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SILVER:
ITS PROPERTIES AND INDUSTRIAL USES

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SILVER: ITS PROPERTIES AND INDUSTRIAL USES

By B. A. Rogers,* Irl C. Schoonover,* and Louis Jordan **

ABSTRACT

Information concerning the properties and industrial uses of silver as obtained from the literature, from visits to plants, and from correspondence is given. The variation in physical properties by mechanical working and heat treatment is emphasized. The chemical properties are discussed with respect to resistance to corrosion. In discussing the alloy systems, emphasis has been placed on those of the base metals which enjoy a considerable consumption. The bactericidal uses of silver, its employment in chemical equipment, and also its application in electrical switching devices have been described.

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PREFACE

This addition to the group of circulars on metals is intended to present, in one place, the more important facts concerning silver. From the traditional point of view, silver is ranked among the precious metals. It has, however, an important position in the industrial field and it is the latter aspect which is of present concern.

The writing of this circular is the outcome of a survey of the engineering uses of silver which has been made by two research associates supported at the National Bureau of Standards by a group of eight of the leading silver-producing companies of the United States. Naturally, the principal source of information has been the papers on various aspects of silver which have appeared in the scientific and technical journals. Much help has been received, however, from the research laboratories of a large number of commercial, chemical, and metallurgical concerns and from correspondents both in this country and abroad.

Examination of the material, which had been collected during the survey, showed that it could be conveniently arranged in three parts. The first part deals with the physical, chemical, and technologic properties of the pure metal. The second part presents the available data concerning the alloys of silver with a number of the commercially important base metals. The final part deals with the industrial uses of silver, which fall mainly into three groups—electrical, chemical, and bactericidal.

Lyman J. Briggs, *Director.*

I. INTRODUCTION

Most of the chemical elements are outstanding because of the degree in which they possess certain particular properties. In this respect, silver is no exception; it may, in fact, be considered as one of the more remarkable metals. It is ordinarily grouped with the noble metals. While its resistance to the more corrosive agents is somewhat inferior to that of other members of this group, its resistance to oxidation is excellent. Its comparatively low melting point and general ease of working have made it a very useful metal.

Silver has the highest-known electrical and thermal conductivities, though for a conductor of given weight per unit length, it is inferior to copper in these respects.

In the molten state, silver is capable of absorbing selectively from the atmosphere an amount of oxygen, which, at atmospheric pressure, is many times its own volume. Upon cooling to the solid state, practically all of this gas is released. The reaction of the halogen salts of silver to the action of light has made it of fundamental importance in the field of photography. In the chemical manufacturing field, the resistance of this metal to alkalies and to organic acids has caused it to be employed in the manufacturing of many food and chemical products.

Its bactericidal properties are also outstanding. Water which contains as little as 0.020 mg per liter of silver will kill certain pathogenic bacteria which are introduced therein. Various compounds of silver are used in pharmaceutical preparations. Silver, unlike lead, mercury, and a number of other metals, is not poisonous when taken internally. Continued internal use of considerable amounts may cause a permanent darkening of the skin, with no other apparent result.

II. PROPERTIES OF SILVER

1. PHYSICAL PROPERTIES

a. ATOMIC PROPERTIES

(1) *Atomic Number.*—The position of silver in the periodic arrangement of the elements is in group I and at the beginning of the last half of the second long period. Its atomic number is 47. The 47 electrons are contained in the first five quantum levels and are distributed as follows: K, 2; L, 8; M, 18; N, 18; O, 1. According to Grimm and Sommerfeld [15],[1] the arrangement of 18 electrons in the fourth quantum level is one of great stability in the second long period of the elements. This statement agrees with the chemical behavior of silver, which almost invariably gives a univalent and colorless ion. The arrangement of the 18 electrons in quantum level 4 is too stable to be broken by chemical means.

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[1] The numbers in brackets appearing throughout the text relate to the numbered selected references in the list at the end of each section.

(2) *Atomic weight.*—The value accepted by the Committee on Atomic Weights of the International Union of Chemistry [4] for the atomic weight of silver is 107.880. G. P. Baxter and Charles H. Greene [6] found 107.880, based on the ratio of ammonia to silver.

(3) *Isotopes.*—Aston [16] has reported two isotopes of silver with masses of 107 and 109, the former being predominant, a fact which is in accord with the chemically determined atomic weight of silver.

(4) *Atomic and ionic radii.*—The size of a neutral atom or an ion of silver is not constant, but depends upon its environment, its charge, the size and charge of the ion or ions with which its is combined, the crystal structure, and the type of compound formed.

For the above reasons, an accurate value of the atomic or ionic radius of silver which is applicable to all conditions, cannot be given. Values ranging between 1.40 and 1.77 A have been reported for the atomic radius of silver. Bragg [22] from crystal measurements on metallic silver gives 1.77 A for the radius. Barth and Lunde [13] found 1.44 A, and Huggins [17], following Bragg's procedure, calculated the radius to be 1.60 A. For the ionic radius, Pauling [12], from calculations based partly on theoretical grounds, obtained a value of 1.26 A, while Goldschmidt [14], from calculations based on crystal data of AgF, found 1.13 A.

(5) *Density.* (a) *Room temperature.*—The density of silver depends to some extent upon its mechanical state. For well-annealed material, either cast or worked, the measurements of Tomlinson [30], Bridgman [18], Honda and Shimizu [7], Lowry and Parker [26], Stahl [21], and others indicate that the density is very close to 10.49 g/cm^3 at room temperature. The density of cold-worked silver is distinctly less. Tomlinson states that hard-drawn silver wire has a density of 10.434 compared with 10.491 for annealed material. Honda and Shimizu give 10.44 g/cm^3 as the density of silver which has been hammered.

(b) *High temperature.*—Most of the measurements of the density of silver at high temperatures have been concerned with the molten material. A few values below the melting point as published by Sauerwald [20] are:

700° C	9.89 g/cm^3.
800° C	9.80 g/cm^3.
900° C	9.72 g/cm^3.

Sauerwald's value of the density at room temperature appears somewhat low but, as he points out, his values at higher temperatures agree fairly well with those calculated from expansion data. His data for molten material also appear to agree fairly well with the results of other observers.

Table 1 has been compiled from data published by Matuyama [10], Sauerwald [20], and Jouniaux [9], whose results agree rather well.

TABLE 1.—*Density of molten silver at various temperatures*

Temperature	Density	Observer	Temperature	Density	Observer
°C	g/cm^3		°C	g/cm^3	
[a] 960	9.30	Matuyama [10].	1,092	9.20	Jouniaux [9].
976	9.285	Do.	1,145	9.15	Do.
1,000	9.259	Do.	1,195	9.10	Do.
1,043	9.210	Do.	1,250	9.05	Do.
1,070	9.188	Do.	1,302	9.00	Do.
1.094	9.17	Sauerwald [20].			

[a] Extrapolated.

(6) *Space Lattice.*—A considerable number of determinations of the crystal structure of silver have been made. These agree in stating that the metal has the face-centered cubic lattice, and the agreement between values given for the parameter is rather satisfactory.

In summarizing the results published previous to 1931, Wyckoff [8] gave a lattice parameter of 4.0776 A, with the last figure in doubt. Masing [1], in the Handbuch der Metallphysik, gives 4.078 A. Among later investigators, Megaw [5] gives the value 4.0774 A for silver powder on the basis that her copper target had the wave lengths $K\alpha_1=1.537395$ and $K\alpha_2=1.541232$ A. Owen and Yates [2] arrived at the result 4.0772 at 15° C, assuming that the radiation from their nickel target had the wave lengths $K\alpha_1=1.65450$ and $K\alpha_2=1.65835$ A. It seems probable, from the data presented, that the lattice parameter of silver may be safely stated to be between 4.077 and 4.078 A.

(7) *Allotropy.*—A number of investigators have stated, on various grounds, that silver has a number of allotropic forms, as many as four having been reported. Allard [11], for example, reported finding lines in his X-ray spectrograms which indicated a noncubic form. His silver was obtained by precipitation from a silver nitrate solution by copper. Kanecke [25] reported a change of form occurring between 118 and 122° C, while others [24, 27, 28, 29] have reported allotropic modifications based on differences such as color.

It appears, however, that the evidence for an allotropic change where other factors can be completely eliminated is entirely lacking. The results of various experimenters studying specific heat have not shown any indication of such change and this fact has been commented upon by Wüst, Meuthen, and Durrer [23], and in the higher temperature ranges by Jaeger, Rosenbohm, and Veenstra [3]. The X-ray data of Owen and Yates [2] for temperatures between normal room temperatures and 600° C give no indication of such a change. It seems logical to conclude that silver which has been completely purified and reduced to the solid state will show no such effect.

(8) *Selected References:*

[1] G. Masing. Handbuch der Metallphysik, **1,** pt. I, p. 43. (Leipzig, 1935).
[2] E. A. Owen and E. L. Yates. *The thermal expansion of the crystal lattices of silver, platinum, and zinc.* Phil. Mag. **17,** 113–131 (1934).
[3] F. M. Jaeger, E. Rosenbohm, and W. A. Veenstra. *Variability of specific heat of fused and solidified silver.* Proc. K. Akad. Wetenschappen. Amsterdam **36,** 291–298 (1933).
[4] G. P. Baxter, Mme. M. Curie, O. Hönigschmid, P. LeBeau, and R. J. Meyer. *Fifth report of the committee on atomic weights of the international union of chemistry.* J. Am. Chem. Soc. **57,** 787 (1935).
[5] Helen Dick Megaw. *Lattice dimensions in copper-silver alloys.* Phil. Mag. (7), **14,** 130–142 (1932).
[6] G. P. Baxter and Charles H. Greene. *The atomic weights of nitrogen and silver: I. The ratio of ammonia to silver.* J. Am. Chem. Soc. **53,** 604 (1931).
[7] Kotaro Honda and Yosomatsu Shimizu. *The effect of cold-working on the magnetic susceptibility of metals.* Sci. Rep. Tohoku Imp. Univ. **20,** 460–488 (1931).
[8] R. W. G. Wyckoff. *The structure of crystals.* (The Chemical Catalog Co., Inc., New York, 1931.)
[9] A. Jouniaux. *Sur les variations avec la temperature de la densité et du poids moléculaire de l'argent fondu.* Bul. Soc. Chim. [4] **47,** 528–531 (1930).

[10] Yosiharu Matuyama. *On a further measurement of the density of molten metals and alloys.* Sci. Rep. Tohoku. Imp. Univ. **18,** 737–744 (1929).

[11] G. Allard. *Sur un etat allotropique de l'argent.* Compt. Rend. **187,** 223 (1928).

[12] L. Pauling. *The sizes of ions and the structure of ionic crystals.* J. Am. Chem. Soc. **49,** 765 (1927).

[13] Tom Barth and Gulbrand Lunde. *X-ray investigations on the platinum metals, silver, and gold.* Norsk Geol. Tids. **8,** 258–269 (1926).

[14] V. M. Goldschmidt. *Geochemische Verteilungsgesetze der Elemente:* VII. Skrifter Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Klasse **2,** 19 (1926).

[15] H. G. Grimm and A. Sommerfeld. *Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit den chemischen Valenzzahlen.* Z. Physik **36,** 36 (1926).

[16] F. W. Aston. Mass Spectra and Isotopes, p. 113. (Edward Arnold & Co., London, 1933.)

[17] M. L. Huggins. *Atomic radii.* Phys. Rev. **21,** 205 (1923).

[18] P. W. Bridgman. *The compressibility of thirty metals as a function of pressure and temperature.* Proc. Am. Acad. Arts Sci. **58,** 166–242 (1922–23).

[19] F. Sauerwald. *Dichtemessungen von Metallen und Legierungen bei hohen Temperaturen mit besonderer Berücksichtigung des flüssigen Zustands.* Z. Metallkunde **14,** 457–461 (1922).

[20] W. Stahl. *Zur Bestimmung der Dichte des Silbers.* *Metall und Erz.* **19,** 213–214. (1922.)

[21] W. L. Bragg. *Arrangement of atoms in crystals.* Phil. Mag. **40,** 169 (1920).

[22] F. Wüst, A. Meuthen, and R. Durrer. *Die Temperatur-Wärmeinhaltskurven der technisch wichtigen Metalle.* Forsch. Gebeite Ingenieur-w. **204,** P45 (1918). See also abstract in Z. Instrk. **39,** 294–296 (1919).

[23] Helderman. *The allotropy of silver.* J. Inst. Metals **16,** 84 (1917).

[24] Ernst Janecke. *Die Umwandlungen der Metalle Zinn, Zink, Wismut, Kadmium, Kupfer, Silber, Blei, und Antimon bestimmt mit dem neuen elektrisch heizbaren Druckapparat.* Z. phys. Chem. **90,** 313–340 (1915).

[25] Thomas Martin Lowry and Reginald George Parker. *The properties of cold-worked metals: I. The density of metallic filings.* J. Chem. Soc. **107,** 1005–1018 (1915).

[26] F. E. Gallagher. *Allotropic silver and its color.* J. Phys. Chem. **10,** 701 (1906).

[27] J. C. Blake. *The colors of allotropic silver.* Am. J. Sci. **16,** 282 (1903).

[28] M. C. Lea. *On allotropic silver.* Phil. Mag. **31,** 320; **32,** 337 (1891).

[29] Herbert Tomlinson. *The influence of stress and strain on the action of physical forces.* Trans. Roy. Soc., (London) (A)**174,** 1–172 (1883).

b. MECHANICAL PROPERTIES

(1) *Elastic Properties.* (a) *Young's Modulus.*—The published values for Young's modulus show considerable variation. Tomlinson [20], on measurements on both annealed and hard-drawn silver, obtained 7.28×10^{11} dynes/cm^2 (converted from Tomlinson's value, g assumed$=980$) for the first and for the latter 7.49×10^{11} dynes/cm^2. By a cantilever flexure method, Andrews [8] obtained 7.28×10^{11} for a thin wire for which the heat treatment was not reported. Gruneisen [17] reported the dynamic Young's modulus to be 7.89×10^{11} dynes/cm^2 (calculated from Gruneisen's value, g assumed$=980$), but nothing was reported as to heat treatment of the pieces tested.

As shown by Andrews [8], the value of Young's modulus decreases with increase of temperature of the specimen. The change in modulus is shown in table 2, reproduced from data presented by Andrews.

TABLE 2.—*Change of Young's modulus with temperature* [*8*]

Temperature	Modulus (Dynes/cm²)	Remarks	Temperature	Modulus (Dynes/cm²)	Remarks
°C	$\times 10^{11}$		°C	$\times 10^{11}$	
30	7.28		448	5.56	
127	7.03		500	5.22	
195	6.95		560	4.22	Slight viscous flow.
260	6.52		619	3.40	
324	6.39		680	2.81	Considerable flow.
388	6.21				

(b) *Modulus of Rigidity* (*Torsion*).—Measurements by Tomlinson [20] of the modulus of rigidity by the torsion pendulum method, yielded 2.66×10^{11} dynes/cm² for annealed silver and 2.69×10^{11} for hard-drawn material. Results obtained by Horton [18] and Kikuta [15] on annealed samples agree very closely with those of Tomlinson, whereas Gruneisen [17] obtained a somewhat higher value.

As would be expected, this modulus also decreases with rise in temperature. Tomlinson [19] observed a decrease of about 3.9 percent and Horton [18], a change from 2.67 to 2.56×10^{11} dynes/cm² in going from 15 to 99° C. Both observed a considerable increase in the logarithmic decrement with increase of temperature. According to Tomlinson, an increase of 177 percent resulted from the temperature increase, 0 to 100° C. A more extended investigation of the variation in torsion properties with temperature was carried out by Kikuta [15], table 3.

TABLE 3.—*Change in torsion properties of silver wire with temperature* [*15*]

[Length 20.4 cm, diameter 0.503 mm]

Temperature	Modulus of rigidity (Dynes/cm²)	Logarithmic decrement	Temperature	Modulus of rigidity (Dynes/cm²)	Logarithmic decrement
°C	$\times 10^{10}$		°C	$\times 10^{10}$	
27	2.68	0.0041	457	1.93	0.0823
130	2.60	.0175	526	1.80	.1028
189	2.48	.0285	590	1.56	.1278
255	2.40	.0323	655	1.42	.1513
283	2.31	.0324	705	1.26	.1803
327	2.25	.0358	755	1.11	.2071
399	2.14	.0557	811	1.04	.2290

Kikuta's data for hard-drawn wire, 0.465 mm diameter, differ considerably from the values given in table 3 for annealed metal in that many of the values for the modulus are higher than the corresponding values for annealed metal and the values for logarithmic decrement are quite uniformly much lower.

(c) *Bulk Modulus*.—Both Tomlinson [20] and Gruneisen [17] calculated the bulk modulus κ from the formula $\kappa=\frac{1}{3}E/1-2\sigma$, where E is Young's modulus and σ represents Poisson's ratio. Bridgman [13] measured the linear compressibility of annealed silver directly and found that up to pressures of $\rho=12{,}000$ kg/cm², the data could be expressed by the formula below:

$$\text{At } 30^\circ\text{ C, } \frac{\Delta V}{V}=-10^{-7}\,(9.87-4.4\times10^{-5}p)\,p.$$

$$\text{At } 70^\circ\text{ C, } \frac{\Delta V}{V}=-10^{-7}\,(10.04-4.5\times10^{-5}p)\,p.$$

From the formula, the initial compressibility at 30° C is 9.87×10^{-7} cm^2kg^{-1}. The values for cubic compressibility given in International Critical Tables (volume 3, page 46) are, for 30° C, 10.20×10^{-7} for $p=0$ and 9.11×10^{-7} for $p=11{,}600$ atmosphere. For higher pressures, the compressibility decreases. The reciprocal of the initial compressibility at 30° C gives a value for bulk modulus of 9.93×10^{11} dynes/cm^2. This result lies between those of Tomlinson and of Gruneisen.

(2) *Tensile Properties.*—Data on the tensile properties of silver show marked lack of agreement. One of the most careful determinations of the ultimate tensile strength of annealed silver has been carried out by Saeftel and Sachs [10], who reported, for the mean of six determinations, 18,200 lb/in.^{2}, obtained with samples, 5 mm in diameter and 20 mm long, which had been annealed in vacuo at 600° C. Price [16] reported a value a little larger than this. Glocker, Kaupp, and Widmann [9] found about the same strength for 99.7-percent silver annealed in air at 900° C, but other values, some of which are several thousand pounds per square inch higher, have been published for supposedly fully annealed material. Values representative of ordinary commercial treatments, as furnished by Handy and Harman, are presented in table 4 from an article by Rogers [1]. This material probably contained about 99.9 percent of silver.

TABLE 4.—*Effect of annealing on the properties of fine silver sheet, 0.032-inch gage, reduced 50 percent in thickness after previous annealing* [1]

	Temperature, in degrees Fahrenheit, of 30-minute anneal							
	As rolled	200°	400°	600°	800°	1,000°	1,200°	1,400°
Scleroscope reading	27	27	11	9	8	7	6	6
Rockwell no. 1/16-inch ball, 60-kg load	91.0	91.0	49.0	39.0	33.0	30.0	11.5	9.8
Cupping depth, inches	--------	0.140	0.301	0.328	0.332	0.330	0.331	0.327
Test load, pounds	--------	750	1,000	1,000	1,000	950	1,000	1,000
Yield strength, lb/in.^{2}	44,300	--------	16,000	13,200	11,500	10,600	7,900	7,800
Ultimate tensile strength, lb/in.^{2}	54,300	--------	26,500	25,000	25,000	24,100	22,900	22,500
Elongation, % in 2 in	2.4	--------	43.7	51.6	51.5	50.8	53.9	48.4

A rough approximation to the yield strength was obtained by taking it as equal to the tensile stress at which dividers set for 2 inches pulled out of the punch marks. These values are also given in table 4.

Shoji's [7] measurements on the rate of elongation of a wire of 0.71 mm diameter and 15.7 cm length which had been annealed in hydrogen at 800° C are summarized in figure 1. The rate of elongation immediately following the application of the load is plotted against the applied stress. It is evident from the stress at which plastic flow starts that the yield strength of annealed silver is very low. Shoji quotes Tammann's figure of 1,220 lb/in.^{2} (86 kg/cm^2) for this property, but apparently made no determination himself.

Using samples of silver wire annealed in vacuo at 600° C, Saeftel and Sachs [10] obtained values for elongation, 20-mm gage length ($12.5 \times \sqrt{\text{cross-sectional area}}$) and reduction of area as follows:

Total elongation	48%
Elongation previous to constriction	42%
Uniform (general) reduction of area (before constriction)	29%
Total reduction of area (including constriction)	91%

Ingall [11] reported a general reduction of about 33 percent and a total reduction of about 88 percent, which are in good agreement with the results of Saeftel and Sachs. Values for commercial material annealed for 30 minute periods are shown in table 4.

(3) *Poisson's Ratio.*—Tomlinson [20] observed the ratio of the lateral contraction to the longitudinal extension in tension for specimens of silver and obtained, for annealed material, a value of 0.369 and, for the hard-drawn, 0.392. Grüneisen's [17] determination by the static method led to a value of 0.379 and by calculations based on dynamically measured quantities he obtained a value of 0.369.

(4) *Compression Properties.*—Coe [12] determined the changes occurring during compression for hard-drawn silver and also for silver which had been annealed for 30 minutes at 800° C. He plotted load on the compression specimens against the corresponding decrease in length of the specimen and found that the resulting curves showed a peak, representing the maximum rate of flow. The stress immediately preceding this maximum rate has been designated by Coe as the "stress giving critical plasticity." His data, on samples 1 inch long by ½ inch diameter, are summarized in table 5.

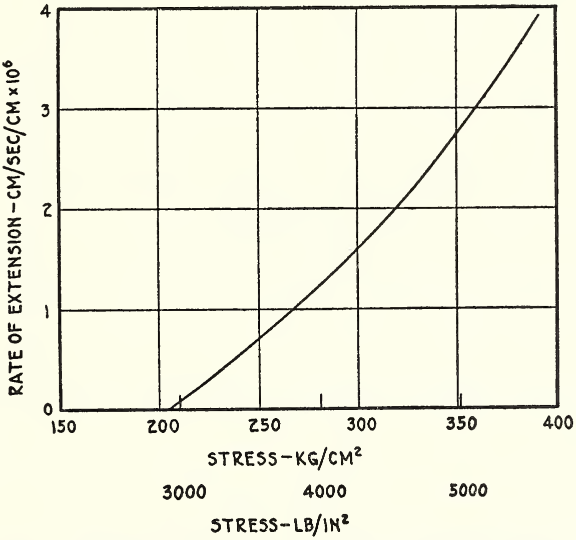

FIGURE 1.—*Rate of initial elongation of annealed silver wire under tensile stress, (Shoji [7]).*

TABLE 5.—*Properties of silver when compressed [12]*

Condition	Elastic limit	Stress giving [1] critical plasticity	Reduction in length at stress giving critical plasticity	Density	Brinell number (10-mm, 1,000-kg, 60-sec)
	lb/in.^{2}	lb/in.^{2}	%	g/cm^3	
Drawn	15, 700	40, 300	21. 6	10. 510	72. 5
Annealed	600	42, 500	31. 1	10. 506	29. 0

[1] Stress for maximum decrease in length for a unit increment of load.

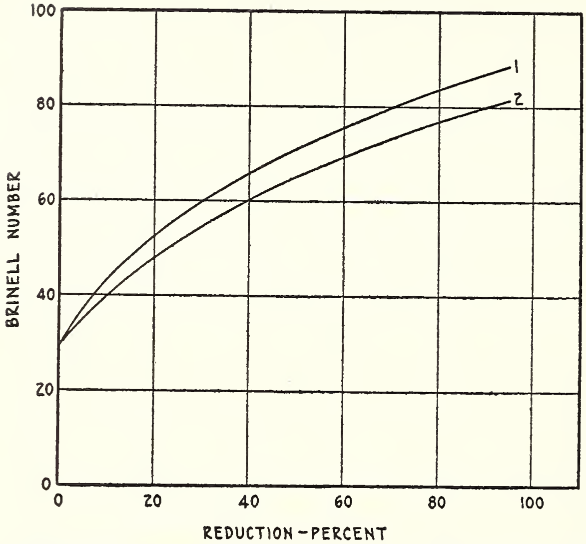

Figure 2.—*Relation between the Brinell number (5-mm 250-kg) of silver and the degree of reduction (Holzmann [4]).*

Curve 1. Rolled in one direction. Curve 2. Rolled in different directions.

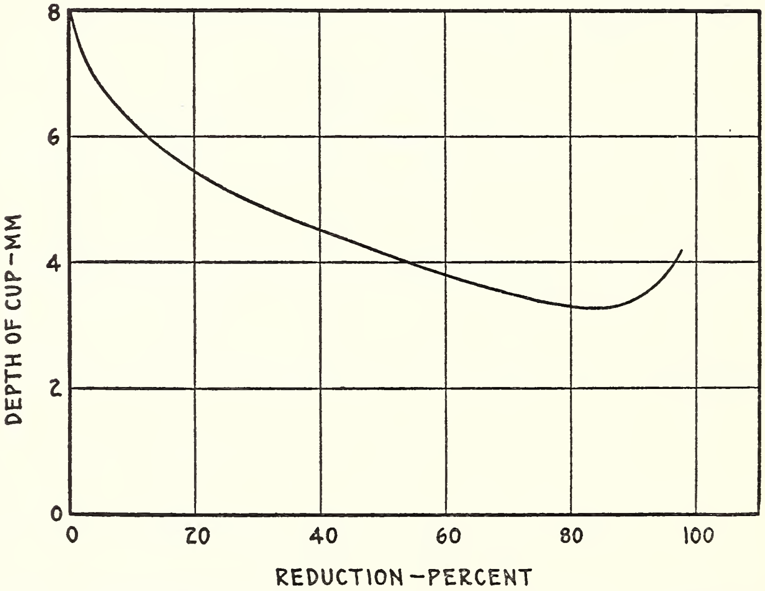

Figure 3.—*The cold-deformability of silver by cupping test as a function of the degree of reduction by rolling in one direction (Holzmann [4]).*

(5) *Hardness.*—The resistance to indentation of silver has been determined by a number of observers. Kurnakow and Achnaserow [14] reported a Brinell number of 27.0 for slowly cooled, annealed silver and 24.4 for rapidly cooled material. Tammann and Dreyer [3] have given a Brinell number of about 32 for material annealed for a short period at 300° C. Coe (table 5) obtained a value of 29 for annealed silver. Other experimenters, for example, Glocker, Kaupp, and Widmann [9], have reported considerably higher values. Brinell readings on silver in the annealed condition and also after being rolled to various reductions are shown in figure 2, based on data of Holzmann [4]. Data on the sceleroscope and Rockwell (60 kg, 1/16-inch ball) readings of silver after various annealing treatments are given in table 4.

(6) *Miscellaneous Properties.*—Data on the depth of impression in cupping tests for material rolled through different reductions are given in figure 3 from Holzmann [4]. The decrease of depth of impression with reduction in thickness in the early rolling is about as expected. The reason for the minimum which occurs is not clear.

Shaw and Leavey [6] studied the friction of silver against itself and other metals in vacuo. At room temperature, the coefficient of friction of silver against itself was about 2.6, which is relatively high for the metals investigated by these authors. The coefficient of friction of silver against iron was about 0.3, the lowest of any combination tested.

In an investigation of nonabrasive wear, which occurs in polishing metals, Hudson [2] found that silver plating was less resistant than platings of palladium, platinum, or nickel. Another interesting investigation worthy of mention is that of Lonsdale [5] on the change of dimensions of silver and other wires subjected to torsion.

