# THE HIGH TEMPERATURE EQUILIBRIUM BETWEEN ZIRCONIUM OXIDE AND CARBON

Thesis

by

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# The High Temperature Equilibrium Between Zirconium Oxide and Carbon.

The present research was begun in the fall of 1923 at the suggestion of Prof. A. A. Noyes as an attempt to devise an apparatus and precision technique for the study of chemical equilibria at incandescent temperatures. The particular subject of interest was the investigation of the stability of refractory oxides. The reduction of zirconium oxide by carbon was chosen as the immediate subject for research.

The earliest work is by Troost and Moissan. Troost reported the formation of $ZrC_2$ by reduction of $ZrO_2$ in a carbon arc furnace. Moissan, working with a carbon resistance furnace, reported ZrC as the product. More recent work is that of Wedekind who reported ZrC. The most significant is probably that of Arkel and deBoer. They report ZrC checked by powder photographs giving a sodium chloride structure. Their method of preparation was to pass $ZrCl_4$ vapor together with $H_2$ and CO over an incandescent tungsten wire which precludes the presence of uncombined carbon, the chief source of uncertainty. The reaction is:

$$ZrCl_4 + 3H_2 + CO = ZrC + 4HCl + H_2O$$

Their structure is checked by Becher and Ebert.

Progress was extremely slow. The order of magnitude was not known for either the equilibrium pressure of CO or the rate of reaction. There were many interfering effects. Also at the start there ~~ware~~ available neither an adequate source of electrical power nor any means of temperature measurement.

The first design of carbon tube furnace has proven entirely adequate. The first containing and accessory apparatus was developed on tha assumption that the equilibrium pressure was small. It consisted of a liter frask with water cooled copper leads (furnace bulb #1) a precision McLeod gauge and standard vacuum pumps. A delay followed while an adequate transformer was built. Then the furnace mounting proved inadequate. Copper clamps and then steel clamps were burnt out. Finally a joint was made by pressing tungsten rods into the ends of the graphite tube.

Gas was evolved from the furnace and inconsistancies in the pressure measured attributed to the presence of inert gases. A gas analysis apparatusbwas developed for the small quantities obtainable. However the gas proved to be entirely carbon monoxide. With larger charges the pressure rose above the range of the McLeod gauge, and and another was built with a higher range. When no consistency was obtained in the pressures reached it was concluded that the reaction went to completion.

The physics department acquired an optical pyrometer, and measurements were made controlling the furnace temperature at pressures up to one atmosphere of CO. But no effect could be observed, the small quantity of gas evolved from the reaction if any was lost in the pressure changes due to fluctuations in the room temperature.

A second apparatus was devised which reduced the enclosed volume to 100cc. But no consistent results were obtained till the pressure range was increased to three atmospheres and all the enclosed gas space put down in a thermostat.

The reaction studied proved completely irreversible, but was later shown to be the emission of carbon monoxide from adsorbed oxygen.

As a diversion a research was made on calcium oxide. But this was found to sublime out of the furnace during the preliminary treatment to remove adsorbed oxygen.

In the light of the information as to adsorbed oxygen, previous work on zirconium oxide was discarded and the research resumed, ending in the determination of the equilibrium in less than two months time.

## The Temperature Scale.

The temperature was measured with a Leeds & Northrup optical pyrometer fitted with an auxiliary lens of 4 diopters which enabled it to be brought to a distance of one foot from the furnace. At the close of the critical experiments this instrument was recalibrated against a standard lamp, #W27, obtained from the Nela Research Laboratory. At the same time the transmission was measured of a water cell made of a section of a 1.5liter flask and a piece of window glass, which closely approximated the conditions of the furnace and thermostat windows with water between.

Since the new calibration agreed to three degrees with the old Bureau of Standards calibration in the range of temperature of the equilibrium measurements, corrections for the emissivity of carbon were used as determined on the old scale. A furnace with an 0.8mm. hole in the center of the wall had been mounted in furnace bulb #1 and the apparent brightness temperature of the adjacent wall compared with the temperature of the hole at a series of temperatures from 1250°K to 2050°K. This correction is

$$T - S = 0.017S - 8 \quad .$$

The transmission of the auxiliary lens is 90.6%, of furnace bulb #1 (a 1 liter pyrex flask) 92.1%, and of the water cell, 83.9%. Corrections were calculated from the Wien radiation law using $c_2 = 14330 \mu$ degree, and $\lambda = .660 \mu$.

As a furnace was used for a long time it developed pits in the surface which would cause a closer approach to black-body conditions. Also a very slight deposit of zirconia or silica formed on the window. Since these are compensating effects and either would introduce but slight error they have been neglected. The effective wave-length of the pyrometer color screen was assumed to be 0.66 , that of Corning 50% transmission red glass. But, since the wave-length and the transmission only occurr together in the radiation law, this assumption introduces no error in the calculated temperature corrections.

During the calibration it was found that readings could be duplicated to within 0.5 milliamperes, corresponding to 1.5 degrees. The emissivity correction probably introduces errors not greater than four degrees. So the temperature measurements as reported are probably relatively good to 2 or 3 degrees, and absolutely to 6 or 7 degrees.

The Wien radiation law as used for calculations in optical pyrometry is:

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda \log t}{c_2 \log e}$$

or

$$\Delta T = -S \frac{S \frac{\lambda \log t}{c_2 \log e}}{1 + S \frac{\lambda \log t}{c_2 \log e}}$$

Calibration of Optical Pyrometer L&N #96848

Against Standard Lamp #W27, Nela Research Laboratory

| Lamp Current | Temperature | T(B of S) | Low | Middle | High scale |
|---|---|---|---|---|---|
| 12.0 amp. | 1145°K | 1126°K | 344.5 | milliamperes | |
| 13.0 | 1250 | 1244 | 371.2 | | |
| 14.25* | 1359 | 1359 | 493.9 | | |
| 15.5 | 1456 | 1453 | 438.5 | 370.5 | |
| 16.75* | 1543 | 1540 | 475.2 | 387.7 | |
| 18.5 | 1650 | 1648 | 528.5 | 411.0 | |
| 22.5 | 1852 | 1849 | 528.5 | 466.5 | 352.1 |
| 27.0 | 2067 | 2066 | | 534.8 | 370.9 |

* interpolated

Correction were applied to the temperatures estimated from the pyrometer current as shown in the following table where θ is the observed temperature, S is the brightness temperature of carbon in which account is taken for the absorption of the optical system, and T is the true thermodynamic temperature , taking account of the emissivity of carbon.

| Current | θ | ΔS | S | ΔT | T |
|---|---|---|---|---|---|
| 460m.a. | 1830.8°K | 27.6° | 1858.4°K | 21.7° | 1880.1°K |
| 470 | 1863.6 | 28.6 | 1892.2 | 22.2 | 1914.4 |
| 480 | 1896.0 | 29.6 | 1925.6 | 22.8 | 1948.4 |
| 490 | 1928.0 | 30.6 | 1958.6 | 23.3 | 1981.9 |
| 500 | 1959.2 | 31.5 | 1990.7 | 23.8 | 2014.5 |

## Apparatus and Procedure.

The furnace is a tube of Atcheson graphite two and a quarter inches long, one quarter inch in diameter at the ends, and one eighth inch at the center for a length of one inch with a sixty-fourth inch wall. This is supported on tungsten rods pressed into the ends of the tube. The charge is retained at the center by graphite plugs resting loosely against the tungsten rods.

The charge was in every case a pellet of compressed zirconium oxide and graphite, aproximately 1/4" long and 90 milligrams in weight, fitting loosely into the furnace.

Furnace bulb #1 was found inadequate for equilibrium measurements, but was used to determine the emissivity of carbon and to run samples to completion in vacuo. The furnace rested horizontally, the tungsten rods resting in steel guides clamped to water cooled copper leads. Electrical connection was made by flexible copper wire fastened by steel clamps to the ends of the tungsten rods. The outer ends of the water cooled leads were tapered to fit ground-glass seals in a pyrex plug which in turn was ground to fit a pyrex one liter flask. Seals were made with Dennison's banker's specie sealing wax, as the ordinary variety pulled away from the glass on cooling the metal to glass seal. The flask was connected by 1/2" pyrex tubing to the vacuum system.

Furnace bulb #2 had silver-soldered leads which developed loose connections, also the walls clouded from material thrown off from the furnace as the clearance was only 1/2", making precise temperature measurements impossible. The design was modified to that of furnace bulb #3.

The tungsten rods were welded in an oxygen blast to flexible copper wire through a nickel intermediary. It was found necessary by sad experience to melt copper completely over the nickel to prevent formation of nickel carbonyl which decomposed and obscured everything. A direct weld was impossible as copper does not wet tungsten. The flexible cord was protected from the flame during the welding by wrapping in a piece of sheet copper to avoid disintegration of the fine wires by oxidation which occurred at the edges of the reducing flame. The flexible cord was welded to a piece of 1/4" copper stock. The welded lead was then silver-soldered through a copper disk seal in the end of a 3/4" pyrex tube. The central section was a 1" tube with a window mounted 2" from the axis, and a 2mm. connecting tube.

The extreme fragility of the furnace necessitated the flexible mounting, also a definite mounting procedure. The furnace was mounted vertically and clamped by the leads in a special support. The lower lead and seal was clamped vertically and the furnace pushed onto the tungsten rod. Then the central tube was placed over tha furnace and down against the seal. The top lead was then clamped somewhat above its final position and lowered gradually as the furnace was worked onto the tungsten rod. Finally the central tube was raised into position and connected up with a hand torch. Support, furnace, and all were then placed in position and the connecting tube sealed to the rest of the apparatus.

The furnace was connected directly to a small trap (T) sufficiently large to protect it if small quantities of mercury got loose. This was connected to a manometer (M) which had a range of two meters. The outlet from the Toepler pump (P) and the connecting tube to the stopcock (A) comprised the rest of the enclosed gas space during measurements, and was therefor placed below the water level in a thermostat. The thermostat was of 300 liters capacity and equiped with a 500 watt heater and an electric fan at opposite ends of the same relay, and two stirrers, one located near the furnace so as to pass by it a constant stream of water from below. It was set at 35°C and could dissipate an extra kilowatt of energy without running away. The thermostat was set on a laboratory desk and had a glass window through which the temperature measurements were made.

Current was supplied by a one killowatt transformer with an 8.5 ohm control resistance in the primary. The furnace current was of the order of 150 amperes at 6 volts.

In the diagram the glassware outside the thermostat is considerably simplified, omitting the vestigial remains of earlier stages of development, but the apparatus is in principle as shown, a Toepler pump (P) to force gas into the furnace bulb, a gas reservoir (R), and a stopcock (R) which isolates them from the McLeod gauge (G) and the vacuum pumps which are connected at V, a single stage mercury diffusion pump backed by a Hyvack oil pump. The top of the manometer is also brought back to the high vacuum line so as to give absolute pressure measurements. Due to high pressures sometimes used it reaches clear to the ceiling as do also the delivery tube and compensating arm of the Toepler pump. The stop-cocks A, B, and C were set in Dennison's banker's specie sealing wax and warmed with a hand torch when turned. They withstood differences of pressure up to 2 1/2 atmospheres and remained tight indefinitely, though A stuck badly and also leaked on one occasion as the wax worked thin after many turnings. A and B were of [illegible] cm. bore.

After the furnace was assembled and installed and the thermostat filled the whole system was evacuated with cocks A and B open, C closed, and pump P connected to the floor vacuum. When a vacuum of $10^{-4}$mm. was obtained it was assumed that the whole system was tight. The furnace was run for a few minutes to drive off any adsorbed inert gases. Then C was opened, and when vacuum was reestablished, B was closed. Carbon monoxide was generated from sodium formate and sulphuric acid, washed in sodium hydroxide and sulphuric acid, passed through a tube of phosphorous pentoxide, and admitted to the apparatus through D, a greased three-way stop-cock. Simultaneously the vacuum was released on the

the pump P. The apparatus was usually filled to one atmosphere, but several times to 1/2 atmosphere as this had to be below the pressure in the furnace tube. Then cocks C and A were closed. Additional gas was pumped into the furnace tube by applying pressure to P from the compressed air line or an oxygen tank. To set the pressure precisely the Toepler pump was operated with the furnace running. The pressure could be reduced to that of the reservoir by opening the cock A. As the thermostat had to be drained a couple of inches whenever this cock was turned, runs were made as much as possible in the order of increasing pressure.

The rate of reaction was so slow, and the quantity of material so small, corresponding to a total change of ten inches pressure in the enclosed volume of about a hundred cubic centimeters, that there was no prospect of waiting for the system to attain equilibrium. Instead it was merely used as an indicator of the distance from equilibrium. Each run constituted a measurement of the rate of reaction at a predetermined temperature and pressure.

The furnace was first thrown on and brought to the approximate temperature. Then gas was pumped in to the proper pressure. Then readings were made on the optical pyrometer and the furnace current readjusted by the control rheostat in the transformer primary till the temperature was that set for the run. Then the pressure was read on the manometer. (With the aid of a ladder borrowed from the janitor) The temperature was adjusted before each of the pressure readings which were taken at intervals of three to ten minutes for periods of one to three hours. The temperature fluctuated considerably, commonly five degrees, often ten, occasionally as much as thirty.

In working up the data the pressures during a run were plotted against the time on a piece of graph paper. The slope of the best straight line gave the rate for the run. Rates at the same temperature were then plotted against the mean pressure for the run. A straight line was then drawn through these rates if possible and the intercept taken as the equilibrium pressure for the temperature. If the data was not so good, an estimate was made from the graph as to the most probable pressure at which the rate should become zero. Since a steel tape graduated to sixteenths of an inch was the only available manometer scale, pressures were determined in feet, inches, and sixteenths of mercury, the final unit being one sixteenth of an inch of mercury. (1 sxinch = 1.5875mm.) Equilibrium pressures were finally converted to atmospheres and a plot made of log(p) against $10^4/T$.

## The Equilibrium Measurements.

With the apparatus and procedure described above it was found impossible to obtain interpretable results till allowance was made for the emission of carbon monoxide from adsorbed oxygen on the carbon furnace. With a blank pellet of powdered graphite rates of emission were found entirely comparable with previous rates of reaction, increasing with the temperature, but entirely independent of the pressure. After baking for five hours at 2000° and 1 1/2 atmospheres rates were zero at lower temperatures. After twelve hours more the rate was also zero at 2000°. There was however a slight emission for a few minutes, presumably adsorbed carbon monoxide, after the furnace had been standing for some time cold. A sharp distinction must be drawn between adsorbed oxygen and adsorbed carbon monoxide. The removal of the former is an irreversible reaction requiring prolonged baking for its completion and is independent of the pressure. The latter probably enters into a true adsorption equilibrium. The extent of the reaction, however is slight, and equilibrium is rapidly attained. It was concluded that satisfactory runs could be obtained provided the furnace was baked over night at the highest temperature to be used in the early life of the furnace. Pressures were employed above the equilibrium pressure of the zirconium-carbon system so that the initial state of the system should be known after the baking.

Pellet #15 spent its whole life at 1880°K. The furnace was evacuated and closed off. It was run for ten minutes developing a pressure of five inches. This was pumped off and the furnace filled to one atmosphere and closed. A short run indicated a rapid rise as was to be expected from adsorbed oxygen. The pressure was then raised to three atmospheres. The pressure fluctuated too much to observe a rate over a short period of time in spite of the fact that the mercury column was damped by a piece of capillary tubing in the bottom of the manometer. Next morning the pressure had dropped an inch. The drop continued throughout the day. The pressure was lowered to one atmosphere at which pressure a very slight decrease continued. The system was then evacuated and a controlled run of three hours was made in which the pressure rose to five inches. This ran the reaction ahead a ways so that the pellet was more active thereafter. Two more uncontrolled runs were made, and then three in which the reaction was followed according to the outlined procedure. The experiment was terminated by a crack in the vacuum system which upset the manometer as the furnace was under reduced pressure. The equilibrium pressure was estimated as 0.522 atmospheres. This is the most uncertain of the points determined due to the lack of enough controlled runs.

