to instruments like those of Thorpe and Rodger and Bingham. Our data do not support Dorsey's view that *m* decreases when Reynolds' number exceeds 700.

Further investigations are being conducted in this Laboratory to determine the value of *m* for capillaries of other shapes.

Summary

1. Within the range of experimental conditions studied, the Hagenbach factor has been found to be 1.124 ± 0.006.

2. The viscosity of methanol at 25° has been determined and a value obtained which agrees with the value of Thorpe and Rodger within 0.3%.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY AND THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

CHEMICAL AFFINITY IN METALLIC ALLOYS, ESPECIALLY SOLID SOLUTIONS: A STUDY IN COMPRESSIBILITY

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The study of the properties of solid solutions is one of the chief aims of metallurgical science. Its practical importance is evidenced by the fact that of the alloys useful because of their superior mechanical properties most are wholly or partly solid solutions. Numerous researches[3] have shown that, with one or two exceptions,[4] terminal solid solutions are simple in structure, showing the space lattice of the solvent metal only, the atoms of the solute having simply replaced atoms of the solvent; intermediate solid solutions are more complicated in structure. The behavior, physical and chemical, of the lattice so modified is, therefore, dependent upon the interaction of the different atoms, and this will be intimately related to their different chemical natures, and also to their specific crystallographic tendencies. From a chemical standpoint the chief effect of interest is that of a partial fixing of the valence electrons, an effect to be expected from the normal chemical affinities between the unlike atoms, and indicated by the enormous decrease in electrical conductivity resulting from solid solution formation. From a mechanical point of view the interaction between unlike atoms is presumably intimately related to the large increase in hardness observed.

Such a partial fixing of the valence electrons is of course not stoichio-

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[1] National Research Fellow.

[2] Contributor to the experimental work on compressibility only.

[3] See G. L. Clarke, "Applied X-Rays," McGraw-Hill Book Co., New York, 1926, page 204.

[4] Notably iron-carbon, manganese-carbon and perhaps copper-tin (see page 66).

metric, and the chemical affinities operative in solid solutions are more nearly like those governing adsorption than like those in saline compounds. The factors determining the composition of intermetallic compounds (which exhibit apparently ambiguous valence relations) have not been explained, though for a complete valence theory such an explanation is obviously necessary. These compounds are highly crystalline, and their heats of formation indicate that the chemical forces at play are commensurable with those in saline compounds.[5] In fact, evidence has been presented[6] in proof of the salt-like nature of certain of these compounds.

Whatever the nature of the chemical forces governing the composition of the intermetallic compounds, it seems reasonable that similar forces should be operative in metallic solid solutions, and it appears likely that an evaluation of the magnitude of these forces should be of value in explaining the behavior of solid solutions, especially the electrical and mechanical, and that ultimately a study of these forces should be of value to the study of chemical affinity in general and the solid state in particular.

It may be said (somewhat truistically) that two metals form solid solutions when the potential energy of their atoms in the state of solid solution is less than that in the elementary states. The problem of measuring the tendency of two metals to form solid solutions (the answer to which would explain quantitatively the phenomenon of limited miscibility) is therefore the problem of evaluating this potential energy decrease. Such an analysis does not now seem possible, though the recent work on lattice energetics may finally lead to this. To be orthodox chemically, such a measurement should be in terms of free energy decrease. For a solid alloy the only practicable method is that involving a measurement of the heat of formation of the alloy and the specific heats of the component metals and of the alloy over a wide temperature range.[7]

[5] Biltz, *Z. anorg. Chem.*, **134**, 37 (1924); **140**, 261 (1924).

[6] Owen and Preston, *Proc. Phys. Soc. London*, **36**, 14 (1923).

[7] Considerable time was spent in attempting to evaluate this quantity calorimetrically. The simplest and most general method for determining the heat of formation is to dissolve the alloyed and the unalloyed metals in similar quantities of a solvent in a system of known heat capacity, and by the difference in the temperature rises observed in the two cases to calculate the heat of formation by application of the law of constant heat summation. The method has been applied especially to intermetallic compounds[5] and to the copper-zinc system, exclusive of the α-solid solutions [Baker, *Z. physik. Chem.*, **38**, 630 (1901)]. The adiabatic calorimetric method developed by Richards [THIS JOURNAL, **32**, 431 (1910)] was used, with hydrochloric acid as a solvent.

The most advisable course seemed to be to investigate those terminal solid solutions in which cubic metals play the role of solvent. Accordingly a series of the α-aluminum-magnesium alloys was prepared. The calorimetric system, including 941.4 g. of $HCl\cdot 20H_2O$, had a heat capacity of 810.0 cal./deg. The reaction between the elementary magnesium and the acid (in the blank determination) was slowed by partly lacquering the magnesium particles (which were roughly $^1/_8$" in diameter) and by imprisoning them

The e.m.f. method is apparently inapplicable because of the practical difficulty in setting up a cell representing the reaction between the component metals to give an alloy of the composition desired, though the Nernst-Reinders theory[8] of the equilibria between solid solutions and aqueous solutions of salts of the component metals appears to make such a determination possible, when the solution pressures of the component metals are not too greatly different.[9] However, because of the difficulties in obtaining a reversible electrode truly representative of the composition of solid solution desired, it is unlikely that the e.m.f. method will be of value for this purpose.

in an inverted platinum cone wired to the bottom of the platinum wire basket. A drop of chlorplatinic acid served to catalyze the dissolution of the aluminum.

Before making any determinations on alloys, the heat of solution of magnesium in $HCl \cdot 20.05H_2O$ was determined. Three determinations using 0.7481 g. of magnesium in each gave temperature rises of 4.193, 4.189 and 4.192°, an average of 4.191° which, multiplied by 810.0 cal./deg., gives 2594.7 cal. at a temperature of 20°.

The aluminum-magnesium alloys were prepared in an apparatus similar to one previously developed by one of the authors [Mehl, *Trans. Amer. Electrochem. Soc.*, **46**, October, 1924) except that argon instead of hydrogen was used for an atmosphere. After preparation the alloys were annealed for 24 hours just below their melting points. The synthetic compositions of the alloys prepared were 5.5, 8.0 and 9.0 percentage of magnesium by weight. The temperature rises observed for 0.6948 g. of each composition were, respectively, 3.964, 3.957 and 3.961°. The blank determinations, using equivalent quantities of the unalloyed metals, gave, for the same compositions, 3.961, 3.963° and 3.960°, apparently identical with the first.

The sensitivity of the calorimetric method as applied to these alloys is probably around 0.006°, indicating that the heat of formation of the α-solid solution in this system is probably less than 8 cal. per gram.

