# Chlorine

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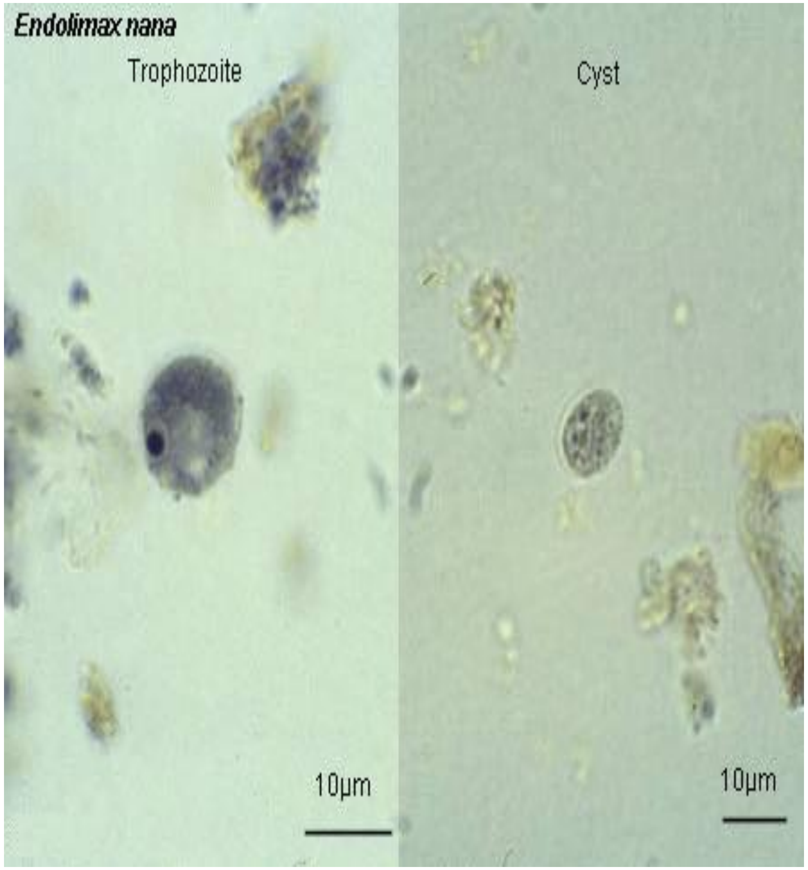
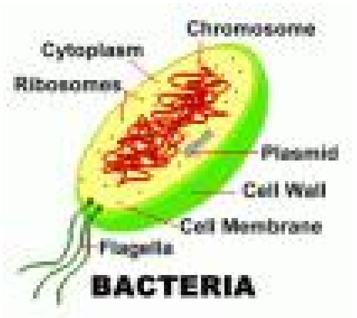
# Pathogens

- Pathogenic organisms are disease causing
- Non-pathogenic organisms are non-disease causing
- Pathogen Types: Bacteria, Viruses, & Protozoa



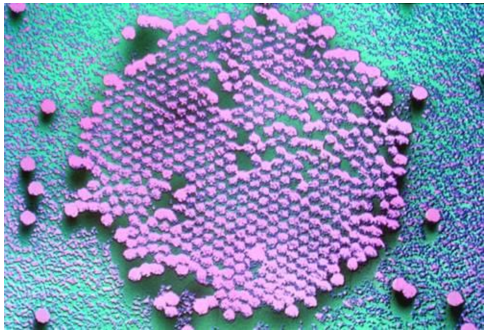
# Bacteria

| Organism | Disease | Primary Source |
| --- | --- | --- |
| Shigella | Bacillary disentary | Human Feces |
| Salmonella | Salmonellosis | Human/animal Feces |
| E. Coli | Gastroenteritis | Human Feces |
| Vibro Cholerae | Cholera | Human Feces |



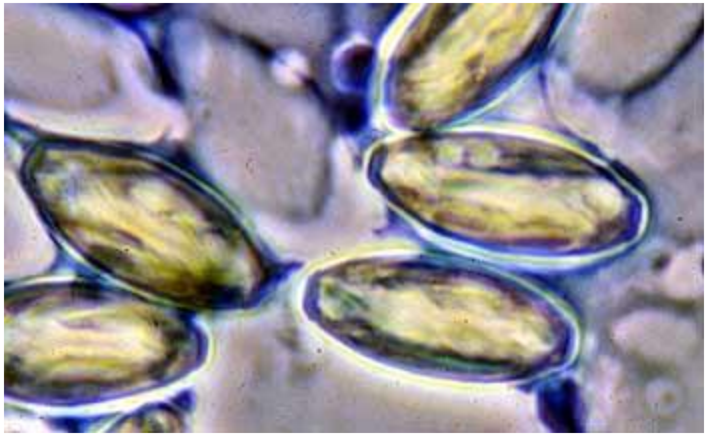
# Viruses

| Organism | Disease | Primary Source |
|---|---|---|
| Hepatitus A | Infectious Hepatitis | Human Feces |
| **Coxsackievirus A&B** | Aseptic meningitis | Human Feces |
| Rotavirus | Gastroenteritis | Human Feces |
| Adenoviruses | Upper respiratory & Gastrointestianilln | Human Feces |



# Protozoans

| Organism | Disease | Primary Source |
|---|---|---|
| Giardia lamblia | Giardiasis | Human/animal Feces |
| Cryptosporidium | Cryptosporidiosis | Human/animal Feces |
| Entamoeba histolytica | Aomebic dysentary | Human/animal Feces |

