hydrous cupric nitrate which was prepared by Guntz and Mason[1] and since there is always a large excess of copper present, it would seem reasonable to assume the presence of a layer of cuprous nitrate on the surface of the copper.

It may be added, in conclusion, that the results given here would lead one to doubt the existence of the compounds which have been stated to be formed by the action of nitrogen peroxide upon other metals.[2]

Summary.

1. Hydrated cuprous oxide has been prepared and its copper content found to confirm the formula $4Cu_2O.H_2O$.

2. It has been shown that copper nitroxyl, Cu_2NO_2, is not formed by the action of nitrogen peroxide on copper, but that the product is a mixture.

3. The presence of the nitrate radical is indicated and it is suggested that the reaction may be the formation of anhydrous cuprous nitrate on the surface of the copper.

SEATTLE, WASHINGTON.

SOLUBILITY VI.   THERMODYNAMIC RELATION BETWEEN SOLUBILITY AND INTERNAL PRESSURE.

By JOEL H. HILDEBRAND.

We are accustomed to attack problems involving molecular weights and equilibria in gaseous systems upon the basis of the laws expressing the behavior of the ideal gas.   In like manner do we attack the problems presented by solutions, including molecular weights, solubility, solvation and dissociation, upon the basis of some "law" supposed to express the behavior of the "ideal solution."   Van't Hoff's law for osmotic pressure has served so well for the derivation of useful relationships that its historical value and plausible analogy with the gas law have obscured its inadequacy for dealing with all but very dilute solutions.   Since we are always inclined to ascribe deviations from our ideal law to changes in molecular species, that is, to chemical changes, it is important that our ideal law be one which is obeyed by all systems in which chemical changes are absent, a criterion by no means fulfilled by van't Hoff's law.

It has been pointed out that Raoult's law is obeyed by more solutions and through much wider ranges of concentration than van't Hoff's law[3] besides having a simpler kinetic basis.   There is, therefore, more justifica-

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[1] Guntz and Mason, *Bull. soc. chim.*, **5**, 1104; **7**, 313 (1909).

[2] Sabatier and Senderens, *loc. cit.*

[3] G. N. Lewis, THIS JOURNAL, **30**, 668 (1908); see also Hildebrand, *ibid*, **38**, 1453 (1917).

tion for considering that deviations from it are due to molecular changes. However, the theory of solubility and the evidence presented in the previous papers of this series[1] indicate that even Raoult's law is not obeyed by a great many solutions in which molecular changes are absent. It has been shown also that this condition exists when there is inequality of internal pressure of the liquids concerned. It is important to discover the exact form of the law expressing the relation between deviations from Raoult's law and differences in internal pressure, but before this is possible it is necessary to define internal pressure in terms having real significance, and set forth its theoretical relation to Raoult's law.

G. N. Lewis has defined an ideal solution as one which obeys Raoult's law at all temperatures and pressures, a limitation which is entirely reasonable in view of the fact that no temperature or pressure has any unique significance. (In order to investigate the vapor pressure of a solution under various pressures it would, of course, be necessary to apply pressure to the liquid phase by means of a piston permeable to the vapor only.) It follows from this definition and the ordinary laws of thermodynamics, as Lewis has shown, that the formation of such a solution from its component liquids will take place without changes in temperature or volume. There is abundant experimental evidence to show that this is true,[2] but since this important relation has never been published, and since it serves as the foundation for what is to follow, it is necessary to set it forth somewhat fully.

We will write Raoult's law in the form $f = f_0 N$, where f_0 is the fugacity[3] of one of the constituents of a binary mixture in the pure liquid state, f its fugacity from the solution, and N its mol-fraction. There is a similar equation for the other component, but since we intend to confine our attention largely to a single component it will not be necessary to use subscripts.

Now the change of fugacity of a pure liquid with temperature, keeping the liquid under constant pressure, is given by the equation

$$(\partial \ln f_0 / \partial T)_P = \Delta / HRT^2,[4]$$

where ΔH is the molecular heat of vaporization. Similarly, the change in fugacity of the same substance from the mixture is connected with the partial molal heat of vaporization; $\Delta \overline{H}$, by[5] the equation $(\partial \ln f / \partial T)_P =$

[1] Hildebrand, THIS JOURNAL, 38, 1452 (1916); 39, 2297 (1917); 41, 1067 (1919); Hildebrand and Jenks, *ibid.*, 42, 2180 (1920); Hildebrand and Buehrer, *ibid.*, 42, 2213 (1920).