The rest of the equilibrium measurements were made on pellet #16. After the preliminary treatment the system was evacuated and run for anhour at 1948°K till the pressure rose to 4". Then a run was made at 46cm, which gave a good forward rate, at92 cm. where the rate was zero, and at 143cm. where the reaction was strongly reversed. Six more runs were spotted in between. Zero rate persisted over quite a range of pressure. This seems to be connected with the fact that the line voltage was fluctuating considerably. The seeing became bad do to the eye-strain of the constant readjustment of the temperature, and this added to the difficulties of the temperature regulation. The effective rate should be an average rate over the temperature fluctions. The persistance of a zero rate may well be due to the necessity of building up an interface before the rate could become appreciable. This interface would be rapidly destroyed in a momentary reversal of the reaction, while there would be an appreciable, lag before it could be reestablished. Thus if the set pressure corresponded to the equilibrium at a temperature well within the range of fluctuation there would be no resultant reaction.

In the series at 2015°K conditions seemed very much better and there were no zero rates, though this may well be due to the higher rate of reaction due to the temperature. However, down at 1914°K the seeing was again exceptionally good, and the temperature required only occasional adjustment. In both these series the rates seem to bear a linear relation to the pressure and the intercepts of the lines drawn appear to be the best determinations of the equilibrium.

In the experiments at 1982°K the physical conditions were at their worst, but enough rates were taken to justify a fairly close estimation of the equilibrium pressure.

However scattered some of the data may be, the most probable value of the equilibrium pressure can be estimated in every case to better than ten per-cent. The points were estimated from the graphs quite independent of other considerations, and before the recalibration of the temperature scale. These points are plotted on the graph of log(p) against the reciprocal temperature as points in circles. The cross and circle at 2015°K represents an estimate made neglecting the linear relation of rate to pressure at this temperature. The similar point at 1880°K represents the intercept of a line connecting the two controlled rates nearest the equilibrium. Neither of these can be regarded as inconsistent with the experimental data, but the most probable value of the equilibrium pressures over the range of the experiments was taken as represented by the straight line on the graph to which the agreement of the individual estimates is better than was anticipated. This gives the relations:

$$\log(p) = 8.592 - 16580/T \quad \text{(in atmospheres)}$$

$$\Delta F^o = 151{,}800 - 78.68T$$

$$\Delta H = 151{,}800 \text{ calories}$$

In the middle of the series at 1982°K the the apparatus was evacuated and run till two inches pressure was developed, now carrying the reaction somewhat over half way to completion instead of a third as before. The agreement of this run and of the subsequent run at 1914°K with the rest of the data afford evidence that the equilibrium is one of one degree of freedom as was hoped from the start.

The values determined for the equilibrium pressure follow below.

| Temperature | Pressure | Log(p) | $10^4/T$ | $\Delta F^{\circ}$ |
|---|---|---|---|---|
| 1880°K | 0.522 atm. | $\bar{1}.7177$ | 5.320 | 4865 cal. |
| 1914 | 0.856 | $\bar{1}.9325$ | 5.223 | 1184 |
| 1948 | 1.21 | 0.0828 | 5.134 | -1478 |
| 1982 | 1.67 | 0.2227 | 5.046 | -4045 |
| 2015 | 2.32 | 0.3655 | 4.963 | -6746 |

The free energy becomes zero at 1930°K.

## Analysis of Reaction products.

The procedure adopted was to weigh a sample onto a platinum foil in an assay balance, ignite in an oxygen bla blast and reweigh. The samples ranged from 9 to 20 milligrams from pellets composed originally of zirconium oxide and graphite. The zirconium was obtained by igniting Kahlbaum zirconium nitrate. The carbon was ground Atcheson graphite. Two different proportions were used, one of approximately molecular proportions to make ZrC, the other, $ZrC_2$. Taking the ignited residue to be $ZrO_2$, the per-cent Zr in the original sample could be computed, and knowing the initial composition, be taken as an indication of the extent to which the reaction had gone.

The first indication of an equilibrium came from a comparison of pellets #10 and #11. the former had gone to a considerable extent at 2000°K and 2 atmospheres pressure. In the latter at 1880°K and 2 atmospheres nothing happened. A comparison of #12 and #13 showed at 1880°K in vacuo little more progress in nineteen hours than in three. This was erroneously taken as evidence that the final product was $ZrC_2$, but the analysis of pellet #20 shows that further progress is possible to compositions corresponding to ZrC as the final product. Presumably the high temperature of this run was necessary to accererate the reaction of particles not in intimate contact.

Analyses of pellets of the second composition gave percentages of Zr corresponding to the exhaustion of the $ZrO_2$. It is of interest to remark that pellet #16 on which most of the equilibrium measurements were made, which was run for a very long time but not to completion, consisted of two parts, a sintered core which had gone to completion, and some loose powder of intermediate composition.

Samples of the original pellets were fairly difficult to ignite, requiring prolonged heating in the blast to oxidise the graphite. Samples high in carbide, however, burned spontaneously when brought up to temperature, being a glowing coal when removed from the blast before complete oxidation. They also expanded about three times in volume, falling to a white powder. The original pellets were quite compact, while the carbide samples were a friable sintered mass, easily broken with ivory tipped tongs.

Pellet #19 was a sample of pure zirconia originally. It was a hard grey-black mass which had to be crushed with steel pliers. It showed some activity in the blast, indicating an appreciable carbide formation by reaction with the carbon of the furnace.

The above data is of interest, but is not conclusive as to the formula of the product. I am greatly indebted to Mr. Hendricks for taking X-ray powder photographs of several of the samples which completely determine the nature of the solid phases in the system.

## Analyses.

| Sample | Zr Content | Temperature | Pressure | Time |
|---|---|---|---|---|
| Original | 55.9% | | | |
| | 56.6 | | | |
| #10 | 71.9 | 2000°K | 2 atm. | |
| #11 | 57.4 | 1880 | 2 atm. | 20 hrs. |
| #12 | 69.0 | 1880 | vacuo | 3 |
| #13 | 73.7 | 1880 | vacuo | 19 |
| #20 | 85.7 | | | |
| | 85.0 | 2200 | vacup | 10 |

If the reaction went to completion by the exhaustion o of $ZrO_2$ to form either Zr or ZrC, the final proportion should be 86.1% Zr. If the reaction went to completion by the exhaustion of C to form $ZrC_2$, the final proportion should be 78.0% Zr.

| Sample | Zr Content | Temperature | Pressure | Time |
|---|---|---|---|---|
| Original | 53.7% | | | |
| #14 | 76.0 | 1880°K | vacuo | 22 hrs. |
| #15* | 75.8 | | | |
| #16* core | 80.0 | | | |
| # core | 78.6 | | | |
| powder | 64.7 | | | |
| #17 | 78.7 | 2100 | vacuo | 8 hrs. |
| #19 ($ZrO_2$) | 75.4 | 2000 | vacuo | 24 hrs. |

Samples #14 - #17 on going to completion should be of composition 78.8% Zr. Sample #19 was originally pure $ZrO_2$.

$$Zr/ZrO_2 = 73.9\%$$

$$Zr/ZrC_2 = 78.8\%$$

$$Zr/ZrC = 88.3\%$$

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* See account of equilibrium measurements for detailed history of pellets #15 and #16

# A Summary of the Data on Zirconium Compounds.

By Courtesy of Mr. Sterling B. Hendricks.

Sample #17 Predominantly ZrC with a slight impurity of monoclinic $ZrO_2$. Impurity does not exceed 5% since only two of the strongest of the powder lines of $ZrO_2$ appear. The structure of ZrC was determined on this sample. It is cubic, having a NaCl type of sruucture. This is borne out by the previous work of Becher and Ebert, etc. All of the powder lines are accounted for, removing the possibility of the presence of an unknown compound in the system.

Sample #13 Chiefly $ZrO_2$, monoclinic, but contains an appreciable amount of ZrC, somewhat above 5%. Since ZrC lines are not shifted from those of #17 the presence of solid solutions is made highly improbable.

Sample #19 Chiefly $ZrO_2$, monoclinic; contains a smaller amount of ZrC than does #13 (almost pure $ZrO_2$). A comparison photograph of $ZrO_2$ obtained by ignition of $Zr(NO_3)_4$ gave exactly the same lines as the $ZrO_2$ of the sample.

The possibility of the presence of ZrO or $Zr_2O_3$, compounds which have probably been prepared by Friedrich and Sittig, is precluded. Other dimorphs of $ZrO_2$ do not appear; cubic and tetragonal forms have been reported. $ZrC_2$ is certainly absent from the entire scheme. This requires the reaction to be:

$$\underset{\text{(monoclinic)}}{ZrO_2} + \underset{\text{(graphite)}}{3C} = \underset{\text{(cubic)}}{ZrC} + \underset{\text{(gas)}}{2CO}$$

## Thermodynamic Calculations.

It has already been seen that the free energy and heat of reaction may be expressed over the range of the experiments by the expressions:

$$ZrO_2 + 3C = ZrC + 2CO$$

$$\Delta F^o = 151{,}800 - 78.68T$$

$$\Delta H = 151{,}800 \text{ calories}$$

The specific heats of graphite and CO were taken from Lewis and Randall, and those of $ZrO_2$ and ZrC estimated from Kopp's law according to the scheme given in Noyes and Sherril.

C $C_p = 1.1 + 0.0048T - 0.0_{5}12T^2$

CO $C_p = 6.50 + 0.0010T$

$ZrO_2$ $C_p = 14.2$

ZrC $C_p = 8.0$

Using the above heat of reaction and the zero value of the free energy at 1930°K gives the following equations for extrapolation down to room temperature:

$$\Delta H = 164{,}050 + 3.5T - 0.0062T^2 + 0.0_{5}12T^3$$

$$\Delta F^o = 164{,}050 - 3.5T\ln T + 0.0062T^2 - 0.0_{6}6T^3 - 59.06T$$

$$\Delta H_{298} = 164{,}580 \text{ calories}$$

$$\Delta F^o_{298} = 141{,}040 \text{ calories}$$

Combining this heat of reaction with the heat of formation of CO at 25°C and the heat of formation of $ZrO_2$ at 18°C - the discrepancy should be only five calories - as determined by Weiss and Neumann, gives a value for the heat of formation of ZrC.

$ZrO_2 + 3C = ZrC + 2CO \qquad \Delta H = 164{,}580$

$2CO = 2C + O_2 \qquad \Delta H = 52{,}280$

$Zr + O_2 = ZrO_2 \qquad \Delta H = -177{,}400$

$Zr + C = ZrC \qquad \Delta H = 39{,}360$

The high temperature heat of reaction is probably good tp 5,000 calories, the extrapolation not in error by more than eight. The determinations of Weiss and Neumann differ among themselves by 600 calories, but there is some doubt of the purity of their zirconium. So the heat of formation of the carbide may well be good to 10,000 calories.

# Critical Resume.

It was hoped at the outset theestablish directly the free energy of formation of zirconium oxide. Due to the formation of carbide, however, this quantity can not be determined without further research. The fact that Moissan prepared zirconium metal by reduction of the oxide by carbon at $2500^\circ$ would indicate that the equilibrium pressure must rise above one atmosphere for the reaction:

$$ZrO_2 + 2ZrC = 3Zr + 2CO$$

A carbon furnace would not be applicable, but the reaction might conceivably be carried out in a zirconia tube, or tungsten lined with zirconia. Difficulties would probably, arxise, because the metal is liquid, and zirconia somewhat volatile in this region, but would presumably be no worse than those already solved in the present research.

The development of a hollow Nernst filament would also open up the possibility of measuring directly the dissociation pressure of a number of oxides of a lower order of stability than zirconia. Mr. Yost has suggested ruthenium oxide as a suitable subject. A platinum tube might be used at the lower temperatures, but would probably have to be protected from the metal formed.

The reactions with nitrogen of both metals and metallic carbides might well yield to similar methods.

But the most immediate extension of the present work is probably the continuation of the study of the reduction of oxides by carbon in the present form of furnace. Beryllium, hafnium, thorium, cerium, and titanium would seem similar enough to zirconium to yield to very similar methods of attack. Magnesium and calcium will probably be available when the furnace itself is sufficiently studied that the preliminary baking can be reduced to a minimum. Aluminum also, if the metal is not too volatile.

The present technique offers many advantages over previous methods. The chief principle is the small size of the furnace. This allows the attainment and very accurate control of high temperatures with a minimum of power. It also makes it possible to completely enclose the apparatus in glass, and the energy evolved is not too great to permit thermostating the furnace and so obtain uniform conditions in the surroundings. The small size will also permit work on rare minerals since a few tenths of a gram of material will be ample for a complete study. Another point is the easy manufacture and replacement of the furnace itself which is bound to deteriorate with time at the temperatures employed.

The limiting factor in the present technique is the temperature control - by pyrometer measurements, in the face of a fluctuating line voltage. But the methods of temperature control in current use in precise optical pyrometry are entirely applicable and would certainly eliminate this source of inaccuracy - and of physical discomfort to the observer.

It is because of the fundamental simplicity of the method, and the possibility of very precise control that it would seem to be applicable to a wide variety of problems in the extention of precise measurements in physical chemistry to high temperatures. The chief fundamental limitation is that it applies directly only to equilibria with only one gaseous component where the reaction is not limited by diffusion in the gas phase, but progresses by direct displacement.

# Summary.

Apparatus and technique have been developed adequate for the study of equilibria between oxides and carbon at temperatures from 1000°K to 2200°K at pressures from a few centimeters to three atmospheres.

Temperatures were measured with an optical pyrometer. The furnace was a graphite tube 1/8" in diameter with a 1/64" wall supported on tungsten rods and enclosed in pyrex glass. The pressures were read on a mercury manometer. The enclosed gas space was about 100cc. and all below the water level of a thermostat at 35°C.

The procedure was to make a run at a set temperature and pressure determining the small rate of change of pressure. A series of such runs at a single temperature allowed an estimation of the equilibrium pressure.

Experiments were made on compressed pellets of $ZrO_2$ and graphite weighing approximately 90milligrams. The composition of the solid phases was determined from X-ray powder photographs taken by Mr. S. B. Hendricks. The free energy and heat of reaction were determined from 1380°K to 2015°K as according to the equations:

$$ZrO_2 + 3C = ZrC + 2CO$$

$$\Delta F^\circ = 151,800 - 78.68T$$

$$\Delta H = 151,800 \text{ calories}$$

# Acknowledgements.

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To Dr. W. E. Forsythe and the Nela Research Laboratory for the accommodation of furnishing the standard lamp, and to Dr. A. G. Worthing for advice. and reprints on pyrometric practice.

To Mr. S. B. Hendricks for the X-ray photographs which established the composition of the solid phases.

To the technical staff of the instute for cooperation in the construction of apparatus.

To Prof. A. A. Noyes for his support and encouragement in the research.