A similar series of measurements was carried out on the α-solid solutions in the aluminum-zinc system, though the method is less satisfactory in its application to these alloys, for it takes approximately 7 g. of zinc to give the desired four degrees rise, as contrasted to 0.7 g. of aluminum. Any segregation in the alloy, therefore, leads to greatly different heats of solution when constant weights of the alloys are dissolved. Prolonged annealing of the castings prevented such segregation in considerable degree, but it soon became apparent that another disturbing factor was present. An alloy of 14.49% of zinc by weight, quenched after twenty-four hours' annealing at 575°, gave a temperature rise of 4.057° (0.8050 g.); after a month this had fallen to 3.988°. An alloy of 19.27% of zinc by weight, quenched after twenty-four hours' annealing at 550°, gave 4.053° (0.8500 g.); after a month this had fallen to 3.990°. It therefore appears that there is some transition in this region of the system, possibly the precipitation of the β-solid solution, resulting in a lower heat content. This point, however, was not the immediate, and the work was abandoned as unfruitful. It is to be noted that the interesting magnesium-cadmium system could be investigated by this method, but only if sufficient refinement of method were developed, for the investigation of this system is likewise made difficult by the disparity in the heats of solution of the component metals.

[8] Nernst, *Z. physik. Chem.*, **22**, 539 (1897); Reinders, *ibid.*, **42**, 225 (1902).

[9] In the case of the α-solid solution in the copper-zinc system, for example, the aqueous solutions of the mixed sulfates of copper and zinc in equilibrium with the solid solution would contain only a trace of the copper ion.

Any measurement of chemical affinity which does not determine free energy change must be considered indirect and from the standpoint of chemical theory less valuable. Such a criticism may be made of the following study, in which changes in compressibility are investigated, but it will be seen that the compressibility point of view has some distinct and unique advantages as applied to metal systems.

The Compressibility of Metallic Alloys, Especially Solid Solutions

That compressibility is a property directly related to the cohesive forces in solids has been repeatedly emphasized by Richards.[10] In elementary solids these cohesive forces are physical in the sense that electrochemical effects involving the displacement of electrons are absent. In compounds the increase in cohesion caused by chemical interplay between unlike atoms is manifested by a decrease in compressibility. This basic idea is very simple in its application to alloys, especially to terminal solid solutions of the simple substitutional type, for here the components in almost every case are solid at room temperature and the effect of the chemical affinity between the unlike atoms may be shown simply by the difference between the compressibility of the unalloyed metals and that of the alloy. That such a comparison leads to results which are of some value to present metallurgical science may be seen in the following.

Some measure of success was assured this work by two determinations made by Adams, Williamson and Johnston,[11] in the course of their investigations of the compressibility of various solids, upon an α-brass and a tin-bismuth alloy. The first was found to give a compressibility coefficient much lower (25%) than the rule of mixtures value, and the second a coefficient very close (within 5%) to the calculated value. No explanation of these results was attempted, except to point out that the copper–zinc system exhibits physical properties which "do not bear a simple relation to the properties of the end members of the series," whereas in the tin–bismuth system many of the physical properties vary linearly with the composition.

The earlier results of Regnault[12] and of Amagat[13] on steel and brass are not comparable in accuracy with modern data.

The extensive work of Lussana on metal systems[14] shows little connection between compressibilty and constitution and in certain cases indicates compressibility coefficients for terminal solid solutions greater than the

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[10] (a) Richards, *Proc. Amer. Acad. Arts Sci.*, **39**, 603 (1904); (b) THIS JOURNAL, **36**, 2417 (1914); (c) *J. Franklin Inst.*, **198**, 25 (1924); (d) *Chem. Rev.*, **2**, 315 (1925).

[11] Adams, Williamson and Johnston, THIS JOURNAL, **41**, 12 (1919).

[12] Regnault, *Mem. de l'acad. des sciences*, **26**, 229 (1847).

[13] Amagat, *Compt. rend.*, **108**, 1199 (1899); *J. phys.*, [2] **8**, 197, 358 (1899).

[14] Lussana, *Nuovo Cimento*, [5] 19, 187 (1910). See also "Piezochemie Kondensierter Systeme," by Cohen and Schut, Leipzig, 1919, page 139.

rule of mixtures values.[15] An inspection of his data for the pure metals discloses the fact that they disagree with the best modern data from —37% for aluminum to +64% for lead, and also indicate abnormal temperature coefficients.[16] It seems necessary to conclude from this that Lussana's data are not to be compared in accuracy with the best of modern data, though there is a qualitative agreement. But for the investigation of alloys, where the *difference* between the calculated (rule of mixtures) value and the observed value is the datum sought, a difference including three experimental inaccuracies, one for each of the component metals and one for the alloy, measurements of high accuracy are essential.

Bridgman[17] has given a value for the compressibility of commercial nichrome wire and also a value for steel, which will be considered later. E. Madelung and R. Fuchs[18] have published values for brass and for steel.

Beckman[19] determined the compressibility for a series of silver-gold alloys. The coefficient given for pure gold, 1.55×10^{-6}, however, is greatly in excess of Bridgman's, 0.572×10^{-6}, and the value extrapolated for pure silver is 1.50×10^{-6}, also greatly in excess of Bridgman's value, 0.987×10^{-6}.[20]

So far as the authors are aware these are the only published data on the direct determination of the compressibility of alloys. Compressibility coefficients have been calculated for a number of alloys from the modulus of elasticity in tension (E, Young's modulus) and the modulus of elasticity in shear (C, the modulus of transverse elasticity or rigidity),[21] especially by E. Grüneisen.[22] Although the compressibility coefficients obtained in this way agree well with those determined directly, except for the soft metals, the method is of less general applicability because of its sensitivity to plastic flow, to slight inhomogeneities in the structure of the material

[15] For example, Lussana's value for an alloy of copper-aluminum, 7% by weight (20% by volume) aluminum, an α-solid solution, is 1.19×10^{-6} between 1 and 1000 atm. whereas the calculated value is 0.88×10^{-6}. In this system seven values are in excess of the rule of mixtures values and only one below.

[16] Lussana gives 0.88×10^{-6} for the compressibility of aluminum at 2000 atm. and 14.7°, whereas Richards gives 1.47×10^{-6} (corrected in the present work to 1.40×10^{-6}) over a range of 100 to 500 megabars at 20°, and Bridgman gives 1.334×10^{-6} at 30° and zero pressure. Lussana gives 0.96×10^{-6} for the same metal at the same pressure and at 27.0° whereas Bridgman finds 1.391×10^{-6} at 75°, an increase of only 4% over a temperature range of 45°. Lussana's value for lead at 500 atm. and 10° is 3.81×10^{-6} whereas Richards finds 2.33×10^{-6} at 20° between 100 and 500 megabars.

