

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SOLUBILITY.

BY JOEL H. HILDEBRAND.

Received May 18, 1916.

CONTENTS.—1. Introduction. 2. Raoult's Law: (a) Kinetic basis; (b) The solubility of gases in liquids; (c) Mutual solubility of liquids; (d) Solubility of solids. 3. Deviations from Raoult's Law: (a) Internal pressure and its effect; (b) Polarity and its effect. 4. Experimental Evidence: (a) Vapor pressure of liquid mixtures; (b) Solubility of gases; (c) Liquids not completely miscible; (d) Solubility of solids; (e) Salt solutions; (f) Metallic solutions. 5. Summary.

1. Introduction.

There is scarcely anything more important for a chemist than a knowledge of solubilities, but unfortunately he finds it more difficult to predict how soluble a substance will be in a given solvent than it is to predict almost any other important property. Bodländer,¹ it is true, has made approximate calculations of the solubility in water of some difficultly soluble salts from the electrode potentials of their ions and the heat of formation of the solid salts. Although this is a remarkable step in advance, it is of a very limited applicability, and it suffers, in common with Berthelot's principle of maximal work from the fact that the free energy of a chemical reaction is not equal to the total energy change. Planck² has pointed out that the relation between the change in free and total energy in forming a solution, and hence solubilities, could be calculated if we knew, in addition to the heat of solution, the specific heats of solution and pure substances down to absolute zero, the treatment being analogous to the calculation of chemical equilibria by means of the Nernst Heat Theorem. At present our meagre knowledge of specific heats of liquids and solutions makes such a treatment impossible. Furthermore, to be of real use, the calculation of solubility must be made from the properties of the pure substances only, and not from a property of the solution, such as its specific heat, the experimental determination of which may be more difficult than that of solubility itself.

Dolezalek³ has shown how, assuming Raoult's Law for the vapor pressure of solutions, it is possible to calculate the solubility of gases in liquids. The validity of his calculations will be discussed later.

Washburn and Read⁴ have also shown how it is possible to calculate the solubility of solids in liquids in cases where the substances obey Raoult's Law in the liquid state. The significance of this method of calculation is very great, but its scope is limited by the relatively small number of the mixtures which obey Raoult's law throughout the entire

¹ *Z. physik. Chem.*, **27**, 55 (1898).

² Planck, "Thermodynamik."

³ Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910).

⁴ Washburn and Read, *Proc. Nat. Acad.*, **1**, 191 (1915); *C. A.*, **9**, 1570 (1915).

range of concentration. If the deviations from this law, occurring in most solutions, could be accurately predicted, it would be possible to make accurate calculations of solubilities in general. It has not been possible up to the present time to give an accurate quantitative treatment for these deviations, and the difficulties in the way, it may be added, are very great. It is possible, however, to make certain generalizations of a more qualitative nature, and with their aid very useful predictions of solubility may be made in an approximate way.

2. Raoult's Law.

(a) **Kinetic Basis.**—A great deal of the older physical chemistry has had for one of its chief foundation stones the law of van't Hoff for the osmotic pressure of dissolved substances. The fruitful use of this law in dealing with the properties of dilute solutions, and its analogy to the laws for perfect gases, have somewhat blinded chemists to its limitations. Nearly all text-books of physical chemistry still use it to derive the ordinary laws for molecular weight determination, electromotive force of concentration cells, etc., and some investigators still ascribe any variations from these formulas to chemical changes, solvation, etc., forgetting that a large part of the deviation may be due to the inaccuracy of the fundamental equation for osmotic pressure. It has been pointed out by G. N. Lewis¹ and others that Raoult's law is a far better fundamental expression, holding for the simplest solutions throughout the entire range of concentration, when the van't Hoff equation leads to absurd values of osmotic pressure. In spite of the apparent probability of the van't Hoff law due to the analogy between gas pressure and osmotic pressure, it should be noted that Raoult's law has a simpler kinetic basis.

Let us consider a binary liquid mixture composed of n_1 molecules of the component X_1 and of n_2 molecules of the other component, X_2 . Let us denote the vapor pressures of the pure liquids by P_1 and P_2 , respectively, and their partial vapor pressures over the solution by p_1 and p_2 , respectively. If the vapors obey the gas laws, and if the molecules of X_1 and X_2 are sufficiently alike so that they are under the same forces in the mixture as in the pure liquids² then it follows, as a mere matter of logic, that since only the fraction $\frac{n_1}{n_1 + n_2}$ of the molecules of the liquid are of the species X_1 , that the partial pressure of X_1 in the vapor phase, p_1 , is the same fraction of what it would be, P_1 , if all the molecules were of the same species. Hence we write

¹ G. N. Lewis, *THIS JOURNAL*, 30, 668 (1908).

² Washburn has defined this limitation by saying that the solution must have "constant thermodynamic environment." *Trans. Amer. Electrochem. Soc.*, 22, 333 (1912).

$$p_1 = P_1 \frac{n_1}{n_1 + n_2}, \text{ and similarly, } p_2 = P_2 \frac{n_2}{n_1 + n_2}. \quad (1)$$

We will consider presently how we may determine whether the molecules of different species are "sufficiently alike" to justify this conclusion, and first indicate, briefly, how the law makes possible the calculation of solubilities of gases and solids in liquids. These calculations have been fully made by the writers referred to, but the repetition seems desirable as an introduction to what is to follow in this paper.

(b) **The Solubility of Gases in Liquids.**—This is expressed in general by the familiar law of Henry, stating that the partial pressure of a gas and its solubility or concentration in a liquid are proportional. Letting X_1 refer to the gas and X_2 to the solvent, we would express this in our notation by the equation

$$p_1 = k \frac{n_1}{n_1 + n_2}.$$

The meaning of the constant k is made clear by putting $n_2 = 0$, when k becomes equal to the vapor pressure of the pure gas, P_1 . If, as may often be the case, the solution is at a temperature higher than the critical temperature of the gas, then P_1 must be an extrapolated value, as shown at X in Fig. 1. The usual equations giving the actual relation between

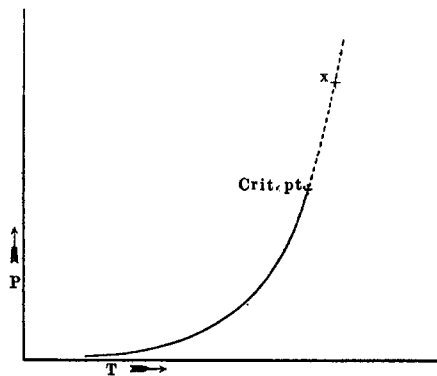


Fig. 1.

vapor pressure and temperature up to the critical temperature must include the effect of the deviation of the vapor from the gas laws as the critical temperature is approached, while Raoult's law, expressed as in this paper, presupposes that the vapor obeys the gas laws. It therefore seems more logical to find P_1 from an equation like the familiar Clausius-Clapeyron equation, than it is to use some one of the empirical equations giving the actual vapor pressures near the critical point. We may say all of this more briefly by stating that P_1 should be considered as the *fugacity* rather than the vapor pressure of the liquid, extrapolated above the critical point.

