

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

### SOLUBILITY. III. RELATIVE VALUES OF INTERNAL PRESSURES AND THEIR PRACTICAL APPLICATION.

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#### I. Introduction.

In the first paper by the writer on this subject,<sup>1</sup> it was shown that deviations from Raoult's law for non-polar substances could be predicted on the basis of differences in internal pressures of cohesions of substances in the liquid state. Since, in systems where it is obeyed, Raoult's law furnishes a method for calculating solubilities of both solids and gases, the prediction of deviations from it makes possible the estimation of relative solubilities. Moreover, we are enabled thereby to understand deviations from a number of fundamental physico-chemical formulas, such as those dealing with molecular weights of dissolved substances, osmotic pressure, Henry's law, the distillation of liquid mixtures, and concentration cells. The wide use to which van't Hoff's law for osmotic pressure is put in deriving physico-chemical formulas emphasizes the importance of an accurate expression for the behavior of substances in solution. The value of Raoult's law in dealing especially with concentrated solutions has begun to be recognized by physical chemists in recent years. Raoult's law is much more accurate at high concentrations than van't Hoff's law and serves quite as well for deriving physico-chemical formulas, in spite of the fact that, as usual in such cases, most text-books in physical chemistry still cling to the historical basis. The present theory, dealing as it does with the deviations from Raoult's law, presents a method of approach to the various problems involving the colligative properties of solutions, concentrated as well as dilute.

In addition to the abundant evidence in support of the theory given in the first paper, still further data were furnished in a second paper on the same subject.<sup>2</sup> It seems safe to say that all of the evidence cited, and this constitutes nearly all at present available, supports the theory that (1) with non-polar substances Raoult's law will be obeyed by mixtures of liquids having equal internal or cohesive pressures, and (2) the greater the difference between the internal pressures the greater will be the escaping tendency of each component of the mixture, and hence the greater the positive deviation of both components from Raoult's law. How this theory could be used to predict solubilities was explained in the first paper, wherein considerable discussion was also included on the effect of polarity.

The most unsatisfactory feature of the previous presentation consisted of the divergent values of the internal pressures, as calculated by other

<sup>1</sup> THIS JOURNAL, 38, 1452 (1916).

<sup>2</sup> *Ibid.*, 39, 2297 (1917).

workers, and the uncertainty involved in any attempt to deal with substances other than those given in the table. A study of their methods for calculating internal pressures has shown clearly the necessity for a careful critique of the whole subject. As a preliminary result of this it has been possible to calculate from every simple data by several independent methods the position of each substance in a table of relative internal pressures. The order of arrangement of the substances considered has turned out to be substantially the same irrespective of the method used, so that it becomes possible for one to find very easily the position of a new substance in the table and to answer a variety of questions regarding its solutions.

No originality is claimed for the fundamental theories used in the following calculations of relative internal pressure, with the exception of the method for relating heat of vaporization to boiling point. A later paper will deal more fully with the theoretical aspects of the problem, this one being designed to present a practical basis for predicting solubilities and for dealing with other problems which may be connected with deviations from Raoult's law.

## 2. Methods for Calculating Internal Pressure.

(a) **Surface Tension.**—It is obvious that work must be done when the surface of a liquid is extended, since a great many molecules are brought from the interior of the liquid, where the attractive forces acting upon a given molecule are the same in all directions, into the surface, where there is an unbalanced attraction towards the interior. This work is numerically equal, on the one hand, to the surface tension, multiplied by the increase in surface. It is equal, on the other hand, to the work done in bringing into the surface against the internal pressure the number of molecules necessary to form the new surface. The work against surface tension is an experimental quantity, and hence would enable us to calculate the internal pressure provided we knew the rate at which this inward attraction decreases as a molecule moves inward from the surface. This idea is contained in the well-known equations of Laplace, which require for their integration an assumption as to the law of molecular attraction. Whatever the law expressing the rate of decrease of the unbalanced internal pressure with the distance below the surface, it is very probable that it is a function of the mean molecular distance, which is proportional to the cube root of the molecular volume  $V^{1/3}$ . Hence we may assume that the work involved in a unit increase in surface, which equals  $\gamma$ , is also proportional to  $\gamma/V^{1/3}$ . Accordingly, the expression

$$\Pi \propto \gamma/V^{1/3} \quad (1)$$

should give relative values of internal pressure, at least for liquids whose molecules do not have a very decided orientation in the liquid surface.

A later communication will deal with the values of the proportionality constant resulting from different assumptions for the law of molecular attraction.

(b) **Heat of Vaporization.**—Stefan<sup>1</sup> has made the well-known assumption that the work involved in bringing a molecule to the surface of a liquid is  $1/2$  of that necessary to overcome the entire attraction of the liquid mass involved in vaporization. This leads to the equation

$$\Pi = 20.65 \frac{L - RT}{V}$$

where  $L$  is the heat of vaporization. The numerical factor is necessary to convert calories into cc. atmospheres.

