

hydrogen. Spectrographic examination of samples of iridium from analysis showed that neither platinum nor lead was present in sufficient quantities to affect the determination. The iridium results tend to be low by a variable but usually small amount. One factor in this error is a slight solution of iridium by aqua regia. A modified procedure for the method is offered which combines the optimum conditions for speed and accuracy in the various details of manipulation.

A full report of this investigation including the actual experimental data will be found in a forthcoming publication of the Bureau of Standards.

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

SOLUBILITY. IX. METALLIC SOLUTIONS

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In a series of papers¹ appearing during the past seven years by the senior author and various collaborators considerable evidence has been presented to show that deviations from Raoult's law, and accompanying effects upon solubilities, can be predicted approximately for substances that are sufficiently non-polar, provided they do not tend to form compounds with each other. These deviations were correlated chiefly with differences in "internal pressure," as estimated by various criteria.

Metallic solutions offer a particularly inviting field for the application of a theory of solubility because a large amount of data is available and also because the metals differ among themselves in surface tension, compressibility, expansion, internal pressure and other characteristics far more than do the familiar non-metallic liquids, so that they offer a much more severe test of a theory than do most non-metallic solutions. For example, although but few non-metallic liquids, excluding water, are sufficiently unlike to yield two liquid phases, there are known no less than 47 metallic pairs which are incompletely miscible in the liquid state.

We do not have data upon the coefficients of compressibility and expansion for molten metals necessary for the calculation of their internal pressure by the expression² $T\alpha/\beta$, used in earlier papers, except for mercury, where the value is 13,200 megabars. This is several times as large as the values for the common non-metallic liquids, which explains, at least partly, their immiscibility with mercury. We may, perhaps, form a rough idea of the internal pressures of liquid metals from the values of α/β of their solid forms. Table I gives some figures of this sort taken

¹ Compare particularly THIS JOURNAL, 38, 1452 (1916); 39, 2301 (1917); 41, 1067 (1919); 42, 2180 (1920); 42, 2213 (1920); 43, 500 (1921); 43, 2172 (1921); 45, 682 (1923). *Phys. Rev.*, 21, 46 (1923).

² α is coefficient of expansion; β of compressibility.

from a paper by T. W. Richards.³ We may also note that the tensile strengths of the metals are in somewhat the same order, nickel, platinum, iron and copper, for example, having high tensile strengths, lead, sodium, bismuth, etc., low strengths.

TABLE I

RELATIVE INTERNAL PRESSURES OF SOLID METALS ESTIMATED FROM EXPANSION AND COMPRESSIBILITY

	$\alpha \times 10^8$	$\beta \times 10^8$	α/β		$\alpha \times 10^8$	$\beta \times 10^8$	α/β
Nickel.....	42	43	98	Mercury (liq.).....	180	395	46
Silicon.....	23	32	72	Lead.....	88	233	38
Platinum.....	27	38	71	Cadmium.....	74	210	35
Gold.....	43	64	67	Tin.....	67	190	35
Copper.....	50	75	67	Sodium.....	220	1560	14
Iron.....	36	60	60	Bismuth.....	40	300	12.5
Silver.....	57	101	56	Potassium.....	250	3170	7.9
Zinc.....	87	170	51	Cesium.....	330?	6100	5.4
Aluminum....	72	147	49				

The surface tension of molten metals may be expected to give a truer indication of the internal forces of the liquid than it does in the case of most compounds, because the molecules are simple and symmetrical and little or no orientation should take place in the surface. We may use the expression $\gamma/V^{1/3}$ or, where data are available, $E_\sigma/V^{1/3}$, where γ is the surface tension, V the molal volume and E_σ the surface energy. We have accurate measurements by Hogness⁴ for the surface tensions of mercury, bismuth, cadmium, lead, tin and zinc. Most values for the other metals are unsatisfactory and conflicting due partly, at least, to failure to prevent

TABLE II

RELATIVE INTERNAL PRESSURES OF METALS FROM SURFACE TENSIONS

	γ	t°	E_σ	$\gamma/V^{1/3}$	$E_\sigma/V^{1/3}$
Platinum.....	1819 ⁵	1800
Iron.....	950 ⁵	1600	...	490	...
Silver.....	782 ⁵	1000	...	348	...
Copper.....	581 ⁵	1100	...	294	...
Gold.....	612 ⁵	1070	...	282	...
Zinc.....	755	450	820	350	380
Cadmium.....	622	450	662	356	274
Mercury.....	393	350	580	157	232
Tin.....	514	450	572	198	222
Lead.....	438	450	494	163	182
Bismuth.....	367	450	413	133	150
Potassium.....	412 ⁴	62	...	114	...
Sodium.....	294 ⁴	90	...	92	...

