LXIII.—*The Influence of Salts on Chemical Equilibria in Solutions.*

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1. *Introduction.*

MOST equilibria into which salts enter in aqueous solution are not distinguished by real constancy of the equilibrium "constant," such as is the case with equilibria between neutral substances. The failure of previous attempts to account for this peculiarity of salt solutions is undoubtedly due to the fact that, directly or indirectly, the method of electric conductivity constituted the basis of the calculations of ionic concentrations, no regard having been taken to the interionic forces originating with the electric charges of the ions.

The difficulties which here and in many other fields the classical theory of salt solution encounters can be overcome in great measure by assuming that strong electrolytes are completely dissociated and that interionic forces are responsible for the abnormalities observed. From the point of view of this theory, which has recently been developed by several authors (Milner, *Phil. Mag.*, 1912, [vi], **23**, 553; 1913, [vi], **25**, 742; Bjerrum, *Zeitsch. Elektrochem.*, 1918, **24**, 321; Ghosh, T., 1918, **113**, 449, 627, 707), the writer has shown (*J. Amer. Chem. Soc.*, 1920, **42**, 761) that the problem of the simple solubility equilibrium can be successfully attacked. It is an obvious conclusion, therefore, that also in the case of more complicated equilibria, involving strong and weak electrolytes in a homogeneous phase, the introduction of the same points of view will enable outstanding anomalies to be removed.

In order to understand the influence of the addition of a salt on a system in chemical equilibrium we must consider the effect of it on any species of molecules or ions present, assuming that neither of them reacts chemically with the added salt. Now it is a well-known fact that the addition of a salt to a solution of a non-electrolyte usually causes the chemical potential or activity of such a substance to increase. This consequence appears most clearly in the solubilities of non-electrolytes, which exhibit—at least in the range of dilute solutions—an almost rectilinear fall with increasing concentration of the added salt. Since in the saturated solution the following thermodynamic equation holds good:

$$\xi = \varepsilon f = \text{constant} \quad . \quad . \quad . \quad (1)$$

where ξ , f , and s indicate respectively activity, activity coefficient, and solubility of the dissolved non-electrolyte, a rectilinear increase of the activity coefficient, or of the activity in the case of constant concentration, follows.

Quite differently run the solubility curves in the case of a sparingly soluble salt as solute. If the salt is uni-univalent, the equation

$$\log s = \frac{1}{3}\sqrt[3]{c_i} + \text{constant}, \quad . \quad . \quad . \quad (2)$$

where s is the solubility and c_i the total ionic concentration of the solution, has been recently shown by the writer to apply approximately. Introducing in (2) the thermodynamic equation:

$$\xi'\xi'' = c^2f'f'' = \text{constant} \quad . \quad . \quad . \quad (3)$$

where ' and '' refer to each one of the two ions of the saturating salt, and assuming the activity coefficients of the ions to be equal and $= f$, we see this coefficient is determined by:

$$\log f = -\frac{1}{3}\sqrt[3]{c}. \quad . \quad . \quad . \quad (4)$$

an expression which agrees fairly well with that given by Bjerrum.

Also when ions of higher valency are considered, solubility measurements can be used to determine their activity coefficients. A series of measurements made in this laboratory, particularly in the group of the metal ammonia salts, shows that the increase in solubility caused by the addition of heteroionic salts is very pronouncedly a function of the valency of the ions of the saturating salt. This is shown in the following table containing the data for the bi-bivalent xanthocobaltic chromate and the ter-tervalent luteocobaltic hexacyanocobaltiate in sodium chloride solutions at 0° . S is the molal solubility at the concentration c of the solvent, S_0 the solubility in pure water.

TABLE I.

Solubility Ratio S/S_0 of Xanthocobaltic Chromate ($S_0 = 0.000257$ mol.) and Luteocobaltic Hexacyanocobaltiate ($S_0 = 0.000007$ mol.) in Sodium Chloride Solutions at 0° .

C .	Xanthocobaltic chromate.	Luteocobaltic hexacyanocobaltiate.
0	1.00	1.00
0.05	1.61	5.40
0.1	2.19	9.30
0.2	3.04	17.8
0.5	4.10	49.6

The extraordinarily increasing values of S/S_0 shown in this table allow us to infer that in the case of multivalent ions we have to do

with very high interionic forces. We obtain most clearly a survey of the influence of the electric charges when considering Fig. 1, in which the solubility ratio S/S_0 is plotted against the concentration c of the solvent for the four cases of saturating substances dealt with above. The curves I, II, III, and IV refer to uncharged molecules, uni-, bi-, and ter-valent ions respectively.

As in the case of uni-univalent salts, equation (3) will also enable us to calculate for salts of higher type the activity coefficients from

FIG. 1.

solubility measurements. On this basis the curves in Fig. 2 are constructed, f_0 , f_1 , and f_2 , here and in the following, indicating the activity coefficient of a non-electrolyte, a univalent, and a bivalent ion respectively.

