

and CH_3COONa , CH_3COOH) were isolated; calcium, zinc, ferric and silver acetates gave negative results.

The results of this work resemble those obtained with sulfate systems in following the general rule previously deduced, that compound formation increases in extent with increasing diversity in the character of the components, the significant variable in systems of this general type $\text{HX}:\text{RX}$ being the position of R relative to H in the electromotive series. An examination of the data for sulfates, formates, acetates, fluorides and hydroxides shows that the rate of decrease in compound formation as we proceed from more positive radicals (such as potassium) or less positive radicals (such as silver) towards hydrogen increases, the weaker the acid radical.

Solubility and compound formation are again found to proceed in parallel throughout the series. Salts which show extensive compound formation (such as salts of the alkali metals) are also extremely soluble. As we pass down the electromotive series towards hydrogen, solubility rapidly diminishes and finally becomes inappreciable.

The correlation of solubility with compound formation and of compound formation with ionization in solutions of metal formates in formic acid will be further dealt with in subsequent communications, and additional rules connecting these properties in systems of the general type $\text{HX}:\text{RX}$ will there be formulated.

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THE PREDICTION OF SOLUBILITY IN POLAR SOLUTIONS.

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If all solutions were ideal, the answer to most of our solubility problems could be very simply stated.¹ At any given temperature the solubility of a solid substance A in a series of different solvents B, C, D, etc. would be, when expressed in terms of mol fractions, a fixed quantity, independent of the particular solvent and immediately calculable from the heat of fusion of A, the temperature of fusion of A and the specific heats of A in the solid and liquid states. All liquids would be completely miscible under all conditions. The solubility of a gas in a liquid, expressed again in terms of mol fractions, would depend only upon the ratio of its partial pressure over the solution to its vapor pressure in the liquid state at the same temperature.²

¹ Roozeboom, "Heterogene Gleichgewichte," [1] 2, 273, et seq. (1904); Washburn, "Principles of Physical Chemistry," Chap. 14 (1915).

² Strictly speaking, this would be true only for a perfect gas. More accurately, solubility is proportional to fugacity instead of to vapor pressure.

Unfortunately, we meet ideal solutions in the laboratory scarcely more frequently than we do infinitely dilute solutions, so that the theory of ideal solutions alone is not much more useful to us in the quantitative prediction of solubilities than is the simple theory of van't Hoff in the quantitative prediction of osmotic pressures or allied relationships. Certainly, for example, the solubility of iodine³ is not the same in a series of solvents such as water, ethyl alcohol, chloroform, carbon disulfide and bromine at the ordinary temperature, even if translated from the units usually employed into terms of mol fractions.

In order to make any further advances on the basis of our modern theory of ideal solutions we require, therefore, to investigate very carefully the various factors which induce non-ideality in solutions and the effect each of these factors has on solubility phenomena. Apparently so many different points⁴ are involved that the complexity of the problem, when first realized, almost compels us to despair of ever reaching definite conclusions; yet on critical examination it becomes possible to disentangle to some extent fundamental from secondary factors, and, by concentrating attention exclusively upon the former, to obtain at least a preliminary outline of the more comprehensive theory of solutions of the future.

This narrowing down of the point of attack may, of course, be carried too far, but in such a case vital disagreements between predicted and experimental results soon appear, necessitating a re-examination of the field already covered and leading either to the modification or to the amplification of the generalizations involved. Thus the tendency of most investigators in the field of non-ideal solutions has been to attribute all divergences from the ideal-solution equations to effects which may be called purely chemical, *i. e.*, to changes in the molecular state of the components on admixture.⁵ In a recent extremely valuable series of articles by Hildebrand and his associates, however, the primary importance of taking into consideration two entirely distinct factors of a more physical nature, internal pressure and polarity, has been indisputably established.⁶ The conclusions of Hildebrand with respect to the solubilities of solids in liquids (that section of the field to which the present article is restricted) may be

³ Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, pp. 325-34; Hildebrand, *THIS JOURNAL*, **39**, 2299 (1917).

⁴ Roozeboom, *op. cit.*, pp. 287-314.

⁵ Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910); **83**, 40 (1913); for other references see Findlay, "Osmotic Pressure," 1919, p. 64, *et seq.* Dhar, *Z. Elektrochem.*, **20**, 57 (1914); also Kendall and Booge, *THIS JOURNAL*, **38**, 1730 (1916); Kendall, Booge and Andrews, *ibid.*, **39**, 2308 (1917).

⁶ Hildebrand, *ibid.*, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); Hildebrand, Ellefsen and Beebe, *ibid.*, **39**, 2301 (1917); Hildebrand and Jenks, *ibid.*, **42**, 2180 (1920); Hildebrand and Buehrer, *ibid.*, **42**, 2213 (1920). Electromagnetic environment as a factor in solubility has also been considered by Harkins (*ibid.*, **41**, 970 (1919)).

summarized as follows: (1) the solubility of a non-polar substance in a non-polar liquid of equal internal pressure is that calculated on the basis of the ideal-solution theory; (2) where the internal pressures are unequal, the solubility is less, to an extent depending on the difference in internal pressures; (3) when one substance is polar and the other non-polar, the solubility is also less; (4) when both substances are polar (leading frequently to the formation of recognizable compounds) the solubility is usually greater than the calculated value.

Numerous examples are given by Hildebrand to illustrate the first three of these rules. The greater difficulties inherent in the study of solutions of the fourth type (polar substances in each other) have also been briefly indicated.⁷

It is with this fourth class of solutions, particularly with those cases in which the formation of addition compounds between the components has already been extensively studied, that the present investigation is concerned. In previous articles⁸ general rules have been formulated connecting the extent of compound formation with the difference in character⁹ of the components of the solution, and for two series of systems of the type HX — RX a parallelism between compound formation and solubility throughout each series has been traced.¹⁰ The fundamental significance of this parallelism is here discussed and its extension to other series attempted.

Before proceeding to a theoretical examination of these solutions (which belong, as indicated above, to the most complex of the 4 divisions made by Hildebrand) it is necessary to determine how many of the disturbing factors may legitimately be neglected, since only through such a clearing of the field in advance is it possible at the present stage to simplify matters sufficiently to enable us to formulate and put to the test any generalizations whatever.

In the first place, for the particular cases here examined, the factor of internal pressure may—in spite of what has been said above—be temporarily left out of consideration. Hildebrand¹¹ himself admits that there is more justification in restricting the discussion to purely chemical factors in mixtures involving a polar liquid; and the components of the mixtures

⁷ Hildebrand, *THIS JOURNAL*, **38**, 1464-1470 (1916).

⁸ See particularly Kendall and Davidson, *THIS JOURNAL*, **43**, 979 (1921); Kendall and Adler, *ibid.*, **43**, 1470 (1921).

⁹ *I. e.*, differences in the positive or negative nature of the constituent groups. In the case of systems of the simple type HX — RX here studied, where the negative radical X is common to both components, the difference in character is dependent on the relative positions of R and H in the electromotive series.