[17] Bridgman, *Proc. Amer. Acad. Arts Sci.*, **58**, 5 (1923).

[18] Madelung and Fuchs, *Ann. Physik*, [4] **65**, 289 (1921).

[19] Beckman, *Dissertation*, Upsala, 1910; International Critical Tables, Vol. II, 215.

[20] The original of this paper was not available. The method of measurement used by Beckman is unknown to the authors.

[21] Compressibility $= \beta = 9C - 3E/CE = 3(1 - 2\sigma)/E$, where σ is Poisson's ratio.

[22] Grüneisen, *Ann. Physik*, **22**, 801 (1907); **25**, 825 (1908).

measured and because of the apparently great difficulty in applying it to the very brittle intermetallic compounds. In addition it gives no indication of the variation of the compressibility with pressure. Grüneisen determined the compressibility of iron, steel, constantan and manganin. G. Angenheister[23] carried out similar measurements on alloys of silver and copper, but the values calculated from his data for the compressibilities of silver and copper, 0.80×10^{-6} and 0.58×10^{-6}, do not agree with those of Grüneisen (0.92×10^{-6} and 0.74×10^{-6}, respectively). The compressibilities calculated for the intermediate compositions show a decided departure from the rule of mixtures values. A minimum comes at 50% by volume and indicates a maximum decrease from the calculated value of 0.26×10^{-6} (from 0.70×10^{-6} to 0.44×10^{-6}). The curve obtained is gently sagging throughout its course and shows no critical points at the limits of solid solubility (copper dissolves 1% by volume of silver and silver 7% copper). The curve shows a progressive departure from a straight line in the heterogeneous fields, where linearity should be strictly observed.

It is clear, therefore, that there are not sufficient data available for the study of the cohesive forces in alloys by means of compressibility. In order to satisfy this lack the present work was undertaken, but as a preliminary study only, for a complete set of data for binary alloys would require investigation of over 400 binary systems. In order first to survey the field, a number of typical alloys was chosen, with the hope that the results would be sufficiently illuminating to indicate the most fertile paths for additional research.

Experimental

Method of Measurement.—The method and apparatus developed by Richards[24] were used without modification. Measurements were made at 25° and required the use of a correction factor for water previously determined by the authors.[25] The piezometers used were of the usual type, sufficiently large to hold an alloy piece with a volume of 25 cm.^{3}. Duplicate determinations were made on each alloy except certain intermediate solid solutions and intermetallic compounds. Divergent results almost always could be traced to the accidental introduction of impurities into the piezometer capillary and when such was the case the results were discarded. Divergencies which could not be traced to such experimental imperfections were discredited by a sufficient number of consistent determinations. In each case, however, the divergent results are noted in the table of data.

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[23] Angenheister, *Ann. Physik,* [4] 11, 188 (1903).

[24] (a) Richards, ref. 10a; (b) THIS JOURNAL, **46**, 935 (1924). Experimental details are given in full in these papers.

[25] Mehl and Mair. *ibid.*, **49**, 1892 (1927).

Materials.—The preparation, heat-treatment and analysis of the alloys presented a task impossible of accomplishment within the time at our disposal, and it was only through the kindly help of a number of industrial metallurgists that the work was made possible; several of the alloys were given additional treatment after their receipt. Table I lists the alloys investigated, with the percentage composition by weight and by volume, and with the heat and mechanical treatment noted for each alloy.

Each alloy was machined into a cylindrical bar 1.516 cm. in diameter and 13.8 cm. long, except the brittle intermetallic compounds, which were cast in graphite tubes.

Table I

Alloys Investigated

Alloy no.	Composition		Treatment
	by weight	by volume	
1	55% Cu; 44% Ni; 1% Fe	55% Cu; 44% Ni; 1% Fe	Cast; rolled; annealed at 1000° for 3 hours
2	36.27% Ni; 63.24% Fe; 0.15% C; 0.49% Mn; 0.15% Si; 0.05% Cr	33.7% Ni; 65.6% Fe; 0.7% Mn	Forged
3	92.34% Cu; 7.66% Al	78.4% Cu; 21.6% Al	Slightly hot-rolled; drawn cold to 0.705″ from 1.000″; annealed 1 hour at 850°
4	87.1% Cu; 12.9% Al	66.9% Cu; 33.1% Al	Hot-rolled to 0.705″ from 1.000″; annealed 1 hour at 850° and quenched in water
5	81.94% Cu; 17.95% Zn; 0.06% Pb; 0.05% Fe	78.5% Cu; 21.5% Zn	Cast; annealed 1 hour at 810°; cold-rolled to $12^1/_2$% reduction in height (to $^3/_4$″ bar); annealed 2 hours at 500°
6	64.27% Cu; 35.61% Zn; 0.09% Pb; 0.03% Fe	59.0% Cu; 41.0% Zn	Cast; annealed 3 hours at 700°; cold-rolled to $12^1/_2$% reduction in height; annealed 2 hours at 500°; cold-rolled to $16^1/_2$% reduction in height (to $^3/_4$″ bar); annealed 2 hours at 600°
7	51.43% Cu; 48.57% Zn; 0.06% Pb; 0.04% Fe	45.8% Cu; 54.2% Zn	Cast; hot-rolled at 600°; annealed 2 hours at 500°; heated to 800°, cooled to 600° and quenched in oil
8	88.53% Cu; 11.44% Sn; 0.03% Fe	86.3% Cu; 13.7% Sn	Cast; annealed 10 hours at 600°; cold-rolled to 20% reduction in height; annealed 2 hours at 650°
9	61.16% Cu; 38.78% Sn; 0.06% Fe	56.3% Cu; 43.7% Sn	Cast in hot graphite tube; annealed 3 hours at 500°
10	67.43% Cu; 32.53% Sn; 0.04% Fe	62.8% Cu; 37.2% Sn	Cast in hot graphite tube; annealed 3 hours at 500°
11	87.24% Al; 12.56% Mg; 0.085% Si; 0.12% Fe	81.7% Al; 18.3% Mg	Extruded; annealed at 430° for 18 hours

TABLE I (*Concluded*)