Now on the assumption that the activity coefficient of any molecule depends only on its number of electric charges and the total, equivalent, ionic concentration of the solution concerned, the results mentioned above give us a means of tracing the influence of salts upon the homogeneous, chemical equilibrium in any particular case. No regard, however, is taken in these calculations to the markedly individual behaviour of ions of identical types, and we have to realise therefore the approximate nature of the results arrived at on this assumption. As it is the purpose of the present article to state only the general principles of chemical equilibria in

salt solutions, consideration of these individualities, although of great importance, may be omitted for the present.

The numerical calculations of homogeneous equilibria stated in the following sections cannot therefore be looked upon as conclusive but only as yielding the average or approximate value of the salt effect in a system of the particular type considered.

On the other hand, as a conclusive result of the above interpretation of the salt effect, we are justified in maintaining the rigid

FIG. 2.

validity of the law of mass-action and of the gas laws in the case of equilibria established in relatively strong salt solutions of unchanged concentrations. This view has recently been fully verified by the writer in a number of instances (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 25. *K. Danske Vid. Selsk. math.-natur. v. Medd.*, 1920, **3**, No. 9).

2. The Dissociation of Water and other Weak Electrolytes.

From quite a different point of view from that given above Le Blanc (*Zeitsch. physikal. Chem.*, 1891, **8**, 314) already suspected the dissociation of water to be augmented by the addition of salts. The same conclusion was reached by von Euler (*ibid.*, 1899, **28**, 626) and Lewis and Wheeler (*ibid.*, 1906, **56**, 190) in the case of other dissociating substances on the ground that the dielectric constant of the solvent was increased by the addition of a salt.

The effects in question, however, are very slight as compared with the influence of the changing activity coefficient according to the assumptions underlying the present theory.

In a diluted, aqueous solution the water activity will be nearly constant, and therefore :

$$\xi_{\text{H}} \cdot \xi_{\text{OH}} = k_{\xi} \quad . \quad . \quad . \quad . \quad (5)$$

where ξ denotes activity and k_{ξ} is a constant which may be termed the thermodynamic dissociation constant. Introducing $\xi = cf$ and assuming the activity coefficient f to be the same for all uni-univalent ions present in the solution, we can write :

$$c_{\text{H}} \cdot c_{\text{OH}} = k_c = \frac{k_{\xi}}{f^2} \quad . \quad . \quad . \quad . \quad (6)$$

which shows that the product of the concentrations of the hydrogen- and hydroxyl-ions—the usual dissociation constant k_c —is not a constant, but increases with increasing ionic concentration since the activity coefficient f decreases. Calculation according to (4) yields for the ratio of k_c at 0.01 and 0.1 normal solution :

$$\frac{(k_c)_{0.01}}{(k_c)_{0.1}} = 0.68,$$

whilst from the measurements of Löwenhertz (*Zeitsch. physikal. Chem.*, 1896, **20**, 291) of the acid-alkali cell at the same concentrations the number 0.71 can be calculated for this ratio, again with the assumption of equal activity coefficient at equal concentration. Not too much weight, however, should be attached to this agreement on account of the adherent uncertainty regarding the liquid junction potential in the experiments of Löwenhertz. For the same reason, most experiments on the acid-alkali cell communicated by other investigators (Poma and his co-workers, *Zeitsch. physikal. Chem.*, 1912, **79**, 55; 1914, **88**, 671*; Lorentz and his co-workers, *ibid.*, 1907, **60**, 422; 1909, **66**, 733; Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2460) can furnish no adequate verification of the theory advanced to account for the varying dissociation of water.

It follows from equations (5) and (6) that the hydrogen-ion potential can be expressed by

$$\pi = RT \log f_{\text{H}} + \text{constant}$$

and

$$\pi = - RT \log f_{\text{OH}} + \text{constant}$$

* The numerical calculations of the ratio of hydrogen-ion concentration are erroneous throughout this paper on account of the use of natural instead of common logarithms.

in solutions containing a strong acid and a strong base of constant concentration respectively. Addition of salts, therefore, will influence the potential of the hydrogen electrode in opposite directions in the two cases to an extent computable by equation (4). This conclusion, too, might easily be tested, sufficient means being provided for the elimination of the liquid junction potential.

Now, when considering a weak electrolyte dissolved in water, for example, a weak acid, dissociating according to the scheme :

it is evident from our theory that the addition of salts will increase the dissociation to a greater extent than in the case of water as the electrolyte. Whilst in both cases the activity coefficients of the ions are decreased, we have for the acid, in addition, an increase in activity of the undissociated molecules. When the acid is sufficiently weak an augmentation of its total activity must ensue.

