

aqueous solution by means of a "semi-permeable" wall, the author said that solutions of salts in water are intimate mixtures which can be separated, to some extent, by mechanical means. This implies, and, indeed, the author said he was of the opinion, that salts preserve their identity when in solution. If this is not the case, on what other assumption can the osmotic phenomena be explained? If we now examine a few well-known examples, we will see that this statement is by no means without experimental proof. As a rule, the solubility of a solid in a liquid increases with rise of temperature; certain substances, however, such as slaked lime, decrease in solubility with rise of temperature; and this has been shown to be due to the fact that as the temperature rises the dissolved substance—in this case the calcium hydrate, $\text{Ca}(\text{OH})_2$ —loses water, and is converted into a less soluble substance—namely, lime, CaO . This is an instance of the dissolved salt actually being dehydrated when in water in the same way as when in solid pieces. This kind of decomposition, if it does not actually prove that the salt retains its identity when in solution, can only be explained with that assumption. If such changes are possible in aqueous solutions, with which metallic solid solutions are analogous, then it is quite reasonable to expect that similar changes may also occur in metallic alloys. Another interesting example is that of sodium sulphate; this salt exists as a solid in three forms—namely, the anhydrous salt Na_2SO_4 , the heptahydrate $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, and the decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The solubility curve of sodium sulphate in water is shown in Fig. 1. The first portion of the curve represents the solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. It will be seen that the solubility of this salt rapidly rises with the temperature up to 34 deg. Cent., after which it gradually diminishes with further rise of temperature. The decahydrated salt decomposes at temperatures above 34 deg. Cent. into the anhydrous salt, and water saturated with that salt; therefore the second portion of the curve corresponds to the solubility of the anhydrous salt in water. Now in such cases of solution the changes which occur in the solution seem quite inexplicable if it is assumed that the dissolved substance is absorbed by the molecules of the solvent, or, as is frequently stated, that the solute actually liquefies.

From these facts we learn that a dissolved hydrate can lose its water of hydration even when the particles of the hydrate are apparently in contact with water; whether the particles of solute and solvent are actually in contact is a matter that will be considered later. In any case it is evident that a dissolved body may undergo the same changes when in solution as when in the pure solid condition.

Van't Hoff's Law.—When the temperature of a system in equilibrium is raised, that reaction takes place which is accompanied by an absorption of heat, and conversely, when the temperature is lowered, that reaction occurs which is accompanied by an evolution of heat.

Le Chatelier's Law.—When the pressure on a system in equilibrium is increased, that reaction takes place which is accompanied by a diminution of volume; and when the pressure is diminished, a reaction ensues which is accompanied by an increase in volume.

These two theories are embraced in Le Chatelier's law, which may be stated as follows:—If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint—i.e., one by which its effect is partially destroyed.

In accordance with this law, increase of solubility with the temperature must occur in those cases where the process of solution is accompanied by an absorption of heat; and a decrease in the solubility with rise of temperature will be found in cases where solution occurs with evolution of heat.

In applying the theorem of Le Chatelier to the course of the solubility curve, it should be noted that by heat of solution there is meant, not the heat effect produced on dissolving the salt in a large amount of solvent, but the heat which is absorbed or evolved when the salt is dissolved in the almost saturated solution. Not only does the heat effect have a different value, but it may even have a different sign. Despite its many forms, it should be noted that the solubility curve of any substance is continuous so long as the solid phase, or solid substance in contact with the solution, remains unchanged. If any "break" or discontinuous change in the direction of the curve occurs, it is a sign that the solid phase has undergone a change. Conversely, if it is known that an alteration of the constitution of the solid phase takes place, a break in the solubility curve can be predicted. From these facts it follows that a salt, even when in solution, may undergo the same changes on heating that solution as when the pure salt is heated alone, and as a logical consequence it follows that it is possible only if the salt retains its identity when in solution. Therefore the author considers he is amply justified in concluding that in all cases solutions are not absolutely homogeneous—that is, though they may have the same composition in all their parts so far as is shown by ordinary analysis or physical tests, yet there is a region beyond which a solution cannot be regarded as homogeneous, or, in other words, the particles of solute are not actually in union with the particles of solvent.

In the discussion on the previous paper it was suggested that this conception as applied to solid solutions was incompatible with the phase rule. Needless to say, the author fully appreciates the value of this important rule, and applies it whenever possible; but he would point out that there are limits to its application, and one of these limits is reached when it is attempted to apply the rule to the molecular constitution of a phase.

In deducing his law, now known as the phase rule, Gibbs regarded a system as possessing only three independent variables—viz., temperature, concentration, and external pressure; among other less important items no account is taken of the internal pressure of a phase, not even in the case of solutions. The rule defines the state of a system in equilibrium by the relation existing between the number of components and the number of phases present, quite independently of the amount of each phase and the internal constitution of the participating substances. Therefore in attempting to determine the internal nature of a solution the phase rule, as expressed by the equation $F = C + 2 - P$, should not be applied, for with this equation it is presupposed that a solution is homogeneous. But because in the application of the phase rule it is supposed that a solution is homogeneous, it does not therefore follow that that is indeed the case; and if it is decided that a solution is a physical mixture coming outside the region of the above equation, it will not detract from the value of the phase rule. For, as a matter of fact, while the author is convinced that the phase rule should be disregarded in trying to decide whether a solution is or is not homogeneous, in the strictest sense of the word, once this question is decided, and if in favor of the author's conception, it becomes even more important to apply the phase rule in order to know exactly what substance is in solution. An example of the limitation of this rule is evident in the case of gaseous solutions, when, from the point of view of the phase rule, there is only one phase present—namely, vapor; and yet there is not the slightest doubt that in gaseous solutions each gas present retains its own properties, and is unaffected by the presence of others.

Another interesting question was raised by Dr. Guertler. He said:—"If it was assumed, with the author, that there existed a very fine mixture of separate crystals in the one solid