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**A Kinetic Model for Predicting
the Composition of Chlorinated
Water Discharged from Power Plant
Cooling Systems**

M. H. Lietzke

Prepared for the U.S. Nuclear Regulatory Commission
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**A KINETIC MODEL FOR PREDICTING THE COMPOSITION
OF CHLORINATED WATER DISCHARGED FROM
POWER PLANT COOLING SYSTEMS**

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A KINETIC MODEL FOR PREDICTING THE COMPOSITION OF CHLORINATED
WATER DISCHARGED FROM POWER PLANT COOLING SYSTEMS¹

M. H. Lietzke

ABSTRACT

A kinetic model for predicting the composition of chlorinated water discharged from power plant cooling systems has been developed. The model incorporates the most important chemical reactions that are known to occur when chlorine is added to natural fresh waters. The simultaneous differential equations, which describe the rates of these chemical reactions, are solved numerically to give the composition of the water as a function of time. A listing of the computer program is included, along with a description of the input variables. A worked-out example illustrates the application of the program to an actual cooling system. An appendix to the report contains a compilation of the known equilibrium and kinetic data for many of the chemical reactions that might be encountered in chlorinating natural fresh waters.

INTRODUCTION

Natural waters used for cooling purposes at power stations may vary widely in composition. Depending on the location of the power station, the cooling water may be either fresh water, seawater, or water of some intermediate composition. The fresh water usually contains traces of organic amines, other organic compounds (mostly humic acid), ammonia or ammonium ion, traces of heavy metals, and various anions, as well as bacteria, algae, spores, and viruses. The seawater, on the other hand, contains approximately 3.45% NaCl and an ammonium ion concentration that is usually lower than in fresh waters. Other abundant (mg/l or greater) cations in seawater include magnesium, calcium, potassium, and strontium ions, while abundant anions include chloride, sulfate, bromide, bicarbonate, borate, silicate, and fluoride ions.

In order to prevent slime formation in the cooling system chlorine is commonly added to the water. The chlorine is rapidly hydrolyzed to yield equimolar quantities of hypochlorous acid and hydrochloric acid. The subsequent chemistry that occurs in fresh water is fairly well understood. The hypochlorous acid dissociates into hydrogen and hypochlorite ions, the extent of dissociation being a function of both pH and temperature. Both the hypochlorous acid and hypochlorite ion are powerful chlorinating agents. They will react rapidly, for example, with ammonia or ammonium ions to produce chloramines, with organic amines to produce N-chlorinated amines, and with amino acids to form N-chloroamino acids. Much of the chlorine is also consumed in satisfying the chlorine demand of the water. The chlorine demand of the water is the difference between the amount of chlorine added and the active (residual) chlorine left. The rates of these various chemical reactions are functions of both the pH and the temperature of the water. The treated cooling water containing the chloramines and other chlorinated molecules is eventually returned to the biosphere, where the N-chloro compounds slowly hydrolyze.

Most of the thermodynamic and kinetic data needed to model the chemistry subsequent to the addition of chlorine to natural fresh waters are available in the literature. Only the rates of hydrolysis of dichloramine and the organic chloramines have not been directly measured. However, in lieu of experimental measurements, reasonable estimates of these quantities may be made and used until measured values become available.

In contrast to the situation with fresh water, the chemistry of what happens when chlorine is added to seawater is unknown. The high concentration of chloride may influence the rates of formation and

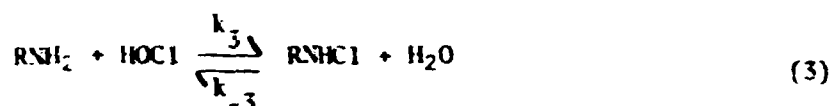
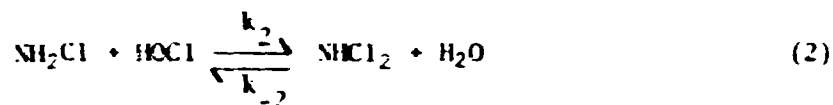
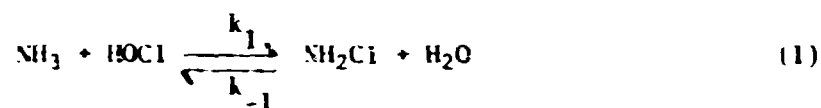
destruction of chloramines. Moreover, the relatively high (ca. 65 ppm) concentration of bromide in seawater² compared to the added chlorine levels will result in the production of hypobromous acid and hypobromite ion. The presence of ammonium ion and organic amines will result in the formation of bromamines as well as chloramines, with the relative concentrations of each dependent upon pH, temperature, and the ammonia to halogen ratio. In addition to the haloamines it is possible that inter-halogen complexes may be formed when chlorine is added to seawater. Hence it is apparent that much experimental work must be done before a reasonable kinetic model can be developed to predict the chemical species present in effluent seawater that has been treated with chlorine.

The reason for developing models to predict the composition of chlorinated cooling water returned to the environment from power plant cooling systems is to provide a means for assessing the environmental impact of such water discharged from existing or proposed power plants. The major concern is the toxic nature of the chloramines and bromamines that may persist for hours or even days after blowdown in the waters of a river or estuary. For example, a massive fish-kill in the cooling waters of a large generating station on the shore of Saginaw Bay³ has been attributed to a lethal concentration of residual chlorine in the water. Halogen residuals in chlorinated waste-water effluents have also been responsible for numerous fish kills in the James River estuary.⁴ Whether the chloramines or other chlorinated compounds will have a long-term effect on man is at present unknown. In any event it is now necessary to take cognizance of this problem in assessing the impact of power generating stations on the environment.

DESCRIPTION OF THE MODEL

In developing the model used in the present program for predicting the composition of water discharged from a power plant cooling system the number of species has been kept small. One reason for this is that the model will be incorporated into a large unified transport model¹ and each species will have to be moved through the environment. The unified transport model is the basis for the large computer program developed from consistent mathematical models to simulate the dispersion of heated water and radioisotopic and chemical effluents from power plant discharges. Another reason for keeping the number of species small is that most of the rate constants that would be needed to refine the model have not been measured as a function of pH and temperature. These are the rate constants for the forward and backward reactions involving organic nitrogen compounds and hypochlorous acid. Of those that have been measured, several of the most common have very similar values (at least in the forward direction) and can be modelled as a group using a single rate constant. In the case of our model we have chosen methylamine as a stand-in for organic nitrogen. Since the total concentration of dissolved organic material amounts in most natural waters to only a few ppm and may be composed of up to 90% humic materials (constituting the chlorine demand of the water), it would, in any case, be difficult to characterize the particular organic compounds present in a given water. Hence, further refinement of the model does not appear at this time warranted.

The model as formulated takes into account the forward and reverse rates of three chemical reactions leading to the formation of chloramines. These are shown as equations (1), (2), and (3).



The species RNH_2 in equation (3) represents a composite of the organic amines present in the water. As previously mentioned, the value of k_3 used in the program is that for the reaction of methylamine with hypochlorous acid. Of the remaining rate constants k_1 , k_{-1} , and k_2 are known. In lieu of measured values of k_{-2} and k_{-3} , k_{-3} has been taken equal to k_{-1} , while k_{-2} has been assumed to be equal to $1/2 k_{-1}$. These six rate constants are the theoretical rate constants for the chemical reactions as written. In practical calculations, however, it is inconvenient to use the theoretical rate constants in the differential equations since the hypochlorous acid will be partially dissociated and the ammonia and organic amines will be in equilibrium with their ammonium ions. Use of the corresponding observed rate constants for the reactions takes into account these equilibria, which are functions of both pH and temperature. The theoretical rate constants are therefore converted in the program into the corresponding observed rate constants for the conditions of pH and temperature specified. Expressions for the conversions are given in Appendix 2. Temperature dependent expressions for the theoretical rate constants are shown in Table 1. Temperatures are in degrees Centigrade.

