Oxidation States

Skills to develop

- Assign an oxidation state (or oxidation number) to an atom in a molecule or ion.
- Describe oxidation and reduction reaction in terms of oxidation state change.

Oxidation State

Oxidation state is a number assigned to an element in a compound according to some rules. This number enable us to describe oxidation-reduction reactions, and balancing redox chemical reactions. You are learning the skill to assign oxidation states (or oxidation numbers) to a variety of compounds and ions.

When an oxidation number is assigned to the element, it does not imply that the element in the compound acquires this as a charge, but rather that it is a convenient number to use for balancing chemical reactions. The guidelines for assigning oxidation states (numbers) are given below:

1. **The oxidation state of any element such as Fe, H_2, O_2, P_4, S_8 is zero (0).**
2. **The oxidation state of oxygen in its compounds is -2, except for peroxides like H_2O_2 and Na_2O_2, in which the oxidation state for O is -1.**
3. **The oxidation state of hydrogen is +1 in its compounds, except for metal hydrides, such as NaH, LiH, etc., in which the oxidation state for H is -1.**
4. **The oxidation states of other elements are then assigned to make the algebraic sum of the oxidation states equal to the net charge on the molecule or ion.**
5. **The following elements usually have the same oxidation states in their compounds:**
   - **+1 for alkali metals - Li, Na, K, Rb, Cs;**
   - **+2 for alkaline earth metals - Be, Mg, Ca, Sr, Ba;**
   - **-1 for halogens except when they form compounds with oxygen or one another;**

These rules are wordy because we have to point out the special cases such as H_2O_2 and Na_2O_2. Rule 3. deals with hydride. Other than these, you may simply remember the oxidation states for H and O are +1 and -2 respectively in a coumpound, and oxidation of other elements can be asigned by making the **algebraic sum** of the oxidation states equal to the net charge on the molecule or ion.

For your practice, we provide some examples below. Please **study the following examples** and derive the oxidation state for all elements. The oxidation numbers of the key element are given in case you need help.

	Oxidation	Compound

Element	state	or ion
H	+1	H^+
Group 1	+1	H_2O^{2-}
	0	H_2
	-1	$NaAlH_4$
Cl	-1	Cl^-
Group 7	0	Cl_2
	+1	ClO^-
	+3	ClO_2^-
	+4	ClO_2
	+5	ClO_3^-
	+7	ClO_4^-
N	-3	NH_3
Group 5	-2	N_2H_4
	-1	NH_2OH
	0	N_2
	+1	N_2O
	+2	NO
	+3	NO_2^-
	+4	NO_2
	+5	NO_3^-

The following are some common oxidants or reductants. Changes of oxidation states in redox reactions of the key elements are given in groups. Please justify the assigned oxidation state to your satisfaction as you read on, and assign the oxidation number to all element in the formulas.

Element	Oxidation state	Compound or ion	
Fe	+2	Fe^{2+}	$Fe = Fe^{2+} + 2\ e^-$
	+3	Fe^{3+}	$Fe^{2+} = Fe^{3+} + e^-$
Zn	0	Zn	Zn is reducing agent
	+2	Zn^{2+}	
O	-1	H_2O_2	$H_2O_2 = O_2 + H_2O$

	0	O_2
	-2	H_2O
Cr	+6	$Cr_2O_7^{2-}$
	+3	Cr^{3+}
	+6	CrO_4^{2-}
Mn	+7	MnO_4^-
	+6	MnO_4^{2-}
	+4	MnO_2
	+2	Mn^{2+}
C	+3	$H_2C_2O_4$
	+4	CO_2
	+4	CO_3^{2-}
	+2	CO

$Cr_2O_7^{2-} + 6\,e = 2\,Cr^{3+}$

$MnO_4^- + 3\,e = MnO_2$

$MnO_4^- + 5\,e = Mn^{2+}$

Oxidation and Reduction in Terms of Oxidation State

In the chemistry of battery, you have learned that oxidation is the loss of electron. A loss of one electron raises the oxidation state by one. We now have another definition for oxidatin and reduction.

> A raise of oxidation state is an **oxidation** whereas a lower of oxidation state is a **reduction**.

