explosive in character. The resulting mass on treatment with water gives a solution containing only selenious acid.

If the monoxide is formed it is likely that the heat of the reaction would decompose it. The experiment was subsequently modified by chilling the bromide to —7°. At this temperature, silver oxide swims unattacked on the surface of the liquid monobromide. No reaction takes place until the whole attains a temperature of + 20°, when the same violent reaction takes place that was before noted. On conducting the experiment in a closed tube, it is noticed that on opening the tube, no pressure exists, hence it is unlikely that a gas has been formed. Should a lower oxide be formed at all in this reaction, the experiments seem to indicate that it immediately dissociates into selenium and the dioxide.

As Pierce has pointed out, it seems very likely that the odor noticed when selenium is roasted in air, is due to the presence of hydrogen selenide, and that efforts to obtain other oxides than the dioxide, thus far have been unsuccessful.

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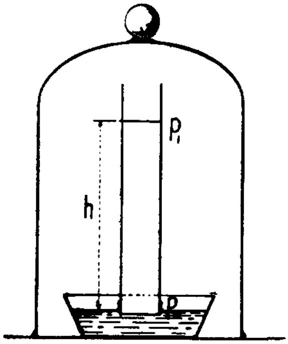
OSMOTIC PRESSURE.

BY C. L. SPEYERS.

Received May 26, 1898.

CONSIDER the following arrangement: The lower vessel contains pure solvent; the tube contains a solution of some non-volatile body in that solvent. The tube is open at the top but closed at the bottom by a diaphragm permeable to the solvent only. At equilibrium, the arrangement is to be so



adjusted that the diaphragm is just at the surface of the solvent in the outer vessel. The tube and vessel holding the solvent are covered by a bell jar, the air being removed so that the only aeriform body under the bell jar is the vapor of the solvent. This is the arrangement described by Arrhenius.[1] At equilibrium, the counter pressure preventing the entrance of the solvent, is commonly given as equal to hs on the unit surface, h being the height of the column of liquid and s the density of the solution whose counter pressure balances the osmotic pressure, π, so that at equilibrium

$$\pi = hs \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The difference between the pressure of the vapor on the top of the solution and the pressure of the vapor on the pure solvent in the lower vessel is so slight compared with π that for our purpose it is negligible. Likewise the coefficient of compressibility of solvent may be neglected by us.

The value of h is *a priori* unknown, but when the system reaches equilibrium, then h must have such a value that the vapor-pressure of the solution equals the vapor-pressure of the pure solvent at height h.

Now

$$dp = -s'dh$$

where s' is the density of the vapor compared with hydrogen.

Experiments by Ramsay and Young, quoted by Noyes and Abbot,[2] show that the density of ether vapor at 12.9° and under pressure p in terms of hydrogen at the same temperature and under the same pressure is $36.08 + 0.0581\,p$. One cc. hydrogen at 12.9° and under p pressure weighs $(0.0_4 8987p/76)$ $273/283.9$ grams.

$$s' = 0.0_4 8987 \frac{p}{76} . \frac{273}{283.9} (36.08 + 0.0581p) \text{ grams.}$$

Wherefore, for ether as solvent,

$$h = \frac{76 \cdot 285.9}{0.0_4 8987.273} \int_{p_1}^{p_0} \frac{dp}{p(36.08 + 0.0581p)} \text{ cm.}$$

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[1] *Ztschr. phys. Chem.*, **3**, 115 (*1889*).

[2] *Ibid.*, **23**, 56 (*1897*).

Integrating by partial fractions, we get

$$h = 24540\ l_\epsilon \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)}\ \text{cm.}$$

Substituting in 1 we get

$$\pi = 24540 \cdot 13.60\ s l_\epsilon \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)}\ \text{in grams} \ldots\ldots (2)$$

The next step is to substitute for s, which in this case is to refer to ether.

