CHAPTER 8

CHEMICAL OXIDATION AND REDUCTION

OXIDATION AND REDUCTION PROCESSES

By chemical oxidation and reduction the oxidation state of the substance is changed. Oxidation is a process in which the oxidation state is increased, while chemical reduction is a process in which the oxidation state is decreased.

An oxidation-reduction (redox) reaction is today defined as a process in which electrons are transferred from one substance to another. An oxidation means loss of electrons and a reduction involves gain of electrons. The concept of electrons exchange is very useful as it affords a simple means of balancing redox reactions. With regard to this balancing, the concept of oxidation stage is introduced. The definition of this concept is based on the following rules:

1. All elements have an oxidation state of zero.
2. All ions have the same oxidation state as their charges.
3. Hydrogen has the oxidation state +1 in all its compounds.
4. Oxygen has the oxidation state -2 in all its compounds except hydrogen peroxide and its derivatives.
5. The sum of the oxidation stages of all atoms in an uncharged molecule is zero.

However, with respect to organic redox reactions, the concept is not directly applicable, because it is difficult to distinguish between different oxidation stages.

To illustrate this point a chlorination can be considered, e.g. $Cl_2 + C_2H_6 \rightleftharpoons C_2H_5Cl + HCl$.

In accordance with Pauling (1960), the oxidation number of each atom in a covalent compound is the charge remaining on the atom when each electron pair is assigned completely to the more electronegative of the atoms sharing the electrons. The three elements involved in the reaction are H, C and Cl. The electronegativity of these three elements is respectively 2.1, 2.5 and 2.8. This means that C in C_2H_6 has the oxidation stage -3, while in C_2H_5Cl it has the oxidation stage - 2. In both C_2H_5Cl and in HCl, Cl has the stage -1.

Redox potential

Nernst's equation expresses the relationship between the electrode potential and concentration of species:

$$E = E_o + \frac{RT}{nF} \cdot \ln\frac{[Ox]}{[Red]} \qquad (8.1)$$

where

R = gas constant = 8.314 joule/C° mol
T = absolute temperature in K
n = the number of electrons exchanged
F = Faraday's constant = 96473 coulomb/equivalent
E_o = standard electrode potential (in volts)
[Ox] = the molar concentration of the oxidizing agent (oxidant)
[Red] = the molar concentration of the reductant

At 25°C (8.1) can be written as:

$$E = E_o + \frac{0.0591}{n} \log\frac{[Ox]}{[Red]} \qquad (8.2)$$

It is possible to control a redox reaction by the use of the redox potential. The redox potential in the equivalent point can be found from Nernst's equation.

Let us consider the reaction:

$$n_2Red_1 + n_1Ox_2 \rightleftharpoons n_2Ox_1 + n_1Red_2 \qquad (8.3)$$

Before the reaction takes place $[Ox_1] = [Red_2] = 0$.

The following equation will always be valid for complete or partial reaction:

$$\frac{[Ox_1]}{[Red_2]} = \frac{n_2}{n_1} \qquad (8.4)$$

At the equivalent point the following equation is valid:

$$\frac{[Red_1] + [Ox_1]}{[Red_2] + [Ox_2]} = \frac{n_2}{n_1} \qquad (8.5)$$

(8.4) and (8.5) involve:

$$\frac{[Red_1]}{[Ox_2]} = \frac{n_2}{n_1} \qquad (8.6)$$

The application of Nernst's equation gives:

$$E = E_{o_1} + \frac{RT}{n_1 F} \cdot \ln \frac{[Ox_1]}{[Red_1]} \tag{8.7}$$

$$E = E_{o_2} + \frac{RT}{n_2 F} \cdot \ln \frac{[Ox_2]}{[Red_2]} \tag{8.8}$$

$E_{o_2} > E_{o_1}$ since Ox_2 oxidize Ox_1.

