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SELECTED THERMODYNAMIC VALUES AND PHASE DIAGRAMS FOR COPPER AND SOME OF ITS BINARY ALLOYS

Ralph Hultgren and Pramod D. Desai

February 1971

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SELECTED THERMODYNAMIC VALUES AND PHASE DIAGRAMS FOR COPPER AND SOME OF ITS BINARY ALLOYS

Sponsored by

The International Copper Research Association

and

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AEC Contract No. W-7405-eng-48

by

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INTRODUCTION

Selected values of the thermodynamic properties of copper and thirty-one of its binary alloys are presented.

Selections have been made by testing experimental data for self-consistency, consistency with known thermodynamic relationships, with the phase diagram, and with other measurements on the same system. Tables, with the exception of the vapor pressure of pure copper, are generally restricted to ranges of temperature and composition actually measured experimentally. Extrapolated values, when presented, are usually placed in parentheses. Melting points and other thermodynamic properties of pure elements wherever needed were taken from Hultgren, Orr, Anderson and Kelley (1963), Supplementary Sheets, with correction to the 1968 International Practical Temperature Scale.

PERSONNEL

This monograph is the result of the effort and cooperation of a large group of people who have been associated with the work. Most of the systems were the primary responsibility of one of the authors (PDD) who conducted the survey and evaluation for the systems under the guidance of the other author (RH). Substantial help was given by Donald T. Hawkins (DTH) and Stuart J. Nelson (SJN) in evaluating a few of the systems.

Initials of the primary evaluator and the date of evaluation are placed on the bottom of the first page of each system.

Each final evaluation was checked and reviewed by other senior members of the group before being accepted.

Mrs. Rebecca C. Palmer and Mrs. Carol Broussard were responsible for typing and layout, and Mrs. Gloria Pelatowski did the line drawings.

METHODS OF EVALUATION

In some cases the quality of the data can be judged by objective criteria. Thus if it is not clear that the sample has been correctly prepared and that both the initial and final states have been adequately charaterized, the estimates of uncertainty are increased, or the data are discarded. In other cases contradictory data are found in which a choice cannot be made on these grounds. In such cases weight is given to the evaluating experience with respect to the method used or to the laboratory in which the measurements were made. In all cases it is intended that all modern measurements be mentioned, and their agreement with selected values be described. Where a given work is mentioned as disagreeing with the selection, the reader should bear in mind that the work may be correct and the selection be wrong.

Heat Capacity Data

Usually, heat capacities (specific heats) are determined by measuring the temperature rise (of one or a few degrees only) caused by the addition of a measured quantity of heat to the specimen. The specimen is usually maintained in a vacuum where the principal source of heat

exchange with the surroundings is by radiation. The radiation heat exchange coefficient increases with T^3; heat exchange is a minor problem at low temperatures, becoming serious as the temperature increases.

In adiabatic calorimeters the attempt is made to keep the surroundings at the same temperature as the specimen during the heating. In isothermal (or isoperibol) calorimeters the surroundings are maintained at a constant temperature so that the heat exchange may be more readily calculated. Both types have upper limits of temperature application; it is extremely difficult to get good measurements above 1000°K. Less conventional methods show some promise of accurate measurements at high temperatures. For example, a sample may be heated to a high temperature in a few milliseconds by a large pulse of electricity. Amperes and voltage drops may be simultaneously recorded electronically, giving the energy input versus time. Temperatures may be deduced from the resistance of the sample or by other means. Heat exchange with the surroundings becomes small because of the small time of the experiment. In another method a sample may be maintained at a high temperature and further heated by a small pulse of current. Analysis of the heating effect gives the heat capacity.

The electronic contribution to heat capacity can be identified and measured only at very low temperatures, usually at the lower end of the liquid helium range, where it may constitute the principal

part of the total heat capacity. At very low temperatures the lattice heat capacity is proportional to T^3, so that

$$Cp = \beta T^3 + \gamma T$$

where γ is the electronic contribution coefficient. It may be found from a plot of Cp/T versus T^2; a straight line results at the lowest temperatures whose intercept at $T^2 = 0$ is γ and whose slope is β.

At very low temperatures, usually below 1°K, there may be a nuclear contribution, caused by the interaction of the nuclear quadrapole moment with electrons. This has not been found for copper.

For alloys there are special problems in heat capacity measurements. The sample should be single-phase and homogeneous. Its degree of order should be known. To attain these requires metallurgical treatments; many measurements in the literature are without value because the workers did not know this. Furthermore, the state of the sample may change during the measurements; for example, the degree of order may become less as the temperature rises during the measurement. Such changes occur only at temperatures where the rate of diffusion is sufficiently rapid. If the rate of change is rapid, the considerable heat involved is included in the measurement. If very slow, it may not be included at all. At intermediate rates, the amount of heat included depends on the time allowed for the measurement.

Heat Content Measurements

In drop calorimetry the sample is dropped from an elevated temperature into a calorimeter, usually near room temperature. The total heat evolved by the sample during cooling is measured. Many alloy samples may not attain equilibrium in the final state; in fact, some may not attain the same final state in successive drops. If the final state is not known, the measured value will be in error by the difference of heat contents of the actual final state and the final state assumed by the experimenter.

The slope of the heat content versus temperature curve is, of course, Cp. Good values of Cp can be determined in this way unless Cp changes rapidly or irregularly with temperature, as, for example, at the λ anomaly at the magnetic Curie temperature.

Standard States

The Gibbs energies, enthalpies, and entropies of formation, as well as the partial molar quantities, the activities, and the activity coefficients, all express the changes when elements in their standard states unite to form the alloy. The numbers have meaning only if the standard states are specified. Nevertheless, even in recent papers the standard state is sometimes left ambiguous, and sometimes errors are made. In the following tables, to ensure precision, the standard states are shown by equations of chemical reactions at the head of each table.

It is a widely understood convention that when the standard state is not specified otherwise, it is taken to be the element at 1 atm. pressure in its equilibrium form at the temperature concerned. This has the advantage of being unambiguous, but has some disadvantages also.

For example, liquid alloys may frequently be stable below the melting points of their components. According to the rule, they would be referred to solid standard states. As the temperature is increased, the enthalpies and entropies of formation change discontinuously as the melting point of the component is passed. Deviations from Raoult's law become purely formal concepts when liquids are referred to solid standards, and activities do not extrapolate to 1.0 as the pure composition is reached. Values from different metallic systems are less directly comparable if one of them is referred to solid standards and the other to liquids.

For these reasons we have adopted the procedure of referring liquid alloys to liquid standard states and solid alloys to solid standard states. In order to do this, the Cp of the pure solid or liquid metals must be assumed at temperatures where the solid or liquid phases are unstable. Extrapolations of measured values are complex, and will be done differently by different workers. Moreover, as the measured values improve, extrapolations are also changed. Thus a measurement with respect to a solid is

tabulated with respect to a hypothetical liquid, and vice versa. If it is recognized that the unstable standard state is purely hypothetical, a simplifying set of properties may be assumed.

In the following it has been assumed that $Cp_{(\ell)} = Cp_{(s)}$. Hence ΔH_m and ΔS_m are constant with temperature for all elements. The same assumption is made for allotropic forms of elements. Tabular values then change continuously with temperature, and, when they are referred to unstable standard states, reference to stable ones may be easily made when desired.

Gibbs Energies of Formation

From electrochemical cells, vapor pressure or chemical equilibrium measurements, the partial molar Gibbs energy $\Delta\bar{G}_B$ of one of the components (and the quantities calculable from it, $\Delta\bar{G}_B^{xs}$, a_B, and γ_B) is derived. If $\Delta\bar{G}_B$ is known over a range of compositions, x ($x = x_B$, the atomic fraction of the component, B), the Gibbs-Duhem relation applies

$$(1-x)d\,\Delta\bar{G}_A + x\,d\,\Delta\bar{G}_B = 0.$$

Integration of this equation gives the values of $\Delta\bar{G}_A$, provided the constant of integration can be determined. For this it is necessary to know the value of $\Delta\bar{G}_A$ at one composition, x_o. For carrying out the integration, for plotting experimental points, and for other tasks of evaluation, it is often particularly convenient to use the

alpha function

$$\alpha_B = \Delta\bar{G}_B^{xs}/(1-x)^2.$$

Integration then gives

$$\Delta\bar{G}_{A,x}^{xs} = \Delta\bar{G}_{A,x_o}^{xs} + x_o(1-x_o)\,\alpha_{B,x_o} - x(1-x)\,\alpha_{B,x} + \int_{x_o}^{x}\alpha_B dx.$$

If the range of compositions includes pure A (x_o = 0.00), the constant of integration can be found from the fact that at this composition

$$\Delta\bar{G}_{A,0} = \Delta\bar{G}_{A,0}^{xs} = 0.$$

Then the above integration simplifies to

$$\Delta\bar{G}_{A,x}^{xs} = -x(1-x)\,\alpha_{B,x} + \int_0^x \alpha_B dx.$$

From both partials, the integral value is found

$$\Delta G = (1-x)\,\Delta\bar{G}_A + x\,\Delta\bar{G}_B.$$

From the temperature coefficient the entropy is found

$$d\Delta\bar{G}_B/dT = -\Delta\bar{S}_B;$$

and consequently the enthalpy

$$\Delta\bar{G}_B = \Delta\bar{H}_B - T\Delta\bar{S}_B.$$

From these partials, the partials for A and the integral values can be found from the Gibbs-Duhem relation as above.

However, it is clear that errors in determination of $\Delta\bar{G}_B$ become larger when temperature coefficients are taken, especially since the range of temperatures favorable for experimentation is usually not large. It is not uncommon to find that acceptable scatter in $\Delta\bar{G}_B$ determinations becomes unacceptably large in the temperature

coefficients. For these cases, calorimetric determinations of ΔH may be preferable, and can be combined with ΔG to give ΔS.

In equilibrium measurements with solid alloys, the equilibrium is with the surface of the alloy. The measurement is not valid unless the surface is in equilibrium with the interior; that is, the measurement must be conducted at a sufficiently high temperature for diffusion to bring about equilibrium between surface and interior. In dynamic methods, such as the Knudsen or Langmuir determination of vapor pressure, where the vapor is continually removed, care must be taken to prevent or allow for depletion of the surface of its more volatile component. These difficulties also apply to liquid alloys, but to a much smaller extent.

Enthalpies of Formation

Enthalpies (or heats) of formation may frequently be measured more accurately in a calorimeter than from temperature coefficients of equilibria. Direct reaction calorimetry may be very difficult for solid alloys. The specimen may need to be maintained for a long time at high temperatures with consequent difficulty in keeping account of heat losses. Furthermore, the reaction may not go to completion; the residue should be investigated. Some attempts on highly exothermic alloys have been made with some success, and attempts are being made on endothermic alloys. For liquid alloys,

the reaction is more readily carried to completion, but the problem of heat losses remains.

Solution calorimetry has been more generally applied. For this the heat of solution of the alloy in a solvent is determined; also the heats of solution of the components. The difference between the values represents the heat of formation of the alloy. Acid solution calorimetry has been tried many times with disappointing precision. The answer sought is the small difference betwen large quantities. Also, there are difficulties; for example, the escaping hydrogen gas may or may not be saturated with water and acid; differences in degree of saturation produce large errors.

Liquid tin solution calorimetry has been much more successful in spite of the fact that the calories are measured at an elevated temperature. This method is applicable to those elements and alloys which will dissolve in a reasonable time in liquid tin. No attempts to apply combustion calorimetry to alloys have been found. Perhaps there is a problem in the final state; for example, the oxides may dissolve one another, possibly forming a glass.

In evaluating enthalpies of formation the function $Q = \Delta H/x(1-x)$ plotted versus x is frequently useful. For example, for regular solutions the plot gives a horizontal line; Q is a constant with x. Where the plot is smooth, meaningful values of $\Delta\bar{H}_A$ and $\Delta\bar{H}_B$ may be derived; their accuracy will be inferior to the integral value.

Phase Diagrams

The phase diagram contains important thermodynamic information. For any two phases, I and II, in equilibrium, it follows that $\Delta\bar{G}_A^{I} = \Delta\bar{G}_A^{II}$, and $\Delta\bar{G}_B^{I} = \Delta\bar{G}_B^{II}$., providing the standard state is the same for both phases. This provides a check of selected Gibbs energies for consistency with the phase diagram.

Although the boundaries of a two-phase region provide relationships of the partial molar Gibbs energies of two phases at an unlimited number of points, the data that can be rigorously calculated from the phase diagram alone is limited. The difficulty is that both the temperature, T, and the composition, x, change simultaneously, so that

$$d\Delta\bar{G}_A/\,dT = (\delta\,\Delta\bar{G}_A/\delta\,T)_x + (\delta\,\bar{G}_A/\delta\,x)_T\,dx/dT$$
$$= -\Delta\bar{S}_A + (\delta\,\bar{G}_A/\delta\,x)_T\,dx/dT.$$

If other information is known, as for example, ΔH values from which $\Delta\bar{S}_A$ values can be calculated or estimated with some accuracy, the phase diagram can be used to calculate Gibbs energies as a function of composition. Even without making use of such information, it has been shown in favorable cases that computer solutions of simultaneous equations (in which the necessary relationships are explicitly or implicitly assumed in the form of the equations) can produce acceptable data. The use of phase diagrams as a source of thermodynamic data is in its infancy.

A further difficulty is the lack of precision with which most phase boundaries have been determined. Most phase diagrams have been sketched in from a few experimental points, often of indifferent accuracy. Solidus lines have mainly been determined from thermal arrests on cooling curves; almost invariably they are many degrees too low. The heat of fusion of a pure metal or congruently melting compound can be rigorously calculated from the slopes of liquidus and solidus. Values of ΔH_m for a single metal have been calculated from many phase diagrams; the results deviate disappointingly, though they are approximately correct.

Thermodynamic values in this work have been confined to actual thermodynamic measurements, using phase diagrams only as an aid in selection, or in a few cases, an extension of other experimental values.

Phase diagrams have been included in most evaluations to give a general view of the system as an aid in understanding the tables. The boundaries have been drawn with reasonable precision, but high precision has not been attempted. The evaluations of Hansen (1958), Elliott (1965), and Shunk (1969) have been taken as a basis. New publications (the above only cover the literature through 1964), have been scanned and revisions adopted where necessary. Crystal structures are from Pearson (1958, 1967), with later revisions where necessary.

Uncertainty Estimates

The uncertainties shown in many of the tables are, unfortunately, to a large extent subjective. Of course, from a large number of measurements the 50% (or 95%) probability can be readily calculated, but this represents only the scatter, or reproducibility of the measurement. What is wanted is to add to this an unknown, systematic error, of the measurement. This can only be estimated from impressions of the concordance of the data with data from other sources, with the phase diagram, etc.

FUNDAMENTAL CONSTANTS

Energy is expressed in terms of the calorie, which is defined in terms of the more fundamental unit, the absolute joule, as follows:

1 thermochemical calorie = 4.1840 absolute joules

All tables are based on the values of the physical constants recommended by the Committee on Fundamental Constants of the National Academy of Sciences - National Research Council and adopted by the National Bureau of Standards (N.B.S. Technical News Bulletin 47 (10), 175-7, October, 1963). The values of those constants most pertinent to the present evaluations are given in the following table.

Constant	Value	Units
Ice point (0°C)	273.150	°K
Thermochemical calorie	4.1840	joules (abs.)
R, gas constant	1.98717 8.3143	cal. /deg. g-atom joules/deg. g-atom
$\mathcal{F}$, Faraday constant	23060.9 96487.0	cal. /volt equiv. coulombs/equiv.

SYMBOLS AND UNITS

The symbols in the tables are defined below with the units used and with remarks on their most common application. All tabulated extensive quantities refer to one gram-atom, i.e., Avogadro's number of atoms, of the substance concerned. Units, except for temperature, are not given explicitly in the tables in order to conserve space.

Many of the symbols should, by convention, properly include a superscript zero, such as G°, H°, or S°, when they refer to an element in its standard state. These, too have been omitted from the tables for the sake of brevity.

Symbol	Units	Definition and Remarks
P	atm	Pressure, most commonly vapor pressure. Gases are assumed to be ideal unless otherwise indicated, so that fugacity (f) is equal to the pressure.
V	cm^3/g-atom	Volume.
T	°K	Absolute temperature.
S	cal/°K g-atom	Entropy.
H	cal/g-atom	Enthalpy or heat content, $H = E + PV$.
G	cal/g-atom	Gibbs energy, $G = H - TS$.
Cp	cal/°K g-atom	Heat capacity at constant pressure, commonly at P = 1 atm.
γ	cal/$(°K)^2$g-atom	Electronic heat capacity coefficient; $C_{(electronic)} = \gamma T$.
st	298.15°K	Subscript denoting standard temperature, as S_{st}.
$H_T - H_{st}$	cal/g-atom	Enthalpy or heat content of a substance at temperature T relative to its standard state at 298.15°K.
$S_T - S_{st}$	cal/°K g-atom	Entropy of a substance at temperature T relative to its standard state at 298.15°K.
$\frac{G_T - H_{st}}{T}$	cal/°K g-atom	The Gibbs energy function of a substance at temperature T relative to its standard state at 298.15°K.

Symbol	Units	Definition and Remarks
ΔH ΔG ΔS	cal/g-atom cal/g-atom cal/°K g-atom	The enthalpy (heat), Gibbs energy, or entropy of formation, vaporization, fusion, etc., corresponding to the process described in the accompanying equation or expressed by a subscript.
ΔCp	cal/°K g-atom	Deviation of heat capacity from Kopp's law of additivity.
ΔG^{xs}	cal/g-atom	Excess Gibbs energy of formation, defined by $\Delta G - RT\,[x \ln x + (1-x) \ln (1-x)]$.
ΔS^{xs}	cal/°K g-atom	Excess entropy of formation, defined by $\Delta S + R\,[x \ln x + (1-x) \ln (1-x)]$.
$\Delta \bar{H}_i$ $\Delta \bar{G}_i$ $\Delta \bar{S}_i$ $\Delta \bar{C}p_i$	cal/g-atom cal/g-atom cal/°K g-atom	Relative partial molar enthalpy (heat content) Gibbs energy, entropy, or heat capacity of component i in an alloy referred to the pure component in its specified reference state.
$\Delta \bar{G}_i^{xs}$	cal/g-atom	Relative partial molar excess Gibbs energy, defined by $\Delta \bar{G}_i^{xs} = \Delta \bar{G}_i - RT \ln x_i$.
$\Delta \bar{S}_i^{xs}$	cal/°K g-atom	Relative partial molar excess entropy, defined by $\Delta \bar{S}_i^{xs} = \Delta \bar{S}_i + R \ln x_i$.
x_i	dimensionless	Atom fraction of component i in an alloy.
a_i	dimensionless	Thermodynamic activity of component i in an alloy referred to the pure component in its specified reference state at the temperature in question $\Delta \bar{G}_i = RT \ln a_i$.
γ_i	dimensionless	Activity coefficient, defined by $\gamma_i = a_i/x_i$.
$\ln$		Natural logarithm, i.e., to the base e.
log		Common logarithm, i.e., to the base 10.
s, ℓ, g, c		Subscripts referring to solid (crystalline), liquid, gaseous, or condensed (solid or liquid) states.
α, β, γ, etc.		Used to designate crystalline phases. May appear as subscript or superscript.
m, v, t		Subscripts referring to melting, vaporization, or a transition between different crystalline phases.

ATOMIC WEIGHTS

Atomic weights used are those based on C^{12}= 12.0000 adopted by the IUPAC in 1961. The following values are from Cameron and Wichers (1962), except for those of Am^{243}, Np^{237}, and Pu^{239} which are from Everling et al. (1960).

Symbol	Element	At. weight	Symbol	Element	
Ag	Silver	107.870	Mo	Molybdenum	95.94
Al	Aluminum	26.9815	N	Nitrogen	14.0067
Am^{243}	Americium	243.061	Na	Sodium	22.9898
Ar	Argon	39.948	Nb	Niobium	92.906
As	Arsenic	74.9216	Nd	Neodymium	144.24
Au	Gold	196.967	Ne	Neon	20.183
B	Boron	10.811	Ni	Nickel	58.71
Ba	Barium	137.34	Np^{237}	Neptunium	237.048
Be	Beryllium	9.0122	O	Oxygen	15.9994
Bi	Bismuth	208.980	Os	Osmium	190.2
Br	Bromine	79.909	P	Phosphorus	30.9738
C	Carbon	12.01115	Pb	Lead	207.19
Ca	Calcium	40.08	Pd	Palladium	106.4
Cd	Cadmium	112.40	Pr	Praseodymium	140.907
Ce	Cerium	140.12	Pt	Platinum	195.09
Cl	Chlorine	35.453	Pu^{239}	Plutonium	239.052
Co	Cobalt	58.9332	Rb	Rubidium	85.47
Cr	Chromium	51.996	Re	Rhenium	186.2
Cs	Cesium	132.905	Rh	Rhodium	102.905
Cu	Copper	63.54	Ru	Ruthenium	101.07
Dy	Dysprosium	162.50	S	Sulfur	32.064
Er	Erbium	167.26	Sb	Antimony	121.75
Eu	Europium	151.96	Sc	Scandium	44.956
F	Fluorine	18.9984	Se	Selenium	78.96
Fe	Iron	55.847	Si	Silicon	28.086
Ga	Gallium	69.72	Sm	Samarium	150.35
Gd	Gadolinium	157.25	Sn	Tin	118.69
Ge	Germanium	72.59	Sr	Strontium	87.62
H	Hydrogen	1.00797	Ta	Tantalum	180.948
He	Helium	4.0026	Tb	Terbium	158.924
Hf	Hafnium	178.49	Te	Tellurium	127.60
Hg	Mercury	200.59	Th	Thorium	232.038
Ho	Holmium	164.930	Ti	Titanium	47.90
I	Iodine	126.9044	Tl	Thallium	204.37
In	Indium	114.82	Tm	Thulium	168.934
Ir	Iridium	192.2	U	Uranium	238.03
K	Potassium	39.102	V	Vanadium	50.942
Kr	Krypton	83.80	W	Tungsten	183.85
La	Lanthanum	138.91	Xe	Xenon	131.30
Li	Lithium	6.939	Y	Yttrium	88.905
Lu	Lutetium	174.97	Yb	Ytterbium	173.04
Mg	Magnesium	24.312	Zn	Zinc	65.37
Mn	Manganese	54.9380	Zr	Zirconium	91.22

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Copper

Part I. Discussion

Phases and Structures. Cu has the fcc (Al) prototype structure (Pearson, 1967). T_m = 1357.6°K was taken from the 1968 International Practical Temperature Scale.

Gas Properties. Values for $Cu_{(g)}$ were taken from Hilsenrath, Messina, and Evans (1964).

Low-Temperature Data. Selected values were taken from the evaluation by Furukawa, Saba, and Reilly (1968), 0°- 300°K. In the table below are listed those references from which the electronic γ could be derived. Values of γ are listed as well as systematic deviations of Cp from selected values over the range of temperature covered by the reference.

Source	Percent Deviation from Selected Values	$\gamma \times 10^4$
Martin (1968), 0.4°- 4°K.	-0.5	1.652
Gmelin and Gobrecht (1967), 0.4°- 30°K.	±0.5	1.663
Osborne, Flotow, and Schreiner (1966, 1967), 1°- 25°K.	agree	1.659
Ahlers (1966), 1.3°- 20°K.	+1	1.661
Clune and Green (1966), 2°- 4°K.	+0.6	1.670
du Chatenier and de Nobel (1966), 1.3°- 30°K.	+5	1.715
Martin (1966), 3°- 30°K.	±0.5	1.663
Isaacs (1965), 1.5°- 4.2°K.	+1	1.668
Isaacs and Massalski (1965), 1.6°- 4.2°K.	+1	1.668
Dixon, Hoare, Holden, and Moody (1965), 1.2°- 4.2°K.	+0.5	1.665
Rorer, Onn, and Meyer (1965), 0.3°- 4.2°K.	+3	1.720
Phillips (1964), 0.1°- 4.2°K.	agree	1.661
Ahlers (1964), 2°- 20°K.	+1	1.683
Kneip, Betterton, and Scarbrough (1963), 1.2°- 4.5°K.	-1	1.664

O'Neal (1963), 0.11°- 1.01°K.	+1	1.678
du Chatenier and de Nobel (1962), 1°- 30°K.	+4 to +16	1.723
Veal and Rayne (1962, 1963), 1.4°- 4.2°K.	agree	1.654
Crane and Zimmerman (1961), 1.5°- 4.2°K (estimated from their graph).	+1 to +7	1.85
Franck, Manchester, and Martin (1961), 0.4°- 30°K.	±1	1.630
Manchester (1959), 1.1°- 4.2°K.	+0.5	1.663
Ramanathan and Srinivasan (1957), 1.3°- 4.2°K.	+4	1.723
Griffel, Vest, and Smith (1957), 1.8°- 4.2°K.	-1	1.651
Corak, Garfunkel, Satterthwaite, and Wexler (1955), 1.2°- 4.2°K.	-0.6	1.644
Rayne (1954), 0.2°- 0.7°K.	-1	1.640
Estermann, Friedberg, and Goldman (1952), 1.8°- 4.2°K.	+8	1.792
Kok and Keesom (1936), 1.2°- 20°K.	0 to +9	1.775
SELECTED VALUE		1.661(±0.01)

Selected values agree within 1% with Cp measurements of Martin (1962), 16°- 90°K; Martin (1960), 20°- 300°K; Huffstutler (1961), 19°- 295°K; Giauque and Meads (1941), 14°- 300°K; Dockerty (1937), 28°- 194°K; Dockerty (1933), 201°- 299°K; Eucken and Werth (1930), 84°- 215°K; and Nernst and Lindemann (1911), 23°- 88°K; except that values of Huffstutler are 2-8% higher below 35°K, those of Giauque and Meads scatter ±2 to ±4% below 35°K, and those of Nernst and Lindemann at 33°K are about 4% lower. Cp values of Sandenaw (1959), 4°- 300°K, scatter ±5% at low temperatures, decreasing to ±1% at high temperatures; values of Aoyama and Kanda (1941), 84°- 274°K, are 0-12% higher; those of Maier and Anderson (1934), 53°- 294°K; and Keesom and Onnes (1914, 1915), 15°- 89°K, scatter within ±6%; and those of Berge and Blanc (1960), 93°- 673°K, are higher by 7% at 93°K, trending to 0-4% lower at 248°K.

High-Temperature Data. Solid. Selected values agree within ±1% with the heat content measurements of Kendall and Hultgren (1960), 315°- 1310°K; Lucks and Deem (1956), 460°- 1345°K; Bronson, Chisholm and Dockerty (1933), 322°- 774°K; Jaeger, Bottema and Rosenbohm (1932), 586°- 1232°K; Seekamp (1931), 373°- 973°K; Ruer and Kramers (1929), 373°- 1123°K; Doerinckel and Werner (1921), 373°- 1074°K; Wüst, Meuthen and Durrer (1918), 373°- 1573°K; and those of Magnus (1910), 510°- 610°K; with the following minor

exceptions: values of Kendall and Hultgren (1960) are lower by about 2% below 800°K; those of Lucks and Deem (1956) trend upward to about 3% higher above 900°K; and those of Wüst, Meuthen and Durrer (1918) are 6% higher below 900°K.

Selected values also agree with the Cp measurements of Berge and Blanc (1960), 93°- 673°K; Lehman (1960), 421°K; Forster and Tschentke (1940), 293°- 1173°K; Persoz (1940), 287°- 640°K; Honda and Tokunaga (1935), 298.4°K; Bronson, Chisholm and Dockerty (1933), 267°- 378°K; Harper (1915), 287°- 320°K; and those of Griffiths and Griffiths (1913), 273°- 371°K; except the values of Forster and Tschentke (1940) are about 1-4% higher above 600°K. Other Cp measurements, when compared with the selected values, are higher as given below:

Source	Percent Higher
Brooks, Norem, Hendrix, Wright, and Northcutt (1968), 313°- 1193°K.	1 to 2
Kraftmakher (1967), 550°- 1250°K.	1 to 2
Norem (1965), 568°- 1193°K.	1 to 4
Pawel and Stansbury (1965), 363°- 883°K.	2
Bronson and Chisholm (1929), 293°- 553°K.	1
Klinkhardt (1927), 373°- 1073°K.	1 to 3

Liquid. Values of ΔH_m and enthalpies are not well established. The following ΔH_m values were found in the literature.

Source	ΔH_m
Vollmer and Kohlhaas (1968)	3107(±50)
Dokken and Elliott (1965)	3290(±275)
Oelsen, Schurmann, and Buchholz (1961)	3030
SELECTED VALUE	3123(±100)

Heat content measurements of Fieldhouse, Hedge, Lang and Waterman (1958), 1362°- 1893°K are 0-3% higher than the selected values. Akhmatova (1967), 1463°- 1638°K reports $Cp_{(\ell)}$ between 6 cal/g-atom deg and 8 cal/g-atom deg. The selected value of ΔH_m was chosen to make $\Delta S_m = 2.300$.

Vapor Pressure Data. Application of the Third Law test to vapor pressure measurements and the Second Law to mass spectrometer measurements yielded the following values of $\Delta H_{v,st}$:

Source	$\Delta H_{v,st}$
Myles and Darby (1968), 1265°- 1356°K. Torsion effusion method.	80530(±50)
Avery, Cuthbert, Prosser, and Silk (1966), 1474°- 1839°K. Mass spectrometer method.	82000*(±1700)
Ponslet and Bariaux (1966), 1223°- 1856°K. Langmuir method.	80510(±200)
McCormack, Myers, and Saxer (1965), 1514°- 1707°K. Knudsen method.	81160(±200)
Krupkowski and Galonka (1964), 1367°- 1523°K. Langmuir method.	80300(±150)
Babeliowsky (1962), 1217°- 1314°K. Mass spectrometer method.	77160*(±3700)
Ackerman and Rauh (1962), 1360°- 1450°K. Mass spectrometer method.	81460*(±900)
Grieveson, Hooper, and Alcock (1961), 1429°- 1846°K. Knudsen method.	80520(±200)
McLellan and Shuttleworth (1960), 987°- 1357°K. Knudsen method.	82090(±250)
Verhaegen (1959), 1314°- 1420°K. Mass spectrometer method.	85040(±200)
Nesmeyanov, Smakhtin, Choporav, and Lebedev (1959), 1192°- 1360°K. Knudsen method.	81170(±600)
Morris and Zellars (1956), 1605°- 1879°K. Transport method.	80670(±150)
Hersh (1953), 1242°- 1563°K. Knudsen method.	81480(±150)
Edwards, Johnston, and Ditmars (1953), 1143°- 1292°K. Knudsen method.	80680(±100)
Marshall, Dornte, and Norton (1937), 1268°- 1466°K. Langmuir method.	80970(±900)
Baur and Brunner (1934), 1768°- 2116°K. Boiling point method.	73610(±600)
Harteck (1928), 1419°- 1463°K. Knudsen method.	81930(±400)
SELECTED VALUE	80600(±300)

*Values reported by the investigators who gave no individual measurements. Grieveson, et al. reported only an equation.

Part II. Tables

Section 1. Low-Temperature Data

T, °K	Cp	T, °K	Cp
0.1	0.0000166	25	0.230
0.5	0.0000845	30	0.405
1	0.000177	40	0.894
2	0.000423	50	1.471
3	0.000806	75	2.843
4	0.00139	100	3.825
5	0.00225	150	4.901
10	0.0133	200	5.408
15	0.0439	250	5.684
20	0.110	298.15	5.840

$C_{(electronic)} = \gamma T$ $\gamma = 1.661(\pm 0.01) \times 10^{-4}$

	Crystal	Gas, $Cu_{(g)}$
$H_{st}-H_0$	1196	1481
S_{st}	7.923(±0.02)	39.742

Section 2. High-Temperature Data

T, °K	Condensed Phase				Gas Phase, Cu(g)			
	Cp	H_T-H_{st}	S_T-S_{st}	$-\frac{G_T-H_{st}}{T}$	Cp	H_T-H_{st}	S_T-S_{st}	$-\frac{G_T-H_{st}}{T}$
298.15	5.840	0	0.000	7.923	4.968	0	0.000	39.742
400	6.032	605	1.744	8.155	4.968	506	1.460	39.938
500	6.177	1216	3.106	8.598	4.968	1003	2.569	40.306
600	6.310	1840	4.245	9.101	4.968	1500	3.474	40.718
700	6.434	2477	5.227	9.611	4.968	1996	4.240	41.131
800	6.557	3127	6.094	10.108	4.968	2493	4.904	41.530
900	6.680	3789	6.873	10.587	4.968	2990	5.489	41.909
1000	6.845	4464	7.585	11.044	4.968	3487	6.012	42.268
1100	7.058	5158	8.247	11.480	4.969	3983	6.486	42.607
1200	7.321	5878	8.873	11.897	4.970	4480	6.918	42.927
1300	7.554	6624	9.469	12.296	4.972	4977	7.316	43.229
1357.6(s)	8.172	7077	9.810	12.520	4.975	5264	7.528	43.393
1357.6(ℓ)	7.800	10200	12.110					
1400	7.800	10530	12.350	12.751	4.977	5475	7.684	43.516
1500	7.800	11310	12.888	13.271	4.985	5973	8.010	43.770
1600	7.800	12090	13.391	13.758	4.997	6472	8.350	44.047
1700	7.800	12870	13.864	14.216	5.016	6973	8.654	44.294
1800	7.800	13650	14.310	14.650	5.041	7475	8.941	44.530
1900	(7.800)	(14430)	(14.732)	(15.060)	5.074	7981	9.214	44.756
2000	(7.800)	(15210)	(15.132)	(15.450)	5.116	8490	9.476	44.973
2200	(7.800)	(16770)	(15.875)	(16.175)	5.229	9524	9.968	45.381
2400	(7.800)	(18330)	(16.554)	(16.839)	5.379	10584	10.429	45.762
2500	(7.800)	(19110)	(16.872)	(17.151)	5.468	11127	10.651	45.943
2600	(7.800)	(19890)	(17.178)	(17.451)	5.564	11678	10.867	46.117
2700	(7.800)	(20670)	(17.473)	(17.740)	5.668	12240	11.079	46.288
2800	(7.800)	(21450)	(17.756)	(18.018)	5.777	12812	11.287	46.454
2839	(7.800)	(21754)	(17.864)	(18.124)	5.822	13038	11.367	46.516
2900	(7.800)	(22230)	(18.030)	(18.287)	5.892	13396	11.492	46.615

T_m = 1357.6°K* ΔH_m = 3123(±100) ΔS_m = 2.300(±0.07)

*Secondary reference point on 1968 International Practical Temperature Scale.

Section 3. Vapor Pressure Data

$$Cu_{(s,\ell)} = Cu_{(g,\ 1\ atm)}$$

T, °K	P	ΔG_T	ΔH_T	P	T, °K
298.15	7.5×10^{-53}	71113	80600	10^{-10}	1048
500	5.0×10^{-29}	64746	80387	10^{-9}	1115
700	5.3×10^{-19}	58536	80119	10^{-8}	1192
800	7.0×10^{-16}	55462	79966	10^{-7}	1280
1000	1.6×10^{-13}	49376	79623	10^{-6}	1383
1100	6.1×10^{-10}	46360	79425	10^{-5}	1511
1200	1.27×10^{-8}	43364	79202	10^{-4}	1663
1300	1.62×10^{-7}	40387	78953	10^{-3}	1852
1357.6(s)	5.92×10^{-7}	38687	78787	10^{-2}	2092
1357.6(ℓ)			75664	10^{-1}	2407
1400	1.38×10^{-6}	37529	75545	1	2839
1500	8.36×10^{-6}	34851	75263		
1600	4.08×10^{-5}	32138	74982		
1700	1.63×10^{-4}	29467	74703		
1800	5.55×10^{-4}	26816	74425		
1900	1.66×10^{-3}	24178	74151		
2000	4.41×10^{-3}	21554	73880		
2200	2.38×10^{-2}	16347	73354		
2400	9.58×10^{-2}	11185	72854		
2500	0.176	8620	72617		
2600	0.309	6068	72388		
2700	0.519	3520	72170		
2800	0.839	979	71962		
2839	1.00	0	71884		
2900	1.31	-1551	71766		

$\Delta S_{v,2839} = 25.32(\pm0.1)$

$\Delta H_{v,0} = 80315(\pm300)$

Part III. References

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Copper-Silver

Part I. Discussion

Phases and Structures. Most determinations of the simple eutectic phase diagram (Hansen 1958) agree within the following limits: liquidus (±5°); eutectic (±1°; ±0.1%); (Ag)-solvus (±0.1%); (Cu)-solvus (±0.2%). Selected thermodynamic values agree with the phase diagram within ±150 cal/g-atom.

Solid Alloys. Data for Table 1 were taken from Cp measurements of Sargent, Isaacs, and Massalski (1966), 1.6°- 4.2°K, x_{Cu} = 0.97-0.99. Selected values of Table 2 agree within 50 cal/g-atom with heats of formation determined by tin solution calorimetry of Oriani and Murphy (1958), 895°K, x_{Cu} = 0.03, 0.05, 0.989, 0.994; and Orr and Hultgren (1960), 320°K, x_{Cu} = 0.11, 0.958, assuming Kopp's law of additivity of Cp values. The ΔG values are readily calculated from the phase diagram. For the limited (Ag) and (Cu) solid solutions, Raoult's law can be assumed for the principal component and Henry's law for the solute without much error. The conditions at the phase boundaries that $\Delta\bar{G}_{Cu}^{(Ag)} = \Delta\bar{G}_{Cu}^{(Cu)}$ and $\Delta\bar{G}_{Ag}^{(Ag)} = \Delta\bar{G}_{Ag}^{(Cu)}$ are sufficient to determine the Henry's law activity coefficients for both phases. ΔS was calculated from ΔG and ΔH.

Liquid Alloys. Selected ΔH values are approximately 10-25 cal/g-atom less endothermic than the direct calorimetric values of Dokken and Elliott (1965), 1373°K, x_{Cu} = 0.5-0.9; and agree with those of Oriani and Murphy (1958), 1373°K, x_{Cu} = 0.1-0.9, except above x_{Cu} = 0.5, where they are more endothermic by 10-80 cal/g-atom. ΔH values from the direct calorimetric measurements of Kawakami (1930), 1473°K, x_{Cu} = 0.22-0.80, scatter widely about the selected values. Selected ΔG_{Ag} values agree within 5% with those determined by vapor pressure measurements of Golonka (1965), 1237°- 1473°K, x_{Cu}=0.1-0.9; and agree above x_{Cu} = 0.7 with the vapor pressure measurements of Edwards and Downing (1956), 1300°- 1560°K, x_{Cu} = 0.14-0.95, but are far more exothermic for x_{Cu}<0.6. ΔS was calculated from ΔG and ΔH.

Part II. Tables

TABLE 1

Low-Temperature Data for (Cu)-Phase Alloys

T, °K	x_{Cu}			
	0.97	0.98	0.99	1.00
	Cp			
1.6	0.000314	0.000315	0.000316	0.000314*
2	0.000427	0.000427	0.000428	0.000426*
3	0.000816	0.000818	0.000819	0.000813*
4	0.00142	0.00142	0.00142	0.00141 *
$\gamma \times 10^4$	1.664	1.664	1.671	1.668 *

*Values differ slightly from selected values (see Cu).

TABLE 2

Integral Quantities for Solid Alloys at 1052°K

$$(1-x)Ag_{(s)} + xCu_{(s)} = Ag_{1-x}Cu_{x(s)}$$

x_{Cu}	Phase	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.05	(Ag)	-215	287	0.477	210	0.073
0.10		-280	537	0.777	400	0.130
0.141*	(Ag)	-288 (±50)	716 (±50)	0.954 (±.1)	562 (±50)	0.146 (±.1)
0.951*	(Cu)	-115	415	0.504	294	0.115
0.98		- 85	181	0.253	120	0.058

*Phase boundary

TABLE 3

Integral Quantities for Liquid Alloys at 1423°K

$$(1-x)Ag_{(\ell)} + xCu_{(\ell)} = Ag_{1-x}Cu_{x(\ell)}$$

x_{Cu}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-614	455	0.751	305	0.105
0.2	-879	748	1.143	536	0.149
0.3	-1026	921	1.368	701	0.154
0.4	-1100	1004	1.479	803	0.142
0.5	-1119	1014	1.499	841	0.121
	(±50)	(±50)	(±.05)	(±50)	(±.05)
0.6	-1091	958	1.440	812	0.102
0.7	-1013	829	1.295	714	0.081
0.8	- 869	629	1.052	546	0.058
0.9	- 611	352	0.677	309	0.030

TABLE 4

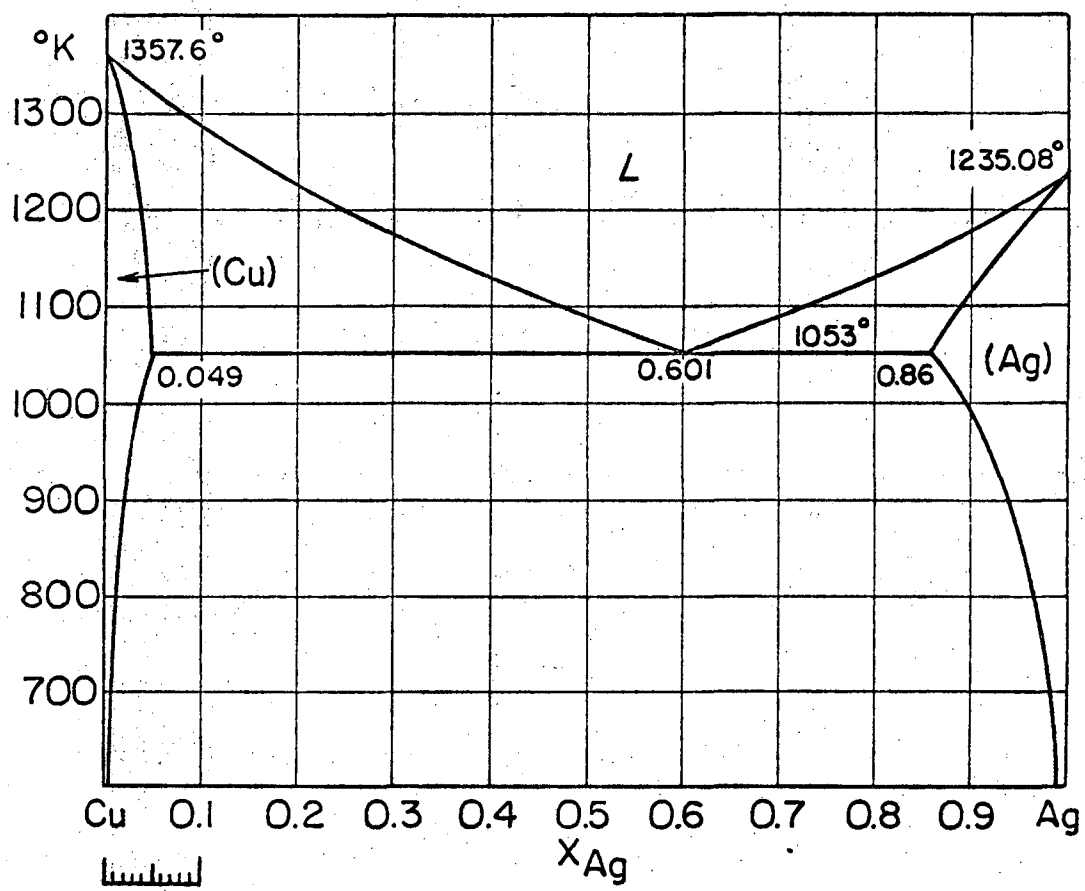
Partial Molar Quantities for Liquid Alloys at 1423°K

Ag Component $Ag_{(\ell)} = Ag(\text{in alloy})_{(\ell)}$

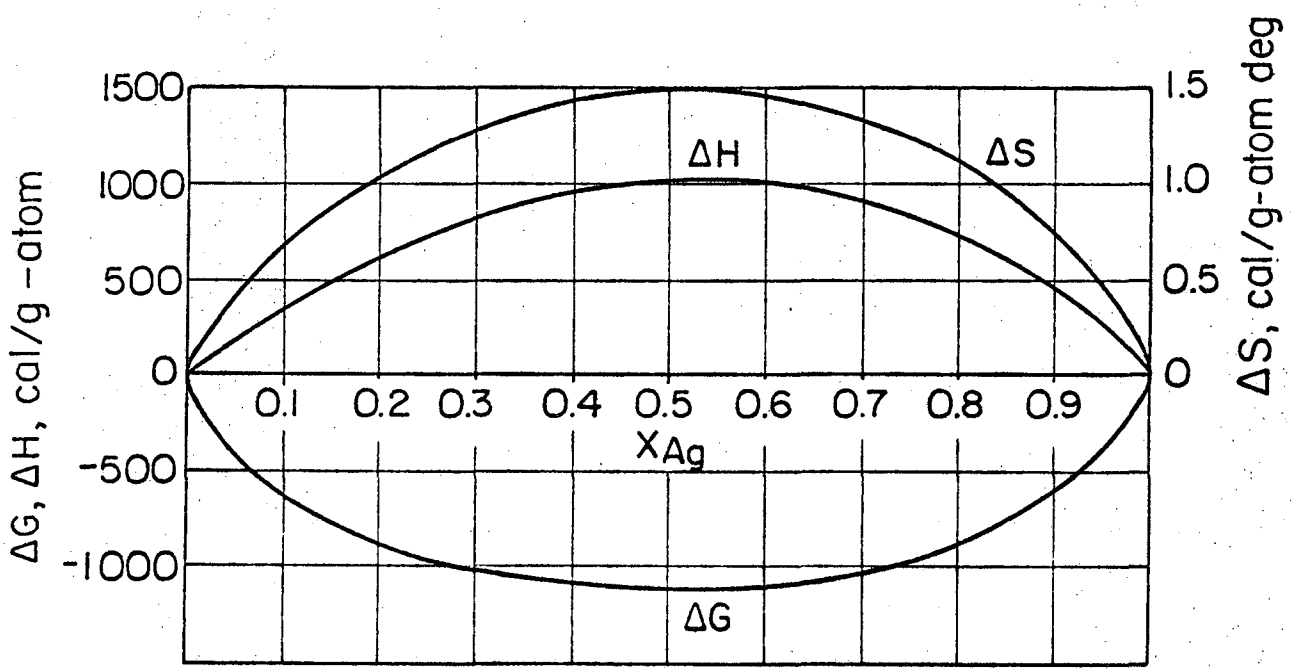
x_{Ag}	a_{Ag}	γ_{Ag}	$\Delta\bar{G}_{Ag}$	$\Delta\bar{G}^{xs}_{Ag}$	$\Delta\bar{H}_{Ag}$	$\Delta\bar{S}_{Ag}$	$\Delta\bar{S}^{xs}_{Ag}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.912	1.014	-259	39	88	0.244	0.035
0.8	0.841	1.052	-489	142	293	0.549	0.106
0.7	0.779	1.113	-707	302	549	0.882	0.174
0.6	0.722	1.203	-921	523	818	1.223	0.207
0.5	0.667	1.334	-1145	815	1126	1.596	0.219
	(±.01)	(±.02)	(±50)	(±50)	(±100)	(±.1)	(±.1)
0.4	0.610	1.525	-1398	1193	1508	2.042	0.221
0.3	0.537	1.790	-1758	1646	1965	2.616	0.224
0.2	0.431	2.154	-2381	2170	2541	3.459	0.261
0.1	0.266	2.656	-3749	2762	3179	4.869	0.293
0.0	0.000	3.375	$-\infty$	3440	3900	∞	0.323

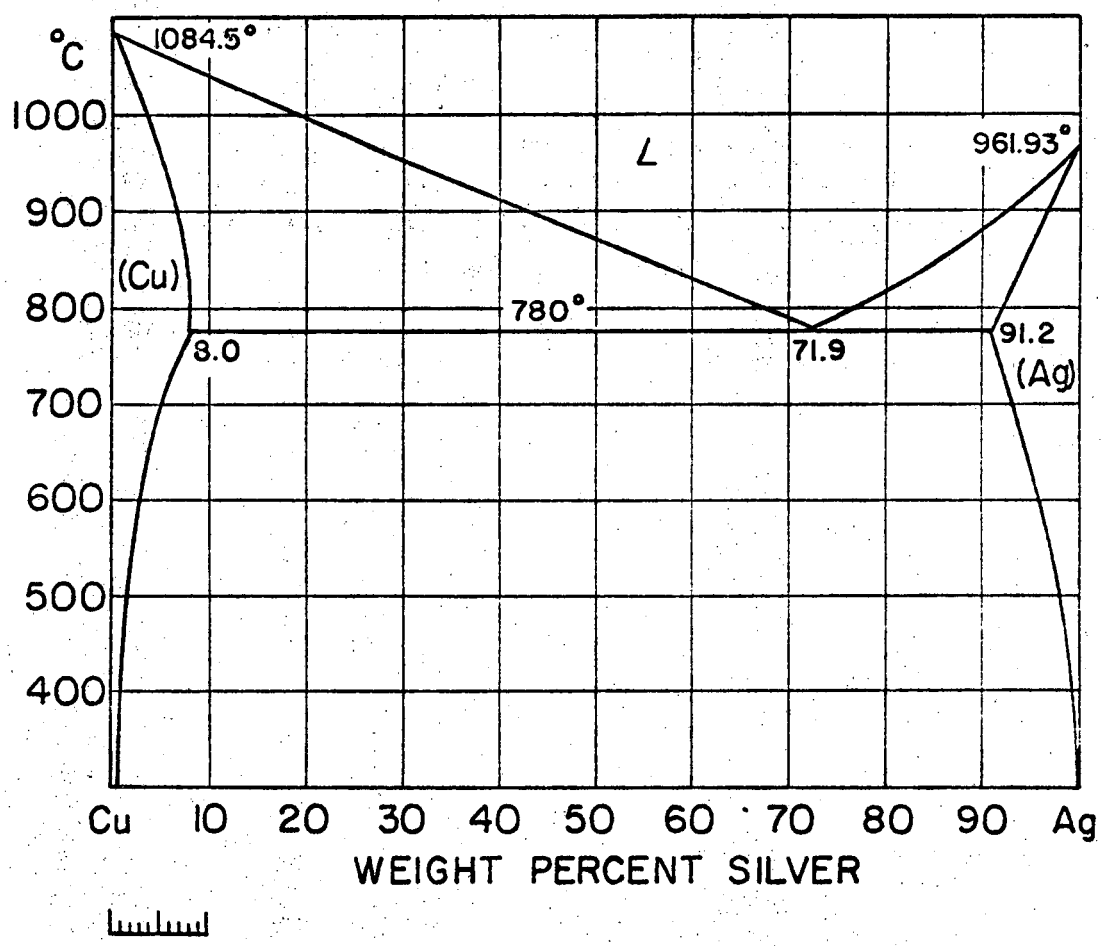
Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.0	0.000	3.406	$-\infty$	3465	5500	∞	1.430
0.1	0.260	2.600	-3809	2702	3750	5.312	0.737
0.2	0.422	2.112	-2437	2114	2570	3.518	0.320
0.3	0.535	1.782	-1771	1634	1788	2.501	0.109
0.4	0.616	1.541	-1368	1223	1283	1.863	0.043
0.5	0.679	1.359	-1093	867	901	1.402	0.024
	(±.01)	(±.02)	(±50)	(±50)	(±100)	(±.1)	(±.1)
0.6	0.731	1.218	-887	558	591	1.038	0.023
0.7	0.782	1.118	-694	314	343	0.729	0.020
0.8	0.841	1.051	-491	140	151	0.451	0.008
0.9	0.912	1.013	-262	36	38	0.211	0.001
1.0	1.000	1.000	0	0	0	0.000	0.000



COPPER - SILVER SYSTEM, 1423°K

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(Cu)
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8.0
71.9
91.2
(Ag)
Cu
10
20
30
40
50
60
70
80
90
Ag
WEIGHT PERCENT SILVER

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Copper-Aluminum

Part I. Discussion

Phases and Structures. The phase diagram with 13 intermediate phases was taken from Hansen (1958) after modifications suggested by Elliott (1965), and by Shunk (1969). Many features are still unresolved. Pearson (1958, 1967) reports four metastable martensite phases and lists the following phases:

θ, "Al_2Cu", with the bc tetragonal (C16) prototype structure.

η_1, "AlCu", with an orthorhombic structure.

η_2, "AlCu", with an end centered orthorhombic structure.

ζ_1, with a hexagonal structure related to $D8_3$.

ζ_2, is probably monoclinic.

ϵ_2, "Al_2Cu_3", probably has a pseudo-cubic structure.

γ_1, with a structure related to γ-brass.

γ_2, "Al_4Cu_9", with the cubic ($D8_3$) prototype structure.

χ, with a structure related to γ-brass

β, with the bcc (A2) structure isotypic with W.

α_2 with a structure conflictingly reported as fcc (A1) isotypic with Cu, or as a cubic (A13) structure isotypic with β-Mn.

The structure of ϵ_1 and δ were not listed.

Solid Alloys. Selected values of Table 1 were taken from Oelsen and Middel (1937), 293°, 1423°K, x_{Cu} = 0.15-0.91, who poured the liquid metals together into a calorimeter at room temperature. Clearly an equilibrium final state may not be attained. Kubaschewski and Heymer (1960), 298°K, x_{Cu} = 0.50, 0.667, measured ΔH by direct reaction calorimetry, at two compositions, agreeing within 10% with Oelsen and Middel, whose other values they accepted. Cp measurements of Ranzetta and West (1961), 733°- 973°K, x_{Cu} = 0.76, found Cp = 7.17 cal/g-atom, invariant with T (which is improbable). Cp measurements of Masumoto, Saito, and Takahashi (1955), 473°- 873°K, x_{Cu} = 0.71-0.87, showed a small anomaly near 578°K, which they attributed to short-range ordering.

Liquid Alloys. Selected values of Table 3 agree well with $\Delta\bar{G}_{Al}$ values calculated from the emf measurements of Wilder (1965), 950°- 1373°K, x_{Cu}= 0.1-0.95; agree within ±300 cal/g-atom with the values from emf studies of Grube and Hantelman (1942), 1005°- 1160°K, x_{Cu} = 0.15-0.49; and within ±150 cal/g-atom with values from the vapor pressure measurements of Hiroyasu and Hiroshi (1969), 1373°, 1473°K, x_{Cu} = 0.088-0.574. Desré (1962) determined the distribution coefficient of Cu between $Pb_{(\ell)}$ and $Al_{(\ell)}$ and also between

$Bi_{(\ell)}$ and $Al_{(\ell)}$. He obtained $\Delta\bar{G}_{Al}$ values 500-3000 cal/g-atom more exothermic than the selected values. Selected ΔH values of Table 2 were taken from the direct reaction calorimetry of Yazawa and Itagaki (1969), 1373°K, x_{Cu} = 0.11-0.9. ΔH values from the direct reaction calorimetry of Oelsen and Middel (1937), 293°, 1373°K, x_{Cu} = 0.15-0.91 (see Solid Alloys) and those of Kawakami (1930), 1473°K, x_{Cu} = 0.28-0.79 are respectively 300-2300 cal/g-atom and 1700-3100 cal/g-atom more exothermic than the selected values. Temperature coefficients of Grube and Hantelman (1942) lead to ΔH values 300-1200 cal/g-atom less exothermic than the selected values. Other quantities of Tables 2 and 3 were calculated with the aid of Gibbs-Duhem integration.

