quantum and after an appreciable interval of time emits another, for it is known that a "collision of the second kind" may involve the atom before the interval is ended, and alter the character of the emitted quantum. This might be made the basis for the distinction between fluorescence and scattering.

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THE USE OF INTERNAL PRESSURE IN METALLIC SYSTEMS

SYSTEM LEAD-ANTIMONY COPPER

UNTIL recently the application of thermodynamic relationships to metallic systems has been almost wholly neglected. J. Johnston,[1] using a method similar to that proposed by Washburn[2] and Read, has shown that the eutectic composition and temperature can be calculated from the solubility curves, and conversely, knowing the eutectic temperature, the solubility can be calculated. In this work, ideal solutions are postulated, but many metallic solutions must closely approach this condition, so that the method should be valuable as a first approximation.

There are three properties of metals which are useful in predicting the miscibility of the liquid phase or even hazarding a guess as to the solid solubility. The most important of these is the internal pressure which is defined by Dupre,[3] as equal to $(-T\frac{\alpha}{\beta})$, where "T" is the absolute temperature, α the coefficient of expansion, and β the coefficient of compression. Liquids with like internal pressures should be more easily miscible than those with unlike. That this assumption is at least followed in substance is demonstrated by Hildebrand[4] with a correlation of existing data on the subject. He shows that those metals which form continuous series of solid solutions have very similar internal pressures, and that those metals which display a miscibility gap are separated in the table by a definite amount. The other two useful properties of the metal are the melting-points and heats of fusion.

The formation of compounds may have a greater effect than the properties named above. The extent of the effect of the compound formation depends on the stability of the compound. When it is stable in the liquid phase, it must be considered a new component with its own internal pressure, melting-point and heat of fusion. On the other hand, compounds which dissociate completely at or before their melting-point have little effect on the miscibility of the liquid phase, since the liquid phase is then composed of only the two original metallic atoms. However, the compound may have a decided bearing on what solid will separate under a given set of conditions. In addition to the melting-points and heats of fusion, the heat of formation of the compound must be taken into consideration. The shape of the liquidus and solidus surfaces depends on these principles. With the help of certain judiciously chosen freezing curves, the surfaces may be accurately known.

APPLICATION TO THE COPPER-LEAD ANTIMONY SYSTEM

In studying the ternary system of lead-antimony copper,[5] there is a good chance to demonstrate the effect of internal pressure in shaping the liquidus surface. In building this surface it is important to have the component binary liquidus lines in mind. In the system lead-antimony[6] no compounds are formed, and there is a solid solubility of antimony in lead as well as a reported solid solubility of lead in antimony.[7] The eutectic occurs at 12.5 per cent. antimony. From Table I it is seen that the internal pressures of lead and antimony are close together. The value for bismuth is shown in the table because it is the only metal other than antimony in the fifth group of the Periodic Table for which any values could be found. General trends in the Periodic Table indicate that internal pressure decreases in going from top to bottom in any group, which places the value for antimony in the vicinity of that for lead. From this consideration,

TABLE I

RELATIVE INTERNAL PRESSURES

Metal	From expansion and compression of solid metals*	Heat of vaporization*	Surface tension*	Boiling points	Viscosity at 1100° C.†
	α/β	L/V	γ/v^3	°C.	η
Cu	67	8850	581	2310	0.036
Ag	56	5500	782	1955	——
Pb	38	2410	444	1525	0.0105
Sb			317	1440	0.0082
Bi	12.5	2030	376	950	0.0065

* Hildebrand, *loc. cit.*, pp. 181–182.

† Bieneas and Sauerwald, *Z. anorg. Chem.*, 161: 51, 1927.

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[1] J. Johnston, *J. Phys. Chem.*, 29: 882, 1925.

[2] Washburn and Read, *Proc. Nat. Acad. Sci.*, 1: 191, 1915.

[3] Dupre, *Ann. chim. Phys.*, 2: 201, 1864.

[4] Joel Hildebrand, "Solubility," Am. Chem. Soc. Monograph, p. 102, 1924.

