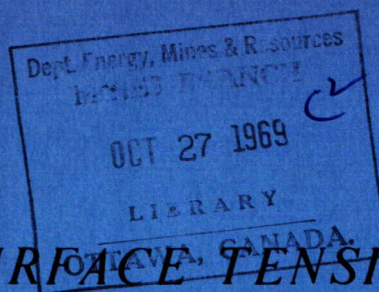


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*THE SURFACE TENSION OF LIQUID  
METALS AND ALLOYS*

D. W. G. WHITE

PHYSICAL METALLURGY DIVISION

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THE SURFACE TENSION OF  
LIQUID METALS & ALLOYS

ABSTRACT

This paper reviews the "state of the art" of liquid metal surface tension measurement. Thus, some basic principles of thermodynamics and surface tension theory are reviewed; selected theoretical and empirical correlations with experimental data are appraised; and experimental methods and techniques are analysed for their sources of error and the means are discussed whereby such errors may be avoided, minimized or corrected for.

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by D. W. G. White

## The surface tension of liquid metals and alloys

AS SHOWN IN Table I, within a narrow margin of error the surface tension of liquid mercury at 25° C is 485 dynes/cm.

This is a simple statement of fact but it is a remarkable one in that it asserts what is probably the only accurately known value for the surface tension of a liquid metal.

It is possible, of course, that accurate values for the surface tension of other metals do exist; but it is fair to say that none is *known* to exist. To the best of the author's knowledge, a selection of values of comparable consistency to that in Table I cannot be written for another liquid metal.

Perhaps it is predictable that mercury would be the first metal whose surface tension would be accurately determined. Nevertheless, although mercury has a combination of physical and chemical properties that make the metal uniquely amenable to experimental manipulation, more than a century has elapsed since Quincke<sup>6</sup> first published his results. With other metals we still have far to go to achieve similar results.

Essentially, the task can be resolved into two basic elements; technology and care. In so far as technology is concerned we have at hand already what we need to make a significant beginning. With the transistor has come zone refining and with the 'Space Age', packaged ultra-high vacuum. If this and other existing technology is used to good effect; if the need for thermal equilibrium is recognised and apparatus built to ensure it; if systematic attention is given to experimental detail whether it is seemingly necessary or not; then it is reasonable to

project that the surface tension of the low-melting-point metals in Groups II<sub>B</sub>, III<sub>B</sub>, IV<sub>B</sub>, and V<sub>B</sub> of the Periodic Table will be known to  $\pm \frac{1}{2}\%$  within the next 20 years.

Although experimental difficulties increase with increasing temperature, it seems reasonable to expect that similar results can be achieved with Sb, Ge, Ag, Cu, and Au, if the objectives are relaxed somewhat. On the other hand, in applying existing materials, techniques, and knowledge to measuring the surface tension of the higher-melting-point metals and the reactive metals, for the time being we must be satisfied with doing what we can.

Certainly any attempt to improve the precision of surface tension measurements is worthwhile, not only for the satisfaction of 'putting a better number in a handbook' but also in the probable expectation that while exercising the necessary effort to be exact, new knowledge will be revealed.

The prospect for further research on the surface tension of liquid metals is an interesting one and it is the author's intent to assist such research by collecting into one review what appear to be 'the best of ideas'. To this end:

- (1) Some basic principles of theory are reviewed.
- (2) Selected theoretical and empirical correlations with experimental data are appraised.
- (3) Experimental methods and techniques are analysed for their sources of error and the means are discussed whereby such errors may be avoided, minimised, or corrected for.

Papers from the published literature will be cited only when, in the judgement of the author, they promote our understanding of the subject. Accordingly, no attempt will be made to produce an all-inclusive survey irrespective of merit.

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Symbols used in this review					
		$M$	Molecular weight	$x'_1, x'_2$	Surface mole fractions of components 1, 2, &c.
		$N$	Avogadro's number		
		$n$	Number of moles: a number when in exponent position	$Z$	Total height of sessile drop
$A$	Surface area	$P$	Pressure	$Z_R$	Height of sessile drop above arbitrary plane below (maximum diameter)
$A_1, A_2$	Molar surface areas of components 1, 2, &c. spread out as monolayers	$p$	Pressure along axis of $Z$ coordinates (across surface thickness)	$Z_{45}$	Height of sessile drop above a point on the outline with a normal at $45^\circ$ to drop axis
$a$	(Chemical) activity: 'capillary constant'	$P_h$	Pressure owing to depth of capillary immersion	$Z_{90}$	Height of sessile drop above a plane through the maximum diameter
$b$	(Spherical) radius at the pole of a sessile drop	$P_\gamma$	Pressure difference across curved surface	$z$	Axis of vertical coordinates
$C$	Constant	$P_{\gamma_1}, P_{\gamma_2}$	Maximum bubble pressures for capillaries 1, 2, &c.	$z', z''$	Thickness of liquid phase, thickness of vapour phase (Flood model <sup>10,11</sup> )
$c$	Specific heat per unit area of surface	$R$	Radius: ratio of maximum to minimum diameters in pendant drop	$\alpha$	Homogenous bulk phase (liquid)
$d_e, d_{max.}$	Maximum diameter of pendant drop	$R$	Molar gas constant	$\beta$	Homogenous bulk phase (vapour): numeric representative of the shape of a liquid drop
$d_{min.}$	Diameter of pendant drop at its waist	$r$	Radius	$\Gamma$	Excess concentration per unit area of surface
$d_s$	Diameter of pendant drop at selected plane	$S$	Entropy: dimensionless function of pendant drop shape	$\gamma$	Surface tension
$E$	(Intrinsic or total) energy	$s\sigma$	Specific entropy or entropy per unit area of surface	$\gamma_0$	A surface tension depending for its value on the critical constants of the liquids
$\Delta E_v$	Energy of evaporation per unit volume	$T$	Absolute temperature		Surface tension of pure components 1, 2, &c.
$e^\sigma$	Specific energy or energy per unit area of surface	$T_c$	Critical temperature	$\mu$	Chemical potential
$F$	Helmholtz free energy	$T_m$	Melting temperature	$\rho$	Density
$f$	A function	$V$	Volume	$\rho_L, \rho_v$	Liquid density, vapour density, &c.
$G$	Gibbs free energy or Gibbs function	$v$	Specific volume (of surface)	$\Sigma$	Sum
$g$	Gravitation constant	$W$	Enthalpy change when $x_1$ moles and $x_2$ moles are mixed, divided by the product $x_1 x_2$	$\sigma$	Superscript to denote interface region (surface)
$H$	Dimensionless function of pendant drop shape	$w$	Weight	$\tau$	Thickness of interface region $\sigma$
$h$	Height of liquid metal surface above tip of capillary	$X$	For non-spherical bubbles equal to $2\gamma/P_\gamma$ (Sugden <sup>127</sup> ): maximum radius of sessile drop	$\varphi$	Contact angle
$i$	Subscript to denote constituent	$x$	One of the two axes of horizontal coordinates	$\omega$	Separation factor (Eberhart <sup>37</sup> )
$K$	Constant	$x_1, x_2$	Bulk mole fractions of components 1, 2, &c.		
$l'$	Fractional factor accounting for difference in bonding between surface and bulk				

## The liquid surface and surface tension

### The nature of surface tension

It is an experimentally observed fact that liquids tend to minimise their surface area. In terms of atomic theory, this fundamental property of a liquid surface is ascribed to the net imbalance of atomic cohesive forces acting inwardly on the atoms in the liquid surface towards the body of the liquid. This situation is indicated schematically in Fig. 1.

In analysing the matter further there is scope for a difference in views and in consequence conflicts have arisen. On the one hand, the presence of free energy in the liquid surface is recognised in the fact that surfaces contract spontaneously. But having noted this much, a number of authors, of whom possibly Adam<sup>7</sup> has been the most influential, have continued with such assertions as '[it is] this free energy in the surface [which] is of fundamental importance' and that surface tension per se lacks physical reality. The 'substitution of a hypothetical tension for a free energy per unit area', the two being dimensionally equivalent, is stated to be a 'mathematical device' used to simplify calculations. The closest Adam comes to offering an argument to support this interpretation is in his reasoning by analogy that the substitution of surface tension for free energy 'is the converse of the

mathematical method of virtual work often used in statics'.

On the other hand, more recently there has been a move to ascribe an independent identity to surface tension. Among others, Brown,<sup>8</sup> Shuttleworth,<sup>9</sup> Flood,<sup>10,11</sup> and Davies and Rideal<sup>12</sup> have affirmed the physical reality of surface tension and by use of such terms as 'plane stress' have emphasised the mechanical aspects of its nature.

Taking two simple examples from common experience, Brown<sup>8</sup> discusses the work processes involved in extending a soap film and either a bubble or a drop, and points out that no matter in what way the surface of a liquid is extended the necessity for performing work on it can be traced to the existence of an opposing force acting tangentially to the surface. He concludes that any theory which accounts for surface energy in liquids must, of necessity, also account for surface tension. Free energy per unit area and surface tension, as force per unit length, are physically equivalent for a pure liquid surface and not just mathematically equivalent.

There are several explanations describing the origin of surface tension in a liquid surface. One, advanced by Brown,<sup>8</sup> stresses the mechanical nature of surface tension. Another argument, thermodynamic in character, has been advanced by a number of authors of whom Davies and Rideal<sup>12</sup> and Gurney<sup>13</sup> are representative. It runs as follows.

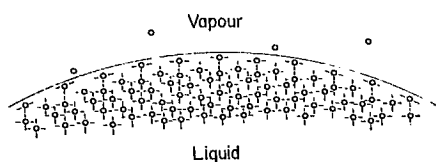
For a liquid in thermodynamic equilibrium, the chemical potential of atoms in the surface must be equal to the chemical potential of the interior atoms. However, surface atoms have fewer nearest neighbours than bulk atoms and accordingly have fewer bonds to break to escape. The tendency of atoms to escape is a measure of chemical potential. Therefore, unless some other factor intervenes, the chemical potential of surface atoms should be higher than that of bulk atoms and not equal to it as is the case. Another factor does intervene, of course, and it is surface tension. Application of a hydrostatic tension to a bulk liquid will reduce the chemical potential of the liquid. Analogously, the existence of a surface tension acts to lower the chemical potential of the surface atoms until it is the same as that of the interior atoms.

**Thermodynamic treatments of surface tension**

In the same way it is possible to account for energy in its various forms for a bulk system by means of suitable thermodynamic expressions, so that one can account for work and energy at the interfacial region (surface) between a liquid and vapour by similar if not identical relations.

There are a number of ways in which surface tension has been represented thermodynamically but they are by no means equally acceptable. To the interested reader with no pretensions to being expert, the situation can be confusing.

To begin with, it will help to clarify matters if we bear in mind that the process we wish to describe involves doing work to extend a planar liquid/vapour interface against the stress of surface tension in a direction in the plane of the surface. For a pure liquid, mechanical work only is involved in this process, but in the general case of a system containing more than one component, allowance must be made for energy changes associated with surface concentration changes.



1 Schematic representation of atom configuration in a liquid.

**Table I. Surface tension of mercury**

Author(s)	Ref.	Method	Year	Surface Tension, dynes/cm at 25° C
Kemball	1	Sessile drop	1946	485.1 ± 1.5*
Zelsing	2	Sessile drop	1953	484.9 ± 1.8
Bering and loileva	3	Max. drop pressure	1954	484.4 ± 0.8
Nicholas <i>et al.</i>	4	Sessile drop	1961	485.8 ± 0.8
Roberts	5	Sessile drop	1964	484.7 ± 1.0*
				485.4 ± 1.2

\* A correction for the particular author's use of the inaccurate form of the Worthington equation has been applied to these results. The correction amounts to +0.27% or 1.2 dynes/cm.

It will, therefore, be necessary to define surface tension in terms of the 'work function' or Helmholtz free energy, which here will be denoted by the symbol *F* (see List of Symbols). At constant temperature this function describes the maximum total reversible work that can be obtained from a given thermodynamic change in state, including work of expansion. The Gibbs free energy (*G*), on the other hand, represents the net work available from a process, exclusive of work of expansion, be it volumetric expansion for a bulk phase or its two-dimensional corollary for a surface.

Thus, following Lewis and Randall,<sup>14</sup> a number of authors, including the writer,<sup>15</sup> have defined the surface tension of a pure liquid in the following way:

$$\left(\frac{\partial G}{\partial A}\right)_{T,P} = \gamma \quad \dots [1]^*$$

This definition is incorrect (e.g., equation [1] is incompatible with equations [10], [11], or [12]), whether or not it has been the authors' intention that the symbol for the Gibbs free energy apply to the entire system including the bulk phases or to the interface region only.

A second approach has involved adapting an equation written for an infinitesimal change in the Helmholtz free energy of a bulk system to include a term associated with the introduction of a planar interface. The equation is usually written thus

$$dF = -SdT - PdV + \gamma dA + \sum \mu_i dn_i \quad \dots [2]^\dagger$$

where the energy changes associated with the surface are accounted for by the third term on the right-hand side.

Then for constant composition at constant temperature and volume

$$\left(\frac{\partial F}{\partial A}\right)_{T,V,n_i} = \gamma \quad \dots [4]$$

This equation represents a process corresponding to a change in the shape of the container of a liquid-vapour system so that the surface area increases while the volume remains constant. The work involved in this process is

\* Followers of the Lewis and Randall school are likely to write equation [1]

$$\left(\frac{\partial F}{\partial A}\right)_{T,P} = \gamma$$

† One way of arriving at equation [2] is as follows. For a bulk system without surfaces, the Helmholtz free energy is a function of the temperature, volume, and the amount of the various constituents present, viz:

$$F = f(T, V, n_1, n_2 \dots n_i)$$

If small changes can occur in the temperature, volume, and amounts of the various constituents, then the change in *F* is given by

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,n_1,n_2 \dots n_i} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n_1,n_2 \dots n_i} dV + \left(\frac{\partial F}{\partial n_1}\right)_{T,V,n_2 \dots n_i} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T,V,n_1 \dots n_i} dn_2 + \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_1,n_2 \dots} dn_i$$

because (as may be found in any standard thermodynamic text)

$$\left(\frac{\partial F}{\partial T}\right)_{V,n_1,n_2 \dots n_i} = -S, \left(\frac{\partial F}{\partial V}\right)_{T,n_1,n_2 \dots n_i} = -P,$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_1,n_2 \dots n_i} = \mu_i$$

$$\text{then } dF = -SdT - PdV + \sum \mu_i dn_i \quad \dots [3]$$

For a system including surfaces it is necessary to add the term  $\gamma dA$  to account for work done in extending the surface, hence

$$dF = -SdT - PdV + \gamma dA + \sum \mu_i dn_i \quad \dots [2]$$

more a measure of the work necessary to change the shape of the liquid than unambiguously to extend its surface independently of the volume. As Flood<sup>10</sup> says 'the operation... does not in general constitute a measure of definite quantity... [and is] capable of yielding a variety of "surface tensions" depending on further particulars not specified...'. Evidently, it is preferable to develop expressions in terms of properties assigned only to the interface region itself.

