13 Disinfection

Chapter 13 in
Bruce E. Crittenden, John C. et al.,
MWH's Water Treatment Principles and Design (3rd Edition),
John Wiley & Sons, 2012

All the figures and tables in this material are from the above reference unless specified otherwise.

Terminology for Disinfection

Term	Definition
Absorbance	Amount of light of a specified wavelength absorbed by the constituents in water.
Biodosimetry	Determination of the dose of a disinfectant to inactivate a specific biological test organism.
Breakpoint chlorination	Process in which chlorine is added to react with all oxidizable substances in water so that if additional chlorine is added it will remain as free chlorine (see below, $HOCl + OCl^-$).
Combined chlorine residual	Concentration of chlorine species resulting from the reaction of chlorine and ammonia, specifically the sum of monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3), expressed as mg/L as Cl_2.
Ct	Product of chlorine residual expressed in mg/L and contact time expressed in min. The term *Ct* is used to assess the effectiveness of the disinfection process for regulatory purposes.
Disinfection	Partial destruction and inactivation of disease-causing organisms from exposure to chemical agents (e.g., chlorine) or physical processes (e.g., UV irradiation).

Term	Definition
Decay rate	Rate at which the concentration of a disinfectant decreases over time.
Disinfection by-products (DBPs)	Undesirable products of reactions between disinfecants and other species in the feed water. DBPs of concern are those that are carcinogenic or have other negative health effects.
Dose–response curve	Relationship between the degree of microorganism inactivation and the dose of a disinfectant.
Free chlorine residual	Sum of the hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) in solution, expressed as mg/L as Cl_2.
Inactivation	Rendering microorganisms incapable of reproducing and thus limiting their ability to cause disease.
Pathogens	Microorganisms capable of causing disease.
Photoreactivation and dark repair	Methods used by microorganisms to repair the damage caused by exposure to UV irradiation.
Reactivation	Process by which organisms repair the damage caused by exposure to a disinfectant.
Sterilization	Total destruction of disease-causing and other organisms.
Transmittance	Ability of water to transmit light. Transmittance is related to absorbance.
Total chlorine residual	Sum of the concentrations of free and combined chlorine.
UV light	Portion of the electromagnetic spectrum between 100 and 400 nm.

