SURFACE TENSION MEASUREMENTS ON IRON
AND IRON-OXYGEN ALLOYS

SURFACE TENSION MEASUREMENTS ON IRON AND IRON-OXYGEN ALLOYS BY THE OSCILLATING DROP TECHNIQUE

By

RAM MURARKA, B.Tech.

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Engineering

McMaster University
October, 1971

MASTER OF ENGINEERING (1971)
(Metallurgy)

McMaster University
Hamilton, Ontario

TITLE: Surface Tension Measurements on Iron and Iron-Oxygen Alloys by the Oscillating Drop Technique

AUTHOR: Ram Niranjan Murarka, B.Tech. (I.I.T., Bombay, India)

SUPERVISOR: Professor W-K. Lu

NUMBER OF PAGES: (vi), 50.

SCOPE AND CONTENTS:

The oscillating drop technique was used to measure the surface tension of pure liquid iron and its oxygen alloys in the range 0 to 600 ppm oxygen. An attempt has been made to investigate how these measurements can be used for future kinetic studies.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. W-K. Lu and Dr. A. E. Hamielec for their supervision and for their helpful and patient assistance during the course of this study.

The author wishes also to express his appreciation of the generous financial support which was provided by the American Iron and Steel Institute. Grateful acknowledgments are due to the technical staff and graduate students of the Department of Metallurgy and Materials Science at McMaster whose help has been invaluable.

Many thanks are given to Miss Lydea de Jong for the excellent typing of this thesis and to Mr. M. vanOosten and Mr. T. Bryner for their assistance with the technical drawings and photographs.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Surface tension of liquid metals is strongly affected by small amounts of adsorbed oxygen or sulphur. It should therefore change appreciably with time during the oxidation of iron and provide a convenient means of following the reaction. Equilibrium values of surface tension at various oxygen levels could be used to estimate adsorbed oxygen in a kinetic experiment provided the surface tension as a function of time is measurable.

Fortunately a suitable dynamic method of surface tension measurement was recently developed at McMaster University(1). The method was originally used with iron and nickel in a reducing atmosphere (6% hydrogen - balance helium)(1). Later, surface tension was measured as a function of oxygen concentration under equilibrium conditions. The oxygen potential was changed by changing the water vapor-hydrogen ratio in a hydrogen-water vapor mixture. Surprisingly, the measured surface tensions corresponding to oxygen contents less than ten parts per million were much higher than those measured by other workers. This suggested and led to the measurement of surface tension of pure iron (at an undetectable oxygen level) in pure hydrogen at various temperatures.

The work was repeated in 6% hydrogen-balance helium mixture making sure that there was no oxygen in the metal. This was accomplished by first purifying the metal in hydrogen for a sufficiently long time and then switching over to the dilute hydrogen-helium mixture. Good agreement was found indicating that helium had no effect on surface tension.

A literature review is presented describing previous measurements of surface tension of liquid iron and showing the effect of surface-active elements. The theory of the oscillating drop technique is briefly described while the experimental apparatus and technique are given in detail with results of experiments for pure iron and iron-oxygen alloys at various temperatures being reported. The experimental errors are evaluated and the measured values of surface tension compared to previously measured values.

Finally, proposed kinetics and mechanism studies of gas-metal (liquid) reactions are discussed in the last section.

CHAPTER II

LITERATURE SURVEY

Methods Used for Measurement of Surface Tension

Most studies on effect of surface active elements on surface tension of liquid metals have been with static methods, viz., maximum bubble pressure method and drop shape method which includes sessile drop and pendant drop methods. The application of static methods with liquid metals has been thoroughly reviewed by White(2) and Semenchenko(3).

Maximum bubble pressure method has certain inherent limitations. With high temperature applications, as with liquid iron, the refractory-tube must be quite thick giving a significant error in the surface tension measurements.

Drop shape methods are also somewhat limited. Accurate geometrical measurements of the drop shape is difficult. The empirical formulae developed in conjunction with Bashforth and Adams tables are very helpful. Any method which involves contacting the metal with a foreign solid surface cannot be used at high temperatures because of contamination of the melt by the supporting material. Most of the previous work on the effect of surface active elements on surface tension of liquid iron has been carried out with static methods of which the sessile drop shape method has been the most popular.

Kozakevitch and Urbain(4) studied the effect of O, S, Se and Te on surface tension of molten iron by the sessile drop technique. Halden and Kingery(5) also studied the effect of C, N, O and S; Wilhelm vor dem Esche and Oscar Peter(6), the effect of O and S, and Kingery(7), the effect of Se and Te.

Some dynamic methods of surface tension measurement are described by Fraser(8). Dynamic methods have some disadvantages over the static methods. Before the development of high speed cinematography, the experimental measurements were highly inaccurate. The dynamic oscillating drop technique(1) employs high speed cinematography. This combined with the advantages of minimal contamination, instantaneous measurement and speed provides a superior method of surface tension measurement. The advantage of an instantaneous measurement will be elaborated upon in a later section.

Precautions to be taken when employing the above methods have been discussed by Fraser(8).

Experimental Results Reported in the Literature

There has been little agreement among the results for the surface tension of pure high melting-point liquid metals, e.g., molten iron. Work done on iron before 1955 shows very low surface tension values compared to more recent results. This is probably due to more efficient control of contaminants in the more recent studies. Among the more recent results, there is good agreement between those after Kozakevitch and Urbain(9) and those after Halden and Kingery(5). Their results on surface tension of Fe-O and Fe-S alloys also show good agreement. Surface tension measured here are later compared with those of the afore-mentioned workers.

The surface tension-composition relationship for the Fe-O alloys obtained by the afore-mentioned workers is shown in Figure 5. Halden and Kingery(5) also found that carbon has no effect on surface tension. Nitrogen was found to be weakly surface active while sulphur was found to be more surface active than oxygen. Kingery(7) also found that selenium was most surface active among the surface active elements. Tellurium had a smaller effect. Kozakevitch and Urbain(4) obtained similar results. For the iron-oxygen system the results obtained by Wilhelm vor dem Esche and Oscar Peter(6) were lowest over the entire range of composition. Surface Tensions measured by Halden and Kingery(5) were the highest.

It should be noted that all previous data mentioned above was measured at only one temperature, 1550°C and that no information is available on the temperature dependence of surface tension at various oxygen levels.

CHAPTER III

THEORETICAL CONSIDERATIONS

This section describes the theory and assumptions upon which is based the oscillating drop technique for surface tension measurement of liquid metals and alloys(1).

This novel dynamic technique using a droplet of metal suspended in an oscillating electromagnetic field employs the relationship between natural frequency of oscillation and surface tension proposed by Rayleigh(10).

This theory considers small vibrations of the liquid mass about its spherical equilibrium shape. The sphere is an incompressible liquid of negligible viscosity surrounded by a second fluid of negligible viscosity and of infinite extent. Hence no damping of the natural oscillations occurs. Motion within the drop is irrotational. Modes of vibration symmetrical about a single axis are considered. The oscillation frequencies are independent of the nature of the forces which tend to keep the drop spherical(11), whether they be due to self-gravitation (e.g., in the case of a liquid globe of the size of the earth) or due to surface tension. The former situation has been solved by Lamb(12) and by Chandrasekhar(13); the latter by Reid(14). In a levitation melting system the tendency to spherical form is due entirely to surface tension.

The differential equations describing the deformation of the drop are derived$^{(15)}$ from a consideration of the relationship between potential energy, P, associated with the surface curvature (potential energy of capillarity) and kinetic energy of motion, K, arising from a small displacement of the surface.

Under dynamic equilibrium and under certain restraint conditions$^{(16)}$ it can be shown that the differential equation describing the deformation of an oscillating drop is

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{a}_n} - \frac{\partial L}{\partial a_n} = 0 \qquad n = 1, 2 \,.\,.\,.\,.\,.$$

where $L = K - P$,

a_n are the generalized co-ordinates (independent variables) representing deviations from the equilibrium radius,

t is the time,

$\dot{a}_n$ are the generalized velocities.

Simplification of the above equation using appropriate expressions for P and K leads to

$$\frac{d^2 a_n}{dt^2} + n(n-1)\,(n+2)\,\frac{\gamma}{\rho a^3}\, a_n = 0 \tag{1}$$

where γ is surface tension, a is drop radius

ρ is drop fluid density, n is the mode of vibration

Equation (1) has the solution of the form

$$a_n \propto \cos (pt + \varepsilon) \qquad (2)$$

where

$$p^2 = n(n-1)(n+2) \frac{\gamma}{\rho a^3} \qquad (3)$$

and

$p/2\pi$ is the frequency of oscillation, w

and

ε is the phase angle.

Setting n equal to 2 for the first mode of symmetrical deformation in a liquid metal system(17) and replacing $4/3\ \pi a^3$ by m, the drop weight, it is seen that

$$\gamma = 3/8\ \pi\ mw^2 \qquad (4)$$

Equation (4) is the working equation for the determination of surface tension from a measure of the oscillation frequency of a fluid droplet of weight, m. It is noteworthy that knowledge of the density of the drop material is unnecessary when using equation (4). Formerly, this has been one of the major sources of disagreement in the surface tension measurements by static methods.

CHAPTER IV

EXPERIMENTAL CONSIDERATIONS

Introduction

The technique of levitation melting was successfully used to measure the frequency of oscillation of a liquid metal drop suspended in an electromagnetic field in a controlled gas atmosphere for long time periods. A controlled low oxygen potential was obtained in the gas phase by saturating pure hydrogen with water vapor. High speed photography was used to record oscillations of the metal drop. Two-colour pyrometry was used to measure the temperature of the levitated drop. The drop was quenched and then analyzed for oxygen after each experiment.

Apparatus

(1) Levitation Chamber:

The levitation chamber is shown schematically in Figure 1. Figure 10 shows a photograph of the chamber. A modified design of the chamber was employed for a number of reasons(1). The main problem with the original design was that it was virtually impossible to prevent condensation of water vapor from the H_2/H_2O gas mixture. The main advantage of the old design was that temperature measurement and photography of the droplet using side and top views could be done simultaneously. With the new design, which has been used many times before for other experiments with levitated metal, the problem of simultaneous temperature measurement and photography has been solved by using a prism which can be rotated through 90^o (details are given later). Another small advantage of the old design was the capability of photographing the top and side view simultaneously. This aided in detecting droplet rotation. Detecting rotation was very difficult and uncertain since it was neither possible to focus the two views together nor to photograph the side view fully through the levitation coil which obstructed part of the view. Moreover, with a carefully wound coil, an experienced worker can judge clearly whether the oscillation movement is influenced by droplet rotation. It was considered adequate to photograph the drop using the top view alone in this investigation.