While this kind of approach was adopted by Gibbs,<sup>16</sup> his concept of an interfacial region has been criticised on other grounds. Although Gibbs did not attempt to define surface tension as such, it was essential to his thermodynamic treatment of the adsorption at the interfaces of solutions to develop a surface model. This work is now regarded as a classic and is admired for its mathematical elegance. Nevertheless, the characteristics of the Gibbs interface have been criticised as arbitrary and obscure by many, including Guggenheim,<sup>17,18\*</sup> in particular, although others such as Scatchard,<sup>19</sup> for example, have attempted to refute the criticism.

In the Gibbs treatment, bulk phases are considered to be separated by a mathematical surface. Each extensive property of an entire system, namely, free energy, content of each component, &c., is imagined to be composed of three parts. In a liquid-vapour system, the first part of the total of an extensive property is assigned to the liquid, it being assumed that the concentration of the property remains homogeneous right up to the mathematical surface. In a similar way, the second portion is associated with the vapour and the balance of the extensive property is assigned to the mathematical surface.

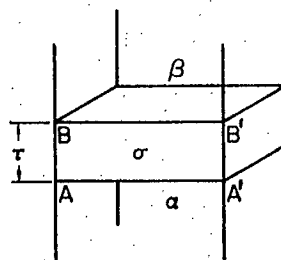
Two main difficulties arise from this treatment. First, several of the extensive properties associated with the mathematical surface depend for their magnitude on the location of the mathematical surface in the region between the liquid and the vapour. This characteristic of the treatment can be exploited mathematically by locating the surface in such a position that certain of the properties become zero. Unquestionably this is mathematically advantageous but conceptually it is abstruse. In addition, the surface has no volume and this too runs counter to our physical picture of an interfacial layer.

Guggenheim and Adam<sup>20</sup> and Guggenheim<sup>17,18</sup> have developed an alternative treatment of the surface based on the work of a number of physicists, notably van der Waals and Bakker<sup>21</sup> and Verschaffelt.<sup>22</sup>

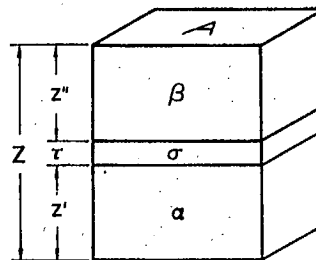
This approach overcomes the difficulties associated with the Gibbs treatment by locating two boundaries, one on either side of a planar interface to include the entire transition region. In this way, a finite thickness is explicitly attributed to the surface region.

A schematic drawing of the model is shown in Fig. 2. Interface region,  $\sigma$ , separates homogeneous bulk phases  $\alpha$  and  $\beta$  which could be liquid and vapour, respectively. Within the interface region  $\sigma$ , properties are uniform in directions parallel to boundaries AA' and BB' but not in a direction normal to these boundaries. Just within the boundary AA', properties are identical with those of the homogeneous liquid  $\alpha$  and similarly at BB' properties on both sides of the vapour boundary are the same.

By considering work done to increase cross-sectional area  $A$  to  $A + dA$  and work done to increase interface region thickness  $\tau$  to  $\tau + d\tau$ , while the material content



2 Model of a liquid/vapour interface. (After Guggenheim.<sup>17,18</sup>)



3 Model of a liquid/vapour interface. (After Flood.<sup>10,11</sup>)

of the interface remains unaltered, an expression  $-PdV^\sigma + \gamma dA$  is developed. This expression is the surface analogue of the term  $-PdV$  in the equation usually written for the most general variation of the Helmholtz free energy of a homogeneous bulk phase, viz:

$$dF = -SdT - PdV + \sum \mu_i dn_i \quad \dots [3]$$

Thus the analogous equation for the interface region is

$$dF^\sigma = -S^\sigma dT - PdV^\sigma + \gamma dA + \sum \mu_i dn_i^\sigma \quad \dots [5]$$

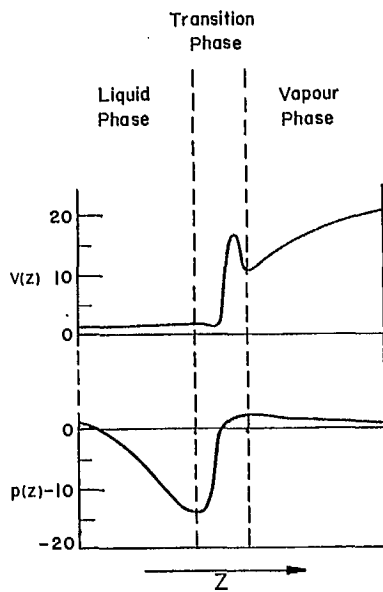
where the superscript  $\sigma$  is used to indicate that the extensive properties are confined to the interface region.

The expression  $-PdV^\sigma + \gamma dA$  describes volumetric work and because of this, unfortunately, ambiguity arises over the nature of the pressure  $P$ . By definition  $P$  is not hydrostatic. It is isotropic within any one lamella parallel to boundaries AA' and BB' but not in a direction normal to these boundaries. Further doubts arise from attempting to imagine the consequences of extending the thickness of the interface region. Both these questions can be vanquished at a stroke, of course, by dropping the term  $-PdV^\sigma$  in equation [5], because its magnitude is negligible. Nevertheless, the ambiguities are inherent in the model and it seems better to avoid them from the outset by adopting another model if a suitable one is to be found. Just this point was made by Guggenheim<sup>18</sup> concerning the Gibbs treatment.

A model for a planar interface that does avoid these difficulties and yet appears to combine some of the convenient characteristics of both the Gibbs and Guggenheim treatments has been proposed by Flood.<sup>10,11</sup> The model is shown diagrammatically in Fig. 3.

Here the liquid phase is denoted by  $\alpha$ , the vapour phase by  $\beta$ , and  $\tau$  is the distance between the two planes located

\* These strictures have been omitted from the 5th edition (1967).



4 The pressure and specific-volume distributions across the liquid/vapour interface. (After Flood.<sup>10,23</sup>)

on either side of the transition region  $\sigma$ . The whole system is allowed to grow in extent from suitable sources of masses but only in directions parallel to the surface layer, i.e.  $z'$ ,  $z''$ , and  $\tau$  (the sum of which is equal to  $Z$ ) remain constant.

Thus for the interfacial region  $\sigma$

$$dF^\sigma = -S^\sigma dT - \bar{p}_z \tau dA + \sum \mu_i dn_i^\sigma \quad \dots [6]$$

where  $-\int_{z'}^{z'+\tau} p(z) dz \equiv -\bar{p}_z \tau$

Equations can be written for the change in Helmholtz free energy of liquid phase  $\alpha$  and vapour phase  $\beta$  that are similar to equation [6] for the surface except that the term  $-\bar{p}_z \tau dA$  is replaced by  $-p z' dA$  and  $-p z'' dA$ , respectively.

It is then supposed that the properties of  $\alpha$ ,  $\beta$ , and  $\sigma$  are measured and compared with a reference system similar in all respects except for the existence of surface region  $\sigma$ . The 'observed' values of the reference system are then subtracted leaving only values for  $\sigma$  remaining.

Hence, putting  $p_z \tau \equiv -\gamma$

$$dF^\sigma = -S^\sigma dT + \gamma dA + \sum \mu_i dn_i^\sigma \quad \dots [7]$$

and at constant temperature and composition

$$\left(\frac{\partial F^\sigma}{\partial A}\right)_{T, n_i} = \gamma = -\bar{p}_z \tau \quad \dots [8]$$

If the planes separated by distance  $\tau$  are located just beyond the limits of the non-uniform region, then  $\gamma$ , the surface tension, is the mean value of the tension in the non-uniform surface layer and is unambiguously equal to the Helmholtz free energy per unit surface.

### Pressure distribution across the liquid/vapour interface

As stated in the derivation of equation [8], the term  $-\bar{p}_z \tau$  is the integral of the pressure distribution over the entire thickness of the liquid-vapour transition region. For liquids such as liquid metals, where the surface tensions are high and the vapour densities much less than the liquid densities, Flood<sup>10,23</sup> has visualised that the pressure  $p(z)$  varies across the surface after the manner shown in Fig. 4. The pressure distribution and the curve for the specific volume  $v(z)$ , have been drawn to correspond physically with a case where the interface adsorbs its own vapour. Thus both the density and the pressure will increase as the interface is entered from the vapour side.

### The thickness of the liquid surface

While studying the nature of surface tension it is natural to wonder how extensive is the region of the liquid surface at temperatures well below  $T_c$ . In attempting to answer this question it seems that there is nothing better than estimates to refer to. These estimates vary from 1 to  $\sim 10$  at. dia.

For example, Mott and Rice<sup>24</sup> appear to agree on 1-2 atom layers for the surface thickness, while Guggenheim,<sup>17,18</sup> Davies and Rideal,<sup>25</sup> and Flood<sup>10</sup> estimate the distance as 10 Å or more. Several writers refer to the optical measurement of Raman and Ramdas<sup>26</sup> on water (1927) which yielded a value of 5 Å. Flood<sup>10</sup> asserts that this is probably more a measure of the thickness of the region of rapid change of refractive index than a measure of the total surface thickness. This region would be essentially identical with the region of rapid increase in specific volume (see Fig. 4), and since this is roughly one-fifth of the total surface thickness, the measurement indicates a total surface thickness of  $\sim 25$  Å.

### The effect of surface curvature on surface tension

It has been implicit in much of the foregoing that discussion of the nature and effects of surface tension has been limited to a consideration of flat surfaces only. However, it is a consequence of the presence of a state of stress in the surface that, if the surface becomes curved, a pressure difference will be set up across the surface. This pressure will be greater on the concave side than on the convex by an amount dependent on the surface tension and radius of curvature. The effect leads to an equation<sup>7,17,18</sup> which may be regarded as a fundamental definition of surface tension and is at the basis of most methods of measuring surface tension, viz :

$$P_\gamma = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad \dots [9]$$

where  $R_1$  and  $R_2$  are the principal radii of curvature.

$P_\gamma$  is imposed on  $-\bar{p}_z$  but, despite its fundamental importance to the measurement of surface tension, the magnitude of  $P_\gamma$  is negligible compared with that of  $-\bar{p}_z$ , as the following extreme example will show.

Suppose that the surface tension of a metal is being measured in a capillary 0.5 mm in dia. and that the thickness of the surface is 25 Å. Neglecting signs, the ratio of the pressure is



$$\frac{P\gamma}{\bar{P}_z} = \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tau = (80) 2.5 \times 10^{-7} = 2/100,000$$

Thus the effect of surface curvature on the surface tension of a liquid is insignificant until the radius of curvature begins to approach the thickness of the surface.

## Theory and empiricism

### Theory

To interpret or to calculate gaseous phenomena it is possible to draw on a self-consistent body of ideas and mathematics known as kinetic theory. To some extent a similar situation exists for the solid state. But not so for liquids. Of course, there are theories of the liquid state but as yet not one of them permits us to predict, to explain, or to calculate a number of liquid properties in the same way that kinetic theory does for gases. Recently, Bernal<sup>27,28</sup> introduced a model of the liquid state that is more promising than any heretofore advanced. The model embodies the concept of a liquid as a 'heap' of particles each in irregular contact with a number of others. But the model awaits the development of a statistical geometry before it can be used for calculation purposes and, hence, it cannot yet be regarded as an adequate theory.

Not only have liquid theories been unable to account satisfactorily for the bulk properties of liquids, they do not seem to have been directed at all to shedding light on the nature of liquid surfaces. In consequence, theoretical activity on liquid surfaces has taken place apart from the main stream of liquid-state theorizing and not, unfortunately, as the natural outgrowth from some of its central concepts.

If liquid theory, generally, is in a parlous state, liquid surface theory, in particular, is no better. Again, there are no unifying concepts. However, some mathematical treatments have been developed and these are reviewed in the following passages. The treatments are of two kinds: thermodynamic and atomistic.

#### Thermodynamic treatments

A number of basic expressions involving surface tension and related properties can be derived. These expressions are now classical in character and are of varying utility. In particular, the Gibbs adsorption equation perhaps calls for special mention.

Apart from these, other expressions have been developed with a view to calculating the surface tension of alloy systems on the basis of certain assumptions. When applied to ideal or near-ideal systems this work has been rewarded by some modest successes.