It should be noted that for the same gas at a given temperature the solubility in all liquids should be the same, according to Raoult's law, when it is expressed in terms of mol-fraction, N . When, however, it is expressed as the amount of gas in a given weight of solvent, the solvent with the higher molecular weight will dissolve less of the gas *per unit*

weight, since there are fewer mols in unit weight of the solvent in this case. Similarly, of two solvents having the same molecular weight, the solubility expressed as amount *per unit volume* of solvent will be greater in the denser solvent, since a unit volume of this solvent would contain more mols.

(c) **The Mutual Solubility of Liquids.**—Whenever liquid mixtures conform to Raoult's law they must be completely miscible, for if there were two liquid phases in equilibrium the partial vapor pressure of each component from each phase would have to be the same, and hence, by Raoult's law, the mol-fractions would be identical, and also the phases.

(d) **Solubility of Solids.**—In considering solutions of solids in liquids we must remember again, letting X_1 denote the species forming the solid phase, that P_1 is the vapor pressure, or better fugacity, of X_1 in the *liquid* form.¹ Since the liquid is the unstable form of X_1 below its melting point, the vapor pressure, or fugacity, of the solid form, which we will call P_1' , is less than P_1 (see Fig. 2). If, then, solid X_1 is gradually added to liquid

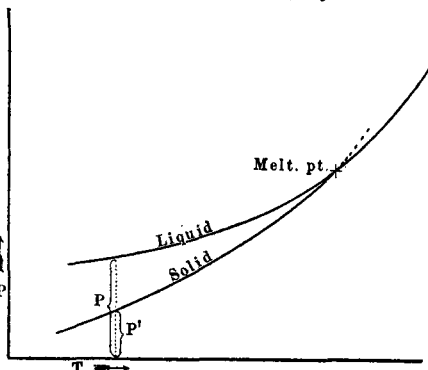


Fig. 2.

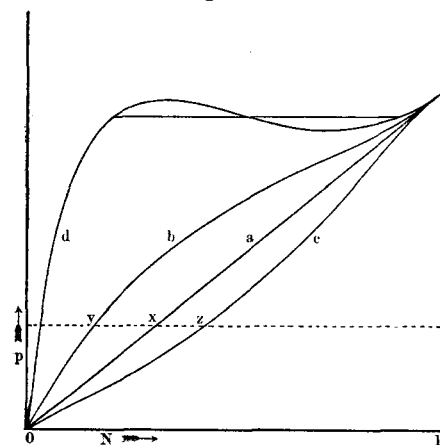


Fig. 3.

X_2 , the partial vapor pressure p_1 will increase in proportion to the mol-fraction $\frac{n_1}{n_1 + n_2}$ (which we will abbreviate into N_1) until it becomes equal to P_1' (at x in Fig. 3), when no further increase is possible and hence the solution is saturated with respect to the solid, and $N_1 = P_1'/P_1$. If, then, P_1'/P_1 can be determined, we can determine the solubility for substances of the class here considered. The ratio P_1'/P_1 is given by the familiar equation²

¹ This important limitation has been overlooked by Strachan, *THIS JOURNAL*, 38, 626 (1196). It allows many solutions to remain in the category of ideal solutions that would be needlessly removed from this class by letting P_1 depend on the appearance of a solid phase.

² This follows simply by taking the difference between the Clausius-Clapeyron equations for the solid and liquid phases.

$$\log \frac{P'}{P} = \frac{-L_0}{4.58T} + \frac{\Delta\Gamma}{1.99} \log T + I, \quad (2)$$

where L_0 is the molal heat of fusion at absolute zero, $\Delta\Gamma$ is the difference in the specific heats per mol of the liquid and solid forms, and I is an integration constant whose value is gotten by putting for T the melting point on the absolute scale, when $\log \frac{P'}{P} = 0$. When $\Delta\Gamma$ is known L_0 can be found from the molal heat of fusion at a temperature T by the relation

$$L = L_0 + \Delta\Gamma T. \quad (3)$$

When $\Delta\Gamma$ is not known we can omit this term without much error, writing Equation 2 simply

$$\log \frac{P'}{P} = \frac{-L}{4.58T} + I. \quad (4)$$

It is obvious that the ratio $\frac{P'}{P}$, and hence the solubility of the solid, is smaller the greater the heat of fusion and the higher the melting point of the substance above the temperature chosen.

3. Deviations from Raoult's Law.

On investigating the actual vapor-pressure curves for mixtures of normal liquids we find rather good agreement with Raoult's law. Perfect agreement is illustrated graphically by Curve *a* in Fig. 3. With practically all solutions, unless dissociation occurs, the law is obeyed by each component when the other is present in but small amount. Graphically this means that the other types of curves for p , such as *b*, *c*, and *d*, in Fig. 3, become tangent to the straight line representing Raoult's law when N approaches unity. In most actual cases, however, as N becomes smaller, that is, as more of the other substance is added, the partial vapor pressure shows more or less deviation from Raoult's law. The actual pressure is greater than that given by Raoult's law in the majority of instances, as illustrated by *b*, Fig. 3, but is less than that calculated by Raoult's law in some cases, such as *c*, Fig. 3, especially when compounds between the two substances are suspected or known to exist. The percentage deviation generally becomes greater as N becomes smaller.¹

These deviations exert a corresponding effect on the solubilities of gaseous or solid substances. Suppose, for example, the behavior is expressed by Curve *b*, Fig. 3, instead of by Curve *a*. This we will call a positive deviation from Raoult's law. It is obvious that saturation with solid X_1 of vapor pressure P_1' will take place at a smaller value of N_1 (point *y*) than it would be if the Curve *a* were followed (when the solution would

¹ For an exposition of these deviations see Roozeboom, "Heterogene Gleichgewichte" vol. 2 (1904).

be saturated at x). Similarly, when a negative deviation from Raoult's law occurs, as shown by Curve c , more of X_1 can be present in the solution before its partial pressure equals that of the pure solid, P_1' (at z). The same considerations hold when X_1 is a gas, when the partial pressure of the gas, p_1 , takes the place of that of the solid, P_1' , in the foregoing discussion.

Two kinds of explanation have been offered to account for these deviations from Raoult's law. Dolezalek¹ assumes that any deviation from Raoult's law is caused by some effect which we may call chemical, a change in the number of mols due to the formation of a chemical compound between the two substances or else to a change in the degree of association of one or both constituents. Raoult's law is supposed to hold for each of the species of molecule present in the mixture. The results of this treatment are often quite plausible, and the writer himself has used it in explaining both the vapor pressure and e. m. f. of certain liquid amalgams.²

The other basis of explanation is that offered by the van der Waals theory, and has been discussed by van der Waals,³ van Laar,⁴ and Kohnstamm.⁵

Van Laar, for example, points out that we should expect deviations from Raoult's law, even when both liquids are normal, provided their critical pressures are different. He gives a formula involving the heat of mixing and van der Waals' " b ," and discusses the various types of vapor-pressure curve gotten by altering the constants in the formula.

Kohnstamm also applies the van der Waals theory in a general discussion of curve types.

