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**THE SIGNIFICANCE OF CONTACT ANGLE
MEASUREMENTS IN SOLDERING**

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SYNOPSIS

The importance of the measurements of contact angles in soldering has been mentioned. The assessment of the spreading power of a solder over a metallic surface involves the determinations of the contact angle between the solder and the metal surface, and the interfacial tension. The theoretical basis for the experimental work done on contact angles has been critically reviewed. Mention is also made of the various fluxes used in soldering. The need for further work involving low-melting solder systems and proper correlation of data is dealt with briefly.

INTRODUCTION

'Soldering' is the process of joining metals by fusion of alloys that have low melting points (most commonly lead-base or tin-base alloys) in the presence of fluxes.

The behaviour of a liquid on a solid is conveniently characterised by a quantity called the contact angle, θ , which finds an interesting application in soldering. For an efficient joint between solder and metal, it is essential that the molten solder shall spread over the surface of the metal, *i.e.*, the contact angle of the liquid solder against the metal must be zero. This implies that the work of adhesion of the solder for the metal shall be equal to, or greater

than, the work of cohesion of the solder. Liquid solder, like other molten metals, has a high surface tension (about 470 dynes per cm. at 300° C.). Consequently, it is essential that the work of adhesion of the solder for the metal shall be as high as possible, *i.e.*, shall not be lowered by physically or chemically adsorbed films. The various precautions and devices adopted in soldering are nearly all directed at removing such films or preventing their formation by keeping the surface clean for which filing, emery-papering, etc., are employed; the solder is then melted on its surface in the presence of a flux—the function of the latter being to remove traces of oxide still present and prevent its further formation by covering the metal with a blanketing layer. While soldering is universally employed, studies utilizing the contact angle as an aid in determining the spreading power of solders over metallic surfaces are limited.

THEORETICAL CONSIDERATIONS

In soldering, if the flux used is volatile, it may be present mainly as a gas, otherwise it will probably be present as a liquid, or it may produce a gas which displaces any liquid residue. The liquid and solid metals may be in contact in (i) a gaseous medium or (ii) a liquid medium. The condition for spreading in case (i) has been discussed by Harkins and Feldman.¹ When a second liquid is present, a simple expression for the spreading coefficient ' ϕ ' can be derived if the following likely assumptions are made²: (a) the liquid flux—solid metal adhesion is a factor opposing solder spread; (b) the flux—liquid metal adhesion is a factor aiding solder spread. The probability of (b) follows from the fact that spreading power of the solder on the solid metal involves an increase in the area of the flux—solder interface, which will take place the more readily the greater the work of adhesion between the two. It can be derived that

