therefore, the value of the Faraday becomes 96,494 absolute coulombs, but for general purposes 96,500 as a round number is recommended.

(4) Inclusions in silver deposits made on smooth platinum surfaces are the same to within the experimental error as when the deposits are made on matte surfaces.

(5) Inclusions between the crystals and cup have been measured by an application of the conductivity method and are found to be a negligible part of the total inclusions which, with pure solutions, were about four parts in a hundred thousand.

(6) In cases where the deposit in large cups exceeds that in small cups (that is where the "volume effect" is appreciable) we do not find that strong heating of the deposits diminishes the difference.

(7) Two experiments on the anode liquid support the Bureau's previous conclusions as to the non-existence of the heavy anode ion.

WASHINGTON. D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

STUDIES OF THE VAPOR PRESSURE OF SOLUTIONS.

THE LOWERING OF THE VAPOR PRESSURE OF WATER PRODUCED BY DISSOLVED POTASSIUM CHLORIDE.

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Introduction.

In a preliminary article[1] the authors described a static method for the study of the vapor tension of aqueous solutions, and gave a sufficient amount of experimental material to demonstrate its reliability. Although these results were apparently very good, when judged by the agreement among the different determinations made on a given solution at various times, extending over periods of several weeks, the authors were not positive that the results obtained were the true vapor tension depressions of the solutions investigated. For this reason certain alterations have been made in the apparatus as originally described. In its improved form it is believed that the apparatus is capable of giving the vapor tension depressions of aqueous solutions correctly to 0.001 mm. or less; and in the present article the authors purpose to describe these alterations in detail and with as little repetition of the portion contained in the first article as will make the description clear. The accompanying illustrations, in which all essential details of the apparatus are given, will assist in making clear such points as are not described here in detail. The measurements on potassium chloride solutions recorded in

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[1] THIS JOURNAL, 36, 2439 (1914); also *Z. physik. Chem.*, 89, 155 (1914).

this article, have been made under these improved conditions and are considered by the authors to be reliable.

The principal changes made in the apparatus are (1) the alterations of the thermostat and thermoregulator designed to secure a more nearly constant temperature, and (2) the introduction of a method for the continuous stirring of the solvent and solutions while in a vacuum.

The Apparatus.

Thermostat.—Fig. 1 shows the construction of the constant temperature bath as seen in cross-section. The bath proper is a cylindrical copper vessel 56 cm. high and 61 cm. in diameter, which rests on a wooden shelf supported by four heavy upright timbers as shown. The arrangement of the interior is such that three separate systems are symmetrically located in the bath, one of which contains the pure solvent, water, and the remaining two, the solutions under investigation. The two bulbs for solutions are shown at F and G. A is a $^1/_4$ H. P. vertical motor of 560 revolutions, the shaft of which is elongated and at B is coupled directly to the propeller shaft C. The propeller D rotates inside the copper cylinder E, which can be raised or lowered and fixed at any desired height on the upright supports, fastened to the bottom of the bath and passing through slots on the side of E. Directly beneath the propeller is situated the compartment L, which is open beneath for the introduction of the electric light N, the source of heat used. About midway between the lateral walls of E and L are fixed the 12 mm. copper coils for the circulation of cool water, the entrance to which is seen at J and the exit at I. At HH are seen two of the vertical plates which are fixed to the interior of E, the purpose of which is to prevent the rotation of the water within E, and thus to provide for more rapid motion of the water upward through the cylinder. In this way a very rapid stream of water is constantly drawn from the bottom of the bath, upward through E and distributed uniformly at the top of the bath, flowing outward and downward over the coils of the thermoregulator R (to be described later) and the bulbs containing the solvent and solutions. By this method of rapid stirring in a symmetrical bath, the temperature of which changes extremely slowly, all parts of the bath are subjected to the same temperature conditions. The form and position of the very sensitive regulator R provides for the control of the temperature within narrow limits over long periods of time, as will be shown by records later on.

The temperature of the bath is maintained by means of the stove N, controlled by R, and the slow stream of cold water flowing through J. The capacity of N is as small as permissible, and the flow of water through J is made such that N will always supply to the bath an amount of heat slightly greater than is withdrawn by the current of water. In order to maintain the same temperature conditions in the bath, when the tem-