¹⁰ Kendall and Davidson, *loc. cit.*, p. 989; Kendall and Adler, *loc. cit.*, p. 1480.

¹¹ Hildebrand, *THIS JOURNAL*, **38**, 1461 (1916); see also Eastman and Hildebrand, *ibid.*, **36**, 2029 (1914).

investigated in this article are *both* polar. In a later section,¹² indeed, it will be shown that it is extremely improbable that the main conclusions here drawn can be significantly affected through not taking into account the differences in internal pressure of our components. The polarity factor, owing to its inherent complexity, cannot be disposed of so readily, but by dissecting the general term "polar," as applied to a liquid, into its particular consequences¹³—increased internal pressure, abnormalities in surface tension and other physico-chemical relationships, increased molecular complexity both in the pure state (association) and in solution with other polar substances (addition compound formation), and an increased tendency towards ionization—we can examine the effect of each of these in turn and so establish its relative importance in inducing deviations from ideality in the special class of solutions under study.

The results obtained in earlier papers of this series¹⁴ lead us to conclude that *compound formation* between the components is the dominating point to be considered. *Internal pressures* in any particular system may vary considerably with the composition, but it has already been indicated that this factor can be here omitted. The abnormalities in other physical properties do not need to be taken into account in this work. *Ionization* has been shown to be a consequence of compound formation, and to parallel it in extent throughout any given series. Any divergences from the ideal solution laws due to compound formation between the components will, therefore, be accentuated by the accompanying ionization, it is true. But it is not to be expected that ionization will change the order of deviations from the ideal curve predicted for a series of systems on the basis of compound formation alone. Rather it will make the "spread" of the different curves with respect both to the ideal and to each other still more pronounced. A detailed discussion of the last remaining factor—*association* of the components—unfortunately cannot be entered into at this point for space considerations. In the final consideration of results,¹⁵ however, it will be shown that the effect of this factor also is here, in general, only of secondary consequence.

We are now in a position to attack the problem in a simpler form, by investigating first of all the influence of compound formation alone upon ideal solution and solubility relationships. Rules for this factor having once been established, we can later proceed more readily to the consideration of the remaining factors.

¹² Page 1498 of this article.

¹³ G. N. Lewis, *THIS JOURNAL*, **38**, 762 (1916).

¹⁴ See especially Kendall and Gross, *ibid.*, **43**, 1416, 1426 (1921).

¹⁵ A preliminary treatment of this complicated subject is given by Roozeboom, "Heterogene Gleichgewichte," [1] **2**, 303-14 (1904).

The Effect of Compound Formation on the Ideal Solubility Curve.

The first stage of the problem consists in indicating qualitatively how the solubility of a fixed substance A will vary in a series of different solvents exhibiting gradually increasing compound formation with A in the liquid state. The complete solubility curves for such a series of systems are shown on a single diagram in Fig. 1. In this diagram, temperature is plotted against the molecular composition of the saturated solution. To facilitate comparison of the curves it is necessary to note that the point A represents the same temperature throughout—the melting point of pure substance A.

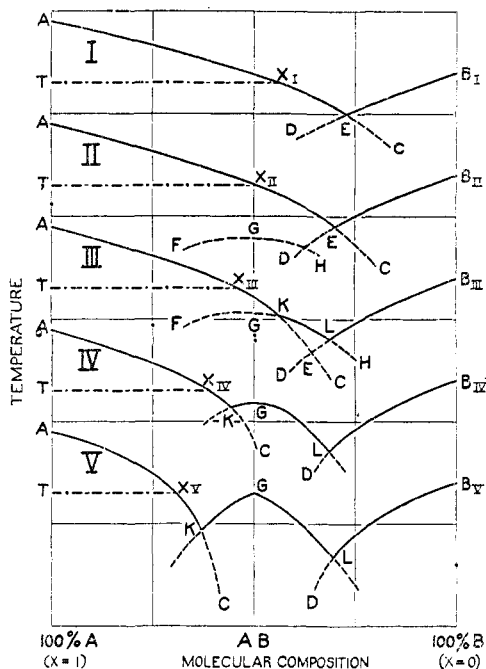


Fig. 1.

Curve I indicates the ideal system A-B_I, where compound formation is entirely absent. The solubility curve of A in B_I, the line AC, represents the ideal solution equation,¹⁶

$$\ln x = (-Q/RT_0T) \cdot (T_0 - T) \tag{I}$$

where x is the mol fraction of A in the saturated solution at the temperature T , Q the differential mol heat of solution¹⁷ of A, T_0 the melting

¹⁶ Roozeboom, *op. cit.*, p. 274; Washburn, *op. cit.*, p. 168.

¹⁷ In the derivation of Equation I an integration has been carried out under the assumption that Q is not variable with the temperature. In actual fact, of course, this is never strictly true. The effect of variations in Q on the course of the curve is discussed in a later section.

point of pure A, and R the gas constant 1.9852. The form and slope of this curve are conditioned solely by the ratio Q/T_0 . If this ratio exceeds the value 4 (as it does for all substances except a few elements) the curve is concave throughout its whole course with respect to the composition axis, but does not change in slope greatly until x becomes very small, when it commences to dip sharply, x finally becoming zero at absolute zero of temperature. The solubility curve of B_I in A, the line $B_I D$, is similar in character (its slope depending, however, on the values of Q and T_0 for B_I). The stable portions of the two curves end at their point of intersection, E, the eutectic point of the system.

Curves II to V illustrate the successive changes which occur in the diagram as compound formation increases.¹⁸ In Curve II the compound formed is so highly dissociated in solution that its solubility curve FGH never enters the stable region of the diagram; in Curve III compound formation is somewhat more extensive and the solubility curve of the compound AB_{III} possesses a limited stable interval KL; in Curve IV this interval has expanded sufficiently to exhibit a maximum point at G (in other words, the compound AB_{IV} is stable at its melting point); in Curve V, finally, the compound AB_V is not dissociated at all into its components in the solution, the system consisting, indeed, of two simple systems of the type shown in Curve I compressed into one composition range.

The essential point to be noted in these systems is the depression of the curve AC from its ideal position, which compound formation in solution necessitates.¹⁹ If only part of the total A in solution exists as uncombined A then, since the solution will not become saturated with respect to A until the mol fraction of *uncombined* A reaches the ideal value, the total mol fraction of A in the saturated solution must exceed this ideal value by an amount depending on the stability of the compound AB in the liquid state. The solubility of A at any fixed temperature T consequently increases regularly as we pass from Curve I to Curve V. This may best be seen by comparing the compositions of the saturated solutions at temperature T (represented by the points X_I , X_{II} , X_{III} , X_{IV} , X_V respectively on the various curves).

Increasing solubility and increasing compound formation, therefore, for a fixed solute A in a series of different solvents, proceed in parallel. A few typical series of systems illustrating this rule are presented below, the solvents in each table being arranged in order of increasing compound formation with the given solute. Although in a few cases it is to be feared

¹⁸ For the sake of simplicity, only a single compound of the type AB is considered. The argument, however, can readily be extended to other types.