For example, in the reaction (unbalanced),

$$MnO_4^- + H^+ \rightarrow Mn^{2+} + H_2O$$

the oxidation of Mn goes from +7 to +2. Thus, Mn is reduced. In the following reaction (unbalanced),

$$H_2C_2O_4 + O_2 \rightarrow CO_2 + H_2O$$

the element C is oxidized, because its oxidation state changes from +3 to +4 in the reaction.

Confidence Building Questions

- **What is the oxidation state of Mo in MoO_4^{2-}?**

Hint . . .

Skill:

Note that (+6) + 4*(-2) = -2, the charge of the ion MoO_4^{2-}. An oxidation state is a signed number; in this case +6.

- **What is the oxidation state of S in SO_3^{2-}?**

  Hint . . .

  Discussion:
  Even though S is in group VIA: O, S, Se, Te, Bi, the sulfur in sulfite ions has an oxidation number +4.

- **What is the oxidation state of As in AsO_4^{3-}?**

  Hint . . .

  Discussion:
  This is the normal oxidation state of group VA: N, P, As, Sb, Bi.

- **What is the oxidation state of Br in BrO_3^-?**

  Hint . . .

  Discussion:
  Br has many oxidation states, e.g. +7 in BrO_4^-.

- **What is the oxidation state of As in As_2S_3?**

  Hint . . .

  Discussion:
  The oxidation for S is -2, since it is in the group VIA: O, S, Se, Te, Po. Super! S being in the same group as O, has an oxidation state of -2.

- **What is the oxidation state of Cr in $Cr(OH)_3$?**

  Hint . . .

  Discussion:
  There are three OH^- groups in the compound. Chromium hydroxide, $Cr(OH)_3$, is a greenish gelatinous solid.

- **In the reaction,**
  $$P_4(s) + 5O_2(g) = P_4O_{10}(s)$$
  What is element reduced?

Hint . . .

Discussion:

What are the oxidation states of O in O_2 and P_4O_{10}? This equation represents the burning of phosphorus in air. P_4O_{10} dissolves in water to form phosphoric acid.

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Gram Equivalent weight:

Atom = $\frac{\text{Atomic weight}}{\text{Valency}}$ = O = $\frac{16}{2}$ = 8

(i) Salt :- $\frac{\text{Molecular weight}}{\text{Charge cation / anion}}$

e.g.

(i) NaCl = $\frac{58.5}{1}$ = 58.5

(ii) $CaCl_2$ = $\frac{110}{2}$ = 55

iii Na_2SO_4

$(23)_2 + 32 + (16)_4$ = $\frac{142}{2}$ = 71 $CaCO_3 = \frac{100}{2} = 50$

1) Acid = $\frac{\text{Molecular weight}}{\text{Basicity: No. of replaceable } H^+ \text{ proton}}$

$HCl + NaOH \rightarrow NaCl + H_2O$

$HCl = \frac{36.5}{1} = 36.5$ Eq. wt. HCl

$H_2SO_4 = \frac{98}{2} = 49$ → Eq. wt. H_2SO_4

Phosphoric acid H_3PO_4 = $\frac{97}{3}$ = 32.3 → Eq. wt. H_3PO_4

$3 + 30 + 64$

Base → Molecular weight

Acidity: No. of replacable (OH^-) hydroxyl ion

(i) NaOH : $\frac{40}{1} = 40$ → Eq. wt. of NaOH.

White Pellet

Hygroscopic → absorb moisture

(ii) $Ca(OH)_2$: $\frac{74}{2} = 37$ → Equivalent wt. of base $Ca(OH)_2$

oxidizing agent :-

oxidation Process

$Na^{\circ} + Cl^{\circ} \longrightarrow Na^{+}Cl^{-}$

Reduction process

Reducing Agent → Looses $\bar{e}$ → neutral

oxidizing agent → gain of $\bar{e}$ → Pick up $\bar{e}$

Always O.S = zero in free state

$Na^{\circ}, H_2^{\circ}, Cl_2^{\circ}, Br_2^{\circ}$

$Na^{\circ} \longrightarrow Na^{+} + 1\bar{e}$

$\frac{1}{2} Cl_2 + 1\bar{e} \rightarrow Cl^-$

O.A

Molecular form

Oxidizing agent: $\frac{\text{Molecular weight}}{\text{No. of gain of electron}}$

