Enthalpy of Hydration (ΔH_{hyd}):

Enthalpy of hydration (ΔH_{hyd}) for $M^{n+}(g)$ ions is the energy released in the hydration reaction.

$$M^{n+}(g) + aQ \longrightarrow M^{n+}(aQ) + \Delta H_{hyd}$$

ΔH_{hyd} is very high due to small size and large nuclear charge on the metal.

Standard Oxidation Potential (E°_{ox}) Values and Reducing Properties of transition elements in aqueous solution:

$$\begin{tikzcd}
M(s) + aQ \arrow[r, "\Delta H"] \arrow[d, "\text{① Enthalpy of sublimation } (+\Delta H_{sub})"] & M^{2+}(aQ) + 2e^- \\
M(g) \arrow[r, "\text{②}\ (IE_1 + IE_2)"'] & M^{2+}(g) \arrow[u, "\text{③ Enthalpy of hydration } (-\Delta H_{hyd})"']
\end{tikzcd}$$

(i) Sublimation: Depends on metallic bonding, stronger the metallic bonding, greater will be sublimation energy. endothermic process.

(ii) $IE_1 + IE_2$ = energy absorbed endothermic process.

(iii) $M^{2+}(g) + aQ \longrightarrow M^{2+}(aQ) + \Delta H$ = enthalpy of hydration
$= -\Delta H_{hyd}$

Smaller the size of $M^{2+}(g)$ ion greater will be the value of ΔH_{hyd}.

On adding ①, Ⅱ & Ⅲ

$$\Delta H = \Delta H_{sub} + (IE_1 + IE_2) - \Delta H_{hyd} \quad \text{—— (1)}$$

Equation ① suggest that

(a) The net electrode potential (E°_{ox}) for the oxidation half reaction.

$$M(s) \longrightarrow M^{2+}(aq) + 2e^-$$

Depends on the net effect of ΔH_{sub}, ($IE_1 + IE_2$) and ΔH_{hyd}

(b) stability of an oxidation state $\propto \frac{1}{\Delta H}$

Transition Elements	$E^\circ(M/M^{2+})$(V)	M/M^{3+}(V)	M^{2+}/M^{3+}(V)
Sc	-	-2.10	-
Ti	+1.60	-	+0.37
V	+1.18	+0.26	+0.26
Cr	+0.91	+0.74	+0.41
Mn	+1.81	-1.57	-1.57
Fe	+0.44	-0.77	-0.77
Co	+0.28	-1.97	-1.97
Ni	+0.25	-	
Cu	-0.34	-	
Zn	+0.76	-	

1. With the exception of Cu, all 3d metals are capable of evolving H_2 gas from acid solution

$$M(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g)$$

→ Cr metal does not evolve H_2 gas from acid solution. This is because formation of Cr_2O_3.

Ti and V are passive to dilute non-oxidising acids at room temp.

2. Since $E^\circ(M/M^{2+}) = +ve$

Except Cu have a strong tendency to get oxidised in aq. solution.

Higher the E°_{ox} stronger is the reducing agent.

(III) With the exception of few elements $E^\circ(M/M^{2+})$ values keep on decreasing on moving from Sc to Zn. This decreasing trend of E°_{ox} values indicates that the reducing ability of transition elements is decreasing from Sc to Zn. This decreasing reducing ability is due to the decreasing size and increasing ionization energies from Sc to Zn. The decreasing reducing ability of the elements from Sc to Zn shows that these elements (M) have a decreasing tendency to form M^{2+} ions.

(IV) There is no regularity in $E^\circ(M/M^{2+})$ values. The irregularity in these values is because of the fact that E° values depend on the sum of ΔH_{sub}, $(IE_1 + IE_2)$ and ΔH_{hyd}. The irregularity is due to the irregular variation in the values of ΔH_{sub} and $(IE_1 + IE_2)$.

(V): $E^\circ(Cu/Cu^{2+})$ value for Cu is $-ve$ because of the reason that the sum of ΔH_{sub} and (IE_1+IE_2) is not balanced by ΔH_{hyd}. Negative values of E° for Cu shows that this metal is not able to liberate H_2 gas from acid solution. This metal is ~~however~~ can reduce oxidising acids like HNO_3 and H_2SO_4.