¹⁹ In Curve I, AC is tangential to the B composition axis ($x = 0$); in Curve V, AC is tangential to the AB composition axis ($x = 0.5$). In the remaining curves AC assumes an intermediate position.

that we are approaching somewhat too closely systems of the type studied by Hildebrand (where internal pressure differences cannot be kept out of consideration), yet a uniform increase in solubility throughout each series is apparent.

TABLE I.^a

Solubility at 40° of Dimethyl-pyrone (M. p., 132.1°).	
Solvent.	Mol. % solute in saturated soln.
Acetic acid	40.2
Formic acid	46.8
Chloro-acetic acid	50.6
Dichloro-acetic acid	53.5
Trichloro-acetic acid	54.3
[Ideal (calc.) ^c	41.5]

^a Kendall, *THIS JOURNAL*, **36**, 1222 (1914).

^b Kendall and Booge, *ibid.*, **38**, 1712 (1916).

^c Poma, *Gazz. chim. ital.*, [II] **41**, 518 (1911). Approximate value only.

TABLE II.^b

Solubility at 10° of Trichloro-acetic Acid (M. p., 58°).	
Solvent.	Mol. % solute in saturated soln.
Benzene	38.0
Phenyl salicylate	57.5
Benzyl benzoate	64.4
Ethyl benzoate	66.0
Ethyl acetate	67.1

TABLE III.^a

Solubility at 50° of Benzoic Acid (M. p., 121°).	
Solvent.	Mol. % solute in saturated soln.
Benzene	17.6
Acetic acid	27.7
Chloro-acetic acid	30.2
Dichloro-acetic acid	42.5
Trichloro-acetic acid	49.5

^a Kendall, *THIS JOURNAL*, **36**, 1722 (1914).

^b Kendall, Booge and Andrews, *ibid.*, **39**, 2303 (1917).

TABLE IV.^b

Solubility at -5° of Ice (M. p., 0°).	
Solvent.	Mol. % solute in saturated soln.
Acetic acid	95.01
β -oxypropionic acid	95.30
α -oxypropionic acid	95.49
<i>d</i> -tartaric acid	95.78
Hydrochloric acid	96.19
[Ideal (calc.)	95.26]

All of the above tables are taken from previous articles of this series,²⁰ freezing-point depression data therein presented being here simply restated in terms of solubilities. We are thus enabled to emphasize (particularly in Table IV) the essential identity of freezing-point depression and solubility relationships. Although this identity is fully recognized in a few standard text-books,²¹ most writers on physical chemistry continue to treat the two subjects as entirely unconnected, and the false distinctions drawn by a past generation between *fusion* and *solution* still flourish in the literature.²²

²⁰ Other shorter examples may be constructed by the reader from the data in Seidell's "Solubilities of Inorganic and Organic Compounds," but the amount of systematic work on the subject is very meagre.

²¹ Roozeboom, *op. cit.*; Washburn, *op. cit.*

²² Thus Forster, in the Emil Fischer Memorial Lecture (*J. Chem. Soc.*, **117**, 1159 (1920) asks the question: "To the man whose sugar 'melts' in tea, how are the beauties of the sixteen stereo-isomeric aldohexoses to be revealed?" To which the answer may be made: "Sugar *does* melt in tea, just as ice melts in iced tea."

Solubilities of Different Substances in a Fixed Solvent.

This second stage of the problem (the comparison of the solubilities of a series of different solutes in the same solvent) is in practice the more important, owing to the supremacy of water as a solvent liquid. Theoretically, however, it is still more difficult to handle, for while the ideal solubility curve for each particular solute is fixed by its own values for Q and T_0 , no relation between the values of either Q or T_0 for *different* solutes has yet been established. We cannot therefore postulate in advance the relative positions of a series of ideal curves, much less make comparisons between them when compound formation causes deviations from the ideal. Under special circumstances, however, it is still possible to make some progress, namely when the solutes possess melting points far above the temperature at which we wish to conduct comparisons. The most interesting of all classes of solutes—neutral salts—fortunately falls under this category. For the discussion of solubility relationships in this field, reference should be made to Fig. 2.

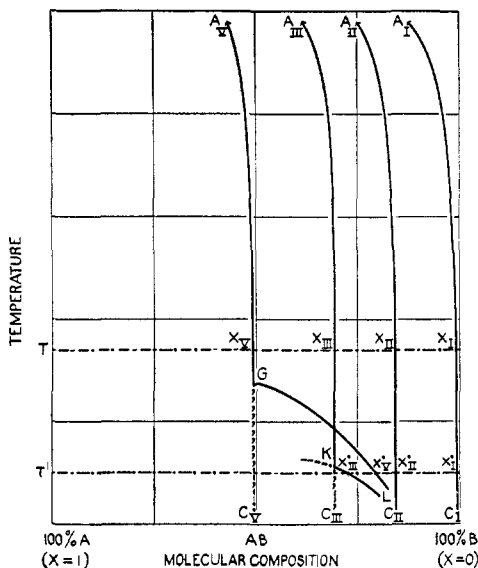


Fig. 2.

Curve I reproduces the course of the ideal solubility curve (Equation I, page 1485) at low temperatures; *i. e.*, points on the curve $A_I C_I$ represent saturated solutions of an ideal solute A_I in a fixed solvent B. At sufficiently low temperatures this line is almost coincident with the B composition axis ($x = 0$) whatever the particular values of Q and T_0 for A_I may be;

in other words, the solubility is *practically zero*. If we take, as an example, the case of potassium chloride (for which Q is 64.10 cal. and T_0 is 1045° abs.) we find that the mol fraction of the salt in a saturated ideal solution at 25° would be only 0.00044.²³

If the salt forms a compound AB with the solvent, however, the solubility curve is depressed (as in Fig. 1) to an extent dependent upon the stability of the compound in solution, the successive changes which occur being shown in Curves II to V, as before.²⁴ The curve $A_V C_V$, which represents saturated solutions of a solute A_V forming a perfectly stable compound of the type AB, is tangential to the AB composition axis ($x = 0.5$); the remaining curves again assume intermediate positions. Furthermore, since the curves are all falling exceedingly sharply in the lower portion of their courses, the variation of x with T at low temperatures is very small. It becomes a matter of minor importance, therefore, what the actual values of Q and T_0 for each particular solute may be, since although the curves for the various salts intersect at random at high temperatures, at low temperatures the order of solubility will be substantially identical with the order of compound formation. As in Fig. 1 this may best be seen by comparing the positions of the points X_I , X_{II} , X_{III} , X_{IV} and X_V on the various curves at a fixed temperature T . For strict purposes of comparison, it must be noted, it is essential that this temperature be so chosen that the solubility of the simple salt is determinable in each case. At still lower temperatures, where a compound may make its appearance as stable phase and the solubility of the simple salt may no longer be measurable, the solubility order may become obscured by the intersection of the stable curves, as indicated by the positions of the points X'_I , X'_{II} , X'_{III} , and X'_V at the temperature T .¹ It must be emphasized that the solubility of the compound under such conditions affords no accurate guide to the actual solubility of the simple salt, but is useful in indicating its *minimum* value.²⁵

For a series of different salts of high melting points in a fixed solvent at a sufficiently low temperature, therefore, solubility and compound formation again proceed in parallel. Two typical series which illustrate this rule (neutral sulfates in sulfuric acid and neutral formates in formic acid) have already been presented in previous articles, to which reference should be made for the complete tables. A third precisely similar series (metal hydroxides in water) may here be added for comparison.