TABLE I

TEMPERATURE DEPENDENT EXPRESSIONS FOR THE
THEORETICAL RATE CONSTANTS OF
EQUATIONS 1, 2, AND 3

$$k_1 = 3.86286 \times 10^6 + 7.69048 \times 10^4 t + 5.52381 \times 10^2 t^2$$

$$k_2 = 1.17429 \times 10^2 + 3.57857 t + 0.212957 t^2$$

$$k_3 = 2.33667 \times 10^8 + 3.26666 \times 10^6 t$$

$$\ln k_{-1} = -13.036 + 0.113091 t - 3.27212 \times 10^{-4} t^2$$

$$k_{-5} = k_{-1}$$

$$k_{-2} = 0.5k_{-1}$$

The rates of the forward reactions resulting in the formation of the chloramines are extremely rapid, while the reverse reactions for the hydrolysis of the chloramines are much slower. For example, in the pH range 7-8 at a temperature of 25° the forward reactions consume the hypochlorous acid in a few minutes, while half-times for the hydrolysis of the chloramines (resulting in the regeneration of the original amines) are measured in hours. The small amount of hypochlorous acid formed by hydrolysis of the chloramines in the cooling system is disregarded after the initial consumption of the added chlorine.

In addition to the three chemical reactions leading to the formation of chloramines, the model includes an equation for the rate of irreversible uptake of chlorine in satisfying the chlorine demand of the water. The value of the rate constant for this reaction must be adjusted by trial and error so that under the conditions prevailing in a natural water of

given composition about 90% of the chlorine added goes into satisfying the chlorine demand of the water. Fast-acting and slow-acting chlorine demand have been combined into this one equation.

In a once-through cooling system the makeup to blowdown ratio is unity and hence chlorine is added to water containing the same concentrations of dissolved substances as the makeup water. In a recirculating system with cooling towers, on the other hand, the chlorine is added to water in which the dissolved substances have become concentrated by a factor equal to the makeup to blowdown ratio. The computer program has been designed to handle either type of configuration. Losses of chlorine by evaporation and by reaction with material attached to the walls of the cooling system are small and have been disregarded.

A final assumption made in this model is that the chlorine added to the water is immediately dispersed throughout the cooling system, rather than being added over a short period of time. Since the time between successive additions of chlorine may be of the order of eight hours this assumption should not have a very large effect on the calculated values of the total residual chlorine discharged from the system after chlorination has ceased.

In developing the foregoing model a survey of the literature was made to compile available information on the necessary equilibrium and rate constants. Unfortunately these data are scattered in the literature⁵ and in many cases difficult to find. Available data on the most important equilibria and reactions involved in chloramine formation have therefore been summarized in Appendix 2 of this report. In each case reference is made to the source of the data.

DESCRIPTION OF THE COMPUTER PROGRAM

The differential equations representing the chemical system are shown as equations (4), (5), (6), and (7).

$$\frac{d[\text{NH}_2\text{Cl}]}{dt} = k_1 [\text{NH}_3] [\text{HOCl}] - k_{-1} [\text{NH}_2\text{Cl}] - k_2 [\text{NH}_2\text{Cl}] [\text{HOCl}] + k_{-2} [\text{NHCl}_2] - F_{\text{BD}} [\text{NH}_2\text{Cl}] \quad (4)$$

$$\frac{d[\text{NHCl}_2]}{dt} = k_2 [\text{NH}_2\text{Cl}] [\text{HOCl}] - k_{-2} [\text{NHCl}_2] - F_{\text{BD}} [\text{NHCl}_2] \quad (5)$$

$$\frac{d[\text{RNHCl}]}{dt} = k_3 [\text{RNH}_2] [\text{HOCl}] - k_{-3} [\text{RNHCl}] - F_{\text{BD}} [\text{RNHCl}] \quad (6)$$

$$\frac{d[X_4]}{dt} = k_4 [\text{CD} - X_4] [\text{HOCl}] - F_{\text{BD}} [X_4] \quad (7)$$

In equation (7) the quantity CD refers to the chlorine demand of the water. X_4 refers to the amount of chlorine consumed in satisfying the chlorine demand, and k_4 is the rate constant for this reaction. The rate constant F_{BD} appearing in all the equations represents the fraction of the total volume of chlorinated water discharged per unit time. It is calculated by dividing the blowdown rate by the total volume of the chlorinated water.

In addition to these four differential equations a fifth differential equation is included to calculate the concentration of HOCl remaining after each time step.

$$\begin{aligned}
 \frac{d[\text{HOCl}]}{dt} = & -k_1 [\text{NH}_3] [\text{HOCl}] + k_{-1} [\text{NH}_2\text{Cl}] - k_2 [\text{NH}_2\text{Cl}] [\text{HOCl}] \\
 & + k_{-2} [\text{NHCl}_2] - k_3 [\text{RNH}_2] [\text{HOCl}] + k_{-3} [\text{RNHCl}] \\
 & - k_4 [\text{CD} - X_4] [\text{HOCl}] - F_{\text{BD}} [\text{HOCl}]
 \end{aligned} \tag{8}$$

These five differential equations are solved simultaneously using a variable step-size Runge-Kutta integration scheme to give the concentrations of NH_2Cl , NHCl_2 , RNHCl , and HOCl remaining in the cooling system after each time step. The concentrations of NH_3 and RNH_2 in the cooling system are calculated after each time step by subtracting the concentrations of NH_2Cl and NHCl_2 from the original concentration of NH_3 and the concentration of RNHCl from the original concentration of RNH_2 . The concentrations of NH_3 and RNH_2 will at first decrease following chlorination, then build up again as fresh make-up water is brought into the cooling system.

Provision is also made in the computer program for a dilution factor in case the blowdown is diluted before discharge. If no further dilution occurs this factor is unity.

DEFINITIONS OF THE VARIABLES WHICH
COMPRISE THE INPUT TO THE PROGRAM

TMP	Temperature of the water in the cooling system in °C.
PH	pH of the water
CL	Amount of chlorine added to the cooling water (ppm). It is assumed that the chlorine is well mixed and instantaneously dispersed throughout the cooling water system.
NH3	Amount of inorganic nitrogen as NH ₃ in the makeup water (ppm).
RNH2	Amount of organic amines in the makeup water (ppm) - modelled by CH ₃ NH ₂ in the program,
CDO	Total chlorine demand of the makeup water (ppm).
RF	Rate at which makeup water is added to the cooling system (gallons per second).
RF1	Blowdown rate (gallons per second) RF/RF1, the makeup to blowdown ratio, is referred to as M ₁ /BD in the output.
VCS	Total volume of the cooling system to which chlorine is added (gallons).
DLF	Dilution factor after blowdown. If no dilution, DLF = 1.0
TO	Time at start of chlorination (TO = 0).
T1	Duration of time in minutes between successive additions of chlorine.
IT	If IT = M output will be in minutes. If IT = S output will be in seconds.
TSTEP	Timestep to be taken at the start of the integration. This must be short. A suggested value is .001 minutes.*
ITS	If ITS = M timestep will be in minutes. If ITS = S timestep will be in seconds.
IFLAG	Integer specifying whether output is to be in molarity or in ppm. If IFLAG = 0 output is in molarity. If IFLAG = 1 output is in ppm.
RK4	Rate constant for equation (7).

The foregoing variables are input to the program on three cards according to the format shown in Table 2.