The reaction chamber is a narrow vycor tube inserted along the vertical axis of the levitation coil. Vycor can adequately tolerate the high temperatures used. The top and bottom portions of this apparatus are made of pyrex glass. The three sections are joined by ground glass fittings. The top portion has an optical flat to get an undistorted beam of light from the drop. There is a side tube for the gas inlet. Downward gas flow direction was used because heating the top portion of this apparatus to prevent moisture condensation was much easier than heating the relatively more complicated bottom part. Heating was done using a nichrome resistance wire.

The bottom section is an eccentric tube to the end of which fits an aluminum disc containing a quartz sliding tube for lifting the sample into the levitation coil, a copper mold for quenching the molten metal drop and an optical flat for observing the bottom view of the drop. There is also a gas outlet used for feeding and withdrawing a sample.

The prism was mounted just over the top optical flat and could be used for temperature measurement in one position and for photography when rotated through 90^0 such that the light beam is turned by 180^0 into the camera placed on the side opposite to the pyrometer.

(2) Gas Train:

The gas used in the present investigation was commercial hydrogen further purified. The purification train is shown in Figure 2. It consists of ascarite (KOH) for CO_2 removal; drierite (anhydrous $CaSO_4$) and silica gel for moisture removal; a cold trap of activated charcoal in liquid nitrogen. The gas then passes through a flow meter with a range of 0.0 to 1.5 litres per minute. The flow rate used in our experiments was between 0.2 and 0.35 litres per minute.

Hydrogen gas is then passed through a series of flasks containing distilled water immersed in a water bath kept at a desired constant temperature. The moisture-saturated gas was then passed into the reaction chamber via a copper tube heated with nichrome wire to prevent condensation of water vapor. Two T-valves were used to by-pass the water-bath when levitating in pure hydrogen. Completing the gas train was a two-stage bubbler from where the gas was taken to exhaust. The purified gas contained very low oxygen and sulphur. This was indicated by the results of O and S analysis of the levitated metal. No oxygen or sulphur could be detected by the existing methods of analysis (see Table II).

Experimental Techniques

(1) Coil Design:

The coil design was similar to that described in a previous study(1), the only difference being that the coil diameter is larger than before.

(2) Temperature Control:

The temperature of the levitated metal could be controlled by changing the coil design, the grid resistance of the high frequency generator, the size of the iron sample and the gas flow rate. A 450 KHz 10KW Tocco generator was coupled to a 7.5:1 step-down transformer in order to reduce power input to the coil to prevent overheating of the sample. The only factor causing small fluctuations in the drop temperature was the fluctuating supply from the mains, a condition which can rarely be avoided except very late at night. As a result most of the runs were done from 10:00 p.m. to 4:00 a.m.

Gas flow was not used as a tool for controlling temperature since it could change the drop oscillation characteristics at high flow rates. The flow rate was kept between 0.2 and 0.35 litres per minute.

(3) Temperature Measurement:

A Milletoon two-colour optical pyrometer and direct reading indicator were used for measuring temperature of the drop. Full details of the calibration method are given by Kershaw(18) so it will suffice to mention that the calibration was performed against a standardized Pt-5% Rh/Pt-20% Rh thermocouple. Calibration checks were frequently made by observing melting and freezing point temperatures of the levitated drop. The actual temperatures reported here are estimated to be within ± 10°C.

(4) Material Preparation:

The samples weighing between 0.5 gms and 0.8 gms were cut from 1" rods of high purity iron, Ferrovac E, purchased from the Crucible Steel Co., Syracuse, N.Y. Table II shows the O and S analysis of this iron. The purity indicated by the manufacturer was 99.94% Fe. The samples were degreased and cleaned in acetone prior to levitation and levitated for a long time (about 6 minutes) in pure hydrogen to remove most of the impurities present in the metal. The amount of O and S in the levitated metal was undetectable by existing methods of analysis.

(5) Photography:

The photographic technique is described in detail elsewhere(1). The film used throughout the present investigation was Kodak 4-X Reversal, Type 7277 with an ASA rating of 400 in day-light. With a frame rate of

1000 frames per second, chosen as the lower limit of reasonable resolution of an estimated oscillation frequency of 40 cps, no artificial illumination was necessary for the molten metal.

(6) Film Analysis:

Film analysis consists of two parts; one, to determine the frame rate and the other, to determine frames per oscillation. The two measurements are described in detail by Fraser(8).

(7) Oxygen Analysis:

The oxygen analysis was carried out with a Leco inert gas fusion apparatus. This apparatus was calibrated against standard samples of known oxygen content.

Procedure

The procedure for both the work on pure iron and iron-oxygen alloys was similar, the only difference being that the water vapor saturation was by-passed during experiments with pure iron.

The sample was prepared and melted in pure hydrogen. The temperature was brought up to 1700°C to allow all oxygen and sulphur to be removed. Then the temperature was brought down and hydrogen was then passed through the saturation tank if needed and the temperature was adjusted to the required level.

To determine the minimum time for equilibrium, the samples were levitated for different lengths of time at a fixed water bath temperature and a constant drop temperature of 1580°C. A plot of time vs. O content is shown in Figure 3. The minimum time is about 5 minutes but the metal was levitated for at least 6 minutes to ensure equilibrium.

The equilibrium oxygen content was about 20% lower than that calculated from Dastur and Chipman's data(19). This discrepancy is thought to be due to thermal diffusion(20).

After equilibrium was reached, the top prism was turned through 90° and thus the levitated metal drop was focussed on the camera-film. The pulse generator was turned on and a recording of the oscillations was made on a full 100 ft. roll of film. The metal was then quenched in the copper mold.

The samples were analysed for oxygen after being cleaned with acetone and dried and the processed film was used to determine the film speed and the number of frames for each oscillation. The ratio was calculated as the frequency of oscillation of the levitated metal drop. The weight and the frequency of oscillation were used to calculate the surface tension using equation (4).

CHAPTER V

RESULTS

The surface tension of pure liquid iron was investigated in the temperature range 1450°C to 1705°C in a purified atmosphere of hydrogen and in the range 1530°C to 1660°C in a purified 6% hydrogen-helium mixture. The latter investigation was done in order to confirm that the previously obtained low surface tension values(1) in this purified hydrogen-helium mixture were solely due to the oxygen and sulphur present initially in the metal and not due to the change of the surrounding medium from pure hydrogen to 6% hydrogen-helium mixture.

The experimentally determined values of frame rate and rate of oscillation of a drop of known weight are shown in Table I and Table IV. The raw data is given in columns 3 to 6. The experimental numbers run from E1 to E16 in Table I and from I1 to I21 in Table IV.

The surface tension was calculated in the following manner. The frame rate (column 4) was divided by frames per oscillation (column 7) giving the drop oscillation frequency which was used to calculate surface tension in dynes per cm (column 9).

In Figure 4, the surface tension vs. temperature is plotted. Also plotted for comparison is the relationship obtained in the previous work(1). The relationship for the present work is

$$\gamma_{Fe} = 0.0794t + 1836 \text{ dynes/cm}$$

where t is the temperature in ^{o}C,

γ_{Fe} is the surface tension of pure iron.

The 95% confidence limits about the slope are 0.559 and -0.401. The correlation coefficient was found to be 0.116. The standard error of estimate (used for plotting 95% confidence intervals in Figure 4) was found to be 45 dynes/cm.

The linear relationship between surface tension and temperature for all samples excluding the supercooled metal was obtained by linear regression analysis. The 95% confidence limits about the regression line are also plotted.

Figure 6 shows the surface tension of pure iron against temperature in an atmosphere of 6% hydrogen-helium mixture.

All the samples for this data were analysed for oxygen and no oxygen could be detected. Some samples were levitated under the same conditions and analysed for sulphur. Sulphur also could not be detected by the existing methods of analysis (Table II).

The effect of oxygen on surface tension of liquid iron was investigated at three different temperatures. Figure 5 shows the data at all three temperatures, plotted on a surface tension vs. ln [%O] plot. A curve is plotted for the combined data of Halden and Kingery(5) and Kozakevitch and Urbain(9) for comparison. Figures 7, 8 and 9 show the data at various temperatures separately. The curves are drawn approximately to show the trend of the variation. Table III shows the raw and calculated data in a manner similar to that for pure iron.

Experimental Errors

The scatter in the values of surface tension as seen in Figures 4, 5, 6, 7, 8 and 9 is associated with the experimental errors in frame rate measurement, temperature measurement and control and oscillation frequency measurement.

In Figure 5 the scatter in the combined data of Kozakevitch and Urbain$^{(9)}$ and Halden and Kingery$^{(5)}$ is not shown because the total number of experimental points based on which the smooth curve in Figure 5 is drawn, is very small compared to the number in the present data.

Differentiating the logarithm of equation (4) we get

$$\frac{\Delta\gamma}{\gamma} = \frac{\Delta m}{m} + 2\,\frac{\Delta w}{w}$$

where $\Delta\gamma$, Δm and Δw are errors in surface tension, drop weight and drop oscillation frequency measurements respectively.

But

$$w = S/D$$

where S is the frame rate measurement and

D is the number of frames for a given number of oscillations.

Thus

$$\frac{\Delta w}{w} = \frac{\Delta S}{S} + \frac{\Delta D}{D}$$

where ΔS and ΔD are errors in frame rate measurements (± 0.2%) and number of frames for a given number of oscillations (± 1 frame in about 100, i.e., ± 1%), respectively.

Δm is approximately ± 0.1%. Therefore

$$\frac{\Delta\gamma}{\gamma} = \frac{\Delta m}{m} + 2\left(\frac{\Delta S}{S} + \frac{\Delta D}{D}\right)$$

$$= [\pm 0.1 + 2(\pm 0.2 \pm 1.0)]\ \%$$

$$= \pm 2.5\%$$

CHAPTER VI

DISCUSSION

For convenience, this section will be presented in two parts.

Part I. Surface Tension of Pure Iron

The surface tension of pure liquid iron levitated in pure hydrogen at four different temperatures, one of which is in the supercooled range, is compared with the results obtained on pure iron previously in our laboratory (Figure 4).