The change in the ordinary mass-action constant k with change of concentration can be computed when in the thermodynamic expression :

$$\frac{\xi_H \cdot \xi_{A'}}{\xi_{AH}} = \frac{c_H \cdot c_{A'} \cdot f_H \cdot f_{A'}}{c_{AH} f_{AH}} = k_\xi \quad . \quad . \quad . \quad (7)$$

the activity coefficients $f_H = f_{A'} = f_1$ and $f_{AH} = f_0$ given in the foregoing section are introduced. Hence it follows that

$$\frac{c_H \cdot c_{A'}}{c_{AH}} = k_e = k_\xi \frac{f_0}{f_1^2} \quad . \quad . \quad . \quad (8)$$

An influence in this direction has already been assumed by Arrhenius in an important paper (*Zeitsch. physikal. Chem.*, 1899, **31**, 197) on the influence of salts on the velocity of inversion caused by weak acids. From experiments on this subject Arrhenius drew the general conclusion that the addition of salts causes an increase of the dissociation constant corresponding with the effect of increasing concentration in a pure solution of a strong electrolyte.

The present theory of the effect of the addition of salts, which in the case under consideration is indicated by equation (8), is compatible with the experimental results of Arrhenius. When the concentration of the weak acid is unchanged and the slighter influence of f_0 is disregarded, equation (8) requires approximate constancy of the product $c_H \cdot f_1$. On the further assumption that the relative speed h of the reaction is directly proportional to the hydrogen-ion concentration, we find $hf_1 = \text{constant}$. The figures in Table II prove this really to be the case.

TABLE II.

Relative Velocity h and Acidity Coefficient f_1 in Mixtures of Acetic Acid (0.025 mol.) and Potassium Chloride (c).

<i>c.</i>	<i>h.</i>	f_1	hf_1
0.125	1.354	0.682	0.92
0.05	1.205	0.752	0.91
0.02	1.135	0.809	0.92
0.0075	1.083	0.855	0.93

When comparing the figures given in the last column, however, we must bear in mind that even in the case of strong acids a salt exerts some influence on the velocity of reaction, the specific, catalytic action increasing slightly with the salt concentration. For this cause a change of 5 per cent. may occur in the values of hf_1 . Nevertheless we are justified in concluding that an alteration of the dissociation of the weak acid in fairly good agreement with our calculations is indicated by these experiments.

From the same point of view we are able to account for the phenomena exhibited by sparingly soluble, weak acids as saturating substances in salt solutions. As was shown by Hoffmann and Langbeck (*Zeitsch. physikal. Chem.*, 1905, **51**, 385), salicylic acid and other weak acids show a maximum of solubility at a certain salt concentration. This result is explained by the fact that in dilute solutions the steeply decreasing course of the activity coefficient of the ions (f_1) must play the chief part in altering the activity of the acid, whilst at higher concentrations the change of f_0 , owing to the salting-out of the undissociated portion of the acid on account of the slight dissociation, will be of greatest effect. Calculation of the experimental data shows a fairly close agreement with the requirements of the activity curves in Fig. 2.

It seems to the writer, therefore, that the theoretical reasons for the assumption of increasing dissociation of a weak electrolyte on the addition of salts, as well as the corroborating, experimental facts, are sufficiently conclusive to settle this question.

In some recent papers McBain and his co-workers (T., 1914, **105**, 1517; 1919, **115**, 1332) have advanced a conflicting opinion, based partly upon the theory developed by Goldschmidt, Snethlage, and others that the catalytic action of acids is due to the influence of the undissociated molecules as well as of the ions, partly upon the argument that the increase in activity of the undissociated molecules of the weak acid produced by the addition of salts is counterbalanced by an equal increase in the activity of the hydrogen ion, no displacement of the equilibrium therefore being bound to occur. The arguments of McBain, however, are not unassailable, because the theory of the catalytic influence of undissociated

molecules, as shown by Bjerrum, possesses very little probability, and the anomalies are much more simply explained by assuming a certain salt effect on the velocity of reaction analogous to the effect exerted by salts on the activity coefficients. It is true that the equilibrating increases in activity of acetic acid and its hydrogen ions have been ascertained approximately through the measurements of McBain and Walpole. This result, however, is a rigid requirement from the thermodynamic law of mass action, if we, with McBain, assume the activity of the acetic ion to be unchanged, and is therefore of no consequence for the question of change in the degree of dissociation. This question cannot be attacked thermodynamically without considering the activities as well as the activity coefficients of the molecules involved.

3. *The Equilibrium in Regulator Mixtures.*

The chemical systems to which the term "regulator mixture" is applied can be characterised by the following equilibrium scheme :

where one of the right-hand substances, for example B , is present in very small concentration as compared with the concentration of two other substances. The best known regulator mixtures are those in which B is the hydrogen- or hydroxyl-ion.

It will be useful to draw a distinction between *acid* and *basic regulators*. This distinction depends, not on the acid or alkaline reaction shown by the solution, but on the scheme of equilibrium belonging to the mixture, namely,

in the case of an acid regulator, for example, acetic acid + sodium acetate, and

in the case of a basic regulator such as ammonia + ammonium chloride.