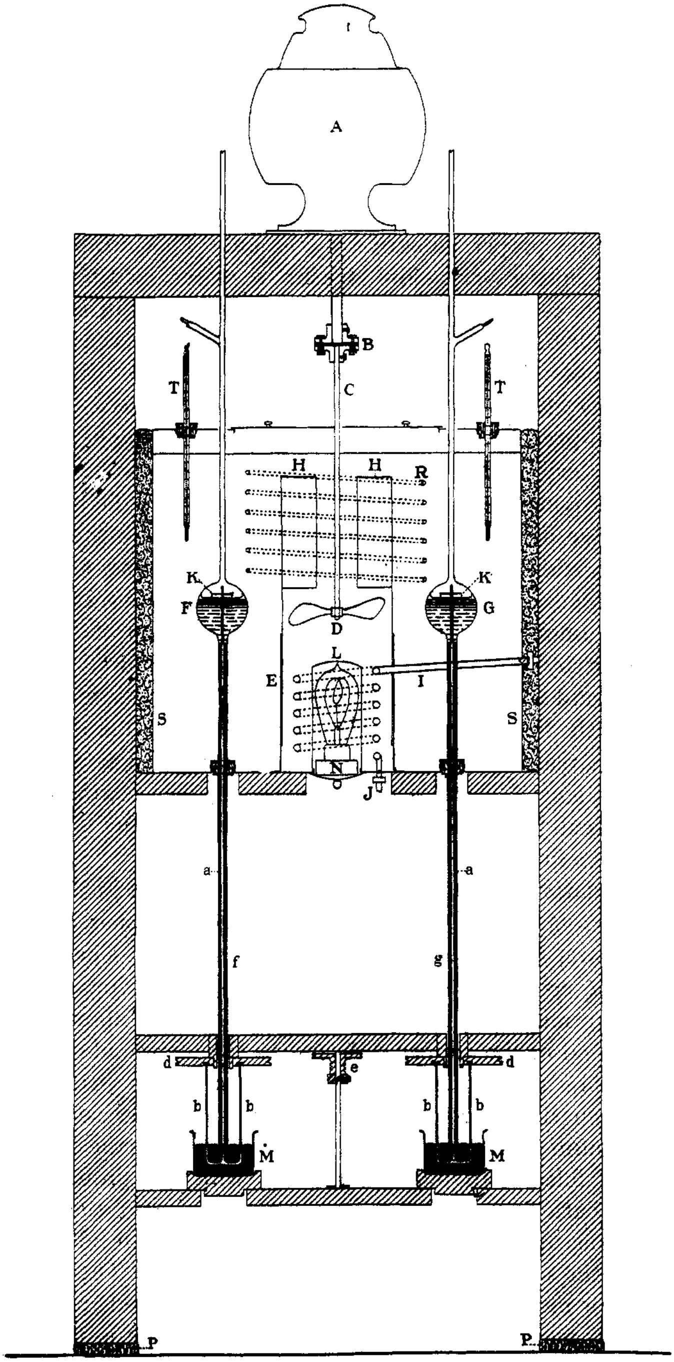

Fig. 1.

perature of the water entering the cooling coil varies, it is necessary to regulate accurately the flow of water through the cooling coil. This is accomplished very simply in the following way: Hydrant water is supplied to a standpipe which gives a constant head of water on the coil. To regulate the flow of water through the coil a section of the water pipe near the standpipe is removed and a glass tube about 25 cm. long inserted. The internal diameter of this tube is small enough to reduce the flow of water the proper amount by friction. This arrangement makes it possible to send a very slow stream of water continuously through the coils, which is not possible with an ordinary stopcock. When the attempt is made to regulate a very slow stream of water by means of a stopcock, the flow will ultimately stop entirely, due to the separation of dissolved air, or the collection of sediment, at the opening of the stopcock. One can prepare a series of such tubes of varying internal diameter and by trial ascertain the diameter required by certain temperature conditions and provide for all desired variations with little trouble. To avoid the change of flow of water through the coil, by the accumulation of air in any portion of the tube, all parts of the cooling system from the standpipe to the exit from the bath are inclined upward at a slight angle so that such quantities of air as may separate from the water will be carried forward by the stream of water and not allowed to accumulate in the system, and thus change the rate of flow. To provide for the maintenance of bath temperatures lower than that of the hydrant water the regulated stream of water is made to pass through a coil of about 4 or 5 meters length of thin-walled copper tubing contained in an ice bath. No difficulty has been encountered in maintaining a bath temperature of 20° in midsummer.

Thermoregulator.—The thermoregulator R is shown in detail in Fig. 2. It is made of about 5 meters of very thin-walled copper tubing bent in the form of spiral about 32 cm. diameter, as shown. The connection at A, between the copper coil and glass portion of the apparatus, is made in the following manner: A short, platinum cylinder about 3 cm. long is brazed to the end of the copper coil; and to the other end of the platinum cylinder the glass portion of the apparatus may be sealed without difficulty. To strengthen this connection a brass cylinder somewhat longer than the platinum cylinder is placed in position over the latter, and the space between filled with plaster of Paris, which is protected from the water of the bath by paraffin. The copper coil and the glass portion of the apparatus up to the level of the mercury in the bulb C, are filled with toluene through B, which is then sealed off. The filling of the thermoregulator must take place when the temperature is near that which it is desired to maintain in the bath. The regulator is then suspended by means of three supports (not shown on the drawing) to the top of the copper cylinder E (Fig. 1), and when the bath temperature is sufficiently near that desired, pure mercury is introduced until its level stands at the desired point in D. Either platinum or tungsten wire may be used as the adjustable contact at N. The side-tube G is for the introduction of a continuous stream of pure hydrogen which aids greatly in maintaining the mercury surface at the point of contact clean.