From equations [7] and [8], it follows that at constant temperature

$$F^\sigma = \gamma A + \sum \mu_i n_i^\sigma \quad \dots [10]$$

Because changes in the Gibbs free energy, or Gibbs function, represent net work available from a process apart from work of expansion

$$G^\sigma = \sum \mu_i n_i^\sigma = F^\sigma - \gamma A = E^\sigma - TS^\sigma - \gamma A \quad \dots [11]$$

$$\text{and for a pure liquid } G^\sigma = 0 \quad \dots [12]$$

Differentiating equation [10] and substituting from equation [7] for  $dF^\sigma$  leads to

$$S^\sigma dT + A d\gamma + \sum n_i^\sigma d\mu_i = 0 \quad \dots [13]$$

Dividing through by  $A$  gives

$$\frac{d\gamma}{dT} = -s^\sigma \text{ for a pure liquid} \quad \dots [14]$$

The surface entropy per unit surface,  $s^\sigma$ , is truly an excess quantity. It represents the additional entropy per unit area possessed by a system with surfaces over and above the amount that the same quantity of fluid would possess under the same conditions of temperature and pressure in the body of a larger quantity of fluid. Thus, the temperature coefficient of surface tension,  $d\gamma/dT$ , gives an indication of the algebraic increase in entropy contributed by a liquid surface. It then becomes possible to say something qualitative<sup>29</sup> about the degree of order in the liquid surface compared with that in the bulk liquid, although attempts have been made to quantify the term by special assumptions concerning surface thickness in the case of metals<sup>30</sup> and in the case of organic liquids.<sup>31</sup> Especially in the case of liquid metals such assumptions are essentially hazardous and hence the significance of the magnitude of the excess entropy calculated in this way is questionable.

Dividing equation [11] through by  $A$ , noting equation [12] for a pure liquid, and substituting for  $s^\sigma$  from equation [14] leads to

$$e^\sigma = \gamma - T \frac{d\gamma}{dT} \quad \dots [15]$$

where  $e^\sigma$  is the internal or total energy of the surface per unit area. It is evident that  $e^\sigma$  can be determined from a plot of surface tension vs. temperature and if  $\gamma$  varies linearly with temperature,  $d\gamma/dT = \text{constant}$  and  $e^\sigma$  is invariant. For many liquids, especially organic liquids,  $\gamma$  has been found to be a linear function of temperature and thus  $e^\sigma$  has come to be regarded by some as a more fundamental characteristic of a substance than the surface tension.

If equation [15] is differentiated

$$\frac{de^\sigma}{dT} = c^\sigma = -T \frac{d^2\gamma}{dT^2} \quad \dots [16]$$

where  $c^\sigma$  is the specific heat. Again, if surface tension varies linearly with temperature  $d^2\gamma/dT^2$  is zero, and so is  $c^\sigma$ . The significance of superficial specific heats with a value of zero has been interpreted by Einstein<sup>32</sup> to mean that the intrinsic energy of the surface,  $e^\sigma$ , goes into the formation of new surface in a potential form.

If equation [13] is divided through by  $A$ , then at constant temperature

$$(\partial\gamma)_T = -\sum \Gamma_i d\mu_i \quad \dots [17]$$

where  $\Gamma_i$  is the number of molecules per unit area of surface,  $n_i^\sigma/A$ . This is the most general form of the well-known Gibbs 'adsorption' equation and as such is

applicable to a system with any number of components. For a binary solution, following Gibbs, equation [17] may be written

$$\Gamma_2 = - \left( \frac{\partial \gamma}{\partial \mu_2} \right)_T \quad \dots [18]$$

where the term  $\Gamma_1 d\mu_1$  has been eliminated by locating the 'dividing surface' so that  $\Gamma_1$  becomes zero. By remembering that  $\mu_1 = \mu^\circ + RT \ln a_1$ , equation [18] can be written

$$\Gamma_2 = - \frac{a_2}{RT} \left( \frac{\partial \gamma}{\partial a_2} \right)_T \quad \dots [19]$$

$\Gamma_2$  is the excess solute over the amount there would have been had the bulk phases remained homogenous right up to the 'dividing surface' and  $a_2$  is the chemical activity of the solute.

Although the Gibbs adsorption equation is usually applied to systems of two components only, Whalen, Kaufman, and Humenik<sup>33</sup> have developed expressions for treating three-component systems exploiting Schuhmann's<sup>34</sup> procedure for dealing with the Gibbs-Duhem equation applied to ternary solutions. In a second paper, Kaufman and Whalen<sup>35</sup> use the same treatment again.

As already noted, the characteristics of the Gibbs treatment—the 'arbitrary' locating of the 'dividing surface', for example—have been the subject of much discussion and even controversy since Gibbs first published his paper in 1878. Recent contributions to this continuing discourse came from Flood,<sup>11</sup> who has written a comparative analysis of the Gibbs and Polanyi descriptions of adsorption; Scatchard,<sup>19</sup> who has explained and defended Gibbs treatment of adsorption; and deBruyn,<sup>36</sup> who has written an explanatory treatise noting, in addition, some recent applications of the equation to nucleation theory.

Although the equation has been applied to some metallurgical problems, it has not enjoyed the extensive use accorded to it in organic chemistry.

Because the energy of a binary solution is minimised when the liquid surface is enriched in the lower-surface-tension component, it is observed experimentally that the surface tension always deviates negatively from a linear function of the mole fraction. However, for those systems where  $\gamma$  is a linear function of the surface-layer mole fraction, Eberhart<sup>37</sup> has developed the expression

$$\gamma = \frac{\omega x_1 \gamma_1 + x_2 \gamma_2}{\omega x_1 + x_2} \quad \dots [20]$$

Here,  $x_1$  and  $x_2$  are the bulk liquid mole fractions and  $\omega$  is a function of temperature only.

Equation [20] fits surface-tension data for a variety of fused-salt, organic, and inorganic mixtures. It has also been found to apply to the copper-nickel system but not to lead-tin alloys.

With some overlapping effort, a number of authors, culminating in Hoar and Melford,<sup>38</sup> have developed expressions of increasing complexity for calculating the surface tension of binary solutions. Results obtained with two of the earlier expressions have been compared

by Taylor<sup>39</sup> with experimental data from six eutectic systems.

This work has all been confined to monomolecular surface models, except for one treatment of a double-layer model by Defay and Prigogine.<sup>40</sup> Although the model with a double-layer surface predicts significant differences in adsorption behaviour compared with the unimolecular surface, surface-tension changes were found to be small enough to justify the unimolecular model as a good first approximation.

Early work was largely applicable to ideal solutions only, but treatments of the unimolecular model now extend to non-ideal mixtures of components with unequal molar surface areas, i.e.,  $A_1 \neq A_2$ .

In a preamble to the derivation of their equations, Hoar and Melford present a succinct résumé of the previous work which it would be redundant to repeat here.

Hence, for a regular solution as defined by Hildebrand,<sup>41</sup> the expression derived by Hoar and Melford is

$$\begin{aligned} \gamma &= \gamma_1 + \frac{RT}{A_1} \ln \frac{x'_1}{x_1} + \frac{W}{A_1} (l'x'_2{}^2 - x_2{}^2) \\ &= \gamma_2 + \frac{RT}{A_2} \ln \frac{x'_2}{x_2} + \frac{W}{A_2} (l'x'_1{}^2 - x_1{}^2) \end{aligned} \quad \dots [21]$$

where the symbols represent quantities as already defined. For values of 0.5 or 0.75 ascribed to  $l'$ , the fractional factor by which bonding in the surface is less than that in the bulk, equation [21] gives a good fit with the experimental data on lead-tin and lead-indium alloys obtained by the authors. There does not appear to be any published record of equation [21] having been applied to other binary systems.

However, for convenience in this treatment no distinction has been made in calculation between the partial molar and the molar surface areas of each component. The one has been taken as the equal of the other. In further work along these lines, Sprow and Prausnitz<sup>42</sup> assume vapour-liquid data to be available and restrict the regular solution treatment to the surface only.

Kaufman and Whalen<sup>43</sup> have presented further thermodynamic manipulations of surface-tension data for binary solutions based on some ideas of Gjostein.<sup>44,45</sup> They conclude that any correlation between surface tension and bulk thermodynamic properties seems unlikely until some new approach is devised.

Possibly it is an effort to provide this new approach that leads Kaufman<sup>46</sup> to abandon the concept of monolayer surfaces on liquids with the thermodynamic properties of regular solutions. Instead, he develops equations for a liquid characterised by stoichiometric groups adsorbed at the surface to the extent of infinite dilution in the bulk. With some convenient assumptions, calculations are matched to selected experimental results for binary systems. This model is also applicable to ternary solutions.

The difficulties in describing the nature of changes in surface tension as a function of composition and temperature in multicomponent alloys are discussed by Ofitserov *et al.*<sup>47</sup> The simple case of an ideal solution with equal partial molar surfaces is compared with some results on the tin-lead-bismuth system. Unfortunately, at the time

of writing, this paper appears to be available only in Russian.

Finally, this section would not be complete without reference to the series of thoughtful papers by Eriksson,<sup>48-52</sup> who has rigorously re-examined and discussed many basic concepts of surface thermodynamics.

#### Atomistic theories and statistical mechanics

While thermodynamic concepts have characterised attempts to account for the properties of alloys, many expressions have been developed to calculate the surface tension of pure liquid metals by considering the details of atomic bonding. In general, the performance of these equations is inconsistent. The excellent agreement with experiment achieved in some cases is offset by large discrepancies in others.

Although many papers have been published in pursuit of this topic, a historical treatment will be eschewed. If, in developing a particular idea, papers have been published more or less in sequence, in general only the most recent will be noted.

In that buffer zone of activity that is neither pure thermodynamics nor yet physics, Skapski<sup>53,54</sup> and Belogurov<sup>55</sup> have published papers. In the first, Skapski<sup>53</sup> derives an expression for the temperature coefficient of surface tension in terms of the entropy changes associated with transferring *N*-Avogadro's atoms from the bulk of a liquid to the surface, and for the same process, develops in a second paper<sup>54</sup> an equation for calculating the total surface energy (equation [15]). From this, of course, surface tension can be determined.

Belogurov<sup>55</sup> arrives at a number of equations for calculating surface tension from such diverse considerations as energy of activation for self-diffusion, first-order phase transformations, and thermal-elastic processes. In some instances agreement between theory and experiment is good; generally, it is not.

From evidence indicating that the first molecular layer of a liquid surface contributes ~90% of the total surface free energy, Lu *et al.*<sup>56</sup> assume a monomolecular layer boundary in order to derive a simple equation for calculating surface tension from significant structure theory. Although, when applied to metals, the agreement between theory and experiment is good for silver and satisfactory for gold, aluminium, and lead, for a number of other metals there is a discrepancy of 20% or more.

In addition, a number of authors have derived equations based on various models within the broad field of electron theory. For example, Stratton<sup>57</sup> has developed expressions for the surface energy of solid metals which at the melting point are in excellent agreement with the experimental results of Taylor<sup>58</sup> for the surface tensions of liquid sodium and lithium. But a similar comparison for potassium reveals a discrepancy of ~50%. Calculated and experimental values for the temperature coefficient of surface tension of all three metals are inconsistent, although agreement here would have been ameliorated had experimental conditions conformed with the need for thermodynamic equilibrium. However, for other metals the expression yields results that simply do not agree with experimental data.

On the other hand, Demchenko,<sup>59</sup> for example, has developed equations that yield results in good agreement with the surface tension of potassium and are in excellent

agreement with the surface tensions of zinc and tin. Yet the surface tensions of sodium and lithium are not predicted as accurately as by Stratton's expression.

Kunin<sup>60</sup> and Zadumkin<sup>61,62</sup> in a series of papers (both alone and with other authors) have applied solid-state theory to yield semi-empirical expressions for calculating the surface energy of metals. Bohdanský and Schins<sup>63</sup> found that Kunin's formula yielded very good agreement with their experimental results on alkali metals—better, in fact, than the match given by any other expression including that of Zadumkin. However, Semenchenko<sup>64</sup> points out that, while Zadumkin's equation produces discordant values for mercury and tin, the results are incomparably better than those given by Kunin's formula. On the basis of his work in calculating the surface tension of pure metals, Zadumkin<sup>65</sup> has also extended his treatment to binary alloys.

In further attempts to determine the surface tension of liquid metals mathematically, Solov'ev and Kaplun<sup>66</sup> have derived a formula from considerations of the 'free volume' and Mayer,<sup>67</sup> too, has developed expressions on the basis of the so-called ionic salt and monoatomic models.

Finally, there are a number of other papers in the literature concerned with calculating surface tension, though not necessarily of liquid metals. The interested reader can gain access to these through the paper of Lu *et al.*<sup>56</sup>

#### Empiricism

There are several expressions remaining from early labours to relate surface tension to other physical properties in pure substances. These expressions hold with good accuracy for many non-associated liquids but their relevance to liquid metals is by no means so certain.

For example, in relating surface tension to temperature, the simplest form of an empirical expression involving  $\gamma$  and  $T$  is

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n \quad \dots [22]$$

In this form, for non-associated liquids, the equation has been found by a number of authors<sup>68</sup> to obtain when  $n \approx 1.2$  and by Guggenheim<sup>69</sup> when  $n = 11/9$ .

Better known, perhaps, is the Eötvös<sup>70</sup> equation

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = K (T_c - T) \quad \dots [23]$$

where  $M$  is the atomic or molecular weight,  $\rho$  the density of the liquid, and  $K$  the Eötvös constant. With  $K = 2.12$ , a number of organic liquids conform to the equation, but according to Semenchenko<sup>64</sup> it does not apply well to liquid metals. However, this opinion has recently been challenged by Groves,<sup>71</sup> who makes out a good case for a verdict of not proven and at the same time advances a value of 0.64 for  $K$ . It may well be, that for many metals, some modified form of equation, such as that of Strauss,<sup>72</sup> for example,

$$\gamma = 0.59 (\Delta E_v)^{5/6} \left(\frac{T_c - T}{T_c - T_m}\right) \quad \dots [24]$$

will be found applicable when more reliable and extensive data become available. In equation [24],  $\Delta E_v$  is the energy of evaporation per unit volume. These equations cannot be expected to apply at temperatures immediately above the melting points of metals whose coefficients of surface tension are positive in this temperature range.

To extend the scope of equation [23] among non-associated liquids many modifications have been proposed. The most enduring of these came from Katayama,<sup>73</sup> who replaced  $\rho$  by  $\rho_L - \rho_v$ .

By combining Katayama's modification of equation [23] with equation [22] and assuming  $n = 1.2$ , Ferguson<sup>74</sup> showed that

$$\frac{\gamma^{1/4}}{(\rho_L - \rho_v)} = C \quad \dots [25]$$

where  $C$  is a constant for each liquid. This equation had earlier been proposed empirically by Macleod<sup>75</sup> and by Bachinski in the Soviet Union. It is widely used with an exponent of  $1/4$ , although Guggenheim<sup>69</sup> asserts that the exponent should be  $3/11$ . According to Semenchenko, this equation, too, is not valid for liquid metals and neither therefore, can be the well-known parachor equation that Sugden<sup>76</sup> derived from equation [25].

