

Gamburg, D. Yu.

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

Zhurnal Fizicheskoi Khimii, Vol. 24, No. 3, PP. 2720278 (1950)

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 existence 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".

The experimental studies have been mainly of dilute solutions. It would

The old ideas, however, proved very durable. It was only gradually, under the influence 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.

The experimental studies have been mainly of dilute solutions. It would

that the thermodynamic properties of these solutions should be expressed by the laws of Henry and Raoult. Combined with general thermodynamic relations, these laws permit us to calculate all the properties of solutions--both volumetric and thermal.

We recall, however, that Mendeleev /4/ in "Basic Chemistry" wrote: "It should be noted that the Henry-Dalton law belongs to a group of approximate laws, similar to the gas laws (Gay-Lussac and Mariott) and many others, i. e., it describes only a part of a complex phenomenon, a limit to which the phenomenon tends. Here the complication arises from the influence of the degree of solubility and the degree of affinity of the solvent gas to water".

The untenability of Henry's Law, both in its classical form, and in its strict thermodynamic form, given to it by Lewis and Randall /5/, has been established by numerous experimental investigations.

The dependence of the Henry coefficient on pressure was first studied by Krichevskii et al /6/. In another paper Krichevskii et al /7/ showed that the limiting Henry law could not give correct values of partial molar volumes of a dissolved gas.

It has been established that the study of volumetric properties of solutions is a delicate method which permits detection of the deviation from the laws of infinitely dilute solutions in the region of extreme dilution /8/.

Accordingly, we also have set up our problem of obtaining experimental data on the volume and phase relations in gaseous solutions.

Because of the considerable experimental difficulties there have been as yet no such investigations for gas-liquid systems. The present work represents the first attempt to overcome these difficulties, and to create an

equipment which would allow reliable measurements of partial molar volumes of liquids dissolved in compressed gases, over a wide range of concentrations. In addition to the volume relationships, the equipment permits a study to be made at the same time of phase equilibria in liquid-gas systems.

This paper is devoted to a description of the technique that we have developed for simultaneous determination of phase and volume relationships in gas-liquid systems in the special high pressure equipment that we have built in the Institute of the Nitrogen Industry.

We shall give the experimental data obtained and their thermodynamic reduction in subsequent articles.

Description of the Equipment and the Principle of its Operation

Values of the partial molar volumes may be calculated from the experimental P - V - T - N_2 data.

In spite of this apparently being the most direct approach, in fact, in an approximate examination, it proves to be the least accurate. In very dilute gas solutions, in which our only interest lies, the unavoidable errors in measuring temperature and pressure may distort the dependence of the volume of a gas solution on the concentration of the dissolved substance. The danger is all the greater, since calculation of the value of the partial molar volume involves the taking of the derivative of molar volume of the solution with respect to the molar fraction of the dissolved substance.

We have developed another experimental technique, whose principle will become clear from the following analogy.

We shall suppose that we require to study the vapor pressures of a solution as a function of its composition.

We may do this by successive measurement of the vapor pressures of the solution at different concentrations. At each measurement we shall then introduce errors in reading the temperatures and pressures, in comparison with the temperature and pressure of the pure solvent. These errors will be compensated if we use a differential tensometer, in one limb of which we place the pure solvent, and in the other--the solution.

In our case we built up an isothermal and isobaric differential volumeter, giving a direct indication of the variation of volume of the gaseous solution during solution of the liquid in it.

The two vessels A and B, joined by a capillary filled with mercury, are immersed in a thermostat 3 (Fig. 1).

Fig. 1. I--trap; II--coil; III--float; IV--mercury level.

If both vessels are simultaneously full of gas at a definite pressure, the mercury in the capillary does not alter its position.

We disconnect the vessels, and add a measured amount of liquid to one of them (B) from the vessel L at constant temperature. Upon solution of the liquid in the compressed gas, the pressure in vessel B changes, and the mercury in the capillary is displaced. By gradual alteration of the volume of the volumeter V connected to vessel B, we may cancel out the fall in pressure which occurred in the system upon solution of the liquid in the gas.

Thus, in the above theoretical approach to solution of the problem, the matter has been reduced to accurate observation of displacement of a mercury level in a capillary, and to accurate measurement of the volumes of liquid in the volumeter.