13-1 Historical Perspective

13-2 Methods of Disinfection Commonly Used in Water Treatment

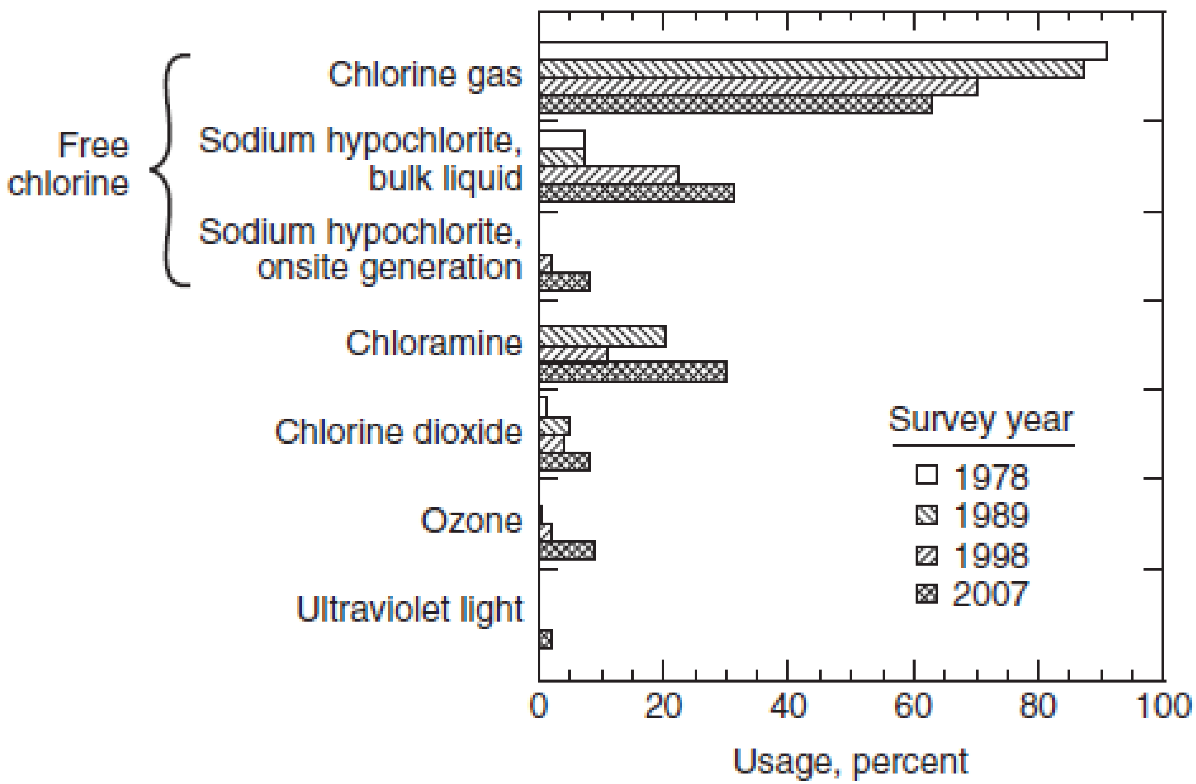


Figure 13-1
Disinfectant use in municipal drinking water treatment in the United States. (Adapted from AWWA 2008.)

Table 13-1
Characteristics of five most common disinfectants

Issue	Free Chlorine	Combined Chlorine	Chlorine Dioxide	Ozone	Ultraviolet Light
	Disinfectant				
Effectiveness in disinfection					
Bacteria	Excellent	Good	Excellent	Excellent	Good
Viruses	Excellent	Fair	Excellent	Excellent	Fair
Protozoa	Fair to poor	Poor	Good	Good	Excellent
Endospores	Good to poor	Poor	Fair	Excellent	Fair
Regulatory limit on residuals	4 mg/L	4 mg/L	0.8 mg/L	—	—
Formation of chemical by-products					
Regulated by-products	Forms 4 THMs[a] and 5 HAAs[b]	Traces of THMs and HAAs	Chlorite	Bromate	None
By-products that may be regulated in future	Several	Cyanogen halides, NDMA[c]	Chlorate	Biodegradable organic carbon	None known
Typical application					
Dose, mg/L (kg/ML)	1–6	2–6	0.2–1.5	1–5	20–100 mJ/cm^2
Dose, lb/MG	8–50	17–50	2–13	8–42	—
Chemical source	Delivered: as liquid gas in tank cars, 1 tonne and 68-kg (150-lb) cylinders, or as liquid bleach. Onsite generation from salt and water using electrolysis. Calcium hypochlorite powder is used for very small applications.	Same sources for chlorine. Ammonia is delivered as aqua ammonia solution, liquid gas in cylinders, or solid ammonium sulfate. Chlorine and ammonia are mixed in treatment process.	ClO_2 is manufactured with an onsite generator from chlorine and chlorite. Same sources for chlorine. Chlorite as powder or stabilized liquid solution.	Manufactured onsite using a corona discharge in dry air or pure oxygen. Oxygen is usually delivered as a liquid. Oxygen can also be manufactured onsite.	Uses low-pressure or low-pressure, high-intensity UV (254-nm) or medium-pressure UV (several wavelengths) lamps in the contactor itself.

13-3 Disinfection Kinetics

Classical Disinfection Kinetics—Chick–Watson

$$r = -k_c N \qquad \text{(Chick, 1908)} \tag{13-1}$$

where r = reaction rate for the decrease in viable organisms with time, org/L·min
k_c = Chick's law rate constant, min^{-1}
N = concentration of organisms, org/L

$$C^n t = \text{constant} \qquad \text{(Watson, 1908)} \tag{13-2}$$

where C = concentration of disinfectant, mg/L
n = empirical constant related to concentration, unitless
t = time required to achieve a constant percentage of inactivation (e.g., 99%)
constant = value for given percentage of inactivation, dimensionless

(Chick-Watson model)

$$r = -\Lambda_{CW} CN \tag{13-3}$$

where Λ_{CW} = coefficient of specific lethality (disinfection rate constant), L/mg·min
C = concentration of disinfectant, mg/L

Most laboratory disinfection studies are conducted using completely mixed batch reactors (CMBR). Using concepts presented in Chap. 6, a mass balance on a batch reactor can be written and integrated, leading to