*Since terms drop out of the differential equations as soon as the HOC_i is consumed, it is necessary to take a very small time step at the start of the integration to ensure that the initial slopes are well determined.

TABLE II
INPUT DATA

Card No.	Field	Variable	Format
1	1 - 10	TMP	F10.0
	11 - 20	PH	F10.0
	21 - 30	CL	F10.0
	31 - 40	NH3	F10.0
	41 - 50	RNH2	F10.0
	51 - 60	CDO	F10.0
	61 - 70	RF	F10.0
	71 - 80	RF1	F10.0
2	1 - 10	VCS	E10.0
	11 - 20	DLF	E10.0
	21 - 30	TO	E10.0
	31 - 39	T1	F 9.0
	40	IT	A1
	41 - 49	TSTEP	F 9.0
	50	ITS	A1
	51 - 55	IFLAG	IS
	56 - 60	NCLC	IS
3	1 - 10	RK4	E10.0

SAMPLE CASE

Three Mile Island Nuclear Station located near Harrisburg, Pennsylvania, uses both a recirculating and a once-through river water cooling system. Data have been taken from a report⁶ on cooling water chlorination practices at this station in order to test the model and computer program presented in this report. The calculations apply to Unit 1 of the recirculating system, for which the most reliable data are available, and to the once-through river water system.

Characteristics of the make-up water, as given in Table 9 of the report, are as follows: pH 7.2; total chlorine demand 2.6 ppm; nitrogen as NH_3 0.17 ppm; temperature 25.5°C. No mention is made of organic amines in the water.

Characteristic values for the once through system are: 29,000 GPM river water straight through; approximate volume of the once through system 1.0×10^6 G. If it is assumed that the water is chlorinated 0.35 ppm above the immediate chlorine demand, this amounts to about 0.85 ppm chlorine in the river water system immediately after chlorination (with the assumption that the chlorine is instantaneously dispersed and well mixed).

Characteristic values for Unit 1 of the recirculating system are: make-up water 11,250 GPM; blowdown 2,000 GPM; volume of the recirculating system 1.3×10^7 G. The blowdown makes up 7% of the total discharge. If it is assumed that the chlorine is instantaneously dispersed and well mixed in the recirculating system, then 6000 lbs of chlorine per day (assume 2000 lbs three times a day) in the total recirculating system would amount to 9.2 ppm chlorine in the water of Unit 1 immediately after chlorination.

Using the above numbers the input parameters for the computer program are:

A. For the River Water System

TMP	25.5	(deg. C)
PH	7.2	(ppm)
CL	0.845	(ppm)
NH3	0.17	(ppm)
RNH2	0	(ppm)
CDO	2.64	(ppm)
RF	483.33	(29,000/60 sec ⁻¹)
RF1	483.33	(29,000/60 sec ⁻¹)
VCS	1.0 × 10 ⁶	(gallons)
DLF	1.0	
TO	0	
T1	480,	(480 min. or 8 hrs)
IT	M	
TSTEP	.001	(min.)
ITS	M	
IFLAG	1	(so that output will be in ppm)
NCLC	8	(eight chlorination cycles)
RK4	1.0 × 10 ⁴	(liters mole ⁻¹ sec. ⁻¹)

B. For the Recirculating System

TMP	43,	(deg.C)
PH	7.2	(ppm)
CL	9.2	(ppm)
NH3	0.17	(ppm)
RNH2	0	(ppm)
CDO	2.64	(ppm)
RF	187.5	(sec ⁻¹)
RF1	33,333	(sec ⁻¹)
VCS	1.3 × 10 ⁷	(gallons)
DLF	14.3	
TO	0.	
TI	480.	(min.)
IT	M	
TSTEP	.001	(min.)
ITS	M	
IFLAG	1	
NCLC	8	
RK4	500.	(liters mole ⁻¹ sec ⁻¹)

When the computer program was run for eight successive chlorination cycles the following results were obtained:

In the case of the river water system the HOCl produced by hydrolysis of the added chlorine is almost immediately consumed by the chlorine demand in the water and by reaction with the ammonia to form NH_2Cl . With the assumption that the chlorine is instantaneously dispersed throughout the system the maximum amount of NH_2Cl formed is .016 ppm. This would lead to ca. .01 ppm total residual chlorine in the discharge for about five minutes. In actual practice, since it takes 15 to 20 minutes for the chlorinated water to reach the discharge point, the effluent water probably never contains as much as .01 ppm total residual chlorine because of chlorination of the river water system. The amount of NHCl_2 formed is insignificant (max. 3.9×10^{-13} m).

In the recirculating system the makeup to blowdown ratio is fairly high (5.63). Both the chlorine demand and the NH_3 become concentrated in the water by this factor. The amount of chlorine added (9.2 ppm) is relatively high while the concentration of NH_3 in the water is rather low. As can be seen in Fig. 1, when chlorine is added to the water the first time the NH_3 is almost immediately consumed, resulting in the formation of both NH_2Cl and NHCl_2 . The remaining HOCl is taken up by the chlorine demand in the water. The amount of NH_2Cl formed is predicted to reach 3.51 ppm, while the NHCl_2 reaches .08 ppm. After a little more than two hours hydrolysis and blowdown reduce the NH_2Cl concentration to below one ppm; this value falls to .04 ppm after 8 hours, while the NHCl_2 concentration falls to less than .01 ppm. The pattern is repeated during subsequent chlorination cycles, with the system coming

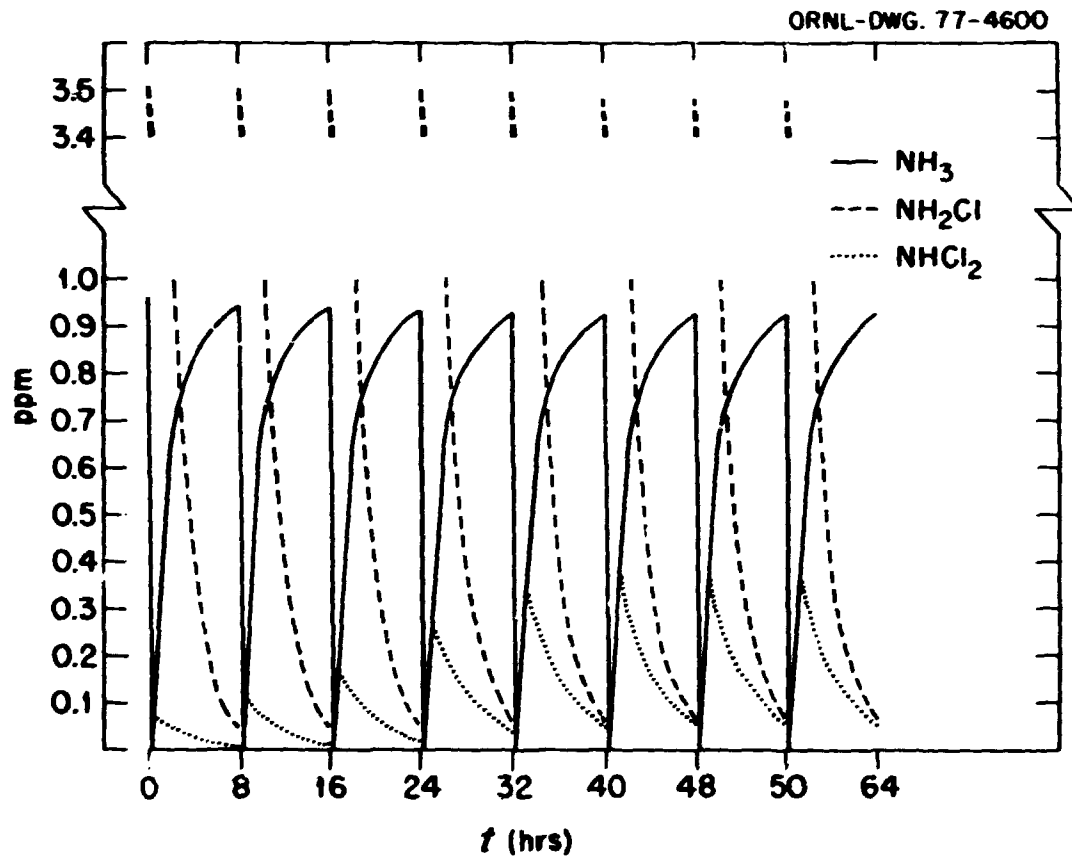


Fig. 1. The Amounts of NH_2Cl , NHCl_2 , and NH_3 in the Recirculating System During Eight Chlorination Cycles