The supercooled metal shows a surface tension value higher than that of liquid metal at a temperature above its melting point. The metal was supercooled by about 60° below the melting point. There was no difficulty in supercooling the metal in the levitation melting apparatus. Gomersall et al(21) achieved a supercooling of 420 ± 20°C for pure iron with the same apparatus. This permits measurement of surface tension for supercooled metals. Other techniques of surface tension measurement cannot work with supercooled metals.

The variation of surface tension with temperature at temperatures above the melting point is not very pronounced as compared to the strong temperature dependence found in a previous study(1). It can also be noted that the surface tension values are much higher than the previous results(1) and the results of Kozakevitch and Urbain(9) at the single temperature of 1550°C. The difference between the present and previous(1) results is much larger at lower temperatures.

The afore-mentioned discrepancies may be explained. Firstly, the amounts of O and S in the metal used in the initial work were both about 10 ppm. The starting iron in our present study, although not very pure (40 ppm oxygen and 25 ppm sulphur) gave an analysis showing undetectable O and S after six minutes of levitation in H_2 (refer to Table II). As found by Halden and Kingery(5) and Kozakevitch and Urbain(9) and as is apparent from our present work on Fe-O alloys (Figures 7, 8, 9), about 10 ppm oxygen can reduce the surface tension of iron by about 30 dynes per cm. An equal amount of sulphur can cause a similar drop in the surface tension of liquid iron as found by Halden and Kingery(5) and Kozakevitch and Urbain(9). The simultaneous presence of O and S would probably cause a reduction in surface tension greater than that found with either alone.

Original data show a greater temperature dependence (see Figure 4). This may be due to the following reasons. In the original study, we levitated the metal in a 6% H_2-He gas mixture for a time insufficient to reach equilibrium between gas and metal. The smaller flow rate of gas did not help. Thus the rate of O and S removal from the metal by the gas was too slow, particularly at lower temperatures close to the melting point. This resulted in surface tension values which were comparable to those of Kozakevitch and Urbain(9) who had the same order of O and S impurities in their samples. At higher temperatures, however, the rate of O and S removal is hastened and the surface tension values are closer to those obtained in the present work with more highly purified iron.

However, the disagreement between our surface tension values with those obtained by previous workers(5,9) may lead one to suspect the validity of the assumptions made by Rayleigh(10) for our system. The only assumption that could possibly be in doubt is the assumption of small vibrations about the spherical equilibrium shape. Rayleigh(10) himself had found a disagreement between the time of vibration (reciprocal of the frequency) of drops in a jet of water calculated from equation (4) and that actually found by using photography. The calculated periodic time was smaller than the actually observed time period. Thus the calculated frequency was larger and the calculated surface tension was larger than what it was in reality.

The maximum deviation from the equilibrium configuration in the present case was less than 11% when samples weighed more than half a gram. This deviation is assumed to be small and does not affect the surface tension values.

There was a smaller amplitude of oscillation observed with larger drop sizes (about 1 gm). Thus it could be suspected that smaller drops would give higher surface tension values at the same temperature. But it was established previously(1) that at a particular temperature there was no significant effect of the sample weight. This means that the difference in the amplitude of small (½ gm) and large drops did not create significant error.

Part II. Surface Tension of Fe-O Alloys

The results showing the effect of oxygen on surface tension of pure iron are shown in Figures 5, 7, 8 and 9.

It is apparent from Figure 5 that the surface tension values at any oxygen level are higher in the present work than those due to Halden and Kingery(5) and Kozakevitch and Urbain(9). The difference at low oxygen levels is more pronounced than at higher oxygen levels. This could be only due to the presence of impurities like sulphur which either lowers its effect on surface tension of iron containing high O amounts or it is removed from the melt at higher oxygen levels thus causing smaller difference in surface tension values at a particular high oxygen level obtained by the above two groups of workers and those obtained presently.

Also it may be noticed that the drop in surface tension in the range 25 to 100 parts per million of oxygen at all temperatures is much faster than obtained by the other two groups of workers. The reason for the above fact is not known.

The surface tension drops up to an oxygen level of 500 to 600 ppm then it practically remains unchanged. The excess surface concentration of oxygen can be calculated by using Gibbs adsorption isotherm which is

$$\Gamma_0 = -\frac{1}{KT}\,\frac{\partial \sigma_G}{\partial \ln a_0} \qquad (5)$$

where Γ_0 = excess oxygen surface concentration, atoms per sq. cm.,

a_0 = oxygen activity in bulk which can be replaced by wt.% O in iron,

K = Boltzmann's constant,

T = absolute temperature, ^{o}K,

σ_G = Gibb's surface tension

$= \sigma_E - T \cdot S$

where σ_E = measured surface tension,

s = surface entropy per unit area.

If an appropriate expression for s is assumed then the above differential equation can be solved numerically or analytically for Γ_0 and this divided by its maximum value will give the fractional surface coverage of the surface by oxygen which can be taken as the activity of oxygen on the surface. This last quantity will be very useful in interpreting the data of many previous workers in the field of gas-metal reactions and in interpreting our own future data. This is dealt with in detail in the section on "Suggestions for Future Work".

Silicon and Chromium Content:

Sometimes at the starting of levitation melting a clearly visible broken layer floating on the molten droplet could be observed. Most of the time this layer used to stay at the bottom of the drop but occasionally it would come up on top and be visible through the pyrometer. Thus it was thought to be an oxide such as SiO_2, Al_2O_3 or Cr_2O_3.

When the metal was heated at 1700°C for some time initially, this floating layer disappeared indicating that the elements like Si, Cr, and Al had escaped in the form of some oxides which have considerably higher vapor pressure at 1700°C. The analysis of the starting material as indicated by the manufacturer shows 0.005% Si, 0.001% Cr, 0.004% V, 0.001% Mo and less than 0.01% Al. Thus there is no doubt that the floating layer was an oxide of the above elements.

Similar to the above, silica films were observed on the surface of the levitated liquid copper drop by Glen and Richardson(22) who also observed that these films could be removed by heating the copper metal to about 1500°C.

CHAPTER VII

SUMMARY

The oscillating drop technique of measuring surface tension of a fluid drop was reviewed. Since not much literature is available in the field of surface activity on liquid metals it has not been possible to go into detail on this particular subject.

The surface tension of pure liquid iron was then found by the measurement of the oscillation frequencies using high speed photography of molten levitated drops in the temperature range 1480°C to 1705°C.

The surface tension of pure liquid iron as a function of temperature was found to be

$$\gamma_{Fe} = (0.0794 \pm 0.480)t + 1836 \text{ dynes cm}^{-1}$$

$$(1555^{o}C \text{ to } 1705^{o}C)$$

where "t" temperature is expressed in ^{o}C.

The present results were compared with our previous results(1) and with results due to Kozakevitch and Urbain(9) and Halden and Kingery(5) and discussed.

The next part was on finding the effect of oxygen on surface tension of Fe-O alloys by the same technique at three different temperatures, 1560°C, 1605°C and 1645°C. These results were compared with those of Halden and Kingery(5) and Kozakevitch and Urbain(9).

CHAPTER VIII

SUGGESTIONS FOR FUTURE WORK

The surface tension of liquid metals has been found to be very susceptible to small amounts of oxygen and sulphur. The effect of oxygen has already been investigated in this report. The effect of sulphur should be investigated in a similar manner. After successfully monitoring changes in surface tension with concentrations of O and S it will be possible to study the mechanism of initial oxidation and sulphidation of liquid iron.

In any gas-metal reaction there are three major steps involved:

1) Mass transfer of reactants and products to and from the interface respectively in the gas phase.
2) Chemical reaction at the interface .
3) Mass transfer in the metal phase.

The second step can further be divided into two parts:

a) Adsorption or desorption of the species at the interface.
b) Dissolution into the metal or desorption into the gaseous phase.

Both the above steps usually need an activation energy to proceed forward.

The slow reaction or the rate-controlling step for the overall reaction could be any one of the above.

If diffusion in the gas phase is the slow step then the surface and the metal-bulk must be at equilibrium. If diffusion in the metal is the slow process, then the gas and the interface must be at equilibrium. The above two problems can be solved without much difficulty with the help of the usual diffusion equations.

If the interfacial reaction is the slow step then during adsorption there is no resistance in the gas phase and during desorption reactions, there is no resistance in the metal phase.

The two steps in the interfacial reaction can be broken down into intermediate steps in various types of reactions. Then the main object is to consider each of these steps one by one and determine which one controls the rate of the overall reaction.

Many previous workers have found that the rate of a particular type of reaction is much slower than predicted from the diffusion model. In all these cases the surface of the liquid metal was "poisoned" by oxygen which decreased the rate. The following are some examples of this behaviour. The decarburisation of iron-carbon melts in CO_2/CO atmospheres was found to be controlled by an interfacial reaction by Swisher and Turkdogan(23). In developing a mathematical model to fit the data, a knowledge of the coverage of the surface of the metal by oxygen, which is assumed to be proportional to the activity of oxygen on the surface, is essential. Swisher and Turkdogan had used the θ_0 values obtained by Halden and Kingery and Kozakevitch and Urbain and their model was consistent with their data.

The oxidation kinetics of free falling iron droplets(24) also seem to be controlled by an interfacial reaction at least in the later stages of oxidation. The rate of desorption of carbon monoxide from liquid iron-carbon melts containing low carbon was also found to be controlled by an interfacial reaction(25). The rate of nitrogen absorption and desorption is also found to be controlled by an interfacial reaction in the presence of oxygen as found by various workers(26,27,28) The rate of sulphurisation of delta-iron is also found to be reduced by the presence of chemisorbed oxygen on the surface(29).

The above observations have not been interpreted well. An attempt can be made to interpret these data in terms of the surface property measured in the present levitation system.

The rate of nitrogen desorption as found by Mori and Suzuki(26) was found to be proportional to the square of the nitrogen content in the melt while that found by Pehlke and Elliott(28) was proportional to the nitrogen content itself. This difference could be due to the fact that the two studies were made under different experimental conditions. The gas used by Pehlke and Elliott was pure nitrogen at one atmosphere pressure within the Sieverts apparatus in which the gas is stationary. Mori and Suzuki used argon flowing over the melt. If the argon removed some oxygen atoms from the surface then some sites could be available for the nitrogen to come to the surface and get desorbed. Thus if the interfacial reaction is the rate controlling step as found by these workers, then the rate will be speeded up as observed by them. In fact, it was found recently(20) that much sulphur is removed from iron-sulphur alloys by helium at flow rates comparable to those used by

Mori and Suzuki. The same behaviour may be expected with oxygen too. The surface tension measurements may give an idea how the oxygen concentration on the surface changes.