³ Richards, *THIS JOURNAL*, **37**, 1643 (1915).

⁴ Hogness, *ibid.*, **43**, 1621 (1921).

⁵ Quincke, *Pogg. Ann.*, **135**, 642 (1868); **138**, 141 (1869).

⁶ Heydweiler, *Wied. Ann.*, **62**, 694 (1897).

the formation of an oxide film. Table II gives values for a number of the more important metals. On account of the difference in temperature the magnitude of $\gamma/V^{1/3}$ for the first five metals is much less than it would be if all of the metals in the table could be compared at the same temperature; accordingly, we are justified in concluding that their internal pressures would be found higher, at the same temperature, than those of the second group, zinc, bismuth, inclusive. It will be noted that the order is not very different from that given in Table I where, of course, crystal structure introduces disturbing factors.

The only other method applicable to the metals is the one using the heat of vaporization. Table III gives values of L/V , which again show approximately the same order, except that the most volatile, mercury and cadmium, are shifted considerably downwards. Table II, however, seems to be more closely correlated with our present knowledge of intermetallic systems.

TABLE III

RELATIVE INTERNAL PRESSURES OF METALS FROM HEATS OF VAPORIZATION

	L	V	t	L/V
Nickel.....	69,200	6.71	1450	10,300
Copper.....	66,900	7.56	1083	8,770
Iron.....	70,600	8.11	1530	8,700
Silver.....	61,800	11.3	961	5,500
Aluminum.....	52,500	11.2	658	4,560
Tin.....	66,200	16.9	232	3,920
Zinc.....	28,800	10.1	419	2,850
Lead.....	45,700	20.0	327	2,410
Thallium.....	39,600	17.2	302	2,300
Bismuth.....	42,200	20.8	269	2,030
Cadmium.....	25,000	14.1	321	1,770
Mercury.....	14,400	15.5	300	973

We will now proceed to examine the solubility data to determine how far the arrangement in these tables corresponds to the mutual solubilities of the metals. We must be prepared, of course, to find solubilities greater than internal pressure differences alone may lead us to expect, due to compound formation, even though the attractions between the compounds may be insufficient to cause the separation in the solid state of any recognizable compounds. If the electron theory were more highly developed with reference to liquid metals we would doubtless be more prepared than we now are to predict compound formation and its attendant effects upon solubility. There is great need of enlightenment regarding the nature of intermetallic compounds.⁸

We will first consider the group of metals, zinc, cadmium, mercury, tin, lead, bismuth, which according to Table II have internal pressures

⁷ Hildebrand, *THIS JOURNAL*, **41**, 1067 (1919).

⁸ However, compare Kraus, *ibid.*, **44**, 1216 (1922).

decreasing in that order. We have very accurate data by Taylor,⁹ concerning the activities, a , of these metals in a number of their liquid alloys, obtained by measuring e. m. f.'s of concentration cells. Taylor found that the pairs given below in Table IV give positive deviations from Raoult's law of the normal type. Writing Raoult's law as $a = N$, where N is the mole fraction, the deviation may be expressed by the value of $\log(a/N)$.

TABLE IV
ACTIVITY COEFFICIENTS IN VARIOUS ALLOYS

Alloy	t	—Log (a/N) for cadmium—		$\Delta(E_{\sigma}/V^{1/3})$
		$N_{Cd}=0.1$	$N_{Cd}=0.2$	
Cd-Sn	483	0.228	0.185	52
Cd-Pb	480	.455	.369	92
Cd-Zn	466	.560	.373	106
		—Log (a/N) for tin—		
		$N_{Sn}=0.1$	$N_{Sn}=0.2$	
Sn-Zn	466	0.460	0.274	158
Sn-Cd	463	.251	.185	52

The values of a/N for the three cadmium alloys are in the same order as the differences between the internal pressures of the components, using $E_{\sigma}/V^{1/3}$ to indicate the latter. It will be seen that the deviations are not, however, strictly proportional to these differences in internal-pressure. The same is true for the two tin alloys. Taylor also obtained results for cadmium-bismuth alloys. We might expect here to find a large deviation on account of their large internal-pressure difference. As a matter of fact, the deviation from Raoult's law is small, but of so irregular a type as to make its non-conformity to the internal-pressure theory not at all strange. The phenomena in this mixture are evidently rather complex.