The equipment consists of three basic parts: the gas compressors with purifying system, the actual equipment for study of volume and phase relationships in gaseous solutions at high pressures, and the control console.

Compression of the gas to 1000 atm was performed by an ordinary GIVD compressor. To give higher pressures, the compressed gas at 1000 atm passed through a further compressor to 5000 atm. Following compression the gas was purified from oil in an oil separator and filter.

The equipment for studying the volume and phase relationships is a system of four high pressure cylinders, appropriately interconnected and fastened to an iron frame, the whole being immersed in the thermostat. All the vessels were designed for a working pressure of 5000 atm.

A general view of the equipment, fastened to the frame, is shown in Fig. 2.

Fig. 2.

Equalizer A (Fig. 1)--a cylinder with a volume of 330 cm^3 , is used to maintain constant pressure during the experiment. In the lower part of the equalizer are located the sensor coils, the float, and the trap for the mercury of the contact-less differential manometer. Below the capillary the equalizer is filled with mercury, and joined to the second cylinder of the system--the mixer B. The mixer has the same dimensions as the equalizer, and its function is to dissolve the liquid in the compressed gas. It is equipped with an electromagnetic stirrer, brought into motion by the solenoid D, mounted on top of the mixer.

The mixer is connected via a special steel ring to a vessel for adding (measured amounts of) liquid to the mixer--the dosimeter L, and to another vessel for measuring the change in volume of the system upon solution of the liquid in the gas--the volumeter V.

The dosimeter is a calibrated cylinder in which a piston travels. The piston is connected at the top to a reduction gear, driven by a motor. The dosimeter fills with liquid when the piston is in the upper extreme position, and when the piston moves down, the liquid batch is put into the mixer. A schematic of the dosimeter is shown in Fig. 3. Its working volume is 6 cm^3 .

The volumeter is a calibrated cylinder with a piston--an exact copy of the dosimeter. By varying the volume of the volumeter (raising or lowering the piston) during the test, we cancel out the drop in pressure created between the equalizer and the mixer upon solution of the liquid in the gas.

The scheme for connecting the dosimeter and the volumeter to the mixer is shown in Fig. 4.

The system in the assembled form is placed in the thermostat filled with transformer oil. The thermostat is equipped with two power shaft stirrers and two heaters mounted on the stirrer shafts. This arrangement of the heaters and stirrers secures a uniform distribution of temperature in the thermostat. Supplementary heaters, directly connected with a contact thermometer and a relay, ensure the constance of the temperature to within $\pm 0.2^\circ \text{C}$ during the test.

The head of the mixer, on which is mounted the solenoid, and into which passes the magnetic end of the stirrer, is separately thermostated. The solenoid is enclosed by an iron jacket into which oil from the thermostat

is supplied by a special pump, returning afterwards to the thermostat. The thermostat is located in a steel enclosure.

Fig. 3. (1) reduction gear; (2) piston; (3) gasket; (4) mixer.

Control of the equipment is concentrated on a panel mounted on the outside wall of the enclosure. There is remote control of all the values, the heater, the stirrer motors, the pump, differential manometer, etc.

As we have pointed out, the basic equipment is two vessels: the equalizer and the mixer, joined together below by a capillary filled with mercury. The capillary with the mercury terminates in the equalizer at a glass tube, on which is mounted a coil of fine wire. Inside the glass tube, at the location of the coil, there is a moving light float of Armco iron. In the mixer the capillary with the mercury terminated in a wide cup. When the pressure changes in the mixer following supply of the liquid into it, the mercury level in the capillary of the equalizer is displaced, displacing the float to a new position in the coil. The coil carries a well stabilized current. The change in position of the float in the coil changes its inductive reactance. The balance of the bridge scheme in which the coil is included is disturbed, and the pressure drop between the vessels may be assessed from the deflection of the needle of a galvanometer. The electrical arrangement of the contact-less differential manometer is shown in Fig. 5.

Fig. 4. (1) volumeter; (2) shut-off valve; (3) dosimeter; (4) mixer.

Fig. 5.

When a pressure drop is established in the system upon solution of the liquid in the gas, the drop is eliminated by moving the piston of the volumeter.

Using this kind of differential manometer one can determine the pressure drop to 0.025 mm Hg, at practically any pressure level.