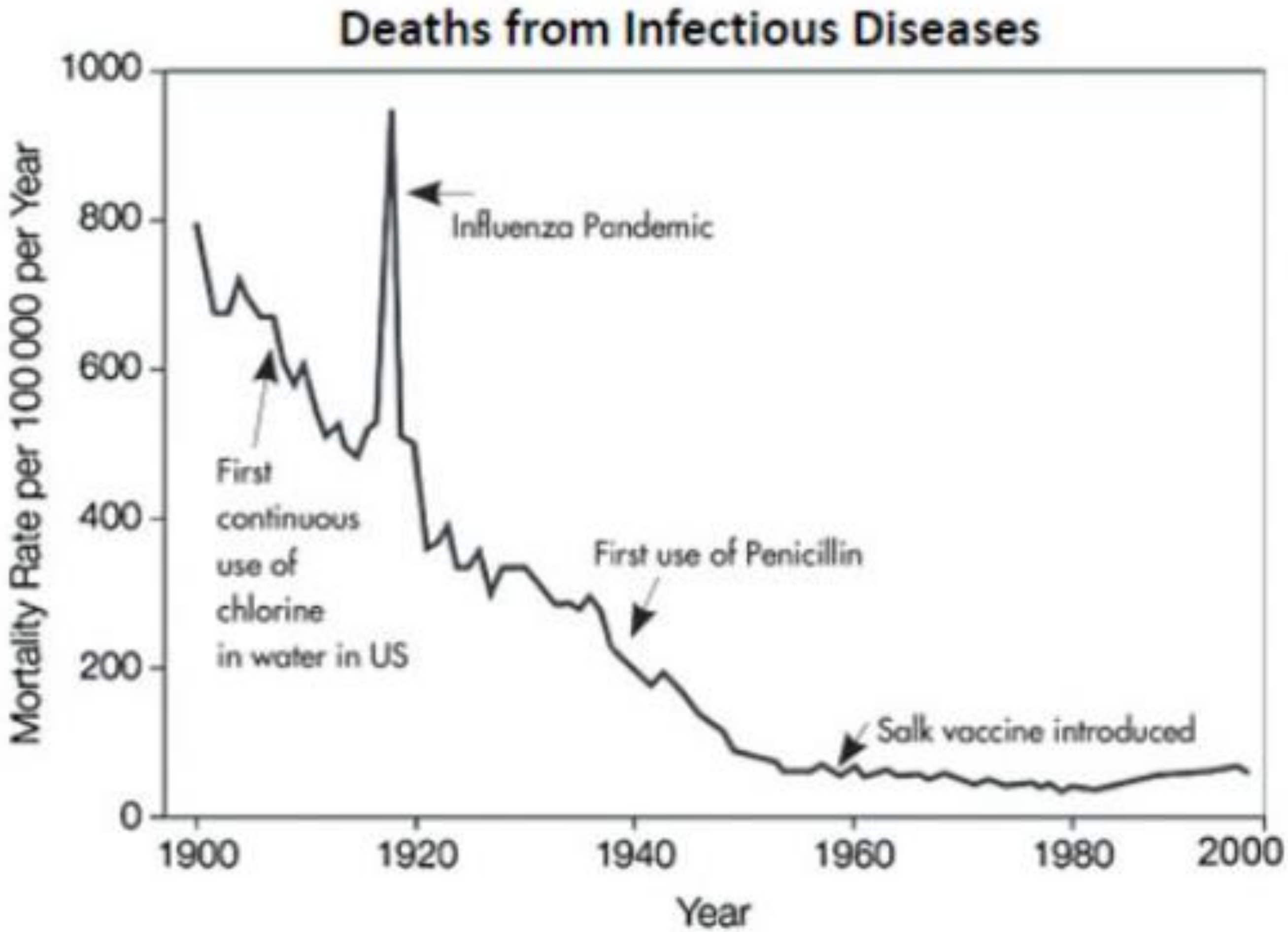


Waterborne human pathogens = disease:

typhoid, dysentery, cholera, …

1900: 25,000 typhoid deaths in US

1960: 20 typhoid deaths


Deaths from Infectious Diseases
1000
800
600
400
200
0
Mortality Rate per 100 000 per Year
1900
1920
1940
1960
1980
2000
Year
Influenza Pandemic
First continuous use of chlorine in water in US
First use of Penicillin
Salk vaccine introduced

# Disinfection

- A unit process for destruction / inactivation of pathogenic microorganisms (including bacteria, amoebic cysts, algae, spores & viruses).

- Emergency Chlorination in 1850 with hypochlorite
- Chlorination for public water supply started in 1904 after an outbreak of typhoid fever in London.

- Ozonation has been widely used in France, Germany, Canada & USSR.

# Disinfection

- The final barrier against human exposure to pathogens

- Disinfectants include:
  heat; boiling – denatures proteins and nucleic acids
  chemicals – uses a variety of mechanisms
  filtration – physical removal of a pathogen
  radiation; UV light – destroys nucleic acids

- Some disinfectants also control taste and odor problems, organic matter, and metals such as iron and manganese

# Factors Influencing Disinfection

- Type of disinfectant
- Type of microorganism
- Disinfectant concentration and time of contact
- pH
- Temperature
- Chemical and physical interference, e.g., clumping of cells or adsorption to larger particles

# Common Disinfectants in Water Treatment

- Chlorine
- Chloramines
- Chlorine dioxide
- Ozone
- Ultraviolet light

# Oxidation Potential of selected Disinfectants in Water at 25°C

| Disinfectant | Molecular weight | Oxidation Potential (V) |
|---|---|---|
| Hydroxyl free radical. $OH^-$ | 17.0 | (-) 2.80 |
| Ozone, $O_3$ | 48.00 | (-) 2.07 |
| Hydrobromous acid, HOBr | 96.91 | (-) 1.59 |
| Hyphochlorous acid, HOCl | 52.46 | (-) 1.49 |
| Chlorine, $Cl_2$ | 70.90 | (-) 1.36 |
| Bromine, $Br_2$ | 156.81 | (-) 1.07 |
| Chlorine dioxide, $ClO_2$(aq.) | 67.50 | (-) 0.95 |
| Mono chloramine, $NH_2Cl$ | 51.47 | (-)0. 75 |
| Dichlormine, $NHCl_2$ | 95.93 | (-)0.74 |

# Chlorine Terms

* Free Chlorine- chlorine remaining in water after chlorination
* Total Chlorine- sum of combined residual chlorine & free available chlorine
* Demand- difference between the chlorine added and the chlorine remaining

# Chlorine Terms

* Pre-chlorination- chlorine injected prior to treatment
* Post-chlorination- chlorine injected after treatment
* Breakpoint chlorination- amount of chlorine added to the water until the demand is satisfied.

