

CHAPTER 9

DISINFECTION

DISINFECTION PROCESSES

Micro-organisms are destroyed or removed by a number of physico-chemical waste water treatment operations, such as coagulation, sedimentation, filtration and adsorption.

However, inclusion of a disinfection step has become common practice in waste water treatment to ensure against transmission of water-borne diseases. The disinfection process must be distinguished from sterilization. Sterilization involves complete destruction of all micro-organisms including bacteria, algae, spores and viruses while disinfection does not provide for the destruction of all micro-organisms, e.g. the hepatitis virus and polio virus are generally not inactivated by most disinfection processes.

The mechanism of disinfection involves at least two steps:

- (1) Penetration of the disinfectant through the cell wall.
- (2) Reaction with enzymes within the cell (Fair et al., 1968).

Chemical agents such as ozone, chlorine dioxide and chlorine probably cause disinfection by direct chemical degradation of the cell matter, including the enzymes, while application of thermal methods or degradation accomplish essentially physical destruction of the micro-organisms.

The large number of organic and inorganic chemicals exert a poisoning effect on the micro-organisms by an interaction with enzymatic proteins or by disruptive structural changes within the cells.

Rate of disinfection

The rate of destruction of micro-organisms has been expressed by a first order reaction referred to as Chick's law:

$$-\frac{dN}{dt} = k \cdot N \quad (9.1)$$

where N is the number of organisms per volume and k is a rate constant.

By integration between the limit $t = 0$ and $t = t_1$:

$$\int_{N_0}^{N(t)} \frac{dN}{N} = -k \int_0^t dt \quad (9.2)$$

or

$$\ln \frac{N(t)}{N_0} = -kt \quad (9.3)$$

$$N = N_0 \cdot e^{-kt} \quad (9.4)$$

Rearrangement of this equation and conversion into common logarithms gives:

$$t = \frac{2.3}{k} \cdot \log \frac{N(t)}{N_0} \quad (9.5)$$

As seen, Chick's law states that the rate of bacterial destruction is directly proportional to the number of organisms remaining at any time. This relation implies a uniform susceptibility of all species at a constant concentration of disinfectant, pH, temperature and ionic strength. Many deviations from Chick's law have been described in the literature. In accordance with Fair et al. (1968) chlorination of pure water shows typical deviations from Chick's law, as seen in Fig. 9.1.

Often deviation from the first order rate expression is due to autocatalytic reaction. In this case the expression can be transformed to:

$$-\frac{dN}{dt} = k_1 \cdot N(t) + k_2 \cdot N(t) \cdot (N_0 - N(t)) \quad (9.6)$$

As pointed out the disinfection rate expression (Chick's law) does not include the effect of disinfectant concentration. The relation between disinfectant concentration and the time required to kill a given percentage of organisms is commonly given by the following expression: $C^n \cdot t = \text{constant}$ (9.7).

Berg (1964) has shown that the concentration/time relationship for HOCl at 0-6°C, to give a 99% kill of Esch. coli is expressed as:

$$C^{0.86} \cdot t = 0.24 \quad (9.7)$$

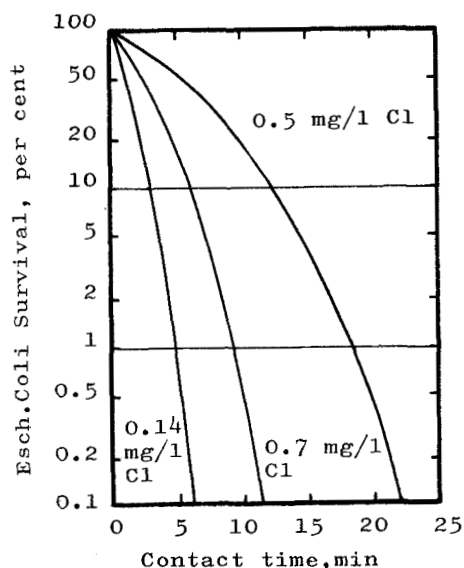


Fig. 9.1. Length of survival of *E. coli* in pure water at pH 8.5 and 2-5°C.

Temperature influences the disinfection rate firstly, by its direct effect on the bactericidal action and secondly, by its effect on the reaction rate. Often an empirical temperature expression is used, such as:

$$k_t = k_{20} \cdot d^{(t-20)} \quad (9.8)$$

where

k_t = the rate constant at $t^{\circ}\text{C}$

k_{20} = the rate constant at 20°C

d = an empirical constant

Most micro-organisms are effectively killed by extreme pH conditions, i.e., a pH below 3.0 and above 11.0.