(7) *Selected References:*

[1] B. A. Rogers. *Silver may answer your corrosion problem.* Chem Met. Eng. **41,** 631–633 (934).

[2] O. F. Hudson. *Wear in the polishing of plated and other surfaces.* J. Inst. Met. **52,** 101–106 (1933).

[3] G. Tammann and K. L. Dreyer. *Die Erholung des elektrische Widerstandes und der Harte von Kupfer, Silber, und Gold sowie von Platin und Palladium von den Folgen der Kaltearbeitung.* Ann. Physik. (5) **16,** 111–118 (1933).

[4] Hermann Holzmann. Festschrift zum Fünfzigjährigenbestehen der Platinschmelze. (Hanau, G. M. Alberti's Hofbuchhandlung, 121–148, 1931).

[5] Thomas Lonsdale. *Changes in the dimensions of metallic wires produced by torsion: II. Silver, gold, aluminum, and nickel.* Phil. Mag. (7) **11,** 1169–1187 (1931).

[6] P. E. Shaw and E. W. Leavey. *Friction of dry solids in vacuo.* Phil. Mag. (7) **10,** 809–822 (1930).

[7] Hikoroku Shoji. *On the plasticity of metals. I.* Sci. Pap. Inst. Phys. Chem. Research, (Tokyo) **4,** 189–201 (1926).

[8] James P. Andrews. *The variation of Young's modulus at high temperatures.* Proc. Phys. Soc. (London) **37,** 169–177 (1925).

[9] R. Glocker, E. Kaupp, and H. Widmann. *Untersuchung über die Rekristallisation gewalzter Silberbleche.* Z. Metallkunde **17,** 353–357 (1925).

[10] F. Saeftel and G. Sachs. *Festigkeitseigenschaften und Struktur einiger begrenzter Mischkristallreihen.* Z. Metallkunde **17,** 155–161 (1925).

[11] Douglas H. Ingall. *Relationship between tensile strength and cold-work in some pure metals and single solid solutions.* J. Inst. Met. **32,** 41–64 (1924).

[12] H. I. Coe. *The behavior of metals under compressive stresses.* J. Inst. Met. **30,** 309–324 (1923).

[13] P. W. Bridgman. *The compressibility of thirty metals as a function of pressure and temperature.* Am. Acad. Arts Sci. **58,** 166–242 (1922–23).

[14] N. S. Kurnakow and A. N. Achnaserow. *Über den Einfluss der Abkühlungsgeschwindigkeit auf die Härte und Mikrostruktur der eutektischen Gemische.* Z. anorg. allgem. Chem. **125,** 185–206 (1922).

[15] Tario Kikuta. *On the change of rigidity and logarithmic decrement in different metals and alloys at high temperatures.* Sci. Rep. Tohoku Imp. Univ. **10,** 139–154 (1921).

[16] Weston A. Price. *Metallurgical studies.* J. Nat. Dental Assn. **4,** 171–175 (1917).

[17] E. Grüneisen. *Die elastische Konstanten der Metalle bei kleinen Deformationen.* Ann. Physik (4) **25,** 825–851 (1908).

[18] Frank Horton. *The effects of changes of temperature on the modulus of torsional rigidity of metal wires.* Trans. Roy. Soc. (London) (A) **204,** 1–55 (1905).

[19] Herbert Tomlinson. *The influence of stress and strain on the physical properties of matter. I. Elasticity (continued). The effect of change on temperature on the internal friction and torsional elasticity of metals.* Proc. Roy. Soc. **60,** 343–345 (1886).

[20] Herbert Tomlinson. *The influence of stress and strain on the action of physical forces.* Trans. Roy. Soc. (London) (A) **174,** 1–172 (1883).

c. THERMAL PROPERTIES

(1) *Change of State (Melting Point, Boiling Point, and Vapor Pressure).*—As the result of a number of investigations, the value accepted for the freezing point of silver is 960.5° C. The freezing point of silver defined as 960.5° C is one of the basic fixed points of the International Temperature Scale [14].

On account of the high solubility of oxygen in silver, special precautions must be taken when determining its melting point. After an extensive investigation of this question Roeser and Dahl [4] concluded that when a graphite crucible and a graphite cover are employed, the melting point obtained is the same as that measured in a vacuum, within the limits of error of the experiment (0.05° C). They also investigated the depression of the freezing point resulting from the passage of air and also of oxygen through the molten bath. The maximum depression obtained in these two cases amounted to 11.2 and 22.6° C, respectively. They, therefore, concluded that 11.2 and 22.6° C, represent the depression of the freezing point of silver when saturated with oxygen at the prevailing pressures of approximately 149 and 760 mm of Hg, respectively.

Allen [5] determined the melting point of silver under mixtures of dry oxygen and nitrogen at atmospheric pressure, and obtained results, table 6, which agree fairly well with those of Roeser and Dahl [4].

TABLE 6.—*Melting point of silver under various pressures of oxygen* [*5*]

Oxygen content of mixture	Melting point
Percent	°C
7.8	958
20.6	951
64.0	942
97.4	938

Silver has an appreciable vapor pressure even in the solid state. Rosenhain and Ewen [28], who measured the loss in weight of small pieces of silver after exposure for various periods in vacuo at 870° C, concluded that fine-grained material lost weight more rapidly than coarse-grained. For example, after a 5-hour exposure a fine-grained strip of silver lost 0.0115 g/cm^2, whereas a coarse-grained one lost only 0.0093 g/cm^2.

Piersol [19] measured the loss of weight of silver filaments at various temperatures and from the data computed the vapor pressure by use of a formula. He then substituted the values of vapor pressure in Hildebrandt's vapor-pressure equation

$$\log p = \frac{0.3140\ C}{T} + 7.85 + \log C,$$

where p is the pressure and T is the temperature, and calculated that $C = 3.95$.

The vapor pressure of silver in the liquid state is somewhat less satisfactorily determined, although the data of Greenwood [29] and of Ruff and Bergdahl [23] agree rather well, as will be seen in table 7, which also includes the data of von Wartenberg [27] taken at lower temperatures.

TABLE 7.—*Vapor pressure of liquid silver at various temperatures* [*23, 27, 29*]

Temperature	Vapor pressure	Observer	Temperature	Vapor pressure	Observer
°C	mm of Hg		°C	mm of Hg	
1,178	0.14	Von Wartenberg [27].	1,758	200	Ruff and Bergdahl [23].
1,316	.81	Do.	1,785	265	Greenwood [29].
1,435	3.9	Do.	1,810	300	Ruff and Bergdahl [23].
1,660	102	Ruff and Bergdahl [23].	1,940	744	Do.
1,660	105	Greenwood [29].	1,955	760	Greenwood [29].
1,680	116	Ruff and Bergdahl [23].			

Greenwood [29] used visual observation to determine the boiling point, while Ruff and Bergdahl [23] deduced their results from the shape of the curve showing the relation between loss of silver and temperature.

The results in table 7 show the good agreement between the determinations of Greenwood and of Ruff and Bergdahl for the boiling point of silver. Greenwood obtained a value of 1,955° C, whereas the latter experimenters gave 1,950° C. It should be noted, however, that when using nitrogen instead of hydrogen over the surface of the metal, the melting point determined by Greenwood was at least 50° C higher. Von Wartenberg [27] argued strongly, on the basis of Greenwood's data with hydrogen and nitrogen and the extrapolation of his own data, that the boiling point of silver must be in the vicinity of 2,100° C. Under the circumstances, it appears inadvisable to set a definite figure for the boiling point of silver.

(2) *Thermal Conductivity.*—The thermal conductivity of silver has been measured by Jaeger and Diesselhorst [33], Lees [31], Bailey [8], Kannuluik [3], and others. Despite the difficulty of measuring this property, the results for room temperature obtained by the different observers agree rather well. The most recent determination has been made by Kannuluik [3], who obtained the value 0.0999 $\frac{\text{cal}}{\text{sec cm}^2\ ^\circ\text{C/cm}}$ at 0° C on material annealed at 550° C. Other figures for the con-

ductivity include 1.006 at 18° C by Jaeger and Diesselhorst, and 0.981 at 0° C obtained by Lees [31] and by Kannuluik [10] in an earlier experiment.

Table 8, from Kannuluik [3], indicates that the thermal conductivity of silver changes only moderately with temperature and very little with previous heat treatment of the metal.

Table 8.—*Thermal conductivity of silver from —183 to 100° C [3]*

Temperature	Conductivity before annealing	Conductivity after annealing	Temperature	Conductivity before annealing	Conductivity after annealing
°C	$\frac{Cal}{sec\ cm^2\ °C/cm}$	$\frac{Cal}{sec\ cm^2\ °C/cm}$	°C	$\frac{Cal}{sec\ cm^2\ °C/cm}$	$\frac{Cal}{sec\ cm^2\ °C/cm}$
−183	1.015	1.018	0	0.999	0.999
−78.5	1.004	1.005	100	.996	.998

The condition before annealing was not stated, however. Kannuluik's [3] data do not confirm the maximum in thermal conductivity reported by Lees [31] and, furthermore, they show a smaller drop in conductivity between 0 and 100° C than was observed by Jaeger and Diesselhorst [33], who reported a decrease of about 0.009 with increase of temperature from 18 to 100° C. Bailey [8] also reported a more rapid falling off than was found by Kannuluik [3]. Bailey's [8] results on the thermal conductivity of silver at temperatures up to 550° C are given in table 9.

Table 9.—*Thermal conductivity of silver from 100 to 550° C [8]*

Temperature	Thermal conductivity	Temperature	Thermal conductivity
°C.	$\frac{Cal}{sec\ cm^2\ °C/cm}$	°C.	$\frac{Cal}{sec\ cm^2\ °C/cm}$
100	0.934	350	0.853
150	.917	400	.844
200	.896	450	.850
250	.880	500	.870
300	.864	550	.901

Although no comment was made by Bailey concerning the condition of the specimen previous to test, the density given, 10.47 g/cm^3, suggests a cold-worked material.

Bridgman has investigated the effect of tension [20] and of hydrostatic pressure [21] on the thermal conductivity of silver. According to his experiments, tension decreases the conductivity slightly. In tests at 30° C under pressure it was possible to obtain more precise data which showed a decrease in conductivity amounting to about 4.3 percent for a pressure of 12,000 kg/cm^2.

Brown [11] was unable to detect any change in the thermal conductivity of specimens subjected to longitudinal magnetic fields of 10,000 oersteds or to transverse fields of 8,000 oersteds. He estimated that a change larger than 0.04 percent could have been detected by his method.

(3) *Thermal Expansion.*—The results of various investigators on the linear expansion of silver in the range between 0 and 100° C agree fairly satisfactorily. The mean value in this interval is prob-

ably close to $1.910\times10^{-5}/^{\circ}C$, as based on the results of Keesom [13], who obtained 1.914×10^{-5} on silver whose purity and treatment were not stated, of Buffington and Latimer [15], who obtained 1.908×10^{-5} for the instantaneous rate at 37° C on cold-worked material which had been cast in graphite, and of Owen and Yates [1], who measured the lattice parameter of powdered silver at elevated temperatures and obtained a coefficient of 1.908×10^{-5}. Dorsey's [32] work on cast silver of density=10.43 g/cm^3 covered temperatures only up to 10° C, for which he gives a value of 1.910×10^{-5} for the instantaneous coefficient. As his values were increasing with rising temperature, the mean for the 0 to 100° C interval would be appreciably higher than the figures given, but probably not so high as those of Scheel [22], who published the value of $1.968\times10^{-5}/^{\circ}C$ for the mean coefficient of linear expansion between 0 and 100° C.

None of the authors mentioned appear to have considered possible changes, due to annealing effects, in this range of temperature.

Investigations of the expansion of silver at temperatures above 100° C have been carried out by Scheel [22] and by Owen and Yates [1]. Scheel [22] used a sample 224 mm long, the temperature of which was maintained in a bath of sodium nitrate. As a result of his investigations, he established the equation

$$\alpha_T=1.939\times10^{-5}+2.95\times10^{-9}\,T$$

for the range from 0 to 500° C. The X-ray investigations of Owen and Yates [1] led them to the expression

$$\alpha_T=1.889\times10^{-5}+3.82\times10^{-9}\,T$$

over the range from 0 to 600° C. It will be noted that for $T=0$ the equation of Owen and Yates is in better agreement with the results of other investigators.

Buffington and Latimer [15] investigated the thermal expansion of silver down to liquid-air temperatures and found that the decrease in coefficient of expansion with temperature became more rapid as low temperatures were reached, table 10.

TABLE 10.—*Linear coefficient of thermal expansion of silver at low temperature* [*15*]

Temperature	Coefficient of thermal expansion per degree centigrade	Temperature	Coefficient of thermal expansion per degree centigrade
°K	$\times10^{-5}$	°K	$\times10^{-5}$
90	1.406	210	1.785
110	1.501	240	1.823
130	1.606	270	1.864
150	1.666	298	1.896
180	1.732	310	1.908

The values of Dorsey [32], who also covered this range, are somewhat higher above 190° K and a little lower below that temperature, but the agreement is fair for data of this kind.

Keesom [13] obtained a mean value for the temperature range between −180 and −250° C of $1.037\times10^{-5}/^{\circ}C$. His work indicates that the coefficient of expansion continues to decrease with temperature, probably at an increasing rate.

(4) *Specific Heat (Atomic Heat).*—Numerous investigations of the specific heat of silver have been made. While the results are generally in fair agreement, the variation in the values of different observers is somewhat greater than can be readily accounted for by experimental errors. After a rather thorough study of the specific heat of different samples of silver, Jaeger, Rosenbohm, and Veenstra [2] concluded that the presence of oxygen was responsible for much of the variability in reported values. Their results, figure 4, show the mean specific heat over various temperatures rather than specific heat as a function of temperature. The variation, however, is approximately the same. Table 11 shows the true specific heat from 0 to 800° C as calculated from the formula

$$C_p=0.055401+0.14414\times10^{-4}\ T-0.16216\times10^{-8}\ T^2$$

given by these authors for "oxygen-free" silver.

Table 11.—*Specific heat of "Oxygen-free" silver at high temperatures [2]*

Temperature	Specific heat	Temperature	Specific heat
°C	cal/g/°C	°C	cal/g/°C
0	0.0559	500	0.0622
100	.0568	600	.0635
200	.0582	700	.0646
300	.0595	800	.0659
400	.0609		

These results may be compared with those of Magnus and Hodler [16], Schuber [26], and Jaeger, Rosenbohm, and Bottema [6] as presented in table 12, which gives both the true specific and true atomic heats.

Table 12.—*Specific heat and atomic heat of silver according to different observers*

Temperature	Magnus, Hodler [16]		Schubel [26]		Jaeger, et al. [6]	
	Specific	Atomic	Specific	Atomic	Specific	Atomic
°C	cal/g/°C	cal/g/at./°C	cal/g/°C	cal/g/at./°C	cal/g/°C	cal/g/at./°C
0	0.0560	6.047	0.0558	6.02	0.0556	6.000
100	.0568	6.129	.0563	6.08	.0571	6.167
200	.0577	6.225	.0569	6.14	.0586	6.324
400	.0598	6.460	.0596	6.43	.0621	6.609
600	.0625	6.753	.0649	7.07	.0635	6.852
800	.0658	7.102	--------	--------	.0654	7.061

The values obtained by Eastman, Williams, and Young [18] are in excellent agreement with those of Jaeger, Rosenbohm, and Bottema, table 12.

Umino [17] has stated that the specific heat of liquid silver is 0.0692 cal/g/°C for all temperatures from the melting point to 1,300° C. Accordingly, therefore, there is a considerable decrease in specific heat at the melting point, which is in agreement with the work of Wüst, Meuthen, and Durrer [24], who found a decrease in specific heat at the melting point but an increase in specific heat with increasing temperature.

On account of its theoretical interest the change of specific heat with temperature at low temperatures has been the subject of a number of investigations. The decrease of atomic heat with temperature is well illustrated by figure 5, from a paper by Eucken, Clusius, and Woitinek [9] giving their own results along with those of Griffiths and Griffiths [25], Nernst [30], and others. The specific heats can be obtained by dividing the values of atomic heat by 107 88

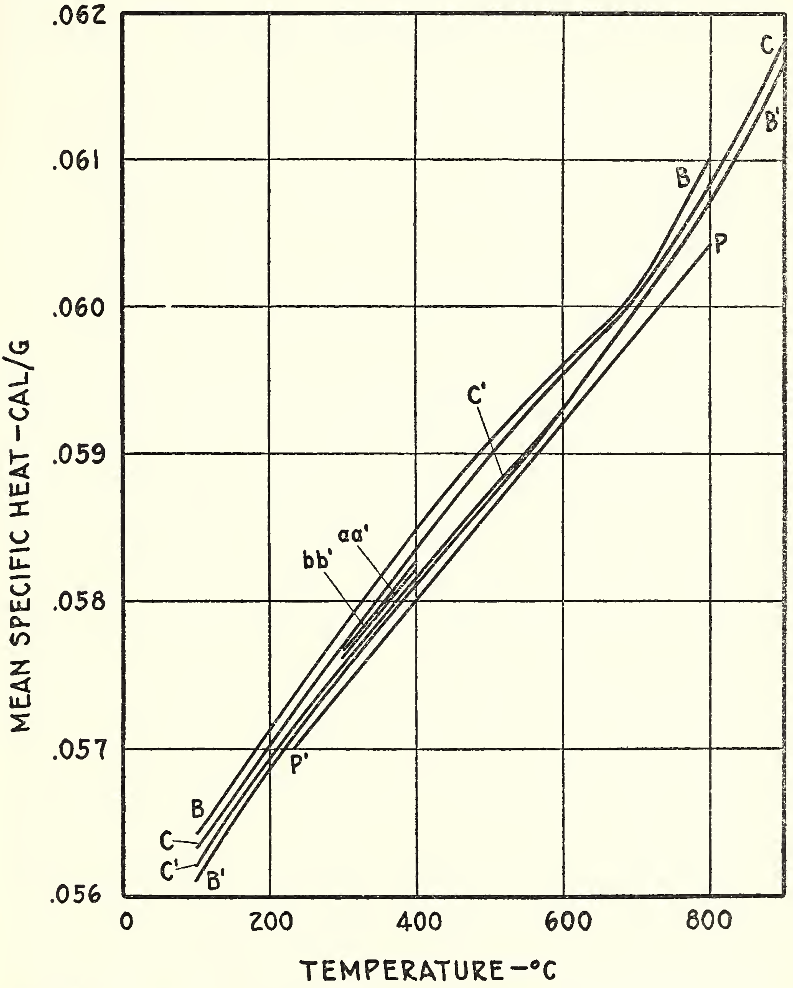

FIGURE 4.—*Variation of mean specific heat of silver with temperature (Jaeger, Rosenbohm, and Veenstra [3]).*

B. Original lump fused and solidified in air.
B'. The same lump preserved for several months.
C. Lump fused and solidified in air shortly before the determination of specific heat.
C'. The same material fused and solidified in vacuo.
aa' and bb'. Specimen B' after heating in air at 940° C for 5 and 10 hours, respectively.
P. Electrodeposited silver.

The investigation of Eucken, Clusius, and Woitinek [9] did not extend to temperatures below 11.4° K. Keesom and Kok [7], however, carried their work down to about 1.4° K with the result shown in table 13. The results of both agree well in their common range. A number of values for the atomic heat above 20° K, from Eucken, Clusius, and Woitinek [9], have been included.

Table 13.—*Atomic heat of silver at low temperatures*

Values below 20° K by [7], values above 20° K by [9]

Temperature	Atomic heat	Temperature	Atomic heat	Temperature	Atomic heat
°K	cal/g at./°C	°K	cal/g at./°C	°K	cal/g at./°C
1.35	0.000254	10	0.0475	60.5	3.452
2	.000626	12	.0830	79.2	4.236
3	.00157	14	.1336	103.1	4.850
4	.00303	16	.2020	124.2	5.156
				144.4	5.468
5	.00509	18	.2898	166.8	5.575
5.4	.00634	20	.3995	183.2	5.655
6	.00891	20.2	.398	205.3	5.754
7	.0151	39.8	2.013		

(5) *Heats of Fusion and Vaporization.*—Consideration of the results of a number of determinations of the heat of fusion of silver indicates that the value is about 25 cal/g. Since no account appears to have been taken of the absorption or evolution of oxygen, it is possible that heat effects other than those due simply to fusion are present. Umino [17] plotted the total heat of silver in both the solid and liquid states against temperature and on extrapolating both curves to the melting point of silver, obtained the result, 24.9 cal/g. Wüst, Meuthen, and Durrer [24] published a value of 26.02 cal/g, but as their values of specific heat are somewhat higher than those generally measured, it is possible that their value for the heat of fusion is also higher. Pionchon [34] in 1887 set forth 24.7 as the result of his experiments.

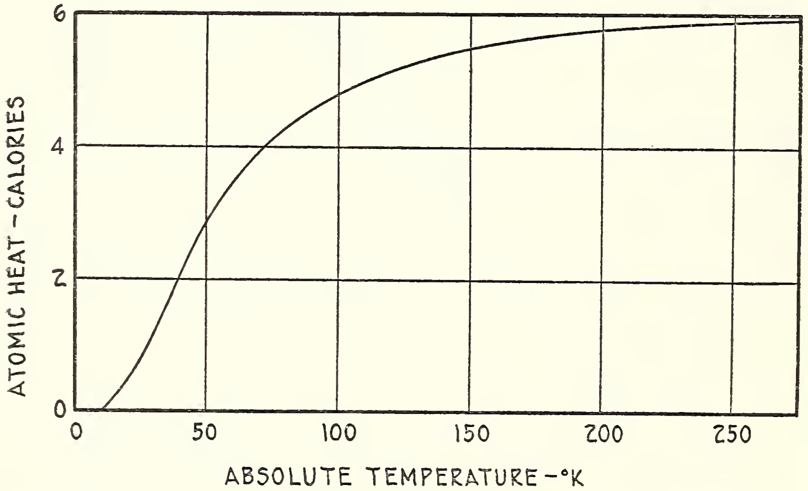

Figure 5.—*Atomic heat of silver at low temperatures* (*Eucken, Clusius and Wortinek* [*9*]).

Direct determinations of the heat of vaporization have not been made. Estimates by Greenwood [29], Von Wartenberg [27], and also by Jones, Langmuir, and Mackay [12] indicate that it is in the vicinity of 60,000 cal/g at., corresponding to 556 cal/g for boiling under 760-mm pressure. Since these estimates involve extrapolation over a considerable range in some cases, the values given should be considered as only approximate.

(6) *Selected References:*

[1] E. A. Owen and E. L. Yates. *The thermal expansion of the crystal lattices of silver, platinum, and zinc.* Phil. Mag. **17,** 113–131 (1934).

[2] F. M. Jaeger, E. Rosenbohm, and W. A. Veenstra. *Variability of specific heat of fused and solidified silver.* Proc. K. Akad. Wetenschappen Amsterdam **36,** 291–298 (1933).

[3] W. G. Kannuluik. *The thermal and electrical conductivities of several metals between −183 and 100° C.* Proc. Roy. Soc., (London) (A) **141,** 159–168 (1933).

[4] William F. Roeser and A. I. Dahl. *Conditions affecting the freezing temperature of silver.* BS J. Research **10,** 661–668 (1933) RP557.

[5] N. P. Allen. *The effect of pressure on the liberation of gases from metals (with special reference to silver and oxygen).* J. Inst. Metals **49,** 317–340 (1932).

[6] F. M. Jaeger, E. Rosenbohm, and J. A. Bottema. *The exact measurement of the specific heats of solid substances at high temperatures: VI. Metals in stabilized and non-stabilized condition: Platinum and silver.* Proc. K. Akad. Wetenschappen Amsterdam, **35,** 763–771 (1932).

[7] W. H. Keesom and J. A. Kok. *Measurements of the specific heats of silver from 1.35 to 20.3° K.* (1932). Proc. K. Akad. Wetenschappen Amsterdam, **35,** 300–306 (1932).

[8] L. C. Bailey. *The thermal conductivities of certain approximately pure metals and alloys at high temperatures.* Proc. Roy. Soc. (London) (A) **134,** 56–76 (1931).

[9] A. Eucken, K. Clusius, and H. Woitinek. *Die bildung einiger Metallhalogenide, insbesondere des bromsilbers vom standpunkt des Nernstschen Wärmesatzes.* Z. anorg. Chem. **203,** 39–56 (1931).

[10] W. G. Kannuluik. *The thermal conductivities of some metal wires.* Proc. Roy. Soc., (London) (A) **131,** 320–335 (1931).

[11] Hugh M. Brown. *Effect of magnetic fields upon thermal conductivity of iron, copper, gold, silver, and zinc.* Phys. Rev. **32,** 508–514 (1928).

[12] Howard A. Jones, Irving Langmuir, and G. M. J. Mackay. *The rates of evaporation and the vapor pressures of tungsten, molybdenum, platinum, nickel, iron, copper, and silver.* Phys. Rev. **30.** 201–214 (1927).

[13] W. H. Keesom. *Über die thermische ausdehnung regular kristallisierender Metalle bei tiefen Temperaturen.* Z. phys. Chem. **130,** 658–661 (1927).

[14] Comptes rendus des Séances de la Septième Conférence Générale des Poids et Mesures. p. 94 (1927). Also, G. K. Burgess, *The International Temperature Scale.* BS J. Research **1,** 635 (1928) RP 22.

[15] Ralph M. Buffington and Wendell M. Latimer. *The measurement of coefficients of expansion at low temperatures.* J. Am. Chem. Soc. **48,** 2305–2319 (1926).

[16] A. Magnus and A. Hodler. *Messungen der Spezifische Wärme des Silbers und des Diamanten im Gebiete hoher Temperaturen.* Ann. Physik (4) **80,** 808–822 (1926).

[17] Saburo Umino. *On the latent heat of fusion of several metals and their specific heats at high temperatures.* Sci. Rep. Tôhoku Imp. Univ. **15,** 597–617 (1926).

[18] E. D. Eastman, A. M. Williams, and T. F. Young. *The specific heats of magnesium, calcium, zinc, aluminum, and silver at high temperatures.* J. Am. Chem. Soc. **46,** 1178–1183 (1924).

[19] Robert J. Piersol. *The vapor pressure constant for silver* (Abst.) Phys. Rev. **23,** 785 (1924).

[20] P. W. Bridgman. *The effect of tension on the thermal and electrical conductivity of metals.* Proc. Am. Acad. Arts. Sci. **59,** 119–137 (1923).

[21] P. W. Bridgman. *The effect of pressure on the thermal conductivity of metals.* Proc. Am. Acad. Arts Sci. **57,** 77–127 (1922).

[22] Karl Scheel. *Über die Wärmeausdehnung einiger Stoffe. I.* Z. Physik. **5,** 167–172 (1921).

[23] Otto Ruff and Bernhard Bergdahl. *Die Messung von Dampfspannung bei sehr hohen Temperaturen nebst einiger Beobachtungen über die Löslichkeit von Kohlenstoff in Metallen.* Z. anorg. Chem. **106,** 76–94 (1919).

[24] F. Wüst, A. Meuthen, and R. Durrer. *Die Temperatur-Wärmeinhaltskurven der technisch wichtigen Metallen.* Forsch. Gebiete Ingenieurw. no. 204, 45 (1918). See abstract in Z. Instrk. **39,** 294–296 (1919).

[25] E. H. and E. Griffiths. *The capacity for heat of metals at low temperatures.* Proc. Roy. Soc. (A) **90,** 557–560 (1914).

[26] Paul Schubel. *Über die Wärmekapazität von Metallen und Metallverbindungen zwischen 18–600°.* Z. anorg. Chem. **87,** 81–119 (1914).