Part II. Tables

TABLE 1

Integral Heats of Formation of Solid Alloys at 298°K

x_{Cu}	Phase	ΔH	x_{Cu}	Phase	ΔH
0.33	θ	-3200	0.66	γ	-5500
0.51	η_2	-4790	0.78	α_2	(-3500)
0.55	ζ	(-4950)	0.85	(Cu)	-2285
0.61	δ	-5100 (± 800)	0.9	(Cu)	-1825 (± 800)

TABLE 2

Integral Quantities for Liquid Alloys at 1373°K

$$(1-x)Al_{(\ell)} + xCu_{(\ell)} = Al_{1-x}Cu_{x(\ell)}$$

x_{Cu}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-1723	- 459	0.921	- 836	0.275
0.2	-2969	- 960	1.463	-1604	0.469
0.3	-3955	-1445	1.828	-2289	0.615
0.4	-4700	-1863	2.066	-2863	0.728
0.5	-5170 (±150)	-2163 (±150)	2.190 (±.1)	-3278 (±150)	0.812 (±.1)
0.6	-5289	-2254	2.210	-3453	0.873
0.7	-4906	-1979	2.132	-3240	0.918
0.8	-3927	-1380	1.855	-2562	0.861
0.9	-2361	- 800	1.137	-1474	0.491

TABLE 3

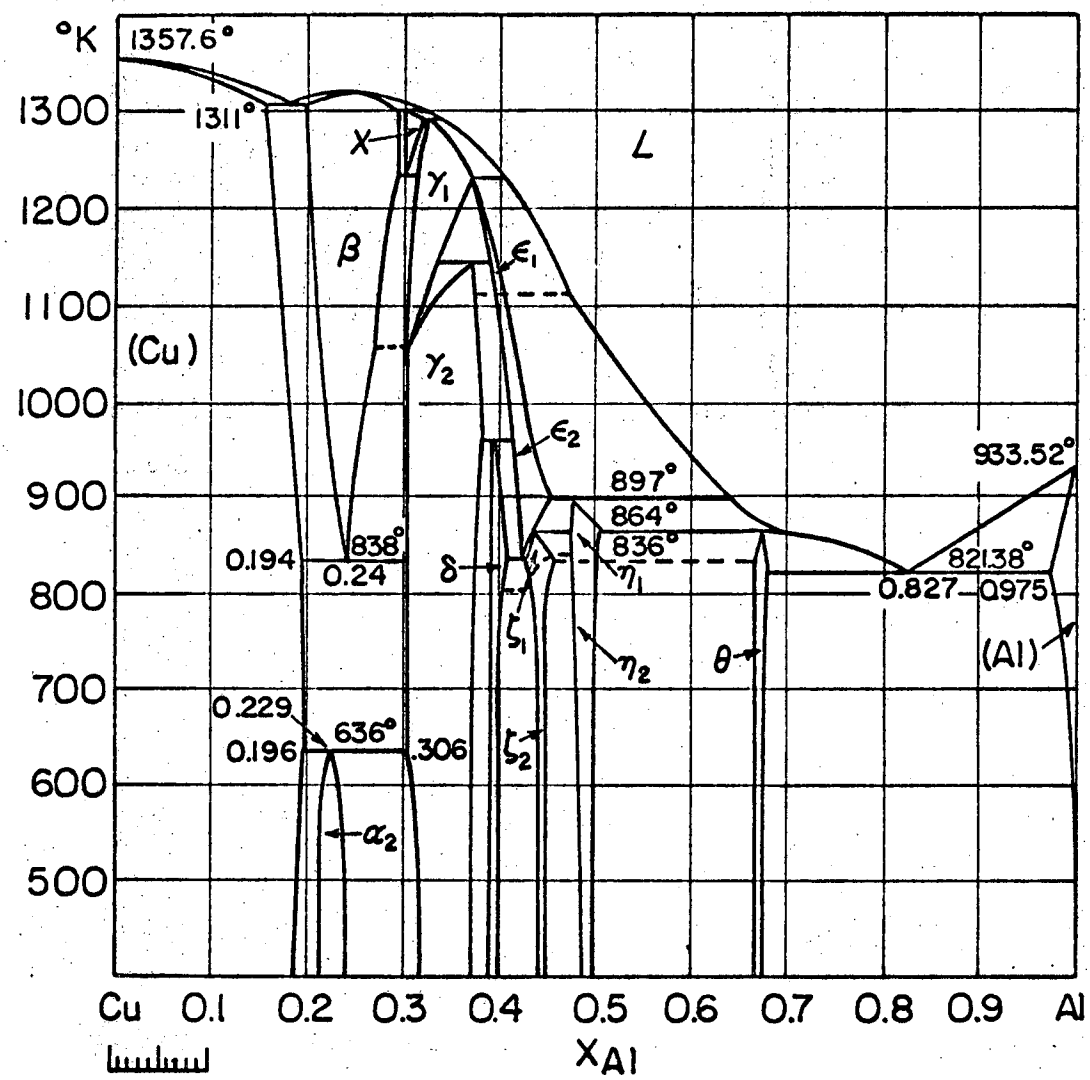
Partial Molar Quantities for Liquid Alloys at 1373°K

Al Component $Al_{(\ell)} = Al(\text{in alloy})_{(\ell)}$

x_{Al}	a_{Al}	γ_{Al}	$\Delta\bar{G}_{Al}$	$\Delta\bar{G}^{xs}_{Al}$	$\Delta\bar{H}_{Al}$	$\Delta\bar{S}_{Al}$	$\Delta\bar{S}^{xs}_{Al}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.889	0.988	- 320	- 32	29	0.254	0.044
0.8	0.759	0.949	- 753	- 144	44	0.580	0.137
0.7	0.609	0.870	- 1354	- 381	-60	0.942	0.234
0.6	0.441	0.735	- 2235	- 842	- 391	1.343	0.328
0.5	0.266	0.532	- 3611	- 1720	-1055	1.862	0.484
	(±.02)	(±.04)	(±150)	(± 150)	(±300)	(±.25)	(±.25)
0.4	0.116	0.290	- 5873	- 3373	-2878	2.181	0.361
0.3	0.028	0.095	- 9709	- 6424	-5012	3.421	1.028
0.2	0.006	0.029	-14062	- 9670	-5864	5.971	2.772
0.1	0.001	0.008	-19307	-13025	-7415	8.661	4.086
0.0	0.000	0.002	- ∞	-16640	-8625	∞	5.838

Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.0	0.000	0.042	- ∞	-8671	-4225	∞	3.238
0.1	0.005	0.052	-14349	-8067	-4849	6.919	2.344
0.2	0.013	0.065	-11833	-7442	-4975	4.995	1.797
0.3	0.025	0.084	-10025	-6741	-4675	3.897	1.505
0.4	0.046	0.115	- 8396	-5896	-4071	3.150	1.329
0.5	0.085	0.170	- 6728	-4837	-3271	2.518	1.141
	(±.005)	(±.01)	(± 150)	(±150)	(±300)	(±.25)	(±.25)
0.6	0.166	0.277	- 4900	-3506	-1838	2.230	1.215
0.7	0.352	0.503	- 2848	-1875	- 679	1.580	0.871
0.8	0.600	0.750	- 1394	- 785	- 259	0.827	0.383
0.9	0.839	0.932	- 478	- 191	- 65	0.301	0.092
1.0	1.000	1.000	0	0	0	0.000	0.000



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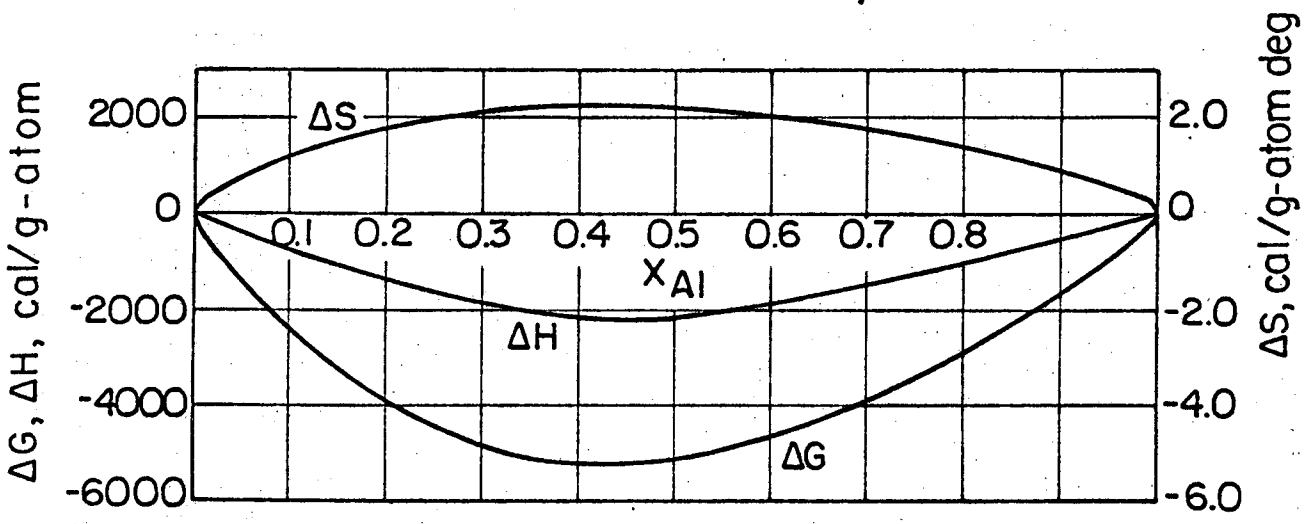

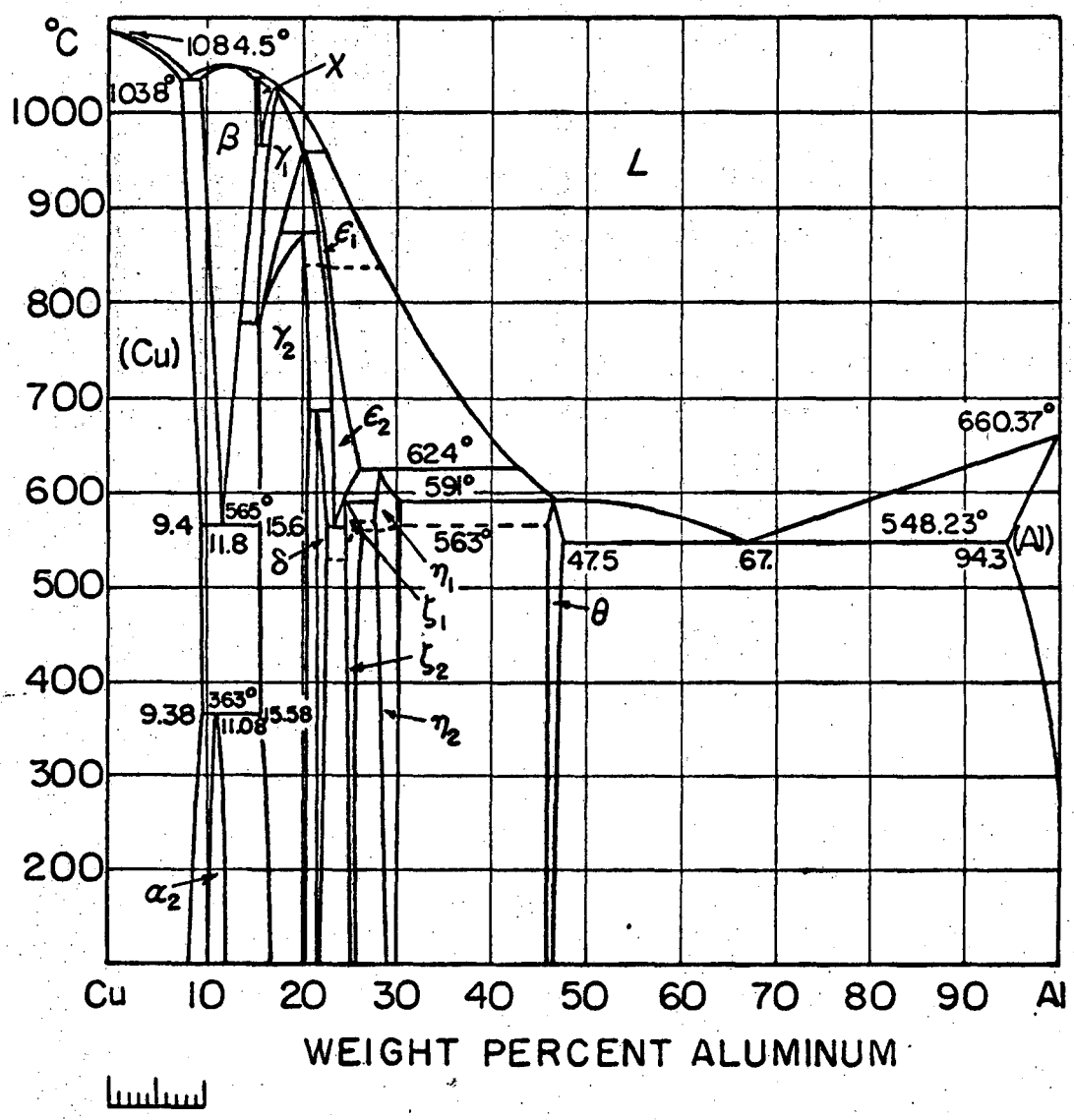
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WEIGHT PERCENT ALUMINUM

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Copper-Arsenic

Part I. Discussion

Phases and Structures. The phase diagram was taken from Elliott (1965), except for the peritectoid decomposition temperature of ϵ. Heyding and Despault (1960) fix this at 598(±25)°K instead of 653°K. Elliott (1965) overlooked the statement of this which occurs in the body of the text and not in the summary. Juza and von Benda (1968) found γ, "$As_4Cu_{9.5}$", to be unstable below 668°K. Their summary, unfortunately, does make this clear and would lead one to fix the peritectoid at T = 623(±10)°K. Pearson (1958, 1967), lists seven structures in this system of which only three occur in the phase diagram:

"As_3Cu_2", has an orthorhombic structure. It was found as a mineral but not in the phase diagram study.

"$AsCu_2$", is hexagonal "mineral or synthetic", not found in the phase diagram.

γ, "As_2Cu_5", was tentatively identified as tetragonal. However, Juza and von Benda (1968), found that this structure was metastable, produced by cooling γ faster than 3°K per minute. Their high-temperature x-ray diffraction study showed that γ is really cubic; they fixed its composition at "$As_4Cu_{9.5}$".

δ, "$AsCu_3$", has the trigonal ($D0_{21}$) structure isotypic with Cu_3P. It is isostructural with the mineral β-domeykite.

α-domeykite, "$AsCu_3$", has the bcc ($D8_6$) structure isotypic with $Cu_{15}Si_4$ except that the 12(a) sites are vacant. This structure was found as a mineral but not in the phase diagram study.

"$AsCu_6$ or $AsCu_7$", with an orthorhombic structure was found as the mineral algodonite, but not in the phase diagram study.

ϵ, "$AsCu_{8-9}$", has the hcp (A3) structure isotypic with Mg. This phase has also been said to be identical with the mineral algodonite.

Liquid Alloys. Selected values of Table 1 were taken from emf measurements of Azakami and Yazawa (1969), 1073°- 1473°K, x_{Cu} = 0.695-0.899, and from the phase diagram. For x_{Cu}>0.83, Azakami and Yazawa's results are approximately 150 cal/g-atom less exothermic than the selected values. The value of $\Delta\bar{G}_{Cu}$ at the liquidus (x_{Cu}=0.94) was calculated assuming the (Cu) phase obeyed Raoult's law; the result was referred to $Cu_{(\ell)}$ assuming for Cu that ΔS_m=2.30, invariant with T (see Cu).

PDD February, 1970

Part II. Tables

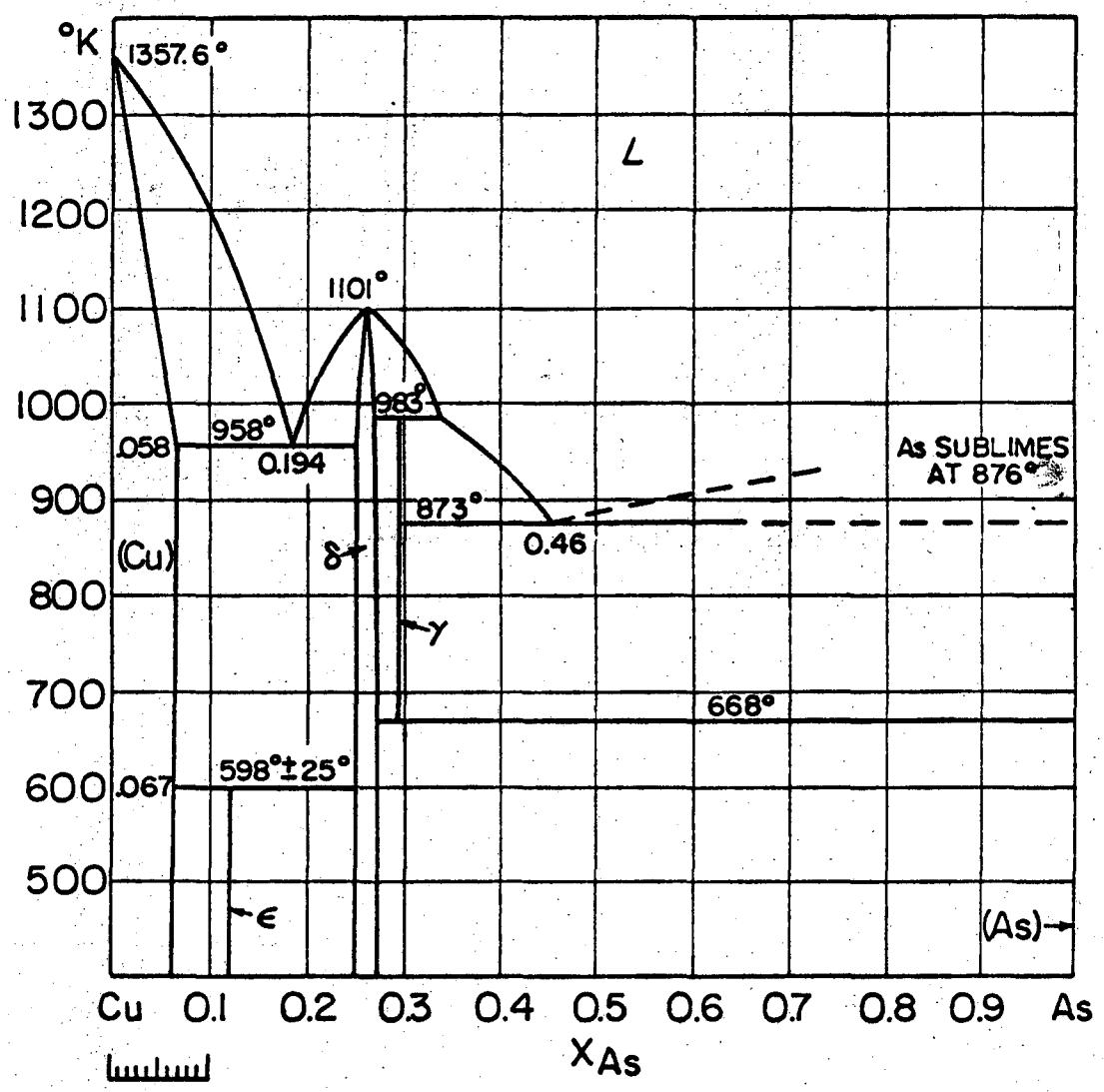
TABLE 1

Partial Molar Quantities for Liquid Alloys at 1273°K

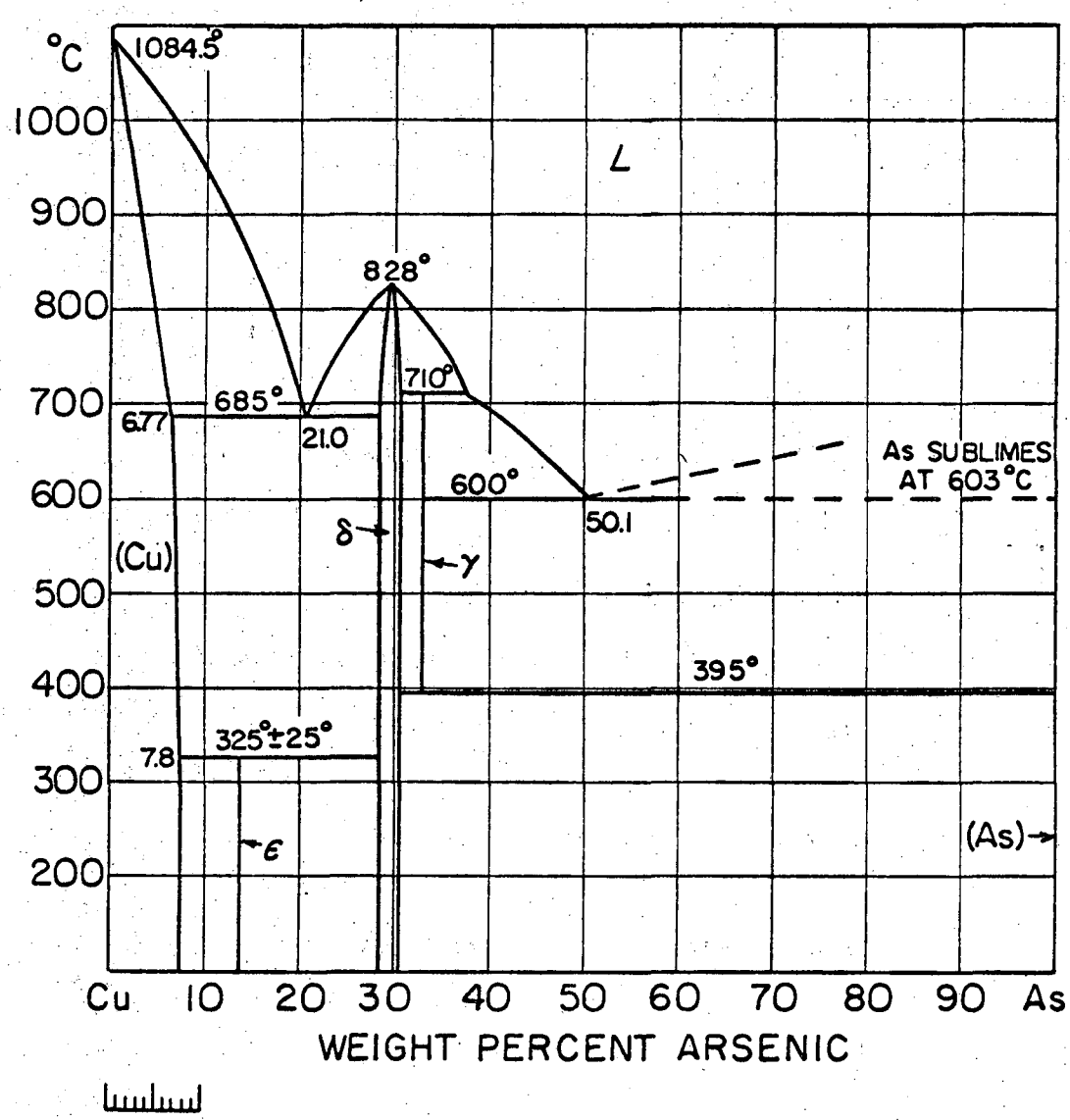
$$Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.70	0.291 (±.018)	0.415 (±.025)	-3127 (±150)	-2225 (±150)
0.80	0.557	0.696	-1482	- 918
0.90	0.828	0.920	- 478	- 211
0.94*	0.913	0.971	- 230	- 73

*Phase boundary



COPPER-ARSENIC SYSTEM



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Copper-Gold

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with modifications of temperatures from Elliott (1965) and Shunk (1969). Au and Cu form a completely miscible series of disordered solid solutions; α has the fcc (A1) structure isotypic with Cu (Pearson, 1958, 1967). At low temperatures, various orderings of the basic lattice are found; in some of them the cubic symmetry is slightly distorted to tetragonal or orthorhombic symmetry. Pearson (1958, 1967) lists the following ordered structures:

- α''', "Au_3Cu", with the ordered fcc ($L1_2$) structure isotypic with $AuCu_3$.
- α''_I, "AuCu I", with the ordered fc tetragonal ($L1_0$) prototype structure.
- α''_{II}, "AuCu II", with a fc orthorhombic structure produced by an antiphase displacement of α''_I.
- α'_I, "$AuCu_3$ I", with the ordered fcc ($L1_2$) prototype structure. Gantois (1968) claims evidence of a two phase region between α_I' and α at x_{Cu} = 0.75.
- α'_{II}, "$AuCu_3$ II", with an ordered fc tetragonal structure produced by an antiphase displacement of α'_I. The region of existence of this structure has not been adequately defined; it has been found at compositions near x_{Cu} = 0.69 in a small range of temperatures adjoining the two-phase region between α and α'_I.

Solid Alloys. Low-Temperature Data. Selected values of Table 1a agree with Cp measurements of Martin (1968), 0.4°- 2.8°K, x_{Cu}=0.75. Cp values of Rayne (1957), 1.5°- 4.2°K, x_{Cu} = 0.75, are 2-6% higher for α'_I alloys and 3-7% lower for α alloys, which would be consistent with the supposition that he had less complete order and less complete disorder in his samples than Martin. Selected values of Table 1b were taken from Cp measurements of Hawkins (1970), 25°- 300°K, x_{Cu}=0.50, and Yoon (1970), 25°- 300°K, x_{Cu} = 0.75.

High-Temperature Data. ΔH values of Table 2 agree within ±75 cal/g-atom with the tin solution calorimetric measurements of Hertz (1967), 432°- 729°K, x_{Cu}= 0.50, Orr (1960), 320°, 720°K, x_{Cu}= 0.10-0.90; Orr, Luciat-Labry, and Hultgren (1960), 318°- 872°K, x_{Cu}=0.50, and Oriani and Murphy (1958b), 652°- 684°K, x_{Cu}= 0.50. Borelius, Larsson, and Selberg (1950), 663°- 674°K, x_{Cu} = 0.5, measured the heat evolved when a disordered sample was rapidly cooled below the critical temperature and equilibrated, thus obtaining directly the heat of ordering of the alloy as a function of temperature. Their results agree with Table 2

except at 675°K, where the selected values are less exothermic by 100-150 cal/g-atom. Dependence of ΔH on T obtained from Cp measurements of Hirabayashi (1951a), 420°- 700°K, x_{Cu} = 0.36-0.64, agrees within ±100 cal/g-atom with the selected values. Other quantities of Table 2 were derived from the selected ΔH values and the ΔS_{st} from Table 1b, assuming $\Delta S_0 = 0$.

Selected ΔH values of Table 3 agree with liquid tin solution calorimetric measurements of Hertz (1966), 558°- 714°K, x_{Cu} = 0.75; Rubin, Leach, and Bever (1955), 273°K, x_{Cu} = 0.75; and Orr (1960), 320°, 720°K, x_{Cu} = 0.10-0.90. Selected Cp values agree with the variation of the selected ΔH with T; they agree closely with Cp measurements of Sykes and Jones (1936), 323°- 823°K, x_{Cu} = 0.75, except at 800°K, where the measured values are about 8% higher. Cp measurements of Hirabayashi, Nagasaki, and Kono (1957), 400°- 1150°K, x_{Cu} = 0.75, scatter about the selected values; those of Kuczynski, Doyama, and Fine (1956), 490°- 1170°K, x_{Cu} = 0.75, are generally 10-25% higher than selected values. Above 800°K, measurements of the latter two works cited show large, positive values of ΔCp (1-2 cal/deg. g-atom). Since Cp measurements at elevated temperatures are difficult, and the two works do not agree with one another, these values were not tabulated. ΔG_{800} was taken from Table 4 by interpolation. From these selections the other values of the table were calculated. The value found for ΔS_{st} agrees with Table 1b if ΔS_0 = 0.066, which is reasonable.

Selected $\Delta\bar{G}_{Cu}$ values of Table 5 agree (±200 cal/g-atom) with the emf measurements of Oriani (1954), 620°- 760°K, x_{Cu} = 0.42-0.78, and with the SO_2 equilibrium studies of Schenck and Keuth (1940), 803°K, x_{Cu} = 0.14-0.4. $\Delta\bar{G}_{Cu}$ values from emf measurements of Chiche (1952), 674°- 1121°K, x_{Cu} = 0.1-0.93 are 500-1000 cal/g-atom less exothermic than the selected values for x_{Cu}<0.525, and scatter about the selected values at higher Cu concentrations, tending to be up to 250 cal/g-atom less exothermic; those of Wagner and Engelhardt (1932) are about 50-900 cal/g-atom less exothermic; and those of Weibke and Quadt (1939) are 80-250 cal/g-atom less exothermic than the selected values. Values of Balesdent and Dode (1954), 800°- 1150°K, x_{Cu} = 0.19-0.49, measured by studying the reduction of Cu_2S by H_2 in the presence of Au, are 150-650 cal/g-atom more exothermic than the selected values. Nesmeyanov, Smakhtin, and Lebedev (1957), 1100°- 1300°K, x_{Cu} = 0.0-1.0, measured vapor pressures of both Au and Cu over Au-Cu alloys. Their $\Delta\bar{G}_{Au}$ values agree well for Au-rich alloys (x_{Cu}<0.1), but are 400-2500 cal/g-atoms less exothermic than the selected values for Cu-rich alloys. Their $\Delta\bar{G}_{Cu}$ values are about 1000 cal/g-atom less exothermic than the selected values. Au vapor pressure measurements of Hall (1951) 1003°- 1219°K, x_{Cu} = 0.0-0.9, lead to $\Delta\bar{G}_{Au}$ values which are 100-3000 cal/g-atom less exothermic than the selected values.

Selected ΔH values of Table 4 agree well with the liquid tin solution calorimetric measurements of Orr (1960); and Oriani and Murphy (1958a), 691°- 708°K, x_{Cu} = 0.15, 0.5, and 0.75. ΔH values calculated by Oriani (1954) from temperature coefficients of his emf measurements and by the Gibbs-Duhem integration tend to be 200-250 cal/g-atom more exothermic than the selected values. Other values in Tables 4 and 5 were calculated with the aid of the Gibbs-Duhem integration.

Selected $\Delta\bar{G}_{Cu}$ values of Table 7 agree with the emf measurements of Oriani (1954), 620°- 760°K, x_{Cu} = 0.42-0.78. Emf measurements of Weibke and Quadt (1939), 623°- 823°K, x_{Cu} = 0.15-0.95; and Wagner and Engelhardt (1932), 662°- 878°K, x_{Cu} = 0.14-0.92, are about 250-400 cal/g-atom less exothermic than the selected values for $x_{Cu} < 0.71$. Other quantities of Tables 6 and 7 were calculated with the aid of the Gibbs-Duhem integration.

Values of Table 8 agree with the measurements of d'Heurle and Gordon (1961), 351°- 496°K, x_{Cu} = 0.275, who measured the heat evolved as a function of time at various temperatures as their sample became ordered, thus obtaining directly the heat of ordering as a function of temperature. Hirabayashi (1951b), 290°- 590°K, x_{Cu} = 0.26, made Cp measurements on a sample slowly cooled and annealed below the temperature of disordering. ΔH_{ord} calculated from his Cp values agrees well with the selected value, but his transformation temperature is ~ 50° higher than that selected, suggesting that his heating rate was too high.

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 10 agree (±350 cal/g-atom) with the values calculated from the Cu vapor pressure measurements of Edwards and Brodsky (1956), 1500°- 1600°K, x_{Cu} = 0.05-0.95; with the emf measurements of Oriani (1956), 1205°- 1310°K, x_{Cu} = 0.15-0.85; and with the mass spectrometric vapor pressure measurements of Neckel and Wagner (1969), 1449°, 1754°K, x_{Cu} = 0.05-0.95 except that the values of Oriani (1956) at x_{Cu} = 0.22 and 0.32 are 1000 and 1500 cal/g-atom less exothermic than the selected values. $\Delta\bar{G}_{Cu}$ values calculated from the oxidation decomposition pressure studies of Meier (1935), 1273°K, x_{Cu} = 0.23-0.31, are about 400-450 cal/g-atom less exothermic than the selected values, while mass spectrometric measurements of Hager, Howard, and Jones (1970), 1823°K, x_{Cu} = 0.1-0.9; and Schmahl and Minzl (1965), 1273°K, x_{Cu} = 0.17-0.35 are highly exothermic. $\Delta\bar{G}_{Cu}$ values were compared with selected values by extrapolating to 1550°K where necessary, using selected $\Delta\bar{S}_{Cu}$ values of Table 10. Selected ΔH values of Table 9 agree well with the direct calorimetric measurements of Yazawa and Itagaki (1969), 1373°K, x_{Cu} = 0.11-0.9. Direct calorimetric measurements of Kawakami (1930), 1473°K, x_{Cu} = 0.26-0.52, are 1000 cal/g-atom less exothermic than the selected values. ΔH values calculated from the ΔG values of Neckel and Wagner (1969) and from their temperature coefficients are much more exothermic than the selected values for $x_{Cu} \leq 0.7$; and less exothermic at higher Cu concentrations. Other quantities in Tables 9 and 10 were calculated with the aid of the Gibbs-Duhem integration.

Part II. Tables

TABLE 1

Low-Temperature Data for Solid Alloys

Table 1a

T, °K	x_{Cu}=0.75	
	α'_I-Phase	α-Phase
	Cp	
0.4	0.0000641	0.0000754
0.5	0.0000809	0.0000936
1.0	0.000176	0.000186
2.0	0.000472	0.000514
3.0	0.00101	0.00113
4.0	0.00190	0.00217

$C_{(electronic)} = \gamma T$ α'_I-Phase: $\gamma = 1.561(\pm 0.03)\times 10^{-4}$

α-Phase: $\gamma = 1.618(\pm 0.03)\times 10^{-4}$

Table 1b

T, °K	x_{Cu}=0.50		x_{Cu}=0.75	
	α'_I-Phase	α-Phase	α'_I-Phase	α-Phase
	Cp		Cp	
20	0.453	0.496	0.284	0.302
25	0.779	0.817	0.509	0.533
30	1.140	1.173	0.771	0.801
40	1.854	1.896	1.398	1.434
50	2.507	2.554	2.044	2.069
75	3.807	3.852	3.349	3.409
100	4.566	4.570	4.234	4.261
150	5.315	5.276	5.101	5.092
200	5.620	5.585	5.461	5.455
250	5.797	5.774	5.690	5.670
298.15	5.920	5.895	5.856	5.835
	x_{Cu}=0.50		x_{Cu}=0.75	
	α'_I-Phase	α-Phase	α'_I-Phase	α-Phase
$S_{st}-S_0$	9.791	9.886	8.880	8.945
$\Delta S_t-\Delta S_0$	0.155	0.250	0.100	0.165
$H_{st}-H_0$	1325	1323	1258	1259
$\Delta H_{st}-\Delta H_0$	14	16	2	3

TABLE 2

Integral Quantities for Solid Alloy as a Function of Temperature, $x_{Cu}=0.50$

$$0.5Au_{(s)} + 0.5Cu_{(s)} = Au_{0.5}Cu_{0.5(s)}$$

T, °K	Cp	H_T-H_{st}	S_T-S_{st}	ΔCp	ΔG_T	ΔH_T	ΔS_T
298.15	5.920	0	0.000	-0.025	-2135	-2089	0.155
400	6.093	612	1.764	0.000	-2151	-2089	0.155
500	6.226	1228	3.139	0.000	-2166	-2089	0.155
520	6.252	1353	3.384	0.000	-2170	-2089	0.155
540	6.276	1479	3.621	0.000	-2173	-2089	0.155
560	6.480	1606	3.853	0.180	-2176	-2089	0.155
580	6.773	1738	4.084	0.450	-2177	-2083	0.163
600	7.161	1877	4.320	0.810	-2182	-2071	0.185
620	8.540	2030	4.570	2.171	-2186	-2045	0.227
640	10.991	2226	4.881	4.600	-2191	-1977	0.335
653(α'')	12.280	2376	5.114	5.874	-2197	-1910	0.440
658(α''_{II})	12.880	2439	5.210	6.469	-2199	-1879	0.487
683(α''_{II})	16.937	2808	5.759	10.499	-2220	-1670	0.806
683(α)	9.237	3143	6.249	2.799	-2220	-1335	1.296
700	8.640	3294	6.468	2.180	-2236	-1294	1.346
750	7.080	3686	7.010	0.524	-2324	-1243	1.442
800	6.571	4019	7.440	0.000	-2379	-1221	1.448
900	6.693	4682	8.220	0.000	-2524	-1221	1.448

at 683°K $\Delta H_{\alpha''_{II}-\alpha} = 335(\pm 50)$ $\Delta S_{\alpha''_{II}-\alpha} = 0.490(\pm 0.073)$

TABLE 3

Integral Quantities for Solid Alloy as Function of Temperature, $x_{Cu} = 0.75$

$$0.25Au_{(s)} + 0.75Cu_{(s)} = Au_{0.25}Cu_{0.75(s)}$$

T, °K	Cp	$H_T - H_{st}$	$S_T - S_{st}$	ΔCp	ΔG_T	ΔH_T	ΔS_T
298.15	5.893	0	0.000	0.000	-1759	-1710	0.166
400	6.085	610	1.758	0.019	-1776	-1709	0.167
500	6.320	1229	3.141	0.111	-1795	-1705	0.180
600	7.590	1906	4.371	1.253	-1815	-1655	0.267
640	9.900	2242	4.912	3.515	-1828	-1573	0.398
653	12.100	2385	5.136	5.699	-1836	-1513	0.494
663(α'_I)	13.500	2512	5.326	7.089	-1838	-1450	0.586
663(α)	7.611	2798	5.757	1.200	-1838	-1164	1.017
680	7.429	2926	5.948	0.999	-1857	-1146	1.045
700	7.275	3073	6.160	0.819	-1876	-1128	1.069
750	7.049	3430	6.653	0.539	-1932	-1094	1.117
800	6.981	3780	7.015	0.410	-1987	-1071	1.145

TABLE 4

Integral Quantities for Solid Alloys at 800°K

$$(1-x)Au_{(s)} + xCu_{(s)} = Au_{1-x}Cu_{x(\alpha)}$$

x_{Cu}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	- 844	- 290	0.693	- 327	0.047
0.2	-1436	- 582	1.068	- 641	0.073
0.3	-1890	- 854	1.295	- 919	0.081
0.4	-2208	-1074	1.417	-1138	0.080
0.5	-2379	-1221	1.448	-1277	0.070
	(±200)	(±75)	(±.27)	(±200)	(±.27)
0.6	-2385	-1279	1.382	-1315	0.045
0.7	-2184	-1189	1.245	-1213	0.031
0.8	-1720	- 894	1.032	- 924	0.037
0.9	-1004	- 440	0.705	- 488	0.059

TABLE 5

Partial Molar Quantities for Solid Alloys at 800°K

Au Component $Au_{(s)} = Au\,(\text{in alloy})_{(\alpha)}$

x_{Au}	a_{Au}	γ_{Au}	ΔG_{Au}	$\Delta\bar{G}^{xs}_{Au}$	$\Delta\bar{H}_{Au}$	$\Delta\bar{S}_{Au}$	$\Delta\bar{S}^{xs}_{Au}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.898	0.998	- 171	- 3	7	0.222	0.012
0.8	0.779	0.974	- 397	- 42	- 11	0.482	0.039
0.7	0.632	0.903	- 729	- 162	- 101	0.784	0.076
0.6	0.465	0.775	-1218	- 405	- 322	1.119	0.104
0.5	0.299	0.598	-1919	- 817	- 677	1.552	0.175
	(±.035)	(±.07)	(±200)	(±200)	(±150)	(±.31)	(±.31)
0.4	0.160	0.400	-2915	-1458	-1343	1.965	0.144
0.3	0.061	0.204	-4440	-2526	-2487	2.441	0.049
0.2	0.016	0.082	-6526	-3968	-4115	3.014	-0.184
0.1	0.005	0.050	-8417	-4757	-4666	4.689	0.114
0.0	0.000	0.045	- ∞	-4935	-3920	∞	1.269

Cu Component $Cu_{(s)} = Cu\,(\text{in alloy})_{(\alpha)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.0	0.000	0.128	- ∞	-3270	-2780	∞	0.612
0.1	0.013	0.130	-6905	-3245	-2956	4.936	0.360
0.2	0.030	0.148	-5593	-3035	-2867	3.408	0.210
0.3	0.055	0.185	-4598	-2684	-2609	2.486	0.094
0.4	0.078	0.245	-3694	-2201	-2237	1.865	0.044
0.5	0.168	0.335	-2839	-1737	-1765	1.343	-0.034
	(±.02)	(±.04)	(±200)	(±200)	(±150)	(±.31)	(±.31)
0.6	0.279	0.464	-2031	-1219	-1237	0.993	-0.022
0.7	0.465	0.664	-1218	- 651	- 632	0.732	0.023
0.8	0.722	0.902	- 518	- 164	- 89	0.536	0.093
0.9	0.893	0.992	- 181	- 13	29	0.263	0.053
1.0	1.000	1.000	0	0	0	0.000	0.000

TABLE 6

Integral Quantities for Ordered Solid Alloys at 653°K

$$(1-x)Au_{(s)} + xCu_{(s)} = Au_{1-x}Cu_{x(s)}$$

x_{Cu}	Phase	ΔG	ΔG^{xs}	x_{Cu}	Phase	ΔG	ΔG^{xs}
0.448*	α''_{II}	-2106	-1213	0.514*	α''_{II}	-2202	-1303
0.486*	α''_{II}	-2172	-1273	0.561*	α''_{II}	-2210	-1320
0.491*	α''_{I}	-2179	-1280	0.720*	α'_{I}	-1945	-1175
0.500		-2197	-1298	0.750		-1836	-1105
		(±200)	(±200)	0.761*	α'_{I}	-1786	-1073
0.510*	α''_{I}	-2199	-1300				

TABLE 7

Partial Molar Quantities for Ordered Solid Alloys at 653°K

	Au Component $Au_{(s)} = Au(\text{in alloy})_{(s)}$					Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(s)}$			
x_{Cu}	Phase	a_{Au}	γ_{Au}	$\Delta\bar{G}_{Au}$	$\Delta\bar{G}^{xs}_{Au}$	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.448*	α''_{II}	0.399	0.722	-1193	- 422	0.083	0.185	-3230	-2188
0.486*	α''_{II}	0.324	0.630	-1464	- 601	0.105	0.217	-2920	-1984
0.491*	α''_{I}	0.324	0.636	-1464	- 588	0.105	0.215	-2920	-1997
0.500		0.279	0.558	-1654	- 755	0.121	0.242	-2740	-1841
		(±.04)	(±.08)	(±200)	(±200)	(±.017)	(±.035)	(±200)	(±200)
0.510*	α''_{I}	0.238	0.485	-1865	- 940	0.143	0.281	-2520	-1646
0.514*	α''_{II}	0.238	0.489	-1865	- 929	0.143	0.279	-2520	-1656
0.561*	α''_{II}	0.156	0.355	-2413	-1345	0.206	0.367	-2052	-1300
0.720*	α'_{I}	0.038	0.135	-4245	-2593	0.445	0.618	-1050	- 624
0.750		0.022	0.088	-4959	-3158	0.542	0.723	- 794	- 421
0.761*	α'_{I}	0.018	0.074	-5246	-3389	0.583	0.766	- 700	- 346

*Phase boundary.

TABLE 8

Heat of Ordering of Solid Alloy, $x_{Cu} = 0.275$

$$Au_{0.725}Cu_{0.275}(\alpha) = Au_{0.725}Cu_{0.275}(\alpha')$$

T, °K	ΔH
360	-315
400	-289
450	-178
483*	- 37
500	- 16

*Critical Temperature

TABLE 9

Integral Quantities for Liquid Alloys at 1550°K

$$(1-x)\,Au_{(\ell)} + xCu_{(\ell)} = Au_{1-x}Cu_x(\text{in alloy})_{(\ell)}$$

x_{Cu}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-1519	- 343	0.758	- 518	0.113
0.2	-2461	- 625	1.185	- 920	0.190
0.3	-3089	- 839	1.452	-1207	0.238
0.4	-3453	- 980	1.595	-1380	0.258
0.5	-3572	-1044	1.631	-1437	0.254
	(±400)	(±100)	(±.27)	(±400)	(±.27)
0.6	-3453	-1024	1.567	-1380	0.230
0.7	-3089	- 915	1.403	-1208	0.189
0.8	-2461	- 711	1.129	- 920	0.135
0.9	-1519	- 408	0.716	- 518	0.071

TABLE 10

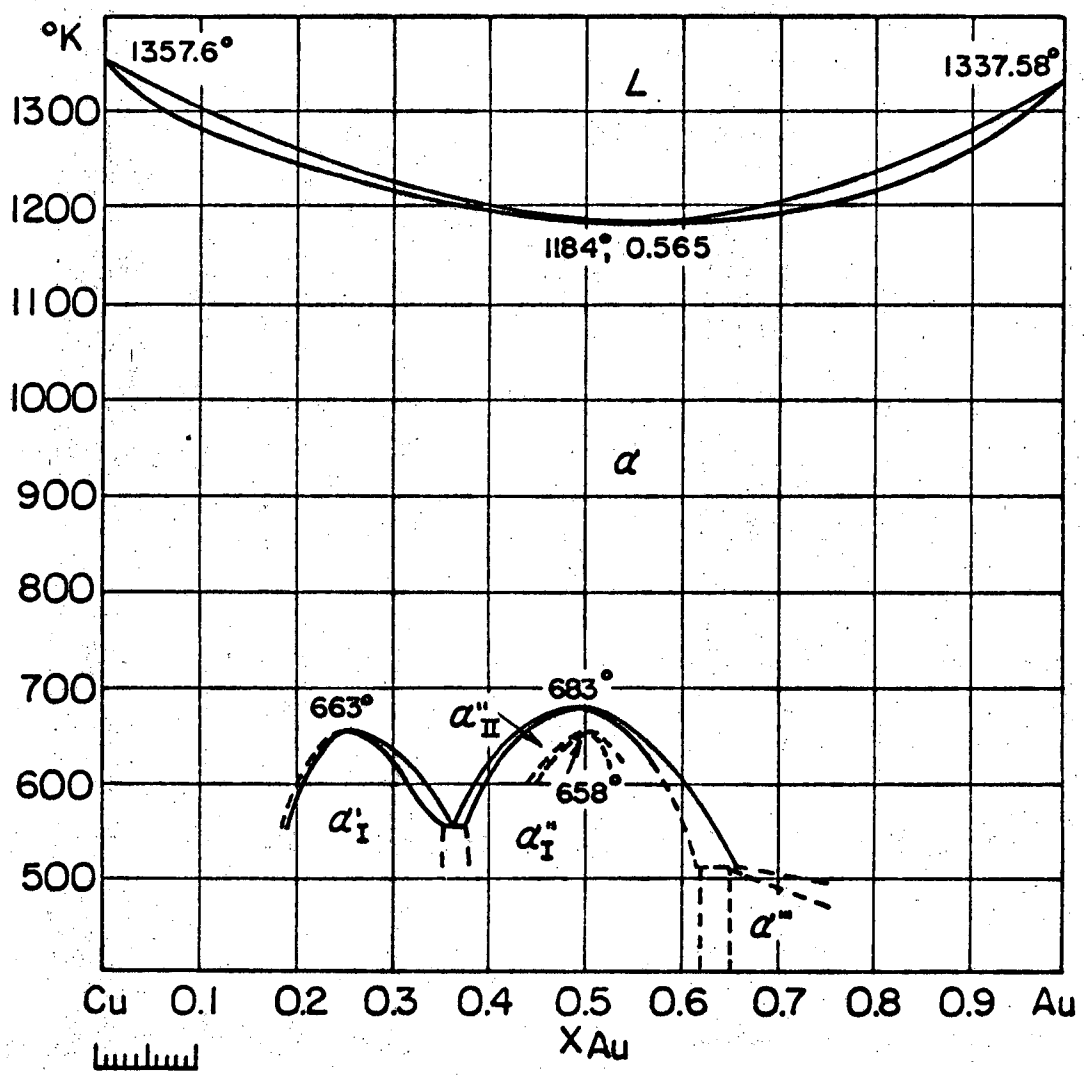
Partial Molar Quantities for Liquid Alloys at 1550°K

Au Component $Au_{(\ell)} = Au(\text{in alloy})_{(\ell)}$

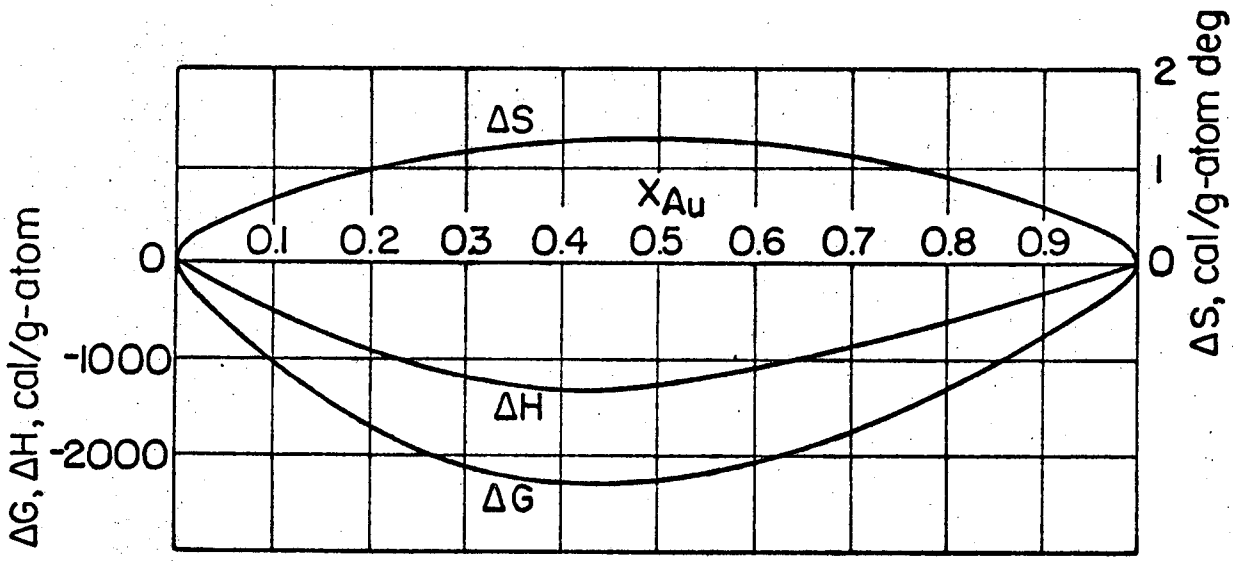
x_{Au}	a_{Au}	γ_{Au}	$\Delta\bar{G}_{Au}$	$\Delta\bar{G}^{xs}_{Au}$	$\Delta\bar{H}_{Au}$	$\Delta\bar{S}_{Au}$	$\Delta\bar{S}^{xs}_{Au}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.883	0.982	- 382	- 58	- 30	0.227	0.018
0.8	0.742	0.928	- 917	- 230	- 127	0.510	0.066
0.7	0.592	0.845	- 1616	- 518	- 303	0.847	0.138
0.6	0.445	0.742	- 2493	- 920	- 567	1.243	0.228
0.5	0.314	0.627	- 3572	-1437	- 931	1.704	0.327
	(±.04)	(±.08)	(±400)	(±400)	(±200)	(±.3)	(±.3)
0.4	0.204	0.511	- 4892	-2070	-1406	2.249	0.428
0.3	0.120	0.401	- 6526	-2817	-2002	2.919	0.526
0.2	0.061	0.303	- 8637	-3680	-2730	3.811	0.613
0.1	0.022	0.220	-11750	-4657	-3600	5.258	0.682
0.0	0.000	0.155	- ∞	-5750	-4625	∞	0.726

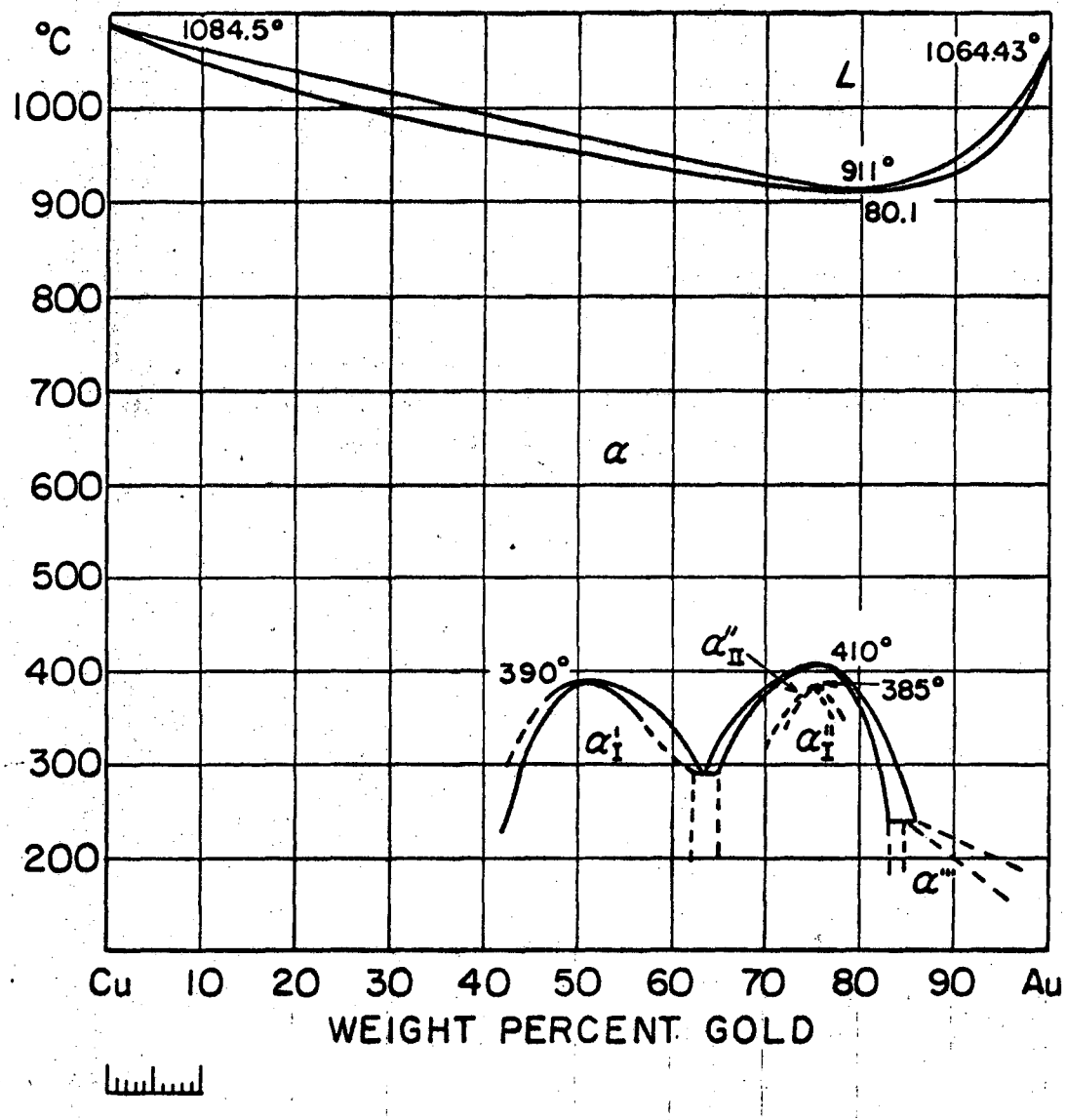
Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.0	0.000	0.155	- ∞	-5750	-3725	∞	1.306
0.1	0.022	0.220	-11750	-4657	-3163	5.540	0.964
0.2	0.061	0.303	- 8637	-3680	-2614	3.886	0.687
0.3	0.120	0.401	- 6526	-2817	-2090	2.862	0.469
0.4	0.204	0.511	- 4892	-2070	-1600	2.124	0.303
0.5	0.314	0.627	- 3572	-1437	-1156	1.559	0.181
	(±.04)	(±.08)	(±400)	(±400)	(±200)	(±.3)	(±.3)
0.6	0.445	0.742	- 2493	- 920	- 769	1.113	0.097
0.7	0.592	0.845	- 1616	- 518	- 449	0.753	0.044
0.8	0.742	0.928	- 917	- 230	- 207	0.458	0.015
0.9	0.883	0.982	- 382	- 58	- 53	0.212	0.003
1.0	1.000	1.000	0	0	0	0.000	0.000



COPPER-GOLD SYSTEM - 800°K

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1084.5°
1064.43°
L
911°
80.1
1000
900
800
700
600
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400
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200
α
390°
α''II
410°
385°
α'I
α''I
α'''
Cu 10 20 30 40 50 60 70 80 90 Au
WEIGHT PERCENT GOLD

Part III. References

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Copper-Beryllium

Part I. Discusssion

Phases and Structures. The phase diagram, from Hansen (1958), Elliott (1965), and Shunk (1969), has been modified to more accurate solid phase boundaries as given by Jacobson and Hammond (1968). The eutectic of (β-Be) and δ has been assumed without direct experimental evidence. Pearson (1958) lists the following intermediate phases:

δ, "Be_2Cu", with the ordered fcc (C15) structure isotypic with Cu_2Mg. However, Magomedova and Davydov (1966) report that "Be_3Cu" has a "hcp structure, like $CuZn_3$", (ϵ-brass).

β', "γ-BeCu", with the ordered bcc (B2) structure isotypic with CsCl.

β, "β-$BeCu_2$", with the disordered bcc (A2) structure isotypic with W.

β' remains ordered as high as 743°K; its disordering temperature, if any, is not known.

Solid Alloys. Selected values of $\Delta\bar{G}_{Be}$ of Table 3 were derived from the emf measurements of Anfinogenov, Smirnov, Ilushchenko, and Belyaeva (1962), 983°- 1108°K, x_{Cu} = 0.004-0.98, corrected to agree with the phase diagram. The measurements scatter considerably and indicate different solid phase boundaries. Other values of Tables 2 and 3 were calculated using Gibbs-Duhem integration.

Liquid Alloys. Selected values for Table 1 were calculated from Bienvenu, Potard, Schaub, and Desré, (1968), 1623°K, x_{Be}~1.00, who measured the distribution coefficient of Cu between $Be_{(l)}$ and $Pb_{(l)}$. However, the selected γ_{Cu}, x_{Pb} = 1.00 was used (see Cu-Pb) rather than the value, 3.18, used by the authors.

Part II. Tables

TABLE 1

Partial Molar Quantities for Liquid Alloys at 1623°K

$Cu_{(l)}$ = Cu(in alloy)$_{(l)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.00	0.000	1.144 (±.2)	-∞	434 (±600)

PDD October, 1969

TABLE 2

Integral Quantities for Solid Alloys at 1073°K

$$(1-x)Be_{(\alpha)} + xCu_{(s)} = Be_{1-x}Cu_{x(s)}$$

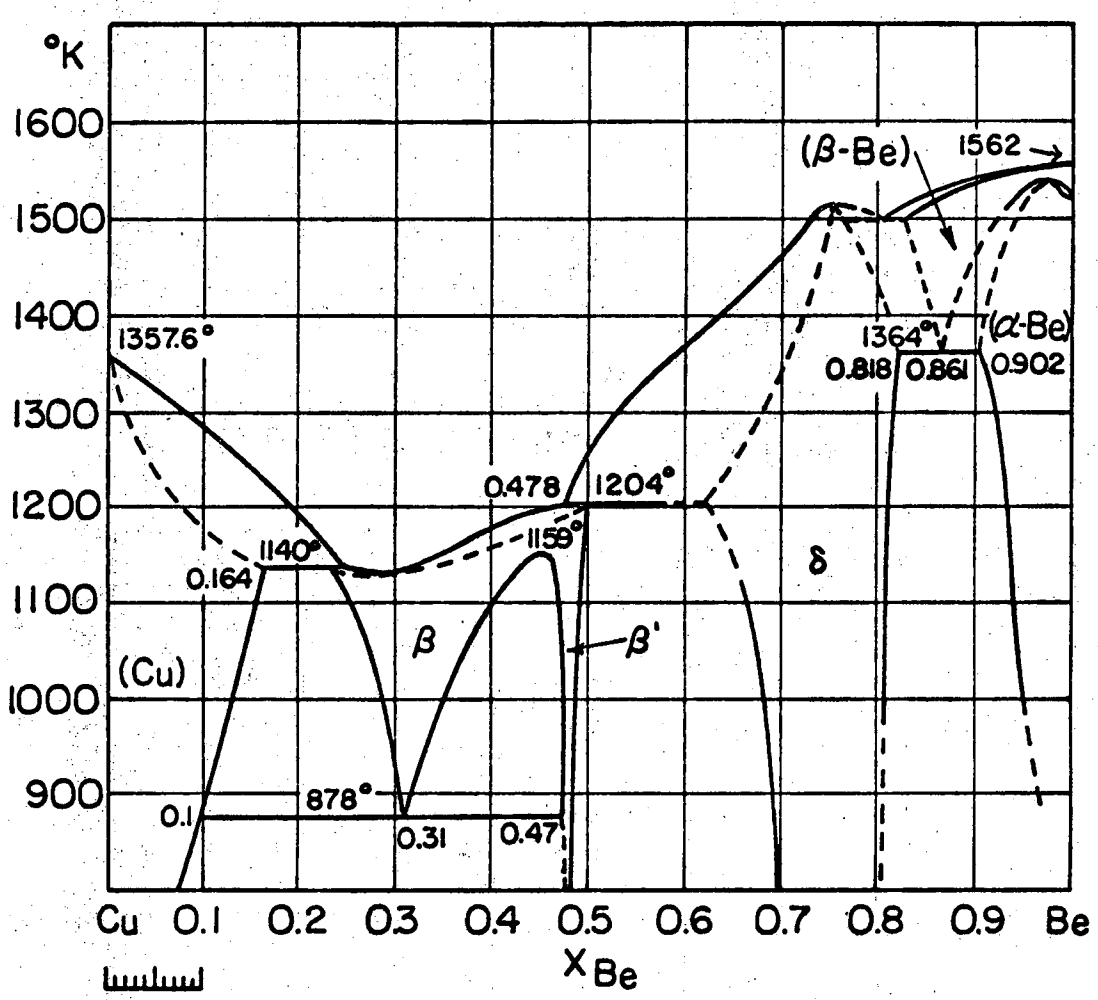
x_{Cu}	Phase	ΔG	ΔG^{xs}	x_{Cu}	Phase	ΔG	ΔG^{xs}
0.057*	(α-Be)	-1290	- 824	0.616*	β	-3407	-1987
				0.65		-3336	-1955
0.191*	δ	-3617	-2578	0.736*	β	-3029	-1798
0.25		-3795	-2596				
0.324*	δ	-3751	-2408	0.851*	(Cu)	-2189	-1292
				0.90*	(Cu)	-1788	-1095
0.509*	β'	-3609	-2131				
0.519*	β'	-3595	-2118				
		(±800)	(±800)				

TABLE 3

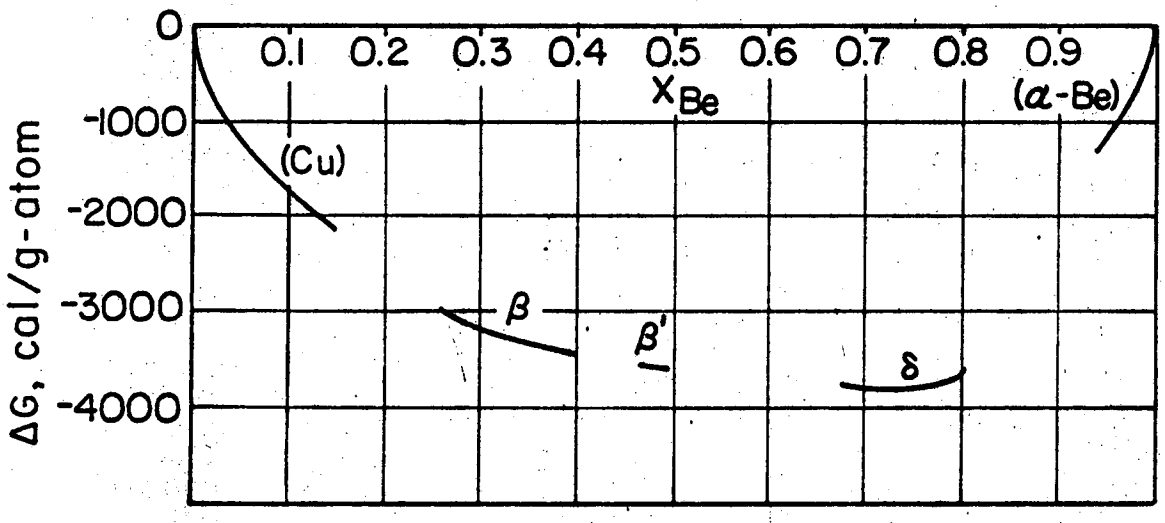
Partial Molar Quantities for Solid Alloys at 1073°K

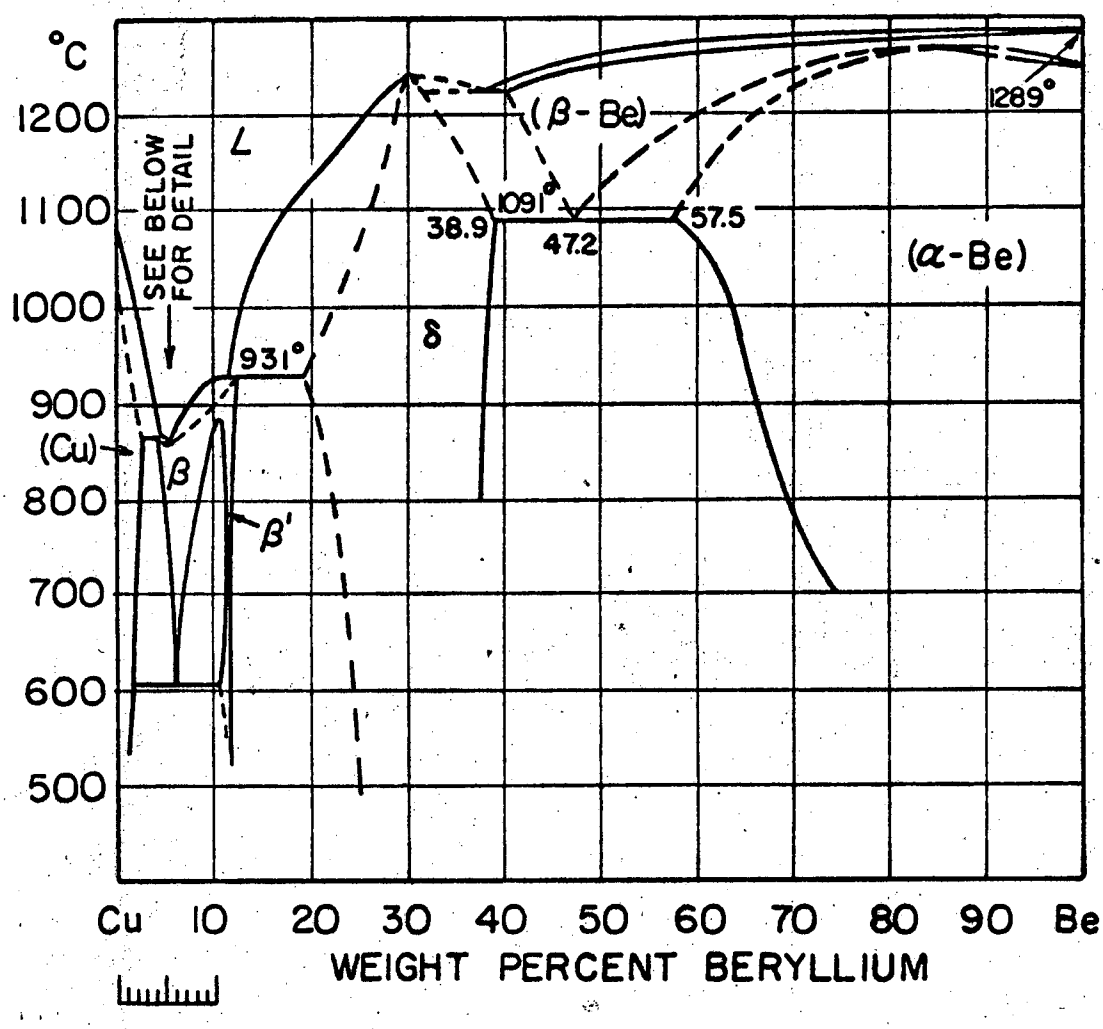
		Be Component $Be_{(\alpha)}$ = Be(in alloy)$_{(s)}$				Cu Component $Cu_{(s)}$ = Cu(in alloy)$_{(s)}$			
x_{Cu}	Phase	a_{Be}	γ_{Be}	$\Delta\bar{G}_{Be}$	$\Delta\bar{G}^{xs}_{Be}$	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.000	(α-Be)	1.000	1.000	0	0	0.000	0.000	$-\infty$	-18962
0.057*	(α-Be)	0.868	0.921	- 300	- 175	0.000	0.004	-17668	-11560
0.191*	δ	0.868	1.073	- 300	152	0.000	0.001	-17668	-14139
0.25		0.164	0.219	- 3850	- 3237	0.182	0.728	- 3628	- 672
0.324*	δ	0.153	0.227	- 4000	- 3165	0.220	0.678	- 3231	- 828
0.509*	β'	0.153	0.312	- 4000	- 2483	0.220	0.432	- 3231	- 1791
0.519*	β'	0.116	0.241	- 4600	- 3039	0.286	0.553	- 2664	- 1265
		(±.04)	(±.07)	(±800)	(±800)	(±.09)	(±.2)	(±800)	(±800)
0.616*	β	0.116	0.301	- 4600	- 2559	0.286	0.465	- 2664	- 1631
0.65		0.105	0.299	- 4810	- 2571	0.306	0.471	- 2543	- 1624
0.736*	β	0.020	0.074	- 8400	- 5561	0.597	0.811	- 1102	- 448
0.851*	(Cu)	0.020	0.131	- 8400	- 4341	0.597	0.701	- 1102	- 758
0.90		0.007	0.073	-10500	- 5591	0.681	0.757	- 820	- 595
1.00	(Cu)	0.000	0.000	$-\infty$	-18000	1.000	1.000	0	0

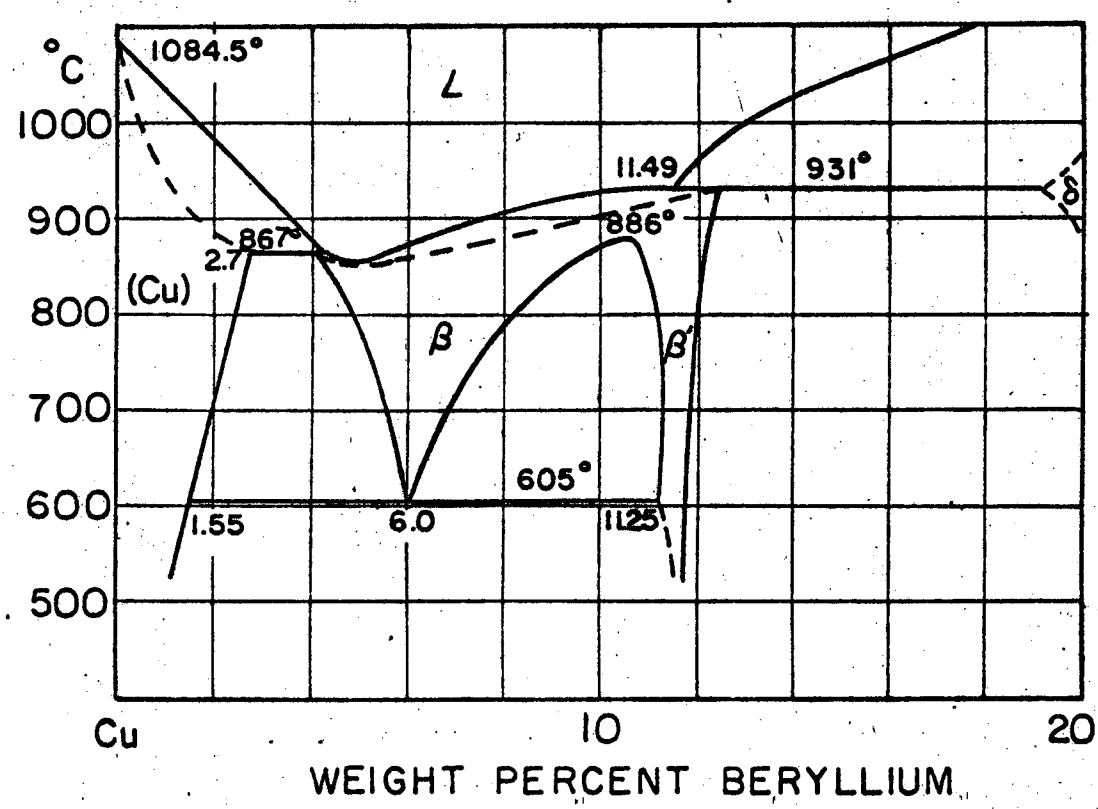
*Phase boundary



COPPER BERYLLIUM SYSTEM, 1073 °K




°C
1200
1100
1000
900
800
700
600
500
L
SEE BELOW FOR DETAIL
(β-Be)
1289°
1091°
38.9
47.2
57.5
(α-Be)
δ
931°
(Cu)
β
β'
Cu 10 20 30 40 50 60 70 80 90 Be
WEIGHT PERCENT BERYLLIUM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L
1000
900
800
700
600
500
11.49
931°
δ
867°
886°
2.7
(Cu)
β
β'
605°
1.55
6.0
11.25
Cu 10 20
WEIGHT PERCENT BERYLLIUM

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Copper-Bismuth

Part I. Discussion

Phases and Structures. The simple eutectic phase diagram was taken from Hansen (1958) with improved precision of the liquidus from Nathans and Leider (1962).

