

CHEM F111: General Chemistry Semester II: AY 2017-18

Lecture-29, 02-04-2018

Notice



Instructor: Dr. Surojit Pande

Q and A discussion from Inorganic Chemistry

Date: 03/04/18

Room No: 5102

Time: 5.10 - 6.10 pm

Summary of lecture 28



Relationship between step wise and overall formation constant

$$\beta_1 = K_1$$
$$\beta_2 = K_1 \cdot K_2$$

$$\beta_3 = [ML_3]/[M][L]^3 = [ML]/[M][L] . [ML_2]/[ML][L] . [ML_3]/[ML_2][L]$$

$$= K_1 . K_2 . K_3$$

$$\beta_n = K_1 . K_2 . K_3 K_n$$

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \dots \log K_n$$

Summary of lecture 28



$$[Cu(NH_3)_4]^{2+}$$
 < $[Cu(en)_2]^{2+}$ < $[Cu(trien)]^{2+}$
Log $\beta = 12.7$ < 19.7 < 20.5

- RT In
$$\beta = \Delta G^0 = \Delta H^0 - T\Delta S^0$$
 (ΔH^0 is negative)

(i)
$$Cd^{2+} + 2en \iff [Cd(en)_2]^{2+} \text{ with log } \beta = 10.6$$

$$\{\Delta H^0 = -56.3 \text{ kJ/mol}, \Delta S^0 = +14.1 \text{ kJ/mol}, - T\Delta S^0 = -4.2 \text{ kJ/mol}$$
and $\Delta G^0 = -60.7 \text{ kJ/mol}\}$

Redox reaction



Reduction
$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$
 Oxidation

- The loss of electrons is Oxidation.
- An element that loses electrons is said to be oxidized.
- The species in which that element is present in a reaction is called the reducing agent.
- The gain of electrons is Reduction.
- An element that gains electrons is said to be reduced.
- The species in which that element is present in a reaction is called the oxidizing agent.

Oxidation state



Oxidation state of an element in a compound is defined as the charge left on the element if all the other elements in the compounds are removed in their usual oxidation states.

e.g. Oxidation state of S in H_2SO_4 is 0 - 2(1) -4(-2) = 6 (+VI)

The stable oxidation does not necessary mean that the corresponding ion exists (e.g. Manganese exists in oxidation state (+VII), but Mn^{7+} doesn't exist, as $KMnO_4$ ionizes into K^+ and MnO_4^- .

Balancing redox equation



Fe²⁺ + MnO₄⁻ + H⁺
$$\longrightarrow$$
 Mn²⁺ + Fe³⁺ + H₂O
MnO₄⁻ \longrightarrow Mn²⁺ (Reduction half reaction)
(+7) (+2)
Fe²⁺ \longrightarrow Fe³⁺ (Oxidation half reaction)
MnO₄⁻ + 8H⁺ + 5e \longrightarrow Mn²⁺ + 4H₂O
5Fe²⁺ \longrightarrow 5Fe³⁺ + 5e
5Fe²⁺ + MnO₄⁻ + 8H⁺ \longrightarrow Mn²⁺ + 5Fe³⁺ + 4H₂O

Nernst Equation



$$aOx_1 + bRed_2 \longrightarrow cRed_1 + dOx_2$$

$$Q = \frac{[Red_1]^c [Ox_2]^d}{[Ox_1]^a [Red_2]^b} \qquad E = E^0 - \frac{RT}{nF} \ln Q$$

The standard reduction potential is related to the change in the standard Gibbs energy by the equation:

$$\Delta G^0 = -nFE^0$$

Elements can be arranged in the increasing order of the standard electrode potential. It is known as electrochemical series.