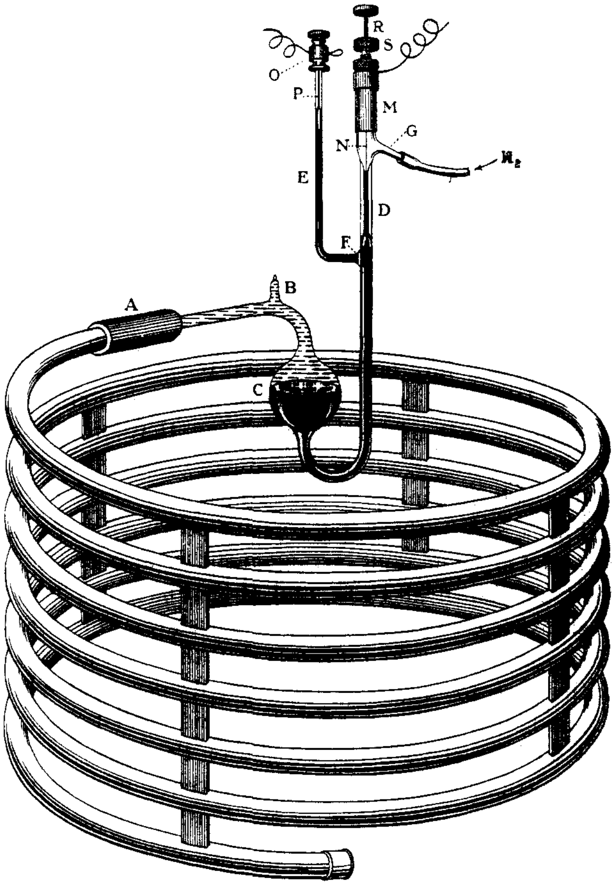

Fig. 2.

The gradual fouling of the mercury surface makes it necessary at intervals of 2 or 3 weeks to withdraw a little of the mercury in D and replace it with fresh mercury—an operation requiring only a few minutes. No attention other than this is given to the thermoregulator for periods of a year or more. With this arrangement, as constructed by the authors, a certain amount of the mercury in the vertical tube D was outside the thermostat and subject to the influence of the temperature of the room rather than that of the thermostat. As a result there was observed an occasional change in the temperature of the thermostat from day to day of not more than 0.002° or 0.003°. This occurred only when there was a marked change in the temperature of the room, and was always provided against when actual measurements were being made. In the case of all measurements here recorded a Beckmann thermometer immersed in the bath showed either no change or a change not exceeding 0.001° over the period of twelve hours during which observations were made.

The following record of the temperature of the thermostat will serve to show the accuracy of regulation which was secured during the interval when measurements were being made. The temperatures are as read on a Beckmann thermometer:

Jan. 26, 1915.	Time, A.M.:	11.00	11.30.	P.M.: 12.10	2.25	3.05	3.25	4.00	5.10
	Temp. °:	1.650	1.650	1.650	1.650	1.650	1.650	1.650	1.650
Jan. 27, 1915.	Time, A.M.:	10.10	10.45	11.15.	P.M.: 12.01	2.00	2.55	3.45	4.35
	Temp. °:	1.649	1.649	1.649	1.649	1.649	1.649	1.649	1.649

Method of Stirring.—It seemed absolutely necessary to provide some means of stirring the solutions while in a vacuum, in order that the surface concentration could at all times be maintained the same as that within the interior of the solution. Changes in surface concentration might be produced by removal of some of the solvent during the process of eliminating the dissolved air as described in our previous article, or the concentration of the surface layer might change spontaneously, due to the effect of the solute on the surface tension of the solvent. It is also very desirable to stir both the solvent and solution as it insures the temperature of solvent and solutions being that of the thermostat, and facilitates the removal of the last traces of dissolved air after the introduction of the solution into the apparatus.

Fig. 1 shows the apparatus for stirring the solutions in the two bulbs F and G. The same arrangement is also provided for stirring the solvent, as shown at F, G, and H in Fig. 3. The device can be described best by referring to Fig. 1, which shows only the two systems for solutions; that for the solvent is not shown, but is identical in all respects with those for the solutions, and its description is unnecessary.