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW} Ct \tag{13-4}$$

where N_0 = concentration of organisms at time = 0, org/L
t = time, min

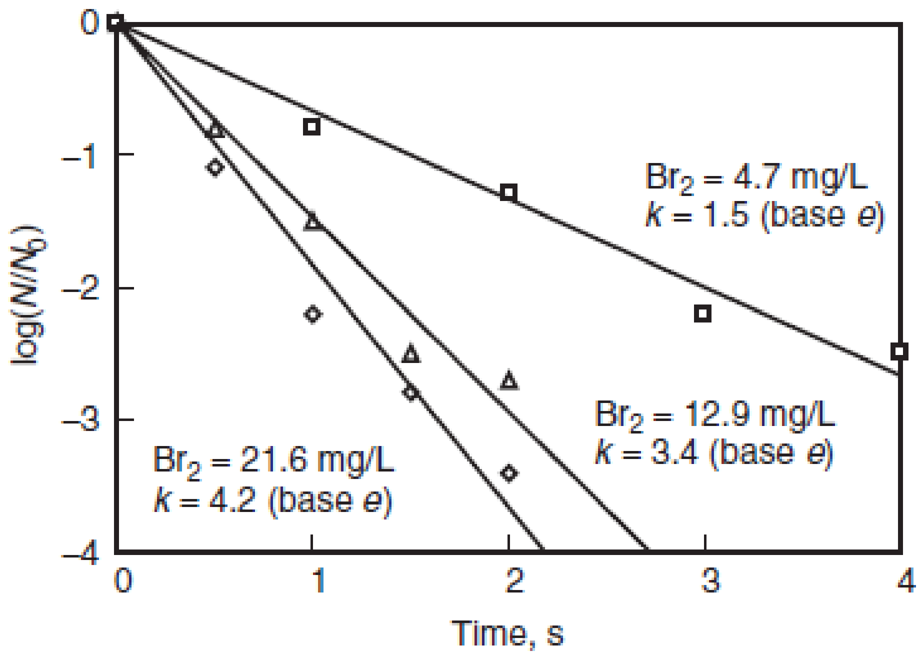
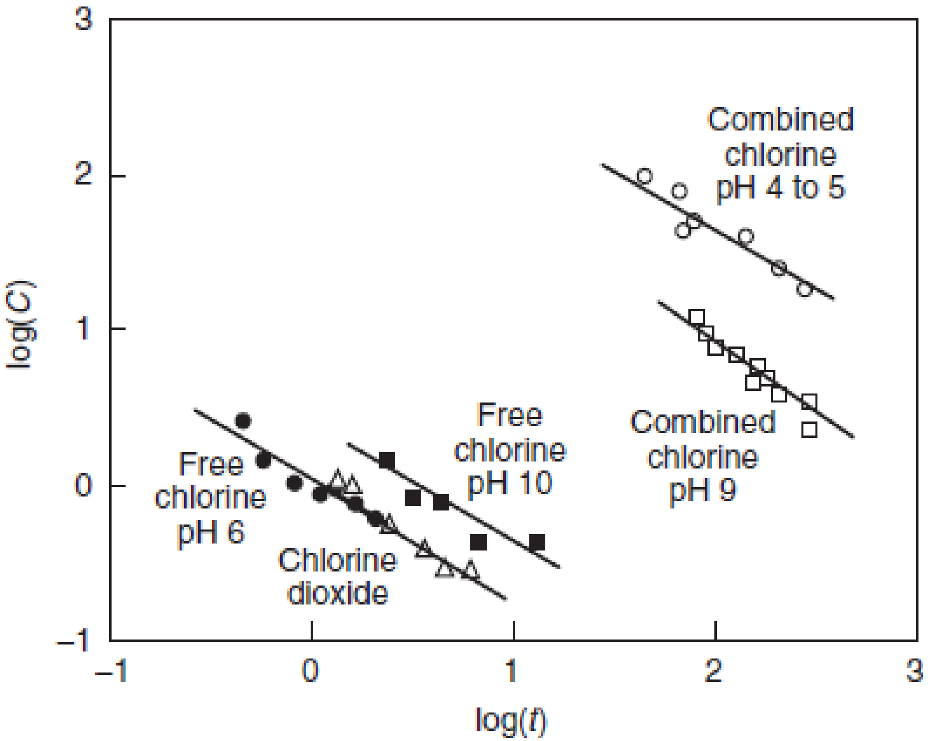


Figure 13-2
Inactivation of poliovirus type I with three concentrations of bromine in a batch reactor. (Adapted from Floyd et al., 1978.)



Ct = constant

Figure 13-3
Watson plot of requirements for 99 percent inactivation of poliovirus type I. (Adapted from Scarpino et al., 1977.)