C. H. Prescott Jr.

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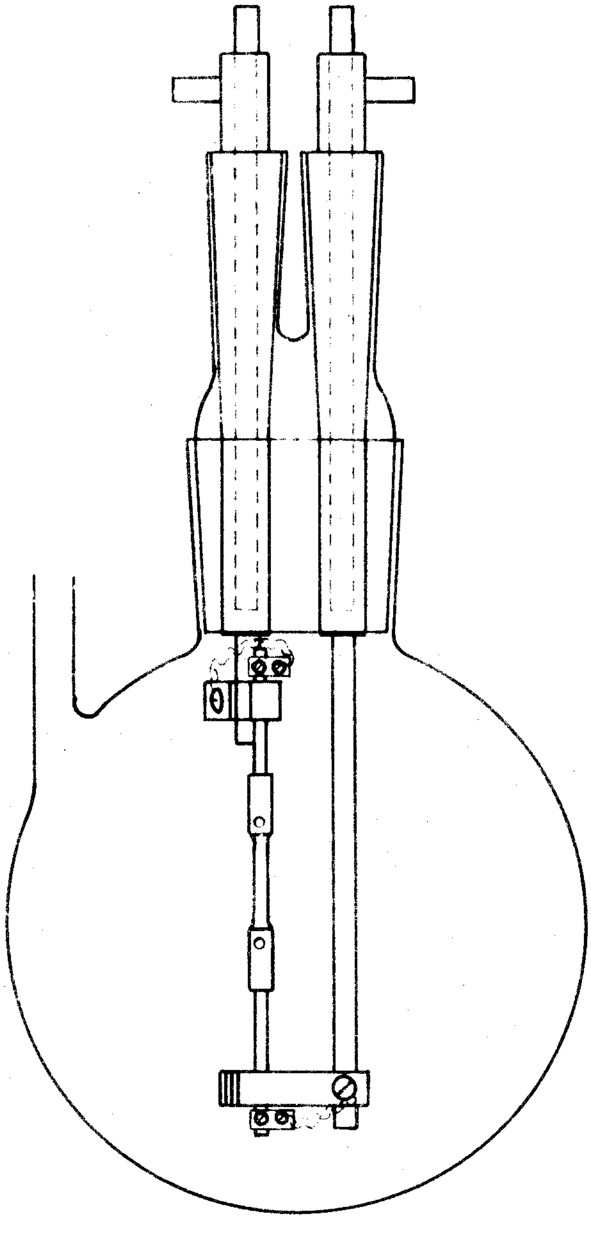
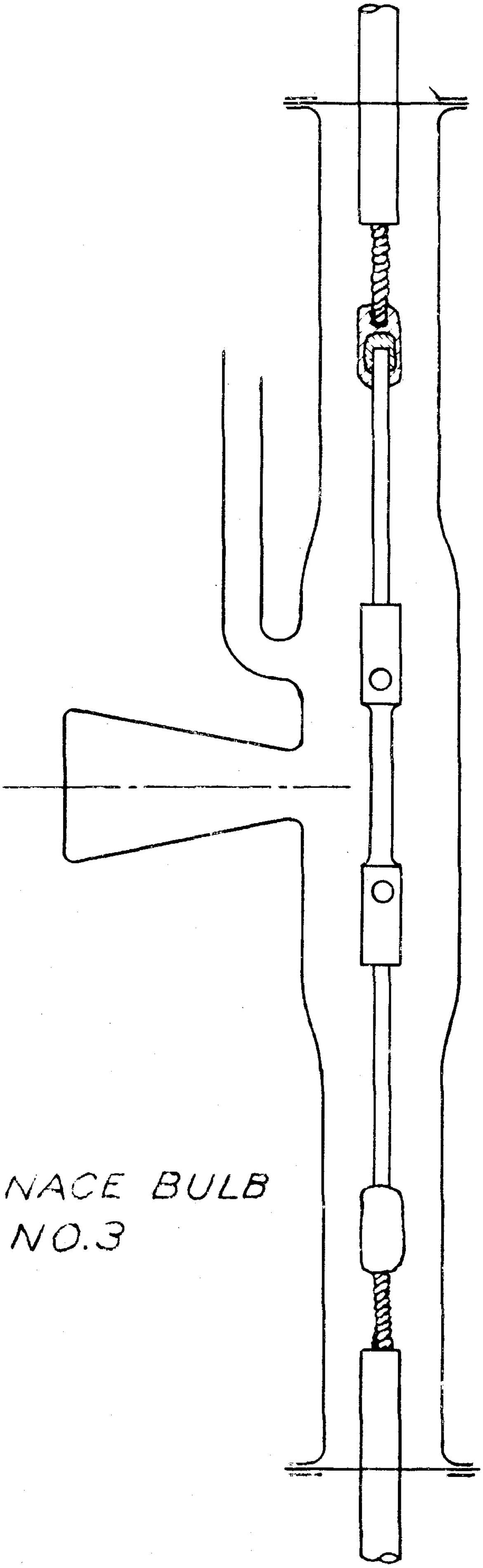


FURNACE BULB
NO. 1



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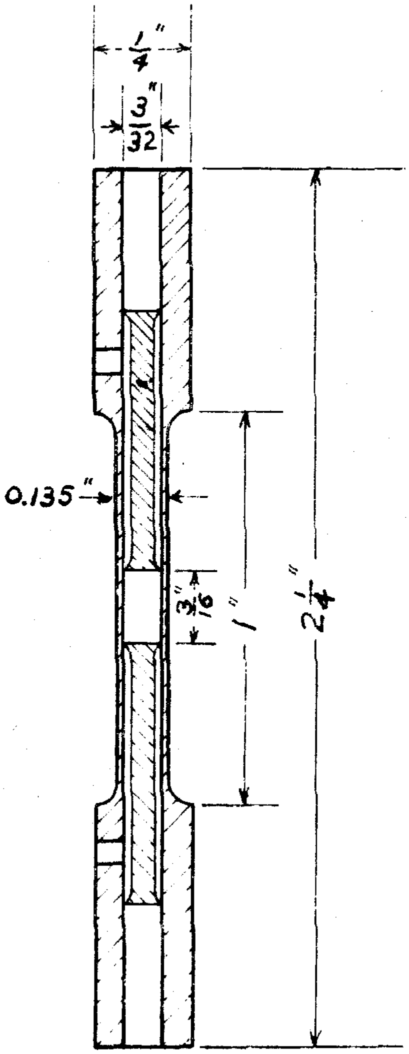


FURNACE

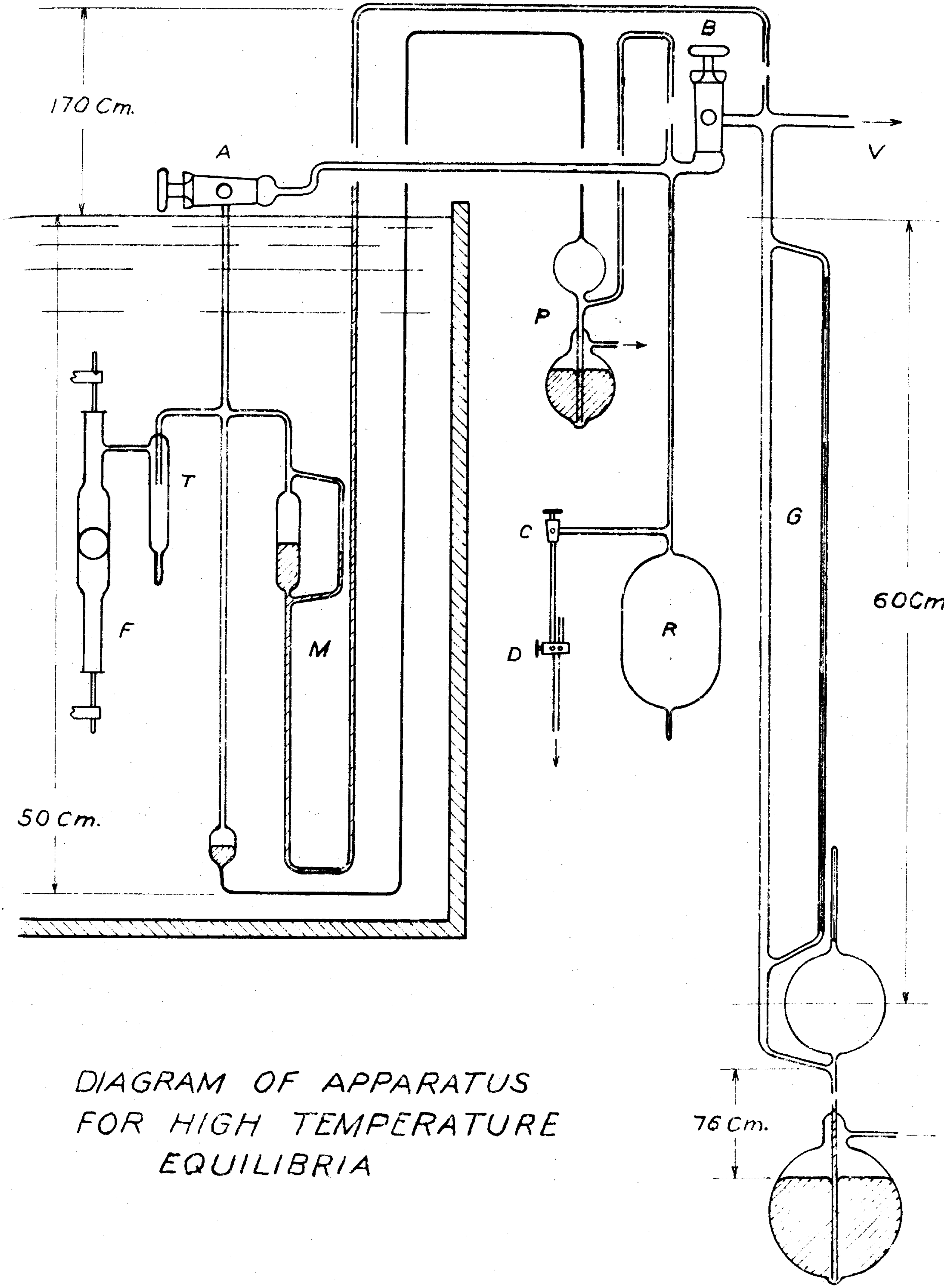
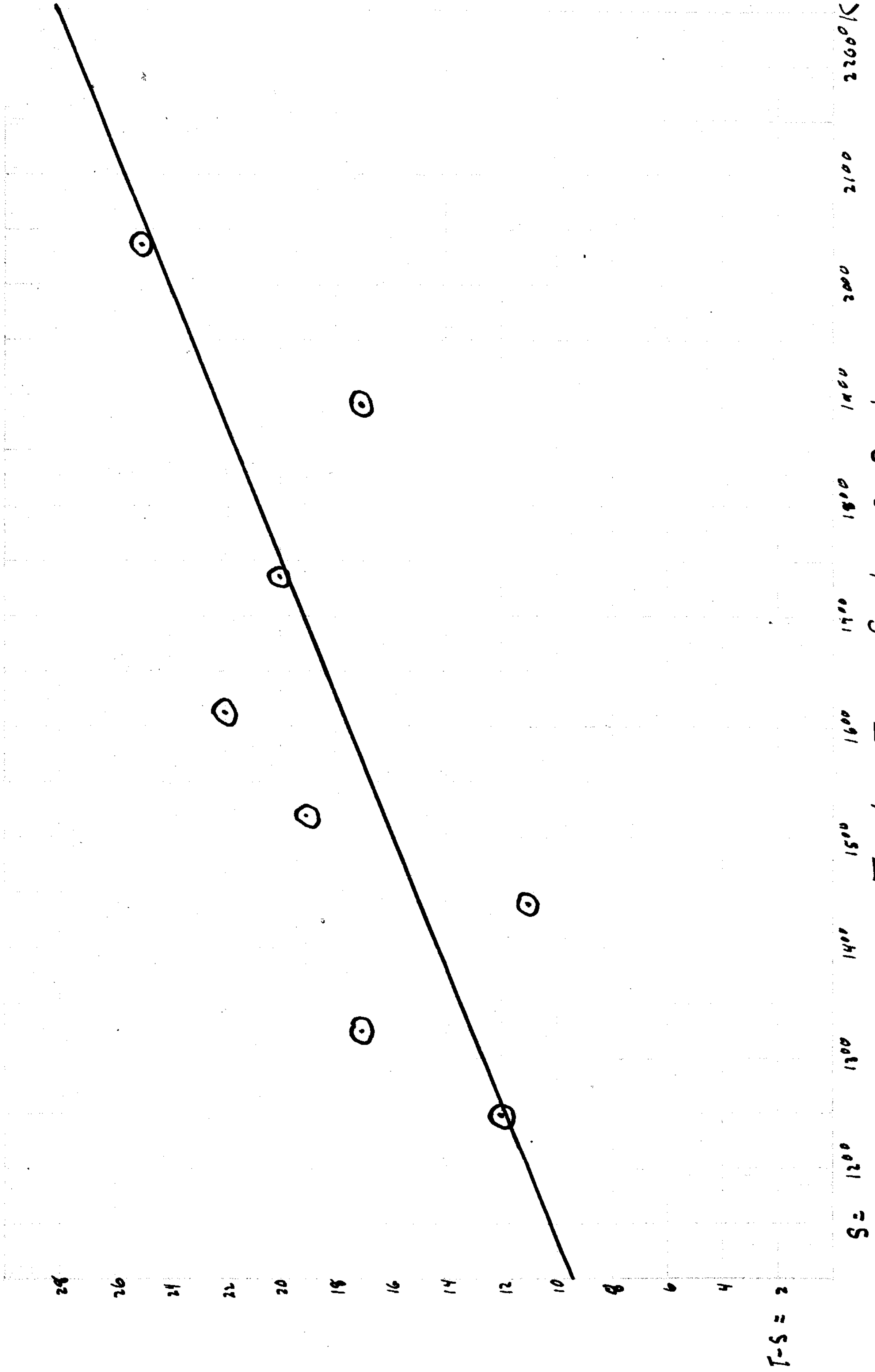
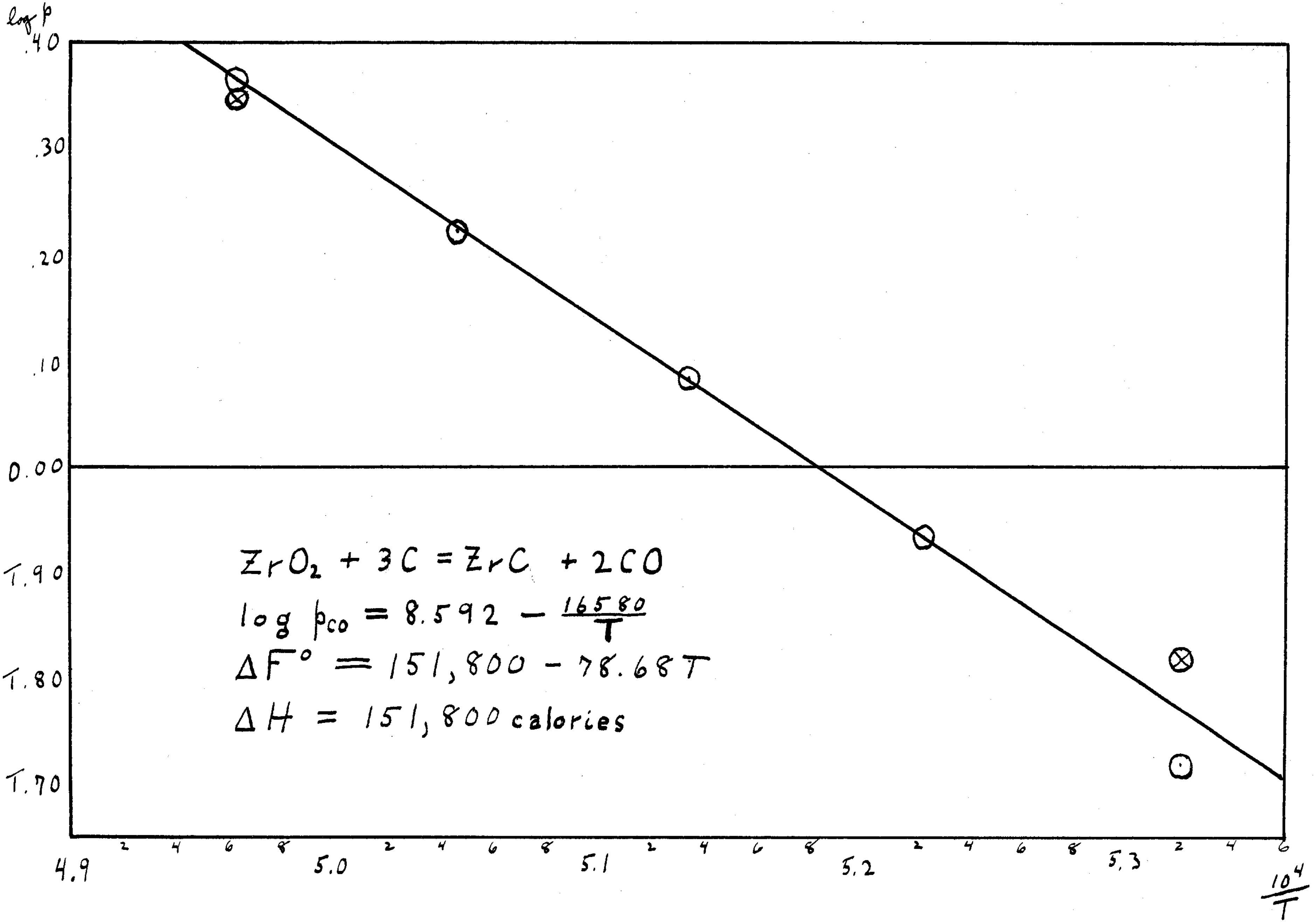