There are many treatments of this topic in the literature. Perhaps the most extensive is that by Partington<sup>77</sup> and the most specific to liquid metals that of Semenchenko.<sup>64</sup>

Attempts to account empirically for the surface-tension behaviour of alloy systems seem to have been largely confined to the Soviet Union. In this connection, Semenchenko's hypothesis of generalised moments has been particularly successful in matching the experimental characteristics of dilute amalgams. Its author has dealt with the subject thoroughly in his book<sup>64</sup> and at the same time has reviewed other empirical concepts comprehensively.

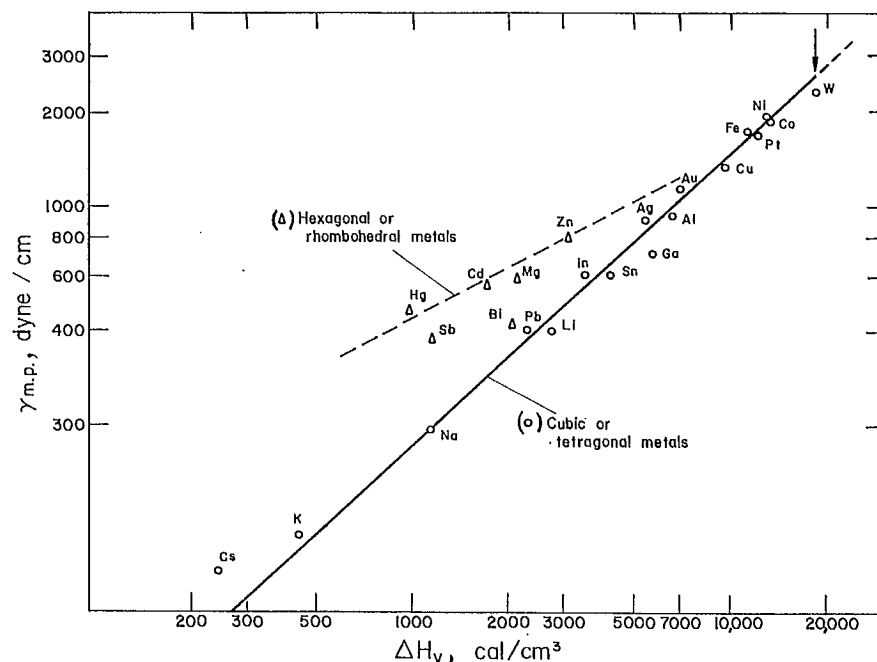
It is an experimentally observed fact that surface tension varies periodically with atomic number and it is recognised that this occurs because surface tension is a function of bond strength. This has led a number of authors to look for empirical correlations between surface tension and other similarly dependent physical properties such as heat of vaporisation, &c., with the purpose of predicting the unknown surface tension of a number of substances. To some extent this work has been hampered by unreliable data. Nevertheless, it has now progressed to the point where predictions with an accuracy of roughly  $\pm 10\%$  can be made.

From calculations based on a correlation between the surface tension and heat of vaporisation of a number of liquid metals, Oriani<sup>78</sup> has shown that the pairwise bonding energy of surface atoms is greater than for bulk atoms. This contradicts a basic assumption of Skapski<sup>53,54</sup> and the upset is substantiated by calculations which show that Skapski's equation leads to incorrect results in the case of eight metals.

In further papers, surface tension has been correlated with atomic volume, heat of sublimation, and an empirical parameter involving elastic modulus and liquid density, by Taylor;<sup>79</sup> heat of fusion, heat of sublimation, atomic volume, the elastic modulus-density parameter, absolute melting point, and absolute melting point plus boiling points, by Siuta and Balicki;<sup>80</sup> vaporisation energy by Strauss;<sup>81</sup> and finally, heat of vaporisation by Grosse,<sup>82</sup> whose graph is reproduced in Fig. 5.

### Experimental methods and their sources of error

In concluding a section on the surface properties of liquid metals as part of a larger review on the structure of liquid metals, Wilson<sup>83</sup> asserts that 'it is not yet possible to draw any conclusions about the structure of liquid metals or alloys from surface-tension measure-



5 A correlation between surface tension and heat of vaporisation. (After Grosse.<sup>82</sup>)

ments. To allow this, measurements of considerably greater accuracy are required . . .<sup>1</sup>

The immediate reason that accurate data have not been obtained is that much experiment, either in method or in the means of executing it, has not been adequate. With a view to improving this situation it is the purpose of this section to examine critically techniques, methods, and apparatus for sources of error and to discuss ways in which error can be averted.

### General experimental precautions

If the surface tension of a liquid metal is to be measured accurately, the liquid should be in thermodynamic equilibrium with its own vapour and be free from extraneous chemical, mechanical, or electrical effects. These necessary restrictions on experimental conditions are quite general in their application, although the means of dealing with them may take particular forms for particular methods of measurement.

### Electrical effects

Apart from mechanical side-effects, spurious effects of electrical origin are possibly the most uncommon and therefore the most readily dealt with.

Experimental techniques involving the redistillation of very large sessile drops of mercury *in situ* are prone to electrostatic effects which can be eliminated by grounding as noted by Kembell<sup>1</sup> and Zeising.<sup>2</sup> Furthermore, the magnitude of electrostatic effects on the surface tension of sessile drops can be calculated for certain limiting cases following the work of Cade.<sup>84,85</sup>

Electron-bombardment heating and induction-heating techniques have been coming into use in connection with attempts to measure the surface tension of reactive metals by the pendant-drop and drop-weight methods. Limitations on the accuracy of surface-tension measurements imposed by electrical-field effects associated with induction heating have been discussed by Peterson *et al.*<sup>86</sup> and by Allen.<sup>87</sup> Peterson *et al.* examined the effect of different coil shapes on magnetic-field distribution within the coil and of the accompanying changes in the apparent surface tension of titanium. It was found, too, that the alternating nature of the field induced vertical oscillations in the liquid drop which also contributed to experimental error. Similar problems attending electron-bombardment heating have also been reported by Tille and Kelly<sup>88</sup> and by Allen.<sup>89</sup>

### Mechanical effects

Although fluctuations in electrical fields are a source of vibration, oscillations will usually have their origins in purely mechanical causes.

In the drop-weight method, vibration causes premature drop break-off and low surface-tension values. In the sessile-drop and pendant-drop methods vibration leads to indistinct photographic images. For a given drop size, drops are more susceptible to vibration the higher the density of the liquid metal and the lower its surface tension.

Vibration may result from uncontrolled inertia forces. In a drop that should be static, vibration is obvious. But uncontrolled inertia forces will be present in all dynamic

methods of measuring surface tension although they may not be very apparent. This is one reason why dynamic methods of measuring surface tension cannot be considered seriously for accurate work.

The maximum-bubble-pressure method is a quasi-static technique that has been used to determine the surface tension of many liquid metals. It is possible that if bubbles are formed too quickly, this method may be susceptible to inertia effects. However, early exploratory work by Bircumshaw<sup>90,91</sup> showed that bubble-formation times in mercury varying from 50 sec to 30 min had no effect on surface tension that was unequivocally attributable to inertia forces. Indeed, Pugachevich<sup>92</sup> has said that bubble-formation times may vary from a few seconds up to 40 min or more for viscous liquids, while Kingery<sup>93</sup> states that for low-viscosity liquids such as metals, times of 1 sec are satisfactory. Nevertheless early studies, especially, were prone to effects from impurities, to variations in degree of thermal non-equilibrium, and to uncertainties concerning the radius (between the inside and outside diameters of the capillary tube) at which the base of the bubble anchored. This work could profitably be repeated to determine whether there is a lower limit to bubble-formation time of practical consequence. In a later section dealing with thermal equilibrium another reason to avoid short bubble-formation times will be indicated.

### Chemical effects

Extraneous chemical reactions with the liquid metal result in contamination and often in a lowering of surface tension. Assuming that an impurity dissolves in the liquid metal and that the quantity transferred is small, there will be little or no effect on surface tension if the impurity is surface-inactive. On the other hand, if the impurity is surface-active, the surface tension of the liquid metal will be reduced and perhaps quite sharply so. However, if the impurity forms a surface film, for example when a metal is oxidised, then surface tension might appear to increase or decrease. In any event, the presence of a film renders the term surface tension rather meaningless.

There is no one criterion for predicting whether an impurity will reduce surface tension. For gaseous ions the concept of polarisability is useful.<sup>94</sup> For metallic contaminants or metalloids, lower surface tension than that of the solvent metal<sup>95</sup> is probably the most convenient rule of thumb, although there are others.<sup>96</sup>

The decrease in the surface tension of a metal to be expected from contamination by an impurity with a lower surface tension may conveniently be expressed in the following way:

$$\left(\frac{d\gamma}{dx_2}\right)_{x_2 \rightarrow 0} < 0 \text{ for } \gamma_2 - \gamma_1 < 0$$

... [26]

Zadumkin and Zvyagina<sup>97,98</sup> found, in fact, that this criterion was substantiated by 94% of the nearly 200 binary systems whose surface-tension data they examined. Complementing the results of this survey summarised in English<sup>97</sup> is a useful table in the Russian original.<sup>98</sup>

For purposes of discussion, sources of contamination can be categorised under three main headings:

- (1) Impurities in the metals themselves.
- (2) Contamination from physical contact with the apparatus.
- (3) Reaction with the experimental environment.

(1) In much of the earlier work, the accuracy of surface-tension data was affected to an important extent by the technology of metal refinement, but with metals of 99.99, 99.999, and even 99.9999% purity becoming increasingly available, this cause of poor data is losing its significance. An example of the effect of metal purity is given below. These data are extracted from a recent paper by White<sup>29</sup> on the surface tension of zinc.

Purity, %	Surface tension at 420° C, dynes/cm
99.99+	757 ± 5
99.999+	761 ± 5
99.9999	767.5 ± 5

(2) If there is contamination from physical contact it will originate with the substances of which such items as crucibles, capillaries, plaques, &c., are made. In selecting materials, not only must possible reactions with the parent material be considered, but also the likelihood of contamination from impurities in the material and from other substances such as binders that might be present. In selecting the parent material there is a large amount of thermochemical data<sup>99</sup> now available of sufficient accuracy to assist intelligent choices. Unfortunately, this is not always matched by information on impurity content, especially with refractory materials. Such information is often regarded as of proprietary interest and is, therefore, decently veiled in obscurity. Kozakevich and Urbain<sup>100</sup> have discussed the thermodynamic stability of various metal-oxide powders, while at the same time emphasising the importance of purity in selecting these materials for making plaques. For those metals that do not form carbides, graphite is an extremely useful, surface-inactive material which is available in high-purity, dense forms.

In practice, contamination by physical contact should not present experimental difficulties, since if reaction with available materials is anticipated, the pendant-drop method should be selected.

(3) Reaction between liquid metals and the experimental environment is really a special case of physical contact. But in itself this source of contamination has several aspects and, thus, it is convenient to consider it separately.

The principal environmental contaminants are oxygen and water vapour and their presence in a surface-tension system, even in trace amounts, can lead to film formation on the metal surface and to spurious surface-tension results. The measures necessary to cope with these gases involve considerable experimental complexity.

Oxygen and water vapour originate in the system in two ways. First, they are present in the apparatus and on the metal charge at the beginning of experiment and may not be completely removed by pumping. Secondly, they can be introduced into the system during experiment by leaks or as impurities in another gas.

All surface-tension equipment should be 'leak-proof', whether it is to be used for experiments in vacuum or in

a gas. For air to diffuse into a system through a pin-hole, a pressure differential is not necessary. Air (outside the system) will readily diffuse down the fugacity gradient against a back pressure of 1 atm of some other gas (inside the system). The other gas, of course, will diffuse out in counter current. In a system of 1 l. or so capacity, a leak rate of  $\sim 1 \times 10^{-4}$  torr/h should be considered the maximum permissible. A lower rate is much to be preferred especially when measuring the surface tension of reactive metals.

When experiments are to be carried out in the presence of gas, if it can be proved that no spurious side effects will result, hydrogen will confer on a system a greater toleration for contamination than will an inert gas. In many cases, however, if a film should form on the surface of the metal, hydrogen will not reduce it even though such a reaction may be energetically favourable. Presumably, the effect is one of kinetics.

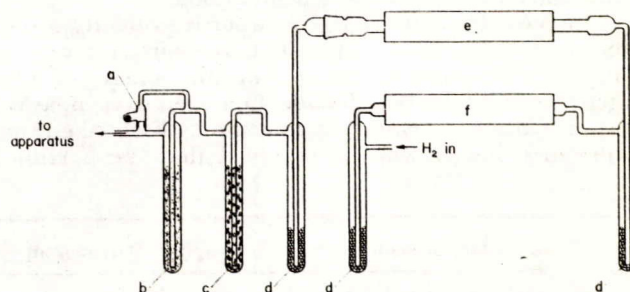
In passing, it is worth noting that if hydrogen is used and if, at any stage in the experimental procedure it is passed through and out of the apparatus, it should not be burnt off at a jet as is often done in laboratories. It should be passed through some form of one-way valve (bubbler) and vented to the outside. When hydrogen is burnt off at a jet, combustion products back-diffuse against the gas stream and contamination results.

No matter what gas is to be used it should be purified carefully. In this respect there are some curious examples of inconsistency in the literature. Gases may be purified by many chemical and adsorptive processes based on sound thermodynamic principles. But to apply these effectively, purification trains must be adequate in extent and gas flow rates not too high. If these principles are respected, there are many ways of satisfactorily purifying a given gas.

Figure 6 depicts a train that has been used by the author for purifying hydrogen and helium. It has given excellent service with very little maintenance for about 5 years and, seemingly, is still in good condition.

A number of workers in the Soviet Union<sup>101,102</sup> purify argon by bubbling the gas through lithium held at 300° C in a suitable iron vessel. NaK at room temperature can be used for the same purpose.