²³ For a saturated aqueous solution, this is equivalent to about 1.8 g. per liter (approximately 0.02 N).

²⁴ Curve IV is omitted in order to avoid crowding and confusion in the diagram. Its position, however, between Curves III and V can readily be visualized with the aid of Fig. 1.

²⁵ The solubility of an unstable solid phase is necessarily greater than that of the stable solid phase.

TABLE V.

Solubilities of Metal Hydroxides in Water. 25°.				
Metal.	Electrode potential.	G. of hydroxide in 100 g. satd. soln.	Solid phase to which saturation refers.	Mol. % hydroxide in satd. soln.
Li	-3.02	11.14 ^a	LiOH, H ₂ O	8.82
K	-2.92	54.2 ^a	KOH, 2H ₂ O	29.13
Ba	-2.8 (?)	4.47 ^b	Ba(OH) ₂ , 8H ₂ O	0.489
Na	-2.72	53.2 ^a	NaOH, H ₂ O	34.01
Sr	-2.7 (?)	1.016 ^c	Sr(OH) ₂ , 8H ₂ O	0.143
Ca	-2.5 (?)	0.152 ^d	Ca(OH) ₂	0.0370
Mg	-1.55	0.0012 ^e	Mg(OH) ₂	0.00052
Al	-1.34	insoluble	Al(OH) ₃	practically zero
Zn	-0.76	0.001 ^f	Zn(OH) ₂	0.00018
Cd	-0.40	0.00026 ^f	Cd(OH) ₂	0.000032
Ni	-0.22	insoluble	Ni(OH) ₂	practically zero
Pb	-0.13	0.0161 (?) ^g	Pb(OH) ₂	0.00121 (?)
Fe (ic)	-0.04	insoluble	Fe(OH) ₃	practically zero
Cu	+0.35	insoluble	Cu(OH) ₂	practically zero
Ag	+0.80	0.0054 ^h	Ag ₂ O	0.00078

^a Pickering, *J. Chem. Soc.*, **63**, 890 (1893).

^b Parsons and Corson, *THIS JOURNAL*, **32**, 1383 (1910).

^c Rothmund, *Z. physik. Chem.*, **69**, 523 (1910).

^d Bassett and Taylor, *J. Chem. Soc.*, **105**, 1926 (1914).

^e Tamm, *Z. physik. Chem.*, **74**, 499 (1910).

^f Bodländer, *ibid.*, **27**, 66 (1898).

^g Sehnal, *Compt. rend.*, **148**, 1394 (1909). In view of the results of earlier observers (see Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, p. 362) this value must be regarded as somewhat uncertain.

^h Rebière, *Bull. soc. chem.*, [IV] **17**, 268 (1915).

The metals are arranged in the order of their electrode potentials. As in the two earlier series, it will be evident that the relative position of each metal to hydrogen in the series is the determining factor in compound formation, ionization and order of solubility. The hydroxides of those metals in the immediate neighborhood of hydrogen form no isolable hydrates, are practically non-ionized in solution and insoluble. As we proceed away from hydrogen towards the more electropositive metals we find isolable hydrates appearing and solubility increasing. The series culminates in the alkali hydroxides, which give a large number of very stable hydrates, are very highly ionized and are exceedingly soluble in water. The irregularities among the alkali metals themselves are to be ascribed to the fact that the solubilities of their non-hydrated hydroxides cannot be directly measured, the figures given being merely minimum values, as explained above.

As in the case of the formates, the available data for confirming an increase in hydration, ionization and solubility for metals below hydrogen are not very plentiful. Silver hydroxide is not stable in the solid state, so

that its solubility cannot be directly measured. It does exist in solution, however, as a moderately strong base,²⁶ and the solubility of this in water must be in excess of that of the more stable silver oxide.

The only marked exception, as before, is offered by aluminum; in spite of the high electrode potential of the metal, aluminum hydroxide is highly insoluble and is an exceedingly weak base. This abnormality²⁷ will be discussed later.

Systems of the Type RX:HOH.

It is not possible to extend the general rules deduced for systems of the type RX:HX to other series of salts in water (where the system contains no radical common to both components) very far at present. The rules outlined above may be tentatively applied, however, to systems of the type RX:HOH for those particular series in which either R is not very different in character from H, or X is not very different in character from OH. In other words, we find that salts of a very weak base exhibit, in general, increasing hydrate formation and increasing solubility in water as the acid radical X diverges from OH, while salts of a very weak acid show the same behavior as the metal radical R diverges from H. Two illustrative series are presented below.

TABLE VI.

Solubility of Ferrous Salts in Water. 25°.

Salt.	Mol. % in satd. soln.	Stable solid phase.
FeCl ₂	8.97 ^a	FeCl ₂ , 4H ₂ O
FeBr ₂	8.99 ^a	FeBr ₂ , 6H ₂ O
Fe(NO ₃) ₂	8.08 ^b	Fe(NO ₃) ₂ , 6H ₂ O
FeSO ₄	3.39 ^c	FeSO ₄ , 7H ₂ O
FeC ₂ O ₄	0.00097 ^d	FeC ₂ O ₄
FeS	0.00013(?) ^e	FeS
Fe(OH) ₂	0.00013(?) ^f	Fe(OH) ₂

TABLE VII.

Solubility of Fluorides in Water. 18°.

Salt.	Mol. % in satd. soln.	Stable solid phase.
KF	14.79 ^g	KF, 4H ₂ O
BaF ₂	0.0166 ^h	BaF ₂
NaF	1.85 ⁱ	NaF
SrF ₂	0.0017 ^h	SrF ₂
CaF ₂	0.00037 ^h	CaF ₂
.....
AgF	18.0(approx.) ^j	AgF, 4H ₂ O

^a Etard, *Ann. chim. phys.*, [7] 2, 537 (1894).^b Funk, *Wiss. Abh. p. i. Reichsanstalt*, 3, 440 (1900).^c Fraenkel, *Z. anorg. Chem.*, 55, 228 (1907).^d Schaefer, *ibid.*, 45, 310 (1905).^e Weigel, *Z. physik. Chem.*, 58, 294 (1907). Approximate value only.^f Bineau, *Compt. rend.*, 41, 510 (1855). Approximate value only.^g De Forcrand, *ibid.*, 152, 1210 (1911).^h Kohlrausch, *Z. physik. Chem.*, 64, 145 (1900).ⁱ Mylius and Funk, *Ber.*, 30, 1718 (1897).^j Guntz and Guntz, *Ann. chim.*, 2, 101 (1914). The solubility of the tetrahydrate is changing very rapidly with temperature at 18°, owing to the proximity of the maximum point.²⁶ Levi, *Gazz. chim. ital.*, [2] 31, 1 (1901).²⁷ See Kendall and Davidson, *THIS JOURNAL*, 43, 988 (1921); also Heyrovsky, *J. Chem. Soc.*, 117, 1024 (1920).