It seems quite evident that calculations after the method of Dolezalek may be very often without significance. There are many mixtures of liquids, normal according to all ordinary criteria, which give vapor pressures greater than demanded by Raoult's law, one component of which would, according to Dolezalek, have to be considered as associated. Such, for example, are the following pairs: benzene and stannic chloride, bromine and carbon tetrachloride, carbon disulfide and methylal, benzene and hexane, benzene and ether, hexane and aniline. The degree of association that would have to be assumed to account for the observed deviations would entirely remove them from the class of normal liquids. In the case of hexane and aniline,⁶ for example, two liquid phases are formed

¹ Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910); **83**, 40 (1913).

² J. H. Hildebrand, *THIS JOURNAL*, **35**, 501 (1913); *Trans. Am. Electrochem. Soc.*, **22**, 319 (1913); E. D. Eastman and J. H. Hildebrand, *THIS JOURNAL*, **36**, 2020 (1914); **37**, 2452 (1915).

³ Van der Waals, "Die Kontinuität."

⁴ Van Laar, *Z. physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).

⁵ Kohnstamm, *Ibid.*, **75**, 527 (1910).

⁶ Unpublished work by Mr. D. B. Keyes of this laboratory.

below 59.3° , which denotes a partial vapor-pressure curve of the type denoted by d in Fig. 3. It is hard to imagine any kind or degree of association that would give this type of curve and still allow Raoult's law to hold for the various molecular species present. Certain it is that the assumption of the existence of double or triple molecular complexes even to a very great extent never leads to a deviation from Raoult's law sufficient to account for the formation of two liquid phases, as with this particular mixture.

Moreover, it is hard to be consistent in the use of this method when dealing with the same component in different mixtures. Thus, for example, acetone is undoubtedly an associated liquid, and account of this would have to be taken in explaining the vapor pressures when it is mixed with carbon disulfide. However, when dealing with the system acetone-chloroform, Dolezalek neglects such association while calculating the equilibrium involving the compound formed between the two substances.

On the other hand, the van der Waals theory, as applied by van Laar, is inadequate when one of the liquids is associated. Thus methyl alcohol and carbon disulfide, though having nearly equal critical pressures, deviate from Raoult's law to the extent of forming two liquid phases. It should be noted, in fairness, that van Laar recognizes the possibility of uncertainties of this nature.

(a) **Internal Pressure.**—If we seek a clue of a kinetic nature to the deviations from Raoult's law, we find it in the limitation stated earlier while giving the kinetic justification for the law, namely, that the molecules of X_1 and X_2 must be "sufficiently alike so that they are under the same forces in the mixture as in the pure liquids." It has seemed to the writer that the most satisfactory conception to serve as a basis for deciding whether the molecular forces are alike or not would be found in internal pressure. This is the force which, together with the external pressure, opposes the thermal pressure which is due to the kinetic energy of the molecules. In terms of the van der Waals equation

$$p - \frac{a}{v^2} = \frac{RT}{v - b},$$

it is the term a/v^2 , the term $RT/(v - b)$ being the thermal pressure. It is the cause of the tendency for the number of molecules in the surface of a liquid to be as small as possible, resulting in the phenomena of surface tension. Unfortunately, however, although the conception of internal pressure is a very fundamental one, its definition in experimental terms is very difficult and unsatisfactory. Several methods for calculating internal pressures have been proposed, and values have been published by a number of men. These values vary widely from one another

in the case of the same liquid, as will be seen in Table I. It is not our present purpose to undertake a critique of these calculations, as we are primarily interested in the relative rather than in the absolute values, and the order was found to be substantially the same by the different methods, except for the highly polar liquids, to be discussed later, where two effects are superimposed.

TABLE I.

| Liquid. | Internal pressures. | | | | | Critical pressure. | Dielectric constant. |
|--------------------------|---------------------|---------|---------|--------|----------|--------------------|----------------------|
| | Winther. | Traube. | Walden. | Lewis. | Mathews. | | |
| Octane..... | | 740 | 1200 | | 1670 | 25 | 1.9 |
| Hexane..... | | 860 | 1250 | | 1700 | 30 | 1.9 |
| Pentane..... | | | 1210 | | 1760 | 33 | ... |
| Ether..... | 1220 | 990 | 1360 | 1930 | 1970 | 36 | 4.3+ |
| Xylene..... | | | 1650 | 2820 | 2400 | 36 | 2.3 |
| Stannic chloride..... | | 1020 | 1680 | | 2500 | 37 | 3.2+ |
| Ethyl acetate..... | 1490 | 1140 | 1730 | 2640 | 2460 | 36 | 6.1 |
| Toluene..... | 1680 | 1180 | 1750 | | 2650 | 42 | 2.3 |
| Methyl acetate..... | 1710 | 1280 | | | 3440 | 46 | 7.0 |
| Carbon tetrachloride.... | 1820 | 1305 | 1680 | 2520 | 2660 | 45 | 2.2 |
| Ethyl chloride..... | 1540 | 1400 | 1740 | | 3000 | 53 | ... |
| Benzene..... | 1790 | 1380 | 1920 | 2640 | 2940 | 48 | 2.3+ |
| Chlorobenzene..... | | 1340 | 1970 | | | 45 | 11.0 |
| Chloroform..... | 1680 | 1410 | 1950 | 2780 | 2910 | 55 | 5.1 |
| Naphthalene..... | | | 1950 | | | 39 | ... |
| Chlorine..... | | | 2020 | | | 89 | 1.9 |
| Ethylene chloride..... | 2060 | 1590 | 2050 | | | 53 | 10.4 |
| Ethyl iodide..... | | | 2060 | | | .. | 7.4 |
| Ethylamine..... | | | 2060 | | | 66 | 6.2+ |
| Iodobenzene..... | | 1420 | 2140 | | | 45 | ... |
| Acetone..... | 1790 | 1390 | 2200 | 3190 | | 56 | 22 |
| Pyridine..... | | | 2340 | | | .. | 12.4 |
| Ethylene bromide..... | 2110 | 1570 | 2400 | | | 71 | 4.9 |
| Arsenic Trichloride.... | | 1590 | 2400 | | | .. | ... |
| Propylalcohol..... | 1900 | 1800 | | | | 50 | 22 |
| Carbon disulfide..... | 2200 | 1980 | 2400 | 2920 | 3950 | 73 | 2.6 |
| Ethyl alcohol..... | 2030 | 2160 | 4000 | | 3600 | 63 | 26 |
| Nitrobenzene..... | | | 2470 | | | ... | 35— |
| Bromoform..... | | | 2550 | | | ... | ... |
| Methyl alcohol..... | 2420 | 3440 | 4100 | | | 79 | 31 |
| Aniline'..... | | | 2600 | | | 52 | 7.3 |
| Bromine..... | | 4800 | 3000 | | | ... | 3.2 |
| Phenol..... | | | 3040 | | | ... | 9.7 |
| Ammonia..... | | | 3900 | | | 114 | 16 |
| Iodine..... | | | 3900 | | | ... | ... |
| Sulfuric acid..... | | | 5300 | | | ... | 84 |
| Water..... | 4900 | 37300 | 10200 | | ... | 218 | 80 |
| Mercury..... | | | 17300 | 12700 | | 456(?) | ... |