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values agree within ±100 cal/g-atom with emf measurements of Lomov and Krestovnikov (1964), 1115°- 1215°K, x_{Cu} = 0.045-0.70; while they are less exothermic by 0-150 cal/g-atom than the values of Nikol'skaya, Lomov, and Gerasimov (1959), 1150°- 1225°K, x_{Cu} = 0.063-0.71, except at x_{Cu} = 0.71, where their value is more exothermic by 320 cal/g-atom. $\Delta\bar{G}_{Bi}$ values from the vapor pressure measurements of Azakami and Yazawa (1967), 1173°- 1473°K, x_{Cu} = 0.2-0.8 when extrapolated to 1200°K using selected $\Delta\bar{S}_{Bi}$ are more exothermic by 50-150 cal/g-atom than selected values.

$\Delta\bar{S}_{Cu}$ values were calculated from the selected $\Delta\bar{G}_{Cu}$ and the phase diagram; the remaining partial and integral values were calculated from Gibbs-Duhem integration. The resultant ΔH values are in most cases more exothermic by 0-200 cal/g-atom than the experimental values of Oelsen, Schürmann, and Buchholz (1961), 1416°K, x_{Cu} = 0.1-0.9; while the direct calorimetric measurements of Kawakami (1930), 1473°K, x_{Cu} = 0.24-0.77, scatter (±200 cal/g-atom) about the selected values except for $x_{Cu} > 0.5$, where they are more exothermic by 0-350 cal/g-atom.

Part II. Tables

TABLE 1

Integral Quantities for Liquid Alloys at 1200°K

$$(1-x)Bi_{(\ell)} + xCu_{(\ell)} = Bi_{1-x}Cu_{x(\ell)}$$

x_{Cu}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-522	468	0.825	254	0.179
0.2	-738	806	1.287	455	0.293
0.3	-849	1052	1.584	608	0.370
0.4	-895	1207	1.752	710	0.415
	(±100)	(±200)	(±.2)	(±100)	(±.2)
0.5	-894	1280	1.812	759	0.435
0.6	-854	1295	1.791	751	0.454
0.7	-772	1224	1.663	685	0.448
0.78*	-675	1073	1.457	581	0.410

*Phase boundary

TABLE 2

Partial Molar Quantities for Liquid Alloys at 1200°K

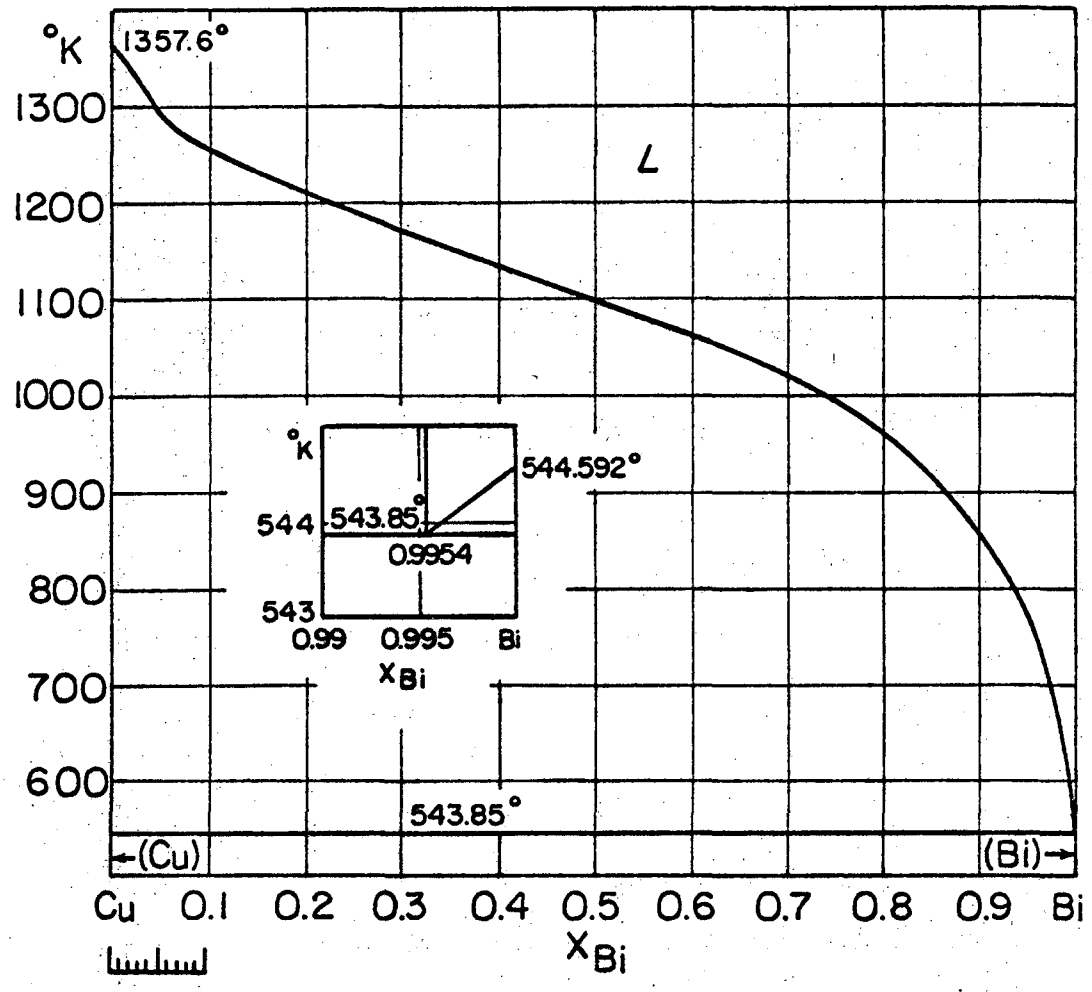
A. Bi Component $Bi_{(\ell)} = Bi(\text{in alloy})_{(\ell)}$

x_{Bi}	a_{Bi}	γ_{Bi}	$\Delta\bar{G}_{Bi}$	$\Delta\bar{G}^{xs}_{Bi}$	$\Delta\bar{H}_{Bi}$	$\Delta\bar{S}_{Bi}$	$\Delta\bar{S}^{xs}_{Bi}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.912	1.013	-225	26	77	0.252	0.043
0.8	0.834	1.043	-431	101	227	0.548	0.105
0.7	0.769	1.099	-625	226	451	0.897	0.188
0.6	0.712	1.187	-810	408	762	1.310	0.295
	(±.01)	(±.02)	(±100)	(±100)	(±300)	(±.26)	(±.26)
0.5	0.658	1.315	-1000	653	1055	1.712	0.335
0.4	0.600	1.500	-1219	966	1439	2.215	0.394
0.3	0.535	1.783	-1492	1379	2128	3.017	0.624
0.22*	0.473	2.149	-1787	1824	3020	4.006	0.997

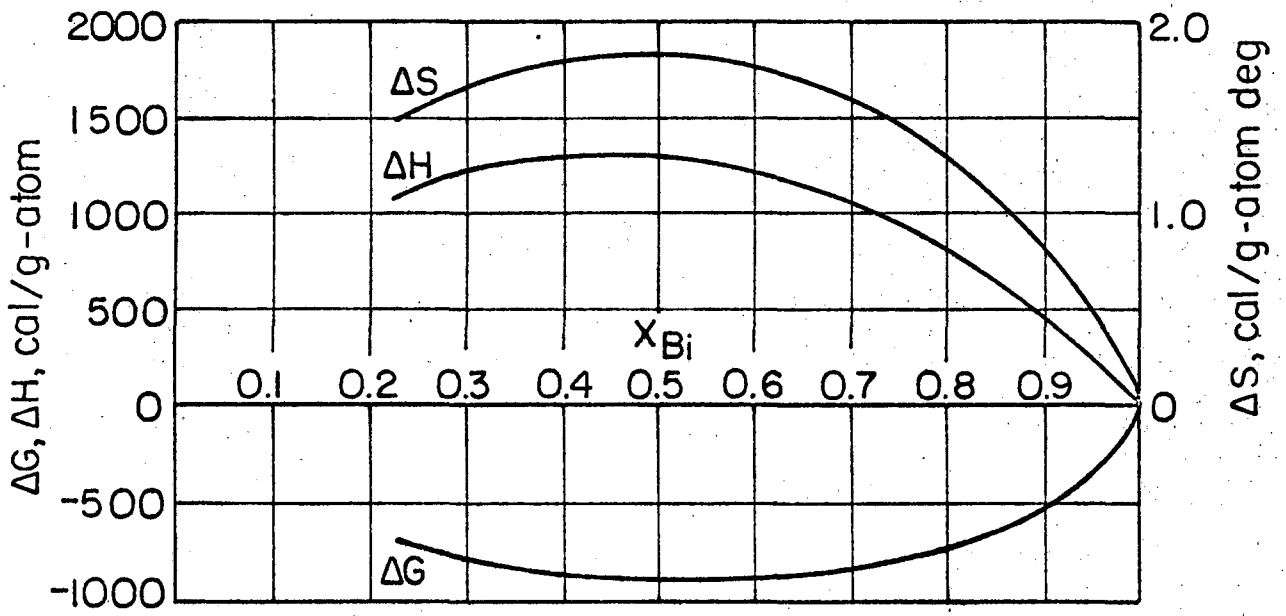
B. Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

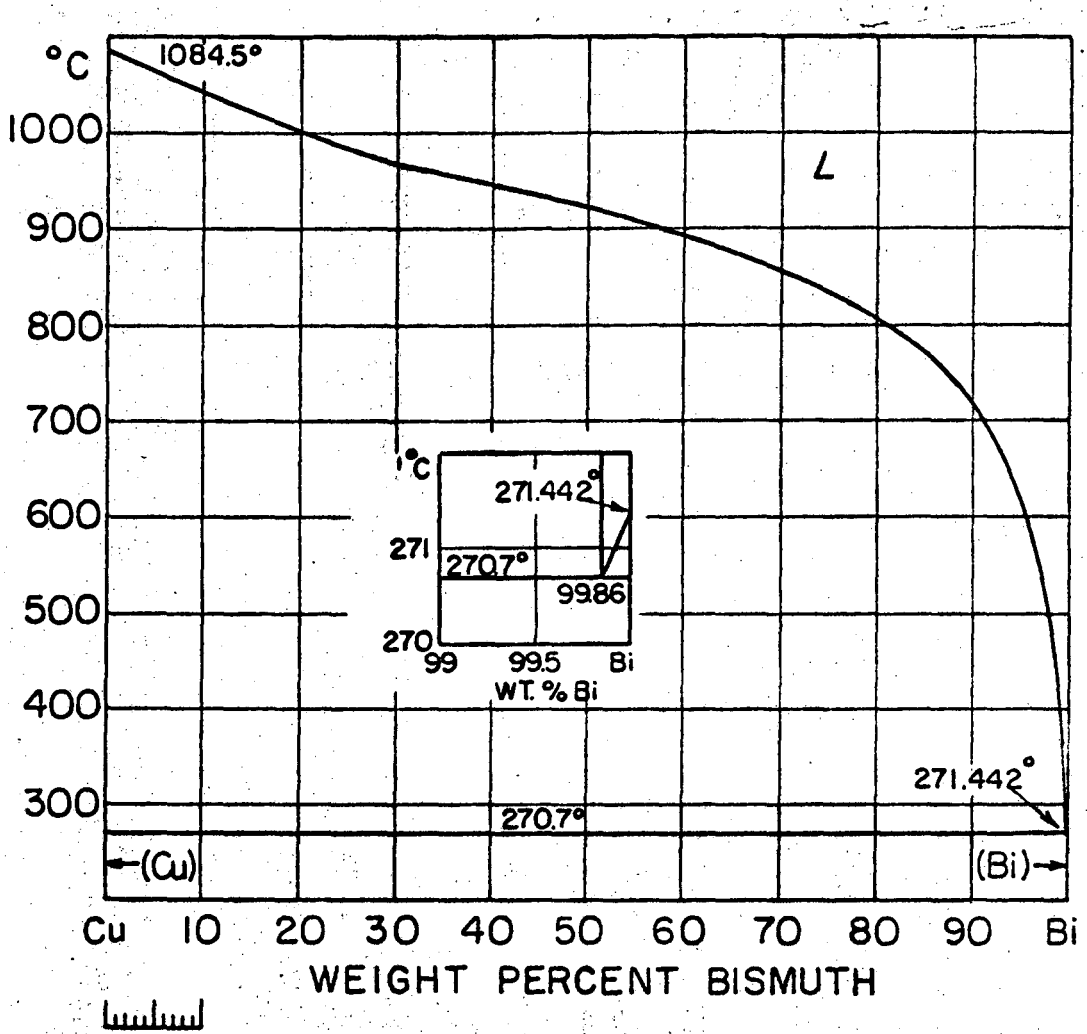
x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.0	0.000	3.236	$-\infty$	2800	5608	∞	2.340
0.1	0.262	2.624	-3191	2300	3981	5.977	1.401
0.2	0.439	2.193	-1965	1873	3124	4.241	1.043
0.3	0.563	1.875	-1372	1499	2452	3.187	0.794
0.4	0.652	1.629	-1022	1163	1876	2.415	0.594
	(±.01)	(±.02)	(±100)	(±100)	(±300)	(±.26)	(±.26)
0.5	0.719	1.437	-789	864	1506	1.912	0.535
0.6	0.774	1.290	-610	608	1200	1.508	0.493
0.7	0.823	1.176	-464	387	834	1.082	0.373
0.78*	0.860	1.102	-361	231	524	0.738	0.244

*Phase boundary



COPPER-BISMUTH SYSTEM, 1200 °K




°C
1084.5°
1000
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L
271.442°
270.7°
(Cu)
(Bi)
Cu 10 20 30 40 50 60 70 80 90 Bi
WEIGHT PERCENT BISMUTH
°C
271.442°
271
270.7°
99.86
270
99 99.5 Bi
WT. % Bi

Part III. References

(For references not in list, see General References)

Azakami, T., and A. Yazawa (1967) J. Mining Met. Inst. Japan 83, 666-72. Vapor pressure (1173°- 1473°K, x_{Cu} = 0.2-0.8).

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Nathans, M. W., and M. Leider (1962) J. Phys. Chem. 66, 2012-5. Phase diagram.

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Oelsen, W., E. Schürman, and D. Buchholz (1961) Arch. Eisenhüttenw. 32, 39-46. ΔH (1416°K, x_{Cu} = 0.1-0.9).

Copper-Calcium

Part I. Discussion

Phases and Structures. The phase diagram, which needs further investigation, is from Hansen (1958). Pearson (1958) reports that:

γ has the hexagonal ($D2_d$) structure isotypic with $CaZn_5$.

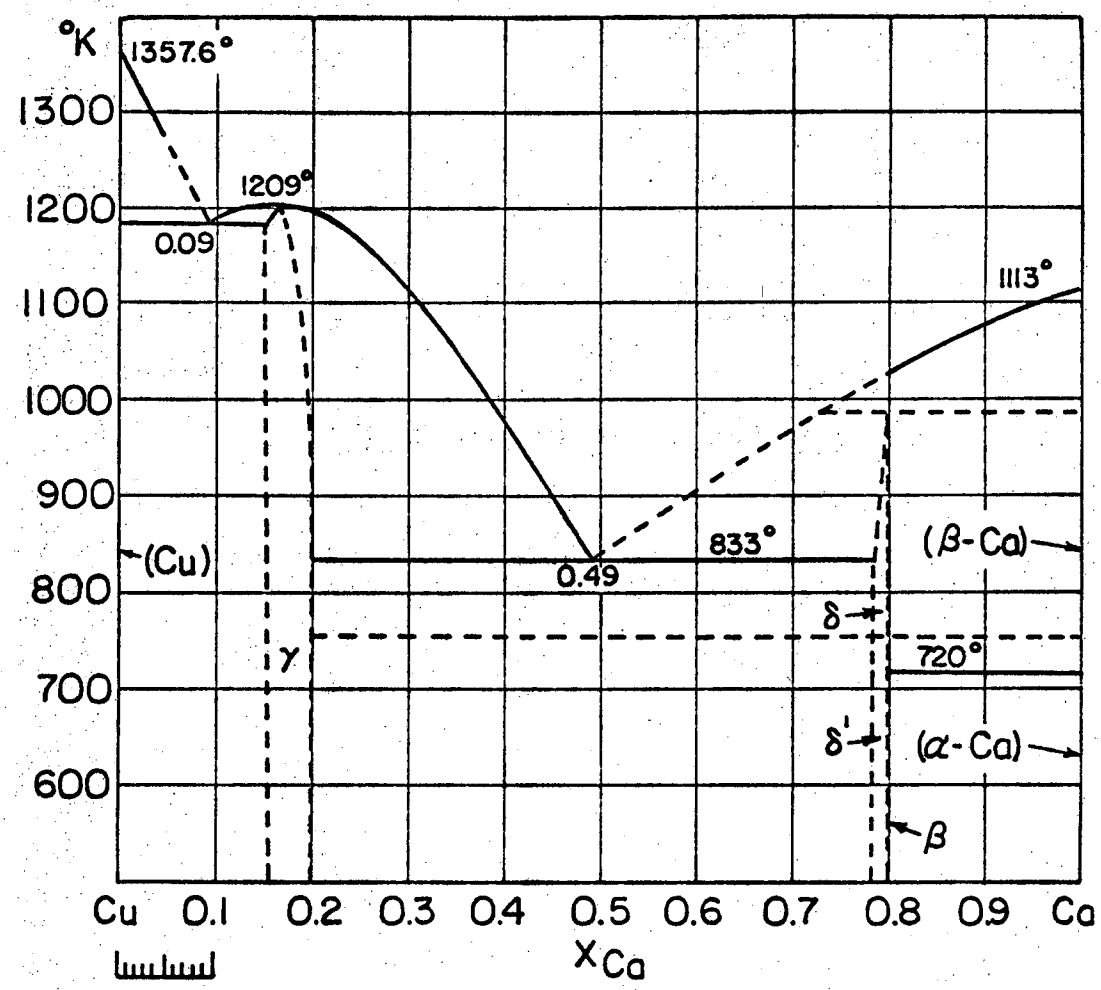
Solid Alloys. Selected values were taken from the measurements of Chiotti, Curtis, and Woerner (1964), of the equilibrium between γ, (Cu), $H_{2(g)}$, and CaH_2. Combining these results with the thermodynamic properties of CaH_2 determined by Curtis and Chiotti (1963), the listed properties were calculated. The selected values were taken from their equation, and differ somewhat from the tabulation of Chiotti et al., which are inconsistent with one another.

Part II. Tables

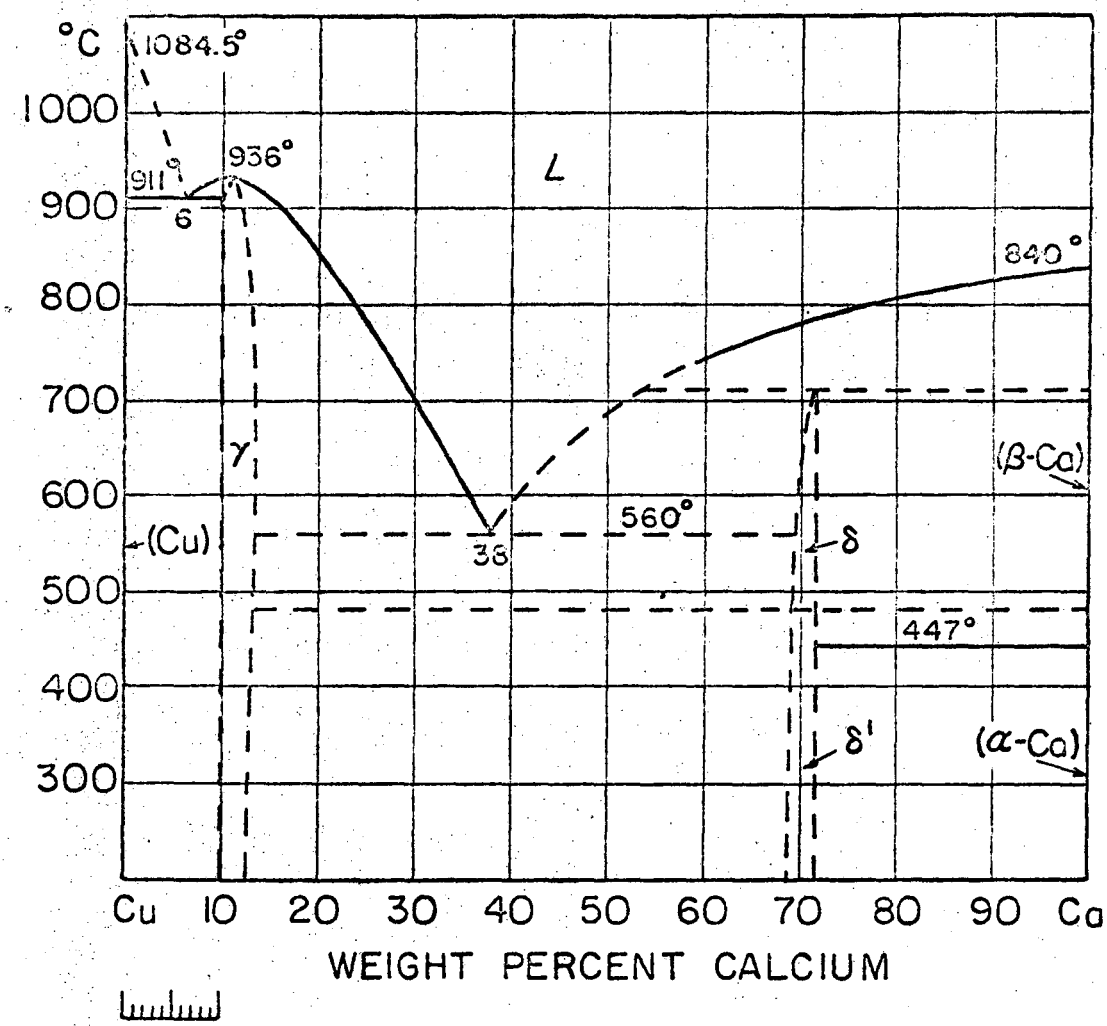
Integral Quantities for γ-Alloy, $x_{Cu} = 0.85$

$$0.15Ca_{(\beta)} + 0.85Cu_{(s)} = Ca_{0.15}Cu_{0.85(\gamma)}$$

T, °K	ΔG	ΔH	ΔS
800	-1862	-1742	0.150
900	-1877	-1742	0.150
1000	-1892	-1742	0.150
	(±300)	(±500)	(±.3)



COPPER-CALCIUM SYSTEM



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Copper-Cadmium

Part I. Discussion

Phases and Structures. The phase diagram of Hansen (1958) has been modified by moving the Cd-rich boundary of the γ-phase to $x_{Cu} = 0.34$, in accord with the work of Nowotny and Bittner (1950). Pearson (1967) reports the following phases:

ϵ, "Cd_3Cu", with a complex hexagonal structure.

γ, "Cd_8Cu_5", with an ordered bcc ($D8_2$) structure isotypic with γ-brass.

δ, "Cd_3Cu_4", was variously reported as having a complex cubic and a complex tetragonal structure. Samson (1967) showed it to be definitely cubic.

β, "$CdCu_2$" with a hexagonal (C36) structure isotypic with $MgNi_2$.

Solid Alloys. Selected values of Table 1 were derived from enthalpy measurements of Kubaschewski (1941), 700° - 1000°K, $x_{Cu} = 0.385, 0.400$, and from Table 2. Selected $\Delta\bar{G}_{Cd}$ values of Table 3 were chosen to agree with the phase diagram and with liquid values (Table 5); they agree within 200 cal/g-atom with values calculated from Cd emf measurements of Vecher and Malets (1967), 373° - 583°K, $x_{Cu} = 0.27, 0.30$; and Vecher and Golikovka (1966), 623° - 773°K, $x_{Cu} = 0.60-0.95$; and with Cd vapor pressure measurements of Borg (1961), 520° - 650°K, $x_{Cu} = 0.26-0.68$, except at $x_{Cu} = 0.399$, where the latter's measurements lead to a value more exothermic by 600 cal/g-atom. ΔG and $\Delta\bar{G}_{Cu}$ values were obtained by Gibbs-Duhem integration of $\Delta\bar{G}_{Cd}$ values. Selected ΔH values of Table 2 were taken from measurements of Kleppa (1956), 723°K, $x_{Cu} = 0.38-0.66$; in referring to $Cd_{(s)}$ as the standard state it was assumed that $\Delta H_m = 1480$ cal/g-atom invariant with T. ΔS was calculated from ΔG and ΔH. Bromine water solution calorimetry of Biltz and Haase (1923), 298°K, $x_{Cu} = 0.40$, gave a value of ΔH less exothermic than the selected value by 800 cal/g-atom. Vecher and Malets (1967) reported $\Delta H = -980$ cal/g-atom for ϵ at $x_{Cu} = 0.25$.

Liquid Alloys. Selected values of $\Delta\bar{G}_{Cd}$ of Table 5 agree well with Cd emf measurements of Nikol'skaya, Otopkov, and Gerasimov (1957), 848° - 923°K, $x_{Cu} = 0.05-0.54$; Riccoboni, Genta, Fiorani, and Valenti (1954), 800° - 875°K, $x_{Cu} = 0.24-0.54$; and with Cd vapor pressure measurements of Azakami and Yazawa (1968), 873° - 1123°K, $x_{Cu} = 0.14-0.82$, except for a single composition, $x_{Cu} = 0.53$, where the latter's value is less exothermic by 140 cal/g-atom. Cd vapor pressure measurements of Jellinek and Rosner (1931), 816° - 1001°K, $x_{Cu} = 0.10-0.60$, scatter and give values of $\Delta\bar{G}_{Cd}$ which tend to be less exothermic by 100-600 cal/g-atom. Other quantities for Tables 4 and 5 were derived by Gibbs-Duhem integration.

Part II. Tables

TABLE 1

Temperature Dependence of Quantities for γ-Phase Alloy, $x_{Cu} = 0.40$

$$0.6Cd_{(s)} + 0.4Cu_{(s)} = Cd_{0.6}Cu_{0.4(s)}$$

$$0.6Cd_{(\ell)} + 0.4Cu_{(\ell)} = Cd_{0.6}Cu_{0.4(\ell)}$$

T, °K	Cp	$H_T - H_{st}$	$S_T - S_{st}$	ΔG	ΔH	ΔS
298.15	6.056	0	0.000	-1069	-1089	-0.066
400	6.317	630	1.814	-1063	-1089	-0.066
500	6.636	1276	3.255	-1057	-1086	-0.058
580	7.005	1821	4.265	-1054	-1073	-0.033
600	7.115	1962	4.502	-1048	-1066	-0.030
700	8.030	2714	5.659	-1051	- 996	0.079
800	9.604	3589	6.826	-1069	- 807	0.328
836(s)	10.347	3948	7.265	-1082	- 695	0.463
836(ℓ)	8.800	6185	9.941	-1207	- 605	0.720
873	8.800	6511	10.322	-1230	- 533	0.799
1000	8.800	7628	11.515	-1346	- 301	1.045

TABLE 2

Integral Quantities for Solid Alloys at 580° K

$$(1-x)Cd_{(s)} + xCu_{(s)} = Cd_{1-x}Cu_{x(s)}$$

x_{Cu}	Phase	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.250*	ε	- 785			-137	
0.340*	γ	- 996			-256	
0.383		-1053	-1173	-0.207	-286	-1.529
0.400		-1054	-1073	-0.033	-278	-1.371
0.425*	γ	-1034 (±100)	- 927 (±50)	0.184 (±.2)	-248 (±100)	-1.171 (±.2)
0.559*	δ	- 860			- 69	
0.572		- 841	- 817	0.041	- 54	-1.315
0.581*	δ	- 825			- 41	
0.667	β	- 666	- 596	0.121	67	-1.143

*Phase boundary

TABLE 3

Partial Molar Quantities for Solid Alloys at 580° K

x_{Cu}	Phase	Cd Component $Cd_{(s)} = Cd(\text{in alloy})_{(s)}$				Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(s)}$			
		a_{Cd}	γ_{Cd}	$\Delta\bar{G}_{Cd}$	$\Delta\bar{G}^{xs}_{Cd}$	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.340*	γ	0.841	1.274	- 200	279	0.110	0.323	-2540	-1296
0.383		0.458	0.742	- 901	-344	0.324	0.846	-1299	- 193
0.400		0.360	0.600	-1178	-589	0.471	1.177	- 868	188
0.425*	γ	0.253	0.439	-1586	-948	0.779	1.834	- 287	699
		(±.04)	(±.07)	(±200)	(±200)	(±.12)	(±.28)	(±200)	(±200)
0.559*	δ	0.253	0.573	-1586	-642	0.779	1.394	- 287	383
0.572		0.215	0.502	-1772	-794	0.883	1.543	- 144	500
0.581*	δ	0.192	0.459	-1900	-897	0.958	1.649	- 50	576

TABLE 4

Integral Quantities for Liquid Alloys at 873° K

$$(1-x)Cd_{(\ell)} + xCu_{(\ell)} = Cd_{(1-x)}Cu_{x(\ell)}$$

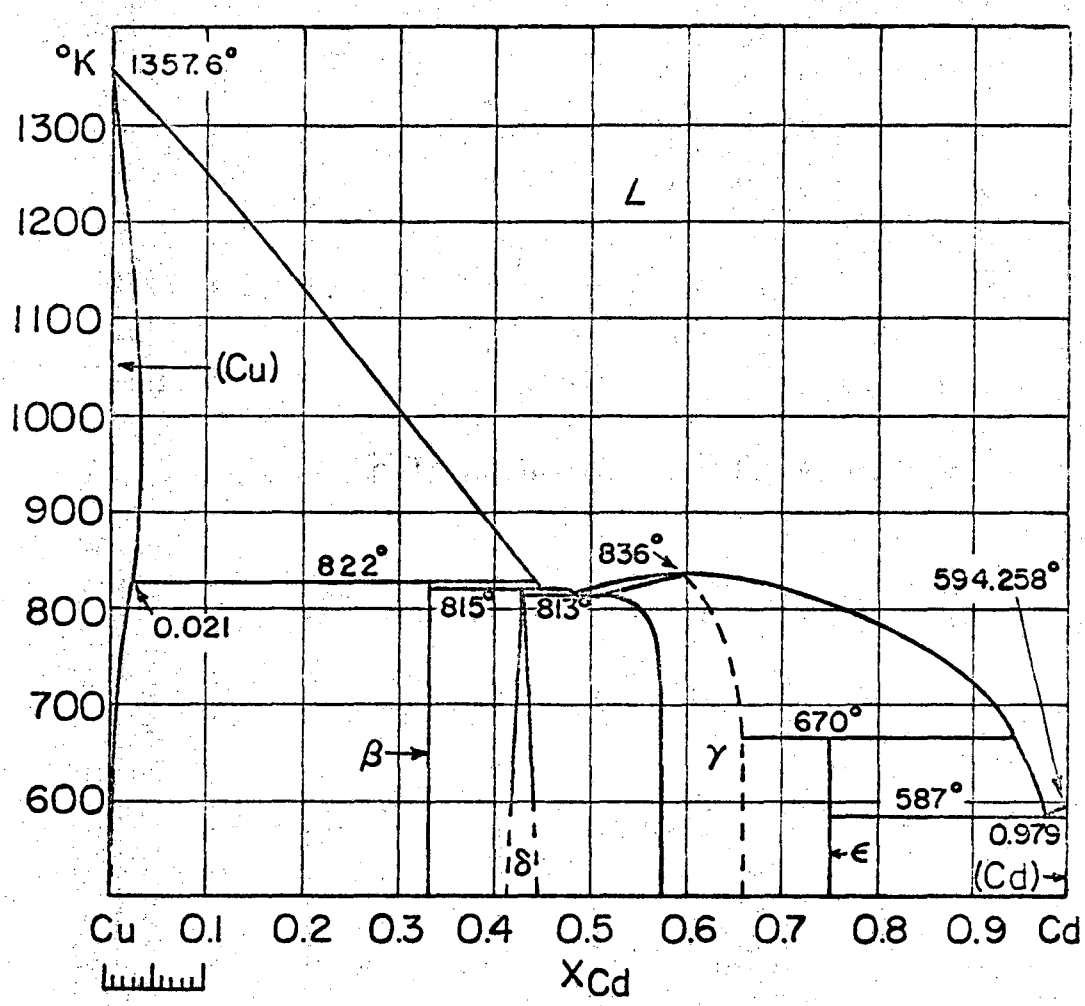
x_{Cu}	ΔG	ΔG^{xs}	x_{Cu}	ΔG	ΔG^{xs}
0.1	- 526	38	0.596*	-1328	-157
0.2	- 835	33			
0.3	-1065	- 5			
0.4	-1230	- 63			
0.5	-1321	-119			
	(±50)	(±50)			

TABLE 5

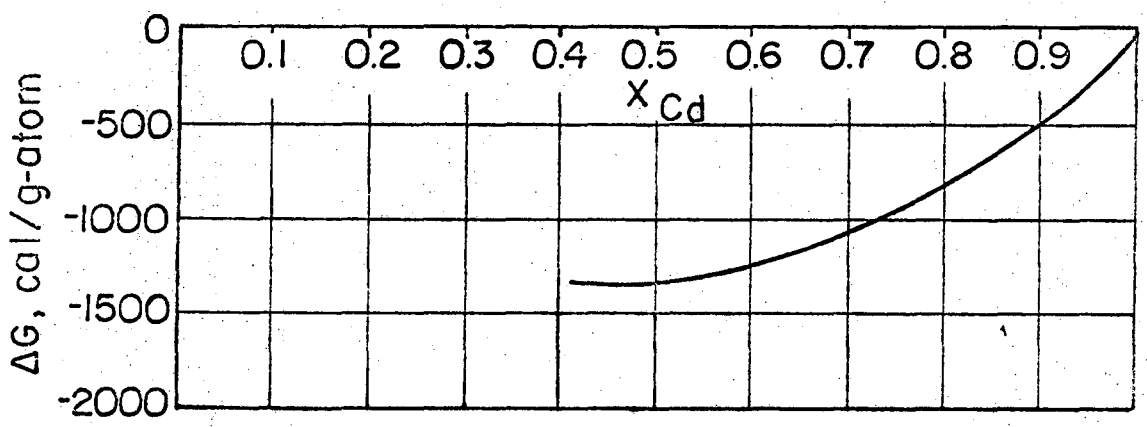
Partial Molar Quantities for Liquid Alloys at 873° K

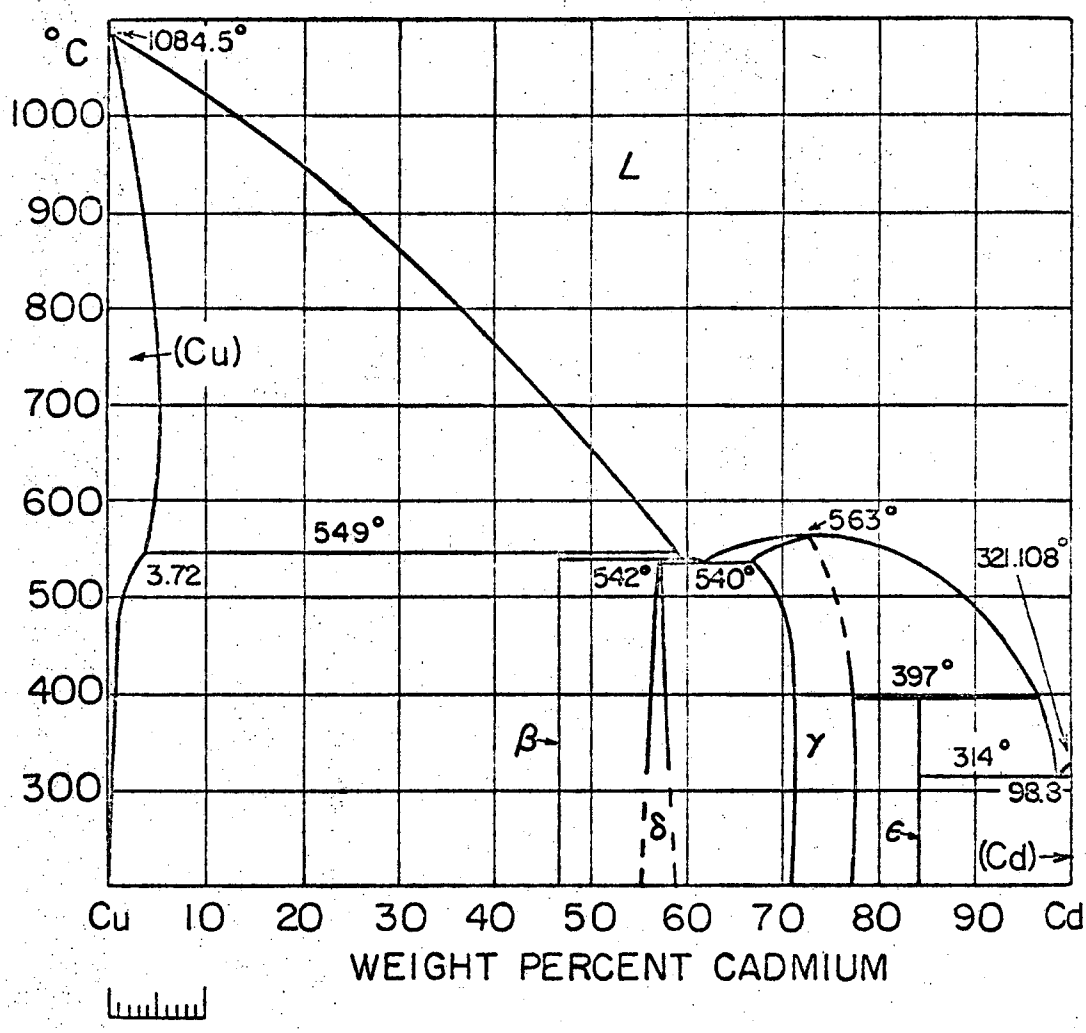
x_{Cu}	Cd Component $Cd_{(\ell)} = Cd(\text{in alloy})_{(\ell)}$				Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$			
	a_{Cd}	γ_{Cd}	$\Delta\bar{G}_{Cd}$	$\Delta\bar{G}^{xs}_{Cd}$	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.0	1.000	1.000	0	0	0.000	1.434	- ∞	626
0.1	0.912	1.013	- 160	23	0.110	1.103	-3824	171
0.2	0.838	1.047	- 307	80	0.183	0.913	-2949	-157
0.3	0.761	1.087	- 475	144	0.245	0.815	-2443	-354
0.4	0.664	1.107	- 710	176	0.314	0.785	-2011	-421
0.5	0.542	1.083	-1064	138	0.403	0.805	-1578	-376
	(±.01)	(±.02)	(±50)	(±50)	(±.01)	(±.02)	(±50)	(±50)
0.596*	0.404	0.678	-1572	-675	0.512	0.859	-1162	-264

*Phase boundary



COPPER-CADMIUM SYSTEM, 873°K




°C
1084.5°
1000
900
800
700
600
500
400
300
L
(Cu)
549°
3.72
542°
540°
563°
321.108°
397°
β
γ
314°
98.3
δ
ε
(Cd)
Cu 10 20 30 40 50 60 70 80 90 Cd
WEIGHT PERCENT CADMIUM

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Biltz, W., and C. Haase (1923) Z. Anorg. Chem. 129, 141-60. ΔH (298°K, x_{Cu} = 0.40).

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Copper-Cobalt

Part I. Discussion

Phases and Structures. The phase diagram, from Hansen (1958) and Elliott (1965) has been adjusted to agree with solid solution boundaries determined by Old and Haworth (1966) and (β-Co) solidus boundaries from the thermodynamic calculations of Dench and Kubaschewski (1969). The α-Co-β-Co transition T is lowered by addition of Cu, but its value remains very uncertain.

Solid Alloys. The selected values of Table 1 were taken from Cp measurements of Crane and Zimmerman (1961), 1.5°- 4.5°K, x_{Cu} =0.974-1.00, and agree approximately with Cp measurements of Du Chatenier and De Nobel (1966), 1°- 4°K, x_{Cu} = 0.999-1.00; and with Tournier, Veyssie, and Weil (1962), 0.7°- 4.5°K, x_{Cu} = 0.978-1.00, which show similar trends. The ΔH values of Table 2 were taken from direct reaction calorimetry of Dokken and Elliott (1965), 1473°K, x_{Cu} = 1.00-0.95. Selected $\Delta\bar{G}_{Co}$ values of Table 4 were taken from emf studies of Dench and Kubaschewski (1969), 1023°- 1548°K, x_{Cu} = 0.02-0.15; and $\Delta\bar{H}_{Co}$ from their temperature coefficients. For $\Delta\bar{G}_{Cu}$, Raoult's law was assumed for the (Cu) phase; other values were calculated from Gibbs-Duhem integration.

Part II. Tables

TABLE 1

Low-Temperature Data for (Cu)-Phase Alloys

T, °K	x_{Cu}			
	0.974	0.984	0.994	1.000*
	Cp			
1.5	0.00176	0.00105	0.00035	0.00031
2	0.00232	0.00138	0.00050	0.00046
3	0.00335	0.00199	0.00093	0.00084
4	0.00422	0.00248	0.00154	0.00140
$\gamma\times10^4$	11.95(±.2)	7.15(±.5)	2.10(±.2)	1.85(±.2)

*Values for pure Cu trend from 5% higher than selected values at 2°K to 5% lower at 4°K (see Cu). They are tabulated for purposes of comparison.

TABLE 2

Heats of Formation of Liquid Alloys at 1473°K

$$(1-x)Co_{(\ell)} + xCu_{(\ell)} = Co_{1-x}Cu_{x(\ell)}$$

$$Co_{(\ell)} = Co(\text{in alloy})_{(\ell)} \qquad Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$$

x_{Cu}	ΔH	$\Delta\bar{H}_{Co}$	$\Delta\bar{H}_{Cu}$
1.00	0	8000	0
0.95	374(±150)	7000(±3000)	25(±10)

TABLE 3

Integral Quantities for Solid Alloys at 1300°K

$$(1-x)Co_{(\beta)} + xCu_{(\beta)} = Co_{1-x}Cu_{x(\beta)}$$

x_{Cu}	Phase	ΔG	ΔG^{xs}	x_{Cu}	Phase	ΔG	ΔG^{xs}
0.05	(β-Co)	-121	391				
0.093*	(β-Co)	-136 (±100)	664 (±100)	0.947*	(Cu)	-141	395

*Phase boundary

TABLE 4

Partial Molar Quantities for Solid Alloys at 1300°K

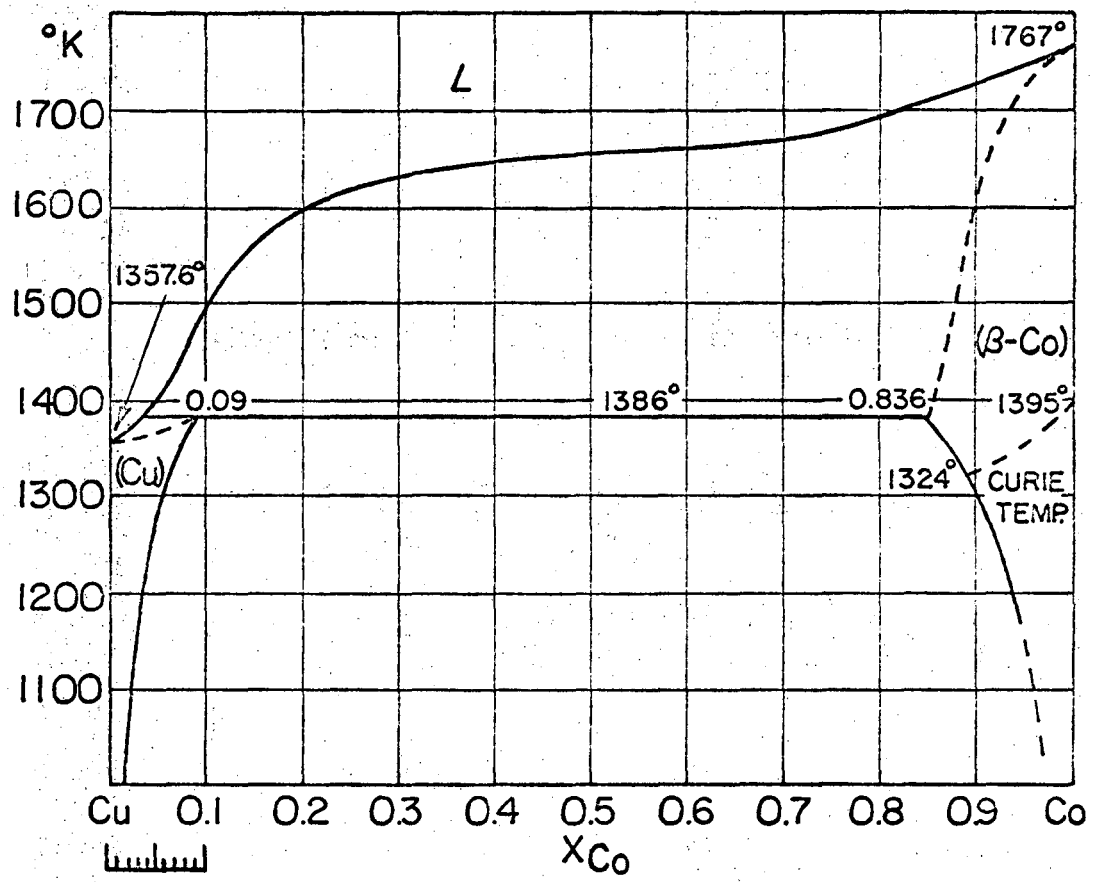
Co Component $Co_{(\beta)} = Co(\text{in alloy})_{(\beta)}$

x_{Co}	Phase	a_{Co}	γ_{Co}	$\Delta\bar{G}_{Co}$	$\Delta\bar{G}^{xs}_{Co}$	$\Delta\bar{H}_{Co}$	$\Delta\bar{S}_{Co}$	$\Delta\bar{S}^{xs}_{Co}$
1.00	(β-Co)	1.000	1.000	0	0	0	0.000	0.000
0.95		0.968	1.019	- 84	48	69	0.118	0.016
0.907*	(β-Co)	0.949 (±.02)	1.046 (±.02)	-135 (±50)	117 (±50)	191 (±50)	0.251 (±.04)	0.057 (±.04)
0.053*	(Cu)	0.949	17.906	-135	7453	—	—	—
0.000	(Cu)	0.000	17.906	- ∞	7453	—	—	—

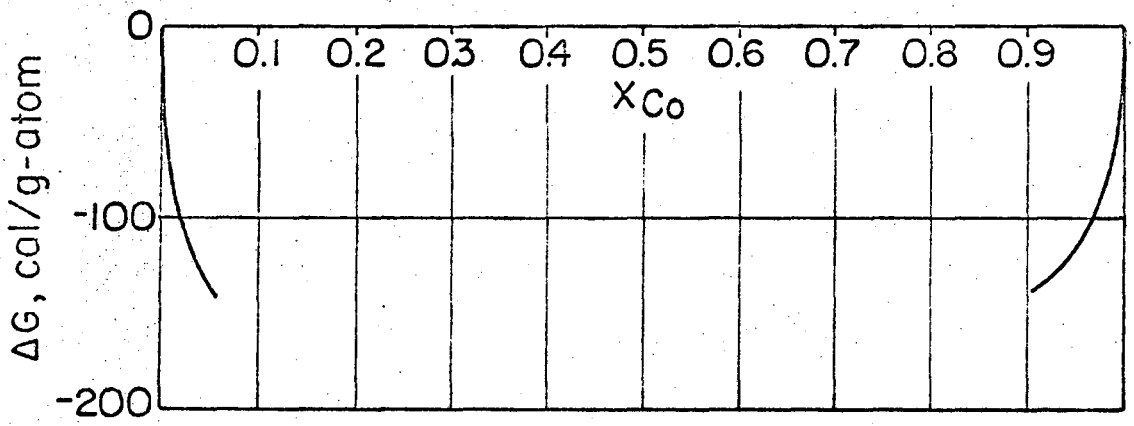
Cu Component $Cu_{(\beta)} = Cu(\text{in alloy})_{(\beta)}$

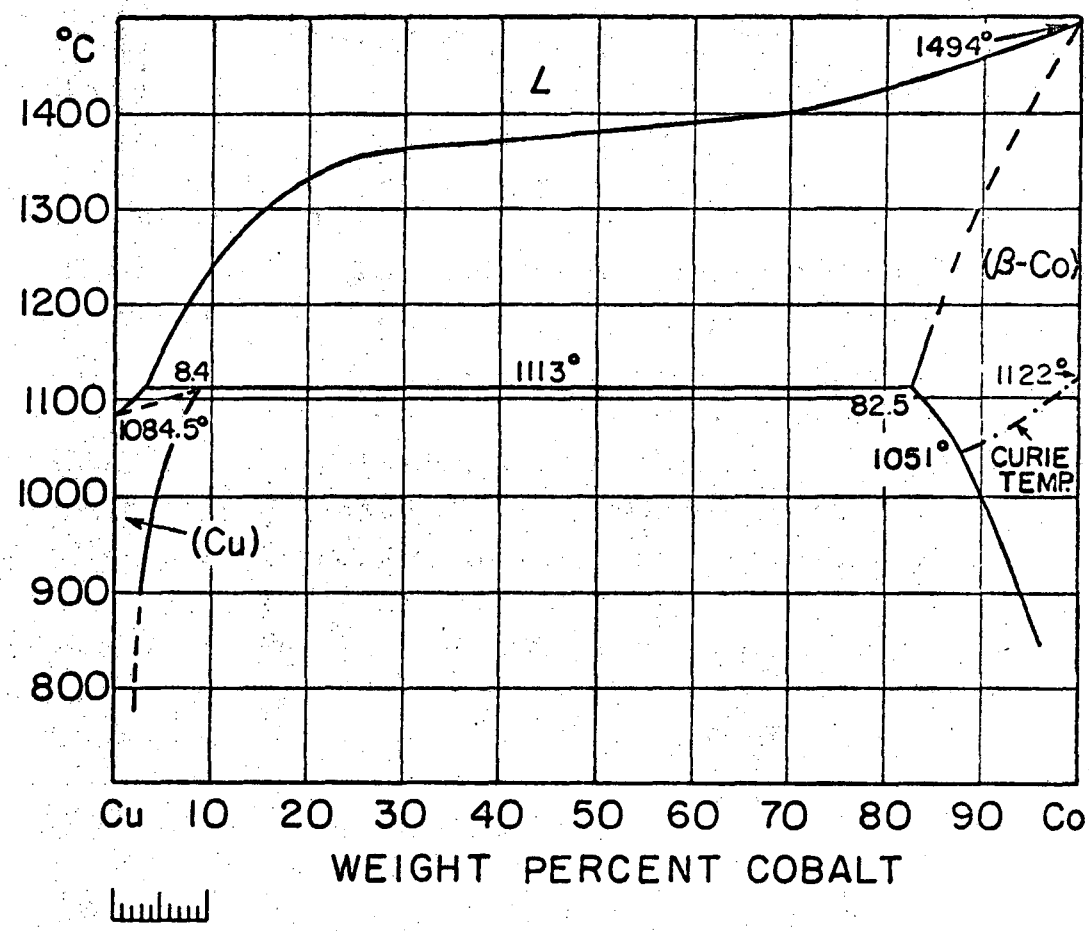
x_{Cu}	Phase	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$
0.00	(β-Cu)	0.000	33.971	- ∞	9108
0.05		0.725	14.500	-832	6907
0.093*	(β-Cu)	0.947 (±.04)	10.183 (±.43)	-141 (±100)	5995 (±100)
0.947*	(Cu)	0.947	1.000	-141	0
1.000	(Cu)	1.000	1.000	0	0

*Phase boundary



COPPER-COBALT SYSTEM, 1300 °K





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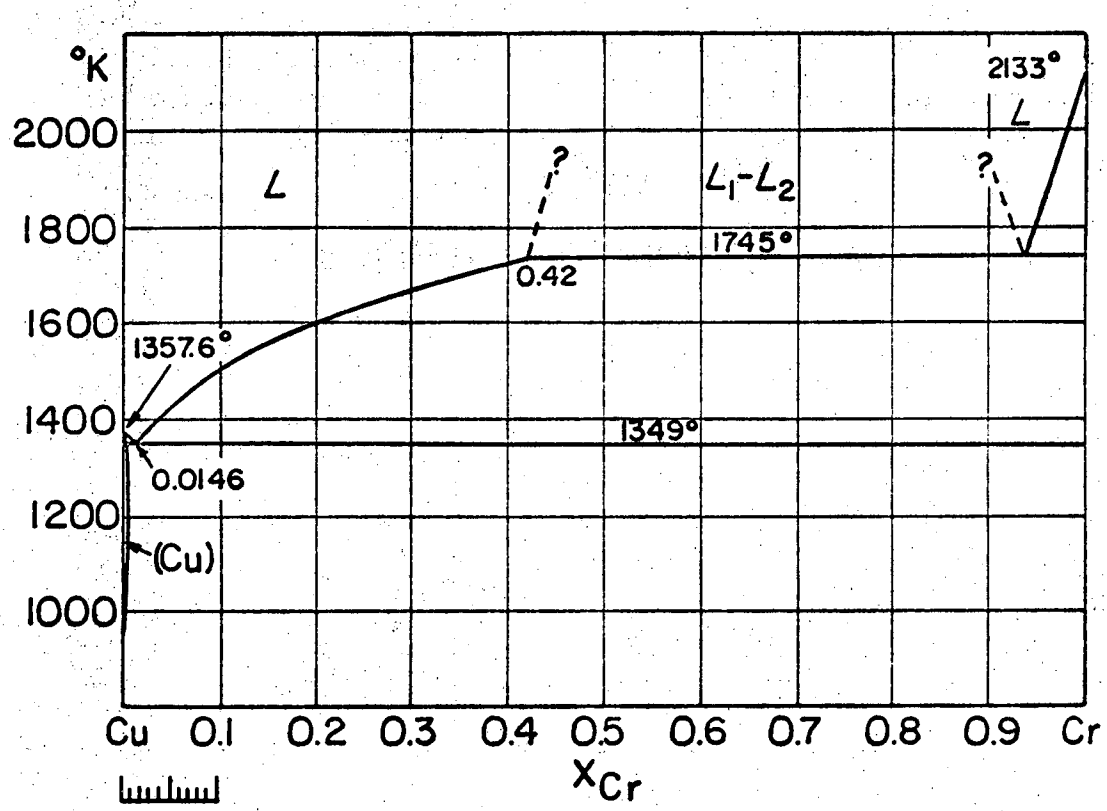
Copper-Chromium

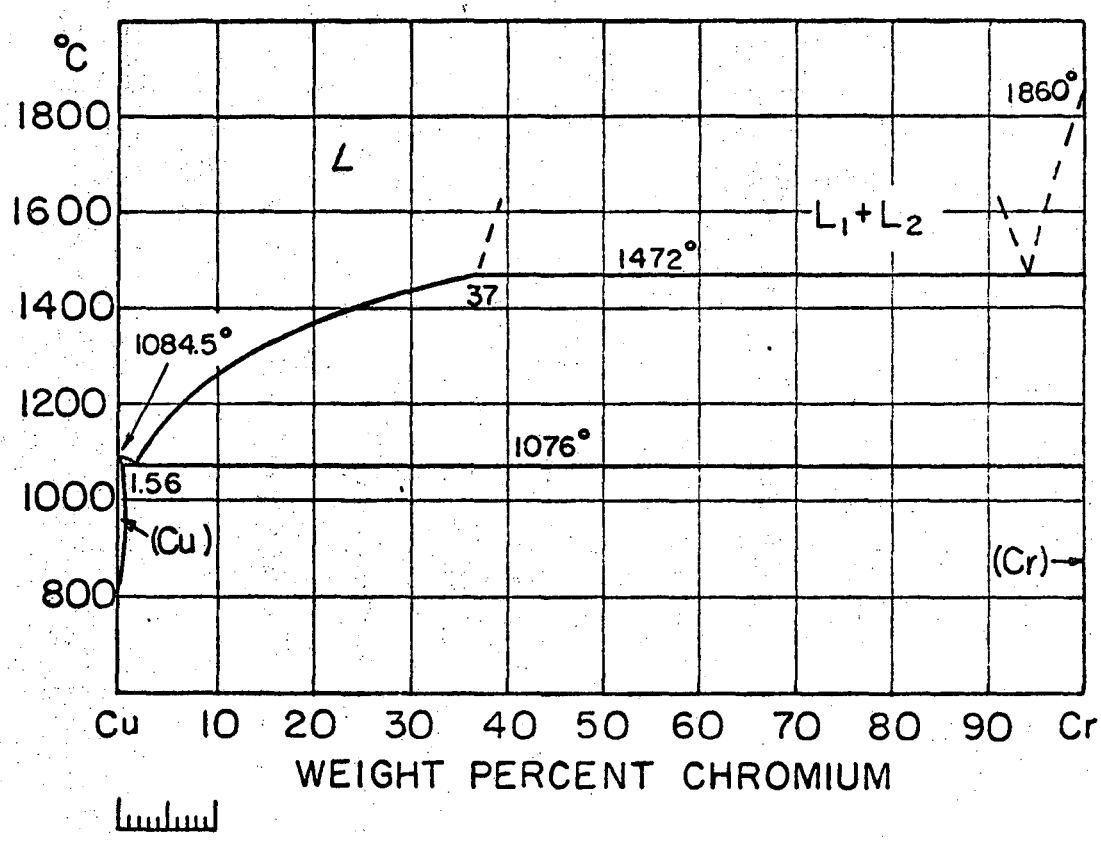
Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with more precise values for the eutectic and (Cu) phase boundaries from Elliott (1965), and T_m = 2133°K for Cr from the 1968 IPTS.

