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SURFACE TENSION OF MOLTEN ZINC AND SOME ZINC ALLOYS

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DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

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SURFACE TENSION OF MOLTEN ZINC AND SOME ZINC ALLOYS

by

D. W. G. White*

ABSTRACT

The surface tension of zinc and of some zinc alloys has been determined by the sessile drop method in a program of work emphasizing detailed experimental care.

From experiments carried out in a closed, isothermal cell, the temperature coefficient of the surface tension of pure zinc over a range of temperature from the melting point (419.6 °C) to 540 °C was found not to be negative but to be positive. However, it was shown that by deliberately inducing continuous vapourization, a temperature coefficient of surface tension with a negative slope can be produced.

In the alloy program, the effects of aluminum, copper, lead and tin on the surface tension of 99.999+% Zn have been determined.

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Direction des mines

Rapport de recherches R 160

TENSION SUPERFICIELLE DU ZINC ET DE
QUELQUES ALLIAGES DE ZINC FONDUS

par

D. W. G. White*

RÉSUMÉ

L'auteur a mesuré la tension superficielle du zinc fondu et de quelques alliages de zinc par la méthode des gouttes posées sur un support, au cours d'une série de travaux qui ont mis en lumière le grand soin apporté aux expériences.

A la suite d'expériences menées à bien dans un compartiment isotherme bien fermé, l'auteur a constaté que le coefficient thermique de la tension superficielle du zinc pur à des températures allant du point de fusion ($419^{\circ}.6$ C.) jusqu'à 540° C. n'est pas négatif, mais positif. L'auteur a montré cependant que s'il provoquait une vaporisation continue du métal la pente du coefficient thermique de la tension superficielle pouvait devenir négative.

En ce qui concerne les alliages, l'auteur a déterminé les effets de l'aluminium, du cuivre, du plomb et de l'étain sur la tension superficielle du zinc à une pureté dépassant 99.999%.

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INTRODUCTION

This report describes work on the measurement of the surface tension of liquid zinc and the determination of the effects of aluminum, copper, tin and lead on the surface tension. The work was undertaken as part of a larger program of fundamental research on the properties of molten zinc and zinc alloys. This program grew out of a continuing interest at the Mines Branch in the behaviour of liquid metals in the foundry and of a desire on the part of the zinc industry for reliable basic data. The work was originally begun in cooperation with the Consolidated Mining and Smelting Company Limited, Trail, B. C., and was subsequently continued from 1960 to date in association with the Canadian Zinc and Lead Research Committee and the International Lead Zinc Research Organization.

The surface tension of liquid zinc has, of course, been measured before: the results of some previous work are shown in Table 1.

TABLE 1

The Surface Tension of Liquid Zinc at 420°C

Author	dynes/cm	Ref.
Korol'kov	750	1
Hogness	754	2
Ryabov and Gratsiansky	782	3
Matuyama	796	4
Saurewald	804	5
Pelzel	820	6
Bircumshaw	830	7

In addition, Korol'kov (1), Ryabov and Gratsiansky (2), and Pelzel (8) have measured the surface tension of some zinc-base alloys.

From Table I, however, it is evident that there is not good agreement among the values. Such disparities arise because sources of experimental error are insufficiently controlled. This situation places the reader in doubt. One result may be correct within narrow limits - even fortuitously - yet, because there is not agreement between several values, none can be accepted with conviction and all become suspect.

It seemed, therefore, in the circumstances, that there was room for further work embodying considerable emphasis on experimental care in order that, within a small margin of error, an accurate value might be obtained. It was in this spirit that the present work was undertaken.

METHOD

There are many experimental methods by which surface tension may be measured, although the maximum bubble pressure method and the drop shape method are the most suitable for liquid metals at elevated temperatures (9). The drop shape method, in particular, has two variants, the pendant drop (hanging drop) and the sessile drop (resting drop). Of these two, the sessile drop method is experimentally flexible, is free from inherent uncertainties, and is an attractive method when substances can be found to support a drop of the liquid metal without any chemical interaction.

The sessile drop method was chosen for this work. In this method, when applied to liquid metals at elevated temperatures, the outline of the meridional section through a drop resting freely on a horizontal surface is recorded photographically. Certain parameters of the drop outline are measured from the photograph and with these the surface tension of the liquid metal may be calculated from data in tables compiled by Bashforth and Adams⁽¹⁰⁾.

Figure 1 illustrates the parameters to be measured for the calculation procedure that has been used. This procedure was proposed by Francis Bashforth in the book of the tables but apparently was lost sight of until recently rediscovered⁽⁹⁾. The method is more reliable than any that was subsequently developed. The parameters to be measured are a set of X-Z co-ordinates (Z_R and Z_R) below the maximum diameter ($2X$), and the maximum diameter ($2X$) itself. The co-ordinates can be defined accurately by making two small incisions in the photographic emulsion with a razor blade on a line just above and parallel to the line corresponding to the horizontal surface of the support.

The simple, fundamental equation relating the tension force acting in a liquid surface to the pressure drop across the surface when it is curved, was manipulated into a dimensionless form by Bashforth⁽¹⁰⁾ to describe the shape of the meridional section of a drop. Because no exact analytical solution to the equation has been devised, tables were drawn up which enable the shape of a drop (β) to be calculated from a pair of X-Z co-ordinates and a measure of the drop size.

For a given size of drop, the shape (β) is determined by a balance between surface tension, tending to draw the liquid up into a sphere, and gravitational forces tending to flatten and spread the liquid. Thus, it is possible to relate the shape of the drop, which can be calculated from tables, to the surface tension of the liquid by the following dimensionless group:

$$\beta = \frac{\rho g b^2}{\gamma}, \quad \text{where:}$$

- γ - surface tension of the liquid (dynes/cm),
- ρ - the density of the liquid determined at the experimental temperature (g/cm^3),
- g - gravitational acceleration constant (cm/sec^2), and
- b - the instantaneous radius at the pole of the drop (cm).

Further discussion of the construction, nature and use of the tables may be found in the original work of Bashforth and Adams⁽¹⁰⁾ and in a paper published elsewhere by the author⁽⁹⁾.

In addition to calculating the surface tension by using the Bashforth and Adams tables in conjunction with the sessile drop method, it is also possible to calculate the contact angle the liquid drop makes with the substance of the support, if the contact angle is greater than 90° . In order to do this it is necessary to measure the maximum height of the drop above the supporting surface (Z), Figure 1, as well as the aforementioned parameters. From a knowledge of the contact angle, two things follow: 1) the work of adhesion - -a thermodynamic measure of how well a liquid and solid stick together- -can be evaluated, and 2) from the tables the volume

of the drop can be calculated. Thus, after an experiment when the drop can be detached from the support and weighed, the density at the experimental temperature can be obtained.

Hence, an evaluation of surface tension by the sessile drop method does not require independent measurement of density. However, as part of the present research program on the properties of liquid metals, the densities of pure zinc and of zinc-base alloys have been measured very accurately by H. R. Thresh⁽¹¹⁾, using a 14 cm³ nuclear-grade graphite pycnometer. The experimental error in this work is confined to $\pm 0.05\%$. This exceptional accuracy is better by a factor of six than the $\pm 0.3\%$ achieved with a small drop. Hence, density data from the pycnometer have been used throughout the surface tension program, both for the calculation of surface tension itself and as a reference with which densities calculated from drop measurements could be compared. Such comparisons were made as a routine check on the optical fidelity of the apparatus.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The sessile drop apparatus has been designed, constructed and operated to render an accurate photographic image of the outline of a meridional section of a drop of liquid zinc or zinc alloy resting freely on a horizontal surface. In a work in which emphasis has been placed on accuracy, many features of apparatus design or experimental technique have been conceived to eliminate, minimize, or correct for sources of

experimental error. Hence, the following account should be assessed in this context.

The experimental precautions adopted are mainly of two kinds: those affecting optical fidelity, and those affecting environmental cleanliness. In later stages of the work the importance of the need to provide the drop with an isolated isothermal environment was fully appreciated, and changes in apparatus and technique were made accordingly.

Essentially, the apparatus was designed to

- 1) isolate a sample or charge in a cool region while the furnace is outgassed in high vacuum at a temperature in excess of the experimental temperature;
- 2) melt the charge and to filter it in an atmosphere of purified hydrogen in order to produce a clean drop; and
- 3) render a magnified photographic image of the outline of the drop.

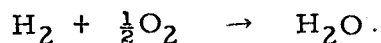
Figure 2 depicts a schematic layout of the apparatus. A charge weighing about 1.8 g, suspended from the end of a 0.005 in. diameter tungsten wire attached to a piece of iron tube, is inserted in side arm (b). The apparatus is closed through ground glass joints on the end of arm (b), at the upper end of the vertical tube carrying the plunger rod assembly (e) and at end cap (h). These joints are sealed with Apeizon "W" wax.

All sources of stop-cock grease on the apparatus are trapped out with liquid nitrogen traps, as at (f) and (p), except the double O-ring seal at (a) where this was not possible. Here it was found by experiment that heating the grease in vacuum to 300 °C before applying it to the O-rings,

and grinding the lower end of the vertical tube internally to fit the liner (k), as shown in Figure 3, eliminated the effects of grease vapour on the surface tension measurements. Details of the experimental work concerning this will be discussed later.

The apparatus is evacuated through trap (p), Figure 2, by a three-stage glass fractionating pump backed by an adequate air ballasting mechanical pump. A liquid-nitrogen-cooled trap (not shown) is interposed between the diffusion and mechanical pumps. The apparatus has a leak rate of about 3×10^{-4} mm Hg per hour in a volume of about 5 litres, and achieves a vacuum of 1×10^{-6} mm Hg. A very small leak rate is important, since, after out-gassing at a temperature about 200 centigrade degrees above the experimental temperature, purified hydrogen is admitted and the system is filled to a pressure of 1 atmosphere over a period of two hours. A low flow rate of hydrogen through the purification train is considered essential to ensure thorough purifying reactions.

Bottled hydrogen of about 99.7% purity is passed through the purification train illustrated schematically in Figure 4. Copper chips at 500°C and ferrochrome granules at 850°C catalyse the reaction



Liquid-nitrogen-cooled traps in sequence remove the water vapour. The equilibrium partial pressure of oxygen over chromium at 850°C is about 10^{-26} atmospheres, and the vapour pressure of water at the boiling point of liquid nitrogen is of the order of 10^{-25} atmospheres. When immersed

in liquid nitrogen, molecular sieve trap (b) containing 13X zeolite and activated charcoal trap (c) remove traces of inert gases, nitrogen, carbon monoxide, and hydrocarbon vapours.

As originally conceived, experimental technique called for passing hydrogen through the system for two to three hours once the pressure had been brought up to 1 atmosphere. The hydrogen entered the system through side arm (g), Figure 2, passed out through the side arm (r), and was burnt off at a jet. Burning the hydrogen off at a jet led to back diffusion of reaction products (water vapour) and air, and gross contamination resulted. The source of contamination proved very elusive to isolate but, when finally determined, the contamination was eliminated by simply removing the purging step from the sequence of events.

After the graphite plunger (l), Figure 3, has been outgassed during the out-gassing cycle, it is raised above the junction with side arm (b), Figure 2. When the system has been filled with hydrogen, the zinc charge is lowered down the vertical tube (d), Figure 3, and melted at the end of the tungsten wire. The wire is then withdrawn, the graphite plunger (l) lowered, and the molten zinc forced through the filtering assembly (o) to form a drop on the graphite plaque (h) below.

When the surface tension of a zinc alloy is to be determined, the alloy is prepared directly in the apparatus. Small holes are drilled in the side of the 1.8 g charge of 99.999+ % Zn, and the requisite quantity of pure solute metal is peened into the holes. Metals of about 99.999% purity are used in all cases for alloying. Advantage is taken of density differences

between the solute and zinc by drilling the holes at the top of the charge, or the bottom, as is appropriate to improve mixing. Homogenization in the molten alloy occurs by some convective mixing and by diffusion while the charge remains in the graphite liner prior to filtering, by mixing during filtering, by mixing again while the drop is being formed on the plaque, and, subsequently, by diffusion. Photographs taken over a two and one-half hour period during a run indicate, by the consistency of surface tension results, that, in general, homogenization is complete before the first photograph is taken. Where an alloy approaches the saturation limit, as in the case of copper and lead, an alloying efficiency of about 80% is achieved, otherwise it is better than 90%.

Early in this work, attempts were made to prepare alloys by careful melting techniques in the laboratory, but erratic surface tension behaviour always followed. Furthermore, a period of about nine months was spent building and experimenting with a vacuum melting and casting apparatus, but it was destroyed in a fire before it had given satisfactory results.

The technique of preparing alloys in the sessile drop apparatus solves problems associated with gas absorption and general cleanliness, and hence yields consistent surface tension data. However, the amount of material available for subsequent analysis is small and analytical accuracy may suffer accordingly.

A definition of the conditions under which surface tension should be measured requires that the liquid be in equilibrium with its own vapour. At temperatures just above its melting point, zinc has a vapour pressure of $> 100\mu\text{Hg}$. Therefore, in the original apparatus design, steps were taken to suppress continuous vapourization losses by attempting to produce in the furnace zone a totally enclosed region with walls and other parts hotter than the drop. To this end, the fused silica furnace tube was constructed in such a way that it could be blocked off at annulus (e), Figure 3, by fused silica stopper (a). Vertical tube (d) was effectively blocked off by liner (k), to which the constricted end of the tube was ground to fit. During the vacuum outgassing cycle, the stopper could be withdrawn to an enlarged section of the furnace tube to improve conductance. A strong magnet to attract ring (b) was used for this purpose. Power inputs to main furnace (m), Figure 2, and auxiliary windings (i), Figure 3, were arranged to produce the longitudinal temperature distribution shown in Figure 3. Although, with this arrangement, vapourization losses still occurred, they were sufficiently small that a nearly correct positive temperature coefficient of surface tension at temperatures just above the melting point was obtained. This is in sharp contrast to the negative coefficients obtained by other workers.

Investigation into the positive temperature coefficient led to the view that the coefficient could be measured accurately only when vapourization had been completely suppressed. Hence, the "open" graphite plaque which had been in use was replaced by a plaque contained in an optical cell as shown in Figure 5.

The fused silica optical cell (17 x 19 x 42 mm) (q) has optically flat windows front and rear. It is carried in stainless steel boat (s) and closed by weighted lid (l) which embraces a fused silica plate 19 x 42 mm. Polished nuclear-grade graphite plaque (r) is housed inside the optical cell. This assembly is loaded into the furnace tube, before a run, with the lid in approximately the same position as shown in the drawing. Pusher (t), consisting of an iron ring and stiff stainless steel wire, replaces fused silica stopper (2), Figure 3.

Details of the experimental technique remain unchanged except that after the drop has been filtered onto the plaque, without de-energizing any of the furnace windings, one half of split main furnace (m), Figure 2, is lowered sufficiently to permit the optical cell to be seen. Pusher (t), Figure 5, is manipulated with a magnet to close the lid of the cell. The pusher is then withdrawn, the furnace closed again, and the temperature restored. With the cell, power inputs to furnace windings are arranged so that the indicated temperature in the furnace at locations corresponding to the windows of the cell is about 1 centigrade degree higher than at the drop position.