Thermodynamic relations



$$\Delta G^0 = - n F \Delta E^0$$

Note: if $\Delta G^0 < 0$, then ΔE^0 must be >0

A reaction is favorable if $\Delta E^0 > 0$

(a)
$$2H^+$$
 (aq) + $2e \longrightarrow H_2(g)$

$$E^{0}(H^{+}, H_{2}) = 0$$

(b)
$$Zn^{2+}$$
 (aq) + 2e \longrightarrow Zn(s)

$$E^{0}(Zn^{2+}, Zn) = -0.76 V$$

$$2H^{+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + H_{2}(g) = +0.76 \text{ V}$$

Reaction is favorable

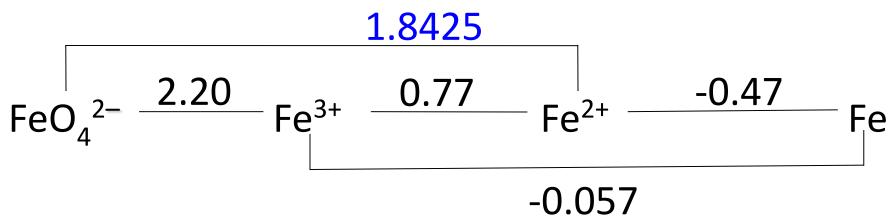
Oxidation-reduction reaction



Many elements can exist in two or more stable oxidation states. For such elements, the reduction of and among all the oxidation states can be written in terms of the half-cell reactions. For example:

Fe²⁺ + 2e⁻
$$\rightarrow$$
 Fe
Fe³⁺ + 3e⁻ \rightarrow Fe
Fe³⁺ + e⁻ \rightarrow Fe²⁺
FeO₄²⁻ + 3e⁻ + 8H⁺ \rightarrow Fe³⁺ + 4H₂O E⁰ = 2.20 V

Latimer diagram $E^{0}(V)$



Latimer diagram



Latimer diagram is useful for summarizing thermodynamic information about the oxidation states of an element.

- Written with the most oxidized species on the left, and the most reduced species on the right.
- Oxidation number decreases from the left to the right and E⁰ values are written on the lines joining the species involved in the couple
- If the potential on the right of a species is higher than the potential on the left then the species would undergo disproportionation

$$FeO_4^{2-} = \frac{2.20}{Fe^{3+}} = \frac{0.77}{Fe^{2+}} = \frac{-0.47}{-0.057}$$

Latimer diagram



Extraction of E^0 for nonadjacent oxidation state

$$ClO_{4} \xrightarrow{+1.2} ClO_{3} \xrightarrow{+1.18} HClO_{2} \xrightarrow{+1.65} HClO \xrightarrow{+1.63} Cl_{2} \xrightarrow{+1.36} Cl_{1}$$
the two redex couples

Identify the two redox couples

Find out the oxidation state of chlorine

HClO(aq) + H⁺(aq) + e
$$\longrightarrow$$
 ½ Cl₂(g) + H₂O(l) +1.63 V
½ Cl₂(g) + e \longrightarrow Cl⁻ (l) +1.36 V

$$\Delta G = \Delta G' + \Delta G''$$
- ν FE = - ν 'FE' - ν "FE"

Disproportionation reaction



Element is simultaneously oxidized and reduced

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

$$E^{0} \qquad 2 \text{M}^{+}(\text{aq}) \stackrel{E^{0'}}{\longrightarrow} \text{M}^{2+}(\text{aq})$$
Basic medium
$$ClO_{4}^{-} \stackrel{+0.37}{\longrightarrow} ClO_{3}^{-} \stackrel{+0.3}{\longrightarrow} ClO_{2}^{-} \stackrel{+0.68}{\longrightarrow} ClO^{-} \stackrel{+0.42}{\longrightarrow} Cl_{2}^{-} \stackrel{+1.36}{\longrightarrow} Cl^{-}$$

'the potential on the left of a species is less positive than that on the right- the species can oxidize and reduce itself, a process known as disproportionation'.