[27] H. von Wartenberg. *Über Metalldampfdrucke, I.* Z. Elektrochem. **19,** 482–489 (1913).

[28] Walter Rosenhain and Donald Ewen. *Intercrystalline cohesion in metals.* J. Inst. Metals **8,** 149–172 (1912).

[29] H. C. Greenwood. *The boiling points of metals.* Chem. News **104,** 31–33, 42–45 (1911).

[30] W. Nernst. *Der Energieinhalt fester Stoffe.* Ann. Physik (4), **36,** 395–440 (1911).

[31] Charles H. Lees. *The effects of temperature and pressure on the thermal conductivities of solids: part II. The effects of low temperatures on the thermal and electrical conductivities of certain approximately pure metals and alloys.* Phil. Trans. Roy. Soc. (A) **208,** 381–443 (1908).

[32] Herbert G. Dorsey. *Coefficient of linear expansion at low temperatures.* Phys. Rev. (1) **25,** 88–102 (1907).

[33] W. Jaeger and H. Diesselhorst. *Wärmeleitung, Elektricitätsleitung, Wärmekapazität und Thermokraft einiger Metalle.* Wiss. Abhandl. physik.-tech. Reichsanstalt, Berlin, **3,** 269 (1900).

[34] M. Pionchon. *Recherches calorimétriques sur les chaleurs spécifique et les changements d'état aux températures elevées.* Ann. Chem. phys. (6) **11,** 33–111 (1887).

d. ELECTRICAL PROPERTIES

(1) *Resistivity.*—(a) *Room Temperature.*—The various values of the electrical resistivity of silver in the literature differ by several percent even for material containing 99.9 percent or more of silver. One of the most careful determinations is that of Linde [4], who used silver obtained from Hilger and stated to show only a trace of calcium and no other impurities upon spectroscopic analysis. For this material, melted in vacuo and annealed in vacuo, the resistivity was found to be 1.59 microhm-cm at 20° C for an annealing temperature of 400° C, and to vary only by about 1 percent for annealing temperatures ranging from 300 to 800° C. Results obtained at the National Bureau of Standards [1] on silver, for which analysis showed less than 0.01 percent of impurities and which was melted in vacuo and annealed in vacuo, did not differ significantly from this value.

(b) *Low Temperatures.*—In presenting the data on the resistance of silver at low temperatures it is convenient to express the resistance at any temperature as a fraction of the resistance of the same specimen at 0° C. In this way corrections for changes of dimensions are avoided, and, furthermore, the data are in their most usuable form. At −78.5° C the values obtained by various observers for well annealed material of high purity agree fairly well, but below this temperature the agreement is less satisfactory. Part of the difference may be due to the sensitiveness of resistivity to change in mechanical condition particularly at low temperatures [2, 22, 10]. These data are assembled in table 14.

TABLE 14.—*Relative resistivity of silver at low temperatures*

Temperature (stated by observer)	R_t/R_0	Reference	Temperature (stated by observer)	R_t/R_0	Reference
°C					
−78	0.684	[18]	−183.6° C	[a]0.247	[24]
−78.5	.685	[2]	−192° C	.207	[18]
−78.4	.682	[5]	20.3° K	[a].0089	[24]
−182.9	.247	[5]	20.4° K	.0100	[14]
−182.8	.235	[14]	1.3° K	.0068	[14]
−183.0	.226	[2]			

[a] Contained 0.18 percent of impurities.

(c) *High Temperatures.*—For the interval between 0° C and the melting point the data may again be conveniently presented as a ratio of the resistance of a given sample at the specified temperature to its resistance at 0° C. Table 15 shows the effect of increasing temperature.

TABLE 15.—*Relative resistivity of silver at high temperatures*

Temperature	R_t/R_0	Reference	Temperature	R_t/R_0	Reference
°C			°C		
100	1.4098	[18]	500	3.19	[a][21]
200	1.8293	[18]	800	4.62	[21]
300	2.2626	[18]	900	5.14	[21]
400	2.710	[18]	960.5 (solid)	5.45	[21]
500	3.168	[18]	960.5 (liquid)	10.8	[21]

[a] Data taken from Northrup's tables or from curves in vicinity of plotted points.

Table 16 shows Northrup's [21] results for silver in the liquid state.

TABLE 16.—*Approximate resistivity of silver in the liquid state* [*21*]

Temperature	Resistivity	Temperature	Resistivity
°C	*Microhm*-cm	°C	*Microhm*-cm
960.5 (solid)	8.4	1,200	19.4
960.5	16.6	1,300	20.5
1,000	17.0	1,340	21.0
1,100	18.2		

Tsutsumi [19] and Matuyama [13] do not agree with Northrup or with each other concerning the resistivity of molten silver. The latter obtained 17.3 microhm-cm for the resistivity at the melting point, while the value obtained by the former is less than that reported by Northrup.

(d) *Effect of Impurities.*—The most complete investigation of the effect of added metals has been made by Linde [4] who used silver from Kahlbaum, apparently somewhat less pure than the metal which he secured from Hilger. His results, presented graphically, are reproduced as figures 6, 7, 8, and 9.

(e) *Effect of Annealing and Cold-Working.*—It is probable that the changes of resistance resulting upon annealing or cold-working silver are complicated by effects caused by gases which have been taken up either in melting or during annealing. A satisfactory explanation of the changes of resistance observed by Takahasi [8], Credner [22], Tammann and Straumanis [12], and Johansson and Linde [11] when annealing their specimens at different temperatures in various gases or in vacuo is not available.

Figure 10, from Tammann and Straumanis [12], shows the resistance of specimens of silver and copper wire in the cold-worked state at room temperature and the changes resulting from annealing at various temperatures in hydrogen. Some results of Credner [22] were included by these authors in this figure. Sieverts [23] measured the resistance of wires at elevated temperatures in a vacuum and then in hydrogen and observed a marked increase in the latter case beginning at approximately 620° C. Subsequent annealing in vacuo and in oxygen failed to restore the original value. According to Jellinek [6] the resistance of silver is increased 13.1 percent by exposure above 500° C to a pressure of 35 atmospheres of hydrogen.

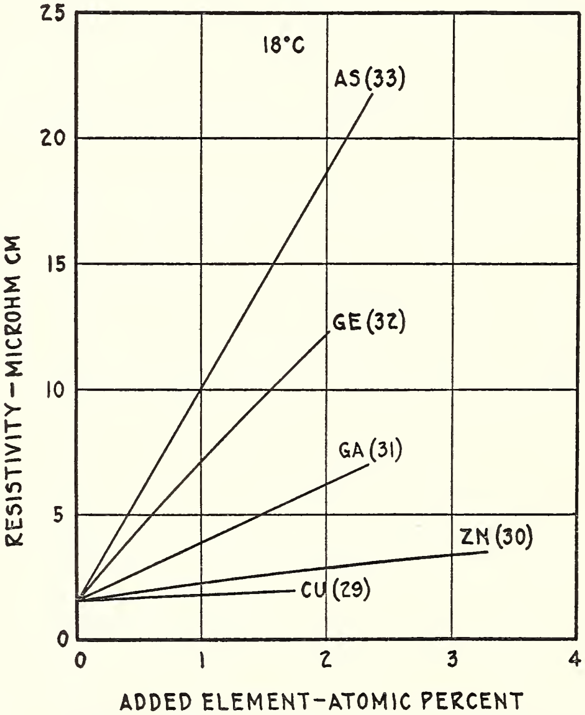

Figure 6.—*Resistivity-concentration curves for alloys of silver with the elements 29 to 33 (Linde [4]).*

The effect of cold-working annealed silver has been studied by Tammann and Dreyer [3] and Takahasi [8]. Both found an increase in resistance with increased reduction by drawing or rolling, but the curve of increase of resistance against percentage reduction of area obtained by Tammann and Dreyer is convex to the reduction axis, whereas that of Takahasi is concave. Tammann and Dreyer reported an increase of approximately 5 percent in resistance for a reduction of about 90 percent, and Takahasi, a value somewhat less.

By twisting a 2-meter length of wire 0.2 mm in diameter which had been fully annealed, Credner [22] found that for 150 turns there was

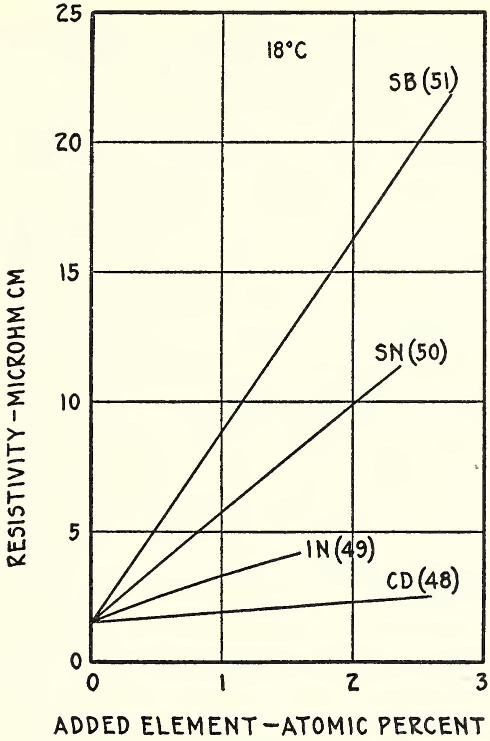

FIGURE 7.—*Resistivity-concentration curves for alloys of silver with the elements 48 to 51 (Linde [4]).*

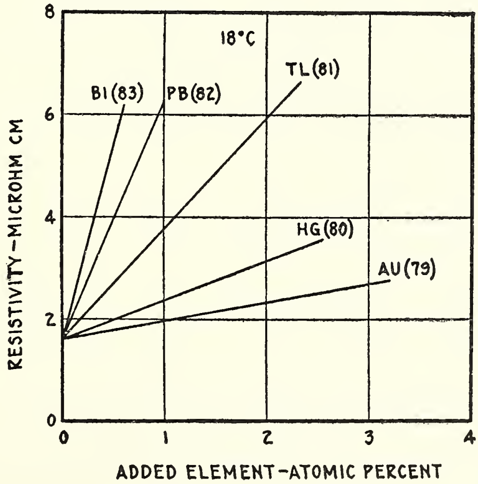

FIGURE 8.—*Resistivity-concentration curves for alloys of silver with the elements 79 to 83 (Linde [4]).*

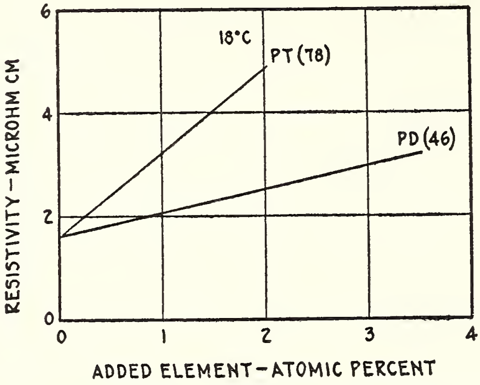

FIGURE 9.—*Resistivity-concentration curves for alloys of silver with the elements 46 and 78 (Linde [4]).*

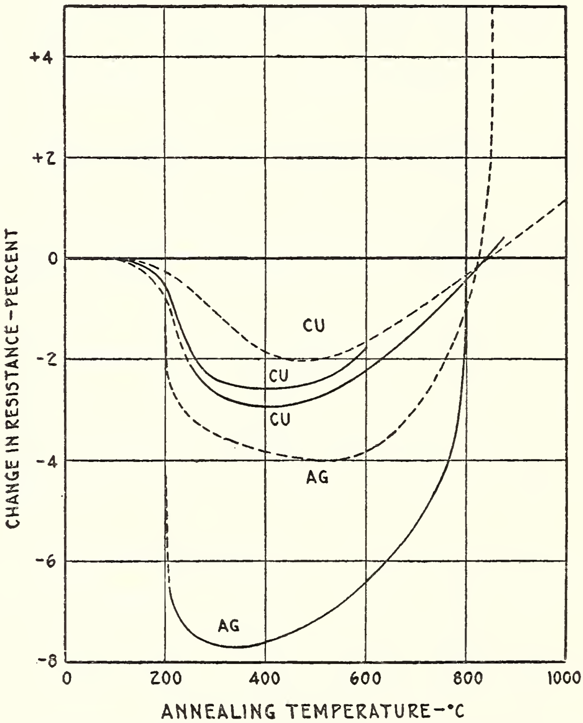

FIGURE 10.—*Change of resistance of silver and copper wires with annealing temperature (Tammann and Straumanis [12]).*

Full line. From data by authors for wire reduced 90 percent in diameter and annealed at successively higher temperatures in hydrogen for 30-minute periods.

Dashed line. From data by Credner [22] for silver wire reduced 42 percent in diameter and copper wire reduced 40 percent in diameter. Both wires annealed at successively higher temperatures in nitrogen for 3-minute periods.

an increase in resistance of 2.2 percent, and this increase remained after annealing at temperatures as high as 480° C. There appeared to be little difference in the temperature coefficient of resistance between wires twisted in this way and wires in the annealed condition.

(2) *Temperature Coefficient of Resistance.*—Measurements on the change of electrical resistance with temperature made by various observers have usually yielded values ranging from 0.00400 to 0.00410 per degree for the interval 0 to 100° C. The earlier determinations have been tabulated by Holborn [18], the highest figure given being obtained in his own investigation. Data by Wensel and Roeser [1] on exceptionally pure silver agree with Holborn's value, and also show very clearly that the value of this coefficient varies markedly with the purity of the material. Table 17 gives the mean temperature coefficients in different temperature ranges as observed by Holborn.

TABLE 17.—*Temperature coefficient of resistance over different temperature intervals* [*18*]

Temperature interval	Mean coefficient	Temperature interval	Mean coefficient
°C		°C	
−192 to −78	0.004185	100 to 200	0.004196
−78 to 0	.004050	200 to 300	.004344
0 to +100	.004098	300 to 400	.004487

The temperature coefficient is somewhat smaller for cold-worked than for annealed silver [1, 22, 18].

(3) *Change of Resistance with Pressure.*—The decrease of resistance with hydrostatic pressure up to 12,000 kg/cm^2 has been measured by Bridgman in the range 0 to 100° C [20] and to 7,000 kg/cm^2 at —78.4 and —182.9° C [5]. The variation in the first case can best be represented by table 18 calculated from Bridgman's [20] results. At the lower temperatures, the change of resistance with pressure is linear.

TABLE 18.—*Relative resistances of silver at various temperatures and pressures* [*20*]

Temperature	Resistance at the pressure indicated (kg/cm^2)			
	0	4,000	8,000	12,000
°C				
0	1.000	0.986	0.974	0.960
50	1.2024	1.185	1.169	1.154
100	1.4047	1.384	1.3 6	1.348

At −78.4° C the average coefficient of change of resistance with pressure over the range of 0 to 7,000 kg/cm^2 is -3.46×10^{-6}, while at −182.9° C it is -4.09×10^{-6}.

(4) *Change of Resistance with Tension.*—Tension also has the effect of decreasing the resistance of silver as has been demonstrated by Tomlinson [27], Bridgman [15], and Rolnick [7]. Bridgman found the effect to be nearly linear up to 250 kg/cm^2 (3,540 lb/in^2) and obtained a value of the tension (longitudinal) coefficient of resistance of 2.86×10^{-6} for room temperature, no correction being made for change in volume. Under loads sufficient to stress the metal beyond its elastic limit, the effect was only about 65 percent as great. The

transverse tension coefficient was only 0.04×10^{-6}, a quantity smaller than the limit of error of measurement.

(5) *Change of Resistance in a Magnetic Field.*—The change of resistance of silver in a magnetic field has been studied by Patterson [26], Grunmach and Weidert [25], and Sanders and Carman [16]. All agree in finding a very slight increase. The data of Sanders and Carman, which are the most complete, are reproduced in table 19.

TABLE 19.—*Fractional increase in resistance of silver in transverse and longitudinal magnetic fields [16] at 23° C*

Field strength	Fractional increase		Field strength	Fractional increase	
	Field transverse	Field longitudinal		Field transverse	Field longitudinal
Oersteds			*Oersteds*		
4, 000	0. 000004	0. 0000024	12, 000	0. 0000356	0. 0000262
6, 000	. 0000084	. 0000052	14, 000	. 0000480	. 0000350
8, 000	. 0000158	. 0000106	16, 000	. 0000630	. 0000456
10, 000	. 0000250	. 0000183			

Patterson's data cover the range of field intensities from 17,300 to 29,200 oersteds. His data at the lower strengths are consistent with

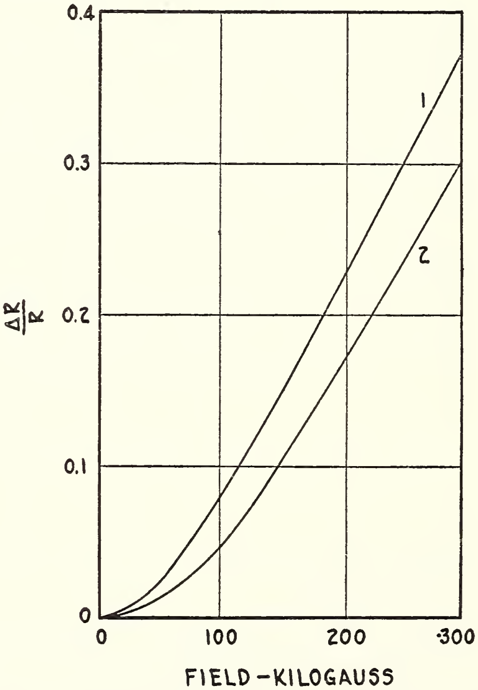

FIGURE 11.—*Change of electrical resistance of silver in strong magnetic fields (Kapitza [9]).*

Magnetic field perpendicular to current.
Curve 1. Annealed silver at temperature of liquid nitrogen.
Curve 2. Hard silver at temperature of liquid air.

those given in table 19. The fractional changes reported by Grunmach and Weidert were roughly 50 percent greater than those given in table 19.

By employing fields up to 300,000 oersteds, Kapitza [9] obtained very considerable increases in resistivity. At room temperature, the maximum increase amounted to about 3 percent, and at the temperature of a mixture of solid carbon dioxide and ether, the increase was 6 percent. The increase was found to be 30 percent for hard-drawn wire in liquid air and 38 percent for annealed wire in liquid nitrogen. Figure 11 shows the fractional change of resistivity with increasing magnetic field for the lower temperatures.

(6) *Change of Reistance at Very High Current Densities.*—Measurements by Bridgman [17] on silver foil indicated that for a current density of 5,000,000 amp/cm^2 there is an apparent increase of resistance of approximately 1 percent.

(7) *Selected References:*

[1] H. T. Wensel and W. F. Roeser. From unpublished work at National Bureau of Standards (1935).

[2] W. G. Kannuluik. *The thermal and electrical conductivities of several metals between —183° C and 100° C* Proc. Roy. Soc. (London) (A) **141,** 159–168 (1933).

[3] G. Tammann and K. L. Dreyer. *Die Erholung des elektrischen Widerstands und der Härte von Kupfer, Silber, und Gold, sowie von Platin und Palladium von den Folgen der Kaltbearbeitung.* Ann. Physik (5) **16,** 111–118 (1933).

[4] J. O. Linde. *Elektrische Eigenschaften verdünnter Mischkristallegierungen. II. Widerstand von Silberlegierungen.* Ann. Physik (5) **14,** 352–366 (1932).

[5] P. W. Bridgman. *The Pressure coefficient of resistance of fifteen metals down to liquid oxygen temperatures.* Proc. Am. Acad. Arts Sci. **67,** 305–344 (1932).

[6] H. Jellinek. *Zur Frage der Gasbeladung von Metallen im Hochdruck.* Z. Physik **66,** 543–557 (1930).

[7] Harry Rolnick. *Tension coefficient of resistance of metals.* Phys. Rev. **36,** 506–512 (1930).

[8] Kinnosuke Takahasi. *On the change of electric resistance produced in cold-worked metals by annealing.* Sci. Rep. Tohoku Imp. Univ. **19,** 265–282 (1930).

[9] P. Kapitza. *The change of electrical conductivity in strong magnetic fields. Part I. Experimental results.* Proc. Roy. Soc., (London) (A) **123,** 342–372 (1929).

[10] P. Kapitza. *The change of electrical conductivity in strong magnetic fields. II. The analysis and the interpretation of experimental results.* Proc. Roy. Soc., (London) (A) **123,** 342–372 (1929).

[11] C. H. Johansson and J. O. Linde. *Elektrische Leitfähigkeit und Zustandsbild der Kupfer-Silberlegierungen.* Z. Metallkunde **20,** 443–444 (1928).

[12] G. Tammann and M. Straumanis. *Die Änderungen der Struktur und des elektrischen Widerstands bei der Kaltbearbeitung von Metallen.* Z. anorg. allgem. Chem. **169,** 365–380 (1928).

[13] Yosiharu Matuyama. *On the electrical resistance of molten metals and alloys.* Sci. Rep. Tohoku Imp. Univ. **16,** 447–474 (1927).

[14] Walther Meissner. *Messungen mit Hilfe von flüssigen Helium. 2. Widerstand von Gold, Zink, Cadmium, Platin, Nickel, Eisen, und Silber, bis herab zu 1.3° abs.* Z. Physik **38,** 647–658 (1926).

[15] P. W. Bridgman. *The effect of tension on the transverse and longitudinal resistance of metals.* Proc. Am. Acad. Arts and Sci. **60,** 423–449 (1925).

[16] W. H. Sanders and A. P. Carman. *Comparison of resistance change in transverse and longitudinal magnetic fields.* Phys. Rev. (2) **21,** 197–198 (1923).

[17] P. W. Bridgman. *The failure of Ohm's law in gold and silver at high current densities.* Proc. Am. Acad. Arts Sci. **57,** 131–172 (1922).

[18] L. Holborn. *Über die Abhängigkeit des Widerstands reiner Metalle von der Temperatur.* Ann. Physik (4) **59,** 145–169 (1919).

[19] Hideo Tsutsumi. *On the variation of electric resistance during the fusion of metals.* Sci. Rep. Tohoku Imp. Univ. **7,** 93–105 (1918).

[20] P. W. Bridgman. *The electrical resistance of metals under pressure.* Proc. Am. Acad. Arts Sci. **52,** 573–646 (1917).

[21] Edwin F. Northrup. *Resistivity of pure silver; solid and molten.* J. Franklin Inst. **178,** 85–87 (1914).

[22] Fritz Credner. *Über die Veränderungen des galvanischen Widerstands welche man beim Ziehen und Tordieren von Drähten und beim Erwärmen gezogener und tordierter Drähte beobachtet; untersucht an Drähten aus Gold, Silber, Kupfer, Nickel, und Eisen.* Z. physik. Chem. **82,** 457–503 (1913).

[23] Adolph Sieverts. *Der Einfluss absorbierter Gase auf den elektrischen Widerstand von Metalldrähten.* Int. Z. Metallog. **3,** 37–56 (1912–13).

[24] H. Kamerlingh Onnes and J. Clay. *On the change of resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures.* Communications Phys. Lab., Univ. Leiden no. 99c (1907).

[25] Leo Grunmach and Franz Weidert. *Über den Einfluss transversaler Magnetisierung auf die elektrische Leitungsfähigkeit der Metalle.* Ann. Physik (4) **22,** 141–179 (1907).

[26] J. Patterson. *On the change of the electrical resistance of metals when placed in a magnetic field.* Phil. Mag. (6) **3,** 643–656 (1902).

[27] Herbert Tomlinson. *The influence of stress and strain on the action of physical forces.* Trans. Roy. Soc. (London) **174,** 1–172 (1883).

e. GALVANOMETRIC AND THERMOMAGNETIC EFFECTS

(1) *Hall Effect.*—Data obtained by Smith [9], Zahn [10], Smith and O'Bryan [1], Raethjen [2], Beckman [7], Ettingshausen and Nernst [11], and others for the value of the Hall coefficient of silver indicate that the correct value at room temperature is in the vicinity of -8.5×10^{-4} cgs magnetic unit, as shown in figure 12.

According to Smith's results the emf observed upon the introduction of a magnetic field is a linear function of the field strength when the temperature is constant. Wait [4] obtained a value of the same magnitude for chemically deposited films but Steinberg's [3] measurements on evaporated films led to the figure -5.2×10^{-4}. Smith [9] obtained a value of -9.2×10^{-4} at $-190°$ C (liquid air), while Beckman [7], whose results are shown in table 20, found a smaller decrease from the value given for room temperature.

TABLE 20.—*Change of Hall coefficient with temperature* [7]

Temperature	Hall coefficient	Temperature	Hall coefficient
°K		°K	
290	-8.0×10^{-4}	20	-10.15×10^{-4}
90	-8.2×10^{-4}	14.5	-9.9×10^{-4}

Onnes and Hof [8] measured the coefficient at 4.25 and 2.8° K and reported the value -16×10^{-4}.

(2) *Other Effects.*—Values of the Nernst, Ettinghausen, Righi-Leduc, and Corbino effects also show a considerable variation. In table 21, the values obtained by various experimenters for these coefficients are given. The literature on the subject has been well analyzed and summarized in the book Galvanometric and Thermomagnetic Effects, by L. L. Campbell. Most of the data will also be found in International Critical Tables, volume VI, pages 414–424.

Table 21.—*Various coefficients of galvanometric and thermomagnetic effects*

Effect	Value of coefficient cgs magnetic units	Observer	Ref. no.
Nernst	-4.3×10^{-6}	Zahn	[10]
Do	-1.8×10^{-6}	Unwin	[5]
Ettingshausen	-1.65×10^{-9}	do	[5]
Righi-Leduc	-4.04×10^{-7}	Zahn	[10]
Do	-2.7×10^{-7}	Unwin	[5]
Corbino	[a] -5.9×10^{-7}	Smith and O'Bryan	[1]
Do	[b] -4.9×10^{-7}	Chapman	[6]

[a] Circular plate. [b] Average.

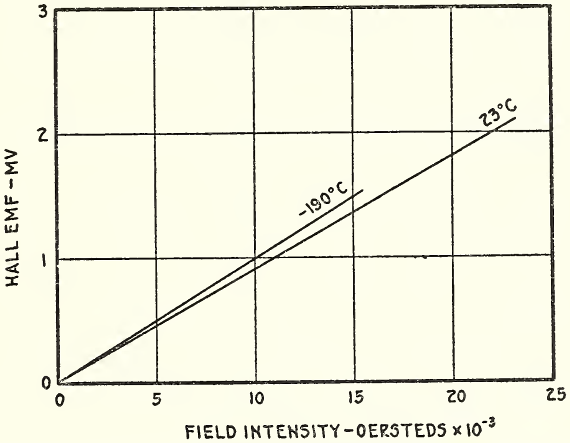

Figure 12.—*The Hall electromotive force of silver as a function of temperature and field intensity* (*Smith* [*9*]).

(3) *Selected References:*

[1] K. K. Smith and H. M. O'Bryan. *Comparison of Hall and Corbino effects in silver and brass.* Phys. Rev. 2, **31,** 149 (1928).

[2] P. Raethjen. *Halleffekt und Thermokraft.* Physik Z. **25,** 84–89 (1924).

[3] J. C. Steinberg. *Hall effect and specific resistance of evaporated films of silver, copper, and iron.* Phys. Rev. (2), **21,** 22–29 (1923).

[4] G. R. Wait. *Hall effect and the specific resistance of silver films.* Phys. Rev. 2, **19,** 615–622 (1922).

[5] F. Unwin. *On the transverse galvanomagnetic and thermomagnetic effects in several metals.* Proc. Roy. Soc. (Edin.) **41,** 44–49 (1920–21).