to equilibrium after five cycles. In the sixth and succeeding cycles the maximum predicted amount of NH_2Cl in the system is 3.48 ppm immediately after chlorination and .666 ppm at the end of the cycle, while the corresponding amounts of NHCl_2 are .48 ppm and .05 ppm.

The amounts of total residual chlorine in the discharge from the recirculating system (after dilution) are shown for seven chlorination cycles in Table 3. Again equilibrium is reached after five cycles. These values probably represent upper limits because of potential losses of chlorine neglected in the model: e.g., losses due to evaporation, cooling tower drift, and other chemical reactions involving chlorine.

The values of the rate constants (RK4) used in both cases for the consumption of chlorine by the chlorine demand of the water were found by trial. Increasing the value above 5×10^5 did not result in a significant increase in the consumption of chlorine by the chlorine demand in the river water system and hence this value was used. The chlorine demand was only about 30% satisfied in this system. In the recirculating water system a value of 500 for RK4 resulted in the total chlorine demand of the water being about 90% satisfied.

The total time required to compile the program and run both cases was 5.3 seconds on the IBM 360/91 computer.

TABLE III
 TOTAL RESIDUAL CHLORINE IN DISCHARGE (ppm)
 Chlorination Cycle

Time	1	2	3	4	5	6	7
1 min.	0.172	0.177	0.192	0.225	0.263	0.276	0.277
10 min.	0.158	0.162	0.168	0.176	0.179	0.180	0.180
1 hr.	0.100	0.103	0.107	0.114	0.118	0.119	0.119
2 hr.	0.059	0.063	0.064	0.069	0.072	0.074	0.074
3 hr.	0.034	0.035	0.037	0.042	0.045	0.046	0.046
4 hr.	0.0199	0.021	0.023	0.026	0.029	0.030	0.030
5 hr.	0.012	0.013	0.014	0.016	0.019	0.019	0.019
6 hr.	<.01	<.01	<.01	<.01	0.012	0.013	0.013
7 hr.	<.01	<.01	<.01	<.01	<.01	<.01	<.01
8 hr.	<.01	<.01	<.01	<.01	<.01	<.01	<.01

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Appendix 1

Listing of the FORTRAN Program

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C THE PURPOSE OF THIS PROGRAM IS TO PREDICT THE CONCENTRATIONS
C OF CHLORAMINES IN WATER DISCHARGED FROM POWER PLANT COOLING
C SYSTEMS
C
C AUTHORS--H. H. LIETZKE AND P. A. OLSEN. EDITED BY I. J. LUCAS
C DEFINITIONS OF INPUT TERMS
C
C TMP TEMPERATURE OF WATER IN THE COOLING SYSTEM
C PH PH OF THE WATER
C CL AMOUNT OF CHLORINE ADDED (PPH)
C NH3 AMOUNT OF INORGANIC NITROGEN AS NH3 IN MAKEUP WATER (PPH)
C RNH2 AMOUNT OF ORGANIC AMINE (CH3NH2) IN MAKEUP WATER (PPH)
C CDO CHLORINE DEMAND OF MAKEUP WATER (PPH)
C RF RATE OF MAKE-UP FLOW INTO COOLING SYSTEM (GALLONS PER SECOND)
C RP1 RATE OF BLOWDOWN FROM COOLING SYSTEM (GALLONS PER SECOND)
C VCS VOLUME OF COOLING SYSTEM (GALLONS)
C DLF DILUTION FACTOR AFTER BLOWDOWN
C TO TIME AT START OF RUN. USUALLY TO = 0.
C T1 DURATION OF RUN (EITHER IN MINUTES OR SECONDS)
C TLG TIME LAG FOLLOWING CHLORINATION BEFORE FIRST RESIDUAL
C CHLORINE APPEARS IN DISCHARGE (MINUTES).
C IT IF IT=N OUTPUT WILL BE IN MINUTES. IF IT=S OUTPUT WILL BE IN
C SECONDS.
C TSTEP TIMESTEP TO BE TAKEN AT THE START OF THE INTEGRATION. THIS
C MUST BE SHORT. SUGGESTED VALUE .001 MINUTES
C ITS IF ITS=N TIMESTEP WILL BE IN MINUTES. IF ITS=S TIMESTEP WILL
C BE IN SECONDS.
C IFLAG INTEGER SPECIFYING WHETHER OUTPUT IS TO BE IN MOLARITY OR IN
C PPM. IF IFLAG=0 OUTPUT IS IN MOLARITY. IF IFLAG=1 OUTPUT IS
C IN PPM
C NCLC NUMBER OF CHLORINATION CYCLES
C
C
C IMPLICIT REAL*8 (A-H,C-Z)
C REAL*8 KA,KECL,KB1,KB2,KB3,KW,KNH
C REAL*8 NHCL/.70906D+02/,NH2CL,KONA,KOHAW,NH3,NHCL2
C REAL*8 KH1,KH2,KH3,NH3O
C
C COMMON /CONC/ CLMOL,NH3,RNH2,RK1OBS,RK2OBS,RK3OBS,DLP,ANOCCL,
C 1NH2CL,NHCL2,RNHCL,ANHCL,NH3O,RNH2O,CLMOL0,X4HGCL,RP,RP1,CDO,DC1
C COMMON /NUM/KN1,KN2,KN3,KN4
C COMMON /RL/ NUL,IFLAG,NSW
C DIMENSION Y(10)
C DATA TEN,THOU/.1D+02,.1D+04/,MCR/'M'/
C DATA ACCURC/1.0D-06/
C
C READ INPUT AND WRITE THE INITIAL VALUES.
C
C 3 READ(5,10,END=105) TME,PH,CL,NH3,RNH2,CDO,RP,RP1
C IF(TME.EQ.0) CALL EXIT
10 FORMAT(8E10.0)
C READ(5,12) VCS,DLF,TO,T1,IT,TSTEP,ITS,IFLAG,NCLC
12 FORMAT(3E10.0,F9.0,A1,E9.0,A1,2I5)
C READ(5,10) RK4
C WRITE(6,20)
20 FORMAT(1H1,T47,'CHLORAMINE MODEL CALCULATIONS',/,/,
C 114X,7HINITIAL,34X,2HFN,10X,2HCL,12X,3HNH3,
C 211X,4HRNH2,5Y.17HINTERNAL H2O TEMP)

```

```

WRITE (6,30) PH,CL,HH3,HH2,THP
30 FORMAT(51X,F7.2,3P14.5,8X,P6.1,1RC)

```

C
C
C

CALCULATE EQUILIBRIUM CONSTANTS BASED ON THE TEMPERATURE (THP)