Thus a knowledge of the surface coverage by oxygen could be very important in studying the data obtained by many previous workers in the field of gas-metal reactions.

For studying the initial rates of oxidation, a simple experimental method can be used. A step-function may be applied to the gas-metal system, i.e., the gas mixture can be instantaneously changed from reducing to oxidizing conditions. Then the high speed cinematography can be used to record the oscillations of the levitated droplet for the first few seconds. The average surface tension values can be determined over a period of a few milliseconds. Thus, knowing the surface tension variation with time, it is possible to know how the surface coverage of oxygen changed with time using the surface tension-concentration relationship at steady-state.

The step function may also be applied by changing the metal temperature instead of changing the gas. This will serve the same purpose since the equilibrium oxygen content of the metal is a strong function of the temperature(19). This may be more suitable since the temperature can be changed much faster in the levitation system than the gas atmosphere.

Suggested future work can be summarised as follows:

1. Apply the dynamic technique to Ag as a check.

2. Establish surface-tension-concentration relationships at various temperatures for Fe-S alloys.
3. Study the nitrogenation and denitrogenation of iron in the presence of oxygen on the surface.
4. Study the surface tension variation of an Fe-O alloy levitated in argon or helium with time.
5. Develop experimental conditions that would cause the interfacial reaction to control the overall reaction and then study the mechanism of reaction during the initial periods of oxidation and sulphidation as well as de-oxidation and desulphidation of liquid iron.
6. Solve the differential equation (5) to obtain a relationship between the fractional surface coverage, θ_O, and wt.% O and thus between θ_O and measured surface tension.

REFERENCES

1. M. E. Fraser, W-K. Lu, A. E. Hamielec, R. Murarka: Met. Trans., March (1971), p. 817.
2. D. W. G. White: Metals and Materials, Review 124 (1968).
3. V. K. Semenchenko: Surface Phenomena in Metals and Alloys, (1962), p. 43-115, Pergamon.
4. P. Kozakevitch and G. Urbain: Mem. Scient. Rev. Met., (1961), 58, p. 517.
5. F. A. Halden and W. D. Kingery: J. Phys. Chem., (1955), 59, p. 557.
6. Wilhelm vor dem Esche and Oscar Peter: Archiv fur des Eisenhutt, June (1956), p. 355.
7. W. D. Kingery: J. Phys. Chem., (1958), 62, p. 878.
8. M. Fraser: M.Sc. Thesis, McMaster University (1970).
9. P. Kozakevitch and G. Urbain: Mem. Scient. Rev. Met., (1961), 58, p. 401.
10. Lord Rayleigh: Theory of Sound, (1945), 2, 2nd edition, p. 371-375, Dover.
11. H. Lamb: Hydrodynamics, (1952), 6th edition, p. 473, Cambridge.
12. H. Lamb: Proc. London Math. Soc., (1881), 13, (1), p. 51.
13. S. Chandrasekhar: Proc. London Math. Soc., (1959), 9 (3), p. 141.
14. W. H. Reid: Quart. Appl. Math., (1960), 18, p. 86.
15. H. Goldstein: Classical Mechanics, (1951), Addison-Wesley.
16. E. C. Okress, P. M. Wroughton, G. Comentez, P. H. Brace and J. C. R. Kelly: J. Appl. Phys., (1952), 5, p. 545.
17. V. G. Levich: Physiochemical Hydrodynamics, (1963), Prentice Hall.
18. P. Kershaw: Ph.D. Thesis, McMaster University (1968).

19. M. Dastur and J. Chipman: Trans. AIME, (1949), 185, p. 441.

20. M. Sunderland, Private Communication.

21. D. W. Gomersall, S. Y. Shiraishi and R. G. Ward: J. Austr. Inst. Metals, (1965), 10, No. 3, p. 220.

22. G. G. Glen and F. D. Richardson: Heterogeneous Kinetics at Elevated Temperatures, (1951), p. 369, edited by Belton and Worrell.

23. J. H. Swisher and E. T. Turkdogan: Trans. Met. Soc. AIME, (1967), 239, p. 602.

24. S. K. Vig, M.Eng. Thesis, McMaster University (1969).

25. King et al: Heterogeneous Kinetics at Elevated Temperatures, (1970), p. 409, edited by Belton and Worrell.

26. K. Mori and K. Suzuki: Trans. ISIJ, (1970), 10, p. 232.

27. E. T. Turkdogan and P. Grieveson: J. Electrochem. Soc., (1967), 114, p. 59.

28. R. D. Pehlke and J. F. Elliott: Trans. AIME, (1963), 227, p. 844.

29. J. H. Swisher: Trans. AIME, (1967), 239, p. 110.

TABLE I

EXPERIMENTAL DATA AND RESULTANT SURFACE TENSION VALUES FOR PURE IRON (in hydrogen)

Expt. No.	Temp. ^{o}C ± 10	Weight grams ±0.001	Frame rate sec^{-1}±2	No. of Oscillations	No. of frames	Frames per Oscillation	Freq. cycles/sec	Surface Tension 1.178xwt. x(freq)^2 dynes/cm
E1	1480	0.5707	1001	20	365	18.25	54.85	2023
E2	1480	0.5569	1001	20	358	17.90	55.92	2052
E3	1480	0.5781	998	25	460	18.40	54.24	2003
E4	1480	0.6181	1000	15	285	19.00	52.63	2017
E5	1555	0.5055	1009	20	351	17.55	57.49	1968
E6	1555	0.6224	1007	25	476	19.04	52.89	2051
E7	1555	0.6021	1007	15	288	19.20	52.45	1951
E8	1555	0.6203	1005	10	196	19.60	51.28	1921
E9	1630	0.6654	1005	30	600	20.00	50.25	1979
E10	1630	0.6708	1006	20	409	20.45	49.19	1912
E11	1630	0.5710	1006	25	472	18.88	53.28	1910
E12	1630	0.6174	1007	15	291	19.40	51.91	1960
E13	1705	0.5723	1007	19	357	18.79	53.59	1936
E14	1705	0.6146	1007	20	384	19.20	52.45	1992
E15	1705	0.6461	1007	22	433	19.68	51.17	1993
E16	1705	0.6602	1005	15	296	19.73	50.94	2018

TABLE II

O AND S ANALYSIS

	Unlevitated Material (part/million)		Levitated in H_2 for at least 6 minutes
Oxygen	36 62 44	47 (average)	Undetectable
Sulphur	27 ppm		Undetectable

TABLE III

EXPERIMENTAL DATA AND RESULTANT SURFACE TENSION VALUES FOR IRON-OXYGEN ALLOYS

Expt. No.	Temp. ^{o}C±10	(% 0)	Weight grams ±0.001	Frame rate sec^{-1}±2	No. of Oscillations	No. of frames	Frames per Oscillation	Freq. cycles/ sec	Surface Tension 1.178xwt. x(freq)^{2} dynes/cm
A1	1560	0.0019	0.5687	967	15	268	17.87	54.113	1962
A2	1560	0.0004	0.5581	971	15	265	17.67	54.952	1985
B1	1560	0.0356	0.6108	974	15	317	21.13	46.12	1530
B2	1560	0.0393	0.6094	958	13	284	21.85	43.85	1380
B3	1560	0.0422	0.6239	979	18	400	22.22	44.06	1427
B4	1560	0.0440	0.5911	955	11	238	21.64	44.15	1357
B5	1560	0.0430	0.6288	960	8	176	22.00	43.62	1409
C1	1560	0.0087	0.6074	944	20	397	19.85	47.54	1617
C2	1560	0.0103	0.5940	952	20	419	20.95	45.44	1445
C3	1560	0.0134	0.5950	960	15	319	21.27	45.12	1427
C4	1560	0.0103	0.6094	958	19	406	21.37	44.82	1442
F1	1560	0.0070	0.5548	998	15	288	19.20	51.98	1766
F2	1560	0.0059	0.6314	1002	10	216	21.60	46.39	1601
F3	1560	0.0065	0.6585	1004	10	223	22.30	45.02	1572
F4	1560	0.0062	0.5491	992	20	403	20.15	49.23	1568
F5	1560	0.0047	0.6205	994	16	335	20.94	47.47	1647
G2	1560	0.0009	0.5339	958	20	346	17.30	55.39	1930
G3	1560	0.0008	0.6037	949	15	276	18.40	52.11	1931

Table III (contd)

A3	1605	0.0010	0.6205	969	15	278	18.53	52.294	1999
B6	1605	0.0501	0.6091	956	10	219	21.90	43.67	1368
B7	1605	0.0514	0.6007	959	10	219	21.90	43.80	1358
B8	1605	0.0508	0.5941	969	15	324	21.60	44.88	1410
B9	1605	0.0514	0.6134	960	8	177	22.125	43.39	1360
B10	1605	0.0525	0.5985	954	12	260	21.67	44.04	1367
G5	1605	0.0015	0.5960	957	15	272	18.13	52.79	1957
G6	1605	0.0018	0.6606	958	5	95	19.00	50.40	1977
G7	1605	0.00065	0.5577	956	15	262	17.47	54.74	1969
G8	1605	0.00043	0.6006	958	5	93	15.60	51.52	1878
J1	1605	0.0080	0.55500	986	17	324	19.06	51.73	1746
J2	1605	0.0080	0.55500	991	15	289	19.27	51.41	1725
J3	1605	0.0080	0.55400	993	10	194	19.40	51.16	1708
J4	1605	0.0080	0.55400	988	15	289	19.27	51.27	1712
J5	1605	0.0080	0.55306	993	15	291	19.40	51.19	1707
J6	1605	0.0123	0.63600	1020	15	326	21.73	46.95	1649
J7	1605	0.0123	0.63500	1017	13	284	21.85	46.56	1619
J8	1605	0.0123	0.63400	985	10	216	21.60	45.59	1552
J9	1605	0.0123	0.63400	990	10	219	21.90	45.19	1523
J10	1605	0.0123	0.63302	992	8	175	21.875	45.33	1532
J16	1605	0.0252	0.63000	983	10	221	22.10	44.46	1466

Table III (concld)