[6] Albert K. Chapman. *The Hall and Corbino effects.* Phil. Mag. (6) **32,** 303–326 (1916).

[7] Bengt Beckman. *On the Hall effect and the change of the electric resistance in a transverse magnetic field at low temperatures down to the melting point of hydrogen.* Communications Phys. Lab., Univ. Leiden, no. 4 to nos. 145–156 (1915).

[8] H. Kamerlingh Onnes and K. Hof. *Further experiments with liquid helium. N. Hall effect and the change of resistance in a magnetic field. X. Measurements on cadmium, graphite, gold, silver, bismuth, lead, tin, and nickel at hydrogen and helium temperatures.* Proc. K. Akad. Wetenschappen Amsterdam **17,** 520–527 (1914).

[9] Alpheus W. Smith. *The variation of the Hall effect in metals with change in temperature.* Phys. Rev. (1), **30,** 1–34 (1910).

[10] H. Zahn. *Über die transversalen galvanometrischen und thermomagnetischen Effekte in verschiedenen Metallen.* Ann. Physik (4), **16,** 148–154 (1905).

[11] Albert V. Ettingshausen and Walther Nernst. *Über das Hall'sche Phänomen.* Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse **94,** 560–610 (1886).

f. THERMOELECTRIC EFFECTS

(1) *Thermoelectromotive Force.*—Table 22 shows the thermoelectromotive force of silver against platinum with one junction of the thermocouple at 0° C and the other at the temperature specified. The values for temperatures above 0° C were obtained at the National Bureau of Standards and each is the average of determinations on four samples of silver, all of which had a purity higher than 99.99 percent. The platinum wire was the Platinum Standard, Pt 27, which is used as a reference material for all thermoelectric measurements at this Bureau. The values for temperatures below 0° C have been computed from data on the thermoelectric power for platinum against a silver-gold alloy determined by Borelius, Keesom, Johansson, and Linde [3] and from data for silver against the same gold-silver alloy by the same authors [2].

Table 22.—*Thermoelectromotive force of silver against platinum*

Temperature of variable junction	Thermoelectromotive force	Temperature of variable junction	Thermoelectromotive force
°C	mv	°C	mv
−200	−0.14	400	4.57
−100	−.35	500	6.36
0	0	600	8.41
100	.74	700	10.75
200	1.77	800	13.36
300	3.05	900	16.20

Positive values (not marked) indicate that current flows from silver to platinum at the cold junction. It will be observed that the data presented here for temperatures above 0° C do not differ markedly from the results obtained by Holborn and Day [9].

The values in table 22 refer to annealed wires. The existence of a thermoelectric force between the annealed and hard-drawn portions of a single wire has been known for a long time and has been investigated for silver by Noll [10], Borelius [5], and Tammann and Bandel [1], all of whom obtained values in the same order of magnitude. Tammann and Bandel, who used this effect as a means of determining the annealing temperature of silver, obtained a thermoelectromotive force of 46μv with the two junctions at 0 and 100° C, respectively. The direction of the current is from the annealed to the worked material at the hot junction.

The effect of pressure on thermoelectromotive force was studied by Bridgman [6], who measured the emf between compressed and uncompressed portions of a silver wire at various pressures up to 12,000 kg/cm^2, figure 13. The current is from uncompressed to compressed metal at the hot junction of such a couple.

(2) *Peltier Coefficient.*—Attempts have been made to determine the Peltier coefficient of a silver-copper junction by direct calorimetric methods. According to Caswell [8], the coefficient has the value of −30 μv, whereas the experiments conducted by Borelius [7] at 0° C led to a value about twice as large numerically and of the same sign. Since the total effect is small, such discrepancies are not surprising. Calculation based on data given by Borelius, Keesom, Johansson, and Linde [3], yields a value of −90 μv. The convention used here is that the Peltier coefficient is positive when there is an absorption of heat with the current going from silver to copper. Hence, the

negative sign means that heat is given off when the current crosses the junction in the direction from silver to copper.

It is noteworthy that Bridgman [6] found a heat absorption when current flowed from the uncompressed to the compressed silver. As would be expected from the data of figure 13, the amount of heat absorbed increased with both temperature and pressure. For temperatures of 0 and 100° C and a pressure of 12,000 kg/cm², the Peltier coefficient for uncompressed and compressed metal is 10.6 μv.

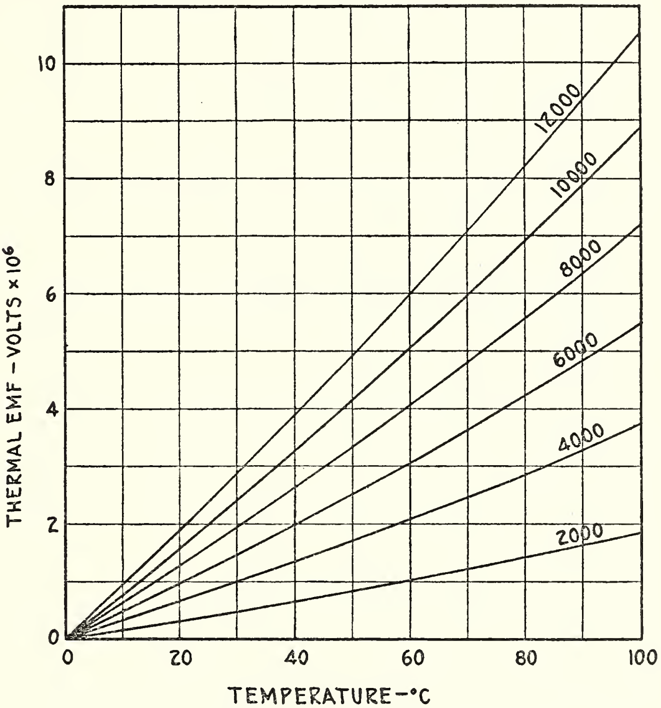

FIGURE 13.—*Thermal electromotive force between compressed and uncompressed silver at various temperatures (Bridgman [6]).*

The values on the individual curves are the pressures used, kg/cm².

(3) *Thomson Effect.*—A direct determination of the Thomson effect was carried out by Borelius and Gunneson [4], the results of which agree well with data calculated from measurements by Borelius, Keesom, Johansson, and Linde [3]. The latter data are given in table 23.

TABLE 23.—*Variation of the Thomson effect with temperature [3]*

Temperature	Thomson effect [a]	Temperaature	Thomson effect [a]
°K	μv/°C	°K	μv/°C
20	1.40	180	0.72
40	.24	200	.84
60	−0.17	220	.96
80	−0.25	240	1.10
100	−0.03	260	1.20
120	.25	280	1.32
140	.44	300	1.44
160	.59		

[a] Positive values correspond to a heat absorption for current passing from the hot to the cold region. Pressure has the effect of increasing the Thomson heat [6].

(4) *Selected References:*

[1] G. Tammann and G. Bandel. *Die Änderung der Thermokraft bei der Erholung der Metalle von der Kaltbearbeitung.* Ann. Physik (5) **16,** 120–128 (1933).

[2] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde. *Measurements on thermoelectric forces down to temperatures obtainable with liquid or solid hydrogen.* Proc. K. Akad. Wetenschappen Amsterdam **35,** 15–24 (1932).

[3] G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde. *Measurements of the thermoelectric force per degree of some pure metals down to the temperature of liquid hydrogen and calculation of Thomson effect.* Proc. K. Akad. Wetenschappen Amsterdam **33,** 17–31 (1930).

[4] G. Borelius and G. Gunneson. *Messungen von Thomsoneffekten bei niederen Temperaturen.* Ann. Physik (4) **65,** 520–540 (1921).

[5] G. Borelius. *Über Thermokräfte in einem chemisch homogenen Leiterkreise: Bearbeitungs und Oberflächenerscheinung.* Ann. Physik (4) **60,** 381–404 (1919).

[6] P. W. Bridgman. *Thermoelectromotive force, peltier heat and Thomson heat under pressure.* Proc. Am. Acad. Arts Sci. **53,** 269–386 (1918).

[7] G. Borelius. *Eine Methode für kombinierte Messung von Peltierwärme und Wärmeleitfähigkeit.* Ann. Physik (4) **52,** 398–414 (1917).

[8] A. E. Caswell. *Determination of Peltier electromotive force for several metals by compensation methods.* Phys. Rev. (1) **33,** 379–402 (1911).

[9] L. Holborn and A. Day. *Über die Thermoelektricität einiger Metalle.* Sitzber. Akad. Berlin Wissensch. 691–695 (1899).

[10] K. Noll. *Thermoelektricität chemischer reiner Metalle.* Ann. Physik (3) **53,** 874–911 (1894).

g. MAGNETIC SUSCEPTIBILITY

Published data on the magnetic susceptibility of silver reveal considerable variation in the values of different experimenters. A survey of the values of Honda [11], Spencer and John [9], Kussmann and Seeman [3], Montgomery and Ross [2], Honda and Shimizu [5], and some others, indicates that the susceptibility is probably between $-.190$ and $-.200\times10^{-6}$ cgs unit.

Owen [10] found that the susceptibility decreased numerically with decrease in temperature to about −183° C. According to the International Critical Tables [7], Owen's value for silver when cooled by liquid air was -0.16×10^{-6}. On the other hand, de Haas and Van Alphen [1] were unable to find an appreciable change in susceptibility at temperatures as low as −259° C. Their values between room temperature and −209° C were all within the range of -0.188 to -0.191×10^{-6}. At lower temperatures, the accuracy was less and only the figure -0.19×10^{-6} was given. Honda [11] measured the susceptibility at high temperatures and found that it increased numerically with temperature. According to the International Critical Tables, the susceptibility at 900° C is -0.25×10^{-6} and in the molten state reaches the value of -0.29×10^{-6}.

Kussmann and Seeman [3], Lowance and Constant [6], and Honda and Shimizu [5] studied the effect of cold-working and found that it caused the susceptibility to drop off rapidly. Honda and Shimizu [5], figure 14, obtained a linear decrease of susceptibility with density for increasing amounts of cold-work. The effect of heating the sample slowly above its annealing temperature is shown in figure 15. Kussmann and Seeman [3] expressed the belief that the change in susceptibility is not caused by the cold-working itself but by the precipitation of small amounts of iron in solid solution in the annealed metal during the plastic deformation of the metal.

Honda [11] and also Vogt [4] found that the susceptibility increased in the negative direction with increasing fluid strengths, but Honda [8] asserts that if no ferrous material is present, the susceptibility is independent of the field strength.

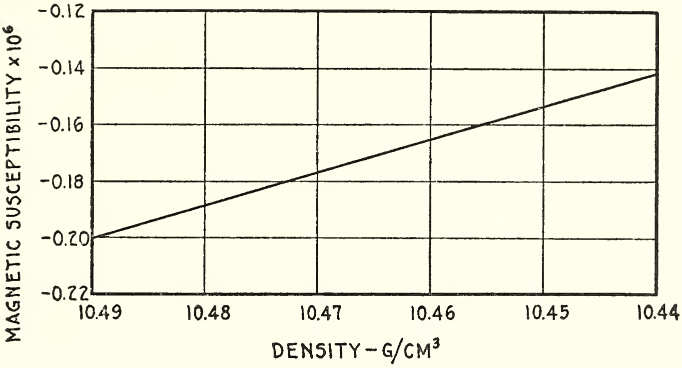

FIGURE 14.—*Relation between the magnetic susceptibility of silver and density changes produced by cold-working (Honda and Shimizu [5]).*

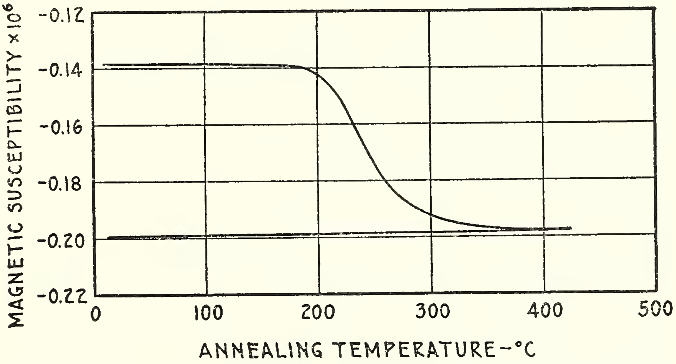

FIGURE 15.—*Change in the magnetic susceptibility on annealing at various temperatures (Honda and Shimizu [5]).*

(1) *Selected References:*

[1] W. J. de Haas and P. M. van Alphen. *Magnetic properties of metals at low temperatures.* Proc. K. Akad. Wetenschappen Amsterdam **36,** 263–270 (1933).

[2] Carol G. Montgomery and William H. Ross. *The Magnetic Susceptibilities of Lead, Silver, and Their Alloys.* Phys. Rev. (2) **43,** 358–360 (1933).

[3] A. Kussmann and H. J. Seeman. *Der Einfluss plastischer Verformung auf die Suszeptibilität dia- und paramagnetischer Metalle.* Z. Physik **77,** 567–580 (1932).

[4] Eckhart Vogt. *Zum Dia- und Paramagenetismus in metallischen Mischkristallreihen.* Ann. Physik (5) **14,** 1–39 (1932).

[5[Kotaro Honda and Yosomatsu Shimizu. *The effect of cold working on the magnetic susceptibility of metals.* Sci. Rep. Tohoku Imp. Univ. **20,** 460–488 (1931).

[6] F. E. Lowance and F. W. Constant. *The structure sensitiveness of magnetism in metals.* Phys. Rev. (2) **38,** 1547–1551 (1931).

[7] Int. Crit. Tables **6,** 354 (1929).

[8] Kotaro Honda. *Magnetic Properties of Matter.* (Tokyo; Syokwabo & Co., p. 128, 1928).

[9] J. F. Spencer and M. E. John. *The magnetic susceptibility of some binary alloys.* Proc. Roy. Soc. (London), (A) **116,** 61–72 (1927).

[10] Morris Owen. *Magnetochemische Untersuchungen. Die thermomagnetischen Eigenschaften der Elemente. II.* Ann. Physik (4) **37,** 657–699 (1912).

[11] Kotaro Honda. *Die thermomagnetischen Eigenschaften der Elemente.* Ann. Physik (4) **32,** 1027–1063 (1910).

h. OPTICAL PROPERTIES

(1) *Reflectivity.*—Silver ranks very high among metals in reflecting power. Through the region of greatest sensitivity of the human eye, its reflectivity is of the order of 95 percent. In the infrared region, the metal may reflect as much as 98 percent of the radiation incident upon its surface. On the other hand, it has been found that its reflecting power diminishes with decreasing wave length and in the region of 3200 A, it falls to a minimum of less than 10 percent.

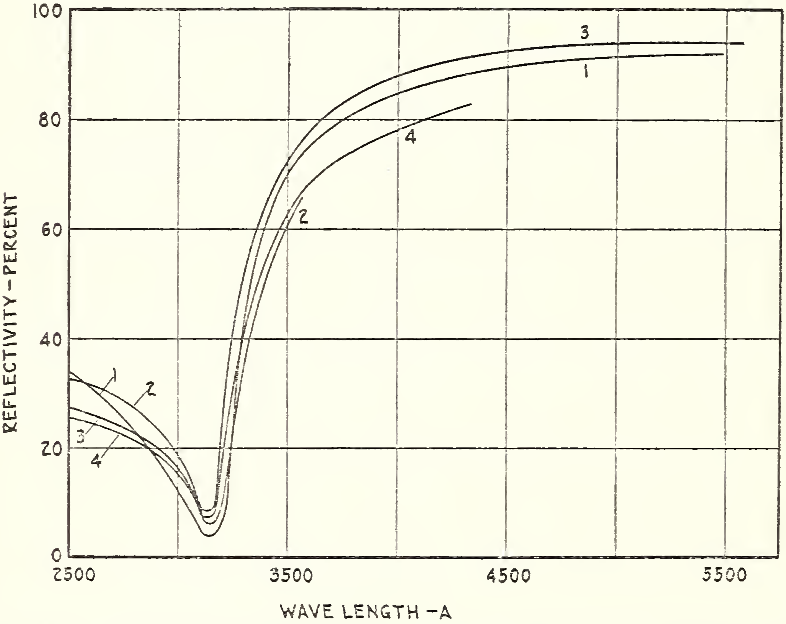

FIGURE 16.—*Change of reflectivity of silver with wave length* (*Coblentz and Stair* [*4*]).

Curve 1. E. Hagen and H. Rubens (Das Reflexionsvermögen von Metallen für ultra-violette Strahlen Verh. d. Deutsch. Phys. Gesell. 3, 163–176 (1901)).
Curve 2. E. O. Hulburt (The Reflecting Power of Metals in the Ultraviolet Region of the Spectrum. Astrophysical Journal 42, 205–230 (1915)).
Curve 3. Coblentz and Stair [4].
Curve 4. Coblentz and Stair [4].

The relation between reflectivity and wave length of the incident light, for the lower visible and near ultraviolet regions, is shown in figure 16, based on data of Coblentz and Stair [4]. This shows the minimum near 3200 A and also indicates the variability in the deposits employed. Some of the variations can no doubt be ascribed to differences in polish. For example, Margenau [6] reported that if the silver had an etched instead of a highly polished surface, the minimum of reflectivity was not so low and occurred about 20 A nearer the blue end of the spectrum.

A factor which, though probably it had no influence in producing the variations to be observed in figure 16, is nevertheless of some interest was observed by Ebeling [7]. He noted that the position of the minimum of reflectivity was displaced considerably toward the red end of the spectrum when the temperature of the reflecting surface was increased from 15 to 200° C. Information on the effect of cooling silver below room temperature, from De Selincourt, [8] is given in table 24.

Table 24.—*Wave length corresponding to minimum reflectivity of silver at various temperatures [8]*

Temperature	Wave length of minimum reflectivity	Temperature	Wave length of minimum reflectivity
°C	A	°C	A
−183	3217	16	3236
−79	3227	150	3247

De Selincourt also investigated the width of the minimum region and found that there was a considerable widening of the band as the temperature was increased.

Information from Coblentz [9] on the reflecting power of silver in the upper visible and infrared portions of the spectrum is given in table 25.

Table 25.—*Reflecting power of silver in the visible and infrared region [9]*

Wave length	Reflecting power	Wave length	Reflecting power	Wave length	Reflecting power
A	%	A	%	A	%
4500	88.0	9000	96.0	15000	97.6
5000	90.0	9500	96.3	17500	97.8
5500	91.5	10000	96.5	20000	97.9
6000	92.7	10500	96.7	25000	98.0
6500	93.5	11000	96.9	30000	98.0
7000	94.1	12000	97.2	35000	98.0
7500	94.7	14000	97.4	40000	98.0
8000	95.1				

(2) *Transmission.*—It is well known that silver deposited in very thin layers on glass is partly transparent. Houston and Moore [5] found that as the wave length is decreased from 7000 to 4600 A, the amount of light reflected by a thin layer of silver decreased while that transmitted increased. It is also true, however, that very thin silver foil, e. g., 3 to 5 $\times 10^{-6}$ cm in thickness, is not entirely opaque. Swamy [2] has mentioned the blue color of silver when viewed by transmitted light. The transmission band which occurs in the region of short wave lengths was found by Rayleigh [3] to change in position when the silver was cooled to the temperature of liquid air. The effect was studied in more detail by McLennan, Smith, and Wilhelm [1] who obtained the results shown in table 26.

(3) *Emissivity.*—The emissivity of silver for a wave length of 6500 A is very low at all temperatures, a fact which would be anticipated from a knowledge of its high reflecting power. In general, experimenters have determined the relative emissivity, that is, the ratio of the intensity of the radiation in the given wave length to that produced by a black body at the same temperature.

TABLE 26.—*Change of the wave length of maximum transmission with temperature of silver sheet* [*1*]

Temperature	Wave length of maximum transmission
°C	A
20	3243
−182	3212
−251	3200
−269	3198

Bidwell [11] measured the actual temperature and the apparent temperature (temperature at which a black body would radiate with the same intensity at the given wave length) of silver from about 700 to 1,800° C and found a linear relationship for a wave length of about 6600 A. For a true temperature of 700° C, the apparent temperature was about 595° C and at 1,800° C, the apparent temperature was about 1,380° C. He obtained a value of 0.055 for the relative emissivity at the low temperatures and a very slightly higher value at high temperatures. The relative emissivity was nearly constant over the entire range and no discontinuity was observed at the melting point.

Burgess and Waltenberg [10] obtained a somewhat higher value of relative emissivity at 940° C (0.044) than at 980° C (0.072) which suggested a higher emissivity in the liquid state. These experimenters used a filter transmitting an average wave length of 6500 A, measured the actual and apparent temperatures of a minute amount of silver placed on a heated platinum strip, and calculated the relative emissivity.

(4) *Selected References:*

[1] J. C. McLennan, C. E. Smith, and J. O. Wilhelm. *The effect of low temperatures on the ultraviolet transmission band of silver.* Phil. Mag. (7) **12,** 833–840 (1931).

[2] S. R. Swamy. *On the transmission of light by thin films of metal.* Proc. Roy. Soc. **131,** 307–320 (1931).

[3] Lord Rayleigh. *The ultraviolet transmission band of metallic silver, as affected by temperature.* Proc. Roy. Soc. (London) (A) **128,** 131–133 (1930).

[4] W. W. Coblentz and R. Stair. *Reflecting power of beryllium, chromium, and several other metals.* BS J. Research **2,** 343–354 (1929) RP39.

[5] W. V. Houston and George Moore. *Transmission and reflection of gold and silver films.* J. Opt. Soc. Am. **16,** 174–176 (1929).

[6] Henry Margenau. *Dependence of ultraviolet reflection of silver on plastic deformation.* Phys. Rev. **33,** 1035–1045 (1929).

[7] Ingo Ebeling. *Metallreflexion I und II.* Z. Physik **32,** 489–501 (1925).

[8] M. de Selincourt. *On the effect of temperature on the anomalous reflection of silver.* Proc. Roy. Soc. (London) (A) **107,** 247–254 (1925).

[9] W. W. Coblentz. *Reflecting power of monel metal, stellite, and zinc.* Sci. Pap. BS **16,** 249–252 (1920) S379.

[10] G. K. Burgess and R. G. Waltenberg. *The emissivity of metals and oxides, II. measurements with the micropyrometer.* Bul. BS **11,** 605 (1915) S243.

[11] Charles C. Bidwell. *A comparison of actual and black-body temperatures.* Phys. Rev. (2) **3,** 439–449 (1914).

2. CHEMICAL PROPERTIES

a. ELECTROCHEMICAL

(1) *Electrolytic Solution Potential.*—In the electrochemical series, silver lies below hydrogen along with copper, thallium, mercury, and gold. Silver is electropositive to such metals as copper, tin, and lead.

It is more resistant to oxidation than these metals and therefore more resistant to corrosion under oxidizing conditions. Silver is slightly less electropositive than gold and more readily oxidized than this metal, but because of the relatively high positive electrolytic solution potential it may be placed on the borderline of that group of metals called "noble." The standard electrolytic solution potential $Ag^+ + e = Ag(s)$ as given in International Critical Tables [8] is +0.7978 volt at 25° C.

(2) *Hydrogen Overvoltage.*—The hydrogen overvoltage at a silver surface in $2N$ H_2SO_4 at 25° C as given in International Critical Tables [4] varies with the current density as shown in table 27.

TABLE 27.—*Hydrogen overvoltage on silver in 2 N* H_2SO_4 *at 25°* C [4]

Current density	Overvoltage	Current density	Overvoltage
ma/cm^2	*Volts*	ma/cm^2	*Volts*
0.1	0.298	100.0	0.875
1.0	.475	200.0	.938
2.0	.579	500.0	1.030
5.0	.692	1000.0	1.089
10.0	.762	1500.0	1.084
50.0	.830		

b. CORROSION

(1) *Introduction.*—Published technical information on the corrosion-resistance of silver is scanty, but articles of a trade nature, especially on the use of silver for construction purposes in chemical plants, are numerous. Most of these articles do not include experimental data and have therefore been excluded from the following discussion.

(2) *Atmospheric.*—Exposure to pure dry or moist air has no effect on silver. Dry or moist oxygen at ordinary temperatures and pressures does not attack silver. Strutt [11], Jirsa and Jelinek [5], Manchot and Kampschulte [14] and others have reported that either dry or moist ozone at ordinary temperatures and pressures forms a black coating on silver. Hydrogen sulphide in moist air very readily tarnishes silver.

(3) *Water.*—According to Krepelka and Toul [6] one liter of doubly distilled water at 20° C dissolved 0.009 mg of pure silver from a silver plate in 7 days. They also reported [3] the solubility of silver in distilled water as determined by nephelometric and electrometric methods to be 0.036 mg of silver per liter of water after 21 days at 20° C. Richards, Collins, and Heimrod [18] reported that the silver deposited in a silver coulometer, when properly washed, neither gained nor lost in weight upon continued digestion with water, a result confirmed by Guthe [15]. Merill [17], however, found that a silver cathode with its coating of silver lost as much as 0.2 mg of silver by being suspended in water at 90° C for 2 hours.

(4) *Acids.*—Watts and Whipple [9] have attributed the resistance of silver to attack by acids to the fact that silver, like gold, platinum, and copper, has an electrode potential in acid solutions which is less than the potential required to discharge hydrogen from its surface. In the absence of suitable depolarizers (oxidizing agents for example) silver should be only slightly attacked by acids. This is generally

true. Most organic acids either do not attack silver or only slightly attack it in the absence of oxidizing agents or similar impurities. Inorganic acids which in themselves are not oxidizing agents only slightly attack pure silver.

(a) *Sulphuric Acid.*—Silver dissolves readily in hot concentrated sulphuric acid with the evolution of sulphur dioxide, a reaction which is utilized in parting gold from silver. Pannain [12] found that pure silver is not attacked by boiling sulphuric acid having a specific gravity lower than 1.710 and that a more dilute acid attacks silver only when the metal is impure. According to Watts and Whipple [9] a strip of pure silver lost .025 mg of silver per square centimeter when immersed in 190 ml of N H_2SO_4 for 45 hours at 37.5° C and the same sample under the same conditions, after 5 ml of a 30-percent H_2O_2 solution had been added, lost 1695.3 mg of silver. Salkowsky [10] also found the solvent action of H_2SO_4 on silver to be augmented by the addition of H_2O_2.

(b) *Phosphoric Acid.*—Unpublished data obtained in the laboratories of Handy and Harman, Inc., Bridgeport, Conn., show that silver is slightly soluble in phosphoric acid. Samples of pure silver having surface areas of 4.5 sq in. (29 cm^2) lost between 2.56 and 3.28 mg of silver per cm^2 per day when immersed for 28 hours in 85 percent H_3PO_4 solution at temperatures ranging between 112 to 121° C. In a similar solution the same samples in a 16-hour test lost between 35.34 and 68.97 mg of silver per cm^2 per day at temperatures ranging between 210° and 231° C. Ruisakov and Bushmakin [1] concludes that a 65 percent H_3PO_4 solution did not attack pure silver at temperatures up to 200° C, but did at 200° C and above when air was bubbled through the solution.

(c) *Nitric Acid.*—According to Millon [23] pure silver is not attacked by nitric acid with a specific gravity less than 1.405, when the composition of the acid is represented by $4HNO_3+7H_2O$, and the temperature does not rise above 20° C. Russell [22] showed that pure silver does not dissolve in nitric acid free from nitrous acid and Stansbie [13] found that silver, like copper and bismuth, is not attacked by nitric acid free from oxides of nitrogen or nitrous acid. Veley [20], Bancroft [7], Hedges [2], and others have also recognized the important part that nitrous acid plays in the solution of silver by nitric acid. According to Veley the silver first reacts with the nitrous acid which is present in the nitric acid, or is formed upon heating, to produce silver nitrate.

$$Ag+2\ HNO_2 \rightleftarrows AgNO_2+NO+H_2O.$$

The silver nitrate then reacts with the nitric acid to form silver nitrate and more nitrous acid.