The effect of disinfection is also strongly dependent on the co-existence of other matter in the waste water, e.g. organic matters. The disinfectant may (1) react with other species to form compounds which are less effective than the parent compounds, or (2) chemically oxidize other impurities present in the water, reducing the concentration of the disinfectants.

Thermal disinfection

The application of heat is one of the oldest, and at the same time most certain, methods for water disinfection. In addition freezing and freeze-drying are effective methods for the preservation of bacteria. However, these techniques are of little practical significance for waste water treatment, as they are too costly. Disinfecting large volumes of water by heating is clearly not suitable for economic reasons.

Irradiation

The wave length region from 250-265 nm, beyond the visual spectrum, has bactericidal effects.

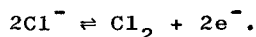
Mercury vapour lamps emit a narrow band at 254 nm and can be used for small-scale disinfection. It is assumed that the nucleic acids in bacterial cells absorb the ultraviolet energy and are consequently destroyed. These nucleic acids include deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The main problem in the application of ultraviolet irradiation for disinfection is to ensure that the energy is delivered to the entire volume of the water. Even distilled water will absorb only 8% of the applied energy to a depth of 3 cm, and turbidity, dyes and other impurities constitute barriers to the penetration of ultraviolet radiation.

This means that only a thin layer of clear water without impurities, able to absorb the ultraviolet light, can be treated. For a 99% level of kill, the use of a 30 W lamp would allow flows of from 2 to 20 m³/h to be disinfected. The use of ultraviolet lamps for disinfection has some important advantages. As nothing is added to the water no desirable qualities will be changed. No tastes or odours result from the treatment. The disadvantage of ultraviolet irradiation is that it provides no residual protection against re-contamination as the application of chlorine does.

Gamma and X-rays are electro-magnetic radiations of very short wave length and have an excellent capacity for destroying micro-organisms. However, their use is expensive. The application of the method requires care, and this will restrict its use considerably.

Chlorine and chlorine derivatives

Chlorine is produced exclusively by electrolytic oxidation of sodium chloride in aqueous solution:



After generation, the chlorine gas is purified by washing in sulphuric acid and the product usually has a purity of more than 99%. The gas is liquified by compression to 1.7 atm between -30°C and -5°C , and stored in steel cylinders or tanks. Chlorine should be handled with caution, as the gas is toxic and has a high chemical activity, with danger of fire and explosion. In the presence of water chlorine is highly corrosive.

When chlorine is added to an aqueous solution it hydrolyzes to yield Cl^- and OCl^- :



As can be seen, the process is a disproportionation, since chlorine in zero oxidation state turns into oxidation states -1 and $+1$. Hypochlorous acid is a weak acid:



The acidity constant K_a :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} \quad (9.11)$$

is dependent on the temperature as illustrated in Table 9.1.

TABLE 9.1

The acidity constant for HOCl

Temperature	K_a
0	$1.5 \cdot 10^{-8}$
5	$1.7 \cdot 10^{-8}$
10	$2.0 \cdot 10^{-8}$
15	$2.2 \cdot 10^{-8}$
20	$2.5 \cdot 10^{-8}$
25	$2.7 \cdot 10^{-8}$

HOCl is a stronger disinfectant than OCl^- ions, which explains why the disinfection is strongly dependent on pH.

Fig. 9.2 shows the time/concentration relationship in disinfection with chlorine (after Fair et al., 1968).

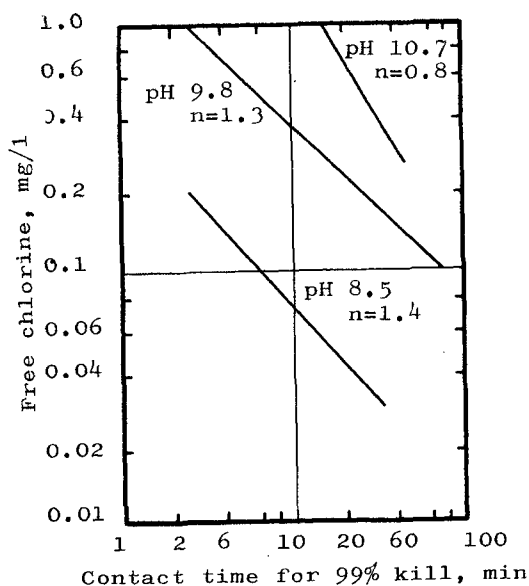


Fig. 9.2. Concentration of free available chlorine required for 99% kill of *E. coli* at 2-5°C.