Table I contains values of the internal pressure in atmospheres accord-

ing to Winther,¹ Traube,² Walden,³ W. C. McC. Lewis,⁴ and Mathews.⁵ The values by Winther, Traube and Lewis are for 0° as calculated by them. Walden gives values only at the boiling point, and in order to obtain values at the same temperature, so that they would be more suitable for comparison, the original values of Walden were reduced to 0° by assuming, according to the van der Waals' theory, that the variation in internal pressure is inversely proportional to v^2 . Considering the uncertainty of the whole calculation, this part of it is relatively unobjectionable. Mathews gives in his paper values for the van der Waals "a." These were calculated to internal pressures at 0° by dividing by the square of the molecular volumes at that temperature. In the same table are given values for the critical pressures, selected from those given in Landolt-Börnstein. It is not surprising that the order for critical pressures, should be substantially the same, in most cases, as that for internal pressure, since in terms of the van der Waals theory critical pressure is given by $\frac{8a}{27b^2}$, while internal pressure is $\frac{a}{v^2}$, and b and v are closely related. It is well known, however, that the van der Waals equation, using the a and b calculated from critical data, does not satisfactorily represent the behavior even of non-associated liquids at much lower temperatures, nor is it possible to do so with any pair of fixed values of a and b . Moreover, it seems likely that, for normal liquids, b varies far more than a .⁶ All of this renders it improbable that equality of critical pressures is the best criterion for our purpose, although it may be exceedingly convenient and useful. We might expect it to be of less value when the b -values (or molecular volumes) of the substances being compared are very different, and accordingly, as we shall frequently see, chlorine, whose b -value is small and which would take a considerably different position in the series if the latter were arranged according to critical pressures, behaves rather as we should expect it to when the series is arranged according to internal pressures.

We shall endeavor presently to show, according to the evidence at hand, that approximate equality of internal pressures of normal liquids is an adequate criterion for sufficient likeness in molecular environment for Raoult's law to hold. We shall also see that inequality of internal pressure indicates that the partial vapor pressures will be found greater than given by Raoult's law. It might be expected that two species of

¹ Winther, *Z. physik. Chem.*, **60**, 603 (1907).

² Traube, *Ibid.*, **68**, 291 (1909).

³ Walden, *Ibid.*, **66**, 385 (1909).

⁴ Lewis, *Phil. Mag.*, [6] **28**, 104 (1914).

⁵ Mathews, *J. phys. Chem.*, **17**, 603 (1913).

⁶ T. W. Richards, *THIS JOURNAL*, **36**, 617 (1914).

molecules of different size and attractive power would pack less closely in the mixture than in the pure state, and that the volume of the mixture would be greater than additive, resulting in smaller attractions and greater vapor pressures. In fact, some preliminary calculations give some promise of a formal relation between this expansion, the assumed resulting decrease in internal pressure, and the increase in vapor pressure.

It may be mentioned that Walden, in the paper above referred to, gives a number of generalizations concerning the relation of internal pressure to constitution, in the case of organic liquids.

(b) **Polar Nature.**—There is another factor besides internal pressure which is of profound importance for which the van der Waals theory has not been able adequately to account, which has doubtless been the chief disturbing factor in its application to the liquid state, and in fact to a great deal of the work involving the mass law. That is the polarity of the substance. The nature of this polarity has been discussed by Bray and Branch,¹ and more fully by G. N. Lewis.² Molecules which are electrically polar will tend to form larger aggregates, or to associate, just as a mass of similar magnets would do. This polarity results in a molecular attraction, and hence an internal pressure and surface tension, which is greater than it would otherwise be. In an electric field such molecules tend to orient themselves according to their polarity, so that the liquid has a considerable dielectric constant. They also tend to form complexes with polar molecules of different species, "addition compounds." There is also a marked tendency for nonpolar or slightly polar substances to become more polar in the presence of polar substances, as shown, for example, by their greater reactivity when dissolved in polar solvents.

In liquids of this sort we should expect not only the b but also the a of van der Waals to be very abnormal and variable, and we can see more justification, in mixtures involving a polar liquid, for applying the method of Dolezalek, though even here we dare not assume that each molecular species present will obey the mass law and Raoult's law. The insuperable objection to this treatment seems to be raised by the liquids incompletely miscible, where we would have to make the paradoxical assumption previously mentioned that the mol-fractions are the same in two liquid phases of different composition.

If X and Y denote nonpolar and polar molecules, respectively, we should expect the attraction between X and Y to be greater than that between X and X, but less than that between Y and Y. This would cause a tendency for the Y molecules to form aggregates, even to the extent of separating as a separate phase of greater or less purity, and the deviations

¹ Bray and Branch, *THIS JOURNAL*, **35**, 1440 (1913).

² G. N. Lewis, *Ibid.*, **38**, 762 (1916).

from Raoult's law would be very great. In fact highly polar liquids nearly always form two-phase liquid systems with nonpolar liquids.

When two polar liquids are mixed we have rather complicated possibilities. If the attractions between Y_1 and Y_2 happened to be the same as those between Y_1 and Y_1 and between Y_2 and Y_2 we might find Raoult's law followed, but in general one species is more electropositive than the other, and the forces between Y_1 and Y_2 are the greatest, resulting in smaller vapor pressures than would otherwise be the case.

The polarity of a liquid is indicated experimentally by a high dielectric constant, an abnormally great entropy of vaporization,¹ deviation from the Eötvös-Ramsay and Shields rule for surface tension, power to give conducting solutions with electrolytic solutes, etc., etc.² A concordant figure for the degree of polarity or the "association factor" can hardly be obtained from the various methods, but we can indicate the polarity roughly by means of the dielectric constant. Values of the dielectric constant are, therefore, given in Table I, selected from those given in Landolt-Börnstein. Where other evidence would modify the conclusions based on the value of the dielectric constant a plus or minus sign is added to the figure to indicate the direction of the modification. For example, stannic chloride is a normal liquid, according to the usual criteria, and gives mixtures with benzene not deviating much from Raoult's law. On the other hand, it is evidently capable of becoming polar, as shown by its solubility and dissociation in water, and its chemical reactivity. It may well be that the symmetry of the molecule gives it, for example, slight moment in an electric field, and hence a small dielectric constant, although the charges within the molecule may be separated considerably, so that the proximity of a strongly polar molecule may distort it, rendering it polar. In the recent paper of G. N. Lewis entitled "The Atom and the Molecule" already cited, it is pointed out that the polar character of a substance is affected by its environment, a slightly polar substance, for example, becoming more polar in the presence of a strongly polar substance. There is no reason to believe that the curve he uses to point out the relation between polarity and "polar influence" would be the same for all substances. We may readily imagine that though two liquids may be equally nonpolar in the pure state they might be influenced unequally by the admixture of a highly polar substance. Such substances as stannic chloride, arsenic chloride, phosphorus trichloride, etc., seem to behave as fairly normal liquids in the pure state, and yet to be capable of polarity in the presence of highly polar substances. The distortion of a symmetrical molecule, previously mentioned, may serve to explain such cases.

If fused salts were included in Table I they would mostly come after

¹ Hildebrand, *THIS JOURNAL*, **37**, 970 (1915).