Bancroft [7] has advanced the opinion that the nitrous acid acts as a catalyst which activates the nitric acid through a dynamic equilibrium possibly of the following type:

$$HNO_3+HNO_2 \rightleftarrows 2NO_2+H_2O.$$

According to Hedges [2], the primary reaction is the formation of an oxide which is converted into a nitrite by the nitrous acid, which is then acted upon by the nitric acid to form a nitrate. Under ordinary conditions, nitrous acid is present or is readily formed when the dilute nitric acid is warmed. This fact accounts for the attack of silver by this acid. Marchlewsky [21] found that nitric acid in concentrations as low as 1 percent, by volume, was capable of dissolving silver at ordinary temperatures, if the silver was finely divided.

(d) *Acetic Acid.*—Silver is widely used as a material for condensers in the manufacture of acetic acid because of its slight solubility in acetic acid. According to Watts and Whipple [9], who studied the action of normal acetic acid and normal acetic acid containing hydrogen peroxide on pure silver, a plate of pure silver lost 0.0266 mg of silver per square centimeter when immersed in 190 ml of normal acetic acid for 45 hours at 37.5° C. The same sample under similar conditions lost 1,799.7 mg after 5 ml of a 30-percent H_2O_2 solution had been added to the acetic acid. Results reported by Salkowsky [10] confirm this behavior. Experiments at the National Bureau of Standards showed that a strip of silver lost 1.19 mg of silver per square centimeter (99.993 percent of Ag) when immersed for 27 hours in glacial acetic acid boiling under a reflux condenser. Lea [19] has also reported that pure silver is insoluble in pure acetic acid free from any oxidizing agents.

(e) *Hydrochloric Acid.*—Experiments at the National Bureau of Standards have shown that boiling hydrochloric acid of each of the following concentrations: 30 percent by volume, 60 percent by volume, and concentrated (specific gravity 1.18) readily attack pure silver and form a surface coating of chloride. In the case of the concentrated and 60 percent acid this chloride coating did not prevent continued attack.

(f) *Lactic Acid.*—An experiment at the National Bureau of Standards showed that a strip of silver (99.993 percent of Ag) having a surface area of 6.8 cm^2 lost 0.011 gram when immersed in a 50-percent solution of lactic acid (by volume) and boiled under a reflux condenser for 26 hours.

(5) *Miscellaneous Chemicals.*—The general action of common solutions and chemical reagents is summarized in table 28.

TABLE 28.—*Attack of various other chemicals on silver*

Severe attack	Slight attack
Hydrogen sulfide+moisture.	Ammonia gas.
Ammonium hydroxide+chloride.	Oxygen below 400° C.
Chlorine vapor+moisture.	Phenol.
Iodine vapor+moisture.	Oxalic acid.
Bromine vapor+moisture.	Hydrofluoric acid.
Potassium cyanide.	Tri-sodium phosphate.
Hydrobromic acid.	Di-sodium phosphate.
Hydriodic acid.	Sodium hydroxide.
Hydrogen selenide.	Potassium hydroxide.
Pyrosulfuric acid.	Sodium chloride.
	Fluorine vapor below 100° C.
	Liquid ammonia free from chlorides.

(6) *Selected References:*

[1] M. V. Ruisakov and I. M. Bushmakin. *Corrosion of metals and alloys by phosphoric acid and phosphorus.* J. Applied Chem. (USSR) **5**, 715 (1932); Chem. Abst. **27**, 54 (1933).

[2] E. S. Hedges. *The action of nitric acid on some metals.* J. Chem. Soc. page 561 (1930).

[3] H. Krepelka and F. Toul. *The solubility of silver in water.* Collection Czechoslov. Chem. Communications **1**, 155 (1929).

[4] Int. Crit. Tables **6**, 339 (1929).

[5] F. Jirsa and J. Jelinek. *A study of the higher oxides of silver. III. Oxidation of silver by ozone.* Z. anorg. allgem. Chem. **158,** 61 (1926).
[6] H. Krepelka and F. Toul. *The solubility of silver in water.* Chem. Listy. **19,** 182; Chem. Abst. **19,** 3194 (1925).
[7] W. D. Bancroft. *Catalytic action of nitrous acid.* J. Phys. Chem. **28,** 973 (1924).
[8] Int. Crit. Tables **6,** p. 334 (1923).
[9] O. P. Watts and N. D. Whipple. *The corrosion of metals by acids.* Trans. Am. Electrochem. Soc. **32,** 257 (1917).
[10] E. Salkowsky. *Über das Verhalten einiger Metalle zu wasserstoffsuperoxydhaltigen Säuren.* Chem.-Ztg. **40,** 448–449 (1916).
[11] J. R. Strutt. *Molecular statistics of some chemical reactions.* Proc. Roy. Soc. (London) (A) **87,** 302–309 (1912).
[12] E. Pannain. *Solution of silver and its alloys in mixtures of acids.* Gaz. Chim. Ital. **39,** II, 234 (1909); Chem. Abst. **5,** 638 (1911).
[13] J. H. Stansbie. *Reaction of copper, bismuth, and silver with nitric acid.* J. Soc. Chem. Ind. **27,** 365 (1908).
[14] W. Manchot and W. Kampschulte. *The action of ozone on metallic silver and mercury.* Ber. deut. chem. Ges. **40,** 2891–2898 (1907).
[15] K. E. Guthe. *A study of the silver voltameter.* Bul. BS **1,** 21 (1905) S2.
[16] W. S. Hendrixson. *Silver as a reducing agent.* J. Am. Chem. Soc. **25,** 637 (1903).
[17] J. F. Merill. *The influence of temperature, pressure, used solutions, and size of anodes on the deposit of silver voltameters.* Phys. Rev. **10,** 167 (1900).
[18] T. W. Richards, E. Collins, and G. W. Heimrod. *The electrochemical equivalents of silver and copper.* Proc. Am. Acad. Sci. **35,** 139 (1899).
[19] M. C. Lea. *Notes on silver.* Am. J. Sci. **44,** 444 (1892).
[20] V. H. Veley. *The conditions of chemical change between nitric acid and certain metals.* Phil. Trans. (A) **182,** 279 (1891).
[21] L. Marchlewski. *Über die Reaction zwischen Arsenwasserstoff und Silnitrat.* Ber. deut. chem Ges. **24,** 2269 (1891).
[22] W. J. Russell. *On the action of hydrogen on silver nitrate.* J. Chem. Soc. **27,** 3 (1874).
[23] E. Millon. *Recherches sur l'acide nitrique.* Ann. chim. Phys. (3) **6,** 98 (1842).

c. CATALYTIC PROPERTIES

Although the catalytic properties of silver and silver salts have been extensively investigated in recent years, detailed discussion of this property has been omitted in this circular because of the wide variety of reactions in which silver or one of its compounds may function as a catalyst. The following selected references include most of the investigations which have been made on this subject.

(1) *Selected References:*

[1] A. F. Benton and T. Bell. *The oxidation of carbon monoxide with a silver catalyst.* J. Am. Chem. Soc. **56,** 501 (1934).
[2] G. A. Rasuvaev and M. M. Koton. *Catalytic decomposition of metals—organic compounds.* Ber. deut. chem Ges. (B) **66,** 845, 1210 (1933).
[3] A. M. Rubenshtein, A. A. Baladin, B. A. Dologoploska, K. A. Morozov, and L. I. Vagranskaya. *The catalytic oxidation of butyl alcohol to butyraldehyde.* J. Applied Chem. (USSR) **6,** 278 (1933).
[4] A. R. Day and A. Eismer. *The catalytic oxidation of propyl alcohol.* J. Phys. Chem. **36,** 1912 (1932).
[5] M. Ya. Kagan and A. L. Shneerson. *Oxidation of ethyl alcohol to acetaldehyde.* J. Applied Chem. (USSR) **5,** 389 (1932).
[6] C. Kröger. *The dependence of detonating gas catalysis upon the quantity of catalyst.* Z. anorg. allgem. Chem. **194,** 73 (1930).
[7] D. L. Chapman and W. K. Hall. *A study of the catalysis by silver of the union of hydrogen and oxygen.* Proc. Roy. Soc. (London) (A) **124,** 478 (1929).
[8] M. Darmois. *Cracking petroleum oils by means of special metallic catalyst.* Chimie & Industrie, Spec. no. 252 (1929).
[9] J. R. Campbell. *Activity of various catalysts in promoting the oxidation of methane by means of oxygen.* J. Soc. Chem. Ind. **48,** 93 (1929).

[10] A. F. Benton and J. C. Elgin. *The synthesis of water with a silver catalyst. II. Energy of activation and mechanism.* J. Am. Chem. Soc. **51, 7** (1929).

[11] B. Neumann. *The reaction mechanism in contact—Sulfuric acid process and the method of action of activators.* Z. Electrochem. **35,** 42 (1929).

[12] L. H. Reyerson and L. E. Swearingen. *The catalytic activity of metallized silica gels.* J. Am. Chem. Soc. **50,** 2872 (1928).

[13] L. H. Reyerson and L. E. Swearingen. *The catalytic activity of metallized silica gels. IV. The oxidation of methane.* J. Phys. Chem. **32,** 192 (1928).

[14] L. E. Swearingen and L. H. Reyerson. *The catalytic activity of metallized silica gels. III. Synthesis of water.* J. Phys. Chem. **32,** 113 (1928).

[15] J. B. Neumann, H. Panzner and E. Goebel. *The activity of various contact substances in the sulfuric acid contact process.* Z. Electrochem. **34,** 696 (1928).

[16] C. H. D. Clark and B. Topley. *The catalytic decomposition of formic acid vapor.* J. Phys. Chem. **32,** 121 (1928).

[17] C. W. Davis. *The glow test for metals of the platinum group.* J. Franklin Inst. **203,** 679 (1927).

[18] A. F. Penton and J. C. Elgin. *The catalytic synthesis of water vapor in contact with metallic silver.* J. Am. Chem. Soc. **48,** 3027 (1926).

[19] H. Dreyfus. Recovering Waste Acetic Acid. British Patent no. 273,810 (1925).

[20] O. Schmidt. *The catalytic hydrogenation of organic substances.* Z. physik. Chem. **118,** 193 (1925).

[21] D. L. Chapman, J. E. Ramsbottom, and C. E. Frotman. *The union of hydrogen and oxygen in the presence of silver and gold.* Proc. Roy. Soc. (London) (A) **107,** 92 (1925).

[22] W. Lommel and R. Engelhardt. *Silver as a catalyst for the absorption of ethylene by sulfuric acid.* Ber. deut. chem. Ges. (B) **57,** 848 (1924).

[23[E. S. Hedges and J. E. Meyers. *The periodic catalytic decomposition of hydrogen peroxide.* J. Chem. Soc. **125,** 1282 (1924).

[24] J. Piccard and E. Thomas. *Catalytic metals.* Helv. Chim. Acta **6,** 1044 (1923).

[25] F. G. Nunez. *Thermal decomposition of tetramethylammonium fluoride.* An. soc. españ. fis. quím. **20,** 539 (1922).

[26] H. C. Tingey and C. N. Hinshelwood. *Catalytic decomposition of formic acid on surfaces of platinum and silver.* J. Chem. Soc. **121,** 1668 (1922).

[27] I. C. Sandonnini. *The behavior of some metals as catalysts.* Gaz. Chim. Ital. **52,** 394 (1922).

[28] J. C. Clancy. Catalysts. Canadian Patent 215,382 (January 1922).

[29] Nitrogen Corporation. Catalytic Agents. British Patent 163,046 (May 1921).

[30] A. Mailke. *Catalysis by means of precious metals.* J. usines gaz. **43,** 177 (1919).

d. CHEMICAL ANALYSIS

Hillebrand and Lundell [5] have discussed in some detail the standard methods for treating various ores of silver for chemical analysis. This reference book should be consulted for detailed procedures.

In the ordinary scheme of analysis, solution of the sulphide-arsenide type of silver ores is best obtained by digesting the ore with nitric acid followed by a sodium carbonate fusion, after which the melt is treated with water, then with nitric acid. The silver from these solutions is removed as a sulphide by hydrogen sulphide following the removal of the silica by dehydration with nitric or sulphuric acid. The silver sulphide is dissolved in nitric acid and the silver determined by one of the following procedures: (A) gravimetric; (B) volumetric; or (C) electrometric.

In the gravimetric method the silver is precipitated from a dilute nitric acid solution by dilute hydrochloric acid, dried at 280° C, and weighed as silver chloride. For very high accuracy, the sample can be transferred to a porcelain crucible and fused at about 455° C.

Copper, mercury, lead, thallium, palladium, bismuth, antimony, cyanides, and thiosulphates interfere with the accuracy of the method.

In the volumetric method a dilute nitric acid solution of silver is titrated with standard ammonium or potassium thiocyanate solution, ferric alum being used as an indicator. The silver is precipitated as white insoluble thiocyanate. A permanent coloration by the red trivalent iron compound does not appear until all of the silver has been precipitated. Strong nitric acid solutions and heat interfere with this reaction. Mercuric mercury, cuprous copper, palladium, nitrous acid, sulfates, and chlorides interfere with the determination.

In the electrometric method, the silver is titrated with a chloride or iodide. The end-point is determined by means of a potentiometer by using silver foil and a mercurous sulphate (calomel) half cell as indicator electrodes.

A number of methods have been described for determining very small amounts of silver in which the concentration of silver is less than 2 mg per liter: Egg [4], Whitby [9], Hickman [8], Wernicke and Modern [6], Johnston, Cuta, and Garrett [2], Jelley [3], and Schoonover [1].

(1) *Selected References:*

[1] Irl C. Schoonover. *A colorimetric method for the quantitative determination of small amounts of silver by the use of p-dimethylaminobenzalrhodanine.* BS J. Research **15,** 377–385 (1935) RP836.

[2] H. L. Johnston, F. Cuta, and A. B. Garrett. *The solubility of silver oxide in water, in alkali, and in alkaline salt solutions. The amphoteric character of silver hydroxide.* J. Am. Chem. Soc. **55,** 2311 (1933).

[3] E. E. Jelley. The *colorimetric determination of small amounts of silver.* S. Soc. Chem. Ind. **51,** I, 191 (1932).

[4] C. Egg. *On the microdetermination of silver in oligodynamic water.* Schweiz. med. Wochschr. **59,** 84 (1929).

[5] W. F. Hillebrand, and G. E. F. Lundell. Applied Inorganic Analysis, 161–166. (J. Wiley & Sons, New York, N. Y., 1929.)

[6] Wernicke and Modern. *Oligodynamic activity of distilled water caused by metallic silver.* Compt. Rend. sec. biol. **99,** 1519–20 (1928).

[7] Kolthoff and Furman. Potentiometric Titrations, 164–184. (J. Wiley & Sons, New York, N. Y., 1926.)

[8] K. C. D. Hickman. *Silver iodide and methylene blue B.* Phot. J. **62,** 512–521 (1922).

[9] G. S. Whitby. *On the detection and estimation of minute amounts of silver and the solubility of sparingly soluble silver salts.* 7th Int. Cong. Applied Chem. **I,** 12 (1909).

3. TECHNOLOGY

a. MECHANICAL WORKING

(1) *Annealing and Recrystallization.* (a) *Temperature of Annealing.*—The temperature at which the properties of cold-worked silver begin to change to those of the annealed metal has formed the basis of a number of investigations. Although the temperature of this change depends, in large measure, on the chemical purity and degree of cold-working of the metal, it has been found to vary considerably according to the property selected as the criterion.

Measurement of one or more of the mechanical properties is the common method for detecting the onset of changes brought about by heating. For example, the hardness of cold-worked silver diminishes when the silver is heated at a particular temperature, which depends, in part, upon the duration of heating at this temperature. Tammann and Dreyer [2] found that softening could be detected after 1-hour periods at the temperatures indicated:

Reduction by rolling at 20°C	Temperature at which softening begins
%	° C
90	65
50	100
10	250

Extremely long periods at these temperatures are required to produce a marked decrease in the hardness. From the facts to be brought out shortly, it appears doubtful whether complete annealing could ever be effected at the temperature at which initial effects are observed.

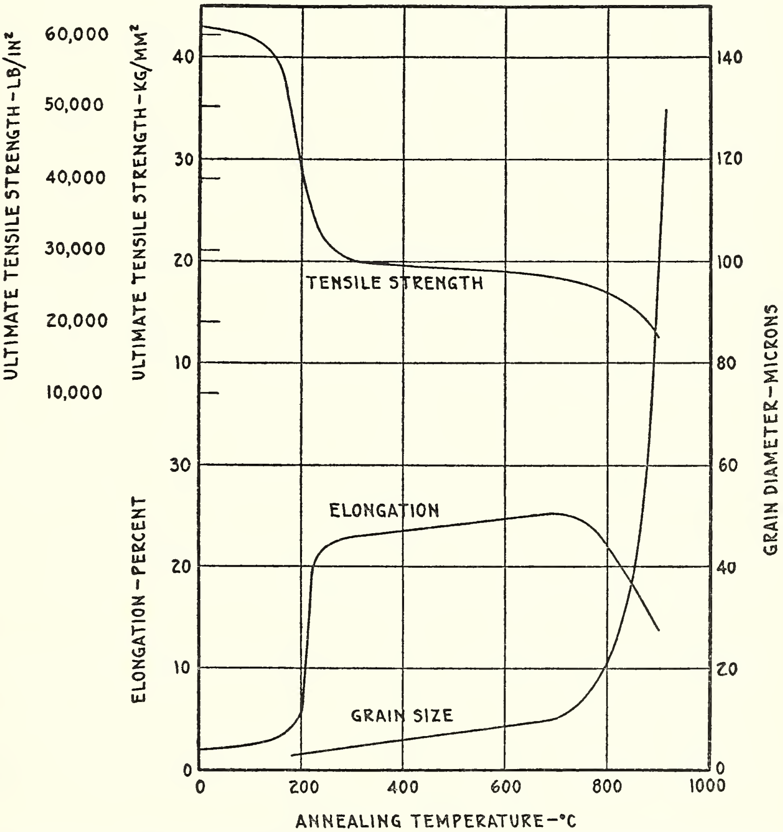

Figure 17.—*Tensile strength, elongation and grain size of rolled silver sheet as functions of annealing temperature (Clark [4] from Glocker, Kaupp and Widmann [9]).*

The effect of temperature on cold-worked silver containing 0.2 percent of copper and some iron was studied by Glocker, Kaupp, and Widmann [9], whose curves showing the changes in ultimate tensile strength, percent of elongation, and grain size, as replotted by Clark [4], are shown in figure 17. It will be noted that marked changes in the mechanical properties resulted on annealing at approximately 200° C. That this temperature is by no means as definite as might be supposed is evident from the authors' statement that in a previous experiment annealing was observed at 150° C on the same material which had been reduced 97 percent in thickness instead of 99 percent as in the present case.

The effect on commercial silver (99.9 percent of silver) of annealing for half-hour periods has been given in table 4. The decrease in hardness and strength, and corresponding changes in other properties, continue to comparatively high temperatures.

Annealing affects different properties at different rates. Thus, Tammann and Dreyer [2], who observed a change in the electrical resistance of cold-worked silver after 5 minutes at 60° C and a marked decrease after short periods at 100° C, state that the electrical resistance reaches the value of the annealed state and the hardness decreases half-way to its value for the annealed condition before any change in the microstructure can be observed.

Other properties change when cold-worked metal is annealed. For example, Tammann and Bandel [1] made thermocouples composed of annealed silver against cold-worked silver. With wire that had been reduced 90 percent by drawing they found that annealing effects appeared at 100° C when the rate of heating was 2.5° per minute. Margenau [5] studied the effect of plastic deformation on the wave length at which the minimum reflecting power of silver occurred and found that the minimum for the deformed material occurred with a wave length 20 smaller than for annealed metal. Magnetic susceptibility, temperature coefficient of resistance, and other properties are also functions of the degree of annealing and have been discussed in connection with the information on these various properties.

(b) *Recrystallization and Structural Changes.*—Changes in the crystalline state of silver may be studied either by X-ray methods or by the microscope. Nishikawa and Asahara [13] examined thin sheets of silver by passing a beam of X-rays perpendicularly through the sheet and found a preferred orientation in the space lattices of the existing crystal grains. They also discovered that the pattern obtained after the sheets had aged for 3 weeks at room temperature was distinctly different from that of freshly rolled sheets.

Experiments of Glocker and Kaupp [10] on sheets which had been reduced 97 percent indicated an initial change after 10 minutes at 140° C. The maximum intensity of the spots constituting the X-ray diffraction pattern of the rolled silver began to diminish after 10 minutes' heating at 170° C. However, complete removal of the rolled structure could not be accomplished by very long annealing periods at approximately 300° C and persisted up to 700° C, according to these authors. No trace of the rolled structure was observed after 10 minutes at 830° C, but Hollabaugh [3] considers this temperature to be insufficient to produce a completely random distribution. According to him, a temperature of 900° C is necessary if the period of annealing is not to exceed one-half hour.

Glocker, Kaupp, and Widmann [9] used both X-ray and microscopic methods. On the basis of the X-ray results, on silver of about 99.7-percent purity, with 10-minute annealing periods they recognized three stages in the annealing of rolled sheet silver:

1. The cold-rolled condition for which the pattern of the as-rolled material persists up to about 200° C.

2. The partly annealed state, from 200 to about 800° C, in which a definite orientation somewhat different from that of the cold-rolled material persists.

3. The condition of random distribution of the space lattice of the grains. The lower temperature limit cannot be stated with certainty, since the change from the X-ray pattern of the partly annealed state to that of a random distribution is very gradual.

No change in the visible microstructure could be detected until an annealing temperature of 212° C had been reached. At this point, some indication of new crystals was observed at a magnification of 1,500 diameters. With increase in the annealing temperature, recrystallization proceeded but with no marked grain growth until, upon reaching about 800° C, marked grain growth set in. This tendency became pronounced with very high annealing temperatures, figure 17.

(c) *Composition vs. Annealing Temperature.*—The presence of small percentages of other elements appears to alter the temperature at which annealing effects set in as determined by the X-ray method, as shown by the data in table 29 from Widmann [7], which have been confirmed by Clark [4].

TABLE 29.—*Annealing temperature of silver containing various impurities* [7]

Element added	Amount	Recrystallization temperature	Element added	Amount	Recrystallization temperature
	Percent	°C		*Percent*	°C
None	----------	150	Nickel	0. 1	137
Copper	0. 303	230	Gold	. 1	112
Do	. 012	200	Do	. 2	110
Do	. 073	175	Palladium	. 1	112
Aluminum	. 20	190	Iron	. 035	110
Zinc	. 119	145	Do	. 055	20
Lead	. 059	145	Do	. 065	20

The temperatures given refer to severely cold-worked material. One statement of Clark's is noteworthy, which is to the effect that silver containing less than 0.0005 percent of iron and 0.00002 percent of lead recrystallizes at room temperature.

(2) *Orientation of Crystals in Cold-Worked Silver.* (a) *Orientation in Wires.*—The tendency of the crystal structure of cold-drawn silver wire to be definitely related to the direction of drawing, that is, to exhibit "preferred orientation", was observed by Ettisch, Polanyi, and Weissenberg [12]. A more detailed study was made by Schmid and Wasserman [6], who stated that the crystals tend to arrange themselves in such a way that either the (100) or (111) planes are approximately parallel to the axis of the wire. These authors also concluded that about 75 percent of the crystals were grouped according to the former arrangement and about 25 percent in the latter.

(b) *Orientation in Sheets.*—Studies of the preferred orientation of the crystals in cold-rolled silver sheet by Mark and Weissenberg [11], by Glocker [8], and by Glocker, Kaupp, and Widmann [9] have given results in good agreement with each other. Figure 18 from Glocker's data is representative. The shaded area represents the rolled sheet or foil with the direction of rolling indicated by the vertical arrow. The preferred orientation of the face-centered cubic crystals is such that the arrow representing the direction of rolling also indicates the (112) direction of the lattice. It will be noted that the (111) direction lies in the plane of the foil and is transverse to the direction of rolling and that the (110) direction is perpendicular to the plane of the sheet. The heavy arrows represent the axes with respect to which the other directions are defined.

Actually, there are two preferred orientations of which figure 18 may be considered to be the first. The second is described by a figure which is the mirror image of figure 18 with the reflection taking place across the plane which contains the direction of rolling and the perpendicular to the sheet.

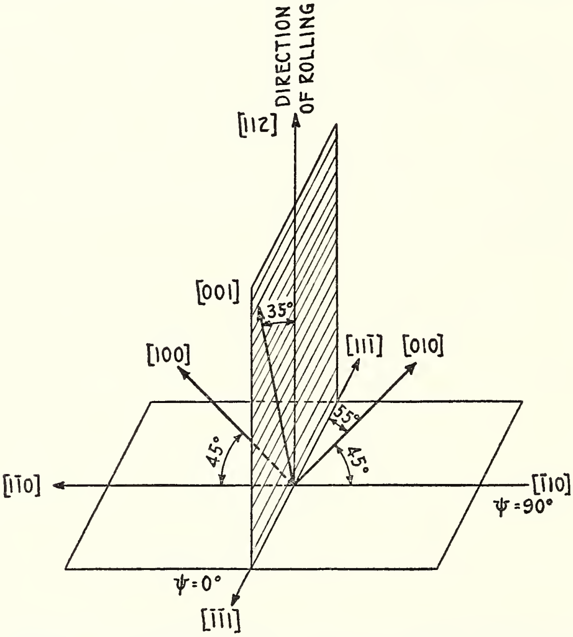

Figure 18.—*Preferred orientation in the grain structure of rolled sheet silver with respect to lattice directions* (*Glocker* [*8*]).

Upon annealing sheet silver at a low temperature, the relations described above are replaced by four preferred orientations. In the new orientations, the (112) planes are still approximately in the direction of rolling but the (311) family of planes has moved into practical coincidence with the normal to the foil. Annealing at a sufficiently high temperature will, of course, produce a completely random distribution of the crystal lattices.

(3) *Selected References:*

[1] G. Tammann and G. Bandel. *Die Änderung der Thermokraft bei der Erholung der Metalle von der Kaltbearbeitung.* Ann. Physik (5) **16,** 120–128 (1933).

[2] G. Tammann and K. L. Dreyer. *Die Erholung des elektrischen Widerstands und der Härte von Kupfer, Silber, und Gold sowie von Platin und Palladium von den Folgen der Kaltbearbeitung.* Ann. Physik (5) **16,** 111–118 (1933).

[3] Cleveland B. Hollabaugh. *Preferred orientation in silver foil produced by cold rolling.* Metals & Alloys **1,** 602–606 (1930).

[4] George L. Clark. *X-ray metallography in 1929.* Metals & Alloys **1,** 14–17, 57–68, 98–111, 153–161, 206–221 (1929–30).

[5] H. Margenau. *Dependence of ultraviolet reflection of silver on plastic deformation.* Phys. Rev. **33,** 1035–1045 (1929).

[6] E. Schmid and G. Wasserman. *Über die Textur hartgezogener Drähte.* Z. Physik **42,** 779–794 (1927).

[7] H. Widmann. *Untersuchungen über die Rekristallisation bei Silber und Kupfer.* Z. Physik **45,** 200–224 (1927).

[8] R. Glocker. *Über Deformations- und Rekristallisationsstrukturen von Metallen.* Z. Physik **31,** 386–410 (1925).

[9] R. Glocker, E. Kaupp, and H. Widmann. *Untersuchungen über die Rekristallisation gewalzter Silber-bleche.* Z. Metallkunde **17,** 353–357 (1925).