The results given above for ferrous salts are paralleled by the salts of other exceedingly weak bases (*e. g.*, $\text{Zn}(\text{OH})_2$; $\text{Cu}(\text{OH})_2$), the halides of these metals being all very soluble, the sulfates somewhat less so, and the carbonates, sulfides, etc. all practically insoluble. The strength of the base cannot be increased very far above that of water, however, before these rules become inapplicable. Thus, for example, lead sulfate is insoluble in water while lead acetate is very soluble.

The fluorides in Table VII form a very striking series. Solubility and compound formation both fall off rapidly as we go down the list from potassium to the less positive metals,²⁸ but with the silver salt the effect of the diversity factor again becomes very apparent. Similar solubility relationships hold, in general, for the salts of other weak acids, such as the carbonates, sulfides and cyanides.²⁹ In all these series, the salts of the alkali metals are very soluble in water, those of the alkali earth metals less soluble and those of the remaining metals practically insoluble. The rule noted in an earlier article³⁰ for systems of the type $\text{HX}:\text{RX}$ when X is varied also applies here, namely that the decrease in solubility as we proceed towards hydrogen in the series is more rapid the weaker the acid radical X. The strength of this radical cannot be increased very far above that of water, however, before we find that all generalizations must be applied with considerable caution. It is somewhat surprising that they should still hold so well in the case of the fluorides.

For salts of a strong acid with a strong base, where we have simultaneously a positive radical very different in character from hydrogen and a negative radical very different in character from hydroxyl, no rules of a general nature can be deduced at present. It is true that Bodländer,³¹ more than twenty years ago, made some extremely significant preliminary advances in this field by showing that the solubility of a difficultly soluble salt in water could be approximately calculated from the electrode potentials of its ions and the heat of formation of the solid salt, but the subsequent development of Bodländer's work has by no means equalled its early

²⁸ The order of barium and sodium is reversed, as in the case of the fluorides in hydrofluoric acid (Kendall and Adler, *loc. cit.*, p. 1479); this point however will be taken up later.

²⁹ Seidell, *op. cit.* It must be noted that the majority of the values given in the literature for these salts do not represent exact equilibrium data. For example, in the case of the carbonates, a definite solubility is obtained only when the partial pressure of CO_2 above the solution is fixed (Johnston, *THIS JOURNAL*, **37**, 2001 (1915)). Similarly a fixed H_2S pressure is necessary in the case of the sulfides, a point hitherto overlooked in the calculation of their solubilities. The current values (*e. g.*, those given by Weigel, *Z. physik. Chem.*, **58**, 293 (1907)) may consequently not be legitimately comparable.

³⁰ Kendall and Adler, *loc. cit.*, p. 1479.

³¹ Bodländer, *Z. physik. Chem.*, **27**, 55 (1898).

promise,³² and criticisms have been abundant.³³ Certain of these criticisms (such as the fact that the heat of formation of a compound is not an exact measure of the free energy change) were forestalled by Bodländer himself, but the really fundamental weakness in his method—the total neglect of the part played by the *solvent* in solubility phenomena—has not previously been sufficiently emphasized. It is due to this neglect that the rules formulated by Bodländer³⁴ regarding the relative solubilities of series of salts containing the same acidic or basic radical (rules which are substantially similar, for certain series, to those developed above) are restricted to aqueous solutions, and even there display disconcerting discrepancies.³⁵ Certainly the equilibria involved in aqueous salt solutions, owing to interaction between solvent and solute, are much more complicated than Bodländer assumed.³⁶ We can, however, by taking into consideration the effect of the formation of solvent-solute complexes on solubility relationships, not only carry the qualitative study of the question for the particular case of aqueous solutions to a point beyond that reached by Bodländer, but we can also apply the rules obtained to the more general field of non-aqueous solutions. A very brief survey of a few typical series is all that can be presented at this stage.

The Solubility of Salts in Non-aqueous Solvents.

It has been claimed by Walden that the solubility of a salt in a series of solvents is greater the greater the degree of association (*i. e.*, the more marked the polar nature) of the solvent.³⁷ In the so-called "indifferent" solvents (such as hexane, benzene, ether) where compound formation is practically non-existent and where, furthermore, the difference in internal

³² Abegg and Bodländer, *Z. anorg. Chem.*, **20**, 457 (1900); **34**, 180 (1903); *Am. Chem. J.*, **28**, 220 (1902).

³³ Ostwald, *Z. physik. Chem.*, **32**, 182 (1900); Locke, *Am. Chem. J.*, **27**, 105 (1902); **28**, 403 (1902); Noyes, *Z. physik. Chem.*, **42**, 507 (1903); Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916). The following comment of Roozeboom upon the work of Bodländer is of particular interest: "To me it seems especially suspicious that temperature of fusion and heat of fusion have been left entirely out of consideration, since in ideal solutions these are the factors which absolutely control the solubility curve" (*Heterogene Gleichgewichte*, [1] **2**, 316 (1904)).

³⁴ Bodländer, *loc. cit.*, p. 69.

³⁵ Especially among *soluble* salts, where it was found necessary to add to the original theory a "law of self-preservation" to account for inverse solubility results (Abegg and Bodländer, *Am. Chem. J.*, **28**, 222 (1902)).

³⁶ Compare Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921); Kendall and Gross, *THIS JOURNAL*, **43**, 1425 (1921).

³⁷ Walden, *Z. physik. Chem.*, **55**, 703 (1906); **61**, 633 (1908). The rate of increase varies with the degree of association of the salt (see Turner, *J. Chem. Soc.*, **99**, 902 (1911)). An attempt to put Walden's rule upon a mathematical basis has been made by van Laar, *Z. physik. Chem.*, **58**, 567 (1907); **59**, 212 (1907).

pressure is extreme, salts are in general insoluble.³⁸ As the polarity of the solvent molecule increases, however, compound formation becomes more and more extensive and solubility increases. Where the compounds are sufficiently stable to be isolated from solution (as, for example, the acetic acid or alcohol addition products of calcium chloride) the solubility of the salt is very high.³⁹

Walden's rule is only a partial statement of the facts, however. For a salt to be soluble it is not sufficient for the solvent molecule to be polar, its radicals must also be diverse in character from those of the solute. This has already been shown in detail for the 3 series of metal sulfates in sulfuric acid, metal formates in formic acid and metal hydroxides in water. Any salt RX in its own acid HX, indeed, necessarily possesses the characteristics of a base,⁴⁰ and the diversity of the radicals R and H will control compound formation and solubility. This rule may be further illustrated from the work of Franklin on liquid ammonia solutions.⁴¹ Here the typical bases are the metal amides, imides and nitrides. Among those that are known only those of the alkali metals (*e. g.*, potassium amide, where the diversity between K and H is extreme) are soluble in ammonia. The ammonobases of the metals nearer to hydrogen (like the corresponding aquo-bases) are not soluble to any extent, and may be conveniently prepared by precipitation.

