

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

## THE SOLUBILITY OF HELIUM IN WATER

BY HAMILTON P. CADY, HOWARD M. ELSEY AND EMILY V. BERGER<sup>1</sup>

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The solubility of helium has attracted some attention, rather more from a theoretical standpoint than an experimental, because of the fact that the published results indicate that as the temperature is raised from 0°, the solubility passes through a minimum. The actual determinations are limited to a single measurement by Ramsay, Travers, and Collie,<sup>2</sup> a single series made by Estreicher<sup>3</sup> working under Ramsay, and two or three series by Antropoff and Ehmcke.<sup>4</sup>

Ramsay, Travers and Collie used Bunsen's method for determining the solubility and secured a lower result than anyone else. Probably they did not obtain complete saturation. Estreicher and Antropoff used the Ostwald method involving a gas buret connected to an absorption bulb by a glass helix, or spiral, to permit vigorous agitation of the water and gas in the absorption bulb. Estreicher's and Antropoff's work do not give as many independent measurements as appears at first sight. Estreicher placed in the apparatus a single sample of gas and water, the latter evidently not air-free<sup>5</sup> and then proceeded to make measurements at different temperatures.

His solubilities are so much greater than those measured by others that it is very probable that his helium was impure. Antropoff<sup>4</sup> used two different fillings of his apparatus with helium and water, making one set of readings at a series of temperatures with the first filling, and two with the second. Antropoff's results are fairly consistent, but as he himself points out, are certainly in error at each end of the series, because of an error of manipulation not discovered until the work on helium was finished.

There are, also, we think, two sources of error in his method which Antropoff did not suspect. These will be discussed later. In our own work, each measurement was made on a new specimen of helium and a fresh sample of water so each is independent and a check on the others. The helium was obtained from natural gas by liquefying the bulk of the other constituents and absorbing the remainder in a large quantity of active coconut charcoal, using only that part which comes off very easily to avoid pumping out with the helium, the more easily absorbed hydrogen and neon. Spectroscopic examination showed it to be pure.

<sup>1</sup> Publication has been greatly retarded by the death of Miss Berger during the progress of the work.

<sup>2</sup> Ramsay, Travers and Collie, *J. Chem. Soc.*, **67**, 697 (1895).

<sup>3</sup> Estreicher, *Z. physik. Chem.*, **31**, 176 (1899).

<sup>4</sup> Antropoff and Ehmcke, *Z. Elektrochem.*, **25**, 269 (1919).

<sup>5</sup> Fox, *Trans. Faraday Soc.*, **4**, 68 (1908). Ref. 4, p. 275.

### Manipulations

The apparatus used is shown in Fig. 1. R is a water thermostat whose temperature was automatically kept to within  $\pm 0.01^\circ$  of that desired. Before starting a measurement, the manometer between the bulb B and C was filled with mercury and the bulb B with dry air under atmospheric pressure. The tip of B was then sealed. At the moment of sealing B, the barometer was read and the observed pressure is given in the data, although, with our experimental procedure, it is not used in the calculation of  $\alpha$ . The volume of B is practically the same as that of the system C. To start a measurement, the bulbs C and F are exhausted through the 3-way stopcock below A, the intermediate

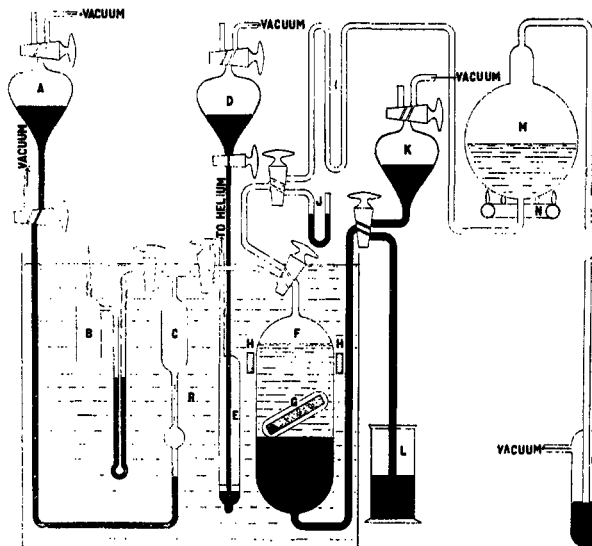


Fig. 1.

stopcocks being properly placed to leave a free passage. During the process, the stopcock between B and C is carefully opened until expansion of air in B has driven the mercury in the manometer up to the stopcock and through its bore. The cock is then closed and the exhaustion of C and F completed.