The other important feature of apparatus design is the optics. The optical arrangement is shown schematically in Figure 6. Light from a 500 W projection lamp fitted with a polaroid filter is collected by a camera lens and a magnified image of the drop is rendered on a photographic plate. A 10X magnification is achieved with a 135 mm Boyer Apo Saphir lens and a lens-to-plate distance of about 5 ft. This lens is a

process lens and is therefore corrected for a finite conjugate distance. A 2 mm telecentric stop is located at the point of second principal focus; which is a distance to the rear of the lens corresponding to the focal length of the lens. A pinhole placed at this point would pass only rays which, before they struck the lens, focused at infinity. Rays on converging or diverging paths before striking the lens, would be focused before or behind the pinhole and, therefore, would be blocked by the stop. In this way, a true meridional section of the drop is photographed. In practice, the hole must be opened out to about 2 mm to avoid objectionable diffraction effects. The telecentric stop confers an enormous depth of focus on the lens and is therefore removed when the camera is being focused.

Because the furnace is at an elevated temperature when photographs are taken, diffraction effects occurring in the gap between the end of the hot furnace and the cool lens can mar the drop image. A lens hood bridges the gap and reduces the effects to negligible proportions.

The lens may be withdrawn back along the camera frame, away from the hot furnace, when the camera is not being focused or a photograph taken. A rod, which is attached to the lens bracket, has a stop at its far end that impinges against the fixed plate holder bracket to produce a set bellows extension. In this way, the lens may be retracted without moving the entire camera and a predetermined lens-to-plate distance preserved.

By impressing a magnified drop image directly onto metallographic plates, errors associated with film shrinkage and the duplication of errors by enlargement are avoided. Following development, the plates

are set on a white background and measured with a cathetometer. The limit of reproducibility of measurement is about 0.002 cm; this reduces (by a factor of 10) to an uncertainty of 2μ in the size of the drop.

The magnification factor of the apparatus has to be determined. This is done by measuring a photograph of an object placed in the furnace tube in the drop position. If care is taken, this affords the opportunity to correct for curvature of the field from the lens and for irregular temperature-induced refraction effects radially normal to the optical axis. These may arise anywhere between the object and the lens. If the correction is to be accurate, however, it is important that experimental conditions be reproduced faithfully when the magnification factor is being determined. Figure 7 illustrates the magnification standard used. It permits the magnification factor to be determined independently in the vertical and horizontal directions on an object located in the same position in the optical field as a drop and whose vertical and horizontal dimensions are about the same as those of a drop. Photographs are taken under the same conditions of temperature and environment as occur in experiment. By making the magnification button from nuclear-grade graphite, the need for an accurate knowledge of thermal expansion behaviour is diminished, compared with what would be necessary if the button were made of steel. A correction for thermal expansion of 0.0001 in. to dimensions measured at room temperature is all that proves necessary.

An indication of the magnitude of the effects involved here is given by the following example. In one case it was found that the magnification factor in the vertical direction was 0.24% greater than in the horizontal direction. With these slightly different magnification factors in the vertical and horizontal directions, the surface tension proved to be a 9.6 dynes/cm lower than when the same magnification factor in the vertical and horizontal directions was used. This error in surface tension is about +1.25%.

Sources of experimental error and the means of overcoming these are more amply discussed in the earlier paper by the author⁽⁹⁾.

RESULTS AND DISCUSSION

Pure Zinc

When details of an apparatus and experimental technique were originally formulated, it was decided that an atmosphere of purified hydrogen would afford the best available safeguard against the undesirable effects of general environmental contamination on surface tension results. However, the possibility was recognized that, in turn, there might be some form of interaction between the metal and hydrogen. Because no unequivocal information on this point seemed to be available in the literature at the time, it was considered desirable to compare the surface tensions of zinc in hydrogen and in helium.

Experiments were carried out at 435 °C with zinc of 99.9999% purity. Duplicate runs in helium gave surface tension values of 753.2 and 753.3 dynes/cm, whereas values averaging 765.7 dynes/cm had been obtained in hydrogen. These values actually contained inaccuracies owing to vapour transport effect and a slightly incorrect magnification factor. The combined error here is about 1.5% but it is a constant error and in no way invalidates the findings. As reproducible as the surface tension in helium appeared to be, it was decided to attempt to eliminate the effects of the stop-cock grease at the double O-ring seal (e), Figure 2, before being satisfied that there was a real difference in the surface tension of zinc in hydrogen and helium. As has already been mentioned, the grease was outgassed at 300 °C in vacuum, a trap was inserted at (f), and the internal surface of the constricted end of vertical tube (d), Figure 3, was ground to fit liner (k). When this was done, the surface tension in helium increased to 767.2 dynes/cm. The agreement was considered satisfactory and the main body of work begun.

Since that time, the very interesting work of Nicholas et al. ⁽¹²⁾ on the effects of various gases on the surface tension of mercury came to the attention of the author. This work on mercury at room temperature supported the present findings with zinc, in that the surface tension of mercury was found to be the same in hydrogen and helium but to be strongly reduced by pump oil and stop-cock grease vapours.

Having determined that there were no unexpected effects from the use of hydrogen as an environment for surface tension measurements and having measured the surface tension at 435 °C, it seemed desirable to check the temperature coefficient of surface tension, in order to compare with the coefficients obtained by other authors, before starting upon experiments with alloys.

A number of runs with double zone-refined zinc having a purity > 99.9999% led to a curve with the strongly positive slope depicted in Figure 8. This curve is in marked contrast to the curves with assorted negative slopes observed by others⁽¹⁻⁸⁾. Experiments showed that the same curve resulted from measuring surface tension on an ascending temperature sequence as on a descending sequence. Replacing the existing furnace tube having a somewhat blemished window with a new tube and window made no significant difference to the results. The magnification factor was checked as a function of temperature and was found to be invariant. The possibility of the coefficient being associated in some obscure way with impurity effects could be eliminated on two grounds. First, measuring surface tension on ascending and descending temperature sequences afforded an opportunity for the time- and temperature-dependent mechanisms of diffusion to reveal some differences in behaviour as might be expected to happen in the presence of impurities, but none occurred. Second, the zinc used was among the purest ever produced*.

* Double zone-refined zinc is produced by applying 20 passes to each of 9 bars of 99.999+% purity. Then the top end and the last 2/3 of each bar are discarded. The remaining 9 pieces are remelted together to make 3 bars. The same procedure is repeated on the 3 bars. The final product is 1 bar of double zone-refined metal.

For comparative purposes the temperature coefficient of surface tension of a 99.99+% grade of zinc was determined and is contrasted with the curve of Figure 8 in Figure 9. That the surface tension of the less pure grade is lower at the melting point of zinc (419.6 °C) than that of the purer metal is in accord with existing ideas. Furthermore, that the surface tension of the less pure metal should increase with increasing temperature, so that its surface tension becomes higher than the surface tension of the purer metal, is in agreement with the observations of Ryabov and Gratsiansky⁽³⁾. However, in the work of these authors the surface tension of 99.999% grade had a shallow negative slope whereas grades less pure had small positive slopes. This kind of effect has, apparently, been observed by a number of workers in the Soviet Union and has led to imprecise ideas about the role of impurities in a positive temperature coefficient.

That impurities have anything to do with a positive slope per se is not supported by the evidence available from this work. Rather, the role of impurities appears to be limited to affecting the magnitude of the slope.

The only factor suspected of playing a role in the formation of a positive coefficient was the small but continuous mass loss by vapour transport. No claim for having determined the surface tension of zinc correctly could be made until this variable had been examined and eliminated, if it was found to affect results. Thus the optical cell was procured and work thenceforth proceeded with it. As a means of arriving at some estimate of the rate of mass loss, the practice was adopted of measuring

the volume change per min at 540 °C for a drop which usually weighed about 1.5 g. With a drop on an "open" plaque this figure was of the order of $25 \times 10^{-5} \text{ cm}^3/\text{min}$. With a drop in the cell the rate of mass loss was $<1 \times 10^{-5} \text{ cm}^3/\text{min}$. It was concluded from this that the cell is effective in suppressing vapourization losses and that the effect of such residual losses on surface tension could be disregarded.

Hence, the temperature coefficients of the surface tension of 99.9999%, 99.999+% and 99.99+% Zn were determined over a range of temperature from the melting point (419.6 °C) to 540 °C in a closed optical cell. The curves obtained are shown respectively in Figures 10, 11 and 12. Points on these curves from separate runs are distinguished by different symbols and are not averages of many experiments but individual values. At the melting point, the surface tension of

- 1) 99.99+% Zn is 760.5 dynes/cm \pm 5 dynes/cm
- 2) 99.999+% Zn is 763.0 dynes/cm \pm 5 dynes/cm
- 3) 99.9999% Zn is 769.5 dynes/cm \pm 5 dynes/cm.

In Figure 13, the curves are superposed for better contrast. All three curves appear to have the same basic form in that data seem to be best fitted by two more or less straight lines joined at a convex upward knee. However, the location of the knee on the temperature scale does not appear to behave in a self-consistent manner; perhaps the knee position reflects not only the quantity of impurity but also the kind of impurity. Above the knee, however, the curves tend to a course, within

experimental error, that is independent of the original purity and is a characteristic of the metal.

By comparing Figure 9 with Figure 13, it is evident that eliminating the vapourization losses induces an increase of about 20 dynes/cm in the surface tension but that the slope of the curves originally obtained are observed to be substantially preserved. Under equilibrium conditions, the surface tension of 99.99+% pure zinc no longer rises with increasing temperature to values above that of the ultra-pure material, although the surface tension of the 99.999+% material does.

Having determined the behaviour of surface tension in the absence of vapourization, it remained to demonstrate convincingly the role of vapourization kinetics in producing a negative temperature coefficient. Power inputs to the various furnace windings were arranged to induce the maximum rate of vapourization of which the apparatus seemed capable. With a drop on an "open" plaque the distribution of surface tension results versus temperature, shown in Figure 14, was obtained. The experimental scatter is somewhat greater than observed under equilibrium conditions and a positive tail lingers still at the low temperature end of the curve, but vapourization has unquestionably changed the slope from sharply positive to shallow negative. The curve has been redrawn in Figure 15, together with a curve obtained when moderate vapourization was inadvertently produced in an experiment, and the two are contrasted with the equilibrium curve for 99.999+% Zn.

Consideration of the data in terms of thermodynamic functions will assist materially in ascribing significance to the results. It is customary to consider the surface transition region separating bulk phases of liquid and vapour as a surface phase. Thermodynamic functions may be assigned to the surface phase, analogous to those possessed by the bulk phases. These functions have units of energy or entropy per unit area and therefore represent intensive thermal properties of the surface phase. These properties exist in excess of what the system would possess if a surface were not there. A standard text on thermodynamics will show that, for a liquid, the surface tension γ is equal to the free energy per unit area F' , thus:

$$\gamma = F' \dots\dots\dots 1)$$

Because the volume contribution of surface may be ignored, PV terms are insignificant and it is of no importance to the present purposes whether F' represents Helmholtz' or Gibbs' free energies.

Also, we may write:

$$\gamma = u - Ts, \dots\dots\dots 2)$$

where u = the intrinsic or total energy per unit area,

s = the entropy per unit area, and

T = absolute temperature °K.

For a single substance at constant pressure or volume, other relations follow immediately:

$$s = -\left(\frac{\delta F'}{\delta T}\right) = -\left(\frac{\delta \gamma}{\delta T}\right) \dots\dots\dots 3)$$

$$u = \gamma - T\left(\frac{\delta \gamma}{\delta T}\right) \dots\dots\dots 4)$$

$$c = \left(\frac{\delta u}{\delta T}\right) = -T\left(\frac{\delta^2 \gamma}{\delta T^2}\right) \dots\dots\dots 5)$$

where c = specific heat per unit area.

From Equation 3 it is evident that the temperature coefficient of surface tension gives an indication of the surface entropy contribution to the system. In particular, by measuring the slope of the temperature coefficient curves and making some assumption concerning the thickness of the surface phase, a molar surface entropy can be calculated⁽¹³⁾ that can be compared quantitatively with entropies of the bulk liquid and vapour. However, the magnitude of the quantity obtained is directly conditioned by the thickness assigned to the surface. Thus, the significance of the magnitude is a matter for reasonable doubt, and it becomes questionable whether trying to consider more than the sign of the entropy function assists or detracts from an understanding of the state of the surface.

The present results indicate that the surface contributes negatively to the entropy of the system and that, therefore, in some way, atoms in the surface of the liquid are less disordered than they would be if there were no surface and they occupied, instead, positions in the bulk liquid. This may merely be a reflection of the fact that surface atoms have available only 8 operative degrees of freedom (6 vibrational and 2 translational),

compared with 9 operative degrees in the bulk (6 vibrational and 3 translational). However, it is not possible to be positive of this because it seems unlikely that the translational degrees of freedom will be operative in the liquid to the same extent as in the surface. On the other hand, since it was originally advanced independently by Langmuir⁽¹⁴⁾ and Harkins⁽¹⁵⁾, chemists have long been familiar with the idea of surface molecular orientation. The concept applies especially to molecules with highly asymmetric fields cooperatively oriented normal to the surface but has been logically extended to embrace monatomic molecules with symmetrical fields. Symmetrical electromagnetic fields, it is argued, become displaced when an atom is the surface. Orientation phenomena occur to make the transition between liquid and vapour less abrupt. Energetically, the driving force for the process is the minimization of surface free energy.

The foregoing indicates the likelihood of some degree of long range orderliness in a direction normal to the surface, but it is also likely that ordering occurs within the plane of the surface because, as Skapski^(16,17) points out, ... "The arrangement in the surface layer of a liquid must correspond to that in the most densely populated plane ... (of a particular species)... because only such an arrangement ensures the minimum of the free surface and, of course, of free energy".

Thus, it seems entirely reasonable to suppose that atoms in the surface of a liquid will have a greater degree of order than if they were to be present in the bulk of the liquid; and it follows, therefore, that the

temperature coefficient of the surface tension of zinc should be initially positive, the burden of theoretical models⁽¹⁸⁾ and the considerable but contrary experimental evidence on liquid metals notwithstanding.

The surface tension versus temperature data do not plot in an invariant straight line or a smooth curve, but seem to be best fitted by two straight lines, the higher temperature leg having a smaller slope than the other. This strongly implies a sharp change from one state of order to a second state of lesser order with increase in temperature. As indicated in Table 2, the slope $\frac{d\gamma}{dT}$ of the higher temperature leg for 99.9999% and 99.99+% Zn is just about one-half of that of the lower temperature portion.

TABLE 2

Temperature Coefficients of the Surface Tension of Zinc

Zinc Purity	$d\gamma / dT$ dynes cm^{-1} deg. C^{-1}	
	Lower temp. slope	Upper temp. slope
99.9999%	0.62	0.32
99.999+%	0.66	0.24
99.99+%	0.85	0.43

Furthermore, because the lines composing the curve are straight,

$$-T \left(\frac{\delta^2 \gamma}{\delta T^2} \right) = c = \left(\frac{\delta u}{\delta T} \right) = 0 \quad \dots 5)$$

Thus, the superficial specific heat is zero. The significance of superficial specific heats with a value of zero was interpreted by Einstein⁽¹⁹⁾ to mean

that all of the energy of formation of a surface u goes into the surface in a potential form which, in turn, implies that the energy is stored up in some configurational way in the surface layer.