(VI) Since $E^\circ_{Cu/Cu^{2+}}$ has negative value, the tendency of Cu(s) to get oxidised to $Cu^{2+}(aq)$ in aqueous solution is extremely small and hence Cu is a poor reducing agent. Thus the following half-R^{xn} proceeds to an extremely small extent.

$$Cu(s) + aq \xrightarrow{\text{oxidation}} Cu^{2+}(aq) + 2e^-$$

(VII) Mn has high value of $E^\circ_{Mn/Mn^{2+}}$ because Mn $3d^5 4s^2$ has high tendency to get oxidised to Mn^{2+} which has a stable half filled configuration. Similarly Zn ($3d^{10}4s^2$) also has high value of $E^\circ_{Zn/Zn^{2+}}$ because this metal has high tendency to get oxidised to Zn^{2+} ion which has stable fully-filled configuration ($Zn^{2+} = 3d^{10}$).

$Mn \xrightarrow{\quad} Mn^{2+} + 2e^-$

$Zn \xrightarrow{\quad} Zn^{2+} + 2e^-$

(VIII) It has been observed that Mn^{3+} and Co^{3+} both are strong oxidising agents in aqueous solution and Co^{3+} ion is a stronger oxidising agent than Mn^{3+} ion.

$Mn^{3+} + 3e^- \xrightarrow{\quad} Mn \quad E^\circ_{Mn^{3+}/Mn} = +1.57V$

$Co^{3+} + 3e^- \xrightarrow{\quad} Co \quad E^\circ_{Co^{3+}/Co} = +1.97V$

Since both E° values are highly positive, both the ions are easily reduced to the metals. Hence both the ions act as strong oxidising agents. Now since $E^\circ_{Co^{3+}/Co}$ value is higher than $E^\circ_{Mn^{3+}/Mn}$ value, Co^{3+} ion is more easily reduced to Co than Mn^{3+} to Mn. Thus Co^{3+} is a stronger oxidising agent than Mn^{3+} ion.

(IX) -ve value of $E^\circ_{Mn^{2+}/Mn^{3+}}$ shows that Mn^{2+} ion is not oxidised to Mn^{3+} ion. i.e. Mn^{2+} is stable. The stability of Mn^{2+} ion is also due to the presence of stable $3d^5$ configuration in Mn^{2+} ion.

$Mn^{2+} \xrightarrow{\quad} Mn^{3+} + e^- \quad (E^\circ_{Mn^{2+}/Mn^{3+}} = -1.57V)$

(X) Co^{3+} ion is a better OA than Co^{2+} ion.

ⓐ $Co^{3+} + e^- \xrightarrow{\quad} Co^{2+} \quad E^\circ_{Red} = 1.97V$

ⓑ $Co^{2+} + 2e^- \xrightarrow{\quad} Co \quad E^\circ_{Red} = -0.28V$

Since E°_{Red} value for reduction half reaction ⓐ is higher than that for reduction half reaction ⓑ. Co^{3+} ion is more easily reduced to Co^{2+} ion than Co^{2+} ion is reduced to Co. Thus Co^{3+} is a better OA.

(XI) $E^\circ_{V^{2+}/V^{3+}}$ value of V is comparatively low

$$\underset{3d^3 (t_{2g}^3)}{V^{2+}} \longrightarrow \underset{3d^2}{V^{3+}} + \bar{e} \qquad E^\circ_{V^{2+}/V^{3+}} = 0.26V$$

Since V^{2+} ion has half filled t_{2g}^3 configuration. V^{2+} ion has little tendency to get oxidised to V^{3+} ion. Hence E° value for the above oxidation half Rx^n is very low.

(XII) Since $E^\circ(Fe^{3+}/Fe^{2+})$ value is low

$$Fe^{3+} + \bar{e} \longrightarrow Fe^{2+} \qquad E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77V.$$

Fe^{3+} ion is not reduced to Fe^{2+} ion. i.e. Fe^{3+} ion is stable. The stability of Fe^{3+} ion is also because of the stable $3d^5$ configuration of Fe^{3+} ion.

(XIII): Since $E^\circ_{Ti^{2+}/Ti^{3+}}$, $E^\circ_{V^{2+}/V^{3+}}$ and $E^\circ_{Cr^{2+}/Cr^{3+}}$ values are positive, Ti^{2+}, V^{2+} and Cr^{2+} are easily oxidised to Ti^{3+}, V^{3+} and Cr^{3+} ions respectively. Thus these ions are strong reducing agents and hence can liberate H_2 gas from an acid. e.g.

$$2Cr^{2+}(aq) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + H_2(g)$$

Variable Oxidation States:

1st Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	~~+2~~							+1	
	(+2)	+2	+2	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$	$\boxed{+2}$
+3	+3	+3	$\boxed{+3}$	+3	$\boxed{+3}$	$\boxed{+3}$	(+3)		
	$\boxed{+4}$	+4	+4	+4	+4	+4	+4		
		$\boxed{+5}$	+5	(+5)					
			$\boxed{+6}$	+6	+6				
				$\boxed{+7}$					

