solution (0.1022 N) with sodium thiosulfate solution (0.1054 N), without starch. Portions of 20 cc. of tetrathionate solution were measured into flasks, diluted, and mixed with measured amounts of solutions of alkalies or alkaline salts, the final volume in each case being 100 cc. The temperature of the laboratory and solutions was somewhat over 30°. The mixture in each flask was left standing 15 minutes, after which it was acidified with dilute hydrochloric acid and methyl orange, then titrated with standard iodine and starch.

Character of medium.	Cc. 0.1022 N iodine.	Character of medium.	Cc 0.1022 N iodine.
Blank	1 drop	NH_4OH, 0.1 N	0.95
NaOH, 0.1 N	9.21	$NaHCO_3$, 0.5 N	2 drops
NaOH, 0.01 N	3.98	$NaHCO_3$, 0.1 N	1 drop
Na_2CO_3, 0.1 N	5.20	$NaHCO_3$, 0.5 N, plus[1] CO_2	1 drop
Na_2CO_3, 0.01 N	0.50		

It is clear that tetrathionates are notably sensitive to even low concentrations of hydroxyl ions, though only slightly affected by sodium bicarbonate, and still less by sodium bicarbonate in presence of carbonic acid. It therefore follows that acid solutions containing tetrathionates, if to be later titrated with iodine, or subjected to any treatment involving assumption that the tetrathionate present has remained unaffected, should never be neutralized by any substance of distinctly alkaline properties. Significant errors may not necessarily result, but a source exists which can produce grave errors through incautious manipulation. Sodium bicarbonate within reasonable limits of excess is appropriate, provided the solution be not left at an elevated temperature a considerable length of time. As a discharging agent for iodine, under such conditions as prevail in the determination of arsenic, it seems safer to abandon the use of thiosulfate altogether, and to substitute therefor a dilute solution of sodium sulfite—about 0.5% of the anhydrous salt.

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NONIDEAL SOLUTIONS. THE ACTIVITY OF A DIFFICULTLY SOLUBLE COMPONENT.

BY E. K. STRACHAN.

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I. Introduction.

The study of the colligative properties of solutions has been greatly facilitated by use of the concept of the ideal solution.[2] This concept

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[1] (50 cc. N $NaHCO_3$ saturated with CO_2 before added to diluted tetrathionate.)

[2] E. W. Washburn, THIS JOURNAL, 32, 660 (1910); G. N. Lewis, *Z. physik. Chem.*, 61, 129 (1907).

has rendered unnecessary the restriction that the solution be dilute, a limitation which was necessarily imposed on all discussions in this field as long as the van't Hoff gas law hypothesis of osmotic pressure was the only one employed. By use of the ideal solution law it is possible to express accurately the colligative properties of an ideal solution in terms of the concentrations of its components. However, the ideal solution law yields quantitative results only when applied to ideal solutions. This very greatly limits its usefulness in dealing with the majority of solutions employed in scientific and technical work. There is, therefore, need of a systematic study of nonideal solutions to the end that quantitative relations between their colligative properties and composition may be discovered.

At the outset it is important to note that deviations from the ideal solution law can be attributed to either or both of two causes: first, the number of molecular species in the solution is different from the number of components, that is, association, dissociation, or a combination of solvent and solute has taken place; and second, the thermodynamic nature of the solution is different from that of the components. Consideration of the first factor is aside from the purpose of this article, since if the number of molecular species and amount of each in the solution were known, the ideal solution law could be applied, provided the last-named cause of deviation played no part. The second factor is frequently called "change in the nature of the medium" or "change in the thermodynamic environment." Solutions exhibiting effects of this latter sort only, form the subject of this paper, and may be termed truly nonideal.

The simplest of such nonideal solutions seems to be one consisting of a solid of only moderate solubility dissolved in a normal liquid forming a mixture in which the number of molecular species is equal to the number of components. Obviously such a solution is not an ideal one as its components are only partially miscible. Were it ideal, however, Henry's law would apply to it, and the desired relation of partial pressure to concentration would be

$$p = (\mathrm{N}/\mathrm{N}_s)\ p_0, \qquad (1)$$

in which p is the partial pressure of the solute when its mol fraction in the liquid is N, p_0 is the vapor pressure of the pure solute, and N_s its mol fraction in a saturated solution. Probably a somewhat similar law governs the behavior of nonideal solutions.

No direct measurements of the partial pressures of a system of the sort described above exist in the literature. However, it is possible to obtain the necessary data by a process of calculation in the case of certain solutions. Those of iodine in carbon tetrachloride, carbon disulfide, and bromoform are particularly suited to this purpose, as they show no association, dissociation, or solvation[1] and so may be regarded as truly nonideal.