DIAGRAM OF APPARATUS
FOR HIGH TEMPERATURE
EQUILIBRIA

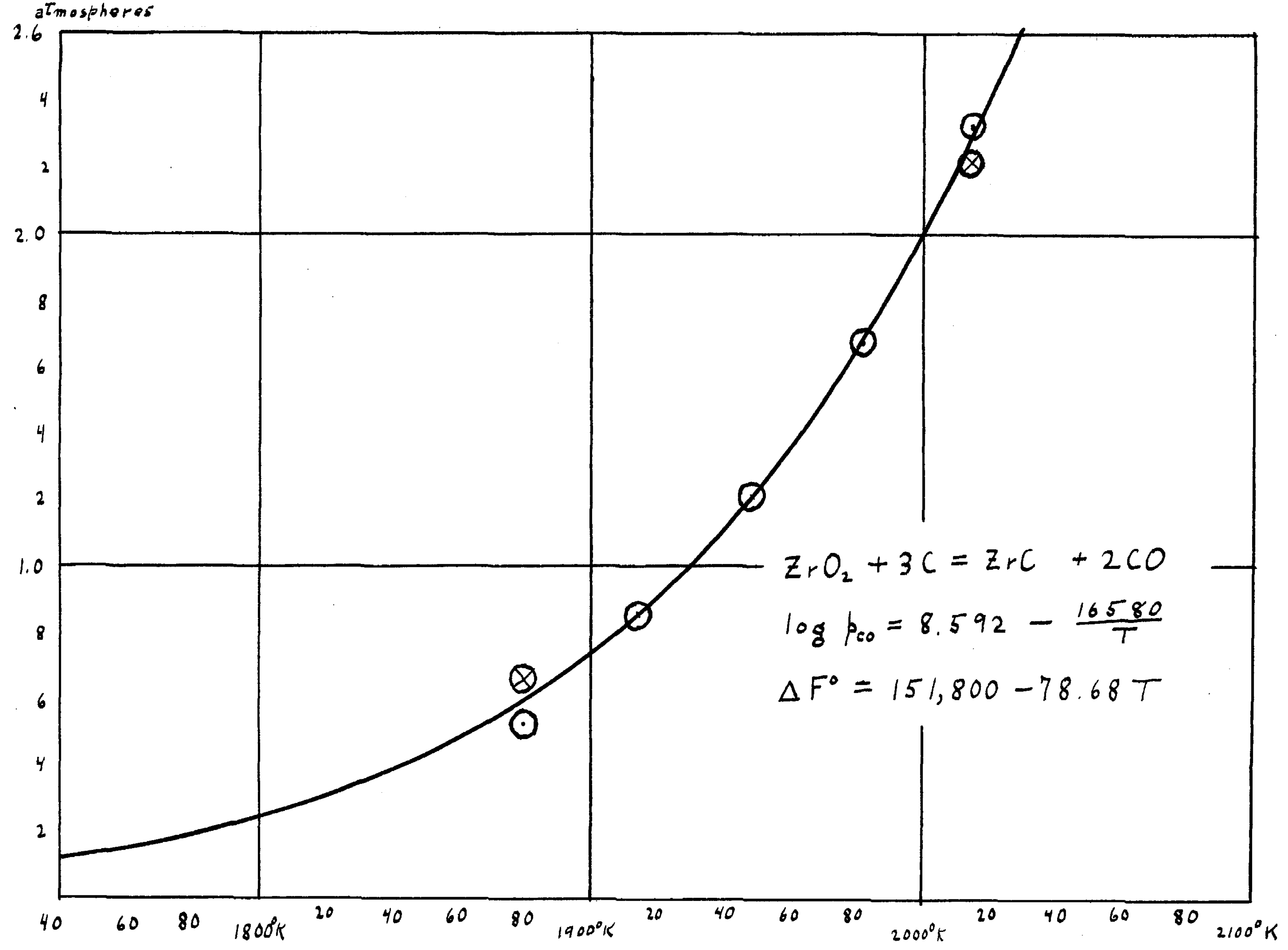


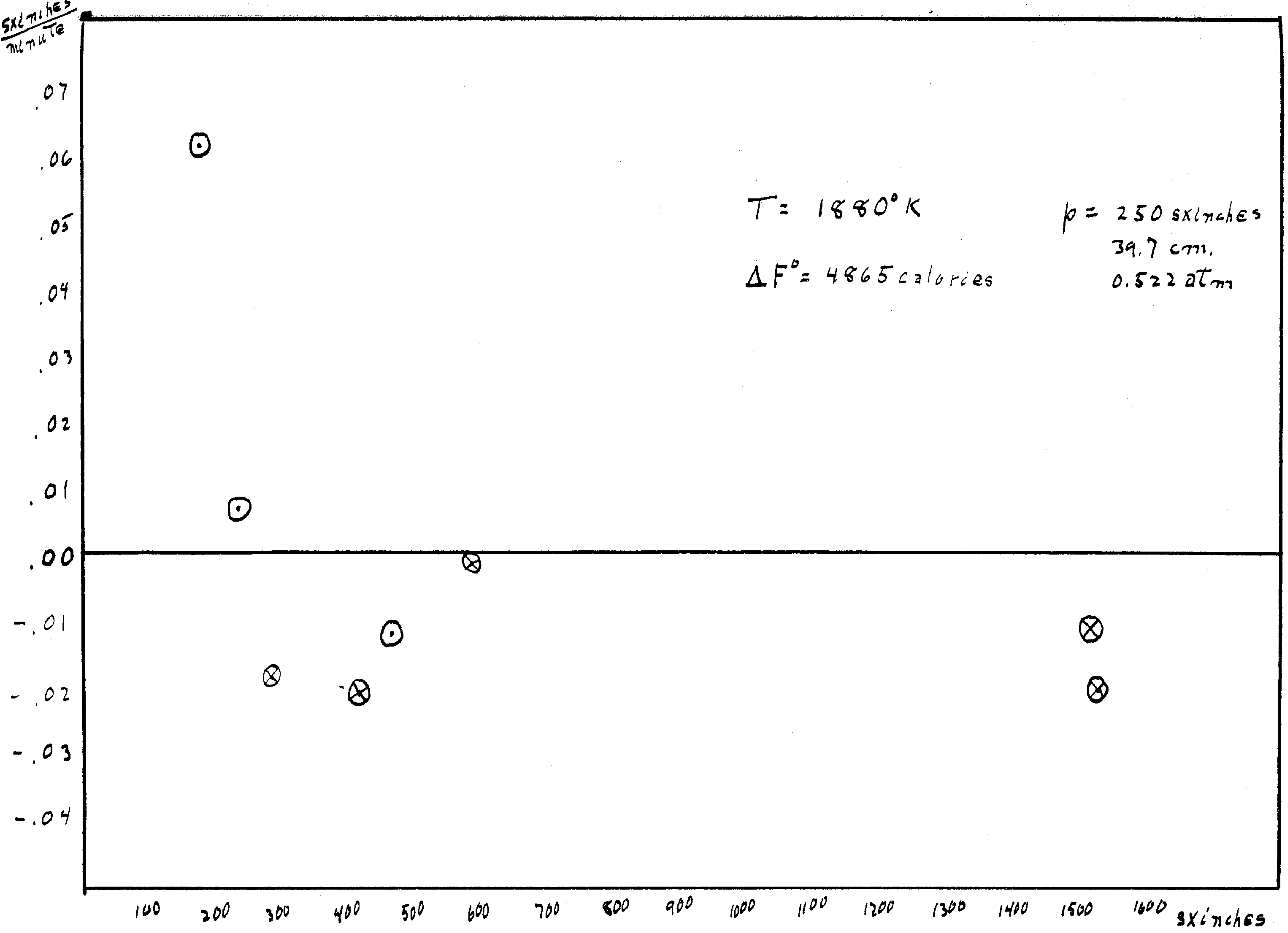
True Temperature Scale of Carbon

$T-S = 0.017S - 8$

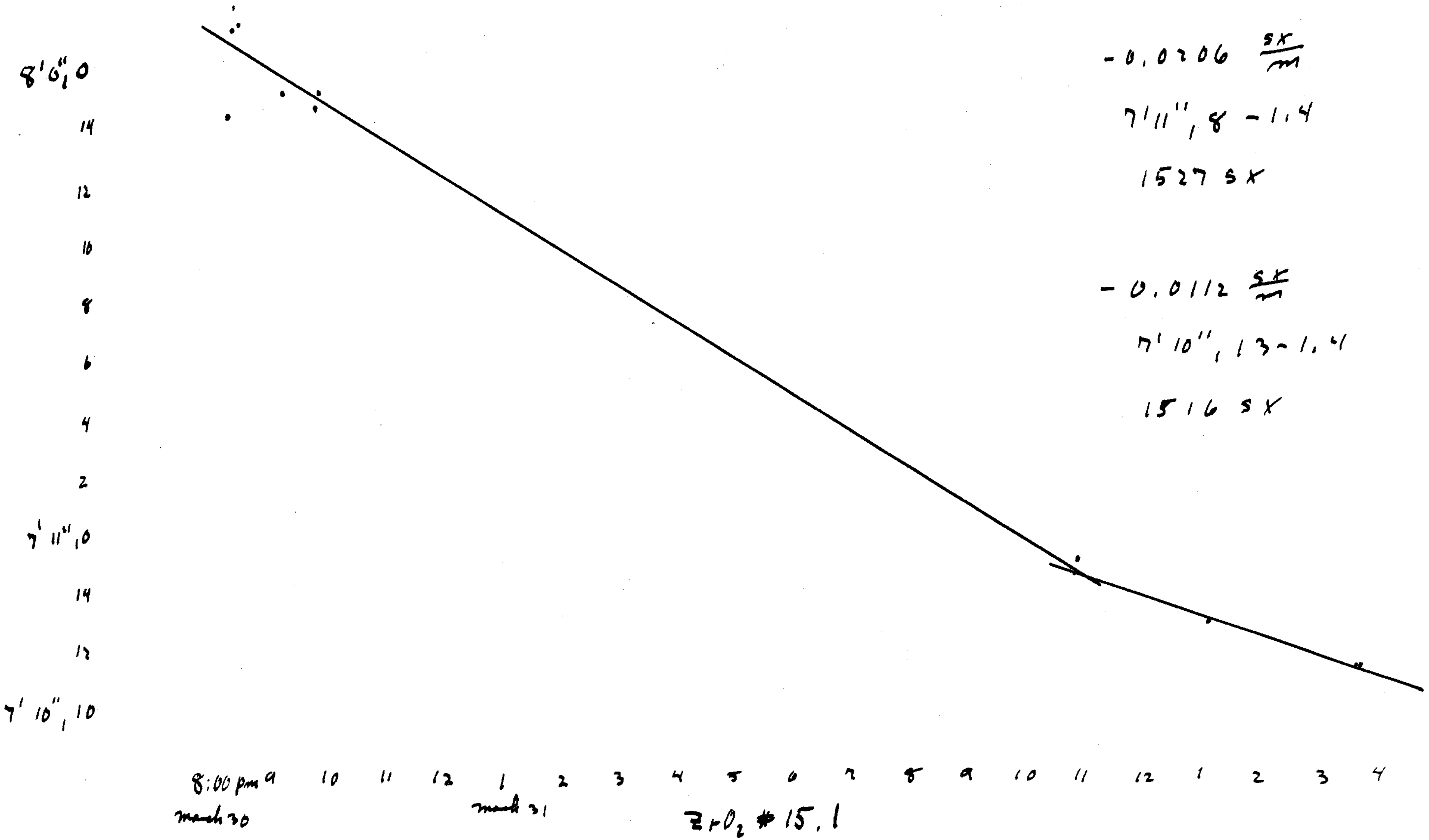


log p
.40
.30
.20
.10
0.00
$\bar{1}.90$
$\bar{1}.80$
$\bar{1}.70$
4.9
2
4
6
8
5.0
2
4
6
8
5.1
2
4
6
8
5.2
2
4
6
8
5.3
2
4
6
$\frac{10^4}{T}$
$ZrO_2 + 3C = ZrC + 2CO$
$\log p_{CO} = 8.592 - \frac{16580}{T}$
$\Delta F^\circ = 151,800 - 78.68T$
$\Delta H = 151,800$ calories


atmospheres
2.6
4
2
2.0
8
6
4
2
1.0
8
6
4
2
40
60
80
1800°K
20
40
60
80
1900°K
20
40
60
80
2000°K
20
40
60
80
2100°K
$ZrO_2 + 3C = ZrC + 2CO$
$\log p_{co} = 8.592 - \frac{16580}{T}$
$\Delta F° = 151,800 - 78.68T$


sxinches/minute
.07
.06
.05
.04
.03
.02
.01
.00
-.01
-.02
-.03
-.04
T = 1880°K
ΔF° = 4865 calories
p = 250 sxinches
39.7 cm.
0.522 atm
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
sxinches