Alloy no.	Composition by weight	Composition by volume	Treatment
12	99.941% Al; 0.013% Si; 0.022% Fe; 0.022% Cu; 0.002% Ti		Cast
13	96% Cu; 4% Si	86.6% Cu; 13.4% Si	Cast; annealed 4 hours at 850°; hammered on anvil to reduce diameter of bar from 0.723″ to 0.690″
14	0.89% C; balance Fe (Armco iron base)		Cast; heated to 900°; quenched in cold water
15	Same as 14		Heated to 940° and cooled at a uniform rate to 480° over a period of $3^1/_2$ hours
16	1.36% C; balance Fe (Armco iron base)		Cast; heated to 900°; quenched in cold water
17	Same as 16		Heated to 940° and cooled at a uniform rate to 480° over a period of $3^1/_2$ hours

Experimental Results.—Two piezometers were used, numbered 1 and 2. Table II gives the standardization data for each. The validity of the standardizations is attested by the agreement among the various separate determinations and also by the agreement between the compressibilities measured and the results obtained by other investigators. All measurements were made at 25°. Two values are given for the quantities of mercury corresponding to a pressure range of 100 to 500 megabars: one was obtained in passing from 500 to 100 megabars, and the other in

TABLE II

PIEZOMETER STANDARDIZATION DATA

Piezometer No. 1			Piezometer No. 2		
Wt. of water	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars calcd. to common quantity of water: 2.7928 g.	Wt. of water	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars calcd. to common quantity of water: 3.1993 g.
2.7928	0.7973	0.7973	3.1993	0.8971	0.8971
	.7966	.7966		.8971	.8971
2.6873	.7764	.7981			
	.7768	.7985	3.2347	.9031	.8959
				.8997	.8925
2.5051	.7350	.7938	2.4985	.7486	.8918
	.7420	.8008		.7490	.8922
2.7236	.7862	.8003			
	.7790	.7931		Average	.8945
0.8928	.4058	.7942			
	.4024	.7908			
	Average	.7964			

passing from 100 to 500 megabars. The agreement within these pairs is a criterion of the success of the individual determinations. The separate standardizations were converted to a common quantity of water by the use of the water correction factor previously determined by the authors.[25]

TABLE III

No. of alloy	No. of piezometer	Wt. of water	Wt. of alloy	Density of alloy	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars corr. to piezometer water standard	$\beta \times 10^6$
1	2	2.8120	222.406	8.910	0.3777	0.4569	0.60
					.3813	.4605	.62
1	2	2.8200	222.406	8.910	.3777	.4566	.64
					.3791	.4552	.63
1	2	2.6580	222.406	8.910	.3464	.4572	.62
					.3466	.4670	.63
2	2	3.0715	199.867	8.402	.4608	.4868	.85
					.4618	.4878	.84
2	2	3.2611	199.867	8.402	.5018	.4891	.85
					.5022	.4895	.85
3	1	2.4564	194.49	7.847	.2811	.3499	.68
					.2793	.3481	.67
3	2	3.1550	194.49	7.847	.4545	.4636	.79
					.4545	.4636	.80
3	2	2.7773	194.49	7.847	.3717	.4580	.75
					.3745	.4608	.77
4	1	2.4631	178.76	7.244	.3008	.3682	.80
					.2974	.3648	.78
5	1	2.2340	214.53	8.669	.2432	.3574	.73
					.2457	.3599	.75
5	1	2.0723	214.53	8.669	.2110	.3583	.74
					.2171	.3644	.78
6	1	2.3273	209.03	8.426	.2724	.3675	.81
					.2685	.3636	.78
6	1	2.3000	309.03	8.426	.2791	.3798	.91
					.2681	.3688	.82
7	1	2.4564	202.95	8.291	.4515	.4083	.93
8	1	2.6398	212.90	8.631	.3421	.3734	.84
8	1	2.5061	212.90	8.631	.3168	.3754	.85
					.3144	.3730	.84
9	1	4.7582	201.38	9.024	.8338	.4321	.99
					.8304	.4287	.96
10	2	4.9141	206.24	8.931	.8528	.5023	.88
					.8556	.5051	.90
11	1	2.6887	63.16	2.553	.4490	.4703	1.57
					.4454	.4667	1.55
11	1	2.5151	63.16	2.553	.4070	.4638	1.52

TABLE III (*Concluded*)

No. of alloy	No. of piezometer	Wt. of water	Wt. of alloy	Density of alloy	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars corr. to piezometer water standard	$\beta \times 10^6$
12	2	3.3096	66.67	2.702	.5670	.5445	1.39
					.5644	.5419	1.37
12	2	3.3053	66.67	2.702	.5672	.5455	1.39
					.5714	.5497	1.43
12	1	2.4649	66.67	2.702	.3807	.4477	1.40
					.3798	.4468	1.39
13	1	2.6564	207.44	8.406	.3646	.3925	.98
					.3620	.3899	.96
13	1	2.6564	207.44	8.406	.3582	.3861	.94
14	2	3.5408	189.61	7.798	.5184	.4486	.62
14	2	3.4924	189.61	7.798	.5104	.4505	.62
					.5064	.4465	.60
15	1	4.2588	181.50	7.835	.6871	.4705	.63
15	1	4.3995	181.50	7.835	.7129	.4676	.60
					.7117	.4664	.59
16	1	3.0380	190.88	7.799	.4238	.3753	.83
					.4254	.3737	.82
					.4252	.3751	.83
17	2	4.3880	184.74	7.807	.7321	.4891	.84
					.7321	.4891	.84
17	1	3.0385	184.74	7.807	.4408	.3906	.84
					.4446	.3944	.87

TABLE IV

No. of alloy	Composition by volume, %	Density (obs.)	Density (calcd.)	$\beta \times 10^6$ (obs.)	$\beta \times 10^6$ (calcd.)	% Decrease in compressibility
1	55 Cu; 44 Ni; 1 Mn	8.910	8.901	0.62	0.64	3
2	33.7 Ni; 65.6 Fe; 0.7 Mn	8.402	8.206	.85		
3	78.4 Cu; 21.6 Al	7.847	7.582	.78	.89	12
4	66.9 Cu; 33.1 Al	7.244	6.870	.79	.98	19
5	75.5 Cu; 21.5 Zn	8.669	8.545	.75	.94	20
6	59.0 Cu; 41.0 Zn	8.426	8.200	.80	1.13	29
7	45.8 Cu; 54.2 Zn	8.291	7.960	.93	1.26	26
8	86.3 Cu; 13.7 Sn	8.631	8.710	.84	0.89	6
9	56.3 Cu; 43.7 Sn	9.024	8.210	.98	1.23	20
10	62.8 Cu; 37.2 Sn	8.913	8.320	.89	1.17	24
11	81.7 Al; 18.3 Mg	2.553	2.474	1.55	1.68	8
12	Pure aluminum	2.702		1.40		
13	86.6 Cu; 13.4 Si	8.406	8.050	.97	0.65	−49
14		7.798		.61		
15		7.835		.61		
16		7.799		.83		
17		7.807		.85		

Experimental Results.—These are given in Tables II, III and IV, together with other data necessary to the calculation of compressibility.