# Chlorine Disinfection Mechanisms*

* Oxidation of membrane-bound enzymes for transport and oxidative phosphorylation
* Oxidation of cytoplasmic enzymes
* Oxidation of cytoplasmic amino acids to nitrites and aldehydes
* Oxidation of nucleotide bases
* Chlorine substitution onto amino acids (more likely)
* DNA mutations
* DNA lesions

*It is possible that none of these mechanisms have been documented

# Chemistry of Chlorine

- Most commonly used disinfectant
- In water chlorine undergoes the following reaction:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (20.1)$$

**HYPOCHLOROUS ACID**

$$\frac{[H^+][Cl^-][HOCl]}{[Cl_2]} = 4 \times 10^{-4} \quad \text{(at 25°C)} \quad (20.2)$$

**Variable with temperature**

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (20.3)$$

**HYPOCHLORITE**

$$\frac{[H^+][OCl^-]}{[HOCl]} = 2.7 \times 10^{-8} \quad \text{(at 20°C)} \quad (20.4)$$

# Chemistry of Chlorine

- HOCl and $OCl^-$ is defined as free available chlorine

* Killing effiency of HOCl is 40 -80 times larger than $OCl^-$ Lower pH favors HOCl.

- Distribution of HOCl and $OCl^-$ is determined by pH

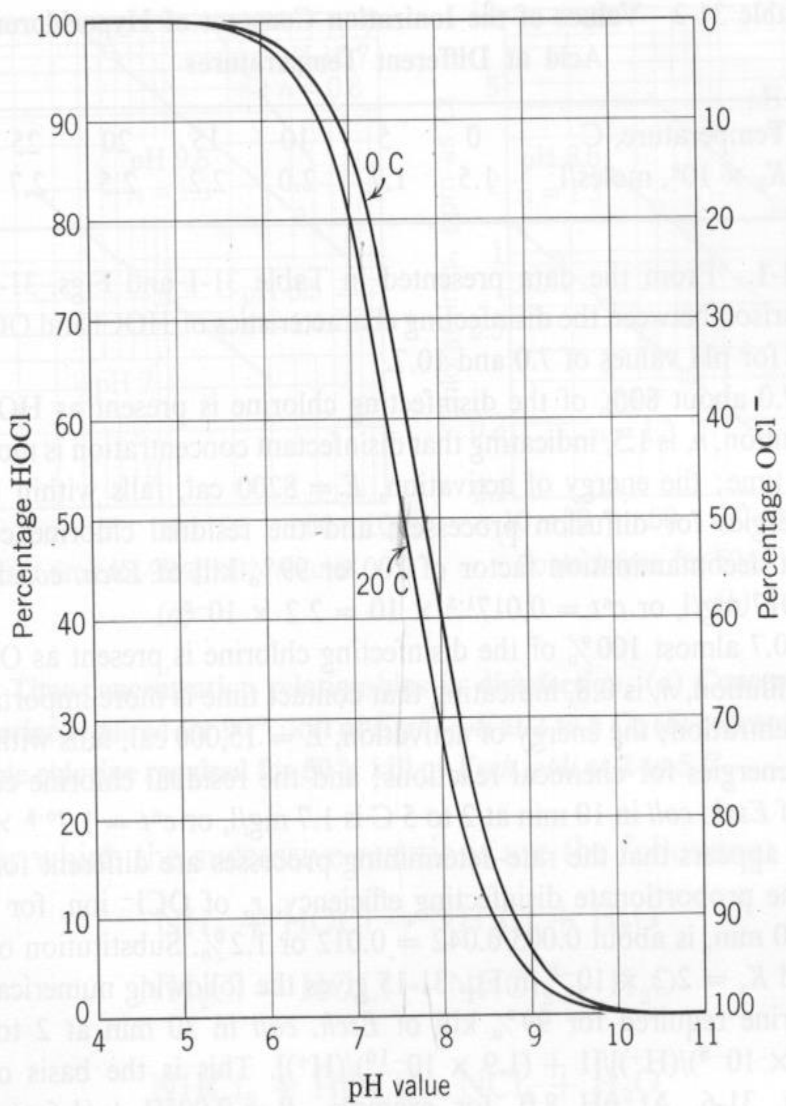
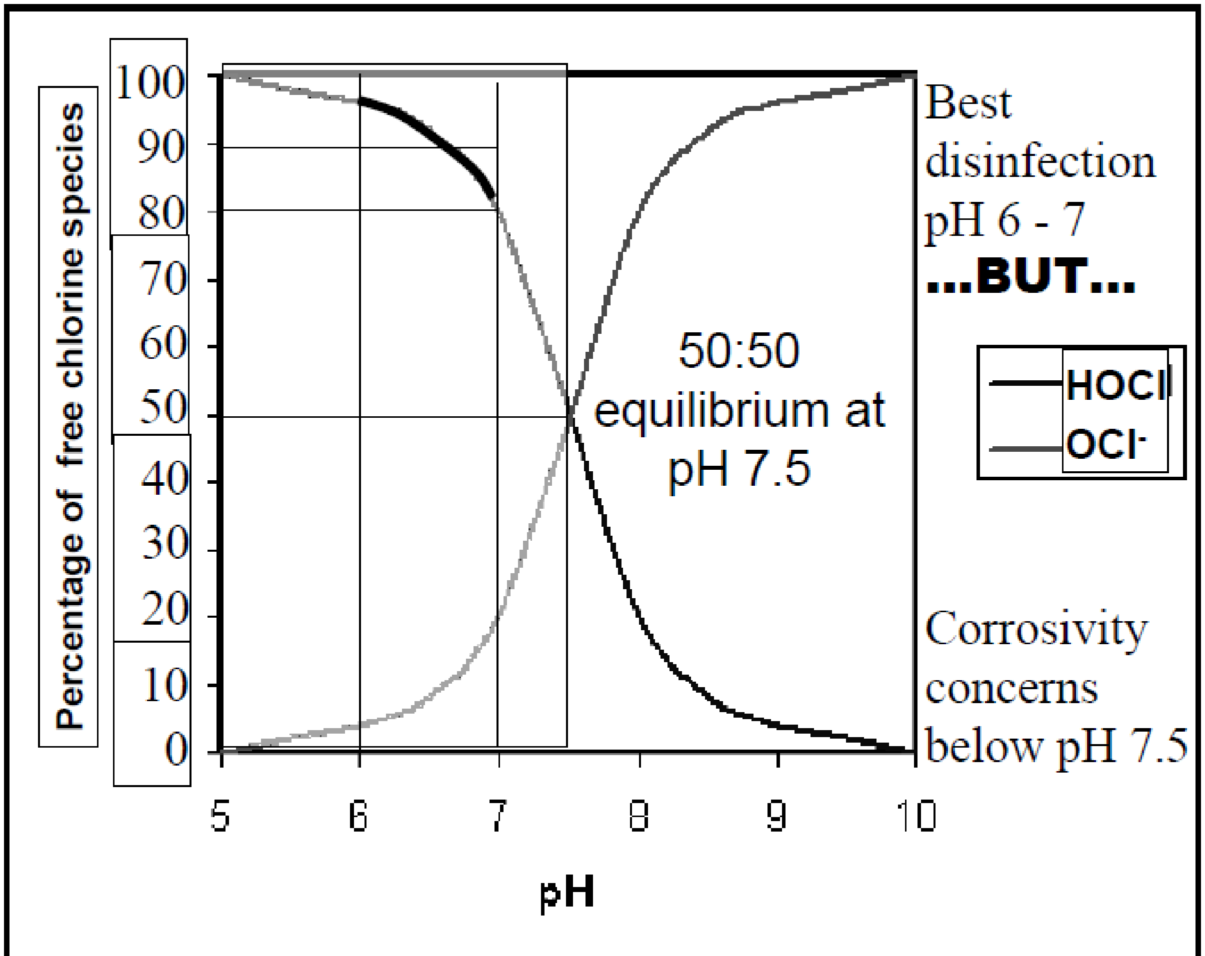