The writer has shown<sup>2</sup> that there is a very simple relation existing between the vapor pressures of all normal liquids which enables one to calculate the entire vapor-pressure curve, and hence the heat of vaporization, from a single point, such as the boiling point. This relation may be used to substitute the more accessible boiling point for the heat of vaporization in making the above calculation. By plotting  $\log p$  against  $\log T$  for the vapor pressure of one normal liquid a curve is obtained which may be superimposed upon the similar curve for any other normal liquid by sliding it along any line whose equation is  $\log p = \log T + \text{const.}$  Consequently, when but a single point on the vapor-pressure curve of one substance is known, such as the boiling point, the entire curve may be constructed by the above means. Furthermore, the tangent to this curve at any point has a slope equal to  $L/RT$ . From this the value of  $L$  at any temperature can be obtained. Subtracting  $RT$  gives the value of the heat of vaporization at constant volume. This was determined for a number of liquids having different boiling points, and it was found that the relation between  $L - RT$  at  $20^\circ$  and the boiling point of the liquid could be expressed by the following equation:

$$L - RT = 5200 + 30t_b$$

where  $t_b$  represents the boiling point.

If Stefan's assumption is correct the internal pressure in atmospheres should accordingly be given by

$$\Pi = 20.65 (5200 + 30t_b)/V_{20}. \quad (3)$$

Even if the assumption is not absolutely correct it may still represent an approximation sufficient to give relative values of internal pressure for different liquids.

(c) **Critical Data.**—As is well known, the term  $a/V^2$  in the van der Waals equation of state represents the internal pressure. If this equation were accurate, values of  $a$  calculated from critical data would give true

<sup>1</sup> Stefan, *Wied. Ann.*, 29, 655 (1886).

<sup>2</sup> Hildebrand, *THIS JOURNAL*, 37, 970 (1915); 40, 45 (1918).

values for internal pressures. Expressing  $a$  in the units ordinarily used for van der Waals' equation, the value of internal pressure in atmospheres would be

$$\Pi = 5.10^8 a/V^2. \quad (4)$$

Inasmuch as critical data are not available for very many substances, it is gratifying to note that van Laar has contributed a method for the calculation of  $a$  on an additive basis.<sup>1</sup> He has shown that  $\sqrt{a}$  for a molecule is the sum of the values of  $\sqrt{a}$  for the atoms composing it. He gives the following values for  $\sqrt{a} \cdot 10^4$ :

H 1.6	P 6.4	Kr 6.9
C 3.1; 1.55; 0	S 6.3	Sb 8.9
N 2.9	Cl 5.4	I 8.8
O 2.7	A 5.2	Xe 9.1
F 2.9	Se 7.1	Hg 11
Ne 2.0	Br 6.9	

There is a constitutive influence apparent, especially with carbon compounds, where the surrounding atoms may exert a partial or even complete screening effect. Thus in compounds like  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_{14}$ , and  $\text{C}_2\text{H}_5\text{Cl}$ , the value of  $\sqrt{a}$  for carbon is 0. In doubly bound carbon, such as in  $\text{C}_6\text{H}_6$ , the value of  $\sqrt{a} \cdot 10^4$  is 1.55. It reaches its full value of 3.1 in  $\text{C}_2\text{H}_2$ ,  $\text{CO}$ , etc.

The following examples are reproduced from van Laar's paper:

$\text{Cl}_2$	$(2 \times 5.4)^2$	$\sqrt{a} \cdot 10^4$	= 108
$\text{CS}_2$	$(3.1 + 2 \times 6.3)^2$		= 246
$\text{C}_6\text{H}_{14}$	$(0 + 14 \times 1.6)^2$		= 502
$\text{C}_6\text{H}_6$	$(6 \times 1.55 + 6 \times 1.6)^2$		= 357
$\text{C}_2\text{H}_5\text{Cl}$	$(0 + 5 \times 1.6 + 5.4)^2$		= 180
$\text{C}_4\text{H}_8\text{S}$	$(4 \times 1.55 + 4 \times 1.6 + 6.3)^2$		= 357

It is thus possible to calculate values of  $a$  with sufficient accuracy for our present purpose of calculating relative internal pressures even where critical data are lacking.