Aquo-acids and ammono-acids are similarly comparable. Although the majority of the common acids have melting points too low to enable us to discuss systems of the type HX:HOH in the same definite manner as systems of the type ROH:HOH in Table V, yet an analogous solubility rule, that strong acids, as a class, are much more soluble than weak acids, is obviously in general accordance with the experimental facts. In liquid ammonia the ammonium salts behave as acids, and here also we find that compound formation and solubility increase with the increasing strength of the acidic radical. Thus ammonium fluoride is insoluble, while the remaining ammonium halides are highly soluble and give very stable addition compounds.⁴²

When we attempt to consider salts of other metals in liquid ammonia,⁴³ we encounter the same difficulties as for salts in aqueous solution. An interesting point⁴⁴ to notice, however, is that while hydrate formation and solubility in water are most extensive, in general, with salts of the most

³⁸ An interesting exception, silver perchlorate in benzene, has recently been critically investigated by Hill, *THIS JOURNAL*, **43**, 254 (1921).

³⁹ Menschutkin, *Mem. Polyt. Inst. Petrograd*, **5**, 355 (1906).

⁴⁰ Schlesinger and Calvert, *THIS JOURNAL*, **33**, 1933 (1911).

⁴¹ Franklin, *Am. Chem. J.*, **47**, 285 (1912).

⁴² Kendall and Davidson (J. G.), *THIS JOURNAL*, **42**, 1141 (1920).

⁴³ Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898).

⁴⁴ Compare Hildebrand, *THIS JOURNAL*, **38**, 1471 (1916).

electro-positive metals (*e. g.*, Li, K), the tendency to combine with and dissolve in ammonia is most marked for the salts of metals at the other extreme of the electrode potential series (*e. g.*, Hg, Ag). A possible explanation of this dissimilarity is the highly electropositive character of the ammonium group.⁴⁵

Systematic solubility determinations for salts in other liquids are now in progress.

The Solubilities of Salts in Aqueous Solutions of Other Salts.

So far, only two-component systems have been discussed. We can also gain information, however, regarding the general applicability of the rules here derived for systems of the type HX:RX to systems of the somewhat more general type RX:R'X (or RX:RY) by examining the effect of the addition of a salt with a common ion upon the solubility of a difficultly soluble salt in water. As a typical illustration, the influence of other chlorides upon the solubility of silver chloride in water may be considered.

Normally, the solubility of silver chloride in water should be depressed practically to zero by the presence of another chloride in quantity, according to the principle of the constancy of the solubility product. If, however, any addition compounds between silver chloride and the added chloride MCl are formed in solution, then the solubility of silver chloride should exceed the calculated value by an amount dependent upon the stability of the compounds formed. The stability of the addition compounds, furthermore, should depend (according to the generalizations developed above) upon the diversity in the positions of the radicals Ag and M in the electrode potential series. Consequently we should expect the solubility of silver chloride in water to increase more and more above the normal value as the radical M is made more electropositive.

That this is so in actual fact is strikingly shown in Fig. 3, which reproduces the accurate determinations of Forbes.⁴⁶ It will be seen that the solubility is tremendously increased in every case shown, the order being $H < Ca < Na < Sr < Ba < K$ or NH_4 . This is exactly the order in the electrode potential series,⁴⁷ as may be seen by reference to Table V. In concentrated

⁴⁵ Although it has been shown by Frenzel (*Z. Elektrochem.*, **6**, 486 (1900)) that the primary dissociation of ammonia is into H^+ and NH_4^{+} , solvation of the positive ion to NH_4^{+} must also be admitted (compare Abegg, "Handbuch anorg. Chem.," [3] **3**, 58 (1907)).

⁴⁶ Forbes, *THIS JOURNAL*, **33**, 1937 (1911). The curves run very close together at low concentrations of added salt, consequently to avoid confusing the diagram the data for high concentrations only (above 2*N*) are there included. The solubility of AgCl in pure water at 25° is 0.0000120 g. equiv. per liter (Glowczynski, *Kolloidchem. Beihefte*, **6**, 147 (1914)); practically zero on the scale in the diagram.

⁴⁷ The position of NH_4 in the series, which cannot of course be directly determined, has been discussed thoroughly by Abegg ("Handbuch anorg. Chem.," [3] **3**, 241-2

aqueous solutions of mercuric chloride, moreover, silver chloride is practically insoluble, as might also have been predicted from the proximity of Ag and Hg (ic) in the same table. For the influence of other chlorides upon the solubility of silver chloride in water no trustworthy data are at present available,⁴⁸ but experiments to complete the series are now being carried out in this laboratory.

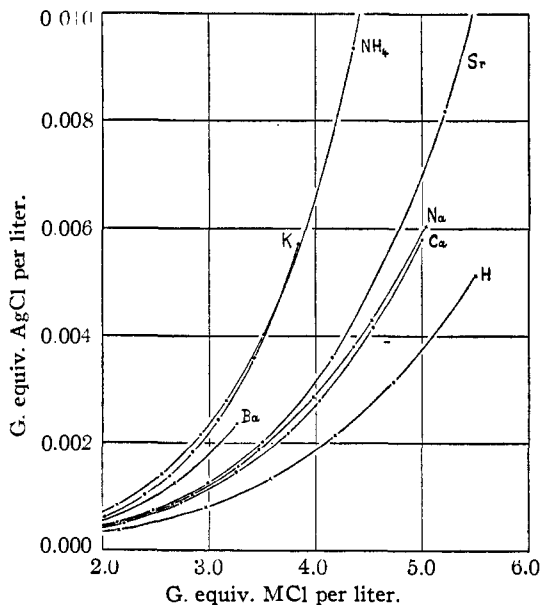


Fig. 3.

A very wide and promising field for future investigation here offers itself, since it will be obvious that any general conclusions deduced will be of importance not only in themselves but also in the further development of the theory and practice of quantitative analysis. From the results for silver chloride discussed above, for example, it appears that the completeness of the precipitation of this salt from aqueous solution is vitally dependent upon the nature and concentration of other chlorides present.

(1907)); experimental analogies place the radical very close to potassium. In preceding solubility comparisons (Kendall and Davidson, *loc. cit.*, p. 989; Kendall and Adler, *loc. cit.*, p. 1480) the ammonium salts have not been included in view of the fact that their melting points are much lower than those of other salts, but here this factor does not come into consideration.

⁴⁸ A few isolated and contradictory determinations are given in Seidell, *op. cit.*, p. 609. A single measurement by Forbes indicating that AgCl is only slightly soluble in concentrated ZnCl₂ solutions, which furnishes the sole incongruity in his whole work with the predictions of the present theory, is being further investigated.