Freezing point-composition diagrams are available which permit us to give the freezing-point lowering for a given solvent and a series of solutes at a fixed composition which, in the absence of "chemical" effects, should

TABLE V
SOLUBILITIES OF BISMUTH, ZINC AND TIN

Solvent	Bi at 250°	Zn at 375°	Sn at 180°
Zn.....	2 liq. ¹⁰	...	0.68 ¹⁰
Cd.....	0.905 ^{13,14}	0.896 ¹⁰	0.71 ^{10,13}
Hg.....	0.920 ¹¹	0.904 ¹¹	0.735 ¹²
Sn.....	0.933 ¹⁰	0.820 ¹⁰	...
Pb.....	0.948 ¹⁴	2 liq.	0.735 ¹³
Bi.....	...	2 liq.	0.76 ¹⁰

⁹ THIS JOURNAL, 45, 2865 (1923).

¹⁰ Heycock and Neville, *J. Chem. Soc.*, 71, 383 (1897).

¹¹ Puschin, *Z. anorg. Chem.*, 36, 201 (1903).

¹² Van Heteren, *ibid.*, 42, 129 (1904).

¹³ Stoffel, *ibid.*, 53, 137 (1907).

¹⁴ Kapp, *Dissertation, Königsberg, 1901.*

place the metals in the order of their internal pressures. It is always most striking to consider the series obtained for the substances of highest and lowest internal pressure, for then there is no ambiguity as to the true order as there is when an element in the middle of the series is chosen for comparison, and when deviations do not differentiate the element of higher internal pressure from the one of lower. Table V, accordingly, gives the solubilities of bismuth and zinc in the series of metals falling between them in Table II also those of tin, in the middle of the series, whose

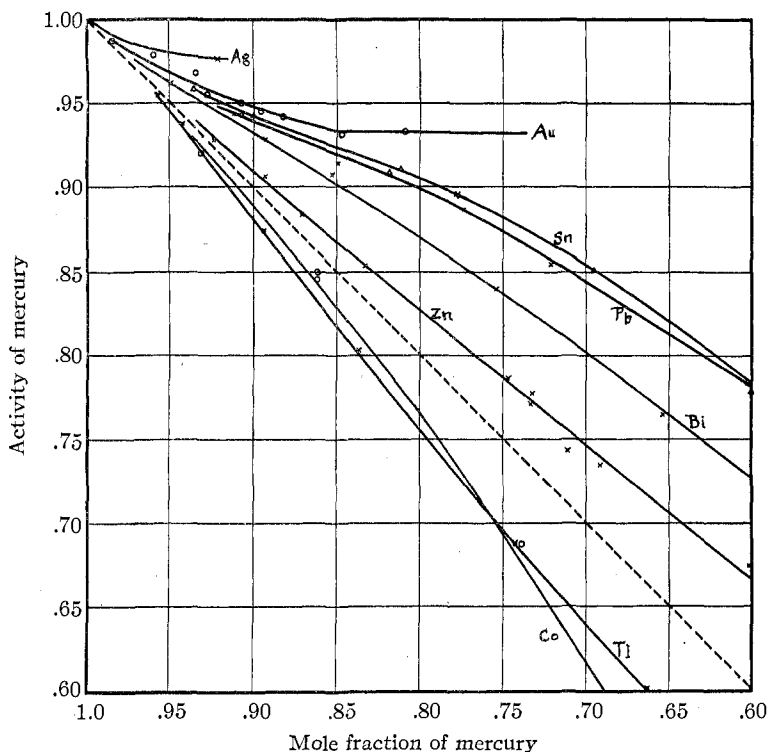


Fig. 1.—Activities of mercury in various amalgams

solubilities should show a maximum in the adjacent members. The figures were obtained from smooth curves drawn through the points given by the observers cited.

It will be seen that the agreement in the case of bismuth is perfect; for zinc it is nearly so, the positions of cadmium and mercury being reversed; for tin the only irregularity is its abnormally great solubility in bismuth, corresponding to the result found by Taylor, previously cited. Similar results are obtained with lead and cadmium.