(d) **From Coefficients of Expansion and Compressibility.**—From van der Waals' equation we get

$$(\partial p / \partial T)_V = R / (V - b) = (p + a/V^2) / T.$$

Since for liquids  $p$  is small compared with  $a/V^2$  we may write

$$(\partial p / \partial T)_V = a / V^2 T.$$

We may also write

$$(\partial p / \partial T)_V = - (\partial p / \partial V)_T (\partial V / \partial T)_p = \alpha / \beta$$

where  $\alpha$  is the coefficient of expansion and  $\beta$  the compressibility. By comparison with the previous expression we get

$$\Pi = a / V^2 = \alpha T / \beta. \quad (5)$$

<sup>1</sup> *J. chim. phys.*, 14, 3 (1916).

(e) **From Coefficient of Expansion.**—Starting again with the van der Waals equation we may differentiate with respect to  $V$ , at constant pressure, getting

$$-\frac{2a}{V^3}(V-b) + \frac{a}{V^2} = R(\partial T/\partial V)_p = -\frac{2a}{V^3} \frac{RT}{p + a/V^2} + \frac{a}{V^2}.$$

Neglecting  $p$  in comparison with  $a/V^2$  and writing  $(\partial V/\partial T)_p = V\alpha$ , we have finally

$$\frac{a}{V^2} = \frac{R}{V} \left( \frac{1}{\alpha} + 2T \right). \quad (6)$$

The values of  $R$  in this equation cannot be evaluated by taking values of  $\alpha$  and  $V$  at different temperatures, since  $a/R$  is constant. We will, therefore, simply take  $R = 82.1$  cc.-atmospheres per degree, giving

$$\Pi = \frac{82.1}{V} \left( \frac{1}{\alpha} + 2T \right). \quad (7)$$

A similar expression can be derived for  $\Pi$  in terms of the compressibility, but it is hardly worth while to multiply further expressions derived from van der Waals' equation.

(f) **Comparison of Values Obtained by Different Methods.**—On applying the above expressions for internal pressure it is found that very different values are obtained for the same substance. This is illustrated by the values in the following table:

TABLE I.  
Internal Pressures at 20°.

	$t_b$ .	$a \cdot 10^4$ .	$\alpha \cdot 10^4$ .	$\beta \cdot 10^6$ .	$V$ .	$\Pi$ (atmospheres).			
						(3).	(4).	(5).	(6).
Ether.....	34.6	346	16.5	187.1	103.8	1240	1600	2590	930
Carbon tetrachloride....	76.5	389	12.4	104.5	86.6	1600	2080	3480	1190
Benzene.....	80	373	12.4	95.3	88.8	1770	2360	3810	1300
Carbon disulfide.....	46	220	12.2	93.2	60.2	2260	3040	3840	1920

The values of  $\beta$  here used are those of Tyrer,<sup>1</sup> the values of  $a$  are calculated from the measurements of Young,<sup>2</sup> except that for carbon disulfide, which is from Hannay and Hogarth.<sup>3</sup>

It is not surprising, in view of the well-known inadequacy of the van der Waals equation for dealing with liquids, that the different formulas derived by its aid lead to inconsistent results. It will be profitable in the future to study the results obtained by a similar treatment of other equations of state. Such treatment, however, lies beyond the scope of the present paper, and is unnecessary for the present purpose, since, it will be observed, the values of  $\Pi$ , calculated in the above various ways, are closely parallel (except the value for carbon disulfide, as calculated by

<sup>1</sup> Tyrer, *J. Chem. Soc.*, 105, 2534 (1914).

<sup>2</sup> Young, *Sc. Proc. Roy. Soc. Dub.*, 12, 374 (1910).

<sup>3</sup> Hannay and Hogarth, *Proc. Roy. Soc.*, 32, 294 (1882).

Equation 5, which should be much higher to correspond to the others). Since we are interested primarily in relative and not in absolute values of internal pressure, in order to apply our theory for the deviations from Raoult's law, it suffices to determine the position of a liquid in the table

TABLE II.  
Relative Internal Pressures at 20°.

