 'inert' or nonlabile.
- A **nonlabile** complex has a **higher activation energy** for ligand substitution.

Examples



Rate Constants for Water Exchange in $[\text{M}(\text{H}_2\text{O})_6]^{n+}$

Complex	$k(\text{s}^{-1})$ (298 K)	Electronic Configuration *
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	1.8×10^5	t_{2g}^1
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	5.0×10^2	t_{2g}^2
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	8.7×10^1	t_{2g}^3
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	2.4×10^{-6}	t_{2g}^3
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	$> 10^8$	$t_{2g}^3 e_g^1$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	1.6×10^2	$t_{2g}^3 e_g^2$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	4.4×10^6	$t_{2g}^4 e_g^2$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	3.2×10^6	$t_{2g}^5 e_g^2$
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	3.2×10^4	$t_{2g}^6 e_g^2$
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	4.4×10^9	$t_{2g}^6 e_g^3$
$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	$> 10^7$	$t_{2g}^6 e_g^4$

*These configurations assume octahedral geometry, even in cases where Jahn–Teller distortion is anticipated.

A Few Generalizations

- ❑ All complexes of s-block ions except the smallest (Be^{2+} and Mg^{2+}) are very labile.
- ❑ Complexes of the M(III) ions of the f block are all very labile.
- ❑ Complexes of the d^{10} ions (Zn^{2+} , Cd^{2+} , and Hg^{2+}) are normally very labile.
- ❑ Across the 3d series, complexes of d-block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
- ❑ Complexes of d-block M(III) ions are distinctly less labile than d-block M(II) ions.
- ❑ *d-Metal complexes with d^3 and low-spin d^6 configurations (for example Cr(III), Fe(II), and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as $[\text{Fe}(\text{phen})_3]^{2+}$, are particularly inert.*
- ❑ Nonlability is common among the complexes of the 4d and 5d series, which reflects the high LFSE and strength of the metal-ligand bonding.

Slow Reactions (Inert)	Moderate Rate	Fast Reactions (Labile)
d^3 , low-spin d^4 , d^5 , and d^6		d^1 , d^2 , high-spin d^4 , d^5 , and d^6
Strong-field d^8 (square planar)	Weak-field d^8	d^7 , d^9 , d^{10}

Representative timescales of chemical and physical processes

Timescale*	Process	Example
10^8 s	Ligand exchange (inert complex)	$[\text{Cr}(\text{OH}_2)_6]^{3+} - \text{H}_2\text{O}$ (c. 6 days)
60 s	Ligand exchange (nonlabile complex)	$[\text{V}(\text{OH}_2)_6]^{3+} - \text{H}_2\text{O}$ (50 s)
1 ms	Ligand exchange (labile complex)	$[\text{Pt}(\text{OH}_2)_4]^{2+} - \text{H}_2\text{O}$ (0.4 ms)
1 μs	Intervalence charge transfer	$(\text{H}_3\text{N})_5\text{Ru}^{\text{II}} - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{Ru}^{\text{III}}(\text{NH}_3)$ (0.5 μs)
1 ns	Ligand exchange (labile complex)	$[\text{Ni}(\text{OH}_2)_5(\text{py})]^{2+} - \text{H}_2\text{O}$ (1 ns)
10 ps	Ligand association	$\text{Cr}(\text{CO})_5 + \text{THF}$ (10 ps)
1 ps	Rotation time in liquid	CH_3CN (1 ps)
1 fs	Molecular vibration	Sn–Cl stretch (300 fs)

* Approximate time at room temperature.

IMPORTANT NOTE

Labile and **nonlabile** (inert) are kinetic terms and must be distinguished from the thermodynamic descriptions **stable** and **unstable**