II. Data and Calculations.

These calculations are based on the fact that the coefficient of distribution of a substance between two solvents is the ratio of its concentration in each when its partial pressure is the same from both. As the ratio of distribution of iodine between water and each of the above solvents has been determined, it is necessary to know only the rate of change of the vapor pressure with the concentration in water in order to be able to calculate it for each of the other solvents. Now, the vapor pressure of iodine from a saturated solution is equal to its sublimation pressure at the same temperature. Hence, by combining the solubility data with those for the sublimation pressure, one obtains the vapor pressure of iodine from its solution at a number of concentrations, each, however, at a different temperature. These values of the vapor pressure can all be reduced to a common temperature by use of the Clausius equation, provided the latent heat of vaporization of iodine from the solution be known. This latter is equal to the difference between the heat of solution and the heat of sublimation, and these in turn can be obtained respectively from the solubility by use of the van't Hoff equation, and from the sublimation-pressure data by use of the Clausius equation.

Table I summarizes the results of these calculations. The solubilities shown in Col. 2 were obtained from the results of Fedotief,[2] Hartley and Campbell,[3] Sammet,[4] and Jakovkin[5] by graphical interpolation. The

TABLE I.—SUBLIMATION PRESSURE AND SOLUBILITY DATA.

1. Temperature. T.	2. Solubility. Mols/liter $\times 10^3$.	3. Heat of soln.	4. Subl. press. p_T.	5. Heat of subl.	6. Heat of vaporization. L_v.	7. Vap. press. at 25°. p_{25}.
0	0.650	....	0.030	...	...	0.150
	...	4.50	...	16.12	10.44	...
10	0.871	....	0.085	...	...	0.210
	...	4.74	...	14.58	10.22	...
20	1.159	...	0.205	...	...	0.250
	...	5.34	...	14.74	9.60	...
30	1.567	....	0.469	...	...	0.360
	...	5.86	...	14.70	9.08	...
40	2.188	....	1.025	...	...	...
	...	6.50	...	14.82	8.44	...
50	3.020	....	2.154	...	...	...
	...	7.00	...	14.66	7.94	...
60	4.188	....	4.266	——	...	...
			Mean,	14.94		

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[1] Beckman, *Z. physik. Chem.*, **58**, 559 (1907).

[2] *Z. anorg. Chem.*, **69**, 30 (1910).

[3] *J. Chem. Soc.*, **93**, 741 (1908).

[4] *Z. physik. Chem.*, **53**, 648 (1905).

[5] *Ibid.*, 18, 590 (1895).

sublimation-pressure data are those of Baxter and Hickey.[1] The latent heat of vaporization of iodine from its aqueous solution, obtained by subtracting the latent heat of solution (Col. 3) from the latent heat of sublimation (Col. 5), is shown in Col. 6, and can be expressed with sufficient accuracy by the equation $L_v = (26950 - 58\,T)$ small calories. Now iodine solutions of the concentrations shown in Col. 2 of the table must have the vapor pressures shown in Col. 4 at the temperatures which appear in Col. 1. By use of the Clausius equation, $dp/dT = L_v/vT$, one can calculate what vapor pressure these solutions would have at any common temperature, say 25°. On substituting the value of L_v obtained above and integrating, it takes the form

$$\log p_{25} = \log p_T + 19.77\,(298 - T)/T - 29.20 \log 298/T.$$

Col. 7 of the table shows the values of the partial pressure of iodine at 25° obtained by substituting the proper values of p and T in this equation. The figures in Col. 2 of Table II were obtained from these by graphical interpolation.

TABLE II.

Conc. in water millimols per liter.	Partial pressure iodine.	Distribution coefficient.			Concentration in millimols per liter in			Mol-fraction × 10^4 in				C for			
		CCl_4.	CS_2.	$CHBr_3$.	CCl_4.	CS_2.	$CHBr_3$.	CCl_4.	CS_2.	$CHBr_3$.	Water.	$CCl_4 \times 10^{-2}$.	$CS_2 \times 10^{-1}$.	$CHBr_3 \times 10^{-1}$.	$H_2O \times 10^{-7}$.
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
0.1	0.025	85.06	585	438	8.5	58.5	43.8	8.28	35.4	38.9	0.018	3.3	2.8	3.0	5
0.2	0.047	85.08	586	443	17.0	117.2	88.4	16.53	71.0	78.0	0.036	2.5	2.1	2.3	3
0.4	0.094	85.10	592	458	34.0	236.8	183.0	33.7	143.0	162.0	0.072	2.1	2.4	2.2	3
0.5	0.118	85.15	599	466	42.6	299.5	233.0	41.5	181.0	205.0	0.090	3.5	2.6	2.3	4
0.6	0.141	85.21	608	476	51.1	364.8	286.0	49.8	220.0	251.0	0.108	3.4	2.5	2.2	4
0.8	0.187	85.70	631	497	68.5	504.8	397.0	66.8	304.0	347.0	0.144	3.3	2.3	2.2	5
1.0	0.232	86.76	651	519	86.7	651.0	519.0	84.6	392.0	450.0	0.180	3.9	2.0	2.2	6
1.2	0.276	88.37	666	541	106.0	781.0	650.0	102.5	467.0	560.0	0.216	4.0	3.4	2.3	(10)
1.34	0.305	.....	...	...	120.0	905.0	745.0	116.0	544.0	644.0	0.244	...	...	...	..
											Mean,	3.2	2.6	2.2	4