Disproportionation reaction



$$Clo^{-+0.42} \longrightarrow Cl_2^{+1.36} Cl^{-1}$$

$$Cl_{2}(g) + 2e^{-} \longrightarrow 2Cl^{-}(aq) + 1.36$$

 $2ClO^{-}(aq) + 2H_{2}O(l) + 2e^{-} \longrightarrow Cl_{2}(g) + 4OH^{-}(aq) + 0.42$

$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$$

$$\Delta E = E^{0} (Cl_{2}/Cl^{-}) - E^{0} (ClO^{-}/Cl_{2}) = 1.36 - +0.42 = 0.94$$

Reaction is spontaneous

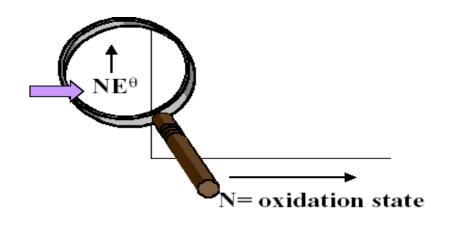
Frost diagram



Arthur A. Frost

Graphically illustration of the stability of different oxidation states relative to its elemental form (i.e., relative to oxidation state = 0)

Note the similarity between this term and $n\Delta E^0 = -\Delta G^0/F$



So, NE⁰ is proportional to the free energy of a compound in oxidation state "N" relative to its elemental form

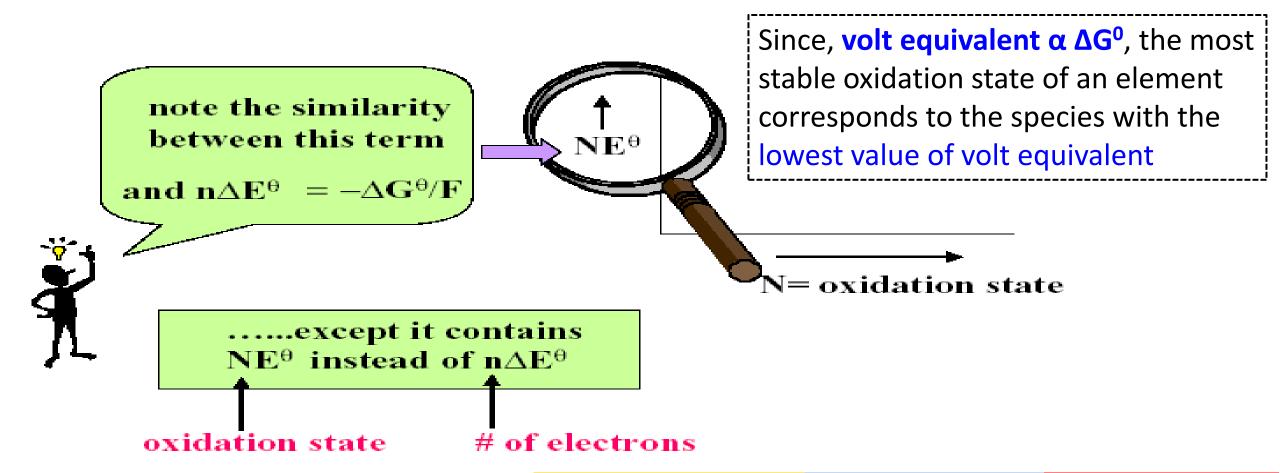
$$X^{N} + Ne^{-} \longrightarrow X^{0}$$

 $NE^{0} = -G^{0}/F$

Frost diagram

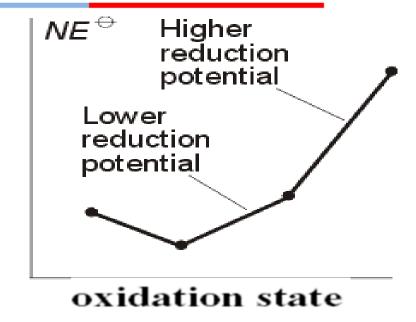


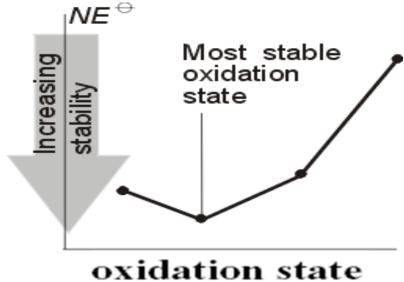
In a Frost diagram the volt equivalent (N x E^0) of a redox couple is plotted against the oxidation state (N) of the element