The compressibility coefficients represent the average compressibility between 100 and 500 megabars. The densities were determined on the bars upon which the compressibility measurements were made and serve as a valuable criterion of the solidity of the samples. It is, of course, essential for this work that the bars be free from voids. The anomalous density found for the copper-silicon alloy seemed to indicate the presence of voids and the excessively high value found for the compressibility also suggested this. In order to eliminate this possible source of confusion five of the alloy bars were subjected to x-ray inspection (numbers 2, 3, 6, 8 and 13) while immersed in methyl iodide. Four of the bars were found to be wholly free from voids, but the copper-silicon alloy was found to be very faulty, the x-ray photograph revealing casting pipe-cones throughout its length. The results on this alloy have, therefore, been discarded.

The densities were determined by the usual water displacement method, using a tare with each weighing and making correction for displacement of air. The data are summarized in Table IV. The calculated densities and compressibilities are obtained from the volume percentage compositions given in the second column. The values for β are the average values from Table III.[26]

Discussion.—In the simplest metallic solid solution, that is, of two metals crystallizing in the same crystal system (such as copper and nickel) and in which solid solution formation takes place by substitution of one atom of the solute for one atom of the solvent, the atoms are arranged crystallographically as they are in the pure component metals. As a consequence of the specific attraction between the unlike atoms (which may be taken as roughly indicated by the relative positions of the elements in the periodic table), the composite lattice will possess a rigidity greater than that of the component metals, in the same volume proportion, originating in the greater attractive (and repulsive) forces. Such a lattice will, therefore, have a smaller compressibility and the difference between the calculated and the observed compressibility coefficients will be indicative of the intensity of the attraction.

In the simplest case this should lead to an increase in density, and in general this is found to be the case, though the x-ray diffraction data on the copper–gold system indicate an exceptional behavior,[27] and a recent

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[26] Compressibility coefficients for the pure metals were taken from the data of Richards, THIS JOURNAL, **37**, 1646 (1915), except for aluminum, which was redetermined, and for nickel and copper (0.53×10^{-6} and 0.72×10^{-6}, respectively), which were calculated from Bridgman's data;[17] the densities of the pure metals are from the International Critical Tables, Vol. I, p. 103.

[27] Lange, *Ann. Physik*, **76**, 476 (1925), plotted *a*, the side of the unit face-centered cell, against atomic percentage composition and found a straight line relation within his experimental error. Kirchner, *Ann. Physik*, **69**, 59 (1922), found an increase in *a*, over the rule of mixtures value, with *a* plotted against atomic percentage composition,

study of the copper-rich copper-tin terminal solid solution is distinctly exceptional.[28] Davey[29] states that solid solutions of aluminum in silver, tin in silver and silicon in copper show in each case an increase in the dimensions of solvent lattice caused by the smaller solute atom. It is evident that it is questionable whether density is of any value as a criterion of the attraction between unlike atoms. Compressibility, however, is unaffected by this argument, since the forces effective in more tightly binding the atoms should also be effective in producing a diminished compressibility.

With respect to solid solutions of metals with different space lattices the foregoing argument requires some elaboration, as noted under the discussion of the experimental results on the various alloys of this type.

The specific attraction between the unlike atoms must be of immediate importance in the mechanical behavior of solid solutions. Solid solutions are much harder than required by the rule of mixtures, and a number of workers[30] have suggested that at least part of the increase in hardness must be caused by the attraction between unlike atoms. Hardness is a complicated property and each method of measurement brings the different factors concerned into play in varying degrees. Empirically it is defined as the resistance to permanent deformation. The tendency among metallurgists at present is to interpret this to mean resistance to slip along atomic planes.[31]

In solid solutions of normal grain size, free from foreign material of any kind and free from mechanical strain, the hardness must, by this theory, be caused only by the warping of the atomic planes, introducing resistance to slip, and by the attraction between the unlike atoms, tending to hold the lattice as a whole more rigid. Abnormally small grain size gives rise to a large increase in hardness, and mechanical strain, caused by cold-work

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amounting at the maximum to 0.9%, which is in excess of the probable experimental error. It is, however, not correct to plot a against atomic percentage composition, though this seems to be the general practice, for not a but a^3 is a linear function of atomic percentage composition when additivity is assumed. The correct procedure is to cube the values of a determined experimentally for the elementary metals, and by means of the atomic percentage composition calculate the values for a^3 for intermediate compositions and then to extract the cube root in order to obtain values for a truly representative of the rule of mixtures. Such a calculation for copper and gold will give a curve for a against atomic percentage composition slightly concave to the composition axis. Kirchner's data very nearly conform to this curve, falling at the greatest 0.5% too high.

[28] Weiss, *Proc. Roy. Soc. (London)*, **108**, 643 (1925), concluded from his x-ray data that this terminal solid solution is not of the simple substitutional type but that an atom of tin replaces several atoms of copper, leading to abnormally low densities.

[29] Davey, *Trans. Am. Soc. Steel Treating*, **6**, 375 (1924).

[30] Desch, *Trans. Faraday Soc.*, **10**, 251 (1914). See especially "Science of Metals," by Jeffries and Archer, McGraw-Hill Book Co., New York, 1924, pp. 232, 260, 270, 396, 412.

[31] The slip-resistance theory of hardness has been summarized by Jeffries and Archer, *Chem. Met. Eng.*, **24**, 1057 (1921).

(plastic deformation), produces a similar result in smaller degree. It is the virtue of compressibility that it measures (in solid solutions) only one of these factors, namely, that caused by the attraction between unlike atoms. Bridgman[32] found that cold-rolled copper and iron gave the same values for compressibility as annealed copper and iron, within the accuracy of the measurements. This significant experiment demonstrates the essential identity of cold-worked and annealed metal, for an amorphous phase, in which the directional forces of the atoms producing the lattice characteristic of the metal are no longer nicely oriented with those of adjacent atoms or, in other words, in which the points of atomic attachment are no longer adjusted, should have a compressibility appreciably greater than that of the crystalline phase.[33]

In pure metals, which are mostly of high symmetry and free from the distortion solid solution formation produces, hardness is a periodic property[34] which, when compared to Richards' periodic curve of compressibility,[35] shows a striking and nearly perfect parallelism.[36] Exceptional metals are those of extraordinarily low symmetry.