J17	1605	0.0252	0.63000	987	14	310	22.14	44.57	1473
J18	1605	0.0252	0.63000	985	13	288	22.15	44.45	1465
J19	1605	0.0252	0.62950	970	5	111	22.20	43.71	1416
J20	1605	0.0252	0.62945	973	13	288	22.15	43.92	1430
A5	1645	0.0003	0.6250	973	15	274	18.27	53.26	2088
A6	1645	0.0003	0.5986	969	15	267	17.80	54.44	2090
B11	1645	0.0662	0.5937	964	12	264	22.00	43.83	1344
B12	1645	0.0630	0.5916	965	14	300	21.43	45.02	1413
B13	1645	0.0626	0.5736	964	11	233	21.18	45.52	1400
C9	1645	0.0199	0.5815	962	15	306	20.40	47.17	1524
C10	1645	0.0166	0.5898	965	14	294	21.00	45.95	1467
C11	1645	0.0169	0.6084	963	15	310	20.67	46.59	1556
C12	1645	0.0186	0.5894	965	14	298	21.29	45.34	1427
F11	1645	0.0052	0.5639	994	15	292	19.47	51.05	1731
F12	1645	0.0053	0.6032	1005	14	286	20.43	49.19	1720
F13	1645	0.0061	0.6162	1007	4	83	20.75	48.53	1710
F14	1645	0.0049	0.6320	1009	8	171	21.375	47.20	1659
F15	1645	0.0060	0.6424	1009	11	240	21.82	46.24	1618
G9	1645	0.0000	0.4346	957	15	240	16.00	49.79	1830
G10	1645	0.00055	0.4689	955	20	327	16.35	58.40	1884
G11	1645	0.0000	0.5253	956	5	85	17.00	56.25	1958
G12	1645	0.00069	0.5784	956	5	89	17.80	53.69	1964

TABLE IV

EXPERIMENTAL DATA AND RESULTANT SURFACE TENSION VALUES FOR PURE IRON

(in 6% H_2/He mixture)

Expt. No.	Temp. ^{o}C±10	Weight grams±0.001	Frame ra rate sec^{-1}±2	No. of Oscillations	No. of frames	Frames per Oscillation	Frequ. cycles/ sec	Surface Tension 1.178xwt. x(freq)^2 dynes/cm
I17	1575	.5549	965	16	279	17.44	55.36	1979
I19	1575	.5549	974	9	158	17.55	55.50	2003
I20	1575	.5549	984	10	178	17.80	55.27	1994
I21	1575	.5549	962	14	243	17.36	55.43	2008
I9	1615	.6133	929	10	178	17.80	52.20	1953
I10	1615	.6095	929	10	178	17.80	52.21	1950
I11	1615	.6075	931	10	176	17.60	52.88	1998
I12	1615	.6055	929	10	176	17.60	52.81	1989
I13	1660	.6025	929	13	227	17.46	53.19	1994
I14	1660	.5983	930	5	87	17.40	53.43	2005
I15	1660	.5953	930	16	278	17.375	53.52	2005
I16	1660	.5923	929	10	174	17.40	53.37	1987

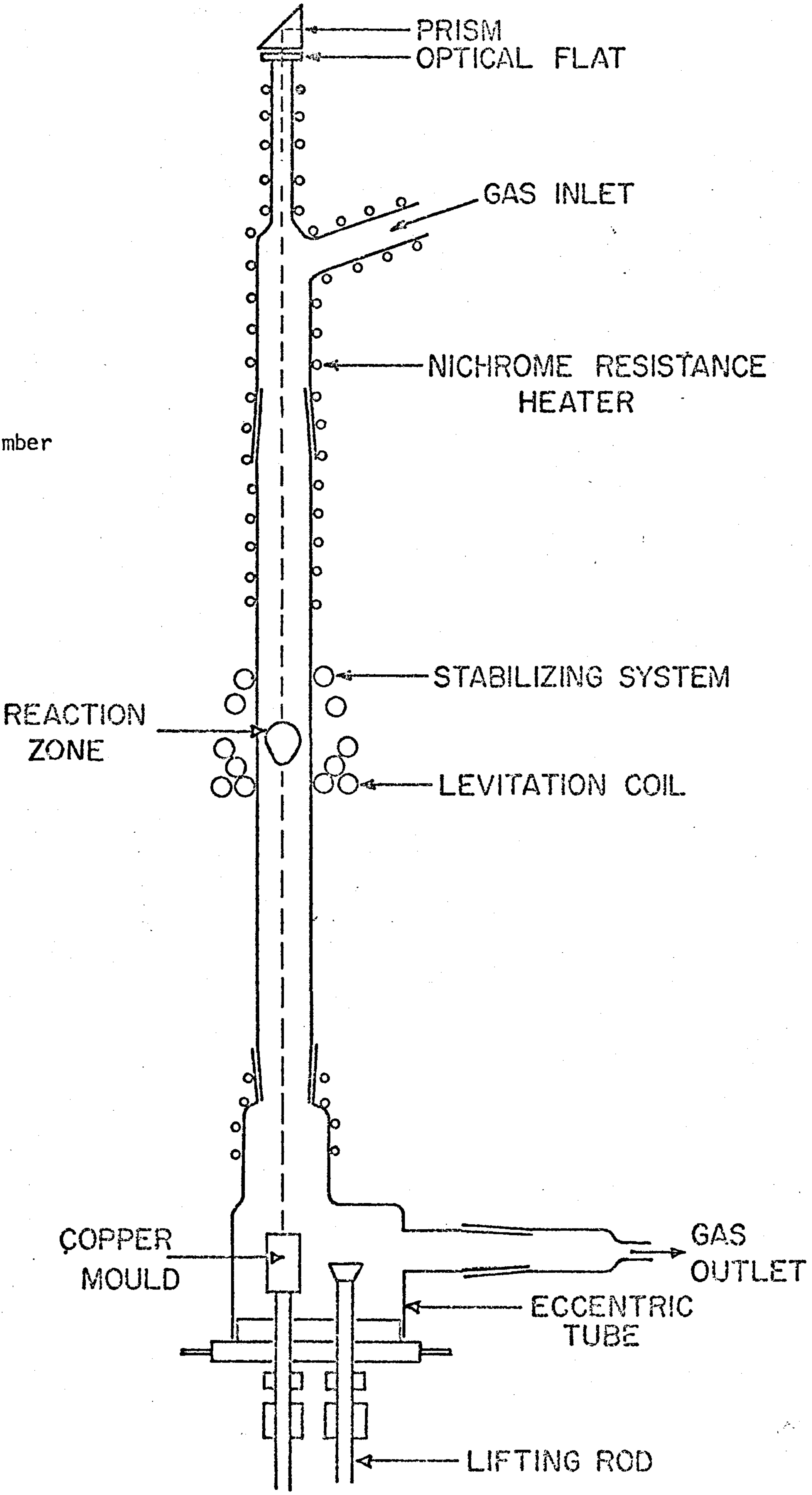

Figure 1.