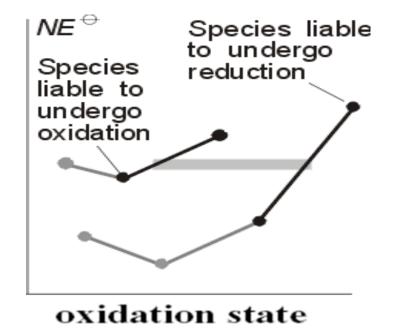


Frost diagrams: Features



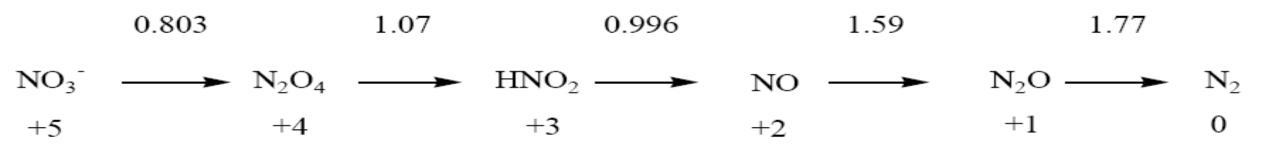


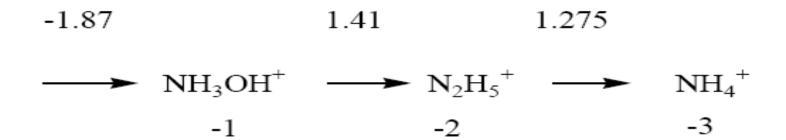




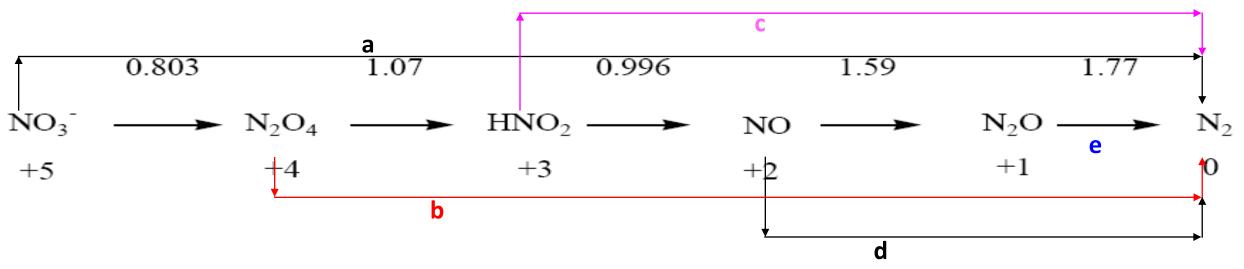


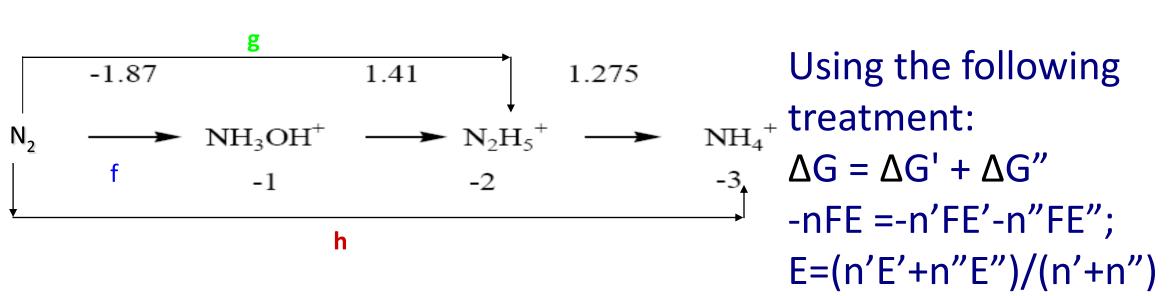
Consider the Latimer diagram for nitrogen in acidic solution













Oxidation state: species NE⁰, N

 $N(V): NO_3^-$

 $N(IV): N_2O_4$

N(III): HNO₂

N(II): NO

 $N(I): N_2O$

N(-1): NH_3OH^+

N(-II): N₂H₅⁺

N(-III): NH₄+

 $(5 \times 1.25, 5)$

(4 x 1.36, 4)

 $(3 \times 1.35, 3)$

(2 x 1.68, 2)