[10] R. Glocker and E. Kaupp. *Beobachtung des Rekristallisationsvorganges mittels Röntgen-strahlen.* Z. Metallkunde **16,** 377–379 (1924).

[11] H. Mark and K. Weissenberg. *Röntgenographische Bestimmung der Struktur gewalzter Metallfolien.* Z. Physik **16,** 314–318 (1923).

[12] M. Ettisch, M. Polanyi, and K. Weissenberg. *Röntgenographische Untersuchungen an Metallen.* Physik. Z. **22,** 646 (1921).

[13] S. Nishikawa and G. Asahara. *Some studies of metals by means of X-rays.* Phys. Rev. **15,** 38–45 (1920).

III. ALLOYS OF SILVER

1. BINARY SYSTEMS

a. IMPORTANT ALLOYS OF SILVER

In conformity with the general plan of emphasizing the technical aspects of silver, the number of binary alloy systems selected for discussion in this circular has been considerably restricted. While certain of the noble-metal alloys are used in technical work in large amounts, it has been considered desirable to take up only base-metal alloys. Since major interest centered in the compositions in which silver is a minor constituent, only those base metals which enjoy a large industrial consumption were selected for discussion.

A still further restriction is necessary because of the very limited extent to which certain base metals will alloy with silver. Included in this class is the very important group which contains iron, nickel, and cobalt. Additions of silver to at least the first two metals of this group, have, however, been made. Faraday [2] added silver to tool steel, and although he was unable to make the steel retain more than 0.2 percent, considered it to be improved by the addition. Other investigators have also reported adding silver to iron. According to Wise [1] the addition of 6 percent of silver to nickel in an experimental alloy made the nickel more machinable. However, little true alloying appears to take place with either nickel or iron.

Examination of the literature indicated that the nonferrous materials of relatively low melting point have been most thoroughly studied. Although none of these systems has been satisfactorily explored, it has seemed desirable to give such information as is available on the alloys of silver with aluminum, cadmium, copper, lead, tin, and zinc.

(1) *Selected References:*

[1] Private communication from E. M. Wise. The International Nickel Co., Research Laboratories, Bayonne, N. J. (1934).

[2] Michael Faraday. Experimental Researches in Chemistry and Physics. p. 57–81, London, Richard Taylor, and William Francis (1859).

b. SILVER-ALUMINUM

(1) *Constitutional Diagram.*—Because of the disagreement among the investigators who have worked on the silver-aluminum system, only the portions of the equilibrium diagram corresponding to the silver-rich and the aluminum-rich alloys are presented. Figure 19 shows the silver-rich end of the diagram from Ageew and Shoyket [3], who based this on their own work and that of Hoar and Rowntree [5]. Westgren and Bradley [8] have confirmed the narrowness of the B′ field. These authors consider this phase to be the compound Ag_3Al and state that it has only a very limited solid solubility for the adjacent phases.

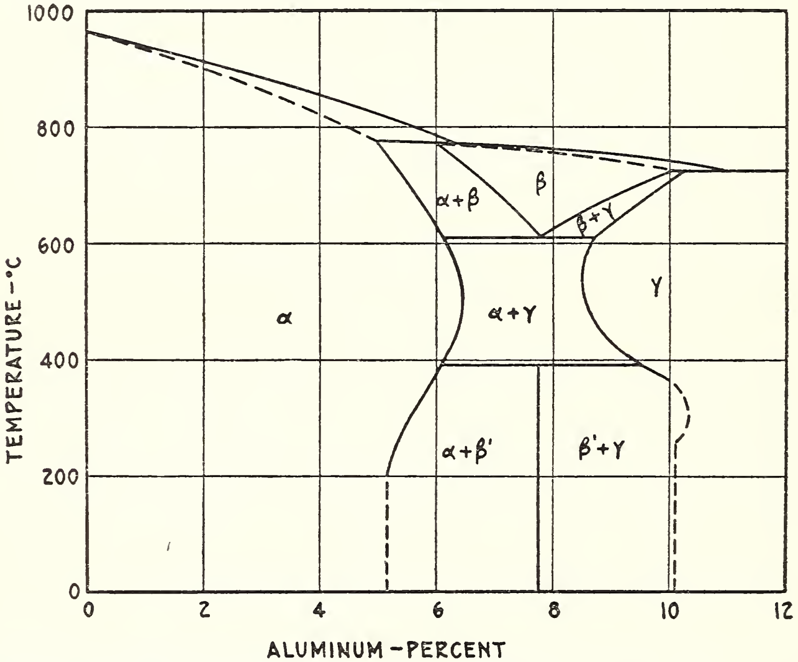

FIGURE 19.—*Portion of the aluminum-silver constitutional diagram (Ageew and Shoyket [3]).*

The only diagram of the aluminum-rich alloys which accounts for the age-hardening properties found by Kroll [10] and Hansen [7] is that of Hansen [6], figure 20. Hansen [6] considered Ag_2Al to be the precipitating substance, but Westgren and Bradley [8] have stated that Ag_3Al is the only compound in this system and have shown that, according to their X-ray data, the phase existing where Ag_2Al would be located is of the solid-solution type. The increase in the solubility of silver in the aluminum-rich phase, as the temperature rises, is rather pronounced.

(2) *Physical Properties.*—Hansen [7] studied the aging characteristics of samples of cast aluminum-silver containing from 0.45 to 11.8 percent of silver quenched from 525° C, figure 21. At 100° C the maximum hardness was not attained after 6-weeks' aging. Aging at 150 to 160° C gave the highest hardness. Quenching from 300° C produced the softest state observed.

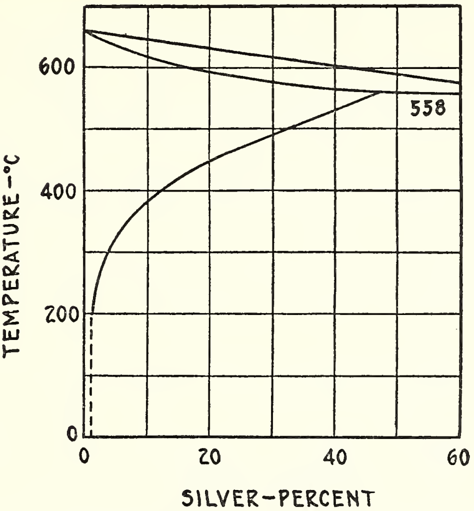

FIGURE 20.—*Portion of the aluminum-silver constitutional diagram (Hansen [6]).*

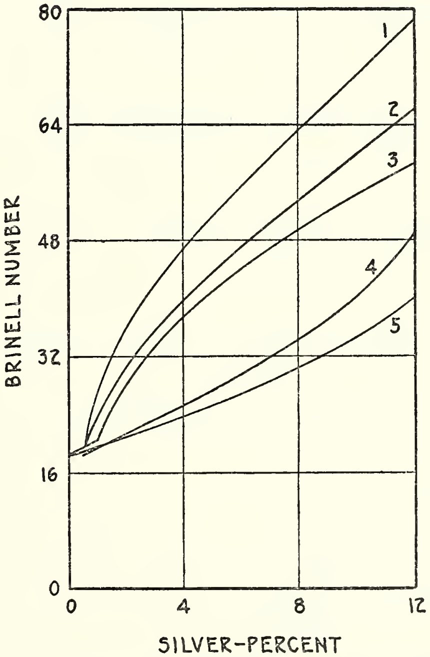

FIGURE 21.—*The Brinell Numbers (5 mm, 62.5 kg, 30 sec) of silver-aluminum alloys of increasing silver content after various heat treatments (Hansen [6]).*

1. Aged for 5 days at 150° C.
2. Aged to maximum hardness at 175° C.
3. Aged for 32 days at 200° C.
4. Heated for 5 hours at 525° C and quenched.
5. Heated for 45 hours at 537° C and quenched, and afterwards heated for 5 days at 300° ± 5° and quenched.

Kroll [10] studied the age-hardening of aluminum containing 1.3 to 9.1 percent of silver. He obtained about the same increase in hardness, as measured on the Brinell scale, as was observed on similar copper-aluminum alloys, but both the initial and the final values were lower. The maximum tensile strength was about 11,400 lb/in.^{2} (8 kg/mm^2), lower than the tensile strength of a copper-aluminum alloy containing 5 percent of copper. The addition of 0.5 percent of magnesium increased the maximum obtainable hardness in both cases, but the effect of magnesium was to raise the aging temperature of the silver-aluminum alloys, whereas it lowered it for the aluminum-copper alloys.

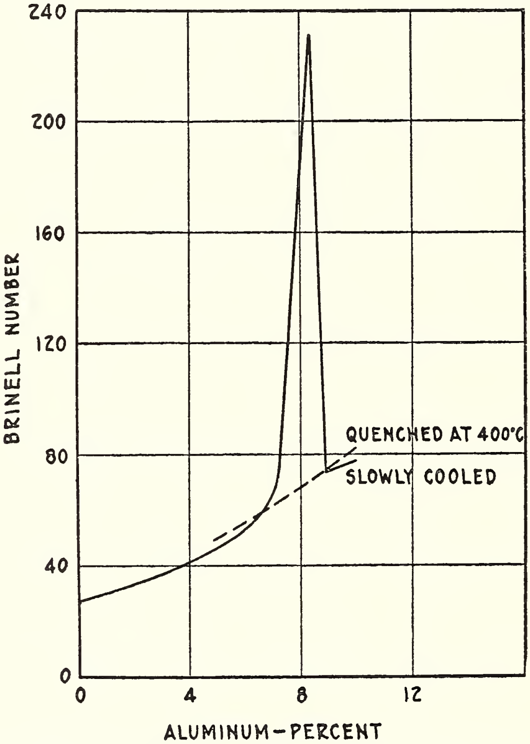

Figure 22.—*Hardness of the aluminum-silver alloys of increasing aluminum content after slow cooling and after quenching from 400° C (Ageew and Shoyket [3]).*

Some work on aluminum-silver alloys has been done at the research laboratory of the Aluminum Company of America [2]. An aluminum alloy containing 5 percent of copper and 3 percent of silver and practically no Mg_2Si showed slightly better mechanical properties than the same alloy without silver, when aged at room temperature, but practically no improvement when aged at 143° C. After salt-spray tests over a period of 4 weeks, the silver-containing alloy was found to have suffered a considerably greater decrease in ultimate tensile strength than the simple 5-percent-copper alloy. Microscopic examination revealed typical intergranular corrosion.

Other tests were made on an alloy of 30-percent silver and 70-percent aluminum. As a solution treatment, the material was held at

540° C for 2 hours and quenched. After aging at 150° C for 20 hours, the ultimate tensile strength was 48,000 lb/in.^{2}, the yield strength 46,000 lb/in.^{2}, and the elongation (2-inch gage length), 2 percent. When the same alloy was aged at room temperature after the same solution treatment, the corresponding values were 51,000 lb/in.^{2}, 37,000 lb/in.^{2}, and 11 percent. Material of this composition could be rolled readily either hot or cold. In cold-rolling, it was necessary to interrupt the process by an annealing after each reduction of 50 percent. Although specimens of this alloy showed little disposition to tarnish, they corroded severely in moist air.

It is of interest to note that in the work done at the laboratories of the Aluminum Company of America, less silver could be gotten into solution than should have been possible according to Hansen's diagram of the aluminum-rich alloys.

The addition of aluminum to silver was found by Jordan, Grenell, and Herschman [9] to increase the hardness rapidly with increasing aluminum content. Likewise Ageew and Shoyket [3], working with cast alloys, found that by cooling the alloy containing 7.9 percent of aluminum rather slowly a marked increase in hardness was obtained. Figure 22 shows the very narrow range over which this peculiar effect occurred.

(3) *Electrical Properties.*—The electrical resistance of aluminum alloys containing small amounts of silver has been investigated by Fraenkel [4] and also by Böhner [1]. The results of the two investigators agree closely and are given in table 30.

TABLE 30.—*Electrical resistance of some aluminum-rich aluminum-silver alloys*

Ag by weight	Resistivity, 20° C	Data from
%	*microhm-cm*	
0.83	30.0	Böhner [1].
2.00	32.4	Fraenkel [4].
2.87	35.8	Böhner [1].
3.85	38.0	Fraenkel [4].

Böhner found little difference between the resistivity of a specimen annealed at 300° C for 14 hours and of a similar sample held at 500° C in a salt bath for 1 hour and then quenched. The values for cold-worked samples were intermediate between those of the annealed and quenched samples.

According to Broniewski [11] alloys containing 0 to 60 percent of silver possessed a higher resistance in the quenched than in the annealed state, the opposite being true with respect to the temperature coefficient of electrical resistance. He also reported a gradually increasing value of thermoelectric power of silver-aluminum alloys against lead with increasing silver content up to 60 percent.

(4) *Selected References:*

[1] H. Böhner. *Über die Beeinflüssung der elektrischen Leitfähigkeit des Aluminiums durch Zusätze.* Z. Metallkunde **26**, 45–47 (1934).

[2] Private communication, W. L. Fink, Aluminum Research Laboratories, New Kensington, Pa. (1934).

[3] N. Ageew and D. Shoyket. *Constitution of the silver-rich aluminum-silver alloys.* J. Inst. Met. **52**, 119–161 (1933).

[4] W. Fraenkel. *Über die Leitfähigkeit von Aluminiummisch kristallen.* Metallwirtschaft **12**, 159–161 (1933).

[5] T. P. Hoar and R. K. Rowntree. *A note on the silver-rich aluminum-silver alloys above 600°C.* J. Inst. Met. **45**, 119–124 (1931).
[6] M. Hansen. *Der Aufbau der Aluminiumreichen Silber-Aluminiumlegierungen.* Z. Metallkunde **20**, 217–222 (1928).
[7] M. Hansen. *Die Alterungshärtung der aluminiumreichen Silber-Aluminiumlegierungen.* Naturwissenschaften **16**, 417–419 (1928).
[8] A. F. Westgren and A. J. Bradley. *X-ray analysis of the silver aluminum alloys.* Phil. Mag. (7) **6**, 280–288 (1928).
[9] Louis Jordan, L. H. Grenell, and H. K. Herschman. *Tarnish-resisting silver alloys.* Tech. Pap. BS **21**, 459–496 (1927) T448.
[10] W. Kroll. *Improvable aluminum-silver alloys.* Metall. u. Erz. **23** (N. F. 14), 555–557 (1926).
[11] W. Browniewski. *Propriétés Electriques des Alliages d'Aluminium:* Ann. chim. phys. (8) **25**, 80–86 (1912).

c. SILVER-CADMIUM

(1) *Constitutional Diagram.*—Although considerable study has been devoted to the constitutional diagram of the silver-cadmium system, the data do not justify the presentation of a complete diagram. Fortunately, the situation concerning the high-cadmium alloys is more satisfactory and the part of the diagram from Durrant [5] is given in figure 23.

Nearly 45 percent of cadmium is soluble in silver at room temperature and somewhat less than this amount at elevated temperatures. The intermediate alloys have been studied by X-ray methods by Astrand and Westgren [10] and by Natta and Freri [11, 12], while Fraenkel and Wolr [8] have used thermal, dilatometric, electrical resistance, and other methods. Ölander [2] measured the electromotive force and the temperature coefficient of electromotive force of a number of the alloys against molten cadmium, the investigation being carried out at elevated temperatures in a molten salt of cadmium as the electrolyte.

(2) *Physical Properties.*—Alloys containing 50 percent by weight, of cadmium are brightly colored, which was first commented upon by Heycock and Neville [16]. Rose [15] noted colors ranging from red to lilac and stated that these appeared upon quenching alloys containing 43 to 50 percent of silver from above a transformation point occurring in the vicinity of 420° C. He attributed the effect to surface oxidation. Schreiner [14] noted a series of colors as the composition was changed. His alloys appear to have cooled rather slowly through the transformation, somewhat above 400° C, but since they were removed from the furnace at a temperature estimated to be above 200° C, they may have dropped rather quickly through the thermal critical point which occurs in this neighborhood [2]. Schreiner also observed that alloys containing 40 to 50 percent of silver showed a marked change in their electromotive force against cadmium after standing for several months at room temperature.

Information on the mechanical properties of the cadmium-silver alloys is scanty. Those of intermediate composition are generally brittle. Schreiner [14] reported that an alloy containing 40 percent of silver broke while being shaken in a flask. Fraenkel and Wolf [8] noted the extraordinary brittleness of alloys containing 37.3 and 42.0 percent of silver and stated that material containing 44.1 percent of silver could be readily broken with a hammer. It appears from their work, however, alloys containing 46 to 59 percent of silver may be worked by the ordinary processes of drawing and rolling.

Rose [15] considered a specimen with 65 percent of silver to be less ductile than those which contained more silver. Fraenkel and Wolf measured the hardness of the intermediate alloys, 40 to 60 percent of silver, by the Brinell method and obtained values from 60 to 70 on alloys which had been annealed for a long time at 180° C. They also found that quenching from 300 and 500° C produced only small changes in hardness. According to Guillet and Cournot [9] alloys containing approximately 60.0 percent of silver exhibited only slight change with heat treatment, the hardness (Brinell scale) being about 35 to 45. Alloys containing 49.3 percent of silver, however, showed appreciable changes with heat treatment, as shown in table 31.

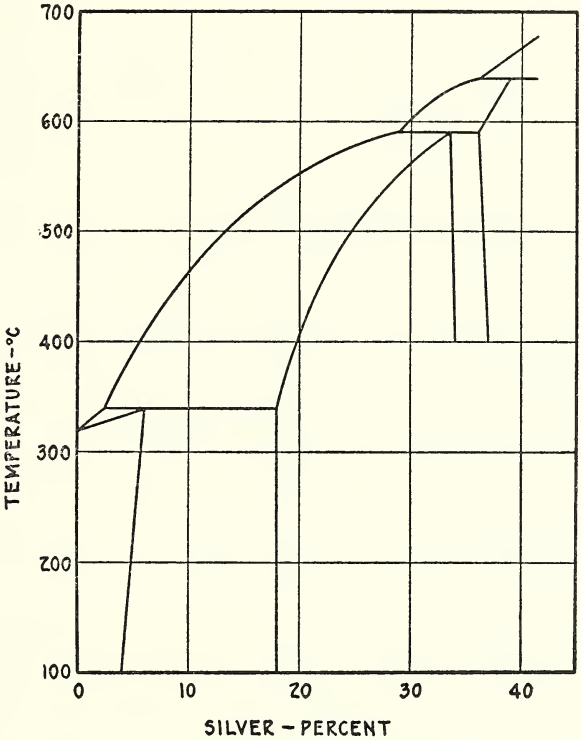

Figure 23.—*Portion of the cadmium-silver constitutional diagram* (*Durrant* [*5*])

Table 31.—*Change of hardness of cadmium-silver alloy* (*49 percent of silver*) *with heat treatment* [*9*]

Treatment	Brinell number (5 mm, 500 kg, 15 sec)
As cast	100
Annealed at 500° C	119
Quenched from 400° C	77
Drawn at 150° C	115
Drawn at 320° C	84

The alloy, 5 percent of silver—95 percent of cadmium, has been investigated in more detail. The data given in table 32 have been supplied by Handy and Harman.

TABLE 32.—*Tensile properties of the 5 percent of silver—95 percent of cadmium alloy at various temperatures*

Temperature of test	Ultimate tensile strength	Elongation in 2 inches	Reduction of area
°F	lb/in.^{2}	*Percent*	*Percent*
Room temperature	16, 400	31. 3	81. 0
300	4, 400	93. 7	91. 0
425	2, 600	93. 7	68. 0
500	1, 700	21. 9	11. 0

The values were obtained on ¼-inch rods at ordinary rate of load application and the values should be considered as only approximate. The load required to produce continuous stretch at room temperature was found to be about 1,200 lb/in^2.

(3) *Chemical Properties.*—Some interest has been shown in the chemical properties of silver-cadmium alloys, principally those containing considerable silver. It was noticed by Rose [15] that silver-cadmium alloys did not tarnish as readily when immersed in a solution of ammonium polysulfide as copper-silver alloys of corresponding composition. He also observed that the brittle alloys of the intermediate range of composition were resistant to cold nitric acid, hydrochloric acid, and some other reagents. The simultaneous electrodeposition of silver and cadmium has been studied by a number of investigators [3, 4, 6, 7, 13]. Stillwell and Stout [4] showed by X-ray methods that the deposits consisted of definite phases of the cadmium-silver system rather than a mixture of the two metals. They also observed that for a given composition, the phases were not generally present in the same proportions as in the corresponding alloy made by melting in the ordinary way.

(4) *Industrial Applications.*—The principal industrial applications of the silver-cadmium alloys are the solder described in table 32 and a silver-cadmium-copper bearing metal. The principal advantage of the silver-cadmium solder over the lead-tin solders is its considerably higher strength at both room and elevated temperatures.

The silver-cadmium-copper bearing alloy contains approximately 2 percent of silver, 0.5 percent of copper and 97 percent of cadmium. According to the manufacturer [1], this bearing has the properties described in table 33.

TABLE 33.—*Tensile strength of the silver-cadmium-copper bearing metal at various temperatures* [**1**]

Temperature of test	Ultimate tensile strength	Elongation in 2 inches	Brinell hardness number (as cast)
°F	lb/in.^{2}	*Percent*	
Room temperature	18, 000	50	40. 2
212	12, 000		19. 0
300	8, 000		13. 2
400	4, 350	68	8. 1

(5) *Selected References:*

[1] Athel F. Denham. New cadmium-silver-copper bearing alloys developed by Federal Mogul. Automotive Industries **71**, 640–642 (1934). Supplemented by private communication Feb. 6, 1936, from E. R. Darby, Federal Mogul Corporation.

[2] Arne Olander, *Eine elektrochemische Untersuchung von Cadmium-Silberlegierunger.* Z. physik. Chem. (A) **163** 107–121 (1933).

[3] Charles W. Stillwell and Henry I. Feinberg. *Structure of electrodeposited alloys. II. Effect of current density and temperature of deposition on the structure of silver-cadmium deposits.* J. Am. Chem. Soc. **55**, 1864–1870 (1933).

[4] Charles W. Stillwell and Lawrence E. Stout. *The Crystal structure of electrodeposited alloys. An X-ray diffraction study of silver-cadmium deposits.* J. Am. Chem. Soc. **54**, 2583–2592 (1932).

[5] P. J. Durrant. *Constitution of the cadmium-rich alloys of the system cadmium-silver.* J. Inst. Metals **45**, 99–113 (1931).

[6] Lawrence E. Stout and William G. Thummel. *The change in reflecting power caused by tarnishing electrodeposited silver-cadmium alloys.* Trans. Electrochem. Soc. **59**, 337–348 (1931).

[7] C. G. Fink and B. G. Gerapostulou. *The electrodeposition of silver-cadmium alloys.* Metal Ind. (New York) **28**, 519–521, 562 (1930).

[8] W. Fraenkel and A. Wolf. *Die Umwandlungen im festen Zustand bei Silber-Cadmiumlegierungen.* Z. anorg. Chem. **189**, 145–167 (1930).

[9] Leon Guillet and Jean Cournot. *Influence des traitement thermiques sur certains alliages argent-zinc et argent-cadmium.* Rev. Mét. **27**, 1–7 (1930).

[10] Halvdan Astrand and Arne Westgren. *Röntgenanalyse der Silber-Cadmiumlegierungen.* Z. anorg. Chem. **175**, 90–96 (1928).

[11] G. Natta and M. Freri. *Analisi coi raggi X e struttura cristallina delle leghe cadmio-argento. Nota III.* Atti accad. Lincei (6) **7** 406–410 (1928).

[12] G. Natta and M. Freri. *Analisi coi raggi X e struttura cristallina delle leghe cadmio-argento. Nota II.* Atti accad. Lincei (6) **6**, 505–511 (1927).

[13] A. H. W. Aten and M. F. van Putten. *The Electrodeposition of silver-cadmium alloys.* Rec. trav. chim. **44**, 861–865 (1925).

[14] Erling Schreiner. *Über das elektromotorische Verhalten von Silber-Cadmiumlegierungen.* Z. anorg. Chem. **125**, 173–184 (1922).

[15] T. Kirke Rose. *On certain properties of the alloys of silver and cadmium.* Proc. Roy. Soc. (London) (A) **74**, 218–230 (1904–05).

[16] C. T. Heycock and F. H. Neville. *On the superficial color of a silver zinc alloy.* Proc. Cambridge Phil. Soc. **9**, 222–224 (1895; 1898).

d. SILVER-COPPER

(1) *Constitutional Diagram.*—Because of their importance in sterling ware and in coinage, the copper-silver alloys have been studied more thoroughly than any other of the alloys of silver with the common metals. The studies of Heycock and Neville [21], Friedrich and Leroux [20], Roeser [12], Stockdale [8], Smith and Lindlief [5], Ageew and Sachs [10], Hansen, Ageew, and Sachs [9] and others, on the constitutional diagram have been critically reviewed by Gregg [2], and the diagram in figure 24 has been taken from that source.

(2) *Physical Properties.*—This diagram suggests that age-hardening should occur in copper alloys containing several percent of silver. Smith and Lindlief [5] found such an effect, but it was small in comparison with that observed in the high-silver alloys. The maximum increase in hardness, B68 to B78, Rockwell scale, which was observed, was on an alloy containing 5 percent of silver which had been heated for 4 hours at 400° C. The observed changes in tensile strength, elongation, and electrical conductivity of this alloy are shown in figure 25.

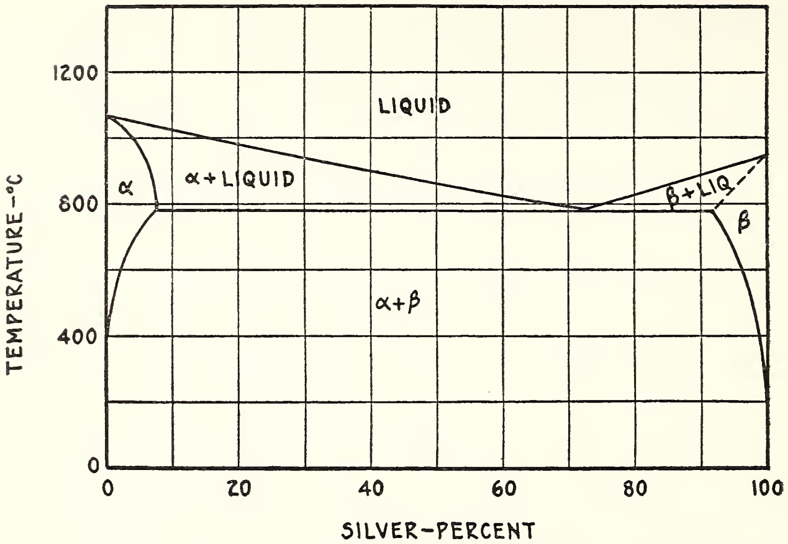

Figure 24.—*Silver-copper constitutional diagram (Gregg [2, p. 66]).*

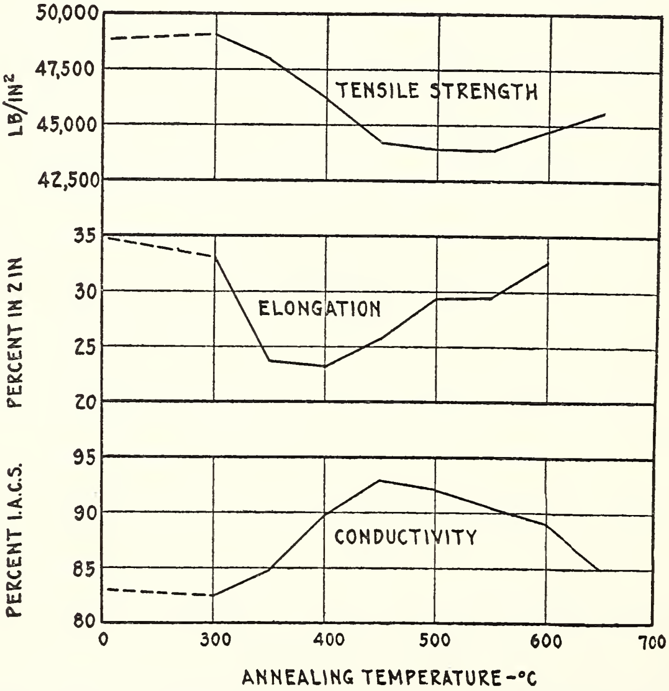

Figure 25.—*Effect of annealing on properties of a copper-silver alloy after being quenched from 750° C (Smith and Lindlief [5]).*

The hardness of annealed cast specimens was found by Kurnakow, Puschin, and Senkowsky [19] to increase from about 40 to 60 on the Brinell scale (10-mm ball, 100-kg load) as the silver content was increased from 0 to approximately 5 percent. On wrought material, Norbury [14] observed a somewhat smaller rise in hardness over the same range.