$ZrO_2$ # 15



$-0.0206 \frac{sx}{m}$

7'11",8 − 1.4

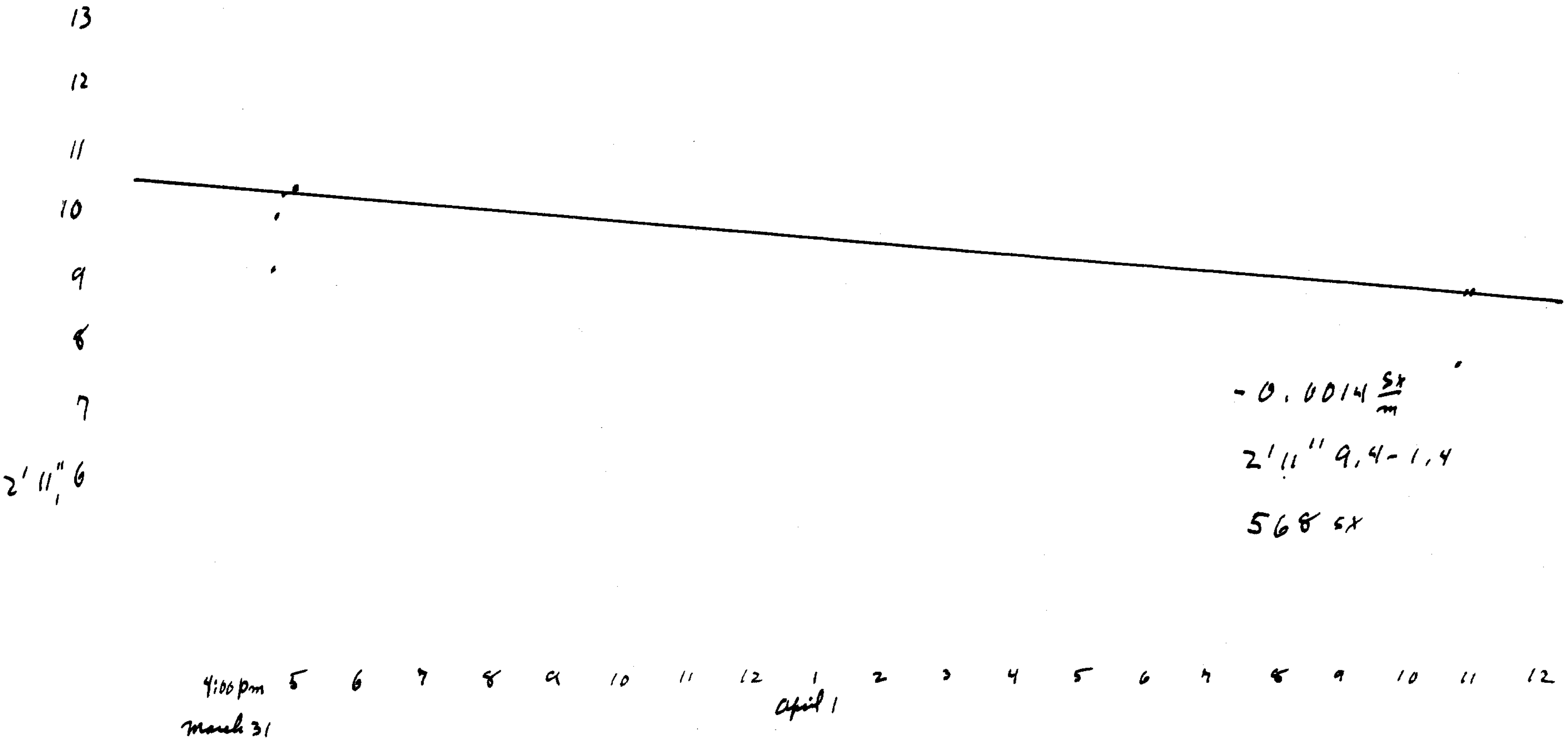
1527 sx

$-0.0112 \frac{sx}{m}$

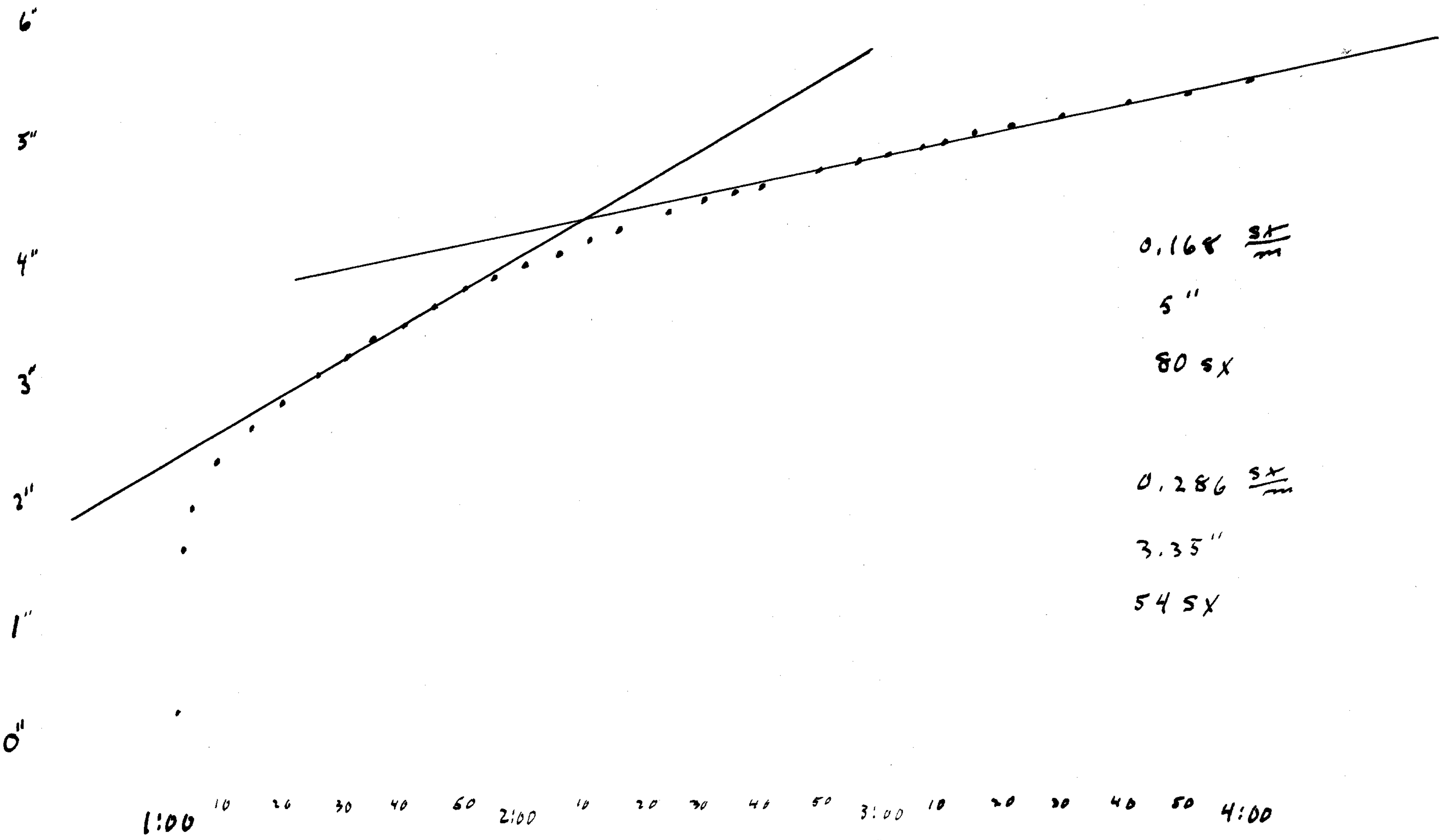
7'10",13 − 1.4

1516 sx

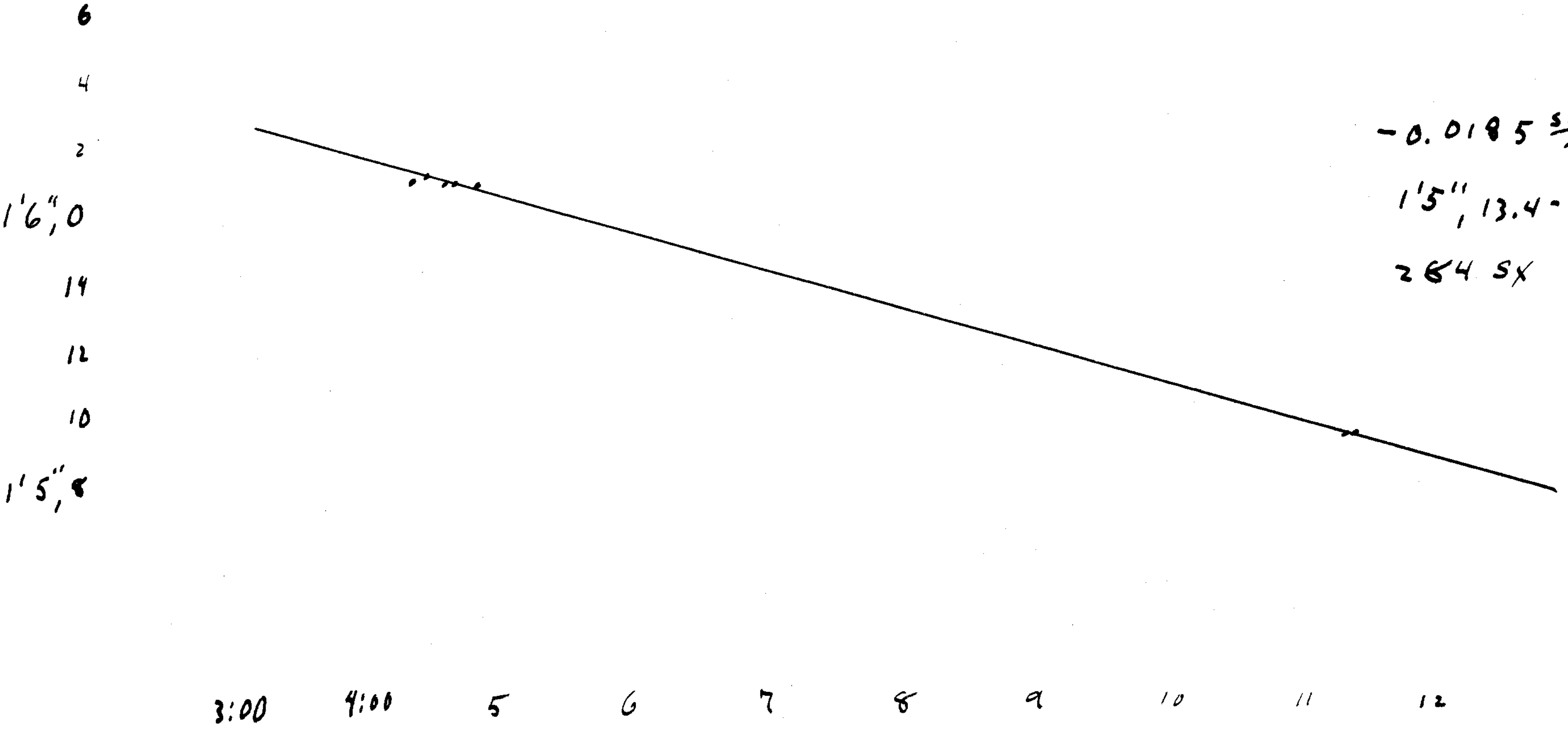
$ZrO_2$ #15.1


13
12
11
10
9
8
7
2' 11" 6
4:00 pm 5 6 7 8 9 10 11 12 1 2 3 4 5 6 7 8 9 10 11 12
March 31
April 1
-0.0014 sx/m
2' 11" 9.4-1.4
568 sx

$ZrO_2$ # 15.2


6"
5"
4"
3"
2"
1"
0"
1:00
10
20
30
40
60
2:00
10
20
30
40
50
3:00
10
20
30
40
50
4:00
0.168 sx/m
5"
80 sx
0.286 sx/m
3.35"
54 sx