If (8.7) is multiplied by n_1 and (8.8) by n_2:

$$n_1 \cdot E = n_1 \cdot E_{o_1} + \frac{RT}{F} \cdot \ln \frac{[Ox_1]}{[Red_1]} \tag{8.9}$$

$$n_2 \cdot E = n_2 \cdot E_{o_2} + \frac{RT}{F} \cdot \ln \frac{[Ox_2]}{[Red_2]} \tag{8.10}$$

By equilibrium found from both equations $E = E_{eqv}$ will be equal and addition of the two equations gives:

$$(n_1 + n_2)E = n_1 \cdot E_{o_1} + n_2 \cdot E_{o_2} + \frac{RT}{F} \cdot \ln \frac{[Ox_1]\,[Ox_2]}{[Red_1]\,[Red_2]} \tag{8.11}$$

In accordance with (8.4) and (8.6)

$$\ln \frac{[Ox_1]\,[Ox_2]}{[Red_1]\,[Red_2]} = 0,$$

and

$$E_{eqv} = \frac{n_1 \cdot E_{o_1} + n_2 \cdot E_{o_2}}{n_1 + n_2} \tag{8.12}$$

The potential before and after the equivalent point can also be calculated, considering the addition of e.g. Ox_2 to Red_1, before the equivalent point Ox_2 has reacted completely. This means:

$Ox_2 = 0$, which involves:

$Red_2 = C_2$, where C_2 is the total concentration of the redox pair 2.

In accordance with (8.6):

$$Ox_1 = \frac{n_2 \cdot C_2}{n_1}, \text{ and}$$

$$Red_1 = C_1 - Ox_1 = C_1 - \frac{n_2 \cdot C_2}{n_1} \qquad (8.13)$$

where C_1 is the total concentration of redox pair 1.

If we introduce this equation into (8.7) it produces:

$$E = E_{o_1} + \frac{RT}{n_1 F} \cdot \ln \frac{n_2 \cdot C_2}{n_1 \cdot C_1 - n_2 \cdot C_2} \qquad (8.14)$$

Correspondingly $Red_1 = 0$ after the equivalent point, which means:

$$Ox_1 = C_1 \cdot Red_2 \frac{n_1 \cdot C_1}{n_2}, \text{ and}$$

$$Ox_2 = C_2 - \frac{n_1 \cdot C_1}{n_2} \qquad (8.15)$$

By introducing (8.15) into equation (8.8):

$$E = E_{o_2} + \frac{RT}{n_2 F} \cdot \ln \frac{n_2 \cdot C_2 - n_1 \cdot C_1}{n_1 \cdot C_1} \qquad (8.16)$$

It is possible to calculate from these equations the redox potential as a function of the addition of either Red_1 or Ox_2, which means that it is possible to follow the process by means of the redox potential.

The redox potential, E, is related to the free energy change, ΔG, involved in the reaction:

$$\Delta G = n \cdot F \cdot E \qquad (8.17)$$

Correspondingly, for the standard state:

$$\Delta G_o = n \cdot F \cdot E_o \qquad (8.18)$$

Since $RT \cdot \ln(K) = -\Delta G_o$, where K is the equilibrium constant, the following equation is valid:

$$K = \exp\left(\frac{n \cdot F \cdot E_o}{RT}\right) \qquad (8.19)$$

The standard electrode potential for a selected group of species of interest in industrial waste water treatment is listed in Table 8.1.

TABLE 8.1

Standard oxidation potentials at 25°C (Latimer, 1952)