The relation of vapor pressure to concentration for solutions of iodine in the other solvents can now be calculated by use of the distribution coefficient. It is important to note, however, that the distribution coefficient is a function of the concentration even in solutions such as these in which there is no change of molecular complexity, a characteristic to be expected, of course, of a nonideal solution. Hence, the values of the distribution coefficient obtained experimentally by Jakovkin[2] and by Washburn and Strachan[3] were plotted against the concentration of iodine

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[1] THIS JOURNAL, 29, 127 (1907).

[2] *Z. physik. Chem.*, 18, 588 (1895).

[3] THIS JOURNAL, 35, 689 (1913).

in the aqueous solution, and a smooth curve drawn through the points so obtained. The value of the distribution coefficient corresponding to any desired concentration could thus be read off the curve. The values of the distribution ratio shown in Cols. 3, 4 and 5 of Table II were obtained in this way. These were multiplied by the figures in Col. 1 in order to obtain the concentrations of iodine in the other solvents, the results appearing in Cols. 6, 7 and 8. The mol-fraction of iodine in each of these solutions was calculated on the assumption that the volume of the solution was the sum of the volumes of its components. Although this is not strictly in accord with the facts, the error involved is too small to affect the ultimate conclusions. The mol fractions obtained in this manner are shown in Cols. 9 to 12 of Table II

The partial pressures shown in the table can be expressed by the equation

$$p = N/N_s\, p_o + C(N_s - N)N, \qquad (2)$$

in which C is an empirical constant and the other letters have the significance already assigned to them. Cols. 13 to 16 show the values of C for each of the four solutions. They are remarkably constant for each solution within the limits of error of the data. Although water, on account of its high degree of association, does not belong to the class of solutions under discussion, for the sake of comparison its constant was calculated. The solubility of iodine is so small in this case that the molecular complexity of the solution is not noticeably altered. Equation 2 differs from Henry's law (Equation 1) only by the term $C(N_s - N)N$. The magnitude of this correction term can be seen by inspection of Figs.

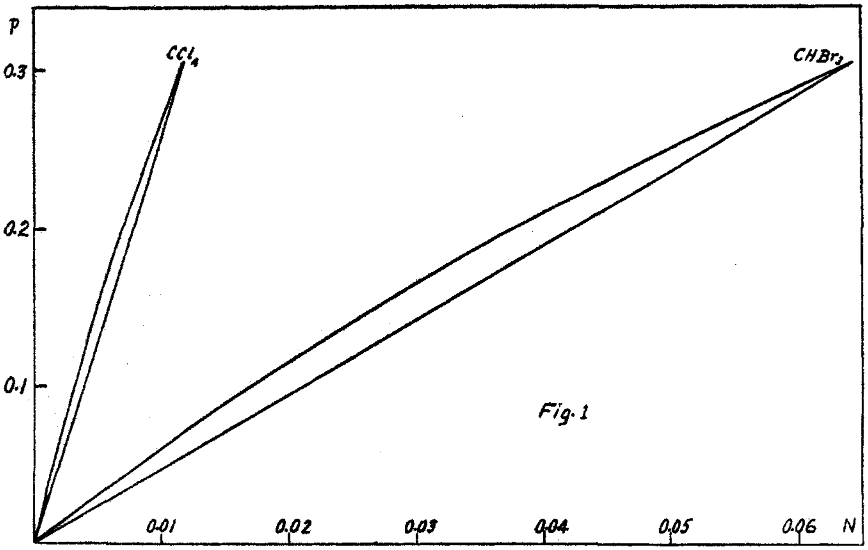

Fig. 1

1 and 2, where the mol fraction of iodine in the solutions is plotted against its partial pressure. The curved lines represent the values calculated from the experimental data and represent Equation 2, while the straight