Substance.	$\gamma$ .	$t_b$	$a \cdot 10^4$ .	$V$ .	$\gamma/\sqrt{V}$ .	$\frac{5200 + 30t_b}{V}$ .	$\frac{a}{V^2} \cdot 10^6$ .
Olein.....	34.4	...	...	994	1.60	...	...
Nickel carbonyl.....	14.59	43.2	548*	135	2.84	48.0	2.46
Octane.....	21.52	125	728	177	3.83	50.5	2.32
Decane.....	22.08	173	968	196.5	3.80	52.8	2.52
Hexane.....	19.25	69	493	130.5	3.80	55.6	2.90
Ethyl ether.....	17.1	34.6	346	103.8	3.64	60.1	3.20
Silicon tetrachloride.....	16.65	59.6	...	114.5	3.42	61.0	...
Mesitylene.....	28.32	165	684	139.0	5.46	73.0	3.56
Stannic chloride.....	...	113	536	117.0	5.44	73.5	3.90
<i>m</i> -Xylene.....	28.07	139	605	123.0	5.64	76.2	4.00
Ethyl benzene.....	28.94	136	570	121.0	5.86	76.7	3.90
Carbon tetrachloride.....	26.56	76.5	389	96.6	5.78	77.5	4.16
Toluene.....	28.63	110.7	480	106.5	6.06	80.0	4.28
Fluorobenzene.....	27.96	85	397	93.8	6.18	82.0	4.52
Phosphorus trichloride.....	29.10	76	...	87.1	6.07	86.0	...
Chlorine.....	...	—33.6	118	50.2	...	84.0	4.60
Benzene.....	28.90	80	373	88.8	6.48	85.6	4.72
Chloroform.....	26.76	61	293	80.4	6.20	87.5	4.54
Ethyl iodide.....	29.08	72	283*	80.7	6.74	91.3	4.35
Chlorobenzene.....	32.90	132	507	101.8	7.05	90.2	4.88
Bromobenzene.....	35	156	569	105.0	7.5	94.1	5.16
Naphthalene.....	...	218	792	123 <sup>1</sup>	...	95.5	5.16
Iodobenzene.....	37.42	188.5	659	112.2	7.80	96.8	5.24
Ethylene chloride.....	32.11	83.7	337	78.8	7.50	97.8	5.44
Thiophene.....	32	84	(413)	79.0	7.5	97.7	(6.62)
			357*				5.72
Phenanthrene.....	...	340	1410*	158 <sup>2</sup>	...	98.0	5.7
<i>p</i> -Dibromobenzene.....	39.0	219	860*	120	7.9	98	6.0
Ethylene-bromide.....	38.36	129	(279)	83.2	8.7	106	(3.9)
			408*				5.5
Phosphoroutribromide.....	...	172	...	95.5	...	108	...
Carbondisulfide.....	34.5	46	220	60.2	8.7	109	6.1
Bromoform.....	...	151	497*	86.6	...	112	6.6
Sulfurmonochloride.....	42.95	138	548*	80.5	9.95	116	8.5
Bromine.....	39	59	191*	51.3	10.5	136	7.3
Iodine.....	...	184	310*	60 <sup>3</sup>	...	180	8.6
Phosphorus.....	51.1	287	659	69.5 <sup>4</sup>	12.4	199	13.7

\*Calculated by the method of van Laar, *Lec. cit.*

<sup>1</sup> Extrapolated from data by Lossen and Zander, *Ann.*, **225**, 111 (1884).

<sup>2</sup> Extrapolated from data by Schiff, *Ibid.*, **223**, 247 (1884).

<sup>3</sup> Extrapolated from data by Billet, *Weim. Inst., France*, **1855**, 292.

<sup>4</sup> Abegg-Auerbach, *Handbuch d. anorg. Chem.*, **5**, p. 373.

arranged in the order of increasing internal pressures. This has been done in the preceding table, where, for the sake of simplicity, the numerical coefficients of the formulas have been omitted, also the values calculated by Formulas 5 and 7, since the other values are sufficient and more reliable. Values of  $\gamma/V^{1/2}$ , Formula 1, have been included, taking the values for  $\gamma$  from the extensive summary by Harkins, Davis and Clark.<sup>1</sup> Values of  $a$  and  $V$  have in general been calculated from data in *Landolt u. Börnstein Tabellen*, except as noted.

The parallelism between the values in the last 3 columns is quite satisfactory, as it is only occasionally that a difference of more than one or two places is indicated by the different values. In several cases the value of  $a/V^2$  calculated by the method of van Laar corresponds more closely with the position according to other methods than does the one obtained from critical data, which may be considered as evidence of inaccuracy of the latter. It may be remarked that a very decided difference in internal pressure is required to produce any considerable deviation from Raoult's law.

(g) **Relative Internal Pressures at  $-203^\circ$  C.**—A table similar to Table II may be calculated for the difficultly liquefiable gases, since data are available for some of the more important ones. Table III gives the values obtained for nitrogen, carbon monoxide, argon, and oxygen at  $-203^\circ$ .

It was found by the graphic method previously described that the following expression gives the heat of vaporization at constant volume at this temperature:

$$L - RT = -1190 + 26T_b.$$

TABLE III.  
Relative Internal Pressure at  $-203^\circ$ .

Substance.	$\gamma$ .	$a \cdot 10^4$ , <sup>2</sup>	$V$ , <sup>1</sup>	$a \cdot 10^4$ , <sup>4</sup>	$\gamma/V^{1/2}$ .	$\frac{L-RT}{V}$ .	$\frac{a}{V^2} \cdot 10^6$ .	$\frac{1}{V} \left( \frac{1}{\alpha} + 140 \right)$ .	
Nitrogen.....	10.53	77.3	27	33.35	5600	3.28	24.2	2.43	10.2
Carbon monoxide	12.84	83	28	33.05	4910	4.00	29.4	2.62	10.4
Argon.....	13.63	87.0° A.	26	26.3	4500	4.59	40.7	3.90	13.8
Oxygen.....	18.35	90.2	27	25.8	3850	6.22	44.6	4.10	15.5

It will be noted that, just as in Table II, there is excellent parallelism between the values in the last four columns obtained by as many independent methods.