	E^o (V)	
	Acidic	Basic
Oxygen related couples:		
$2H_2O = O_2 + 4H^+ + 4e^-$	-1.229	
$4OH^- = O_2 + 2H_2O + 4e^-$		-0.401
$2H_2O = O_2 + 4H^+$ (pH 7) $+ 4e^-$	(-0.815)	
$H_2O = O(g) + 2H^+ + 2e^-$	-2.42	
$2OH^- = O(g) + H_2O + 2e^-$		-1.59
$H_2O_2 = O_2 + 2H^+ + 2e^-$	-0.682	
$OH^- + HO_2^- = O_2 + H_2O + 2e^-$		+0.076
$3OH^- = HO_2^- + H_2O + 2e^-$		-0.88
$2H_2O = H_2O_2 + 2H^+ + 2e^-$	-1.77	
$O_2 + H_2O = O_3 + 2H^+ + 2e^-$	-2.07	
$O_2 + 2OH^- = O_3 + H_2O + 2e^-$		-1.24
$H_2O_2 = HO_2 + H^+ + e^-$	-1.50	
$OH^- + HO_2 = O_2^- + H_2O + e^-$		-0.4
$2H_2O = HO_2 + 3H^+ + 3e^-$	-1.70	
$4OH^- = O_2^- + 2H_2O + 3e^-$		-0.7
$HO_2 = O_2 + H^+ + e^-$	+0.13	
$O_2^- = O_2 + e^-$		+0.56
$H_2O = OH + H^+ + e^-$	-2.80	
$OH^- = OH + e^-$		-2.0
$OH + H_2O = H_2O_2 + H^+ + e^-$	-0.72	
$OH + 2OH^- = HO_2^- + H_2O + e^-$		+0.24
Chlorine related couples:		
$2Cl^- = Cl_2 + 2e^-$	-1.36	
$Cl^- + 2OH^- = ClO^- + H_2O + 2e^-$		-0.89
$1/2Cl_2 + H_2O = HClO + H^+ + e^-$	-1.63	
$Cl^- + H_2O = HClO + H^+ + 2e^-$	-1.49	
$HClO + H_2O = HClO_2 + 2H^+ + 2e^-$	-1.64	
$ClO^- + 2OH^- = ClO_2^- + H_2O + 2e^-$		-0.66
$HClO_2 = ClO_2 + H^+ + e^-$	-1.275	
$ClO_2^- = ClO_2 + e^-$		-1.16
$ClO_2 + H_2O = ClO_3^- + 2H^+ + e^-$	-1.15	
$ClO_2 + 2OH^- = ClO_3^- + H_2O + e^-$		+0.50
Manganese related couples:		
$Mn^{2+} = Mn^{3+} + e^-$	~+1.5	
$Mn^{2+} + 2H_2O = MnO_2(s) + 4H^+ + 2e^-$	-1.23	
$Mn(OH)_2 + 2OH^- = MnO_2(s) + 2H_2O + 2e^-$		+0.05
$MnO_2(s) + 4OH^- = MnO_4^- + 2H_2O + 3e^-$		-0.588
$MnO_2(s) + 2H_2O = MnO_4^- + 4H^+ + 3e^-$	-1.695	
$MnO_4^{2-} = MnO_4^- + e^-$	-0.564	
$MnO_2(s) + 2H_2O = MnO_4^{2-} + 4H^+ + 2e^-$	-2.26	
$MnO_2(s) + 4OH^- = MnO_4^{2-} + 2H_2O + 2e^-$		-0.60
$4H_2O + Mn^{2+} = MnO_4^- + 8H^+ + 5e^-$	-1.51	

The kinetics of redox reactions

The reaction rate of a redox process is affected by concentration of reactants, temperature, catalysts, pH and the nature of the reactions.

The influence of pH is a result of one of the following effects:

1. H^+ or OH^- taking part in that reaction.
2. H^+ or OH^- changing the activity of other reactions.
3. H^+ or OH^- acting as catalysts.

The following reaction illustrates effect (1):

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2 + 4H^+ \qquad (8.20)$$

The reduction of chromate with H_2SO_3 is dependent on pH, since the concentration of H_2SO_3 is in accordance with Henderson-Hasselbalch's equation:

$$pH = pK + \log\frac{[HSO_3^-]}{[H_2SO_3]} = 1.89 + \log\frac{100 - \%acid}{\%acid} \qquad (8.21)$$

Fig. 8.1 illustrates the percentage of H_2SO_3 as function of the pH. The curve is constructed in accordance with equation (8.21).

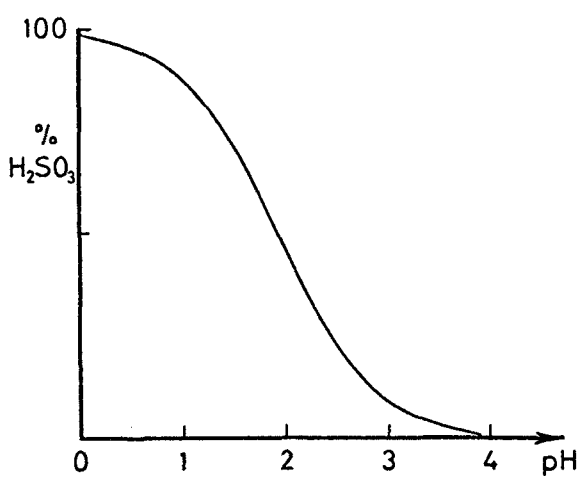

Fig. 8.1. % H_2SO_3 as a function of pH.