Thus compressibility may be taken as a measure of the lattice rigidity factor in hardness. For solid solutions, the difference in compressibility of the solid solution and the value calculated on the basis of the rule of mixtures may be taken as a measure of the additional interatomic forces resulting from the chemical affinity operative between the unlike atoms, resulting in an increase in the lattice rigidity. Applied to alloys in this way, compressibility may be said to measure "chemical hardness." The other effects promoting slip resistance may be said to produce "physical hardness."[37]

Without doubt the chemical factor is subordinate in magnitude to the physical, but the latter must be considered as intimately related to the chemical, for the warping of the atom planes, as a result of the introduction

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[32] (a) Bridgman, *Proc. Am. Acad. Arts Sci.*, **44**, 265 (1909); (b) **58**, 168 (1923).

[33] Bridgman's experiment (in which linear compressibility was measured) likewise points out the complete compressibility isotropy of these cubic lattices, for the process of cold-rolling inevitably produces preferred orientation. Similar experiments on a non-cubic metal, such as zinc, would, however, show nothing concerning the nature of cold-worked metal, since the preferred orientation produced by cold-rolling would cause a very appreciable difference because of the well-known difference in compressibility along the different crystallographic axes.

[34] Rydberg, *Z. physik. Chem.*, **33**, 353 (1900); Edwards, *J. Inst. Metals*, [2] **20**, 61 (1918).

[35] Ref. 26, p. 1643.

[36] Traube, *Z. anorg. Chem.*, **34**, 413 (1903), pointed out the parallelism between hardness and internal pressure. This had been suggested (with the help of a few examples) by Richards in 1901. *Proc. Am. Acad. Arts Sci.*, **37**, 1 (1901).

[37] The value in the use of such terms is purely utilitarian: they serve to classify descriptively a series of facts or conditions producing a common effect.

of solute atoms, is caused by the difference in atomic volumes, modified in some way by the chemical attraction between the unlike atoms and the relative compressibilities of the partially ionized atoms.

System Copper–Nickel.—The only previous determination of an alloy in this system was made by Grüneisen,[22b] who determined E and σ for a sample of commercial constantan. The compressibility coefficient calculated was 0.62×10^{-6}, agreeing with the value here determined.

The alloy measured was "Constantan," containing approximately 55% copper, 44% nickel, and 1% manganese, by weight. No analysis was made of this alloy since the compressibility coefficients of these three metals are so nearly equal that only a very large departure from the reported composition could cause an appreciable variation in the calculated compressibility. The calculated compressibility was obtained from the value for nickel obtained by Bridgman expressed in terms of average compressibility between 100 and 500 megabars, namely, 0.53×10^{-6}.[38] The value 0.73×10^{-6} was taken as the most representative value for copper.[39] The calculated coefficient, 0.64×10^{-6}, is only very slightly greater than the observed value, 0.62×10^{-6}. The density increase, 0.1%, is also slight. Copper and nickel both crystallize in face-centered cubes, with approximately the same lattice constants, 3.597 and 3.499 Å., respectively,[40] and are very similar chemically. No great decrease in compressibility is therefore to be expected.

System Iron–Nickel.—The only measurement made in this system was on a commercial alloy "Invar," received in the forged condition, containing 36.27% nickel. Filings of the alloy were examined by x-rays for structure, using the Hull powder method, and found to consist wholly of face-centered cubes, characteristic of nickel and γ-iron.[41] The compressibility coefficient found, 0.85×10^{-6}, is much higher than that calculated using the coefficient of α-iron (which is 0.60×10^{-6}), namely, 0.58×10^{-6}, and appears to mean that the compressibility of γ-iron is much greater than that of α-iron.

System Copper–Aluminum.—Alloy 3 is in the α-field near the limit of solid solubility. Alloy 4 is a β-solid solution. There appears to be an appreciable increase in the cohesive forces in the β-solid solution, but a lower symmetry doubtless favors a greater hardness.

An accident prevented an investigation of annealed and age-hardened duralumin, but on the basis of the results presented here, especially those on steel, it may be predicted that the age-hardening, now known to be produced by the resistance to slip offered by submicroscopic particles of $CuAl_2$ (in a pure copper-aluminum alloy)[42] will have only a very slight, probably inappreciable, effect upon the compressibility.

System Copper–Zinc.—A number of measurements have been reported on "brass," but with one exception there has been no accompanying analysis. Adams, Williamson and Johnston measured the compressibility of a leaded brass with 61.76% copper, 35.92% zinc, 2.26% lead and 0.05% iron. Their value (corrected) at zero pressure is 0.86×10^{-6}. For a brass of unstated composition Madelung and Fuchs found 0.90×10^{-6}

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[38] Richards' value for nickel, 0.43×10^{-6}, is apparently low.

[39] Bridgman's value (recalculated) is 0.730×10^{-6}, and the value found by Adams, Williamson and Johnston (corrected) is 0.725×10^{-6}. The above value is taken in preference to the slightly higher value of 0.75×10^{-6} given by Richards and Grüneisen.

[40] Davey, *Phys. Rev.*, **25**, 753 (1925).

[41] This is in confirmation of the work of McKeehan, *Phys. Rev.*, **18**, 657 (1921), and Osawa, *J. Iron Steel Inst. London*, May, 1926.

[42] Merica, Waltenberg and Scott, *Bull. Am. Inst. Min. Eng.*, June, 1919, p. 913.

between 50 and 200 megabars. The other data appearing in the literature are of inferior accuracy, most of the values reported being higher than those obtained here. The higher value found by Adams, Williamson and Johnston may be explained in part by the lead present. The other higher values probably refer to copper-zinc alloys of higher zinc content.

Three compositions were investigated. An α-brass, half-saturated (18% zinc by weight), gave a compressibility of 0.75×10^{-6}, a decrease of 20% from the rule of mixtures value. An α-brass very near to the limit of solid solubility (35.6% zinc by weight), gave 0.80×10^{-6}, a decrease of 29% from the rule of mixtures value. Despite this tremendous decrease, the hardness increase at the limit of solid solubility is only about 15%.[43] It is possible that this discrepancy is in some way related to the extraordinary elongation recently observed in a single crystal of α-brass,[44] a condition indicating, apparently, that certain of the factors which produce "physical hardness" in elementary zinc are no longer present when the zinc atom crystallizes on the copper lattice.