### 3. Use of the Table of Relative Internal Pressures.

(a) **Solubility Predictions, Solids.**—The previous papers have discussed the use of the table so far as concerns the substances already in it. The

<sup>1</sup> Harkins, Davis and Clark, *THIS JOURNAL*, **39**, 541 (1917).

<sup>2</sup> Baly and Donnan, *Trans. Chem. Soc.*, **81**, 907 (1902).

<sup>3</sup> Cf. values in *Landolt-Börnstein Tabellen*.

<sup>4</sup> Calculated from Baly and Donnan, *Loc. cit.*

consideration of new substances requires, first, a knowledge of the molecular volume. Where the substance exists in the liquid state this is easily calculated from the molecular weight and the density. When the substance is a gas or a solid at ordinary temperatures its volume as a liquid must be gotten either by extrapolating from its density in the liquid state or by determining its solution volume, preferably in a liquid which would dissolve it obeying Raoult's law. To be very accurate this would, of course, involve one or two successive approximations.

In addition to the molecular volume of the liquid at 20° we must know also either (a) the surface tension at 20°, (b) the boiling point, or (c) the value of the van der Waals *a*. Where the last is not known from determinations of the critical pressure and temperature it may usually be calculated quite satisfactorily by the method of van Laar explained above.

As examples let us see how successfully we could have predicted the relative solubilities of some of the solids given in the second paper of this series, here reproduced in Table IV.

TABLE IV.  
Solubilities in terms of mol fraction.

Solvent.	<i>p</i> -Dibromobenzene, 25°.	Phenanthrene, 25°.	Triphenylmethane, 20°.
Hexane.....	0.086	0.042	0.030
Ether.....	0.183	0.151	...
Carbon tetrachloride.....	0.193	0.186	...
Benzene.....	0.217	0.207	...
Chloroform.....	...	...	0.258
Carbon disulfide.....	0.224	0.255	0.191
Calc. from Raoult's law.....	0.248	0.221	0.229

Consider first the solubilities of *p*-dibromobenzene. To find the position of this substance in the table, and hence the solvents which would dissolve it giving solutions obeying Raoult's law, we must know its molecular volume in the (supercooled) liquid state, the melting point being 89.3°. Schiff<sup>1</sup> gives an expression for the density of the liquid as follows:

$$d^t = 1.8408 - 0.0009696(t - 89.3) - 0.0002023(t - 89.6)^2.$$

The decimal point in the last coefficient is evidently a misprint, as it leads to absurd results. The coefficient is doubtless either 0.00002023 or 0.000002023, leading to a density at 20° of 1.916 or 1.909, respectively, and a molecular volume of 123 cc. or 124 cc., respectively. Tyrer<sup>2</sup> gives the solution volume per gram at 25° as 0.513 in carbon disulfide, 0.514 in benzene, and 0.506 in chloroform. From these figures we may calculate the molecular volume at 25° to be about 121 cc., which would become about 116 cc. at 20°. We will select 120 cc. as the mean of these two values. The surface tension given in the table is extrapolated from that

<sup>1</sup> Schiff, *Ann.*, 223, 263 (1884).

<sup>2</sup> Tyrer, *J. Chem. Soc.*, 97, 2620 (1910).



measured above its melting point. The value of  $a$  has been calculated by van Laar's method, which gives  $a \cdot 10^4 = (6 \times 1.55 + 4 \times 1.6 + 2 \times 6.9)^2 = 860$ . Substituting in our formulas we get values in all 3 cases which agree closely in placing *p*-dibromobenzene close to and a little above carbon disulfide in the table. Its solubility in carbon disulfide should therefore be very close to that calculated from Raoult's law by the aid of the melting point and heat of fusion. Its solubility in liquids higher up in the table should be progressively less. We see that this is the case.

With phenanthrene we have likewise solution volumes from the measurements of Tyrer,<sup>1</sup> from which we may calculate  $V = 158$  cc. An expression for the density of the liquid given by Schiff,<sup>2</sup>  $1.06305 - 0.0005(t - 100.5)$ , gives a closely agreeing value, 160 cc. Although we do not possess measurements of the surface tension, both the boiling point and the value of  $a$  calculated by van Laar's method agree in placing phenanthrene just above *p*-dibromobenzene, so that a similar decrease in solubility is noted as we go to solvents further up the table.