Solid Alloys. Du Chatenier and De Nobel (1966), 1°- 8°K, x_{Cu} = 0.9944-1.00; and Du Chatenier and Miedema (1966), 0.04°- 10°K, x_{Cu} = 0.9944, 0.9993; quenched liquid copper alloyed with small additions of Cr. They found the Cp of these probably two-phase solid alloys were considerably higher than the Cp of pure Cu below 8°K; the electronic $\gamma = 4.3\times10^{-4}$ for all the alloys compared with 1.66×10^{-4} for pure Cu. Results were not tabulated.



COPPER-CHROMIUM SYSTEM



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Cp (0.04°- 10°K, x_{Cu} = 0.9944, 0.9993).

Copper-Iron

Part I. Discussion

Phases and Structures. The phase diagram is from Hansen (1958), with more accurate boundaries from Elliott (1965) and Klement (1963). The (γ-Fe) solidus was taken from Bochvar, Ekatova, Panchenko, and Sidokhin (1966). The (γ-Fe)-(Cu) boundary was taken from Speich, Gula, and Fisher (1966). There are no intermediate phases.

Solid Alloys. (Cu)-Phase. Selected values of Table 1 were taken from Cp measurements of Franck, Manchester, and Martin (1961), 0.4°-30°K, x_{Fe} = 0.0005, 0.0013, 0.0024, who found small iron impurities greatly increased Cp below 10°K but had little effect above (see Cu).

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values were taken from vapor pressure measurements of Morris and Zellars (1956), 1730°-1850°K, x_{Fe}=0.03-0.88. Several determinations have been made of $\Delta\bar{G}^{xs}_{Cu}$ at x_{Fe} = 1, which give values less endothermic than the selected value of 8160:

Source	$\Delta\bar{G}^{xs}_{Cu}(x_{Fe}=1)$
Onillon (1967) 1823°-1923°K, $x_{Fe}\sim 1$. Vapor composition versus liquid composition.	7630
Langenberg (1956), 1873°K, $x_{Fe}\sim 1$. Distribution coefficient between $Fe_{(\ell)}$ and $Pb_{(\ell)}$.	7880
Koros and Chipman (1956), 1873°K, $x_{Fe}\sim 1$. Distribution coefficient between $Fe_{(\ell)}$ and $Ag_{(\ell)}$.	7510
Chou (1947), 1873°K, $x_{Fe}\sim 1$. Distribution coefficient between $Fe_{(\ell)}$ and $Ag_{(\ell)}$.	8010

ΔG and $\Delta\bar{G}_{Fe}$ values were calculated by Gibbs-Duhem integration of the selected $\Delta\bar{G}_{Cu}$.

Selected ΔH values agree closely with the direct calorimetric measurements of Woolley and Elliott (1967), 1873°K, x_{Fe} = 0.85-1.0, and within ±50 cal/g-atom with the calorimetric measurements of Podgornik (1961), 1873°K, x_{Fe} = 0.1-0.9, except for being 225 cal/g-atom less endothermic at x_{Fe} = 0.1; and with the dynamic drop calorimetry of Oelsen, Schürmann, and Florin (1961), 1873°K, x_{Fe} = 0.21-0.81,

except that the latter's values were less endothermic at x_{Fe} = 0.21 and 0.81 by 125 cal/g-atom. From the dependence of ΔH on T, Oelsen, et al. were able to calculate values of ΔG which were only 0-60 cal more exothermic than selected ones. The other values in Tables 2 and 3 were calculated from the selected values.

Part II. Tables

TABLE 1

Low-Temperature Data for (Cu)-Phase, x_{Fe} = 0.0024

T, °K	Cp	T, °K	Cp
0.4	0.00029	10	0.0141
1	0.00070	15	0.0445
2	0.00114	20	0.112
3	0.00159	25	0.232
4	0.00219	30	0.410
5	0.00309		

TABLE 2

Integral Quantities for Liquid Alloys at 1823°K

$$(1-x)Cu_{(\ell)} + xFe_{(\ell)} = Cu_{1-x}Fe_{x(\ell)}$$

x_{Fe}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-443	804	0.684	735	0.038
0.2	-560	1387	1.068	1253	0.073
0.3	-624	1789	1.324	1589	0.110
0.4	-663	2033	1.479	1775	0.141
0.5	-674	2132	1.540	1837	0.162
	(±100)	(±100)	(±0.08)	(±100)	(±0.08)
0.6	-662	2093	1.511	1776	0.174
0.7	-632	1917	1.399	1581	0.185
0.8	-580	1562	1.175	1232	0.181
0.9	-465	950	0.777	712	0.131

TABLE 3

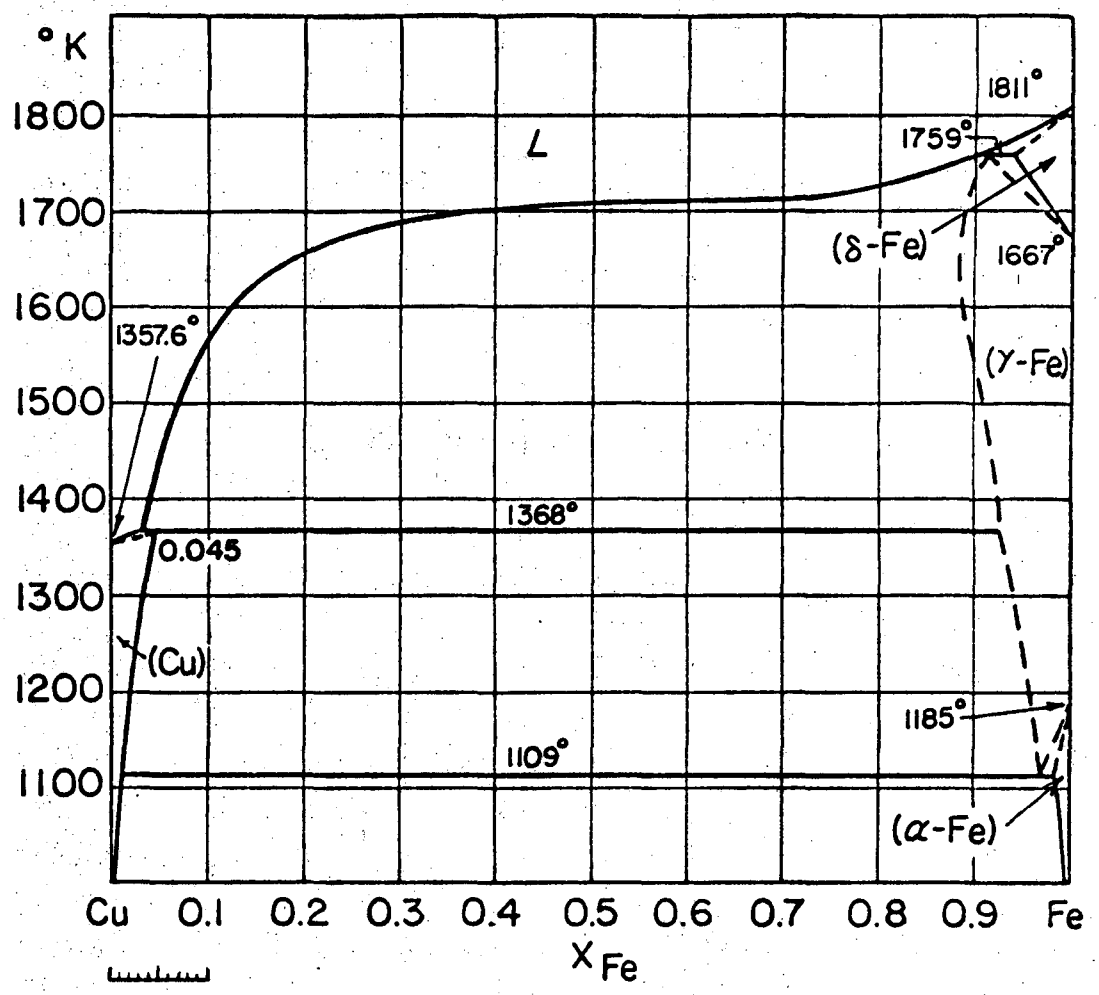
Partial Molar Quantities for Liquid Alloys at 1823°K

A. Cu Component $Cu_{(\ell)} = Cu\,(\text{in alloy})_{(\ell)}$

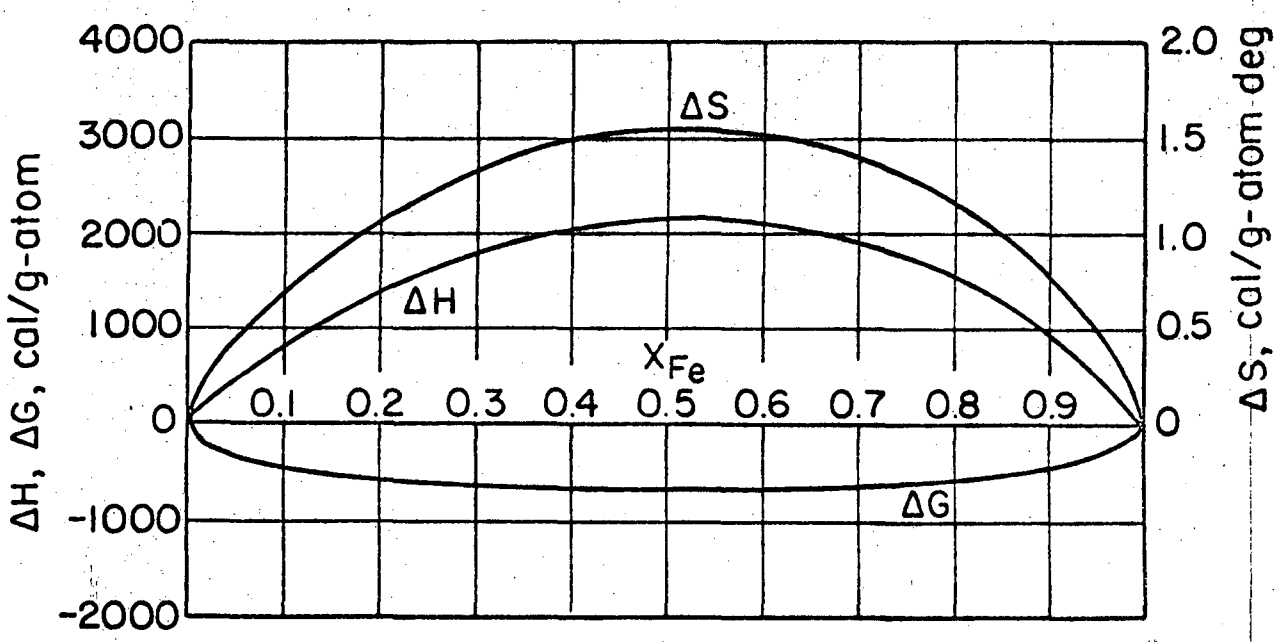
x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.929	1.032	-267	114	118	0.211	0.002
0.8	0.896	1.120	-397	411	409	0.442	-0.001
0.7	0.878	1.254	-471	821	830	0.713	0.005
0.6	0.857	1.428	-560	1290	1355	1.051	0.035
0.5	0.829	1.657	-681	1830	1982	1.461	0.084
	(±.01)	(±.02)	(±100)	(±100)	(±200)	(±.12)	(±.12)
0.4	0.804	2.010	-790	2529	2714	1.922	0.102
0.3	0.780	2.598	-902	3459	3702	2.525	0.133
0.2	0.728	3.641	-1149	4682	5312	3.544	0.346
0.1	0.557	5.575	-2117	6225	7897	5.493	0.917
0.0	0.000	9.512	$-\infty$	8160	11370	∞	1.761

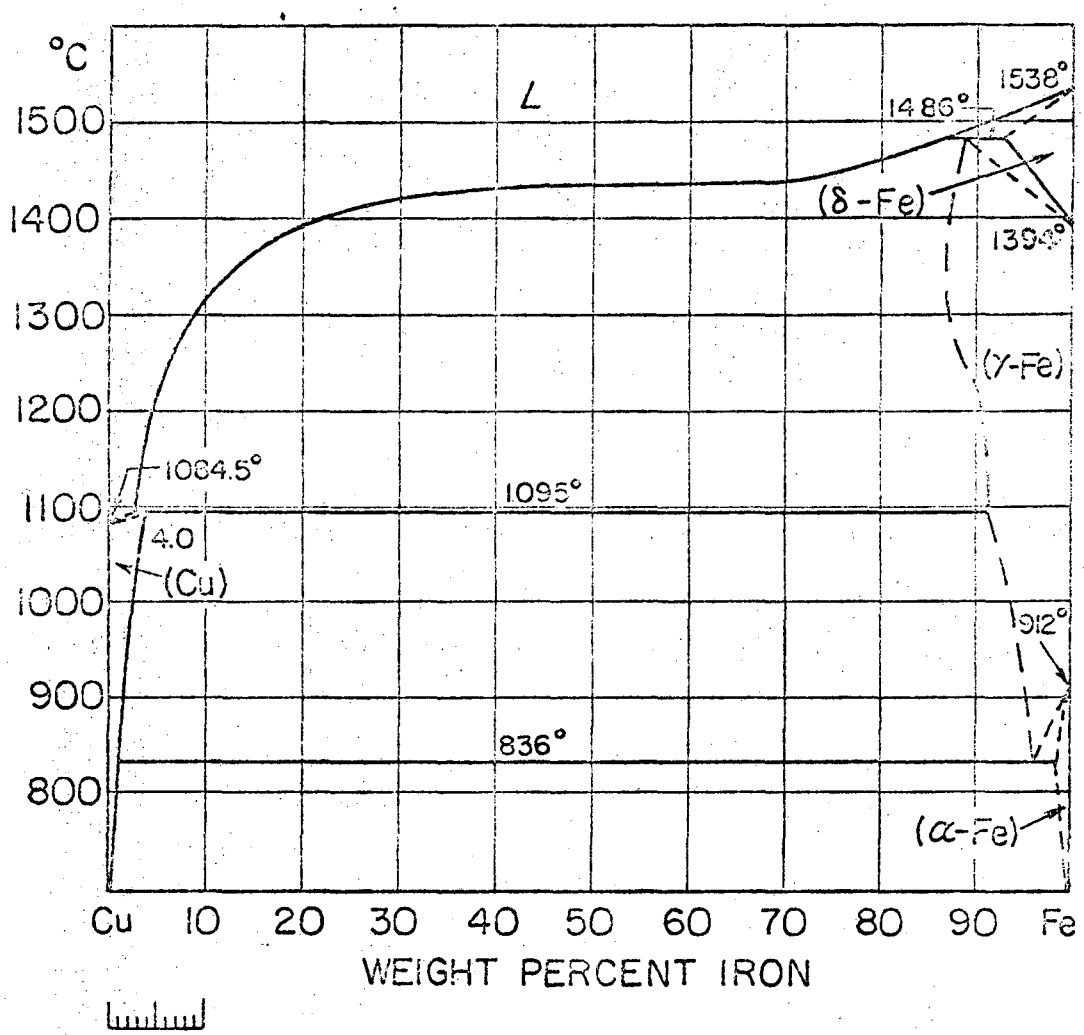
B. Fe Component $Fe_{(\ell)} = Fe\,(\text{in alloy})_{(\ell)}$

x_{Fe}	a_{Fe}	γ_{Fe}	$\Delta\bar{G}_{Fe}$	$\Delta\bar{G}^{xs}_{Fe}$	$\Delta\bar{H}_{Fe}$	$\Delta\bar{S}_{Fe}$	$\Delta\bar{S}^{xs}_{Fe}$
0.0	0.000	10.570	$-\infty$	8550	9300	∞	0.411
0.1	0.573	5.728	-2019	6323	6978	4.935	0.359
0.2	0.716	3.582	-1208	4622	5299	3.570	0.371
0.3	0.763	2.542	-981	3380	4028	2.748	0.355
0.4	0.798	1.996	-816	2503	3049	2.120	0.300
0.5	0.832	1.663	-668	1843	2282	1.618	0.241
	(±.01)	(±.02)	(±100)	(±100)	(±200)	(±.12)	(±.12)
0.6	0.853	1.421	-577	1274	1678	1.237	0.222
0.7	0.867	1.239	-517	775	1152	0.916	0.207
0.8	0.886	1.107	-438	370	624	0.583	0.139
0.9	0.925	1.028	-282	100	178	0.253	0.043
1.0	1.000	1.000	0	0	0	0.000	0.000



COPPER - IRON SYSTEM, 1823 °K




°C
1500
1400
1300
1200
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L
1538°
1486°
(δ-Fe)
1394°
(γ-Fe)
1084.5°
1095°
4.0
(Cu)
912°
836°
(α-Fe)
Cu
10
20
30
40
50
60
70
80
90
Fe
WEIGHT PERCENT IRON

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Copper-Gallium

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) as modified by Kittl and Massalski (1965), T<900°K, x_{Ga} = 0.18-0.30. Pearson (1958, 1967) lists the following intermediate phases:

- β, with the bcc (A2) structure isotypic with W;
- ζ, with the hcp (A3) structure isotypic with Mg;
- γ and γ_1, with the cubic ($D8_3$) structure isotypic with Al_4Cu_9. The two phases are distinguished from thermal analysis and from a slight inflection in the lattice constant versus T;
- γ_2 and γ_3, with the bcc ($D8_2$) structure isotypic with γ-brass. The two phases are distinguished by changes in intensity of weak diffraction lines; they are separated by a two-phase region;
- θ, also called "ϕ" and "$CuGa_2$", with a tetragonal structure; Pearson quotes x_{Ga}~0.58, but Betterton and Hume-Rothery are positive that x_{Ga}~0.665.

In addition, Kittl and Massalski (1965) give the phase

- ζ', with probably an ordered structure which is a distortion of the ($D0_{19}$), Ni_3Sn type.

Solid Alloys. Selected values were taken from liquid tin solution calorimetry of Kleppa and King (1962), 298°K, x_{Ga}=0.068-0.177.

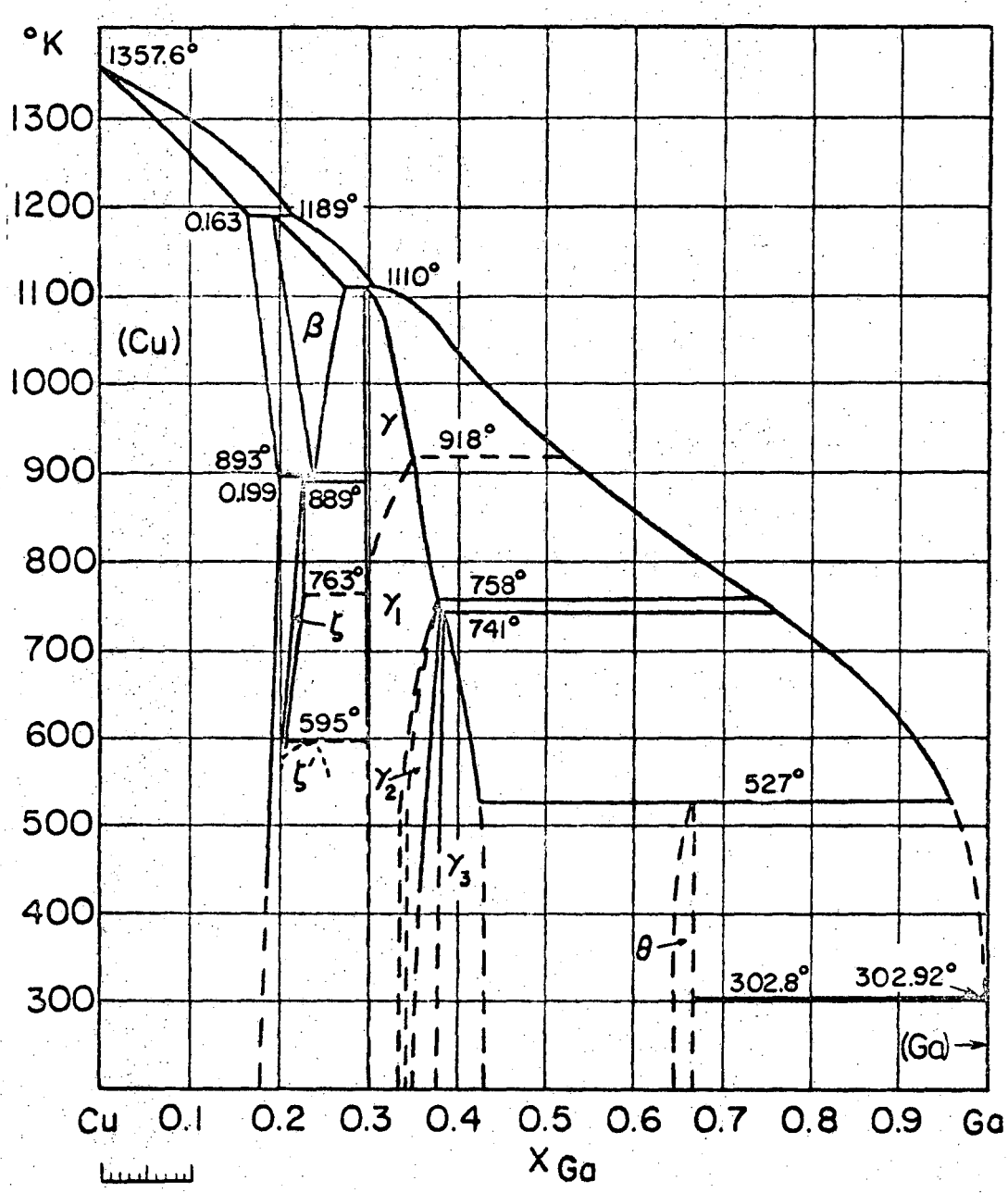
Part II. Tables

Heats of Formation of (Cu)-Phase Alloys at 298°K

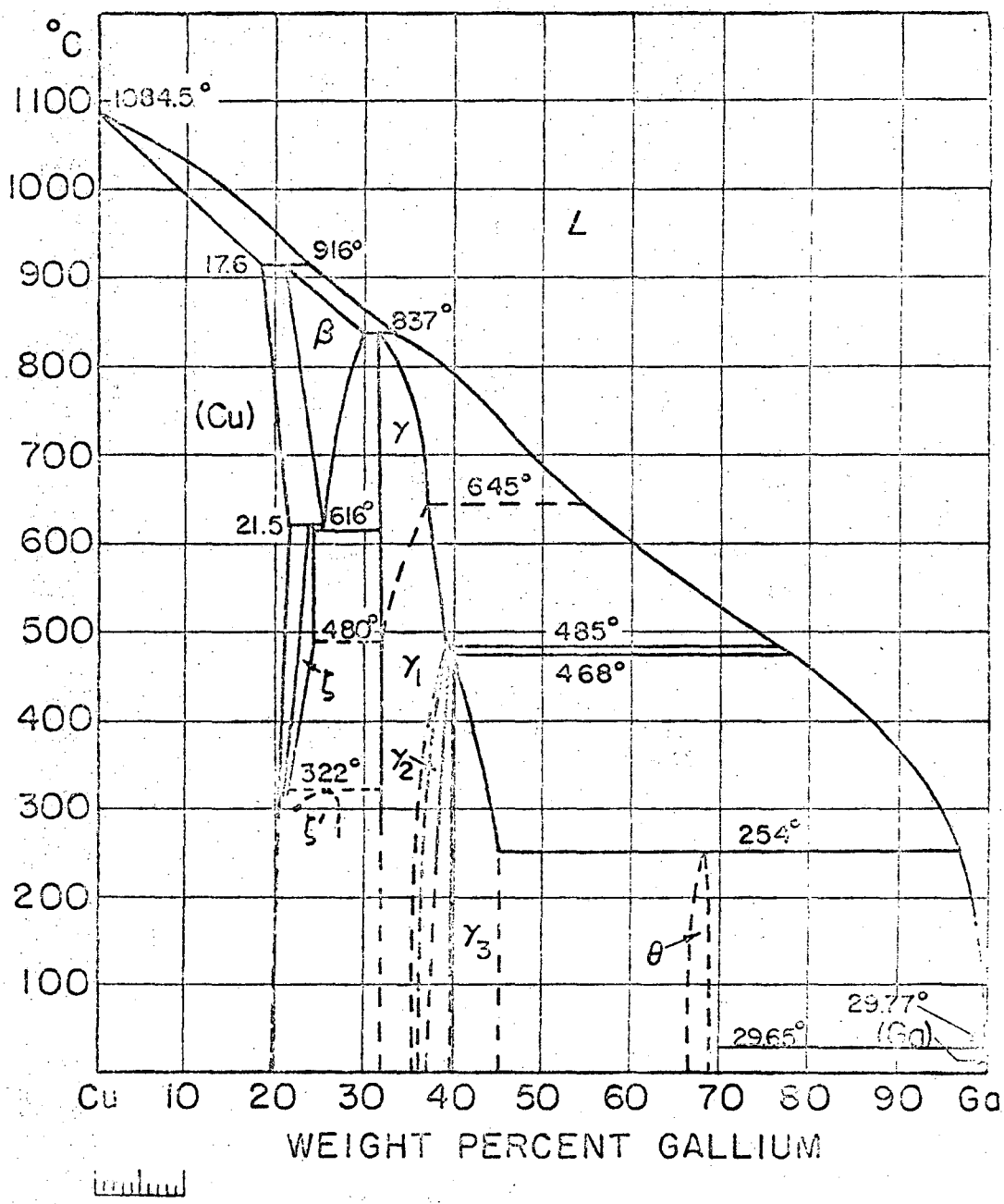
$$(1-x)Cu_{(s)} + xGa_{(s)} = Cu_{1-x}Ga_{x(s)}$$

x_{Ga}	ΔH	$\Delta\bar{H}_{Cu}$	$\Delta\bar{H}_{Ga}$
0.05	-700	-32	-13383
0.10	-1335	-134	-12144
0.15	-1900	-319	-10858
0.177*	-2170 (±50)	-467 (±100)	-10092 (±500)

*Phase boundary



COPPER - GALLIUM SYSTEM



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ΔH (298°K, x_{Ga} = 0.068-0.177).

Cu-Ge

Copper-Germanium

Part I. Discussion

Phases and Structures. The phase diagram from Hansen (1958) has been modified to the more accurate liquidus boundaries from Elliott (1965). Pearson (1958, 1967) lists the following intermediate phases.

ζ, "Cu_5Ge", with the hcp (A3) structure isotypic with Mg.

ϵ, "Cu_3Ge", has a trigonally distorted bcc (A2) structure.

ϵ_1, "Cu_3Ge", has an orthorhombic structure isotypic with β-Cu_3Ti.

ϵ_2, "Cu_3Ge", with a bcc (A2) structure isotypic with W.

In addition "CuGe" with a hcp (A3) structure isotypic with Mg has been reported.

The extremely low solubilities of Cu in (Ge) have been measured by Dorward and Kirkaldy (1968); Hall (1957); and Thurmond and Struthers (1953).

Solid Alloys. Selected values of Table 1 have been taken from Cp measurements of Rayne (1958), 1°- 4.2°K, x_{Ge} = 0.004-0.109. Selected ΔH values of Table 2 were taken from tin solution calorimetry of Kleppa and King (1962), 298°K, x_{Ge} = 0.043-0.162.

Part II. Tables

TABLE 1

Low-Temperature Data for (Cu)-Phase

T,°K	x_{Ge}				
	0.00	0.005	0.01	0.05	0.10
	Cp				
1	.000175	.000180	.00183	.000190	.000196
2	.000419	.000429	.000434	.000453	.000478
3	.000799	.000814	.000821	.000864	.000935
4	.00138	.00140	.00141	.00149	.00165
$\gamma \times 10^4$	1.641(±.03)	1.687	1.711	1.778	1.811

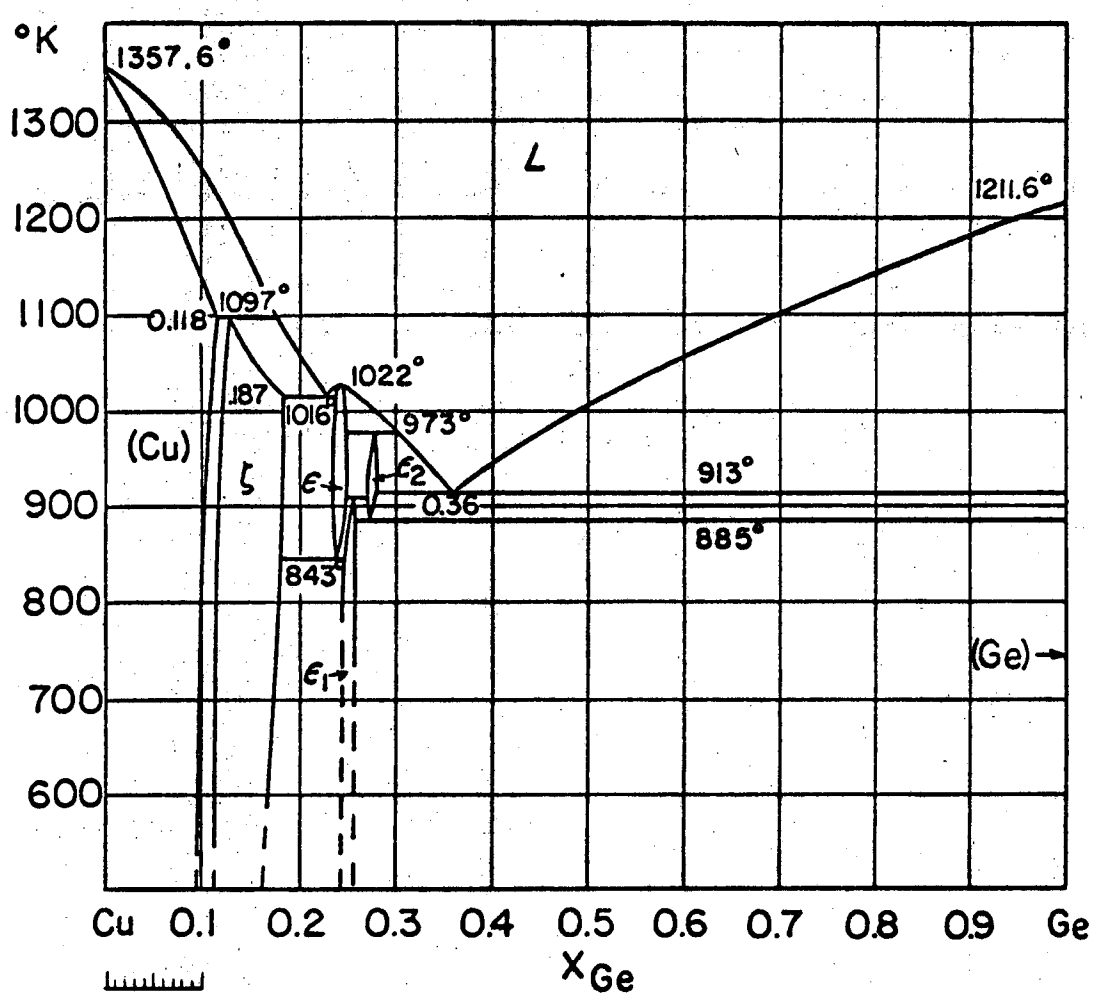
TABLE 2

Heats of Formation for (Cu)-Phase Alloys at 298.15°K

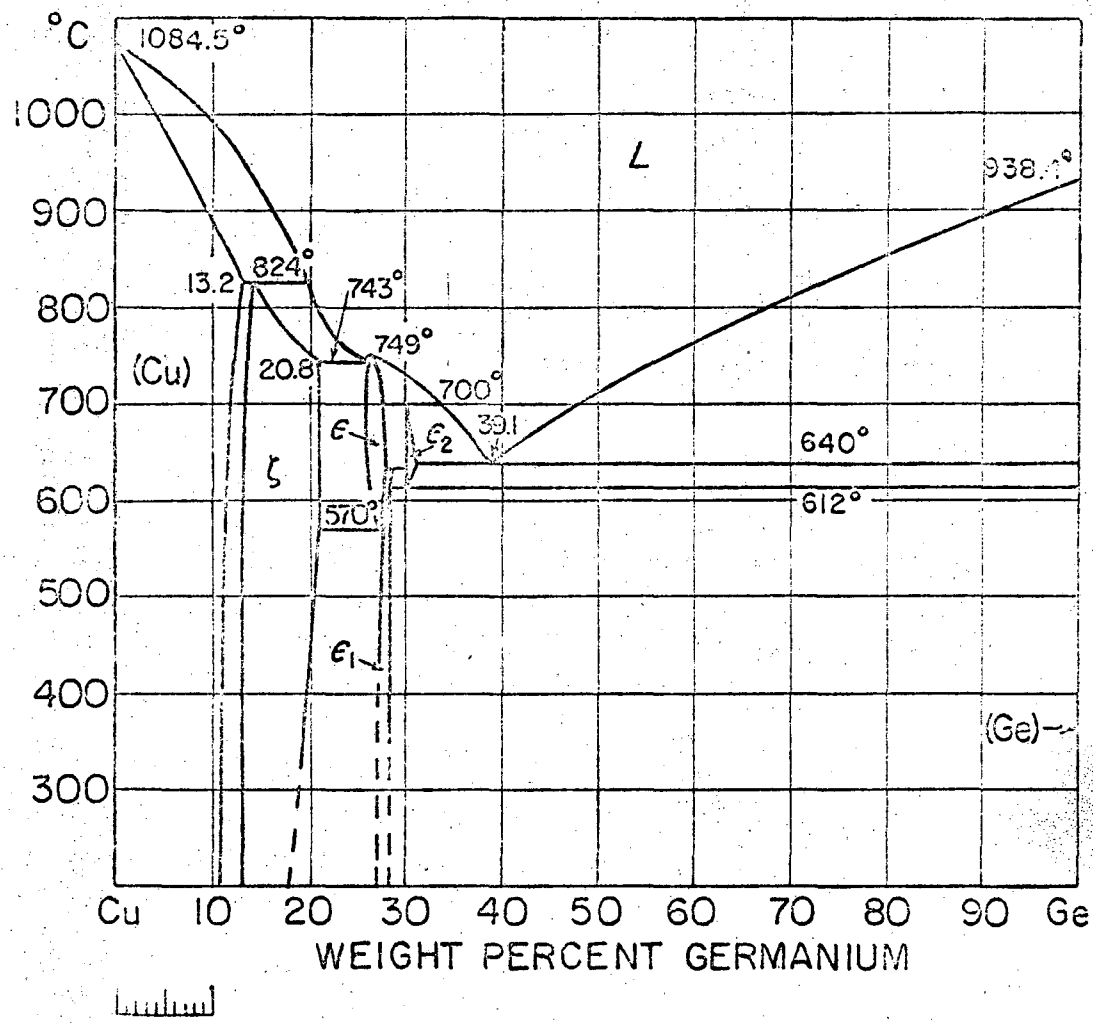
$$(1-x)Cu_{(s)} + xGe_{(s)} = Cu_{1-x}Ge_{x(s)}$$

x_{Ge}	ΔH
0.05	-210
0.10	-430
0.116*	-512 (±50)

*Phase boundary



COPPER - GERMANIUM SYSTEM



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Copper-Indium

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958). Pearson (1958) lists the following intermediate phases:

β, "Cu_4In", with the bcc (A2) structure isotypic with W.

γ, has a complex cubic ($D8_{1-3}$) structure isotypic with Fe_3Zn_{10}, Cu_5Zn_8, or Cu_9Al_4.

δ, with a complex structure resembling ($D8_{1-3}$) which has been variously described as cubic, tetragonal, or hexagonal, (see Shunk, 1969).

η, "Cu_2In", has a hexagonal ($B8_2$) structure isotypic with Ni_2In.

The structure of the ϕ phase has not been reported.

Solid Alloys. Selected values of Table 1 were taken from liquid tin solution calorimetric measurements of Kleppa (1956), 723°K, x_{In}=0.089-0.375; 0.92-0.98.

Liquid Alloys. Selected $\Delta\bar{G}_{In}$ values of Table 3 were taken from the emf studies of Azakami and Yazawa (1969), 973°-1273°K, x_{In}=0.2-0.8, who have reported emf versus temperature curves. Selected ΔH values of Table 2 agree well with the direct reaction calorimetric measurements of Yazawa and Itagaki (1969), 1373°K, x_{In} = 0.10-0.90, and with liquid tin solution calorimetric measurements of Kleppa (1956). Other quantities of Tables 2 and 3 were calculated with the aid of Gibbs-Duhem integration.

Part II. Tables

TABLE 1

Heats of Formation of Solid Alloys at 723°K

$$(1-x)Cu_{(s)} + xIn_{(s)} = Cu_{1-x}In_{x(s)}$$

x_{In}	Phase	ΔH
0.05	α	0
0.30	δ	-2040
0.34	η	-1900
0.39	η	-1800(±50)

TABLE 2

Integral Quantities for Liquid Alloys at 1073°K

$(1-x)Cu_{(\ell)} + xIn_{(\ell)} = Cu_{1-x}In_{x(\ell)}$

x_{In}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.175*	-1661	-774	0.827	-672	-0.095
0.2	-1767	-802	0.899	-700	-0.095
0.3	-1991	-749	1.157	-688	-0.057
0.4	-2005	-497	1.405	-570	0.068
0.5	-1891	-240	1.538	-412	0.160
	(±150)	(±150)	(±.14)	(±150)	(±.14)
0.6	-1689	- 74	1.505	-254	0.168
0.7	-1421	23	1.346	-119	0.132
0.8	-1088	70	1.079	- 21	0.085
0.9	- 669	66	0.685	24	0.039

TABLE 3

Partial Molar Quantities for Liquid Alloys at 1073°K

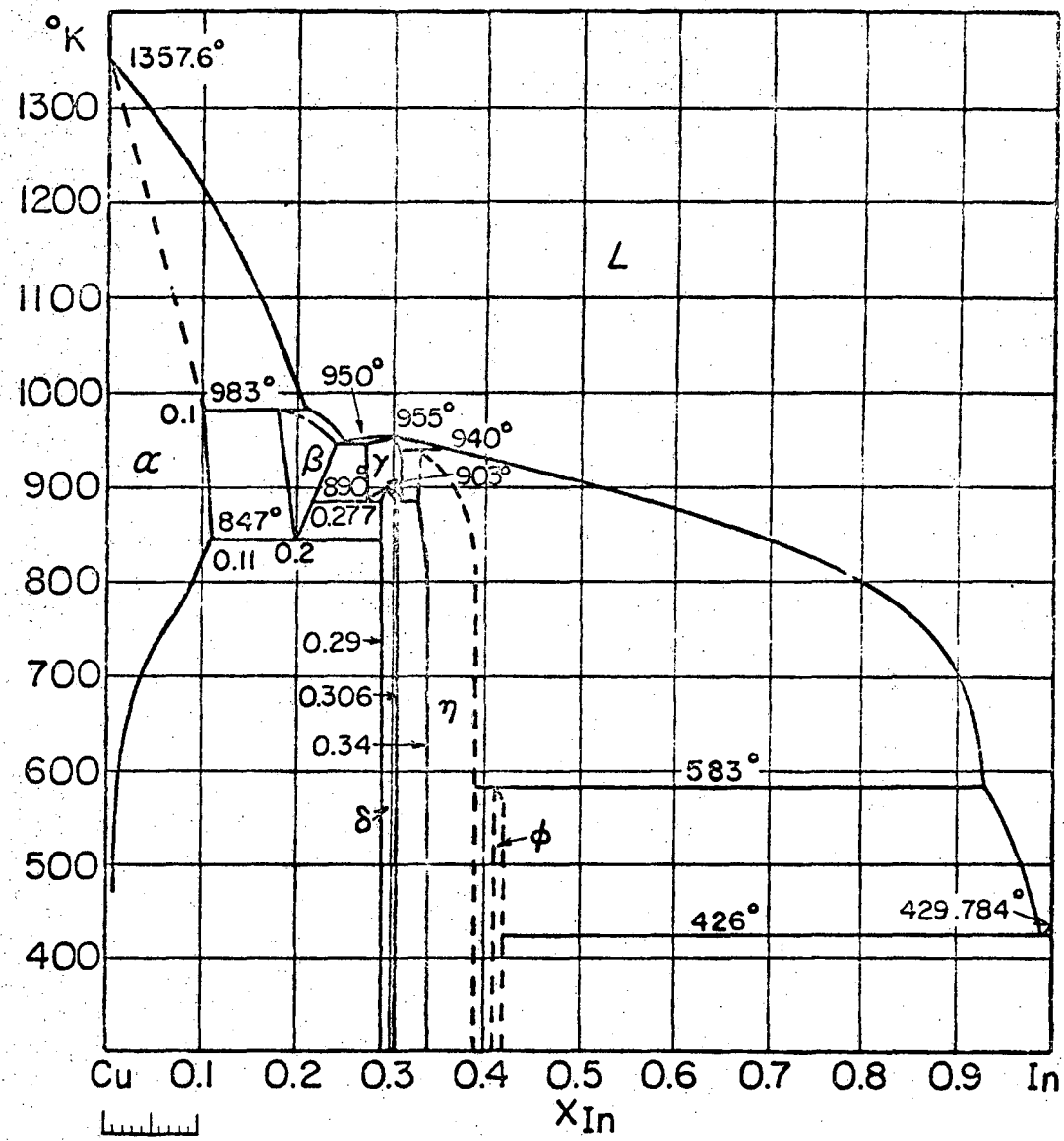
Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.825*	0.680	0.824	- 823	- 413	- 508	0.294	-0.088
0.8	0.620	0.775	-1020	- 544	- 645	0.349	-0.094
0.7	0.453	0.647	-1690	- 930	-1269	0.392	-0.316
0.6	0.349	0.582	-2243	-1154	-1622	0.579	-0.436
0.5	0.282	0.563	-2702	-1224	-1309	1.298	-0.079
	(±.02)	(±.04)	(±150)	(±150)	(±300)	(±.35)	(±.35)
0.4	0.233	0.582	-3109	-1155	- 853	2.102	0.281
0.3	0.192	0.640	-3520	- 953	- 468	2.844	0.452
0.2	0.151	0.753	-4037	- 605	- 16	3.747	0.548
0.1	0.096	0.958	-5002	- 92	296	4.938	0.362
0.0	0.000	1.328	- ∞	606	1010	∞	0.376

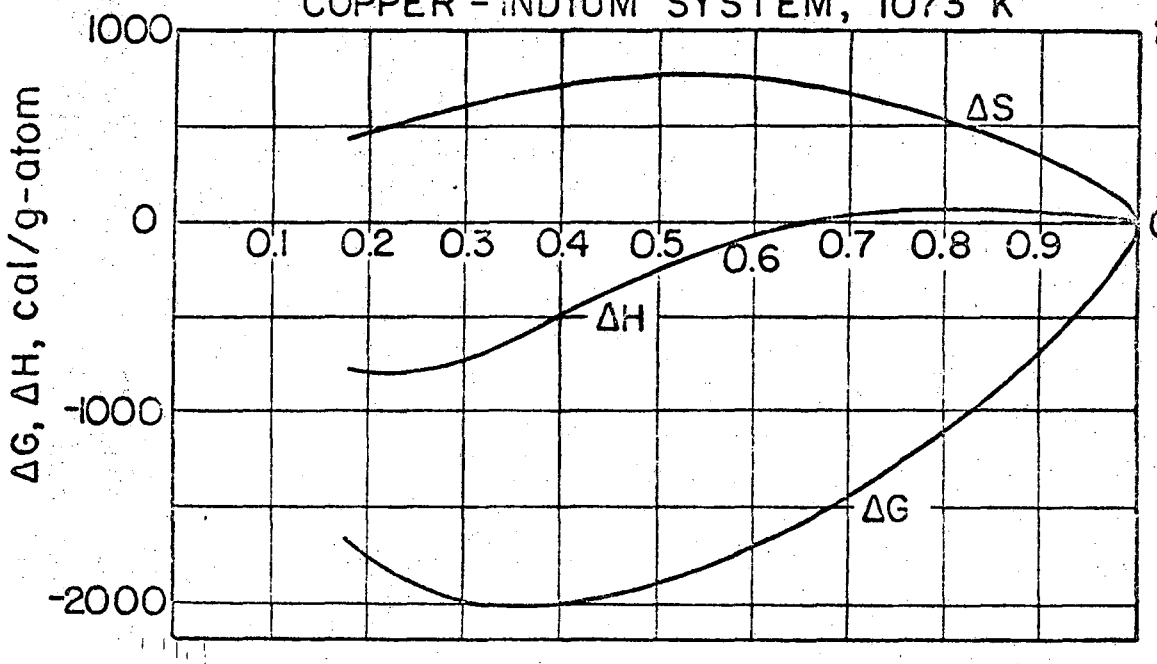
In Component $In_{(\ell)} = In(\text{in alloy})_{(\ell)}$

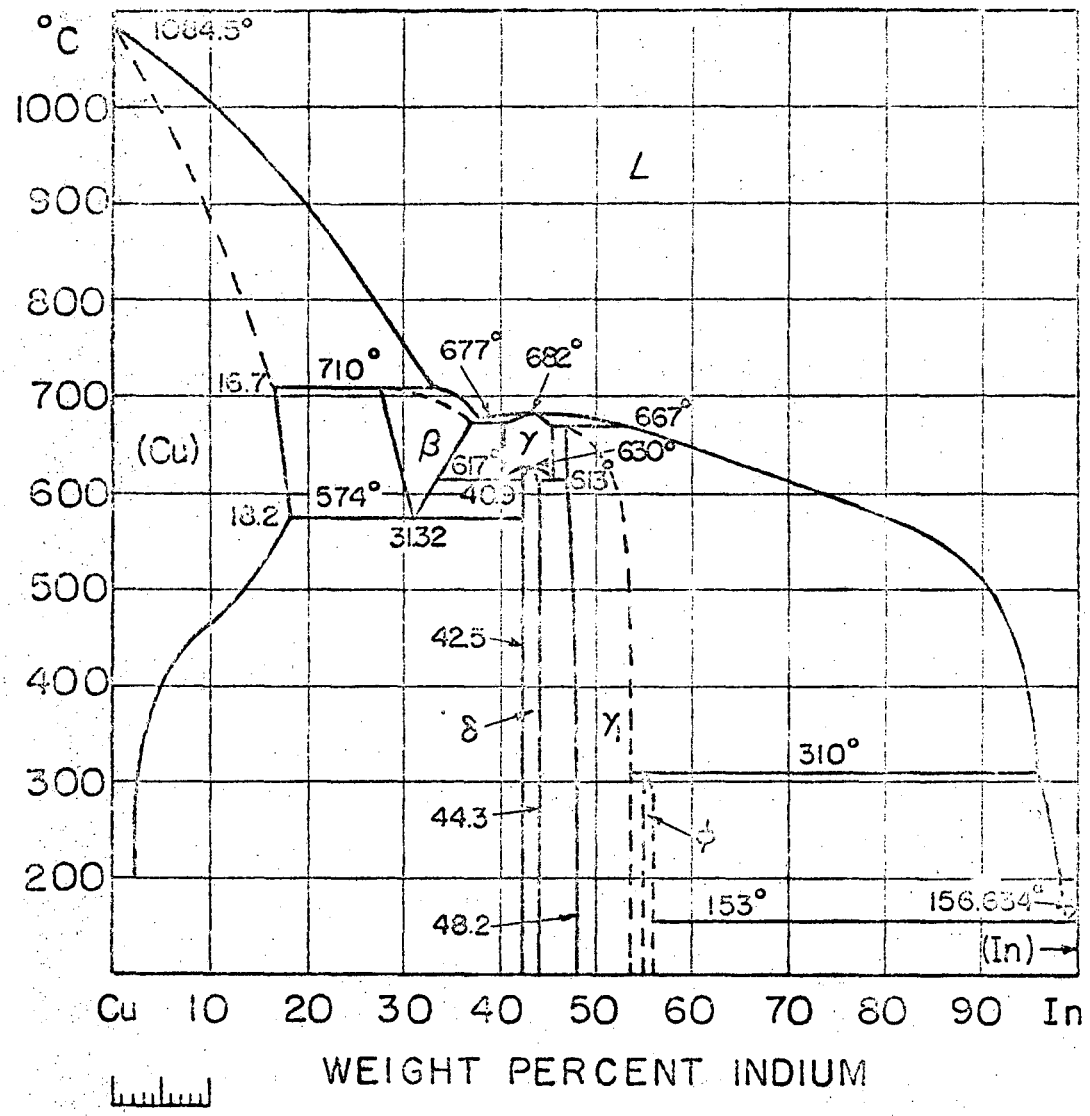
x_{In}	a_{In}	γ_{In}	$\Delta\bar{G}_{In}$	$\Delta\bar{G}^{xs}_{In}$	$\Delta\bar{H}_{In}$	$\Delta\bar{S}_{In}$	$\Delta\bar{S}^{xs}_{In}$
0.175*	0.072	0.412	-5609	-1892	-2028	3.337	-0.127
0.2	0.107	0.537	-4756	-1325	-1427	3.102	-0.095
0.3	0.283	0.943	-2692	- 125	465	2.942	0.550
0.4	0.462	1.154	-1648	306	1192	2.647	0.826
0.5	0.603	1.206	-1079	399	829	1.778	0.401
	(±.04)	(±.08)	(±150)	(±150)	(±300)	(±.35)	(±.35)
0.6	0.706	1.177	- 743	346	445	1.107	0.092
0.7	0.783	1.118	- 521	239	233	0.703	-0.006
0.8	0.848	1.060	- 351	125	91	0.412	-0.032
0.9	0.916	1.018	- 188	37	40	0.212	0.003
1.0	1.000	1.000	0	0	0	0.000	0.000

*Phase boundary



COPPER - INDIUM SYSTEM, 1073°K





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Yazawa, A., and K. Itagaki (1969) Private Communication, Tohoku University, Sendai, Japan. ΔH (1373°K, x_{In} = 0.1-0.9).

Copper-Magnesium

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with more accurate (Cu)-phase boundaries from Elliott (1965). Pearson (1958, 1967) lists two intermediate phases.

- β, "Cu_2Mg", with the ordered fcc (C15) prototype structure. There is some evidence that disordering occurs above 600° K (see Solid Alloys).
- γ, "$CuMg_2$", with an ordered orthorhombic structure.

Solid Alloys. Low-Temperature Data. Selected values of Table 1 were taken from Cp measurements of Slick, Massena, and Craig (1965), 1.7° - 4° K, x_{Mg} = 0.333.

High-Temperature Data. Selected values of Table 2 agree with the enthalpy measurements of Schübel (1914), 291° - 773° K, x_{Mg} = 0.333, and Schimpff (1910), 83° - 373° K, x_{Mg} = 0.333, 0.667. At 600° K and above, ΔCp becomes positive, possibly indicating disordering; drop calorimetry is not a precise method for determining enthalpy under these conditions. ΔH_{st} values were obtained from liquid tin solution calorimetry of King and Kleppa (1964), 298.15° K, x_{Mg} = 0.333, 0.667.

Selected $\Delta\bar{G}_{Mg}$ values of Table 4 were calculated from emf measurements of Eremenko, Lukashenko, and Polotskaya (1968), 673° - 873° K, x_{Mg} = 0.175-0.585. Mg vapor pressure measurements of Smith and Christian (1960), 675° - 1020° K, x_{Mg} = 0.12-0.89 lead to values of $\Delta\bar{G}_{Mg}$ which are less exothermic by 960 cal/g-atom than the selected values for x_{Mg}<0.33, and 2240 cal/g-atom more exothermic than the selected values between 0.33 and 0.667. Their results would imply that γ was more stable than β, whereas β has much the higher melting point. Smith and Christian's results were therefore not accepted. From the selected $\Delta\bar{G}_{Mg}$ values and a value of $\Delta\bar{G}_{Cu}$ from the phase boundary of the (Cu)-phase, assuming Raoult's law, the remaining Gibbs energies of Tables 3 and 4 were calculated. From the selected ΔG_{750} and ΔH_{st}, and the heat content data, the remaining ΔG, ΔH, and ΔS values of Table 2 were calculated.

Liquid Alloys. Selected $\Delta\bar{G}_{Mg}$ values of Table 6 agree (±150 cal/g-atom) with the Mg vapor pressure measurements of Sieben and Schmahl (1966), 865° - 1200° K, x_{Mg} = 0.22-0.94, and with the phase diagram. The Gibbs-Duhem integration constant was obtained from the phase diagram, assuming Raoult's law for a_{Cu} in the (Cu)-phase. Temperature coefficients of Sieben and Schmahl agree well (±0.1 eu) with selected $\Delta\bar{S}_{Mg}$, except they scatter more (±0.8 eu) for x_{Mg}<0.4. Selected values also agree with the phase diagram.

