THE DOUBLE DECOMPOSITION REACTION

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The many new methods of investigating sub-atomic phenomena that have been developed chiefly by physicists during the last twenty-five or thirty years have given us a knowledge of the nature of chemical reactions and chemical compounds that entirely overshadows the theoretical knowledge of the chemists at the beginning of the present century. Merely a partial list for the last twenty years alone includes such significant discoveries and theories as Rutherford's nuclear atom, Laue's X-ray crystal analysis and the modifications and improvements by the Braggs and others, Moseley's determination of the relative atomic numbers and Chadwick's absolute determination, the Bohr theory, the Lewis-Langmuir theory, polar and non-polar compounds, electrovalence and covalence, the Debye-Huckel theory of complete ionization and interionic attraction of strong electrolytes, Millikan's exact determination of $\frac{e}{m}$, Rutherford's artificial disintegration of light atoms, Aston's mass spectrograph and the isotopes, the packing effect and evidence of the change of mass into energy, the cosmic rays and Millikan's theory of the synthesis of matter from radiation, the theory of wave mechanics, and the Heisenberg atom.

These subjects may all be said to fall within the scope of atomic and sub-atomic physics, and yet they have changed the appearance of a large part of theoretical chemistry to such an extent as to make it an almost unrecognizable science to a chemist of 1900.

In contrast to the situation that existed at that date we now know how many elements there are between hydrogen and uranium; why most atomic weights deviate largely from whole numbers while some do not; that atoms, molecules, and ions are now established facts, for we can measure their individual sizes and weights, their relative positions with respect to each other in substances and the number of them in a gram. We can even measure changes in the size of atoms due to the loss of valence electrons when they are oxidized to positive ions or the gain of such when they are reduced to negative ions.

These and many other recent advances certainly suggest the fitness of re-examining the stock ideas of the presentation of general chemistry. It is the purpose of this paper to do so for the double decomposition reaction.

Most of the reactions that a student in inorganic chemistry and qualitative analysis deals with have been included by conventional classification in this type. The most common examples have been reactions in which a precipitate is formed, such as the formation of in-

soluble silver chloride by mixing solutions of silver nitrate and sodium chloride,

(I) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

and the formation of two insoluble precipitates, silver chloride and barium sulfate, as illustrated by substituting barium chloride for the sodium chloride in equation (I) and silver sulfate for the silver nitrate,

(II) $Ag_2SO_4 + BaCl_2 \rightarrow 2AgCl + BaSO_4$

That something happens in these two cases is obvious. But even when no precipitate is formed an imaginary reaction has been supposed to occur, as when sodium nitrate and potassium chloride solutions are mixed. This has been written

(III) $NaNO_3 + KCl \rightarrow NaCl + KNO_3$

and has been widely used for years.

The other most important kind of reaction that has been grouped with these is the neutralization reaction, for example

(IV) $NaOH + HCl \rightarrow NaCl + H_2O$

and we have characterized this by the formation of a slightly ionized substance rather than an insoluble one.

In addition to the above cases this category has been made to include complex ion formation and reactions at electrodes during electrolysis (Schlesinger, *General Chemistry*, 1930, p. 271), which seems to the writer to be like adding further burdens to an already broken down horse. At least this paper is an attempt to show that the double decomposition reaction is such.
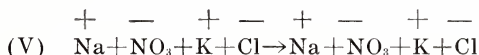
The justification for the name "double decomposition," or "transposition," or the more high sounding synonym, "metathesis," has been the statement that the two substances written on the left in the equation both decompose. This statement assumes that *molecules* of these substances, which in most instances are strong electrolytes, really exist in the solution. This idea is greatly emphasized by the mistaken but unfortunately general custom of writing molecular formulas for strong electrolytes.

To a student in elementary chemistry it seems curiously inconsistent for his instructor to make such use of molecules and molecular formulas and then to tell him that nearly fifty years ago Arrhenius produced excellent evidence that most of the material in solution was present as ions rather than as molecules. In fact Arrhenius and his contemporaries had no evidence that any molecules were present. They simply found that a certain part of the substance did not show the activity that was characteristic of ions. It was, therefore, supposed that this part must be present as molecules. This explanation was very successful for weak electrolytes, the degree of ionization of which found quantitative expression in Ostwald's dilution law.

The assumption of the existence of molecules of strong electrolytes by the chemists of fifty years ago was a natural one. A particular importance was being attached to them in those days. It was less than thirty years since Cannizzaro had pointed out the use of molecular

weights in the method of determining atomic weights. It was only nine years before Arrhenius proposed the ionic theory that Victor Meyer devised his vapor density method for determining molecular weights.

The fact that the Ostwald dilution law does not hold for strong electrolytes has been known for years, nevertheless, many chemists still continue to treat strong electrolytes qualitatively in the same way as they do weak electrolytes. Other evidence of this inconsistency is to be found in their failure to accept the implications of the constant heat of neutralization of strong acids and bases, and of Hess' law of thermoneutrality, which was discovered as early as 1841. The latter states that if two neutral salt solutions at the same temperature are mixed together, no change of temperature occurs. The theory of complete ionization is strikingly successful in explaining the reason for this. No temperature change means no reaction at the time of mixing. Consequently equation (III) does not represent the situation as it exists. The substances are ions and mixing ions does not necessarily produce a reaction. See equation V.

$$\text{(V)} \quad \overset{+}{\text{Na}} + \overset{-}{\text{NO}_3} + \overset{+}{\text{K}} + \overset{-}{\text{Cl}} \rightarrow \overset{+}{\text{Na}} + \overset{-}{\text{NO}_3} + \overset{+}{\text{K}} + \overset{-}{\text{Cl}}$$

The combination of the ions into the four possible kinds of crystals occurs only when the solution is evaporated to dryness. The difference from the cases shown in (I) and (II) is in degree of solubility only.

In recent years the conception of complete ionization of strong electrolytes has received practicaly conclusive verification from X-ray crystal analysis, which has been applied to the crystalline forms of many strong electrolytes and has shown that they are composed entirely of ions. There are no molecules distinguishable in the crystal. If such is the case then there certainly are none in a solution of the crystal, for the ions are then farther apart than they are in the crystal itself.

In 1923 Debye and Huckel contributed further to the cause of complete ionization when they proposed an interionic attraction theory to explain the behavior of strong electrolytes. It has done so very successfully. We need no longer be concerned about their failure to follow the Ostwald dilution law, which would postulate the presence of molecules. Neither do we need to suppose that molecules are present in strong electrolytes.

In conclusion the writer suggests that it is inaccurate, misleading, and a waste of time to use molecular formulas for strong electrolytes in any instance. The time-honored double decomposition reaction does not exist. In its place we have several different kinds of changes, for instance, crystallization when precipitates are formed, or a change from electrovalence to covalence in neutralization reactions. Complex ion formation is a matter of co-ordinate covalence, and electrolytic reactions are best considered as oxidation-reduction changes.