The System $(NH_4)_2SO_4$-NH_4Cl-Ag_2SO_4-$AgCl$-H_2O

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CONTENTS

C O N T E N T S

INTRODUCTION

Considering a system derived from water and two electrolytes which do not yield a common ion, the equilibrium which must exist between the two electrolytes can be expressed by the equation:

$$AM + BN = AN + BM$$

Such equilibria involve a simple interchange between the acidic and basic constituents. Systems of this kind were designated by Meyerhoffer (14) "reciprocal salt pairs", but the term is now generally applied to systems of this kind in which water is present as an additional component. In the presence of water the equilibria are determined almost entirely by the extent to which the four salts are dissociated and by the relative solubilities of these salts and their different hydrates. If the salts are capable of forming double salts or solid solutions the solubility of these are also important factors in the equilibria.

Investigations of such systems are not common in literature but perhaps one of the most interesting is the system $CuSO_4$ - $CuCl_2$ - $(NH_4)_2SO_4$ - NH_4Cl - H_2O studied by Schreinemakers (21) (22). As will be shown in the sequel a case of "reciprocal salt pairs" constitutes a quaternary system; that is, a system of four components and such studies are of interest not only from the point of view of the individual properties of the substances participating but also from the view of the mode of representation. The investigation of Schreinemakers produced several double salts and also introduced a new method of representing quaternary systems.

Somewhat similar to the work of Schreinemakers, this investigation concerns the system $(NH_4)_2SO_4$ - NH_4Cl - Ag_2SO_4 - $AgCl$ - H_2O. The participating substances are connected by the equation:

$$2NH_4Cl + Ag_2SO_4 = (NH_4)_2SO_4 + 2AgCl$$

A complete study of this equilibrium involves the investigation of the four ternary systems making up the quaternary. These are as follows:

(a) Ag_2SO_4 - $AgCl$ - H_2O

(b) $(NH_4)_2SO_4$ - Ag_2SO_4 - H_2O

(c) NH_4Cl - $AgCl$ - H_2O

(d) $(NH_4)_2SO_4$ - NH_4Cl - H_2O

Since Schreinemakers investigated the ternary system $(NH_4)_2SO_4$ - NH_4Cl - H_2O, his results will be used in this work.

A further point of interest in the investigation involves the formation of double salts. The copper ion and ammonia form a complex in solution and Schreinemakers was able to find double salts of the two salt pairs $CuSO_4$-$(NH_4)_2SO_4$ and $CuCl_2$ - NH_4Cl. It is a well known fact that silver chloride because of the complex formed between silver and ammonia will dissolve in dilute ammonia water. It might then be expected that double salts would exist between the pairs $(NH_4)_2SO_4$ - Ag_2SO_4 and NH_4Cl - $AgCl$. Although such double salts were not found at the temperature of the investigation, evidence from increased solubility of the silver salts and constancy obtained in the equilibrium expression indicates their existence.

In industrial analysis valuable silver from silver chloride is recovered by a dangerous process involving nitric acid and alcohol. It was thought possible through the existence of the equilibrium

$$2NH_4Cl + Ag_2SO_4 = (NH_4)_2SO_4 + 2AgCl$$

or through formation of double salt, that silver chloride could be reintroduced into solution in some usable form. However, by the ordinary means of analysis no silver ion could be found in solution from the action of a saturated solution of ammonium sulphate on silver chloride, and although the solubility of silver chloride was increased many thousands in ammonium chloride solution, it still was insufficient to warrant use industrially.

THEORETICAL CONSIDERATIONS

The Investigation and Graphical Representation of Two Salts and Water -

As stated previously a complete investigation of the system $(NH_4)_2 SO_4$ - NH_4Cl - Ag_2SO_4 - $AgCl$ - H_2O involves the study of the four ternary systems:

(a) Ag_2SO_4 - $AgCl$ - H_2O

(b) $(NH_4)_2 SO_4$ - Ag_2SO_4 - H_2O

(c) NH_4Cl - $AgCl$ - H_2O

(d) $(NH_4)_2 SO_4$ - NH_4Cl - H_2O

These are special cases of ternary systems since they are all composed of water and two salts with a common ion. The problem of representation of such systems has been solved in many ways [(15), (23), (30), (19), (10)]. The method to be used in this work was first suggested by Gibbs [(7)] and later independently by Stokes [(28)]. It has since been greatly elaborated by Roozeboom [(20)]. The method of representation consists in employing an equilateral triangle with lines ruled parallel to each side of the triangle, the length of a side is made equal to unity or one hundred; the sum of the fractional or percentage amounts of the three components being represented therefore by a side of the triangle. The composition of a ternary mixture is obtained by determining the distance in a direction parallel to the three sides of the triangle (Figure 1). Conversely, in order to represent a mixture consisting of say a, b, and c parts of the components A, B and C respectively, where $a \neq b \neq c = 100$, divide one side, say AB of the triangle into

100 parts. Since apex A represents 100% A we plot from B, the distance Bx representing a parts of A, and since apex B represents 100% B we plot from A the distance Ax' representing b parts of B (Figure 1). Since AB = 100 and a + b + c = 100 the remainder xx' represents c parts of C. From x and x' lines are drawn parallel to the sides of the triangle and the point of intersection P represents the composition of the ternary mixture of given composition; for as is evident from the figure, the distance of the point P from the three sides of the triangle, when measured in directions parallel to the sides is equal to a, b and c respectively. Since all investigations in this work were carried out at 30°, isothermal diagrams only will be considered here.

We now consider the form that will be taken by the equilibrium diagram of an aqueous solution of two salts when plotted on the equilateral triangle. In the simplest case where no double salts are present a two-branch curve results, represented by acb in Figure 2. In this diagram a represents the solubility of salt A, b represents the solubility of salt B, while the curves ac and bc represent ternary solutions in equilibrium with solid salt A and solid salt B respectively. At c we have an isothermally invariant system in which the solution is in equilibrium with both salts as solid phases.

Where the two components A and B form a compound,

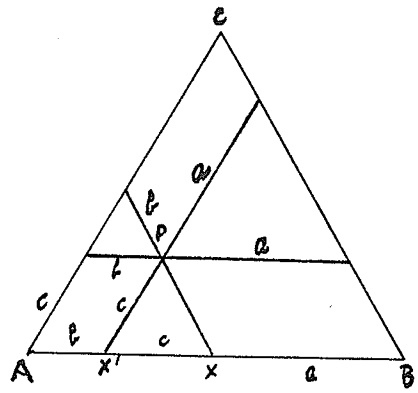

Fig. 1

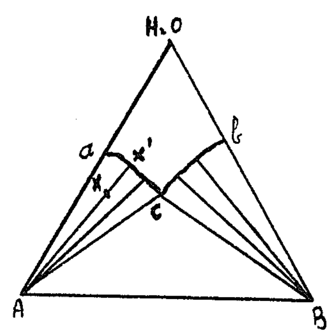

Fig. 2

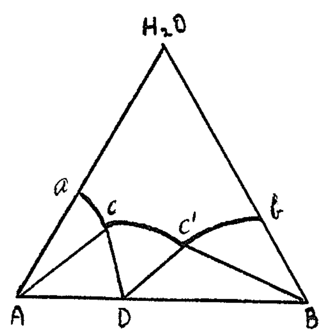

Fig. 3