Levitation Chamber

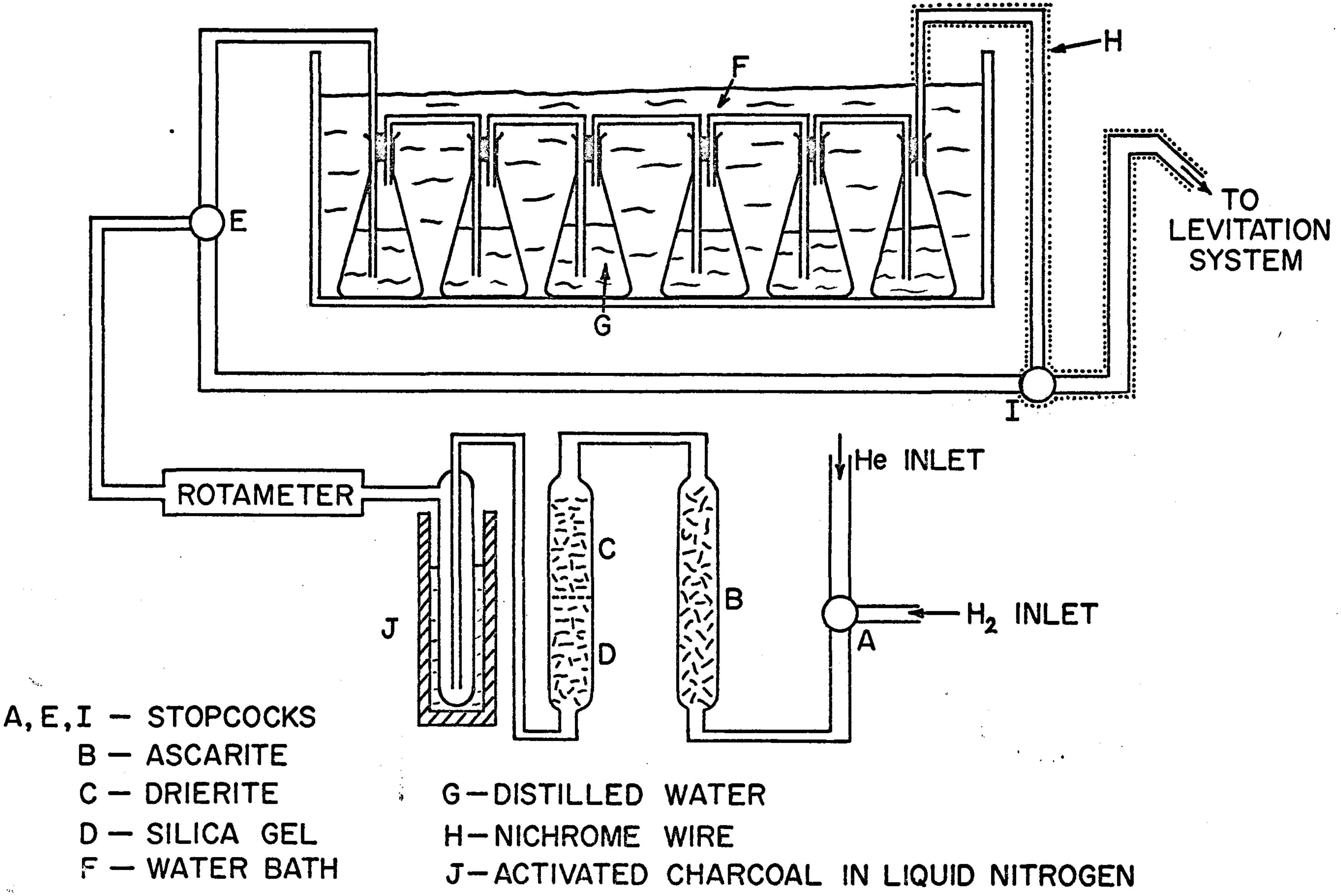

Figure 2. Purification and Water Vapor Saturation Train

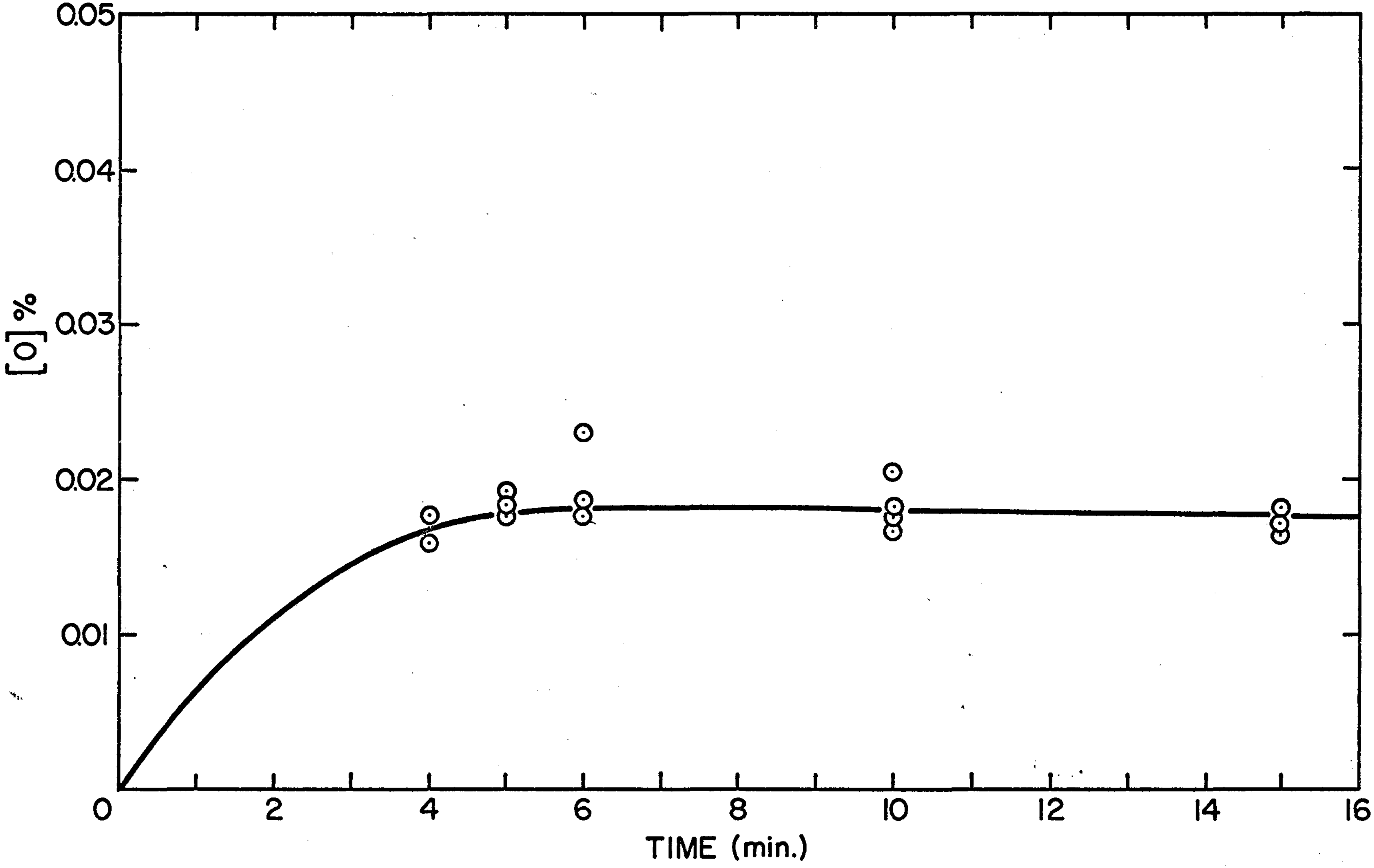

Figure 3. Oxygen Transferred to Metal vs. Time

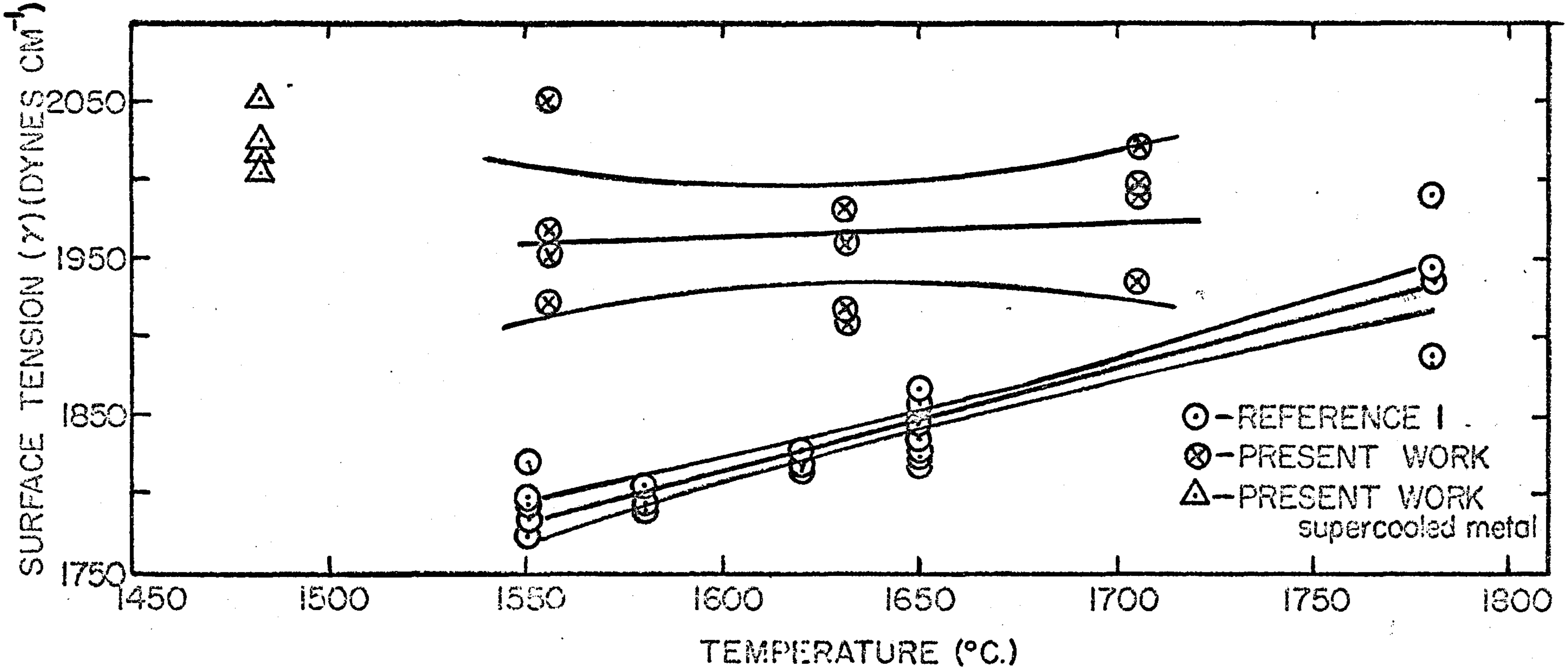

Figure 4 Surface Tension of Iron vs. Temperature

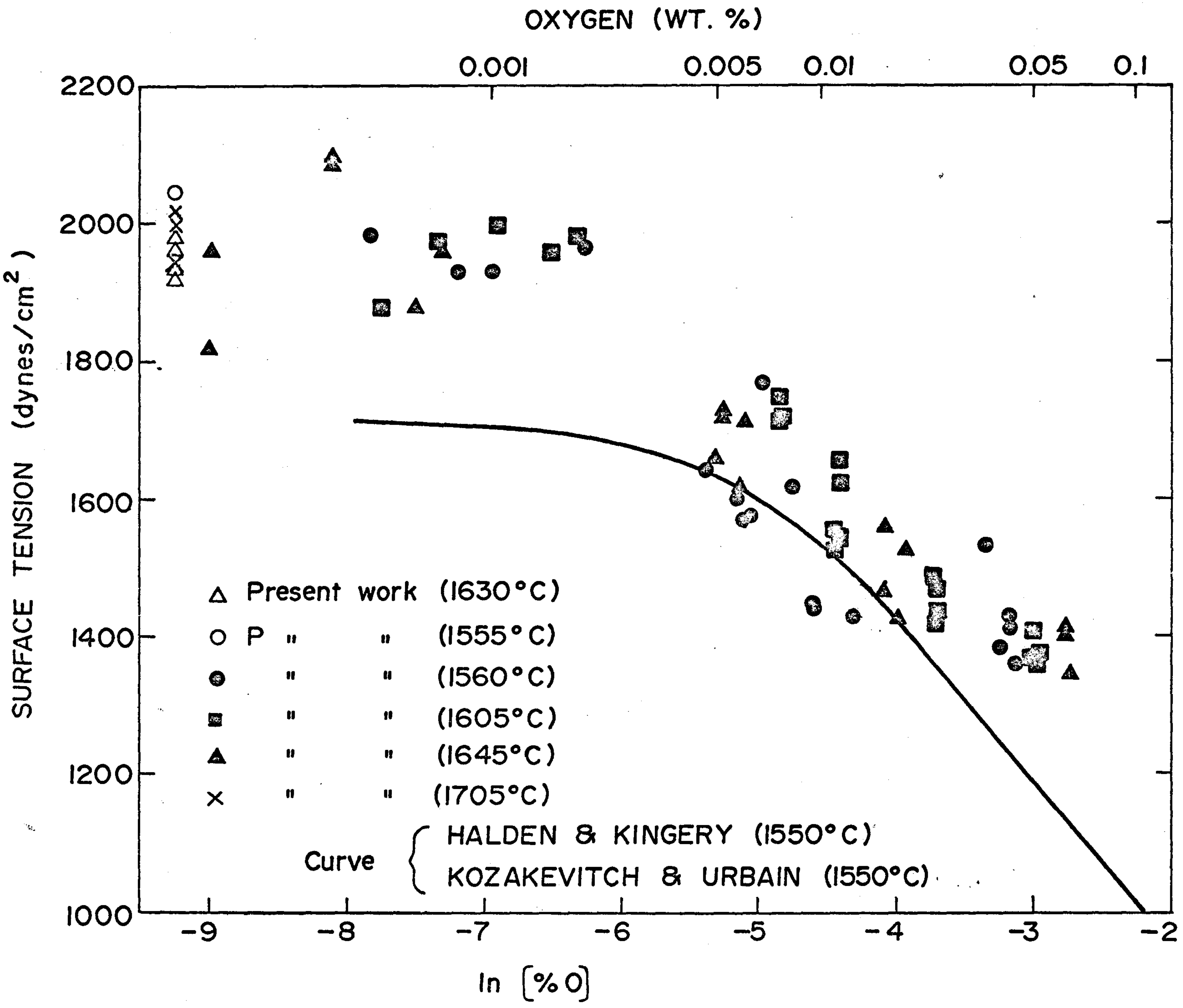

Figure 5. Surface Tension of Iron-Oxygen Alloys vs. Oxygen wt.% in Alloy.