As shown in Fig. 1, the bulbs F and G containing the solutions are situated on a level with the middle of the bath, communicating above with the portion of the apparatus for the elimination of dissolved gases and the measurement of the vapor tension (Fig. 3), and below with a tube 16 mm. diameter and somewhat more than barometric height. The lower open ends of these tubes, *f* and *g*, dip beneath the surface of the mercury contained in the glass vessels M,M. The whole apparatus is completely exhausted and, after the preliminary removal of the greater part of the dissolved air in closed glass vessels, as described in our original article, the solution is left in the glass vessel (Fig. 4), under a partial vacuum. The transfer of the solution from the flask to the solution bulb F or G, as the case may be, is accomplished in the following manner to avoid contact with air: File marks are made on the glass tubes A and C (Fig. 4). One end, A, is connected by means of a rubber tube to a reservoir filled with clean mercury, care being taken to see that the rubber tube is completely filled with mercury, and that A is well immersed in the mercury at the open end of the rubber tube before A is broken off. When these precautions are taken the space in the flask (Fig. 4) not filled by solution,

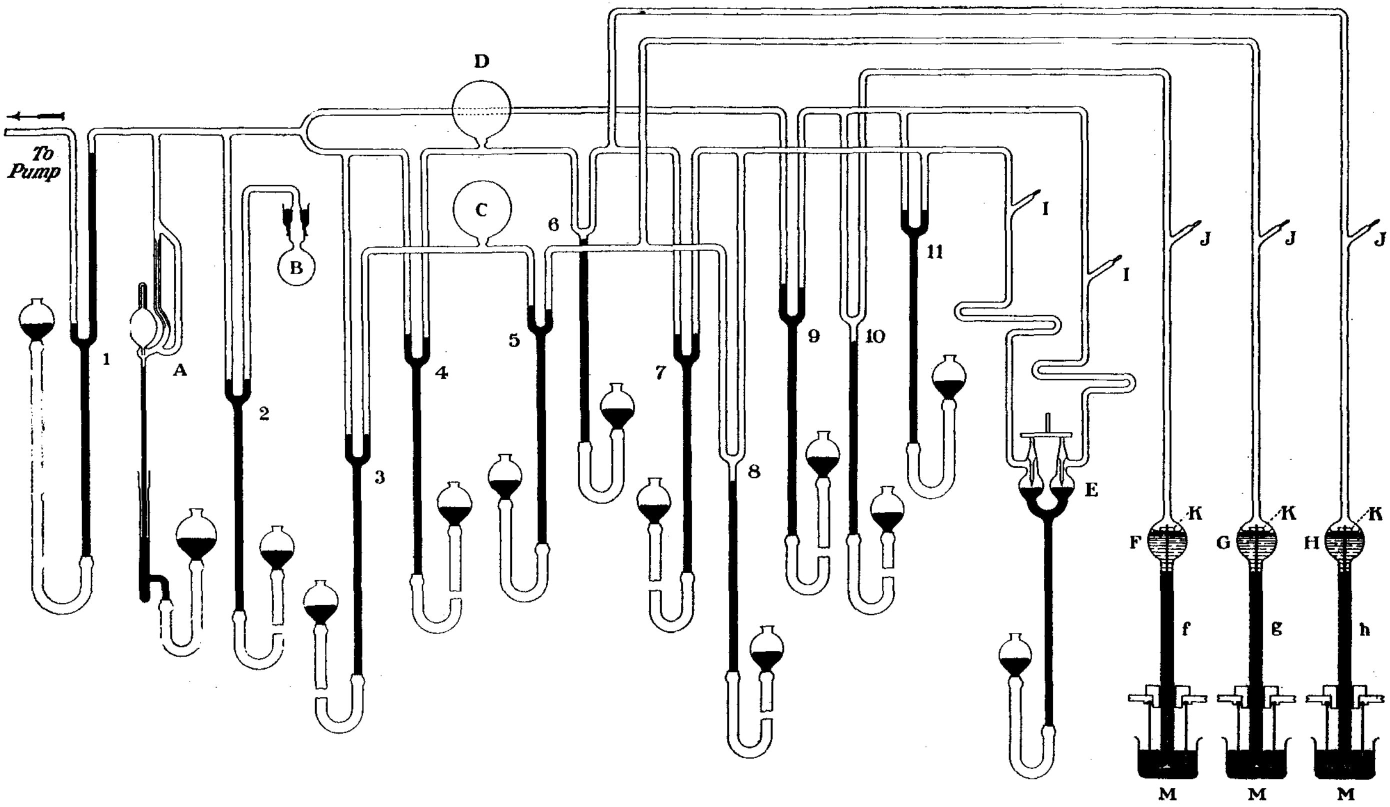

Fig. 3.