**Fig. 31-5. Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures. (After Morris, Sec. 31-11, footnote 14.)**

# Free Chlorine Distribution with pH



## pH & disinfection (chlorine):
### What you need to know

1. The best disinfection occurs at lower pH.
2. If you have high alkalinity and high pH (> 8) consider longer chlorine contact time due to reduced efficiency of the hypochlorite form.

# HW

Consider the effect of pH on the distribution of the free chlorine species:
a) Construct a figure showing the percent distribution of HOCl and OCl-1 as a function of pH on Microsoft Excel worksheet
(3 to 11) using an equilibrium acidity constant (Ka) of 2.7x10-8.
b) Calculate directly (do not read from the figure) the % HOCl existing at pHs of 5.5, 6.5, 7.5, and 8.5.

# Three Forms of Chlorine

- POWDER
  - Calcium Hypochlorite→ applicable for small systems or for intermittent usage
- LIQUID-Sodium Hypochlorite
  - Bleach 5%
- GAS 99.9%

  *extremely corrosive with water/humic

  *compressible

  *changes to liquid at 5.6 atm

  *2.5 times heavier than air

  *greenish-yellow color



# Gas Chlorine

- Heavier than air
- Boiling Point -34 °C
- Liquid form expands 460 times
- Lowers pH of the water

# Reactions with ammonia

- When $Cl_2$ & $NH_3$ are both present in water, they react to form products collectively known as Chloramines.

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad \text{(monochloramine)} \quad (20.6)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad \text{(dichloramine)} \quad (20.7)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad \text{(trichloramine)} \quad (20.8)$$

- Mono and di chloramines have significant disinfecting power→ **Combined Chlorine**
- Chloramines effective against bacteria but not viruses
- Two most common end product of Ammonia Oxidation by $Cl_2$ are $N_2$ gas

$3Cl_2 + 2NH_3 \Leftrightarrow N_2(g) + 6\ HCl$

# Chloramines stink!

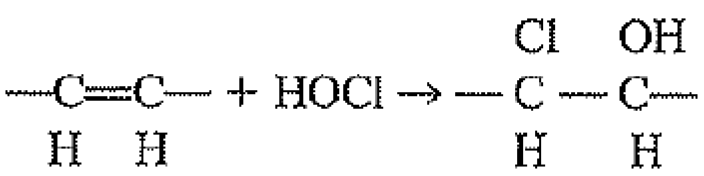
Taste and odor threshold concentrations:

- Free chlorine (HOCl): 20 mg/L
- Monochloramine ($NH_2Cl$): 5.0 mg/L
- Dichloramine ($NHCl_2$): 0.8 mg/L
- Trichloramine ($NCl_3$): 0.02 mg/L

# Extraneous Reactions

- Chlorine combines with a wide variety of materials, especially with reducing agents
- e.g. $Fe^{2+}$ , $Mn^{2+}$ , $H_2S$ , organic matter

$$H_2S + Cl_2 \rightarrow 2HCl + S \qquad (20.9)$$




(20.10)

# Extraneous Reactions

* Chlorine also reacts with halogens in water

$$Br^- + HOCl \rightarrow HOBr + Cl^- \quad (20.11)$$

* Reacts with phenols to produce mono, di-, tri- phenols→ can impart taste and odors

# Reactions with Humic Acid

- **Naturally occurring organic matter $\xrightarrow{\text{Disinfection}}$ Contaminants**