$$\phi = W_{SL} + W_{LF} - W_{FS} - W_{LL}$$

where

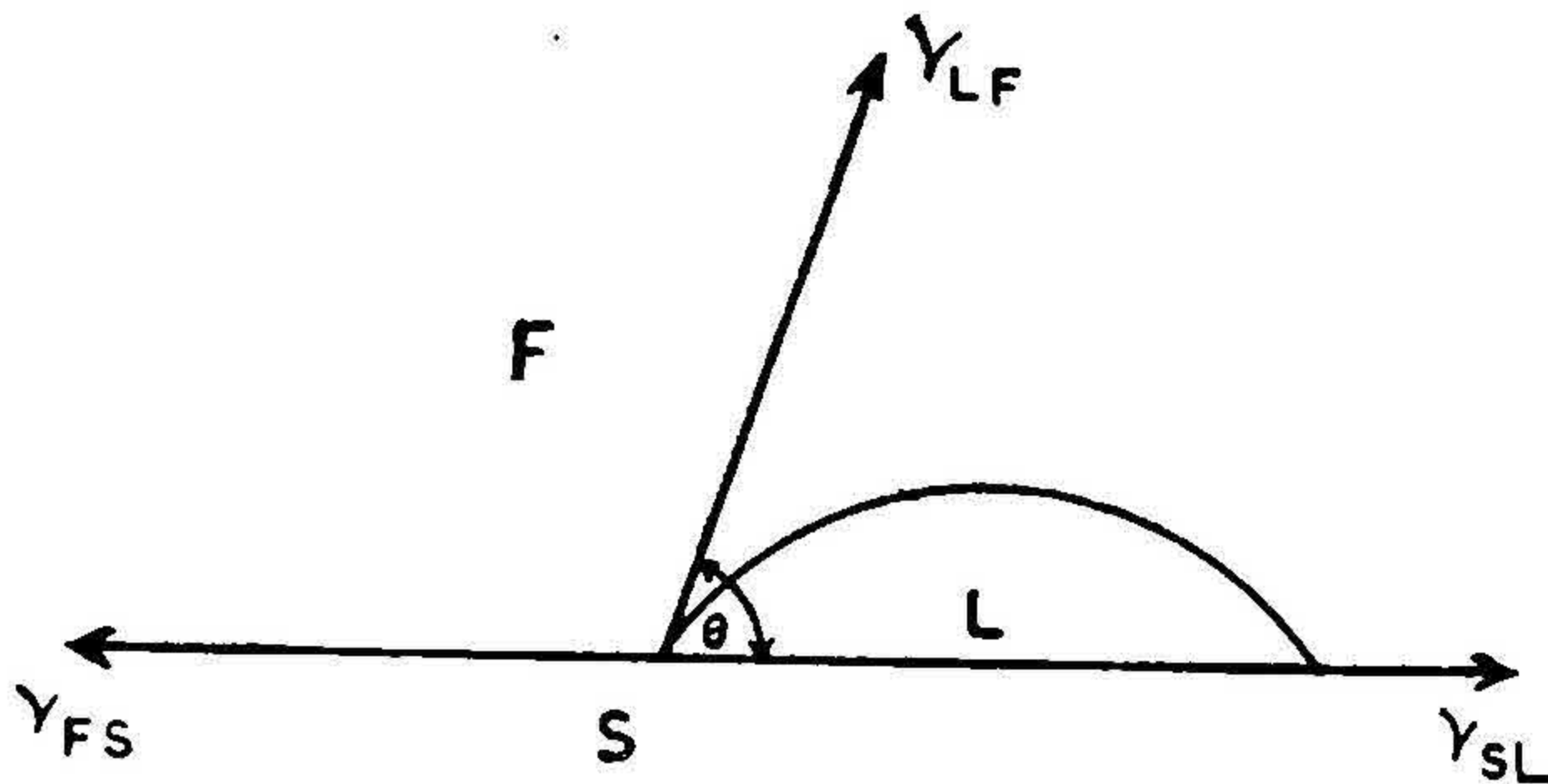
- W_{SL} = work of adhesion between solid and liquid metals,
 W_{LF} = ,, ,, liquid metal and liquid flux,
 W_{FS} = ,, ,, flux and solid metal,
 W_{LL} = work of cohesion of the liquid metal.

Substituting in terms of surface and interfacial tensions, we have

$$\phi = \gamma_{FS} - \gamma_{SL} - \gamma_{LF}$$

where γ_{FS} is the interfacial tension between flux and solid metal, and similarly for the other terms.

An expression for ' ϕ ' has been derived^{2, 3} in terms of the contact angle θ and surface and interfacial tensions.



F = Flux, S = Solid metal, L = Liquid solder.