fills with mercury from the reservoir. The other glass tube C is connected by a rubber tube to a strong glass tube, the other end of which is drawn out and bent upward so that it may be inserted beneath the lower ends of *f* and *g*. C is broken off at the file mark and a few cubic centimeters of the solution forced over by the mercury in the reservoir while the open end of the curved glass tube dips beneath the mercury in M. The open end of the glass tube is then inserted beneath the lower end of *f* or *g*, as the case may be. The solution is then forced from the flask by the mercury contained in the reservoir, and passes upward through the mercury column and collects in the glass bulb F or G above. Care is taken to introduce just enough in each case to bring the level of the liquid within the bulb to a mark made on the outside of F and G. When the surface of the liquid in the bulb is at this level, the platinum vanes K,K are about two-thirds immersed in the liquid within. The rotation of these vanes is accomplished in the following manner: The vanes are firmly sealed into the upper ends of the long glass rods *a,a,* which extend down through the mercury columns in *f* and *g*, and at the bottom are sealed to the middle of the U-shaped rods *b,b*. The upper ends of *b,b* fit into depressions on the under surfaces of the wooden pulleys *d,d,* each of which is grooved and belted by a very light belt to the central loose pulley *e*, which in turn is belted to a small motor, the speed of which can be regulated within wide limits. In this way the simultaneous stirring of the liquids in all three bulbs can be easily accomplished and can be continued for any length of time without any thermal effect on the solutions or solvent, and while the whole system is evacuated. It is not necessary to provide any means of keeping these stirring devices in position as the buoyancy of the glass rods *a,a* in the mercury is sufficient. No trouble whatever has been experienced from the apparently fragile character of this device. It only requires careful construction in the beginning. The whole arrangement is so satisfactory that, when air has been completely removed, equilibrium is apparently established in the Rayleigh manometer E (Fig. 3), within the time (3-5 min.) required to adjust the manometer for a reading. Readings, however, are never taken until after the lapse of fifteen or twenty minutes after the adjustment of the traps and it has been shown that subsequent readings for periods of days do not vary from these first readings by more than the variations among themselves. During the preliminary removal of air in the closed flasks and the complete removal of air after introduction into the apparatus, a certain amount of water is removed from the solution, the concentration of which is thereby increased. The amount of water removed after introduction into the apparatus can be calculated quite accurately from the

Fig. 4.

volume filled by the vapor at each exhaustion and the number of exhaustions. The change of concentration of the solution during the complete process of removing the dissolved air has been determined on many of the solutions of potassium chloride investigated in this article by evaporating a known weight of the solution and weighing the residual potassium chloride. The greatest change of concentration observed corresponded to a change of 0.0002 mm. in the vapor tension of the solution, and we have made no correction for it on account of the small change.

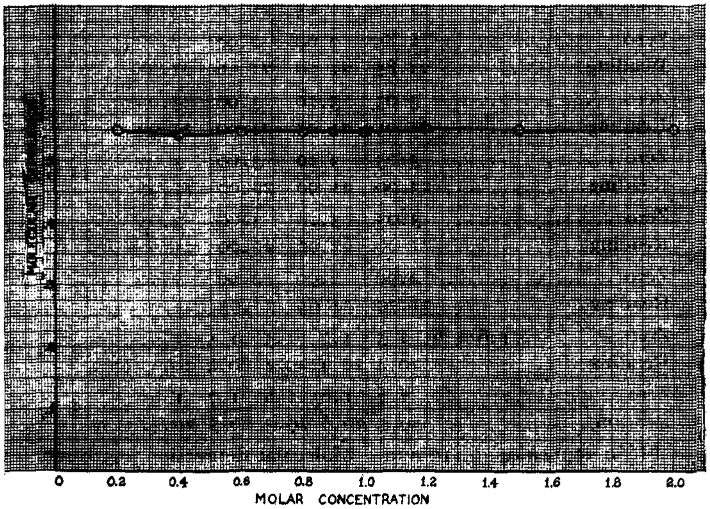

Fig. 5.

It will be noticed that the plan of the apparatus as shown in Fig. 3 is somewhat different from the former apparatus. This is due to the fact that the capacity of the apparatus has been doubled by introducing two systems for solutions and to the fact that each system has been made independent of the other two.

The results obtained from a study of aqueous solutions of potassium chloride at 20° are given below and are summarized in the ensuing table and curve. The concentrations employed here express the number of gram molecules of solute dissolved in 1000 grams of solvent.

Experimental.

