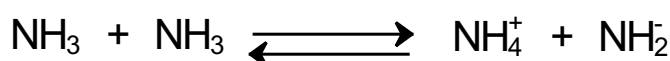


## Acid base equilibria 1

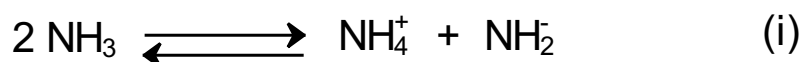
Indicate the equilibrium equation and the constant expression for the auto-protolysis of liquid ammonia. If  $K_{\text{NH}_3} = 10^{-22}$ , how many molecules of ammonia are ionized in a single mole of ammonia? Assume the density of ammonia is 0.771 g/ml.

### Solution:

Auto-protolysis is the phenomenon whereby an ammonia molecule can donate a proton to another  $\text{NH}_3$  molecule to form a positive and a negative charged species. The equation of the auto-protolysis can be written as



or



To find the constant expression, consider the equilibrium constant expression for the reaction:

$$K_1 = \frac{(\text{NH}_4^+) \cdot (\text{NH}_2^-)}{(\text{NH}_3)^2}$$

Note that the concentration of  $\text{NH}_3$  in pure ammonia is always constant. By the analogy of the auto-protolysis of water (where the  $K_w$  expression is written  $(\text{OH}^-)(\text{H}_3\text{O}^+)$ , - without  $(\text{H}_2\text{O})^2$  in the denominator), the constant expression for the auto-protolysis of  $\text{NH}_3$  is

$$K_{\text{NH}_3} = (\text{NH}_4^+) \cdot (\text{NH}_2^-) \quad (\text{ii})$$

To find the number of molecules of ammonia ionized in a single mole of ammonia, use the equation

$$K_1 = \frac{(\text{NH}_4^+) \cdot (\text{NH}_2^-)}{(\text{NH}_3)^2}$$

Let  $x$  be the number of moles of ammonia ionized. Then the  $\text{NH}_3$  remaining non-ionized is  $1 - x$  moles. Since each 2 ammonia molecules must ionize to produce a single  $\text{NH}_4^+$  and one  $\text{NH}_2^-$ , the number of  $\text{NH}_4^+$  is equal to the number of  $\text{NH}_2^- = x/2$ . Let  $V$  be the volume of one mole of ammonia. The concentration of  $\text{NH}_4^+$  and  $\text{NH}_2^-$  can be written as  $(x/2)/V$ , and the concentration of non-ionized  $\text{NH}_3$

is  $(1 - x) / V$ . The equation for  $K_1$  can be rewritten as

$$K_1 = \frac{\left(\frac{x}{V_1}\right) \cdot \left(\frac{x}{V_1}\right)}{\left(\frac{1-x}{V_1}\right)^2} = \frac{\frac{x^2}{4}}{(1-x)^2} \cdot \frac{\frac{1}{V_1^2}}{\frac{1}{V_1^2}} = \frac{x^2}{4(1-x)^2} \quad (\text{iii})$$

X, the number of moles of ionized ammonia, can be calculated if  $K_1$  is known. To solve  $K_1$ , consider a more general case of the equation

$$K_1 = \frac{(\text{NH}_4^+) \cdot (\text{NH}_2^-)}{(\text{NH}_3)^2}$$

The numerator  $(\text{NH}_4^+) (\text{NH}_2^-)$  is the constant expression for the auto-protolysis of  $\text{NH}_3$  and must always equal  $K_{\text{NH}_3} \cdot K_{\text{NH}_3}$  and is given as  $10^{-22}$ .

To find  $(\text{NH}_3)^2$ , use the fact that the density of ammonia is 0.771 g/ml. The mole weight of ammonia is

$$\frac{0.771 \text{ g}}{17.03 \text{ g/mol}} = 0.045 \text{ kg mol kg}^{-1}$$

and the density of ammonia is 0.0453 mol/ml = 45.3 mol / liter, so  $(\text{NH}_3) = 45.3 \text{ M}$ . Substitute these results in

$$K_1 = \frac{(\text{NH}_4^+) \cdot (\text{NH}_2^-)}{(\text{NH}_3)^2}$$

$$K_1 := \frac{10^{-22}}{45.3^2}$$

$$K_1 = 4.873\text{e-}26 \quad (\text{iv})$$

Substitute this value of  $K_1$  into (iii)

$$4.8731 \times 10^{-26} = \frac{x^2}{4(1-x)^2} \quad (\text{v})$$

To simplify the problem, note that the dissociation of ammonia is very small and  $x \ll 1$ . Approximate  $(1-x)^2$  as 1, then (v) becomes

$$\frac{x^2}{4} = 4.873 \times 10^{-26} \quad (\text{vi})$$

Now solve to obtain  $x = 4.42 \times 10^{-13}$ . This is the number of moles of  $\text{NH}_3$  that is ionized. To find the number of molecules, remember that 1 mole =  $6.02 \times 10^{23}$  molecules.

$$x := 4.42 \cdot 10^{-13} \cdot \text{mol} \quad y := 6.02 \cdot 10^{23} \cdot \text{molecules/mol}$$

$$X := x y$$

$$X = 266084000000.000 \text{ molecules mol mol}^{-1}$$

So,  $2.66 \times 10^{11}$  molecules of ammonia are ionized.