Consider a drop of liquid solder (L) in equilibrium on a solid metal surface (S) in the medium of flux (F) as in the figure. γ_{LF} , γ_{FS} and γ_{SL} are the interfacial tensions between liquid solder-flux, flux-solid and solid-liquid solder respectively and ' θ ' the contact angle. Then

$$\gamma_{FS} = \gamma_{SL} + \gamma_{LF} \cos \theta \quad (1)$$

Work of adhesion⁴ is the work which has to be done to pull asunder a solid-liquid joint one sq.cm. in cross-section, *i.e.*,

$$W_{SL} = \gamma_{FS} + \gamma_{LF} - \gamma_{SL} \quad (2)$$

Substituting (1) in (2) we have

$$W_{SL} = \gamma_{LF} (1 + \cos \theta) \quad (3)$$

The Spreading Coefficient 'φ'.—Spreading will occur if $\theta = 0$ or

$$W_{SL} \geq 2\gamma_{LF} \text{ or } \geq W_{LL}$$

In other words, a liquid will spread over a solid if the work of adhesion W_{SL} of the liquid for the solid surface is equal to or greater than the work of cohesion W_{LL} of the liquid for itself. ($W_{SL} - W_{LL}$) has been called by Harkins⁴ the spreading coefficient ' ϕ ' of the liquid over the solid.

$$\phi = W_{SL} - W_{LL} = (\gamma_{FS} - \gamma_{SL}) - \gamma_{LF}$$

But

$$\gamma_{FS} - \gamma_{SL} = \gamma_{LF} \cos \theta$$

$$\phi = \gamma_{LF} (\cos \theta - 1) \quad (4)$$

FLUXES IN SOLDERING

The mechanism of the action of fluxes in soldering has been studied by Latin.² The main question appears to be whether (a) fluxes act purely in

a cleansing capacity or (b) fluxes besides acting as cleansing agents, also lower considerably the surface tension of the molten solder, and this effect is important in aiding efficient spreading. Ladon⁵ inclines to the latter view, but Crow⁶ to the former from considerations and experiments of a largely qualitative nature. Coffman and Parr⁷ measured the effect of hydrogen chloride on the surface tension of molten solders and concluded from spreading tests that chemical cleansing alone is not sufficient to account for spreading and that diminution of surface tension is of importance. Dean and Wilson⁸ also came to the same conclusion from their experiments.

Nightingale⁹ considers fluxes in two classes: (a) "protective" (resin, tallow and most organic fluxes) and (b) "chemically active" (zinc chloride, ammonium chloride and others). It is well known that residues from the flux used in soldering may give rise to corrosion which if persistent may lead to the failure of the metal adjoining the soldered joint. One of the best soldering fluxes, zinc chloride is particularly objectionable from this angle. The practical alternatives to corrosive zinc chloride are few, and considered solely on their ability as fluxes, they are all inferior when used upon the commonly soldered metals.¹⁰ The safest is natural resin since it never causes corrosion but its fluxing action is weak. Tallow and palm oil are also very mild and slow acting. Oleic acid is slow acting and not popular because of its rancid smell. The features of orthophosphoric acid as a flux and the properties of fluxes containing organic phosphates have been investigated.¹¹ Fluxes based on organic phosphates permit easy soldering of many materials without residues of fluxes causing corrosion.

The above were the only fluxes in common use a quarter of a century ago when a patent was taken out covering the use of aniline hydrochloride as soldering flux. At soldering temperature some decomposition occurs into aniline and hydrochloric acid which acts as a flux. The discovery that aniline hydrochloride could serve as a flux encouraged experiments with a number of other amine hydrochlorides and bromides chiefly for incorporating in resin as "activators" which would be destroyed at soldering temperature and leave no ionisable halide on the work. The majority of modern cored solders are now filled with such activated resins.¹⁰

DETERMINATION OF INTERFACIAL TENSIONS AND CONTACT ANGLES

The assessment of the spreading power of a solder over a metal surface depends on the determinations of (a) interfacial tension between solder and flux on the solid metal and (b) contact angle.

(a) *Interfacial Tension*.—Most determinations of metal surface tensions have been made using the method of maximum bubble-pressure;¹²⁻¹⁵ but the drop-weight,^{16, 17} sessile-drop,¹⁸⁻²⁰ sessile-bubble,²¹ hanging drop,²² and capillary height²³ methods have also been used. Such quantitative determinations of the contact angles of molten metals with solids as have been made have usually been

incidental to the determination of surface tension by the sessile-drop or capillary height²⁴ methods.