Example 13-1 Application of the Chick–Watson model

Plot the data shown on Fig. 13-2, as given below, according to Eq. 13-4. Determine the coefficient of specific lethality and the coefficient of determination (r^2). The data for the inactivation of poliovirus type I with bromine (Floyd et al., 1978) are provided in the following table:

C, mg/L	Time, s	$\log(N/N_0)$	C, mg/L	Time, s	$\log(N/N_0)$
21.6	0	0	12.9	1.5	−2.5
21.6	0.5	−1.1	12.9	2	−2.7
21.6	1	−2.2	4.7	1	−0.8
21.6	1.5	−2.8	4.7	2	−1.3
21.6	2	−3.4	4.7	3	−2.2
12.9	0.5	−0.8	4.7	4	−2.5
12.9	1	−1.5			

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW}Ct$$

Solution

1. Determine the values of Ct and $\ln(N/N_0)$ for each organism survival value.
   a. Ct is calculated simply by multiplying C by t.
   b. To convert from base 10 to base e logarithms, recall the logarithmic identity $\log_b(x) = \log_a(x)/\log_a(b)$, thus:

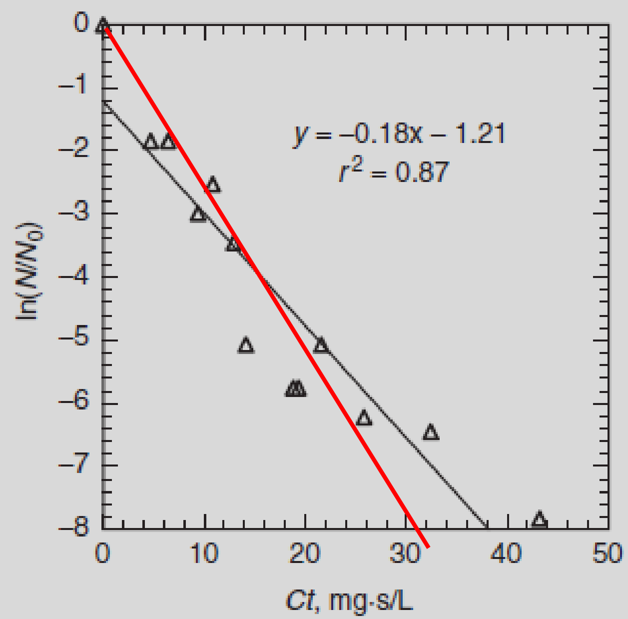
$$\ln(N/N_0) = \frac{\log(N/N_0)}{\log(e)} = 2.303\log\left(\frac{N}{N_0}\right)$$

c. The required data table is shown below:

Time, s	C, mg/L	Ct, mg · s/L	ln(N/N₀)	Time, s	C, mg/L	Ct, mg · s/L	ln(N/N₀)
0.5	21.6	10.8	−2.53	1.5	12.9	19.4	−5.76
1	21.6	21.6	−5.07	2	12.9	25.8	−6.22
1.5	21.6	32.4	−6.45	1	4.7	4.7	−1.84
2	21.6	43.2	−7.83	2	4.7	9.4	−2.99
0.5	12.9	6.5	−1.84	3	4.7	14.1	−5.07
1	12.9	12.9	−3.45	4	4.7	18.8	−5.76

2. Prepare a plot of $\ln(N/N_0)$ as a function of Ct and fit a linear trendline through the data. Select trendline options to display the equation and r^2 value.
3. The required plot is shown below.

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW} Ct$$



4. The slope of the line in the above plot corresponds to the coefficient of specific lethality, Λ_{CW}. From the plot $\Lambda_{CW} = 0.18$ and $r^2 = 0.87$.