PDD, SJN June, 1969

Part II. Tables

TABLE 1

Low-Temperature Data for β-Phase Alloy, $x_{Mg} = 0.333$

T, °K	Cp
2	0.000598
3	0.00109
4	0.00182

$C_{(electronic)} = \gamma T \qquad \gamma = 2.48(\pm 0.01)\times 10^{-4}$

TABLE 2

Temperature Dependence of Quantities for Solid Alloys

$$(1-x)Cu_{(s)} + xMg_{(s)} = Cu_{1-x}Mg_{x(s)}$$

T, °K	Cp	H_T-H_{st}	S_T-S_{st}	ΔCp	ΔG	ΔH	ΔS
	(β-Phase) $x_{Mg}=0.333$						
298.15	5.810	0	0.000	-0.067	-2715 (±200)	-2670 (±50)	0.152 (±.7)
400	5.996	601	1.732	-0.111	-2729	-2679	0.125
500	6.238	1212	3.095	-0.062	-2742	-2689	0.105
600	6.570	1851	4.260	0.083	-2752	-2690	0.103
700	6.985	2529	5.304	0.325	-2762	-2669	0.133
750	7.199	2884	5.793	0.452	-2769	-2649	0.160
800	7.417	3249	6.265	0.574	-2779	-2624	0.194
	(γ-Phase) $x_{Mg}=0.667$						
298.15						-2280	
373		441					
750					-2141		

TABLE 3

Integral Quantities for Solid Alloys at 750°K

$$(1-x)Cu_{(s)} + xMg_{(s)} = Cu_{(1-x)}Mg_{x(s)}$$

x_{Mg}	Phase	ΔG	ΔG^{xs}
0.041*	(Cu)	- 396	- 141
0.328*	β	-2732	-1789
0.333		-2769	-1820
0.357*	β	-2820 (±150)	-1848 (±150)
0.667	γ	-2139	-1190

TABLE 4

Partial Molar Quantities for Solid Alloys at 750°K

x_{Mg}	Phase	Cu Component $Cu_{(s)}$ = Cu(in alloy)$_{(s)}$				Mg Component $Mg_{(s)}$ = Mg(in alloy)$_{(s)}$			
		a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Mg}	γ_{Mg}	$\Delta\bar{G}_{Mg}$	$\Delta\bar{G}^{xs}_{Mg}$
0.041*	(Cu)	0.959	1.000	- 62	0	0.004	0.099	-8203	-3442
0.328*	β	0.959	1.427	- 62	530	0.004	0.012	-8203	-6541
0.333		0.650	0.975	- 641	- 37	0.009	0.027	-7031	-5392
0.357*	β	0.089 (±.008)	0.139 (±.012)	-3604 (±150)	-2946 (±150)	0.391 (±.039)	1.094 (±.11)	-1407 (±150)	129 (±150)

TABLE 5

Integral Quantities for Liquid Alloys at 1100°K

$$(1-x)Cu_{(\ell)} + xMg_{(\ell)} = Cu_{(1-x)}Mg_{x(\ell)}$$

x_{Mg}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.168*	-2072	-1643	0.390	-1083	-0.509
0.2	-2316	-1841	0.432	-1222	-0.562
0.3	-2865	-2285	0.527	-1529	-0.687
0.4	-3123	-2485	0.580	-1652	-0.757
0.5	-3131 (±300)	-2465 (±500)	0.605 (±.54)	-1616 (±300)	-0.772 (±.54)
0.6	-2916	-2265	0.591	-1444	-0.746
0.7	-2501	-1933	0.516	-1165	-0.698
0.8	-1905	-1492	0.375	- 811	-0.619
0.9	-1124	- 908	0.197	- 414	-0.449

*Phase boundary

TABLE 6

Partial Molar Quantities for Liquid Alloys at 1100°K

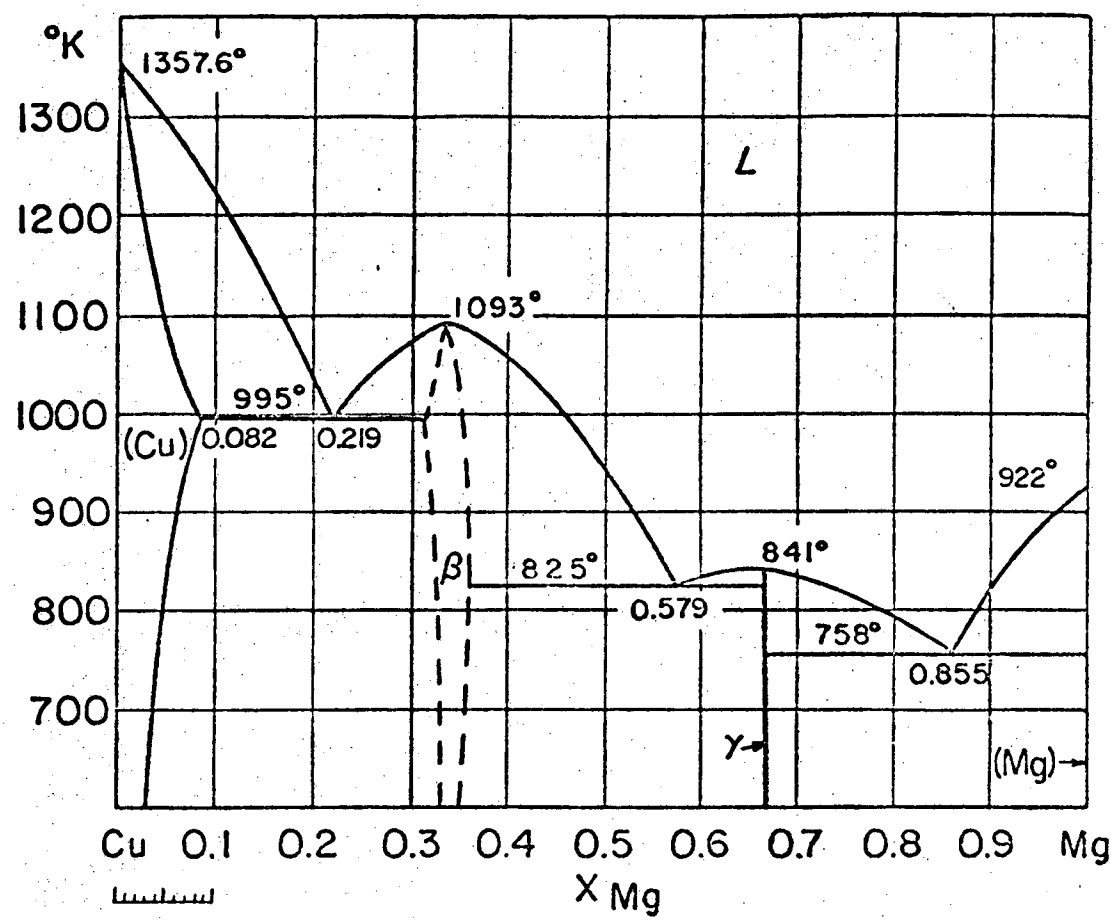
Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.832*	0.725	0.872	- 701	- 299	- 542	0.144	-0.221
0.8	0.661	0.826	- 904	- 416	- 695	0.189	-0.254
0.7	0.465	0.664	-1674	- 894	- 1327	0.315	-0.394
0.6	0.302	0.504	-2613	-1496	- 2145	0.425	-0.590
0.5	0.187	0.373	-3670	-2155	- 3056	0.558	-0.819
	(±.024)	(±.048)	(±300)	(±300)	(±500)	(±.54)	(±.54)
0.4	0.110	0.275	-4829	-2826	- 3902	0.843	-0.978
0.3	0.063	0.209	-6054	-3422	- 4642	1.283	-1.109
0.2	0.034	0.171	-7374	-3856	- 5475	1.726	-1.472
0.1	0.015	0.154	-9127	-4094	- 7206	1.747	-2.829
0.0	0.000	0.000	- ∞	-4168	-11762	∞	-6.904

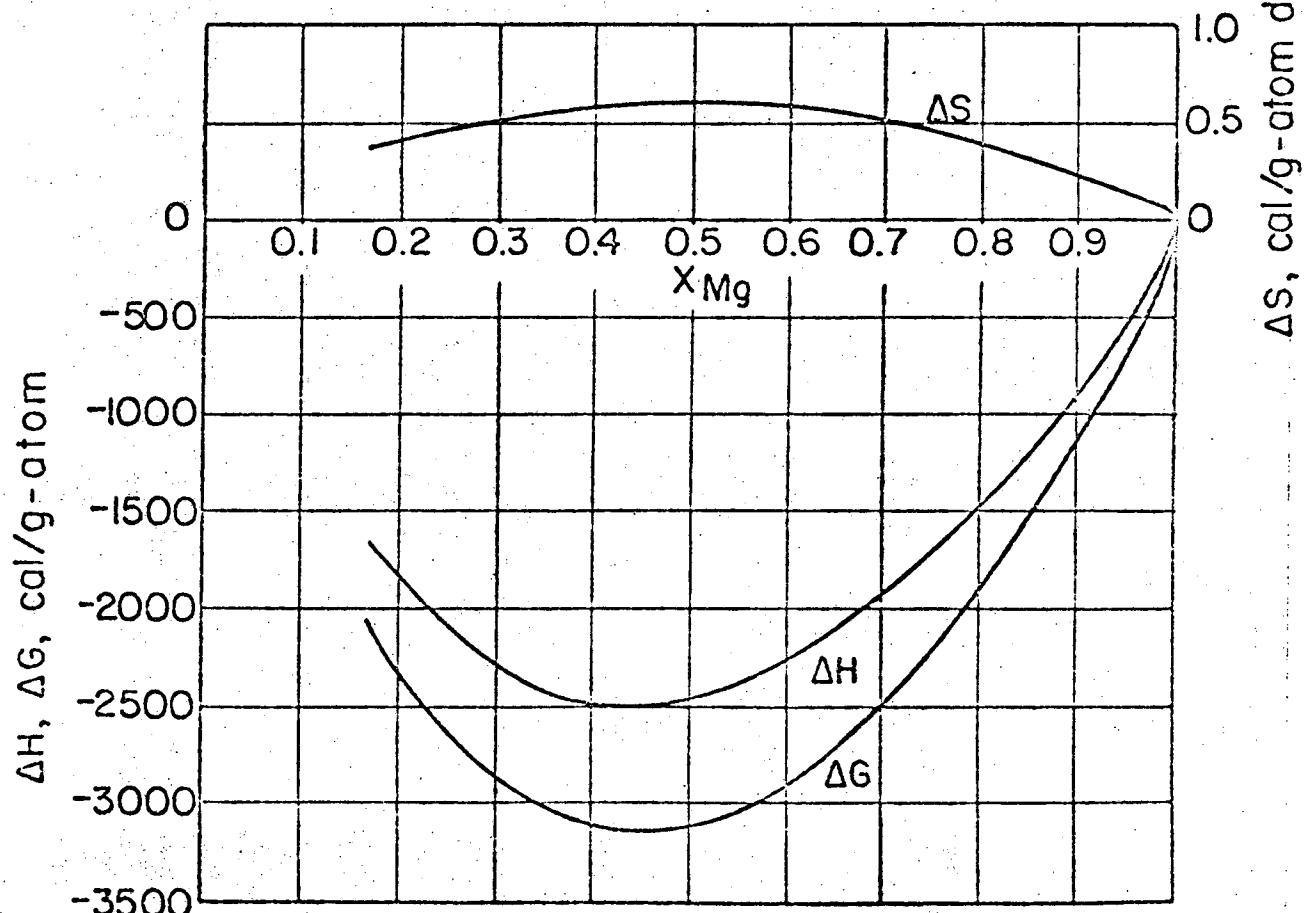
Mg Component $Mg_{(\ell)} = Mg(\text{in alloy})_{(\ell)}$

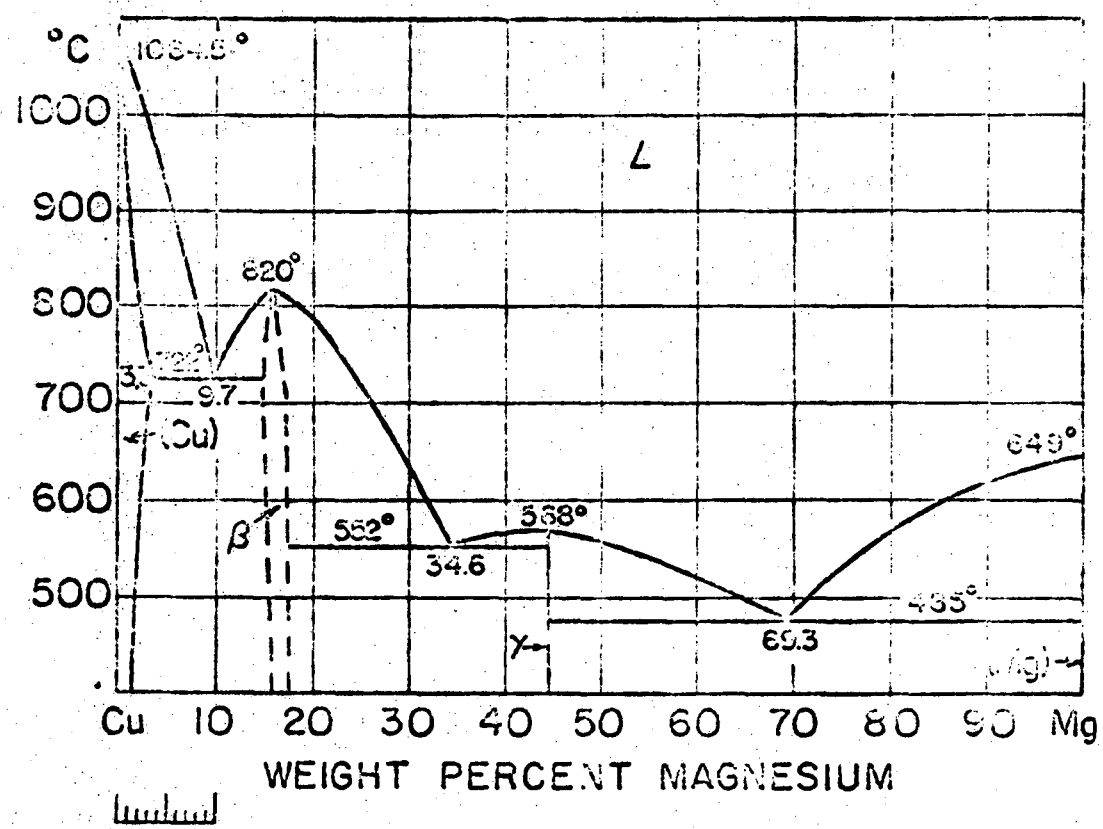
x_{Mg}	a_{Mg}	γ_{Mg}	$\Delta\bar{G}_{Mg}$	$\Delta\bar{G}^{xs}_{Mg}$	$\Delta\bar{H}_{Mg}$	$\Delta\bar{S}_{Mg}$	$\Delta\bar{S}^{xs}_{Mg}$
0.168*	0.017	0.103	-8862	-4963	-7095	1.607	-1.938
0.2	0.026	0.131	-7966	-4448	-6419	1.406	-1.792
0.3	0.076	0.252	-5643	-3011	-4520	1.021	-1.372
0.4	0.169	0.422	-3889	-1886	-2995	0.813	-1.008
0.5	0.306	0.611	-2591	-1076	-1873	0.652	-0.725
	(±.04)	(±.08)	(±300)	(±300)	(±500)	(±.54)	(±.54)
0.6	0.472	0.787	-1640	- 523	-1174	0.423	-0.592
0.7	0.639	0.913	- 978	- 198	- 772	0.187	-0.522
0.8	0.782	0.978	- 538	- 50	- 497	0.037	-0.406
0.9	0.898	0.998	- 235	- 5	- 208	0.024	-0.185
1.0	1.000	1.000	0	0	0	0.000	0.000

*Phase boundary



COPPER – MAGNESIUM SYSTEM, 1100°K




°C
1000
900
800
700
600
500
L
820°
9.7
(Cu)
β
552°
34.6
568°
γ
69.3
649°
485°
(Mg)
Cu 10 20 30 40 50 60 70 80 90 Mg
WEIGHT PERCENT MAGNESIUM

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(For references not in list, see General References)

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Slick, P. I., C. W. Massena, and R. S. Craig (1965) J. Chem. Phys. 43, 2788-94. Cp (1.7°- 4°K, x_{Mg} = 0.333).

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Copper-Manganese

Part I. Discussion

Phases and Structures. The phase diagram, from Shunk (1969), has been altered lowering the transformation $T_{\alpha-\beta}$ of Mn by 20°K to agree with selected values. The α-phase has the fcc (A1) structure isotypic with Cu. At high Mn concentrations γ quenched to room temperature distorts slightly to a fc tetragonal structure. The γ' and γ'' phases indicated are thought to be ordered structures of γ, but this could not be confirmed by X-ray diffraction because of the nearly equal atomic numbers of Cu and Mn.

Solid Alloys. Low-Temperature Data. Selected values of Table 1 were taken from Cp measurements of Ho (1965), 0.07°- 1.2°K, x_{Mn} = 0.00057-0.939; 0.06°- 4.2°K, x_{Mn} = 1.00. Ho found a pronounced rise in Cp at the lowest temperature, resulting in minima in Cp at 0.1°- 0.8°K, depending on the concentration. This result, not found in pure Cu, was no doubt due to nuclear contributions. Cp measurements of Du Chatenier and Miedema (1965), 0.06°- 10°K, x_{Mn} = 0.0015, 0.0115, found minima at approximately the same temperatures, though their Cp values only roughly agreed with those of Ho (1965).

Cp measurements at numerous compositions up to 10°K seemed to change regularly with composition, so that Tables 1b and 1c were derived at smoothed compositions. Selected values of Table 1b agree well with Cp measurements of Zimmerman and Sato (1961) 1.5°- 4.2°K, x_{Mn} = 0.11-0.96; and of Zimmerman and Hoare (1960), 2°- 4°K, x_{Mn} = 0.0058-0.114; 2°- 15°K, x_{Mn} = 0.0016, 0.0055; but are slightly lower than those of De Nobel and Du Chatenier (1959), 1.6°- 20°K, x_{Mn} = 0.0013; Du Chatenier and De Nobel (1966), 0.1°- 10°K, x_{Mn} = 0.00-0.0115. Selected values of Table 1c agree within a few percent with Cp measurements of Du Chatenier and De Nobel (1966), De Nobel and Du Chatenier (1959), and with those of Zimmerman and Hoare (1960), with the following exceptions: values of Du Chatenier and De Nobel (1966) are about 10% lower near x_{Mn} = 0.01 and 5°K. Cp measurements of Du Chatenier and Miedema (1965) are about 10% higher at 5°K than selected values.

All workers found that small additions of Mn to Cu greatly increased Cp, the result becoming less prominent at higher temperatures. The cause for this is not clear; Zimmerman and Hoare (1960) attributed it to an antiferromagnetic transformation.

High-Temperature Data. Selected values of Table 2 were taken from Cp measurements of Scheil and Norman (1960), 293°- 823°K, x_{Mn}=0.231. They attributed the small anomaly near 523°K to "short-range ordering"; more likely it is connected with the ordered γ' phase. Cp measurements of Hirano, Maniwa, and Takagi (1958), 273°- 573°K, x_{Mn}=0.534, 0.743, 0.817; and heat content measurements of Naylor (1946), 723°- 1123°K, x_{Mn} =0.28-0.91, were not evaluated because they involved the two-phase region, making initial or final states uncertain.

Selected $\Delta\bar{G}_{Mn}$ values of Table 4 agree within 200 cal/g atom with emf measurements of Peters and Wiles (1963), 1091°- 1119°K, x_{Mn} = 0.20-1.00, except for one experimental point (x_{Mn} = 0.297) which is less exothermic by about 400 cal/g atom. $\Delta\bar{G}_{Mn}$ values derived from Mn vapor pressure measurements of Krenzer and Pool (1969), 1043°- 1323°K, x_{Mn} = 0.13-1.00 are less exothermic by 70-450 cal/g atom for $x_{Mn}<0.25$ and more exothermic by about 200-550 cal/g atom for $x_{Mn}>0.25$. It should be noted that Krenzer and Pool (1969) erred in extrapolating some of their values for fcc γ-phase to x_{Mn} = 1.0. Since they used β-Mn for their standard state, extrapolation of the γ-phase should lead to $a_{Mn}>1.00$, with corresponding changes in Gibbs function plots. They are aware of the difficulty, but state that they have "followed experimental data", which unconvincingly violate the laws of thermodynamics. They suggest their experimental data may be wrong because of surface depletion, but this is less likely at high Mn contents. Values of $\Delta\bar{G}_{Mn}$ derived from emf measurements of Eremenko, Lukashenko, and Sidorko (1964, 1968), 923°- 1123°K, x_{Mn}= 0.06-0.82 are more exothermic than selected values by 50-250 cal/g atom for most compositions but as much as 900 cal/g atom for $x_{Mn}<0.25$. Values of $\Delta\bar{G}_{Mn}$ at 1163°K derived from Mn vapor pressure measurements of Evseeva and Evseev (1963), 1163°, 1211°K, x_{Mn} = 0.1-0.95 are in rough agreement with the selected values but extrapolating to 1100°K using their temperature coefficients gave absurd results. The value of $\Delta\bar{G}_{Mn}$ at x_{Mn} = 0.885 was taken from the phase diagram. Conversion to the γ-Mn standard state was made assuming for Mn that $\Delta S_{\beta-\gamma}$= 0.37, invariant with T.

Selected ΔH values of Table 3 were taken from the liquid tin solution calorimetric measurements of Pratt and Bryant (1969), 320°K, x_{Mn}= 0.1-0.9. Temperature coefficients of Eremenko et al. (1964, 1968) lead to improbably large endothermic values for ΔH and ΔS.

Liquid Alloys. Selected values of Table 6 were derived from Mn vapor pressure measurements of Spencer and Pratt (1968), 1278°- 1596°K, x_{Mn}= 0.05-0.85.

Part II. Tables

TABLE 1

Low-Temperature Data for γ-Phase Alloys

Table 1a

x_{Mn}	T, °K					
	0.08	0.10	0.20	0.50	0.80	1.00
	Cp					
0.000*	0.0000133	0.0000166	0.0000333	0.0000845	0.000139	0.000177
0.00057	0.00018	0.00016	0.00017	0.00037	0.00062	0.00077
0.0014	0.00033	0.00025	0.00019	0.00037	0.00058	0.00072
0.0059	0.00114	0.00077	0.00031	0.00034	0.00051	0.00063
0.0107	0.00248	0.00166	0.00055	0.00041	0.00058	0.00071
0.0319	0.00614	0.00406	0.00118	0.00055	0.00068	0.00081
0.435			0.00617	0.00144	0.00115	0.00121
0.586			0.00591	0.00178	0.00177	0.00200
0.939			0.00267	0.00165	0.00222	0.00269
1.000**	0.0100	0.00653	0.00202	0.00135	0.00186	0.00227

Table 1b

x_{Mn}	T, °K			$\gamma \times 10^4 (\pm .1)$
	2	3	4	
	Cp			
0.00*	0.000423	0.000806	0.00139	1.66
0.10	0.00248	0.00415	0.00636	
0.20	0.00166	0.00275	0.00416	
0.30	0.00129	0.00230	0.00376	5.45
0.40	0.00162	0.00269	0.00407	7.40
0.50	0.00225	0.00372	0.00550	10.45
0.60	0.00400	0.00606	0.00816	19.86
0.70	0.00497	0.00777	0.0110	24.00
0.80	0.00546	0.00852	0.0120	26.45
0.90	0.00525	0.00795	0.0113	24.25
1.00**	0.00452	0.00696	0.00964	21.99

Table 1c

x_{Mn}	T, °K			
	5	10	15	20
	Cp			
0.000*	0.00225	0.0133	0.0439	0.110
0.001	0.0036	0.015		0.116
0.005	0.0084	0.021	0.052	
0.01	0.011	0.028		

*Selected values (see (Cu)

**For γ-Mn

TABLE 2

High-Temperature Data for γ-Phase Alloy, $x_{Mn} = 0.231$

$$0.769Cu_{(s)} + 0.231Mn_{(\gamma)} = Cu_{0.769}Mn_{0.231(\gamma)}$$

T, °K	Cp	ΔCp	T, °K	Cp	ΔCp
298.15	6.05	0.02	523	7.40	0.85
400	6.30	0.02	550	7.01	0.39
473	6.56	0.11	600	7.05	0.33
500	6.88	0.37	700	7.15	0.23

TABLE 3

Integral Quantities for γ-Phase Alloys at 1100°K

$$(1-x)Cu_{(s)} + xMn_{(\gamma)} = Cu_{1-x}Mn_{x(\gamma)}$$

x_{Mn}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.10	- 755	240	0.904	- 45	0.259
0.20	-1105	456	1.419	- 12	0.425
0.30	-1270	608	1.707	66	0.493
0.40	-1299	701	1.798	172	0.481
0.50	-1226	764	1.809	289	0.432
	(±350)	(±100)	(±.33)	(±350)	(±.33)
0.60	-1072	871	1.766	399	0.429
0.70	- 860	1009	1.699	475	0.485
0.80	- 615	1096	1.555	479	0.561
0.885*	- 396	720	1.014	384	0.305
0.90		625**			

TABLE 4

Partial Molar Quantities for γ-Phase Alloys at 1100°K

	Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(\gamma)}$				Mn Component $Mn_{(\gamma)} = Mn(\text{in alloy})_{(\gamma)}$			
x_{Mn}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Mn}	γ_{Mn}	$\Delta\bar{G}_{Mn}$	$\Delta\bar{G}^{xs}_{Mn}$
0.00	1.000	1.000	0	0	0.000	0.669	- ∞	-880
0.10	0.883	0.982	- 271	- 41	0.096	0.964	-5114	- 81
0.20	0.776	0.944	- 613	- 125	0.245	1.224	-3076	442
0.30	0.633	0.904	- 999	- 219	0.419	1.396	-1902	730
0.40	0.526	0.876	-1406	- 289	0.594	1.485	-1139	864
0.50	0.437	0.874	-1809	- 294	0.745	1.491	- 643	872
	(±.07)	(±.14)	(±350)	(±350)	(±.11)	(±.22)	(±350)	(±350)
0.60	0.367	0.917	-2192	- 189	0.861	1.436	- 326	790
0.70	0.319	1.064	-2496	136	0.930	1.328	- 159	621
0.80	0.299	1.494	-2641	877	0.952	1.190	- 108	380
0.885*	0.290	2.526	-2702	2026	0.957	1.081	- 96	171

*Phase boundary

**Measured at 320°K, phase is unstable at 1100°K.

TABLE 5

Integral Quantities for Liquid Alloys at 1500°K

$$(1-x)Cu_{(\ell)} + xMn_{(\ell)} = Cu_{(1-x)}Mn_{x(\ell)}$$

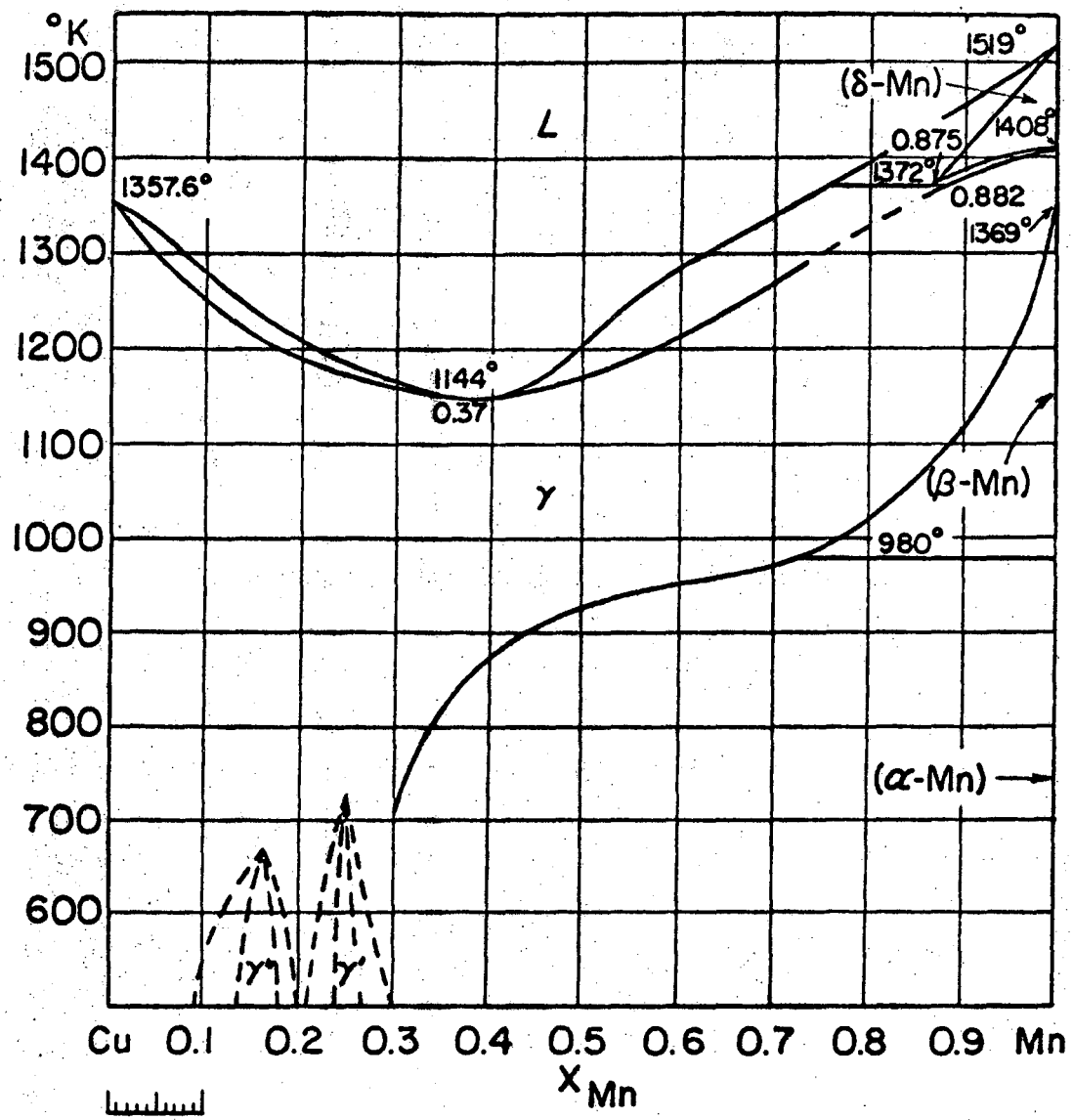
x_{Mn}	ΔG	ΔG^{xs}	x_{Mn}	ΔG	ΔG^{xs}
0.1	-1082	-113	0.6	-1377	629
0.2	-1555	- 64	0.7	-1099	722
0.3	-1724	97	0.8	- 785	707
0.4	-1714	292	0.9	- 456	513
0.5	-1591	476	0.96*	- 226	275
	(±100)	(±100)		(±100)	(±100)

TABLE 6

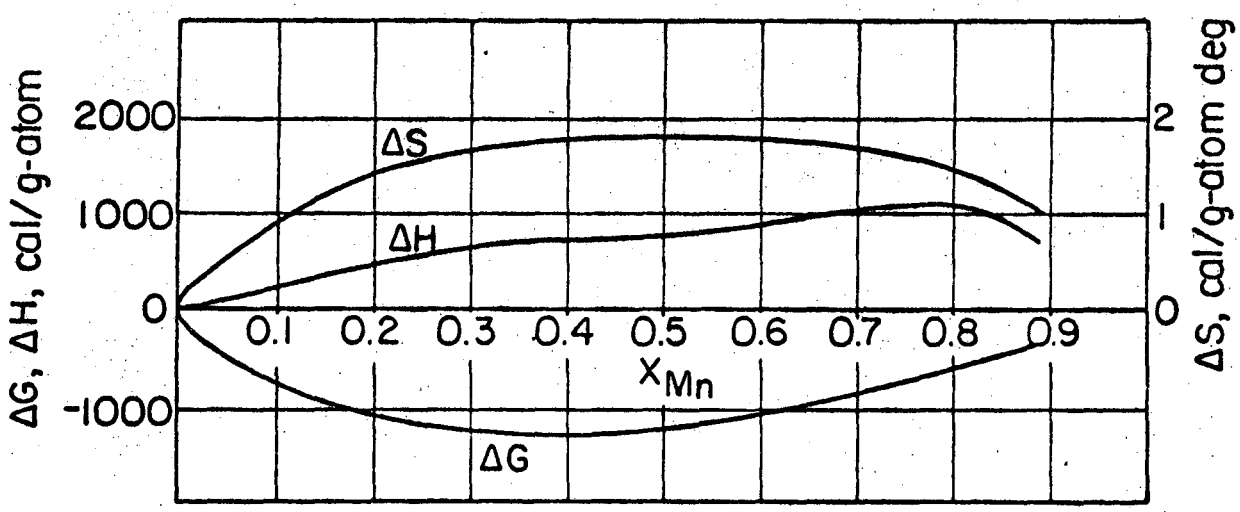
Partial Molar Quantities for Liquid Alloys at 1500°K

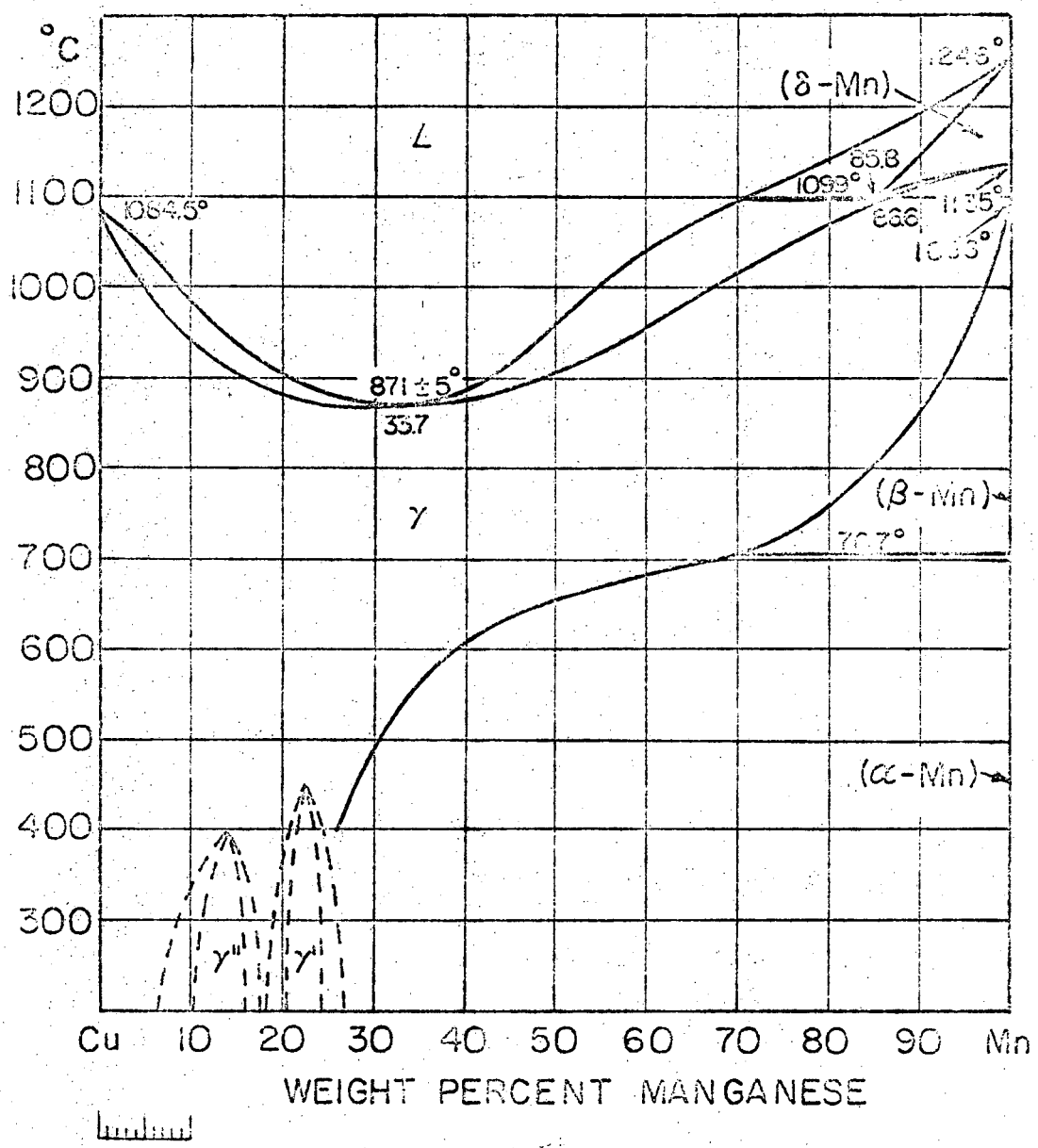
	Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$				Mn Component $Mn_{(\ell)} = Mn(\text{in alloy})_{(\ell)}$			
x_{Mn}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Mn}	γ_{Mn}	$\Delta\bar{G}_{Mn}$	$\Delta\bar{G}^{xs}_{Mn}$
0.0	1.000	1.000	0	0	0.000	0.511	- ∞	-2000
0.1	0.875	0.972	- 400	- 86	0.089	0.887	-7219	- 356
0.2	0.724	0.905	- 964	- 299	0.268	1.342	-3920	877
0.3	0.598	0.854	-1532	- 469	0.482	1.608	-2173	1416
0.4	0.511	0.851	-2004	- 481	0.651	1.627	-1280	1451
0.5	0.440	0.879	-2450	- 384	0.782	1.565	- 731	1335
	(±.015)	(±.03)	(±100)	(±100)	(±.025)	(±.05)	(±100)	(±100)
0.6	0.380	0.951	-2882	- 151	0.882	1.470	- 374	1149
0.7	0.340	1.133	-3216	373	0.938	1.340	- 191	872
0.8	0.327	1.637	-3328	1469	0.951	1.189	- 149	516
0.9	0.301	3.011	-3577	3286	0.964	1.071	- 109	205
0.96*	0.250	6.261	-4127	5468	0.987	1.028	- 41	81

*Phase boundary



COPPER - MANGANESE SYSTEM, 1100°K





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Copper-Molybdenum

Part I. Discussion

Phases and Structures. Hansen (1958) reports a complete miscibility gap in the liquid state and vanishingly small solubility of Mo in (Cu). Elliott (1965) reports a solubility of Cu in (Mo) at 950°C of about 1.5 wt.%.

Part II. Tables

No thermodynamic data were found for this system.

Part III. References

(For references not in list, see General References.)

Copper-Nickel

Part I. Discussion

Phases and Structures. The phase diagram, from Hansen (1958), shows complete miscibility in the solid and liquid states. The liquidus is well established, the solidus probably is too low. Elford, Müller, and Kubaschewski (1969), calculated from thermodynamic data that there should be a miscibility gap below 600°K.

Solid Alloys. Low Temperature Data. Below 4°K Cp measurements were found for numerous compositions. Since they agreed reasonably well, it was possible to draw credible Cp versus x_{Ni} curves, obtaining the smoothed values of Table 1. For compositions x_{Ni} = 0.35 to 0.55, Cp values are anomalously high, reaching a maximum at x_{Ni} = 0.43-0.45, and Cp/T increases as the temperature decreases. The selected values of Table 1 agree within a few percent with the Cp measurements of Dixon, Hoare, and Holden (1968), 1.2°- 4.2°K, x_{Ni}= 0.0-0.9; and Gupta, Cheng, and Beck (1964), 1.3°- 4.2°K, x_{Ni} = 0.45-0.90. Cp measurements of Keesom and Kurrelmeyer (1940), 1°- 20°K, x_{Ni} = 0.216-0.816, are higher by 0-6% and show a pronounced anomaly at 2°K not found by the others; Manchester (1959), 1°- 4.2°K, x_{Ni} = 0.313, whose own values are lower by 10-30%, believes this anomaly may be due to desorption of He. Values of Guthrie, Friedberg, and Goldman (1959), 1.3°- 4.2°K, x_{Ni} = 0.108, 0.265, 0.37, are higher by 0-9%.

Cp values of Keesom and Kurrelmeyer (1940), above 5°K are shown in Table 2 and agree with Table 3. Values of Table 3 were taken from Cp measurements of Eucken and Werth (1930), 15°- 202°K, x_{Ni} = 0.42, whose values were extrapolated to agree with Table 4. Values of Table 4 were taken from Cp measurements of Honda and Tokunaga (1935), 297.9°K, x_{Ni} = 0.0-1.0, except that their measurements at x_{Ni} = 0.522 and 0.574 are about 4% lower than the smoothed curve, which also agrees with Table 5. Yee and Zimmerman (1966), 0.05-0.15°K, x_{Ni} = 0.43, and Ho, O'Neal, and Phillips (1963), 0.3°- 4°K, x_{Ni} = 0.43, have measured the Cp of commercial constantan.

High-Temperature Data. Selected values of Table 5 were taken from Cp measurements of Pawel and Stansbury (1965), 323°- 883°K, x_{Ni} = 0.520, 0.764, 0.907, 1.000; and Grew (1934), 83°, 196°, 293°- 670°K, x_{Ni} = 0.801, 0.881, 0.944. At the measured compositions, except x_{Ni} = 0.764, the maximum Cp anomaly occurs at

the magnetic Curie temperature. At x_{Ni}=0.764, the maximum Cp lies about 60°K higher than the selected Curie temperature. The reason for this is not clear, except that the composition is in a range found not to give reproducible results by Elford, Müller, and Kubaschewski (1969).

Selected ΔH values agree well (±100 cal/g-atom) with the direct reaction calorimetry of Elford, Müller, and Kubaschewski (1969), 773°-1273°K, x_{Ni}=0.1-0.9, and with the tin solution calorimetry of Oriani and Murphy (1960), 913°K, x_{Ni}=0.03-0.94. Elford, et al., found that in the composition range x_{Ni}=0.5-0.8 the values scattered widely, being as much as 650 cal/g-atom lower than selected ones. They made Cp measurements at x_{Ni}=0.7, finding the values very high and scattered. After annealing the alloy for 11 weeks at 773°K, they found lower, more consistent Cp values. They concluded that the deviations were caused by nonequilibrium effects, and selected interpolated values, which also agree better with work of others. Their Cp values, even after the long anneal, are higher than interpolated values by more than 10%, so they have not been tabulated. Oriani and Murphy's values of ΔH were also lower than selected ones in the range x_{Ni}=0.5-0.8.

Tin solution calorimetric measurements of Leach and Bever (1959), 273°K, x_{Ni}=0.12-0.40, yielded more endothermic values by as much as 600 cal/g-atom; this could be reconciled only by an average ΔCp=-0.85. Direct reaction calorimetric measurements of Kubaschewski, Dench, and Genta (1958), 995°K, x_{Ni}=0.5, 0.6, give ΔH values which are 75-100 cal/g-atom more endothermic than selected values.

Selected $\Delta\bar{G}_{Ni}$ values of Table 7 agree closely with emf measurements of Rapp and Maak (1962), 973°, 1273°K, x_{Ni}=0.1-0.9; values of Nanis (1954), 973°K, x_{Ni}=0.01-0.77, which scatter widely, are less endothermic by 0-900 cal/g-atom. Other values of Tables 6 and 7 were calculated from selected ΔH, and $\Delta\bar{G}_{Ni}$ values. The emf values reported by Vecher and Gerasimov (1963), 873°-1023°K, x_{Ni} = 0.10-0.93, modifying slightly earlier measurements of Gerasimov, Vecher, and Geiderikh (1958), 883°-1038°K, x_{Ni} = 0.07-0.90, yield values of $\Delta\bar{G}_{Cu}$ which are more endothermic than selected values by 40-140 cal/g-atom, except for x_{Ni} >0.8, where they deviate in the same direction by larger amounts. Temperature coefficients of Rapp and Maak (1961) and Vecher and Gerasimov (1963) lead to values of ΔH which agree with selected values within 50 cal/g-atom.

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 9 agree (±100 cal/g-atom) with the Cu vapor pressure measurements of Schultz, Zellars, Payne, and Foerster (1964), 1796°-1866°K, x_{Ni} = 0.05-0.90. Elford, et al. (1969), from thermodynamic values for the solid alloys, the liquidus of the phase diagram, and assuming ideal entropy for the liquid alloys, were

able to calculate ΔG^{xs} values (assumed = ΔH) over the entire concentration range which were more endothermic than the selected values by less than 180 cal/g-atom. Considering experimental uncertainties and the assumptions necessary, this should be regarded as good agreement. We have chosen to tabulate the experimental values. Selected ΔH values of Table 8 were taken from the direct calorimetric measurements of Dokken and Elliott (1965), 1473°K, x_{Ni} = 0.00-0.15, and Benz and Elliott (1964), 1473°K, x_{Ni} = 0.007-0.088. Von Samson-Himmelstjerna (1936), 1773°K, x_{Ni} = 0.00-1.00, measured heat contents of liquid alloys by pouring them into a calorimeter at room temperature. Elford, et al. (1969), analysed the data, finding, with the aid of reasonable assumptions, that $\Delta H = 2360 x_{Ni}(1-x_{Ni})$, in good agreement with the selected values. However, the method is somewhat crude and this result was not used. El'Khasan, Abdel-Aziz, Vertman, and Samarin (1966), 1773°K, x_{Ni} = 0.18-0.90, found large exothermic values of ΔH (maximum -1890 cal/g-atom), in agreement, they report, with earlier work by Sryvalin, Esin, and Nikitin (1958), but the result is not in accord with other data. A graphite resistance tube was used for heating; possibly this contaminated the Ni with C.

Part II. Tables

TABLE 1

Low-Temperature Data for Solid Alloys

x_{Ni}	T, °K				$\gamma \times 10^4$ (±.1)
	1	2	3	4	
	Cp				
0.0*	0.000177	0.000423	0.000806	0.00139	1.66(±.01)
0.1	0.00024	0.00054	0.000948	0.00153	2.31
0.2	0.00035	0.00075	0.00125	0.00190	3.40
0.3	0.00058	0.00120	0.00189	0.00268	5.78
0.4	0.00135	0.00240	0.00319	0.00421	
0.45	0.00267	0.00430	0.00597	0.00798	
0.5	0.00212	0.00380	0.00560	0.00770	
0.6	0.00156	0.00313	0.00474	0.00638	15.56
0.7	0.00149	0.00302	0.00461	0.00632	14.88
0.8	0.00155	0.00315	0.00486	0.00672	15.43
0.9	0.00167	0.00338	0.00516	0.00706	16.65
1.0*	0.00168	0.00340	0.00518	0.00704	16.80

*From selected values

TABLE 2

Low-Temperature Data for Solid Alloys
(According to Keesom and Kurrelmeyer)

T, °K	x_{Ni}					
	0.000*	0.216	0.42	0.62	0.816	1.000*
	Cp					
5	0.00225	0.00382	0.00933	0.00882	0.00891	0.0091
10	0.0133	0.0168	0.0248	0.0249	0.0239	0.023
15	0.0439	0.0483	0.0527	0.0557	0.0511	0.0434
20	0.110	0.107	0.0990	0.108	0.0965	0.0770
$\gamma \times 10^4$	1.66(±.01)	4.57(±.1)	16.6(±.2)	15.2(±.1)	15.8(±.1)	16.8(±.1)

*From selected values.

TABLE 3

Low-Temperature Data for Solid Alloys, $x_{Ni} = 0.42$

T, °K	Cp	T, °K	Cp
5	0.00933	50	1.206
10	0.0248	75	2.455
15	0.0527	100	3.490
20	0.0990	150	4.745
25	0.191	200	5.326
30	0.326	250	5.561
40	0.695	298.15	5.644

$Cp_{(electronic)} = \gamma T \qquad \gamma = 16.6(\pm.2)\times 10^{-4}$

$\Delta H_{st} - \Delta H_0 = -23$

$\Delta S_{st} - \Delta S_0 = -0.16$

TABLE 4

Heat Capacities of Solid Alloys at 298.15°K

x_{Ni}	Cp	x_{Ni}	Cp
0.0	5.840	0.6	5.988
0.1	5.664	0.7	6.171
0.2	5.570	0.8	6.310
0.3	5.550	0.9	6.350
0.4	5.618	1.0	6.230
0.5	5.780		

TABLE 5

High-Temperature Data for Solid Alloys

T, °K	x_{Ni}						
	0.520**	0.764**	0.801***	0.881***	0.907**	0.944***	1.000
	Cp						
298.15	5.824	6.268	6.312	6.352	6.348	6.327	6.230
350	6.128	6.480	6.686	6.660	6.644	6.704	6.536
400	6.260	6.762	7.012	6.984	6.946	7.074	6.800
404	6.270	6.786	7.040*	7.012	6.972	7.106	6.820
450	6.388	6.709	6.936	7.343	7.294	7.481	7.062
495	6.496	6.736	7.926	7.660*	7.628	7.852	7.340
500	6.509	6.742	6.930	7.572	7.666	7.894	7.374
525	6.565	6.776	6.962	7.276	7.860*	8.093	7.575
550	6.620	6.814	6.992	7.154	7.360	8.276	7.813
567	6.656	6.842	7.012	7.136	7.252	8.400*	7.965
580	6.684	6.862	7.028	7.130	7.212	7.940	8.095
600	6.726	6.896	7.054	7.135	7.182	7.568	8.314
620	6.769	6.932	7.082	7.146	7.146	7.538	8.660
631	6.792	6.954	7.096	7.154	7.176	7.536	9.300*
650	6.829	6.994	7.123	7.168	7.188	7.537	7.640
700	6.922	7.104	(7.196)	(7.216)	7.234	(7.556)	7.370
800	7.072	7.307	(7.346)	(7.350)	7.360	(7.591)	7.440
900	7.182	7.460	(7.498)	(7.503)	7.510	(7.638)	7.640

*Curie temperature

**According to Pawel and Stansbury (for x_{Ni} = 0.764, the maximum Cp at 404°K does not coincide with the magnetic Curie temperature, 340°K).

***According to Grew

TABLE 6

Integral Quantities for Solid Alloys at 973°K

$$(1-x)Cu_{(s)} + xNi_{(s)} = Cu_{1-x}Ni_{x(s)}$$

x_{Ni}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-415	74	0.502	213	-0.144
0.2	-578	166	0.765	390	-0.230
0.3	-654	265	0.944	527	-0.269
0.4	-679	355	1.063	622	-0.274
0.5	-667	425	1.122	673	-0.255
	(±100)	(±100)	(±.11)	(±100)	(±.11)
0.6	-625	461	1.116	676	-0.221
0.7	-559	449	1.036	622	-0.179
0.8	-469	378	0.870	499	-0.124
0.9	-334	232	0.582	295	-0.665

TABLE 7

Partial Molar Quantities for Solid Alloys at 973°K

Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(s)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.908	1.009	- 186	18	- 12	0.179	-0.031
0.8	0.832	1.040	- 356	75	- 29	0.336	-0.107
0.7	0.767	1.096	- 582	177	- 25	0.572	-0.208
0.6	0.713	1.188	- 654	333	26	0.699	-0.315
0.5	0.659	1.319	- 804	535	150	0.980	-0.396
	(±.03)	(±.07)	(±100)	(±100)	(±200)	(±.23)	(±.23)
0.4	0.610	1.526	- 954	818	374	1.365	-0.456
0.3	0.566	1.888	-1099	1229	725	1.875	-0.518
0.2	0.506	2.531	-1317	1795	1229	2.617	-0.582
0.1	0.369	3.693	-1926	2526	1912	3.944	-0.631
0.0	0.000	5.900	- ∞	3432	2800	∞	-0.649

Ni Component $Ni_{(s)} = Ni(\text{in alloy})_{(s)}$

x_{Ni}	a_{Ni}	γ_{Ni}	$\Delta\bar{G}_{Ni}$	$\Delta\bar{G}^{xs}_{Ni}$	$\Delta\bar{H}_{Ni}$	$\Delta\bar{S}_{Ni}$	$\Delta\bar{S}^{xs}_{Ni}$
0.0	0.000	3.286	- ∞	2300	600	∞	-1.747
0.1	0.277	2.773	-2480	1972	842	3.414	-1.161
0.2	0.469	2.345	-1464	1648	947	2.478	-0.720
0.3	0.601	2.002	- 985	1343	941	1.979	-0.413
0.4	0.690	1.725	- 717	1055	850	1.610	-0.211
0.5	0.761	1.521	- 529	811	700	1.263	-0.114
	(±.04)	(±.08)	(±100)	(±100)	(±200)	(±.23)	(±.23)
0.6	0.811	1.351	- 406	582	518	0.950	-0.066
0.7	0.844	1.206	- 327	362	331	0.676	-0.032
0.8	0.876	1.095	- 257	175	165	0.434	-0.010
0.9	0.922	1.024	- 157	47	46	0.209	-0.001
1.0	1.000	1.000	0	0	0	0.000	0.000

TABLE 8

Integral Quantities for Liquid Alloys at 1823°K

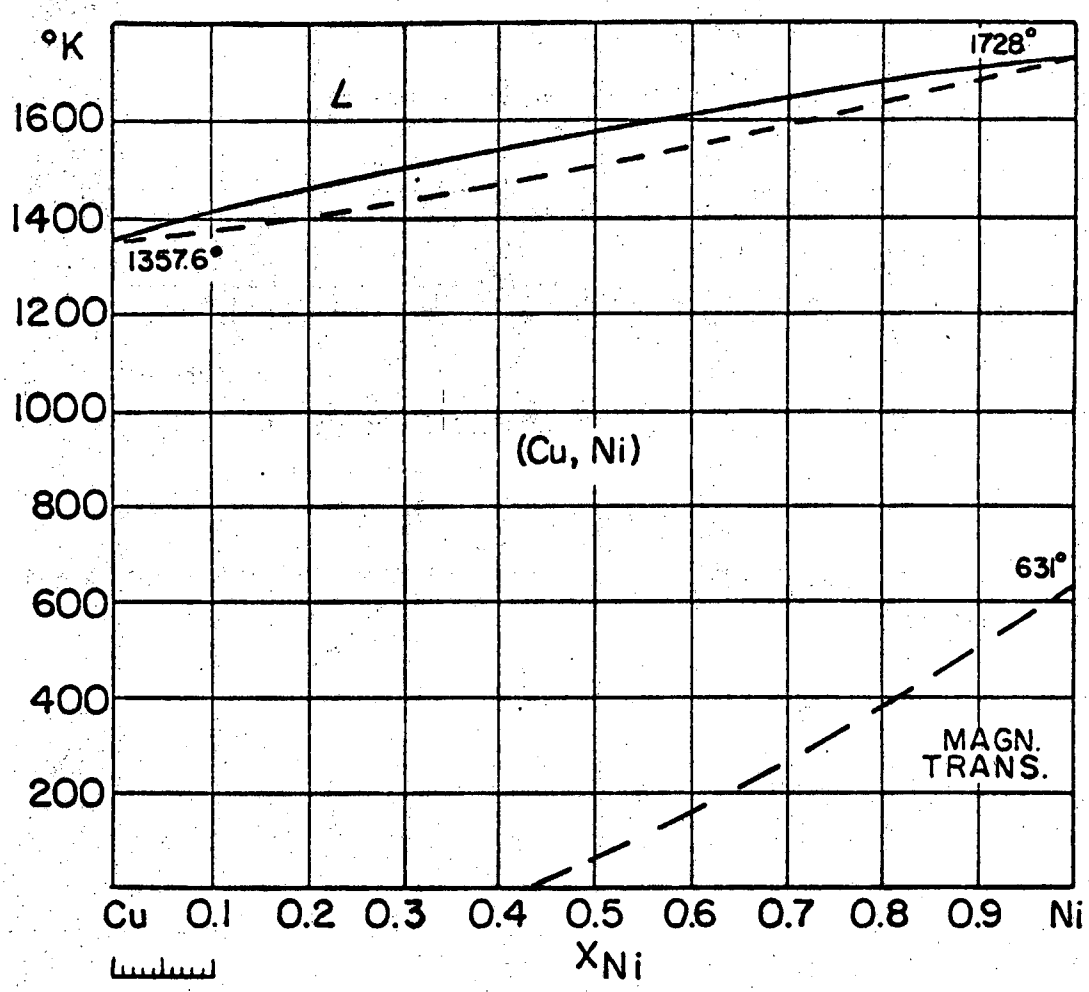
$$(1-x)Cu_{(\ell)} + xNi_{(\ell)} = Cu_{(1-x)}Ni_{x(\ell)}$$

x_{Ni}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	- 948	240	0.652	229	-0.006
0.15	-1195	341	0.842	336	-0.003
0.2	-1377			435	
0.3	-1617			596	
0.4	-1745			693	
0.5	-1786			725	
	(±100)			(±100)	
0.6	-1742			696	
0.7	-1604			609	
0.8	-1349			464	
0.9	- 917			261	

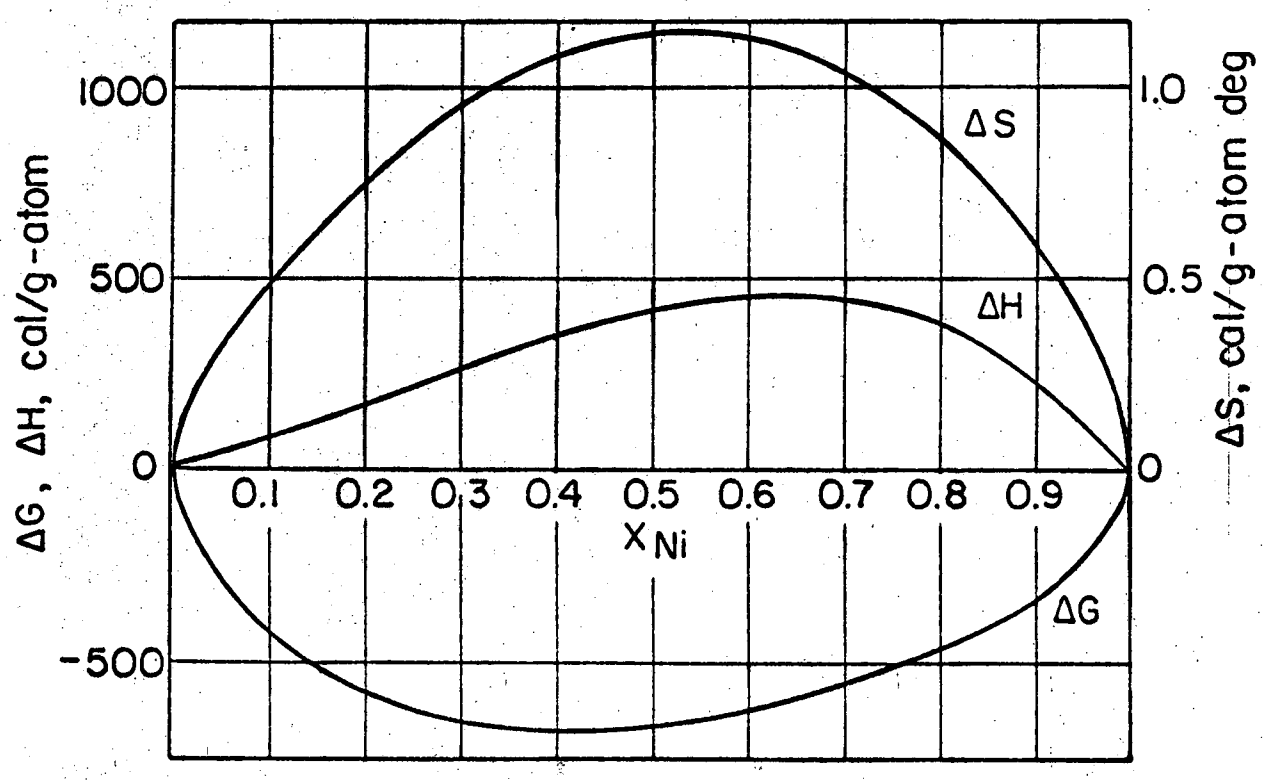
TABLE 9

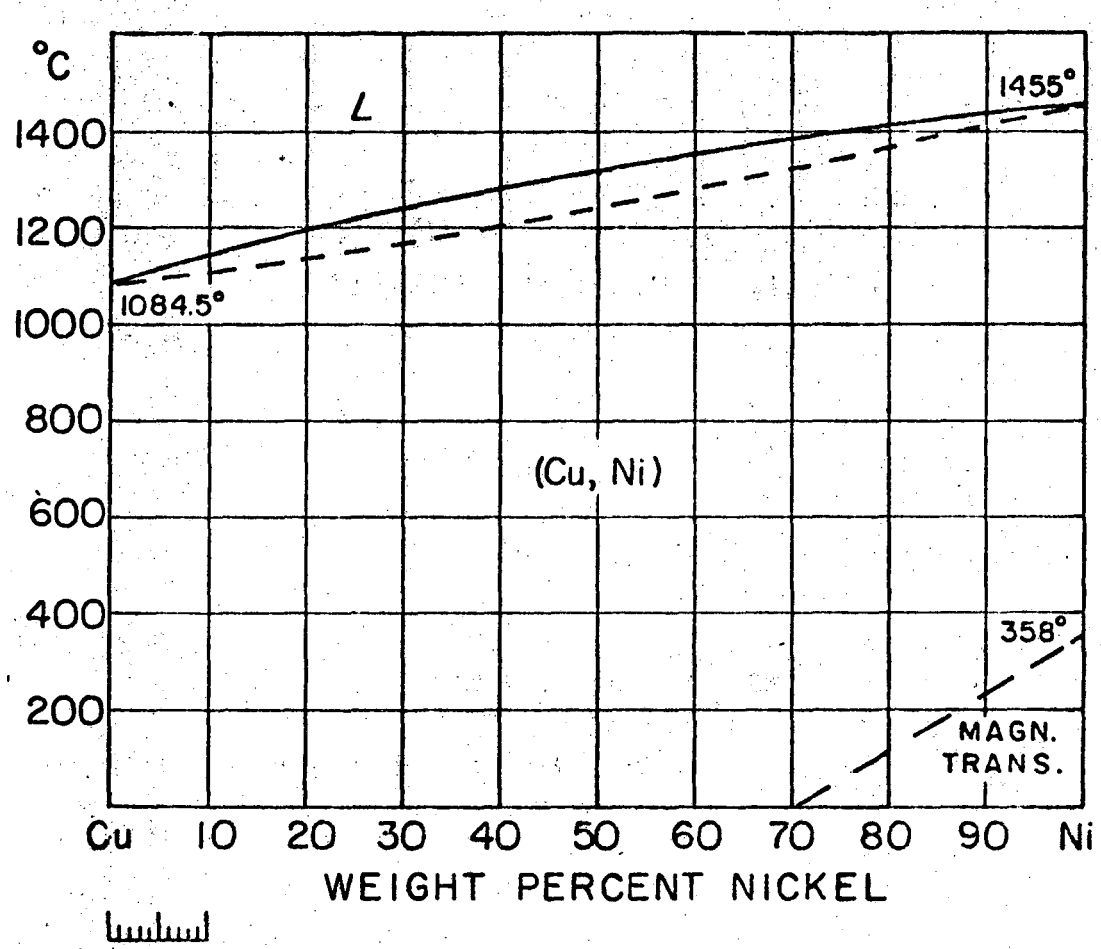
Partial Molar Quantities for Liquid Alloys at 1823°K

	Cu Component $Cu_{(\ell)}$ = Cu(in alloy)$_{(\ell)}$				Ni Component $Ni_{(\ell)}$ = Ni(in alloy)$_{(\ell)}$			
x_{Ni}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Ni}	γ_{Ni}	$\Delta\bar{G}_{Ni}$	$\Delta\bar{G}^{xs}_{Ni}$
0.0	1.000	1.000	0	0	0.000	1.906	- ∞	2336
0.1	0.902	1.002	- 374	8	0.185	1.864	-6120	2222
0.2	0.814	1.017	- 747	61	0.341	1.704	-3899	1931
0.3	0.740	1.058	-1088	204	0.455	1.517	-2851	1510
0.4	0.677	1.128	-1414	436	0.539	1.347	-2241	1079
0.5	0.611	1.222	-1786	725	0.611	1.222	-1786	725
	(±.02)	(±.03)	(±100)	(±100)	(±.02)	(±.03)	(±100)	(±100)
0.6	0.534	1.334	-2275	1044	0.682	1.136	-1337	464
0.7	0.444	1.480	-2941	1421	0.752	1.075	-1031	261
0.8	0.334	1.669	-3974	1856	0.826	1.032	- 692	116
0.9	0.191	1.912	-5992	2349	0.907	1.008	- 353	29
1.0	0.000	2.227	- ∞	2900	1.000	1.000	0	0



COPPER-NICKEL SYSTEM, 973 °K





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Copper-Lead

Part I. Discussion

Phases and Structures. The phase diagram, from Hansen (1958) and Elliott (1965), with the critical temperature of the miscibility gap, T_c = 1254°K from Jacobs, Maes, and de Strycker (1967), shows almost complete immiscibility in the solid state and a miscibility gap in the liquid.

