

E379091

EPA-600/3-79-091
August 1979

**AQUEOUS AMMONIA EQUILIBRIUM -
TABULATION OF PERCENT UN-IONIZED AMMONIA**

by

**Robert V. Thurston, Rosemarie C. Russo, and Kenneth Emerson
Fisheries Bioassay Laboratory
Montana State University
Bozeman, Montana 59717**

Grant No. R8J0861

Project Officer

**Kenneth E.F. Hokanson
Monticello Ecological Research Station
Environmental Research Laboratory - Duluth
Monticello, Minnesota 55362**

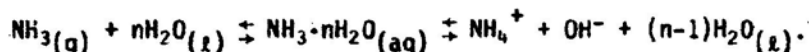
**ENVIRONMENTAL RESEARCH LABORATORY-DULUTH
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
DULUTH, MINNESOTA 55804**

i.a

SECTION I

INTRODUCTION

Ammonia, when dissolved in water, exists in both an un-ionized form (NH_3), and in an ionized form (NH_4^+). This relationship is principally a function of the pH, temperature, and ionic strength of the aqueous solution. The equation expressing the aqueous ammonia equilibrium can be written as



As indicated in this equation, the dissolved ammonia molecule exists in hydrated form; it is hydrogen-bonded to at least three water molecules (Butler 1964).

Research by Chipman (1934), Wuhrmann et al. (1947), and Wuhrmann and Woker (1948) has established that the NH_3 species of total aqueous ammonia is relatively more toxic than the NH_4^+ species. Based on this and other research, a water quality criterion of 0.02 mg/liter NH_3 has been established by the U.S. Environmental Protection Agency (1977) to protect freshwater aquatic life. There is at present no Environmental Protection Agency criterion for NH_4^+ or for total ammonia.

Tabata (1962) has attributed toxicity to fishes and aquatic invertebrates to the NH_4^+ fraction as well as to the NH_3 fraction, and has estimated NH_4^+ to be perhaps 1/50th as toxic as NH_3 . More recently, Armstrong et al. (1978) have reported the toxicity of NH_4^+ to be greater than that reported by Tabata, under the conditions of their tests on prawn (*Macrobrachium rosenbergii*) larvae. Experiments conducted on fishes in our laboratory (unpublished data) also indicate that the toxicity of the NH_4^+ species and/or the effect of pH on the toxicity of NH_3 is greater than previously reported in the literature.

Regardless of the relative toxicity of these two chemical species, an exact understanding of their aqueous equilibrium relationship is essential. A number of analytical methods are available for direct determination of total ammonia concentrations in aqueous solutions. NH_3 may be measured directly by a selective membrane probe, although the lower limit of detection by commercially available probes is on the order of 10^{-6} M, which is above the NH_3 concentration of most natural water systems. If the pH of the solution measured is altered to facilitate measurement of NH_3 , the original composition must be computed; if total ammonia is measured, NH_3 must be computed. Either way, the percent of total ammonia initially present as NH_3 or as NH_4^+ must be determined by calculation based on the ammonia-water equilibrium at the original pH and temperature.

Analysis of data generated in our studies on the toxicity of ammonia to fishes and aquatic invertebrates created a need for the best possible data on the equilibrium relationship between NH_3 and NH_4^+ . We therefore conducted a critical evaluation of the literature data on the ammonia-water equilibrium system and developed equations for calculation of pK_a as a function of temperature and of percent NH_3 and NH_4^+ for total ammonia solutions as a function of pH and temperature. Results of our evaluation have already been discussed in detail elsewhere (Thurston *et al.*, 1974; Emerson *et al.*, 1975). The purpose of the present report is to provide water pollution workers with a reference table of percent un-ionized ammonia values based on the results of the previously published research, and at smaller increments of pH and temperature than in other abbreviated tables provided in our previous publications.