 $(1 \times 1.77, 1)$

 $[-1 \times (-1.87), -1]$

 $[-2 \times (-0.23), -2]$

 $(-3 \times 0.27, -3)$

The most stable oxidation state of an element will lie lowest in its Frost diagram

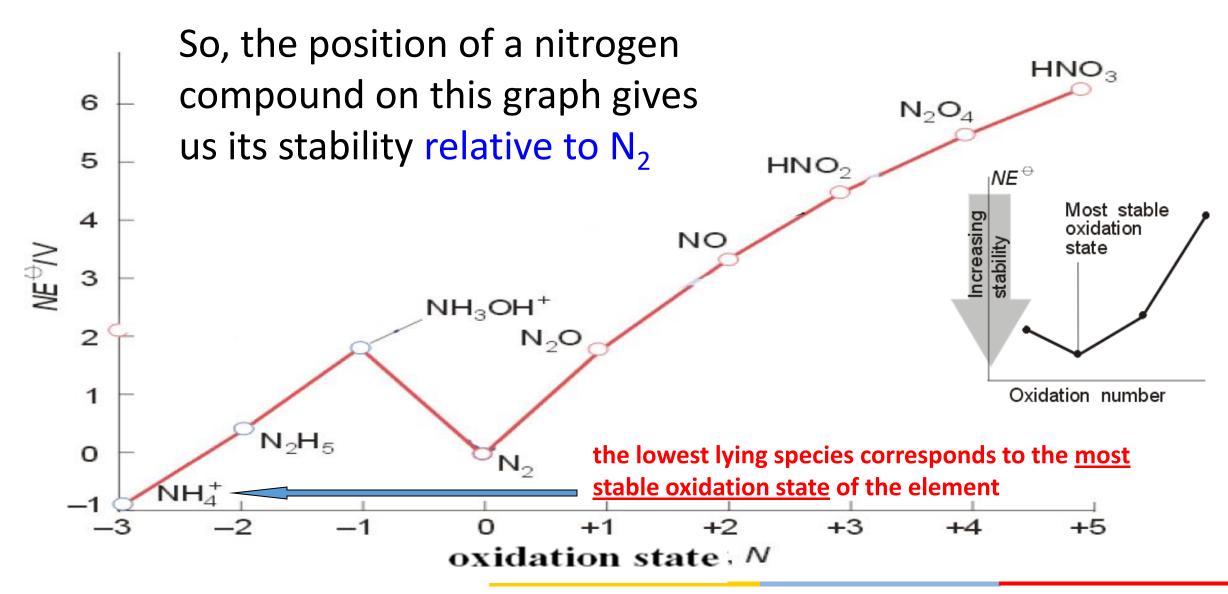


We obtain

$E^0 = 1.25V$	a
$E^0 = 1.36V$	b
$E^0 = 1.45V$	C
$E^0 = 1.68V$	d
$E^0 = 1.77V$	е
$E^0 = -1.87V$	f
$E^0 = -0.23V$	g
$E^0 = 0.27V$	h
	$E^{0} = 1.36V$ $E^{0} = 1.45V$ $E^{0} = 1.68V$ $E^{0} = 1.77V$ $E^{0} = -1.87V$ $E^{0} = -0.23V$