It is evident that the total surface energy u can be calculated by Equation 4) from the graphs in Figures 10, 11 and 12. While γ remains a linear function of temperature, $\frac{d\gamma}{dT} = \text{constant}$ and the total surface energy is independent of temperature. Because of its constancy, u is regarded by many as very much more a characteristic function of a substance than the free surface energy γ . Values of u are recorded in Table 3 so that when accurate data for other metals become available, comparisons can be made.

TABLE 3

The Total Surface Energy of Zinc

Zinc Purity	u ergs cm ⁻²	
	Lower temp. slope	Upper temp. slope
99.9999%	340	558
99.9994%	306	625
99.994%	171	473

When continuous vapourization occurs during surface tension measurements, the effect is twofold. Equilibrium conditions no longer prevail and the free surface energy or surface tension γ cannot be expected to remain a minimum. Therefore, surface tension is likely to increase. In addition, vapourization leads to a continuous loss of atoms from the

surface which, if great enough, should detract from surface order and increase surface entropy. This, in turn, will exert a negative effect on the slope of the temperature coefficient. In a given set of conditions, the entropy increase will be proportional to the vapour pressure and should, therefore, first manifest itself as a negative slope at high temperatures. As Figure 15 indicates, with increasing severity of vapourizing conditions, the entropy increase progressively transforms the slope of the curve from positive to negative, proceeding down the temperature scale.

Although it has been shown that the temperature coefficient of the surface tension of zinc is positive and explanations for the phenomenon have been advanced, it is not to be expected that the coefficient continues indefinitely to be positive. As the temperature increases, so will the equilibrium concentration of atoms in the vapour phase and the thermal agitation of atoms in the bulk of the liquid: the degree of surface "unsharpness"⁽¹⁶⁾ will increase and the surface entropy will change similarly. At the point where surface tension is a maximum, the excess of surface entropy will be zero; that is, the molar surface entropy⁽¹³⁾ and the bulk entropy will be the same. Beyond the temperature corresponding to the maximum surface tension, the free and the total surface energies will decrease with increasing temperature until at the critical temperature both become zero⁽¹⁵⁾.

This work represents the first occasion on which a positive temperature coefficient has been measured for zinc. But it is not the first time a positive coefficient has been determined for a liquid metal. To the

author's knowledge, positive coefficients have been measured twice for cadmium^(2,7), twice for copper^(5,20) (as well as a number of negative coefficients), once for iron-nitrogen alloys⁽²¹⁾, and once for other iron alloys⁽⁵⁾. In addition, an interesting qualitative observation on indium was reported by Bergh⁽²²⁾. But in all cases the results have been treated in the nature of an embarrassing anomaly and no satisfactory explanation of them has been given.

Zinc Alloys

The effects of aluminum, copper, lead and tin on the surface tension of 99.999+% Zn at 435 °C have been determined and the data plotted in Figures 16, 17, 18 and 19, respectively. Each point results from a separate run and, in general, is the arithmetic mean of four values determined over a two and one-half hour period. Within the group of four values from a run, scatter was usually <1%. Curves are shown of surface tension versus weight per cent to a limit of about 1% Pb, 1.1% Sn, 1.6% Cu and 2.75 % Al. These limits have been set by ease of solution at 435 °C in the case of lead and copper, the solubility limits being about 1.2% and 1.9% respectively; by industrial interest in alloys up to 1% only in the case of tin; and by the onset of experimental difficulties in the case of aluminum.

Up to their maximum concentrations, the Zn-Cu, Zn-Pb and Zn-Sn solutions are sufficiently dilute that an atom fraction scale and a weight per cent scale remain linearly proportional. Thus, no fundamental significance is lost by plotting the results on a weight per cent basis. Towards the

maximum concentration, an atom fraction scale in the Zn-Al system does cease to be proportional to solute weight, but because there is very little change in surface tension, here too no significance will be missed.

For the Zn-Pb system, thermodynamic data of sufficient accuracy are available to permit the activity of lead to be calculated^(23, 24). Plotting surface tension against activity offers the most meaningful way of presenting the data. But again, because the solutions remain dilute, the activity coefficient changes only from 305 at 0.25% Pb to 284 at 1.0% Pb and an activity scale remains substantially proportional to weight per cent. However, if surface tension is replotted against the natural logarithm of the activity of lead, the shape of the curve does change and a good straight line emerges, as shown in Figure 20.

The slope of the curves may be summarized in the following way:

- 1) in concentrations up to about 2.75%, aluminum has no effect on the surface tension of zinc;
- 2) up to about 1.6%, copper increases the surface tension of zinc about 2%;
- 3) lead has an appreciable effect on the surface tension of zinc, 1% lead reducing the surface tension more than 40%; and
- 4) in concentrations up to 1.1%, tin reduces the surface tension of zinc by about 7%.

In each of Figures 16, 17, 18 and 19 two curves are given: one uncorrected and the other corrected, with the bulk of experimental results documenting the uncorrected curve. This occurs because the data were originally determined on an open plaque while the delivery of optical cells was being awaited. The original data were later corrected by redetermining

the surface tension of selected compositions from each alloy system in a cell. The details are as follows.

It will be observed that the original data for each alloy do not extrapolate back at zero composition to the correct value for the surface tension of 99.999+% Zn at 435 °C. Neither do the curves extrapolate back to the same inexact value. It was thought, therefore, that if, when a surface tension value had been determined for a low solute concentration and another at a high concentration, the uncorrected curve could be uniformly displaced to fit the two points and extrapolate at zero composition to the value for the surface tension of 99.999+% Zn at 435 °C taken from Figure 11, then the corrected curve could be accepted with confidence as accurate within ± 5 dynes/cm. This proved to be the case for zinc-aluminum alloys and zinc-copper alloys, Figures 16 and 17. For the zinc-aluminum alloys the correction for vapour transport effect was +7 dynes/cm and for the zinc-copper alloys, + 15 dynes/cm.

With zinc-lead alloys, Figure 18, the correction procedure was not so straightforward. At 0.15% Pb, a positive correction of 10 dynes/cm was indicated, while at 0.78% Pb the correction appeared to be negative by the same amount. A repeat experiment at 0.68% Pb confirmed the need for a negative correction with a value of -9 dynes/cm. Without changing the shape of the original curve, therefore, the curve was tipped to fit the three experimental points and to extrapolate back to 773 dynes/cm at zero lead concentration.

The dominant feature of the zinc-lead constitution diagram is a miscibility gap, which at 435 °C extends from about 1.2% Pb to about 98% Pb. This implies that the activity coefficient of lead is likely to be greater than unity and, indeed, as already mentioned, the activity coefficient at 435 °C has the remarkable value of about 300. Thus, although the mole fraction of a 1% Pb solution is only 0.00318, the activity is 0.903, and because at the same time the activity coefficient of the solvent remains about 1⁽²³⁾, there is no cause for alarm if such a non-ideal solution behaves in an unexpected fashion, especially if the magnitude of the effect is not large.

The behaviour of zinc-tin alloys, Figure 19, is anomalous and not completely resolved. It will be noticed that in its uncorrected form, the plot of surface tension versus tin concentration extrapolates at zero tin composition to a surface tension value which is greater than that of 99.999+% Zn at 435 °C and not to a value which is less as is the case with zinc-aluminum, zinc-copper and zinc-lead alloys. Correcting for vapour transport effect increases the surface tension roughly 10 dynes/cm in conformity with the general direction and magnitude of this correction for the other systems. This, of course, serves only to exacerbate the discrepancy when the curve is extrapolated to zero tin concentration.

A limited investigation of the matter revealed the following information:

- 1) Some hypothetical interaction between Zn-Sn alloys and hydrogen is not responsible for the surface tension curve's being "too high", because experiments in helium resulted in surface tension values approximately 10 dynes/cm higher still. This, in turn, is in seeming conflict with early experiments on pure zinc, which indicated no difference between the surface tension in hydrogen and that in helium.
- 2) Experiments suggested by Dr. E. A. Flood of the National Research Council, involving grounding the sessile drop through the plaque and the boat, showed that there are no electrical effects arising from contact potentials to obscure the true surface tension.
- 3) As indicated by the point for 0.085% Sn, the surface tension of zinc-tin alloys does fall off sharply to the correct value for pure zinc as the zero tin axis is approached. Nevertheless, the effect is anomalous and but for the pressure of program commitments it would have been worthwhile to have carefully documented the phenomena. In view, therefore, of the vestiges of doubt remaining about the true behaviour of zinc-tin alloys, it seems reasonable to set the limits of error at ± 10 dynes/cm, as compared with ± 5 dynes/cm for the other alloy systems.

Many mathematical relations of a theoretical, semi-empirical and empirical nature have been developed, to match the results from surface tension experiments on solutions. Undoubtedly, the purpose of these equations is to help in analysing the nature of the liquid surface - its thickness, the configuration of the atoms, etc., - or to predict the surface tension of solutions from a knowledge of the surface tension of the pure components and their concentrations. Of these equations, probably the most widely used is the Gibbs adsorption equation. This is often written in the form

$$\Gamma_2 = - \frac{1}{RT} \left(\frac{\delta \gamma_M}{\delta \ln a_2} \right)_T, \quad \dots\dots\dots 6)$$

where Γ_2 = excess surface concentration of solute compared with the concentration in the bulk liquid.

γ_M = surface tension of the solution,

a_2 = activity of the solute in the bulk liquid, and

R and T are the gas constant and absolute temperature, respectively.

Expressed in this form, the equation embodies the assumption that the surface of the solution is composed of particles external to an imaginary boundary that separates them from the bulk liquid and is located in such a position that the excess of the solvent, Γ_1 , in the surface is zero.

When Γ_2 has been calculated it has the units of moles/cm². To this point the treatment of data is rigorous. But difficulties arise in translating this information into more meaningful terms. Assumptions must be made about the nature of the surface thickness and this is a hazardous step. In general, a monolayer is assumed and an area per atom

calculated. This area (in a two-dimensional liquid surface) is then usually compared with a value calculated from parameters of the three-dimensional solid. The results usually are not very illuminating⁽²⁵⁾.

In the Soviet literature, in particular, a number of relations of an empirical or semi-empirical nature have been derived, some of them from statistical or atomistic models. Korol'kov⁽¹⁾ and Semenchko⁽¹⁸⁾ discuss those extant up to about 1960. These equations often prove successful in a specific application but lack a general validity. The Theory of Generalized Moments⁽¹⁸⁾ and its application to amalgams are an example. Furthermore, the task of evaluating the worth of these relationships by the data of the authors is hampered by the knowledge that, with the exception of some work on mercury, all other data must embody errors deriving from the vapour transport effect to a greater or lesser extent.

In connection with their work on lead-tin and lead-indium alloys, Hoar and Melford⁽²⁶⁾ extended a thermodynamic approach developed by others to produce equations for purposes of predicting the surface tension of a solution from that of its pure components. They propose two pairs of equations, the first set of which are stated to be exact and the second to be based on the assumption of a regular solution⁽²⁷⁾. Respectively, these equations are:

$$\gamma_M = \frac{A_1}{\bar{A}_1} \gamma_1 + \frac{RT \ln a_1'}{\bar{A}_1 a_1} = \frac{A_2}{\bar{A}_2} \gamma_2 + \frac{RT \ln a_2'}{\bar{A}_2 a_2} \dots\dots\dots 7)$$

$$\text{and } \gamma_M = \gamma_1 + \frac{RT \ln x_1'}{A_1 x_1} + \frac{W}{A_1} (l' x_2' - x_2^2) \dots\dots\dots 8)$$

$$= \gamma_2 + \frac{RT \ln x_2'}{A_2 x_2} + \frac{W}{A_2} (l' x_1' - x_1^2),$$

where γ_1, γ_2 = surface tensions of the pure components 1, 2,

x_1, x_2 = mole fractions of components 1, 2 in the bulk liquid,

x_1', x_2' = mole fractions of components 1, 2 in the surface,

a_1, a_2 = activities of components 1, 2 in the bulk liquid,

a_1', a_2' = activities of components 1, 2 in the surface,

A_1, A_2 = molar surface areas of components 1, 2,

\bar{A}_1, \bar{A}_2 = partial molar surface areas of components 1, 2,

$W = \frac{H^M}{x_1 x_2}$ = and H^M = heat of mixing of the solution, and

$l' = 0.5 - 0.75$ is a factor to allow for the difference in surface and bulk coordination numbers.

The Gibbs adsorption equation must be invoked to calculate x_1' and x_2' , and the usefulness of the equations is debilitated by the need for assumptions about surface thickness. Nevertheless, a thermodynamic treatment seems inherently sound and worthy of effort to extend it further in order to embrace solutions which depart widely from Raoult's Law.

Of the systems studied in this program, only for zinc-lead alloys are thermodynamic data of sufficient accuracy available to justify an attempt to compare values calculated from Hoar and Melford's equations with

experimental results. Unfortunately, as noted before, the zinc-lead system exhibits a highly positive deviation from ideality. Thus, the entropy of mixing is non-ideal, alloys do not conform with the assumption of a regular solution, and it is found that Equations 8) do not vary sharply enough with change in x_2 to produce even semi-quantitative agreement with Figure 18. Furthermore, difficulties arise with Equations 7) concerning the interpretation and calculation of a_2' which largely negate the value of the equations in practice.

In an effort to match the form of the surface tension versus lead concentration curve in Figure 18, attempts were made to develop an equation for predicting the surface tension of a solution from that of its components. In doing so, forms involving molar quantities, as in Hoar and Melford's treatment, were avoided in order to avert the accompanying necessity for assumptions concerning surface thickness. Terms, therefore, were restricted to intensive quantities or pure numbers. Because of the pressure of program commitments very little time could be given to this work, and the result is a simple model which can only be considered a partial success.

If it is assumed that, whatever the differences between the surface and the bulk in the equilibrium concentrations of the components in a binary solution, the surface and bulk activities are the same, then it seems reasonable to suppose that the thermodynamic behaviour of each component in the surface is controlled by its activity in the body of the liquid. If all

interactions between the components are accounted for by the magnitude of the value of their respective activities, then the surface tension of a solution should simply be the sum of the surface tensions of the pure components weighted by their respective activities, viz:

$$\gamma_M = \frac{a_1 \gamma_1 + a_2 \gamma_2}{a_1 + a_2} . \quad \dots\dots\dots 9)$$

Equation 9) has approximately the right form, which Equations 8) do not, but it gives results that are consistently high by about 100 dynes/cm. Agreement with experiment, therefore, is only semi-quantitative and the model is probably incomplete, since it seems difficult to believe that it is basically incorrect.

Indeed, qualitatively, we expect that in small concentrations the influence of a solute on the surface tension of a solution will be proportional to the difference between its surface tension and that of the solvent and that, additionally, its effects will be conditioned by the magnitude of its activity in the solution. Therefore, solutes with smaller surface tensions than those of the solvent, and suffering positive deviations from ideality ($f_2 > 1$) when dissolved, will significantly reduce the surface tension of a solution. Solutes with higher surface tensions than the solvents or solutes undergoing negative deviations ($f_2 < 1$) in solutions, in small amounts will not have much effect on surface tension.

All the systems investigated conform to these ideas. Lead has the lowest surface tension (~ 450 dynes/cm) and the greatest positive

deviation from Raoult's Law ($f_{\text{Pb}} \approx 300$). Lead, therefore, strongly depresses the surface tension of zinc. Tin, too, has a lower surface tension than that of zinc (~ 500 dynes/cm) but, from inspection of the binary phase diagram, is not expected to deviate appreciably from an ideal solution and thus its effect on the surface tension of zinc is not as strong as that of lead.