[2] Cf. Hubbard, *Z. physik. Chem.*, 74, 217 (1910).

[3] G. N. Lewis, *Proc. Am. Acad. Arts Sci.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907). This quantity is identical with the vapor pressure when the vapor behaves as a perfect gas.

[4] G. N. Lewis, *loc. cit.*, for the equations in this paragraph and the next.

[5] This is the heat absorbed when one mol is evaporated from an infinitely large amount of the *solution*.

$\Delta \overline{H}/RT^2$, and since Raoult's law holds through a range of temperature, $\partial \, ln \, f_o = \partial \, ln \, f$, whence $\Delta H = \Delta \overline{H}$; from which it follows that the liquids mix without any heat effect.

When the fugacity is altered by altering the pressure at constant temperature we have the equations $(\partial \, ln \, f_o/\partial P)_T = V/RT;$ and $(\partial \, ln \, f/\partial P)_T = \overline{V}/RT;$[1] from which we see that, when Raoult's law holds, $V = \overline{V}$, which implies that there are no volume changes upon mixing.[2]

The relations just deduced render it highly probable that Raoult's law will be obeyed by any mixture which is formed without volume or heat change, and enable us to predict, at least in a general way, the sign and the magnitude of the deviation from Raoult's law from the sign and magnitude of the heat and volume changes. However, this is not of very great practical value, for it connects one property of a solution with 2 others without enabling us to make the vastly more useful prediction of the properties of the solution from the properties of its *pure component substances*. We will now proceed to show that the above relations can be made to yield a connection between the properties of the pure components and the likelihood that the system will obey Raoult's law.

If Raoult's law holds at all temperatures and pressures, it will also hold when the temperature and pressure are varied in such a way as to keep the volume of the liquid constant, so that $(\partial \, ln \, f/\partial T)_V = (\partial \, ln \, f_o/\partial T)_V$. The following mathematical identity relates the partial differential quantities previously mentioned:

$$(\partial \, ln \, f/\partial T)_V = (\partial \, lnf/\partial P)_T(\partial P/\partial T)_V + (\partial \, ln \, f/\partial T)_P;$$

and similarly, for the pure substance,

$$(\partial \, lnf_o/\partial \mathrm{T})_V = (\partial \, ln \, f_o/\partial P)_T(\partial P_o/\partial T)_V + (\partial \, ln \, f_o/\partial T)_P.$$

Now, when Raoult's law is obeyed, the corresponding terms involving the fugacity are equal for the solution and the pure substance, whence the remaining terms must also be equal, or $(\partial P/\partial T)_V = (\partial P_o/\partial T)_V$. This very significant relation shows that *the value of* $(\partial P/\partial T)_V$ *for a solution which obeys Raoult's law at all temperatures and pressures is independent of its composition, and, therefore, must be the same for the 2 components in the pure state.*

It does not follow that 2 liquids having the same $(\partial P/\partial T)_V$ will yield an ideal mixture, although the presumption is that they will when both are normal liquids which do not react with each other. In the accompanying figure are illustrated several possible types of mixture, so far as concerns the variation of $(\partial P/\partial T)_V$ with composition. Curve A corre-

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[1] The partial molal volume $\overline{V}$ is the increase in volume when one mol is added to an infinite amount of the solution. It is also given by the partial differential coefficient $(\partial V/\partial N)_{P,T}$.

[2] It can easily be shown that when the above relations hold for one component of binary mixture they hold also for the other.

sponds to the ideal solution. Curves B and C imply deviations from Raoult's law, even where the pure components have identical values of this quantity, as would be the case where the liquids are unequally polar, or where association or solvation exists. The system represented by Curve D would obey Raoult's law for one component and Henry's law for the other only in the range of composition for which the $\left(\frac{\partial P}{\partial T}\right)_V$ curve is horizontal. This case would doubtless be rather uncommon, and in a sense accidental. Curves E and F represent the probable behavior of normal liquids having different values of $(\partial P/\partial T)_V$, and where we may assume that the difference would determine, at least to a large extent, the magnitude of the deviation from Raoult's law.
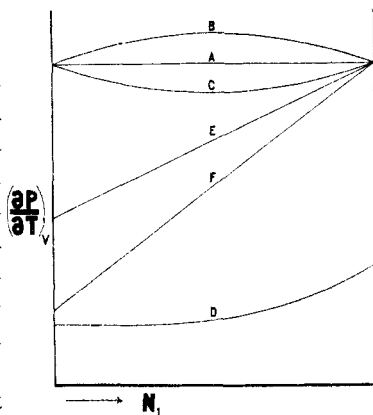

Fig. 1.—Curve types; relation between $(\partial P/\partial T)_v$ and composition of binary liquid mixtures.