  - **Humic Substances $\xrightarrow{Cl_2}$ Trihalomethanes**

- **Trihalomethanes are the most common by-products of water chlorination**

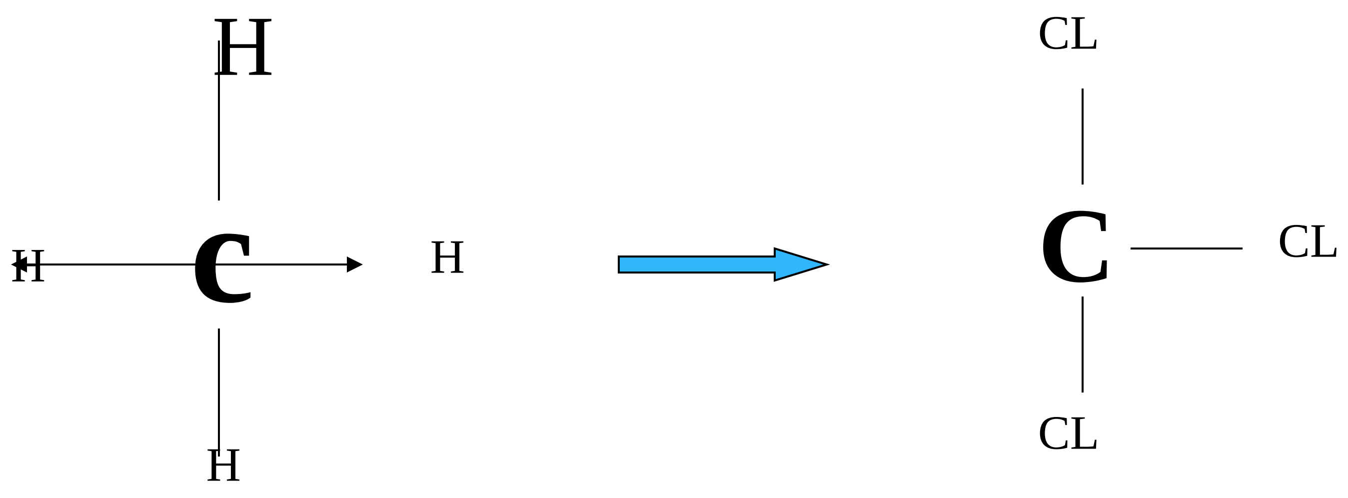
- **THMs represent structural variation of methane molecule ($CH_4$) in which 4 halogen atoms ( F, Cl, Br, I) are substituted for hydrogen.**

# TRIHALOMETHANES

"TRI"= MEANING THREE SITES

"HALO" = FROM THE HALOGEN GROUP

"METHANE" = DERIVED FROM METHANE




METHANE

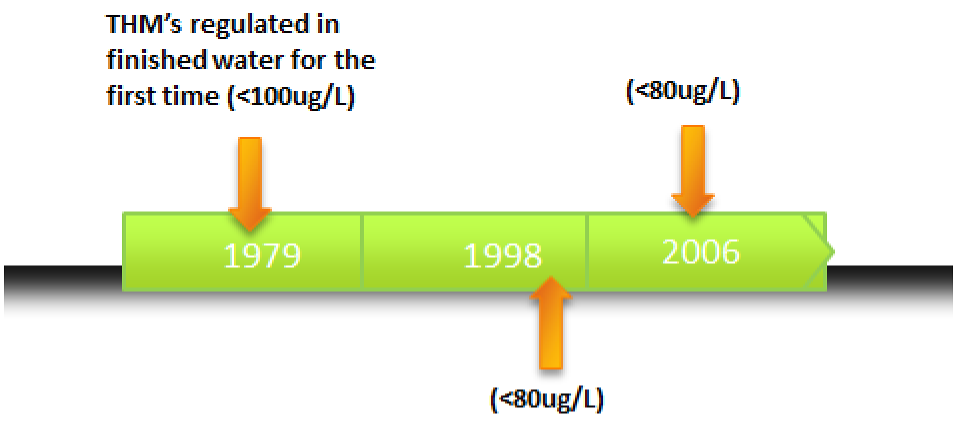
TRIHALOMETHANE

- **THMs commonly found in drinking water include**

  - **Chloroform, Trichloromethane ($CHCl_3$)**
  - **Bromodichloromethane ($CHBrCl_2$)**
  - **Dibromochloromethane ($CHBr_2Cl$)**
  - **Bromofrom ($CHBr_3$)**
  - **Dichloro iodomethane ($CHCl_2I$)**
  - **Bromochloroiodomethane (CHIBrCl)**

# THM regulation

* USEPA regulation→




* European Standard < 100 µg/L
* Turkish Standard: <80µg/L

- Because of the interest in reducing the THM levels in water, consideration for other disinfectants. However,
  - $Cl_2$ is the only disinfectant to provide residual protection within the distribution system
  - Ozone may be used as primary disinfectant, then $Cl_2$ application

# Interfering Substances

- Turbidity can prevent adequate contact between chlorine and pathogens
- Chlorine reacts with organic and inorganic nitrogenous compounds, iron, manganese, and hydrogen sulfide.
- Dissolved organic compounds exert a chlorine demand
- Knowing the concentrations of interfering substances is important in determining chlorine dose

# Break- point chlorination

•When $Cl_2$ is added to water, it is consumed to oxidise various organic compounds in water & that represents initial $Cl_2$ demand.

•Then $Cl_2$ reacts with $NH_3$ to from combined chlorine residual.

•With addition of $Cl_2$, combined $Cl_2$ residual reaches a max. value & further addition of $Cl_2$ causes a decrease in combined residual.

•This is called Break-point Chlorination.

•At this point, Chloramines are oxidised to $N_2$ gas.

•After break point chlorination is reached, free chlorine residual develops @ the same rate as that of applied dose.

# Break point curve

- **If inorganic chlorine demand (e.g. Iron & Mn) is present, initial $Cl_2$ dose produces no residual $Cl_2$.**