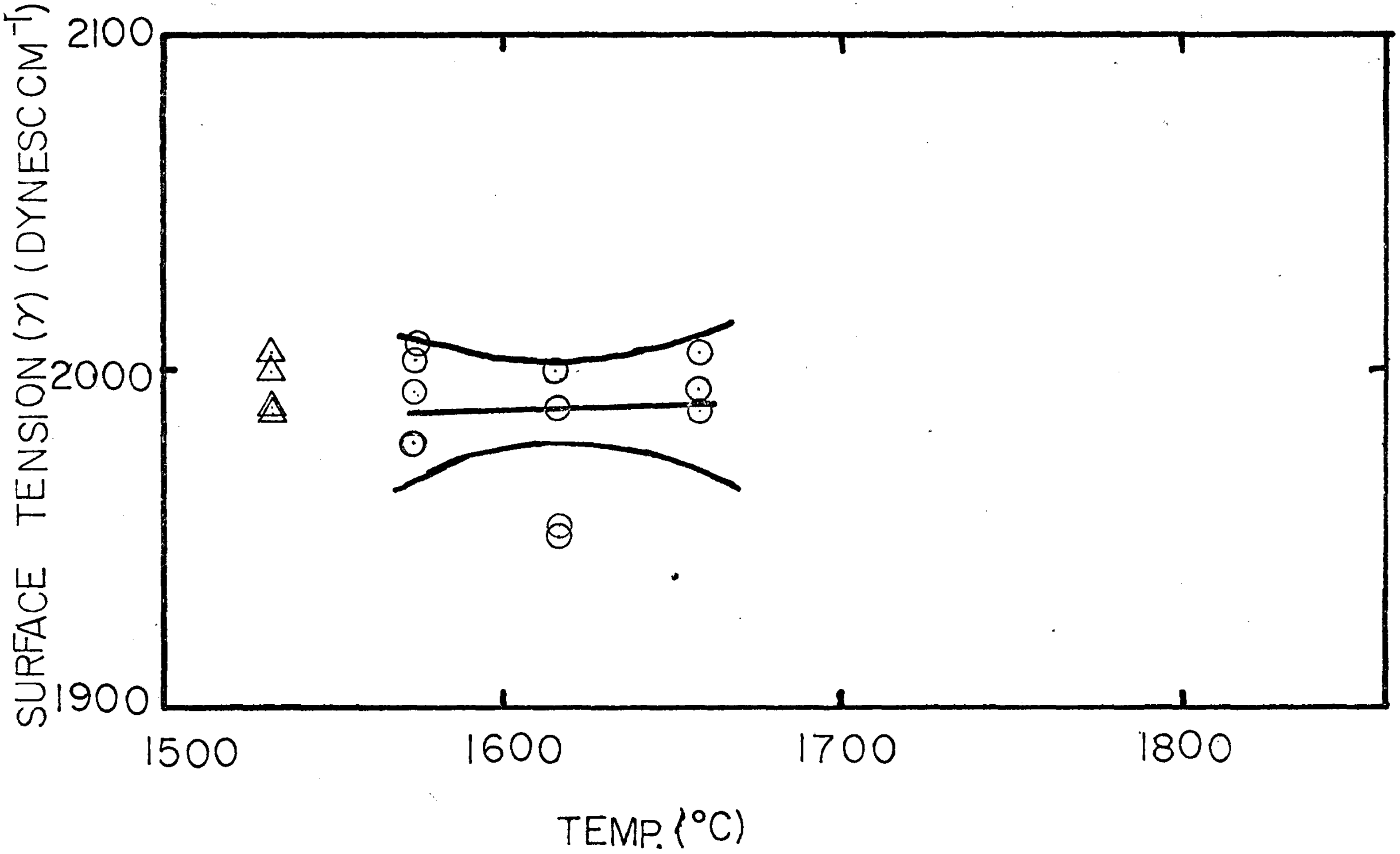

Figure 6. Surface Tension of Iron vs. Temperature (6% H_2- balance He).

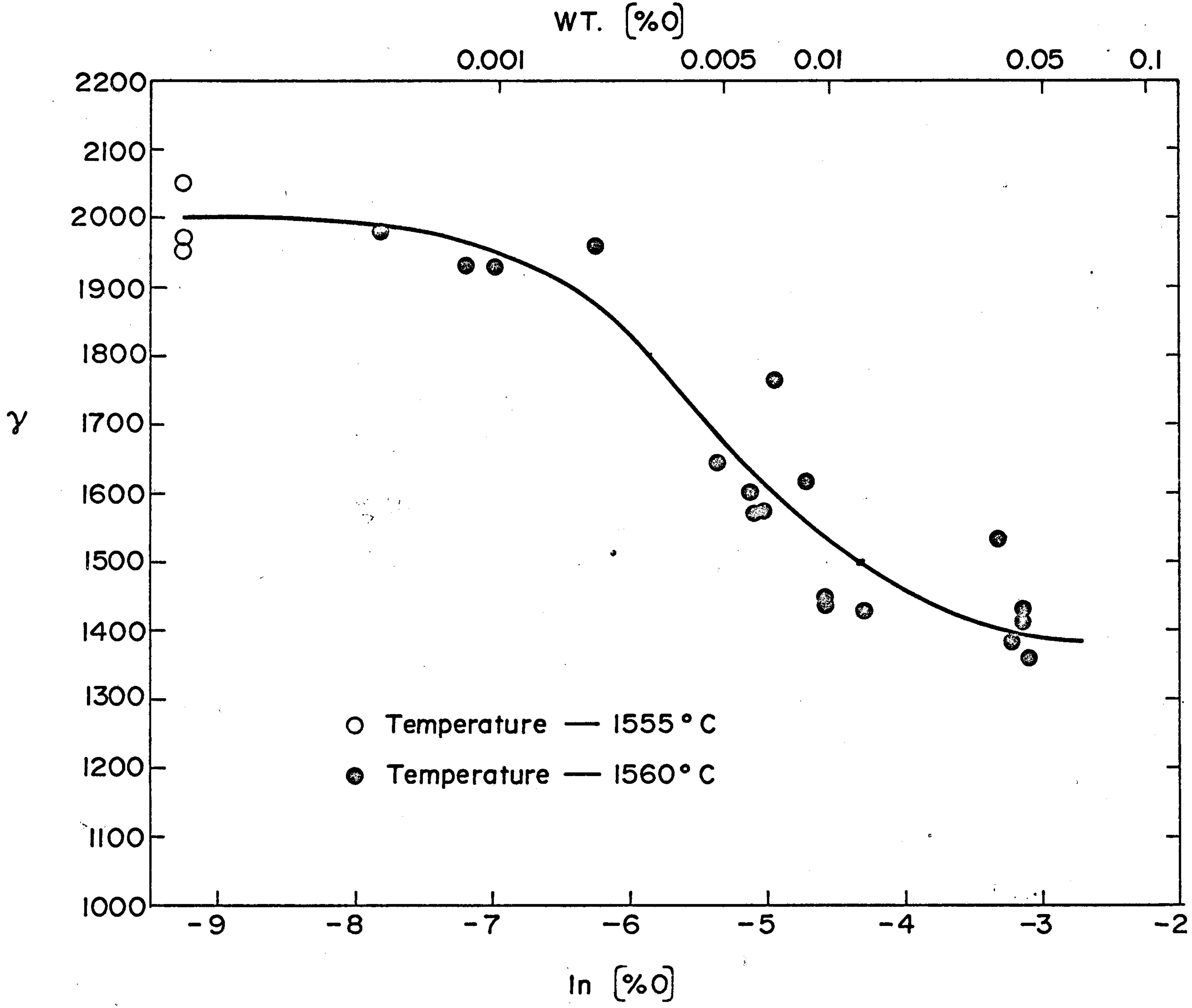

Figure 7. Surface Tension of Iron-Oxygen Alloys vs. Oxygen wt.% in Alloy (1560°C).