The decrease in compressibility is paralleled by an increase in density, which is 2.8% at the maximum.[45] In the elementary state the zinc is the more compressible element and it seems likely that the increase in density is taken up mostly by the zinc atoms, which on the copper lattice are forced out of their normal shape (that of a prolate spheroid) into approximately a sphere. The distance of closest approach of the zinc atoms in elementary zinc is 2.66 Å.,[46] whereas the distance of closest approach in copper is 2.56 Å.,[40] and the saturated solid solution 2.56 Å.,[47] so that the zinc atoms in α-brass are compressed on all sides, but mostly at the poles. It is possible that the zinc atom in brass is rotated in such a way that its major axis lies in the [111] direction in the copper lattice. If this were the case, a denser packing could result without any great compression of the zinc, assuming that the zinc atom lies wholly within the periphery of a prolate spheroid. Whether the copper atom is also compressed, as suggested by the increase in density, or expanded, as suggested by the apparent decrease in the cohesive forces (the compressibilities of the brasses are all less than that of pure copper, and it will be shown in a subsequent publication that the internal pressures are probably also less), appears at present to be beyond the reach of experiment.

The compressibility of the β-solid solution shows a decrease from the rule of mixtures value of 26%. The greater hardness of the β-solid solution is doubtless to be ascribed to a lower order of symmetry.[47]

System Copper-Tin.—The α-solid solution shows a compressibility slightly smaller than the rule of mixtures value, despite the fact that each tin atom replaces not one but several copper atoms.[28] Alloy 10, which is the δ-solid solution, appears to show a greater decrease than Alloy 9, the compound Cu_3Sn, and also exhibits a greater Brinell hardness,[48] though it is claimed that Cu_3Sn shows a greater scratch hardness.[49]

System Aluminum-Magnesium.—The composition investigated, 12.56% by weight of magnesium, is in the $\alpha + \beta$ field[50] near the limit of solid solubility. The percentage decrease in compressibility observed, 8%, is relatively small, as is the percentage increase in density, which is 3%.

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[43] Harris, *J. Inst. Metals*, **28**, 327 (1922) states that the Brinell number of a 66–34 α-brass is 48. The Brinell number of pure copper is ordinarily taken as 40.

[44] Elam, *Proc. Roy. Soc. (London)*, 115A, 133 (1927).

[45] Jeffries and Archer, *Chem. Met. Eng.*, **29**, 925 (1923).

[46] Hull, *Phys. Rev.*, **17**, 571 (1921).

[47] Ref. 4, p. 49.

[48] Bauer and Vollenbruck, *Z. Metallkunde*, **16**, 426 (1924).

[49] International Critical Tables, Vol. II, p. 561.

[50] Hanson and Gaylor, *J. Inst. Metals*, [2] **24**, 201 (1920).

Two determinations by other workers remain to be discussed. Bridgman[17] determined the linear compressibility at 30° of a piece of nichrome wire, approximating in composition to 80% nickel and 20% chromium by weight, or 76% nickel and 24% chromium by volume. Taking the compressibility coefficient of nickel from Bridgman's data, 0.53×10^{-6}, and that of chromium from Richards's data (after approximate conversion to Bridgman's units), 0.89×10^{-6}, the rule of mixtures value for this composition may be calculated to be 0.72×10^{-6}. Bridgman found 0.55×10^{-6}, which is considerably lower.

Grüneisen's[22b] determination of the elastic constants for manganin leads to a compressibility coefficient of 0.81×10^{-6}. The calculated value for this alloy, assuming a composition of 82.1% copper, 0.6% iron, 15.0% manganese and 2.3% nickel, is 0.76×10^{-6}, appreciably lower than the determined value. There is some uncertainty concerning the composition of the alloy measured by Grüneisen (who gives no analysis), but the possible variation in composition from that assumed could hardly reconcile the calculated and the assumed values. It is the author's opinion that a direct measurement of the compressibility of thoroughly equilibrated manganin would show a compressibility coefficient only slightly different from the rule of mixtures value and that this difference would be negative, that is, that the coefficient calculated would be greater than that measured.

System Iron–Carbon.—The superior hardness of quenched steels has engaged the attention of metallurgists for many years. Although the problem is by no means solved, it is certain that the quenching hardness is related to the partially arrested transformation of austenite into pearlite and is directly caused by the constituent martensite. Most recent theories tacitly assume that the hardness of martensite is chiefly the aforenamed "physical hardness," that is, it is caused by factors which impede slip without increasing the cohesive forces in the alloy.[51]

Most investigators of compressibility have made measurements on iron and steel but none seem to have investigated the special point of the effect of heat-treatment. The early values for the compressibility of iron were actually obtained from measurements on mild steel. Grüneisen,[22b] from measurements of the elastic moduli, calculated the compressibility of iron and of "steel," and found them to be the same, namely, 0.60×10^{-6}. Bridgman[52] measured the linear compressibility of Bessemer boiler plate and of annealed tool steel (1.25% carbon), and for the first found 0.530×10^{-6} (an average of two determinations, one made parallel to the direction of rolling and the other perpendicular to it) and for the second 0.525×10^{-6}. These figures are probably too low.[17]

Adams, Williamson and Johnston[11] measured the volume compressibility of Bessemer steel (0.2% carbon) and of tool steel (0.8% carbon), finding 0.575×10^{-6} for each. Madelung and Fuchs[18] found 0.61×10^{-6} for both iron and steel ("silver steel").

The present work confirms previous work in the similarity of the compressibilities of annealed steel and iron, but gives a higher compressibility for hypereutectoid steel than would be expected from the measurements of Bridgman on annealed 1.25% carbon steel.

In order to determine whether quenched steel possesses any superior cohesive forces, two sets of experiments were performed. A eutectoid steel (0.89% carbon) was quenched drastically (the heat treatments of these steels are given in Table I), a treatment which rendered it highly martensitic, and increased its hardness almost three-fold

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[51] Modern opinion on the nature of martensite and on the factors causing hardness in quenched steel has recently been summarized by Sauveur, *Trans. Am. Inst. Mining Met. Eng.*, No. 1532-C, 1926.

[52] Ref. 32 a, p. 255.

(from a Brinell number, 3000 kg. load, of 241, to 653). The compressibility of this steel, an average of three determinations, was found to be 0.61 × 10^{-6}. The steel was then annealed thoroughly and its compressibility again determined, giving an average of three determinations, a value of 0.61 × 10^{-6}.

Similarly a hypereutectoid steel (1.36% carbon) was quenched as before and its compressibility found to be 0.83 × 10^{-6}, an average of three determinations. After annealing, the value found, an average of four determinations, was 0.85 × 10^{-6}, which within the possible error is identical with the first value.