The bulb F is then filled with mercury from K and the connecting system between F and M filled with mercury. M was now filled with conductivity water through a tube at the top, not shown in the drawing, which was then sealed off. A vacuum was applied to O and the water in M boiled at least  $\frac{1}{2}$  hour, the pressure being gradually raised until the boiling was finished at atmospheric pressure. Previous workers have shown that these conditions are favorable for the removal of gases and we feel that there is no question but that the water used by us was air-free.

In the meantime, the helium has been introduced into the system as follows. The bulb E is exhausted through one side of a 3-way stopcock, not shown, between E and the helium supply, not shown in the drawing. E is then filled with mercury from D and a small quantity of freshly boiled water introduced into E through the stopcock previously used for its exhaustion. With the aid of a vacuum, the mercury is then partially withdrawn from E and the water boiled under diminished pressure to remove the air. Helium was then introduced and the water boiled again by reducing the pressure, insuring the removal of air from the water. Finally, E was left filled with pure helium under atmospheric pressure and in contact with water.

The exhausted gas-measuring system C was then rinsed out by repeatedly admitting a little helium and exhausting and finally filling with mercury from A. It was then put in connection with E and B and mercury withdrawn from C, into A and admitted to E from D, the manometer between B and C being carefully watched to keep the gas at the pressure of the air in B. The stopcock on C was then opened to let helium into the tube between C and F, the cock on F being closed. Boiling, air-free water was now transferred from M to F by withdrawing mercury into K until the connecting system of glass tubing was filled with water just through the bore of the stopcock at the top of F. The 3-way stopcock below K was then turned to allow the mercury to pass into the weighed dish L and the desired quantity of water introduced into F. This was done very slowly in order that the temperature of the water might be lowered by the cooling coils shown diagrammatically at I, to such a point that the stopcock lubricant is not softened. Another reason for transferring the water slowly was to allow it to take on the temperature of the water in the thermostat in order that the mass and the volume of water might be calculated from the weight of the mercury displaced. To this same end, after the desired amount of water had been passed into F, the stopcock at the top of F was closed while that between F and L was left open until thermal equilibrium between F and the thermostat R had been reached. L was then removed and weighed. From its increase in weight, the temperature of the bath, the density of mercury and that of water, the mass and volume of the latter can be calculated.

When the system had been so filled with water and helium, it was ready for the measurement. K was put into communication with F and the stopcock at the top of F opened to allow a little water to enter the capillary tube connecting F and C. The water meniscus was adjusted to a line on this tube near F's stopcock. This brought a little water in contact with the unmeasured helium and introduced a theoretical error, but the volume of helium which can dissolve in this very small quantity of water is altogether too small to be measured, so that no observable error is caused here. Now, with the stopcock F closed and that on either side of C open toward B, in the one case, and F, in the other, the pressure in C was carefully adjusted by letting mercury run in from A, or sucking it out as might be required until the mercury in the manometer stood at the same level in either limb.

These levels were read very carefully, using a cathometer as a zero instrument. The position of the mercury meniscus in the gas buret C was then read with care using a tello-microscope. Of course, this buret was carefully calibrated so that its volume and errors of graduation were known. The greater part of the gas was now transferred to F and its solution started.