Many redox processes are influenced catalytically by OH^- or H^+, for example in the oxidation of alcohol, which reacts very slowly with neutral solutions. The OH^- has a strong catalytical effect and the oxidation process is extremely rapid in basic solutions (Stewart, 1964).

As can be seen, pH is one of the most influential parameters in a redox process and pH should therefore be carefully monitored or controlled in chemical redox reactions. The oxidation of Fe^{2+} to Fe^{3+}:

$$2Fe^{2+} + \frac{1}{2}O_2 + 5H_2O \rightleftharpoons 2Fe(OH)_3\downarrow + 4H^+$$

is catalyzed by cations, such as Cu^{2+} and Co^{2+}, but also anions, such as HPO_4^{2-} and $H_3SO_4^-$ forming complexes with iron(III)-ions are able to catalyze this reaction. The influence of the concentrations of reactants on the reaction rate is usually not quantitatively predictable, and must be obtained experimentally. In some instances, however, it is possible to set up equations. Stumm and Lee (1961) have produced the following rate equation, based on an experimental investigation:

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)][OH^-]^2 P_{O_2} \quad (P_{O_2} = \text{partial pressure } O_2) \qquad (8.22)$$

It is possible to give some general views about the activity of organic compounds with respect to oxidation, but the rules must be used cautiously and then only give qualitative estimations.

Phenols, aldehydes, thio-organic compounds and aromatic amines all show high activity, while halogenated hydrocarbons, saturated aliphatic compounds and benzenes all have low reactivity. Many other compounds, such as alcohols, unsaturated alkyl compounds, carbohydrates, acids, ketones, esters and aliphatic amines show an intermediate activity in respect of oxidation.

Oxidants

The application of oxidation is largely limited, mainly for the reasons of economics.

There are several aspects to be considered in the selection of a suitable oxidizing agent for industrial waste water treatment. These are:

(1) Ideally no residue of oxygen should remain after the treatment and there should be no residual toxic or other effects.
(2) The effectiveness of the treatment must be high.
(3) The cost must be as low as possible.
(4) The handling should be easy.

It is understandable that only few oxidants are capable of meeting these requirements. The following oxidants are in use today for treatment of water and waste water:

(1) Oxygen or air.
(2) Ozone.
(3) Potassium permanganate.
(4) Hydrogen peroxide.
(5) Chlorine.
(6) Chlorine dioxide.

Oxygen has its significance in biological oxidation, but also plays an important role in chemical oxidation.

The primary attraction of oxygen is that it can be applied in the form of air. It is used for removal of volatile gases such as methane, hydrogen sulphide and carbon dioxide or even some organic compounds with low boiling points, by stripping. Furthermore, it is used for the oxidation of divalent iron and manganese.

The oxidation of divalent iron and manganese is strongly dependent on pH (see equation (8.22) and Morgan, 1964; Morgan and Stumm, 1963).

Divalent manganese is adsorbed on manganese dioxide:

$$Mn^{2+} + MnO_2 \rightarrow Mn^{2+},MnO_2 \qquad (8.23)$$

This process can be utilized by passing the water containing divalent manganese through a bed of activated carbon coated with manganese dioxide.

Organic material including phenol can be catalytically oxidized by the use of suitable catalysts, such as oxides of copper, nickel, cobolt, zinc, chromium, iron, magnesium, platinum and palladium, but this process is as yet not developed for use on a technical scale.

Ozone is a more powerful oxidant than oxygen and is able to react rapidly with a wide spectrum of organic compounds and micro-organisms present in waste water.

It is produced from oxygen by means of electrical energy, which is a highly attractive process since air is used. One of the advantages of using ozone is that it does not impart taste and odour to the treated water. Ozone is used in the following areas of water treatment:

1. Removal of colour, taste and odour (Holluta, 1963).
2. Disinfection, see also chapter 9.
3. For the oxidation of organic substances e.g. phenol surfactants (Eisenhauer, 1968; Wynn et al., 1972) and cyanides (Khandelwal et al., 1959; Anon, 1958).
4. For removal of iron and manganese (Hopf, 1964).