1915 Experiment using 0.2 *M* KCl Final observations as follows:

					Mean.	Deflection.	Depression.
May 4	Zero	3.50	3.40	3.30	3.40	18.95	0.1105
	Reading	22.40	22.40	22.25	22.35		
	Zero	3.05	3.00	3.10	3.05	18.78	0.1095
	Reading	22.00	21.80	21.80	21.83		

								Mean.	Deflect.	Depres.
May 5	Zero	3.25	3.30	3.20				3.25	18.77	0.1095
	Reading	22.00	22.05	22.00				22.02		
	Zero	3.25	3.30	3.20				3.25	19.08	0.1113
	Reading	22.25	22.40	22.35				22.33		
	Zero	3.25	3.30	3.20				3.25	18.77	0.1095
	Reading	21.90	22.15	22.00				22.02		
	Zero	2.90	2.90	2.90				2.90	19.08	0.1113
	Reading	22.15	22.00	21.80				21.98		
May 6	Zero	2.85	2.90	2.90				2.88	19.00	0.1108
	Reading	21.90	21.85	21.90				21.88		
	Zero	2.85	2.90	2.90				2.88	19.00	0.1108
	Reading	21.85	21.90	21.90				21.88		
	Zero	3.05	3.10	3.00				3.05	18.88	0.1102
	Reading	21.95	21.95	21.90				21.93		
	Zero	3.05	3.10	3.00				3.05	18.93	0.1104
	Reading	22.00	21.90	22.00				21.98		
	Zero	3.05	3.10	3.00				3.05	18.93	0.1104
	Reading	21.90	22.00	22.00				21.98		
	Zero	2.90	2.90	2.90				2.90	18.77	0.1095
	Reading	21.70	21.65	21.65				21.67		
June 9	Zero	1.6	1.6	1.5	1.7	1.5	1.5	1.57	18.83	0.1098
	Reading	20.4	20.4	20.4	20.4			20.4		
June 10	Zero	1.7	1.65	1.6	1.7			1.65	18.87	0.1102
	Reading	20.5	20.6	20.5	20.5			20.52		

Mean depression, 0.110 mm. Molecular depression, 0.550 mm.

Experiment using 0.4 *M* KCl. Final observations as follows:

								Mean.	Deflect.	Depres.
Aug. 3	Zero	3.0	3.1	3.1	3.1			3.1	37.30	0.2175
	Reading	40.3	40.4	40.5	40.3			40.4		
Aug. 6	Zero	2.4	2.4	2.3	2.3			2.35	37.22	0.2171
	Reading	39.4	39.5	39.7	39.7	39.5	39.6	39.57		
	Zero	2.4	2.4	2.3	2.3			2.35	37.25	0.2172
	Reading	39.5	39.7	39.6	39.6			39.6		
Aug. 7	Zero	1.9	1.8	2.0	2.0	2.0		1.94	37.36	0.2178
	Reading	39.2	39.3	39.4	39.3			39.3		

Mean depression, 0.217 mm. Molecula: depression, 0.542 mm.

1915. Experiment using 0.6 *M* KCl. Final observations as follows:

											Mean.	Deflect.	Depres.
June 9	Zero	1.4	1.4	1.5	1.5	1.25	1.25	1.4	1.4	1.5	1.4	56.65	0.3303
	Reading	58.0	50.0	58.1	58.1						58.05		
	Zero	1.6	1.6	1.5	1.7	1.5	1.5				1.57	56.43	0.329
	Reading	58.0	58.0	58.0							58.0		
June 10	Zero	1.65	1.65	1.80	1.6	1.6					1.66	56.45	0.3291
	Reading	58.2	58.0	58.1	58.15						58.1		
	Zero	1.7	1.6	1.65	1.7						1.65	56.48	0.3293
	Reading	58.1	58.15	58.2	58.1						58.13		

Mean depression, 0.329 mm. Molecular depression, 0.548 mm.

Experiment using 0.8 *M* KCl. Final observations as follows:

						Mean.	Deflect.	Depres.
July 15	Zero	1.2	1.3	1.3		1.27	75.23	0.4385
	Reading	76.5	76.5	76.5		76.5		
July 16	Zero	0.9	0.9	0.9		0.9	75.25	0.4386
	Reading	76.1	76.2	76.2	76.1	76.15		
	Zero	0.9	0.9	0.9	0.9	0.9	75.15	0.4381
	Reading	76.0	76.1	76.0	76.1	76.05		

Mean depression, 0.438 mm. Molecular depression, 0.547 mm.

1915. Experiment using 0.9 *M* KCl. Final observations as follows:

June 30	Zero	−1.65	−1.55	−1.60	(negative)	−1.60	84.65	0.4935
	Reading	83.1	83.1	83.0	83.0	83.05		
July 2	Zero	2.2	2.2	2.25	2.30	2.25	84.51	0.4927
	Reading	86.8	86.8	86.75	86.7	86.76		
July 8	Zero	1.8	1.9	2.0	2.0	1.92	84.68	0.4937
	Reading	86.6	86.6	86.5	86.7	86.6		
July 9	Zero	2.0	2.1	2.0	2.1	2.05	84.65	0.4935
	Reading	86.6	86.8	86.7	86.7	86.7		
July 16	Zero	0.9	0.9	0.9		0.9	84.65	0.4935
	Reading	85.5	85.6	85.5	85.6	85.55		

Mean depression, 0.493 mm. Molecular depression, 0.548 mm.