² See W. E. S. Turner, "Molecular Association," Longmans, Green & Co., 1915.

water. All the evidence we have goes to show that many molten salts are far more polar than are even the dissociating solvents such as water and ammonia. The latter are not much ionized in the pure state, and their polarity must be due to a separation of the charges in the molecule. Fused salts, on the other hand, seem to be very highly ionized in the pure state, the separation of the charged parts being more or less complete into charged ions, as shown by the high conductivity of fused salts. The resulting liquids are highly abnormal, from the standpoint of the usual criteria, so far as they can be applied, although the term associated is hardly adequate to express their condition. The term polar is far more pertinent. The abnormal character and high internal pressure consequent upon this polar condition is evidenced chiefly by the high surface tension and the deviation from the Eötvös-Ramsay and Shields relation, such as are seen in the following values,¹ figures for water being included for comparison:

TABLE II.

| | Temp. | Surface tension. | R. and S. constant. | "Assoc. factor." |
|--------------------------------------|---------|------------------|---------------------|------------------|
| NaNO ₃ ² | 339 | 106 | 0.445 | 10.68 |
| KNO ₃ ² | 338 | 110 | 0.503 | 8.73 |
| AgCl ³ | 446-580 | ... | 0.959 | 3.29 |
| PbCl ₂ ³ | 480-600 | ... | 0.903 | 3.60 |
| BaCl ₂ ⁴ | 960 | 180 | | |
| H ₂ O..... | 20 | 73 | 1.13 | 3.56 |

Although our knowledge of fused salts is very meagre, we may doubtless make approximate predictions of their relative polarity to serve the purpose to be described later. We may assume that the polarity of a liquid salt is conditioned primarily by the electropositive and electronegative character of its constituents. This is indicated by the electrode potentials, and the electrochemical replacement series, where elements are concerned. This electrochemical character usually accords with the position of the element in the periodic table, the elements becoming increasingly electropositive as we go towards the alkali group, and also as we go from top to bottom of the principal groups. (In the subgroups, such as that including zinc, cadmium and mercury, the most electropositive elements may be found at the top.) The reverse is true for the electronegative character. Information is also gained from the relative strengths of acids and bases, the strongest being those showing the greatest tendency to ionize, and hence being most polar. In accordance with this the alkali halides, for example, would be highly polar, those of silver much less so, silver iodide being less polar than silver chloride. A

¹ See also Walden, *Z. Electrochem.*, **14**, 713 (1908).

² Bottomley, *J. Chem. Soc.*, **83**, 1421 (1903).

³ Lorenz and Kauffler, *Ber.*, **41**, 3727 (1908).

⁴ Motylewski, *Z. anorg. Chem.*, **38**, 410 (1903).

substance like lead chloride would be moderately polar, while lead acetate would be but slightly polar. The silicates of the heavier metals would be but slightly polar. An increase of polarity would result from increasing the electronegative character of a weak anion by the formation of a poly-anion, for example, a dichromate would be more polar than a chromate.

It seems, further, that atomic volumes have a great deal to do with polarity. Where these are great there would doubtless be more opportunity for the separation of the charges which produce polarity, the molecule being less compact, and we find, as a matter of fact, that the alkali metals, having the highest atomic volumes of all the elements, give highly polar compounds, followed in this respect by the halogens and the alkaline earths. The element having the smallest atomic volume of all, carbon, gives the least polar of all compounds. The "most normal" liquids we possess are the hydrocarbons of the paraffin series. The difference in atomic volumes may be responsible for the greater polarity of elementary iodine than of chlorine, as shown by the fact that its electrical conductivity in the liquid state is greater than that of chlorine,¹ and also by its greater reactivity. This polarity cannot be due to any difference in the two atoms composing the molecule, but rather to the electron being held under less constraint in the molecule, due possibly to the greater atomic volume as compared with chlorine.

The larger number of factors to be considered with polar liquids, and the lack of information as to their fundamental nature, cause our generalizations in the case of solutions of polar substances in each other to be much less accurate, but even here our predictions may have considerable value.

It will be remarked that in many respects the foregoing considerations concerning salts are essentially the same as those put forward by Abegg and Bodländer² in their theory of electro-affinity, which they also apply to the question of solubility. However, there are many serious contradictions that may be drawn from their considerations alone, which may be minimized by considering other factors simultaneously, especially the melting point and the heat of fusion. It must constantly be borne in mind that we are basing our discussion of the deviation from Raoult's law of a mixture of two *liquids*, and that where the solubility of solids is under discussion we must take into account, first, the polarity, internal pressure, etc., of the supercooled liquid, so far as we know them or are able to predict them, and, second, the instability of the supercooled liquid with respect to the solid form under discussion, as expressed by the ratio

¹ Linde, *Wied. Ann.*, **56**, 563 (1895); Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906).

² *Z. anorg. Chem.*, **20**, 453 (1899).

P'/P , which may be calculated by the aid of Equation 2 or 4. A discussion of examples later will make this plainer.

The molten metals follow the fused salts at the bottom of the table, being represented by mercury. Here we probably have extreme polarity, the metal being highly dissociated into ions and electrons. However, it may still behave as a normal liquid according to some of the criteria. Mercury, for example, though abnormal according to the surface tension relationship,¹ is quite normal from the standpoint of the entropy of vaporization.² Certain it is that the internal pressures of the metals are so high as to preclude mixing with the other liquids, except in the case of the alkali metals in liquid ammonia, and in some fused salts.

We have little basis, as yet, for arranging the metals in the order of their internal pressures, but are left to infer the relative magnitudes of internal pressures from the surface tension, compressibility, and from the tenacity of the metal in the solid form. Table III gives a few values of surface tension selected from Landolt-Börnstein; also values of the compressibility, at 20° C., according to T. W. Richards.³ One may infer that the internal pressures at the same temperature may increase in the order given in the table.

TABLE III.

| | K. | Hg. | Pb. | Ag. | Fe. | Pt. |
|---|------|------|------|------|------|------|
| Temperature..... | 62° | 15° | 325° | 1000 | 1500 | 2000 |
| Surface tension..... | 412 | 436 | 510 | 782 | 1000 | 1800 |
| Compressibility $\times 10^6$ at 20°..... | 31.7 | 3.95 | 2.33 | 1.01 | 0.60 | 0.38 |

Thus, in spite of the high temperature at which it was observed, it will be noted that the surface tension of molten iron is very high compared with that of the softer metals. This, with the small compressibility and high tensile strength of solid iron, undoubtedly indicates a high internal pressure.

To summarize the effect of internal pressure and polarity, we may say that (1) Raoult's law should be obeyed by mixtures of nonpolar liquids having the same internal pressures; (2) nonpolar liquids of different internal pressures will show greater vapor pressures in the mixture than would be expected from Raoult's law; (3) the same holds true for mixtures of polar with nonpolar liquids; (4) mixtures of polar liquids may show either positive or negative deviations from Raoult's law, but in most cases the latter will predominate; (5) these deviations will modify the predictions of solubility for gases, liquids, and solids, based upon Raoult's law alone, the solubilities being greater where negative deviations occur, and *vice versa*.

¹ Cenac, *Ann. chim. phys.*, [8] 28, 298 (1913); see also J. L. R. Morgan, *Ibid.*, [9] 1, 326 (1914).

² Hildebrand, *Loc. cit.*

³ T. W. RICHARDS, THIS JOURNAL, 37, 1643 (1915).