Triphenyl-methane has a molecular solution volume in benzene and in chloroform, according to Tyrer, of 264 cc. at 25°, which we may call approximately 260 cc. at 20°. From this, together with the values  $\gamma = 44.7$ ,<sup>3</sup>  $t_b = 360$ ,  $a = 2850 \times 10^{-4}$ , (calculated) we calculate the following values:  $\gamma/V^{1/2} = 7.1$ ;  $(5200 + 30t_b)/V_{20} = 64$ ;  $a/V^2 \times 10^5 = 4.6$ . Although these figures do not agree very closely as to the position of liquid triphenyl-methane in the table, they indicate that it belongs in the general region of carbon tetrachloride, benzene and chloroform. As is to be expected from this, we find that its solubility is much greater in chloroform than in carbon disulfide or in hexane.

(b) **Solubility Predictions, Liquids.**—It requires a great difference in internal pressures to cause two nonpolar liquids to become incompletely miscible, but the internal pressure of phosphorus is so high that this is possible with all of the liquids at the top of the table. Molten phosphorus forms two liquid phases with carbon tetrachloride and benzene, while with carbon disulfide it is completely miscible at ordinary temperatures. (Molten phosphorus can be greatly supercooled.) It is to be expected that, except as relative internal pressures may be altered by changing temperature, there will be a progressive rise in the critical temperatures of mixing of molten phosphorus with another liquid as we ascend the table. Data upon this are now being obtained.

(c) **Solubility of Gases.**—It will be noted that the values expressing relative internal pressures of the gases given in Table III are not far from the values for the liquids at the top of Table II, although Table III is

<sup>1</sup> Tyrer, *J. Chem. Soc.*, 97, 2620 (1910).

<sup>2</sup> Schiff, *Loc. cit.*

<sup>3</sup> Harkins, Davies and Clark, *Ibid.*

for  $-203^{\circ}$  and Table II is for  $20^{\circ}$ . Since the internal pressure decreases with the temperature, due to decrease in  $V$ , the liquids nitrogen, oxygen, etc., could they exist at  $20^{\circ}$ , would undoubtedly have very low internal pressures. Hence the substances in Table III properly belong at the top of Table II, and should be much less soluble than corresponds to Raoult's law in all the liquids in Table II, and should, moreover, dissolve most readily in those liquids at the top of Table II. That this is true, so far as existing data are concerned, is seen by reference to the table of gas solubilities given in the first paper of this series.

It is obvious, further, that the solubility of oxygen should be considerably greater than that of nitrogen in all the solvents in Table II, not only because of its higher boiling point, but also because of its higher internal pressure.

During the war there was some discussion of the possibility of finding a good solvent for carbon monoxide. It is here seen that the best solvents for this gas should be the liquids at the top of Table II, but even in these it should dissolve to a smaller extent than Raoult's law would indicate, and on account of its low boiling point Raoult's law leads us to expect at best but low solubility. The only hope of finding a high solubility would lie in the direction of negative deviation from Raoult's law caused by a solvent with which it would unite reversibly to form a compound in solution.

(d) **Distillation of Liquid Mixtures.**—The results obtained in the distillation of liquid mixtures may be related to the partial vapor pressures of the components, and accurately predicted in cases where Raoult's law holds. By adding the possibility of predicting approximately the extent of any deviation from this law we are enabled to get a general idea of what to expect in any case.

Suppose, for example, it were a question of the separation of nitrogen from argon, Table III would lead us to expect a smaller deviation from Raoult's law with this mixture than occurs with mixtures of nitrogen and oxygen, which have been fully investigated.<sup>1</sup>

Again, bromoform and mesitylene, though not differing much in boiling point ( $151^{\circ}$  and  $165^{\circ}$ , respectively) should give vapor pressures enough greater than Raoult's law, on account of their very different internal pressures, to give a vapor-pressure curve with a maximum, hence a boiling-point curve with a minimum, which would prevent their separation by fractional distillation.

(e) **Molecular Weights and "Association."**—In most determinations of molecular weight with nonpolar substances the figures would indicate an

<sup>1</sup> Inglis, *Proc. Phys. Soc.*, 20, 640 (1906). Since writing the above the author has discovered measurements of the system argon-nitrogen by Holt and Hamburger (*Z. physik. Chem.*, 91, 513 (1916)) which confirm this prediction.

increasing association as the concentration of the solute is increased. Investigators have in such cases often used different expressions for concentration in order to make the molecular weight appear as nearly constant as possible. There has been much discussion as to whether the concentration should be expressed in terms of weight of solute per unit volume or per unit weight of solvent, or per unit volume or per unit weight of solution. The question can be decided in the light of the theory that Raoult's law holds for liquids for equal internal pressure. Accordingly, in determining molecular weights that solvent should be chosen which will have approximately the same internal pressure and polarity as the solute, and the concentration should be expressed in terms of mol-fraction.

