

Ellery, professor of chemistry and chairman of the faculty of Union College at the chemical laboratory, papers will be presented. The visitors will then go to Troy and will inspect the new aeronautical, chemical and metallurgical engineering laboratory of Rensselaer Polytechnic Institute. An informal dinner will be held at 7:00 P. M. at which the president of the institute, Dr. William O. Hotchkiss, will greet the visitors. At 8:30 P. M. Dr. C. E. K. Mees, of the research department of the Eastman Kodak Company, will give an illustrated lecture on "Color Photography and the Kodachrome Process." Saturday morning will be given over to the presentation of papers at the Walker Chemical Laboratory.

IN order to have as its guest and principal speaker Dr. Robert A. Millikan, of the California Institute of Technology, the annual meeting of the U. S. Institute

for Textile Research will be postponed from November 7 to November 14, but will be held as originally planned at the Waldorf-Astoria, New York, N. Y. To celebrate the end of its fifth year, and to honor Dr. Millikan, the institute will give a dinner that evening at which President Francis P. Garvan, who is also president of the Chemical Foundation, will act as toastmaster. Another feature of the dinner will be reports of several applications of scientific textile research in the mills by technicians responsible for them. Dr. J. R. Katz, director of the institute's warp sizing research, now in progress at the Massachusetts Institute of Technology, will also speak. The regular annual meeting and meeting of the board of directors will be held in the morning. In the afternoon the Research Council will hold an open conference on the subject of creping of regenerated rayon and acetate fabrics, to which all who are interested are invited.

DISCUSSION

THE SOLUTE AS LIQUID

ONE of van't Hoff's great achievements was the proof that in dilute solutions a dissolved substance behaves in some respects like an ideal gas. A corollary, not drawn by van't Hoff, was to consider the solute as in all respects like a gas. Nernst¹ stated that a third substance, added in small amounts, has no more effect on the solubility than a gas will have on the partial pressure of a solid. This is not true experimentally, because any addition of alcohol to a saturated solution of sugar or sodium chloride will cause a decrease in solubility.² There is no need of speaking of a change in thermodynamic environment.

If we start with ether and methyl alcohol, the alcohol is called a gas and the ether a liquid at all concentrations if one has a rubber diaphragm, while the ether will be called a gas and the alcohol a liquid at all concentrations if one uses an animal bladder membrane. On the other hand, one of the criteria of two ideal liquids, benzene and toluene at 35°, is that the two shall mix without volume expansion or contraction. So far as volume relations are concerned, neither liquid behaves as a gas at any concentration.

This has been recognized by Lumsden,³ who stated that a binary, non-aqueous solution is a mixture of two liquids. He excluded aqueous solutions because of difficulties in connection with ionization, hydration, etc. While these present problems experimentally, they do not affect the general principles. Putting Lumsden's concept in a broader form, all liquid solu-

tions are mixtures of liquids, regardless whether any or all of the pure components are solids, liquids, vapors or gases at the temperature of the experiment. As such, all the components will show some of the properties of liquids.

If either component of a binary solution may act in some respects as a liquid and in other respects as a gas, we must clear up the apparent discrepancy. That is merely a question of wording. Instead of saying that at low concentrations the solute behaves more or less like an ideal gas so far as osmotic pressure relations are concerned, we say that at low concentrations a solute (present as liquid) or a suspended particle (present as solid, liquid or gas) behaves more or less like an ideal gas so far as osmotic pressure is concerned. This includes both the van't Hoff generalization and also the Einstein⁴ generalization that suspended particles behave like an ideal gas when the sol is dilute.

Perrin⁵ speaks of gamboge granules large enough to be visible in sunlight under a strong lens as behaving like an ideal gas with a molecular weight of two hundred thousand tons. Nobody supposes that these gamboge particles are gases or that the crystals of gold in a red gold sol are not solid. When we call a solute a gas, it is a purely metaphysical gas.

Some interesting consequences follow. A fused salt is a liquid. If the fused salt is considered to be completely dissociated, the ions must be liquids at the temperature in question. If the fused salt is not completely dissociated, the ions must either be liquids or

¹ Nernst, "Theoretische Chemie," 386, 1893; Nernst-Codd, "Theoretical Chemistry," 564, 1923.

² Lash Miller, *Jour. Phys. Chem.*, 1: 633, 1897.

³ Lumsden, *Jour. Chem. Soc.*, 91: 24, 1907.

⁴ Einstein, *Ann. Physik*, (4) 17: 549, 1905; 19: 280, 371, 1906.