The solubility of ozone is dependent upon the temperature. Henry's coefficient as a function of the temperature for ozone and oxygen is shown in Table 8.2.

TABLE 8.2

Henry's coefficient for oxygen and ozone in water

Temperature (^{o}C)	$H \cdot 10^{-4}$ Oxygen	Ozone
0	2.5	0.25
5	2.9	0.29
10	3.3	0.33
15	3.6	0.38
20	4.0	0.45
25	4.4	0.52
30	4.8	0.60
35	5.1	0.73
40	5.4	0.89
45	5.6	1.0
50	5.9	1.2

Henry's coefficient, H, is used in Henry's law:

$$p = H \cdot x \qquad (8.24)$$

where

p = the partial pressure in atm.

x = the mole fraction in solution

Ozone has low thermodynamic stability at normal temperature and pressure (Kirk-Othmer, 1967). It decomposes both in the gas phase and in solution. Decomposition is more likely in aqueous solutions, where it is strongly catalyzed by hydroxide ions, see Table 8.2, (Stumm, 1958).

TABLE 8.2

Influence of pH on half life of ozone in water (Stumm, 1958)

pH	Half-life(min)
7.6	41
8.5	11
8.9	7
9.2	4
9.7	2
10.4	0.5

The oxidation of phenol by gaseous ozone has been studied by Gould et al. (1976) under a number of conditions.

Virtually complete removal of phenol and its aromatic degradation products is realized when 4-6 moles of ozone have been consumed for each mole of phenol originally present. At this point approximately $\frac{1}{3}$ of the initial organic carbon will remain and 70-80% reduction of the COD-number will have been achieved. Concentrations of the non-aromatic degradation products will be less than 0.5 mg/l. Subsequent dilution of the discharge of this effluent should reduce the concentration of the various components in the receiving body of water to tolerable levels.

Ozone is extremely toxic, having a maximum tolerable concentration for continuous exposure of 0.1 ppm. However, the half life of ozone is reduced by high pH as demonstrated in Table 8.2.

The ozone concentration can be analyzed either by ultraviolet absorption spectroscopy or by iodide titration:

$$O_3 + 3I^- + H_2O \rightarrow I_3^- + O_2 + 2OH^- \qquad (8.25)$$

The liberated iodine is titrated with thiosulphate (Kirk-Othmer, 1967). As indicated above, ozone is generated from dry air by a high voltage electric discharge. A potential of 5000 to 40,000 volts between the electrodes is used. Cooling is usually employed to minimize ozone decomposition in the reactor. Theoretically 1058 g of ozone can be produced per kWh of electrical energy, but in practice a production of 150 g/kWh is more usual.

Permanganate is a powerful oxidizing agent and is widely used by many municipal water plants for taste and odour control and for removal of iron and manganese. Furthermore, it can be used as an oxidant for the removal of impurities such as Fe^{2+}, Mn^{2+}, S^{2-}, CN^- and phenols present in industrial waste water.

In strongly acidic solutions permanganate is able to take up 5 electrons:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons 4H_2O + Mn^{2+} \qquad (8.26)$$

while in the pH range from approximately 3 to 12 only three electrons are transferred and the insoluble manganese dioxide is formed:

$$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons 2H_2O + MnO_2 \qquad (8.27)$$

or

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons 4OH^- + MnO_2 \qquad (8.28)$$

Permanganate can, as mentioned above, oxidize manganese(II):

$$3Mn_2^{2+} + 2MnO_4^- + 2H_2O \rightleftharpoons 5MnO_2 + 4H^+ \qquad (8.29)$$

This process was extensively investigated by Ladbury et al. (1958).

The theoretical stoichiometric amount of permanganate, 1.92 parts $KMnO_4$ per part Mn^{2+}, is generally not required, since Mn^{2+} is adsorped on precipitated manganese dioxide. The adsorption on divalent manganese dioxide is a function of pH as is shown in Fig. 8.2, (after Morgan and Stumm, 1964).