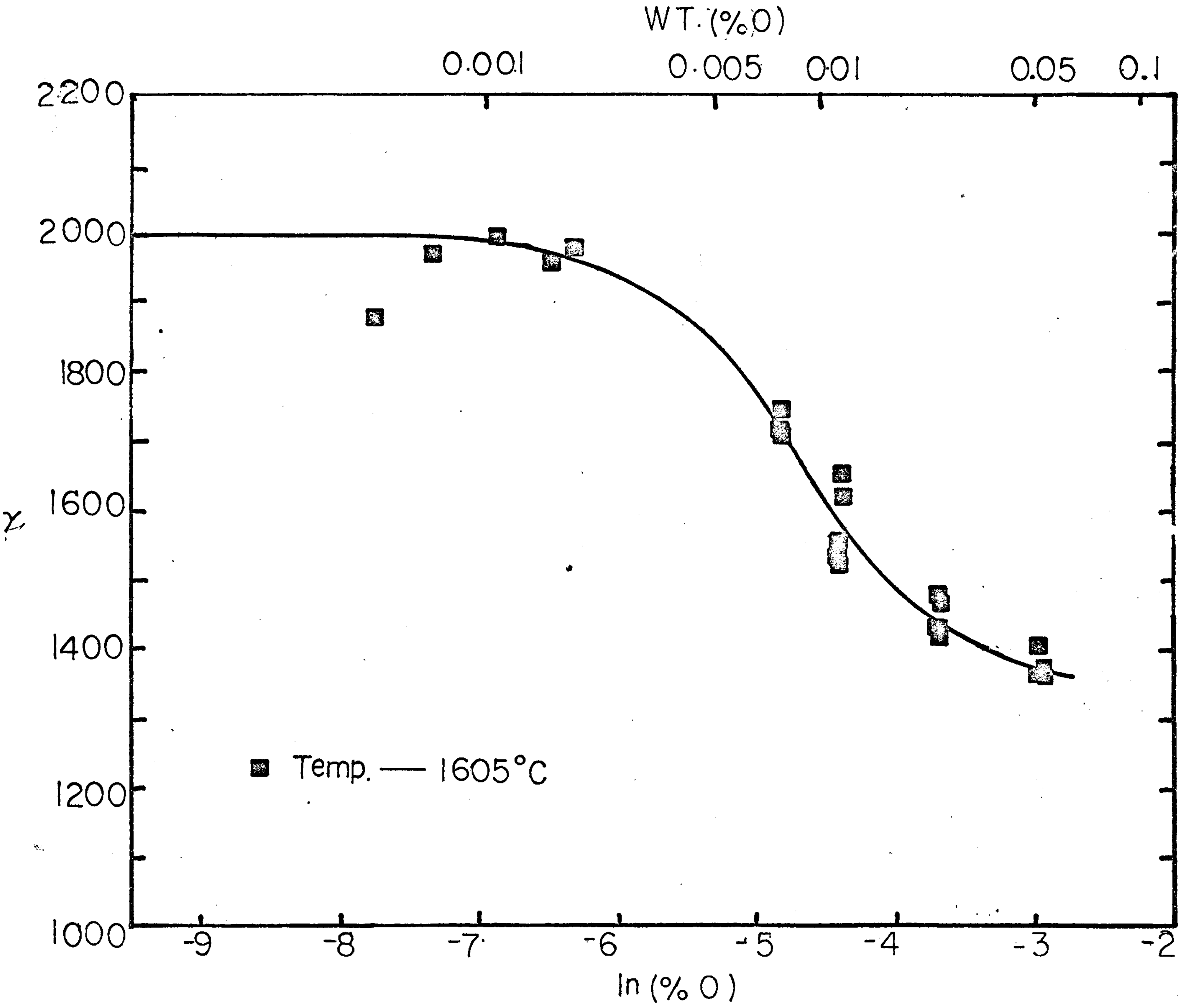

Figure 8. Surface Tension of Iron-Oxygen Alloy vs. Oxygen wt.% in Alloy (1605°C)

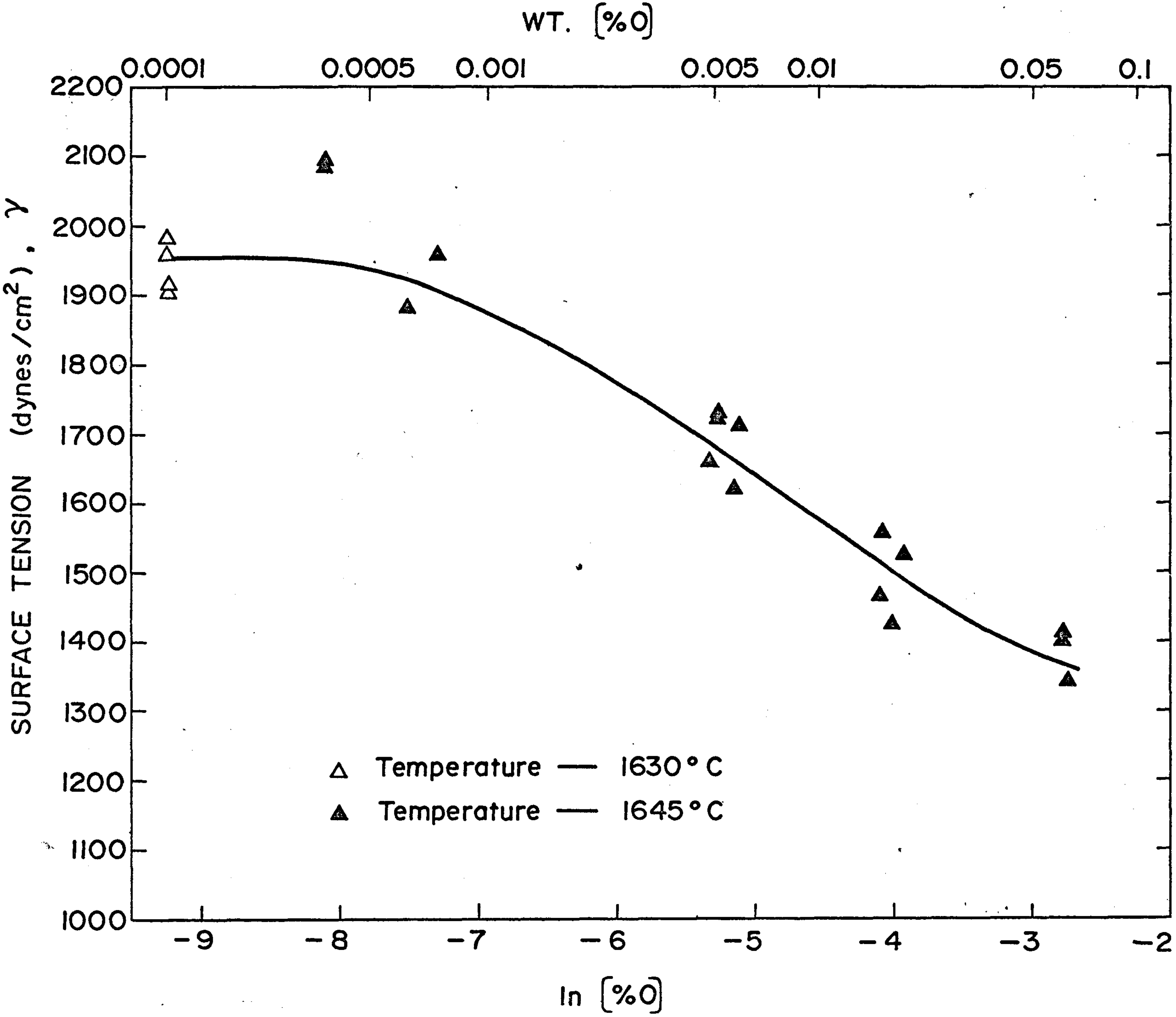

Figure 9. Surface Tension of Iron-Oxygen Alloys vs. Oxygen wt.% in Alloy (1645°C).

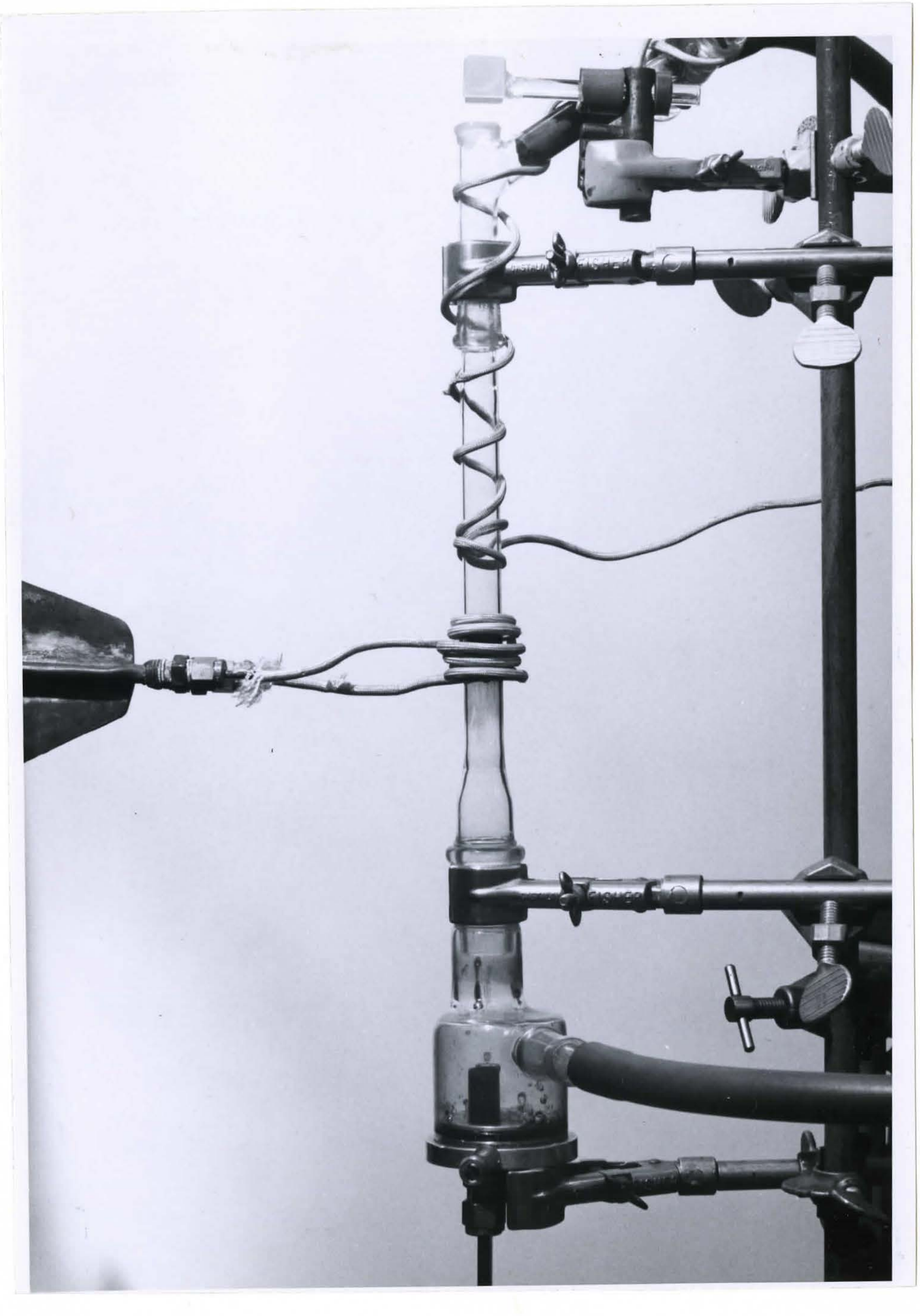

Figure 10