Acid base equilibria 1

Indicate the equilibrium equation and the constant expression for the auto-protolysis of liquid ammonia. If $K_{NH3} = 10^{-22}$, 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-proteolysis is the phenomenon whereby an ammonia molecule can donate a proton to another NH_3 molecule to form a positive and a negative charged species. The equation of the auto-protolysis can be written as

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

or

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^- \qquad \text{(i)}$$

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

$$K_1 = \frac{(NH_4^+)\cdot(NH_2^-)}{(NH_3)^2}$$

Note that the concentration of NH_3 in pure ammonia is always constant. By the analogy of the auto-protolysis of water (where the K_W expression is written $(OH^-)\,(H_3O^+)$, - without $(H_2O)^2$ in the denominator), the constant expression for the auto-protolysis of NH_3 is

$$K_{NH3} = (NH_4^+)\cdot(NH_2^-) \qquad \text{(ii)}$$

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

$$K_1 = \frac{(NH_4^+)\cdot(NH_2^-)}{(NH_3)^2}$$

Let x be the number of moles of ammonia ionized. Then the NH_3 remaining non-ionized is 1 - x moles. Since each 2 ammonia molecules must ionize to produce a single NH_4^+ and one NH_2^-, the number of NH_4^+ is equal to the number of NH_2^- = x / 2. Let V be the volume of one mole of ammonia. The concentration of NH_4^+ and NH_2^- can be written as (x / 2) / V_1, and the concentration of non-ionized NH_3

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

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

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

$$K_1 = \frac{(NH_4^+) \cdot (NH_2^-)}{(NH_3)^2}$$

The numerator (NH_4^+) (NH_2^-) is the constant expression for the auto-protolysis of NH_3 and must always equal $K_{NH3} \cdot K_{NH3}$ and is given as $10^{-22.}$

To find $(NH_3)^2$,use the fact that the density of ammonia is 0.771 g/ml. The mole weight of ammonia is

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

and the density of ammonia is 0.0453 mol/ml = 45.3mol / liter, so (NH_3) = 45.3 M. Substitute these results in

$$K_1 = \frac{(NH_4^+) \cdot (NH_2^-)}{(NH_3)^2}$$

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

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

Substitute this value of K_1 into (iii)

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

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

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

Now solve to obtain $x = 4.42 \times 10^{-13}$. This is the number of moles of NH_3 that is ionized. To find the number of molecules, remember that 1 mole = 6.02×10^{23} molecules.

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

$$X := x\,y$$

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

So, 2.66×10^{11} molecules of ammonia are ionized.