On the other hand, both aluminum (~ 900 dynes/cm) and copper (~ 1300 dynes/cm) have higher surface tensions than that of zinc. Existing data⁽²³⁾ indicate that any significant departure from ideality, in the case of aluminum, is not expected; but that in zinc-copper alloys, copper would be expected to show a negative deviation. Hence, we find that in small concentrations, aluminum does not have any effect at all on the surface tension of zinc, whereas the much higher surface tension of copper prevails over the attenuating effect of a negative deviation.

SUMMARY AND CONCLUSIONS

The surface tension of zinc and some zinc alloys has been determined by the sessile drop method in a program emphasizing detailed experimental care. The surface tension of the pure metal was measured over a range of temperature from the melting point (419.6°C) to 540°C , while that of the alloys was measured at a constant temperature of 435°C .

At the melting point the surface tension of zinc is:

1) 99.99+% Zn	-	760.5 dynes/cm	\pm 5 dynes/cm
2) 99.999+% Zn	-	763.0	" "
3) 99.9999% Zn	-	769.5	" "

From experiments carried out in a closed, isothermal cell, the temperature coefficient of the surface tension $(\frac{\delta\gamma}{\delta T})_{P,n}$ of zinc was found to be, not negative, but positive. A positive temperature coefficient reflects a negative surface excess of entropy which, in turn, indicates a greater degree of order in the surface than in the body of the liquid. The driving force for this state is the minimization of surface free energy which occurs atomistically through a systematic displacement of the electromagnetic field in a direction normal to the liquid surface and by close atomic packing in the plane of the surface. The straight-line behaviour of surface tension with respect to temperature indicates a zero superficial specific heat, which supports the general conclusion of greater order in the surface than in the bulk by implying that the energy of surface formation is stored in the surface in some configurational way.

It is expected that with increasing temperature the degree of surface order will decrease, the surface zone will progressively thicken, and the surface tension will pass through a maximum and rapidly become zero as the critical temperature is approached.

By deliberately inducing continuous vapourization, a temperature coefficient of surface tension with a negative slope can be produced. To date, the effect of vapour transport on surface tension has not been recognized by others as an important variable, and with few exceptions it

is to be expected that all previous work will embody errors from its presence to a greater or lesser extent.

Continuous vapourization exerts a twofold effect on the temperature coefficient curve. Free surface energy (surface tension) tends to increase because thermodynamic equilibrium no longer prevails. At the same time, as surface order decreases, surface entropy increases in a manner proportional to temperature. Thus, the change from a positive to a negative slope is first observed at higher temperatures.

In the alloy program, the effects of aluminum, copper, lead and tin on the surface tension of 99.999+% Zn have been determined and the data have been corrected for vapour transport effect. The findings are that:

- 1) in concentrations up to about 2.75%, aluminum has no effect on the surface tension of zinc;
- 2) up to about 1.6%, copper increases the surface tension of zinc about 2%;
- 3) lead has an appreciable effect on the surface tension of zinc, 1% lead reducing the surface tension more than 40%; and
- 4) in amounts up to 1.1%, tin reduces the surface tension of zinc by about 7%.

Qualitatively, the results agree with the prediction that the effect of a solute will be proportional to the difference between its surface tension and that of the solvent, conditioned by the magnitude of the solute activity in the solution. Thus, solutes with much smaller surface tensions than the solvent, and suffering positive deviations from Raoult's Law, will strongly

reduce surface tension when in solution. Such, for example, is the case for lead dissolved in zinc.

For zinc-lead alloys, attempts were made to fit results to existing models for liquid solutions. Unfortunately, the zinc-lead system exhibits a very large positive deviation from Raoult's Law ($f_{Pb} \approx 300$). Thus, the equations of Hoar and Melford were not suitable in this instance. Attempts to derive another equation, avoiding assumptions concerning surface thickness, were only partially successful. The simple relation devised predicted a surface tension versus composition curve of about the right form, but was approximately 100 dynes/cm too high.

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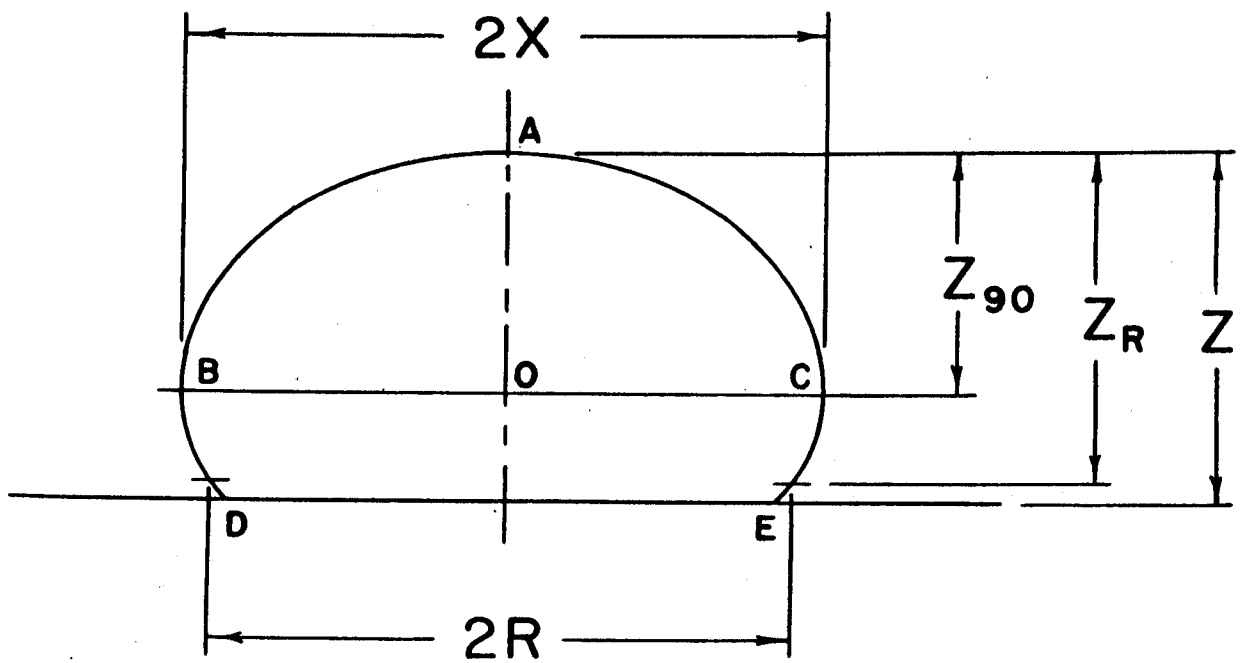


Figure 1. The Sessile Drop.

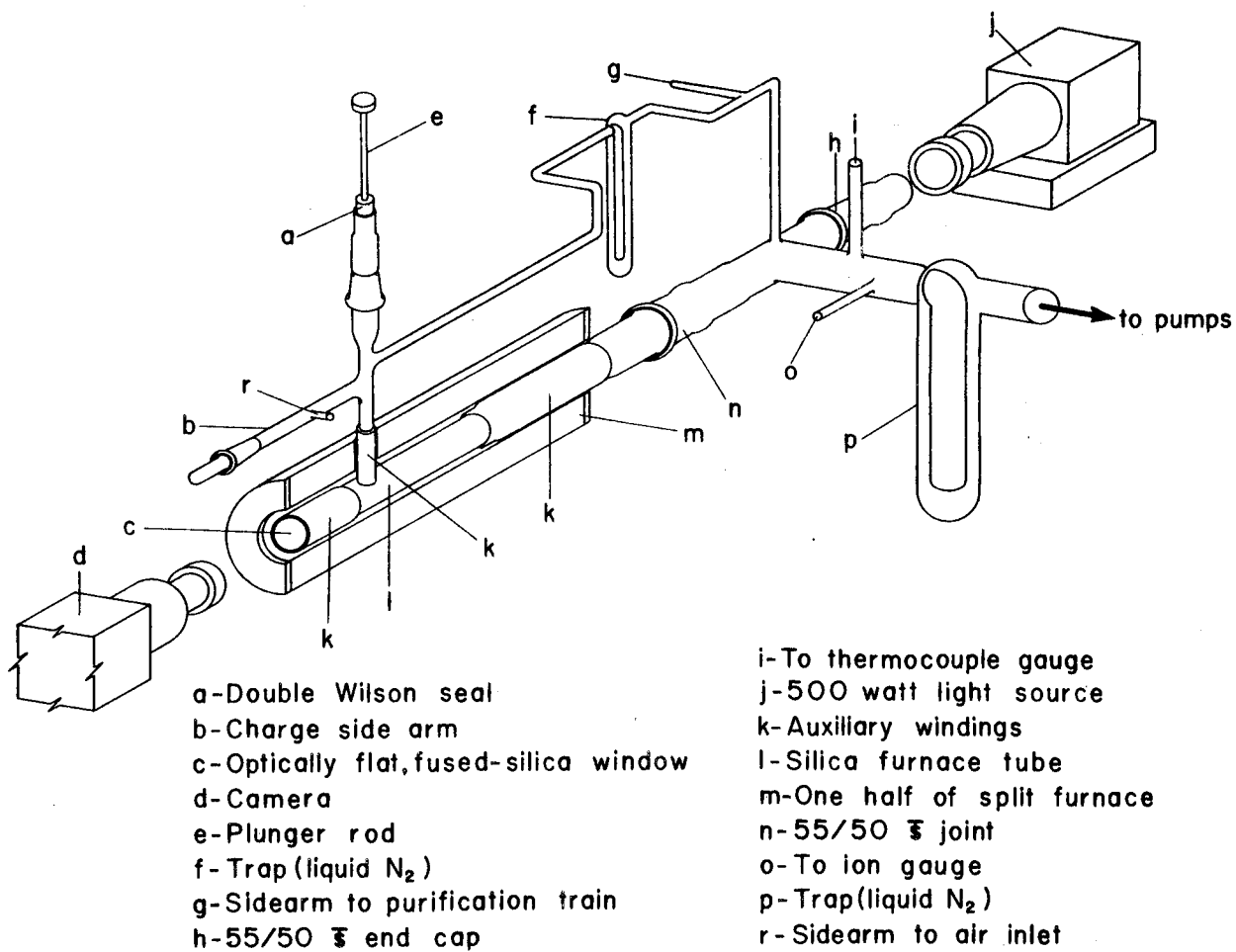


Figure 2. Schematic Layout of Sessile Drop Apparatus .

- a-Fused silica stopper.
- b-Iron ring attached around stopper.
- c-Fused silica window sealed to furnace tube.
- d-Tube to introduce charge to furnace tube.
- e-Fused silica annulus sealed to furnace tube.
- f-Thermocouple protection tube and stop.
- g-Stainless steel boat.
- h-Polished graphite plaque.
- i-Auxiliary heater windings.
- j-Fused silica furnace tube 35mm. diameter.
- k-Graphite liner.
- l-Graphite plunger.
- m-Plunger rod.
- n-Zinc charge.
- o-Filter assembly, comprising silica wool between two graphite filters.

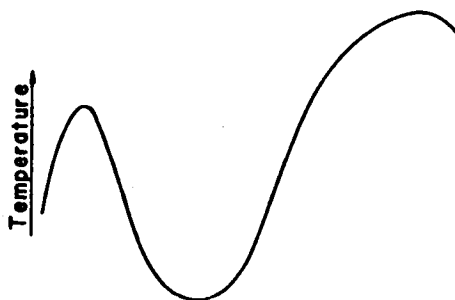
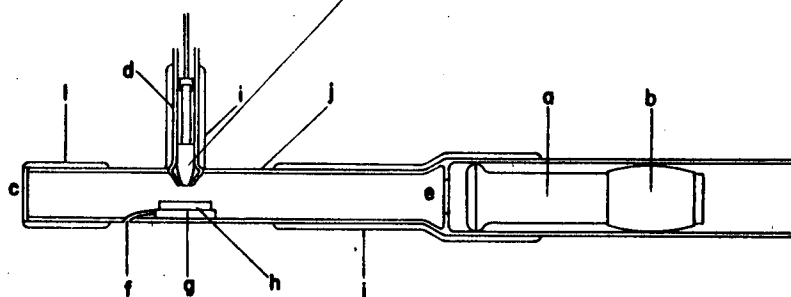
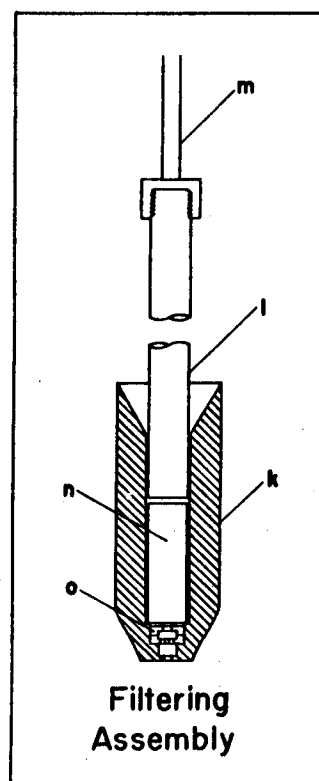


Figure 3. Furnace Tube Details 1.

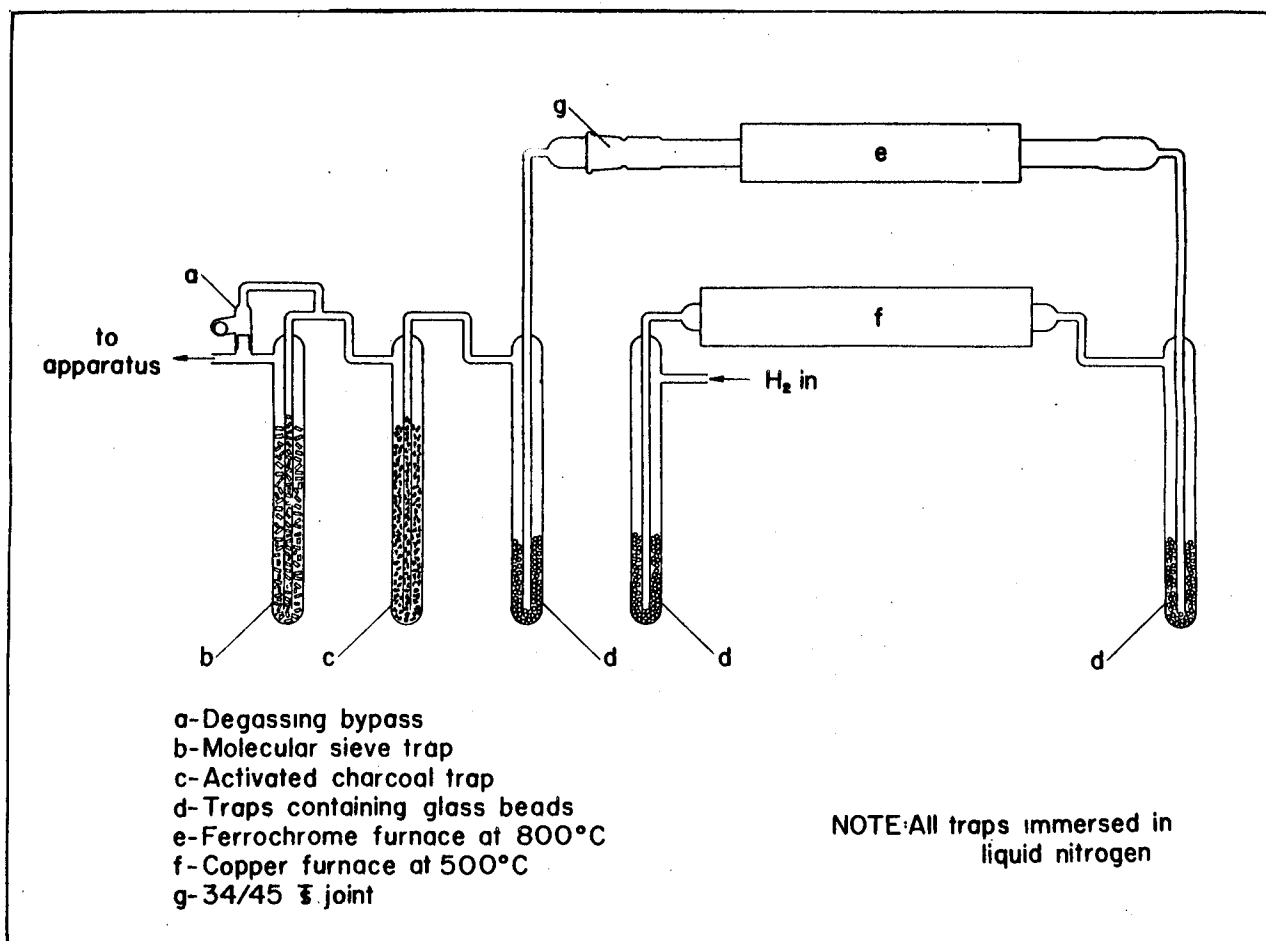


Figure 4. Schematic Layout of Hydrogen Purification Train.