The diffusion of a gas into a liquid is a very slow process, so it is necessary to stir the liquid. This was done by the magnetic stirrer G consisting of a piece of soft iron sealed in a glass tube, the whole adjusted to sink in the water and yet to be brought easily to the surface by the electromagnet represented by H and I. The latter was automatically energized at regular intervals to keep up the stirring without attention. This gently stirred the water without subjecting it to the violent shaking which was used by others and which is open to objections, as shown later.

Working in this way, at room temperatures it required at least 24 hours, at lower temperatures much longer, to obtain equilibrium. During this time, the pressure was kept constant as shown by the manometer through frequent adjustments from A. The next day, the gas was driven back into C by introducing mercury from K until the water reached the mark on the capillary near the stopcock F. The pressure was then finally adjusted and the volume of the remaining gas read.

The volume of the bulb between the two graduations of the gas buret and the quantity of water were so chosen that the mercury was now on the upper scale. The helium was then re-introduced into F and the process repeated until successive measurements

made at intervals of several hours showed no change which was not within the error of reading. From the volume of helium absorbed and the data for the water, the absorption coefficient of helium was calculated.

The results obtained are shown in the table where  $t$  is the temperature on the Centigrade scale,  $V$  is the volume of water,  $V_1$  is the volume of helium absorbed in  $V$  volumes of water, and  $\alpha$  is the coefficient of absorption defined by the equation,<sup>6</sup>  $\alpha = \frac{273.1 \times V_1}{T \times V}$ , where  $V$  and  $V_1$  are defined as above and  $T$  is the temperature on the absolute scale.

$t$	$V$	$V_1$	$\alpha$
30	244.0	2.265	0.00836
30	276.0	2.516	0.00821
30	274.6	2.447	0.00803
30	274.3	2.465	0.00810
25	279.3	2.618	0.00859
25	280.7	2.642	0.00862
10	273.8	2.521	0.00888
10	271.8	2.545	0.00903
2	271.5	2.559	0.00936
2	271.6	2.567	0.00938

The curves in Fig. 2 give a comparison of our values with those of Estreicher, Antropoff and Ramsay. Curve A represents Estreicher's results, B those of Antropoff, C our own, and D Ramsay's single value. It will be seen at once that ours are lower than Estreicher's and Antropoff's but higher than Ramsay's single reading. The discrepancies cannot be

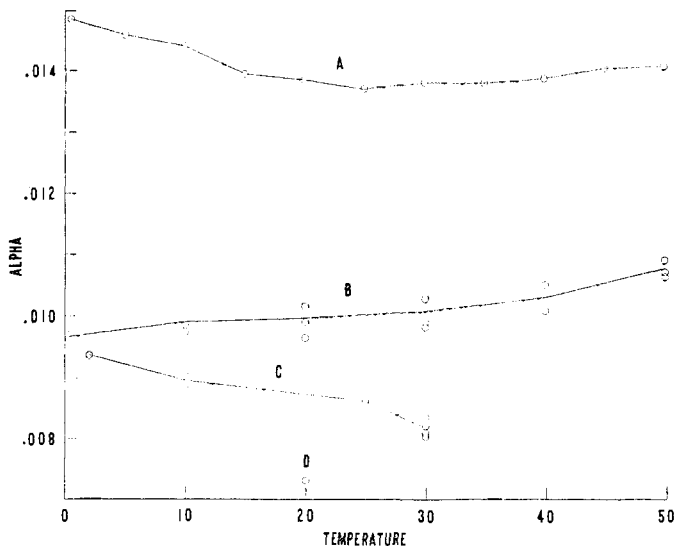


Fig. 2.

<sup>6</sup> Ostwald "Solutions," Translated by Muir, Longmans, Green and Co., 1891.

due to either hydrogen or neon in the helium, because each of the first two is more soluble than the last and each, if present, would tend to increase the apparent solubility of the helium. Estreicher's helium was probably impure and we need not concern ourselves further with his results.