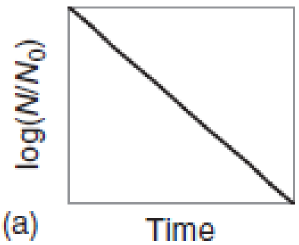
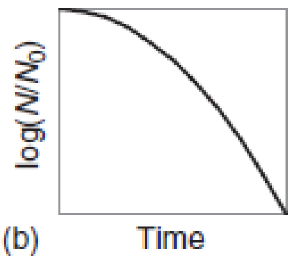
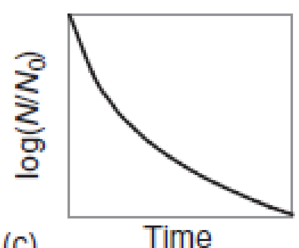
Shape of semilog plot of disinfection data	Reasons for shape	Examples
 (a)	**Pseudo-first order** The most common form of disinfection data. 1. Data fit Chick's law.	**Free chlorine**: *E. coli*, poliovirus **Ozone**: Poliovirus, *E. coli*, *G. Lamblia*, and *C. parvum* **UV**: *C. parvum*, MS2 (<4 log), and *G. lamblia* (<3 log)
 (b)	**Accelerating rate** Often observed at low disinfectant doses. Possible reasons include: 1. Disinfectant must react with more than one critical site in organism (Rahn, 1973; et al., 1975). 2. Disinfectant must take time to diffuse to critical site (Collins and Selleck, 1971). 3. Natural heterogeniety in resistance among organisms (Kim et al., 2002a).	**Combined chlorine**: Most organisms at low inactivation **Any disinfectant**: Suspension of aggregated virus particles of multicellular organisms **Chlorine dioxide**: *C. parvum*, endospores
 (c)	**Decelerating rate** Often observed after several logs of inactivations. Possible reasons include: 1. Decrease in germicidal properties of the disinfecting agent with time (Gard, 1957; Collins and Selleck, 1971). 2. Resistance to the disinfectant increases with increasing exposure (Gard, 1957; Collins and Selleck, 1971). 3. Natural heterogeniety in resistance among organisms (Hess, 1953). 4. Interference of particles with disinfection (Severin, 1980; Qualls et al, 1983; Parker and Darby, 1995). 5. Organisms are in clumps that test as one unit but must be inactivated individually (Hunt and Mariñas, 1997).	**Combined chlorine**: Most any organism at high removals **UV**: Total coliform in secondary effluent, *G. lamblia* above 3 log removal

Figure 13-4
Graphical forms of disinfection data.

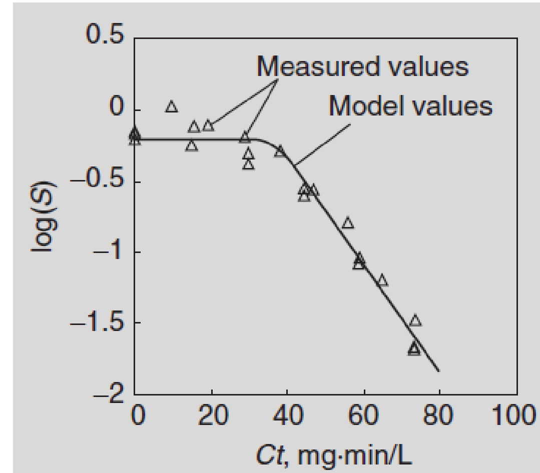
Contemporary Kinetic Models

√ RENNECKER–MARI ˜ NAS MODEL (ACCELERATING RATE)

$$\ln\left(\frac{N}{N_0}\right) = \begin{cases} 0 & \text{for } Ct < b \quad (13\text{-}5) \\ -\Lambda_{CW}(Ct - b) & \text{for } Ct \geq b \quad (13\text{-}6) \end{cases}$$

where b = lag coefficient, mg · min/L

Example 13-2

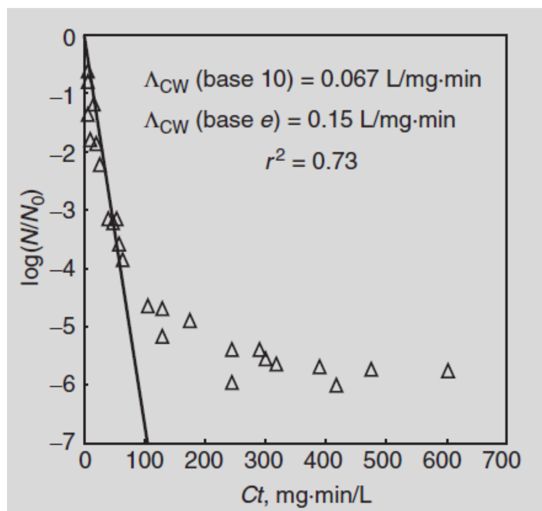


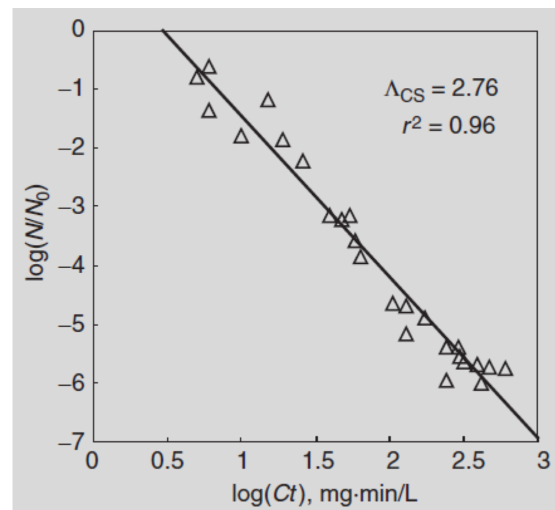
√ COLLINS–SELLECK MODEL (DECELERATING RATE)

$$\ln\left(\frac{N}{N_0}\right) = \begin{cases} 0 & \text{for } Ct < b \quad (13\text{-}7) \\ -\Lambda_{CS}[\ln(Ct) - \ln(b)] & \text{for } Ct \geq b \quad (13\text{-}8) \end{cases}$$

where Λ_{CS} = Collins–Selleck coefficient of specific lethality, unitless
b = lag coefficient, mg · min/L