In the first case the equation :

$$\frac{\xi_1}{\xi_0} = \frac{k_\xi}{\xi_{H'}} \quad . \quad . \quad . \quad . \quad (9)$$

applies thermodynamically. From this we derive :

$$\log \frac{f_1}{f_0} = k_\xi + p_{H'} + \log \frac{c_0}{c_1} \quad . \quad . \quad (10)$$

where $p_{H'} = -\log H'$ according to Sørensen (*Medd. Carlsberg*

Lab., 1909, **8**, 1) is termed the hydrogen exponent. In the case of a basic regulator we have

$$\frac{\xi_1}{\xi_0} = k_{\xi} \xi_{H^+} \quad . \quad . \quad . \quad . \quad (11)$$

and correspondingly

$$\log \frac{f_1}{f_0} = k_{\xi} - p_{H^+} + \log \frac{c_0}{c_1} \quad . \quad . \quad (12)$$

Of course these equations also hold good in the case of solutions of pure weak acids or weak bases. They can be applied much more advantageously to regulator mixtures, however, because the ionic concentration c_1 is known here from the composition of the mixture, when the salts in this are considered to be completely dissociated. By measuring p_{H^+} electrometrically in the regulator mixtures at various concentrations, or when various amounts of salts are added, we are therefore enabled to calculate the corresponding changes in f_1/f_0 and thus to test the validity of the theory given in the first section. It is a point of importance for the application of formulæ (10) and (12) to such a system as a regulator mixture that the influence of the changing medium on the activity of the hydrogen ion manifests itself independently of the influence on its activity coefficient. On account of the very small hydrogen-ion concentration displacement of the equilibrium will cause no sensible changes in c_0 and c_1 , the changes in f_0 and f_1 therefore affording the only causes for the measured alteration of ξ_{H^+} .

Regulator mixtures of this kind have been very thoroughly investigated, especially by Sørensen and his pupils (*Medd. Carlsberg Lab.*, 1909, **8**, 1; 1910, **8**, 373; 1910, **9**, 10; 1911, **10**, 146). Valuable material for a verification of formulæ (10), (12) and (13) has thereby been obtained.

We shall first consider the *phosphate mixtures* produced by mixing 1/15 molal solutions of primary and secondary alkali phosphates. The equilibrium in these is represented by

and the corresponding equilibrium equation analogous to (10); therefore :

$$\log \frac{f_2}{f_1} = k_{\xi} + p_{H^+} + \log \frac{c_1}{c_2} \quad . \quad . \quad (13)$$

Sørensen's measurements of the ratios c_p/c_s in which the solutions of primary and secondary phosphates are mixed, the p_{H^+} found, and $\rho = \log f_2/f_1 + k$ calculated from (13), k being an arbitrary constant, are given in Table III.

TABLE III.

c_p/c_s	p_{H^+}	ρ	c_p/c_s	p_{H^+}	ρ
0.0101	8.68	0.683	1.500	6.643	0.819
0.0256	8.338	0.746	2.333	6.468	0.836
0.0526	8.043	0.764	4.0	6.239	0.841
0.111	7.731	0.777	9.0	5.906	0.860
0.250	7.381	0.779	19.0	5.589	0.868
0.429	7.168	0.800	39.0	5.288	0.879
0.667	6.979	0.803	99.0	4.944	0.940
1.000	6.813	0.813			

As seen from the figures in the last column, $\log f_2/f_1$ exhibits no constant value, but increases gradually as the solution changes from secondary to primary phosphate. This is explained by the fact that the equivalent concentration of the primary phosphate is only one-half of that of the secondary salt. The change is shown more clearly in the accompanying diagram (Fig. 3), where the equivalent

FIG. 3.

Equivalent concentrations of primary and secondary phosphates.

concentrations ranging from 0.067 to 0.133 are plotted as abscissæ and the values of $\log f_2/f_1$ in Table III are indicated by white circles. By means of a straight line drawn through these points a difference of 0.12 is found between the values of $\log f_2/f_1$ at pure primary and pure secondary salt, whilst the most fitting curve gives 0.10. Since the corresponding value taken from the curves in Fig. 2 is 0.09, we see that our theory accounts rather satisfactorily for the salt effect measured in this system.

The black points in Fig. 3 belong to a series of measurements in

which the specimen of secondary phosphate used contained a few units per cent. of the primary salt. The strongly diverging course exhibited by these measurements shows that such an impurity can easily be detected by means of calculations of this kind. A content of 2.6 per cent. of primary salt is conformably computed from the last three points.

Other regulator mixtures measured by Sorensen were glycine + 0.1*N*-hydrochloric acid and glycine + 0.1*N*-sodium hydroxide, representing a basic and an acid regulator respectively. As the glycine solution was decinormal with respect to sodium chloride and no change in the salt concentration therefore occurred on mixing the solutions, a constant value of f_1/f_0 was expected to be calculated from equations (10) and (12). This was found to be the case when due regard was taken to the amount of hydrogen- and hydroxyl-ions in these mixtures, which was so great as to have a sensible influence on c_1 .