Now this little paper centers around this quantity s. I wish to show that for s we should substitute the value for the pure solvent, in this case ether, and not the value for the solution which is in the tube at the time of consideration. This latter value was used by Arrhenius.[1]

Does not the great advantage of the modern theory of solution lie in the notion that the constituents of a liquid homogeneous mixture, are independent of each other? Is not this far more suggestive than the assumption of a peculiar, characteristic, almost chemical, action between the constituents, which assumption even the originators of the modern theory of solution seem at times inclined to make? For when the constituents are independent of each other, then we must seek the apparently peculiar characteristic action of one constituent upon the other constituent of a homogeneous liquid mixture, in a difference of condition offered by the one constituent to the other. For instance, suppose we have ammonium chlorid in the form of partially dissociated vapor and we introduce some nitrogen, keeping temperature and total pressure constant. Then the ammonium chloride is believed to dissociate still more; but not because the nitrogen acts chemically upon this system or in any other characteristic way upon it. Not at all. But because the introduction of nitrogen necessitates a change in the condition of the system. Of course the change in condition in this case is readily detected, whereas the changes in condition produced when one of the constituents of a homogeneous liquid mixture is changed are not so easily followed up. Nevertheless, it would seem more profitable to seek for the cause of apparently specific

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[1] *Loc. cit.*

action in this direction rather than in the direction of chemical affinity or chemical action; the latter notion is so vague.

Granting this independence of the constituents, the notion of a diaphragm permeable to one constituent but not to the other, becomes clear enough.

In the arrangement considered above, the diaphragm is permeable to the constituent present in larger quantities and therefore generally called the solvent. In this case ether is the solvent. As the diaphragm is impermeable to the solute, should we not claim that it receives the full pressure of the solute, not allowing any activity on the part of the solute to pass through the diaphragm? How can we claim anything else? But then when we do this, how can we claim that the hydrostatic pressure preventing the entrance of the ether, comes from anything else than the column of pure ether in the solution, which column of pure ether has the height of the column of solution? We cannot, consistently, with what we have assumed regarding the independence of the constituents of the liquid mixture. For we are not to look upon a molecule of ether locked to a molecule of solute, so that whither the ether molecule goes, the other molecule must go. Not at all, not even for an instant. And yet, how can we mean otherwise when we say that s in equation (1) shall refer to the solution as a whole and not to the solvent in it.

Now in the paper of Noyes and Abbot[1] from which paper the above calculations have been taken, there is a collection of data which will be useful in testing this view.

In that paper they describe an arrangement which we must look upon as purely imaginary; the arrangement cannot be looked upon as possible in fact, though perhaps interesting from a theoretical point of view. Instead of putting the diaphragm at the bottom of the tube, they put it at the top of it and assume that the pure solvent rises in the tube until its hydrostatic pressure balances the osmotic pressure of the solute. But in their development of the necessary formulas, they do not take into account the external air pressure needed to force up the column of liquid supposing the arrangement to be subject to the air-pressure, or if in a partial vacuum such as we have assumed in our arrangement, they do not show how such a column of

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[1] *Loc. cit.*

liquid could possibly rise in the tube, for the difference in pressure, p_0-p_1, is insignificant compared with π. In either case, so far as their results depend upon their theoretical deductions, they are valueless, but considered by themselves, the data are very valuable, and will serve us a good turn.

Substituting in (2) the value for s for pure ether, given by Noyes and Abbott, equal to 0.7206, and passing to Briggs' logarithms, we get

$$\pi = 553900\left(l\frac{63.08 - 0.0581p_1}{p_1} - 0.0607\right)\cdots\cdots(3)$$

On the other hand, knowing the concentration, we can calculate π by Avogadro's law. The two values should agree. In the following table, largely from Noyes and Abbot, c is the quantity of solute, in one series naphthalene, in the other azobenzene, in one part of ether at 12.9°, p is the vapor-pressure of the solution in cm. of mercury, s is its density, π_1 is the osmotic pressure calculated from (3), π_2 is the osmotic pressure calculated from (3) but substituting the density of the solution for the density of the pure solvent, π_0 is the osmotic pressure calculated according to Avogadro's law, $\Delta\pi_1$ is the percentage variation of π_1, compared with π_0 as the standard, $\Delta\pi_2$ is the percentage variation of π_2, compared with π_0 as the standard.