- c-Fused silica window sealed to furnace tube
- d-Tube to introduce charge to furnace tube
- e-Fused silica annulus sealed to furnace tube
- f-Thermocouple protection tube and stop
- i-Auxiliary heater windings
- j-Fused silica furnace tube 35mm. diameter
- k-Graphite liner
- l-Graphite plunger
- p-Weighted stainless steel cover embracing 1mm. thick fused silica
- q-Fused silica optical cell
- r-Graphite plaque
- s-Stainless steel boat
- t-Pusher

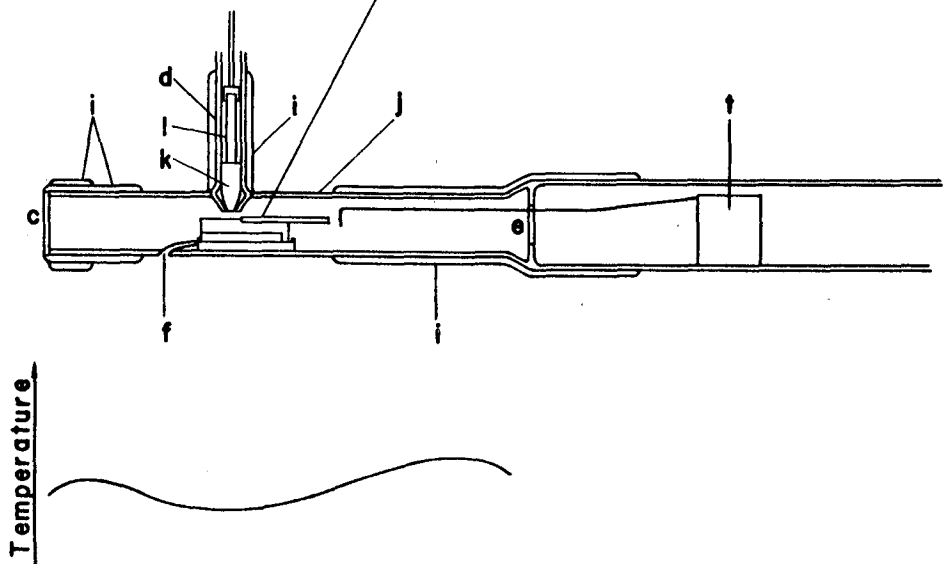
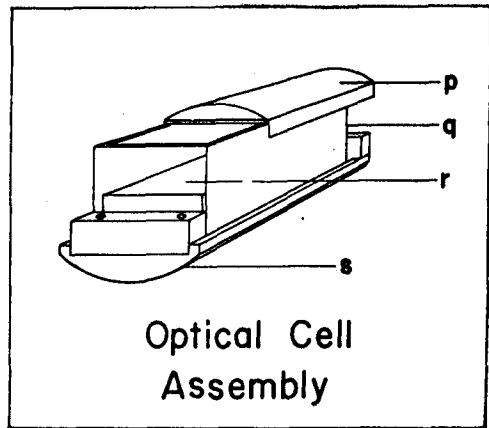


Figure 5. Furnace Tube Details 2.

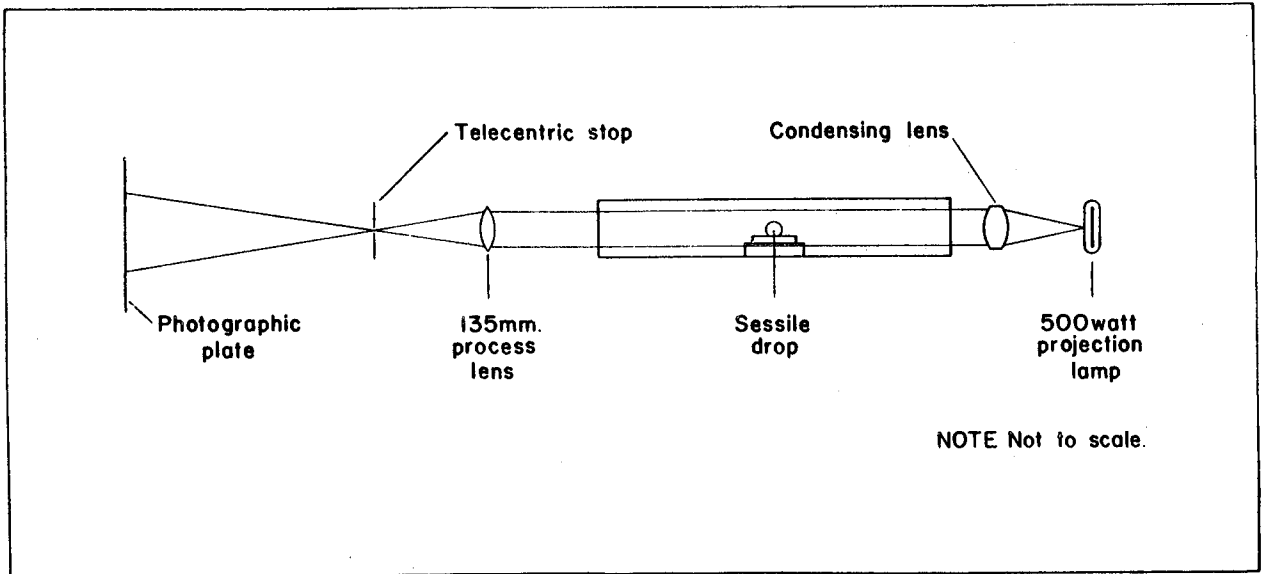


Figure 6. Optical Arrangement of Sessile Drop Apparatus .

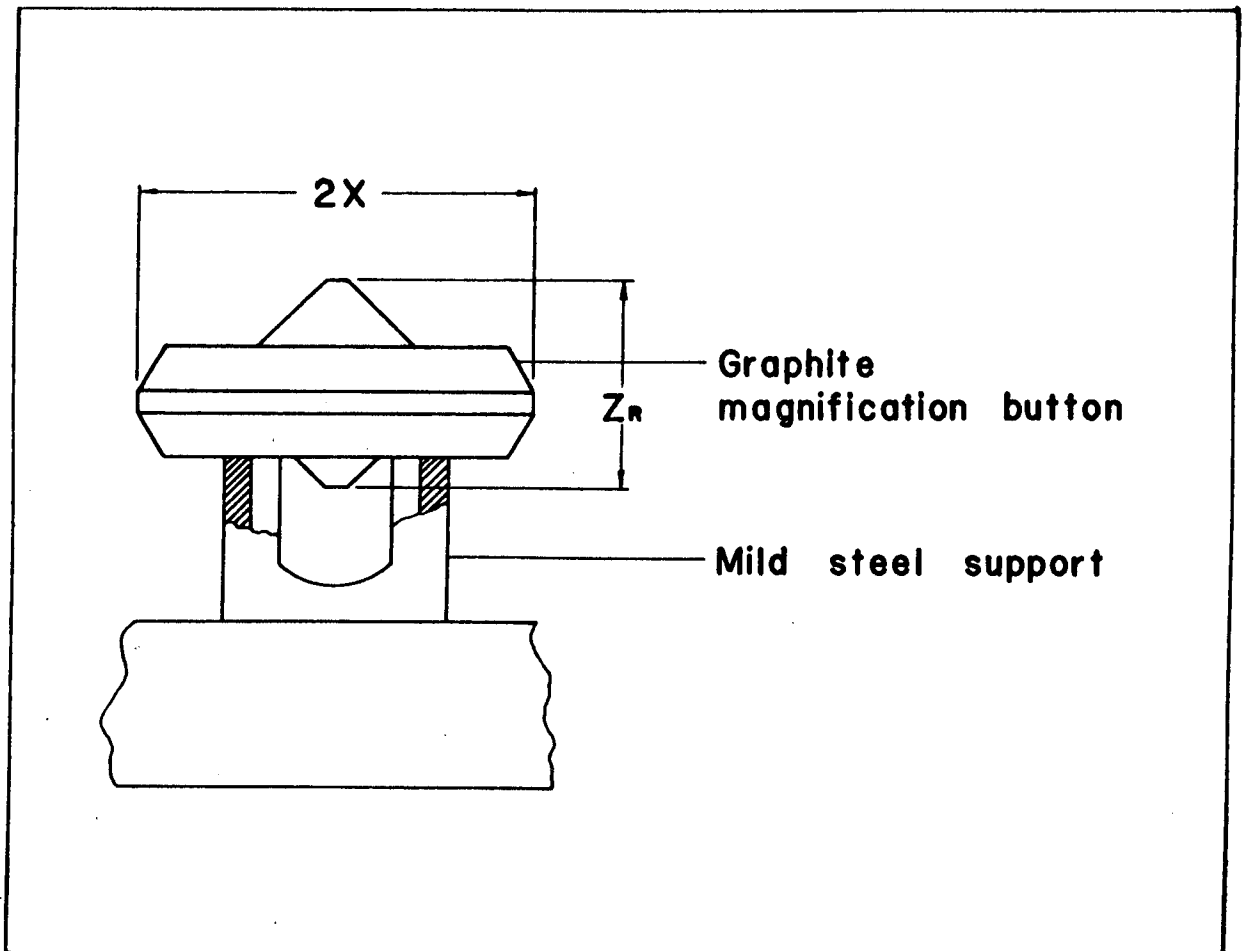


Figure 7. Magnification Determination Button.

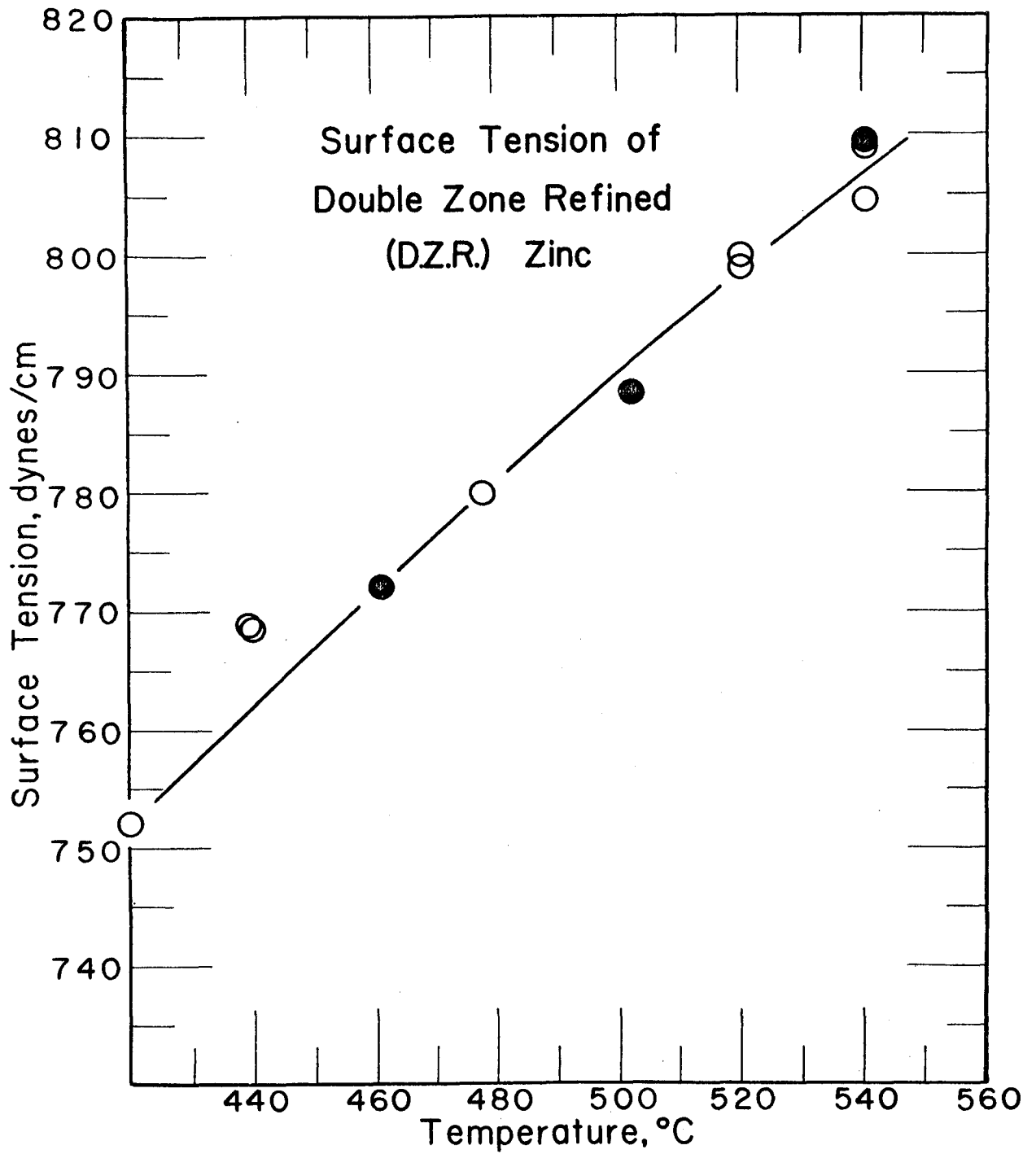


Figure 8. Surface Tension of Double Zone Refined (D.Z.R.) Zinc.