Measurement of the volume change of the volumeter was carried out to an accuracy of $\pm 0.005 \text{ cm}^3$. The volume of liquid supplied to the system was measured to the same accuracy. Reading of the displacement of the pistons of the dosimeter and of the volumeter was done using a height gauge.

The Experimental Procedure

The course of the test may be examined according to the scheme of the equipment shown in Fig. 1.

To fill the equipment with gas, we use the piston motors to bring the volumeter piston to the extreme low position, and the dosimeter piston to the extreme up position. We separate the dosimeter from the mixer by valve 1. We open valve 2 and evacuate the dosimeter with a vacuum pump, after which the liquid is admitted to it, and valve 2 is closed. To fill the equipment with gas, we open valves 3, 4, and 5 and close valve 6. We fill the equipment with gas to the test pressure, and then wait, to allow the system to take up the temperature of the thermostat. Thereafter we uncouple vessels A and B, by closing valves 4 and 5, and note the null position of the galvanometer needle. We open valve 1. The pressure in the mixer then falls off somewhat since the liquid has not been compressed. Then with the motor we begin to move the dosimeter piston until the galvanometer needle returns to the null position, and therefore the liquid has been compressed to the test pressure.

Pressures up to 1500 atm were measured firstly with the coarse manometer I, and then with the precision Bourdon manometer K, to an accuracy of

± 2 atm; pressures above 1500 atm were measured on a manganin manometer L on the equalizer A.

During the test the tube leading from the equipment to the manometer was shut off by valves 3, 4, and 5; thus all the gas in the system was thermostated.

When the galvanometer needle was steady in the null position, we began to admit liquid into the mixer.

To accelerate solution of the liquid in the gas, we switched on the electromagnetic stirrer. On the galvanometer we noted a fall in pressure between the mixer and the equalizer.

When the fall became steady, by raising the volumeter piston, we added the additional volume to the system that completely cancelled out the pressure drop. The differential manometer galvanometer needle came back to its original position at the start of the experiment.

On the height gauges of the dosimeter E and volumeter G we read the volume of the liquid admitted to the system, and the change in volume of the system upon solution of this liquid into the compressed gas.

By plotting the movement of the dosimeter piston (volume of liquid admitted) against movement of the volumeter piston (change of volume of the system upon solution of the liquid), we obtain a graph. The slope of the curve relative to the x axis gives the value of the partial molar volume of the liquid in the compressed gas, in the homogeneous region.

Upon further supply of liquid there is a discontinuity in the curve. The point of discontinuity indicates saturation of the gas by the liquid.

Fig. 6.

The slope of the curve after the discontinuity, upon further addition of liquid, gives the value of the partial molar volume of liquid in the heterogeneous region.

The general form of the curve obtained, for example for the nitrogen-benzene system (at 50 atm and 50°C), is shown in Fig. 6.

Conclusions

1. An equipment has been built for measurement of the partial molar volumes of liquid dissolved in compressed gases.
2. The equipment permits data on partial molar volumes to be obtained in both the homogeneous and heterogeneous regions.
3. In addition to study of the volume relationships, the equipment allows data on phase equilibria to be obtained.
4. The equipment has been designed to operate at pressures from 1 to 5000 atm.

The Institute of the Nitrogen Industry
Moscow, Russia
Received 4 April 1949

References

1. John Dalton, Collected Works on Atomicity (1801-1810) (translated from English), GNTI, Leningrad, 1940.
2. D. I. Mendeleev, Works, 4, p. 283, 1937.
3. D. G. Hildebrand, Solubility of Non-electrolytes (translated from the 2nd English edition), GONTI, Moscow, 1938.
4. D. I. Mendeleev, Basic Chemistry, ed. 13, Vol. 1. p. 68, 1947.
5. Lewis and Randall, Chemical Thermodynamics (translation from English), ONTI, Leningrad, 1936.
6. I. R. Krichevskii, and Y. S. Kazarnovskii, Zhur, fiz. khim., 6, 1930, 1935.
7. I. R. Krichevskii, and A. A. Il'inskaya, Zhur, fiz. khim., 19, 621, 1945.
8. I. R. Krichevskii, Phase Equilibria in Solutions at High Pressures, GKHI, 1946.