Direct measurement of the surface tension of a liquid metal in contact with a flux phase is possible by several methods which are independent of the contact angle. Bircumshaw²⁵ gives values for a number of tin-lead solders in contact with hydrogen; Chalmers and Wadie²⁶ obtained similar data employing a resin flux; and Latin² determined the surface tension of tin and tin-lead solder of eutectic composition in contact with resin, zinc-ammonium chloride and stannous chloride fluxes (see Table I).

TABLE I
*Surface Tensions of Tin, Lead and Tin-Lead Eutectic (Dynes/cm.)
at Temperatures just above the Liquidus*

Metal	Flux				
	Hydrogen (Bircumshaw ²⁵)	Resin (Chalmers and Wadie ²⁶)	Resin (Latin ²)	Zinc- ammonium chloride (Latin ²)	Stannous Chloride (Latin ²)
Tin ..	550	420	456	422	342
Tin-lead eutectic	490	380	390	331	..
Lead ..	440	316

(b) *Contact Angle*.—The determination of contact angle has been made by (i) direct measurement, (ii) photography or other optical means, and (iii) by the measurements of the dimensions of the drop.

The determinations of interfacial tension γ and contact angle θ for tin and tin-lead solders on copper in the presence of various fluxes, viz., resin, zinc-ammonium chloride and stannous chloride in order to evaluate the spreading powers of solders on copper, have been made by Latin. The contact angle has been measured by solidifying the melted solder drop on a horizontal copper surface, mounting in bakelite, sectioning diametrically and measuring the angle at the point of contact by an optical means (see Table II).

Latin has also suggested determining spreading power ϕ directly (without the knowledge of γ and θ) by the equation $\phi = -\frac{1}{2}gh^2(D - d)$, where h = height of the solder drop, D the density of the solder and d density of the flux. To determine the solder-flux interfacial tension, he has employed the "maximum bubble pressure" method as modified by Sugden.²⁷ Since Latin measured the contact angles on a solidified drop, sources of inaccuracy are likely to arise

TABLE II
*Contact Angles of Tin and Eutectic Tin-Lead Solder on Copper
 as determined by Latin*

Solder	Flux	Temperature °C.	Contact Angle θ
(1) Tin	.. Resin	250	70°
		265	65°
		325	55°
	Zinc-ammonium Chloride	250	50°
		300	40°
(2) Eutectic Tin-lead Solder	Resin	195	70°
		265	50°
		320	small, difficult to measure
	Zinc-ammonium Chloride	200	35°
		260	0°
		(approx.)	

from changes in the shape of the drop after solidifying. He could not photograph the molten drops owing to the presence of excess of flux. In his experiments he has noted that, around tin and solder drops heated in contact with copper in zinc-ammonium chloride flux, blue coloured areas are formed. He concludes that this blue colouration is due to tin which has deposited from the flux and has subsequently alloyed with the copper. He considers that this accounts for the greater spreading in zinc-ammonium chloride flux than resin flux. From a comparison of areas of spread of tin and eutectic tin-lead solder in either flux, he has deduced that the greater spreading of the eutectic solder is probably due to its lower surface tension. Bailey and Watkins²⁸ point out, that if this were the only reason for the greater spreading of the eutectic composition, it might be expected from measurements of surface tension in resin made by Chalmers and Wadie (Table I) that the best spreading of all would be obtained with pure lead. Latin gives no evidence that this is so, and in fact lead does not spread as well as solders containing about 50% tin. The formation of "haloes" around tin drops of solder when a chloride flux is used as observed by Latin, has also been noted by Fine and Dowdell.²⁹ Bailey and Watkins indicate that the formation of haloes may probably take place by diffusion from the liquid metal or by deposition from some liquid fluxes. Daniels and Macnaughtan,³⁰ in their

review on the wetting of metals with particular reference to tinning and soldering, comment that it is unknown whether the formation of 'halo' always accompanies the spreading of a drop of molten metal on a solid metal or if it is an indispensable preliminary to the spreading of the main drop. They state that the flux will assist the spreading of the drop of molten metal if it causes a reduction in the surface tension of the drop and quote work by Coffman and Parr⁷ and by Latin in which the extent to which the surface tension of solders is reduced in various fluxes has been measured.