$KMnO_4$

$K_2Cr_2O_7$ Potassium dichromate

K_2CrO_4 Potassium Chromate

$\frac{158}{5} = 31.5$ → Equivt. wt of $KMnO_4$; 158 → Mol. wt. of $KMnO_4$

Reducing agent: $\frac{\text{Molecular weight}}{\text{No. of loss of electron}}$

$FeSO_4$

$Na_2C_2O_4$ Sodium oxalate $\frac{134}{2} = 67$

$H_2C_2O_4 \cdot 2H_2O$ Oxalic acid $\frac{126}{2} = 63$ or $\frac{90}{2} = 45$

$\frac{152}{1} = 152$ → Eq. wt of $FeSO_4$

$\frac{152}{1} = 152$

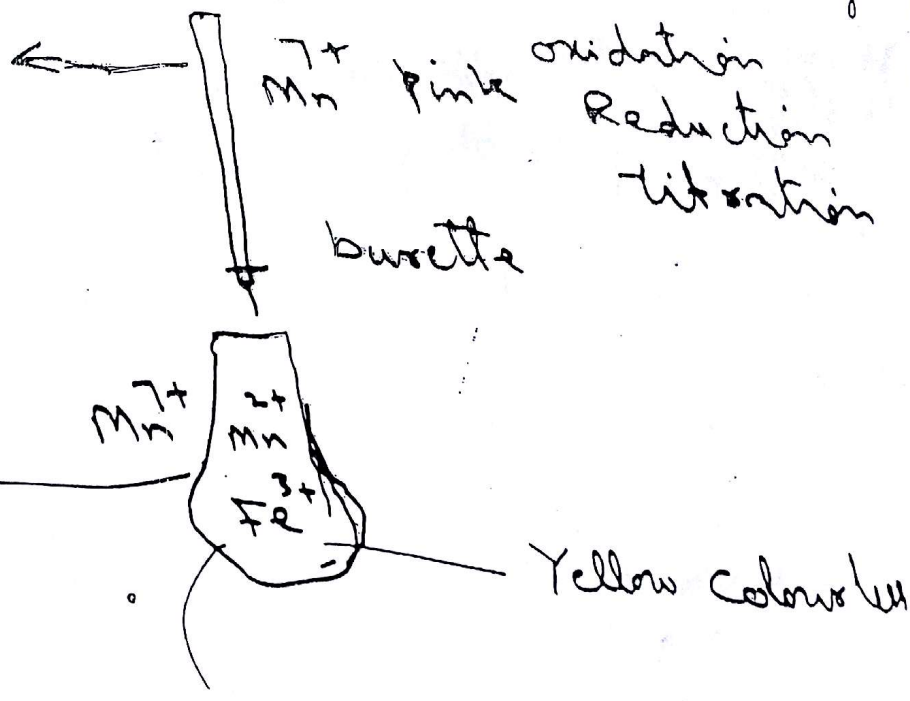
warm 70°

Volumetric Analysis

K_2CrO_4

$K_2Cr_2O_7$

O.A



10 ml $FeSO_4$

A H_2SO_4 (dil)

10 ml

23 23 46 24 64 134

Oxidation State

$KMnO_4 + H^+_{(aq)} + FeSO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + H_2O$

$KMnO_4$ solid

Potassium permanganate

$Mn^{7+}O_4^- + 5\bar{e} \rightarrow Mn^{2+}SO_4$ Reduction half

Permanganate

$Fe^{2+} \rightarrow Fe^{3+} + 1\bar{e}$ Oxidation half

Balance by cross multiplication

$2KMnO_4 + 4H_2SO_4 + 10FeSO_4 \rightarrow 2MnSO_4 + 5Fe(SO_4)_3$ (dil)

Never: use HCl, HNO_3, Conc./hot H_2SO_4

Always: but use only dil H_2SO_4 as medium

Normal (N) = Gm. Eq. wt / lit

Molar (M) = Mole. wt / lit

Molal (m) = Mol. wt / Kg

Preparation of solutions solid compounds

2 (i) Prepare 1N & 0.1N solution of NaOH in lit

1st Calculate Gm. Eq. wt. = $\frac{\text{M.wt.}}{\text{acidity (no. of replaced OH)}}$

$\frac{40}{1} = 40.$

(i) 40 gm dissolve in 1 litre = 1 Normal solution of NaOH

(ii) 4.0 gm = 1 litre solvent = 0.1N sol. of NaOH.