The connection between this last statement and the exposition of the theory of solubility in the earlier papers of this series becomes evident if we note that $T(\partial P/\partial T)_V$ is a term in the thermodynamic equation of state, $P + (\partial E/\partial V)_T = T(\partial P/\partial T)_V$, where E denotes total energy. The terms of this equation have the dimensions of pressure, so that we may define "internal pressure" as $T(\partial P/\partial T)_V$, which is substantially equal to $(\partial E/\partial V)_T$, since P is small compared with the other members. There have been many papers written upon the subject of internal pressure in liquids, but almost none defining it in experimental terms. These discussions have almost invariably been dominated by the billiard-ball conception of molecules, with attractive forces different in nature from the repulsive forces and therefore capable of differentiation and separate measurement. Although we may speculate upon the pressure that the molecules of a liquid would exert if there were no attractive forces acting between them, it is impossible, since the forces of attraction and repulsion are of common electronic origin, to make such speculations serve as a basis for accurate calculations. On the other hand, by defining internal pressure by the aid of the above thermodynamic equation of state we introduce quantities which have not only great theoretical significance, but which are capable of accurate measurement.

It is not at all surprising to find that liquids having identical values for corresponding terms in the thermodynamic equation of state are also sufficiently alike to obey Raoult's law, provided that no molecular changes occur upon mixing. It may be added that if the equation of van der Waals applied accurately to the liquid state its terms, when written in

the form $P + a/V^2 = RT/(V—b)$, would correspond exactly to those of the thermodynamic equation, since upon differentiation with respect to temperature at constant volume, we get $(\partial P/\partial T)_V = R(V—b)$. The approximate validity of the van der Waals equation accounts for the fact that the values of a/V^2 calculated from it have been of considerable value in the treatment of the subject of solubility in the earlier papers of this series, particularly the third.

In order to determine the internal pressure of liquids, as here defined, we can avail ourselves of the relationship

$$(\partial P/\partial T)_V = —(\partial P/\partial V)_T \, (\partial V/\partial T)_P = \alpha/\beta,$$

where α, the coefficient of expansion, is $(\partial V/\partial T)_P/V$, and β, the compressibility, is $—(\partial V/\partial P)_T/V$. In the table are given illustrative values for the internal pressure, $T\alpha/\beta$, for a number of liquids.

INTERNAL PRESSURES IN MEGABARS AT 20°.

	$\alpha 10^6$.	$\beta 10^7$.	E_S.	$293\alpha/\beta$.	$270 E_S/V^{\frac{1}{3}}$.
iso-Hexane................	1445	1450	....	2920	....
Octane....................	1181	1167	48.4	2970	2330
Ethyl benzene.............	961	807	60.9	3490	3320
m-Xylene.................	994	789	59.5–67.8	3690	3320–3970
Carbon tetrachloride.......	1229	978	62.2–63.4	3690	3650–3730
Toluene...................	1099	842	62.1–65.9	3830	3540–3750
Chloroform...............	1276	963	59.7–66.3	3880	3730–4130
Benzene..................	1242	888	67.2–70.8	4100	4080–4300
Ethylene chloride..........	1172	773	73.0–73.3	4450	4600
Ethylene bromide..........	967	596	76.4	4760	4700
Bromine..................	1111	602	195.5(?)	5400	....