The ammonium present in the water is able to react with the chlorine or hypochlorous acid:



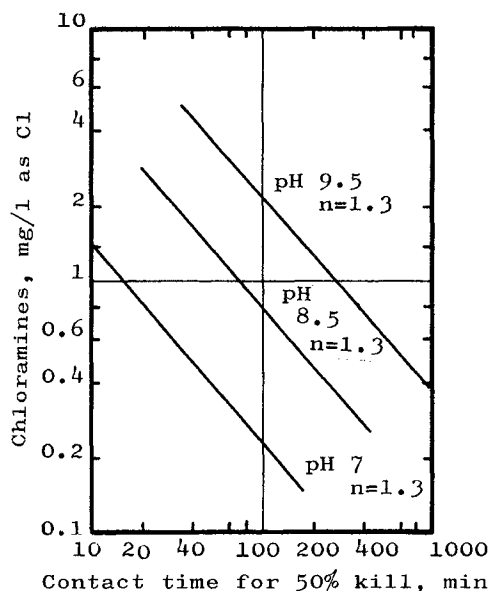
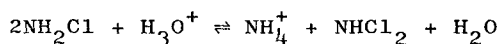


Fig. 9.3. Concentration of combined available chlorine required for 50% kill of *E. coli* at 2-5°C.

The rates of chlorine formation depend mainly on pH and the ratio of the reactants employed. Moore (1951) infers that the distribution of chlorine is based on the equation



for which

$$K = \frac{[\text{NH}_4^+][\text{NHCl}_2]}{[\text{H}_3\text{O}^+][\text{NH}_2\text{Cl}]^2} = 6.7 \cdot 10^5 \quad (25^\circ\text{C}) \quad (9.18)$$

The disinfection power of chloramines measured in terms of contact time for a given percentage kill, is less than that of chlorine. This is seen by comparing Fig. 9.3 with Fig. 9.2.

The bactericidal properties of chlorine are probably based on the formation of free hypochlorous acid:



However, the reaction of chlorine with ammonia or amino compounds presents a problem in the practice of chlorination of waste water containing such nitrogen compounds.

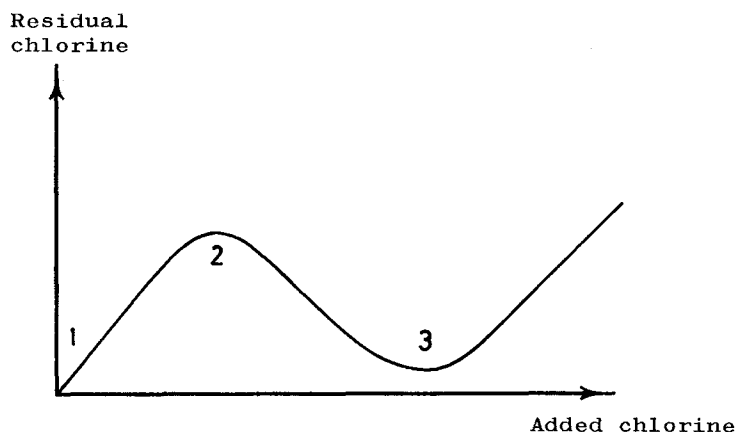
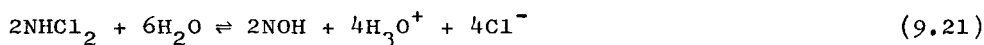
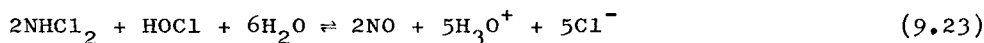


Fig. 9.4. Break-point chlorination.