2nd T.S

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
								+1	
		(+2)	+2	+2	+2	+2	+2	(+2)	+2
+3	(+3)	(+3)	+3		+3	+3	(+3)	(+3)	
	+4	(+4)	+4	(+4)	+4	+4	+4		
		+5	+5	(+5)	(+5)				
			+6		(+6)	(+6)			
					(+7)				
					(+8)				

3rd T.S

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
				(+1)				+1	+1
		(+2)	+2	(+2)	+2	+2	+2		+2
+3	(+3)	(+3)	(+3)	+3	+3	+3	(+3)	+3	-
		(+4)	+4	+4	+4	+4	+4		
		+5	+5	+5			(+5)		
			+6	(+6)	+6	(+6)	(+6)		
				+7					
					+8				

Explanation for O.S:

1. With the exception of first and last transition elements in each series, all other elements show more than one oxidation states (O.S.)
2. The most common oxidation state of the element belonging to the first transition series (except Sc) is +2 which arises from the loss of two 4s electrons. This indicates that after scandium d-orbitals become more stable than the s-orbital.
3. Stabilisation of low (unstable) oxidation states. Transition elements also show low oxidation states like -1, 0, +1 etc. These oxidation states are unstable.

However these states get stabilized when the metals form compounds or complexes with π-acid ligands like CO, NO, N_2, PR_3, AsR_3 CNR, CN^-, C_6H_6, α-α' dipyridyl, ethylene etc.

e.g. CuCl (+1)

$Ni(CO)_4$ $Fe(CO)_5$

(4) Highest oxidation states

(i) The highest oxidation state for the first five elements (Sc to Mn) is equal to sum of the electrons in 4s and 3d orbitals. On the other hand the highest oxidation state for the remaining five elements (Fe to Zn) is not equal to sum of the electrons in the 4s and 3d orbitals. The stability of higher o.s lying after Mn decreases successively.

(ii) The high o.s of many transition metals like V(V) Cr(VI) Mn(IV), Mn(VI), Fe(VI) Co(IV), Ni(III) Cu(III), Ag(III) etc are oxidising (i.e. unstable). These unstable o.s which are high oxidation states get stabilized by forming complexes with small highly electronegative ligands like O^{2-}, F^-, Cl^- per iodate (IO_6^{5-}), tellurate (TeO_6^{6-}) etc.

(III) within a group the maximum oxidation state increases with atomic number.

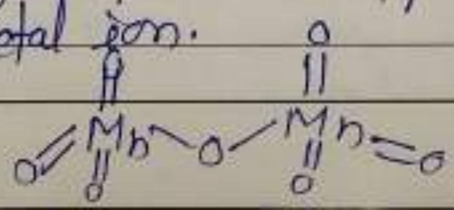
e.g Fe +2, +3

Ru & Os, +2, +3, +4, +6 & +8 also.

(IV) The highest o.s. of transition metals are found in their fluorides and oxides.

Oxygen form more stable complexes than fluorine because oxygen forms multiple bonds with the transition metal ion.

e.g. Mn_2O_7



CLASSTIME

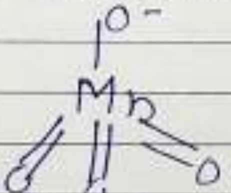
④ The highest O.S shown by transition metal is 8, shown by Ru and Os.

⑤ Ionic/ covalent character of compounds of a given metal in various oxidation states

Elements in +2 and +3 O.S. form ionic compounds and in higher oxidation states form covalent compounds.

e.g.	VCl_2	VCl_3	VCl_4
	Ionic	Less Ionic	covalent

MnO_4^-



covalent

⑥ Acidic/basic character of the compounds of a given transition metal in various oxidation states.

+2	+3	+4	+5
VO	V_2O_3	VO_2	V_2O_5
Basic	Basic	Amphoteric	Acidic

CrO	Cr_2O_3	CrO_2	CrO_3
+2	+3	+4	+6
Basic	Amphoteric	Ampho	acidic

MnO	Mn_3O_4	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7
+2	+8/3	+3	+4	+6	+7
Basic	amphoteric			weakly acidic	strong acidic

$\overset{+2}{TiCl_2}$ $\overset{+3}{TiCl_3}$ $\overset{+4}{TiCl_4}$

$TiCl_2 < TiCl_3 < TiCl_4$

$\overset{+2}{VCl_2} < \overset{+3}{VCl_3} < \overset{+5}{VOCl_3}$