1914. Experiment using 1.0 *M* KCl. Final observations as follows:

							Mean.	Deflect.	Depres.
Dec. 11	Zero	8.2	8.2	8.2			8.20	93.80	0.547
	Reading	102.0	102.0	102.0			102.00		
	Zero	8.2	8.2	8.2			8.20	93.80	0.547
	Reading	102.0	102.0	102.0			102.00		
Dec. 12	Zero	8.1	8.1	8.2			8.13	93.74	0.5466
	Reading	101.9	101.9	101.8			101.87		
Dec. 16	Zero	8.8	8.8	8.8	8.7	8.9	8.80	93.80	0.547
	Reading	102.6	102.5	102.7			102.60		

Mean depression, 0.547 mm. Molecular depression, 0.547 mm.

Experiment using 1.2 *M* KCl. Final observation as follows:

Aug. 3	Zero	3.0	3.1	3.1	3.1			3.1	113.80	0.6634
	Reading	117.0	116.9	116.9	116.85	116.9	117.0	116.90		
Aug. 4	Zero	2.8	2.9	3.0	2.9			2.9	113.73	0.6628
	Reading	116.65	116.65	116.6	116.6			116.63		
Aug. 5	Zero	2.8	3.0	3.0	3.0			2.95	113.65	0.6625
	Reading	116.6	116.5	116.6	116.8	116.6		116.6		
	Zero	2.9	3.0					2.95	113.65	0.6625
	Reading	116.6	116.6	116.8	116.5	116.7		116.6		
Aug. 7	Zero	1.8	1.9	1.9	1.9			1.87	113.63	0.6623
	Reading	115.5	115.5	115.5	115.5			115.5		

Mean depression, 0.663 mm. Molecular depression, 0.552 mm.

1915. Experiment using 1.5 *M* KCl. Final observations as follows:

								Mean	Deflect.	Depres.
Mar. 9	Zero.....	7.10	7.20	7.10				7.13	141.57	0.8255
	Reading	148.60	148.80	148.70				148.70		
Mar. 10	Zero.....	6.25	6.35	6.40	6.40			6.35	141.77	0.8267
	Reading	148.15	148.10	148.10	148.15			148.12		
	Zero.....	6.00	6.00	6.00				6.00	141.81	0.827
	Reading	147.70	147.95	147.70	147.90			147.81		
Mar. 12	Zero.....	6.10	6.10	6.05				6.08	141.64	0.826
	Reading	147.70		147.65	147.80			147.72		
	Zero.....	7.00	7.05	7.10				7.05	141.61	0.8257
	Reading	148.60	148.70	148.85	148.60			148.66		
	*Zero.....	6.10	6.10	6.05				6.08	140.90	0.8216
	Reading	146.95	147.00	147.00				146.98		
	*Zero.....	7.00	7.05	7.10				7.05	140.92	0.8217
	Reading	148.00	147.90	148.00				147.97		
	Zero.....	7.10	7.05	7.20	7.00	7.15	7.10	7.10	141.36	0.8244
	Reading	148.40	148.45	148.50	148.50			148.46		
Mar. 16	Zero.....	6.30	6.30	6.30				6.30	141.55	0.8255
	Reading	147.95	147.80	147.75	147.90			147.85		
	Zero.....	6.95	7.00	6.95				6.97	141.64	0.826
	Reading	148.50	148.65	148.65	148.65			148.61		
Mar. 17	Zero.....	6.15	6.20	6.15				6.17	141.71	0.8263
	Reading	147.90	147.90	147.85				147.88		
	Zero....	6.90	6.90	6.95				6.92	141.58	0.8257
	Reading	148.45	148.60	148.50	148.45			148.50		
Mar. 18	Zero.....	6.05	6.10	6.05				6.07	141.68	0.8262
	Reading	147.75	147.65	147.85	147.75			147.75		
	Zero.....	6.80	6.80	6.85				6.82	141.55	0.8255
	Reading	148.30	148.35	148.40	148.45			148.37		
	Zero.....	6.05	6.10	6.05				6.07	141.66	0.826
	Reading	147.65	147.75	147.80				147.73		
	Zero.....	6.80	6.80	6.85				6.82	141.55	0.8255
	Reading	148.40	148.35	148.35				148.37		

Mean depression, 0.826 mm. Molecular depression, 0.550 mm.

Experiment using 2.0 *M* KCl. Final observations as follows:

						Mean.	Deflect.	Depres.
Mar. 20	Zero........	6.95	7.00	7.05		7.00	189.02	1.1018
	Reading.....	196.00	196.05	196.00		196.02		
Mar. 22	Zero........	6.70	6.80	6.85	6.75	6.78	189.12	1.1023
	Reading....	195.85	195.90	195.95		195.90		
	Zero........	6.35	6.30	6.40		6.35	189.02	1.1018
	Reading....	195.30	195.40	195.40		195.37		
	Zero........	6.40	6.30	6.30		6.33	188.90	1.1012
	Reading....	195.20	195.25	195.20		195.22		

*These readings have been omitted in taking the mean, since it is apparent that the deviation is too great to admit of their being correct.