$ZrO_2$ #15.3

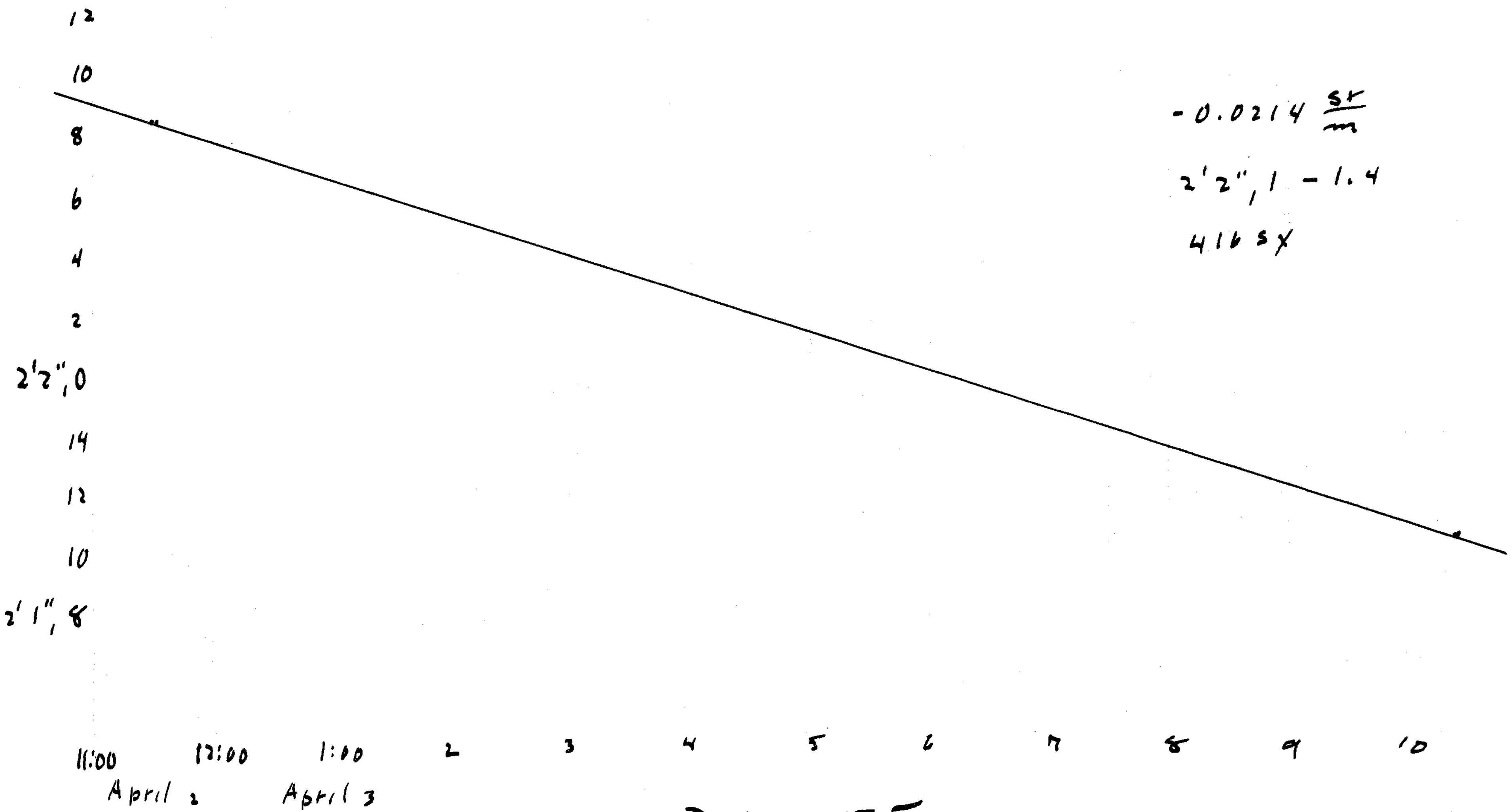


-0.0185 sx/m

1'5",13.4-1.4

264 sx

$ZrO_2$ # 15.4

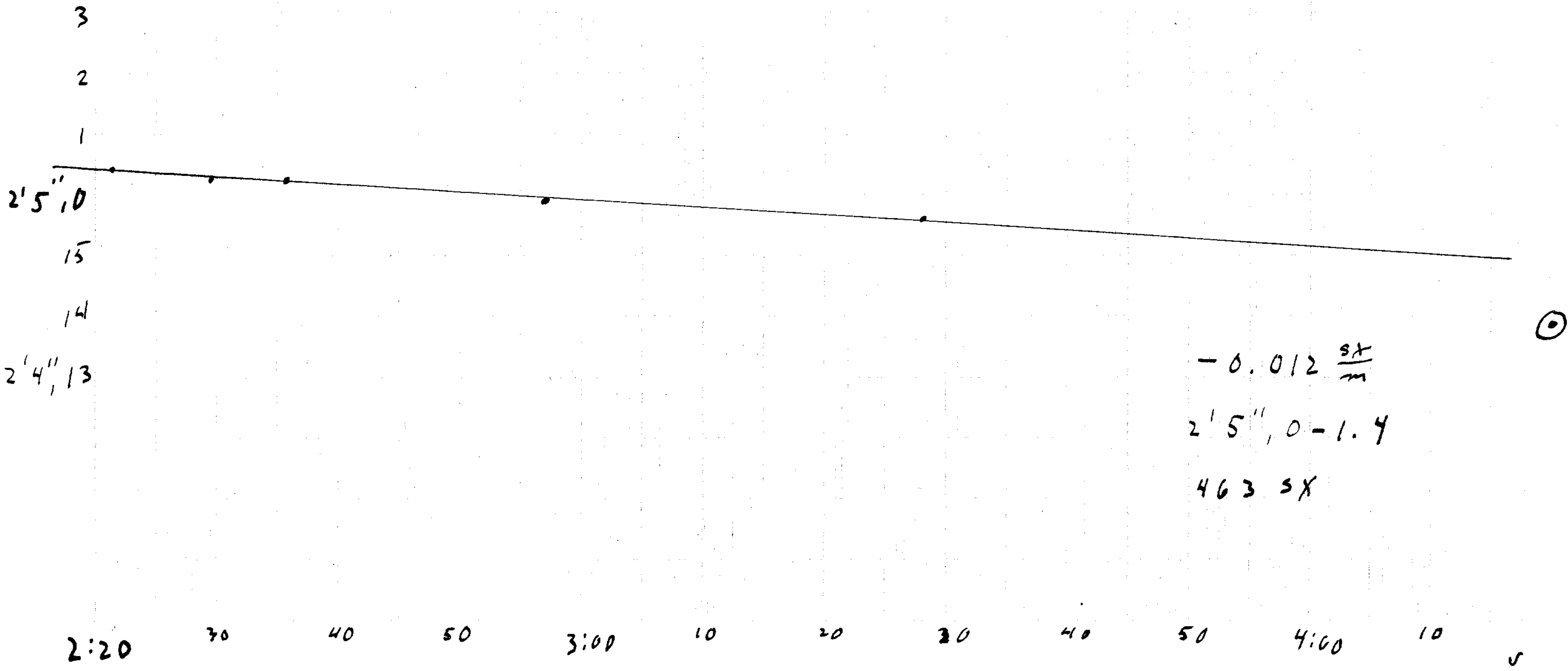


$-0.0214 \frac{st}{m}$

2'2",1 - 1.4

416 sx

$ZrO_2$ # 15.5

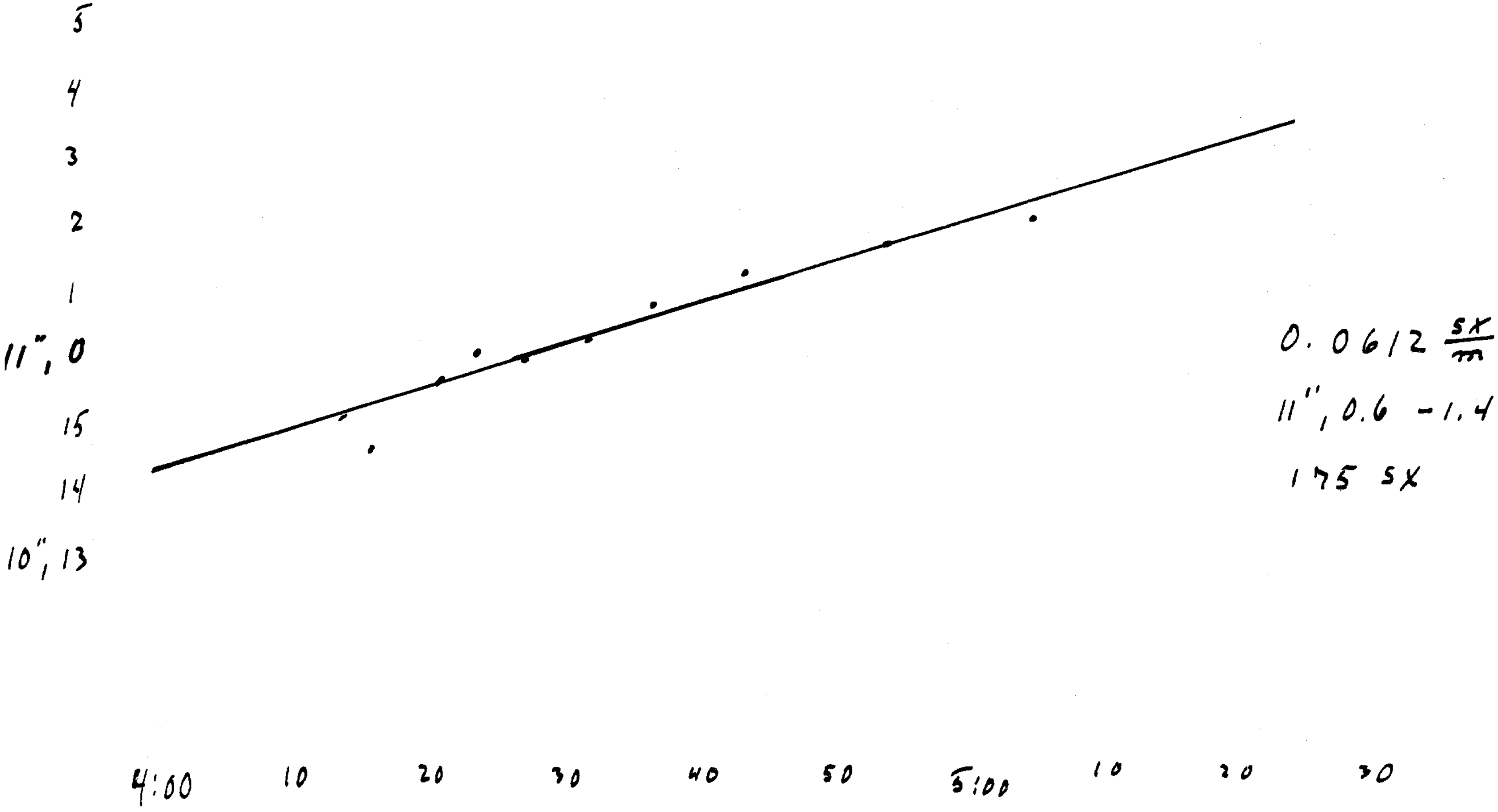


$-0.012\ \frac{sx}{m}$

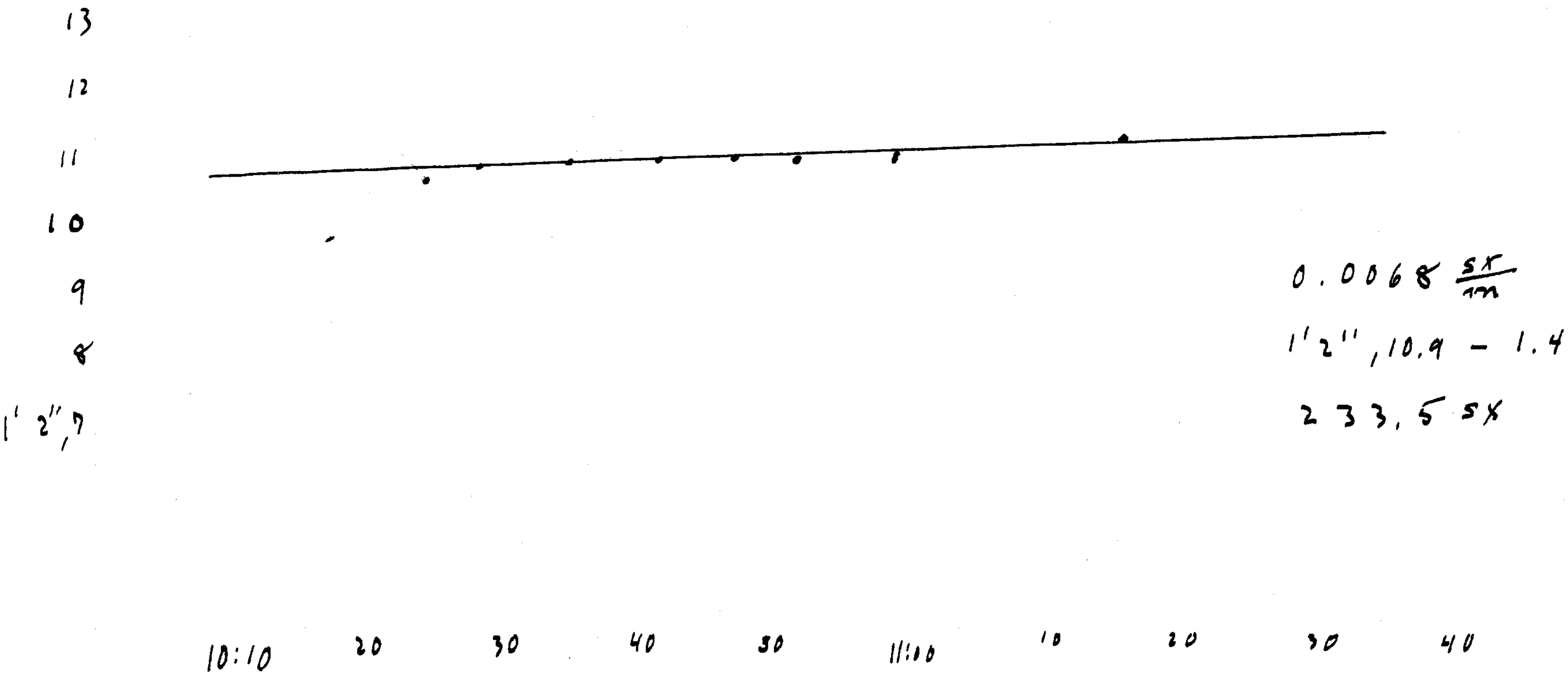
2'5'',0 − 1.4

463 sx

Z + $O_2$ #15.6


5
4
3
2
1
11", 0
15
14
10", 13
4:00
10
20
30
40
50
5:00
10
20
30
0.0612 $\frac{sx}{m}$
11", 0.6 - 1.4
175 sx

$ZrO_2$ # 15.7

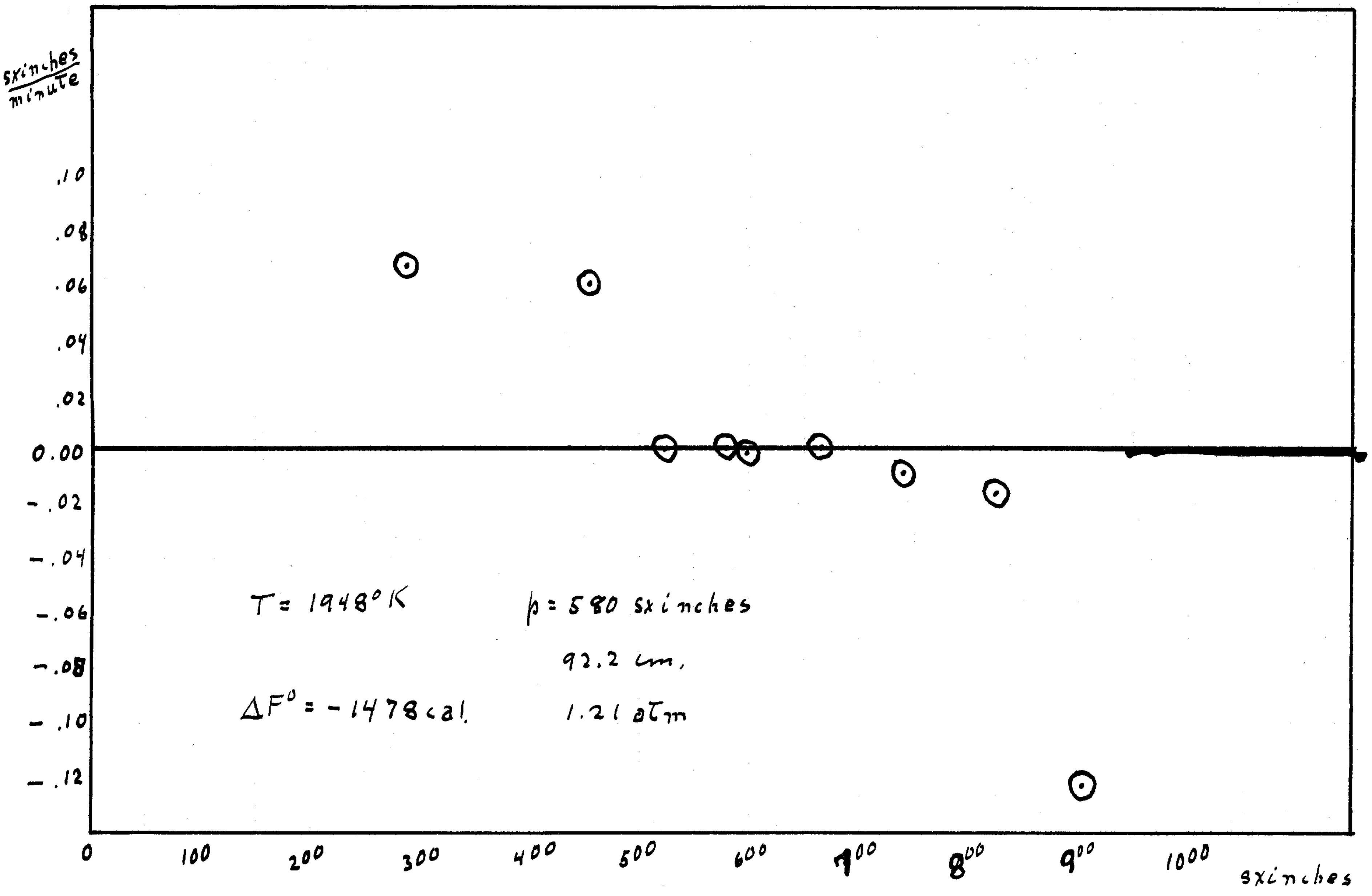


0.0068 $\frac{sx}{m}$

1'2'',10.9 - 1.4

233,5 sx

$ZrO_2$ # 15.8

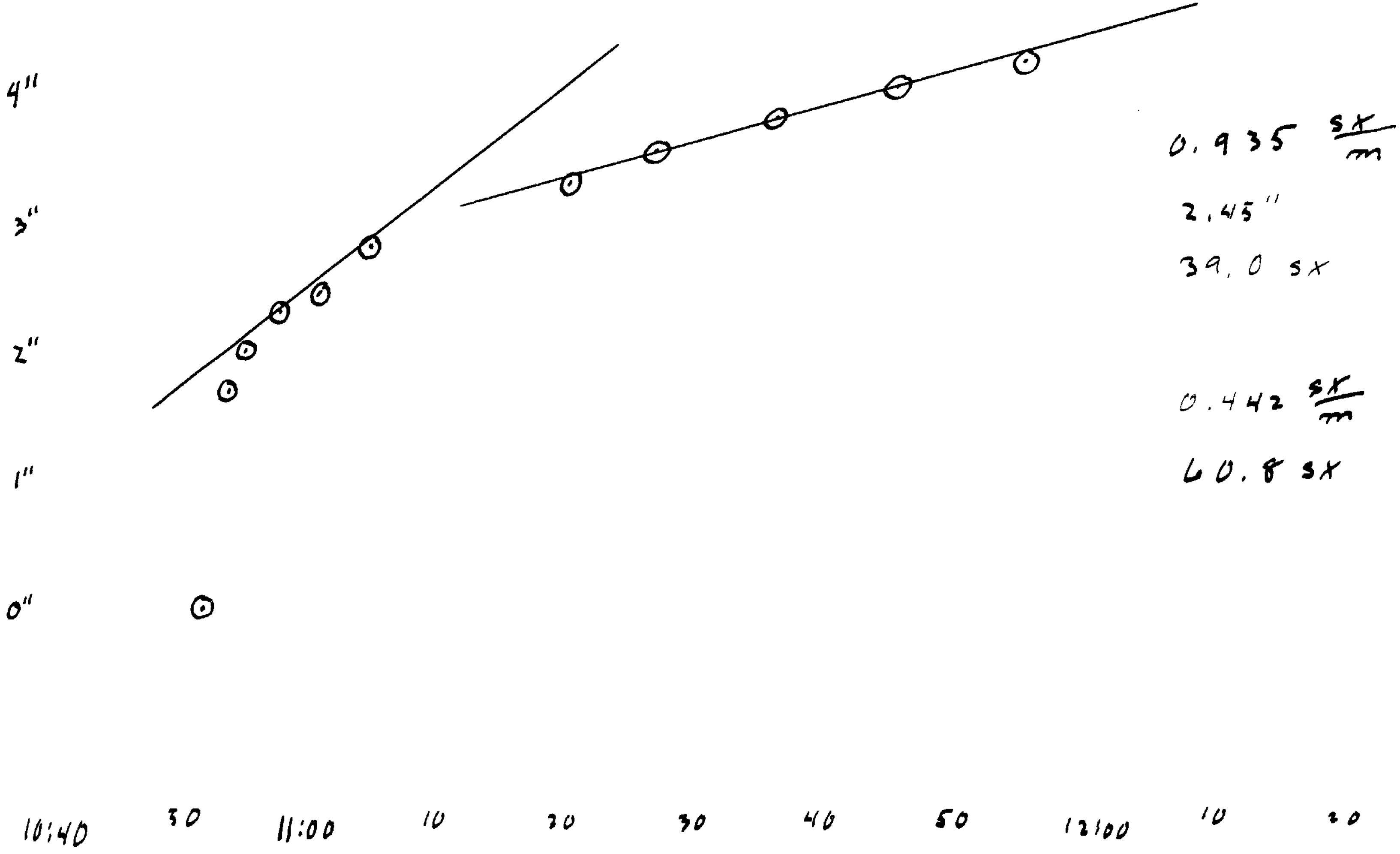


T = 1948°K

p = 580 sxinches
92.2 cm.
1.21 atm

$\Delta F^0$ = -1478 cal.