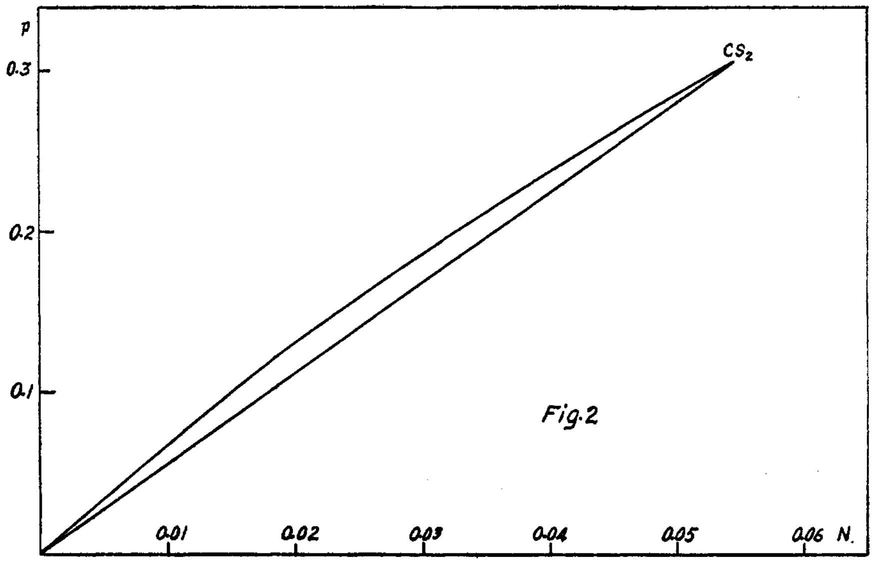

Fig. 2

lines were obtained by use of Henry's law. The curve for water is omitted, as the deviation from Henry's law would be apparent only in a very large figure.

III. Discussion of Results.

It is worthy of note that the value of C is in every case almost inversely proportional to the square of the solubility of iodine in the solution, the proportionality constant being 9×10^{-2} for bromoform, 8×10^{-2} for carbon disulfide, 4×10^{-2} for carbon tetrachloride, and 2×10^{-2} for water. The decrease in these four values of the proportionality constant with the solubility may be accidental, or may be due to the increase of the mol-fraction of solvent as that of the solute decreases. However, the agreement is very close, considering that the solubility of iodine in the different solvents varies more than 10^5-fold, and its square, more than 10^{10}-fold. It further suggests that Equation 2 is the limiting form approached by a more general expression when the solubility becomes sufficiently small, and is not a mere power-series interpolation formula. Investigations are now in progress in this laboratory to determine the relation of vapor pressure to concentration prevailing in other nonideal solutions, and to inquire into the exact significance of the constant C. It is hoped that thus a more general equation may be obtained expressing vapor pressure or activity in terms of concentration.

This equation is important not merely because it relates vapor pressure to concentration for this type of nonideal solution, but rather because it can be used to express thermodynamic activity[1] or "active mass" in terms of concentration. Consequently, any property of a solution of this type which can be expressed in terms of thermodynamic activity can also be expressed in terms of concentration. This fact is of especial value in the discussion of chemical equilibria in solutions of this sort, as they constitute one of the most common and interesting types. In such cases, the mass-action law, depending as it does on Henry's law, cannot express the equilibrium relations accurately, except at infinite dilution or when compensation effects are present. But by combining this equation with the laws of thermodynamics it is possible to determine the relation which must exist between the mol-fractions of the reacting substances in an equilibrium mixture in this kind of a solution.

In a qualitative way this equation shows that the distribution coefficient will increase with increasing concentration, if the concentration of solute in the solution in which it is most soluble is placed in the numerator, provided both solutions are truly nonideal. This conclusion agrees with the available data, not only for the particular systems employed in this article, but also quite generally. It shows at once that not all cases of inconstancy of the distribution ratio can be attributed to change of molecular complexity of the solute, and, as a corollary, that inconstancy of the distribution ratio is not a sufficient basis for concluding that a solute has different molecular weights in the different solvents. This, of course does not exclude change of molecular complexity from also being a cause of variation of the distribution ratio with the concentration.

IV. Summary.

(1) The partial pressure of a difficultly soluble component from its solution in several solvents has been calculated.

(2) The partial pressure of a difficultly soluble component of a truly nonideal solution can be expressed by the relation

$$p = (N/N_s)\ p_o + C(N_s - N)N$$

in which p is the partial pressure of the solute when its mol fraction is N, p_0 is the vapor pressure of the pure solute, and N_s its mol fraction in a saturated solution.

(3) C is a constant approximately inversely proportional to the square of the solubility.

MINNEAPOLIS, MINN.

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[1] As defined by Lewis (*Z. physik. Chem.*, 61, 129 (1907)) for these solutions the activity, $\xi = N/RT\ [P_0/N_s + C(N_s - N)]$ if the vapor is a perfect gas.