				Mean.	Deflect.	Depres.
Zero........	6.90	7.00	6.90	6.93	189.02	1.1018
Reading....	196.00	195.95	195.90	195.95		
Zero........	6.90	7.00	6.90	6.93	189.02	1.1018
Reading....	196.00	195.95	195.90	195.95		
Zero........	6.40	6.30	6.30	6.33	188.95	1.1015
Reading....	195.30	195.30	195.25	195.28		
Zero........	6.30	6.30	6.30	6.30	188.92	1.1013
Reading....	195.20	195.20	195.25	195.22		
Zero........	7.00	6.95	7.00	6.98	188.95	1.1015
Reading....	195.90	195.90	195.90	195.90		

Mean depression, 1.1017 mm. Molecular depression, 0.551 mm.

TABULATION OF RESULTS, TEMPERATURE 20.0°.

Concentration. Mols KCl per 1000 g. H_2O.	Observed depression.	Molecular depression.
0.2	0.110	0.550
0.4	0.217	0.542
0.6	0.329	0.548
0.8	0.438	0.547
0.9	0.493	0.548
1.0	0.547	0.547
1.2	0.663	0.552
1.5	0.826	0.550
2.0	1.102	0.551

Summary.

(1) In the foregoing article the authors have described certain changes which have been made in the form of the apparatus since the publication of their original article, including (*a*): A thermostat, the temperature of which can be maintained constant to 0.001° for periods of twelve hours or more; (*b*) a simple mechanical device for continuous stirring of the solution and solvent while in vacuum, and (*c*) a more sensitive McLeod gauge for measuring the residual air pressure after the absorption of the water vapor.

(2) Actual observations of the vapor pressure lowering are made only after the McLeod gauge shows a residual air pressure of less than 0.0001 mm.

(3) Under these conditions the vapor pressure lowering of a given solution remains constant for days to 0.001 mm. as shown in the table of measurements above.

(4) Solutions of potassium chloride varying in concentration from 0.2 *M* to 2.0 *M* have been studied.

(5) It has been shown by the analysis of the solutions from the apparatus after the measurements have been made, that the change of concentration of the solutions during the process of removing the dissolved air and measuring the vapor tension lowerings is small enough to be neglected.

(6) The most striking feature of the experimental results is, that for all concentrations investigated, the molecular lowering of vapor tension is the same. Thus the lowering of a 0.2 *M* solution is 0.110 mm., while that of the 2.0 *M* solution is 1.1102 mm. Similar results have been obtained by Tower and Germann[1] from a study of the vapor tension of alcoholic solutions of potassium bromide and lithium chloride. Whether this phenomenon can be explained by the combination of the solvent and solute, as suggested by Tower and Germann, cannot be decided until the rigid applicability of Raoult's law has been tested with some non-electrolyte over the same range of concentration. This the authors purpose doing as soon as possible.

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THE EQUATION OF STATE FOR GASES AND LIQUIDS.

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Van der Waals' equation, $(p + a/v^2)(v - b) = \mathrm{RT}$, has for thirty years been accepted by chemists and physicists as a most valuable guide in the study of the behavior of gases and liquids. On the other hand, the limitations of the equation of the distinguished Hollander have also come to be generally recognized. From any two of the three quantities, critical temperature, critical pressure and critical volume, the theory of van der Waals enables us to calculate *a* and *b*. But if from the values of *a* and *b* so obtained, we calculate the third critical quantity, our result will be widely at variance with the facts. This is also evident when we remember that the theory of van der Waals requires that the critical density shall be 2.67 times that of an "ideal" gas under the same conditions of temperature and pressure, whereas in all cases hitherto investigated the ratio is much larger, usually about 3.7. Most of the modifications of the equation attempt to meet this condition of affairs, but are unable to raise the ratio above three.

Now there seems to be no doubt that the general ideas underlying the theory of van der Waals are of great value, enabling us to obtain a better insight into the nature of gases and liquids. It would seem to be worth while inquiring whether another method of deriving the equation of state is not theoretically sounder and more justifiable.

Van der Waals' method of applying a correction to the volume of the gas seems to be correct in principle, although the correction represented by the letter *b* may not be a "constant." Leaving out of account the surface layer of unknown thickness, the pressure throughout the fluid should undoubtedly be represented by the expression $\mathrm{RT}/v - b$. Owing, however, to unbalanced molecular forces in the surface layer directed to-

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[1] THIS JOURNAL, 36, 2449 (1914).