We may illustrate by using determinations by Beckman of the rise in boiling point of carbon disulfide, using as solutes naphthalene<sup>1</sup> and phosphorus.<sup>2</sup> Table V gives part of the original data, together with values of the mol-fraction of solute  $N$ , and the quotient of this into the rise in boiling point, which is the "molecular rise" and can be calculated from the heat of vaporization of the solvent. The values of the latter given in the literature are as follows: 6670,<sup>3</sup> 6420,<sup>4</sup> 6380,<sup>5</sup> 6600.<sup>6</sup> The mean of these is 6520, whence  $RT^2/L = 30.8$ .

TABLE V.

G. CS <sub>2</sub> .	G. solute.	Rise in b. p. $\Delta t$ .	Mol fraction, solute, $N$ .	$\Delta t/N$ .	
				30.8	calculated
49.65	3.746	1.293	0.0438	29.5	} solute
49.65	6.719	2.268	0.0762	29.8	
54.65	3.129	0.980	0.0339	28.8	} solute
54.65	6.523	1.810	0.0681	26.6	
49.75	9.349	2.630	0.1032	25.4	

It will be noted that the rise in the boiling point with naphthalene solutions is but slightly less than that calculated from Raoult's law, whereas with phosphorus it is considerably less for similar concentrations. This is exactly what follows from the table of relative internal pressures. Naphthalene and carbon disulfide are not very different in internal pressure, hence the lowering of vapor pressure or the rise in the boiling point of carbon disulfide when naphthalene is dissolved should be a little less than that calculated by the aid of Raoult's law. With carbon disulfide and phosphorus, however, the difference in internal pressure is much greater, hence the lowering of vapor pressure or the rise in boiling point is found to be considerably less than Raoult's law would lead us to expect.

<sup>1</sup> *Z. physik. Chem.*, 6, 437 (1890).

<sup>2</sup> *Ibid.*, 5, 76 (1890).

<sup>3</sup> Regnault, *Mem. Acad.*, 26, 1, 262 (1862).

<sup>4</sup> Winkelmann, *Ann. d. Physik*, 9, 208, 358 (1880).

<sup>5</sup> Wirtz, *Ibid.*, 40, 446 (1890).

<sup>6</sup> Andrews, *Pogg. Ann.*, 75, 501 (1848).

It is therefore desirable, in determining molecular weights, as well as in determining the "molecular rise," to select solvents having internal pressures approximating those of the solutes. Thus, in the light of the previous discussion concerning the solubilities of *p*-dibromobenzene and triphenyl methane, it is evident that the former would give the normal figure for molecular weight in benzene more closely than in carbon disulfide, whereas with the latter the reverse would be true.

Considerations of this sort may prove very important in such questions as the distinction between  $S_6$  and  $S_8$  for the molecular weight of sulfur, and in work such as that of Gomberg on the trivalent carbon compounds.

It may be well to direct attention to an error easily made in this connection. The vapor pressures of the components of a mixture are related by the Duhem equation  $N_1 d \ln p_1 + N_2 d \ln p_2 = 0$ , which shows that when the vapor pressure of one component deviates from Raoult's law that of the other will deviate in the same direction. Accordingly, a polar solvent, which we may legitimately regard as associated, will give a smaller boiling or freezing point change with a normal solute than Raoult's law would indicate, causing a high figure, and apparent association, for the molecular weight of the solute. Such a conclusion is, however, quite unjustifiable, since, if the roles of solvent and solute are reversed, the other component would appear to be associated. For example, J. H. Mathews<sup>1</sup> has concluded that anthracene is associated in solution in fused cinnamic acid. Since, however, the latter is a far more polar substance, it, and not the anthracene, is to be regarded as associated, and hence the cause of the deviation from the normal freezing point lowering.

Similarly, Dolezalek<sup>2</sup> has assumed that the deviation from Raoult's law shown by mixtures of benzene and carbon tetrachloride is caused by partial association of carbon tetrachloride. There is, however, more reason to regard the benzene as the slightly associated liquid, so that the assumption is hardly justifiable. The theory here advanced would rather indicate that the difference in internal pressures is responsible for the deviation rather than any difference in polarity. Similar objections apply, of course, to the explanation used by the writer to account for abnormal behavior of various amalgams.<sup>3</sup>

(f) **Deviations from the Mass Law.**—Since it is possible to predict when Raoult's law will hold, it is also possible to predict when the mass law will hold for concentrated solutions. The mass law is usually derived for substance in solution by the use of van't Hoff's law for osmotic pressure. This we know to fail at higher concentrations, so that the mass

<sup>1</sup> Mathews, *THIS JOURNAL*, 39, 1125 (1917).