In the case of borate and citrate regulators calculations of this kind meet with difficulties owing to the fact that no single equilibrium prevails in these mixtures. In mixtures of boric acid and alkali various condensed acids and ions are present, and in the case of citrate mixtures simultaneous equilibria between CiH_3 , CiH'_2 , CiH'' , and Ci''' (where $\text{Ci} = \text{C}_6\text{H}_5\text{O}_7$) prevail in all ranges of mixtures used in the measurements.

In the foregoing measurements with phosphate mixtures the concentration changed only from 1/15 to 2/15. Palitzsch has examined the same mixtures with the addition of sodium chloride, using a much wider range of total concentration. The results of his measurements are collected in Table IV.

TABLE IV.

	$m.$	$c_{\text{NaCl.}}$	$c.$	p_{H^+}	p_f	p_c
$c_p/c_s = 39$	1/150	0	0.0067	5.48	0.00	0.00
	1/60	0	0.0167	5.43	— 0.05	— 0.04
	1/15	0	0.067	5.29	— 0.19	— 0.14
	1/150	0.1	0.107	5.19	— 0.29	— 0.21
	1/150	0.25	0.257	5.03	— 0.45	— 0.34
	1/150	0.5	0.507	4.91	— 0.57	— 0.43
	1/60	0.5	0.517	4.85	— 0.63	— 0.44
	1/15	0.5	0.567	4.84	— 0.64	— 0.47
	1/15	0.7	0.767	4.74	— 0.74	— 0.54
	1/150	1.0	1.007	4.65	— 0.83	— 0.63
$c_p/c_s = 11.5$	1/15	0	0.068	5.81	0.00	0.00
	1/15	0.5	0.568	5.35	— 0.46	— 0.33
	1/15	0.7	0.768	5.25	— 0.56	— 0.40
$c_p/c_s = 5.67$	1/15	0.0	0.072	6.10	0.00	0.00
	1/15	0.5	0.572	5.67	— 0.43	— 0.33
	1/15	0.7	0.772	5.55	— 0.55	— 0.40

In this table, m indicates the molal concentration of the phosphate mixture, c_{NaCl} the concentration of the added sodium chloride, c the total equivalent concentration, p_{H^+} the measured hydrogen exponent, ρ_f the value of $\log f_2/f_1 + k$ calculated from equation (13) and ρ_e the value obtained from the curves in Fig. 2.

As our theory requires, the value of ρ_f is found to decrease steadily with increasing ionic concentration. Comparison with the values of ρ_e shows a fairly good agreement, the calculated values, however, always being somewhat smaller than those found. As emphasised in the introduction, the basis of our calculation is not sufficiently defined to permit us to expect a close agreement, no allowance having been made for the peculiarities of the various salt systems. There can be no doubt, however, that the figures in Table IV lend strong support to the general theory which underlies these calculations.

Very thorough investigations on acetate regulator mixtures have been published by Walpole (T., 1914, **105**, 2501, 2521). His work contains three series of measurements, namely (i) acetic acid-sodium acetate mixtures in which the total "acetate" was 0.2*N*, (ii) acetic acid-sodium acetate-sodium chloride solutions in which the total "acetate" was 0.2*N* and the total sodium was 0.2*N*, and (iii) mixtures of acetic acid and sodium acetate in equal concentration ("standard acetate" at various dilutions). The three kinds of mixtures can be characterised by the following equations:

The results of the first series are given in Table V. The figures in the first column are the concentrations of the acetic acid; in the second and the third columns are given the observed *E.M.F.*'s and the hydrogen-ion concentrations calculated by Walpole. The figures in the last column are the values of $\rho = \log f_1/f_0 + k$ calculated by means of equation (10).

In equation (10) used for the calculation of ρ we have to introduce $c_0 = c_{\text{C}_2\text{H}_4\text{O}_2} - c_{\text{H}^+}$ and $c_1 = c_{\text{C}_2\text{H}_3\text{O}_2\text{Na}} + c_{\text{H}^+}$. Whilst c_{H^+} is negligible at concentrations of acetic acid lower than 0.16, we have to correct for it at higher concentrations. The figures under c_{H^+} are calculated by Walpole from the equation $\pi = 0.3377 + 0.0577 \log \frac{1}{c_{\text{H}^+}}$ on the assumptions that the dissociation is

92 per cent. in 0.1*N*-hydrochloric acid and that the gas laws are valid in the case of the solutions concerned. Since both assumptions are erroneous, the values of c_{H^+} can be accurate only until $c_{\text{C}_2\text{H}_4\text{O}_2}$,

TABLE V.