Titanium, zirconium, uranium, and other substances have all been used successfully for cleaning up gases. Whenever possible it is an advantage, however, to use materials that can be restored or regenerated *in situ*. Thus, they may be used indefinitely.



NOTE: All traps immersed in liquid nitrogen

- a Degassing bypass
- b Molecular-sieve trap
- c Activated-charcoal trap
- d Traps containing glass beads
- e Ferrocchrome furnace at 800° C
- f Copper furnace at 500° C

6 A purification train for hydrogen and helium.

A text by Farkas and Melville<sup>103</sup> published in 1939 still appears to be the only book devoted to handling gases in the laboratory, although more recent information is to be found in works dealing with laboratory practices.<sup>104</sup>

While it is essential to adopt adequate measures to minimise the ingress of contamination during the course of experiments, it is equally important to design the apparatus in such a way that it can be thoroughly cleaned up after being open to atmosphere. Thus, it is important first to degas the apparatus in vacuum even though experiments may be carried out in a gaseous atmosphere. An apparatus cannot be cleaned up satisfactorily by purging it with a gas. The application of heat as extensively as possible helps considerably to remove adsorbed gases. In particular, in the furnace zone of the apparatus it is an obvious advantage to be able to degas at temperatures in excess of the experimental temperature range, if at all possible.

Cleaning the metal charge in the apparatus is a more difficult problem. Films and adsorbed gases on the surface are not easily removed. But the difficulty will be exacerbated if the metal is allowed to become hot during the degassing cycle. It should be isolated in the apparatus and kept cool. After degassing, hydrogen may be used to renew the surface of easily reducible metals, such as iron or copper, whether in the liquid or solid states. Ion-bombardment, and filtration too, are satisfactory cleaning methods.

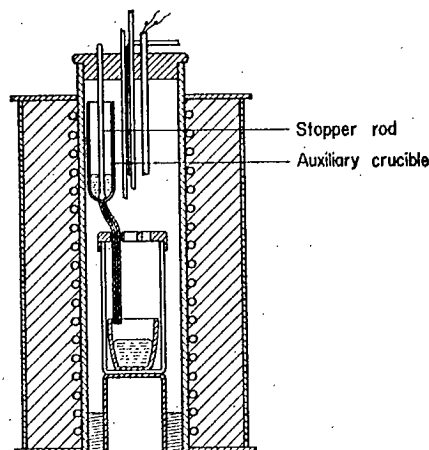
In a brief review, Roberts<sup>105</sup> has enumerated methods for generating clean surfaces in vacuum. While his remarks are aimed primarily at solid surfaces, much of the discussion is also germane to liquids.

Many workers in liquid metals use apparatus capable of achieving  $10^{-6}$ – $10^{-7}$  torr, yet physicists engaged in surface studies of solid metals have long employed ultra-high vacua to ensure meaningful results. To the author's knowledge there is only one example<sup>106</sup> of ultra-high vacuum being used in surface-tension research.

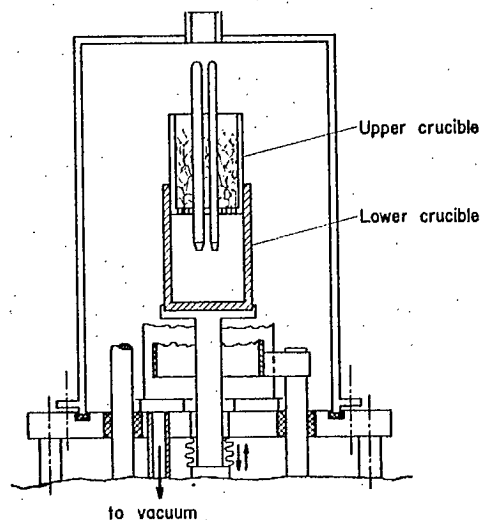
Of the excellent texts devoted to vacuum techniques, Dushman<sup>107</sup> is an outstanding example of a general treatment, while Redhead, Hobson, and Kornelsen<sup>108</sup> have compiled a review confined to the field of ultra-high vacuum.

Application of the foregoing principles leads in practice to metal that sparkles and results that are closely self-consistent. Yet the matter is not as straightforward as this and in the interests of objective reporting it is necessary to introduce a dissenting note.

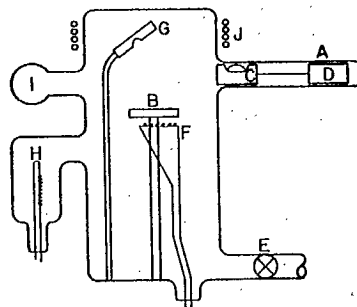
In 1961, Nicholas *et al.*,<sup>4</sup> in what is evidently a piece of very careful work, found that the surface tension of mercury remained unchanged in atmospheres of nitrogen, methane, carbon dioxide, and even oxygen, as well as in hydrogen, helium, and vacuum. From the results quoted below, it will be observed that the maximum



7 Furnace zone of a maximum-bubble-pressure apparatus. (After Krause, Sauerwald, and Michalke.<sup>113</sup>)



8 Maximum-bubble-pressure apparatus of Lazarev and Pershikov.<sup>114</sup>



A Side arm F Thermocouple-heater  
 B Sample plate G Aluminum vapour source  
 C Indium container H Titanium sorption pump  
 D Magnetic slug I Redhead magnetron gauge  
 E Bakeable ultrahigh vacuum valve J Induction coil

9 Ultra-high-vacuum, sessile-drop apparatus of Aldrich and Keller.<sup>108</sup>

Gas: 1 atm pressure	$\gamma_{Hg}$ (25° C) dynes/cm
Vacuum ( $< 1 \times 10^{-7}$ torr)	484.7
H <sub>2</sub>	484.6
He	483.4
N <sub>2</sub>	483.3
O <sub>2</sub>	484.3
CO <sub>2</sub>	485.4
CH <sub>4</sub>	485.5

scatter is only 2.2 dynes/cm. (On the other hand, water vapour, propane, and pump oil were found to reduce the surface tension of mercury quite sharply. Other workers<sup>1,29,109</sup> too have noted the deleterious effects of pump oil and stop-cock grease vapours.)

That the surface tension of mercury should be the same in carbon dioxide and oxygen as it is in hydrogen and helium, however carefully these gases may have been purified, runs contrary to expectations. But bearing in mind the effect of water vapour, the results suggest that in the oxidation of mercury by air, with its accompanying effect of lowering surface tension, water vapour plays a vital role that is probably catalytic. However, it is not possible to generalise from this one result, because as Kubaschewski and Hopkins<sup>110</sup> note '... moisture normally present in air may have a catalytic effect... but may also have a reverse effect...'

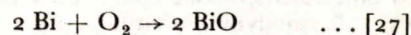
Further anomalous evidence concerning the handling of mercury is afforded by Roberts<sup>5</sup> who observed that 'it was found that the usual recommended "cleaning methods" do not alter the surface tension obtained in the "uncleaned" vessel'.

Immunity to contamination in certain circumstances does not appear to be confined to mercury at room temperature. For example, Aldrich and Keller<sup>111</sup> discovered that a bond formed between indium and aluminium at 160° C in nitrogen or hydrogen at pressures < 1 torr was weaker than a similar bond formed in a vacuum of 10<sup>-10</sup> torr. However, the bond was not weakened if the gases were admitted after the bond had been formed. Furthermore, compared with the values

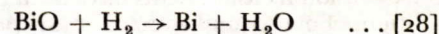
obtained in ultra-high vacuum, the surface tension and contact angle of the indium remained unchanged, whether the gases were introduced before or after the two metals were brought together.

Again, in measuring the surface tension of liquid bismuth by the drop-weight method, Addison and Raynor<sup>112</sup> observed that although experimental scatter was greater, above 400° C the results obtained in hydrogen contaminated with traces of oxygen and water vapour were the same as results obtained in purified hydrogen. Below 400° C, however, the surface tension when measured in impure hydrogen departed from linear behaviour by increasing sharply to values as much as 100 dynes/cm greater than the correct value at temperatures of ~ 300° C.

The authors advance an explanation for the effect in terms of the rates of the two reactions



and



Above 400° C, it is proposed, reaction [28] is much faster than [27] and clean metal exists, but at temperatures below 400° C reaction [28] becomes progressively slower with respect to [27] and an oxide film results.

An understanding of the circumstances in which contamination can be prevented or induced will come only from careful quantitative work with sophisticated equipment involving low-energy electron diffraction (LEED), vacuum X-ray fluorescence analysis, or mass spectrography. Hence, until we know much more of what we are about, we should ignore the temptation to deviate from a systematic improvement of the materials, equipment, and techniques used for measuring the surface tension of liquid metals.

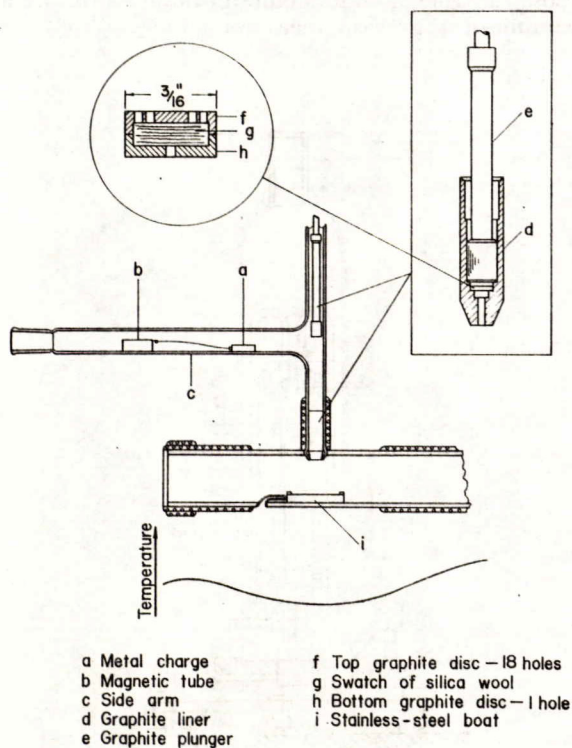
To illustrate some of the foregoing ideas, Fig. 7-10 have been selected from many drawings of apparatus in the literature because they provide examples of worthwhile design features. However, the selection of these apparatus does not necessarily imply that their design is regarded as ideal in all respects.

Figure 7 illustrates the principle of initially placing the metal apart from the main furnace zone and is taken from some of the early work of Sauerwald (cited by Krause, Sauerwald, and Michalke<sup>113</sup>). This particular apparatus was used to determine the surface tension of zinc by the maximum-bubble-pressure method.

Figure 8 depicts an attempt by Lazarev and Pershikov<sup>114</sup> to renew the surface of strontium by gravitational filtration. The capillary tubes and the upper and lower crucibles are made of stainless steel.

Figure 9 is a drawing of the apparatus of Aldrich and Keller<sup>106</sup> used to investigate the contact angle between liquid indium and an aluminium substrate by the sessile-drop method. In operation this system is capable of vacua in the 10<sup>-11</sup> torr range. An atomically clean surface is restored to the aluminium substrate after degassing by evaporation of a ½-g aluminium source (G). During degassing, the indium charge is held in container (C), set off in side arm (A).

Figure 10 shows the apparatus used by the present author to measure the surface tension of zinc<sup>29</sup> and other metals by the sessile-drop method. During the degassing cycle, charge (a) manipulated by magnet through tube (b), is isolated in side arm (c). After degassing, the



10 Furnace zone of a sessile-drop apparatus with filtering facility. (After White.<sup>29</sup>)



charge is lowered into graphite liner (d), melted off, and forced through the filters by graphite plunger (e).

With differences in emphases, some of the foregoing material has been reviewed in an earlier paper by White.<sup>15</sup>

**Thermodynamic equilibrium**

When surface tension is measured, the liquid should be in thermodynamic equilibrium with the vapour. This means that while there will be a steady-state interchange of atoms across the liquid/vapour interface, there should be no net continuous loss of atoms from the liquid through the vapour to a sink.

That thermodynamic equilibrium is a necessary pre-condition for accurate surface-tension measurements is very widely known. Yet few people in the metallurgical field outside the Soviet Union have built apparatus to ensure thermodynamic equilibrium. This means that surface-tension measurements have been made in various conditions of non-equilibrium. For any particular metal, differences in degree of non-equilibrium will engender differences in rates of continuous vaporisation.

The effect of continuous vaporisation on surface tension is purely thermal in nature and has little or nothing to do with the presence of impurities as some seem to believe. Indeed, White<sup>20</sup> has shown that by deliberately inducing vaporisation, the positive temperature coefficient of the surface tension of a 99.999 + % zinc could be made negative. Continuous vaporisation has a randomising effect on the liquid surface. This in turn increases the absolute magnitude of the surface entropy with an accompanying effect on surface tension which may be understood through equation [14],  $d\gamma/dT = -s^{\sigma}$ .

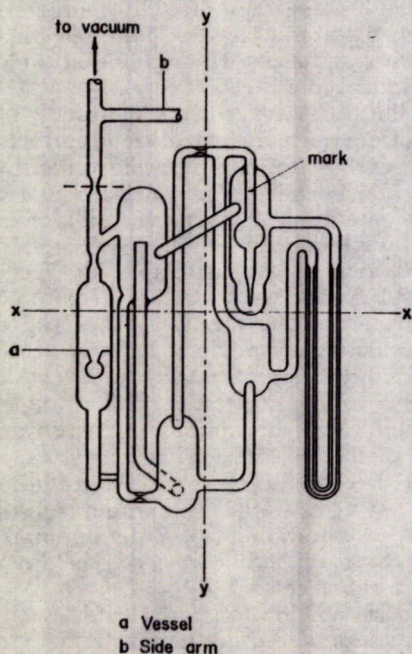
Unfortunately, the magnitude of the vaporisation

effect on the surface tension of liquid metals is not negligible. While it was shown that a particular degree of non-equilibrium induced an increase in the surface tension of zinc<sup>20</sup> of roughly 40 dynes/cm, in later work<sup>115</sup> the same arbitrary conditions were found to decrease the surface tension of tin from 7 dynes/cm at 260° C to 15 dynes/cm at 520° C. Over this temperature range, the vapour pressure of tin varies from  $10^{-23}$  to  $10^{-13}$  torr.