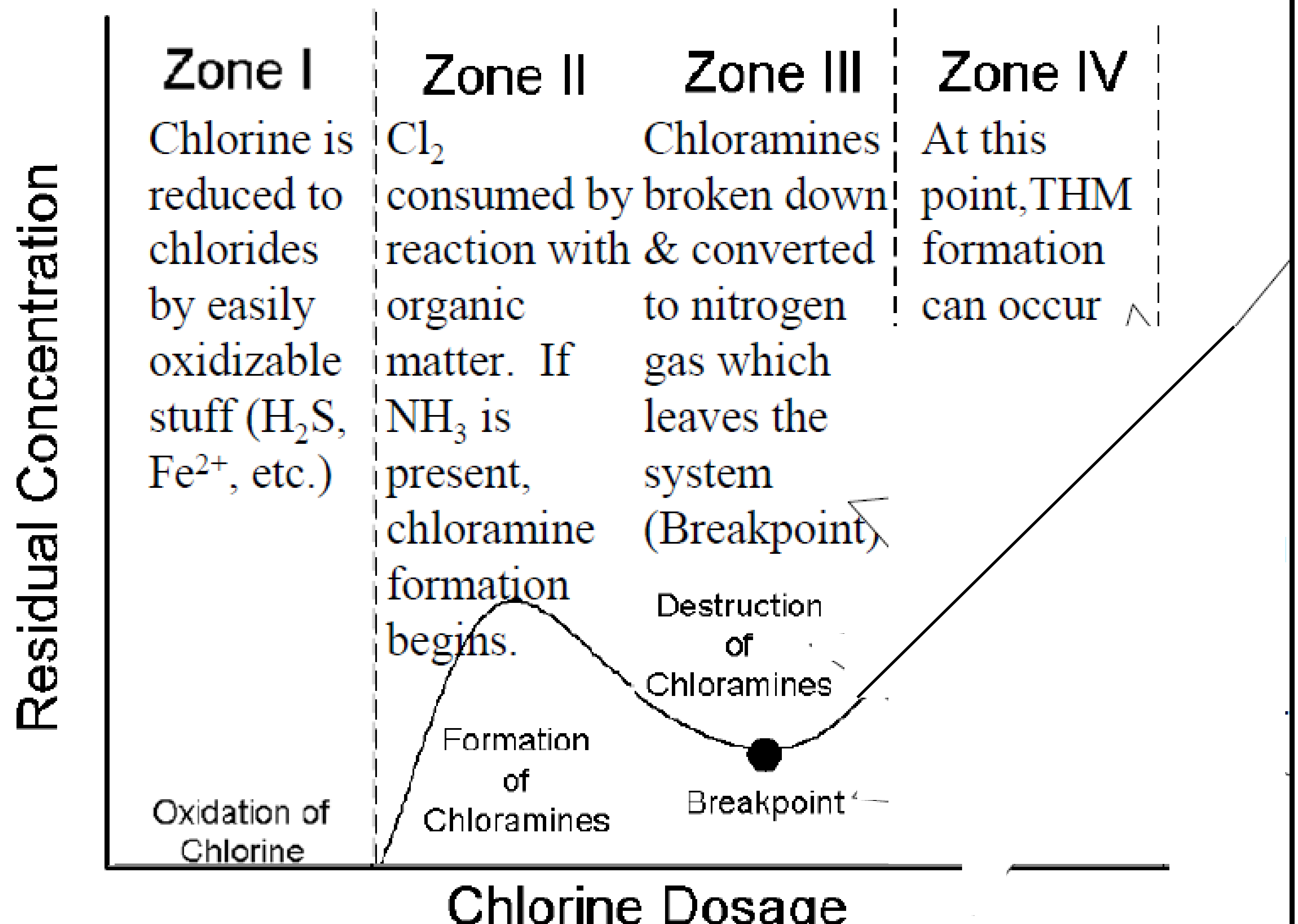
- **Residual $Cl_2$ Vs $Cl_2$ dose Curve would be flat until the demand is satisfied.**

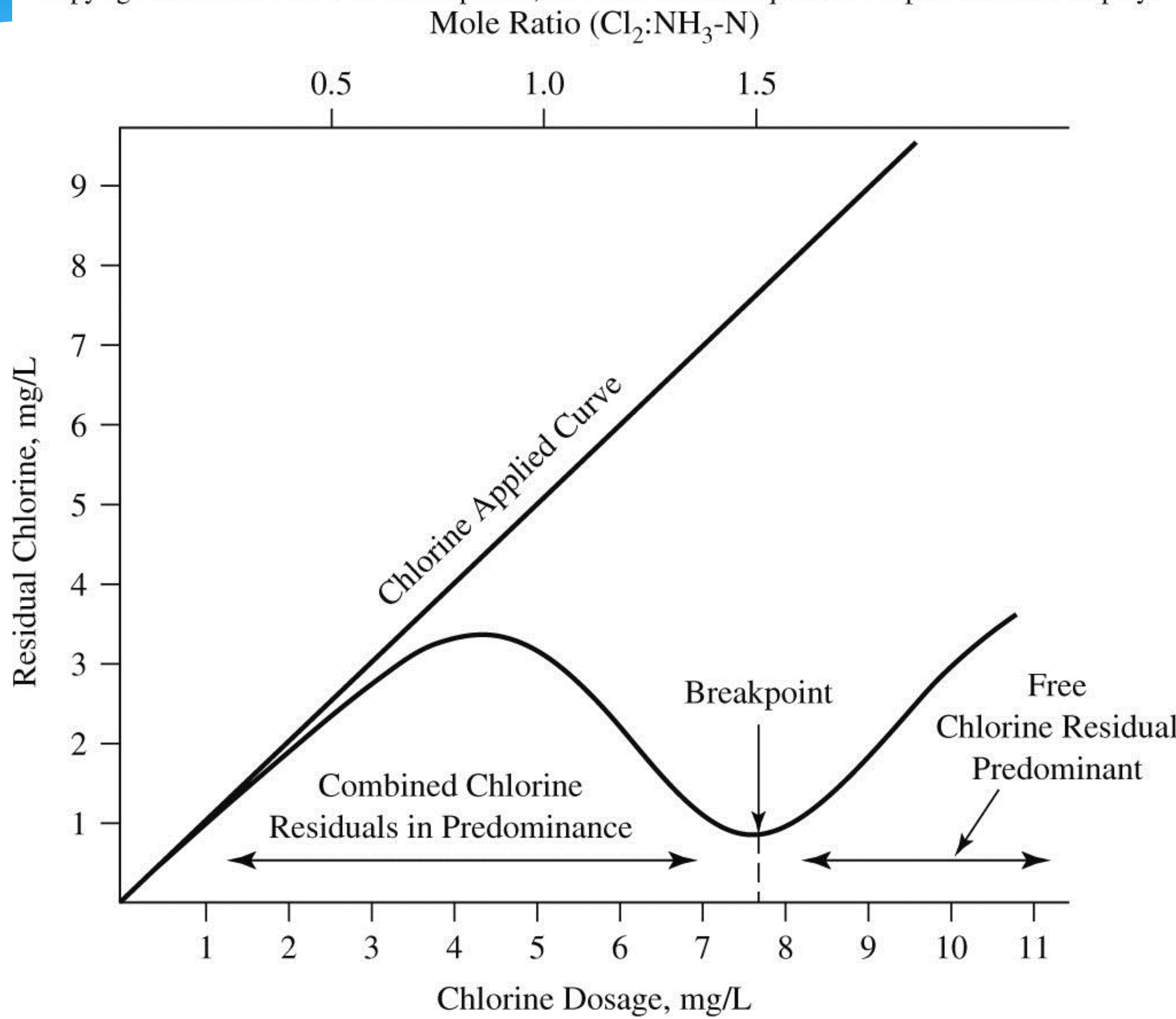
- **As the $Cl_2$ dose increase, $Cl_2$ residual first rises to a max. & then declines to a min.**