The deviations of amalgams from ideality are shown by the vapor-pres-

sure measurements by the senior author and his collaborators,¹⁵ summarized in the plot of a against N shown in Fig. 1. We see here more irregularity than in the other cases. With cadmium there is negative deviation, showing that the atoms of these elements attract each other to a greater extent than they attract their own kind. With zinc the deviation is positive but, just as in Table V, less than we might have expected, which may indicate the same sort of effect that is shown more obviously with cadmium, its nearer neighbor in sub-group 2 of the Periodic System. Again bismuth, which is below tin and lead in Table II, shows a smaller deviation than lead and tin. In brief, mercury seems to show more evidence than we have previously seen of greater attractions for certain other elements than internal pressures alone would lead us to expect. Cases of this sort multiply greatly with other systems to be considered in the following paragraphs. It is interesting to note the great deviations with silver and gold, which will be found in harmony with the positions of these metals in a later and more extensive table.

The construction of a more general table of internal pressures of metals is made difficult by the lack of accurate data concerning their physical properties in the liquid state, by the inferior accuracy of much of the solubility data, and by the frequency with which solid solutions and compounds occur, the former making the freezing-point data of less significance for our purpose, and the latter introducing a factor with which the simple internal-pressure theory is incompetent to deal. The table we have attempted to construct is, therefore, somewhat approximate in character and subject to later modification as our knowledge of the field is extended. In its construction we have been guided by what knowledge we possess of the physical properties of the metals, by the freezing-point data in cases where simple eutectics occur, by the existence of two liquid phases in many cases, showing extreme mutual insolubility, by the existence of solid solutions of simple type showing great similarity between the components, and by the Periodic System, which we have assumed to indicate the approximate positions of elements that belong to series already established. We have noted in general that internal pressure decreases from top to bottom of a group. Upon finding, for example, as in Table II, that internal pressures decrease from zinc to mercury, we feel justified in assuming that the internal pressure of magnesium is higher than that of zinc.

The evidence is so large in volume but so inconclusive in many of its individual items, that it does not seem worth while to attempt to present it in detail beyond what is shown in Table VI, itself. This table lists the

¹⁵ Zinc: Hildebrand, *Trans. Am. Electrochem. Soc.*, **22**, 319 (1923). Silver, gold, bismuth and thallium: Hildebrand and Eastman, *THIS JOURNAL*, **36**, 2020 (1914); **38**, 785 (1916). Cadmium, tin and lead: Hildebrand, Foster and Beebe, *ibid.*, **42**, 545 (1920).

cases in which binary alloys show either two liquid phases or solid solutions, and omits the compounds, which introduce complications rather than contradictions to the internal-pressure theory. The data have been derived from the usual sources, beginning with the Landolt-Börnstein "Tabellen."

TABLE VI
INTERNAL PRESSURE SERIES FOR LIQUID METALS^a
High ← Internal Pressure → Low

	C	Si	Cr	Mn	Fe	Co	Ni	Al	Cu	Mg	Ag	Au	Zn	Cd	Hg	Sn	Pb	Tl	Bi	Na	K	
C																						
Si												s	s				s	i	i	i		
Cr												i					i	i	i	i		
Mn					S	S	S					i						i	i	i		
Fe				S		S	S					i						i	i	i		
Co				S	S		S					i	s					i	i	i		
Ni				S	S	S						i	s					i	i	i		
Al			i												s	i		s	i	i	i	i
Cu			i	S	s		S							S					i	i	s	
Mg																						
Ag		s	i	i	i	i	i					S						s	s	i		i
Au		s		S	s	s			S		S									s		
Zn																						
Cd																						
Hg			i																			
Sn		s	i																			
Pb		i	i	i	i	i	i	i	i			s										
Tl		i		i		i	i	i			s	s	i									
Bi		i	i		i	i		i	s			i	s	s								
Na																						
K																						

^a The letters have the following significance: i, 2 liquid phases; S, complete solubility in the solid state; s, limited solubility in the solid state.

Each space in Table VI corresponds to the mixture of the two metals whose symbols are at the left-hand side and at the top, respectively. The diagonal is drawn through the intersection of each symbol with itself, so that the nearer a space is to this diagonal the closer are the two metals to each other in internal pressure. The portions of the table on the two sides of the diagonal are, of course, essentially identical, but the presence of both will be found convenient. Those combinations which yield two liquid phases are denoted by "i" (insoluble), those which yield a complete series of solid solutions by "S," and those showing limited solubility in the solid state are denoted by "s." Where the system has not been investigated, or where compounds have been found, the space has been left blank, so as not to complicate the table.

