Part III

Temperature Dependence of the Resistivity of Solid Solutions of Zinc, Gallium, Germanium, and Arsenic in Copper from 5° to 300° K.

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The resistivities of a series of alloys in the solid solution region of the copper-zinc, copper-gallium, copper-germanium, and copper-arsenic systems from 5° to 300° K. are presented.

THE TEMPERATURE DEPENDENCE, from 5° to 300° K., of the thermopowers of the copper based solid solutions with zinc, gallium, germanium, and arsenic as solutes has been reported (*1*, *2*). The temperature dependence of the resistivity of the alloys also was measured. The room temperature resistivities were useful in discussing the room temperature thermopower. The Grüneisen θ_R's, determined from the approximately linear portions of the resistivities curves, were useful in discussing the concentration dependence of the phonon-drag peak position. The resistivity data as such were not, however, presented, but will be published separately as they have intrinsic merit.

The agreement with earlier work (*4*) at room temperature is good. The present data extend, however, to considerably higher concentrations and over a range of temperature (Figure 1).

EXPERIMENTAL

The preparation of the alloys, the wire specimens, the apparatus, and the method of measurement have been described (*1*, *2*). Aside from the error in the form factor, the ratio of the area to the length, the accuracy of the measurements is at least ±1.0%. The error in the determination of the cross-sectional area introduces an error of up to ±1.0%. The results are not corrected for the volume change with temperature. The errors in the compositions of the alloys are believed to be not greater then 1% of the minor constituent.

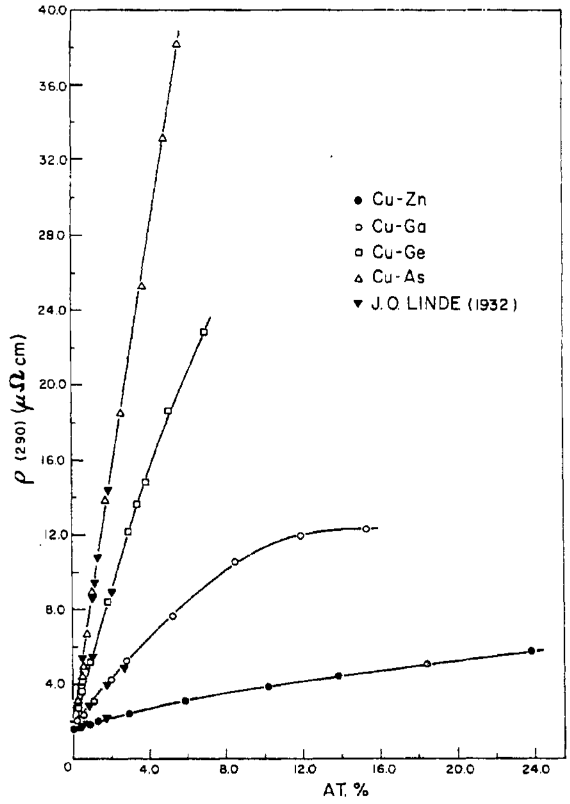

Figure 1. Concentration dependence of the restivities of the solid solutions of zinc, gallium, germanium, and arsenic in copper at 290° K.

The measurements were made at 5° intervals, plus or minus a few tenths of a degree. The data were interpolated

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linearly to 5° intervals and smoothed using a nine-point cubic over the whole range (*3*). The standard deviations from the curves are not greater then 0.005 microohm cm.

The results for the four systems are given in Tables I-IV (which have been deposited with ADI), and are shown at 290° K. in Figure 1.

LITERATURE CITED

(1) Crisp, R.S., Henry, W.G., Schroeder, P.A., *Phil. Mag.* **10,** 553 (1964).

(2) Henry, W.G., Schroeder, P.A., *Can. J. Phys.* **41,** 1076 (1963).

(3) Guest, P.G., "Numerical Methods of Curve Fitting," p. 358, Cambridge University Press, 1961.

(4) Linde, J.O., *Ann. Phys. Lpz.* **15,** 219 (1932).

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Ternary Systems of Sulfur and Sulfur Compounds

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New experimental observations are presented for 15 ternary systems of elemental sulfur, mostly near its melting point, 113° C.; 52 systems of sulfuric acid of various strengths including oleum and sulfur trioxide; 43 systems of methyl sulfate, 16 systems of ethyl sulfate, and ten systems of other sulfur compounds, a total of 102 (because 34 are in two categories). Sulfur was found completely unselective between any two hydrocarbons, even when liquid or in solution. The distortion of phase diagrams resulting from high reactivity of sulfuric acid or oleum with organic compounds was minimized by rapid observation and by dilution with alkyl sulfates or methanesulfuric acid. These reagents mix even with oleum, without evolution of appreciable amounts of heat, and so are probably true diluents. Yet a few systems show decided distortion because of the resulting quaternary systems. This is readily detected by the shapes. The unusual phase relations between sulfuric acid, sulfur trioxide, chlorosulfonic acid, hydrogen chloride, and water are shown in two graphs. Eleven systems of methyl sulfate and nine of ethyl sulfate, which do not have sulfuric acid as a component, contained usual features including isooptics, isopycnics, solutropes, and three liquid phases, but no island curves.

THIS is the seventh in a series of twelve papers presenting 1070 ternary systems mostly involving two liquid phases. Those involving sulfuric acid are necessarily approximate because of reaction. Means of minimizing the effects are presented.

SULFUR

Liquid sulfur was considered as a possible solvent for selective extraction of hydrocarbons since above the melting point, 113° C., it is miscible in all proportions with bicyclic hydrocarbons such as naphthalene, biphenyl, tetralin, 1- and 2-methylnaphthalene, and also with phenanthrene and fluorene (*1*). Its CST's with benzene, toluene, and *o*- and *p*-xylenes (*1*) are not excessively high; while the mutual miscibilities of sulfur with nonaromatic hydrocarbons are very low until it begins to react with them at about 135° C. Twenty-five ternary systems of sulfur have been published (mostly compiled in *8* pp. 187, 218), many of them involving an aromatic amine. Those with liquid ammonia (*5*; graphs 7, 29-33) show a deep purple color in the ammonia-rich layer. Two quaternary systems, with water, sulfur, hexane, and aniline or phenol (*12*) separate into four liquid layers at about 96° C.

Fifteen new ternary systems of elemental sulfur are presented in Figure 1, most of them at or near the melting point, so as to have two liquid phases. Systems were made up by weight with sulfur and a liquid not miscible with it near its melting point; and then titrated with the other component as shown in the graphs. Tie lines were observed by adjusting the compositions near 113° C. with substantial volumes of each liquid layer in equilibrium. The layers were separated and cooled to crystallize out the sulfur. The refractive indices from both layers and that of the original hydrocarbon mixture always agreed within 0.001. To the two layers of the systems of graphs 11 and 12, in which crystallization of naphthalene would prevent that procedure, a small addendum of naphthalene, added to the two liquid layers, was found to be distributed less than 5% to the sulfur layer.

In every case tried, all of the tie lines were found to be isologous, pointing directly toward the sulfur corner. This would indicate no selectivity for any hydrocarbon over another one. The proportions of the two hydrocarbons in the extract layer were the same as those of the same two hydrocarbons in the raffinate layer. A corollary is that the plait point in the graph is at the point of contact of the tangent to the binodal curve which passes through the sulfur corner. Thus in graph 11, which illustrates two systems including cetane and decane, respectively, both plait points are at 32% naphthalene and the apices of the curve are at 48% naphthalene.

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