The values[1] of α have been taken from various sources. Since the data upon compressibility published by different observers are not always very concordant, and since relative rather than absolute values are here desired, we have restricted ourselves to data from a single reliable source, viz., from Richards[2] and co-workers. These observers, in common with most others, do not give compressibility as above defined, but, instead, the mean compressibility over a large pressure range. Since the compressibility varies considerably with the pressure it is necessary for our purpose to extrapolate their data to atmospheric pressure, at which the values of expansion have been measured. The pressure unit is the megabar.[3]

It may be noted that compressibility could doubtless be determined indirectly through measurements of $(\partial P/\partial T)_V$ and α more accurately than

[1] Thorpe, THIS JOURNAL, 37, 141, 225 (1880); 63, 273 (1893). Louguinine, Ann. chim. phys., [4] 11, 453 (1867); Pierre, ibid., [3] 20, 1, (1847); 21, 336 (1847); 33, 199 (1851); Pinette, Ann., 243, 32 (1888); Weger, ibid., 221, 67 (1883).

[2] Richards, Stull, Mathews and Speyers, THIS JOURNAL, 34, 971 (1912); Richards and Shipley, ibid., 38, 989 (1916).

[3] 1 megabar = 0.987 atmosphere = 10⁶ dynes.

by direct measurement, since pressure at constant volume can be measured with ease, and since, according to the work of Amagat, $(\partial P/\partial T)_V$ is constant or nearly so.

The order of the substances in the table is the same as that given by the criteria used in the third paper of this series, so that the previous discussions of relative solubilities remain valid in the light of the present definition of internal pressure. It may be of interest to show why the quantities L_V/V and $\gamma/V^{\frac{2}{3}}$, γ being the surface tension, may be expected to give essentially the correct arrangement of liquids in the table of internal pressures.

We have seen that, when P is small, the internal pressure of a liquid is also given by $(\partial E/\partial V)_T$. If, as seems probable, this quantity is approximately proportional inversely to some power of the volume, we may write

$$(\partial E/\partial V)_T = a/V^n.\text{[1]}$$

Now, if the liquid could be expanded isothermally until the volume of the saturated vapor v is reached, the energy absorbed would be the same as that absorbed in ordinary vaporization, L_V, so that

$$L_V = \int_V^v \frac{a}{V^n}\, dV = \frac{a}{1-n}\left(\frac{1}{v^{n-1}} - \frac{1}{V^{n-1}}\right).$$

If n is not much less than 2 the term involving v can be neglected, giving $L_V a\, V^{n-1}/(n-1)$, whence $a/V^n = (n-1)\,L_V/V = (\partial E/\partial V)_T$. This is dimensionally identical with the well-known Stefan relation for calculating internal pressure. W. C. McC. Lewis[2] has published essentially the same equation, i. e., $L_V/V = T\alpha/\beta$, but his derivation of it appears to be invalid, for there is no thermodynamic justification for replacing the heat of expansion, with which he begins, by the heat of vaporization, which he later inserts in its place. Dupré[3] has derived expressions for the limiting attraction between 2 layers as the distance separating them becomes zero, an attraction which has served very frequently as a theoretical definition of internal pressure, although of doubtful significance, since this attraction would go through a maximum and then fall off to zero as the layers approach each other. His expressions are essentially identical with the 2 terms in the preceding equation.

The relation of surface tension to internal pressure may be traced through the quantity L_V/V as follows. Let us take 1 mol. of liquid, having a volume, V, and break it up into n drops of equal radius, r. The volume of these drops will be $V = 4/3\pi r^3 n$, and their surface, $s = 4\pi r^2 n$. Elim-

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[1] In the van der Waals equation $n = 2$. The following discussion would also apply if we should use the more general expression $a/(V - c)^n$.

[2] W. C. McC. Lewis, *Phil. Mag.*, [6] 22, 268 (1911).

[3] Dupré, *Ann. chim. phys.*, [4] 2, 200 (1864); [4] 6, 283 (1865); cf. W. C. McC. Lewis, *Trans. Faraday Soc.*, 7, 94 (1911).

inating r we have $s = 4.84V^{2/3}n^{1/3}$. Let E_s denote the energy absorbed in the formation of 1 sq. cm. of surface, which is related to the surface tension by the thermodynamic equation $E_s = \gamma - Td\gamma/dT$. The energy absorbed in forming n drops from one would be $sE_s = 4.84V^{2/3}E_s$ $(n^{1/3} - 1)$. If the surface tension remained constant down to "drops" each containing but a single molecule, when n becomes $6.06.10^{23}$, the energy absorbed would equal the internal heat of vaporization, and we would have $L_V = 40.9V^{2/3} E_s$ joules. If, as is probably the case, the surface tension remains constant at least to drops containing 13 molecules, where, with hexagonal packing, one molecule would be completely shielded by those on the surface, we can calculate a lower limit for the value of L_V, obtaining $17.4 \ V^{2/3}E_s$. As a matter of fact, the heat of vaporization lies between the limits given and corresponds approximately to the expression $L_V = 25 \ V^{2/3}E_s$. We see, therefore, that $E_s/V^{1/3}$ is proportional to L_V/V, and hence, by the earlier discussion, proportional also to internal pressure.