Example 13-3





Comparison of Disinfection Models

Table 13-2
Comparison of disinfection models

Disinfection Model	Form of Data	Plots as Straight Line On	Number of Coefficients	Comment
Chick[a]: $\ln\left(\frac{N}{N_0}\right) = -k_c t$ where k_c = Chick's law rate constant, time^{-1}	Pseudo–first order	Semilog graph: $\log(N/N_o)$ vs. t	1	Widely used in microbiology. Approximates a lot of disinfection data.
Rennecker–Mariñas: For $Ct < b$ $\ln\left(\frac{N}{N_0}\right) = 0$; For $Ct > b$ $\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW}(Ct - b)$ where Λ_{CW} = coefficient of specific lethality, $1/(\text{mg} \cdot \text{min/L})$; b = lag coefficient, $\text{mg} \cdot \text{min/L}$	Pseudo–first order with lag	Semilog graph: $\log(N/N_o)$ vs. Ct	2	Equation is consistent with "Ct" concept. Can approximate most disinfection data. Performs poorly only if the disinfection reaction truly shows an accelerating rate from the start or if a decelerating rate of reaction is observed. When $b = 0$, this equation simplifies to the Chick–Watson equation.
Collins–Selleck: For $Ct < b$ $\ln\left(\frac{N}{N_0}\right) = 0$; For $Ct > b$ $\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CS}[\ln(Ct) - \ln(b)]$ where Λ_{CS} = log-based coefficient of specific lethality; b = lag coefficient, $\text{mg} \cdot \text{min/L}$	Decelerating rate with lag	Log–log graph: $\log(N/N_o)$ vs. $\log(Ct)$	2	Equation is also consistent with "Ct" concept. Can approximate most disinfection data. Performs poorly if only the accelerating phase is of interest or if several logs of first-order behavior are observed.

[a]The Chick–Watson model is not shown because it is a special case of the Rennecker–Mariñas model when $b = 0$.

Table 13-3
Selected kinetic parameters (base *e*) based on data in the literature[a]

Organism	Disinfectant	Chick–Watson and Rennecker–Mariñas: Λ_{CW}, L/mg·min or m^2/J	*b*, mg·min/L or J/m^2	Collins–Selleck: Λ_{CS}	Source of constant or data used to develop constant
E. coli	Cl_2, pH 8.5, $T = 2–5°C$	3.75	0.2	—	Butterfield et al. (1943)
	NH_2Cl	0.0375	10	—	Butterfield and Wattie (1946)
	NH_2Cl	0.0327	—	—	Butterfield and Wattie (1946)
	ClO_2	3.3	0.33	—	Scarpino et al. (1977)
	O_3	8330	—	—	Hunt and Mariñas (1999)
	UV	0.83	—	—	Harris et al. (1987)
Total coliform (wastewater or wastewater seed)	HOCl	—	0.005	1.2	Selleck and Saunier (1978)
	OCl^-	—	0.1	1.9	Selleck and Saunier (1978)
	NH_2Cl	—	3.0	2.8	Selleck and Saunier (1978)
	ClO_2	—	0.9	2.2	Roberts et al. (1980)
	UV	—	4	26	Tchobanoglous et al. (2003)
Poliovirus	HOCl	0.2	—	—	Floyd and Sharp (1979)
	NH_2Cl	—	—	—	—
	ClO_2	0.47	28	—	Scarpino et al. (1977)
	O_3	0.85	—	—	Katzenelson et al. (1974)
	UV	3	—	—	Cooper et al. 2001 (sewage)
MS-2	Cl_2	3.4	—	—	Haas et al. (1996)
	NH_2Cl	0.005	—	—	Cooper et al. (2001) (buffer)
	ClO_2	—	—	—	—
	O_3	—	—	—	—
	UV	0.96	—	—	Oppenheimer et al. (2001)

(*continued*)