```

KHH=8.44167D-11+6.22812D-12*THP+3.69317D-13*THP**2-5.97755D-17*
THP**3+2.52447D-16*THP**4
KA= 1.99643D-08+THP*5.90714D-10+THP*THP*3.57143D-12
KECL= 1.42691D-04+THP*9.53501D-06+THP*THP*1.91076D-08
KB1= 1.50677D-05+THP*1.22903D-07
KB3= 3.56464D-04+THP*4.35750D-06-THP*THP*6.58928D-08
KB2= 1.17429D+02+THP*3.57857D+00+THP*THP*2.12857D-01
BK1T= 3.86286D+06+THP*7.69048D+04+THP*THP*5.52381D+02
BK3T= 2.33667D+08+THP*3.26666D+06
TDK=THP+273.15
EKNLOG=3.1286D+04/TKR+98.9734*DLG(TDK)-0.097611*TDK-2.17087D+06/
1 TDK**2-606.522
KH=10.**EKWLOG
EKN1=-13.036+THP*.113091-THP*THP*3.27212D-04
KH1=DEXE(EKN1)
KH2=KH1/2.
KH3=KH1
CDO=CEO/(THCU*HWCL)
RF=BF/VCS
BF1=BF1/VCS
BDR=BE/BF1
CDO=CEO*BDR
DC:=CDO

```

C
C
C
C

CALCULATE H+ CONC. (HCON) AND MOLALITY OF NH3 (HH3), HH2
(HH2) AND CL (CLMOL).

```

HCON=1EH**(-PH)
HH3=HH3/(THOU*14.007)
HH2=HH2/(THCU*14.007)
CLMOL=CL/(THOU*HWCL)

```

C
C
C

CALCULATE HOCL, OCL AND CL2 CONC.

```

KONA=KA/HCON+1
KONAW=(KA+HCON)/KH
BK1OBS=BK1T/(KONA+KONAW*KE1)
BK2OBS=KB2*KHH/HCON
BK3OBS=BK3T/(KONA+KONAW*KE3)
HOCL=CLMOL/KONA
OCL=CLMOL-HOCL
CL2=CLMOL*CLMOL*HCCN/KECL

```

C

```

WRITE (6,40)
40 FORMAT(1H0,T14,'CALCULATED',T48,'CL DEMAND',T62,
1'CI HCLAR',6X,'NH3 MOLAR',5X,'NH2 MOLAR')
WRITE (6,45) CDO,CLMOL,HH3,HH2
45 FORMAT(T14,'INITIAL',25X,P5.1,6X,1P3G14.5)
WRITE (6,50) HCON,HOCL,OCL,CL2
50 FORMAT(T14,'VALUES',/,T48,'H+',T62,'HOCL',T76,
1'OCL',T90,'CL2',/,T45,1P4G14.5)
WRITE (6,70) DLF,BDR
70 FORMAT(1H0,46X,'DLF',11X,'HC/BD',/,44X,0P7.2,8X,P7.2)

```

```

WRITE(6,110) BK1OBS,BK2OBS,BK3OBS,BK4
110  FORMAT(1H0,T10,'CONSTANTS:',T46,'K1OBS=',T61.5,
      & 'K2OBS=',G11.5,'K3OBS=',G11.5,5X,3BK4=',G11.5)

C
C   SOLVE DIFFERENTIAL EQNS USING SUBROUTINES KUTA AND EQUA.
C
WRITE(6,60) T0,IT,T1,IT,TSTEP,ITS
60  FORMAT(1H0,/,T21,'T0=',
      & 'P6.2,A1,/,T21,'T1=',P8.2,A1,/,T21,'1ST TIME STEP=',F8.4,A1,/)
WRITE(6,95)
95  FORMAT(T75,5X,T100,'DISCHARGE',
      & '1/,T75,8X,T106,'VALUES')
WRITE(6,100)
100  FORMAT(5X,'TIME',5X,'NHCL',6X,'NH2CL',5X,'NH3',
      & '7X,'NH2',6X,'NHCL',5X,'NHCL2',4X,'CL DEMAND',2X,'X4',8X,
      & 'NH2CLO',4X,'NHCL2C',4X,'NHCLCLO',4X,'T2CLO',/)

DLF=1.000/DLF
NH3=NH3*BDL
NH2=NH2*BCR
NH30=NH3
NH20=NH2
NHCL1=0.
DO 101 I=1,8
101 Y(I)=0.
NH2CL=Y(1)
NHCL2=Y(2)
NHCL=Y(3)
NOL=1
IF(IT.NE.NCR) GO TO 62
TO=TO*60.
TI=TI*60.
62 IF(ITS.EQ.NCR) NOL=60
TSTEP=TSTEP*NOL
DO 200 K=1,NCLC
N=5
TO=TO
T1=TI
DEL=TSTEP
INAX=700
CLNOL=CLNOL
CALL KUTA(T0,T1,Y,N,DEL,ACCURC,INAX)
CLNOL=CL/(THOU*NHCL)
199 T1=T1/60.
200 CONTINUE
GO TO 3
105 CONTINUE
STOP
END

```

SUBROUTINE ROTA (XL, X0, Y, NE, DLL, ACCORC, INAR)

```

C
C
      IMPLICIT REAL*8 (A-H, O-Z)
      REAL*8 K1, K2, K3, K4, K5, NH3, NH2CL, NHCL2, XH1, KH2, KH3
      REAL*8 NH2CLP, NH3P, NHCL2P, DCLAP, NH30, NH2CLO, NHCL20
C
      DIMENSION Y (10), YI (10), YH (10), K1 (10), K2 (10), K3 (10), K4 (10), K5 (10),
      I F (10), E (10), P1 (10), YH (10)
C
C
      COMMON /CONC/ CLBCL, NH3, RHH2, RK10B5, RK20B5, RK30B5, DLP, ANOCLL,
      IHH2CL, HHCL2, RHHCL, ANOCL, NH30, RHH20, CLH0L0, XHNOCL, RP, RP1, CDO, DCI
      COMMON /NUN/ KH1, KH2, KH3, KH4
      COMMON /NL/ NUL, IFLAG, NSW
      LOGICAL QUIT, FIRST
C
      HINC=ISQRT(DSQRT(2.00))
      NSW=0
      ITER=0
      N=NE
      IN=XL
      ANOCL=CLH0L0+ANOCLL
      Y (4)=ANOCL
      XHNOCL=Y (5)
      TRCLO=.689*Y (6)+.826*Y (7)+.541*Y (8)+.676*ANOCLL*DLP
      IF (IFLAG .EQ. 1) GO TO 600
      WRITE (6, 71) IN, ANOCL, NH2CL, NH3, RHH2, RHHCL, NHCL2, CDO, XHNOCL,
      IY (6), Y (7), Y (8), TRCLO
71      FORMAT (1X, F8.3, 3X, 1E12E10.2)
      GO TO 601
600 ANCLL=ANOCLL*5.246E+4
      CLH0L=CLH0L*7.0906E+4
      ANOCL=ANOCL*5.246E+4
      CDOP=CDO*7.0906E+4
      NH3P=NH3*1.4007E+4
      RHH2P=RHH2*1.4007E+4
      NH2CLE=Y (1)*5.1476E+4
      NHCL2E=Y (2)*8.5921E+4
      RHHCLE=Y (3)*6.5503E+4
      XHCL=XHNOCL*7.0906E+4
      HCLAP=Y (6)*5.1476E+4
      DCLAP=Y (7)*8.592E+4
      OCLAP=Y (8)*6.5503E+4
      TRCLPC=.689*HCLAP+.541*OCLAP+.825*DCLAP+.676*ANCLL*DLP
      WRITE (6, 671) IN, CLH0LP, NH2CLP, NH3P, RHH2P, RHHCLP, NHCL2P, CDOP, XHCL
      IP, HCLAP, DCLAP, OCLAP, TRCLP
671      FORMAT (1X, F8.3, 2X, F8.3, 11F10.4)
601 H=DLL
      FIRST=.TRUE.
      QUIT=.FALSE.
      DO 10 I=1, N
10      YH (I)=Y (I)
20 IF (H .GT. 360.) H=360.
      IF (XH+H .LT. X0) GO TO 30

```

