> **Associative v.s Dissociative Mechanism:**

**(1) Effect of $d^n$-configuration:** For oh complexes $[M(H_2O)]_6^{n+}$, the associative path involves the approach of the entering solvent molecule along the $C_3$-axis of the complexes. Thus, greater $e^-$ density in the $t_{2g}$ level will disfavour the approach of entering nucleophile electrostatically. This is why for the early members of $M^{2+}$ of the first row transition series having less $e^-$ density in the $t_{2g}$ level, the associative path is favoured while for the late members, of the series (where the $t_{2g}$ level is filled in), the associative path is highly disfavoured (i.e. dissociative path is favoured).

**(2) Effect of Bulkyness of solvent:** With the increase in bulkyness of the solvent, the associative path leading to an increase in the coordination no. in attaining the T.S is disfavoured. This is why for a particular metal center $\Delta V^{\neq}$ increases in the order: DMSO > DMF > $H_2O$. For the solvent exchange process $\Delta V^{\neq}$ is positive (dissociative path) for $[Mn(DMF)_6]^{2+}$ and $\Delta V^{\neq}$ is negative for $[Mn(H_2O)_6]^{2+}$ (i.e. associative path)

**(3) Effect of the charge on the metal ion:** For the $M^{3+}$ ions, e.g $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$ the associative path is operated. Higher positive charge favours the binding of the entering ligand.

**(4) Effect of electron density in the $t_{2g}$ level:** In case of $[M(H_2O)]_6^{3+}$ species, the associative character for the solvent exchange process decreases with increase of $e^-$ density in the $t_{2g}$ level.
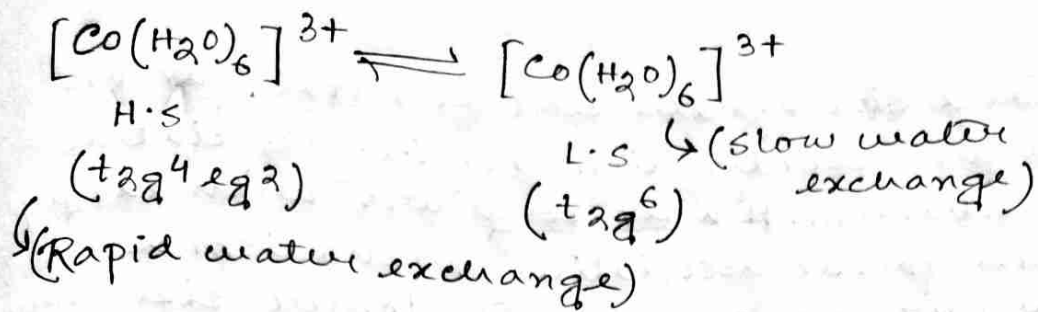
Q. Associative path is operated for $[M(H_2O)_6]^{3+}$, (M = Fe, Cr) but for their hydrolysed species $[M(OH)(H_2O)_5]^{2+}$, the dissociative path operates.

→ $[M(OH)(H_2O)_5]^{2+}$ behaves like bivalent metal ions of the late members of the 1st transition series. The dissociative character is introduced into the hydrolysed species, $[M(OH)(H_2O)_5]^{2+}$ because of two reasons :—

(i) Lower positive charge and labilizing effect of the good σ-donor & π-donor (-)OH ligand.

Q. Unusually high lability of $[Co(H_2O)_6]^{3+}$ → Explain why ?

→ Co(III), $d^6$ complexes are generally more inert than corresponding Cr(III), $d^3$ complexes. But the rate of $H_2O$ exchange in $[Cr(OH_2)_6]^{3+}$ is much slower than that for $[Co(H_2O)_6]^{3+}$ i.e. $H_2O$ exchange of $[Co(H_2O)_6]^{3+}$ is fairly high because $[Co(H_2O)_6]^{3+}$ is highly oxidising and it can oxidize water to release oxygen slowly and it is itself reduced to $\overline{[Co(H_2O)]^{2+}}$ $Co(aq)^{2+}$. $Co(aq)^{3+}$ is labile and which is invariably contaminated to $[Co(H_2O)_6]^{3+}$. This contaminated $Co^{3+}$ catalyse the water exchange of inert $[Co(H_2O)_6]^{3+}$. There is another reason for the enhanced water exchange rate for $[Co(H_2O)_6]^{3+}$. In $[Co(H_2O)_6]^{3+}$, 10 Dq value provided by $H_2O$ ligand is critical 10 Dq value (10 Dq ≈ P). It allows the spin isomerism (H·S ⇌ L·S). The L·S $[Co(H_2O)_6]^{3+}$ is inert because of the very high crystal field activation energy but the high spin $[Co(H_2O)_6]^{3+}$ is more labile because of the lower crystal field activation energy.

$$[Co(H_2O)_6]^{3+} \rightleftharpoons [Co(H_2O)_6]^{3+}$$

H.S

$(t_{2g}^4 e_g^2)$         L.S ↳(slow water

                $(t_{2g}^6)$     exchange)

↳(Rapid water exchange)


**q. Why V(III) is more labile than V(II)?**

→ V(III), $d^2$ and V(II), $d^3$

Due to charge effect, V(III) is expected to be more inert than V(II) but in reality V(III), $d^2$ is more labile than V(II), $d^3$. This can be explained by considering higher crystal field activation energy (CFAE) for V(II) in compared to V(III).


**q. The heavier congeners are relatively inert → Explain.**

→ With increase in 10Dq value, lability gradually decreases i.e. inertness increases. We know crystal field spliting power of (10Dq value) for heavier congeners is higher i.e. lability is lower. That is why the lability order of Co(III) > Rh(III) > Ir(III) and

Ni(II) > Pd(II) > Pt(II).


**q. Write down the factors favouring the associative path.**

(i) High effective nuclear charge & high overall (+ve) charge of the complex

favouring a new M-L bond formation, which favours associative mechanism. Higher valent metal ion favours associative path whereas lower valent metal ion favours dissociative path. Similarly heavier congeners favour associative path & ligher congeners favour dissociative path.

(ii) Large size of the central metal favours higher coordination no. i.e. associative mechanism. Heavier congeners with larger size favour associative mechanism & lighter congeners with lower size favour dissociative mechanism.

(iii) Low $d\,e^-$ density in the $t_{2g}$ level for Oh complexes favours associative mechanism. That is why early members of 1st row transition element are relatively labile than late members.