Forbes⁴⁹ has calculated that the salt is most insoluble in 0.01 *N* chloride solutions; Glowczynski,⁵⁰ on the other hand, has found experimentally that the addition of potassium chloride and ammonium chloride in much lower concentrations already involves an appreciable increase above the original solubility value. Evidently the presence of salts of the alkali metals in considerable quantity could easily introduce very significant errors in the analytical procedure at present employed.⁵¹ The magnitude of such errors might, according to the results here obtained, be reduced by the addition of salts of less electropositive metals, but this is a point which requires direct experimental confirmation.⁵² Whether the rules outlined in this article could legitimately be expanded to predict the optimum conditions for precipitations in general is a question for future investigation. The available data for other difficultly soluble salts are in few instances sufficiently extensive or reliable to enable us to obtain any such definite indications of the applicability of the generalizations here developed as in the case of silver chloride, but several typical examples are now being more systematically examined, and we hope to report further on this topic shortly.⁵³

When the original solute is markedly soluble in water, the effect of the addition of other solutes containing a common ion becomes more complex, and solubility curves with minimum and maximum points may result. Such curves are discussed in the succeeding article, in connection with a study of systems of the type $HX:HY:H_2O$. Where the second solute contains no common ion at all (*i. e.*, in systems of the type $RX:R'Y:H_2O$) the equilibria involved naturally present still greater intricacies, as the experience of previous investigators in this portion of the field serves to testify.⁵⁴ The satisfactory elucidation of such elaborate systems necessarily awaits the prior formulation of acceptable general rules for systems with a smaller number of variables.

⁴⁹ Forbes, *loc. cit.*, p. 1946.

⁵⁰ Glowczynski, *ibid.*, p. 172.

⁵¹ Treadwell and Hall, "Analytical Chemistry," 2, 317 (1914).

⁵² It is possible that complete precipitation might be ensured only at the expense of introducing other and more significant errors, such as adsorption of added salt by the precipitate.

⁵³ The particular series under investigation are: (a) $AgCl$ and $PbCl_2$ in other chloride solutions, (b) slightly soluble fluorides in AgF and KF solutions, (c) the sulfates of the alkaline earth metals in other sulfate solutions, (d) the sulfates and hydroxides of the alkaline earth metals in solutions of more soluble salts of the same metals. These are not mentioned with any intention of reserving the field, but merely to obviate possible duplication of effort.

⁵⁴ See the extensive work of Noyes and his collaborators, beginning in *THIS JOURNAL*, 33, 1643 (1911) and continued more recently by Harkins, *ibid.*, 38, 2679 (1916); 41, 1155 (1919).

General Consideration of Results.

It remains to discuss, somewhat more fully than was done in the introductory section, the validity of the principle adopted as a basis for all of the comparisons here carried out, namely that compound formation between the components is the dominating factor in inducing deviations from ideality in polar solutions. The satisfactory agreement of our predictions with the facts of experiment furnishes in itself, of course, support for this view-point, indicating as it does that the disturbances due to other factors are, in general, subsidiary in their nature. In order to establish this more directly, however, the effect of these factors may here be subjected to brief analysis.

Internal Pressure.—Undoubtedly in many of the systems examined in the preceding pages the internal pressures of the components are very unequal. Exact data are not available, but since we know that fused salts, as a class, are far more polar than water and also vary considerably in polar character among themselves, we should expect to find solubilities much below the ideal value in many cases. It has been shown above, however, that the ideal solubility for salts of high melting point in solvents at ordinary temperatures is already practically zero, so that while the internal pressure factor may help to account for abnormally minute solubilities in isolated instances (*e. g.*, silver chloride in water) it can scarcely affect the present argument, which is based upon much larger divergences from the ideal in the opposite direction. True, the possibility exists that the internal pressure effect might increase proportionately with the solubility as compound formation becomes more extensive, but no indications that this is so are found in the present work. It appears, therefore, that under the special conditions here encountered, the internal pressure factor can be neglected.

Heat of Fusion.—Owing to the fact that the specific heats of substances in the solid and liquid states are not identical, the factor Q in Equation I (p. 1485) is not a true constant, even for ideal solutions, but varies with the temperature. The variation thus induced is, however, in general relatively small, and can be omitted without much error. More serious, in non-ideal solutions, is the variation in the differential heat of solution Q due to interactions between the components on admixture. As is well known, the heat effect of such interactions may be so great in certain aqueous salt solutions as to reverse the sign of Q , in which case we obtain *decreasing* solubility values with increase of temperature.⁵⁵

This "heat of admixture" factor has been discussed in detail for the case of dilute solutions in an earlier article,⁵⁶ to which reference should be

⁵⁵ Most calcium salts, for example, exhibit this peculiarity in aqueous solution.

⁵⁶ Kendall, Booge and Andrews, *THIS JOURNAL*, 39, 2312 (1917).

made. It must be admitted here that the factor is not one which can be definitely correlated with the character of the components, and that consequently the relative positions of the various curves in a series may be very significantly affected, even to the extent of confusing the predicted order of solubilities. This is particularly the case in systems of the type $RX : H_2O$, in which heat of admixture variations are very pronounced, and it will undoubtedly be necessary to study the effect of this factor more intensively in the case of such systems before their solubility relationships are satisfactorily established. In systems of simpler types (*e. g.*, $HX : RX$) heats of admixture are in general smaller and more uniform, being positive in sign (the addition compounds formed becoming less stable as the temperature rises) and increasing in magnitude as the extent of compound formation increases. In such series it is unlikely that the relative positions of the curves for different salts with respect to the ideal will be confused by variations in Q , consequently the comparisons carried out without taking this factor into consideration are still, in most instances, substantially valid.

Ionization.—With our views on the ionization of strong electrolytes at present undergoing fundamental modification, it is difficult to treat this factor rigorously. If, on the one hand, we regard the Arrhenius equation $RX \rightleftharpoons R^+ + X^-$ as valid, and apply to it Nernst's principle of the constancy of the undissociated salt concentration in saturated solutions,⁵⁷ then it would follow that the solubility of a salt in an ionizing solvent should exceed the ideal value by an amount immediately calculable from the degree of ionization. For example, in the case of potassium chloride in water (p. 1489), the ideal solubility value 0.00044 at 25° would refer to the undissociated salt only, and correction for ionization⁵⁸ would increase it to approximately 0.0025. In other words, the change would not be large and would be in the same direction for all salts. If, on the other hand, we follow Milner and Ghosh in regarding salts as completely ionized both in the solid state and in water solution, no correction of this nature is necessary, although other factors (such as changes in the attractive forces between oppositely charged ions due to changes in the dielectric constant)⁵⁹ might enter into consideration.

Association.—In the solubility tables shown above, x (the mol fraction of solute in the solution) has been calculated from the experimental data on the assumption that solvent and solute are both non-associated. If the solvent is associated, however, values of x so obtained are too high for comparison with the ideal equation, which assumes the use of the actual

⁵⁷ Nernst, *Z. physik. Chem.*, **4**, 372 (1889); see also Stieglitz, *THIS JOURNAL*, **30**, 946 (1908); Kendall, *Proc. Roy. Soc.*, **85A**, 200 (1911).

⁵⁸ Using the conductivity ratio Λ_v/Λ_∞ as a measure of the degree of ionization.