Liquid Alloys. Selected ΔH values of Table 1 were taken from heat content measurements of Schürmann and Kaune (1965), 1225°-1473°K, x_{Pb}=0.1-0.9, except that slightly less endothermic values were taken at x_{Pb} = 0.8 and 0.9, in order to agree better with the phase diagram. Usual errors in the method caused by segregation in freezing should be absent in this system. Direct calorimetric measurements of Kawakami (1930), 1473°K, x_{Pb}=0.24-0.80, yield ΔH values more endothermic by 200-400 cal/g-atom. ΔH values calculated by Kleppa (1952) from the phase diagram agree with selected values within ±50 cal/g-atom at most concentrations. From the ΔH vs x_{Pb} curve, $\Delta\bar{H}_{Cu}$ and $\Delta\bar{H}_{Pb}$ were obtained graphically.

The selected $\Delta\bar{G}_{Cu}$ values agree within ±50 cal/g-atom with values calculated from the liquidus and also those calculated by Kleppa (1952) from the phase diagram. In the calculation $\Delta\bar{H}_{Cu}$ and $\Delta\bar{S}_{Cu}$ were assumed to be invariant with T, that is, $\Delta\bar{C}p_{Cu}$ = 0. Values were referred to $Cu_{(\ell)}$ assuming for Cu that ΔH_m = 3140 cal/g-atom, ΔS_m = 2.315 cal/deg g-atom, invariant with T. Vapor pressure measurements of Yazawa, Azakami, and Kawashima (1966), 1273°- 1473°K, x_{Pb} = 0.10-0.78, yield values of $\Delta\bar{G}_{Pb}$ which agree with selected values within ±100 cal/g-atom except for x_{Pb}<0.2 where they trend to 280 cal/g-atom more exothermic; those of Kim and Abdeev (1963), 1373°K, x_{Pb} = 0.0003-0.015 scatter (±1000 cal/g-atom) about selected values; while those of Abdeev and Miller (1958), 1273°- 1473°K, x_{Pb} = 0.08-0.55 are less exothermic by 400-1600 cal/g-atom. Langenberg (1956), 1873°K, x_{Pb} = 0.96-1.00, measured the distribution coefficient of Cu between $Fe_{(\ell)}$ and $Pb_{(\ell)}$. From the selected values for Cu-Fe (see Cu-Fe), the $\Delta\bar{G}_{Cu}$ values calculated from the distribution coefficient are about 900 cal/g-atom more exothermic than selected values. ΔG values calculated by Schürmann and Kaune (1965) from their heat content curves are slightly (0-45 cal/g-atom) less exothermic than selected values.

PDD August, 1968

Part II. Tables

TABLE 1

Integral Quantities for Liquid Alloys at 1473°K

$$(1-x)Cu_{(\ell)} + xPb_{(\ell)} = Cu_{1-x}Pb_{x(\ell)}$$

x_{Pb}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-500	707	0.819	452	0.173
0.2	-645	1154	1.221	820	0.227
0.3	-712	1422	1.448	1076	0.234
0.4	-762	1567	1.581	1208	0.244
0.5	-793	1607	1.630	1235	0.252
	(±100)	(±100)	(±.068)	(±100)	(±.068)
0.6	-803	1534	1.586	1167	0.249
0.7	-782	1338	1.439	1006	0.225
0.8	-707	1026	1.176	757	0.182
0.9	-530	584	0.756	421	0.110

TABLE 2

Partial Molar Quantities for Liquid Alloys at 1473°K

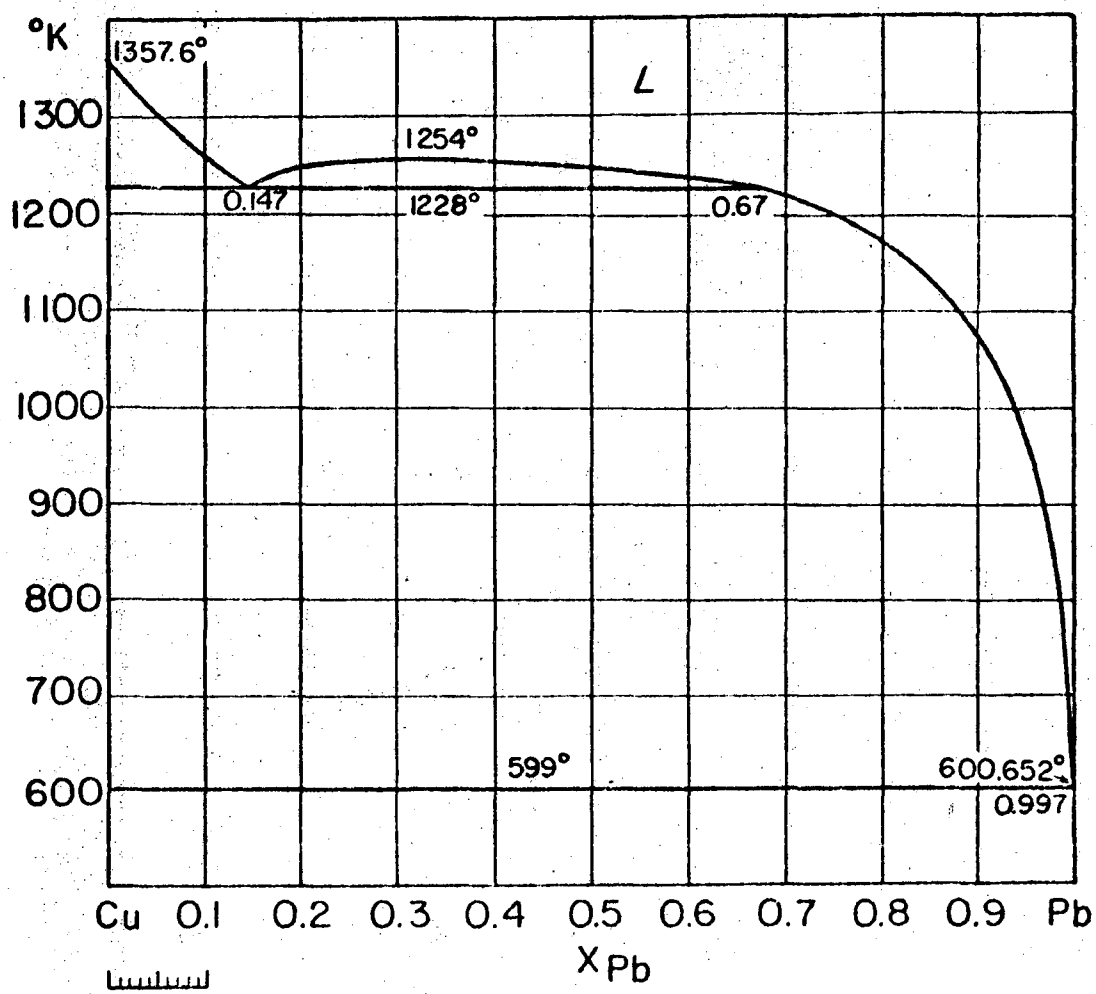
Cu Component $\quad Cu_{(\ell)} = Cu_{(\text{in alloy})(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.912	1.013	- 270	38	143	0.280	0.071
0.8	0.852	1.065	- 468	185	468	0.635	0.192
0.7	0.832	1.188	- 539	505	824	0.925	0.216
0.6	0.815	1.359	- 598	897	1198	1.220	0.205
0.5	0.791	1.581	- 688	1341	1670	1.601	0.223
	(±.027)	(±.055)	(± 100)	(±100)	(±150)	(±.12)	(±.12)
0.4	0.755	1.886	- 824	1858	2344	2.151	0.330
0.3	0.691	2.304	-1082	2443	3121	2.853	0.461
0.2	0.577	2.884	-1610	3101	4013	3.817	0.619
0.1	0.370	3.702	-2909	3831	5184	5.494	0.918
0.0	0.000	4.872	- ∞	4635	6600	∞	1.334

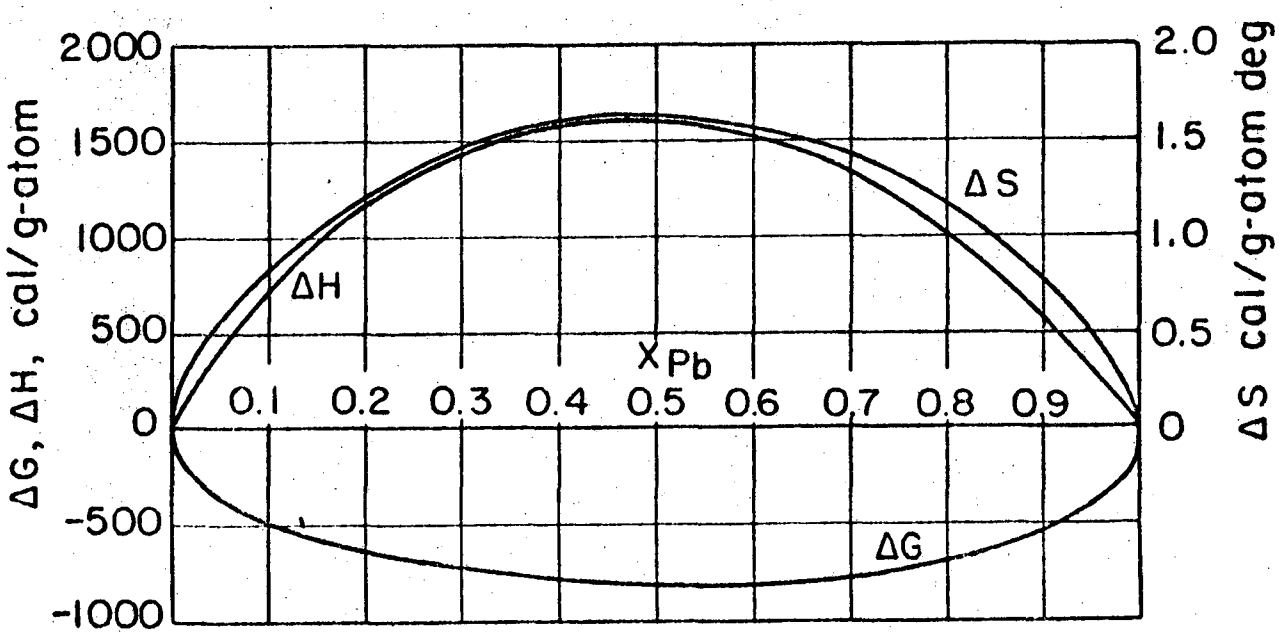
TABLE 2 (Cont'd)

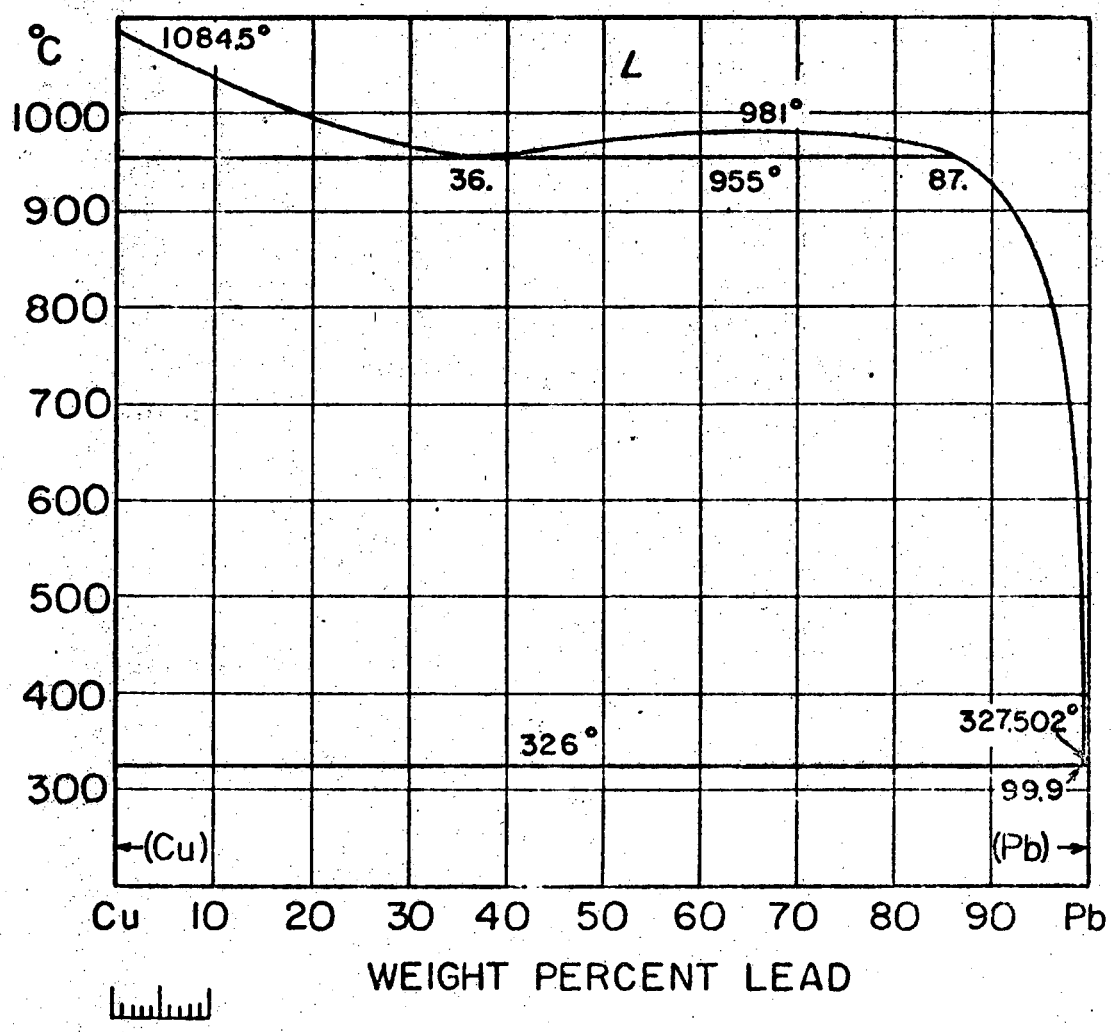
Pb Component $Pb_{(\ell)} = Pb(\text{in alloy})_{(\ell)}$

x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta\bar{G}_{Pb}$	$\Delta\bar{G}^{xs}_{Pb}$	$\Delta\bar{H}_{Pb}$	$\Delta\bar{S}_{Pb}$	$\Delta\bar{S}^{xs}_{Pb}$
0.0	0.000	5.271	$-\infty$	4865	8620	∞	2.549
0.1	0.417	4.166	-2563	4177	5791	5.672	1.096
0.2	0.630	3.148	-1354	3357	3898	3.565	0.367
0.3	0.683	2.278	-1115	2409	2817	2.670	0.277
0.4	0.709	1.772	-1008	1674	2120	2.124	0.303
0.5	0.736	1.471	- 899	1130	1545	1.659	0.282
	(±.025)	(±.051)	(± 100)	(±100)	(±150)	(±.12)	(±.12)
0.6	0.764	1.273	- 789	707	994	1.210	0.195
0.7	0.800	1.143	- 653	391	573	0.833	0.124
0.8	0.848	1.060	- 482	171	279	0.516	0.073
0.9	0.913	1.015	- 266	42	73	0.230	0.021
1.0	1.000	1.000	0	0	0	0.000	0.000



COPPER - LEAD SYSTEM, 1473 °K

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(Cu)
(Pb)
Cu 10 20 30 40 50 60 70 80 90 Pb
WEIGHT PERCENT LEAD

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Copper-Palladium

Part I. Discussion

Phases and Structures. The phase diagram, from Hansen (1958), shows a complete series of solid solutions with fcc (A1) structures. At lower temperatures complex ordering phenomena occur; Hansen shows tentative boundaries of three regions. Pearson (1958, 1967) describes the ordered structures as follows:

α' has the ordered fcc ($L1_2$) structure isotypic with $AuCu_3$.

α'' has an ordered tetragonal structure, a distortion of ($L1_2$), which is best described through antiphase domains.

β has an ordered bcc (B2) structure isotypic with CsCl.

Numerous investigations have been and are being made of the ordering process and structures, especially for α''.

Solid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 2 agree within ±100 cal/g-atom with vapor pressure measurements of Myles and Darby (1968), 1350°K, x_{Pd} = 0.1-0.9. Values of $\Delta\bar{G}_{Cu}$ from other measurements were brought to 1350°K with the use of the selected $\Delta\bar{S}_{Cu}$ values and were found to agree as follows: Emf measurements of Vecher and Gerasimov (1963), 873°- 1033°K, x_{Pd} = 0.11-0.92, agree within ±125 cal/g-atom, except at x_{Pd} = 0.5 and 0.7, where their values are more exothermic by about 500 cal/g-atom. Earlier emf measurements of Vecher and Gerasimov (1958), 873°- 1073°K, x_{Pd} = 0.11-0.92, are mostly less exothermic than selected $\Delta\bar{G}_{Cu}$ values by 150-1000 cal/g-atom. Emf measurements of Pratt and Bugden (1967), 900°- 1200°K, x_{Pd} = 0.1-0.9, scatter (±350 cal/g-atom) about the selected values except for $x_{Pd} > 0.8$, where they are less exothermic by 800-1100 cal/g-atom. Equilibrium data of Schenck and Keuth (1940), 883°K, x_{Pd} = 0.08-0.17, are about 100-175 cal/g-atom less exothermic. Gibbs-Duhem integration of the selected $\Delta\bar{G}_{Cu}$ values gave the ΔG and $\Delta\bar{G}_{Pd}$ values of Tables 1 and 2.

Selected ΔH values of Table 1 agree within the experimental scatter of ±100 cal/g-atom with tin solution calorimetric measurements of Guadagno, Orr, and Hultgren (1961), 1000°K, x_{Pd} = 0.16-0.90, and the 915°K measurements of Oriani and Murphy (1962), 915°K, x_{Pd} = 0.05-0.30, 0.51; 769°- 940°K, x_{Pd} = 0.40. The measurements of the latter at x_{Pd} = 0.40 were intended to determine the heat of transformation of β to α. However, as seen in Table 3, ΔH appeared to be constant with T to the critical temperature, 873°K; above this temperature no first-order latent heat appears, but $\Delta Cp \sim 6.4$. The hypothesis of Oriani and

Murphy is that above 873°K the ordered bcc β structure transforms to an ordered structure with practically no latent heat; the ordered structure then disorders over a range of temperature of 873° to 1000°K; above this $\Delta Cp = 0$ and the ΔH values agree with those selected. This is a curious behavior, especially since thermal effects were found in determining the β-α transformation temperature (Hansen, 1968). However, the other ΔH values found by Oriani and Murphy in this and other systems generally agree with selected values. ΔS was calculated from ΔG and ΔH.

$\Delta\bar{S}_{Cu}$ values were chosen so that Gibbs-Duhem integration yielded the selected ΔS values and which agreed as well as possible with temperature coefficients found by vapor pressure and emf measurements. Agreement was fair with temperature coefficients of Vecher and Gerasimov and Myles and Darby; Pratt and Bugden's values were much too positive (they themselves note their temperature coefficients appear unreliable).

Part II. Tables

TABLE 1

Integral Quantities for Solid Alloys at 1350°K

$$(1-x)Cu_{(s)} + xPd_{(s)} = Cu_{(1-x)}Pd_{x(s)}$$

x_{Pd}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-1675	-1005	0.496	-803	-0.150
0.2	-2665	-1830	0.618	-1323	-0.376
0.3	-3217	-2440	0.575	-1578	-0.639
0.4	-3400	-2621	0.577	-1594	-0.760
0.5	-3274	-2557	0.531	-1415	-0.846
	(±100)	(±100)	(±.07)	(±100)	(±.07)
0.6	-2919	-2422	0.369	-1114	-0.969
0.7	-2414	-2108	0.227	-776	-0.987
0.8	-1797	-1664	0.099	-455	-0.896
0.9	-1056	-904	0.113	-183	-0.533

TABLE 2

Partial Molar Quantities for Solid Alloys at 1350°K

A. Cu Component $Cu_{(s)} = Cu\,(\text{in alloy})_{(s)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.853	0.947	-428	-145	-87	0.253	0.043
0.8	0.650	0.813	-1154	-555	-368	0.582	0.139
0.7	0.450	0.643	-2142	-1185	-1178	0.714	0.005
0.6	0.286	0.477	-3354	-1984	-2554	0.593	-0.422
0.5	0.184	0.367	-4547	-2687	-3057	1.103	-0.274
	(±0.01)	(±0.02)	(±100)	(±100)	(±500)	(±.4)	(±.4)
0.4	0.126	0.314	-5561	-3103	-3748	1.343	-0.477
0.3	0.094	0.321	-6351	-3121	-4949	1.039	-1.354
0.2	0.068	0.343	-7191	-2874	-6656	0.396	-2.802
0.1	0.043	0.427	-8461	-2287	-8132	0.244	-4.332
0.0	0.000	0.627	$-\infty$	-1250	-10040	∞	-6.511

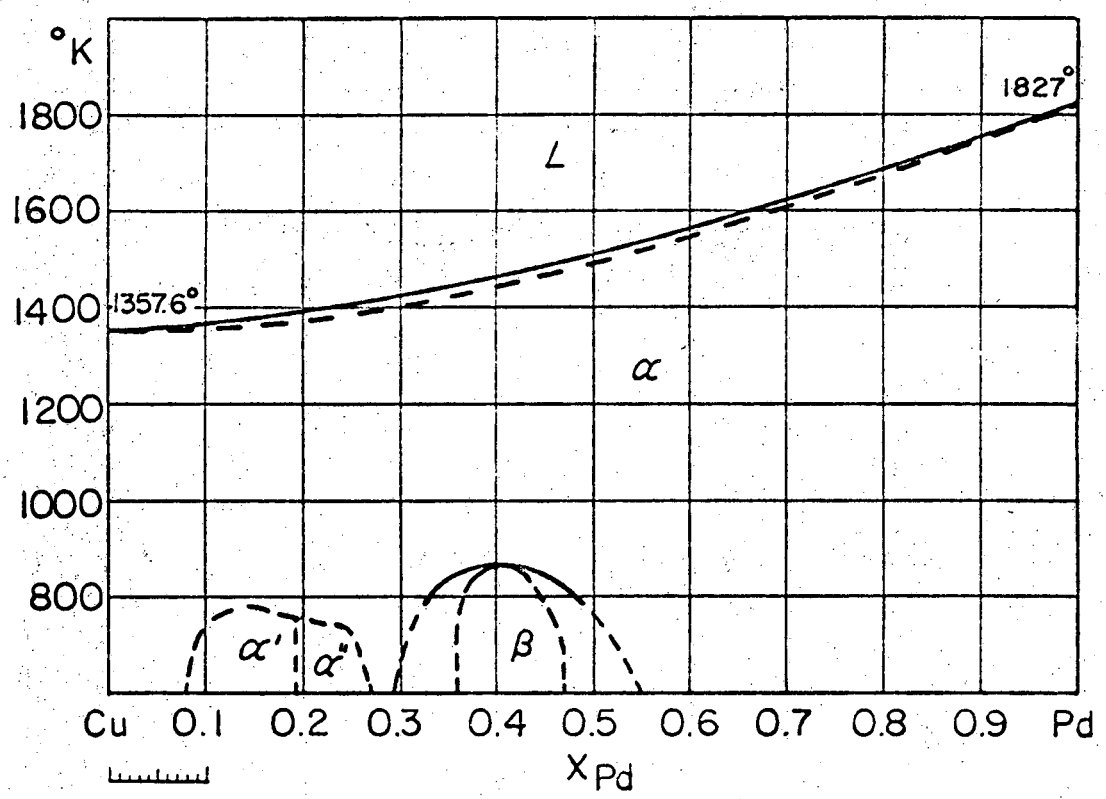
B. Pd Component $Pd_{(s)} = Pd\,(\text{in alloy})_{(s)}$

x_{Pd}	a_{Pd}	γ_{Pd}	$\Delta\bar{G}_{Pd}$	$\Delta\bar{G}^{xs}_{Pd}$	$\Delta\bar{H}_{Pd}$	$\Delta\bar{S}_{Pd}$	$\Delta\bar{S}^{xs}_{Pd}$
0.0	0.000	0.008	$-\infty$	-9519	-10900	∞	-1.023
0.1	0.008	0.081	-12905	-6727	-9274	2.689	-1.887
0.2	0.039	0.194	-8711	-4393	-7680	0.764	-2.434
0.3	0.118	0.395	-5724	-2493	-5385	0.251	-2.141
0.4	0.274	0.686	-3468	-1010	-2722	0.553	-1.268
0.5	0.474	0.948	-2001	-142	-2057	-0.042	-1.419
	(±0.01)	(±0.02)	(±100)	(±100)	(±500)	(±.4)	(±.4)
0.6	0.649	1.082	-1158	212	-1538	-0.281	-1.296
0.7	0.763	1.089	-727	230	-891	-0.121	-0.830
0.8	0.846	1.057	-449	150	-416	0.024	-0.419
0.9	0.917	1.019	-233	50	-100	0.098	-0.111
1.0	1.000	1.000	0	0	0	0.000	0.000

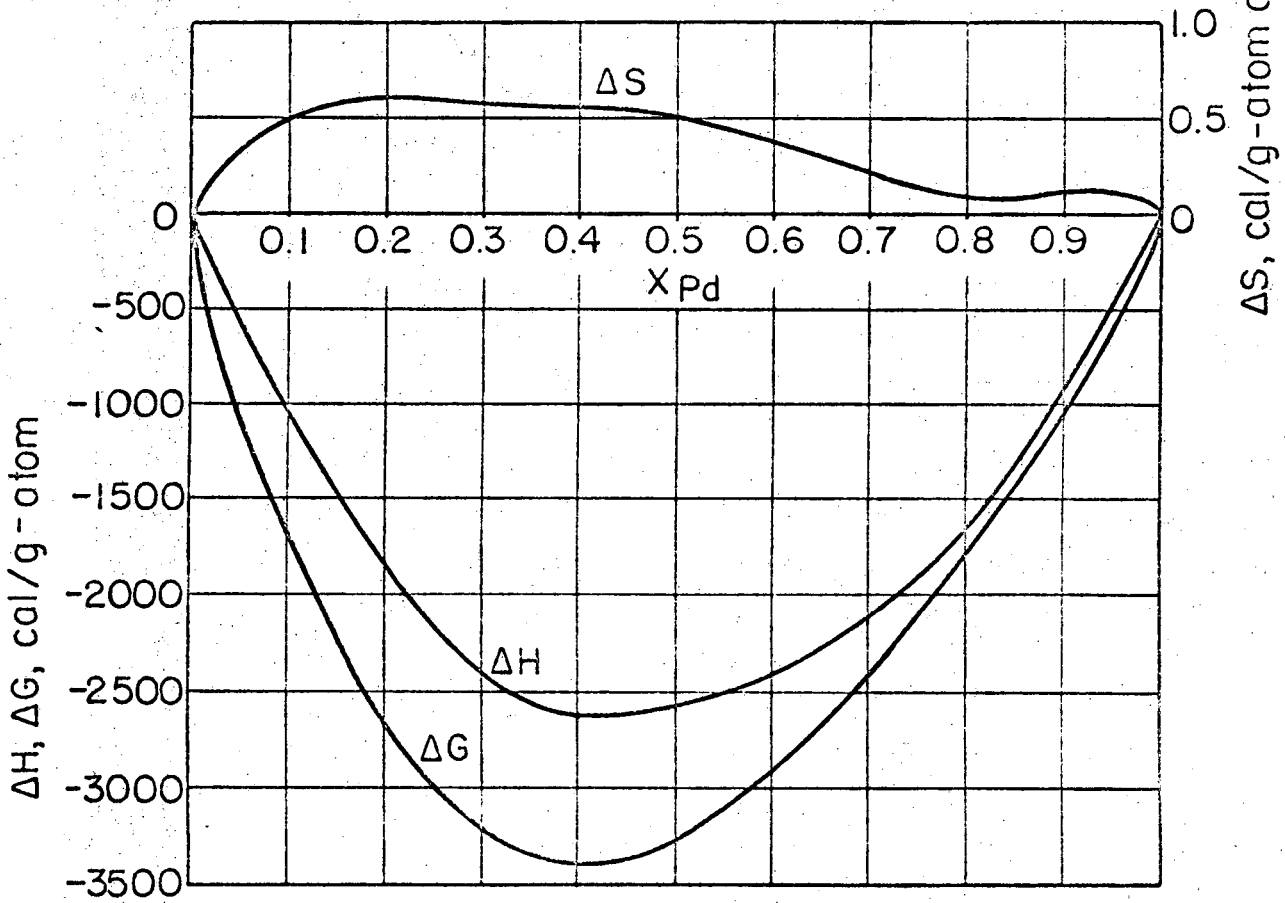
TABLE 3

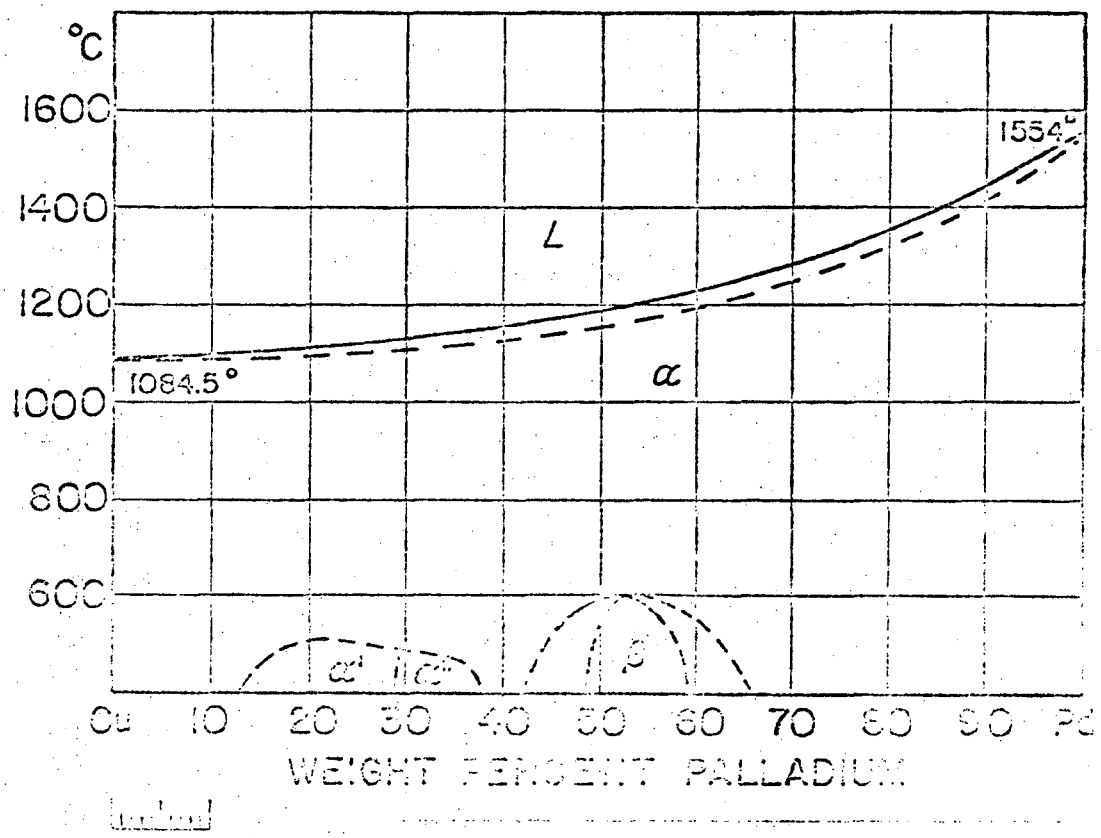
Heats of Formation for Ordered Alloy, $x_{Pd} = 0.4$

T, °K	Phase	ΔH
773	β	-3280
800	β	-3280
873	β-α	-3280
900	α	-3080
940	α	-2850



COPPER-PALLADIUM SYSTEM, 1350 °K





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Copper-Platinum

Part I. Discussion

Phases and Structures. Cu and Pt form a continuous series of fcc solid solutions with ordered states where indicated. The phase diagram is from Hansen (1958) except that the ordering temperature at $x_{Pt} = 0.50$ has been increased to 1100°K to agree with Geiken (1967). Pearson (1958) describes the ordered structures as follows:

α' has the ordered ($L1_2$) structure isotypic with $AuCu_3$.

α'' has a structure based on a cell of 32 atoms. At $x_{Pt} = 0.50$ the structure is ordered rhombohedral ($L1_1$), becoming cubic at $x_{Pt} = 0.75$.

Solid Alloys. Low-temperature data of Table 1 were taken from Rayne and Roessler (1965), 1.5°- 4.2°K, $x_{Pt} = 0.501$.

Selected ΔH versus T values of Table 2 were taken from heats of formation measured by Geiken (1967), 368°- 1164°K, $x_{Pt} = 0.50$. Selected $\Delta\bar{G}_{Cu}$ values of Table 4 agree with vapor pressure measurements of Myles and Darby (1968), 1350°K, $x_{Pt} = 0.1-0.9$, except for $x_{Pt} \leq 0.2$, where the measured values fluctuate by ±70 cal/g-atom. Vapor pressure measurements of McCormack, Myers, and Saxer (1966), 1542°- 1673°K, $x_{Pt} = 0.6-0.9$, (after correcting their analytical expression by multiplying their value of A by 10), scatter by ±300 cal/g-atom about the selected values. Emf measurements of Weibke and Matthes (1940), 673°- 1073°K, $x_{Pt} = 0.14-0.86$, agree within ±100 cal/g-atom with selected ΔG_{Cu} values except for a deviant point at $x_{Pt} = 0.86$. Emf measurements of Bidwell, Schulz, and Saxer (1966), 823°- 1073°K, $x_{Pt} = 0.069-0.492$ yield values usually less exothermic by 100-350 cal/g-atom, as do equilibrium measurements of Schenck and Keuth (1946), 883°K, $x_{Pt} = 0.05-0.15$; and Schmahl and Minzl (1965), 1273°K, $x_{Pt} = 0.65-0.83$; while equilibrium measurements of Assayag (1955), 1025°- 1200°K, $x_{Pt} = 0.40-0.92$ yield values more exothermic by 600-2000 cal/g-atom. ΔG and $\Delta\bar{G}_{Pt}$ values of Tables 3 and 4 were calculated from the selected $\Delta\bar{G}_{Cu}$ by Gibbs-Duhem integration. Selected ΔH values of Table 5 were taken from Sn solution calorimetry of quenched alloys by Myles and Darby (1968), 298°K, $x_{Pt} = 0.1-0.9$. For $x_{Pt} = 0.50$, the value for $\Delta H_{1350°K}$ of Table 2 can be reconciled with $\Delta H_{298°K}$ of Table 5 by taking $\Delta Cp = -0.19$. This value is reasonable as shown by the similar trend with temperature between 298°- 900°K of the ordered alloys of Table 2. High-temperature values of ΔH of Table 3 were calculated from the low-temperature values of

Table 5, assuming ΔCp has a parabolic dependence on composition, as indicated in Table 3. Liquid Sn solution calorimetry measurements of Oriani and Murphy (1962), 914°K, x_{Pt} = 0.06-0.51, were made on alloys which, depending on composition, were in ordered, disordered, or intermediate states and agree only approximately with selected values.

Liquid Alloys. McCormack, Myers, and Saxer (1966), 1542°- 1673°K, x_{Pt} = 0.10, 0.26, measured the vapor pressure of Cu above two compositions in the liquid state. They found considerable negative deviations from Raoult's law. The results were not tabulated because of the few points measured and the lack of a Gibbs-Duhem constant of integration, except from the phase diagram, of which the solidus is uncertain.

Part II. Tables

TABLE 1

Low-Temperature Data for Ordered and Disordered Solid Alloy x_{Pt} = 0.50

T, °K	Cp Ordered	Cp Disordered
1.5	0.00022	0.00033
2	0.00032	0.00048
3	0.00060	0.00087
4	0.00103	0.00144
γ	1.27×10^{-4}	1.97×10^{-4}

TABLE 2

High-Temperature Data for Solid Alloys: x_{Pt} = 0.5

$$0.5Cu_{(s)} + 0.5Pt_{(s)} = Cu_{0.5}Pt_{0.5(s)}$$

T	Phase	ΔG	ΔH	ΔS
298.15	α''	-4006	-4018	-0.041
400		-3999	-4037	-0.094
500		-3989	-4056	-0.134
600		-3974	-4074	-0.167
700		-3957	-4093	-0.195
800		-3936	-4111	-0.219
900		-3914	-4130	-0.24
1000		-3901	-3870	0.031
1100	α''	-3935	-3150	0.714
1100	α	-3935	-2650	1.168
1200		-4052	-2650	1.168
1350	α	-4228	-2650	1.168
		(±150)	(±150)	(±.05)

TABLE 3

Integral Quantities for Solid Alloys at 1350°K

$$(1-x)Cu_{(s)} + xPt_{(s)} = Cu_{(1-x)}Pt_{x(s)}$$

x_{Pt}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}	ΔCp
0.1	-1970	-1228	0.550	-1098	-0.096	(-0.07)
0.2	-3166	-2023	0.847	-1824	-0.148	(-0.12)
0.3	-3879	-2482	1.035	-2241	-0.179	(-0.16)
0.4	-4211	-2674	1.139	-2406	-0.198	(-0.18)
0.5	-4227	-2650	1.168	-2368	-0.209	-0.19
	(±100)	(±150)	(±.07)	(±100)	(±.07)	(±.05)
0.6	-3964	-2477	1.102	-2158	-0.236	(-0.18)
0.7	-3450	-1979	1.089	-1811	-0.125	(-0.16)
0.8	-2686	-1355	0.986	-1343	-0.009	(-0.12)
0.9	-1615	-689	0.685	-742	0.039	(-0.07)

TABLE 4

Partial Molar Quantities for Solid Alloys at 1350°K

Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(s)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.836	0.929	-480	-197	-234	0.182	-0.027
0.8	0.616	0.770	-1300	-702	-795	0.374	-0.070
0.7	0.416	0.594	-2354	-1397	-1539	0.603	-0.106
0.6	0.266	0.444	-3548	-2178	-2363	0.878	-0.138
0.5	0.163	0.326	-4869	-3010	-3131	1.288	-0.089
	(±.01)	(±.02)	(±100)	(±100)	(±200)	(±.12)	(±.12)
0.4	0.095	0.237	-6321	-3863	-4536	1.322	-0.499
0.3	0.053	0.177	-7878	-4648	-6044	1.358	-1.034
0.2	0.025	0.124	-9918	-5600	-6547	2.497	-0.702
0.1	0.008	0.080	-12965	-6788	-6844	4.534	-0.042
0.0	0.000	0.048	-∞	-8120	-6870	∞	0.926

Pt Component $Pt_{(s)} = Pt(\text{in alloy})_{(s)}$

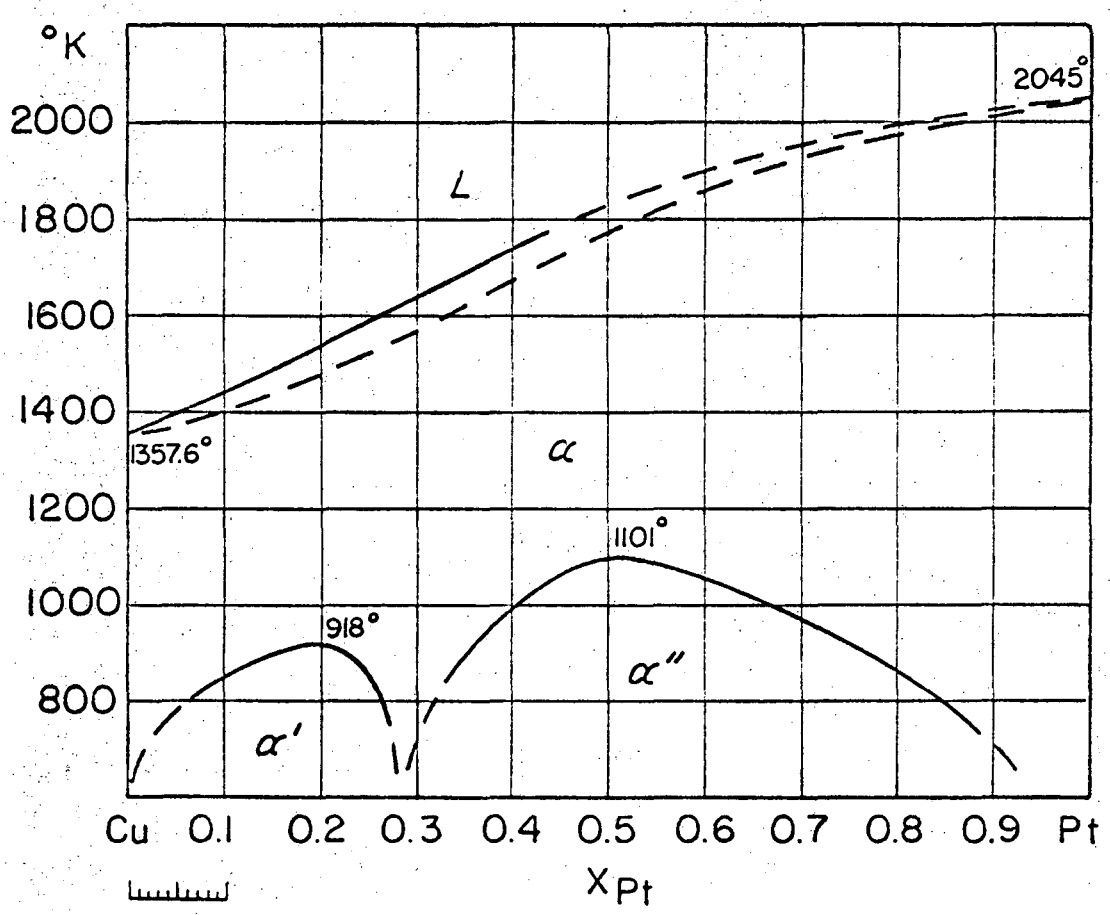
x_{Pt}	a_{Pt}	γ_{Pt}	$\Delta\bar{G}_{Pt}$	$\Delta\bar{G}^{xs}_{Pt}$	$\Delta\bar{H}_{Pt}$	$\Delta\bar{S}_{Pt}$	$\Delta\bar{S}^{xs}_{Pt}$
0.0	0.000	0.008	-∞	-13067	-14760	∞	-1.254
0.1	0.003	0.032	-15385	-9208	-10178	3.857	-0.718
0.2	0.019	0.095	-10631	-6314	-6934	2.739	-0.460
0.3	0.062	0.208	-7439	-4209	-4682	2.042	-0.350
0.4	0.144	0.359	-5207	-2749	-3139	1.532	-0.289
0.5	0.263	0.526	-3585	-1725	-2169	1.049	-0.328
	(±.01)	(±.02)	(±100)	(±100)	(±200)	(±.12)	(±.12)
0.6	0.410	0.683	-2393	-1022	-1104	0.955	-0.061
0.7	0.561	0.801	-1552	-595	-237	0.974	0.265
0.8	0.721	0.901	-878	-279	-57	0.608	0.164
0.9	0.877	0.974	-353	-71	-5	0.258	0.048
1.0	1.000	1.000	0	0	0	0.000	0.000

TABLE 5

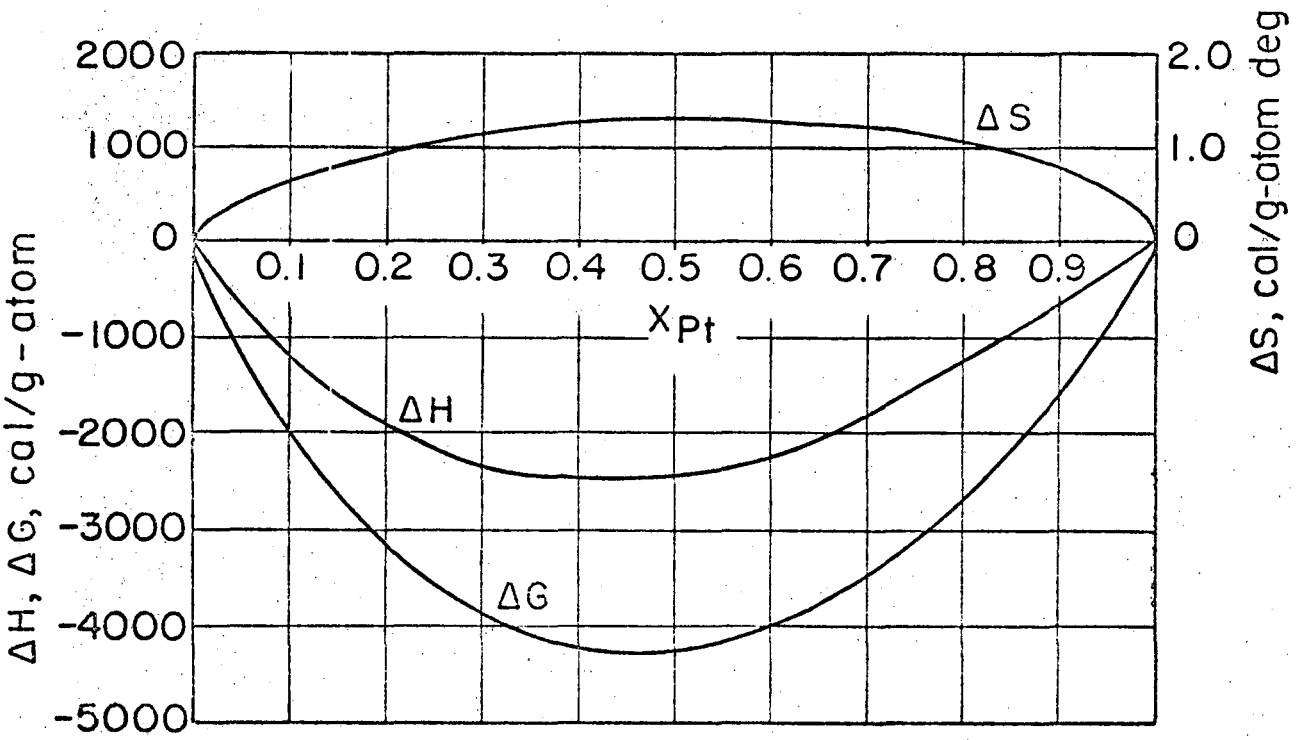
Heats of Formation of Disordered Quenched Alloys at 298°K

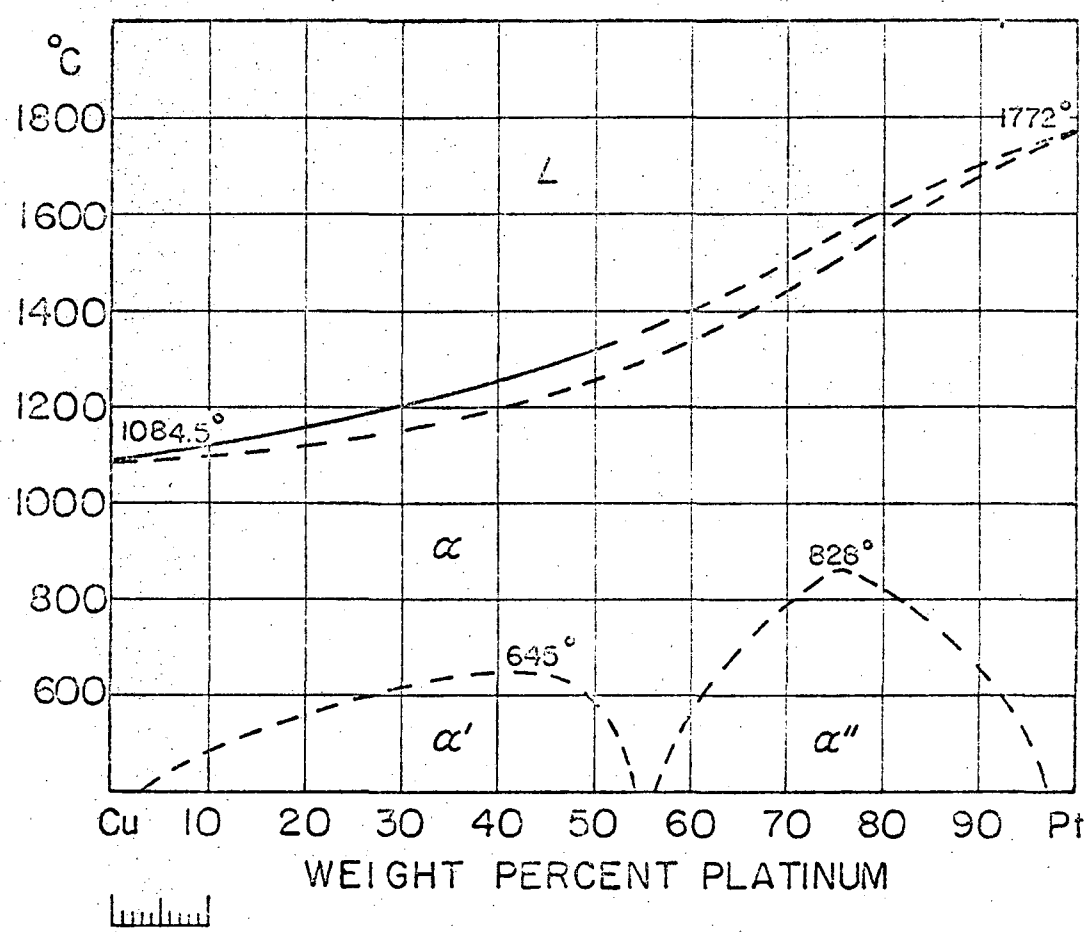
$$(1-x)Cu_{(s)} + xPt_{(s)} = Cu_{1-x}Pt_{x(s,\,disordered)}$$

x_{Pt}	ΔH	x_{Pt}	ΔH
0.1	-1160	0.6	-2294
0.2	-1902	0.7	-1820
0.3	-2323	0.8	-1234
0.4	-2491	0.9	-621
0.5	-2460 (±100)		



COPPER PLATINUM SYSTEM, 1350°K

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1800
1600
1400
1200
1000
800
600
1772°
L
1084.5°
α
826°
645°
α'
α''
Cu 10 20 30 40 50 60 70 80 90 Pt
WEIGHT PERCENT PLATINUM

Part III. References

(For references not in list, see General References)

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Equilibrium (1025°- 1200°K, x_{Pt} = 0.4-0.92).

Bidwell, L. R., W. J. Schulz, and R. K. Saxer (1967) Acta Met. 15, 1143-51. Emf (823°- 1073°K, x_{Pt} = 0.069-0.492).

Geiken, G. (1967) M.S. Thesis, Lawrence Radiation Lab., University of California, UCRL-17615.
ΔH (368°- 1164°K, x_{Pt} = 0.5).

McCormack, J. M., J. R. Myers, and R. K. Saxer (1966) Trans. Met. Soc. AIME 236, 1635-7. Vapor pressure (1542°- 1673°K, x_{Pt} = 0.1-0.9).

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Vapor pressure (1350°K, x_{Pt} = 0.1-0.9); ΔH (298°K, x_{Pt} = 0.1-0.9).

Oriani, R., and W. K. Murphy (1962) Acta Met. 10, 879-85.
ΔH (914°K, x_{Pt} = 0.06-0.51).

Rayne, J., and B. Roessler (1965) Proc. Low-Temp. Physics LT9, 1964, 1074-7. Cp (1.5°- 4.2°K, x_{Pt} = 0.501).

Schenck, R., and H. Keuth (1940) Z. Elektrochem. 46, 298-308.
Equilibrium (883°K, x_{Pt} = 0.05-0.15).

Schmahl, N. G., and E. Minzl (1965) Z. Physik Chem. 47, 164-82.
Equilibrium (1273°K, x_{Pt} = 0.65-0.83).

Weibke, F., and H. Matthes (1941) Z. Elektrochem. 47, 421-3.
Emf (673°- 1073°K, x_{Pt} = 0.14-0.86).

Copper-Antimony

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with modifications of Elliott (1965). Pearson (1958, 1967) lists five intermediate phases.

η, "$Cu_{5.5}Sb$", with the hcp (A3) structure isotypic with Mg.

ϵ, "$Cu_{4.5}Sb$", with a hexagonal superlattice related to the ($D0_{19}$) type.

ϵ', with a hcp superlattice based on the (A3) structure. Pearson (1967) lists two phases, "$Cu_{3.3}Sb$", and "$Cu_{3.65}Sb$". From the original references cited by Pearson, it seems clear only one phase is involved, with a composition near "$Cu_{3.65}Sb$". The formula "$Cu_{3.3}Sb$", was devised to fit atomic positions in a hypothetical, fully-ordered structure.

κ, "Cu_3Sb", with the orthorhombic structure isotypic with Cu_3Ti.

β, "Cu_3Sb", with the ordered fcc ($D0_3$) structure isotypic with BiF_3.

γ, "Cu_2Sb", with the ordered tetragonal (C38) prototype structure.

Solid Alloys. Selected ΔH values of Table 1 were taken from liquid tin solution calorimetric measurements of Kleppa (1956), 723°K, x_{Sb} = 0.06-0.335; those of Table 2 were taken from the same source, assuming ΔH to be invariant with T.

Selected $\Delta\bar{G}_{Cu}$ values of Table 3 agree closer than 100 cal/g-atom with emf measurements of Vecher and Gerasimov (1958), 643°- 883°K, x_{Sb} = 0.04-0.34, although the indicated phase boundaries vary somewhat. The other quantities of Table 3 and Table 2 were calculated from the selected $\Delta\bar{G}_{Cu}$ and ΔH values, using Gibbs-Duhem integration where necessary.

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 5 agree with emf measurements of Krestovnikov and Lomov (1963), 1115°- 1215°K, x_{Sb} = 0.1-0.95, and also with emf measurements of Vecher, Nikol'skaya and Gerasimov (1957), 975°- 1050°K, x_{Sb} = 0.18-0.93, except for $x_{Sb} < 0.34$, where they diverge to as much as 200 cal/g-atom more exothermic than selected values. $\Delta\bar{G}_{Sb}$ values calculated from vapor pressure measurements of Azakami and Yazawa (1967), 1173°- 1473°K, x_{Sb} = 0.2-0.8, are 0-400 cal/g-atom more exothermic than selected values, except that the value at x_{Sb} = 0.2 is 1000 cal/g-atom more exothermic.

Selected $\Delta\bar{S}_{Cu}$ values were taken from the reasonably agreeing temperature coefficients of the emf measurements of Krestovnikov and Lomov

(1963) and Vecher et al. (1957). The remaining values of Tables 4 and 5 were calculated from these selected values. Directly measured ΔH values of Kawakami (1930), 1473° K, x_{Sb} = 0.25-0.75 are much more symmetrical about x_{Sb} = 0.5, diverging to 0-675 cal/g-atom less exothermic below this composition and 0-450 cal/g-atom above. Temperature coefficients of Azakami and Yazawa (1968) lead to ΔH values more exothermic by 150-1600 cal/g-atom.