SECTION II

CALCULATION OF PERCENT UN-IONIZED AMMONIA

To calculate the temperature dependence of the pK for NH_3 , and to calculate the fraction of NH_3 , we used the equations from Emerson et al. (1975). Values of the NH_3 fraction, expressed as percentage of total ammonia, are listed in Table A-1 at temperature intervals of 0.2 degree from 0.0 to 40.0 C, and pH intervals of 0.01 pH unit from pH 5.00 to 12.00. If percent NH_3 values for smaller increments of temperature within the range reported are desired, these can readily be linearly interpolated from Table A-1. It should be noted by users of Table A-1 that the equation used for pK_a is invalid outside the temperature range 0 to 50 C because it was obtained empirically. Extrapolations to temperatures above 50 C or below 0 C should not be made.

It should also be noted that, although pH and temperature are the most important factors which determine the percentage of total ammonia in either the ionized or un-ionized form, ionic strength is another important influence on this equilibrium. There is a decrease in the percentage of un-ionized ammonia as the ionic strength increases in hard water or in dilute saline solution. In most natural freshwater systems, even up to 200-300 mg/liter dissolved solids, the reduction of percent NH_3 attributable to dissolved solids is negligible. In more saline or very hard waters there will be small but significant decreases in the percent NH_3 ; these cannot be readily calculated or derived from the data presented here.

SECTION III

PROCEDURE FOR USE OF THE PERCENT UN-IONIZED AMMONIA TABLE

Concentrations of ammonia have been reported in the literature as a variety of different forms, such as NH_3 , NH_4^+ , $\text{NH}_3\text{-N}$, NH_4OH , NH_4Cl , and others. Standard analytical methods for determining ammonia measure total ammonia, often referred to as the "analytical concentration" of ammonia. If the total ammonia concentration is expressed in one form and you wish to convert it to some other desired form, you can always do so by multiplying the expressed value by the ratio of the formula weight (F.W.) of the desired form over the formula weight of the expressed form; i.e.,

$$\text{Concentration as expressed form} \times \frac{\text{F.W. of desired form}}{\text{F.W. of expressed form}} = \text{Concentration as desired form.}$$

Several examples of these conversion factors, to convert total ammonia in one form to total ammonia in another form, are given below; to convert from the expressed form to the desired form, multiply the expressed form by the conversion factor.

<u>Total Ammonia Expressed Form (F.W.)</u>	<u>Total Ammonia Desired Form (F.W.)</u>	<u>Conversion Factor</u>
$\text{NH}_3\text{-N}$ (14.0)	NH_3 (17.0)	17/14
NH_4^+ (18.0)	NH_3 (17.0)	17/18
NH_4^+ (18.0)	$\text{NH}_3\text{-N}$ (14.0)	14/18
NH_4OH (35.0)	$\text{NH}_3\text{-N}$ (14.0)	14/35
NH_4Cl (53.5)	NH_3 (17.0)	17/53.5

Table A-1 gives the percent of the total ammonia concentration which is present as un-ionized ammonia at the desired temperature and pH. The table may be used with any units which express the total ammonia concentration as weight per unit volume; examples are mg/liter, grains/gallon, ppm. Given the total ammonia concentration, temperature, and pH, multiply the total ammonia concentration by the appropriate fraction (percent/100) taken from Table A-1. The un-ionized ammonia concentration obtained will be in the same form and units as the total ammonia concentration.

Example 1. Suppose the total ammonia concentration, expressed as NH_3 , is 12.0 mg/liter at a pH of 7.80 and a temperature of 13.0 C. What is the concentration of un-ionized ammonia, expressed as NH_3 , under these conditions?

Solution: From Table A-1 the percent of un-ionized ammonia at the pH and temperature is 1.52. Hence the concentration of un-ionized ammonia as NH_3 is

$$12.0 \text{ mg/l} \times 0.0152 = 0.182 \text{ mg/l}$$

Example 2. Suppose the total ammonia concentration, expressed as NH_4Cl , is 8.50 mg/liter, at a pH of 6.90 and a temperature of 18.0 C. What is the concentration of un-ionized ammonia expressed as NH_3 ?

Solution: To convert from mg/liter NH_4Cl to mg/liter NH_3 , multiply by the factor 17/53.5 (see example in conversion table above). The percent of un-ionized ammonia is obtained from Table A-1 as before; in this case it is 0.272. The result is then

$$8.50 \text{ mg/l} \times 17/53.5 \times 0.00272 = 0.00735 \text{ mg/l un-ionized ammonia as } \text{NH}_3.$$