⁵⁹ Ghosh, *J. Chem. Soc.*, **113**, 457 (1918).

molecular types existent in the solution.⁶⁰ We do not know the exact association factors for the common solvents, nor the variation in these factors on addition of solute. The necessary correction, nevertheless, will be for any fixed solvent approximately proportional to the concentration of solute unless α is very large,⁶¹ hence it cannot affect significantly the accuracy of the comparisons here made.

Association of the solute is again a point which it is difficult to discuss at present. If the high association factors quoted for fused salts⁶² are accepted, then it is evident that very extensive disassociation must occur as their concentration in a solution diminishes. Changes in the assumed molecular state of the solvent do not, however, change the position of the solubility curve appreciably, as has been shown in a previous article.⁶³ If, on the other hand, we regard highly polar substances, such as the common inorganic salts, as entirely ionized both in the solid state and in aqueous solution, no need to consider their association ever arises.

Other Factors.—The subsidiary effect of other factors (such as atomic volume, valence, etc.,) is being further studied, and will be discussed in a subsequent paper. One point, nevertheless, in connection with valence must be mentioned here. It has been assumed in comparing curves throughout this article,⁶⁴ for the sake of simplicity, that the addition compounds formed are of the same monomolecular type AB. Two solutes, however, of different valence character (*e. g.*, a uni-univalent salt R'X and a uni-divalent salt R''X₂) might be expected to give different types of addition compounds with the same solvent B (*e. g.*, R'X, B and R''X₂, B₂).⁶⁵ Since the limiting value which X approaches at low temperatures for a perfectly stable compound of the type AB is 0.50, while for a compound of the type AB₂ it is 0.33, it is obvious that the relative positions of the solubility curves will not, unless consideration is paid to the variation in type, furnish us with valid information regarding the stability of the compounds.⁶⁶ When it is furthermore remembered that in cases where the constituent

⁶⁰ For water, for example, at ordinary temperatures, a molecular weight much greater than 18.016 should be employed in accordance with the average molecular type (H₂O)_n.

⁶¹ At very high concentrations of solute the relative correction necessarily diminishes. Disassociation, furthermore, will be extensive in such solutions.

⁶² See Kendall and Gross, *THIS JOURNAL*, **43**, 1419 (1921).

⁶³ Kendall, Booge and Andrews, *ibid.*, **39**, 2310 (1917). A more detailed treatment of this topic may be found in Roozeboom, *op. cit.*, [1] **2**, 303 (1904).

⁶⁴ See Diagrams I and II and the discussion on these diagrams; pp. 1486, 1489.

⁶⁵ Thus esters of monobasic acids give monomolecular compounds AB with trichloroacetic acid, while esters of dibasic acids give compounds of the type AB₂ (Kendall and Booge, *THIS JOURNAL*, **38**, 1712 (1916)).

⁶⁶ Or, *vice versa*, we cannot from the diversity of the constituent radicals make valid predictions of relative solubilities, unless we take account of the difference in composition of the compounds.

radicals are very diverse in character several different complex addition products between the components may simultaneously be present in a solution,⁶⁷ it will not seem remarkable that occasional minor reversals of solubility orders are manifest in the tables presented above. It is a matter for comment, rather, that such divergences from prediction are not more frequent.

The Electrode Potential Series.—As a final point, the use of the electrode potential series as the basis for establishing "diversity of radicals" must be justified. Strictly speaking, instead of the experimentally determined electrode-potential values we should employ for each radical what is more fundamental and important, the real "electro-affinity." Until exact free-energy data are more numerous, however, we must be satisfied with the series as it stands, relying on the generally accepted view that it is substantially accurate.⁶⁸

In view of the multiplicity of the disturbing factors discussed above, the question may pertinently be raised (as it was previously against Abegg and Bodländer) whether the generalizations deduced in this work are valid at all. The answer to the question consists in the substantial agreement of the predictions made with the facts of experiment. Criticism can, of course, be readily directed against certain discrepancies, but just as Abegg and Bodländer's general conclusions were not invalidated by the discovery of cases where their predicted solubilities were apparently in error by 10^6 or so, in the same way the citation of isolated abnormalities will not suffice to destroy the validity of the arguments here advanced. The justification of the present work lies in the fact that it enables us to obtain a general survey of a very important and intricate subject, with the main features involved duly emphasized. So much having been done, we can now continue more easily with the further development of the topic and with the examination of the remaining factors.

Summary.

The various factors inducing deviations from the ideal solubility curve in polar solutions have been critically discussed, and it has been shown

⁶⁷ As, for example, in the systems of H_2SO_4 with the sulfates of the alkali metals (Kendall and Landon, *THIS JOURNAL*, **42**, 2131 (1920)). In aqueous systems variations in compound types become still more extreme, as may be seen by comparing the isolable hydrates in Table V of this article.

⁶⁸ Compare Lewis, "System of Physical Chemistry," **2**, 301-6 (1919). Our current method of interpreting electromotive-force measurements is not free from error, as will be shown in a later article (see also Kendall, *Proc. Nat. Acad. Sci.*, **7**, 60 (1921)). That the data for lead salts fall slightly out of line throughout the present work is presumably due in part to this factor. In all 3 series examined (sulfates, formates, hydroxides), ionization and solubility values are systematically somewhat too high (compare Heyrovsky, *J. Chem. Soc.*, **117**, 1024 (1920)).

that the predominant disturbing factor is addition compound formation between the components of the solution.

In previous articles it has been established that the extent of such compound formation in any series is dependent upon the diversity in character of the constituent radicals of the components, the basis of diversity being the relative position of the variable radicals in the electrode potential series. Ionization, furthermore, has been found to increase uniformly with compound formation.

These generalizations have here been employed to predict solubility relationships in systems of various types. It has been shown that:

(a) For a fixed solute in a series of different solvents, increasing solubility and increasing compound formation proceed in parallel.

(b) For a series of different solutes of high melting point in a fixed solvent, increasing solubility and increasing compound formation also proceed in parallel at low temperatures.

Illustrations of these rules for non-aqueous and aqueous solutions have been presented which indicate their agreement with the facts of experiment.

A general discussion of solubility relationships in systems of increasingly complex nature (*e. g.*, $RX:HX$, $RX:H_2O$, $RX:R'X:H_2O$) has been made, and the rules deduced for the simpler types of systems have been found to be applicable, to a limited extent, to the more complex types. For example:

(a) Salts of a very weak base exhibit increasing hydrate formation and increasing solubility in water as the acid radical X diverges from OH; salts of a very weak acid show the same behavior as R diverges from H.

(b) The increase in the solubility of a difficultly soluble salt in water on addition of a second salt containing a common ion, due to complex salt formation, is dependent upon the diversity of the variable radicals.

The extension of the first of these rules to non-aqueous solutions, and the importance of the second in analytical chemistry, have been noted.

The disturbing effect of other factors upon the ideal solubility curve has been briefly examined, and the possibility of accounting for existent abnormalities in solubility relationships by a more intensive study of the field has been indicated.