$C_2H_4O_2$.	π .	$C_H \times 10^3$.	ρ .
0.0025	0.7138	—	0.473
0.005	0.6961	—	0.473
0.0075	0.6853	—	0.468
0.01	0.6778	—	0.468
0.02	0.6593	—	0.473
0.03	0.6478	—	0.474
0.04	0.6393	—	0.477
0.05	0.6316	—	0.469
0.06	0.6256	—	0.474
0.08	0.6148	—	0.479
0.1	0.6046	—	0.478
0.12	0.5947	—	0.483
0.14	0.5841	—	0.491
0.16	0.5712	0.09	0.500
0.18	0.5525	0.19	0.525
0.185	0.5450	0.26	0.528
0.190	0.5348	0.38	0.531
0.192	0.5290	0.48	0.522
0.194	0.5225	0.63	0.520
0.195	0.5193	0.71	0.531
0.196	0.5155	0.83	0.540
0.197	0.5105	1.01	0.537
0.198	0.5057	1.23	0.552
0.199	0.4995	1.57	0.545
0.2	0.4931	2.01	0.541

= 0.194. At higher concentrations the ρ -values, therefore, will be somewhat untrustworthy.

The results of the second series are given in Table VI.

TABLE VI.

$C_2H_4O_2$.	π .	$C_H \times 10^3$.	ρ .
0.004	0.7015	—	0.468
0.0105	0.6762	—	0.462
0.04	0.6375	—	0.447
0.06	0.6235	—	0.438
0.08	0.6126	—	0.441
0.1	0.6019	—	0.432
0.12	0.5908	—	0.405
0.14	0.5793	—	0.438
0.16	0.5654	0.142	0.399
0.17	0.5564	0.162	0.394
0.18	0.5461	0.244	0.414
0.185	0.5389	0.326	0.420
0.189	0.5297	0.471	0.395
0.19	0.5274	0.515	0.396
0.194	0.5159	0.817	0.393
0.195	0.5129	0.920	0.405
0.199	0.4949	1.89	0.376
0.2	0.4902	2.77	0.436

The notation and the calculation are here the same as in the foregoing case.

Finally in Table VII the third series of measurements is pre-

sented; c here indicates the equal concentrations of acetic acid and sodium acetate.

TABLE VII.

c .	π .	ρ .
0.2	0.60345	0.458
0.1	0.60445	0.476
0.04	0.60575	0.496
0.02	0.60678	0.517
0.016	0.60735	0.526
0.01	0.60798	0.536
0.005	0.60923	0.558
0.002	0.61100	0.589
0.001	0.61223	0.611

The results of the three series are shown diagrammatically in Fig. 4, which can most conveniently be made a basis for discussion. The values of ρ , differing from the values of $\log f_1/f_0$ only by a constant, are here plotted as ordinates against the concentrations of sodium acetate as abscissæ. The data belonging to series (i), (ii) and (iii) are indicated by $\circ$, $\bullet$ and $\bullet$ respectively.

FIG. 4.

First of all, through the mutual position of the points in the diagram, we obtain information about the experimental error.

This amounts in many cases to 0.05 or more, expressed in p_H values. Nevertheless, there can be no doubt how to draw the most fitting curve through the experimental points. It is evident that the measurements in series (i) and (iii) are represented by a strongly bent curve, *a*, identical for both series. The measurements of series (ii), on the other hand, lie probably on a straight line *b*.

This, however, is just what we have to expect from the point of view of our theory. In (i) and (iii) no salt is present other than sodium acetate. Independently of the amounts of acetic acid, which differ largely in the two series, we must find concordant values of f_1/f_0 at the same concentration of sodium acetate. The shape of the curve, furthermore, agrees well with the theoretical one given in Fig. 2. In the second series, on the other hand, the salt present in the solution changes gradually from 0.2 molal sodium chloride to 0.2 molal sodium acetate, the total salt concentration being constant. Here we have to expect a salt effect changing proportionately with the change in composition, that is, a rectilinear change in f_1/f_0 , as exhibited by the experiments.

The course of the line *b*, inclining strongly from sodium acetate to sodium chloride solution, gives evidence of the fact that the salt effect is markedly a function of the nature of the salt in question. On the assumption that the effect of the two salts is an additive one, the curve *c* in the figure is calculated as expressing the interdependence of $\log f_1/f_0$ and the concentration in a solution containing no other salt than sodium chloride. The theoretical curve based upon the solubility measurements referred to in the introduction is inserted in Fig. 4 as *d*. This curve evidently agrees rather closely with the sodium chloride curve, *c*, in accordance with the fact that acetates deviate more than chlorides from the average salt effect as given in the theoretical curves in Fig. 2.

4. *The Indicator Equilibrium.*

Another field in which our theory can be applied advantageously is the much discussed problem of the influence of salts on the colours of indicators. (For the literature, see Bjerrum: "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen, Sammlung Ahrens," 1914.) Since the functions of indicators, according to the view introduced by Ostwald, are due to their properties as weak acids and weak bases, this problem is a special case of the one treated in the foregoing.