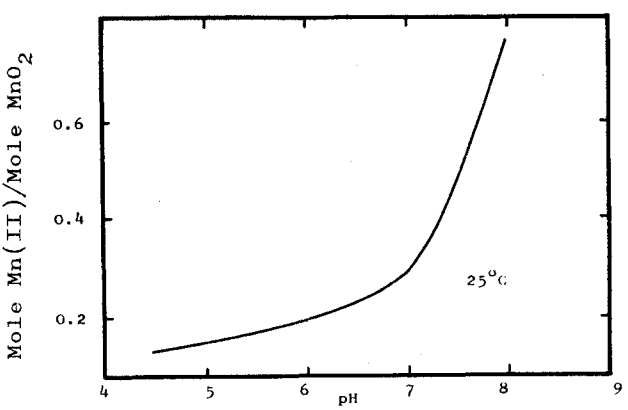

Fig. 8.2. Mn(II) sorption by MnO_2 as a function of pH.

Aeration is normally more economic for oxidation of hydrogen sulphide, but permanganate finds an application in cases where only small concentrations of hydrogen sulphide are considered. The stoichiometry for this oxidation (Willey et al., 1963) is:

$$4KMnO_4 + 3H_2S \rightleftharpoons 2K_2SO_4 + S + 3MnO + MnO_2 + 3H_2O \qquad (8.29)$$

The stoichiometry for the oxidation of cyanide in a hydroxide solution of pH 12-14 is:

$$2MnO_4^- + CN^- + 2OH^- \rightleftharpoons 2MnO_4^{2-} + CNO^- + H_2O \qquad (8.30)$$

In saturated solution of calcium hydroxide (Posselt, 1966), the reaction takes the form:

$$2MnO_4^- + 3CN^- + H_2O \rightarrow 3CNO^- + 2MnO_2 + 2OH^- \qquad (8.31)$$

The presence of calcium ions affects the rate of manganate(IV) disproportionately:

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + 4OH^- + MnO_2 \qquad (8.32)$$

The permanganate concentration can be determined by spectrophotometry (absorption maximum at 526 mμ) or by a titrimetric method.

Table 8.4 gives a survey of the oxidation of organic compounds by permanganate.

TABLE 8.4

Permanganate oxidation of organic compounds

-CH = CH-	⟶	-CH(OH) - CH(OH)-
R - CH_2OH	⟶	R - COOH
R - CHO	⟶	R - COOH
R_2 - CHOH	⟶	R_2 - C = O
R - SH	⟶	R - SO_3H
Alkyl amines	⟶	R - COOH + NH_3
R_1 - S - R_2	⟶	R_1 - SO_3 - R_2
R_1 - S - S - R	⟶	R_1 - SO_3H + R_2 - SO_3H
R_1 - SO - R_2	⟶	R - SO_2 - R_2

Chlorine is known to be a successful disinfectant in waste water treatment, but it is also able to oxidize effectively such compounds as hydrogen sulphide, nitrite, divalent manganese and iron and cyanide. The oxidation effectiveness usually increases with increasing pH.

Cyanide which is present in a number of different industrial waste waters is typically oxidized with chlorine at a high pH. The oxidation to the much less toxic cyanate (CNO^-) is generally satisfactory, but in other cases complete degradation of cyanide to carbon dioxide and nitrogen is required, see chapter 13.

The disadvantage of chlorine is that it forms aromatic chlorocompounds, which are highly toxic, e.g. chlorophenols when phenol-bearing water is treated with chlorine (Aston, 1947).

This fact has caused the more widespread use of chlorine dioxide. Chlorine dioxide is as unstable as ozone and therefore must be generated in situ.

The industrial generation of chlorine dioxide is carried out by means of a reaction between chlorine and sodium chlorite in acid solution (Granstrom and Lee, 1958):

$$Cl_2 + 2NaClO_2 \rightleftharpoons 2ClO_2 + 2NaCl \qquad (8.33)$$

As chlorine dioxide is a mixed anhydride of chlorous and chloric acid disproportionation to the corresponding anions occurs in basic solutions:

$$2ClO_2 + 2OH^- \rightleftharpoons ClO_2^- + ClO_3^- + H_2O \qquad (8.34)$$

This process becomes negligible under acidic conditions. The equilibrium:

$$2ClO_2 + H_2O \rightleftharpoons HClO_2 + HClO_3 \qquad (8.35)$$

shifts to the left at lower pH.

According to Myhrstad and Samdal (1969) chlorine dioxide can be analysed with acid chrome violet K, and determined spectrophotometrically without interference by Cl_2, ClO^-, ClO_2^- and ClO_3^-.