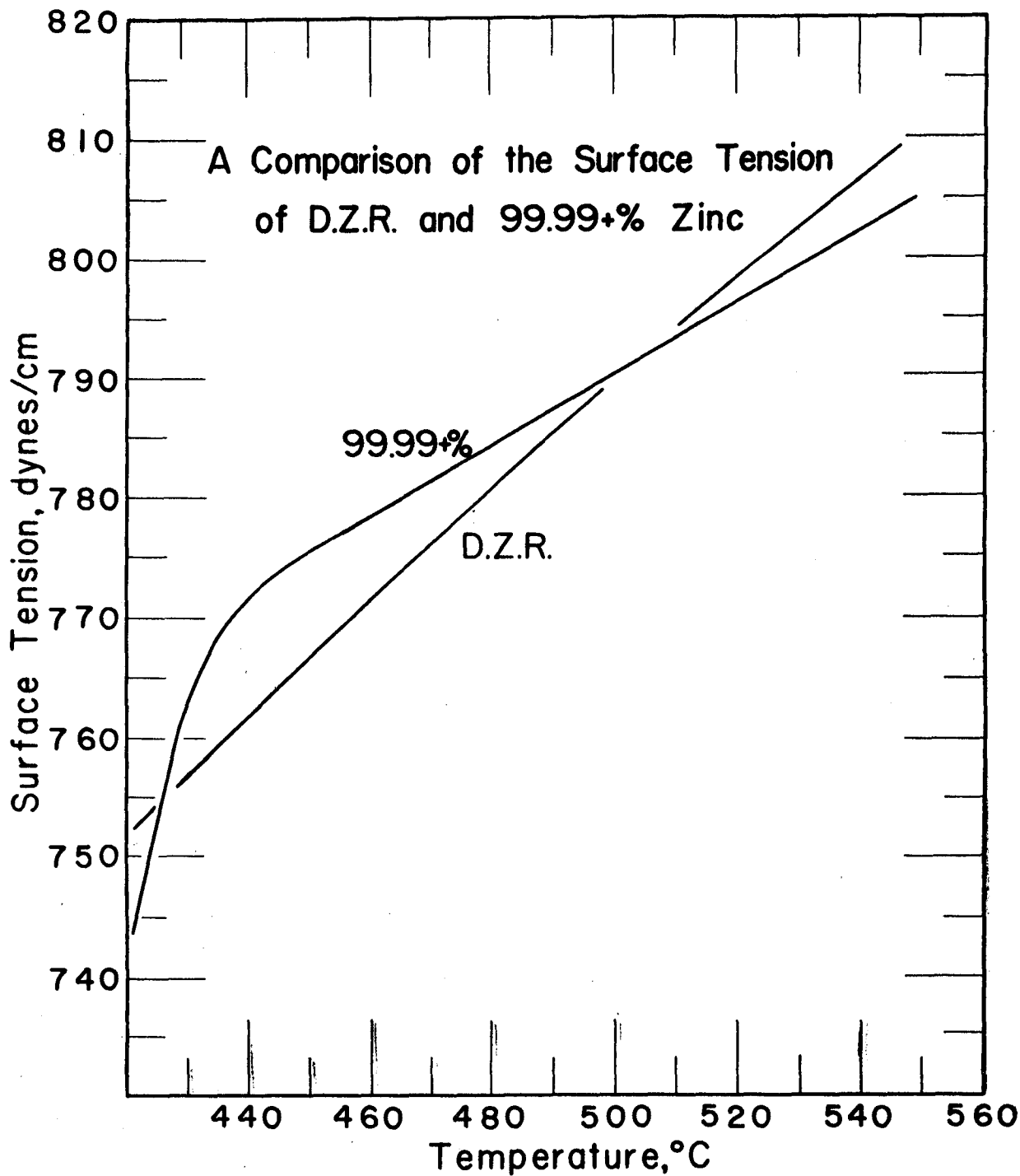


Figure 9. A Comparison of the Surface Tension of D.Z.R. and 99.99% Zinc.

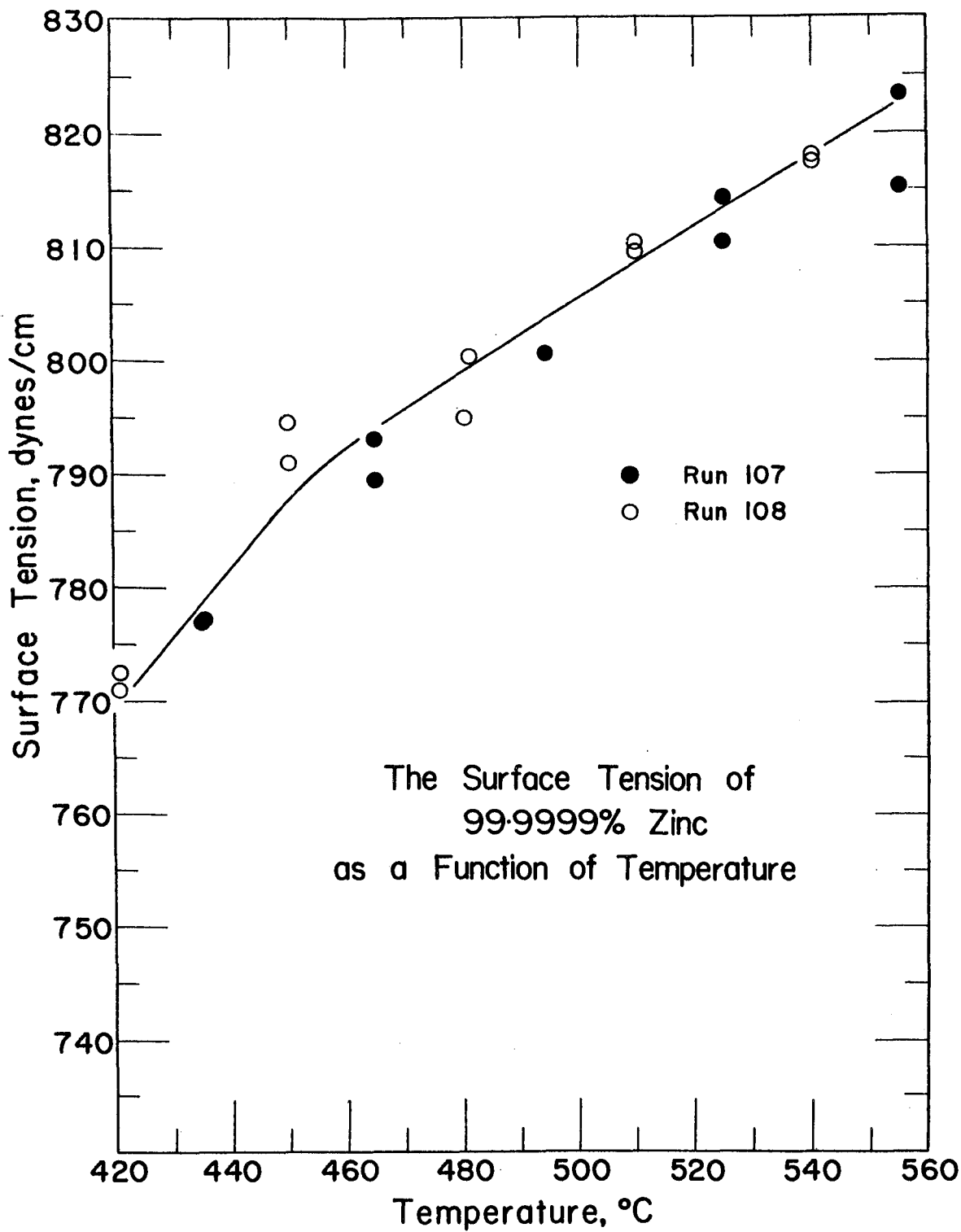


Figure 10. The Surface Tension of 99.9999% Zinc as a Function of Temperature.

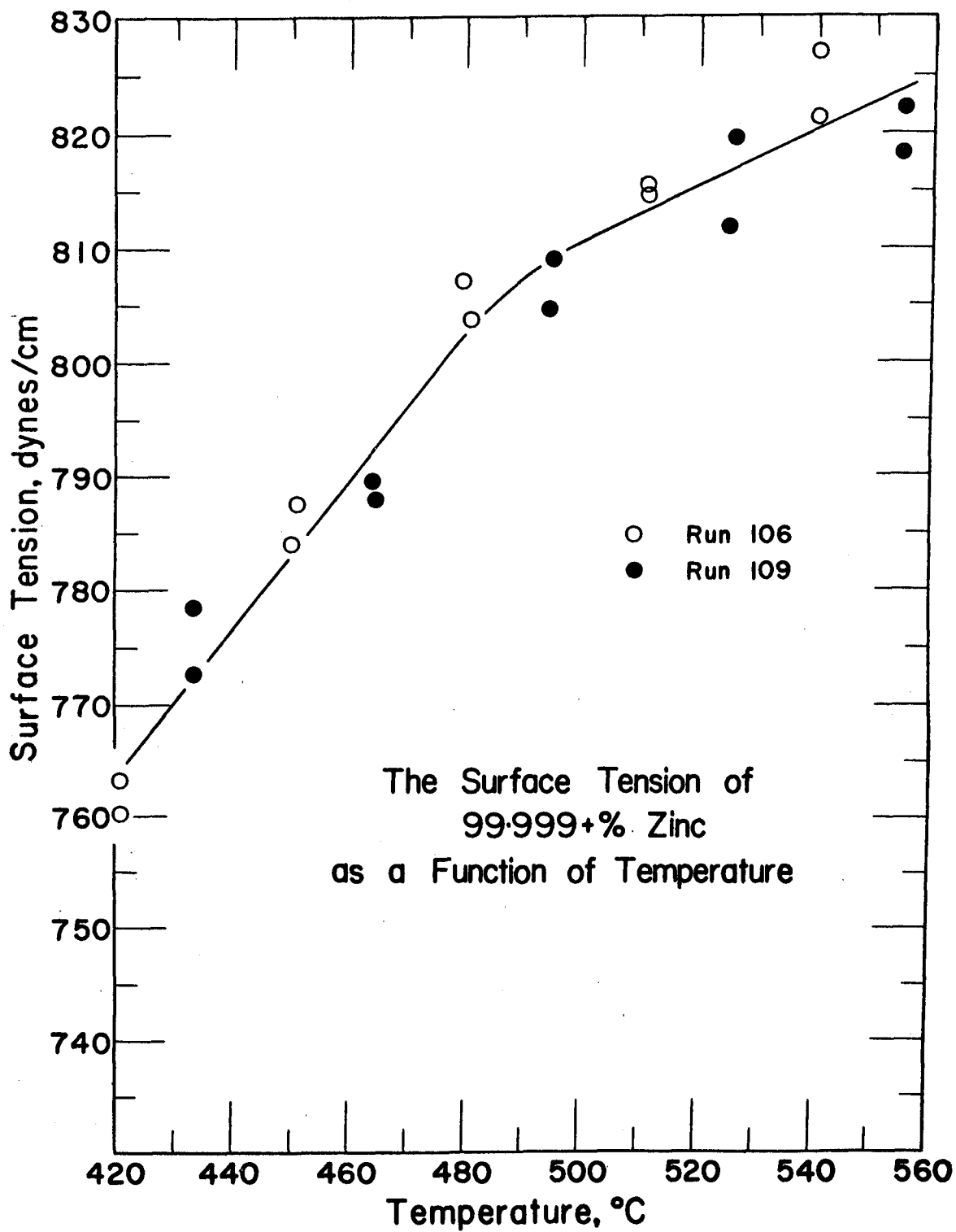


Figure 11. The Surface Tension of 99.999+% Zinc as a Function of Temperature.

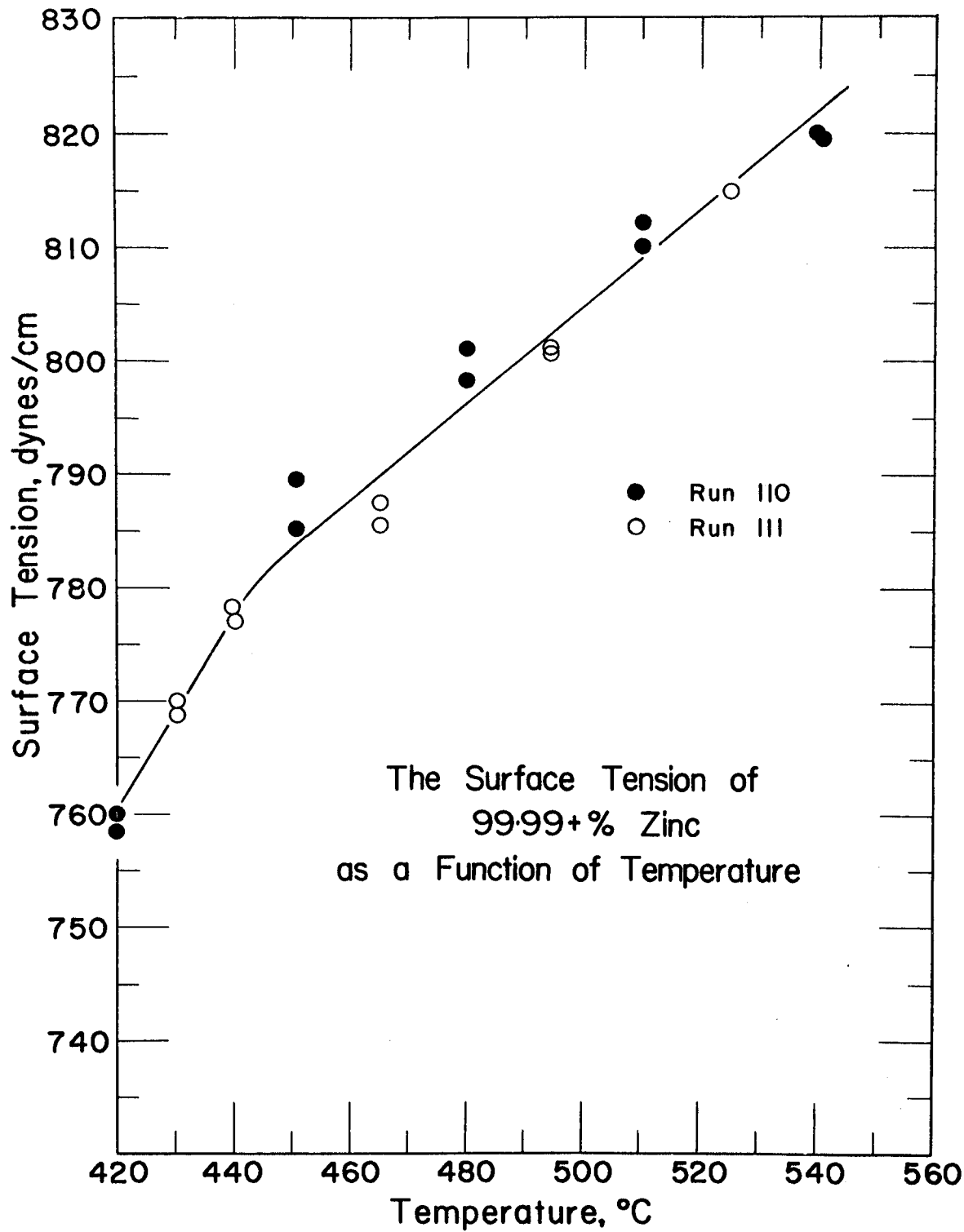


Figure 12. The Surface Tension of 99.99+% Zinc as a Function of Temperature.