The particular advantage of using solutions of indicators consists in the possibility of deducing from the colour the ratio in which the undissociated and the dissociated portions are present in the

solutions. Assume the case of an acid indicator dissociating according to the scheme :

then equation (10) will apply thermodynamically to this equilibrium. When the solutions considered show the same colour, c_1/c_0 in this equation will be a constant and therefore :

$$\log \frac{f_1}{f_0} = k + p_{H^+} \quad . \quad . \quad . \quad . \quad (14)$$

As a consequence of this equation a given activity of the hydrogen ion will produce the same colour only in solutions having the same value of f_1/f_0 . The colorimetric method for the determination of hydrogen-ion activities, based upon the principle of comparing the colour of a series of regulator mixtures with the colour of the solution the hydrogen-ion activity of which is to be determined, will therefore to a certain degree be untrustworthy if the concentration of the solution differs from that of the regulator mixtures. Equation (14) teaches that in the case of an acid indicator the addition of salts, that is, decreasing values of f_1/f_0 , implies decreasing values of p_{H^+} . The more concentrated solution is more acid than the less concentrated which gives the same colour. The colorimetric method consequently leads us to accept too small a hydrogen-ion activity in the concentrated solution.

In the case of a basic indicator we can write, instead of (14),

$$\log \frac{f_1}{f_0} = k - p_{H^+} \quad . \quad . \quad . \quad . \quad (15)$$

and therefore follow an effect in the opposite direction. The colorimetric method leads us to accept too high a hydrogen-ion activity in the more concentrated solution.

A verification of these conclusions is furnished by the investigations of Sørensen (*loc. cit.*) and his co-workers, who have done important work for the elaboration of the colorimetric method. The test is made a quantitative one by introducing in equations (14) and (15) the values of f_1/f_0 and f_2/f_1 calculated on the principles given in the introduction.

Sørensen's data are tabulated in Table VIII. The first column gives the indicator used. The column headed $(p_{H^+})_c$ contains the values of p_{H^+} found colorimetrically by comparison with the pure regulator without added salt; $(p_{H^+})_e$ is the electrometric or true value of p_{H^+} in the solution. The "salt error" is defined by :

$$\Delta = (p_{H^+})_c - (p_{H^+})_e$$

Δ_o and Δ_c indicating the observed and the calculated values of the salt error respectively.

TABLE VIII.

Indicator.	$(pH')_e$	Δ_f	Δ_c
(1) Solution : Phosphate (0.07N) + NaCl (0.5N); $(pH')_e = 5.65$.			
<i>p</i> -Nitrophenol	5.81	+ 0.16	+ 0.15
<i>p</i> -Sulphobenzeneazo- α -naphthylamine	5.55	- 0.10	- 0.15
Alizarinsulphonic acid	5.91	+ 0.26	+ 0.23
(2) Solution : Phosphate (0.11N) + NaCl (0.5N); $(pH')_e = 6.66$.			
<i>p</i> -Nitrophenol	6.80	+ 0.14	+ 0.14
Neutral-red	6.57	- 0.09	- 0.14
Rosolic acid	6.72	+ 0.06	+ 0.14
(3) Solution : Borate (0.08N) + NaCl (0.5N); $(pH')_e = 8.02$.			
<i>p</i> -Sulphobenzeneazo- α -naphthol ...	8.14	+ 0.12	+ 0.15
Phenolphthalein	8.14	+ 0.12	+ 0.15

It is seen that the effect of the salt on the various indicators in nearly all cases agrees well with the calculated effect. Only in the case of rosolic acid is the agreement less satisfactory.

In Table IX are given some other data from some measurements of Sørensen and Palitzsch (*Medd. Carlsberg Lab.*, 1913, **10**, 228).

TABLE IX.

<i>c</i> .	Δ_f	Δ_c	Δ_f	Δ_c
0.01	- 0.09	- 0.06	- 0.14	- 0.11
0.02	- 0.05	- 0.04	- 0.12	- 0.09
0.05	- 0.02	0	- 0.07	- 0.05
0.1	+ 0.05	+ 0.03	- 0.02	- 0.02
0.2	+ 0.11	+ 0.07	+ 0.05	+ 0.02
0.5	+ 0.20	+ 0.15	+ 0.14	+ 0.10
	(I.)		(II.)	

c is the concentration of the salt solution and Δ_f and Δ_c have the same meaning as above. Series I refers to measurements in which phenolphthalein and naphtholphthalein were used as indicators in solutions of a borate mixture of concentration 0.05. In series II phenolphthalein and phosphate mixtures were employed. A comparison of Δ_f and Δ_c shows the anticipated salt effect. That the calculated values are somewhat smaller than those found is perhaps due to the assumption, made in calculations according to equation (14), that the indicators are monobasic acids. Assuming the indicators to dissociate as dibasic acids—and for this assumption some evidence has been brought forward (Wegscheider, *Zeitsch. Elektrochem.*, 1908, **14**, 510)—we must introduce f_2/f_1 instead of f_1/f_0 , and then obtain small deviations in the opposite direction.