As iodo metric titration gives Cl_2:

$Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2$ (pH = 7.0)

and iodo metric titration at pH = 2.5 - 3.0 gives the total amount of $Cl_2 + ClO_2 + ClO_2^-$:

$$Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2 \qquad (8.36)$$

$$2ClO_2 + 8H^+ + 10I^- \rightleftharpoons 2Cl^- + 4H_2O + 5I_2 \qquad (8.37)$$

$$ClO_2^- + H_4 + 4I^- \rightleftharpoons Cl^- + 2H_2O + 2I_2 \qquad (8.38)$$

it is possible to make a simultaneous determination of ClO_2, ClO_2^- and Cl_2 independently.

Chlorine dioxide is used for taste and odour control and for the oxidation of manganese(II) ions. It has been reported to be a selective oxidant for industrial waste water containing cyanide, phenol, sulphides and mercaptans (Wheeler, 1976).

Hydrogen peroxide can be used as an oxidant for sulphide in water (Cole et al., 1976). Recently this oxidizing ability has been applied to control odour and corrosion in domestic and industrial waste water.

The hydrogen peroxide is believed to act in three different ways to control the sulphide production and resulting odours:

$H_2S + H_2O_2 \rightarrow H_2O + S$ (acidic - neutral)

$H_2S + H_2O_2 \rightarrow H_2O +$ sulphate (alkaline).

It is possible to oxidize sulphide catalytically in aqueous solution using hydroquinone and hydroquinone iron(III)-chloride, ammonium peroxydisulphate acting as catalyst.

The volume of air needed for complete removal of sodium sulphide is 8-40 times the stoichiometrical amount.

The application of reductants

Reduction is a process in which soluble metallic ions are reduced through a redox reaction. Generally, the process is used in the treatment of plating waste water containing chromate. This water, from chromate acid baths used in electroplating and anodizing processes, contains chromate in the form of CrO_3 or $Na_2Cr_2O_7 \cdot 2H_2O$. The pH in such waste water is low and the Cr(VI) concentration is often very high - up to 20,000 ppm or more. The most commonly used reducing agents are iron(II)-sulphate, sodium meta hydrogen sulphite or sulphur dioxide. Since the reduction of chromate is most effective at low pH, it is of course an advantage if the waste water itself contains acid, which is often the case. Iron(II)-ions react with chromate by reducing the chromium to a trivalent state and the iron(II)-ions are oxidized to iron(III) ones.

The reaction occurs rapidly at pH below 3.0, but since the acidic properties of iron(II)-sulphate are low at high dilution, acid must often be added for pH adjustment.

The reactions are:

$$CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \qquad (8.39)$$

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 \rightleftharpoons Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O \qquad (8.40)$$

$$Cr_2O_7^{2-} + 6FeSO_4 + 7H_2SO_4 \rightleftharpoons Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + SO_4^{2-} \qquad (8.41)$$

It is possible to show that 1 mg of Cr will require 16 mg $FeSO_4$, $7H_2O$ and 6 mg H_2SO_4 based on stoichiometry.

After the reduction, the Cr^{3+} formed is precipitated by means of calcium hydroxide (see chapter 3).

Reduction of chromium can also be accomplished by the use of meta-hydrogen sulphite or sulphur dioxide. When meta-hydrogen sulphite is used the salt hydrolyzes to hydrogen sulphite:

$$S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^- \quad (8.42)$$

The hydrogen sulphite reacts to form sulphurous acid:

$$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^- \quad (8.43)$$

Sulphurous acid is also formed when sulphur dioxide is used, since:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \quad (8.44)$$

As mentioned previously, the reaction is strongly dependent upon pH and temperature (see p. 102).

The redox process is:

$$2H_2CrO_4 + 3H_2SO_3 \rightleftharpoons Cr_2(SO_4)_3 + 5H_2O \quad (8.45)$$

Based on stoichiometry, the following amounts of chemicals are required for 1 mg of chromium: 2.8 mg $Na_2S_2O_5$ or 1.85 mg SO_2.