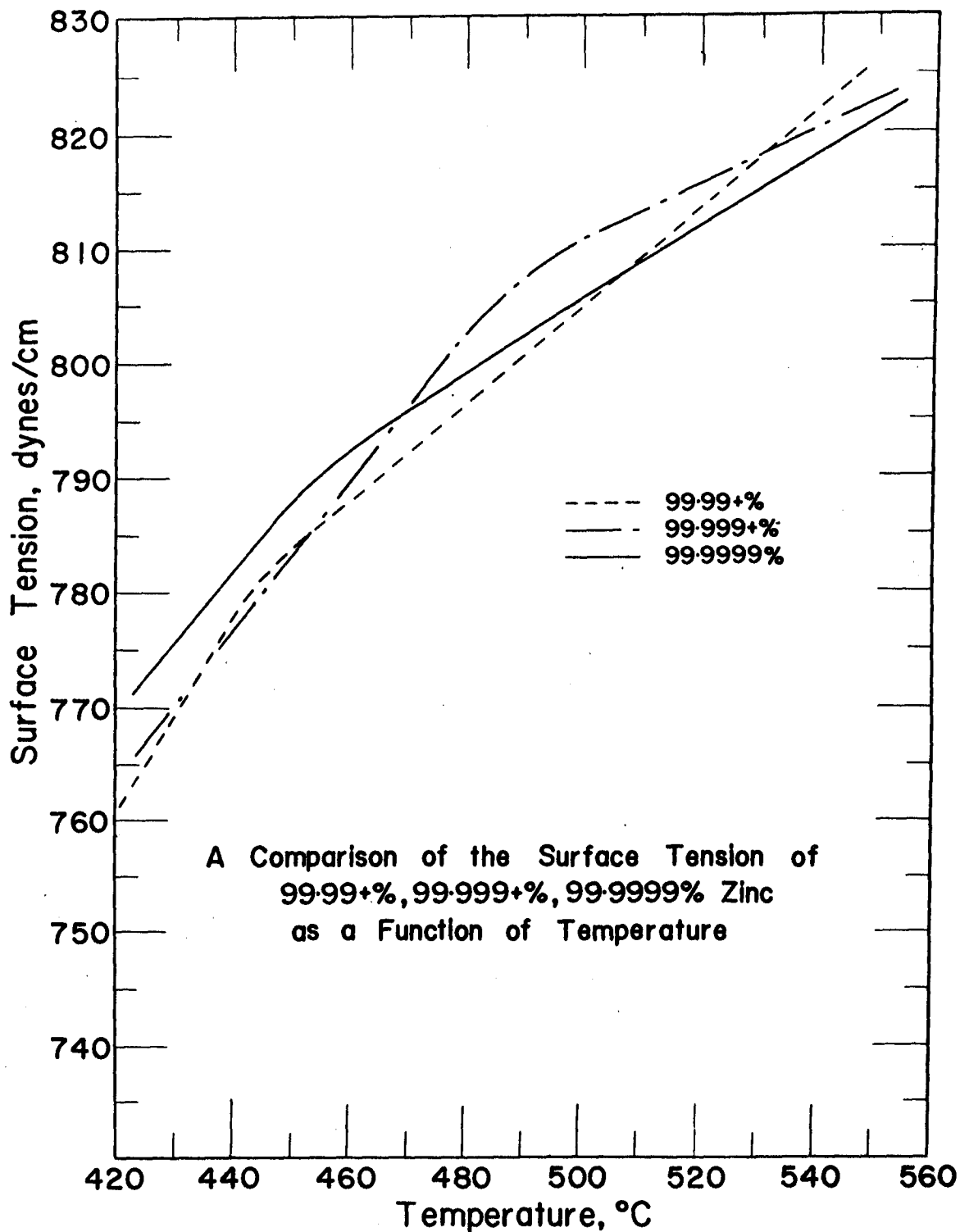


Figure 13. A Comparison of the Surface Tension of 99.99+%, 99.999+%, and 99.9999% Zinc as a Function of Temperature.

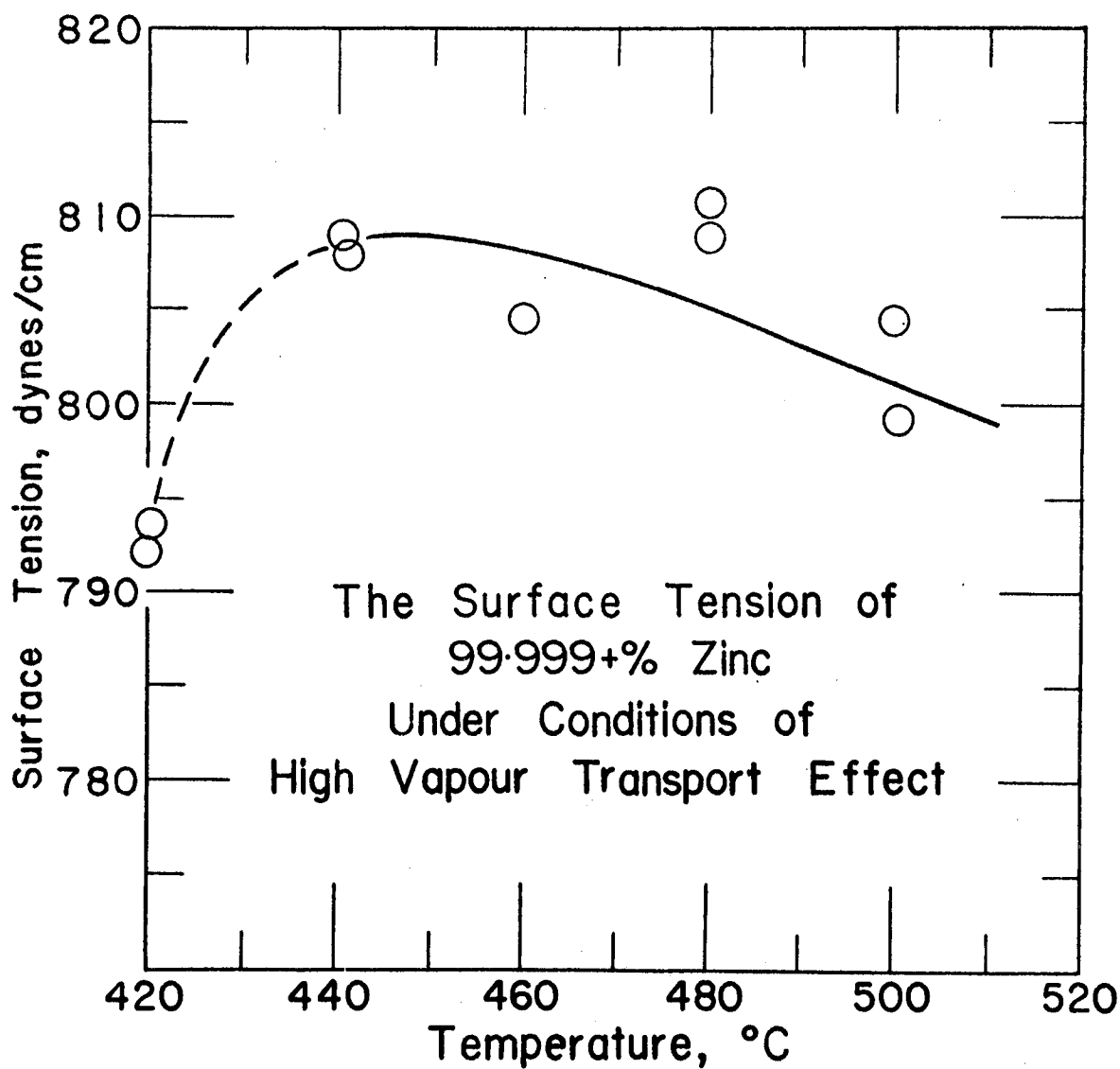


Figure 14 The Surface Tension of 99.999+% Zinc under Conditions of High Vapour Transport Effect.

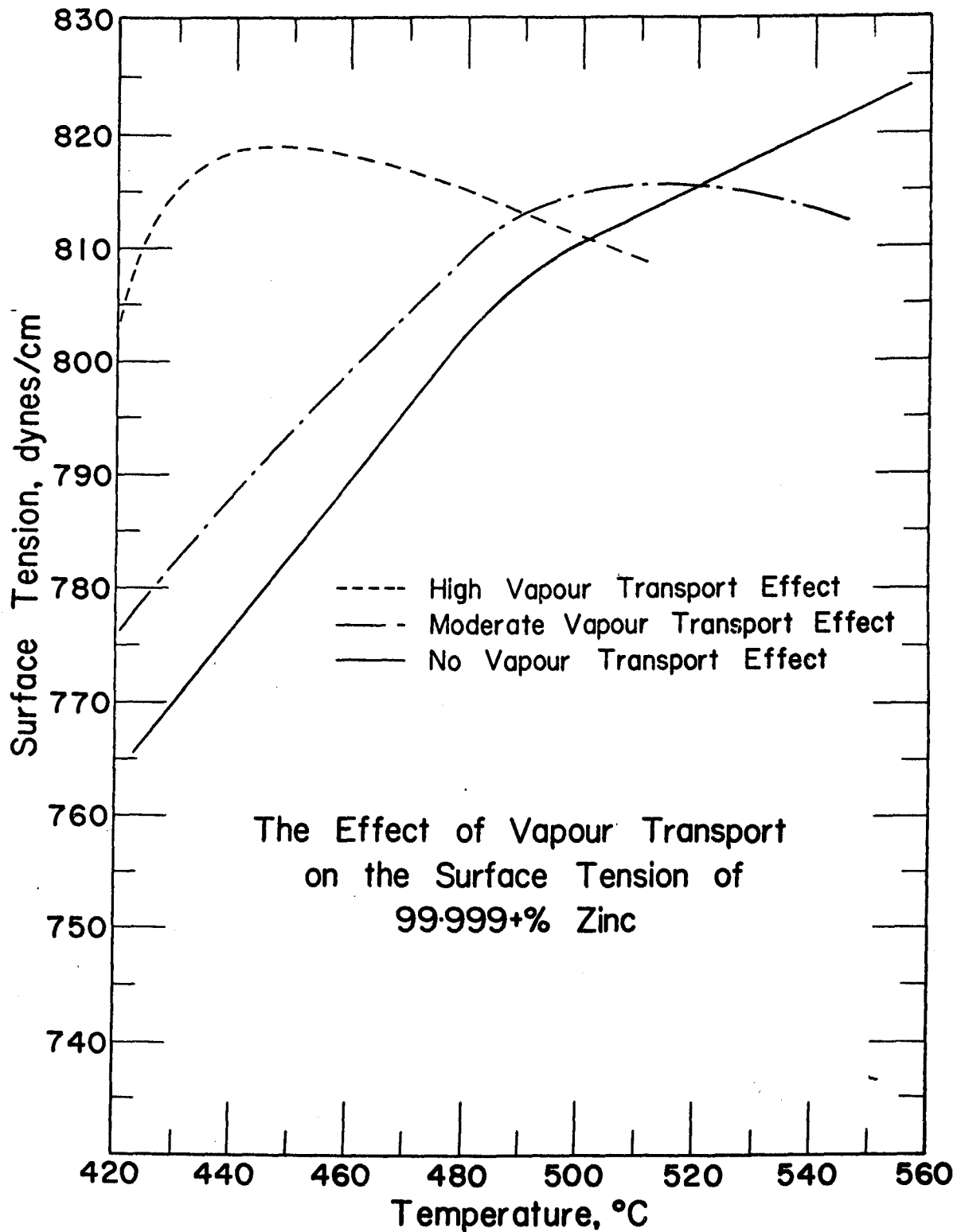


Figure 15. The Effect of Vapour Transport on the Surface Tension of 99.999+% Zinc.

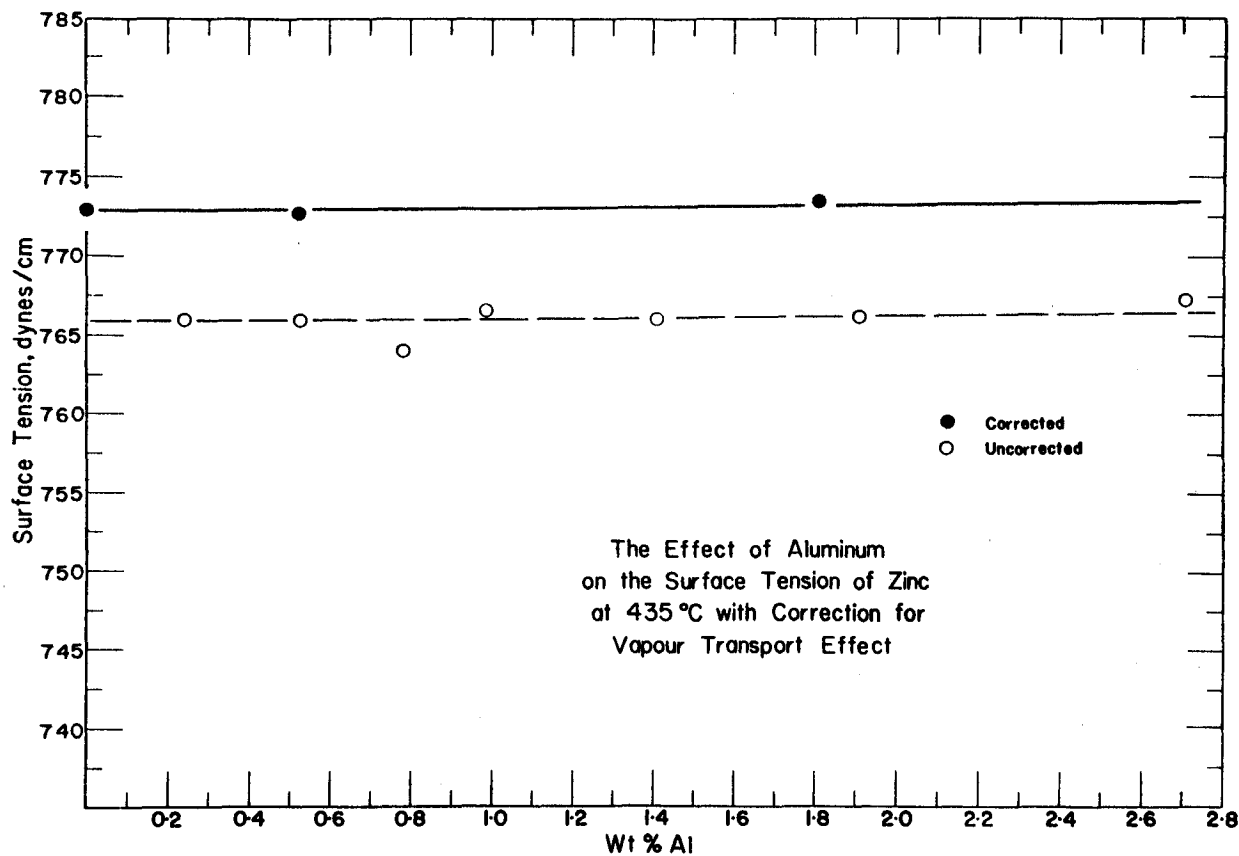


Figure 16. The Effect of Aluminum on the Surface Tension of Zinc at 435°C, with Correction for Vapour Transport Effect.