It is therefore apparent that the hardening of steel by quenching is not caused by any appreciable increase in the normal cohesive forces, for the compressibility is not changed by quenching or annealing. It seems extraordinary indeed that a glass-hard steel should suffer the same volume decrease with increase in pressure as an annealed steel, but the result is not strange when examined in the light of the slip interference theory of hardness (with which it is in full accord), for this theory postulates no increase in the binding forces between the atoms in steel and assumes the hardness to be caused only by the mechanical arrangement of the structural units. It seems highly probable from the apparent identity of the compressibility values of the steels in the quenched and annealed conditions that the structural *units* in quenched steel are not greatly different from those in annealed steel, and this is in agreement with the explanation of the hardening of steel by the slip interference theory enunciated by Jeffries,[53] in which martensite is taken to be an aggregate of submicroscopic cementite and ferrite, differing from pearlite only in the size and arrangement of the cementite and ferrite grains.

Judging from Bridgman's experiment on rolled metals[32] neither variations in grain size nor mechanical strain appear to make any difference in compressibility (though it is conceivable that a decrease in density resulting from cold work or very small grain size should result in a slightly higher compressibility), so that an increase in hardness caused by either or both of these effects would make no difference in compressibility. On the other hand, lattice distortion, which has been postulated as a cause of hardness in steel, could be produced presumably only by an alteration in the interatomic forces, and this should result in an appreciable compressibility difference. The Hanemann-Schrader theory[54] assumes an ϵ- and an η-phase in equilibrium with austenite, and designates the η-phase as the bearer of the martensitic hardness because this phase is assumed to contain a hard iron carbide of the formula $Fe_{24}C$. It is assumed that the "hardness of martensite" is "caused by a definite arrangement of the iron and carbon atoms in an iron-carbon compound" ($Fe_{24}C$), and that this compound is hard because of the nature of its space lattice and because of the directional forces which inhere in the lattice. It is obvious that the compressibility results here presented limit the possible interpretations of this theory. The inherent hardness of the hypothetical compound $Fe_{24}C$, which is assumed to be much greater than that of ferrite or pearlite, must be explained either by (1) an extraordinarily low symmetry, or (2) interatomic forces between the iron and carbon atoms very much greater than those in austenite or pearlite, or by both (1) and (2). The assumption of the presence of large quantities of a compound of low symmetry seems to be untenable in the light of the results of x-ray diffraction studies on the structure of steel, for only the face-centered cube (characteristic of γ-iron) and the body-centered cube (characteristic of α-iron) have been found,[55] both lattices of high symmetry. The alternative (2) seems definitely denied by the compressibility measurements, which show no appreciable difference in the cohesive forces in quenched and an-

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[53] See Sauveur, ref. 51, p. 39.

[54] *Trans. Am. Soc. Steel Treat.*, 9, 229 (1926).

[55] X-ray research on steel has recently been summarized by G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, 1926, p. 210.

nealed steel. It is not impossible, of course, that there should be small quantities of a carbide such as $Fe_{24}C$ present in quenched steel, but the only large contribution such a compound could make to the superior hardness of martensite would be by virtue of a very fine state of subdivision. In such a form the Hanemann-Schrader is nearly indistinguishable from the more generally accepted slip-resistance theory, and in the assumption of the presence of an unknown compound of iron and carbon seems much less likely.

The compressibility of the eutectoid steel is only slightly higher than that of iron (0.61×10^{-6} and 0.60×10^{-6}, respectively), whereas the compressibility of the hypereutectoid steel is proportionately much greater (0.83×10^{-6}). The reason for this lack of proportionality is not now evident. The presence of voids in the hypereutectoid steel would of course account for the proportionately higher value, but this possibility is denied by the normal density (Table II). It is to be noted that though the compressibilities of eutectoid steel and of pure iron are nearly identical, the Brinell numbers are 241 and 75, respectively.

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Summary

1. The importance of a knowledge of the chemical affinity operative between unlike atoms in metallic solid solutions is emphasized. An attempt to measure the heat of formation of certain aluminum-magnesium and aluminum-zinc alloys is reported, in which the heat of solution of magnesium in $HCl.20H_2O$ is determined.

2. The compressibility of solid solutions is discussed and it is pointed out that in certain simple solid solutions the compressibility is a datum by which the intensity of the chemical affinity therein operative may be estimated.

3. Previous data on the compressibility of alloys are critically reviewed

and a series of new measurements on sixteen alloys, differing widely in type, is presented. It is shown that the greatest departure from simple additivity occurs in solid solutions of metals differing greatly in chemical type and that this departure is negative in every case under observation.

4. The basic importance of compressibility as a criterion of lattice rigidity in the study of the mechanical properties of metals and alloys, especially hardness, is emphasized, and the results of the compressibility measurements are correlated with the known mechanical properties and are interpreted to be in harmony with the slip-resistance theory of hardness. Measurements on quenched and annealed carbon steels are interpreted to indicate that the quenching hardness in these steels is not caused by an increase in the cohesive forces.

[Contribution from the Wolcott Gibbs Memorial Laboratory and the Metallurgical Laboratories of Harvard University]

INTERNAL PRESSURES IN METALLIC SOLID SOLUTIONS

By Robert Franklin Mehl[1]

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The importance of compressibility in the study of chemical affinity in metallic solid solutions and intermetallic compounds has recently been emphasized, and it has been shown that from compressibility data interesting conclusions may be drawn concerning the metallurgical behavior of alloys.[2]

The problem of the attraction between unlike atoms in solid solutions may be attacked in a different way, namely, by the use of the concept of internal pressure. T. W. Richards,[3] and others,[4] have emphasized the importance of internal pressures among the factors which determine the existence and behavior of solids. Richards has correlated the conception with his equation of state for solids.[5,3a]

The quantity π_0, the internal pressure, was first calculated by the equation

$$\pi_0 = \frac{R}{V_A \, \alpha_s} \tag{1}$$

where V_A is the atomic volume, α_s the coefficient of cubic thermal expansion and R the gas constant. Richards recently modified this equation,[6] and now regards (1) as only an approximation. The new equation is

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[1] National Research Fellow.

[2] Mehl and Mair, This Journal, **50**, 55 (1928).

[3] The most recent treatment of internal pressures is given by (a) Richards, This Journal, **48**, 3063 (1926). The first of his many papers on this subject appeared in 1901; (b) *Proc. Amer. Acad. Arts Sci.*, **37**, 1 (1901).

[4] Traube, *Z. anorg. Chem.*, **34**, 413 (1903); Benedicks, *ibid.*, **47**, 455 (1905); Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, pp. 69, 185.

[5] Richards, This Journal, **46**, 1419 (1924).

[6] Ref. 3a, p. 3067.