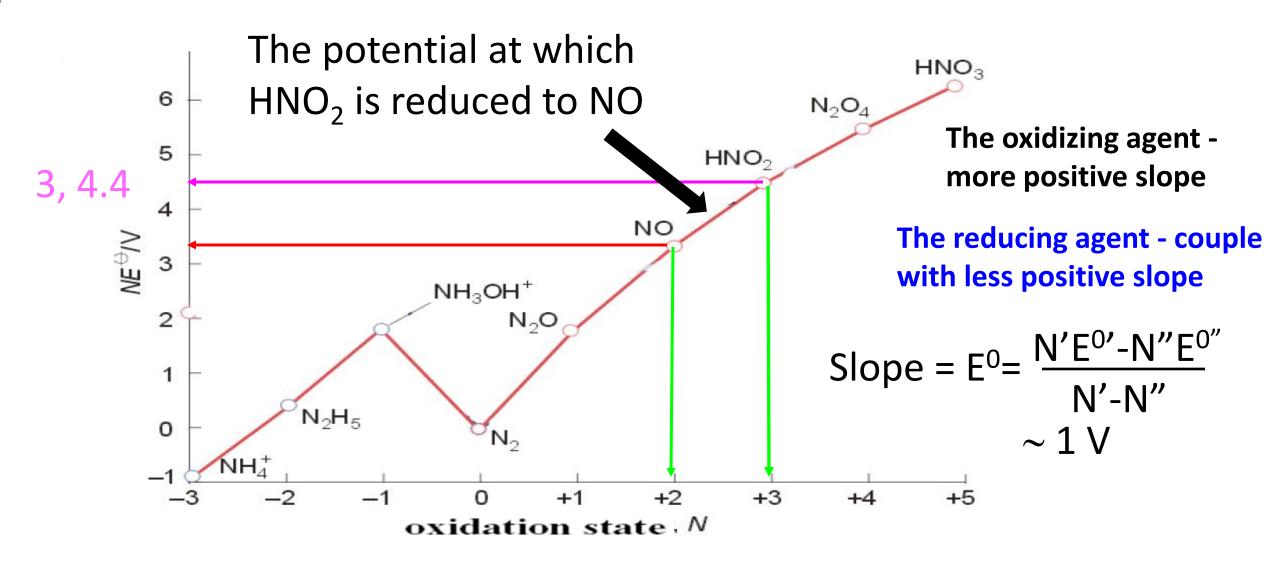
Frost diagram of N₂





Frost diagram of N₂





Discussed topics.....



- ✓ Latimer diagram
- ✓ Frost diagram
- ✓ Example of disproportionation reaction
- ✓ Different features from Frost diagram
- ✓ Combined Latimer and Frost diagram

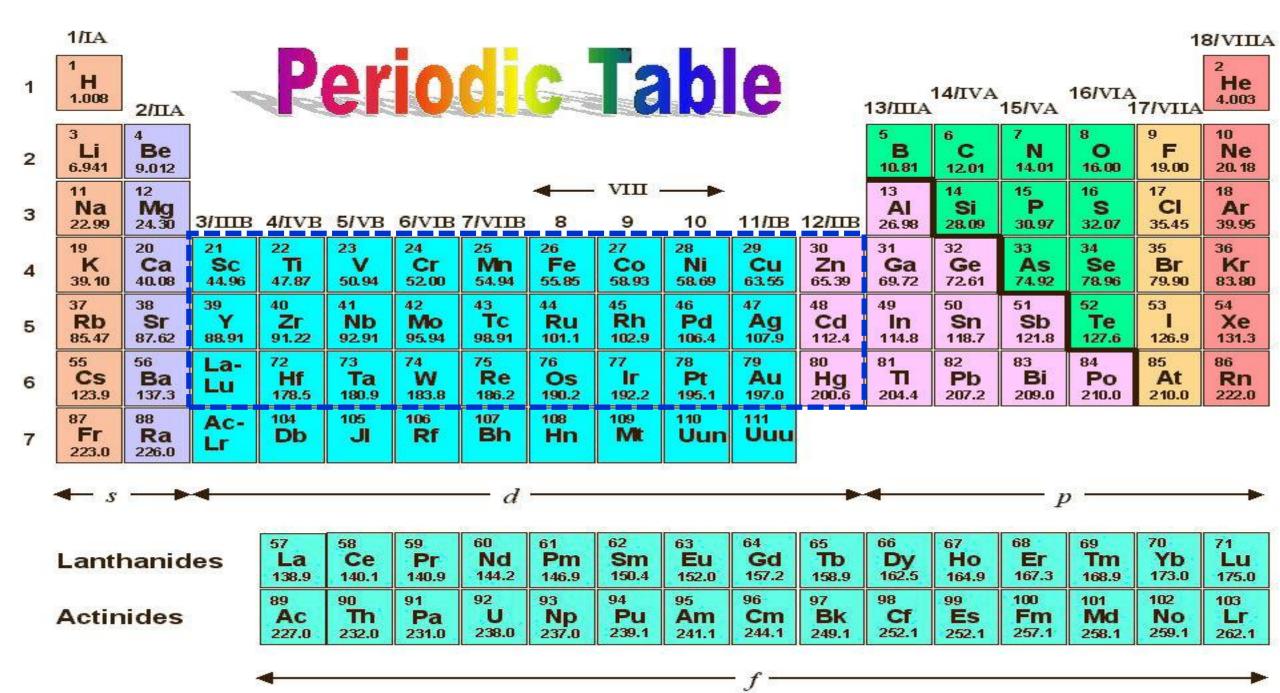
21-23	Coordination Chemistry: Coordination compounds	Double salts and coordination compounds. Werner's work; effective atomic no. concept.; Chelates and isomerism; shapes of d orbitals, crystal field theory, octahedral complexes, spectrochemical series	R1: p194-200 (SS); p202-214; p222-224, p232- 235	•	The concept of chelates and coordination compounds Development of coordination complexes in light of various theories
24- 26	Distortion of Complexes; Tetrahedral, Octahedral, and Square planar arrangement Jahn-Teller distortion: Effect of geometrical distortions on stability, stability in other geometries	R1: p214-222	•	Nature of ligand, idea of different orbitals and their effect in inorganic complexes	
				•	Idea of distortion in tetrahedral, octahedral, and square planar complexes
27- 29	Coordination Chemistry: Octahedral complex, CFSE, and Electronic spectrasof octahedral complexes, Applications of term symbols, Thermodynamic and kinetic aspects of Inorganic complexes, Latimar and Frost diagram	Electronic spectra of octahedral complexes, p	p219-222 R1: p947-960 R3: p262-264, 380-381, 385-389	•	Spectral nature of inorganic complexes
		Thermodynamic and kinetic aspects of Inorganic complexes, Latimar and Frost		•	Effect of strength and the symmetry of ligand field on various energy levels
		agrain		•	Identify the nature of stable and unstable complexes