4. Experimental Evidence.

(a) **Liquid Mixtures.**—Having laid down our general principles, let us now compare their application with the observed facts. The following pairs of liquids give mixtures which obey Raoult's law exactly or nearly so: benzene and carbon tetrachloride,¹ benzene and chlorobenzene,² benzene and chloroform,² benzene and ethylene chloride,¹ chlorobenzene and toluene.² It will be observed that all of these liquids have nearly the same values of internal pressure. A small positive deviation, as we would expect, is found in the cases of ethyl iodide with ethyl acetate³ and benzene with stannic chloride.⁴ Larger deviations occur with benzene and carbon disulfide,^{5,6} carbon disulfide and carbon tetrachloride,⁷ benzene and hexane,⁸ benzene and ether⁹ and carbon disulfide and methylal.¹⁰ Methylal is not given in the table but it is nonpolar, with a dielectric constant of only 2.7, and it must have a very low internal pressure, as Walden gives for acetal an internal pressure of 1000 atmospheres at 103°. The partial pressure of bromine in dilute solution in carbon tetrachloride is over twice the value calculated from Raoult's law.¹¹

Chlorine, on the other hand, obeys Raoult's law rather closely in carbon tetrachloride solution. From the measurements of Jakowkin¹² on the solubility of chlorine in carbon tetrachloride we have calculated the following values for the mol-fraction of chlorine, N , and the ratio of the partial vapor pressure of chlorine to that of liquid chlorine at the same temperature, p/P .

| | | | | |
|-------------|---------|---------|---------|---------|
| N | 0.00086 | 0.00225 | 0.00423 | 0.00718 |
| p/P | 0.00092 | 0.00208 | 0.00410 | 0.00673 |

The corresponding values are obviously almost within the limit of experimental error. This case is significant as showing that the internal pressures furnish a more reliable criterion than do critical pressures. In this case, as may be seen from the table, the former are much more nearly alike than the latter. If our table were arranged according to critical pressures chlorine would have a very different place.

(b) **Solubility of Gases.**—As explained previously, the ratio p/P for

¹ Zawidzski, *Z. physik. Chem.*, **35**, 129 (1900).

² Linebarger, *THIS JOURNAL*, **17**, 615, 690 (1895).

³ Zawidzski, *Loc. cit.*

⁴ Schulze and Hock, *Z. physik. Chem.*, **86**, 445 (1914).

⁵ Brown, *J. Chem. Soc.*, **35**, 547 (1879).

⁶ Carveth, *J. phys. Chem.*, **3**, 193 (1899).

⁷ Brown, *J. Chem. Soc.*, **39**, 517 (1881).

⁸ Given without reference by Noyes and Sherrill, "General Principles of Chemistry," p. 27 (1914).

⁹ Haywood, *THIS JOURNAL*, **21**, 994 (1899).

¹⁰ Zawidzski, *Loc. cit.*

¹¹ Unpublished measurements by Lewis and Storch of this laboratory.

¹² Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

a solution of a gas in a liquid gives its solubility where Raoult's law holds, even though the value of P for the gas has to be extrapolated above its critical pressure. The deviations from Raoult's law cannot be predicted with as much satisfaction as in the case of most of the solutions heretofore considered, because we have no knowledge of what places the gases should occupy in the table except as critical pressures may be used for the purpose. However, with the same gas, the solubility in various solvents should depend on the order of the internal pressures of the latter, subject, as always, to the further influence of polarity. The extent to which this is true is seen in Table IV. In calculating the figures here given use is made of the measurements of Just¹ on the solubilities of hydrogen, nitrogen, carbon monoxide and carbon dioxide. The values for methane, ethane, and ethylene are calculated from solubility measurements by MacDaniel,² and for ammonia in methyl and ethyl alcohol by de Bruyn.³

TABLE IV.⁴

Solubilities of Gases in Terms of Mol-Fraction, $N \times 10^4$, when $p = 1$ Atmosphere.

| p/P for gas Solvent. | 20° C. | | | | 25° C. | | | |
|---------------------------|------------------|------------------|------|-------------------|-------------------|---------------------------------|---------------------------------|-------------------|
| | H ₂ . | N ₂ . | CO. | CO ₂ . | CH ₄ . | C ₂ H ₆ . | C ₂ H ₄ . | NH ₃ . |
| | 10 | 11 | 178 | | 32 | 240 | 148 | 1020 |
| Hexane..... | ... | ... | ... | ... | 31 | 171 | 159 | |
| Xylene..... | 4.0 | 6.1 | 8.9 | ... | 26 | ... | ... | |
| Ethylacetate..... | 3.2 | 6.8 | 9.9 | ... | ... | 123 | ... | |
| Toluene..... | 3.7 | 5.3 | 7.7 | 108 | 21 | ... | ... | |
| Chloroform..... | ... | 4.3 | 6.3 | 123 | .. | ... | ... | |
| Benzene..... | 2.6 | 4.1 | 6.1 | 94 | 18 | ... | 125 | |
| Acetone..... | 2.1 | 4.2 | 6.5 | 211 | .. | ... | 75 | |
| Ethylalcohol..... | 2.1 | 3.3 | 4.5 | 70 | 11 | 55 | ... | 2300 |
| Nitrobenzene..... | 1.5 | 2.6 | 3.9 | 112 | .. | ... | ... | |
| Methylalcohol..... | 1.5 | 2.2 | 3.0 | 70 | 7.4 | 33 | ... | 2730 |
| Aniline..... | 1.16 | 1.1 | 1.9 | 55 | .. | ... | ... | |
| Carbon disulfide..... | ... | 1.3 | 2.0 | 23 | .. | ... | ... | |
| Water..... | 0.15 | 0.13 | 0.19 | ... | 2.4 | 3.2 | 8.4 | 3300 |

The values of p/P were gotten by using the data found in Landolt-Börnstein, extrapolating above the critical pressure, where necessary, by the aid of the straight line plot obtained on plotting $\log p$ against $1/T$. P is the pressure the liquefied gas would have at 20° and 25° , respectively; p is taken as 1 atmosphere. The solubilities, in terms of mol-fraction, are calculated also for a gas pressure of one atmosphere.

It will be seen that for nitrogen, carbon monoxide, methane, ethane and ethylene, the solubility in the various solvents decreases in essentially

¹ Just, *Z. physik. Chem.*, **37**, 342 (1901).

² MacDaniel, *J. phys. Chem.*, **15**, 587 (1911).

³ de Bruyn, *Rec. trav. chim.*, **11**, 112 (1892).

⁴ The writer wishes to express his thanks to Mr. D. B. Keyes for help in the calculations required to prepare this table.

the order given in the table of internal pressures, the gas behaving, in this respect, as would a liquid of low internal pressure. The order for the different gases is not quite identical, but the slight discrepancies are hardly greater than the errors involved. As before, the greatest uncertainty is where the polar solvents are concerned. This is not surprising, as the uncertainties are necessarily greater in such cases on account of our inability to determine how much of the internal pressure is due to the polarity. Carbon dioxide is obviously, from its chemical reactivity, much more polar than the gases previously mentioned, and additional uncertainties are thus introduced, though a distinct increase in solubility in the more polar solvents is evident.

When we come to ammonia, itself highly polar, we find a solubility in polar solvents greater than that indicated by Raoult's law alone.