Perhaps the most interesting result of adding small amounts of silver to copper is the increase in "annealing temperature", as illustrated in figure 26 from Kenny and Craig [3]. Annealing periods of ½ hour were employed and the hardness was measured by a Rockwell hardness tester.

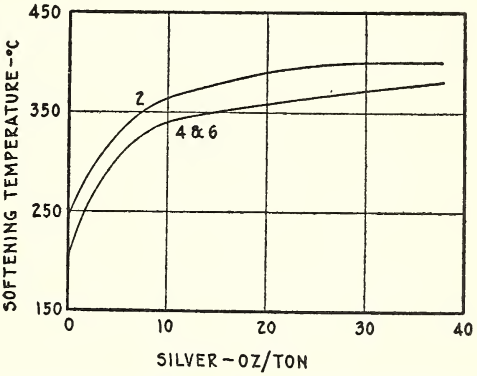

Figure 26.—*Influence of silver on the softening temperature on annealing of hard copper sheet (Kenny and Craig [3]).*

Upper curve, sheet reduced 20 percent; 2 numbers hard. Lower curve, sheets reduced 37 and 50 percent; 4 and 6 numbers hard, respectively (oz/ton×0.00343=percent Ag).

The effect of annealing at 200° C for long periods upon the ultimate tensile strength of argentiferous copper wires drawn from 5/16-inch hot-rolled rods to 0.050-inch wire without annealing is shown in figure 27. It will be observed that the silver content exercises a considerable effect. For an annealing temperature of 150° C the decrease in tensile strength of the alloys very low in silver was much less marked. The strength of alloys containing above 0.03 percent of silver fell off slightly in the beginning but showed practically no change in the interval from 150 to 365

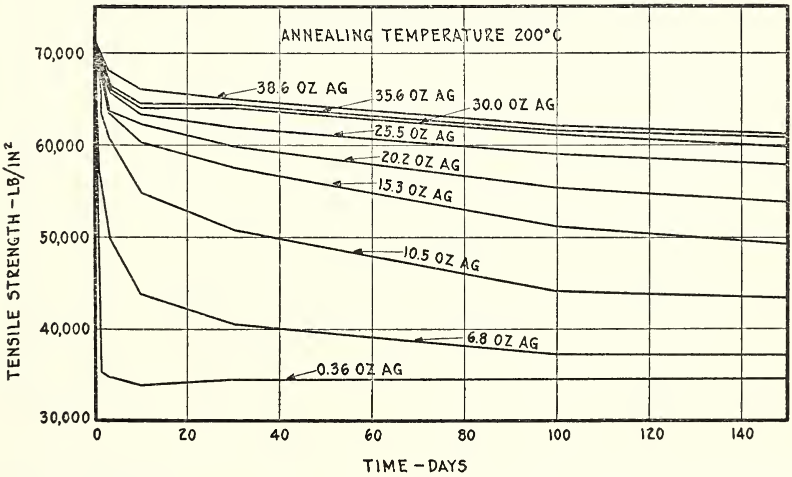

Figure 27.—*Tensile strength of 16-gage (0.050 in.) wire after heating at 200° C (Kenny and Craig [3]).*

Silver content expressed as oz/ton. (Oz/ton×0.00343=percent Ag).

days. Annealing periods of 2 minutes were found by Kenny and Craig [3] to have marked effect on the tensile strength of hard drawn argentiferous copper wire, figure 28. The amount of silver has an important influence on the amount of softening which takes place.

Among earlier investigators who studied the effect of small amounts of silver on copper may be mentioned Caesar and Gerner [18], Johnson [17], Hudson and McKeown [4], Tapsell and Johnson [6] and Hudson, Herbert, Ball, and Buckell [11]. The last investigators found that additions of silver, iron, tin, and other elements were effective in raising the limit of proportionality of copper which had been cold-worked and then annealed at 300° C. In their opinion silver was the most effective. They also stated that, "The highest limits of proportionality observed in all alloys except copper containing silver were only obtained at the expense of ductility or with a hardness greater than that desired, or both."

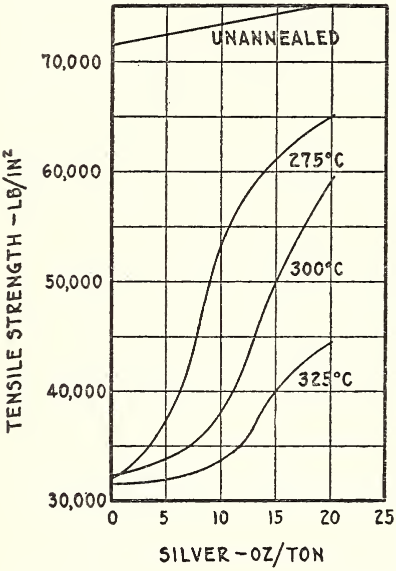

Figure 28.—*Tensile strength of 24-gage (0.020* in.) *wire after annealing for 2 minutes at several temperatures (Kenny and Craig* [3]).

(Oz/ton×0.00343=percent Ag).

Hudson and McKeown [4] investigated the effect of variable amounts of silver in copper-silver and copper-silver-arsenic material for locomotive fire-box stays and plates. The silver content was of the order of 0.1 percent and the arsenic about 0.33 percent. In tests at room temperature, the addition of silver was found to improve the tensile properties of both plain copper and the copper-arsenic alloy, particularly after annealing at about 300° C. The results in table 34 are representative. The copper which contained silver had previously been reduced 10 percent in area and the other specimens 7 percent in area.

Table 34.—*Limit of proportionality and ultimate tensile strength of plain copper and some alloyed copper, annealed for 2 hours at 300° C* [4]

Material	Limit of proportionality	Ultimate tensile strength	Elongation [gage length= 4 $\sqrt{area}$]
	lb/in.^{2}	lb/in.^{2}	*Percent*
High-conductivity copper	5, 100	32, 500	52
Arsenical copper	10, 300	33, 200	46. 5
Silver-copper	7, 200	34, 300	51. 0
Silver-arsenical copper	11, 200	35, 200	51. 0

These investigators also studied the behavior of arsenical and silver-arsenical copper at 300 and 350° C under compression at 7,800, 11,100, and 16,800 lb/in^2. The silver-arsenical copper was deformed less than the arsenical copper at the high and low loads, but comparatively little difference was noted in the two kinds of material for 11,100 lb/in^2.

Tapsell and Johnson [6] conducted creep tests on arsenical copper containing about 0.33 percent of arsenic and on silver-arsenical copper containing a like amount of arsenic and about 0.07 percent of silver. Table 35 contains their data for tests at 300° C on material previously annealed at 350° C.

TABLE 35.—*Creep values of arsenical and silver-arsenical coppers at 300° C [6]*

Material	Stress	Approximate initial strain	Approximate minimum rate of strain	Duration of test
	lb/in.^{2}	in./in.	in./in./day	*Days*
Arsenical	11, 200	0. 0019	0. 00206	4B[a]
	9, 000	. 0016	. 00056	12B
	6, 700	. 0006	. 00014	49B
Silver-arsenical	11, 200	. 0009	. 00037	7. 5B
	9, 000	. 0007	. 000091	26B
	6, 700	. 0006	. 000020	42U[b]

[a] B=broken.
[b] U=unbroken.

According to Bassett [16] the presence of 0.06 percent of silver calls for increasing the annealing temperature from 250 to 350° C for work in the rolling mill.

An interesting observation on the effect of silver on electrolytic copper used for castings has been made by Ash [1]. By using the spiral-casting method developed by Saeger and Krynitsky [7] for testing the fluidity of molten metals, Ash found that, while copper containing 0.04 or 0.10 percent of silver did not produce as long a spiral as copper alone, yet it filled the mold better and gave a much sharper corner, which suggested a decreased surface tension.

(3) *Electrical Properties.*—The electrical conductivity of copper is altered surprisingly little by the addition of small amounts of silver. Data quoted by Gregg [2, page 86] indicate that the presence of 0.1 percent of silver lowers the conductivity by only 0.7 percent, whereas the same percentage of arsenic lowers it about 25 percent [15]. Norbury [14] has shown that silver has the least effect of all the metals in lowering the conductivity of copper, and according to Johansson and Linde [13], the conductivity of the silver-copper series does not fall below 75 percent of that of copper for any composition in the series, all the specimens being in the hard condition. For alloys annealed for 100 hours at 350° C, the conductivity did not fall below 90 percent of that of annealed copper.

(4) *Chemical Properties.*—There is very little published information on either atmospheric or chemical corrosion of argentiferous copper. Experiments at the U. S. Naval Engineering Experiment Station on the corrosive action of brackish river water (5,500 ppm of chlorine) on copper containing 5 percent of silver indicated no superiority to ordinary copper. Red brass (15 percent of zinc) containing 1 or 5 percent of silver showed considerably more corrosion damage than corresponding alloys without silver.

(5) *Industrial Applications.*—Silver-rich alloys of silver-copper series have long been of great importance because of their use in coinage and sterling ware. However, the possibility of improving copper by the addition of silver has not been seriously considered until rather recently. This material has been found particularly useful when soldering is involved, since the heat of soldering does not cause undue softening of the metal. Commutator bars are frequently made of a similar alloy to insure that their hardness will be maintained when warmed.

(6) *Selected References:*

[1] E. J. Ash. An Investigation of the Casting Properties of Lake Versus Electrolytic Copper and Their Alloys. Progress Report of the Metallurgical and Testing Division, U. S. Naval Gun Factory, Navy Yard, Washington, D. C. June 4 (1934).

[2] J. L. Gregg. Arsenical and Argentiferous Copper. (Monograph Series Am.-Chem. Soc.) Chemical Catalog Co., Inc., N. Y. (1934).

[3] H. C. Kenny and G. L. Craig. *Influence of silver on the softening of cold-worked copper.* Trans. Am. Inst. Mining Met. Eng. (Inst. Met. Div.) **111,** 196-204 (1934).

[4] O. F. Hudson and J. McKeown. *The properties of copper in relation to low stresses. The effect of cold-work, heat-treatment, and composition.* J. Inst. Metals **48,** 69–87 (1932).

[5] C. S. Smith and W. E. Lindlief. *The equilibrium diagram of the copper-rich copper-silver alloys.* Trans. Am. Inst. Mining Met. Eng. **99,** 101–114 (1932).

[6] H. J. Tapsell and A. E. Johnson. *The properties of copper in relation to low stresses. The effect of cold-work, heat-treatment, and composition.* J. Inst. Metals **48,** 87–94 (1932).

[7] C. M. Saeger, Jr., and A. I. Krynitsky. *A practical method for studying the running quality of a metal cast in foundry molds.* Trans. & Bul. Am. Foundrymen's Assn. **2,** 513–540 (1931).

[8] D. Stockdale. *The solid solutions of the copper silver systems.* J. Inst. Metals **45,** 127–140 (1931).

[9] N. Ageew, M. Hansen, and G. Sachs. *Entmischung und Eigenschaftsänderungen übersättigter Silber-Kuperlegierungen.* Z. Physik **66,** 350–376 (1930).

[10] N. Ageew and G. Sachs. *Röntgenographische Bestimmung der Löslichkeit von Kuper in Silber.* Z. Physik **66,** 293–303 (1930).

[11] O. F. Hudson, T. M. Herbert, F. E. Ball, and E. H. Bucknall. *The properties of locomotive firebox stays and plates. The oxidation of arsenical copper and effects of small quantities of added elements on the softening temperature and mechancial properties of copper.* J. Inst. Metals **42,** 221–300 (1929).

[12] W. F. Roeser. *Thermoelectric temperature scales.* BS J. Research **3,** 343–358 (1929) RP99.

[13] C. H. Johansson and J. O. Linde. *Electrische Leitfähigkeit und Zustandschaubild der Kupfer-Silberlegierungen.* Z. Metallkunde **20,** 443–444 (1928).

[14] A. L. Norbury. *The effect of quenching and tempering on the mechanical properties of silver.* J. Inst. Metals **39,** 145–161 (1928).

[15] D. Hanson and C. B. Marryat. *Investigation of the effect of impurities on copper. Part III—The effect of arsenic on copper. Part IV—The effect of arsenic plus oxygen on copper.* J. Inst. Metals **37,** 121–163 (1927).

[16] W. H. Bassett, *Researches affecting copper and brass.* Mining and Met. **5,** 73–75 (1924).

[17] F. Johnson. *Experiments in the working and annealing of copper.* J. Inst. Metals **26,** 173–197 (1921).

[18] G. V. Caesar and C. C. Gerner. *The annealing properties of copper at temperatures below 500° C with particular reference to the effect of oxygen and of silver.* Trans. Am. Inst. Met. **10,** 208–248 (1916).

[19] N. Kurnakow, N. Puschin, and N. Senkowsky. *Die elektrische Leitfähigkeit und Härte der Silber-Kupferlegierungen.* Z. anorg. Chem. **68,** 123–140 (1910).

[20] K. Friedrich and A. Leroux. *Kupfer, Silber, und Blei.* Metallurgie **4,** 293–315 (1907).

[21] C. T. Heycock and F. H. Neville. *Complete freezing point curves of binary alloys containing silver or copper together with another metal.* Trans. Roy. Soc. (London) (A) **189,** 25–69 (1897).

e. SILVER-LEAD

(1) *Constitutional Diagram.*—The diagram of the lead-silver system shown in figure 29, which is taken from the International Critical Tables, is based on the work of Friedrich [13]. Friedrich, as well as Heycock and Neville [14], and Petrenko [12] found difficulty in detecting arrest points on that part of the liquidus curve between 90 percent of lead and the eutectic composition. In a study of alloys with less than 10 percent of silver, Yoldi [6] reported that he observed double arrests quite close to the eutectic composition, which he placed at 2.30 percent of silver. He also reported that he detected an arrest at the eutectic temperature in an alloy containing only 0.3 percent of silver.

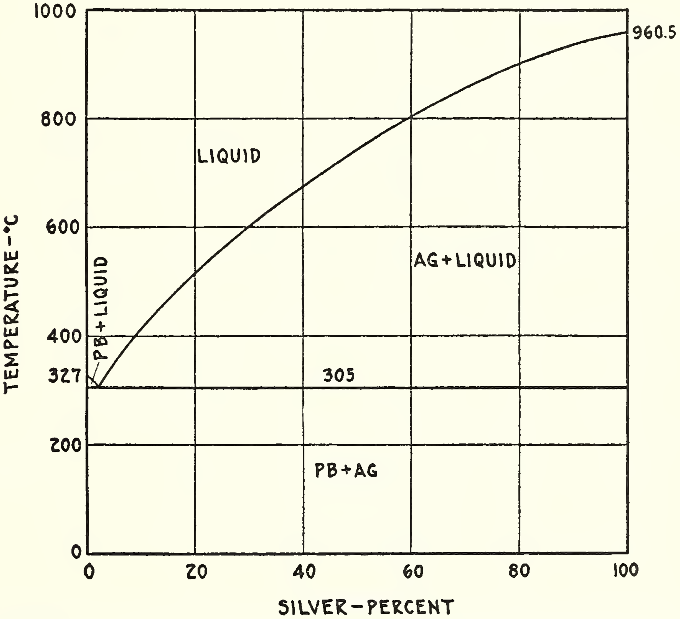

FIGURE 29.—*Silver-lead constitutional diagram (Int. Crit. Tables [9] from Friedrich [13]).*

Practically no solid-solution phase has been detected at either end of the lead-silver diagram. However, Garre and Vollmert [3] found that the compounds Ag_3Sn, $AgCd_4$, and Ag_2Cd_3 were all soluble in lead up to several percent. The hardness of the alloys was always greater after quenching than after slow cooling and the $AgCd_4$ appeared to produce age hardening.

(2) *Physical Properties.*—Russell [1] studied the recrystallization of cold-worked lead containing relatively small amounts of silver. To

lead containing less than 0.0005 percent of impurities, he added silver in various amounts to produce very pure alloys which were cast in vacuo, annealed in vacuo, then distorted and the period required for recrystallization to be completed was noted. The results are summarized in table 36.

Table 36.—*Effect of small amounts of silver on the recrystallization of lead* [*1*]

Added silver	Distortion	Temperature during recrystallization	Time for recrystallization
Percent	*Percent*	°C	
0	5	Room temperature	5 minutes.
0.0001	5	do	24 hours.
.0005	5	do	60 days.
.005	5	125	20 hours.

Ludwik [11] measured the hardness of lead and three lead-silver alloys with an Amsler machine using a 90-degree cone, his results being given in table 37.

Table 37.—*Hardness of some silver-lead alloys* [**11**]

Silver	Hardness [1]	
	As quenched	Annealed at 300° C for 2 to 3 hours
Percent		
0		About 5
.5	9.5 to 9.8	10.0 to 10.6
1.0	10.3 to 11.4	11.2 to 11.4
2.0	11.0 to 12.0	12.3 to 12.5

[1] Ratio of load to projected area of indentation.

(3) *Chemical Properties.*—It was demonstrated by Fink and Pan [10] that the addition, even in small amounts, of lead to a silver anode or silver to a lead anode used in the electrolysis of sodium chloride, reduced the voltage required and also the corrosion of the anode. Additional work on an alloy containing 61 percent of silver, reported by them to be the best composition for the purpose, has been carried out by Rabinovich and Rubantchik [4] and Zhivotinskii [5].

In the attempt to find alloys of lead more resistant to sulphuric acid than pure lead, Garre and Mikulla [2] added $AgCd_4$ in amounts up to 2 percent, by weight, of the compound. They reported a considerably decreased loss of weight in both dilute and concentrated acid. At 100 and 200° C, the loss of weight was markedly less for the alloy than for lead.

(4) *Industrial Applications.*—Two lead-silver solders have been employed to some extent, the 5 percent of silver—95 percent of lead alloy being one and the other, the solder containing 2.5 percent of silver, 0.25 percent of copper, and 97.25 percent of lead described by Silberstein [8]. The principal advantage of these solders is that they melt at a higher temperature than ordinary lead-tin solder.

An important use of the lead-silver alloys is their employment as anodes in the production of electrolytic zinc. It was found by

Tainton, Taylor, and Ehrlinger [7] that the addition of 0.5 to 1 percent of silver to the lead used in making these anodes produced metallic zinc of much lower lead content than when pure lead anodes were employed.

(5) *Selected References:*

[1] R. S. Russell, *The influence of silver on the rate of recrystallization of distorted lead.* Proc. Australasian Inst. Mining Met. **95,** 125–157 (1934).
[2] B. Garre, and H. J. Mikulla. *Schwefelsäurebeständige Bleilegierungen.* Z. anorg. Chem. **212,** 326–328 (1933).
[3] B. Garre and F. Vollmert. *Härtbare Bleilegierungen.* Z. anorg. Chem. **210,** 77–80 (1933).
[4] M. A. Rabinovich and A. S. Rubanchik. I *Chlorine-resistant lead-silver electrodes.* Ukrain. Khem. Zhur. (Wiss Teil) **6,** 245–251 (1931).
[5] P. B. Zhivotinskii. II *Chlorine-resistant lead-silver electrodes.* Ukrain. Khem. Zhur. (Wiss Teil) **6,** 252–261 (1931).
[6] F. Yoldi. *The lead-silver system.* Anales soc. españ. fís. quím. **28,** 1055–1065 (1930).
[7] U. C. Tainton, A. G. Taylor, and H. P. Ehrlinger. *Lead alloys for anodes in electrolytic production of zinc of high purity.* Trans. Am. Inst. Mining Met. Eng. **85,** 192–200 (1929).
[8] James Silberstein. *The development of a new high-temperature solder.* Elec. J. **25,** 543–546 (1928).
[9] Int. Crit. Tables (Silver-Lead Diagram) **2,** 414 (1927).
[10] C. G. Fink and Li Chi Pan. *Insoluble anodes for the electrolysis of brine.* Trans. Am. Electrochem. Soc. **49,** 89–131 (1926).

[11] P. Ludwik. *Über die Härte Metallegierungen.* Z. anorg. Chem. **94,** 161–192 (1916).
[12] G. J. Petrenko. *Über die Legierungen des Silbers mit Blei und Zink.* Z. anorg. Chem, **53,** 202–211 (1907).
[13] K. Friedrich. *Blei u. Silber.* Metallurgie **3,** 393–406 (1906).
[14] Heycock and Neville. *Complete freezing point curves of binary alloys containing silver or copper together with another metal.* Trans. Roy Soc. (London) (A) **189,** 25–69 (1897).

f. SILVER-TIN

(1) *Constitutional Diagram.*—A comprehensive study on the constitution of the silver-tin alloys has been made by Murphy [6], who used thermal-analysis, microscopic-examination, and electrical-resistance methods. Murphy reported a new phase lying in the region between 12.5 and 19 percent of tin at room temperature, with somewhat wider boundaries at high temperatures, which had escaped the attention of Petrenko [8].

Its existence has been confirmed by the X-ray investigation of Nial, Almin, and Westgren [3]. Murphy estimated the solid solubility of silver in tin to be less than 0.1 percent, which is in general agreement with the change of properties found for tin containing 0.02 percent of silver by Hanson, Sanford, and Stevens [1]. Murphy's diagram is given in figure 30.

The observation made by Murphy that the presence of silver greatly retards the allotropic transformation from white to gray tin at low temperatures is noteworthy. Tin of 99.99-percent purity, when maintained at −78° C, began to change to the gray state in 6 days when in the worked condition and in 11 days when cast material was used. However, cast tin containing 0.2 percent or more of silver maintained at the same low temperature for 3 weeks and showed no evidence of change. The same sample, removed from its low-temperature surroundings and subjected to cold-work, showed no effect after an additional period of 3 weeks at −78° C. Inoculation of the argentiferous tin with gray tin also failed to produce any effect in 6 weeks.

(2) *Physical Properties.*—Data on the physical properties of the tin-rich alloys of the silver-tin series are scanty. According to Ireland [5] alloys containing 2.5 to 5.0 percent of silver are suitable for valves for refrigeration equipment and similar apparatus. Material of this composition is more resistant to cold plastic flow than pure tin, but is sufficiently soft to allow hard objects to be pressed into it when desired.

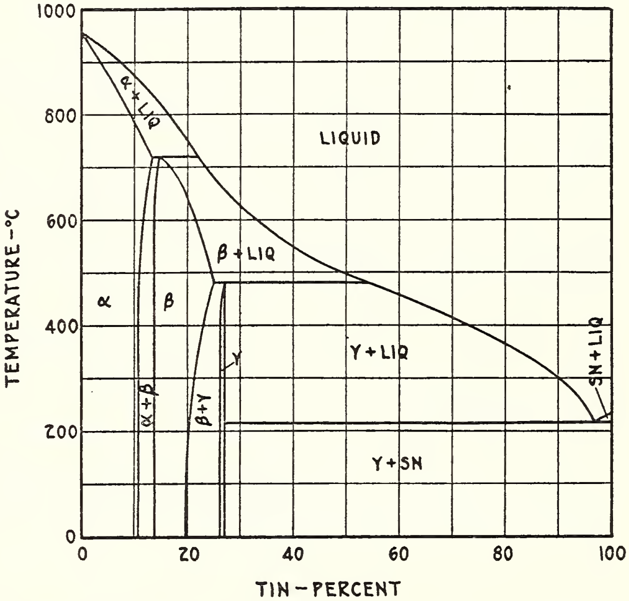

FIGURE 30.—*Silver-tin constitutional diagram* (*Murphy* [*6*]).

Hanson, Sanford, and Stevens [1] demonstrated that the grain size of tin was noticeably decreased as silver was added up to 0.1 percent and that tin containing 0.2 percent of silver has the very high tensile strength, as compared with pure tin of 7,500 lb/in.^{2} after quenching from 210° C. However, the increase in strength over that of tin largely disappeared after 22 weeks at room temperature. On the other hand, the lead-silver eutectic alloy (3.5 percent of silver) had maintained its high strength better as is shown in table 38.

TABLE 38.—*Ultimate tensile strength of the eutectic silver-tin alloy* [*1*]

Condition	Ultimate tensile strength
	lb/in.^{2}
15 days after rolling	8,100
Annealed for 3 hours at 100 °C	7,800
Annealed for 3 hours at 210° C	5,200
Quenched from 210° C	8,300

The results of some experiments at the National Bureau of Standards on silver-tin alloys containing up to about 10 percent of silver are given in table 39. The specimens, about 0.040 inch thick, which had been rolled from ingots approximately 0.5 inch thick, were tested about 14 days after rolling.

TABLE 39.—*Tensile properties of some silver-tin alloys*

Nominal silver content	Actual silver content average of top and bottom	Yield point [1]	Ultimate tensile strength	Elongation in 2 inches
Percent	*Percent*	lb/in.^{2}	lb/in.^{2}	*Percent*
1.0	0.98	2,350	3,000	57
2.0	1.86	3,900	4,500	47
3.5	3.65	4,500	5,300	37
6.0	5.64	3,650	4,650	49
10.0	9,87	3,600	4,850	40
(99.99 Sn)	----------	----------	2,200	68

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[1] Divider method.

The tensile strength was considerably lower than the value reported by Hanson, Sanford, and Stevens [1]. The alloy of approximately eutectic composition possessed the greatest strength but also the lowest elongation. Tests were also made on the bursting strength of silver-tin pipe which had been extruded through the die used for the size known as ⅜-in. 5-oz tin pipe. Water pressure was used and the test completed in about 1 minute. The following comparative values of the strength of the ordinary tin and the silver-tin pipes were obtained:

Material	Pressure (lb/in.^{2})	
	Ballooning begins	Leaking begins
Tin pipe	1,300	1,700
Silver-tin pipe	2,300	2,550

(3) *Industrial applications.*—An important application of silver-tin alloys is for dental amalgams [7]. According to Leschke [2], there is some evidence that the absorption of mercury from amalgam fillings is less when silver is the alloying element than when copper is used.

A number of minor uses for silver-tin alloys have been noted and there has lately appeared in England a pewter bearing the trade name "Pewsil", which is stated to contain silver.

(4) *Selected References:*

[1] D. Hanson, E. J. Sanford, and H. Stevens. *Some properties of tin containing small amounts of silver, iron, nickel, or copper.* J. Inst. Metals **55,** 115–131 (1934).

[2] Erich Leschke (Translated by C. P. Stewart and O. Dorrer), Clinical Toxicology, page 52, William Wood & Co., Baltimore, Md. (1934).

[3] O. Nial, A. Almin and A. Westgren. *Röntgenanalyse der Systeme Gold-Antimon und Silber-Zinn.* Z. physik. Chem (B) **14,** 81–90 (1931).