° C.	p naphthalene.	p azobenzene.	s naphthalene.	s azobenzene.	π_1 naphthalene.	π_1 azobenzene.	π_2 naphthalene.	π_2 azobenzene.	π_0 naphthalene.	π_0 azobenzene.	$\Delta\pi_1$ naphthalene.	$\Delta\pi_2$ naphthalene.	$\Delta\pi_1$ azobenzene.	$\Delta\pi_2$ azobenzene.
0.00	33.05	33.05	0.7206	0.7206	....	.....	.....	.....	....	.....	....	....	....	....
0.01	32.82	32.91	0.7232	0.7234	1495	886.2	1500	889.4	1347	947.6	+11.0	+11.0	—6.9	—6.1
0.02	32.62	32.77	0.7258	0.7262	2880	1938.0	2901	1953.0	2673	1883.0	+7.7	+8.5	+2.8	+3.7
0.03	32.43	32.64	0.7283	0.7290	4265	2825.0	4301	2858.0	3991	2809.0	+6.9	+7.9	+0.6	+1.7
0.05	32.07	32.39	0.7330	0.7345	6868	4541.0	6985	4629.0	6567	4629.0	+4.6	+6.4	—1.9	0.0
0.07	31.72	32.14	0.7376	0.7399	9250	6370.0	9470	6539.0	9080	6403.0	+1.9	+4.3	—0.5	+2.1
0.10	31.24	31.79	0.7443	0.7473	12730	8806.0	13150	9132.0	12730	8988.0	0.0	+3.3	—2.0	+1.6
0.13	30.78	31.46	0.7512	0.7548	16280	11240.0	16960	11770.0	16260	11490.0	+0.1	+4.3	—2.2	+2.4
0.16	30.34	31.13	0.7578	0.7617	19550	13620.0	20550	14390.0	19660	13900.0	—0.6	+4.5	—2.0	+3.5
0.20	29.79	30.72	0.7663	0.7704	23700	16670.0	25200	17820.0	24030	16980.0	—1.4	+4.9	—2.0	+4.9
0.24	29.27	30.33	0.7746	0.7792	27740	19660.0	29810	21260.0	28200	19950.0	—1.7	+5.7	—1.9	+6.6
0.27	....	30.06	.....	0.7859	.....	21650.0	.....	23780.0	.....	22110.0	....	....	—2.0	+7.6

Judging from these figures, there can hardly be any question that the density of the solvent and not that of the solution is to be used in computing π by the hydrostatic method.

RUTGERS COLLEGE, May, 1898.

METHOD OF PREPARING A STRICTLY NEUTRAL AMMONIUM CITRATE SOLUTION.

BY A. D. COOK.

Received June 8, 1898.

FOR the benefit of many analytical chemists who are engaged in fertilizer work and for the purpose of securing uniformity in results, I respectfully submit the following pertaining to the neutrality and preparation of the chemical reagent "ammonium citrate."

This reagent has caused more trouble than all the other reagents required in fertilizer work, and yet it is an extremely easy matter to get a strictly neutral reaction.

The method adopted by the Association of Official Agricultural Chemists does not state the most essential fact in the preparation of this reagent, and the one which, if universally adopted, would overcome many obstacles in its preparation.

The failure to obtain a strictly neutral solution of ammonium citrate has caused great discrepancy in results among chemists who have analyzed the same material. I refer more particularly to the analysis of concentrated phosphates where there is a large per cent. of available phosphoric acid. The total phosphoric acid running as high as fifty per cent., the insoluble eleven per cent., making the available thirty-nine per cent. In the chemical laboratory at this station, where from 800 to 1000 samples of commercial fertilizers are analyzed annually, I have had ample opportunity to try different methods and to compare results obtained by chemists working with different solutions of ammonium citrate. It has been pointed out by fellow-workers in this field that a strictly neutral solution may be obtained by allowing the solution to stand after ammonia has been added to the citric acid and the proper dilution made. I have found that the practicability of this procedure depends upon the temperature of the solution. If vigorous stirring is neglected the solution will be slightly alkaline. Vigorous stirring, thus causing