What next.....



Draw backs of CFT: no covalent bond formation between meal and ligand, it is electrostatic......

Further modified theory is Ligand Field Theory (LFT): not in syllabus



Question



$$Cr(VI) \xrightarrow{0.55 \text{ V}} Cr(V) \xrightarrow{1.34 \text{ V}} Cr(IV) \xrightarrow{2.1 \text{ V}} Cr(III) \xrightarrow{-0.42 \text{ V}} Cr(II) \xrightarrow{-0.9 \text{ V}} Cr(0)$$

(Latimer diagram of Cr species)

Based on the reduction potential value from Latimer diagram of Cr species, conversion of Cr(V) to Cr(VI) is not spontaneous, however, Cr(V) converts to Cr(VI). Justify your answer.

Yes, Cr(V) converts into Cr(VI) and the reaction is spontaneous. This is due to Cr(V) undergo disproportionation reaction.

In aqueous medium the disproportionation reactions are

$$Cr(VI) + e \longrightarrow Cr(V), E^0 = 0.55 V$$
 (equ. 1)

$$Cr(V) + e \longrightarrow Cr(IV), E^0 = 1.34 V$$
 (equ. 2)

To check the spontaneity of Cr(V) to Cr(VI) we have to consider the reverse reaction of (equ. 1)

Therefore, $E^0 = 1.34 + (-0.55) = 0.79$, which is greater than 0.

So, the reaction is spontaneous and Cr(V) converts into Cr(VI).

Question



Convert the following Latimer diagram for vanadium into Frost diagram by mentioning the coordinates of the different points. Identify the most effective oxidizing agent and most stable oxidation state of V.

$$VO_2^+ \xrightarrow{1.0 \text{ V}} VO^{2+} \xrightarrow{0.34 \text{ V}} V^{3+} \xrightarrow{-0.26 \text{ V}} V^{2+} \xrightarrow{-1.130 \text{ V}} V$$

Answer: The coordinates are for V(0)

$$(0,0)$$
; $V^{2+} = (2, -2.26V)$; $V^{3+} = (3, -2.52V)$; $VO^{2+} = (4, -2.18V)$; $VO_2^+ = (5, -1.18V)$

The most stable oxidation state is V^{3+} Most effective oxidizing agent is VO_2^+