(c) **Liquids not Completely Miscible.**—Mr. Keyes and the writer have sought a pair of normal liquids that would be incompletely miscible, and have found that aniline, far down in the table, will not mix completely at lower temperatures with the paraffins, standing at the head of the table, though it will mix with all of the normal liquids standing nearer to it. Aniline is slightly polar, which helps to account for this behavior, but it is impossible to account for the deviation from Raoult's law evident in this case by any ordinary assumption as to association according to the method of Dolezalek.

As is well known, the highly polar liquids given in the table do not mix completely with the nonpolar liquids. The internal pressures and the polarity together make relative predictions quite trustworthy. Thus methyl alcohol, more polar than ethyl alcohol, does not mix completely with carbon disulfide whereas ethyl alcohol does. Water, still more polar, is scarcely soluble at all in carbon disulfide. Phenol is more polar than aniline and is accordingly much more soluble in water. Ethyl acetate, though having the same internal pressure as toluene, is much more polar, and hence is far more soluble in water. Other familiar facts are in general accord with the figures in the table.

(d) **Solubility of Solids.**—Iodine, calculated as a supercooled liquid, has the highest internal pressure of any of the normal substances in the table, and accordingly its solutions in most of the liquids represented show large deviations from Raoult's law. To make this evident we must calculate the ratio of vapor pressures for solid and liquid iodine for temperatures in the region of existing solubility measurements. Lewis and Randall¹ give the free energy of liquid iodine at 25° as 460 cal. per gram atom, corresponding to 920 cal. per mol. Since $920 = -4.58 \times 298 \log P'/P$, we have $P'/P = 0.212$. If Raoult's law held, this figure should represent also the solubility of iodine in terms of its mol-fraction at this tem-

¹ Lewis and Randall, *THIS JOURNAL*, 36, 2259 (1914).

perature. We have calculated the solubility in terms of mol-fraction in bromoform and carbon tetrachloride from measurements by Jakowkin.¹ The solubility in bromoform is given by him only in terms of amount of iodine per liter, so that we have had to make the assumption that the volume of the solution is additive, using for the volume of liquid iodine 59 cc. per mol.² The solubilities in carbon disulfide and benzene are gotten from measurements by Arctowski,³ an extrapolation being necessary in the case of benzene to get the value at 25°. The solubility in chloroform is gotten from data by Hantzsch and Vagt,⁴ an interpolation being necessary to reduce to 25°. The following are the resulting values:

$$P'/P = 0.212; N = \begin{array}{cccccc} \text{CHBr}_3 & \text{CS}_2 & \text{C}_6\text{H}_6 & \text{CCl}_4 & \text{CHCl}_3 & \\ 0.066 & 0.058 & 0.047 & 0.026 & 0.022 & \end{array}$$

Comparing the order of solubilities with that for internal pressures, we see that the solubility is greatest in bromoform, with the highest internal pressure, and the one nearest to iodine. The value in carbon disulfide comes next, as is to be expected. The internal pressures of the next three liquids are not far apart, and we might expect the solubilities in these liquids to be about the same. This is the case for chloroform and carbon tetrachloride. It is true the order here is reversed, but the moderate uncertainties of the figures for both the internal pressures and solubilities make the small discrepancy of scant significance. The only apparent exception of any magnitude is in the case of benzene, whose internal pressure is very close to those of carbon tetrachloride and chloroform but whose power of dissolving iodine appears to be nearly double what we might expect it to be. This is undoubtedly due to the fact that the solid phase is not pure iodine, but becomes a solid solution of benzene in iodine, as discovered by Beckmann and Stock,⁵ allowing more iodine to enter the solution.

Solutions of naphthalene likewise show excellent agreement with the predictions made with the aid of the table. The mol-fraction of naphthalene in saturated solutions in several solvents is given in the following table, in comparison with the value P'/P , calculated from the measurements of Bogojawlenski⁶ by means of Equation 2. The heat of fusion per mol is 4440 cal., $\Delta T = 5.1$, the melting point is $T = 353.1$.

| | CS ₂ | CHCl ₃ | C ₆ H ₆ CH ₂ | C ₆ H ₁₄ | C ₂ H ₅ OH | P'/P | Temp. |
|--------|--------------------|--------------------|---|--------------------------------|----------------------------------|-------|-------|
| N..... | 0.253 ⁸ | 0.303 ⁷ | | 0.101 ⁷ | 0.033 ⁸ | 0.286 | 20° |
| | | | 0.188 ⁹ | | | 0.263 | 16.5° |

¹ Jakowkin, *Z. physik. Chem.*, **18**, 585 (1895).

² Cf. Dawson, *J. Chem. Soc.*, **97**, 1046 (1910).

³ Arctowski, *Z. anorg. Chem.*, **6**, 392 (1894); **11**, 272 (1896).

⁴ Hantzsch and Vagt, *Z. physik. Chem.*, **38**, 705 (1901).

⁵ Beckmann and Stock, *Ibid.*, **17**, 107 (1895).

⁶ Bogojawlenski, *Chem. Zentr.*, **76**, II, 945 (1905).

⁷ Etard, *Bull. soc. chim.*, [3] **9**, 82 (1893).

⁸ Lobry, *Z. physik. Chem.*, **10**, 784 (1892).

⁹ Bechi, *Ber.*, **12**, 1978 (1879).

As would be expected from the position of naphthalene in Table I, the values of P'/P are very close to the values of N in chloroform, a little less in carbon disulfide with its higher internal pressure, falling off, on the other hand, in toluene and hexane, with their successively lower internal pressures. The polar character of alcohol accounts for the very low solubility in that solvent.

Other data of similar nature is being obtained in this laboratory and will soon be ready for publication, all of which, thus far, is in entire accord with the predictions made.

(e) **Salt Solutions.**—We know so little about the properties of fused salts that we cannot predict relative solubilities in such cases with the certainty that is possible with less polar substances. Several generalizations, however, are possible.

The highly polar character of fused salts, previously referred to, causes all salts, so far as we have been able to determine, to be completely miscible in the liquid state.

The most highly polar salts would be the halides, nitrates, etc., of the alkali and alkaline earth metals, and accordingly these are generally very soluble in polar solvents, showing negative deviations from Raoult's law, in accordance with the principles earlier set forth. This is illustrated in Table V, where the solubility in water at 25° is given in terms

TABLE V.

| | Melting point. | Molal heat of fusion. | P'/P calc. | N solubility. |
|---|-------------------|--------------------------|-----------------|--------------------|
| $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ | 30° | 8900 | 0.84 | 0.44 |
| H_3BO_3 | 185 | | | 0.016 |
| AgNO_3 | 218 | 2580 | 0.17 | 0.19 |
| HgI_2 | 250 | 4440 | 0.04 | $2 \cdot 10^{-6}$ |
| NaNO_3 | 333 | 3690 | 0.03 | 0.18 |
| $\text{K}_2\text{Cr}_2\text{O}_7$ | 397 | 2980 | 0.06 | 0.018 |
| AgCl | 455 | 3050 | 0.05 | $2 \cdot 10^{-7}$ |
| KCl | 772 | 6410 | 0.0004 | 0.08 |
| BaCO_3 | 795 | | | $2 \cdot 10^{-6}$ |
| Ag_2S | 830 | | | $2 \cdot 10^{-7}$ |
| PbSO_4 | 1100 | | | $3 \cdot 10^{-6}$ |
| CaF_2 | 1400 | | | $4 \cdot 10^{-6}$ |
| CaSiO_3 | 1510 | | | 0+ |
| BaSO_4 | 1580 | | | $2 \cdot 10^{-7}$ |
| Al_2O_3 | 2020 | | | 0+ |

of mol-fraction, along with values of the melting point, and, where the heat of fusion is known,¹ values of P'/P , which would equal the solubilities if Raoult's law held. Calcium fluoride and barium sulfate we might