Table 13-3 *(Continued)*

Organism	Disinfectant	Chick–Watson and Rennecker–Mariñas: Λ_{CW}, L/mg·min or m^2/J	b, mg·min/L or J/m^2	Collins–Selleck: Λ_{CS}	Source of constant or data used to develop constant
Giardia	Cl_2, pH 7	—	68	3.8	Haas and Heller (1990)
	NH_2Cl	—	300	5	JMM (1991) (*G. muris*)
	ClO_2	0.21	—	—	Wallis et al. (1989)
	O_3	—	0.02	1.77	JMM (1991) (*G. muris*)
	O_3	1.9	—	—	Wallis et al. (1989)
	UV	38	—	—	Oppenheimer et al. (2001) (*G. muris*)
C. parvum	Cl_2, pH 6	0.0013	375	—	Driedger et al. (2000)
	NH_2Cl	0.00077	5500	—	Rennecker et al. (2001)
	ClO_2	0.083	35	—	Corona-Vasquez et al. (2002)
	O_3	1.7	0.22	—	Driedger et al. (2001)
	O_3	0.83	—	—	Oppenheimer et al. (2000)
	UV	25	—	—	Oppenheimer et al. (2001)
B. subtilis	Cl_2, pH 6	0.0006	—	—	Brazis et al. (1958) (*B. anthracis*)
	NH_2Cl	0.00054	4560	—	Larson and Mariñas (2003)
	ClO_2	0.13	—	—	Radziminski et al. (2002)
	O_3	2.12	4.91	—	Larson and Mariñas (2003)
	UV	0.004	170	—	Knudson (1986) (*B. anthracis*)

[a]Unless otherwise noted all kinetic parameters are given for 25°C.

Declining Concentration of Chemical Disinfectant

$$r_d = -k_d C \tag{13-9}$$

where r_d = reaction rate for the decline in disinfectant concentration with time, mg/L·s or mol/L·s
k_d = first-order decay rate, s^{-1}
C = disinfectant concentration, mg/L or mol/L

$$r_d = -xk_{d1}C - (1-x)k_{d2}C \tag{13-10}$$

where x = fraction of disinfectant decaying by the first mechanism, unitless
C = concentration of disinfectant, mg/L or mol/L
k_{d1}, k_{d2} = decay coefficient for two different mechanisms, s^{-1}

Influence of Temperature on Disinfection Kinetics

$$\ln(k_r) = \ln(A) + \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (5\text{-}85)$$

where k_r = appropriate reaction rate constant, k_c, Λ_{CW}, Λ_{CS}, or k_d.
E_a = activation energy, J/mol
R = universal gas constant, 8.314 J/(mol · K)
T = reaction temperature, K (273 + °C)
A = collision frequency parameter

$$\frac{k_{r,T_1}}{k_{r,T_2}} = \theta^{T_1 - T_2} \quad (13\text{-}11)$$

where k_{r,T_1} = reaction rate constant at temperature 1
k_{r,T_2} = reaction rate constant at temperature 2
θ = empirical constant, dimensionless
T_1 = temperature corresponding to known rate constant k_{r,T_1}, K (273 + °C)
T_2 = temperature corresponding to known rate constant k_{r,T_2}, K (273 + °C)

Combining Eqs. 5-85 and 13-11 and solving for θ, the following expression is obtained:

$$\theta = e^{E_a / RT_1 T_2} \quad (13\text{-}12)$$

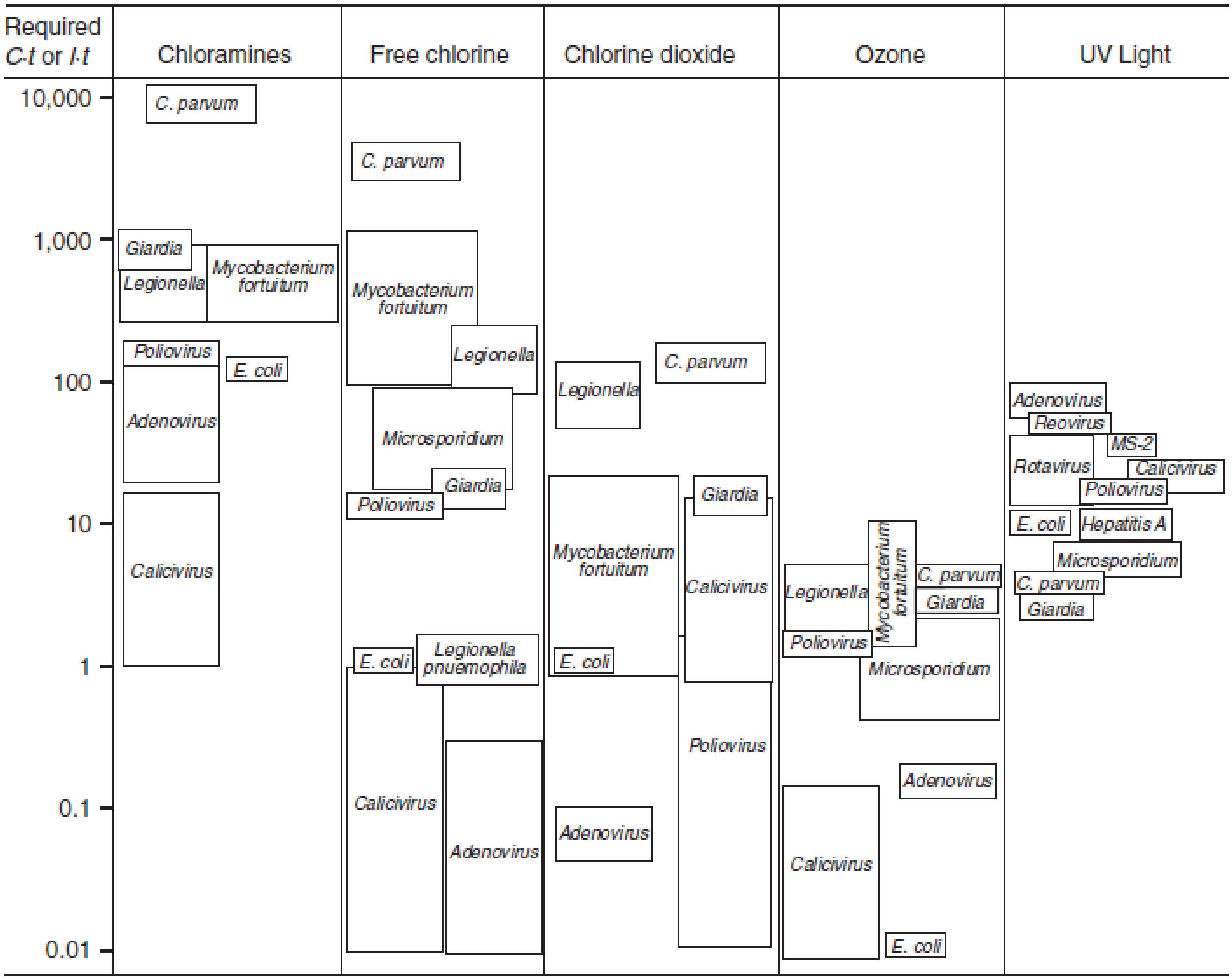
Table 13-4
Activation energies for a variety of disinfection reactions

Microorganism	Disinfectant	E_a, kJ/mol	$K_{25°C}/K_{5°C}$	Reference
C. parvum	HOCl	71.9		Rennecker et al. (2001)
C. parvum	HOCl	64.7		Corona-Vasquez et al. (2002)
		72[a]	6.4	
C. parvum	ClO_2	67.5		Corona-Vasquez et al. (2002)
C. parvum	ClO_2	86.3		Ruffell et al. (2000)
		77[a]	8.0	
C. parvum	NH_2Cl	75.6		Driedger et al. (2001)
C. parvum	NH_2Cl	78.7		Rennecker et al. (2001)
C. parvum	NH_2Cl	59.2[b]		Corona-Vasquez et al. (2002)
		77[a]	8.0	
C. parvum	O_3	102		Oppenheimer et al. (2001)
C. Parvum	O_3	75.7		Driedger et al. (2001)
C. Parvum	O_3	81.2		Rennecker et al. (1999)
C. Parvum	O_3	47.6		Finch et al. (2001)
		76[a]	7.8	
C. muris	O_3	92.8	12	Kim et al. (2002b)
E. coli	O_3	37.1	2.7	Hunt and Mariñas (1997)
G. lamblia	O_3	39.2	2.9	Wickramanyake et al. (1984b)
G. muris	O_3	70	6.6	Wickramanyake et al. (1984a)
N. gruberi	O_3	31.4	2.3	Wickramanyake et al. (1984a)
B. subtilis	O_3	46.8	3.6	Larson and Mariñas (2003)
B. subtilis	NH_2Cl	79.6	8.7	Larson and Mariñas (2003)

[a]Recommended value.
[b]Old oocysts.

The Ct Approach to Disinfection

Figure 13-5
Overview of disinfection requirements for 99 percent inactivation. (Adapted from Jacangelo et al., 1997.)



- Constant CT values are available only in the cases where the Chick-Watson model can applied (No dependence on the initial microorganism population)