Fig. 9.4 shows the residual chlorine as a function of the chlorine applied. Between the points 1 and 2 in the figure mono- and di-chloramine are formed. The oxidation processes with chlorine occurring between points 2 and 3 give a decline in residual chlorine. Point 3 is called the breakpoint. Addition of chlorine in this interval probably produces free nitrogen gas as the predominant product of oxidation. Fair et al. (1968) even propose that the reaction involving the formation of NOH as an intermediate, followed by the formation of nitric oxide, NO, could explain the observations between points 2 and 3:



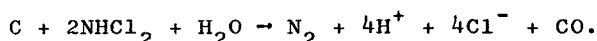
Totally:



Further addition of chlorine beyond the break-point gives an increasing residue of free chlorine.

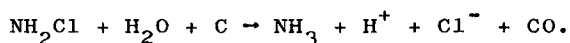
Chlorine doses below the break-point requirement can be used to oxidize ammonia if chlorination is followed by contact with activated carbon (Bauer et al., 1973).

Dichloramine has been shown to be rapidly converted to the end product, the most likely reaction being:

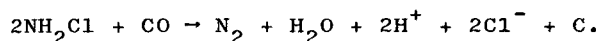


Further study is, however, needed to show conclusively that surface oxidation results from this reaction. Furthermore, it is important to know that the $\text{Cl}_2/\text{NH}_3\text{-N}$ oxidized mole ratio is 2:1, which is required for ammonium oxidation by this pathway.

The monochloramine reaction with carbon appears more complex. On fresh carbon the reaction is most probably:



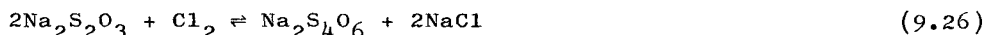
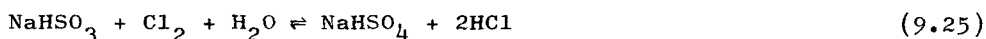
After this reaction has proceeded to a certain extent, partial oxidation of monochloramine was observed. Possibly according to the reaction:



It has been observed that acclimation of fresh carbon is necessary before monochloramine can be oxidized.

In the removal of ammonia with a dose of chlorine less than the break-point followed by contact with activated carbon, pH control can be used to determine the major chlorine species. The studies reported herein indicate that a pH value near 4.5 should be avoided, because NHCl_2 predominates and thus 10 parts by weight of chlorine are required for each part of $\text{NH}_3\text{-N}$ oxidized to N_2 . At a slightly higher pH and acclimated carbon, the portion of monochloramine increases and the chlorine required per unit weight of $\text{NH}_3\text{-N}$ oxidized should approach 7.6 parts, neglecting the chlorine demand resulting from other substances. However, further testing should be used to verify this conclusion in each individual case.

When accidental overdosing of chlorine has occurred or after an intentional addition of large quantities of chlorine to accelerate disinfection it will be desirable to remove the excess chlorine. This is possible with a reducing agent, such as sulphur dioxide, sodium hydrogen sulphite or sodium thiosulphate:



Oxidative degradation by chlorine is limited to a small number of compounds. Nevertheless, oxidation of these compounds contributes to overall reduction of BOD_5 in wastes treated with chlorine. A disadvantage is that chlorinated organic compounds may be formed in large quantities. A variety of chlorine compounds is applied in waste water treatment. For these compounds the available chlorine can be calculated. Generally this is expressed as percentage chlorine having the same oxidation ability. Data for the different chlorine-containing compounds are given in Table 9.2.

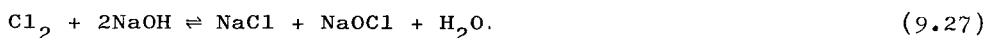
TABLE 9.2

Actual and available chlorine in pure chlorine-containing compounds

Compound	Mol. weight	Chlorine equiv. (moles of Cl_2)	Actual chlorine (%)	Available chlorine(
Cl_2	71	1	100	100
Cl_2O	87	2	81.7	163.4
ClO_2	67.5	2.5	52.5	260
NaOCl	74.5	1	47.7	95.4
CaClOCl	127	1	56	56
$\text{Ca}(\text{OCl})_2$	143	2	49.6	99.2
HOCl	52.5	1	67.7	135.4
NHCl_2	86	2	82.5	165
NH_2Cl	51.5	1	69	138

It can be seen that the actual chlorine percentage in chlordioxide is 52.5, but the available chlorine is 260%. This is of course due to the fact that the oxidation state of chlorine in chlordioxide is +4 which means that 5 electrons are transferred per chlorine atom, while Cl_2 only transfers one electron per chlorine atom.