The effect of salts on indicators has been examined from the point of view that the hydrogen-ion activity is the deciding factor in the indicator equilibrium. The displacement of the equilibrium in an indicator-regulator mixture, however, can be considered from another point of view, namely, that the equilibrium can be represented with no hydrogen ions entering in the equilibrium scheme.

Denoting the neutral molecules of an acid and a basic regulator by AH and B respectively, and the neutral molecules of an acid and a basic indicator by SH and M , all possible equilibria and the effect of the addition of salts on any of these can be given by the following scheme :

	Indicator.	Regulator.	Equilibrium.	Effect.
(I)	acid	acid	$SH + A' \rightleftharpoons S' + AH$	none
(II)	acid	basic	$SH + B \rightleftharpoons S' + BH'$	more basic
(III)	basic	acid	$MH' + A' \rightleftharpoons M + AH$	more acid
(IV)	basic	basic	$MH' + B \rightleftharpoons M + BH'$	none

The requirements of this scheme seem actually to be fulfilled in most cases of observations with indicators of known chemical nature, especially when it is noted that the requirement of "none" effect cannot be at all a rigid one, because even very small deviations from equal salt effect on ions of the same type will be able to produce a change in colour of the indicator.

As an example we may quote the very accurate investigation carried out in this field by Rosenstein (*J. Amer. Chem. Soc.*, 1912, **34**, 1125) who evaluated directly the colour change of phenolphthalein to determine the degree of dissociation of this indicator in an ammonia-ammonium chloride regulator in which $c_{NH_4^+}/c_{NH_3}$

was kept constant. In Table X the ratios $\frac{\alpha}{1-\alpha}$ are given together with the corresponding total salt concentrations c_t , the values of f_1/f_0 taken from the diagram (Fig. 2) and finally the value of $r = \frac{\alpha}{1-\alpha} / \left(\frac{f_1}{f_0}\right)^2$.

TABLE X.

c_t .	$\frac{\alpha}{1-\alpha}$	f_1/f_0 .	r .
0.10	0.246	0.69	0.116
0.13	0.261	0.67	0.118
0.20	0.310	0.63	0.122
0.60	0.469	0.50	0.117

Since we have here a basic regulator and an acid indicator the system will be represented by the equilibrium (II) in the above scheme. Increasing salt concentration, therefore, must render the solution more basic, as is really shown by the figures in the second column. For the equilibrium (II) the thermodynamic mass-action law requires

$$\left(\frac{\xi_1}{\xi_0}\right)^2 = \frac{c_{NH_4^+}}{c_{NH_3}} \cdot \frac{\alpha}{1-\alpha} \left(\frac{f_1}{f_0}\right)^2 = \text{constant}$$

or as $\frac{c_{NH_4^+}}{c_{NH_3}}$ was unchanged

$$\frac{\alpha}{1-\alpha} \cdot \left(\frac{f_1}{f_0}\right)^2 = \text{constant}.$$

The constancy of this term is exhibited by the values of r given in the last column.

Some other series of the measurements of Rosenstein harmonise more fully with the assumption of the dissociation of phenolphthalein as a dibasic acid.

As a chief result of our considerations of the effects of salts on the indicator equilibrium we may record the complete agreement of the theory in regard to the sign, and the partial agreement in regard to the magnitude, of the effect with the evidence furnished by various materials and in various fields of investigation. For reasons stated in the introduction, however, all our calculations are to a certain degree approximate, and in the case of indicators a special uncertainty attends the numerical results on account of the chemical nature of such substances not being fully elucidated; for example, methyl-orange, which is usually regarded as a basic indicator on account of its character as amine. Simultaneously acting as a strong acid, the anion of this will be the form in which the indicator will be present in alkaline solution, and the equilibrium scheme of the dissociation therefore will be represented by

fully corresponding with the dissociation of an acid indicator if we are allowed to regard the right-hand molecule as electrically a neutral one. This, however, is doubtful, because one hydrogen ion has been removed from one end of the molecule and added to the other and the electric charges produced do not necessarily neutralise one another; therefore, it can be foretold that the behaviour of such a substance will be uncertain.

Similar uncertainties, and also others due to the possibly colloidal nature of the indicator, are encountered in many cases.

Summary.

From the point of view of the theory of complete dissociation of strong electrolytes, the interpretation of the solubility phenomena exhibited by slightly soluble salts leads us to surmise an increase in the dissociation of weak electrolytes on the addition of salts to their solutions. Evidence corroborative of this conclusion has been advanced from various fields of investigation, and an explanation of the salt effect on regulator mixtures and indicator equilibria has been given from the same point of view.

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