Since dissolved oxygen reacts with sulphur dioxide, excess SO_2 must be added to account for this oxidation:

$$H_2SO_3 + \frac{1}{2}O_2 \rightleftharpoons H_2SO_4 \quad (8.46)$$

REFERENCES

Anon, 1958. Ozone counters waste cyanide's lethal punch. Chem. Eng., 65: 63.

Aston, R.N., 1947. Chlorine dioxide use in plants on the Niagara border. J. Amer. Water Works Assoc., 39: 687.

Catzer, J.R., Ficke, H.H. and Sadana, A., 1976. Evaluation of aqueous phase catalytical oxidation. J. Wat. Poll. Contr. Fed., 48: 920.

Cole, C.A., Paul, P.E. and Brewer, H.P., 1976. Odour control by hydrogen peroxide. J. Wat. Poll. Contr. Fed., 48: 297.

Eisenhauer, H.R., 1968. Ozonization of phenolic wastes. J. Wat. Poll. Contr. Fed., 40: 1887.

Granstrom, M.L. and Lee, G.F., 1958. Generation and use of chlorine dioxide. J. Amer. Water Works Assoc., 50: 1453.

Gould, J.P. and Weber, W.J., 1976. Oxidation of phenols by ozone. J. Wat. Poll. Contr. Fed., 48:

Holluta, T., 1963. Das Ozon in der Wasserchemie. GWF, 104: 1261.

Hopf, W., 1964. Fortschritte in der Wasseraufbereitung. Tech. Forsch., 15: (4), 49.

Khandelwal, K.K., Barduhn, A.J. and Grove, C.S.,Jr., 1959. Kinetics of ozonation of cyanides. Ozone Chemistry and Technology, Advan. Chem. Ser., 21, 78, Amer. Chem. Soc., Washington, D.C.

Kirk-Othmer, 1967. Encyclopedia of Chemical Technology. John Wliley, New York. Sec. Ed., 14: 410-432.
Ladbury, J.W. and Cullis, C.F., 1958. Kinetics and mechanisms of oxidation by permanganate. Chem. Rev., 58: 403.
Latimer, W.M., 1952. The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Prentice Hall, New York.
Lewis, W.K. and Whitman, W.G., 1924. Ind. Eng. Chem., 16: 1215.
Morgan, J.J. and Stumm, W., 1963. Oxygenation of aqueous manganese(II). Division of Water and Waste Chemistry, Amer. Chem. Soc., 145th Meeting, New York.
Morgan, J.J., 1964. The Chemistry of Aqueous Manganese II and IV. Thesis, Harvard University, Cambridge, Mass., U.S.A.
Morgan, J.J. and Stumm, W., 1964. Colloid chemical properties of manganese dioxide. J. Coll. Sci., 19: 4, 437.
Myhrstad, J.A. and Sandal, J.E., 1969. Behavior and determination of chlorine dioxide. J. Amer. Water Works Assoc., 61: 205.
Pauling, L., 1960. The Nature of Chemical Bond. Cornell University Press, Ithaca, N.Y., U.S.A.
Posselt, H.S., 1966. Sodium and potassium ferrate (VI). A Bibliography and Literature Review. Unpublished Research Report, Carus Chemical Company, Inc., LaSalle, Ill.
Stewart, R., 1964. Oxidation Mechanisms: Application to Organic Chemistry. W. A. Benjamin, Inc. New York.
Stumm, W., 1958. Ozone as a disinfectant for water and sewage. J. Boston Soc. Civ. Eng., 45: (1), 68.
Stumm, W. and Lee, F.G., 1961. Oxygenation of ferrous iron. Ind. Eng. Chem., 53: 143.
Ueno, Y., 1976. Catalytic removal of sodium sulphide from aqueous solution and application to waste water treatment. Water Research, 10: 317.
Wheeler, G.L., 1976. Chlorine dioxide a selective oxidant for industrial waste water treatment. 4th Annual Ind. Poll. Conf., April 1976.
Willey, B.F., Jennings, H. and Muroski, F., 1963. Removal of hydrogen sulfide from water using permanganate. Paper presented before the Division of Water, Air and Waste Chemistry. Amer. Chem. Soc., Los Angeles, (April 1-5, 1963).
Wynn, C.S., Kirk, B.S. and McNabney, R., 1972. Pilot plant for tertiary treatment of waste water with ozone. Water, 69: 42.