- **Prior to the break point, $Cl_2$ residual is a combined residual.**

- **After the break point, there is no ammonia left to react with $Cl_2$.**

# Chlorination & Breakpoint




Mole Ratio ($Cl_2$:$NH_3$-N)
0.5
1.0
1.5
Residual Chlorine, mg/L
9
8
7
6
5
4
3
2
1
Chlorine Applied Curve
Breakpoint
Free
Chlorine Residual
Predominant
Combined Chlorine
Residuals in Predominance
1
2
3
4
5
6
7
8
9
10
11
Chlorine Dosage, mg/L

# Break Point Chlorination

* $Cl_2$ / $NH_3$ ratio 1:1 for the formation of mono , dichloroamines.
* Further increase in mole ratio → trichloramine, oxidation of part of ammonia to $N_2$ or $NO_{3-}$.
* These rxns. are completed at mole ratio 1.5:1
* Chloramine residuals maximum @1:1mol
* Then decline to a minimum till 1,5:1

# Breakpoint Chlorination

- Chlorination of a water to the extent that all the ammonia is converted to $N_2$ or higher oxidation states.

**Theoretically**

3 mole chlorine → conversion to trichloramine
4 mole chlorine →complete oxidation to nitrate

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6H^+ + 6Cl^-$$

* Breakpoint chlorination → for better disinfection, required to obtain free chlorine residual , if ammonia is present.
* Method of ammonia removal in ww

* Combined chlorine residuals → Longer lasting ( final treatment with ammonia )

* Chlorine demand : Amount of chlorine that must be added to reach a desired level of residual.

# Chlorine Residual Determination

* Old Methods → total chlorine
* New Methods → free and combined chlorine

**Total Chlorine Residual**

* Measurement depend on measuring the oxidizing power
* Other oxidizing agents present may interfere → manganese, nitrites

# Starch – Iodide Method :

- Oxidizing power of free and combined chlorine to convert iodide to iodine.

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \quad (20.14)$$

$$I_2 + \text{starch} \rightarrow \text{blue color} \quad \text{(qualitative test)} \quad (20.15)$$

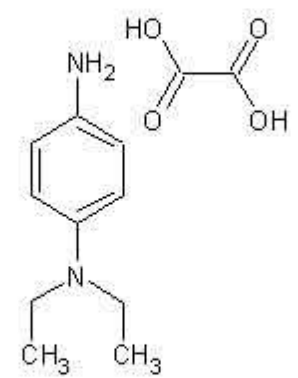
- Blue color → shows the presence of free chlorine.
- Titration with thiosulfate to check the endpoint for quantitative results

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad (20.16)$$

- Appropriate for total Cl2>1 mg/L.

# DPD Method

- DPD + $Cl_2$ containing water→Red color
- Titrate with Ferrous Ammonium Sulfate (FES)→endpoint: colorless
- This is free chlorine




*N,N*-diethyl-*p*-phenylenediamine (DPD)

# Chlorine Dioxide

- First used in Niagara Fall, NY in 1944 to control phenolic tastes and algae problems
- Used in 600 WTP (84 in the US) in 1970's as primary disinfectant and for taste and odor control
- Very soluble in water; generated as a gas or a liquid on-site, usually by reaction of $Cl_2$ gas with $NaClO_2$ :
  - $2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$
- Usage became limited after discovery of it's toxicity in 1970's & 1980's
  - thyroid, neurological disorders and anemia in experimental animals by chlorate
- Recommended maximum combined concentration of chlorine dioxide and it's by-products < 0.5 mg/L (by US EPA in 1990's)

# Chlorine Dioxide

- High solubility in water
  - 5 times greater than free chlorine
- Strong Oxidant; high oxidative potentials;
- Neutral compound of chlorine in the +IV oxidation state; stable free radical
  - Degrades in alkaline water by disproportionating to chlorate and chlorite.
- Generation:  On-site by acid activation of chlorite or reaction of chlorine gas with chlorite
- About 0.5 mg/L doses in drinking water
  - toxicity of its by-products discourages higher doses

# Ozone: $O_3$

- Very strong oxidant (very low C▪t values) but has no residual disinfection power
- More expensive than chlorination but does not produce trihalomethanes which are suspected carcinogens
- Widely used in Europe, limited use in U.S.