Regarding the nature of the solid surface over which the solder spreads, Bailey and Watkins point out that the development of particular low contact angles which are formed against copper by tin-lead solders appears to be preceded by the formation of an alloy layer. The possibility of changes of contact angle taking place as a consequence of intermetallic diffusion has been pointed out by Tammann and Arntz,³¹ and Alty and Clark.³² Daniels³³ while ascribing the prime cause of wetting to the attraction between the base and coating metals, mentions that the affinity results in the formation of an intermetallic compound or solid solution which is due to intermetallic diffusion. Work on the spreading of metals on metals by Bondi,³⁴ suggests that, interaction, whether compound formation or solution, is always accompanied by initial spreading. But where as with solution, the final spreading coefficient remains positive (*i.e.*, low θ). With compound formation, it becomes negative (*i.e.*, high θ). It is as well to point out that the converse—that initial spreading signifies interaction—is certainly not true. A simple example is the system air-water-platinum, where the contact angle approaches zero; the water spreads over the platinum surface, but there is no reaction. Bailey and Watkins³⁵ in their determination of the surface tensions occurring in the systems copper-hydrogen and copper-lead-hydrogen at temperatures of 850° C. have observed that the value of surface tension in the latter case is lower. They suggest that the reduction is due to the adsorption of lead (which is in the vapour state at the high temperature employed) at the copper-gas surface.

The importance of the time factor in any method of quantitatively evaluating the jointing capacity of a soldering system has been discussed by Earle.³⁶ It is shown that 'jointing capacity' may be analysed into two independent characteristics of the soldering system: its time/temperature wetting characteristic and its interfacial tension characteristic. An apparatus called the Kollagraph for measuring the two independent characteristics is described. The effect of tin content of the solder, the alloy additions to the solder, the basis stock, the thickness of the stock, the type of flux and preheating are discussed; the general conclusion is reached that most types of solder are selective in their reaction to different basis stocks, and fluxes. The theoretical basis involved in the study has been given by Latin *et al.*³⁷ who have expressed the time t taken for molten solder to penetrate a distance l into a capillary space between flat horizontal plates separated by a distance d , thus:

$$t = \frac{3l^2 (\eta_1 + \eta_2)}{d\gamma \cos \theta}$$

where θ = contact angle, γ = interfacial tension, η_1 = viscosity of solder and η_2 = viscosity of flux.

Chalmers and Wadie in their investigation on the dewetting of tin and some tin alloys from hot-dipped oxygen-free high conductivity copper, have used the receding contact angle as a measure of the tendency to dewet and have discussed the influence of the surface tension of the liquid and their experimental variables upon the measured receding contact angles. They have determined the angles of contact of tin drops by means of an optical arrangement devised by them. The interfacial tension between the solder and the flux has been determined, thus: a standard quantity of the solder is melted in a fireclay dish, and molten flux is poured on it. After the solder is solidified, the procedure is to invert the drop so that the flat surface rests on a glass plate and measure the height 'h' of the drop optically. The interfacial tension $T = \frac{1}{2}gh^2(D - d)$, where 'D' is the density of the solder and 'd' that of the flux.

The method of determining contact angles and surface tensions by measuring the dimensions of small bubbles and drops^{38, 39} has been utilised in the case of metals. The acute contact angle $\theta = 2 \tan^{-1}(h/x)$, where h is the greatest height of the drop and x the radius of its base. Since h is difficult to measure, Mack has determined h in terms of the volume of the drop. The obtuse contact angle is a function of z/r and r/b , where z is the vertical height of the drop, r the greatest horizontal radius and b the radius of curvature at the apex of the drop. By reference to Bashforth and Adams tables, the values of θ could be known as a function of z/r and r/b . Ellefson and Taylor,³⁹ by applying the above method, have measured γ and θ of molten silicates and glasses on gold and platinum. The values of θ , as measured by them, of sodium silicate glass on gold are given in Table III.