We must recall, first of all, that the internal-pressure theory cannot predict tendencies towards the formation of compounds, or abnormally great attractions between the atoms of unlike metals, so that negative deviations from Raoult's law, or even abnormally small positive deviations or, in other words, abnormally great solubilities, are not contradictory to the theory. All that can be expected is that insolubility cannot occur unless

there is sufficient difference in internal pressure, although even then it may not occur if tendency towards compound formation exists. Let us now examine the table with this in mind. It will be seen that there are no i's within a certain distance of the heavy diagonal, denoted by the dotted lines, indicating that there are no cases of insolubility in the liquid state among the metals adjacent to each other. A separation of at least five places is necessary. This may not seem very great, but reference to Table II will show that it corresponds to about 100% difference in internal pressure, almost as great as the entire difference from top to bottom of the table in our third paper¹⁶ for non-metallic liquids. There would undoubtedly be found still more insoluble pairs if it were not for differences in boiling point, as between mercury and iron, which make it difficult or impossible to investigate the system. Even in such cases, however, the table is significant with regard to other phenomena, such as wetting, which likewise requires sufficiently great attractive forces between the two metals concerned. It is well known, for example, that pure mercury will not wet iron.

Turning to the consideration of solubility in the solid phases as an indication of probable likeness in the internal pressures of the liquids, when compounds are not formed, we find that 21 cases of solid solution are found in the spaces between the dotted line and the heavy diagonal, the region in which insolubility in the liquid form is absent, while but 17 cases occur outside this region, although the possible combinations in the other two regions are 57 in the former and 153 in the latter. In other words, solid solutions are known to occur in 37% of the possible combinations among metals within five places of each other in the internal-pressure series, while they are known among but 11% of the possible combinations of metals more than four places removed. If we consider metals removed less than eight places from each other, as compared with those eight or more places removed, giving equal numbers of possibilities in the two groups, we find 42 instances of solid solution among the former group and only 6 among the latter.

Table VI will be found useful, therefore, in predicting and correlating (a) the solubilities of metals in the liquid, and to some extent in the solid state; (b) the relative freezing-point depressions and apparent molecular weights; (c) the ability of a molten metal to wet solid metal.

It is expected, also, that it will prove very significant in connection with another phenomenon now under investigation in this Laboratory, namely, the initial overvoltage required to start the deposition of one metal upon another.

Whenever it shall prove possible to predict the chemical combinations of metals with one another, this knowledge, together with Table VI, or a

¹⁶ THIS JOURNAL, 41, 1067 (1919).

perfected form of it, should make it possible to correlate completely all of the intermetallic systems.

Summary

1. Various means of estimating the relative internal pressures of metals are discussed and tables are given.
2. Data are given showing the correlation between these tables and the behavior of binary metallic solutions.

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EXTREMELY DRY LIQUIDS

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The very important discoveries of Baker¹ concerning the boiling points and other properties of highly desiccated liquids have opened a large and most promising field of physicochemical investigation. The startling results which have already been obtained have aroused some degree of skepticism, because of a suspicion that they were irreconcilable with fundamental thermodynamic principles; but I am convinced that no essential conflict exists, and that the chief observations which have so far been made not only may be interpreted thermodynamically, but also permit, with the aid of thermodynamics, some valuable predictions.

At first the experiments seemed to indicate that the removal of the smallest traces of water produced profound changes in the static properties of a liquid, such as might be explained by a large shift of inner equilibrium through the formation of a larger number of complex molecules from simple molecules. Smits² believes that such a change in equilibrium is thermodynamically possible and that it is in fact the explanation of the facts observed by Baker.

With this conclusion I can by no means agree. It is not absolutely prohibited by the laws of thermodynamics alone, but any one who will read the chapter on dilute solutions in the recent treatise on thermodynamics by Professor Randall and myself will see how little is required, besides the laws of thermodynamics, to prove Raoult's law for the infinitely dilute solution. For solutions of moderate concentration its approximate validity has been attested by hundreds of observations of the most varied sorts. The only marked exceptions occur when the solute dissociates, and then the activity of the solvent is diminished two, three, or more times as much as Raoult's law predicts, according as the solute molecule dissociates into two, three, or more molecules. Smits' hypothesis seems

¹ Baker, *Phil. Trans.*, 79A, 583 (1888); *J. Chem. Soc.*, 65, 611 (1893); 81, 400 (1902); 91, 1862 (1907); 101, 2339 (1912); 121, 568 (1922).

² Smits, *Proc. acad. Sci. Amsterdam*, 26, No. 3 (1923).