$ZrO_2$ # 16.0



0.935 $\frac{sx}{m}$

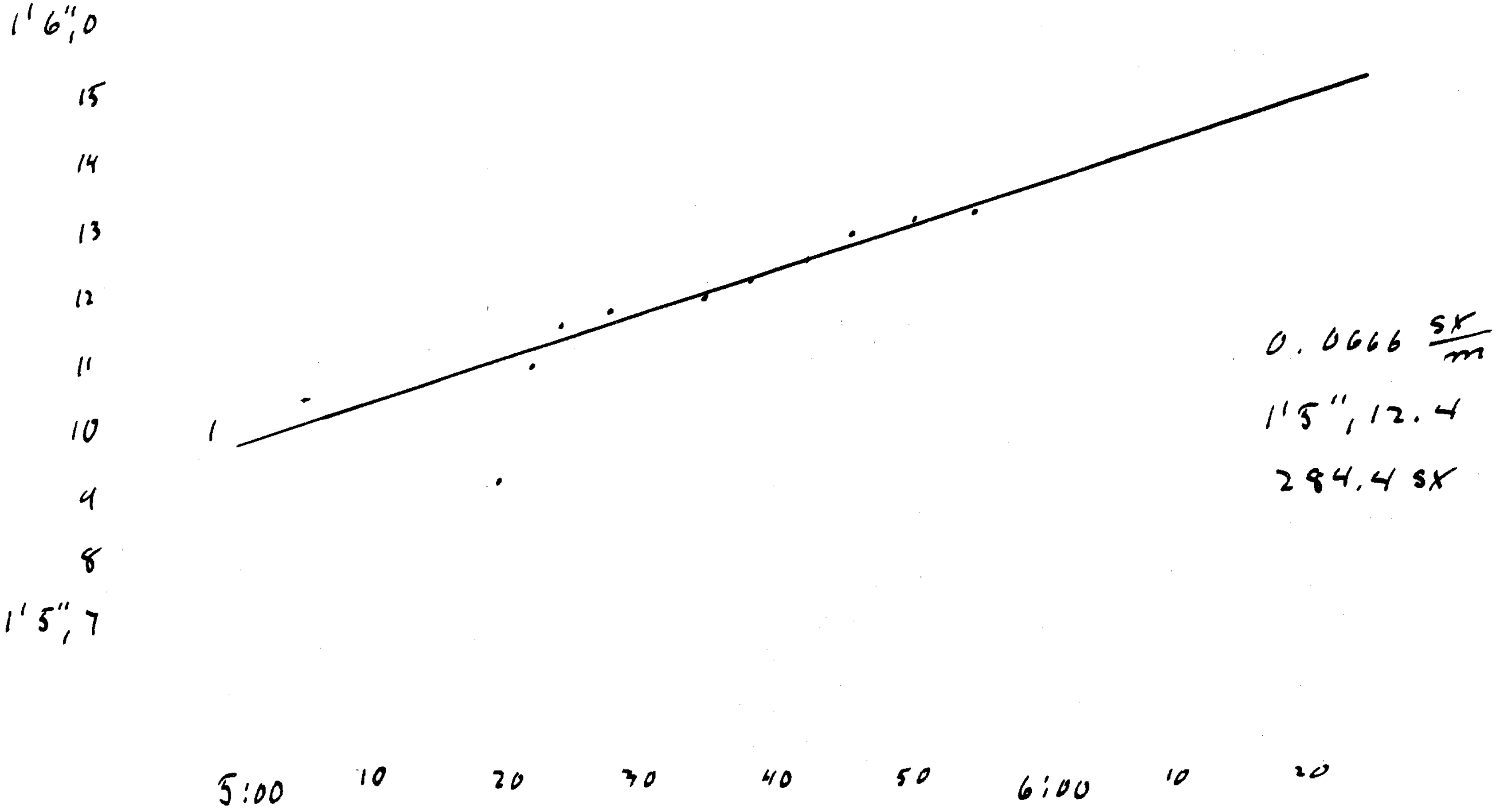
2.45"

39.0 sx

0.442 $\frac{sx}{m}$

60.8 sx

$ZrO_2$ # 16.01

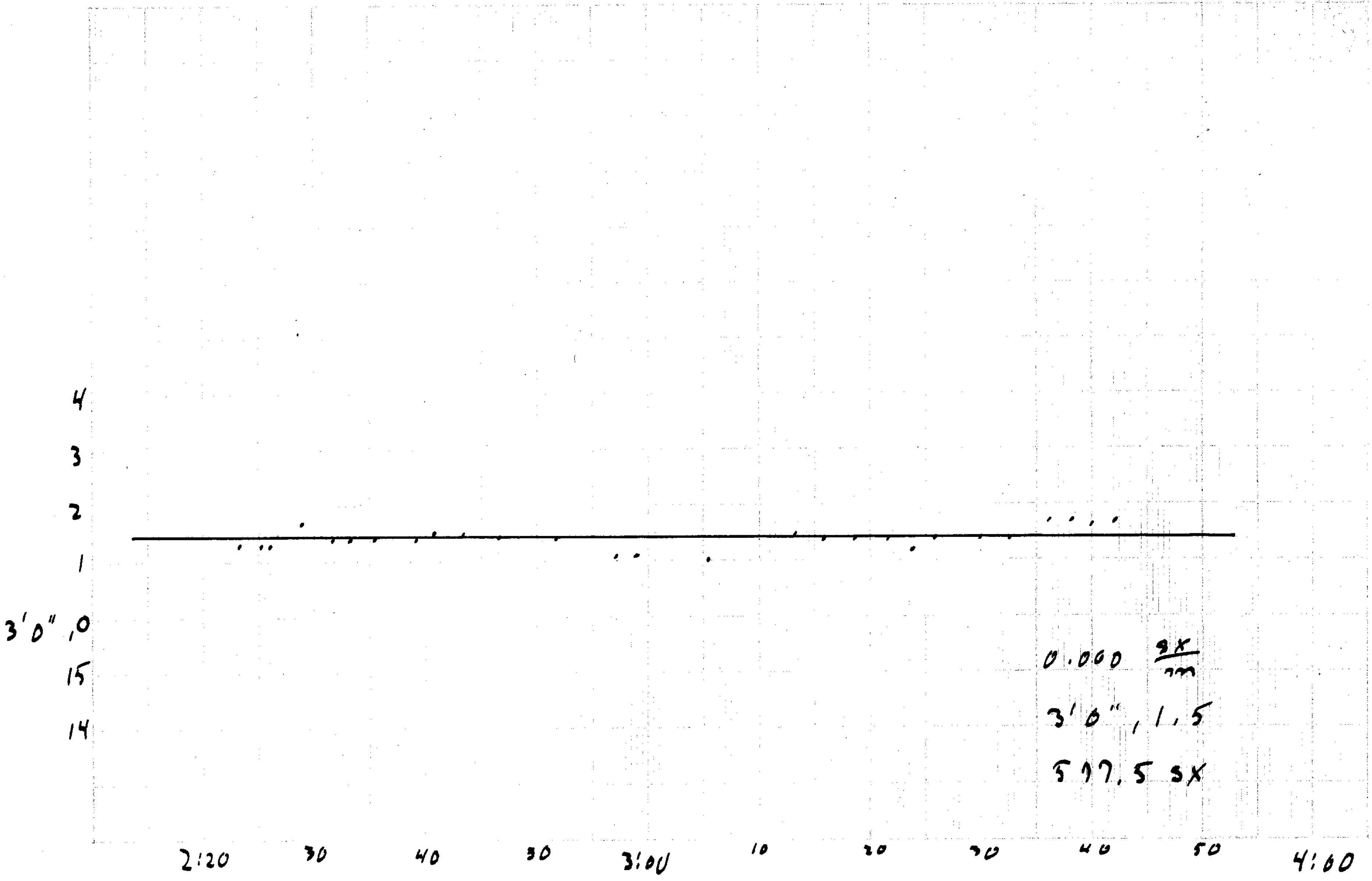


0.0666 $\frac{sx}{m}$

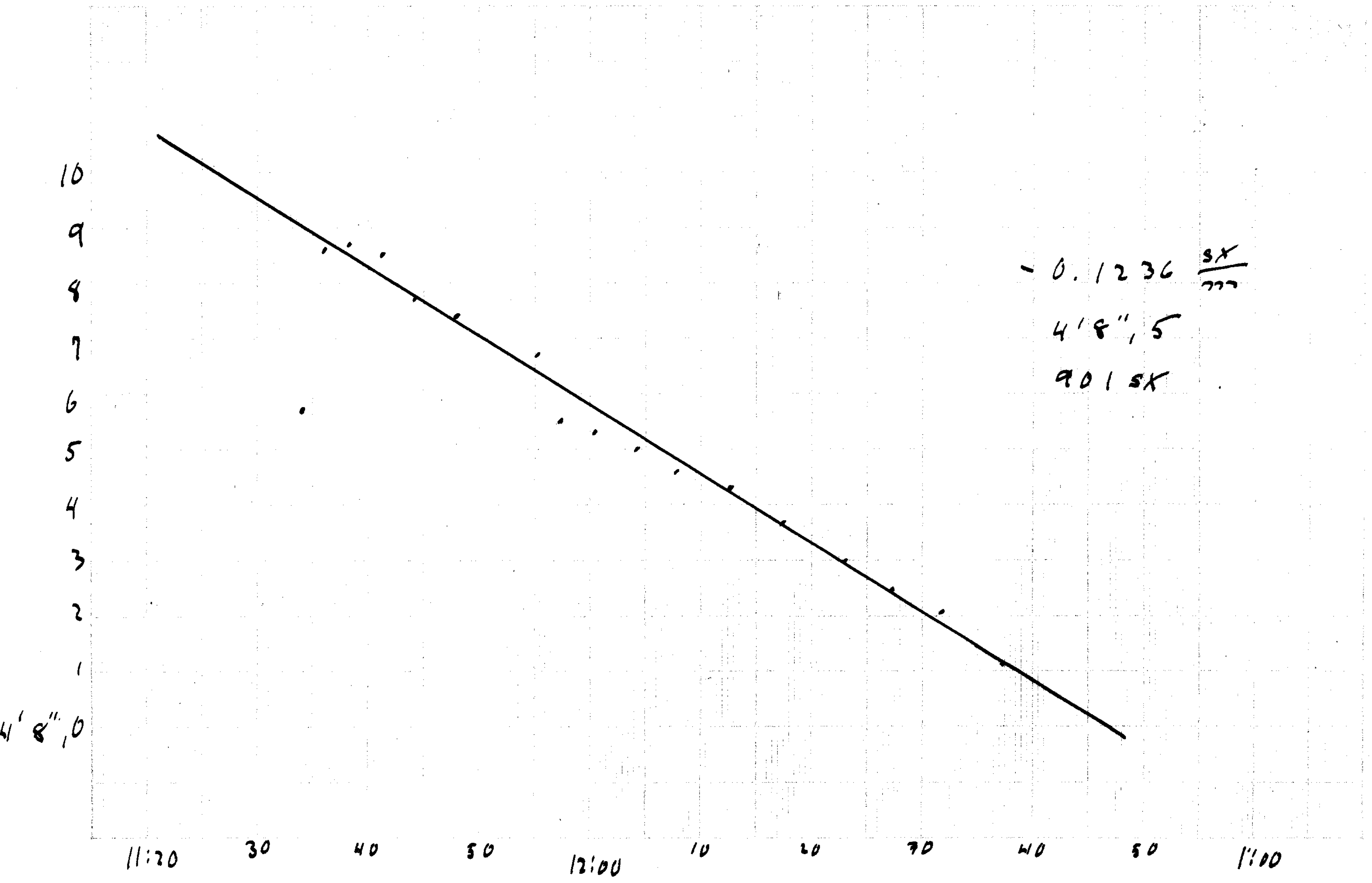
1'5",12.4

284.4 sx

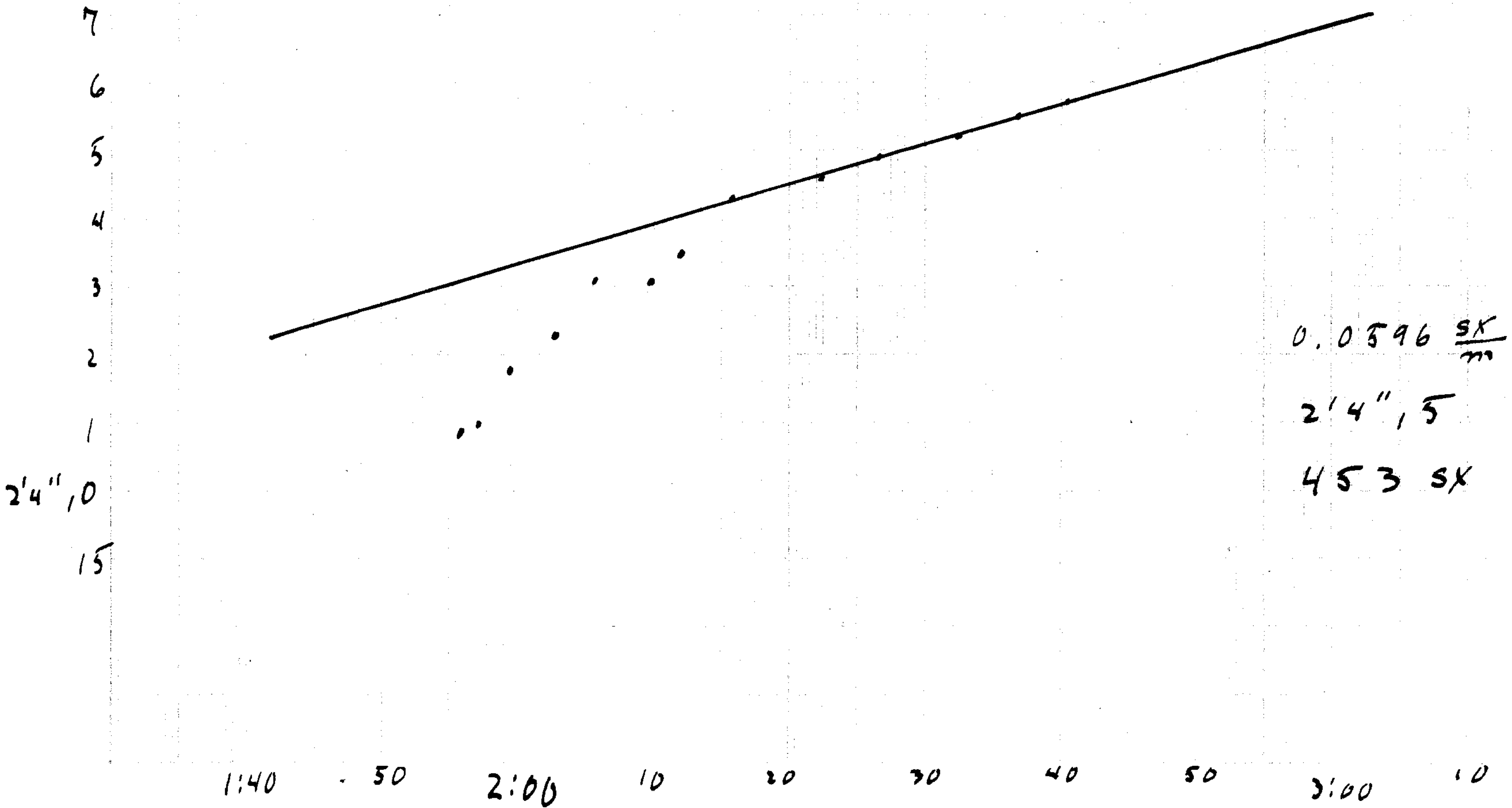
$ZrO_2$ #16.02


4
3
2
1
3'0",0
15
14
0.000 $\frac{sx}{mm}$
3'0", 1.5
517.5 sx
2:20
30
40
50
3:00
10
20
30
40
50
4:00