TABLE III

Sodium Silicate on Gold

Weight of Silicate on the Gold Surface = 0.5994 gm.

Atmosphere	Temperature °C.	Time hours	θ Calculated
<i>Vacuum</i> .. Nitrogen allowed to enter after 5 hrs. of vacuum.	996	0	57°
<i>Nitrogen</i> .. Vacuum applied just after reading and retained for 25 hrs.; then oxygen allowed to enter.	1,000	24	57°
<i>Oxygen</i> ..	1,000	50	56°

It is concluded that there is a definite wetting of the gold metal as such by the molten silicate and that the degree of wetting is not significantly affected by the kind of atmosphere present.

The contact angles of some sodium silicate glasses on metals copper, silver, gold, palladium, platinum and nickel in vacuum, hydrogen, helium, oxygen and air atmospheres at 900° C. have been measured⁴⁰ directly by means of a telescope with a protractor scale attached to it. The study of contact angles of various slags on refractories⁴¹ has also been made. It is concluded that the optimum condition for the reduction of slag attack is a high contact angle preferably associated with a high interfacial free energy between slag and refractory. Furthermore, it is shown that the factor most likely to produce this condition is low surface energy of the refractory relative to that of the slag. A technique for measuring contact angle continuously at high temperatures has been devised and results are given for various slags on platinum and alumina. Some values of the contact angle are cited in Table IV.

TABLE IV⁴¹
Solid Surface: Platinum
Gas: Air

Slag		Temperature °C.	θ
CaO	SiO ₂		
40	60	1,500	49.5°
44	56	1,550	48°
		1,590	48.5°
48.2	51.8	1,590	49°
52	48	1,540	44.5°

Conclusions reached are that the contact angle varies little with temperature or composition, showing a slight decrease only at the most basic composition.

The measurements of γ and θ have been made by the sitting-drop method⁴² between, on the one hand, fused lead (with and without sodium) and on the other hand fused zinc and zinc saturated with lead (with and without the addition of sodium). Non-equilibrium systems (not mutually saturated) give somewhat varying results, $\gamma = 112$ and $\theta = 45^\circ$ on graphite, 109 and 69° on magnesite. On account of the known capillary activity of sodium even small additions of sodium cause a significant decrease of γ and increase of θ . Also, the simultaneous determinations of surface tensions of molten metals and their contact angles with silica or other refractory solids upto 1,200° C. have been made^{43, 44} by measuring the pressures required to force the molten metal into two capillaries of the

solid, at least one of which is conical. Experimental and mathematical details of the method, especially as applied to molten metals, are described. The surface tension of molten tin between 400° and 800° C. in a hydrogen atmosphere determined by the method is $(700 \pm 25) - (0.17 \mp 0.015)T$ dynes/cm., where T is the temperature in °K. The contact angle of tin with fused or polished silica surfaces, determined by the same experiments, is $145^\circ \pm 10^\circ$, independent of temperature but sensitive to the degree of roughness of the surface.

It can be seen from the above that work on the measurement of contact angles, especially those of molten solders on metallic surfaces in the presence of fluxes and other variables, has been rather limited. Investigations on some aspects of this problem of the determination of ' θ ' have been undertaken. For this purpose, a special apparatus has been constructed.