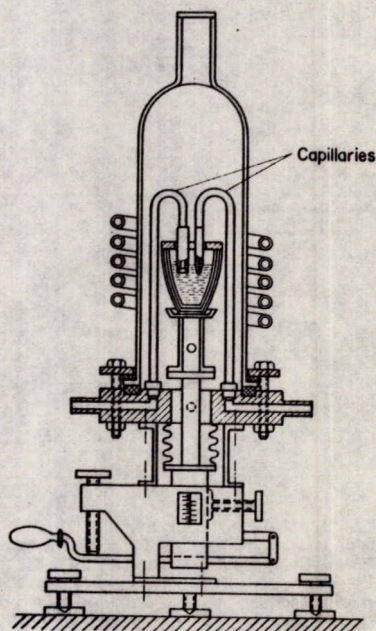
The need to achieve thermodynamic equilibrium in an apparatus has several practical consequences. Thus, while the surface tension of metals may be measured in a static vacuum, all parts of the apparatus accessible to the metal vapours must be at temperatures not less than that of the metal. On the other hand, surface-tension measurements should never be attempted in a dynamic vacuum, whatever the temperature distribution. A gas in the system (say, at 1 atm pressure) will considerably reduce vapour diffusion rates in the presence of a 'cold spot'. Nevertheless, for accurate work these rates will remain unacceptably high.

It is the need to preserve thermodynamic equilibrium that will impose lower limits on bubble and drop formation times in the maximum-bubble- and drop-pressure methods, even if inertia effects are absent.

Russian awareness of the need for thermodynamic equilibrium has led to considerable ingenuity in the design of maximum-bubble-pressure and maximum-drop-pressure apparatus to ensure equilibrium. Figure 11 is representative of the layout of a type of apparatus used for work at temperatures that can be conveniently handled in a thermostat. The distinguishing feature of this type of apparatus is that it may be operated while completely immersed in the thermostat. This particular instrument, designed by Timofeevicheva<sup>116</sup> is dual-purpose, capable of both maximum-bubble-pressure and maximum-drop-pressure measurements.

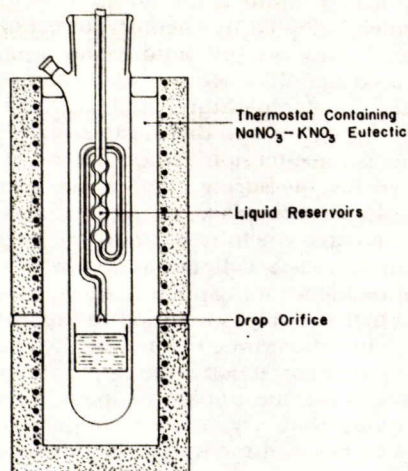


11 Dual-purpose, maximum-bubble-pressure/maximum-drop-pressure apparatus of Timofeevicheva.<sup>116</sup>

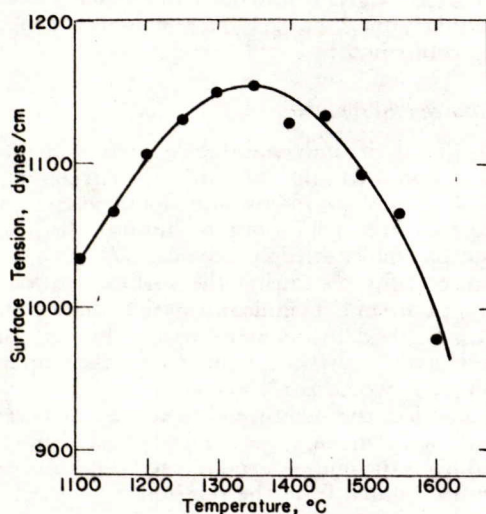


12 High-temperature, maximum-bubble-pressure apparatus. (After Pugachevich.<sup>121,122</sup>)

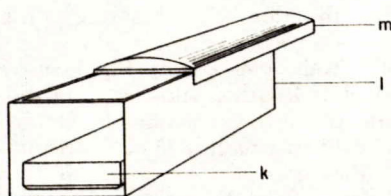
After degassing in vacuum, clean metal is admitted to vessel (a), gas is introduced through side arm (b), and the apparatus sealed off at the dotted line with a torch. This instrument is operated by suitable rotational and tipping movements to transfer metal to other vessels.



13 Drop-weight apparatus of Addison and Raynor.<sup>112</sup>



14 Surface tension of copper from 1100 to 1600° C, according to Pugachevich and Yashkichev.<sup>120</sup>



k Graphite plaque  
l Fused-silica optical cell  
m Weighted stainless-steel cover embracing 1mm.-thick fused silica

15 Optical cell used in the sessile-drop apparatus of White.<sup>29</sup>

Descriptions of other single- or dual-purpose apparatus of this kind are to be found in the literature.<sup>92,102,117-119</sup>

For high-temperature work with the maximum-bubble-pressure method, Pugachevich<sup>120-122</sup> has designed the apparatus shown in Fig. 12. While it cannot be expected that this apparatus would be completely immune to continuous vaporisation the convoluted capillaries add one bend and a considerable increase to the length of the diffusion path through the hot zone. It seems reasonable to expect that this arrangement will satisfy to a greater extent the conditions necessary for thermal equilibrium than apparatus with classical straight-through-type capillaries.

This design feature of the convoluted tube is even more effectively used in the drop-weight apparatus of Addison and Raynor<sup>112</sup> shown in Fig. 13.

Application of the same feature in some form to the maximum-bubble-pressure apparatus of Bohdansky and Schins<sup>63</sup> would have been preferable to the straight-bore tube that was employed. However, the authors were able to create a hot zone with only a slight temperature gradient over a considerable length of their furnace tube by taking advantage of the very interesting 'heat-pipe' effect. This technique is applicable to metals developing vapour pressures of > 20 torr and has been described by the authors in an earlier paper.<sup>123</sup>

With the apparatus shown in Fig. 12, Pugachevich and Yashkichev<sup>120</sup> measured the surface tension of copper from the melting point (1083° C) to 1600° C. The results, shown in Fig. 14, were described in a subsequent paper<sup>124</sup> from the same author by a word which translates into English as 'fantastic'. Fantastic or not, there is no reason to suspect that, assuming the author's description of experimental conditions to be acceptable at face value, the results are not more correct than any other published results for copper.

For preserving thermodynamic equilibrium in a sessile-drop apparatus at temperatures that are not too high, the following scheme has been found practical. When liquid metal is filtered in the apparatus shown in Fig. 10, a drop forms on the graphite plaque (k) in the silica optical cell (l) depicted in Fig. 15. The optical cell fits into the stainless-steel boat (i) of Fig. 10. The lid (m) is closed by magnetic manipulation of a stiff wire. By controlling the power inputs to various furnace windings the kind of temperature distribution indicated schematically in Fig. 10 is achieved. As a result, the lid and the front and rear windows of the cell are approximately 1 degC hotter than the drop.

#### Density

Surface tension is determined by measuring some parameter on a liquid metal that is in mechanical equilibrium between gravitational and surface-tension forces. To calculate surface tension, the measured parameter is substituted in an equation which, among other variables, contains a value for the density of the liquid metal at the experimental temperature. Thus, unless errors in other quantities fortuitously reduce errors due to density, the accuracy of the calculated surface tension can be no better than the accuracy of the density.

Flint,<sup>125</sup> in a recent review, and Kozakevich<sup>126</sup> also, have drawn attention to the uncertainties in some existing density data. Using the density of liquid copper as an example, Flint elucidates the inbred nature of a lot

of data that all ultimately derive from some early pioneer work. On the other hand, Kozakevich points out that discrepancies in surface-tension results between different investigators can sometimes be resolved by normalising for the differences in the density values used.

Although, quite clearly, density is an important factor affecting the accuracy of surface-tension measurements, an extensive treatment of the subject cannot be undertaken in this review. May it suffice to note that until completely reliable data are available, it is preferable that the experimenter make his own density measurements and that these should be characterised by the same care as the surface-tension measurements they are designed to facilitate. If, however, published density values are to be used, it is essential to search the literature thoroughly and to be aware of the likely limitations on the data's accuracy.

While a linear sensitivity to density errors is a common characteristic of surface-tension measuring methods, there is one notable exception. This method is the Sugden<sup>127</sup> treatment of the maximum-bubble-pressure method which will be discussed in the following section. The mathematics of the method are such that surface tension is not directly proportional to density. Indeed, uncertainties in density engender uncertainties in surface tension that are smaller by about one order of magnitude. Obviously, this is a distinct advantage.

#### Methods and specific precautions

There are a number of means by which surface tension may be determined. Each method has its own characteristics. Thus some are more adapted than others for accurate work on liquid metals at elevated temperatures or again may be more suitable to surface-tension measurements at high pressures.<sup>128</sup>

In general, the two most useful are the maximum-bubble-pressure method and the sessile-drop method. But for one reason or another different techniques are used and these will be discussed first. These are the Wilhelmy plate method, the capillary method, the drop-weight method, the Worthington approximation method, and the pendant-drop method. For clarity in presentation, the last two are best considered together with the sessile-drop method, because all three are drop-shape methods.

#### Wilhelmy plate method

The Wilhelmy or vertical-plate method is better suited to wetting studies than for accurate surface-tension measurements. The method has been used by Addison<sup>129</sup> and his co-workers in a continuing programme of experimentation on the wetting characteristics of some liquid alkali and alkaline-earth metals against other (solid) metals.

In this technique, the maximum force exerted on a thin plate as it is withdrawn from the liquid is measured by a torsion balance. The contact angle of the liquid metal against the plate must be known if the surface tension of the liquid metal is to be calculated. Corrections must be applied for the weight of liquid adhering to the plate and further errors can be incurred by 'end effects'.

The method has been used extensively by chemists and, therefore, more complete discussions of its charac-

teristics will be found in standard texts on surface chemistry,<sup>7,12,130</sup> as well as in the first paper of the Addison *et al.*<sup>112</sup> series.

#### Capillary method

In one form or another, the capillary technique has also been widely adopted by chemists to measure the surface tension of many organic liquids and aqueous solutions. When used carefully with liquids that completely wet glass and at temperatures that can be comfortably handled in air or oil thermostats, the method yields accurate surface-tension data. However, it is not so attractive for measuring the surface tension of liquid metals. In the first place, its application will be limited to those metals which by virtue of melting point and/or chemical inertness will not react with materials from which precision-bore capillary tubes can be made, e.g. silica. Furthermore, in addition to the usual experimental problems concerning the uniformity of capillary bores and meniscus corrections, the apparatus is complicated compared with the apparatus for other methods, and with liquids that are neither completely wetting nor completely non-wetting the contact angle must be taken into account.

Nevertheless, a serious attempt to measure the surface tension of tin, lead, and indium<sup>30</sup> and some lead-tin and lead-indium alloys<sup>38</sup> has been made with a variant of the capillary method. As yet, the results have not been closely confirmed.

#### The drop-weight method

It is difficult to understand how a method that incorporates experimentally determined 'correction' terms of up to ~40% of the magnitude of a measured parameter can be accurate. Yet for organic liquids, the drop-weight method has had its ardent advocates.<sup>132</sup>

However, for measuring the surface tension of high-melting-point and chemically active metals, the drop-weight method (together with the pendant-drop method) avoids physical contact with the apparatus and is, therefore, worth persevering with.

In practice, the drop-weight method involves collecting and weighing a known number of drops carefully melted from the end of a rod of radius  $r$ . Surface tension is then calculated from the relation

$$\gamma = \frac{w}{f2\pi r} \quad \dots [29]$$

where  $f$  is a function of  $r/V^{1/3}$  and  $V$  is the volume of a drop.

When the weight of a drop has been determined,  $V$  can be calculated with a knowledge of the density.  $f$  is then obtained from graphs or tables in the original Harkins and Brown paper,<sup>133</sup> or from the International Critical Tables.<sup>134</sup>

It may appear from discussions of the method,<sup>135,136,88</sup> that the theory is incorrect and that the identity of  $f$  is not that of a correction factor for the ratio of the actual drop weight to the 'ideal drop' weight  $2\pi r\gamma$ . However, the mathematical authenticity of the method is supported by fresh insights arising from the dimensional analysis of Brown and McCormick.<sup>137</sup> At the same time, these authors point to the advantages of forming drops

on conical tips—a variant of the method that might be applicable to some low-melting-point metals.

Apart from sources of experimental error originating with drop instability and continuous vaporisation that have already been discussed in previous sections, there are further difficulties associated with steep temperature gradients, temperature measurement, and gases evolving from the metal. Calverley,<sup>138</sup> Kelly,<sup>139</sup> Allen,<sup>87</sup> Tille and Kelly,<sup>88</sup> and Allen<sup>89</sup> have all contributed to a discussion of these problems.

#### The maximum-bubble-pressure and drop-pressure methods

In the maximum-bubble-pressure method, the pressure of a gas is slowly increased until a bubble forms and detaches itself from the tip of a capillary tube immersed in liquid metal. In the maximum-drop-pressure method it is the liquid metal that is forced through the capillary to form a drop either in a vacuum or in a gaseous atmosphere.

If the diameter of the capillary is small enough, the bubble will be essentially hemispherical. In this case the maximum pressure necessary to form the bubble will be given by

$$P_h + P_\gamma = gh\rho + \frac{2\gamma}{r} \quad \dots [30]$$

The first term accounts for the pressure necessary to overcome the liquid-metal head; the second term for the pressure necessary to create new surface against the collapsing force of surface tension.  $h$  is the depth of capillary immersion and  $r$  is the appropriate capillary radius. The second term on the right-hand side of equation [30] is the limiting case of equation [9] for a spherical surface. For an error of  $< 0.1\%$ , equation [30] is valid for a range of capillary diameters dependent on the liquid metal whose surface tension is to be measured. This range varies from a low limit of  $< 0.23$  mm dia. for mercury to a high limit of  $< 0.68$  mm dia. for aluminium.

