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Phase and Volume Relations in Gas-Liquid Systems at High Pressures: Experimental Technique

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During the period of more than seventy years from the beginning of the 19th Century (1801-1873), problems of gaseous solutions did not exist in science.

In 1801, Dalton /1/ asserted in his law that the pressures of gases in a mixture are independent, which in principle eliminates the question of solubility of a liquid in gases. The dispute between the antagonists Berthollet, Saussure and Le Rou, who defended the chemical point of view of solution of water by air, and Dalton, was decided in favor of Dalton and his followers. The concept of the gas mixture, which asserted the independent existence of water vapor in the gaseous medium, regardless of its composition and density, was maintained in science and in practical work for a long time.

The first chemist to come forward against these firmly entrenched incorrect ideas was Mendeleev. In a course of theoretical chemistry given by him in 1873-4, he wrote /2/: "By solutions we usually mean only solutions of gases, liquids, and solids in liquids. But this concept is narrow and therefore incorrect. There may also occur solution of a gas in a solid, of a liquid in gases, etc. Regnault made some remarks about the existance of the last phenomenon. He noted that the pressure of vapor in air is not equal to the pressure in an evacuated space, although one should expect the contrary, taking into account the properties of gases. From (#1) this fact the conclusion may be drawn that between vapors and air there exists a more intimate connection than a simple mixing, such as that between a solvent and a dissolved substance; we have here, it seems, an indication of the existence of solution of a liquid in gases".

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The old ideas, however, proved very durable. It was only gradually, under the influrence of practice, and of the experimental material accumulated in laboratories and in industry, that the old views of Dalton, on the incorrectness of which Mendeleev first spoke out, began to be replaced by the new ideas.

In some areas this had begun some time earlier, and had entered firmly into scientific and technical usage (the equations of state of real gases), while in other areas the process is still going on at the present time, particularly as regards solutions of liquids in compressed gases.

A typical example is the well-known monograph by Hildebrandt "Solubility of Non-Electrolytes" /3/, in which, 60 years after the work of Mendeleev, there is not a single line devoted to gaseous solutions.

Expressions like "the content of ammonia vapor in a mixture of hydrogen and nitrogen under pressure"-instead of "the solubility of liquid ammonia in a mixture of hydrogen and nitrogen under pressure"-are still regarded as usual in scientific and technical literature.

The practice of using high pressures in the chemical industry in the last 25 years has led to the final triumph of Mendeleev's ideas concerning gaseous solutions. In the periodic literature one now encounters, more and more frequently, papers on investigations of gaseous solutions, particularly by Soviet authors.

However, until now these papers dealt only with the study of solubility of liquids in high pressure gases, and vice versa, and as the most recent investigations have shown, these data are not sufficient to form a basis for the problem as a whole.

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