TABLE 1

Heats of Formation of Solid Alloys at 723° K

$$(1-x)Cu_{(s)} + xSb_{(s)} = Cu_{(1-x)}Sb_{x(s)}$$

x_{Sb}	Phase	ΔH	x_{Sb}	Phase	ΔH
0.052*	(Cu)	108	0.248*	β	280
0.155*	η	- 63	0.274*	β	- 47
0.19	ε	-186	0.322*	γ	-778
		(±100)	0.334*	γ	-1006

TABLE 2

Integral Quantities for Solid Alloys at 775° K

$$(1-x)Cu_{(s)} + xSb_{(s)} = Cu_{1-x}Sb_{x(s)}$$

x_{Sb}	Phase	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.058*	(Cu)	- 462	120	0.751	-121	0.311
0.211*	β	-1438			-644	
0.25		-1622	250	2.415	-756	1.298
0.295*	β	-1744			-810	
0.327*	γ	-1813			-840	
0.33		-1817	- 912	1.168	-840	-0.093
0.334*	γ	-1812	-1006	1.040	-831	-0.226

TABLE 3

Partial Molar Quantities for Solid Alloys at 775° K

		Cu Component $Cu_{(s)}$ = Cu(in alloy)$_{(s)}$				Sb Component $Sb_{(s)}$ = Sb(in alloy)$_{(s)}$			
x_{Sb}	Phase	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Sb}	γ_{Sb}	$\Delta\bar{G}_{Sb}$	$\Delta\bar{G}^{xs}_{Sb}$
0.000	(Cu)	1.000	1.000	0	0	0.000	0.258	- ∞	-2085
0.058*	(Cu)	0.942	1.000	- 92	0	0.015	0.258	-6470	-2085
0.211*	β	0.942	1.194	- 92	273	0.015	0.071	-6470	-4074
0.25		0.596	0.795	- 796	- 353	0.070	0.279	-4101	-1966
0.295*	β	0.486	0.690	-1110	- 572	0.120	0.408	-3260	-1380
0.327*	γ	0.486	0.723	-1110	- 500	0.120	0.368	-3260	-1539
0.33		0.314	0.892	-1784	-1167	0.294	0.872	-1883	- 176
0.334*	γ	0.171	0.257	-2720	-2094	1.000	2.994	0	1689
		(±.01)	(±.03)	(±100)	(±100)	(±.01)	(±.01)	(±100)	(±100)

*Phase boundary

TABLE 4

Integral Quantities for Liquid Alloys at 1190°K

$(1-x)Cu_{(\ell)} + xSb_{(\ell)} = Cu_{1-x}Sb_{x(\ell)}$

x_{Sb}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.108*	-1797	- 983	0.684	- 988	0.004
0.2	-2657	-1348	1.100	-1474	0.106
0.3	-3119	-1344	1.492	-1675	0.278
0.4	-3189	-1054	1.794	-1598	0.457
0.5	-3025	- 697	1.956	-1386	0.579
	(±100)	(±550)	(±.45)	(±100)	(±.45)
0.6	-2709	- 388	1.950	-1117	0.613
0.7	-2274	- 151	1.784	- 829	0.570
0.8	-1719	17	1.459	- 537	0.465
0.9	-1022	82	0.928	- 253	0.282

TABLE 5

Partial Molar Quantities for Liquid Alloys at 1190°K

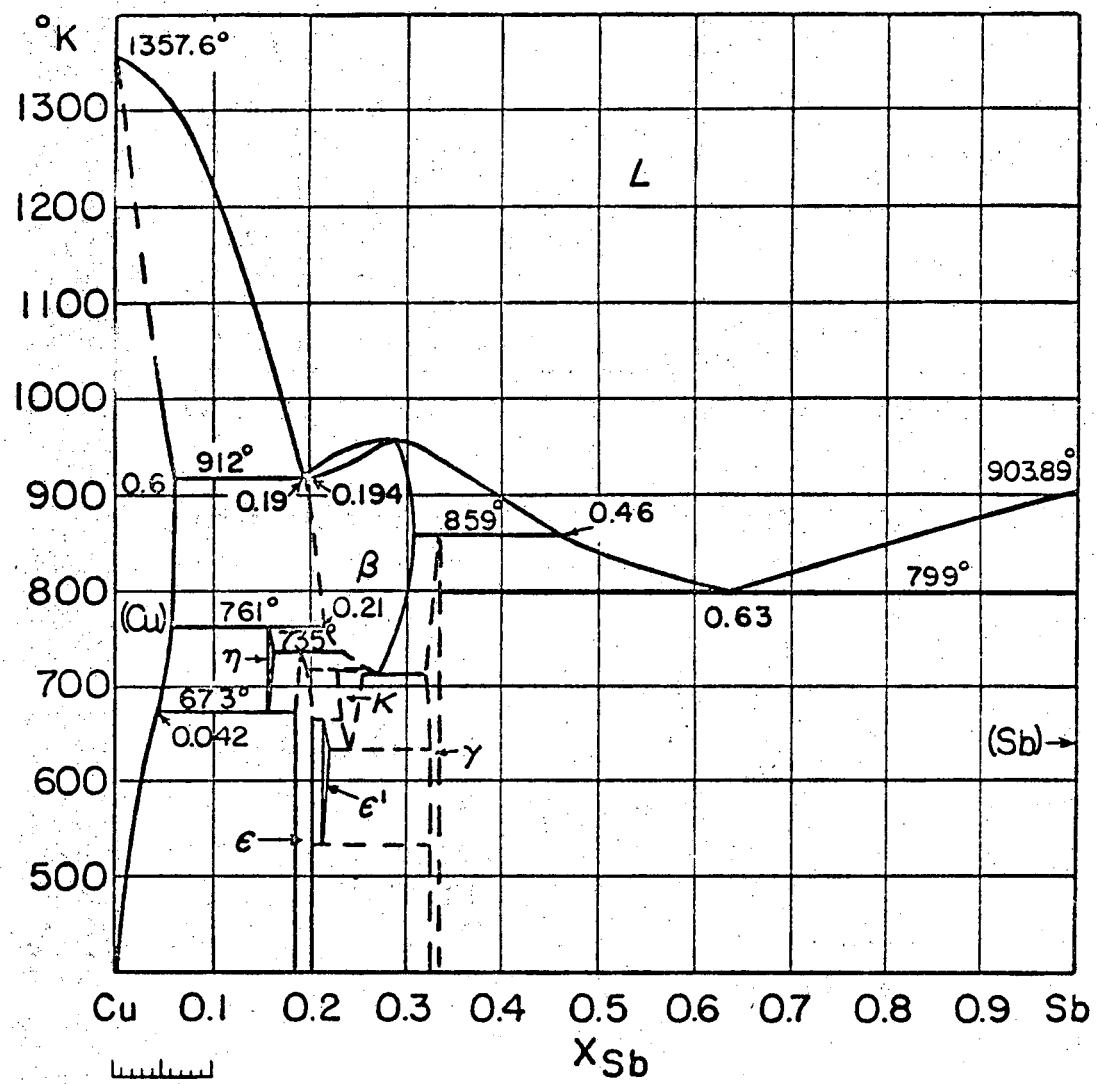
Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
0.892*	0.814	0.912	- 488	- 217	- 290	0.166	-0.061
0.8	0.587	0.734	-1259	- 732	- 952	0.258	-0.185
0.7	0.363	0.518	-2399	-1555	-1892	0.426	-0.283
0.6	0.232	0.387	-3454	-2246	-2458	0.837	-0.178
0.5	0.160	0.319	-4343	-2705	-2487	1.560	0.183
	(±0.007)	(±.014)	(±100)	(±100)	(±550)	(±.45)	(±.45)
0.4	0.122	0.306	-4968	-2801	-2017	2.480	0.659
0.3	0.089	0.295	-5728	-2881	-1586	3.481	1.088
0.2	0.059	0.297	-6672	-2867	- 978	4.785	1.587
0.1	0.032	0.320	-8143	-2697	98	6.925	2.349
0.0	0.000	0.378	- ∞	-2300	1746	∞	3.400

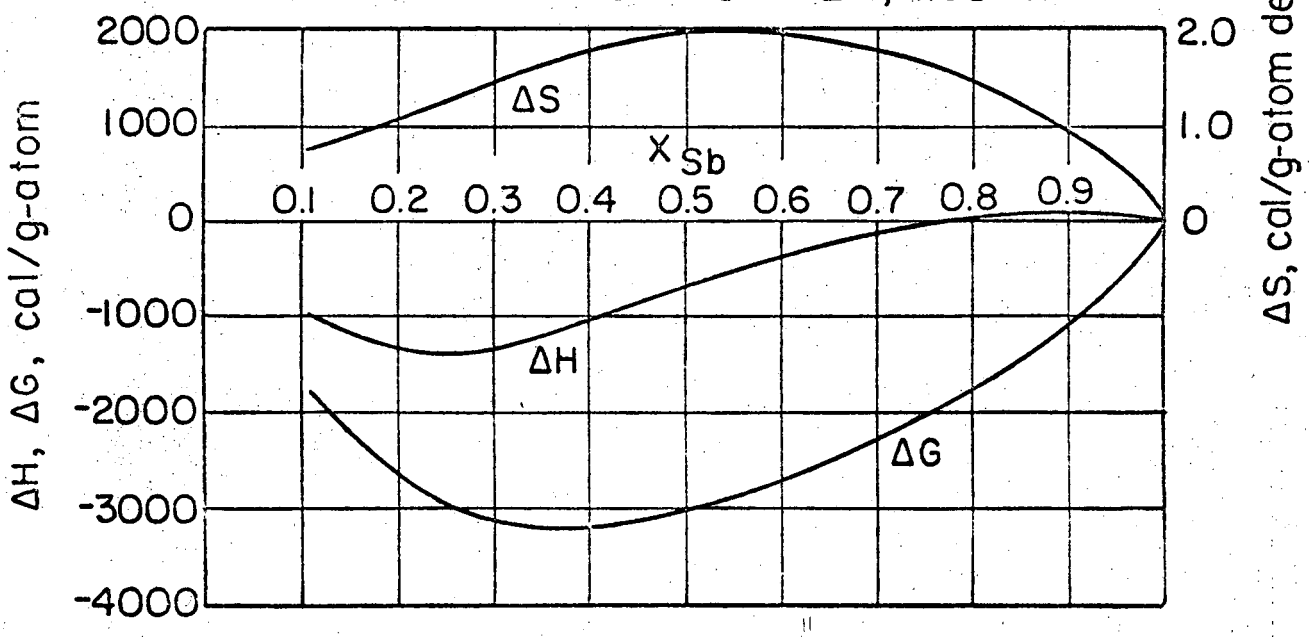
Sb Component $Sb_{(\ell)} = Sb(\text{in alloy})_{(\ell)}$

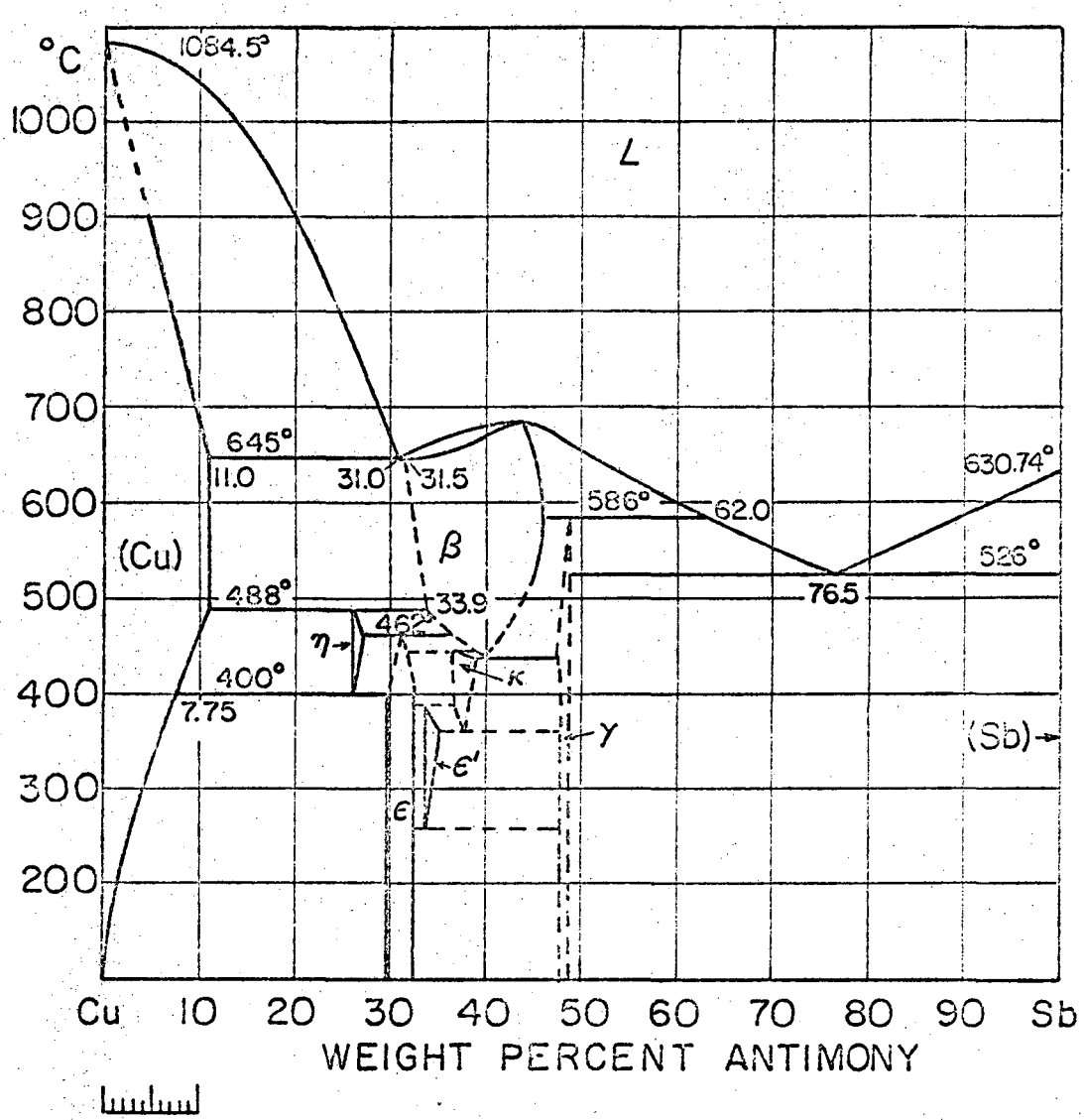
x_{Sb}	a_{Sb}	γ_{Sb}	$\Delta\bar{G}_{Sb}$	$\Delta\bar{G}^{xs}_{Sb}$	$\Delta\bar{H}_{Sb}$	$\Delta\bar{S}_{Sb}$	$\Delta\bar{S}^{xs}_{Sb}$
0.108*	0.005	0.045	-12616	-7353	-6709	4.964	0.541
0.2	0.031	0.153	- 8248	-4443	-2929	4.470	1.272
0.3	0.131	0.437	- 4802	-1955	- 66	3.980	1.587
0.4	0.307	0.768	- 2792	- 625	1053	3.231	1.410
0.5	0.486	0.972	- 1706	- 67	1093	2.352	0.975
	(±.02)	(±.04)	(±100)	(±100)	(±550)	(±.45)	(±.45)
0.6	0.601	1.002	- 1202	5	698	1.597	0.582
0.7	0.715	1.022	- 793	51	465	1.057	0.348
0.8	0.816	1.020	- 481	46	266	0.628	0.185
0.9	0.907	1.008	- 230	19	81	0.261	0.052
1.0	1.000	1.000	0	0	0	0.000	0.000

*Phase boundary



COPPER-ANTIMONY SYSTEM, 1190 °K

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500
400
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200
L
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11.0
31.0
31.5
586°
62.0
630.74°
(Cu)
β
526°
488°
33.9
76.5
462°
η
κ
400°
7.75
γ
(Sb)
ε'
ε
Cu
10
20
30
40
50
60
70
80
90
Sb
WEIGHT PERCENT ANTIMONY

Part III. References

(For references not in list, see General References)

Azakami, T., and A. Yazawa (1967) J. Mining Metal. Inst. Japan, 83, 666-72. Vapor pressure (1172° - 1473°K, x_{Sb} = 0.2-0.8).

Kawakami, M. (1930) Sci. Repts. Tohoku Imp. Univ. 19, 521-49. ΔH (1473°K, x_{Sb} = 0.25-0.75).

Kleppa, O. J. (1956) J. Phys. Chem. 60, 852-8. ΔH (723°K, x_{Sb} = 0.06-0.335).

Krestovnikov, A. N., and A. L. Lomov (1963) Izv. Vysshikkh Uchebn. Zavedenii, Tsvetn. Met. 6, 75-82. Emf (1115° - 1215°K, x_{Sb} = 0.1-0.95).

Vecher, A. A., and Ya. I. Gerasimov (1958) Zhur. Fiz. Khim. 32, 2835-40. Emf (643° - 883°K, x_{Sb} = 0.04-0.34).

Vecher, A. A., A. V. Nikol'skaya, and Ya. I. Gerasimov (1957) Zhur. Fiz. Khim. 31, 1395-1400. Emf (975° - 1050°K, x_{Sb} = 0.18-0.93).

Copper-Silicon

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958), with modifications of Elliott (1965). For Si, T_m = 1687.15 was taken from the 1968 International Practical Temperature Scale. Pearson (1958, 1967) lists the structures of six intermediate phases; however, recent high-temperature diffraction studies of Mukherjee, Bandyopadhyaya, and Gupta, (1969), indicated modifications of structure of three of them.

κ, "ζCu-Si", with the hcp (A3) structure isotypic with Mg.

β, "βCu-Si", possibly with the bcc (A2) structure isotypic with W.

γ, "γ-Cu_5Si", with the complex cubic (A13) structure isotypic with β-Mn.

ϵ, "ϵ-$Cu_{15}Si_4$"; Mukherjee, et al. (1969) state this phase is not bcc as stated by Pearson (1967), but is complex cubic. They found evidence of a transformation near 873°K, by X-ray diffraction but not by differential thermal analysis.

δ, "δ Cu-Si"; Murkherjee et al. (1969) state that this phase has a complex tetragonal structure, not the slightly deformed ($D8_2$) structure isotypic with γ-brass listed by Pearson (1967).

η, η', η''; data on these phases are contradictory. Elliott (1965), cites one work indicating two low-temperature transformations as shown in the diagram; others found no low-temperature changes. Mukherjee et al. (1969) found a low-temperature phase, η', with a complex tetragonal cell; at high temperatures there were drastic changes in intensity of some of the lines, probably indicating some sort of transformation between 823°- 979°K.

Dorward and Kirkaldy (1968) made a recent determination of the solubility of Cu in (Si). Luo and Andres (1970) found κ to be superconducting below 0.61°K.

Liquid Alloys. $\Delta\bar{G}_{Si}$ values determined by the H_2, H_2O, SiO equilibria of Bowles, Ramstad, and Richardson (1964), 1833°K, x_{Si} = 0.0036, 0.051, agree with selected values of Table 2, in which Henry's law was assumed. The other values of Tables 1 and 2 were calculated from this selection. Emf measurements of Nikitin (1962), 1673°K, x_{Si} = 0.027-0.24, were reported in terms of activities, with a_{Si} = 1.0 at x_{Si} = 0.24. In view of uncertainities of interpretation, these values were not tabulated.

PDD August, 1970

Part II. Tables

TABLE 1

Integral Quantities for Liquid Alloys at 1833°K

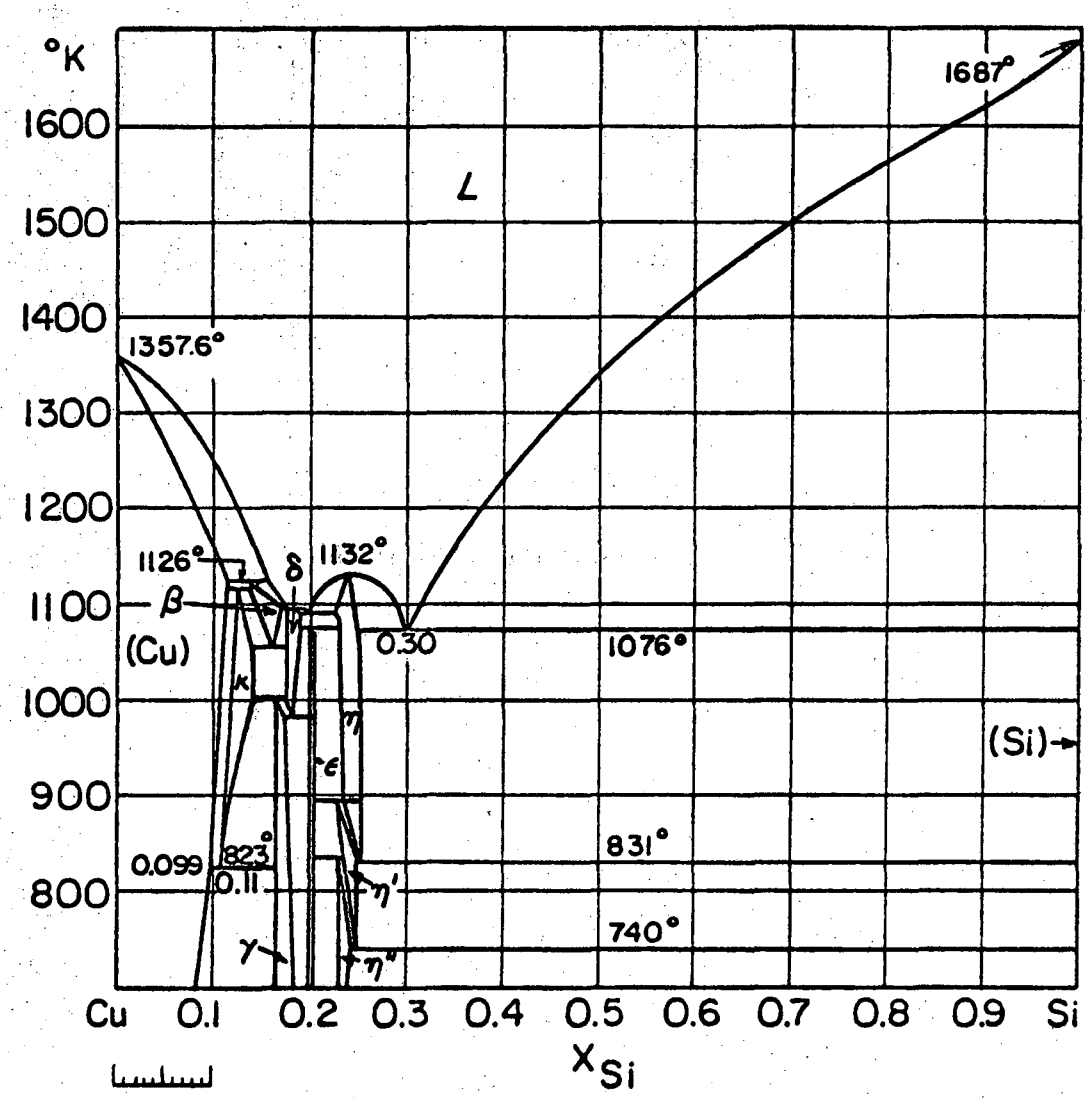
$$(1-x)Cu_{(\ell)} + xSi_{(\ell)} = Cu_{1-x}Si_{x\,(\ell)}$$

x_{Si}	ΔG	ΔG^{xs}
0.05	-1473(±70)	-750(±70)

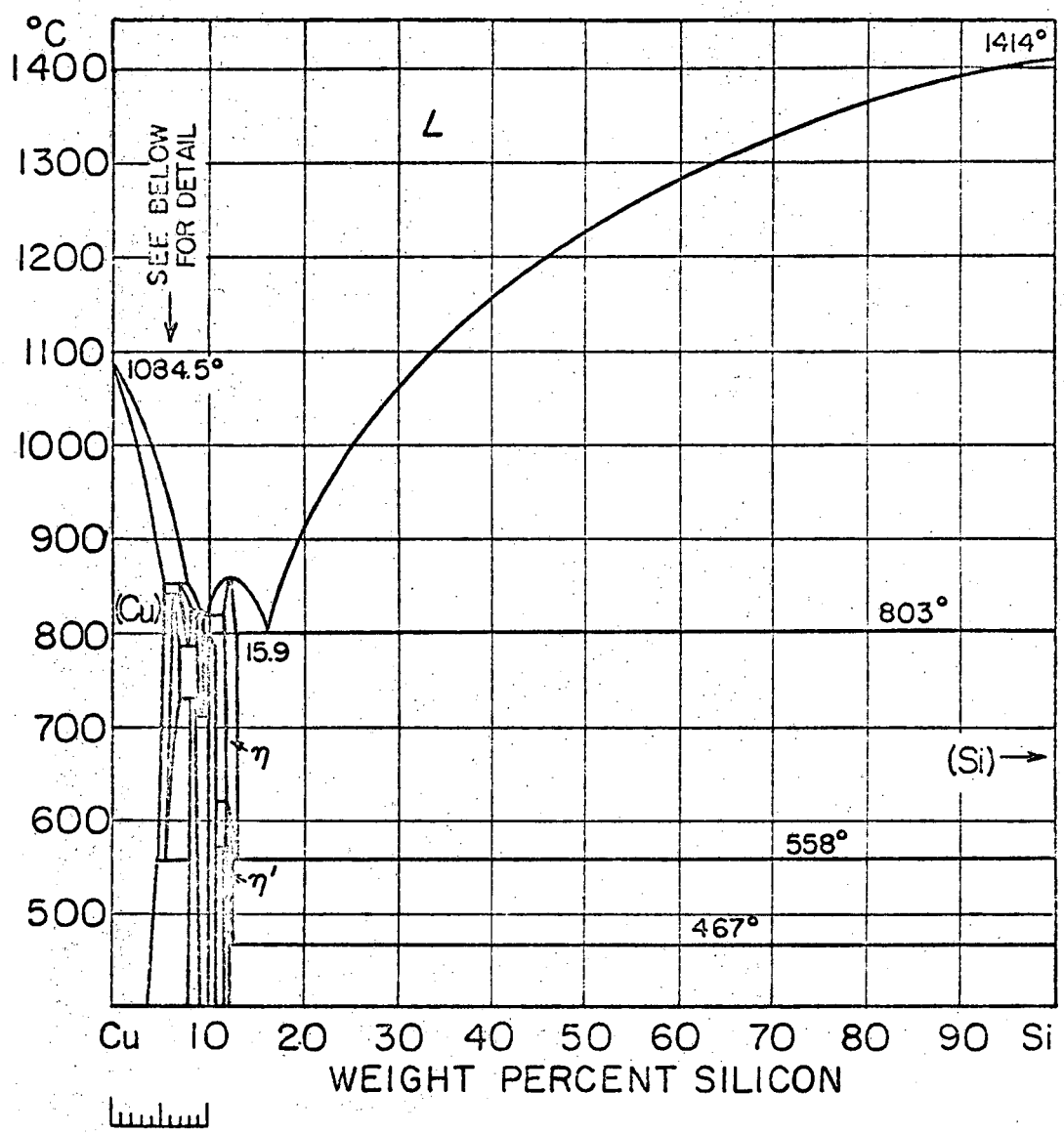
TABLE 2

Partial Molar Quantities for Liquid Alloys at 1833°K

	Cu Component $Cu_{(\ell)}$ = Cu(in alloy)$_{(\ell)}$				Si Component $Si_{(\ell)}$ = Si(in alloy)$_{(\ell)}$			
x_{Si}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Si}	γ_{Si}	$\Delta\bar{G}_{Si}$	$\Delta\bar{G}^{xs}_{Si}$
0.00	1.000	1.000	0	0	0.000	0.016	$-\infty$	-15000
0.05	0.950 (±.013)	1.000 (±.014)	-187 (±50)	0 (±50)	0.0008 (±.0002)	0.016 (±.004)	-25912 (±1000)	-15000 (±1000)



COPPER - SILICON SYSTEM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800
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1414°
L
SEE BELOW FOR DETAIL
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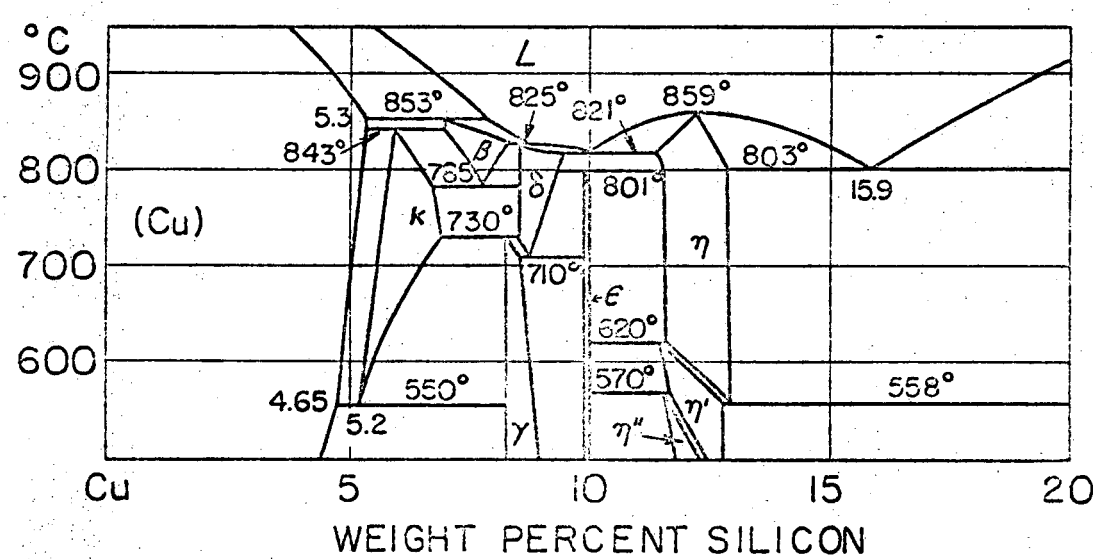
(Cu)
15.9
803°
η
(Si)
558°
η'
467°
Cu 10 20 30 40 50 60 70 80 90 Si
WEIGHT PERCENT SILICON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843°
β
803°
785
δ
801°
15.9
(Cu)
κ
730°
η
710°
ε
620°
570°
558°
4.65
550°
5.2
γ
η''
η'
Cu 5 10 15 20
WEIGHT PERCENT SILICON

Part III. References

(For references not in list, see General References)

Bowles, F. J., H. F. Ramstad, and F. D. Richardson (1964) J. Iron Steel Inst. (London) 202, 113-21. H_2, H_2O, SiO equilibria (1833°K, x_{Si} = 0.0036, 0.051).

Dorward, R. C., and J. S. Kirkaldy (1968) Trans. Met. Soc. AIME 242, 2055-61. Solubility of Cu in (Si).

Luo, K. L., and K. Andres (1970) Phys. Rev. B1, 3007. Superconductivity.

Mukherjee, K. P., J. Bandyopadhyaya, and K. P. Gupta (1969) Trans. Met. Soc. AIME 245, 2335-8. Phase diagram.

Nikitin, Yu. P., (1962) Tsvetnaya Met. 5, 56-7. Emf (1673°K, x_{Si} = 0.027-0.24).

Copper-Tin

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958). Pearson (1958, 1967) reports the following intermediate phases and structures:

β, with the bcc (A2) structure isotypic with W.

γ, with the fcc ($D0_3$) structure isotypic with BiF_3.

δ, "$Cu_{31}Sn_8$", with a cubic structure similar to ($D8_{1-3}$) isotypic with Fe_3Zn_{20}, Cu_5Zn_8, or Cu_9Al_4.

ζ, "$Cu_{20}Sn_6$", with a trigonal structure.

ϵ, "Cu_3Sn", with a pseudo hexagonal structure similar to (A3) isotypic with Mg.

η', "Cu_6Sn_5", with a hexagonal structure which is a superlattice of ($B8_1$) isotypic with NiAs. On heating it transforms to the η-phase, of unknown structure.

Knödler (1966) confirms the structures of β and γ. Pearson (1967) also reported two metastable phases. On quenching from the β region, γ', with a hexagonal structure isotypic with ζ-AgZn, is formed. On quenching from the γ region at 973°K, ϵ'-Cu_3Sn, having an orthorhombic structure, is obtained.

Solid Alloys. Low-Temperature Data. Selected values of Table 1 were taken from Cp measurements of Clune and Green (1966), 2°- 4°K, x_{Sn} = 0.00-0.062. Selected ΔH values of Table 2 agree well within ±100 cal with the liquid tin calorimetric measurements of Kleppa (1956), 723°K, x_{Sn} = 0.074-0.255, 0.84-0.96; Cohen, Leach, and Bever (1954), 273°K, x_{Sn} = 0.042, 0.247; Ticknor and Bever (1952), 573°K, x_{Sn} = 0.98-0.99, and with the direct calorimetric measurements of Körber and Oelsen (1937), 293°K, 1423°K, x_{Sn} = 0.14-0.81, except the value of Kleppa (1956) for an unknown reason is about 400 cal/g-atom less exothermic in the (Cu) + δ region at x_{Sn} = 0.086. The Br_2 aqueous solution calorimetric value of Biltz, Wagner, Pieper, and Holverscheit (1924), 293°K, x_{Sn} = 0.25 is about 200 cal/g-atom more exothermic than the selected value. Honda and Tokunaga (1935), 299°K, x_{Sn} = 0.00-0.06 found by true Cp measurements of the (Cu) phase that ΔCp = 0 (±0.2), in agreement with ΔH measurements at differing temperatures.

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Liquid Alloys. Several direct measurements of the heat of solution of $Cu_{(s)}$ in $Sn_{(\ell)}$ near $x_{Sn} = 1$ have been found.

Source	$\Delta\bar{H}_{Cu(s)}$, T, °K	$\Delta\bar{H}_{Cu(\ell)}$, 723°K
Orr (1960), 700°K	2840	-236
Oriani and Murphy (1959), 691°K	2816	-243
Kleppa (1956), 723°K	2792	-328
Ticknor and Bever (1952), 573°K	2570	-281
	SELECTED VALUE	-260

The values have been transferred to $\Delta\bar{H}_{Cu(\ell)}$ at 723°K, assuming for Cu, $\Delta H_m = 3120$, invariant with T, and $\Delta\bar{C}p_{Cu(\ell)} = 1.9\ (\pm 2)$.

Selected $\Delta\bar{G}_{Sn}$ values of Table 4 agree within ±200 cal with the vapor pressure measurements of Azakami and Yazawa (1969), 1403°K, $x_{Sn} = 0.1-0.9$; with the mass-spectrometric vapor pressure measurements of Alcock, Sridhar, and Svedberg (1970), 1450°- 1680°K, $x_{Sn} = 0.1-0.9$, and of Hager, Howard, and Jones (1970), 1250°- 1820°K, $x_{Sn} = 0.1-0.9$, with the following exceptions: The value of Azakami and Yazawa is less exothermic by 3000 cal/g-atom at $x_{Sn} = 0.1$. Values of Alcock, Sridhar, and Svedberg are highly exothermic for $x_{Sn} \leqslant 0.4$, and those of Hager, Howard, and Jones scatter up to ±1500 cal on the Cu-rich side. Values of Alcock et al. (1969), and Hager et al. (1969) were transferred to 1400°K with the aid of the selected temperature coefficient (see next paragraph).

Selected ΔH values of Table 3 agree within ±200 cal with the direct reaction calorimetric measurements of Yazawa and Itagaki (1969), 1373°K, $x_{Sn} = 0.08-0.88$; Körber and Oelsen (1937) 293°, 1423°K, $x_{Sn} = 0.14-0.81$; Kawakami (1930), 1473°K, $x_{Sn} = 0.16-0.68$; and with the solution calorimetric measurements of Benz and Elliott (1964), 1400°K, $x_{Sn} = 0.003-0.125$ with the following exceptions: Values of Kawakami (1930) are more exothermic by 200-500 cal for $x_{Sn} > 0.28$. Values reported by Alcock et al. (1969) from the temperature coefficient scatter (±150 cal/g-atom) about the selected values; those of Hager et al. (1969) are 0-170 cal more and less exothermic, respectively for $x_{Sn} < 0.32$ and for $x_{Sn} > 0.32$. Other quantities of Tables 3 and 4 were calculated with the aid of Gibbs-Duhem integration.

Selected $\Delta\bar{G}_{Sn}$ values of Table 5 were taken from the emf studies of Dinh-Pham-Thai (1967), 633°K, $x_{Sn} = 0.975-0.995$, who has reported only activity curves.

Ackerman, Drowart, Stafford, and Verhaegen (1961), 1632°- 1852°K, $x_{Sn} = 0.5$ have reported a dissociation energy of 20700 cal/g-atom for the CuSn molecule at 0°K.

TABLE 1

Low-Temperature Data for (Cu)-Phase Alloys

T, °K	x_{Sn}				
	0.000	0.005	0.010	0.030	0.060
	Cp				
2.0	0.000423	0.000423	0.000432	0.000447	0.000474
3.0	0.000806	0.000816	0.000827	0.000868	0.000943
4.0	0.00139	0.00142	0.00144	0.00153	0.00168
$\gamma \times 10^4$	1.66	1.67	1.69	1.71	1.76

TABLE 2

Heats of Formation of Solid and Liquid Alloys at 723°K

$$(1-x)Cu_{(s)} + xSn_{(s)} = Cu_{1-x}Sn_{x(s)}$$

$$(1-x)Cu_{(\ell)} + xSn_{(\ell)} = Cu_{1-x}Sn_{x(\ell)}$$

$$Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$$

x_{Sn}	Phase	ΔH	x_{Sn}	Phase	ΔH	ΔCp	$\Delta\bar{H}_{Cu}$	$\Delta\overline{Cp}_{Cu(\ell)}$
0.091*	(Cu)	- 280	0.825*	ℓ	-1105	1.7		
			0.850		- 990			
0.204*	δ	-1300	0.900		- 760	1.2		
0.209*	δ	-1260	0.950		- 530			
					(±50)			
0.244*	ϵ	-1686	1.000	ℓ	0		-260	1.9(±2)
0.250		-1800						
0.255*	ϵ	-1920						
		(±100)						

*Phase boundary.

TABLE 3

Integral Quantities for Liquid Alloys at 1400°K

$$(1-x)Cu_{(\ell)} + xSn_{(\ell)} = Cu_{1-x}Sn_{(\ell)}$$

x_{Sn}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-1922	-666	0.897	-1018	0.251
0.2	-2834	-979	1.325	-1442	0.331
0.3	-3195	-934	1.614	-1495	0.400
0.4	-3300	-715	1.846	-1427	0.509
0.5	-3167	-475	1.923	-1238	0.545
	(±300)	(±150)	(±.24)	(±300)	(±.24)
0.6	-2889	-264	1.875	-1017	0.538
0.7	-2483	- 97	1.705	- 784	0.491
0.8	-1937	13	1.392	- 545	0.398
0.9	-1196	52	0.891	- 291	0.245

TABLE 4

Partial Molar Quantities for Liquid Alloys at 1400°K

Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.802	0.891	- 613	- 320	- 159	0.325	0.115
0.8	0.539	0.674	-1717	-1096	- 749	0.691	0.248
0.7	0.389	0.556	-2626	-1633	-1443	0.845	0.136
0.6	0.284	0.474	-3497	-2076	-1662	1.311	0.295
0.5	0.220	0.440	-4215	-2287	-1631	1.845	0.468
	(±.025)	(±.05)	(±300)	(±300)	(±250)	(±.3)	(±.3)
0.4	0.169	0.422	-4949	-2400	-1418	2.522	0.701
0.3	0.125	0.417	-5781	-2432	-1049	3.380	0.988
0.2	0.082	0.408	-6971	-2493	- 640	4.522	1.324
0.1	0.038	0.379	-9104	-2698	81	6.561	1.985
0.0	0.000	0.317	- ∞	-3197	1050	∞	3.034

Sn Component $Sn_{(\ell)} = Sn(\text{in alloy})_{(\ell)}$

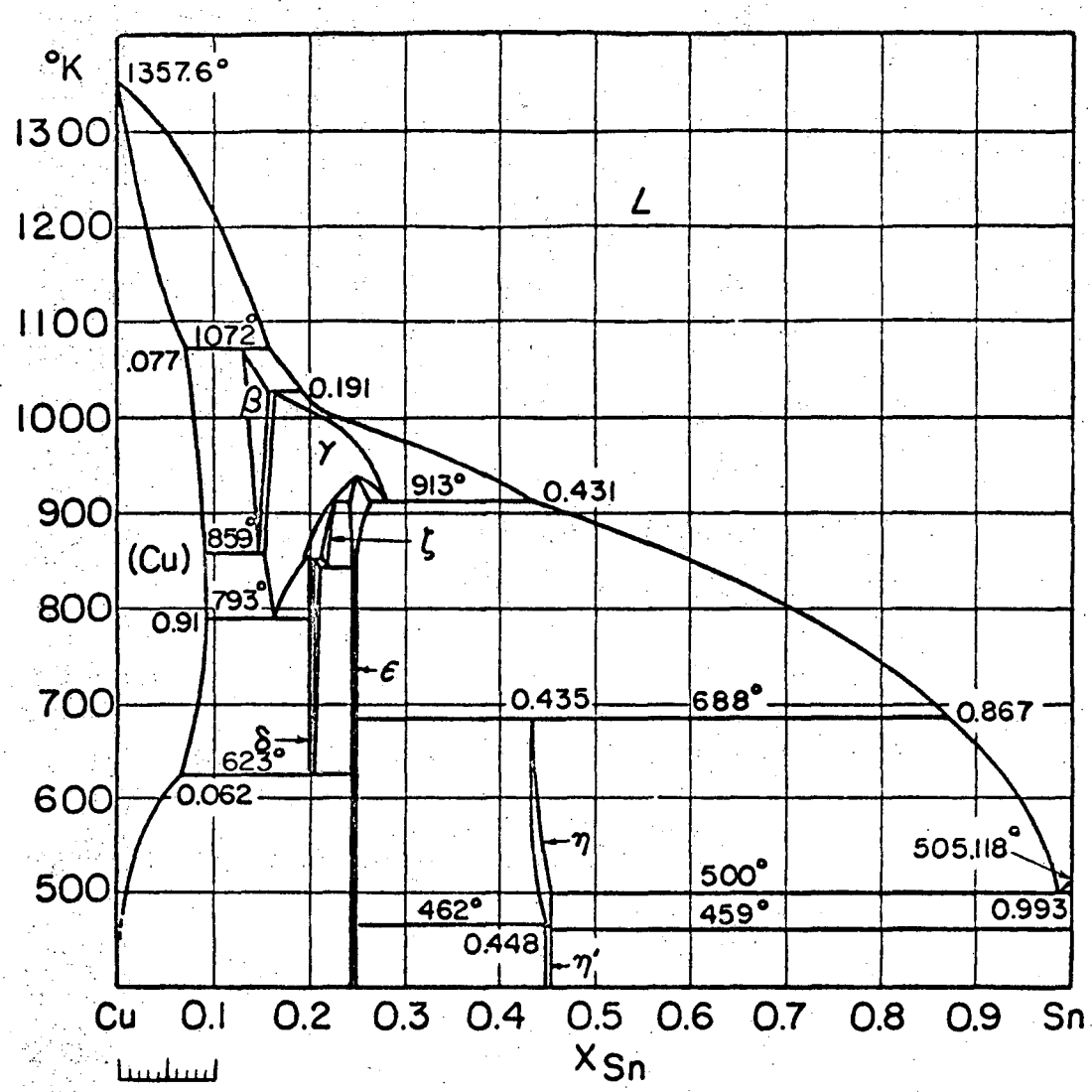
x_{Sn}	a_{Sn}	γ_{Sn}	$\Delta\bar{G}_{Sn}$	$\Delta\bar{G}^{xs}_{Sn}$	$\Delta\bar{H}_{Sn}$	$\Delta\bar{S}_{Sn}$	$\Delta\bar{S}^{xs}_{Sn}$
0.0	0.000	0.007	- ∞	-13609	-8000	∞	4.006
0.1	0.007	0.072	-13706	- 7301	-5233	6.053	1.477
0.2	0.072	0.362	- 7304	- 2827	-1901	3.860	0.661
0.3	0.197	0.656	- 4523	- 1173	252	3.411	1.018
0.4	0.340	0.849	- 3003	- 454	706	2.649	0.828
0.5	0.467	0.934	- 2119	- 190	681	2.000	0.622
	(±.05)	(±.1)	(± 300)	(± 300)	(±250)	(±.3)	(±.3)
0.6	0.580	0.966	- 1516	- 95	506	1.444	0.429
0.7	0.681	0.973	- 1069	- 77	311	0.986	0.277
0.8	0.784	0.979	- 678	- 57	176	0.610	0.167
0.9	0.892	0.991	- 317	- 24	49	0.261	0.052
1.0	1.000	1.000	0	0	0	0.000	0.000

TABLE 5

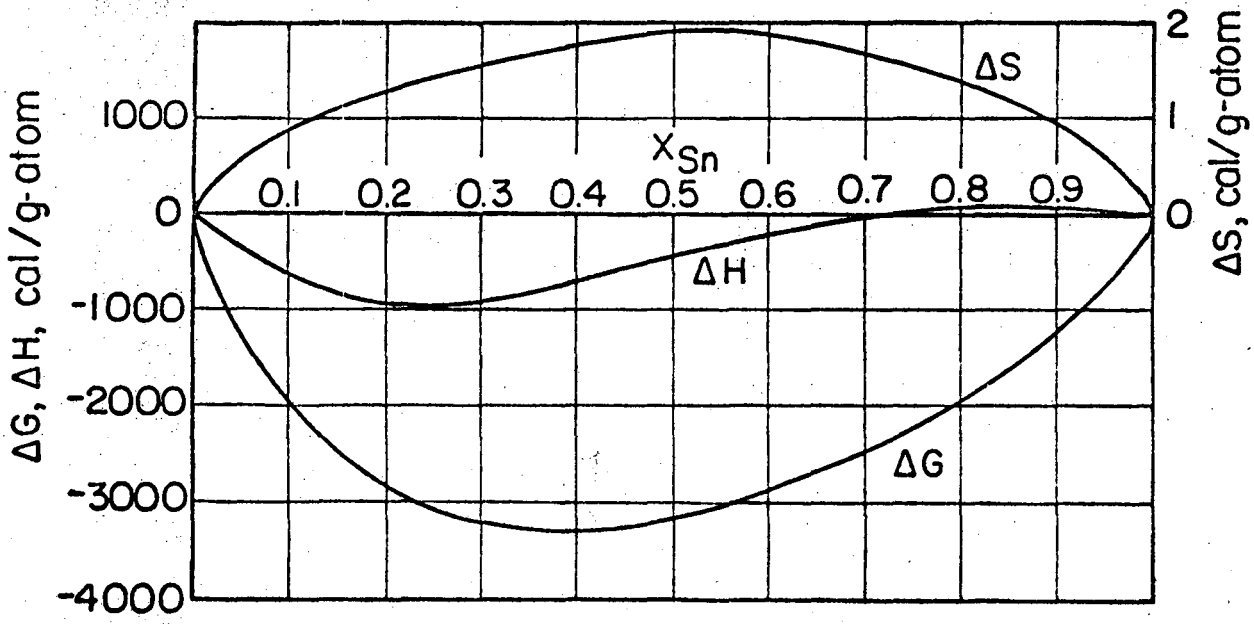
Partial Molar Quantities for Liquid Alloys at 633°K

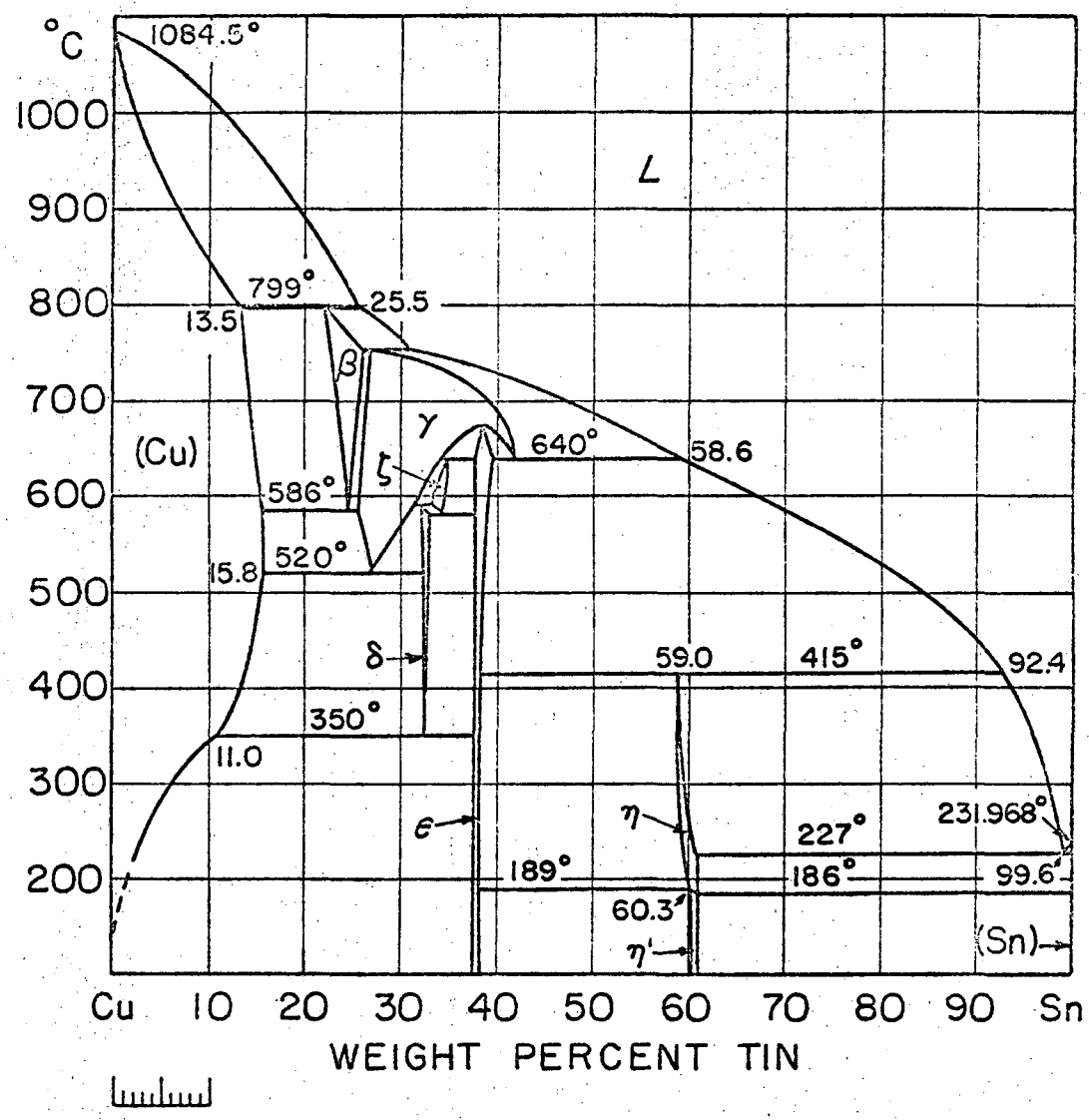
$Sn_{(\ell)} = Sn(\text{in alloy})_{(\ell)}$

x_{Sn}	a_{Sn}	γ_{Sn}	$\Delta\bar{G}_{Sn}$	$\Delta\bar{G}^{xs}_{Sn}$
0.98	0.965	0.985	-47	-20
0.99	0.985	0.995	-13	- 7
	(±.005)	(±.005)	(±5)	(±5)



COPPER - TIN SYSTEM, 1400°K

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(Cu)
640°
58.6
ζ
586°
520°
15.8
δ
59.0
415°
92.4
350°
11.0
ε
η
227°
231.968°
189°
186°
99.6
60.3
η'
(Sn)
Cu 10 20 30 40 50 60 70 80 90 Sn
WEIGHT PERCENT TIN

Part III. References

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Orr, R. L. (1960) Acta Met. 8, 489-93. ΔH (700°K, x_{Sn} = 1.0).

Ticknor, L. B., and M. B. Bever (1952) J. Metals 4, 941-5. ΔH (573°K, x_{Sn} = 0.98-0.99).

Yazawa, A., and K. Itagaki (1969) Private Communication, Tohoku Univ. Sendai, Japan. ΔH (1373°K, x_{Sn} = 0.08-0.88).

Copper-Tellurium

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with additional information from Elliott (1965). Pearson (1958, 1967) lists the following phases:

- β, "Cu_2Te" a high temperature phase with a complex fc cubic structure.
- γ, "Cu_2Te" a low temperature phase with a hexagonal structure. Three superlattices of this structure have been reported.
- ϵ, "Cu_4Te_3" with a complex tetragonal structure.
- ζ, "CuTe" with an orthorhombic structure.

Baranova (1969) reports a phase,

"Cu_7Te_4", with a hexagonal structure. This is probably δ.

Solid Alloys. The selected ΔH value of Table 1 was taken from the compilation of Wagman, Evans, Parker, Halow, Bailey, and Shumm (1969).

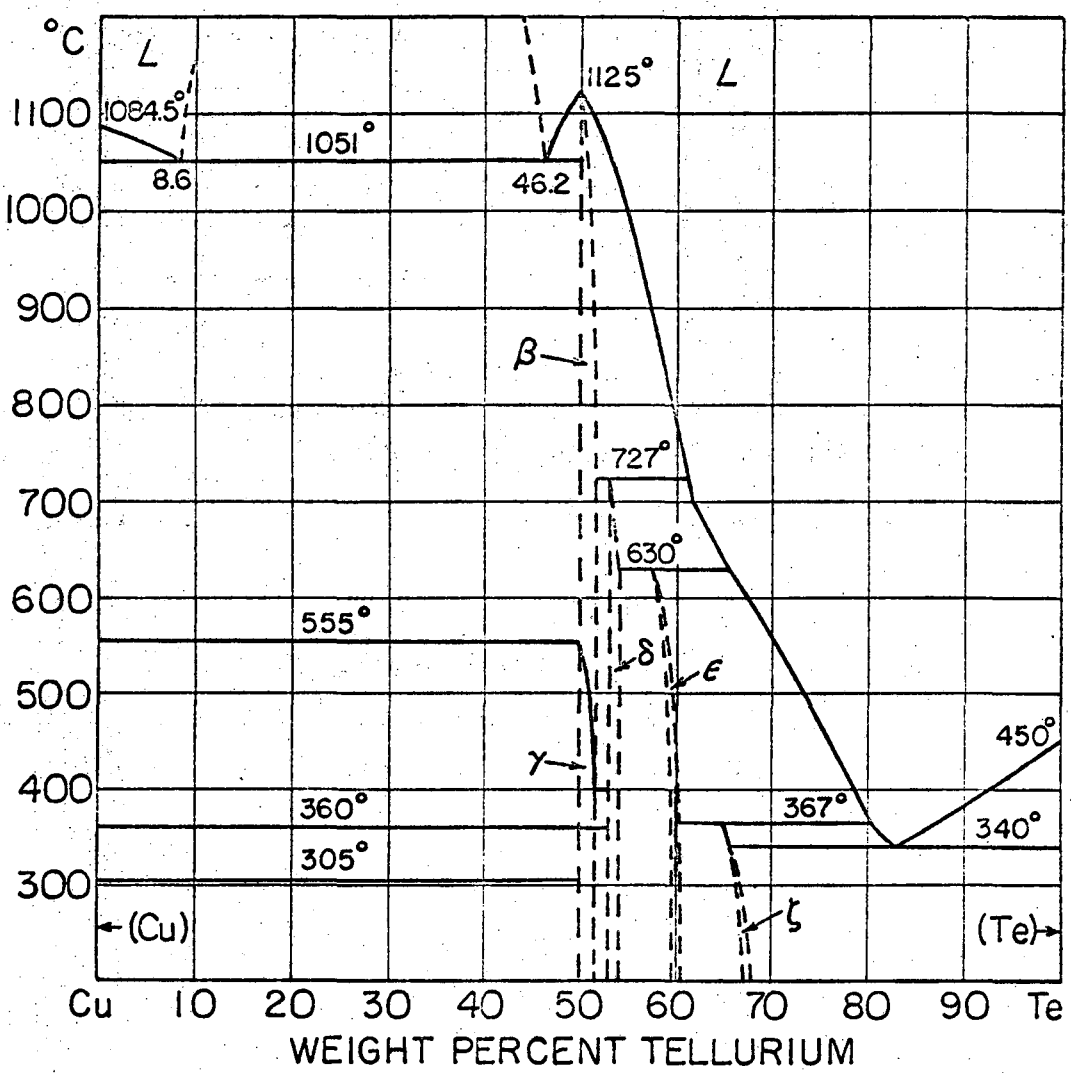
Part II. Tables

TABLE 1

Heats of Formation of the γ-Phase Alloy, $x_{Te} = 0.33$, at 298.15°K

$$0.67Cu_{(s)} + 0.33Te_{(s)} = Cu_{0.67}Te_{0.33(\gamma)}$$

x_{Te}	ΔH
0.33	1667



Part III. References

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Copper-Thorium

Part I. Discussion

Phases and Structures. The phase diagram was taken from Elliott (1965), with corrections for the selected $T_{\alpha-\beta}$ = 1638°K and T_m = 2031°K. Pearson (1958, 1967) lists the two intermediate phases:

δ, "Cu_2Th", with the hexagonal (C32) structure isotypic with AlB_2.

ϵ, "γ-$CuTh_2$", with the bc tetragonal (C16) structure isotypic with Al_2Cu.

The structure of the γ, "Cu_4Th", phase has not been reported. There are considerable uncertainties in regard to the ϵ-(α-Th) eutectic. Thomson (1965) found that it occurred at x_{Th} = 0.73 at 1310 (±12)°K; about 96°K higher than shown. The melting temperature of ϵ obviously must also be considerably raised.

Solid Alloys. Selected values of Table 1 were calculated from the emf studies of Magnani (1968), 850°- 946°K, x_{Th} = 0.05; 0.07.

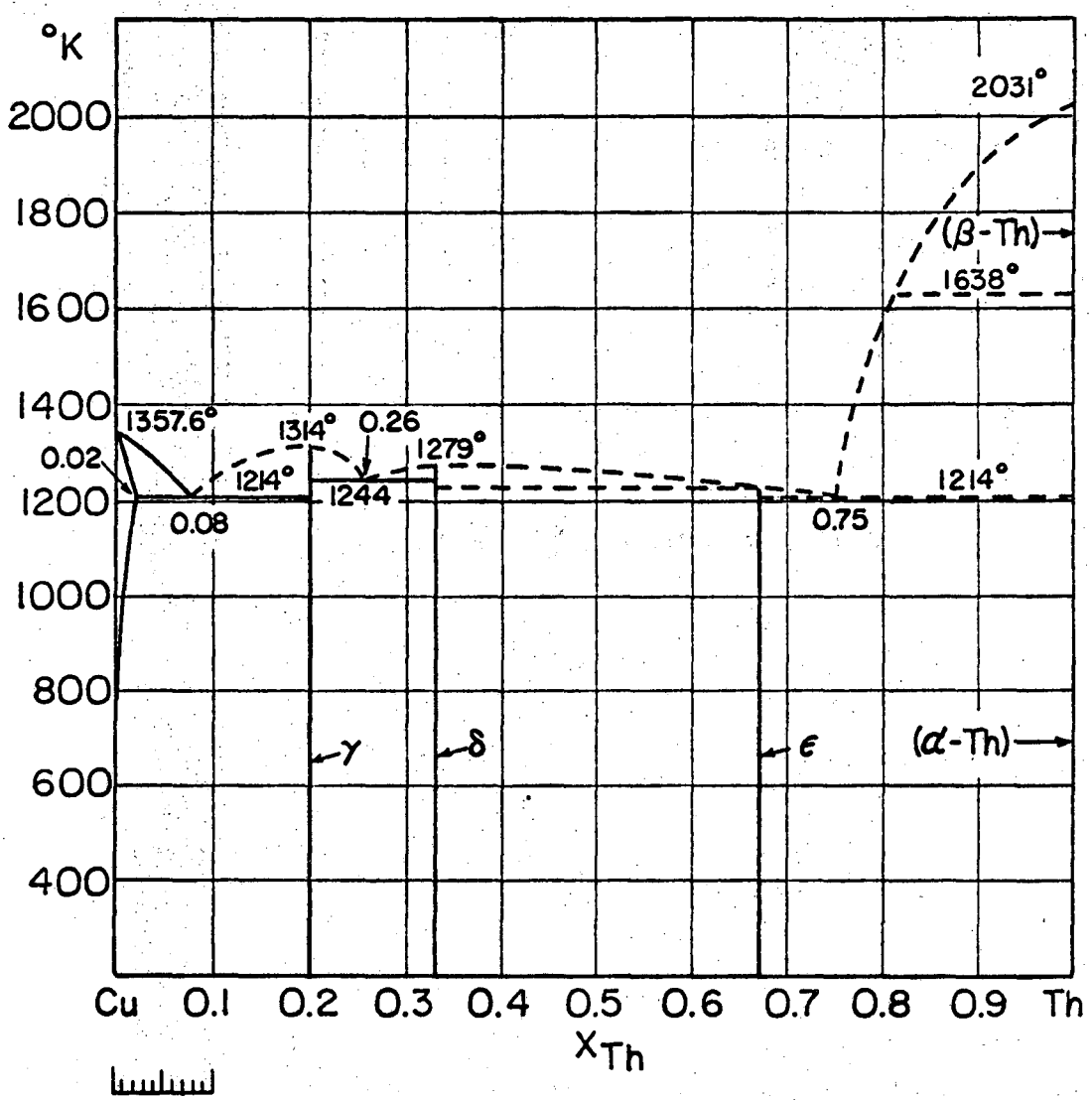
Part II. Tables

TABLE 1

Integral Quantities for γ-Phase Alloys at 900°K, x_{Th} = 0.2

$$0.8Cu_{(s)} + 0.2Th_{(\alpha)} = Cu_{0.8}Th_{0.2(\gamma)}$$

x_{Th}	ΔG	ΔH	ΔS
0.20	-4280 (±50)	-2939 (±150)	1.490 (±.2)



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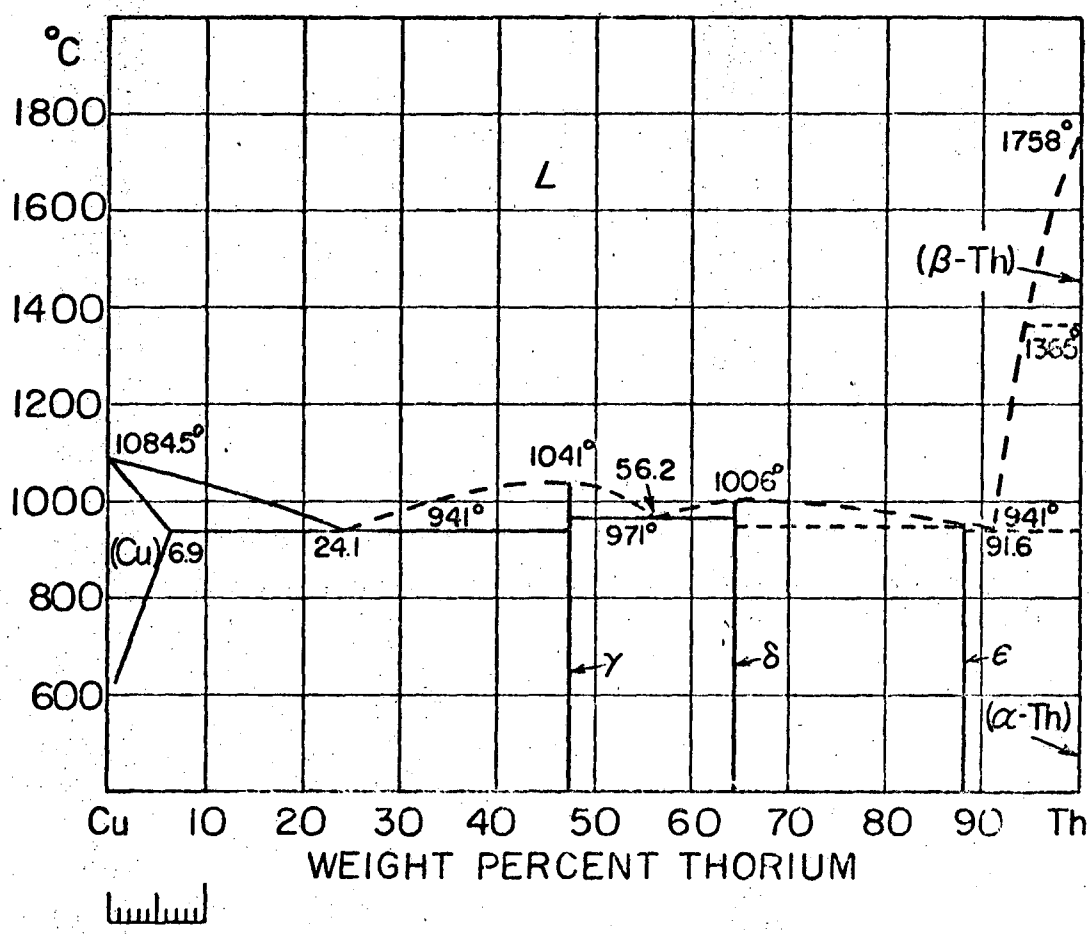

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Copper-Titanium

Part I. Discussion

Phases and Structures. Many contradictory reports were found of phases and structures in this system; possibly due to unidentified impurities such as O or N. The diagram from Hansen (1958) has been modified to include additional information from Elliott (1965), modifications suggested by Shunk (1969), by Eremenko, Buyanov, and Prima (1966), and by Eremenko, Buyanov, and Pancheko (1969). Eremenko, Buyanov, and Prima (1966) list the following intermediate phases:

δ, "Cu_4Ti", with a rhombohedral structure. Pfeifer, Bhan, and Schubert (1968), and Sinha (1969) report the orthorhombic structure isotypic with Au_4Zr. The "Cu_3Ti"-phase reported by Hansen (1958), and the "Cu_7Ti_2"-phase reported by Shunk (1969) are essentially this phase.

ϵ, "Cu_2Ti", with the orthorhombic structure isotypic with Au_2V (Confirmed by Schubert, 1965).

η, "Cu_3Ti_2", with the tetragonal structure isotypic with Al_3Os_2. Schubert (1965) found it to be a complex tetragonal structure with a different space group.

γ, "Cu_4Ti_3", with a tetragonal structure confirmed by Schubert (1965) and Pfeifer et al. (1968).

ζ, "CuTi", with the ordered tetragonal (B11) prototype structure. Pearson (1958) lists an additional phase, "δ-CuTi" ($x_{Ti} = 0.55$), with an ordered tetragonal ($L1_0$) structure isotypic with AuCu I.