⁵ Perrin, "Brownian Movement and Molecular Reality," 46, 1910.

they must be gases dissolved in the liquid, undissociated salt. Owing to the practically complete absence of salt ions in the vapor phase under ordinary conditions, it is improbable that the ions of a fused salt are to be considered as dissolved gases. We conclude, therefore, that a fused salt consists of liquid ions and an unknown amount of liquid undissociated salt. As liquids, the two ions and the undissociated salt singly must have solvent or precipitating action, and this action must be selective. With sodium nitrate, potassium nitrate and lithium nitrate, each salt lowers the freezing point of either of the others.

In aqueous solutions of two salts with a common ion, we have, theoretically at least, a decrease of solubility, on account of the precipitating action of the common ion and an increase in the solubility due to the mutual solvent action of the two salts. If one of the salts is sparingly soluble, the solvent action of the other will be negligible in low concentrations and the precipitating effect of the common ion will be practically the whole thing.

There is no evidence of a complex salt between sodium and potassium nitrate; but potassium nitrate is more soluble in a sodium nitrate solution than in pure water. This is probably due to solvent action by liquid sodium nitrate and its liquid ions, anhydrous or hydrated as the case may be. One can predict that, at high enough temperatures, all the isotherms for water and two salts with a common ion, forming no other solid phases than these two pure salts, will be concave to the water corner of the triangular diagram, instead of being convex, as most of them now are.

If a sparingly soluble salt behaves like a dissociating gas, the concentration of the undissociated portion in a saturated solution should be constant, irrespective of the addition of another salt with a common ion. Arrhenius⁶ showed that addition of sodium monochloracetate to a saturated solution of silver monochloracetate forced the total solubility of the silver salt below the calculated concentration of the undissociated silver salt in water. Similar results were obtained with silver propionate and butyrate and the corresponding sodium salts. We do not yet know why this should be; but we know now that the belief that the concentration of the undissociated portion of the silver salt must remain constant was based on the false assumption that the solute must behave in all respects like a gas.

When solid benzene dissolves in liquid toluene at -20° , we do not postulate solvation. We merely say that benzene is soluble in toluene—as it is. When sodium nitrate dissolves in nearly pure nitric acid, sodium acetate in pure acetic acid or lead sulfate in

pure sulfuric acid, we do not postulate solvation, though it may occur. We say that these substances are soluble in these liquids, just as we say that sodium chloride or sugar is soluble in water. If we start with a saturated solution of lead sulfate in water and add sulfuric acid continuously, there is at first a decrease in solubility owing to the presence of a common ion, and then an increase in solubility.⁷ One should say that lead sulfate is soluble in sulfuric acid and is precipitated by water. There is a minimum solubility for lead chloride and hydrochloric acid, calcium sulfate and sulfuric acid, fluorides and hydrofluoric acid, and doubtless in many other cases.

Schukow⁸ showed that potassium chloride and sodium chloride increase the solubility of sugar in water, but nobody knows whether this means that sodium and potassium chlorides are soluble in melted sugar.

The general results of this paper are:

(1) All liquid solutions are mixtures of liquids, regardless whether any or all of the pure components are solids, liquids, vapors or gases at the temperature of the experiment.

(2) The ions in a fused salt or in a solution are present as liquids and may exert a precipitating or solvent action.

(3) In low concentration a dissolved liquid or a suspended particle will behave in some respects like a gas. This postulate reconciles the conclusion of van't Hoff on true solutions and of Einstein on sols with the fact that true solutions are mixtures of liquids, showing in some cases the properties of liquids, and with the fact that the dispersed phase in a sol is rarely a gas.

(4) While it is customary and profitable in physical chemistry to treat the solute thermodynamically as a gas under certain circumstances, it is actually a liquid and is a gas only in a metaphysical sense. It is then not preposterous to say that the osmotic pressure may be that of a gas in a volume into which the liquid solute could not possibly be compressed.

(5) When dealing with the effect of one salt on the solubility of another salt, it is not safe to ignore the direct or indirect solvent or precipitating effect of the third ion or the undissociated salt on the solubility of the second salt.

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ON THE FORMATION OF LAKE BALLS

UNDER this heading in *SCIENCE* for August 30, A. G. Huntsman describes certain balls obtained by Dr. H.

⁷ Ditz and Kanhäuser, *Z. anorg. allgem. Chem.*, 98: 128, 1916.

⁸ Schukow, *Z. Vereins deutsch. Zucker-Industrie*, 50: 291, 1900.

⁶ Arrhenius, *Z. physik. Chem.*, 31: 225, 1899.