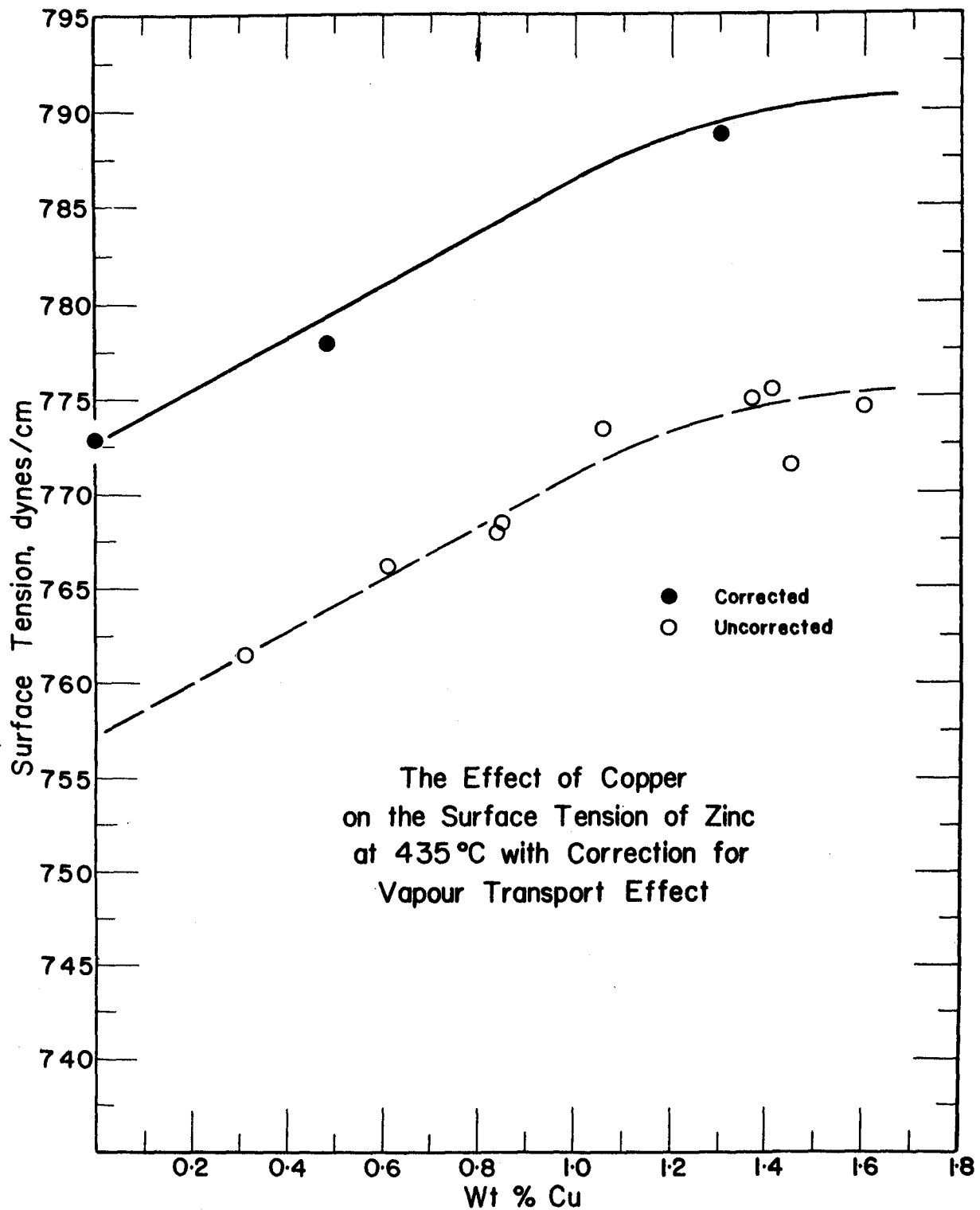


Figure 17. The Effect of Copper on the Surface Tension of Zinc at 435°C, with Correction for Vapour Transport Effect.

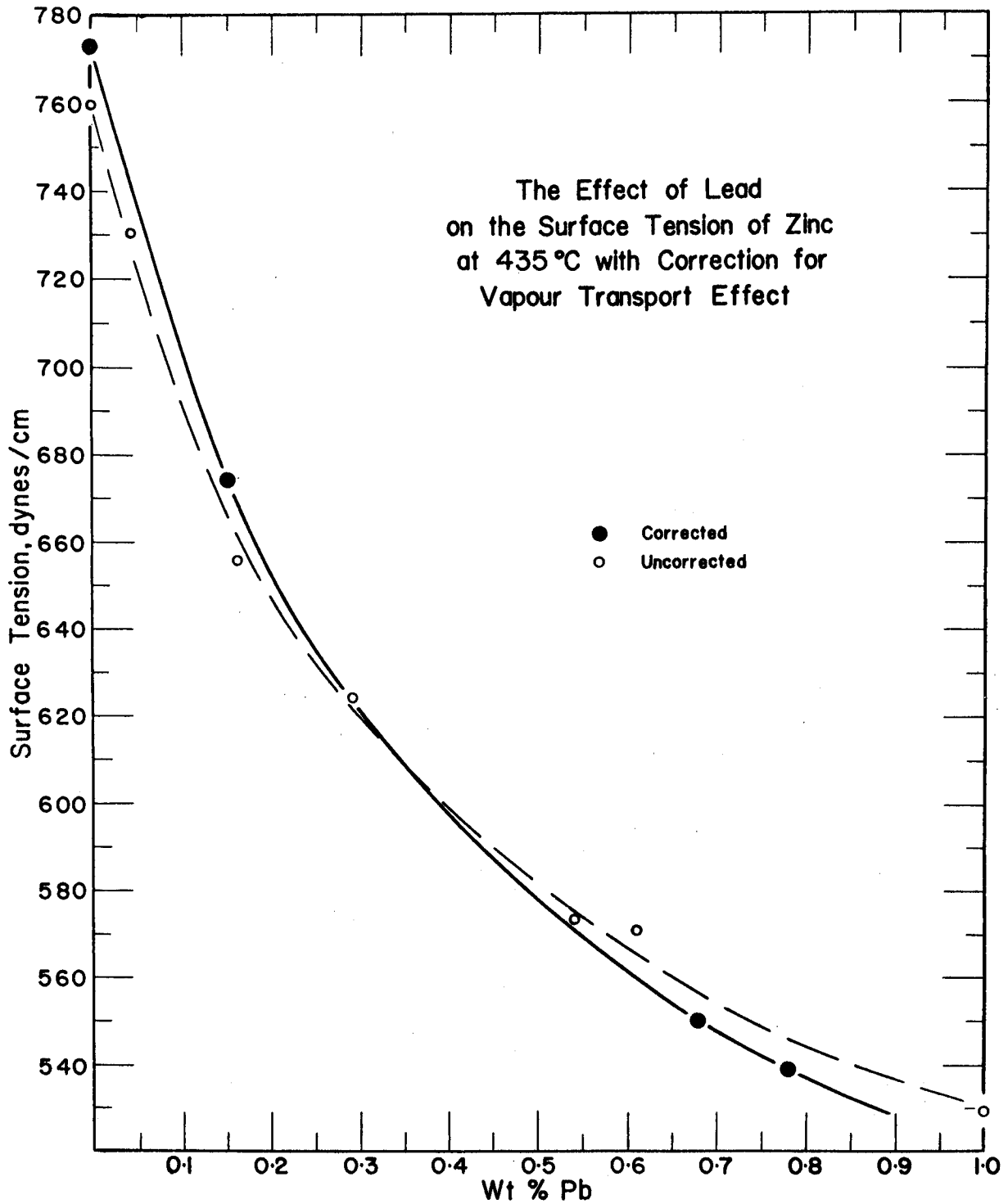


Figure 18. The Effect of Lead on the Surface Tension of Zinc at 435°C, with Correction for Vapour Transport Effect.

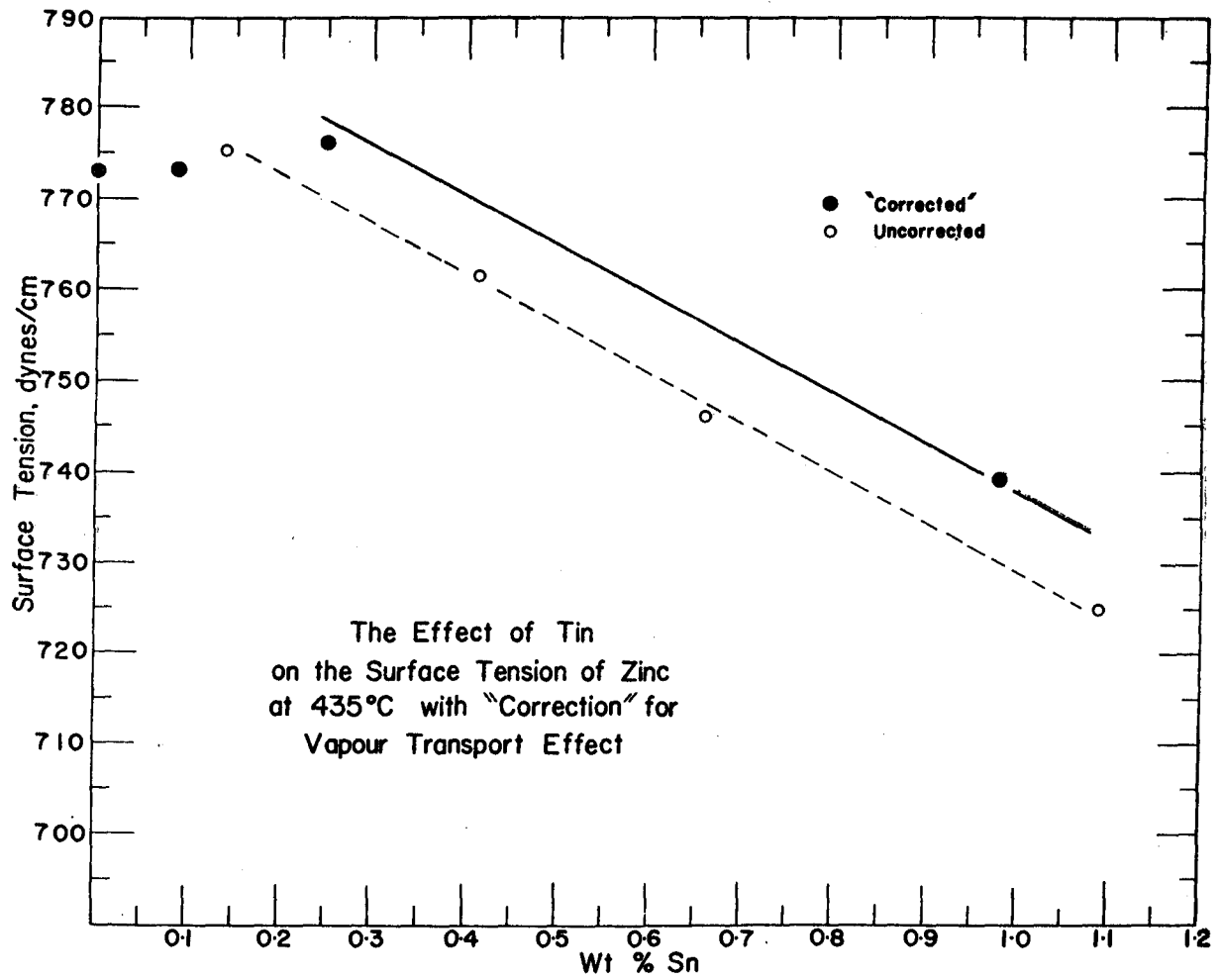


Figure 19. The Effect of Tin on the Surface Tension of Zinc at 435°C, with 'Correction' for Vapour Transport Effect.

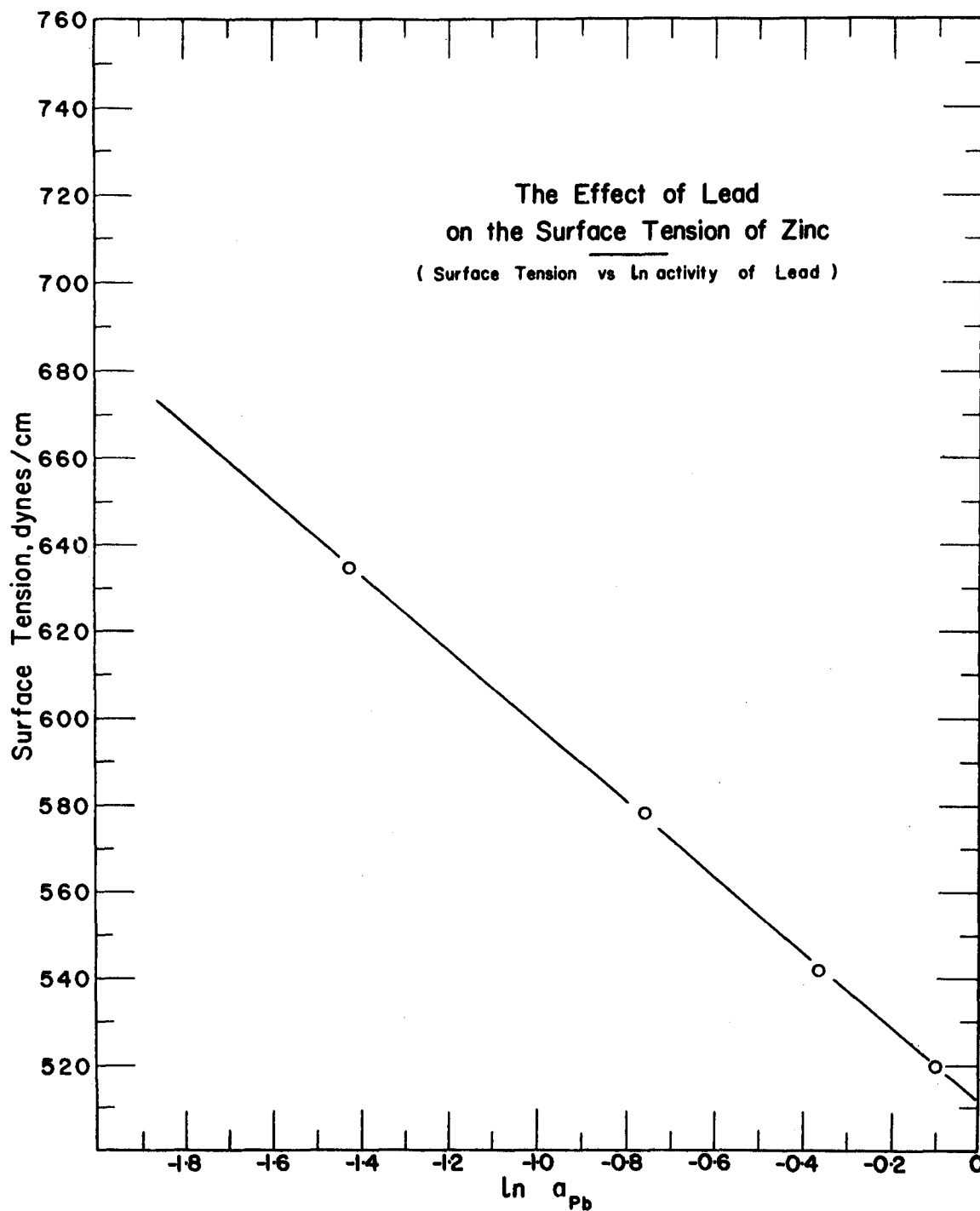


Figure 20. The Effect of Lead on the Surface Tension of Zinc.