<sup>2</sup> Dolezalek, *Z. physik. Chem.*, 64, 727 (1908).

<sup>3</sup> Hildebrand, *THIS JOURNAL*, 35, 501 (1913); Eastman and Hildebrand, *Ibid.*, 36, 2020 (1914); 37, 2452 (1915).

law derived from it must also be inexact. However, derived from Raoult's law, which teaches us to express active mass or concentration in terms of mol-fraction, we can predict that it will hold *at all concentrations* for substances having approximately equal internal pressure, and, moreover, we can predict the direction of the deviation where this is not the case by determining by the aid of differences in internal pressures the relative deviations from Raoult's law.

(g) **Partition Coefficients.**—The table enables us to state that in the partition of such a substance as iodine between water and carbon disulfide, there will be for a given concentration in the water layer more iodine in the carbon disulfide than there would be in carbon tetrachloride, in partition between it and water. Illustrations might be multiplied indefinitely.

(h) **Recrystallization.**—In purifying substances by crystallizing from hot solution it is desirable to use a solvent in which the substance is not very soluble at ordinary temperatures, but in which its solubility increases as rapidly as possible with the temperature. It is well, also, to choose a solvent in which the impurities which may be present will be as soluble as possible at the lower temperatures. When the substance to be purified has a low melting point it will be very soluble in liquids having a similar internal pressure and polarity, hence it is better to select a solvent different from the solute in one or the other of these factors, so as to produce a smaller solubility. This has the additional advantage of giving a larger temperature coefficient of solubility, for Raoult's law is almost invariably approached more closely at higher temperatures than at lower. For example, a paraffin of melting point below  $100^{\circ}$  would be most soluble (in terms of mol-fraction) in liquids like hexane, silicon tetrachloride and mesitylene, and its solubility being already a maximum, so far as the choice of solvent is concerned, would not increase so rapidly with temperature as would its solubility in a liquid like carbon disulfide, its solutions with which would deviate considerably from Raoult's law on account of the difference in internal pressure; or in a liquid like alcohol where the deviation would be due to difference in polarity. Hence, in cooling from say  $50^{\circ}$  to  $20^{\circ}$ , a greater portion of the paraffin would separate from its solutions in carbon disulfide or alcohol than from a solution in hexane. Moreover, in this case the impurities present would likely be substances of higher internal pressure than the paraffin, such as unsaturated bodies, which would remain in the mother liquor more readily, if the solvent were one of higher internal pressure or polarity.

Where a substance of high melting point, such as anthracene, is being recrystallized, it may be desirable to use a solvent of similar internal pressure in order to secure larger solubility than would be possible in a liquid of very different internal pressure or of high polarity.

In future papers it is planned to discuss the absolute magnitude of

internal pressure in the hope of making possible the calculation of the absolute deviation from Raoult's law. Additional solubility data are to be obtained, and the internal pressures of metals are to be examined, so as to make possible the treatment of such quantities as the e. m. f. of amalgam concentration cells, and freezing-point diagrams.

#### Summary.

Various independent methods for calculating internal pressures of liquids are reviewed, and though the values they yield differ considerably, they are seen to be closely parallel. Pending a theoretical critique of the subject tables of relative internal pressures of relatively nonpolar substances are given for the sake of their practical value.

Other substances may be placed with reference to those already given by knowing their densities (as pure liquids or in solution), together with either surface tension; boiling point; the constant  $a$  in the van der Waals equation (which may be calculated from critical data or from the atomic values given by van Laar); the coefficient of expansion; or this last, together with the compressibility.

The use of these values is discussed in connection with predictions concerning the solubilities of solids, liquids and gases; the distillation of liquid mixtures; molecular weights and "association;" deviations from the mass law; partition coefficients; and the choice of solvent in recrystallization.

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[JOINT CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA AND NEW HAMPSHIRE COLLEGE.]

### THE DETERMINATION OF CERIUM IN THE PRESENCE OF OTHER RARE EARTHS BY PRECIPITATION AS CERIC IODATE.

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Cerous iodate and the iodates of the other rare earth elements are soluble in the presence of nitric acid, although very difficultly soluble in water. Scandium iodate is soluble in nitric acid, but less easily so than the rare earth iodates. Thorium, zirconium, and ceric iodates are almost insoluble in nitric acid provided a considerable excess of iodate ion be present.

Meyer and Speter<sup>1</sup> have developed a method for the separation of thorium from the rare earth compounds by precipitation as thorium iodate, from a solution strongly acid with nitric acid. It is evident that for the success of this method for thorium any cerium present must be in the trivalent form.

<sup>1</sup> *Chem. Ztg.*, 34, 306 (1910).