Hypochlorite can be obtained by the reaction of chlorine with hydroxide in aqueous solution:



Chlorinated lime, also called bleaching powder, is formed by reaction of chlorine with lime:



A higher content of available chlorine is present in calcium hypochloride, Ca(OC1)_2 . As mentioned in chapter 8, p. 119, chlorine dioxide is generated in situ by the reaction of chlorine with sodium chloride:



Halogens other than chlorine

Theoretically fluorine could be used for disinfection, but nothing is known as regards the bactericidal effectiveness of this element at low concentrations. However, bromine is used mainly for disinfection of swimming pools. The reason is that monobromamine, unlike chloramine, is a strong bactericide. There is therefore no need to proceed to break-point bromination. Bromine has a tendency to form compounds with organic matter, resulting in a high bromine demand. This and the higher cost are the major factors limiting the use of bromine for treatment of waste water.

Iodine can also be used as a disinfectant. It dissolves sparingly in water unless iodide is present:



It reacts similarly with water in accordance with the scheme for chlorine and bromine:



It has a number of advantages over chlorination. Iodine does not combine with the ammonium to form iodamines, but rather oxidizes the ammonia. Also it does not combine with organic matter very easily, e.g. it oxidizes phenol rather than forming iodo-phenols. However, iodine is costly and it has, up till now, found a use only for swimming pool disinfection.

Ozone

Ozone is produced by passing compressed air through a commercial electric discharge ozone generator. From the generator the ozone travels through a gas washer and a coarse centred filter. A dispersion apparatus produces small bubbles with a large surface area exposed to the solution.

Ozone is used extensively in water treatment for disinfection and for the removal of taste, odour, colour, iron and manganese.

Ingols and Fetner (1957) have shown that the destruction of *Escherichia coli* cells with ozone is considerably more rapid than with chlorine when the initial ozone demand of water has been satisfied (see Fig. 9.5).

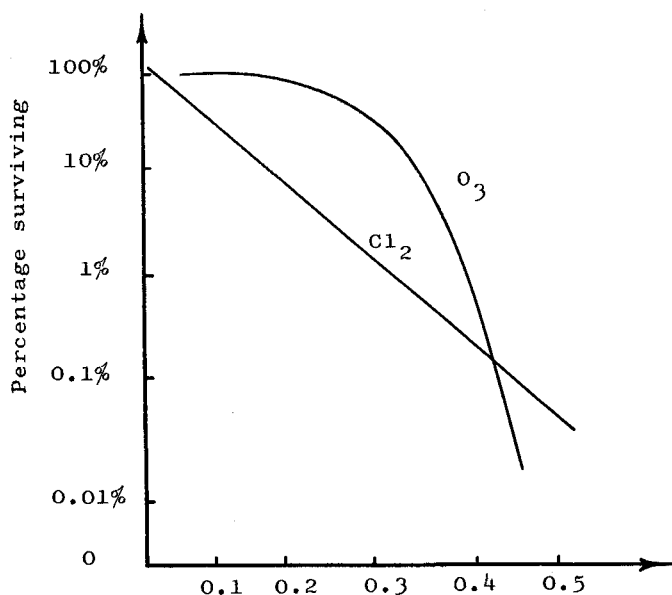


Fig. 9.5. Disinfection of *E. coli* by chlorine and ozone (dosage mg/l).

The activity of ozone is a problem in the disinfection of water containing high concentration of organic matter or other oxidizable compounds. A further problem arises from the fact that the decomposition of ozone in water does not permit long-term protection against pathogenic regrowth. However, ozone has the advantage of being effective against some chlorine resistant pathogens, like certain virus forms (Stumm, 1958).

The simultaneous removal of other compounds makes ozonation an advantageous water treatment process.

An excellent colloidal removal can be obtained by ozone. In all the dye waste water samples colour can be reduced dramatically by the application of about 1 g ozone per litre of waste water. However, generally the cost has been in the range of 4-7 times the cost of conventional waste water treatment systems. This cost may be greatly reduced in the near future. It seems at the present stage of development, that ozone might be excellently applied to textile dye waste treatment, as a final polishing agent to remove those dyes that are inert to conventional treatment.

Ozone can be used to alleviate the toxic and oxygen demanding characteristic of waste water containing ammonia by converting the ammonia to nitrate.