```

DLL=N
N=10-18
IF (FIRST) DLL=N
QUIT=.TRUE.
30 DEL=0
CALL ECUA(XN,YN,F1,DEL)
40 DO 50 I=1,N
    K1(I)=N*F1(I)/3.
50    Y1(I)=YN(I)+K1(I)
    DEL=N/3.
    CALL ECUA(XN+N/3.,Y1,F,DEL)
    DO 60 I=1,N
        K2(I)=E*F(I)/3.
60    Y1(I)=YN(I)+K1(I)/2.+K2(I)/2.
    DEL=N/3.
    CALL ECUA(XN+N/3.,Y1,F,DEL)
    DO 70 I=1,N
        K3(I)=N*F(I)/3.
70    Y1(I)=YN(I)+3.*K1(I)/8.+9.*K3(I)/8.
    DEL=N/2.
    CALL ECUA(XN+N/2.,Y1,F,DEL)
    DO 80 I=1,N
        K4(I)=N*F(I)/3.
80    Y1(I)=YN(I)+3.*K1(I)/2.-9.*K3(I)/2.+6.*K4(I)
    DEL=N
    CALL ECUA(XN+N,Y1,F,DEL)
    TEST=0.0
    DO 90 I=1,N
        K5(I)=N*F(I)/3.
        E(I)=(K1(I)-9.*K3(I)/2.+4.*K4(I)-K5(I)/2.)/5.
        TEST=DMAX1(TPST,DABS(E(I)))
90    CONTINUE
    IF (TEST.LT.ACCURC) GO TO 100
    ITER=ITER+1
    IF (ITER.GE.IMAX) GO TO 100
    N=N/2.
    QUIT=.FALSE.
    FIRST=.FALSE.
    GO TO 40
100 DO 110 I=1,N
    YN(I)=YN(I)
110    YN(I)=YN(I)+(K1(I)+4.*K4(I)+K5(I))/2.
    XN=XN+N
    DO 500 I=1,N
    IF (YN(I) .GE. 0) GO TO 500
    IF (I .EQ. 4) NSW=1
    YN(I)=0.
500 CONTINUE
C
111    NH2CL=YN(1)
    NHCL2=YN(2)
    BHHCL=YN(3)
    ANOCL=YN(4)
    I*NOCL=YN(5)
470 IF (I*NOCL .GE. DC1) I*NOCL=DC1
472 NH3=NH30-NH2CL-NHCL2
    IF (NH3 .GT. 0.) GO TO 473
    NH2CL=NH2CL/(1.-NH3/NH30)

```

```

      BHCL2=BHCL2/(1.-BH3/BH30)
      BH3=0.
473  BH2=BH20-BHCL
      IF(BH2 .GT. 0.) GO TO 474
      IF(BH20 .LE. 0.) GO TO 474
      BHCL=BHCL/(1.-BH2/BH20)
      BH2=0.
474  CDO=DC1-X4HCL
      IF(BH2 .LE. 0) BH2=0.
      YH(1)=BH2CL
      YH(2)=BHCL2
      YH(3)=BHCL
      ANOCL1=ANOCL
      BH2CLO=BH2CL*DLP
      BHCL2O=BHCL2*DLP
      BHCLLO=BHCL*DLP
      Y(6)=BH2CLO
      Y(7)=BHCL2O
      Y(8)=BHCLLO
      TBCLO=.689*BH2CLO+.547*BHCLLO+.825*BHCL2O+.676*ANOCL*DLP
      TY=YH/BUL
480  IF(IPLAG .EQ. 1) GO TO 700
      WRITE(6,271) TY,ANOCL,BH2CL, BH3, BH2, BHCL, BHCL2, CDO ,X4HCL,
      1BH2CLO, BHCL2O, BHCLLO, TBCLO
271  FORMAT(1X, F8.3, 3X, 1E12E10.2)
      GO TO 118
700  ANOCLP=ANOCL*5.246D+4
      CLCIP=CLDIS*4.7932D+4
      CDOP=CDO*7.0906D+4
      BH2CLF=BH2CL*5.1476D+4
      BH3P=BH3*1.4007D+4
      BH2P=BH2*1.4007D+4
      BHCLF=BHCL*6.5503D+4
      BHCL2F=BHCL2*8.5921E+4
      X4HCLF=X4HCL*7.0906E+4
      HCLAP=BH2CLO*5.1476D+4
      DCLAP=BHCL2O*8.592D+4
      OCLAP=BHCLLO*6.5503D+4
      TBCLPO=.689*HCLAP+.547*OCLAP+.825*DCLAP+.676*ANOCLP*DLP
      WRITE(6,671) TY,ANOCLP, BH2CLP, BH3P, BH2P, BHCLP, BHCL2P, CDOP , X4HCL
      1P, HCLAP, DCLAP, OCLAP, TBCLPO
C
      IXL=IX/3600
118  FIRST=.FALSE.
      IF (TEST_GE_ACCURC/32.) GO TO 120
      B=B*HINC
      ITER=ITER-1
120  IF (.NOT.QUIT) GO TO 20
      DO 130 I=1,N
130   Y(I)=YH(I)
      GO TO 150
140  WRITE(6,10000)
150  RETURN
10000 FORMAT(1X, 'IBX EXCEEDED')
      END

```