# Ozone

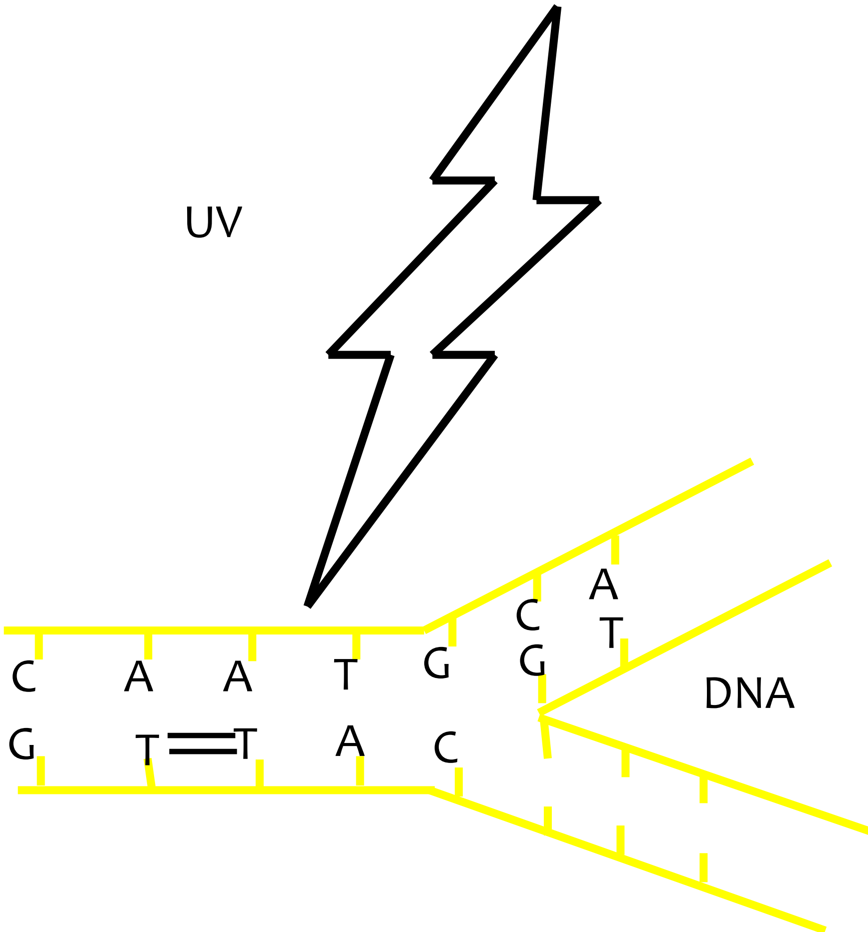
- First used in 1893 at Oudshoon
- Used in 40 WTPs in US in 1990 (growing use since then), but more than 1000WTPs in European countries
- Increased interest as an alternative to free chlorine (strong oxidant; strong microbiocidal activity; perhaps less toxic DBPs)
  - A secondary disinfectant giving a stable residual may be needed to protect water after ozonation, due to short-lasting ozone residual.
- Colorless gas; relatively unstable; reacts with itself and with $OH^-$ in water; less stable at higher pH
- Formed by passing dry air (or oxygen) through high voltage electrodes to produce gaseous ozone that is bubbled into the water to be treated.

# UV Disinfection

- Optimum ultraviolet light wavelength range for germicidal effect:  250 nm - 270 nm
- Low pressure mercury lamps emit 253.7 nm
- Damages microbial/viral DNA and viral RNA by causing dimerization, blocking nucleic acid replication
- Does not produce toxic by-products
- Higher costs than chemical disinfection, no residual disinfection

# Ultraviolet Radiation and Effects

- Physical process
- Energy absorbed by DNA
- Inhibits replication
- Pyrimidine Dimers
- Strand Breaks
- Other Damage



# Two important factors: Concentration and contact time

Effectiveness of disinfection depends primarily on the concentration used and the time of exposure

$$\text{Kill} \propto C^n \times t \qquad (n > 0) \tag{20.12}$$

# Chick's Law

* The death of microorganisms is first order with respect to time
* Thus, the remaining number of viable microorganisms, N, decreases with time, t, according to:

$$\frac{dN}{dt} = -kN$$

* where k is an empirical constant descriptive of the microorganism, pH and disinfectant used.
* Integrating with respect to time, and replacing limits (N = $N_o$ at t = 0) yields:

$$N = N_0 e^{-kt} \qquad \ln \frac{N}{N_0} = -kt$$

**20.12** According to Chick's law, the rate of kill of bacteria by chlorination follows first-order reaction kinetics. Assuming this to be true, how much contact time is required to kill 99 percent of the bacteria with a chlorine residual of 0.1 mg/L, if 80 percent are killed in 2 min with this residual? (See Sec. 3.10.)

# CT value

- Disinfectant effectiveness can be expressed as a C ▪ t value where:
  - C = disinfectant concentration
  - t = time required to inactivate a 99% of the population under specific conditions

  - The lower the C ▪ t, the more effective the disinfectant

- In general, resistance to disinfection is in the following order:
- **vegetative bacteria < enteric viruses < spore-forming bacteria < protozoan cysts**

# Inactivation of *Cryptosporidium* Oocysts in Water by Chemical Disinfectants

| Disinfectant | $CT_{99}$ (mg-min/L) | Reference |
|---|---|---|
| Free Chlorine | 7,200+ | Korich et al., 1990 |
| Monochloramine | 7,200+ | Korich et al., 1990 |
| Chlorine Dioxide | >78 | Korich et al., 1990 |
| Mixed oxidants | <120 | Venczel et al., 1997 |
| Ozone | ~3-18 | Finch et al., 1994<br>Korich et al., 1990<br>Owens et al., 1994 |

| Oxidant | Advantages | Disadvantages |
| --- | --- | --- |
| **Chlorine** | Strong oxidant<br>Persistant residual | Chlorinated by-products<br>Taste and odor problems<br>pH influences effectiveness |
| **Chloramines** | No trihalomethane formation<br>Persistant residual | Weak oxidant<br>Some organic halide formation<br>Taste, odor, and growth problems |
| **Chlorine dioxide** | Strong oxidant<br>Relatively persistant residual<br>No trihalomethane prod.<br>No pH effect | Total organic halide formation<br>ClO3 and ClO2 by products<br>On-site generation required<br>Hydrocarbon odors possible |
| **Ozone** | Strong oxidant<br>No trihalomethane or organic halide formed<br>No taste or odor prob.<br>Little pH effects<br>Coagulant aid<br>Some by products biodegradable | Short half-life<br>On-site generation required<br>Energy intensive<br>Some by products biodegradable<br>Complex generation<br>Corrosive |

| | Characteristics | Chloramines | Free $Cl_2$ | $ClO_2$ | $O_3$ | UV |
|---|---|---|---|---|---|---|
| 1. | Disinfection | Moderate | Excellent | Excellent | Excellent | Good |
| 2. | $p^H$ influence | Not significant | Decreases as pH increases | Not significant | | |
| 3. | Residual in distribution system | Yes | Yes | Yes | No | No |
| 4. | By products (THMs) | Unlikely | Yes | Unlikely | Unlikely | Unlikely |
| 5. | Typical applied dosage (mg/L) | 0.5-3 | 2-20 | Not available | 1-5 | Not available |