θ, "$CuTi_2$" with the tetragonal ($C11_b$) structure isotypic with $MoSi_2$.

In addition Pearson (1958, 1967) lists the following phases whose existence is doubtful and which are not included in the phase diagram:

"β-Cu_3Ti (H. T.)", with a disordered end-centered orthorhombic structure.

"β'-Cu_3Ti (L. T.)", with an ordered orthorhombic structure.

"ϵ-$CuTi_3$", with an ordered tetragonal prototype structure. Recently Gardina, Gordeeva, Timonina, and Zifferman (1967) have reported the existence of this phase obtaining a similar crystal structure.

Solid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 2 were taken from the measurements of Hackworth, Hoch, and Gegel (1969), 1423°- 1523°K, x_{Ti} = 0.914-0.966; 1718°- 1803°K, x_{Ti} = 0.86, 0.919, who measured the ratio of the vapor pressure of $Cu^{65}_{(g)}$ and $Cu^{63}_{(g)}$ coming from a triple Knudsen cell with the aid of a mass spectrometer. Inside the main cell were two Knudsen cells, one containing the pure isotope, Cu^{65}, and the other the alloy of Cu of the normal isotopic concentration with Ti. From the ratio of the isotopes in the gas, the authors were able to determine $\Delta\bar{G}_{Cu}$ in the alloy. Other quantities of Table 1 and 2 were calculated from the selected ones using the Gibbs-Duhem relation.

Liquid Alloys. Selected $\Delta\bar{G}_{Cu}$ values of Table 4 were taken from Hackworth et al. (1969) (see Solid Alloys). Other quantities of Tables 3 and 4 were calculated from the selected ones with the aid of the Gibbs-Duhem relation [assuming the Raoult's law value for $\Delta\bar{G}_{Ti}$ in (β-Ti) at the phase boundary.] Values were referred to $Cu_{(\ell)}$ or $Cu_{(s)}$ assuming, for Cu, that ΔS_m = 2.3, invariant with T.

Part II. Tables

TABLE 1

Integral Quantities for (β-Ti) Alloys at 1473°K

$$(1-x)Cu_{(s)} + xTi_{(\beta)} = Cu_{1-x}Ti_{x(\beta\text{-}Ti)}$$

x_{Ti}	ΔG	ΔG^{xs}
0.905*	-773	146
0.95	-500	80
	(±25)	(±25)

TABLE 2

Partial Molar Quantities for (β-Ti) Alloys at 1473°K

	Cu Component $Cu_{(s)}$ = Cu(in alloy)$_{(s)}$				Ti Component $Ti_{(s)}$ = Ti(in alloy)$_{(s)}$			
x_{Ti}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Ti}	γ_{Ti}	$\Delta\bar{G}_{Ti}$	$\Delta\bar{G}^{xs}_{Ti}$
0.905*	0.152	1.604	-5506	1384	0.910	1.005	-276	16
0.95	0.084	1.689	-7237	1532	0.951	1.001	-146	4
	(±.006)	(±.12)	(±250)	(±250)	(±.003)	(±.003)	(±10)	(±10)
1.00	0.000	1.790	- ∞	1705	1.000	1.000	0	0

*Phase boundary

TABLE 3

Integral Quantities for Liquid Alloys at 1800°K

$$(1-x)Cu_{(\ell)} + xTi_{(\ell)} = Cu_{1-x}Ti_{x(\ell)}$$

x_{Ti}	ΔG	ΔG^{xs}
0.86	-1408	40
0.93*	- 938	-30
	(± 40)	(±40)

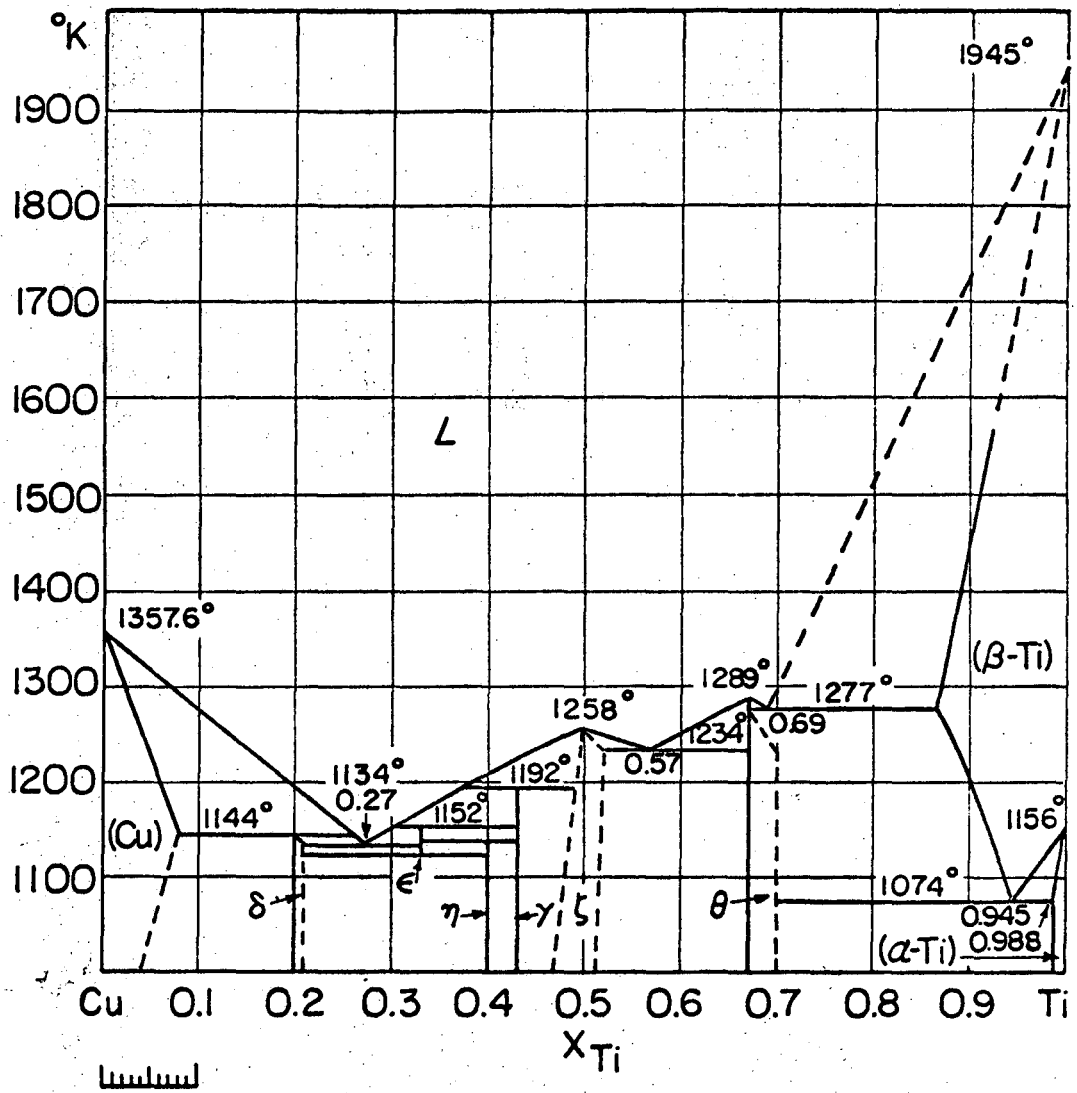
*Phase boundary

TABLE 4

Partial Molar Quantities for Liquid Alloys at 1800°K

	Cu Component $Cu_{(\ell)}$ = Cu(in alloy)$_{(\ell)}$				Ti Component $Ti_{(\ell)}$ = Ti(in alloy)$_{(\ell)}$			
x_{Ti}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Ti}	γ_{Ti}	$\Delta\bar{G}_{Ti}$	$\Delta\bar{G}^{xs}_{Ti}$
0.86	0.177	1.264	-6197	836	0.839	0.975	-629	- 90
0.93*	0.092	1.309	-8535	977	0.903	0.971	-366	-106
	(±.007)	(±.10)	(±250)	(±250)	(±.005)	(±.005)	(±20)	(±20)

*Phase boundary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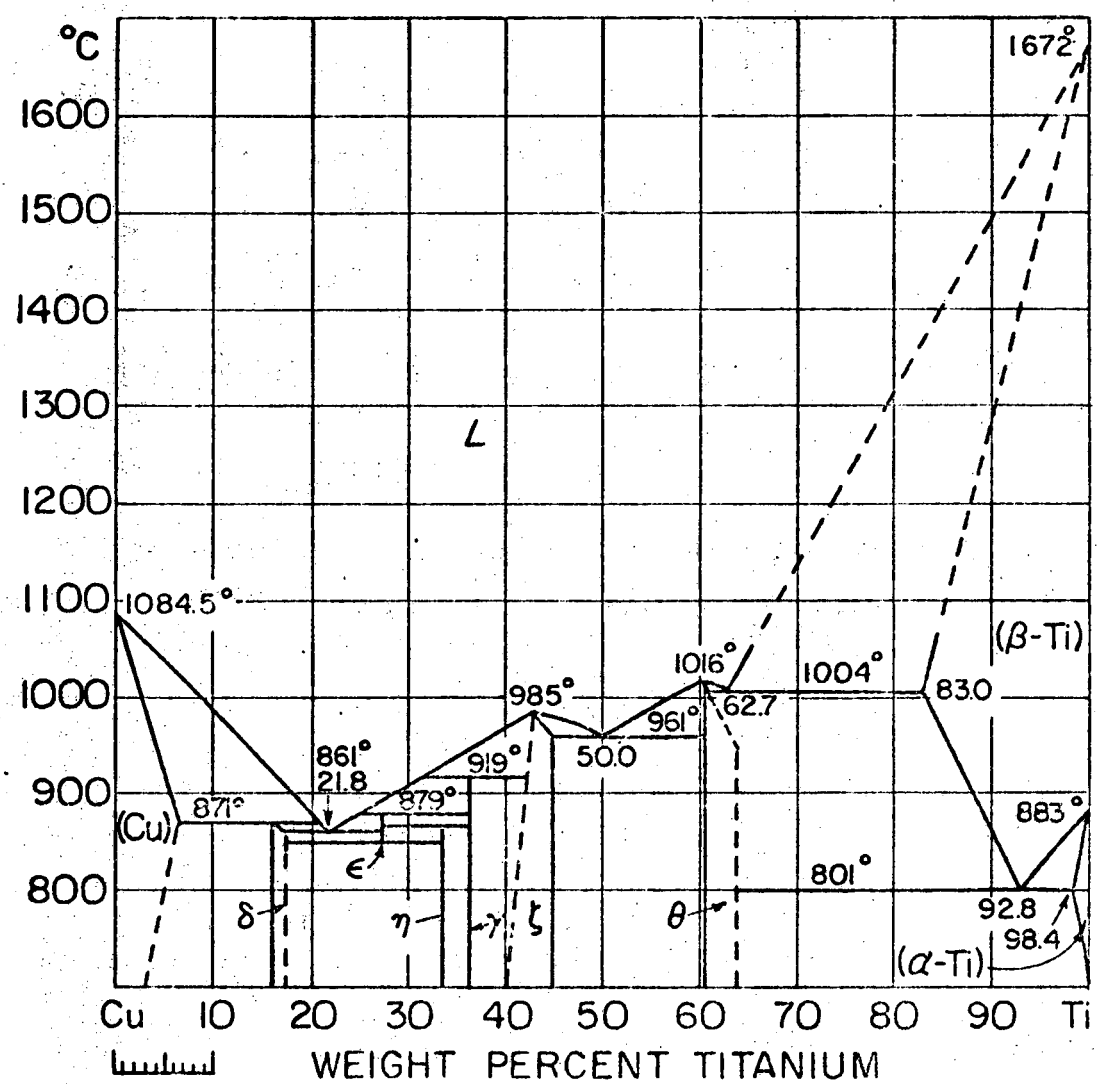
Cu
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Ti
X_Ti



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Copper-Thallium

Part I. Discussion

Phases and Structures. The phase diagram of Hansen (1958) and Elliott (1965) has been extended to include the miscibility gap determination of Predel and Sandig (1969), and the $T_{\alpha-\beta}$ = 507°K for Tl.

Liquid Alloys. Selected enthalpies of formation of Tables 1 and 2 were taken from the direct reaction calorimetry of Predel and Sandig (1969), T = ?, x_{Tl} = 0.1-0.9, who report their results only graphically and do not give the temperature of measurement. Their measurements scatter as much as ±400 cal/g-atom, though most of them are within ±150 cal/g-atom.

Selected $\Delta\bar{G}_{Tl}$ values of Table 2 were calculated from Tl vapor pressure measurements of Yazawa, Azakami, and Kawashima (1966), 1273°, 1473°K, x_{Tl} = 0.065-0.9; they present the results only as activity curves. Values were transferred to 1573°K with the aid of the selected $\Delta\bar{H}_{Tl}$. Other quantities of Table 1 and 2 were calculated from ΔH and $\Delta\bar{G}_{Tl}$. ΔH values calculated by Yazawa et al. (1966) from temperature coefficients are more endothermic by 200-800 cal/g-atom; those calculated by Kleppa (1952) from the phase diagram are more endothermic by 500-1500 cal/g-atom.

Part II. Tables

TABLE 1

Integral Quantities for Liquid Alloys at 1573°K

$$(1-x)Cu_{(\ell)} + xTl_{(\ell)} = Cu_{1-x}Tl_{x(\ell)}$$

x_{Tl}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-466	647	0.708	550	0.062
0.2	-614	1214	1.163	950	0.168
0.3	-702	1661	1.502	1207	0.288
0.4	-776	1954	1.735	1328	0.398
0.5	-845	2050	1.840	1322	0.463
	(±150)	(±200)	(±.2)	(±150)	(±.2)
0.6	-899	1930	1.798	1205	0.461
0.7	-915	1582	1.587	995	0.374
0.8	-854	1088	1.234	711	0.240
0.9	-644	543	0.755	372	0.109

PDD January, 1970

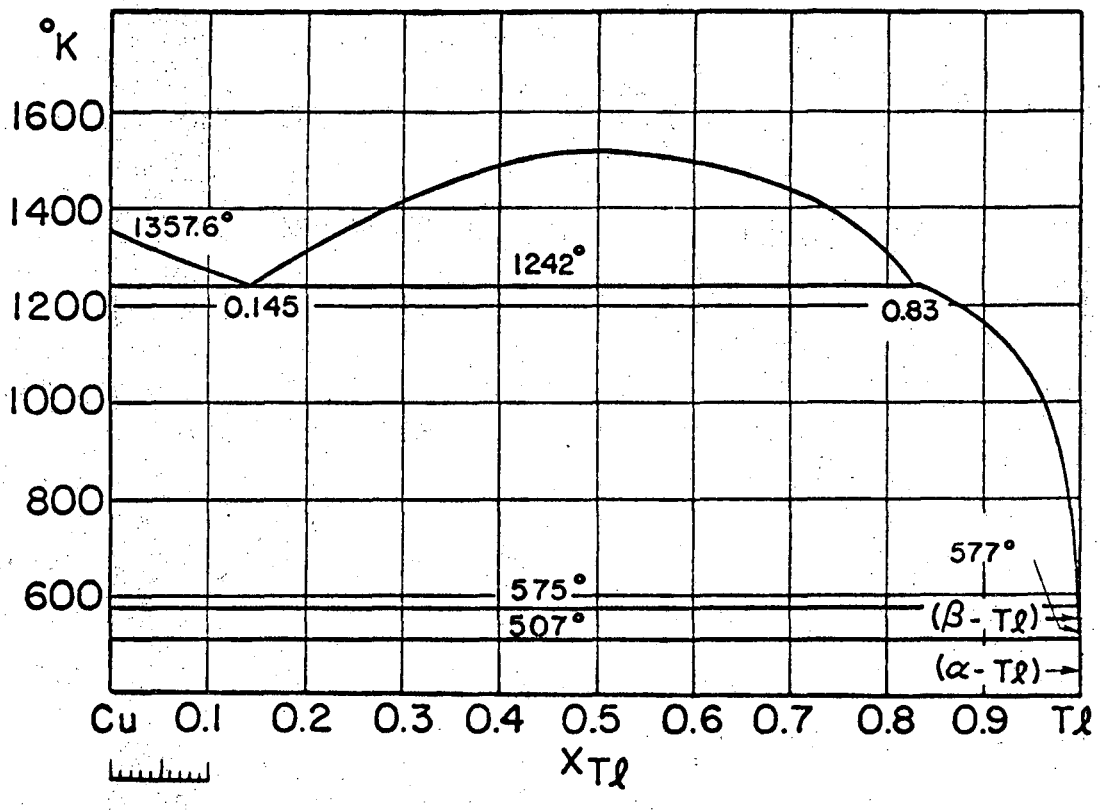
Partial Molar Quantities for Liquid Alloys at 1573°K

Cu Component $Cu_{(\ell)} = Cu(\text{in alloy})_{(\ell)}$

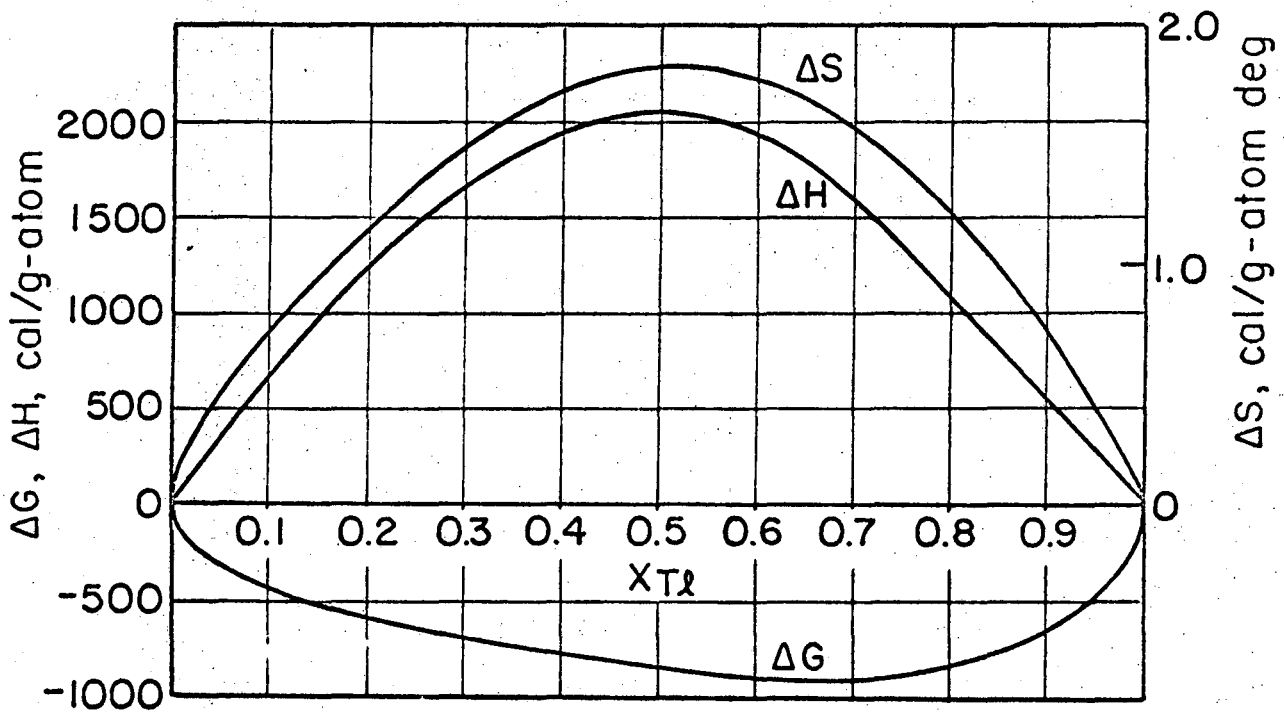
x_{Cu}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.922	1.024	- 255	74	34	0.184	-0.026
0.8	0.879	1.098	- 405	293	185	0.375	-0.068
0.7	0.860	1.229	- 471	643	535	0.640	-0.069
0.6	0.855	1.425	- 489	1107	1158	1.048	0.032
0.5	0.847	1.693	- 520	1646	2069	1.646	0.269
	(±.04)	(±.08)	(±150)	(±150)	(±400)	(±.3)	(±.3)
0.4	0.810	2.024	- 660	2204	3391	2.576	0.755
0.3	0.723	2.409	-1015	2748	4670	3.614	1.221
0.2	0.561	2.807	-1805	3226	5299	4.516	1.318
0.1	0.316	3.163	-3598	3600	5528	5.802	1.226
0.0	0.000	3.403	- ∞	3828	5230	∞	0.891

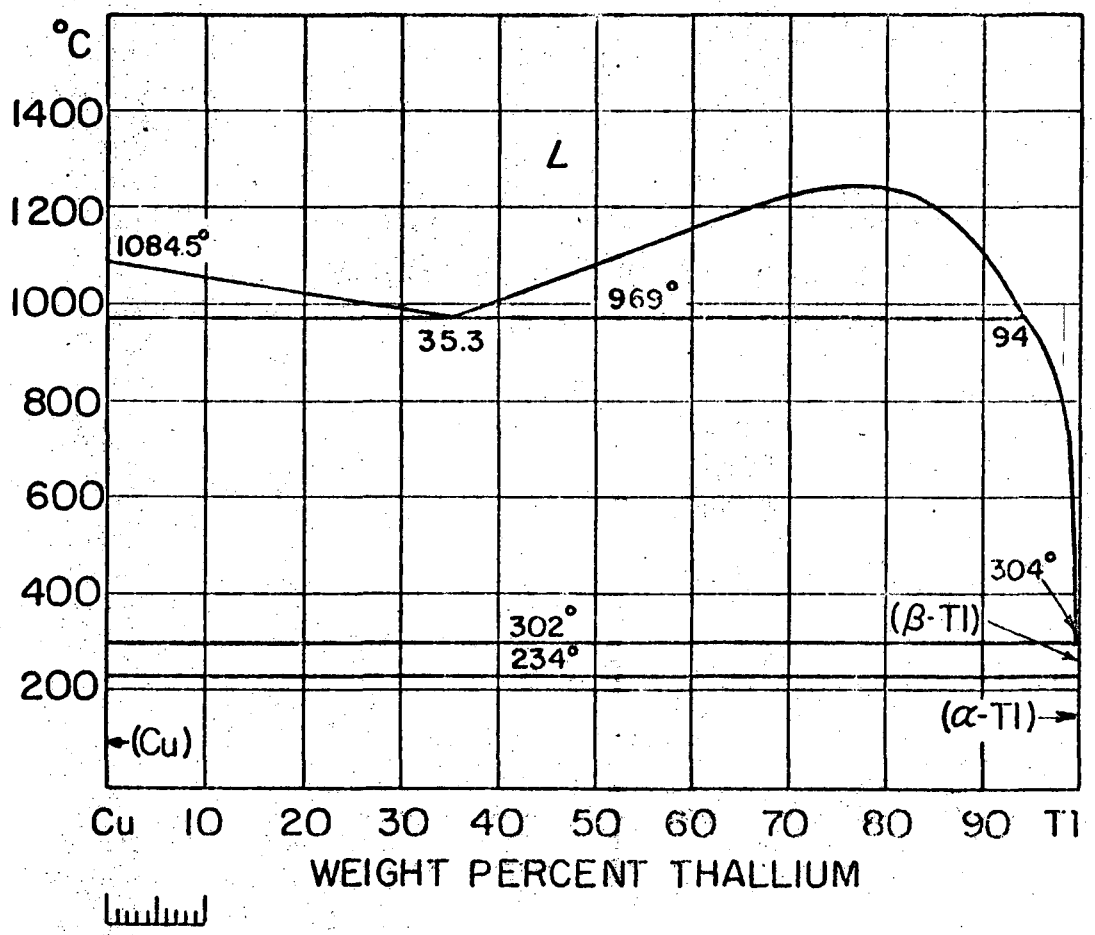
Tl Component $Tl_{(\ell)} = Tl(\text{in alloy})_{(\ell)}$

x_{Tl}	a_{Tl}	γ_{Tl}	$\Delta\bar{G}_{Tl}$	$\Delta\bar{G}^{xs}_{Tl}$	$\Delta\bar{H}_{Tl}$	$\Delta\bar{S}_{Tl}$	$\Delta\bar{S}^{xs}_{Tl}$
0.0	0.000	7.385	- ∞	6250	6730	∞	0.305
0.1	0.468	4.685	-2370	4828	6164	5.425	0.850
0.2	0.628	3.141	-1453	3578	5331	4.313	1.115
0.3	0.672	2.242	-1240	2523	4287	3.514	1.121
0.4	0.680	1.700	-1205	1660	3146	2.766	0.945
0.5	0.688	1.376	-1169	997	2031	2.035	0.657
	(±.03)	(±.07)	(±150)	(±150)	(±400)	(±.3)	(±.3)
0.6	0.713	1.188	-1058	538	955	1.280	0.265
0.7	0.757	1.081	- 872	243	259	0.719	0.010
0.8	0.821	1.026	- 616	82	35	0.414	-0.029
0.9	0.904	1.004	- 316	14	-11	0.194	-0.016
1.0	1.000	1.000	0	0	0	0.000	0.000



COPPER-THALLIUM SYSTEM, 1573°K





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ΔH (T = ?, 0.1-0.9).

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Copper-Tungsten

Part I. Discussion

Phases and Structures. Hansen (1958) reports that tungsten is insoluble in liquid Cu; and that the so called Cu-W alloys used technically are mixtures of the two pure metals phases.

Part II. Tables

No thermodynamic data were found for this system.

Part III. References

(For references not in list, see General References.)

Copper-Zinc

Part I. Discussion

Phases and Structures. The phase diagram was taken from Hansen (1958) with the following modifications: Shinoda and Amano (1960) report an extremely slow eutectoid decomposition of β' at 523°K and a rapid decrease of solubility of Zn in (Cu) below this temperature. The latter has been confirmed by X-ray diffraction studies of Erez (1962), 426°- 533°K, x_{Zn} = 0.308-0.360. Pearson (1967) lists the following crystal structures:

β has the bcc (A2) structure isotypic with W.

β' has the ordered bcc (B2) structure isotypic with CsCl.

γ has the ordered bcc ($D8_2$) prototype structure.

δ has the ordered bcc (B2) structure isotypic with CsCl.

ϵ has the hcp (A3) structure isotypic with Mg.

Melikhov and Presnyakov (1966) report that after annealing at 513°K for 600 hours, a two-phase region develops in the γ region, between x_{Zn} = 0.645 to 0.657. Both phases have the γ-brass structure, but the one with higher zinc content is somewhat deformed.

Solid Alloys. Low-Temperature Data. Selected values of Tables 1 and 2 agree, usually closer than 1%, with Cp measurements of Veal and Rayne (1963a), 1.4°- 4.2°K, x_{Zn} = 0.0-0.34; Veal and Rayne (1962), 1.4°- 4.2°K, x_{Zn} = 0.42-0.50; Veal and Rayne (1963b), 1.4°- 4.2°K, x_{Zn} = 0.59-0.66; Clune and Green (1966), 2°- 4°K, x_{Zn} = 0.00-0.027; and Huffstutler (1961), 15°- 303°K, x_{Zn} = 0.1-0.35. Cp measurements of Isaacs and Massalski (1965), 1.6°- 4.2°K, x_{Zn} = 0.0-0.38, are 0-2% lower; those of Rayne (1957), 1.4°- 4.2°K, x_{Zn} = 0.00-0.33, are 2-4% higher than selected values. Selected electronic γ values agree with the above except the values of Veal and Rayne (1963a) and Clune and Green (1966) are about 1% higher; those of Isaacs and Massalski (1965), and Rayne (1965) are, respectively, about 2% lower and 5% higher. Isaacs and Massalski (1965) found a considerable decrease of γ between x_{Zn} = 0.02-0.08; this was not found by others.

High-Temperature Data. Selected values of Table 3 were derived from heat content measurements of Ruer and Kremers (1929), 573°- 823°K, x_{Zn} = 0.19-0.54. Selected values of Table 4 agree with Cp measurements of Moser (1936), 380°- 892°K, x_{Zn} = 0.475 and Sykes and Wilkinson (1937), 513°- 773°K, x_{Zn} = 0.35-0.49; and heat contents of Table 3.

PDD, SJN November, 1968

Cp anomalies in the (Cu) phase were found by Kussmann and Wollenberger (1959), 373°- 673°K, x_{Zn} = 0.1-0.35; and by Masumoto, Saito, and Sugihara (1952), 373°- 715°K, x_{Zn} = 0.04-0.36. The anomalies occur at 450°- 550°K, they are quite small, and the two sets of work do not agree on their magnitude or temperature. Both attribute the anomalies to destruction of order of nearest neighbors, but no proof is presented.

(Cu) Phase. Selected values of ΔH in Table 5 are 20-100 cal/g-atom more exothermic than liquid tin solution calorimetric measurements of Orr and Argent (1965), 573°K, x_{Zn} = 0.01-0.33; and 50-100 cal/g-atom less exothermic than those of Kleppa and King (1962), 298°K, x_{Zn} = 0.05-0.34, except that the latter's value at x_{Zn} = 0.34 is more exothermic than selected values by 300 cal/g-atom. ΔH was determined by Körber and Oelsen (1937), 298°K, x_{Zn} = 0.11-0.88; and by von Samson-Himmelstjerna (1936), 298°K, x_{Zn} = 0.13-0.88; by pouring $Cu_{(\ell)}$ into a calorimeter at 298°K containing $Zn_{(s)}$. Assuming the final state was the equilibrium phase, they calculated ΔH values which were, respectively, 0-170 cal/g-atom more exothermic and about 500 cal/g-atom less exothermic than the selected values. Weibke (1937), 363°K, x_{Zn} = 0.016-0.63, by aqueous bromine solution calorimetry, obtained ΔH values more exothermic than the selected values by 0-200 cal/g-atom.

$\Delta\bar{G}_{Zn}$ values at 1000°K were selected which agree within ±150 cal/g-atom with those obtained from vapor pressure measurements of Hargreaves (1939), 800°- 1283°K, x_{Zn} = 0.05-0.50; and within ±500 cal/g-atom with those derived from vapor pressure measurements of Argent and Wakeman (1958), 1000°K, x_{Zn} = 0.02-0.34, except that the latter's values for x_{Zn}>0.22 trend to 500-1000 cal/g-atom less exothermic. Vapor pressure measurements of Herbenar, Siebert, and Duffendack (1950), 923°- 1243°K, x_{Zn} = 0.05-0.29 yield values of $\Delta\bar{G}_{Zn}$ which are 300-500 cal/g-atom more exothermic than the selected values. $\Delta\bar{G}_{Zn}$ values at 1000°K were transferred to 773°K using the selected $\Delta\bar{S}_{Zn}$ values which in turn were obtained from the selected $\Delta\bar{G}_{Zn}$ and $\Delta\bar{H}_{Zn}$ assuming ΔCp = 0. The other quantities of Tables 5 and 6 were calculated by the Gibbs-Duhem integration. The resulting $\Delta\bar{G}_{Zn}$ values agree within ±300 cal/g-atom with the vapor pressure measurements of Pemsler and Rapperport (1968), 523°- 823°K, x_{Zn} = 0.05-0.35.

β, γ, and ε Phases. Selected values were calculated from emf measurements of Ölander (1933), 685°- 899°K, x_{Zn} = 0.44-0.84. The selected $\Delta\bar{G}_{Zn}$ values trend smoothly with composition in one-phase regions and are remarkably constant in two-phase regions. However, the compositions of the phase boundaries differ by 0.00-0.02 from those selected by Hansen (1958). Tables 5 and 6 show the phase boundaries determined by Ölander. $\Delta\bar{S}_{Zn}$ and $\Delta\bar{H}_{Zn}$ values were calculated from Ölander's tempera-

ture coefficients. The other partial and integral Gibbs energies, enthalpies, and entropies were determined by Gibbs-Duhem integration. Surprisingly, there seems to be no reliable calorimetric work for these phases. These studies already have been referred in the earlier section (see (Cu)-phase). Measurements of Körber and Oelsen (1937) are about 200 cal/g-atom more exothermic for β and γ and about 300 cal/g-atom less exothermic for ϵ; those of von Samson-Himmelstjerna (1936) are about 600 cal/g-atom more exothermic for γ; and those of Weibke (1937) are about 200 cal/g-atom more exothermic for β and γ.

β'-Phase. Values of Table 7 for the β'-phase were calculated from Tables 5 and 4. Emf values of Ölander at 685°K are consistent with values from these tables.

δ-Phase. Selected values of Table 8 were calculated from Ölander's measurements in the $\gamma + \delta$ and $\delta + \epsilon$ regions. In the absence of an integration constant, no Gibbs-Duhem integration was attempted.

Liquid Alloys. Selected $\Delta\bar{G}_{Zn}$ values of Table 10 agree well (±50 cal/g-atom) with extrapolated emf measurements of Kleppa and Thalmayer (1959), 900°K, x_{Zn} = 0.80-0.92; and with vapor pressure measurements (±100 cal/g-atom) of Downie (1964), 1200°K, x_{Zn} = 0.25-0.68; except that the latter's values at x_{Zn} = 0.61 and 0.63 are less exothermic by about 220 cal/g-atom. Vapor pressure measurements of Schneider and Schmid (1942), 923°- 1123°K, x_{Zn} = 0.43-0.80, lead to values more exothermic by 100-400 cal/g-atom at most concentrations; as do those of Everett, Jacobs, and Kitchener (1957), 1069°- 1303°K, x_{Zn} = 0.16-0.79, but they are more exothermic by 700-1400 cal/g-atom for $x_{Zn} < 0.70$. Boiling point measurements of Leitgebel (1931), 1188°- 1773°K, x_{Zn} = 0.06-0.87, led to a boiling point of 1200°K at x_{Zn} = 0.82; this gives a value of $\Delta\bar{G}_{Zn}$ which is 120 cal/g-atom less exothermic than the selected value at that composition. Vapor pressure measurements of Yazawa and Azakami (1968), 1073°- 1473°K, x_{Zn} = 0.15-0.90 lead to values of $\Delta\bar{G}_{Zn}$ which are more exothermic than selected values by 400-700 cal/g-atom. The constant for the Gibbs-Duhem integration was taken from values of $\Delta\bar{G}_{Cu}$ in the (Cu) phase and the liquidus and solidus at 1200°K.

Part II. Tables

TABLE 1

Low-Temperature Data for (Cu)-Alloys

T, °K	x_{Zn}				
	0.0*	0.1	0.2	0.3	0.35
	Cp				
2	0.000423	0.000436	0.000446	0.000456	0.000462
3	0.000805	0.000834	0.000867	0.000909	0.000933
4	0.00139	0.00145	0.00152	0.00163	0.00169
5	(0.00225)	(0.00236)	(0.00250)	(0.00272)	(0.00284)
10	(0.0144)	(0.0138)	(0.0149)	(0.0167)	(0.0177)
15	(0.0453)	0.0487	0.0500	0.0532	0.0560
25	0.230	0.255	0.291	0.324	0.338
50	1.476	1.570	1.672	1.765	1.797
75	2.841	2.978	3.051	3.177	3.220
100	3.842	3.950	3.989	4.084	4.141
150	4.894	4.943	4.998	5.051	5.081
200	5.405	5.416	5.456	5.483	5.495
250	5.673	5.669	5.689	5.696	5.697
298.15	5.838	5.788	5.792	5.800	5.802
$\gamma \times 10^4$	1.66(±.05)	1.69(±.05)	1.70(±.05)	1.68(±.05)	1.67(±.05)
$H_{st}-H_0$	1196	1208	1221	1235	1241
$S_{st}-S_0$	7.925 (±.06)	8.094 (±.06)	8.246 (±.06)	8.424 (±.06)	8.498 (±.06)

*Values for pure Cu are slightly(<1%) different above 5°K from the selected values. They are tabulated for the purpose of comparison.

TABLE 2

Low-Temperature Data for β and γ Phases

x_{Zn}	Phase	Cp			$\gamma \times 10^4$
		2°K	3°K	4°K	
0.43	β	0.000548	0.00124	0.00243	1.63(±.05)
0.47	β	0.000514	0.00113	0.00218	1.60(±.05)
0.58	γ	0.000316	0.000651	0.00121	1.08(±.05)
0.60		0.000264	0.000549	0.00103	0.92(±.05)
0.65	γ	0.000176	0.000402	0.000812	0.48(±.05)

TABLE 3

Heat Content Data for Solid Alloys

x_{Zn}	Phase	$H_{773}-H_{st}$	$\Delta H_{773}-\Delta H_{st}$
0.2	(Cu)	2975	-26
0.25		2987	-26
0.35	(Cu)	3045 (±50)	10 (±50)
0.46	β	3593	533
0.47		3628	566
0.48	β	3663	598

TABLE 4

High-Temperature Data for the β and β′ Phases, $x_{Zn} = 0.475$

T, °K	Cp	$H_{st}-H_T$	S_T-S_{st}	ΔCp	$\Delta H_T-\Delta H_{st}$	$\Delta S_T-\Delta S_{st}$
β′-Phase						
298.15	5.875	0	0.000	-0.074	0	0.000
400	6.097	608	1.752	-0.071	-9	-0.018
500	6.660	1242	3.164	0.299	0	-0.007
600	7.892	1962	4.474	1.344	73	0.125
700	10.778	2870	5.907	3.829	315	0.532
738	(16.600)	(3344)	(6.565)	(9.630)	(524)	(0.836)
β-Phase						
773	7.780	3645	6.964	0.784	582	0.908
800	7.508	3852	7.227	0.496	599	0.920
900	7.450 (±.1)	4595 (±50)	8.102 (±.1)	0.370 (±.1)	636 (±50)	0.966 (±.1)

TABLE 5

Integral Quantities for Solid Alloys at 773°K

$$(1-x)Cu_{(s)} + xZn_{(s)} = Cu_{1-x}Zn_{x(s)}$$

x_{Zn}	Phase	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	(Cu)	-1111	-627	0.626	-612	-0.020
0.2		-1896	-1309	0.759	-1127	-0.235
0.3		-2419	-1754	0.861	-1481	-0.353
0.381	(Cu)	-2677	-1969	0.916	-1657	-0.404
		(±300)	(±150)	(±.4)	(±150)	(±.4)
0.44*	β	-2815	-2112	0.909	-1761	-0.454
0.45		-2837	-2141	0.900	-1780	-0.467
0.47		-2873	-2199	0.872	-1811	-0.502
0.488*	β	-2896	-2251	0.834	-1832	-0.542
		(±200)	(±300)	(±.5)	(±200)	(±.5)
0.582*	γ	-2995	-2625	0.479	-1951	-0.872
0.6		-3026	-2726	0.388	-1992	-0.949
0.65		-2917	-2718	0.257	-1922	-1.030
0.672*	γ	-2805	-2588	0.281	-1832	-0.978
0.761*	ε	-2267	-2050	0.281	-1422	-0.813
0.80		-2007	-1836	0.221	-1238	-0.773
0.82		-1854	-1700	0.199	-1130	-0.738
0.847	ε	-1627	-1484	0.185	-969	-0.666

*Phase boundaries according to Ölander's emf data. They are slightly different from the selected phase diagram.

TABLE 6

Partial Molar Quantities for Solid Alloys at 773°K

Cu Component $Cu_{(s)} = Cu(\text{in alloy})_{(s)}$

x_{Cu}	Phase	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	$\Delta\bar{H}_{Cu}$	$\Delta\bar{S}_{Cu}$	$\Delta\bar{S}^{xs}_{Cu}$
1.0	(Cu)	1.000	1.000	0	0	0	0.000	0.000
0.9		0.877	0.974	-202	-40	64	0.344	0.135
0.8		0.678	0.847	-598	-255	-164	0.561	0.118
0.7		0.458	0.655	-1198	-650	-727	0.609	-0.099
0.619	(Cu)	0.313	0.505	-1786	-1050	-1212	0.743	-0.210
		(±.02)	(±.03)	(±300)	(±300)	(±400)	(±.65)	(±.65)
0.56*	β	0.313	0.559	-1786	-895	-840	1.223	0.071
0.55		0.290	0.527	-1901	-983	-840	1.373	0.184
0.53		0.248	0.467	-2146	-1171	-840	1.690	0.428
0.512*	β	0.212	0.413	-2385	-1357	-840	1.999	0.668
		(±.03)	(±.05)	(±200)	(±200)	(±500)	(±.7)	(±.7)
0.418*	γ	0.212	0.507	-2385	-1046	355	3.546	1.813
0.4		0.125	0.312	-3198	-1790	-725	3.199	1.378
0.35		0.026	0.074	-5620	-4007	-5759	-0.180	-2.266
0.328*	γ	0.011	0.035	-6865	-5152	-7418	-0.715	-2.931
0.239*	ε	0.011	0.048	-6865	-4666	-5697	1.511	-1.334
0.20		0.006	0.030	-7856	-5384	-6888	1.252	-1.946
0.18		0.004	0.022	-8463	-5829	-7697	0.991	-2.417
0.153	ε	0.003	0.018	-9065	-6181	-9033	0.041	-3.689

*Phase boundaries according to Ölander's emf data. They are slightly different from the selected phase diagram.

TABLE 6 (cont'd.)

Partial Molar Quantities for Solid Alloys at 773°K

Zn Component $Zn_{(s)} = Zn(\text{in alloy})_{(s)}$

x_{Zn}	Phase	a_{Zn}	γ_{Zn}	$\Delta\bar{G}_{Zn}$	$\Delta\bar{G}^{xs}_{Zn}$	$\Delta\bar{H}_{Zn}$	$\Delta\bar{S}_{Zn}$	$\Delta\bar{S}^{xs}_{Zn}$
0.0	(Cu)	0.000	0.014	-∞	-6505	-5500	∞	1.300
0.1		0.002	0.024	-9296	-5759	-6853	3.160	-1.415
0.2		0.010	0.050	-7087	-4615	-5888	1.551	-1.647
0.3		0.032	0.108	-5268	-3419	-4149	1.448	-0.944
0.381	(Cu)	0.068	0.179	-4125	-2642	-3199	1.198	-0.720
		(±.01)	(±.03)	(±300)	(±300)	(±400)	(±.65)	(±.65)
0.44*	β	0.068	0.155	-4125	-2864	-3731	0.510	-1.122
0.45		0.075	0.166	-3982	-2755	-3731	0.325	-1.263
0.47		0.090	0.192	-3693	-2533	-3731	-0.049	-1.550
0.488*	β	0.107	0.219	-3433	-2331	-3731	-0.386	-1.811
		(±.01)	(±.03)	(±200)	(±200)	(±500)	(±.7)	(±.7)
0.582*	γ	0.107	0.184	-3433	-2601	-4765	-1.723	-2.800
0.6		0.150	0.250	-2911	-2126	-4059	-1.485	-2.500
0.65		0.386	0.594	-1461	-799	-1081	0.492	-0.365
0.672*	γ	0.585	0.871	-823	-212	-231	0.766	-0.025
0.761*	ε	0.585	0.769	-823	-403	-905	-0.106	-0.650
0.80		0.702	0.877	-545	-202	-573	-0.036	-0.48
0.82		0.769	0.938	-403	-98	-384	0.025	-0.37
0.847	ε	0.832	0.982	-283	-28	-121	0.210	-0.120

*Phase boundaries according to Ölander's emf data. They are slightly different from the selected phase diagram.

TABLE 7

Thermodynamic Properties of β'-Phase at 600°K

$$0.525Cu_{(s)} + 0.475Zn_{(s)} = Cu_{0.525}Zn_{0.475(s)}$$

ΔG	ΔH	ΔS
-2755 (±200)	-2657 (±300)	0.164 (±.6)

TABLE 8

Partial Quantities for δ-Phase at 860°K

Zn Component

$$Zn_{(s)} = Zn(\text{in alloy})_{(s)}$$

x_{Zn}	a_{Zn}	γ_{Zn}	$\Delta\bar{G}_{Zn}$	$\Delta\bar{G}^{xs}_{Zn}$
0.730*	0.594	0.814	-890	-352
0.753*	0.636 (±.2)	0.775 (±.3)	-775 (±200)	-290 (±200)

TABLE 9

Integral Quantities for Liquid Alloys at 1200°K

$$(1-x)Cu_{(\ell)} + xZn_{(\ell)} = Cu_{1-x}Zn_{x(\ell)}$$

x_{Zn}	ΔG	ΔG^{xs}	x_{Zn}	ΔG	ΔG^{xs}
0.334*	-2942	-1423	0.6	-2860	-1255
0.4	-3071	-1466	0.7	-2462	-1005
0.5	-3071 (±400)	-1418 (±400)	0.8	-1889	-695
			0.9	-1126	-351

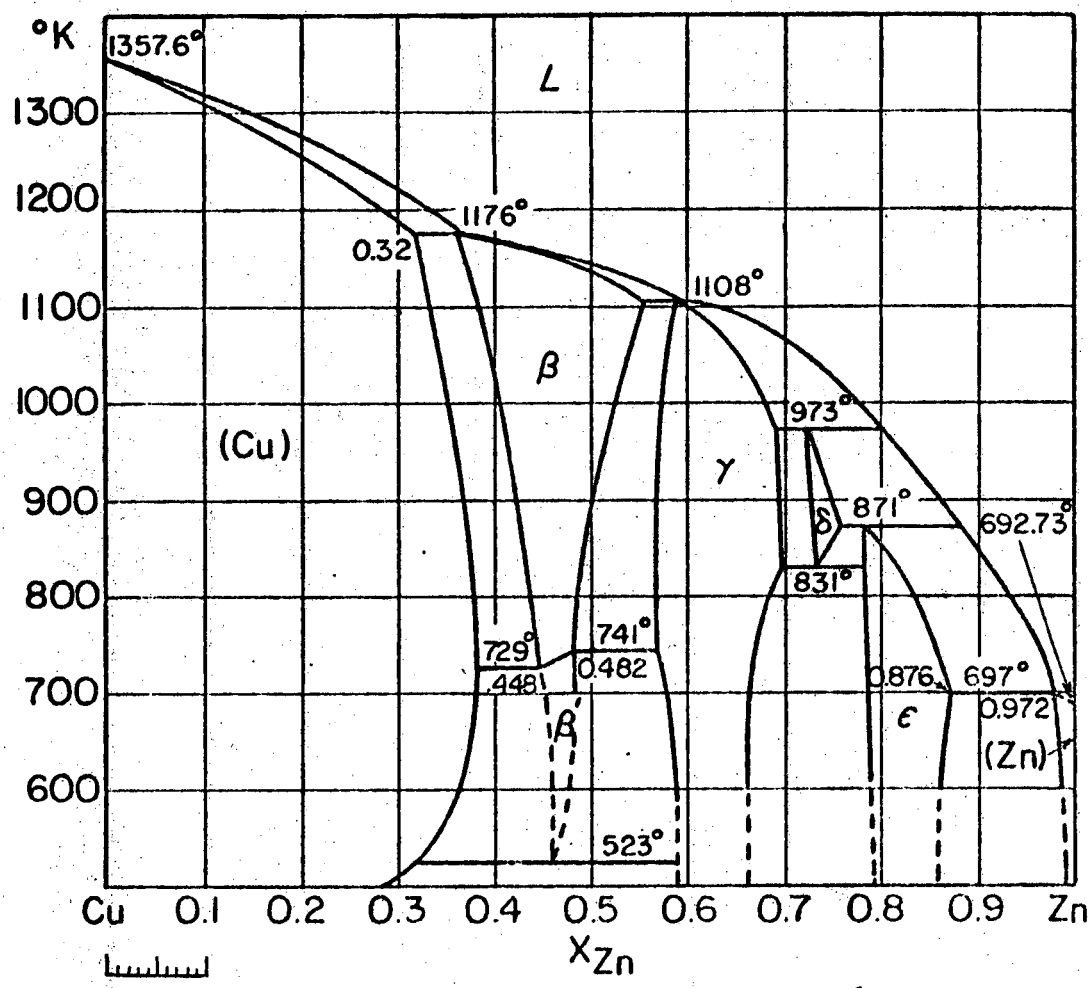
*Phase boundary

TABLE 10

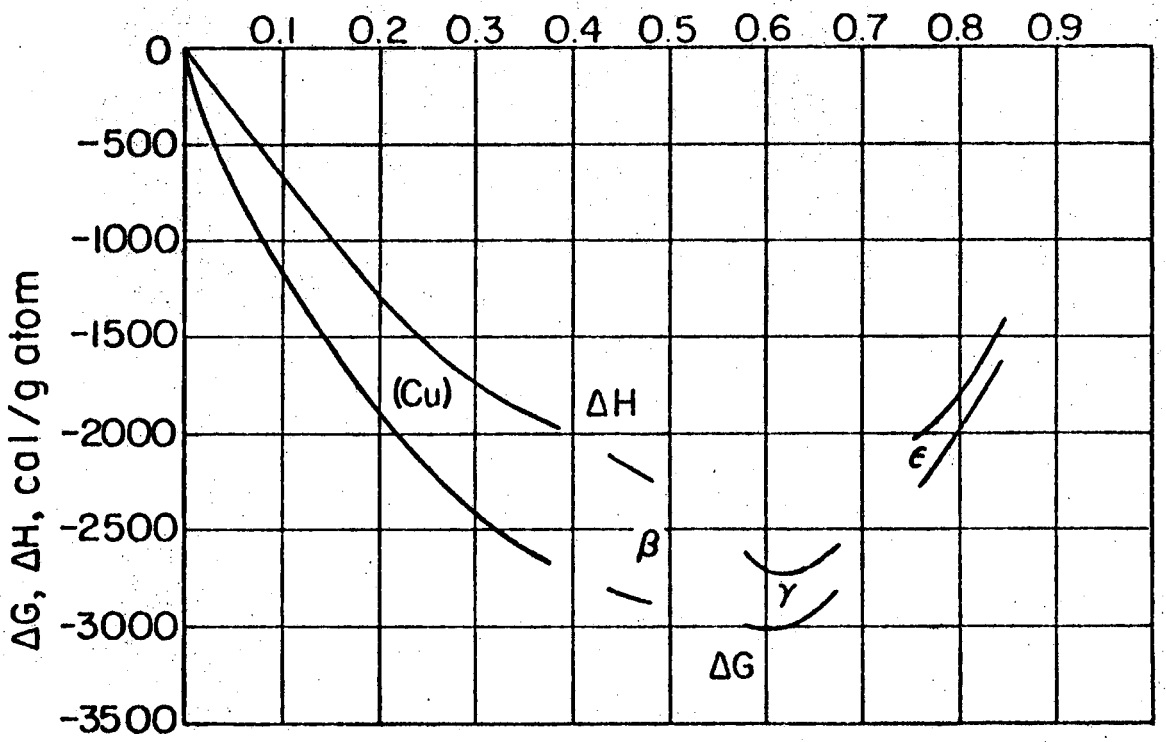
Partial Molar Quantities for Liquid Alloys at 1200°K

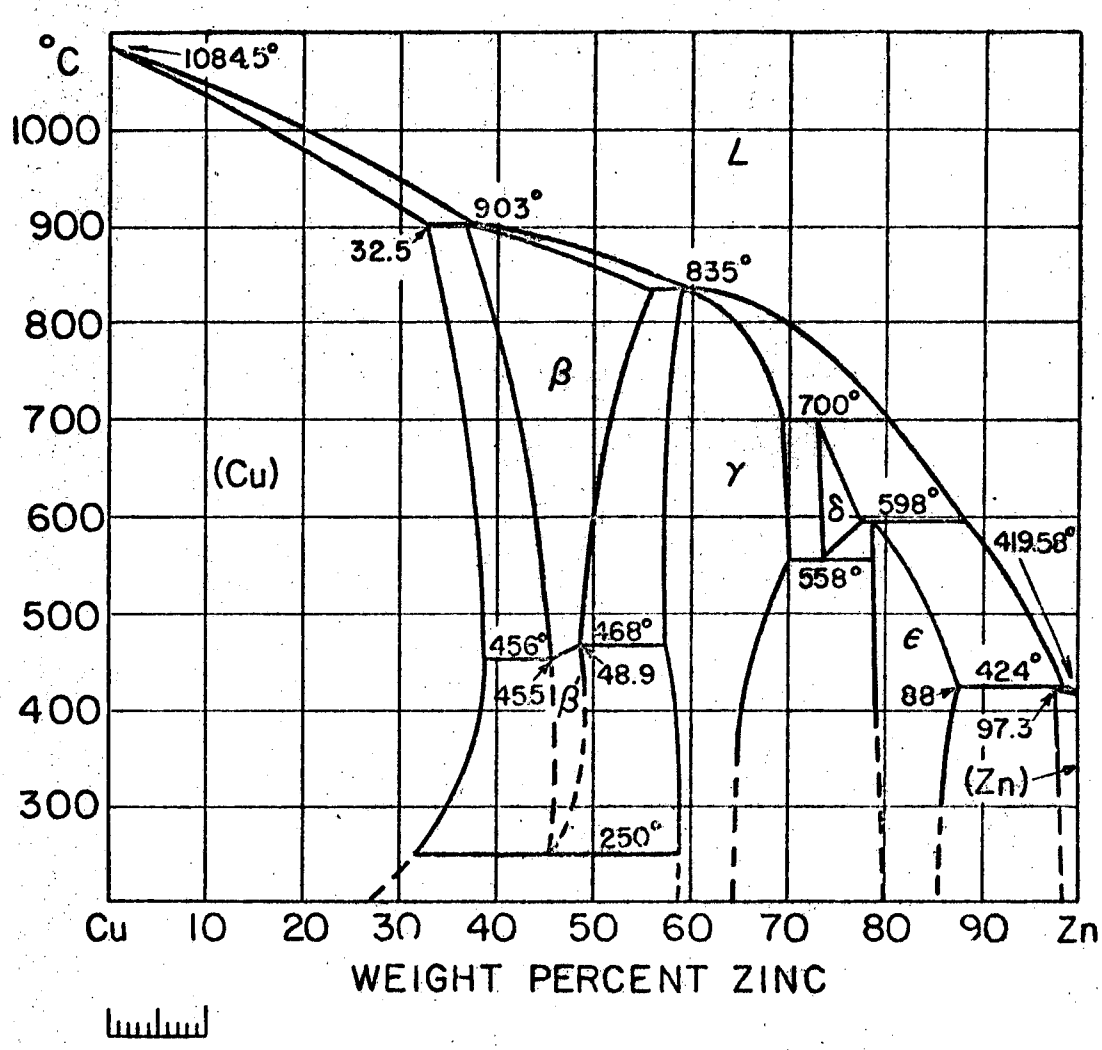
	Cu Component $Cu_{(\ell)}$ = Cu(in alloy)$_{(\ell)}$				Zn Component $Zn_{(\ell)}$ = Zn(in alloy)$_{(\ell)}$			
x_{Zn}	a_{Cu}	γ_{Cu}	$\Delta\bar{G}_{Cu}$	$\Delta\bar{G}^{xs}_{Cu}$	a_{Zn}	γ_{Zn}	$\Delta\bar{G}_{Zn}$	$\Delta\bar{G}^{xs}_{Zn}$
0.334*	0.432	0.648	-2003	-1034	0.132	0.398	-4814	-2199
0.4	0.334	0.557	-2614	-1396	0.207	0.517	-3757	-1572
0.5	0.219	0.438	-3621	-1968	0.347	0.695	-2521	-868
	(±.05)	(±.1)	(±400)	(±400)	(±.05)	(±.1)	(±400)	(±400)
0.6	0.139	0.348	-4705	-2520	0.505	0.841	-1630	-412
0.7	0.085	0.284	-5869	-2998	0.657	0.939	-1002	-151
0.8	0.049	0.245	-7187	-3349	0.789	0.986	-564	-32
0.9	0.023	0.229	-9010	-3519	0.900	1.000	-250	1
1.0	0.000	0.235	-∞	-3454	1.000	1.000	0	0

*Phase boundary



COPPER - ZINC SYSTEM, 773 °K




°C
1084.5°
1000
900
800
700
600
500
400
300
L
903°
32.5
835°
β
700°
(Cu)
γ
δ
598°
419.58°
558°
456°
468°
ε
455
β'
48.9
424°
88
97.3
(Zn)
250°
Cu
10
20
30
40
50
60
70
80
90
Zn
WEIGHT PERCENT ZINC

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Copper-Zirconium

Part I. Discussion

Phases and Structures. The phase diagram from Hansen (1958) has been modified to include recent studies from Elliott (1965), Shunk (1969) and Meny and Champigny (1966). Many features are still unresolved. There have been conflicting reports about various intermediate phases. Pearson (1958, 1967) lists the following phases:

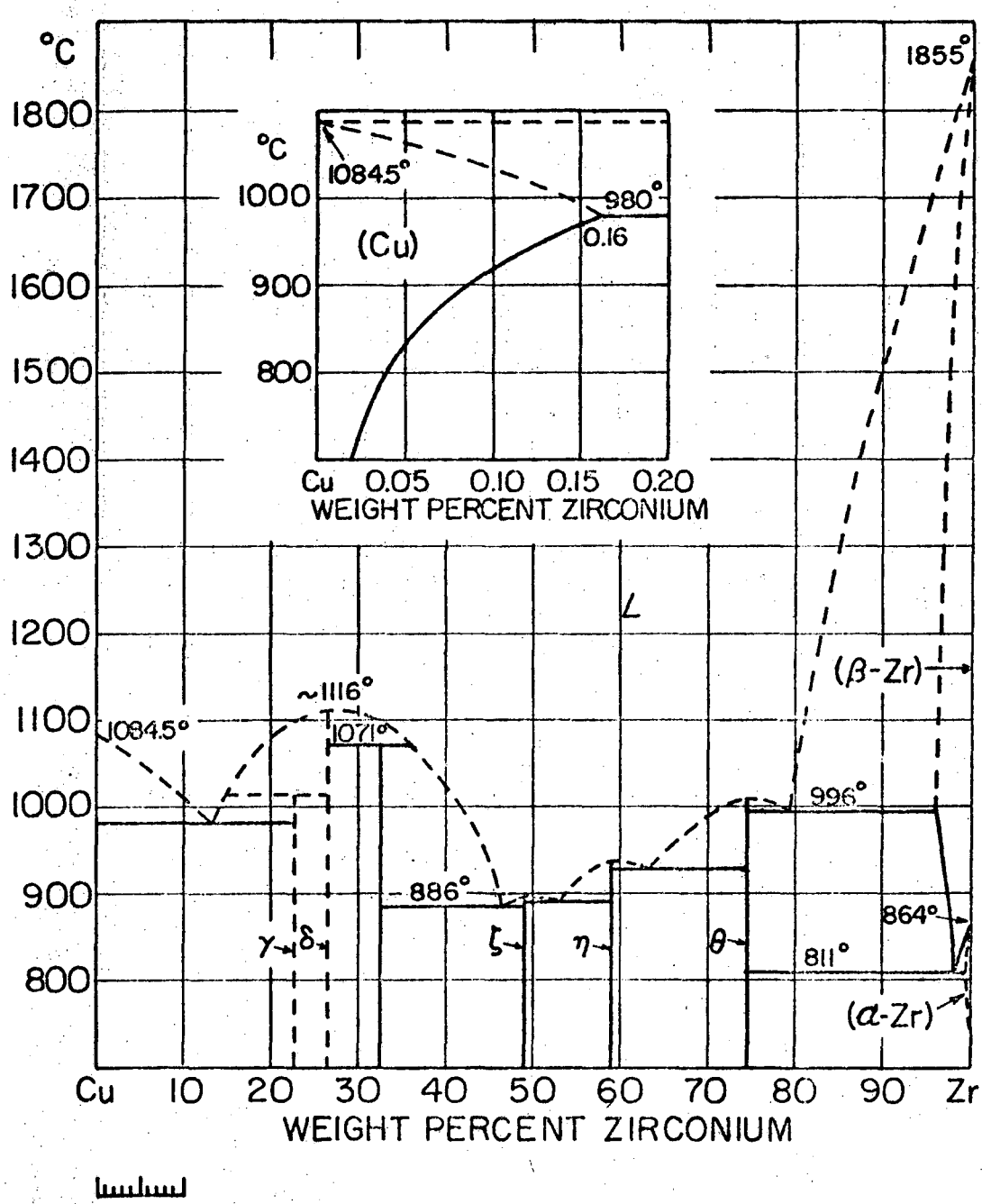
θ, "$CuZr_2$" with an ordered bc tetragonal ($C11_b$) structure isotypic with $MoSi_2$. This phase has been well established.

"$CuZr_3$" with an ordered tetragonal structure isotypic with "ϵ-$CuTi_3$". The existence of this phase is disputed and it is not included in the phase diagram.

Structures of γ, "Cu_5Zr"; δ, "Cu_4Zr"; ζ, "Cu_3Zr_2"; and η, "CuZr" have not been found. In addition, Hansen (1958) reports a questionable "Cu_5Zr_2" phase, not included in the phase diagram.

Part II. Tables

No thermodynamic data were found for this system.



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