In the earlier paper $\gamma/V^{1/3}$ was used instead of $E_s/V^{1/3}$. That this gave approximately the correct order of arrangement of liquids in the table of relative internal pressures is doubtless due to the fact that γ for the substances considered is roughly one-half of E_s.[1] Harkins[2] has pointed out that E_s should be more closely connected with internal pressure.

In the table are given values of E_s taken from the extensive tables of Harkins, Davies and Clark.[1] The figures for $d\gamma/dT$ obtained by different observers are often rather discordant, so that the calculated values for E_s often vary rather widely for the same substance, as shown in the table, where the extreme values are given. In the last column will be found figures for internal pressures in megabars given by the expression $270 \ E_s/V^{1/3}$. The numerical coefficient, although falling within the limits above determined, may be regarded as arbitrarily chosen so as to make the values of internal pressure agree with those given by the expression $293 \ \alpha/\beta$ in the preceding column. The agreement between the last 2 columns is as good as the inaccuracy in the experimental values of E_s could lead us to expect.

We may conclude, therefore, that for practical purposes, the methods used in the third paper for determining relative values of internal pressure may still be used in the light of the new definition of internal pressure here given, although the expression $E_s/V^{1/3}$ is to be preferred theoretically to $\gamma/V^{1/3}$.

The further development of the theory necessitates measurement of $(\partial P/\partial T)_V$ for both pure substances and solutions.

[1] Cf. Harkins, Davies and Clark, THIS JOURNAL, **39**, 555 (1917).

[2] Harkins, *Proc. Nat. Acad. Sci.*, **5**, 566 (1919).

Summary.

1. It has been shown thermodynamically that only such liquids as have identical values of $(\partial P/\partial T)_V$ are capable of yielding solutions obeying Raoult's law under all conditions, i. e., at all temperatures, pressures and compositions.

2. It is proposed to define internal pressure as $T(\partial P/\partial T)_V$, one of the terms of the thermodynamic equation of state.

3. Illustrative values are given for the internal pressures of certain liquids calculated in this way.

4. Since the internal pressure of a solution of non-polar liquids is probably a linear function of the composition expressed in terms of mol-fraction, it is probable that the difference between the internal pressures of the 2 pure liquids would determine, at least to a considerable extent, the deviation of the solution from Raoult's law. This is essentially the theory of solubility heretofore outlined and supported by abundant experimental data.

5. The criteria previously used for estimating relative values of internal pressure are shown to be in substantial accord with the thermodynamic definition of internal pressure here used, although it is theoretically preferable to use surface energy in place of surface tension.

BERKELEY, CAL.

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. I. THE REDUCTION OF NICKELOUS OXIDE.

BY GREGORY PAUL BAXTER AND LEON WOODMAN PARSONS.

Because of recent suggestions as to the constitution of the atoms, especially as to the existence of isotopes, comparisons of material from different sources have become especially important. Nickel in particular is interesting from this point of view. The following investigation upon the atomic weight of meteoric nickel was completed several years ago and a brief preliminary report has already been published.[1] A similar comparison had previously been made between terrestrial and meteoric iron,[2] and the 2 varieties of material were found to be identical within the limit of experimental error. As nickel is the metallic element second in abundance in iron meteorites, it was a natural choice for further

[1] *Carnegie Inst., Yearbook* 14, 350 (1915).

[2] Baxter and Thorvaldson, THIS JOURNAL, 33, 337 (1911); Z. anorg. Chem., 70, 348 (1911); Baxter and Hoover, Orig. Comm. Eighth Inter. Congr. Applied Chem., 2, 37 (1912); THIS JOURNAL. 34, 1657 (1912); Z. anorg. Chem., 80, 201 (1913).