¹ Taken from the data given by Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909), see also Goodwin, *Trans. Am. Electrochem. Soc.*, **21**, 113 (1912) with the exception of the value for KCl by Plato, *Z. physik. Chem.*, **55**, 737 (1906), and that for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, by Person, *Ann. chim. phys.*, [3] **27**, 250 (1847).

expect to be highly polar in the liquid state. Their insolubility, in spite of polarity, is due to their high melting points, corresponding to a very small value of P'/P . If the heat of fusion were known, so that P'/P could be calculated, we would doubtless find that it is less than N in both cases, so that here, just as with potassium chloride and sodium nitrate, the deviation from Raoult's law would be negative, in accordance with the general principle. The negative deviation from Raoult's law has practically disappeared when we come to the salt of a much less electro-positive metal like silver nitrate, and we find in general that the salts of the nobler and hence less electropositive metals become much less polar and less soluble in polar solvents, even if the melting point is not very high. Boric acid, in spite of its low melting point, has obviously very slight polarity, and is accordingly not very soluble in water. When we consider the sulfides of the heavier metals, and especially the silicates, we encounter both small polarity and high melting points, and consequently they are relatively insoluble. With the slightly polar compounds of lower melting point, however, like the acetates, mercuric iodide, etc., we find solubility in the weakly polar organic solvents, for here, as we should expect, the liquids do not show the strong positive divergence from Raoult's law that we find when a polar and a nonpolar substance are mixed.

It must be frankly stated that the mere guess as to the polarity of a molten salt is not sufficient to explain all of the facts. For example, silver iodide, which we might expect to be weakly polar, is far less soluble in water than it would be if Raoult's law held, but it is at the same time far more soluble in liquid ammonia, which is also very polar, although less so than water. We may make a generalization that cannot be deduced from the simple criteria of polarity that we have announced, though it, too, ought ultimately to be brought into accord with the physical properties of the substances, namely, that the tendency to form hydrates, and hence to give negative deviations from Raoult's law and greater solubility in water solution, is greatest for elements at the top of the Periodic Table, whereas the tendency to unite with ammonia, and hence, presumably, to be more soluble in liquid ammonia, is greatest for elements at the bottom of the table. This is illustrated by the abnormally high solubility of magnesium chloride in water, on the one hand, and by the abnormally high solubility of mercuric iodide and silver iodide in liquid ammonia, on the other hand.

In this connection it should be pointed out that the values of P' and P which determine the solubility are those of the actual phase which is in equilibrium with the solution. Thus it is the melting point and the heat of fusion of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, not of CaCl_2 , which determine the solubility of calcium chloride at room temperatures. The same applies, of course,

to all solids with solvate of crystallization. Similar modifications must be made when the solid is a solid solution.

It may be stated, finally, that from our standpoint it probably makes little difference whether the solute and the solvent associate with each other to form a new polar complex, or whether there follows a separation of the parts of the original solute molecules into distinct solvated parts, which is electrolytic dissociation. The effect in either case is to reduce greatly the fugacity of the solute, p , and hence to give strongly negative deviations from Raoult's law. On the other hand, if electrical conductivity is being investigated, it would make a great deal of difference whether or not such dissociation took place, for only then would the ions be free to migrate. This point of view may serve to explain the difference in the values for the degree of dissociation obtained by thermodynamic and by conductivity methods. It is probably folly to expect them to agree, just as it doubtless is folly to expect the different methods for determining the "association factor" of polar liquids to agree.

(f) **Metallic Solutions.**—Here again, our meagre knowledge of the substances in the liquid state prevents any such comparisons as were made earlier. We have discussed previously the probable relative values of the internal pressures of molten metals.

There are many pairs of metals not completely miscible in the liquid state, corresponding to large positive deviations from Raoult's law. These pairs are in accord with what little basis we have at present for prediction. The following examples may be cited: iron-lead, copper-lead, bismuth-iron, aluminum-sodium, chromium-tin, nickel-thallium.

On the other hand, metals near together in the above respects mix readily, giving solid solutions, in many cases, indicating close approximation to Raoult's law in the liquid phase. Examples are silver-gold, bismuth-copper, cadmium-mercury, nickel-cobalt, iron-manganese.

5. Summary.

1. The following conclusions can be drawn when Raoult's law holds for a mixture of two liquids:

(a) The solubility of a vapor or gas in terms of its mol-fraction in the solution is given by p/P , the ratio of the partial pressure of the gas to its saturation pressure. The latter may have to be gotten by extrapolation above the critical pressure.

(b) The solubility of a solid in terms of mol-fraction is given by the ratio of the vapor pressures of its solid and liquid forms at the temperature in question. This can be calculated from the heat of fusion and the melting point, and will be smallest for solids having a high melting point and a large heat of fusion.

(c) When solubility is expressed as weight of solute in a given weight of solvent, other things being equal, will be greatest for

solutes of high molecular weight, and for solvents of low molecular weight. When the solubility is expressed as amount of solute in a given volume of the solvent, it is greatest for solvents having low molecular weight and high density.

(2) Deviations from Raoult's law may be ascribed primarily to inequality of internal pressure and to polarity. These factors, and their approximate prediction, have been discussed at some length for various kinds of liquids.

(a) Nonpolar liquids having approximately equal internal pressures obey Raoult's law, and are subject to the previous generalizations.

(b) A difference in internal pressure, with nonpolar liquids, produces a positive deviation from Raoult's law for both components, decreasing the solubility, whether considered with respect to a gaseous or a solid form of the component in question. Very great differences in internal pressure are necessary for incomplete miscibility of the two components in the liquid form.

(c) A polar and a nonpolar liquid show strong positive deviations from Raoult's law, with accompanying effects on solubilities. Most liquids which are not completely miscible belong to this class.

(d) Two polar liquids may show either positive or negative deviations from Raoult's law, usually positive where there is considerable difference in polarity, and negative when both are highly polar. The effects on solubility correspond to the direction of these deviations.

Numerous examples are given justifying the points of view presented.

BERKELEY, CAL.

{CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.}

AN ADIABATIC CALORIMETER.

BY FARRINGTON DANIELS.

Received May 2, 1916.

The cooling correction, which is essential in ordinary calorimetry, is troublesome and uncertain. The adiabatic calorimeter as devised by Richards eliminates this correction, but since it has not received the general acceptance which, in the opinion of the author, it deserves,¹ an attempt has been made in this laboratory to modify the construction so as to bring it into more popular favor. Electrolytic heating, as used by Derby, has made possible the development of a calorimeter which it is hoped will accomplish this purpose.

In common calorimetric practice the temperature is read at frequent intervals and the correction for radiation is calculated by one of several

¹ See criticisms of Dickinson, Bureau of Standards, *Bull.* 11, 206 (1914), and of Jaeger and von Steinwehr, *Z. physik. Chem.*, 54, 428 (1906).