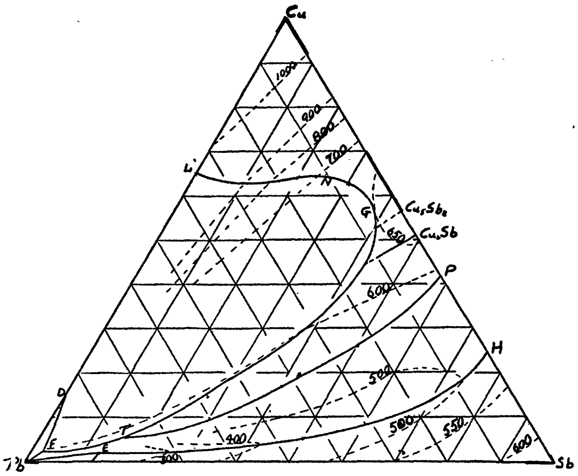
[5] R. A. Morgen, L. G. Swenson and F. C. Nix, Tech. Pub. 43, Am. Inst. Mining and Met. Eng., 1928.

[6] R. S. Dean, *J. Am. Chem. Soc.*, 45: 1683, 1923.

[7] Endo, Sci. Repts., Tohoku Imp. Univ. 14: 503, 1925.

complications in the liquid phase of the lead-antimony system are not to be expected. The internal pressures of copper and lead on the other hand are widely separated, and the effect of this wide difference is shown in the binary system.[8] There are no compounds formed so a miscibility gap appears. Between 15 per cent. and 65 per cent. copper by weight, there are two liquid phases. An eutectic between copper and lead appears at about 0.05 per cent. copper. Copper and antimony are just as widely separated in internal pressure values as copper and lead. However, the fact that a compound,[9] Cu_5Sb_2, forms, which is stable at its melting-point, changes the consideration. Two other compounds, Cu_3Sb and Cu_2Sb, are known in this system, but they are unstable at their melting-points and are formed by the decomposition of Cu_5Sb_2 on cooling. For this purpose, therefore, we shall consider the copper antimony system as divided into two parts, namely, copper-Cu_5Sb_2 and Cu_5Sb_2-antimony. The fact that solid solubility occurs at both ends of the system and that both copper and antimony dissolve in the Cu_5Sb_2 crystals indicates that the internal pressure of Cu_5Sb_2 is between that of antimony and copper.

With this information, it is now possible to see how the shape of the immiscibility gap in the ternary system copper-lead antimony checks with the theory. Since there is a break on the copper-lead side and none on the copper-antimony line, the curve of immiscibility must close on itself. Fig. 1 is a representation of the system reproduced from the paper of Morgen,[10] Swenson and Nix. The two liquid layer region found experimentally is bounded by the line DFTGL. Starting at D the boundary drops sharply towards F, which corresponds to about 2.5 per cent. antimony by weight. This is the amount of antimony which has solid solubility in lead, so that up to this amount in the liquid state, the antimony just acts to replace so much lead, probably approaching a perfect solution. The following generalization then seems to follow: Over the range where a solid solution separates, the liquid behaves like the pure solvent or approaches a perfect solution of the two constituents. From F to K the line is practically horizontal. This is the region in which lead is the primary crystal and so further addition of antimony, over 2.5 per cent., makes little difference in the ternary liquid mixture. K probably corresponds to the point at which lead and antimony are in the proportions in which they exist in the eutectic. From K to T the line starts to curve, but since in this region an antimony compound, Cu_2Sb, is the primary crystal, the effect of the low internal pressure of antimony is still noticeable, tending to extend the area of immiscibility. After the line PT is passed, the primary crystal is Cu_5Sb_2, and so this compound is the dominating factor, and the curve turns away from the antimony corner. The point G, the nearest approach to the copper-antimony line, is at 5 per cent. antimony. This corresponds to the solid solubility of lead in antimony and agrees with the generalization made previously. From G the curve returns sharply to the copper-lead axis. In this region the three substances to be considered are copper, Cu_5Sb_2, and the copper-lead mixture indicated by L. These three have effective internal pressures close enough together so that they are completely miscible in the liquid phase.



System Copper-Lead-Antimony

FIG. 1

CONCLUSIONS

A method has been suggested whereby the shape of miscibility gaps may be predicted.

A relation is pointed out between solid solution formation and an effect on the liquidus surface.

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DIMORPHISM IN THE DEVELOPMENTAL HISTORY OF THE SEX VEINS OF THE RABBIT

THE right sex vein of the adult male rabbit is described by Krause (1884)[1] as entering the vena cava inferior at the level of the fifth lumbar vertebra. The left sex vein of the adult male rabbit is described in the same account as entering the left renal vein. According to Krause, both sex veins of the adult female rabbit directly enter vena cava inferior

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[8] F. Friedrich, *Met. u. Erz.*, 10: 578, 1913.

[9] H. Reimann, *Z. Metallkunde*, 12: 321, 1921.

[10] *Loc. cit.*

[1] Krause, W., "Topographische Anatomie des Kaninchens," II Aufl., Leipzig, 1884.