For larger capillaries, the expression for the pressure term corresponding to the creation of new surface must be replaced by one compensating for the deviations from sphericity imposed by gravitational forces. Several approximation formulae have been proposed, of which that of Schroedinger<sup>140</sup> is probably the best known, viz:

$$\gamma = \frac{rP_\gamma}{2} \left[ 1 - \frac{2}{3} \left( \frac{r\rho g}{P_\gamma} \right) - \frac{1}{6} \left( \frac{r\rho g}{P_\gamma} \right)^2 \right] \quad \dots [31]$$

This equation is applicable with very little error to systems for which  $r/a$  is  $< 0.2$ , where  $a \equiv \sqrt{\frac{2\gamma}{\rho g}}$  and is known variously as the 'capillary constant' or 'specific cohesion'.

More rigorously, Sugden<sup>127</sup> applied the capillarity relations expressed in numerical form in the Bashforth and Adams<sup>141</sup> tables to the case of a bubble in a liquid. Setting  $X = 2\gamma/P_\gamma$  for the general case of non-spherical surfaces where  $r \neq 2\gamma/P_\gamma$ , he constructed a table of minimum  $X/r$  values for values of  $r/a$  between 0 and 1.5. Starting with values resulting from the assumption of a hemispherical bubble, the table facilitates the calcula-

tion of an exact value for  $a$  and hence  $\gamma$ , by a sequence of successive approximations.

Furthermore, Sugden realised that if apparatus were built embodying two tubes of different diameters immersed to exactly the same depth in the liquid, the surface tension could be calculated directly from the expression

$$\gamma = \frac{\Delta P_\gamma}{2 \left( \frac{1}{X_1} - \frac{1}{X_2} \right)} \quad \dots [32]$$

without a knowledge of the actual depth to which the tubes were immersed. In equation [32],  $\Delta P_\gamma = P_{\gamma_1} - P_{\gamma_2}$  and the subscripts 1 and 2 refer to the smaller and larger tubes respectively.

Thus, a mathematically exact method of determining surface tension is available which, if used in conjunction with two tubes, is insensitive to metal-density errors and is independent of the depth to which the tubes are immersed in the liquid. It is surprising that Sugden's method has not been more widely used.

In the manner of an epilogue to this work, in a later paper, Sugden<sup>142</sup> developed an approximation expression based on equation [32] which in use saves calculation time at the expense of some accuracy.

However, in a conventional single-capillary apparatus the depth of capillary immersion must be measured and uncertainties in the measured depth must be limited to  $\sim 0.001$  cm if attendant errors in surface tension are to be limited to  $< 0.1\%$ . To the apparent depth of immersion must be added the increase in the metal head arising from the volume of metal displaced by the capillary and, if it is large enough, the volume displaced by the bubbles themselves. Changes in the curvature of the metal surface arising from the presence of a tube must be taken into account, as must the length increase from thermal expansion of the capillary, if the magnitude of this also is large enough.

These potential sources of error have been discussed in greater detail in an earlier treatment of surface-tension methods.<sup>15</sup>

Some of the Russian single-capillary maximum-bubble-pressure instrument designs, which can be completely isolated in a thermostat, function independently of the depth of capillary immersion. Pugachevich,<sup>92</sup> in particular, has discussed the theory and operation of one of these. However, the design depends for its efficacy on measurements from a reference surface of the liquid in a 'wide' arm devoid of capillarity effects<sup>143</sup> and is said to be most suitable for liquids that wet glass. Except, perhaps, for uncommon metals like caesium<sup>102</sup> that do wet glass, application of the design to liquid metals should be treated with reserve.

No discussion of the maximum-bubble-pressure method is complete without commenting on a serious shortcoming. The method is not independent of the contact angle between the liquid and the material of the capillary. If the liquid completely wets the capillary, accurate values for surface tension can be calculated by using the internal diameter of the capillary. With the maximum-drop-pressure method, use of the internal diameter leads to accurate surface-tension values for liquids that are completely non-wetting.

But because, in general, most liquid metals display

a contact angle of  $\sim 130^\circ$  or more towards most of the materials from which capillaries are made, bubbles do not anchor at the internal diameter. Neither, unfortunately, do bubbles always locate exactly at the external diameter. In some instances, use of the outside diameter for calculation purposes leads to results that are much too high.

One obvious way round this difficulty is to reduce the capillary tip to a circular 'knife edge' by grinding and polishing a low-angle chamfer. With stainless-steel capillaries, e.g. for measuring the surface tension of strontium,<sup>114</sup> there is no especial problem in reducing the wall thickness to 0.001 mm at the tip. But with refractory capillaries, there are practical difficulties in producing a 'knife edge' finer than  $\sim 2-3\%$  of the internal diameter. This, of course, is especially so if the capillary bore is small; but there is an upper limit imposed on tube diameters by uncertainties in pressure measurement.

Porter<sup>144</sup> approached the matter by postulating a mechanism of bubble formation at the tip of a tube and as a result established certain criteria of diameter: wall-thickness ratios for small capillaries to ensure that bubbles would locate at the outside diameter. This analysis was later re-examined by several Russian workers and comparable criteria extended to larger tubes, as noted by Pugachevich.<sup>124</sup>

A fresh approach to the problem was adopted by Vashchenko and Rudoi<sup>145</sup> who developed a sensitive electric micromanometer for continuously recording the pressure in a small system. Two pressure maxima were observed, as shown schematically in Fig. 16 and the second was used in conjunction with the external diameter for calculating the surface tension.

However, all difficulties have not been resolved by the foregoing work, and as Pugachevich<sup>124</sup> concludes in his excellent digest of the subject, there is yet room 'for a number of methodical investigations'.

**Drop-shape methods**

The surface tension of a liquid may be determined by measuring certain parameters on the outline of a section through a drop. If the drop rests freely on a horizontal surface it is known as a sessile drop. If the drop is suspended, it is known as a pendant drop. Within these two classes of drop, the shape will be determined by a balance between gravitational and surface-tension forces and will, therefore, be a function of the size of the drop as well as the density and surface tension of the liquid.

Although in some limited instances the form of a

drop outline can be characterised accurately by 'approximation' formulae, numerical solutions to the fundamental differential equation have been tabulated for a wide range of drop shapes in the well-known Bashforth and Adams tables.<sup>141</sup>

**Sessile-drop method.** For the general case of a liquid that makes a contact angle of  $> 90^\circ$  with the substrate material, it has long been possible to calculate surface tension by the sessile-drop method without a knowledge of the contact angle. Indeed, the contact angle itself can be calculated. More recently, methods have been developed facilitating the calculation of surface tension from measurements on drops with contact angles  $> 45^\circ$ .

A number of methods exist for calculating surface tension from measurements on non-wetting drops ( $\phi > 90^\circ$ ). While most of these methods have been based on some use of the Bashforth and Adams tables, or an adaptation of the tables, the original method devised by Bashforth himself was lost sight of. This method is simple, direct, and exact.

It seems likely that even if Bashforth's method had not been 'lost', the Worthington<sup>146</sup> method would have become established independently. For large drops of liquids with favourable density: surface-tension ratios, the radius  $b$  at the pole of the drop approaches infinity. In this event a simplified mathematical treatment becomes feasible. For drops of  $\sim 5$  cm dia. the method is applicable to mercury.

Worthington was the first to take advantage of this fact. Having derived the rigorous equation

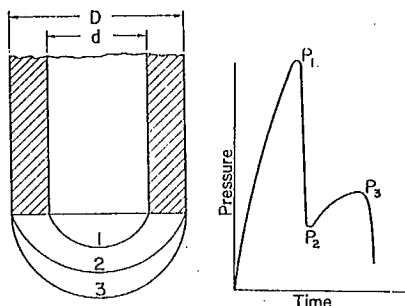
$$\gamma = \frac{1}{2} \rho g Z_{90}^2 + 2/b \gamma Z_{90} - \gamma \int_0^{Z_{90}} \left( \frac{\sin \phi}{dx} \right) dz \quad \dots [33]$$

he then reduced it to a form which, when later modified by others, became

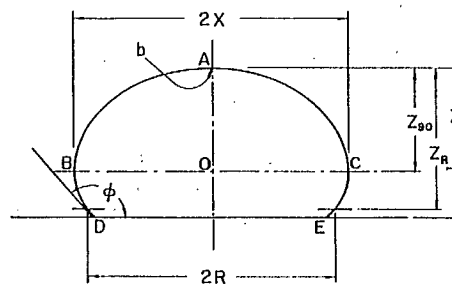
$$\gamma = \frac{1}{2} \rho g Z_{90}^2 \left( \frac{1.641X}{1.641X + Z_{90}} \right) \quad \dots [34]$$

where the significance of the symbols is as shown in Fig. 17. For mercury drops, 5 cm in dia., Zeising<sup>2</sup> examined equation [34] and calculated the error it involved by comparing results with calculations from equation [33]. A difference of 0.27% or 1.2 dynes/cm was found.

Thus, although the mathematics now appears to be satisfactorily known, application of the method to



16 Pressure fluctuations during the development of a bubble at the outside diameter of a capillary tube.<sup>145</sup>



17 The sessile drop.

experiment involves locating a plane precisely through the maximum diameter in order to measure  $Z_{90}$  accurately. The difficulties in doing this are well known and are regarded as insuperable when measurements are attempted on photographs. Nevertheless, in the work on mercury, measurements are made directly on the drop itself and with such evident care that claims from the authors to accuracies of the order of 0.25% must be treated seriously. To others engaged in the more conventional pursuits of the sessile drop, a study of this literature<sup>1,2,147</sup> is interesting and instructive, especially for its discussions of optical errors.

While the Worthington method is suitable only for large drops, even of mercury, Porter<sup>148,149</sup> was able to work out an approximation procedure applicable to a broad gamut of drop sizes. However, the method does involve measurements of  $Z_{90}$  and for other reasons again the author felt unable to claim an accuracy of better than 1% even for certain drop sizes to which he considered the method best suited.

The major field of surface-tension activity is centred on drops at elevated temperatures whose shape is such that they can be treated from the Bashforth and Adams tables. Typically these drops are of  $\sim 1$  cm dia. and thus measuring techniques are usually applied to enlarged photographic images of the drops.

Much of the past work on non-wetting sessile drops, especially in North America, has followed a procedure founded on a limited use of the Bashforth and Adams tables. This procedure goes back to work by Ellefson and Taylor.<sup>150</sup> It was these authors who first located a line through the maximum diameter of the drop by a special geometrical construction technique, measured the height  $Z_{90}$  between the line and the crest of the drop, and determined the (dimensionless) shape factor  $\beta$  immediately from the ratio  $X/Z_{90}$  by interpolation in Table I of the tables. Surface tension is then calculated by means of equation [35]. The errors inherent in this procedure depend, as already noted, on the accurate location of the line through the maximum diameter and are a function of the drop shape and size as emphasized with clarity by Dismukes.<sup>151</sup>

Probably the ultimate development of this technique has come from Staicopolus, who has prepared a digital computer programme<sup>152,153</sup> and nomographs<sup>154</sup> for calculating surface tension from a measured ratio of  $X/Z_{90}$ .

To side-step the necessity of having to locate a line accurately through the maximum diameter, Dorsey<sup>155</sup> derived an empirical equation for calculating surface tension by a special adaptation of the Bashforth and Adams tables. Particularly for drops with a shape parameter,  $\beta$ ,  $> \sim 4$  the equation is quite accurate. The measured quantities are  $X$  and a height that depends on a geometrical construction involving the intersection of the polar axis of the drop and a  $45^\circ$  tangent to the drop surface above the major diameter.

Kozakevich<sup>100</sup> and his co-workers employ a technique that is essentially an elaborated variant of the Dorsey construction. In practice, a special grating is applied to drop photographs, certain parameters between the grating and the drop are measured, and these are then processed through tables derived from Bashforth and Adams to calculate values for the drop-shape factor,  $\beta$ , and the radius at the pole of the drop,  $b$ . These lead ultimately to a value for the surface tension.

The method, however, is very sensitive to error in the geometrical construction or positioning of the grating. Dorsey, for example, estimated that an error of 0.001 in the ratio of measured quantities gave rise to an error of 0.8% in surface tension. The Kozakevich variant is probably more accurate than this, though Smolders and Duyvis<sup>156</sup> put the limit at 1-2%.

In turn, these two authors devised another scheme which involves drawing an accurately scaled enlargement of a portion of the drop contour, the  $\beta$  value for which is identified by graphical interpolation between curves of known  $\beta$ .

The method is probably more accurate than any preceding it but seems vulnerable on two counts. First, the enlarged curve is constructed from about 10 pairs of measured  $X-Z$  co-ordinates which must make the method time-consuming. Secondly, because curve fitting is confined to an arc of only  $\sim 45^\circ$ , the method is probably less accurate than the authors' estimate of 0.1%.

A recent treatment of sessile drops by Butler and Bloom<sup>157</sup> embodies an approach that is essentially similar, although there are two important differences. Graphical interpolation is replaced by a computer programme and curve fitting is extended to an arc of  $180^\circ$  across the top of the drop from one point of maximum diameter to the other. Starting with the equation to an ellipse, values of  $\beta$  and  $b$  are determined by an iterative procedure that give the best fit to a series of  $\sim 20$   $X-Z$  co-ordinates.

The method is evidently a worthwhile development of the Smolders and Duyvis treatment, yet the objection to time-consuming measurement remains, the authors trespassing on our credulity by their assertion that this can be done in 15 min.

Thus, there have been a number of methods for calculating surface tension from measurements on sessile drops, yet none of these is superior to the original Bashforth method. The method was outlined and referenced in an earlier paper.<sup>15</sup> However, because it is evident that it has largely gone unnoticed, the method will be described again briefly here, supported by a worked example in the Appendix.