Antropoff probably had pure helium, but he himself found, after he had finished his work on this gas, that his method contained a serious source of error. He measured the gas in a gas buret in a dry condition, brought a small part of it through a long narrow glass spiral into contact with the water in the absorption vessel, shook the latter for 10 minutes and assumed that equilibrium had been reached and that the gas in the measuring buret was completely saturated with water vapor; so, in correcting the volume he subtracted the aqueous tension from the barometric reading. In his work upon krypton, he showed that the diffusion of water vapor was so slow that this assumption was wrong and that the error was great enough to change the entire shape of the curve, giving an apparent minimum of solubility when none exists. Antropoff also points out that with his method of work the results at lower temperatures are in error because, in the absence of liquid water in the gas-measuring buret and since he went from higher to lower temperature, the gas at lower temperatures would be supersaturated with water vapor; he thinks, therefore, that only the results in the middle of his series are correct.

There are, however, in our opinion, two sources of error in his method which he did not suspect. First, no correction was applied for the change of volume in the liquid when the helium was dissolved. This change was in all probability small but Antropoff has shown that if, when using his apparatus, one neglected the change in volume of the water with the change of the temperature, an error of 100% would result, so that even a very small change in volume would make an error of many per cent. Ramsay's<sup>2</sup> single determination gives us the only clew to the magnitude of this effect and his figures are incredibly large. "The tube contained 162.3 arbitrary divisions, of which 26.0 were occupied by helium and 136.3 by water. After shaking, the volume of the helium was reduced to 25.0 divisions, and that of the water was increased to 137.3. As 137.3 absorb 1.0, one volume of water absorbs 0.0073 volume." These figures would indicate that the increase in volume of the liquid was equal to the gaseous volume of the helium absorbed.

Much more serious than this is, we think, the way in which Estreicher and Antropoff secured equilibrium between the gas and the liquid. Gas is absorbed very slowly by a liquid unless the surface of the latter is changed constantly. Estreicher and Antropoff secured this change by connecting the gas-measuring buret with the absorption vessel by a flexible helix or spiral of glass tubing and shaking the absorption bulb violently with a motor. This enabled them to reach a static condition in 10 minutes.

Now, it is well known that violent hammering results when a vessel, partly filled with water and free from air or other gases, is shaken. This has been used as a test for the presence of air in the vessel because even a small quantity of gas will so cushion the blow that no such effect is found. A moment's reflection will show that, when a gas is acting to stop the blow of the water against the glass, it is put under a pressure greater than that exerted by the rest of the gas and is, in a manner, driven into the water forming a supersaturated solution. The effect of even a small increase in pressure is easily noticed in gas solubilities. Winkler has shown that, when a gas is bubbled through the liquid, a correction must be applied for the hydrostatic pressure of the liquid.<sup>7</sup> All workers in gas solubility are agreed that it is much easier to get a gas into solution than it is to get it out again, so we are convinced that all measurements made in the manner described above are in error because of supersaturation.

In our experiments, the necessary stirring was secured by the comparatively gentle movement of the magnetic stirrer G, Fig. 1. The result was that the equilibrium was reached much more slowly, in 24 to 36 hours, but we can rest assured that the solutions so obtained were not supersaturated. Sufficient readings were taken, after the last noticed change of volume, so that we are confident that the solutions were saturated.

No attempt was made to get readings at higher temperatures than 30°, because the stopcock grease gave distinct signs of softening even at this temperature; in fact, the lack of concordance in our results at this temperature can be attributed to this. To work at higher temperatures, a new apparatus must be built, eliminating stopcocks, and we believe that an attempt should be made to determine directly the helium dissolved by a known volume of water. There are many difficulties in the way, but the obvious advantage of directly measuring the volume of the small quantity of gas dissolved instead of getting it by the difference between two relatively large volumes is so great that we believe the attempt is justified.

### Summary

The solubility of helium has been determined between +2° and 30°.

The value of the coefficient of the solubility is smaller than that obtained by other observers with the exception of a single value by Ramsay. The coefficient of solubility decreases with rising temperature and there is no sign of a minimum of solubility.

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<sup>7</sup> Winkler, *Ber.*, **24**, 89 (1891).