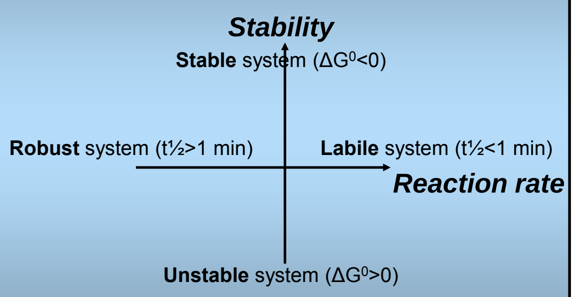
Thermodynamic and kinetic stability



Kinetics of substitution

$[M(OH_2)_x]^{n+} + H_2O \leftrightarrows [M(OH_2)_{x-1}(OH_2)]^{n+} + H_2O$

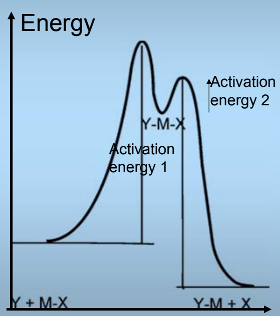
Rate= $k \cdot [M(OH_2)_x]^{n+}$

Reaction rates; magnitudes

Typical rates of substitution of water on metal ions

11 > log(k·s) > 8	8 > log(k·s) > 4	4 > log(k·s) > 0	-3 > log(k·s) > -6
Cs^+, K^+, Na^+, Li^+.			
Ba^{2+}, Ca^{2+}	Mg^{2+}	Be^{2+}	
	In^{3+}	Ga^{3+}, Al^{3+}	
La^{3+}	Sc^{3+} Y^{3+}		
Sm^{3+} Ce^{3+}	Lu^{3+} Dy^{3+}		
Cr^{2+} Cu^{2+}	Mn^{2+}, Fe^{2+} Co^{2+}	Ni^{2+} V^{2+}	Cr^{3+}
Hg^{2+} Cd^{2+}	Zn^{2+}		Pt^{2+}, Co^{3+}-Ir^{3+}

Reaction profile model



Maxima: transition states

Minima: ground states or intermediates

Energy of activation

Substitution mechanism

Associative: $L_5MX + Y \rightarrow X[L_5M]Y \rightarrow X + L_5MY$

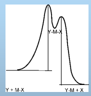
rate=k·[M-X] ·[Y]

Dissociative: $L_5MX + Y \rightarrow X + [L_5M] + Y \rightarrow X + L_5MY$

rate=k·[M-X]

rate determining step fast

No intermediate (activation energy 2 too small or absent):



Interchange associative or interchange dissociative

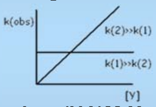
Some further details

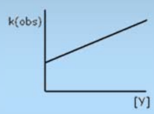
Solvent assistance mechanism in M-X + Y→ M-Y + X

rate=k_1·[M-X] + k_2·[Y]·[M-X]

First term: M-X + H_2O→M-OH_2 + X (slow)

M-OH_2 +Y → M-Y (fast)





Conjugate base mechanism (HA)M-X + Y→(HA)M-Y + X

rate=k·[Y] ·[(HA)M-X] [OH^-]

(HA)M-X + OH^- ⇆ (A)M-X (fast equilibration)

(A)M-X + Y → (A)M-Y + X (slow)

(A)M-Y + H^+ → (HA)M-Y (fast)

Square planar substitution

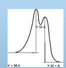
ML_2TX +Y → ML_2TY +X; (X and Y trans to T) :

Second order rate constant (same X and Y) increase in the order of T:

H_2O, OH^-,NH_3 ,py<Cl^-<Br^-<SCN^-<I^-< NO_2^-< $C_6H_5^-$< $SC(NH_2)_2$< CH_3^- <NO, CN^- ,CO

Trans-influence: higher ground state energy

Trans effect: stabilise transition state/intermediate



26.5

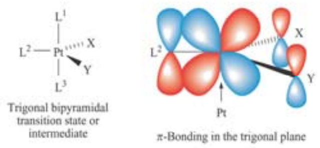


Fig. 26.5 In the trigonal plane of the 5-coordinate transition state or intermediate, a π-bonding interaction can occur between a metal *d* orbital (e.g. d_{xy}) and suitable orbitals (e.g. *p* atomic orbitals, or molecular orbitals of π-symmetry) of ligand L^2 (the ligand *trans* to the leaving group), X (the leaving group) and Y (the entering group). Note that ligands may not necessarily contribute to the π-bonding scheme, e.g. NH_3.

End of chapter 26 problem

26.4: $k_{obs}=k_a+k_b \cdot [py]$

$k_a=26.0 s^{-1}$; $k_b=3.2 \cdot 10^2 (Ms)^{-1}$

26.5: $PtCl_4^{2-} \rightarrow$ cis & tr- $PtCl_2NH_3NO_2^-$

$PtCl_4^{2-} + P(C_2H_5) \rightarrow ?$

26.7: $k_{obs}=k_1+k_2 \cdot [tu]$; k_1 very small

solvent assisted path negligible