The oxidation is a first order reaction with respect to the concentration of ammonia and is catalyzed by OH^- over the pH range 7-9. The average value of the reaction rate constant at pH 9.0 is $5.2 \pm 0.3 \cdot 10^{-2} \text{ min}^{-1}$. Ammonia competes for ozone with the dissolved organic constituents comprising the BOD and is oxidized preferentially relative to the refractory organic compounds provided alkaline pH values can be maintained. Due to the elevated pH required, ammonia oxidation by ozone is attractive in the process of lime clarification and precipitation of phosphate.

The reaction of ozone with simple organic molecules has been extensively studied in recent years.

The reactions are usually complex, subject to general and specific catalysts and yield a multitude of partially degraded products.

It has been indicated that the reaction between ozone and organic compounds does not depend on the ozone concentration, but rather on the concentration of the decomposed product of ozone. It has been proposed by Hawes (1971) that the free radicals and ions formed by ozone degradation are the chief reacting species. The mechanism proposed by Hawes for the decomposition of ozone in water is as follows:



These mechanisms are supported by numerous kinetic experiments. The subsequent reaction between the ozone decomposition product and the organic compounds is as follows:



It is proposed that peroxide degradation occurs as follows:



The chain of terminating steps are then:



As a specific example, Eisenhauer (1968) has studied the reaction of ozone with phenol, which is a common part of many dye structures. He has proposed that phenol is first converted to catechol and then to o-quinone. The o-quinone then undergoes a cleavage reaction.

REFERENCES

- Bauer, Robert C. and Vernon, L. Snoeyink., 1973. Reaction of chloramines with active carbon. *J.W.P.Cr.Fed.*, 45: 2290.
- Berg, A.P., Kinman, R.C., Thomas, W.C. Freund, G. and Bird, E.D., 1965. Use of iodine for disinfection. *J.Amer.Water Works Assoc.*, 57: 1401.
- Eisenhauer, H.R., 1968. The ozonation of phenolic wastes. *J.W.P.Contr.Fed.*, 40: 1896.
- Fair, G.M., Geyer, J.C. and Okun, D.A., 1968. *Water and Waste Engineering*. J. Wiley & Sons, Inc. New York.
- Hawes, C.G. and Davidson, R.R., 1971. Kinetic of ozone decomposition and reaction with organics in water. *Chem.Kin Eng.Journal*, 17: 141.
- Ingols, R.S. and Fetner, R.H., 1957. *Proc. Soc. Water Treatment Exam.*, 6: 8.
- Moore, E.W., 1951. Fundamentals of chlorination of sewage and wastes. *Water and Sewage Works*, 98: (No. 3), 130.
- Singer, Philip C. and Zilly, William B., 1975. Ozonation of ammonium in waste water. *Water Research*, 9: 127.
- Snider, Erich H. and Porter, John J., 1974. Ozone treatment of dye waste, 46: *J. of W.P. Contr. Fed.*, 46: 887.
- Stumm, W., 1958. Ozone as a disinfectant for water and sewage. *J. Boston Soc. Civ. Eng.*, 45: (1), 68.

CHAPTER 10

AERATION AND STRIPPING

GAS TRANSFER

The process of aeration is used for transferring oxygen to waste water. Stripping is for removing volatile gases such as hydrogen sulphide, hydrogen cyanide and ammonia from waste water. Both aeration and stripping involve a gas-liquid mass-transfer process in which the driving force is created by a departure from equilibrium. In other words, the driving force in the gas phase is a partial pressure gradient and, in the liquid phase, is a concentration gradient.

The transfer of a gas can be treated as a four-step process. The first step involves passage of the gas from the vapour phase to the gas-liquid interface. The gas must then pass through a gas film on the vapour side of the interface. The third step is the passage of the gas through a liquid film on the liquid side of the interface. In the final step the gas must be dispersed throughout the bulk of the liquid. General conditions are such that one of the steps is rate-limiting and the overall gas-transfer rate can be calculated on the basis of this step. The remaining steps are insignificant in the overall process.

In stagnant conditions diffusion of the gas through the bulk solution is generally the slowest step and an expression for molecular diffusion can be used to predict the transfer rate.

The diffusion can be calculated by means of Fick's Law:

$$N = -D \cdot A \cdot \frac{dc}{dy} \quad (10.1)$$

where

N = mass transfer per unit time

A = the cross-sectional area across which diffusion occurs

$\frac{dc}{dy}$ = the concentration gradient perpendicular to the cross-sectional area, A

D = diffusion coefficient