[4] C. L. Mantell. Tin ACS Monograph no. 51, p. 220 (Chemical Catalog Co., Inc., New York, N. Y., 1929).

[5] Ward S. Ireland. U. S. Patent 1,626,038, April 26, 1927.
[6] A. J. Murphy. *The constitution of the alloys of silver and tin.* J. Inst. Metals **35**, 107–124 (1926).
[7] Reginald Arthur Joyner. *Amalgams containing silver and tin.* J. Chem. Soc. **99**, 195–208 (1911).
[8] G. I. Petrenko. *Über die Legierungen des Silbers mit Blei und Zinn.* Z. anorg. Chem. **53**, 200–211 (1907).

g. SILVER-ZINC

(1) *Constitutional Diagram.*—The diagram of the silver-zinc system, figure 31, is based upon the work of Carpenter and Whiteley [11] and modified in accordance with more recent work. The portions concerning which there is uncertainty have been shown in dashed lines although some of the solid lines are not well established. There is obviously need for much more work on this system.

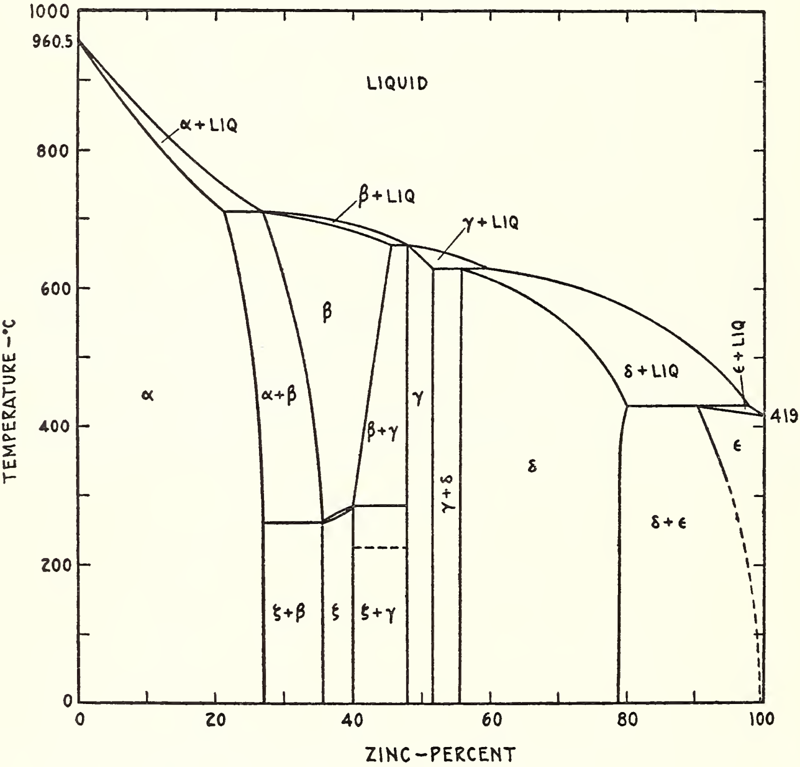

FIGURE 31.—*Silver-zinc constitutional diagram.*

In the region between 25 and 50 percent of zinc, the transformation of the β phase as indicated by the thermal data of B. G. Petrenko [7], and G. I. Petrenko [9] and the X-ray data of Westgren and Phragmen [10], and Weerts [3] has replaced the simple eutectoid change of Carpenter and Whiteley. The portion between 40 to 60 percent of zinc has been revised to agree with the thermal data of G. I. Petrenko and B. G. Petrenko [6] and the X-ray results of Owen and Edmunds [1]. The line at about 79 percent of zinc has been extended vertically to agree with the results of Owen and Edmunds. At the zinc end, the portion based on the hypothesis of an allotropic change in zinc at approximately 335° C, now shown to be incorrect [4], has been simplified to conform to the microscopic evidence of Carpenter and Whiteley [11].

(2) *Physical Properties.*—Heycock and Neville [13] observed that the alloys containing about 38 percent of zinc were sometimes highly colored. If quenched from a temperature of 285° C or higher, the alloy had a pronounced red color, which disappeared, however, upon heating the specimen to 150° C. The red color persisted despite attack by sulphuric and hydrochloric acids and alkalies. Although apparently a surface effect, the color appeared even when the alloy was prepared in the presence of hydrogen. The color of the zinc-silver alloys has also been noted by Puschin [12], Guillet, Petit, and Cournot [2], and others.

There is little precise information on the mechanical properties of alloys of this system. Some general information from Heycock and Neville [13] is summarized in table 40.

TABLE 40.—*Mechanical properties of some silver-zinc alloys [13]*

Zinc content (percent)	Nature of alloys
0 to 24.0	Malleable.
25.0 to 26.7	Brittle.
At 29.5	Tough.
39.0 to 53.0	Very brittle.
At 57.5	Quite tough.
At 60.5	Fairly tough.

Guillet, Petit, and Cournot, who conducted experiments on rolling the alloys containing 10, 20, 30, and 40 percent of zinc, confirmed these results as did also Jordan, Grenell, and Herschman [8].

(3) *Chemical Properties.*—There is very little reliable information on the chemical properties of this series of alloys. According to Centnerszwer and Straumanis [5] the presence of small amounts of silver in specimens of zinc, provided other impurities are absent, has very little effect on the solubility rate of zinc in $0.01N$ to $2N$ solutions of hydrochloric and sulphuric acids. Jordan, Grenell, and Herschman [8] reported that the high-silver alloys of this series were very resistant to tarnishing.

(4) *Selected References:*

[1] E. A. Owen, and I. G. Edmunds. *The determination of certain phase boundaries in the silver-zinc thermal diagram by X-ray analysis.* J. Inst. Metals **57,** (Adv. Copy) 706 (1935).

[2] Leon Guillet, Alfred Petit; and Jean Cournot. *Étude sur les alliages d'argent.* Rev. Mét. **29,** 113–132 (1932).

[3] J. Weerts, *Über Umwandlungsvorgänge im β-Messing und in β-Silber-Zinklegierungen.* Z. Metallkunde **24,** 265–270 (1932).

[4] Cir. BS 359, p. 172–174 (1931).

[5] M. Centnerszwer and M. Straumanis. *Lösungsgeschwindigkeit einiger Zink-Silberlegierungen in Säuren.* Z. physik Chem. (A) **156,** 23–37 (1931).

[6] G. 1. Petrenko and B. G. Petrenko. *Zur Frage des Aufbaus der γ-Phase in den Legierungen Ag-Zn.* Z. anorg. allgem. Chem. **185,** 96–100 (1930).

[7] B. G. Petrenko. *Zum Aufbau der δ-Phase von Silber-Zinklegierungen.* Z. anorg. allgem. Chem. **184,** 369–375 (1929).

[8] L. Jordan, L. H. Grenell, and H. K. Herschman. *Tarnish resisting silver alloys.* Tech. Pap. BS **21,** 467 (1927) T 348.

[9] G. I. Petrenko. *Über die Umwandlungen der Silber-Zinklegierungen im kristallinschen Zustande.* Z. anorg. allgem. Chem. **165,** 297–304 (1927).

[10] A. Westgren and G. Phragmen. *X-ray analysis of copper-zinc, silver-zinc, and gold-zinc alloys.* Phil. Mag. **50**, 311–341 (1925).

[11] H. C. Carpenter and W. Whiteley. *The silver-zinc equilibrium with an appendix on the* Cu-Zn, Ag-Zn, Ag-Cd *equilibria.* Int. Z. Metallog. **3,** 145–175 (1912–13).

[12] N. A. Pushin. *Potential and nature of metallic alloys.* J. Russ. Phys. Chem. Soc. **39,** 353–399 (1907).

[13] C. T. Heycock and F. H. Neville. *The freezing point of alloys containing zinc and another metal.* J. Chem. Soc. **71,** 383–422 (1897).

IV. INDUSTRIAL USES OF PURE SILVER

1. CONSUMPTION OF SILVER IN THE UNITED STATES

Merrill [1] has estimated that at least three-fourths of the world's production of silver is used for monetary purposes. No more than one-fourth of the yearly production of silver is consumed by the arts and industries. Merrill lists the non-monetary consumptions in the United States for 1929 in the following order:

Silver consumed by industries making products for ultimate consumption

Uses	*Percent*
Sterling silver industry	34. 4
Photographic industry	26. 6
Electroplating industry	14. 4
Jewelry, optical goods, and novelties	9. 0
Engineering applications, including silver solder	6. 9
Chemical uses (exclusive of photography and electroplating)	6. 2
Dental supplies	2. 1
Miscellaneous	. 3
Losses (difference)	. 1

The four largest fields of consumption of silver have been arbitrarily excluded from the present survey of industrial and engineering applications. The uses of greatest concern here are those included under items [5] and [6]. Among the engineering uses of silver, solders constitute one of the most important items. Those who are interested in this subject will find essential information in papers by Leach [2, 3].

The primary purpose of this section is to direct attention to the recent applications of silver and especially to those uses which appear to have the possibility of further development. These will be considered under the three headings: bactericidal, chemical, and electrical uses.

(a) SELECTED REFERENCES

[1] Charles White Merrill. *Consumption of Silver in the Arts and Industries of the United States.* Econ. Pap. no. 14, U. S. Bur. Mines (1932).

[2] R. H. Leach. *Silver solders and their use.* Metals and Alloys **2,** 278–283 (1931).

[3] R. H. Leach. *Silver solders.* Proc. Am. Soc. Testing Materials, part II, **30,** 493–511 (1930).

2. BACTERICIDAL USES

Silver has been used in a variety of medicinal preparations, many of which, no doubt, involve the disinfecting action of silver. In this section, however, the type of bactericidal action of concern is that described by Nägeli [15].

In 1893 Nägeli reported that the presence of copper in solution in amount so minute as almost to defy analysis had a marked bactericidal effect. To this action he gave the name "Oligodynamic Effect", a term still used to designate the bactericidal action of certain metals in dilute solution. Little interest was manifested in the subject until during the World War when experiments on the purification of water by finely divided silver were conducted. Since that time, the literature of the subject has become increasingly voluminous.

A large part of this work has been devoted to silver and its salts because of the remarkable sterilizing power which this metal and its compounds exert. Most of the results of investigations have appeared in journals published in Germany, in which country the process has met with considerable commercial success. An excellent analytical summary of most of the investigations of the oligodynamic action of silver and other metals is that of Raadsveld [4] which is recommended particularly to those who are interested in the theories advanced concerning the germ-killing power.

Before 1928 little was known of this method of sterilization in the United States. Since that time a number of commercial, college, and university laboratories have become interested in the phenomenon, this interest resulting in part from the establishment of an American branch of the original German company in New York.

Some unpublished information on the oligodynamic action of silver was obtained for use in this circular from a study made by the Research Laboratories of the National Dairy Products Corporation, Inc., Baltimore, Maryland. Most of the experiments carried out on water containing *Eschericia coli* in concentrations between 3,200 and 8,000 germs per cubic centimeter. Silver was introduced in different ways: as the salts, silver nitrate, silver acetate, silver chloride, in colloidal form, and by the commercial electrolytic method. The concentration of silver ion was comparable in each case and varied between 0.10 and 0.15 ppm. Distilled water to which 10 ppm of calcium carbonate had been added was used. The pH values of the solutions were 7.0 and 7.2 and the temperature was maintained at 20° C. The solutions became sterile in periods ranging from 1½ hours to less than 3 hours. Silver introduced by the electrolytic method or as the chloride produced a sterile condition a little more quickly than the other methods.

Some further information was also obtained by an investigation made at the bacteriological laboratories of Dr. Robert Keilty [1] in Washington, D. C. The bactericidal powers of copper, bronze, silver, and silver-plated disks were studied. It was found that pure silver and silver-plated disks might eventually effect bacteriolysis when kept in direct contact with bacteria on nutrient media; but that when the influence of the silver was removed from those tests which showed bacteriostasis over a period of 12 hours, bacteriolysis had not taken place. Copper had the same effect as silver but to a somewhat lesser extent. Bronze seemed to have very little action.

Krause's [8] work on the practical application of the oligodynamic effect of silver is outstanding. The following method used by Krause for sterilizing is typical. The suspected water is made to dissolve silver ions to the extent of 0.02 to 0.10 ppm and is then allowed to stand for a period ranging from one-half hour to several hours, according to the dosage of silver and other conditions, after which coli and pathogenic bacteria, such as those which cause typhoid fever, have been found to be completely killed. In his earlier experiments, Krause introduced silver to the desired concentration into the water by means of silver-coated sand, the water to be purified being passed through an ordinary filter filled with sand which had been coated with a porous deposit of silver. Recently, a more effective method has largely supplanted the older sand-filter method. In this, water is passed between silver electrodes, between which a small potential difference is maintained. The amount of silver thus introduced can be readily controlled.

According to the technical literature the bactericidal use of silver is not confined to the sterilization of drinking water. The following applications have been reported, some of which are being commercially applied in this country and abroad, the sterilization of spirit vinegar [3], water used in factories [10, 12], water used in making ice [7], drinking water on ships [8], the preservation of fish [11], bottled mineral waters [9], [14], the preparation of mouth washes and gargles [2], bactericidal soaps containing silver [5], and salves containing silver [2]. Certain dental fillings, such as silver manganite, have been reported to have a bactericidal action [6].

(a) SELECTED REFERENCES

[1] Robert A. Keilty. Experiments on the Bacteriostatic and Bacteriolytic Influence of Silver as Determined by the Direct Action of Metallic Discs. (From a report submitted to the Sponsors of the Associateships on Silver at the Bureau of Standards.) (1935).

[2] Rudolph Freund. *Experimentelle Beiträge zur Wirkungsweise Antiseptischer Stoffe.* Biochem. Z. **273,** 365–380 (1934).

[3] H. Kreipe. *The sterilization of spirit vinegar by means of the catadyn process.* Fruit Products J. **13,** 337 (1934).

[4] C. W. Raadsveld. *The oligodynamic effect of metals and metal salts.* Chem. Weekblad **31,** 497–504 (1934).

[5] A. C. Buchman, Jr., (Editor). *Patent issued for soap containing silver.* Sci. Am. **144,** 150–151 (1934).

[6] W. Dieck. *Silbermanganit.* Deut. Zahnärztliche Wochschr. **36,** 419–426 (1933).

[7] C. H. Herter. *Activated-water ice.* Refrigerating World **68,** 22–23 (1933).

[8] G. A. Krause. *Purification of water by the electro-catadyn method.* Wasser, **7,** 74 (1933).

[9] L. Fresenius. *The applicability of the catadyn process in the mineral water industry.* Z. Untersuch. Lebensm. **64,** 42 (1932).

[10] O. Fruehwald. *The catadyn process for the sterilization of water and an experiment in sausage manufacture.* Deut. Schlachtof. Ztg. **32,** 223 (1932).

[11] F. Ruësenberg. Fighting Fish Parasites. Aquarie- Terrarienkunde no. 49 (1932).

[12] H. Vierman. *On washing water for mills.* Z. ges. Getreidew- Mühlenw. **19,** 188 (1932).

[13] K. J. Demeter. On the Action of Catadyn Silver Upon the Microflora of Milk. Int. Milchwirtschaftskongress. Addresses nos. 37–77, 183 (1931).

[14] P. Haertl. *New ways of sterilizing water and mineral waters.* Veröff. Zentralst. Balneologie (N. S.) **14,** 51 (1929).

[15] von Nägeli. *On the oligodynamic phenomenon in swing cells.* Denkschriften der Schweiz. Naturforsch. Ges. **33,** 1 (1893).

3. SILVER IN CHEMICAL EQUIPMENT

Another major industrial use of silver is the fabrication of chemical equipment. Despite the cost, pure silver and, to a lesser extent, silver-lined materials, are used extensively for this purpose. The high initial cost is partially offset, first, by the ease of recovery of the silver from scrap metals, and its relatively high value in the recovered form, and second, by the fact that silver-lined equipment has practically all the advantages of silver without the high initial cost. Rogers [1] has discussed the latter factor.

Much of the following information on the applications of and possibilities in the use of silver in chemical equipment was obtained by visits to about 20 representative chemical plants. This has been supplemented by correspondence with representative users both in this country and abroad. The information from both these sources has been largely confirmed by such references in the literature as are available. Among the papers which are of particular interest are those by McDonald [7, 9] and Schoonover [2].

No attempt will be made to describe any particular apparatus or to give estimates as to the quantity of silver involved. In some plants only a few small pieces were found, whereas in others, as much as 3,000 pounds of silver was in use.

Small installations of silver equipment have been used successfully for processes in which dilute hydrochloric acid is one of the products. The handling of chlorine, wet or dry, in silver is fairly common practice in filtration plants employing chlorination. Although fine or pure silver appears to have only a limited application with the halogens and their acids, certain high-silver alloys may be useful in this field.

Fusions of sodium and potassium hydroxide have long been carried out in silver crucibles, evaporating pans, molds, and ladles of silver are used in the preparation of the best grades of sodium and potassium chlorides and hydroxides. An interesting application of pure silver in this field is for plugs for alkali burettes.

Since many organic acids do not attack silver, it is in this field of the chemical manufacturing industry that a large portion of the silver equipment is used at the present time. For acetic acid, which manifests its greatest corrosive action at the point where the hot vapors condense during distillation, silver condensers, stills, vats, and taps are extensively used with marked success. Some of the equipment is very large and may be constructed of pure silver or lined with silver. A part of the success of silver in this field can be attributed to the fact that many organic compounds of silver are colorless and, hence, no objectionable color effects appear, even if some contamination by silver does occur. The absence of color is considered important in the manufacture of white vinegar for pickling, where even very slight discoloration is objectionable. Silver-lined vats have also been used for the handling of acetic anhydride.

In preparing phenol, especially the better grades for pharmaceutical purposes, silver stills, condensers, and taps are used. Silver-lined steel barrels have been used to transport pharmaceutical glycerin. Much silver equipment is used in the manufacture of lactic acid. Steam-jacketed silver kettles have given many years of satisfactory service in the preparation of the sodium salts of phosphoric acid.

In the production of foodstuffs, jams, jellies, and beverages, silver has been used more widely abroad than in this country. Silver pipe lines, siphons, taps, nozzles and containers have long been used for the handling and dispensing of beverages. Pure silver and silver-lined stills, condensers, and pipe lines have been used in the preparation of fruit juices and extracts. Jams, jellies, and allied products are made in pure silver and silver-lined autoclaves, evaporating pans, vacuum stills, and similar equipment.

In the food industries, silver is widely used for one or more of the following reasons: freedom from any appreciable metallic contamination which might have toxic effects or be objectionable because of discoloration or an undesirable metallic taste; the ease with which the surface of silver containers may be kept free from bacteria, an all-important factor in the preparation of foodstuffs and beverages; and the absence of catalytic effects which might cause decomposition of the essential oils which are necessary in preserving the characteristic flavors of many products.

Probably the largest quantity of silver chemical equipment is used in the photographic industry. Photographic emulsions must be free from foreign metals and must be handled in tanks which can be kept scrupulously clean, especially free from bacteria. Silver is used for tanks, evaporating kettles, rolls, and other equipment.

Silver condensers are used in the preparation of certain coal-tar products and in the recovery of solvents used in the rayon industry. Silver and silver-lined vacuum pans are used in the tanning industry. Some silver equipment is used in the preparation of aniline dyes and dyestuffs, and silver catalysts are used in many processes. Chains of silver are sometimes used for packing still columns. Silver vessels are often employed in the preparation of ordinary ink.

This list of uses of silver, while representative, is by no means complete. A number of other instances in which silver has been employed successfully as equipment are known but are considered as trade secrets and have not been included. Numerous suggested uses of silver which have been given consideration and appear worthy of mention are silver-lined bottles for hydrofluoric acid, fine silver and silver-lined bottles for the finer grades of perfumes, etc.

(a) SELECTED REFERENCES

[1] B. A. Rogers. *Silver may answer your corrosion problem.* Chem. and Met. Eng. **41,** 631 (1934).

[2] I. C. Schoonover. Silver equipment in chemical plants. Chem. and Met. Eng. **41,** 545 (1934).

[3] Editorial, *Silver in chemical plant construction.* Can. Chem. and Met. **18,** 65 (1934).

[4] I. G. Farbenind. Silver Alloys Resistant to Chemical Action. Brit. Pat. 297, 665 (1927).

[5] B. E. Roetheli, H. O. Forrest. *Materials used in chemical engineering.* Ind. Eng. Chem. **24,** 1018 (1932).

[6] R. S. McBride. *Chemical engineering problems in hardwood distillation.* Chem. Met. Eng. **39,** 604 (1932).

[7] D. McDonald. *Metallic silver and its alloys.* Chem. Engineer **18,** 171 (1931).

[8] Editorial, *Silver for chemical plant.* Chem. Age **24,** 163 (1931).

[9] D. McDonald. *Applications of silver to the chemical plant.* Chem. Age **24,** 142 (1931).

[10] *Materials resistant to various chemicals and other substances.* Brit. Non-Ferrous Research Assoc. Monograph, Serial 11, 496 (1932).

[11] W. R. Huey. *Materials for construction of chemical plant.* Ind. Eng. Chem. **26,** 1 (1933).

[12] J. H. Thompson, H. J. Krase, K. H. Clark. *Resistance of metals to the system area—Water ammonium carbonate.* Ind. Eng. Chem. **22,** 735 (1930).

[13] W. Guertler. *The future of silver and its alloys.* Metal Ind. (London) **37,** 33 (1930).

[14] C. Zeigler. The Use of Gold and Silver Covered Metals for Making Equipment for the Chemical Industry. Chimie et industrie, Special no. 220 (1932).
[15] J. M. Bryan. *Metal in the food industry.* Food Manuf. **8,** 399 (1933).
[16] W. R. Huey. *Silver. A metal of specialized uses in chemical plants.* Chem. and Met. Eng. **36,** 522 (1929).
[17] I. G. Farbenind. Coal Tars and Mineral Oil Derivatives. French Pat. no. 35, 831 (1928).
[18] W. Guertler. *The problem of acid-proof metallic materials.* Z. Metallkunde **18,** 365 (1926).
[19] C. J. Elliott. *Metals used in the chemical industry plants.* Metal Ind. (London) **41,** 511 (1932).
[20] A. Bergman. *New uses for metals.* Metal Ind. (N. Y.) **22,** 1 (1924).
[21] C. E. Sholes. *Choosing a metal for corrosion resistance.* Inco. **4,** 19 (1923).
[22] L. Irwell. *The commercial uses of silver.* Metal Ind. (N. Y.) **8,** 329 (1910).

4. SILVER IN ELECTRICAL EQUIPMENT

Another major engineering use of silver is in the electrical field. Pure silver, its alloys with the noble metals, and to a lesser extent its alloys with the base metals have all been found valuable as material for electrical contacts and similar purposes.

A study of various pure metals and alloys with respect to their suitability as contact materials for telephone circuits has been made by Kingsbury [6]. Since telephone circuits vary widely with respect to resistance, inductance, and capacity, materials suitable in some circuits do not always perform satisfactorily in others. With the very light pressure used in part of the equipment, contact resistance is inclined to be variable and results in objectionable microphonic effects in certain circuits. For such circuits a number of the alloys of silver with the noble metals give good service. According to Kingsbury, silver is particularly suitable for those contacts in which there is a slight rubbing action in opening or closing.

Alloys of silver with the common metals—copper, zinc, and cadmium—have been employed in various applications particularly as contact metals. Mabb [3] mentions the use of silver-copper alloys containing 80 to 90 percent of silver in radio equipment. Silver-nickel contact points made by compressing and sintering mixed metal powders have found a limited application.

Recently, silver contacts have been used considerably in power equipment. A marked advantage of silver contacts is the small increase in resistance, and consequently of temperature, with time, as illustrated in figure 32 from Paxton and Strang [4]. For contacts which operate infrequently, this property is important. Paxton and Strang have also described silver-surfaced bus-bar ends and silver-surfaced plates for splicing bus bars. Silver contacts of 12 mm diameter, which can be used at very high current densities, have been described by Hopp [2]. Graphite-silver contacts are also in use. A noteworthy application of silver contacts in small equipment is found in the Burgess microswitch and the Burgess vacuum contact [1].

In a recent investigation by the Westinghouse Electric and Manufacturing Co. in cooperation with the National Bureau of Standards, the operation of a silver commutator on a 220-volt, 5 horsepower generator was studied. It was found that the contact resistance between the silver commutator and a graphite brush is insufficient to take care of the reactance voltage at full load. Although the wear characteristics have not been fully determined, the loss of silver appears to be slightly greater than for similar copper equipment, but not enough to discourage the use of silver in lower voltage equipment, where it may have some advantage.

A recent development in the electrical industry which involves a new use for silver is in photoelectric cells. The peculiar properties of silver which lead to its use in these cells are its ease of oxidation at low temperatures in a glow discharge and the instability of the oxide so formed as the temperature rises. A description of the cesium-oxygen-silver photoelectric cell has been given by Prescott and Kelly [5].

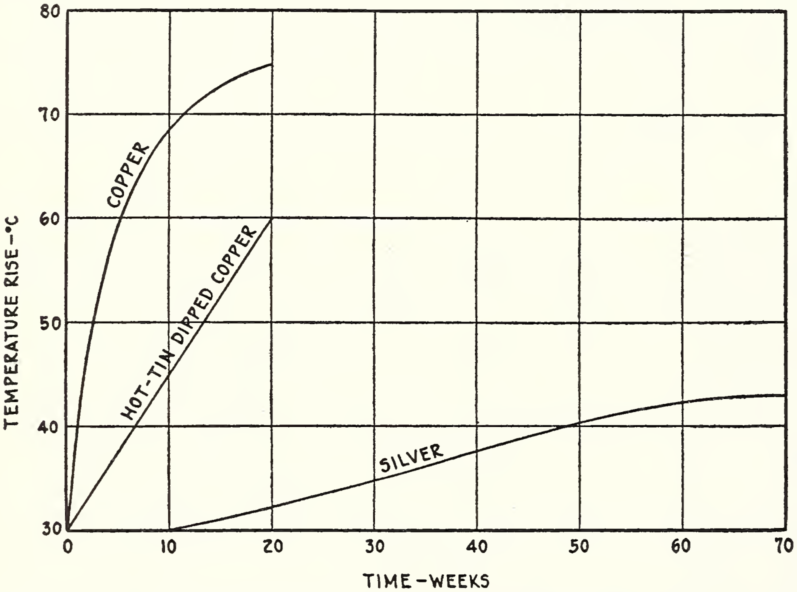

Figure 32.—*Rise of temperature in electrical contacts of copper, hot-tin dipped copper, and silver in oil; intermittent duty (Paxton and Strang [4]).*

Area, 1⅛ in. by ¾ in. Current, 600 amp. Pressure, 20 lb. Ambient temperature, 40° C.

(a) SELECTED REFERENCES

[1] Instruments **7,** (May) advtg. p. A1 (1934).
[2] W. Höpp. *Neuartige Bauweise von Schaltgeraten.* Elektrotech. Z. **54,** 203–205 (1933).
[3] P. Mabb. *Contact metals and contact care.* Metal Ind. (London) **43,** 3–5 (1933).
[4] R. Paxton and H. E. Strang. *Designs of current-carrying contacts in modern switchgear.* Gen. Elec. Rev. **36,** 524–528 (1933).
[5] C. H. Prescott, Jr., and M. J. Kelly. *The caesium-oxygen-silver photoelectric cell.* Trans. Electrochem. Soc. **62,** 297–322 (1932).
[6] E. F. Kingsbury. *Use of noble metals for electrical contacts.* Trans. Am. Inst. Mining Met. Eng. **78,** 804–822 (1928).

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