REFERENCES

1. Harkins and Feldman .. *J. Am. Chem. Soc.*, 1922, 44, 2665.
2. Latin .. *Trans. Faraday Soc.*, 1938, 34, 1384.
3. Gregg .. *The Surface Chemistry of Solids*, 1951, p. 183.
4. Harkins .. *J. Am. Chem. Soc.*, 1917, 39, 356.
5. Ladon .. *Chem. and Met. Eng.*, 1921, 24, 981.
6. Crow .. *Trans. Faraday Soc.*, 1924, 20, 199.
7. Coffman and Parr .. *Ind. Eng. Chem.*, 1927, 19, 1308.
8. Dean and Wilson .. *Ibid.*, 1927, 19, 1312.
9. Nightingale .. *British Non-Ferrous Metals Research Association*, 1932, p. 65.
10. .. *Tin and its Uses*, Tin Research Association Publication, May 1954, No. 30.
11. Willstrop *et al.* .. *Monthly J. Inst. Metals*, 1936, 3, 175.
12. Bircumshaw .. *Phil. Mag.*, 1926, 2 (vii), 341.
13. Sauerwald and Drath .. *Z. anorg. Chem.*, 1926, 154, 79; 1927, 162, 301.
14. Hogness .. *J. Am. Chem. Soc.*, 1921, 43, 1621.
15. Pelzel .. *Berg-u. hüttenmänn Monatsh, montan. Hochschule. Leoben*, 1948, 93, 248; (*C.A.*, 1953, 47, 9233 a).
16. Quincke .. *Ann. Chem.*, 1859, 55, 227.
17. Matuyama .. *Sci. Rep. Tôhoku Imp. Uni.*, 1927, 16 (i), 555; (*C.A.*, 1953, 47, 9233 a).
18. Siedentopf .. *Ann. Physik. u. Chem.*, 1897, 61, 235.
19. Herzfeld .. *Ibid.*, 1897, 62, 450.
20. Kemball .. *Trans. Far. Soc.*, 1946, 42, 246.
21. Portevin and Bastien .. *Proc. Inst. Brit. Found.*, 1935-36, 29, 88; *Found. Trade Journ.*, 1936, 55, 28.
22. Smirnova and Ormont .. *Doklady Akad. Nauk S.S.S.R.*, 1952, 82, 751; (*C.A.*, 1953, 47, 9233 a).
23. Smith .. *J. Inst. Metals*, 1914, 12, 168.
24. Libmann .. *Uni. Illinois Eng. Exptl. Station Bull.*, 1928, 173.
25. Bircumshaw .. *Phil. Mag.*, 1934, 17 (vii), 181.

26. Chalmers and Wadie .. *J. Inst. Metals*, 1940, 66, 241.
27. Sugden .. *J. Chem. Soc.*, 1922, 121, 258.
28. Bailey and Watkins .. *J. Inst. Metals*, 1951-52, 80, 57.
29. Fine and Dowdell .. *Trans. Am. Soc. Metals*, 1946, 37, 245.
30. Daniels and Macnaughtan *Tech. Publ. Internat. Tin Research Develop. Council*, 1937, Series B, 6.
31. Tammann and Arntz .. *Z. anorg. Chem.*, 1930, 192, 45.
32. Alty and Clark .. *Trans. Far. Soc.*, 1935, 31, 648.
33. Daniels .. *Ibid.*, 1935, 31, 1277.
34. Bondi .. *Chemical Reviews*, 1953, 52 (2), 417.
35. Bailey and Watkins .. *Proc. Phys. Soc.*, 1950, 63 B, 350.
36. Earle .. *J. Inst. Metals*, 1945, 71, 45.
37. Latin .. *Brit. N-F Metals Research Assoc.*, Rep. No. R.R.A. 647.
38. Mack .. *J. Phys. Chem.*, 1936, 40, 159.
39. Ellefson and Taylor .. *J. Am. Cer. Soc.*, 1938, 21, 193.
40. Zackay *et al.* .. *Ibid.*, 1953, 36, 84.
41. Towers .. *Trans. Brit. Cer. Soc.*, 1954, 53, 180.
42. Gel'd and Chuchmarev .. *Doklady Akad. Nauk S.S.S.R.*, 1952, 83, 877; (*C.A.*, 1952, 46, 7954 g).
43. Atterton and Hoar .. *J. Inst. Metals*, 1952-53, 81, 541.
44. Hoar and Atterton .. *Research*, 1951, 4, 42.