```

SUBROUTINE EQUA(X,Y,YF,DEL)
IMPLICIT REAL*8(A-H,C-Z)
REAL*8 UN3,KN1,KN2,KN3,UNCL2,UN2CL,UN30

COMMON /CONC/ CLMOL,UN3,UNH2,KN1OBS,KN2OBS,KN3OBS,OLP,ANOCCL,
1UN2CL,UNCL2,UNCL,ANOC,UN30,UNH2O,CLMOL0,YOOCCL,RF,RF1,CDO,DC1
COMMON /MOM/KN1,KN2,KN3,KN4
COMMON /AL/ UNL,IPLAG,NSW
DIMENSION YP(10),Y(10)
AUN3=UN3
AUNH2=UNH2
I41=Y(5)
IF(I41 .GE. DC1) I41=DC1
CDO=DC1-I41
YP(1)=Y(4)*(KN1OBS*AUN3-KN2OBS*Y(1))-KN1*Y(1)+KN2*Y(2)-RF1*Y(1)
YP(2)=KN2OBS*Y(1)*Y(4)-KN2*Y(2)-RF1*Y(2)
YP(3)=KN3OBS*AUNH2*Y(4)-KN3*Y(3)-RF1*Y(3)
IF(NSW .EQ. 0) GO TO 50
YP(4)=0.
GO TO 51
50 YP(4)=-KN1OBS*AUN3*Y(4)+KN1*Y(1)+KN2*Y(2)-KN2OBS*Y(4)*Y(1)-KN3OBS*
1Y(4)*AUNH2+KN3*Y(3)-UNH2*CDO*Y(4)-RF1*Y(4)
51 YP(5)=KN4*CDO*Y(4)-RF1*Y(5)
RETURN
END

```

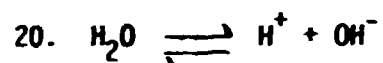
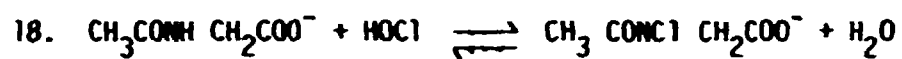
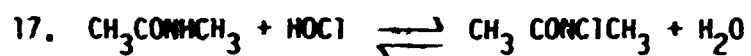
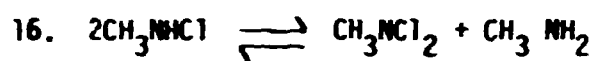
Appendix 2

**Compilation of Thermodynamic and Kinetic Data for Reactions
Involving N-Chlorination of a Number of Organic
and Inorganic Compounds**

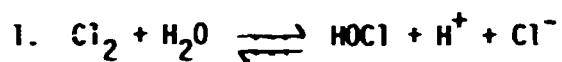
APPENDIX 2

Thermodynamic and kinetic data on the following reactions are summarized:

1. $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^-$
2. $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$
3. $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
4. $\text{NH}_4^+ (\text{H}_2\text{O}) \rightleftharpoons \text{NH}_3 + \text{H}^+$
5. $\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{HOCl}$
6. $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$
7. $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$
8. $(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$
9. $\text{NH}_3 + \text{HOCl} \rightleftharpoons \text{NH}_2\text{Cl} + \text{H}_2\text{O}$
10. $\text{NH}_2\text{Cl} + \text{HOCl} \rightleftharpoons \text{NHCl}_2 + \text{H}_2\text{O}$
11. $2\text{NH}_2\text{Cl} + \text{H}^+ \rightleftharpoons \text{NH}_4^+ + \text{NHCl}_2$
12. $2\text{NH}_2\text{Cl} \longrightarrow \text{NHCl}_2 + \text{NH}_3$
13. $\text{CH}_3\text{NH}_2 + \text{HOCl} \rightleftharpoons \text{CH}_3\text{NHCl} + \text{H}_2\text{O}$
14. $(\text{CH}_3)_2\text{NH} + \text{HOCl} \rightleftharpoons (\text{CH}_3)_2\text{NCl} + \text{H}_2\text{O}$
15. $\text{CH}_3\text{NHCl} + \text{HOCl} \rightleftharpoons \text{CH}_3\text{NCl}_2 + \text{H}_2\text{O}$



21. Rate constants for N-chlorination of a number of additional compounds relative to ammonia.



$$K_1 = \frac{[\text{Cl}^-] [\text{H}^+] [\text{HOCl}]}{[\text{Cl}_2]}$$

<u>t^oc</u>	<u>K₁ x 10⁴</u>
0	1.46
15	2.81
25	3.94
35	5.10
45	6.05

ref: R. E. Connick & Yuan - tsan Chia, J. Am. Chem. Soc., 81 1280 (1959)

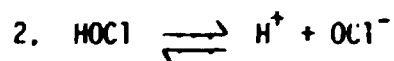
rate constants

$k_1 = 5.60 \text{ sec}^{-1} \pm 0.45$ if the reaction is monomolecular

$k_1 = 0.1 \text{ l/mole} \cdot \text{sec}$ if the reaction is bimolecular

(this has not been resolved)

ref: A. Lifshitz and B. Perlmutter - Hayman, J. phys. chem, 64, 1663 (1960).

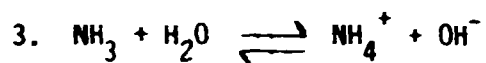


$$K_2 = \frac{[\text{H}^+] [\text{OCl}^-]}{[\text{HOCl}]}$$

2. (concl.)

<u>t °C</u>	<u>K₂ x 10⁸</u>
0	2.0
5	2.3
10	2.6
15	3.0
20	3.3
25	3.7

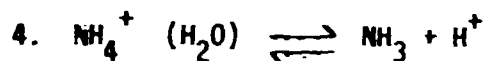
ref: G. M. Fair, J. C. Morris, S. L. Chang, I. Weil, R. P. Burden, J. Am. Water Works Assoc. 40, 1051 (1948).



$$K_3 = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

<u>t °C</u>	<u>K₃ x 10⁵</u>	<u>t °C</u>	<u>K₃ x 10⁵</u>
0	1.51	25	1.81
10	1.62	40	2.00
15	1.70	50	1.95

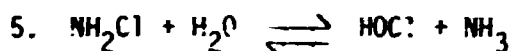
ref: H. Lunden, J. chim. phys. 5, 574 (1907)



$$K_4 = \frac{[\text{NH}_3] [\text{H}^+]}{[\text{NH}_4^+]}$$

$t^\circ\text{C}$	$K_4 \times 10^{10}$	$t^\circ\text{C}$	$K_4 \times 10^{10}$
0	(0.83)	30	8.06
5	1.25	35	11.3
10	1.86	40	15.7
15	2.73	45	21.4
20	3.98	50	28.9
25	5.68		

ref: R. G. Bates and G. D. Pinching, J. Res. Nat. Bur. Stand. 42, 419 (1949)



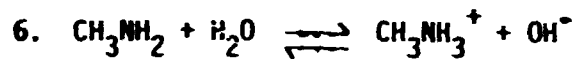
$$K_5 = \frac{[\text{HOCl}] [\text{NH}_3]}{[\text{NH}_2\text{Cl}]}$$

$$K_5 = 9.0 \times 10^{-2} \exp(-14,000/RT) \text{ moles/l.}$$

rate constant: as a first order process (in the absence of competing NH_3) the specific rate is given by

$$k_5 = 8.7 \times 10^7 \exp(-17,000/RT) \text{ sec}^{-1}$$

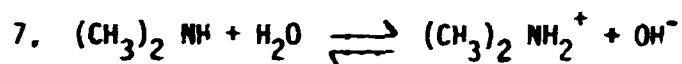
ref: M. L. Granstram, PhD Thesis, Harvard University, Nov. 1954,



$$K_6 = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

$t^\circ\text{C}$	$-\log K_6$	$K_6 \times 10^4$
0	3.449	3.56
10	3.405	3.94
20	3.380	4.17
30	3.367	4.30
40	3.375	4.22
50	3.386	4.11

ref: D. H. Everett and W. F. K. Wynne - Jones, Proc. Roy. Soc (London),
177A, 499 (1941)

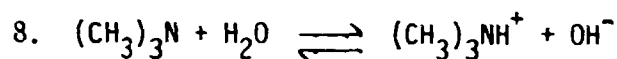


$$K_7 = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

$t^\circ\text{C}$	$-\log K_7$	$K_7 \times 10^4$
0	3.392	4.055
10	3.307	4.932
20	3.245	5.689
30	3.203	6.266
40	3.183	6.561
50	3.175	6.683

7. (concl.)

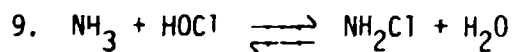
ref: D. H. Everett and W. F. K. Wynne - Jones, loc. cit.



$$K_8 = \frac{[(\text{CH}_3)_3\text{NH}^+] [\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$

<u>t°C</u>	<u>-log K₈</u>	<u>K₈ x 10⁵</u>
0	4,591	2,564
10	4,407	3,917
20	4,261	5,483
30	4,141	7,228
40	4,059	7,297
50	3,992	10,19

ref: D. H. Everett and W. F. K. Wynne - Jones, loc. cit.