The mathematical foundation of the Bashforth and Adams tables has been discussed by a number of authors,<sup>15,156,157</sup> including a most detailed account by Bashforth<sup>141</sup> himself. Suffice it to say here that, starting from equation [9], the variables defining the contour of a surface have been manipulated in such a way that it is possible to calculate the surface tension from three parameters measured on a non-wetting drop, by interpolating in B.A. Table II\* for exact values of  $\beta$  and  $b$  and inserting these values in the equation

$$\beta = \frac{\rho g b^2}{\gamma} \quad \dots [35]$$

The parameters to be measured are indicated in Fig. 17. These are the maximum diameter  $2X$  and any one set of  $X-Z$  co-ordinates below the maximum diameter, such as  $2R$  and  $Z_R$ . These are then processed as shown in the Appendix to yield values for  $\beta$  and  $b$ , which, together with a value for the density of the liquid metal

\* This and subsequent mention of table numbers refers to the Bashforth and Adams tables, as indicated by the letters B.A.

$\rho$ , lead to a solution of equation [35] for  $\gamma$ . Experience shows that the  $X$ - $Z$  co-ordinates are best defined by a slot  $\sim 0.5$ - $1$  mm wide cut in the photographic emulsion with a razor blade or surgical scalpel, as illustrated in Fig. 18.

If, in addition, the overall height of the drop  $Z$  is measured, the contact angle  $\phi$  can be calculated. This, together with values for  $\beta$  and  $b$ , enables the volume of the drop to be interpolated from B.A. Table III for  $V/b^3$ . After experiment, the drop can be weighed and, hence, the density at the experimental temperature calculated. Densities with a random error of  $\sim \pm 0.25\%$  can be obtained in this way.

Error may be incurred by the linear-interpolation procedures for  $\beta$  and  $b$  in Table II. The magnitude of the error is difficult to assess but may be as high as 2% at low  $\beta$  values ( $\sim 1$ ). Therefore, in any sustained campaign of surface-tension measurements it is worth while to construct a series of large curves from data in those parts of B.A. Tables II and V that are of interest. This will not only considerably improve accuracy, it will expedite calculation. Accordingly, considering all sources of error involved in a graphical procedure, it is possible to claim conservatively an accuracy of  $< \pm 0.5\%$  for the method.

Francis Bashforth was aware that interpolation in the tables as published would lead to some error and it was for this reason that in the preface he offered his notes to anyone willing to attempt to augment the tables. This work has been undertaken at the Canadian Department of Energy, Mines, and Resources. In consequence, supplementary tables<sup>158</sup> have been published which limit calculation error to a maximum of  $< 0.1\%$  for a range of drop shapes from  $\beta = 0$  to  $\beta = 50$ .

For wetting-type drops with contact angles  $> 45^\circ$ , the surface tension may be calculated from the computer programme of Staicopolus<sup>152,153</sup> written for an appropriate polynomial function of the measured ratio  $X/Z_{45}$ . On the other hand, for drops with contact angles  $> 60^\circ$ , the method of Ivashchenko *et al.*<sup>159</sup> also becomes applicable. This employs a geometrical construction technique essentially similar to that of Dorsey. The method makes possible the measurement of parameters that lead eventually, through tables derived from Bashforth and Adams, to values for surface tension.

Although surface tension when calculated by these methods will not be as accurate as when calculated from measurements on non-wetting drops, the methods do represent a considerable advance over techniques discussed by White<sup>15,160</sup> involving the direct measurement of  $\phi$  or  $b$ .

In reproducing photographic images of drops, great care is imperative to ensure that true meridional sections are rendered. The drop image should be enlarged only in the camera and should be rendered on plates rather than on film. The camera should be fitted with a lens corrected to work at short distances (process lens) and have a telecentric stop of  $\sim 2$  mm dia. at the point of second principal focus. For drops not photographed from their own illumination, collimated light or at least a polaroid filter will sharpen the image, although the most important source of indistinct images are heat-induced refraction effects.

The magnitude of errors in surface tension arising from uncertainties in the magnification factor of the optical system are greater by a factor of two. But if the

magnification factor is determined carefully in both the horizontal and vertical directions on a special button such as that depicted in Fig. 19, errors arising from curvature of the lens field or irregular radially distributed refraction effects can be submerged. For the greatest accuracy, it is important to machine the button with similar height and diameter characteristics to the sessile drop and to locate the button in the same part of the optical field as occupied by drops.

A fuller treatment of optical errors is given in the earlier review by the present author.<sup>15</sup>

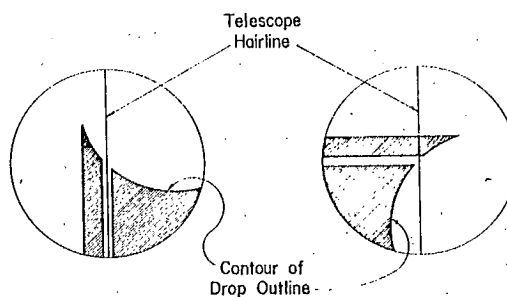
**Pendant-drop method.** In contrast to the scarred maturity of the sessile-drop method, the pendant-drop method is a newcomer with a record of almost clinical purity.

Although no one appears to have done so, as pointed out by Parvatikar,<sup>161</sup> it is possible to calculate surface tension from measurements on pendant drops in a way that is completely analogous with the much used procedure first developed by Ellefson and Taylor<sup>160</sup> for sessile drops. But while it is not necessary to restrict measurements to fully developed, and thus unstable, drops as the author seems to imply, the method does not have a very promising future because other and more accurate methods are just as convenient.

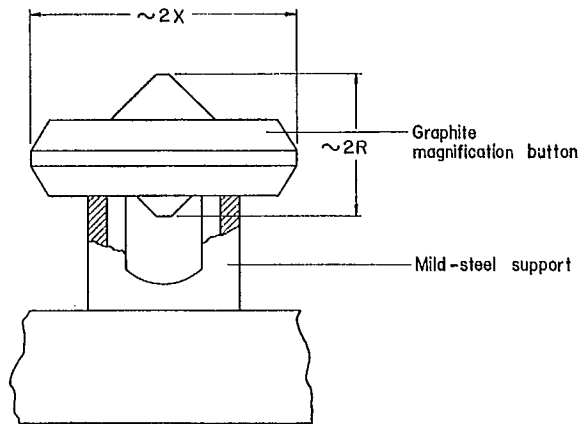
It is also possible to apply Bashforth's method to pendant drops, although no one appears to have done this either. The fact is that the advantages of this method are not so obvious as when the method is applied to sessile drops. On the one hand, although data in B.A. Table IV have been augmented to some extent by the work of Fordham<sup>162</sup> and of Niederhauser and Bartell,<sup>163</sup> they are inadequate for accurate calculation and are presented in irregular increments of  $\phi$ . On the other hand, in its present state of development, the method originated by Andreas, Hauser, and Tucker<sup>164</sup> is more convenient. Nevertheless, if suitable tables are prepared, especially at low  $\beta$  values, Bashforth's method should become more attractive for precise liquid-metals research.

The Andreas, Hauser, and Tucker method of 'a selected plane' is an adaptation of the Bashforth treatment of the drop profile. In this technique, variables have been rearranged in such a way that the Bashforth dimensionless group (equation [35]) becomes transformed to

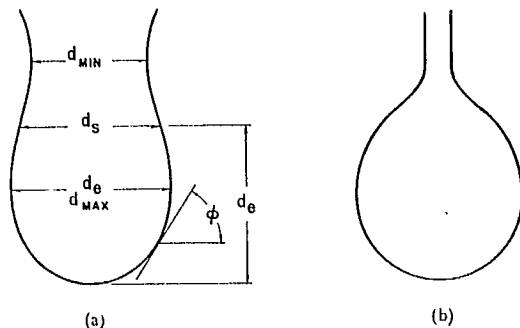
$$H = \frac{g\rho d^2 c}{\gamma} \dots [36]$$



18 Portion of sessile-drop photograph as seen through cathetometer telescope, showing slot cut in the emulsion to define  $X$ - $Z$  co-ordinates.



19 Graphite magnification button.



20 Pendant drops.

where the identity of  $\beta$  has been replaced by a shape parameter  $S = d_s/d_e$  and  $H = \beta (d_e/b)^2$ . As indicated in Fig. 20a,  $d_s$  is the diameter of a plane arbitrarily located at a height above the origin equal to  $d_e$ , the maximum diameter of the drop.

Originally, the method was supported by a table of  $S$  versus  $1/H$  for  $S$  between 0.70 and 1.00, that had been evaluated empirically from measurements on drops of water. Subsequently, this table was found to contain errors as great as 1.4% when Fordham<sup>162</sup> and Niederhauser and Bartell<sup>163</sup> independently computed similar tables to five decimal places—the latter authors a little more accurately than Fordham. Fordham's table covers the range of  $S$  from 0.66 to 1.00, and Neiderhauser and Bartell the range of  $S$  from 0.67 to 1.00. Niederhauser and Bartell's table has also been published in Adamson's<sup>165</sup> book.

These tables facilitate the rigorous calculation of surface tension for many liquids, but both Stauffer<sup>166</sup> and Bidwell *et al.*<sup>167</sup> recognised that the lower limit of the tables was too high to embrace the shapes assumed by liquid-metal drops of reasonable size. Accordingly, from suitable computer programmes, Stauffer prepared

a table for  $S$  between 0.30 and 0.66; similarly, Bidwell *et al.* have published a table for  $S$  covering the range 0.2–1.10.

In addition to his table, Stauffer\* presents an instructive error analysis of the method, which emphasises that because  $d_s$  is dependent on  $d_e$ , errors arising from inaccurate measurement can seriously cascade. Aware of the same point, Winkel<sup>168</sup> has proposed a variant of the method in which the drop-shape parameter  $S$  is replaced by the ratio  $R$  of two independent quantities, where  $R = d_{\max}/d_{\min} = d_e/d_{\min}$ . (Fig. 20a). This method is to be supported by a table of  $R$  vs.  $H$ , which at the time of writing does not appear to be in print.

However, because of the surface tension: density ratios, drops of liquid metals tend to lose their waists ( $d_{\min}$ ) thereby assuming a shape more like that shown in Fig. 20b than in Fig. 20a. Thus, Winkel's variant would not be applicable and in these circumstances, given a convenient table, Bashforth's treatment may well be found to possess some advantages.†

There has been a sharp increase in the use of the pendant-drop method in the past few years, as pioneering attempts to measure the surface tension of high-melting-point and refractory metals have been undertaken. In practice the method is susceptible to the same sources of error as afflict the drop-weight method, in addition to errors of an optical nature<sup>169–171</sup> similar to those encountered with the sessile-drop method. As the following references attest<sup>87–89,138,139,172</sup>, the experimental problems in applying the method are intimidating. Yet some of these difficulties are amenable to control. In particular, gas in the metal and drop instability can be diminished, if not eliminated, by vacuum degassing and reworking the metal to a rod and by abandoning electron-bombardment heating in vacuum, in favour of, say, graphite resistance-heating in an inert gas. In conjunction with an illuminating source of X-rays, it might be possible to enclose a drop almost totally by heaters and in this way secure a greater measure of thermodynamic equilibrium than prevails in present apparatus.

If work is to continue on measuring the surface tension of many challenging metals there are, for the time being, no alternatives to the drop methods.

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To Dr. E. Alison Flood, National Research Council, Ottawa, Canada, who provided the stimulus of some very useful discussions and who read and commented on the first section of this review, the author acknowledges with considerable pleasure his debt for the help received. Similarly, thanks are due to Dr. James G. Eberhart of the Sandia Corporation, Albuquerque, New Mexico, who sent copies of several extensive articles and who read and commented minutely on the section on 'The Liquid Surface and Surface Tension'.

\* A good error analysis is to be found in *J. Phys. Chem.*, 1967, 71, 4190.

† White's supplement to the tables of Bashforth and Adams<sup>163</sup> does not contain this table.



## APPENDIX

99.9999% tin; temp: 246° C; atm H<sub>2</sub>

	$Z_R$	$2X$	$2R$
Cathetometer Readings, cm	53.845 49.715	55.247 46.333	54.990 46.595
	4.130	8.914	8.395
		$X = 4.457$	$R = 4.1975$

 $\beta = 4.9$ 

$$\frac{x}{b' \varphi = 90^\circ} = 0.70713 \quad \therefore b' = \frac{4.457}{0.70713} = 6.3029$$

$$\left. \begin{aligned} \frac{R}{b'} &= \frac{4.1975}{6.3029} = 0.6659_6 \\ \frac{Z}{b'} &= \frac{4.130}{6.3029} = 0.6553 \end{aligned} \right\} \text{From graphs}$$

$$\frac{x}{b'} = 0.6664_6$$

$$\varphi = 121.53^\circ$$

$$\frac{R}{b'} - \frac{x}{b'} = 0.6659_6 - 0.6664_6 = -0.0005$$

 $\beta = 5.0$ 

$$\frac{x}{b' \varphi = 90^\circ} = 0.70441 \quad \therefore b' = \frac{4.457}{0.70441} = 6.3273$$

$$\left. \begin{aligned} \frac{R}{b'} &= \frac{4.1975}{6.3273} = 0.6634 \\ \frac{Z}{b'} &= \frac{4.130}{6.3273} = 0.6527 \end{aligned} \right\} \text{From graphs}$$

$$\frac{x}{b'} = 0.6627$$

$$\varphi = 122.13^\circ$$

$$\frac{R}{b'} - \frac{x}{b'} = 0.6634 - 0.6627 = +0.0007$$

$$\Delta \beta = 0.1 \quad \Delta \frac{x}{b'} = 0.0012 \quad \Delta b' = 0.0244$$

$$\beta = 4.9 + 0.1 \times \frac{5}{12} = 4.9417$$

$$b' = 6.3029 + 0.0244 \times 0.41667 = 6.3131; b = \frac{6.3131}{9.992^*} = 0.63182 \text{ cm}$$

$$b^2 = 0.39919 \text{ cm}^2$$

$$g_{\text{ottawa}} = 980.6$$

$$\rho_{\text{Sn}}, \uparrow 246^\circ \text{ C} = 6.978$$

$$\gamma = \frac{g \rho b^2}{\beta} = \frac{980.6 \times 6.978 \times 0.39919}{4.9417} = 552.7 \text{ dynes/cm}$$

\* Magnification factor.  
 † Mines Branch density data; to be published.

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