2. Prepare 0.1M solution of NaOH

40 gm of NaOH dissolve in 1 litre

= 1M

4.0 gm = = 0.1M of NaOH

Formula

Amt. of substance required = $\frac{\text{Concentration required} \times \text{Gm. equivalent weight} \times \text{Vol. required}}{1000}$

or

Amt. gm = $\frac{\text{Conc. req} \times \text{Gm. eq. wt} \times \text{Vol. req}}{1000}$

For Prepare 1N Solution of NaOH

Amt = $\frac{1 \times 40 \times 1000}{1000}$

= 40 gm of NaOH dissolve in 1 litre

Prepare 0.1N of NaOH

Amt = $\frac{0.1 \times 40 \times 1000}{1000}$

4.0 gm of NaOH in 1 litre

For prepare 1M Solution of NaOH

Amt wt. = $\frac{1 \times \text{Mol. wt (40)} \times 1000}{1000}$

= 40 gm NaOH dissolve in 1 litre

Oxalic acid soln:

$H_2C_2O_4 \cdot 2H_2O$ hydrated = 126

$H_2C_2O_4$ anhydrous = (without water molecule) 90

gm. Eq. wt: $\frac{126}{2} = 63$

anhydrous $\frac{90}{2} = 45$

Prepare 0.1N solution of oxalic acid.

wt. req. $= \frac{0.1 \times 63 \times 1000}{1000}$

6.3 gm of oxalic acid in 1 litre

Prepare 0.1M solution of oxalic acid

wt $= \frac{0.1 \times 126 \times 1000}{1000}$

12.6 gm of oxalic acid dissolve in 1 litre

Prepare 0.8N of NaOH in 1 litre

$$\text{wt. eq.} = \frac{0.8 \times 40 \times 1000}{1000}$$

$$= 32.0 \text{ gm dissolve in 1 litre}$$

Problem : $\frac{0.8 \times 40 \times 250}{1000}$

$$\frac{32.0}{4} = 8 \text{ gm dissolved}$$

Calculate Normality of solution that contains 8 gm of NaOH in 250 ml solution

$$\text{wt. of subst} = \frac{N = ? \times 40 \times 250}{1000}$$

$$8$$

$$\frac{8 \times 1000}{40 \times 250} = N$$

$$= \frac{32}{40} = 0.8N \text{ of NaOH}$$

(a) 1st Find N/M

$$N = \frac{\text{gm. eq. wt} \times 100}{\text{specific gravity} \times \% \text{ purity}}$$

$$N = \frac{\% \text{ Purity} \times \text{specific gravity}}{\text{gm. eq. wt.} \times 100}$$

(b) Sol. $N_1V_1 = N_2V_2$ — 95% purity, 1.83 sp. gm

$1 \times 500 = 36 \times V_2$

$\frac{1 \times 500}{36} = V_2$

$= 13.88$ ml of H_2SO_4 dissolve in 500 ml make up.

Problem 0.1 N solution of 250 ml

$N_1V_1 = N_2V_2$ — % Purity × sp. gravity / 100 — 12 N HCl

$0.1 \times 250 = 12 \times V_2$

$\frac{0.1 \times 250}{12} = V_2$

2.08 ml of HCl dissolve in 250 ml

Prepare 0.01, 0.02, 0.03, 0.05 solution from stock solution of 5N of NaOH

(i) $N_1V_1 = N_2V_2$

$0.01 \times 10ml = 5 \times V_2$

$V_2 = ?$

$$\frac{0.01 \times 10^2}{5} = V_2$$

$= 0.02ml$ of NaOH in 10ml

(ii) $N_1V_1 = N_2V_2$

$0.02 \times 10 = 5 \times V_2$

$$\frac{0.02 \times 10^2}{5} = V_2$$

$= 0.04ml$ of NaOH in 10ml

(iii) $N_1V_1 = N_2V_2$

$0.03 \times 10 = 5 \times V_2$

$$\frac{0.03 \times 10^2}{5} = 0.06ml \text{ of NaOH}$$

(iv) $N_1V_1 = N_2V_2$

$0.5 \times 10 = 5 \times V_2$

$= 1ml$ of NaOH