$$K_9 = \frac{[\text{NH}_2\text{Cl}]}{[\text{NH}_3] [\text{HOCl}]}$$

$$K_9 = 3.6 \times 10^9 \text{ at } 25^\circ\text{C}$$

ref: J. E. Draley, ANL/ES - 12 (1972)

9. (concl.)

rate constant: Over the temperature range 5 - 35°C the activation energy for the reaction is 3 kcal.

The theoretical rate constant is given by

$$k_g = 9.7 \times 10^8 \exp(-3000/RT) \text{ l/mole} \cdot \text{sec.}$$

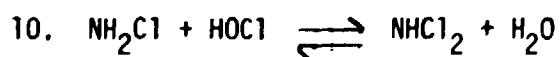
ref: J. C. Morris in Principles and Applications of Water Chemistry, S. D. Faust and J. V. Hunter (ed.), John Wiley and Sons, Inc., N.Y. (1967), p. 27

k_g (theoretical) is related to k_g (obs.) by

$$k_g \text{ (obs.)} = \frac{k_g \text{ (theoret)}}{1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[H^+]} + \frac{K_b}{K_w} [H^+]}$$

where $K_a = K_2$; $K_b = K_3$; and K_w is given by K_{20}

ref: I. Weil & J. C. Morris, J. Am. Chem. Soc, 71, 1664 (1949)



$$K_{10} = \frac{[\text{NHC1}_2]}{[\text{NH}_2\text{Cl}] [\text{HOCl}]}$$

10. (concl.)

$$K_{10} = 1,35 \times 10^6 \text{ at } 25^\circ\text{C}$$

ref: Draley, loc. cit.

rate constant: the activation energy for this reaction is 7.3 kcal.

The theoretical rate constant is given by

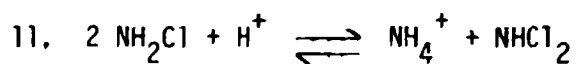
$$k_{10} = 7.6 \times 10^7 \exp(-7300/RT) \text{ 1/mole - sec.}$$

In mildly acid solutions

$$k'_{10} = k_{10} K_a / [H^+]$$

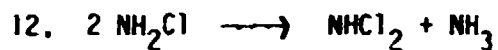
where $K_a = K_4$

ref: J. C. Morris (1967) loc. cit., p. 28.



$$K_{11} = \frac{[\text{NH}_4^+] [\text{NHC1}_2]}{[\text{H}^+] [\text{NH}_2\text{Cl}]^2}$$

$$K_{11} = 6.7 \times 10^5 \text{ at } 25^\circ$$

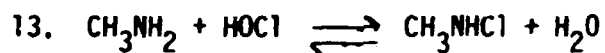


The activation energy for this reaction in the temperature range 7 - 49°C is 4.3 kcal.

rate constant:

$$k_{12} = 80 \exp(-4300/RT) \text{ l/mole} \cdot \text{sec.}$$

ref: M. L. Granstrom, loc. cit.



rate constant: over the temperature range 5 - 25°C the activation energy for the reaction is 1.9 kcal.

The theoretical rate constant is given by

$$k_{13} = 7.8 \times 10^9 \exp(-1900/RT) \text{ l/mole} \cdot \text{sec.}$$

ref: J. C. Morris (1967), loc. cit., p. 32.

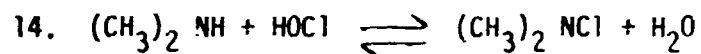
k_{13} (theoretical) is related to k_{13} (obs.) by

$$k_{13} \text{ (obs.)} = \frac{k_{13} \text{ (theoret)}}{1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[\text{H}^+]} + \frac{K_b}{K_w} [\text{H}^+]}$$

13. (concl.)

where $K_a = K_2$; $K_b = K_6$; and $K_w = K_{20}$

ref: I. Weil and J. C. Morris, loc. cit.



rate constant: over the temperature range 5 - 38°C (no change with temperature) the theoretical rate constant is given by

$$k_{14} = 3.3 \times 10^8 \text{ 1/mole - sec.}$$

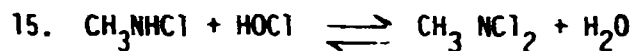
ref: J. C. Morris (1967), loc. cit., p, 34

k_{14} (theoretical) is related to k_{14} (obs) by

$$k_{14} \text{ (obs)} = \frac{k_{14} \text{ (theoret)}}{1 + \frac{K_a K_b}{K_w} + \frac{K_a}{[\text{H}^+]} - \frac{K_b}{K_w} [\text{H}^+]}$$

where $K_a = K_2$; $K_b = K_7$; and $K_w = K_{20}$

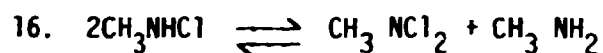
ref: I. Weil and J. C. Morris, loc. cit.



rate constant: $k_{15} = 1.1 \times 10^3$ 1/mole - sec at 25°C.

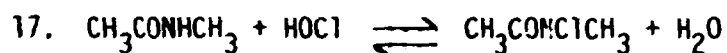
The temperature coefficient has not been determined.

ref: J. C. Morris (1967), loc. cit., p. 32.



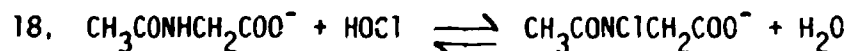
rate constant: $k_{16} = 4.7 \times 10^{-2}$ 1/mole - sec at 25°C

The temperature coefficient has not been determined.



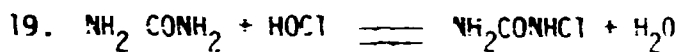
reaction rate: At 25° the rate constant is

$$k_{17} = 1.4 \times 10^{-3} \text{ 1/mole - sec.}$$



reaction rate: At 25° the rate constant is

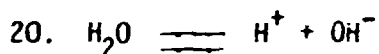
$$k_{18} = 5 \times 10^{-2} \text{ 1/mole - sec.}$$



reaction rate: At 25° the rate constant is

$$k_{19} = 7.5 \times 10^{-2} \text{ 1/mole - sec.}$$

ref: (16, 17, 18, 19): J. C. Morris (1967), loc. cit.



$$K_{20} = K_w = [\text{H}^+] [\text{OH}^-]$$

The temperature dependence of K_w (at saturation vapor pressure) is given by

$$\log K_w = \frac{P_1}{T} + P_2 \ln T + P_3 T + \frac{P_4}{T^2} + P_5,$$

where

$$P_1 = 3.12867 \times 10^4$$

$$P_4 = -2.17087 \times 10^6$$

$$P_2 = 94.9734$$

$$P_5 = -6.06522 \times 10^2$$

$$P_3 = -0.097611$$

$$T = T^\circ\text{K}$$

ref: F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr., J. Solution Chem, 3, 191 (1974).

21. Summary of rate constants for N - chlorination of a number of nitrogenous compounds relative to NH_3 . F_o is the ratio of the rate constant for the particular reaction relative to that for the reaction with NH_3

TABLE I RATE CONSTANTS FOR
N-CHLORINATION RELATIVE TO NH_3 (a)

Nitrogenous Compound	$\text{pK}_o(25^\circ\text{C})$	$F_o = k_u/k_r$	$\log F_o$
Methylamine	3.376	60 (b)	1.78
Dimethylamine	3.226	54 (b)	1.73
Diethylamine	3.067	23	1.36
Morpholine	5.30	9	0.95
Diethanolamine	5.12	9.3	0.97
Ethylaminoacetate	6.27	2.0	0.30
Glycine	4.221	22	1.34
Alanine	4.133	19	1.28
Leucine	4.256	14	1.15
-Alanine	3.765	33	1.52
Serine	4.795	6.7	0.83
Glycylglycylglycine	6.09	2.3	0.36
Chloramide	ca 15	5.5×10^{-5}	-4.26
N-chlormethylamine	ca 13.8	1.8×10^{-4}	-3.74

(a) Based on reaction between HOCl and basic form of N compound,

(b) Computed from individual rate constants.

ref: J. C. Morris (1967), loc. cit., p. 37.