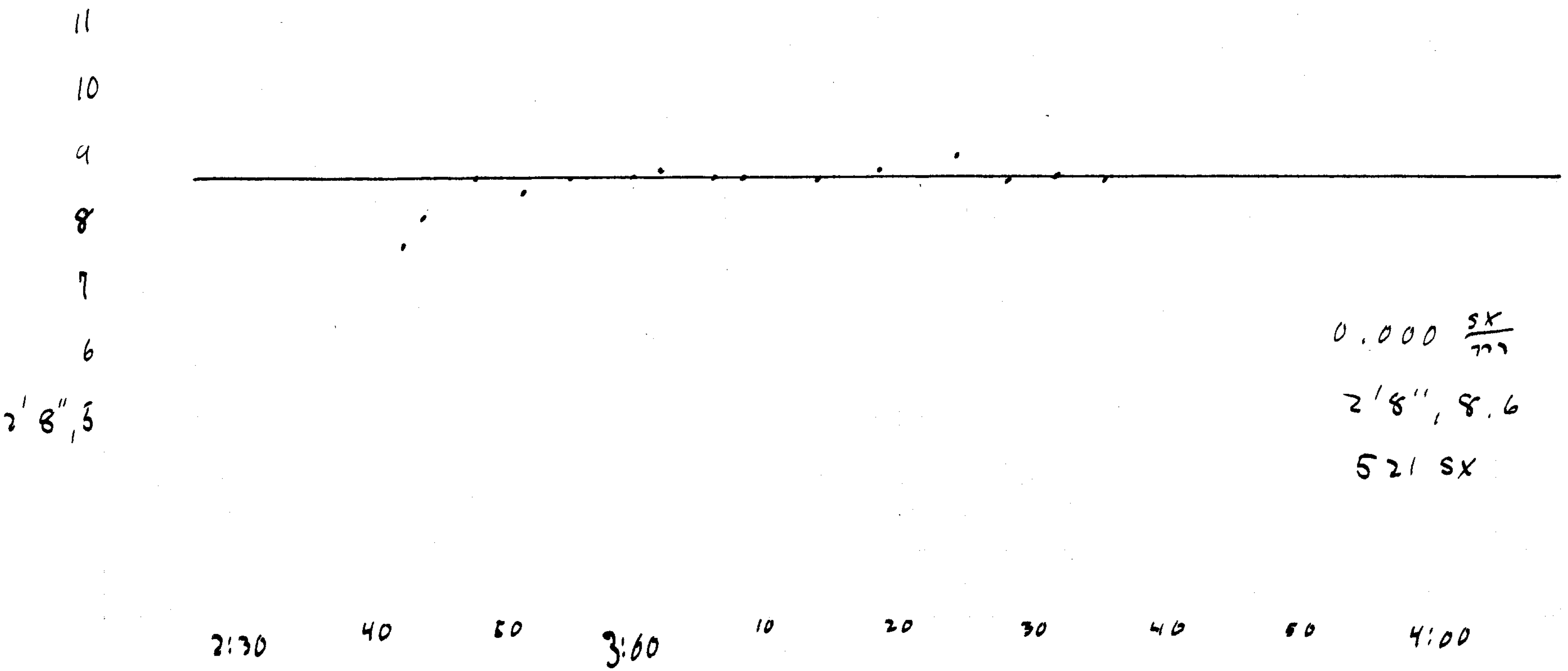
$ZrO_2$ #16.03

-0.1236 sx/m
4'8",5
901 sx
10
9
8
7
6
5
4
3
2
1
4'8",0
11:20
30
40
50
12:00
10
20
30
40
50
1:00

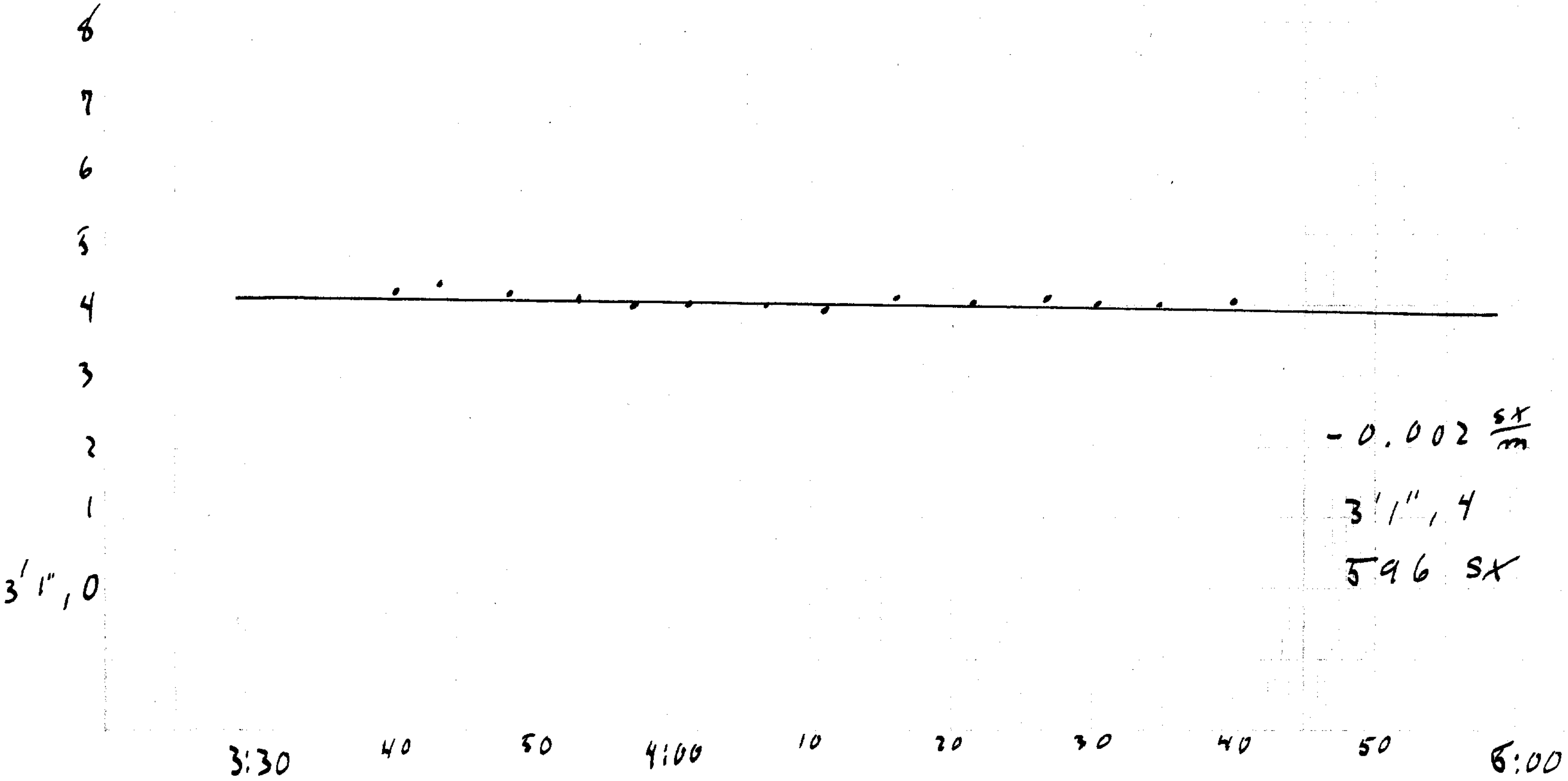
$ZrO_2$ #16.04


7
6
5
4
3
2
1
2'4",0
15
0.0596 sx/m
2'4",5
453 sx
1:40
50
2:00
10
20
30
40
50
3:00
10

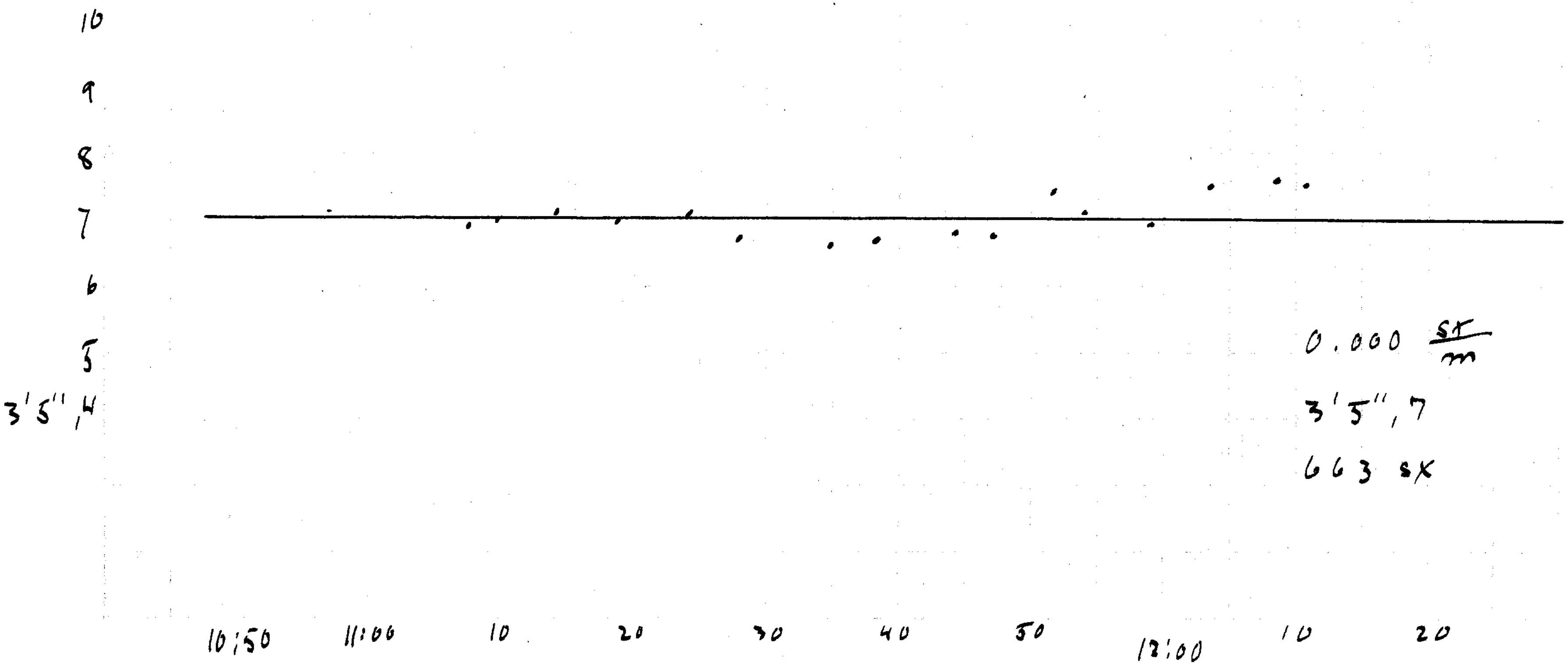
$ZrO_2$ #16.05


11
10
9
8
7
6
2'8",5
0.000 sx/m
2'8", 8.6
521 sx
2:30
40
50
3:00
10
20
30
40
50
4:00

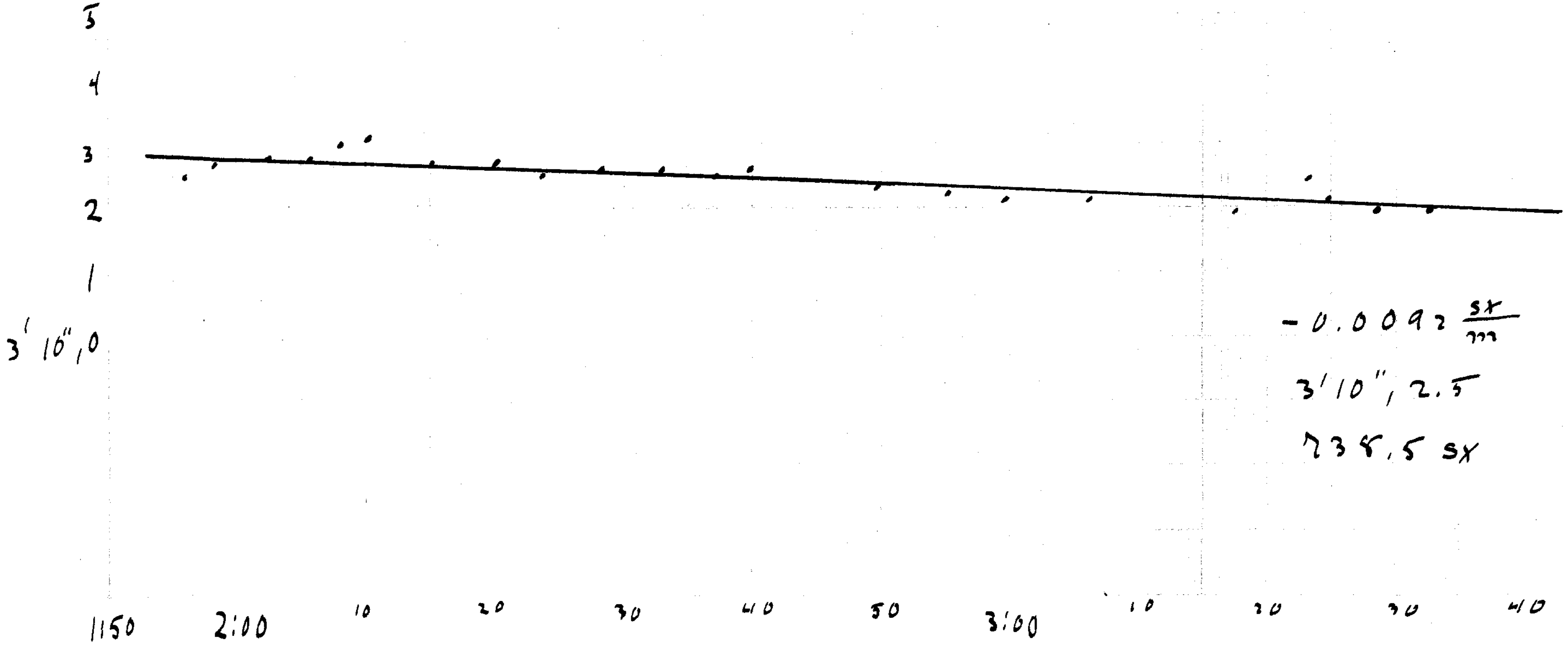
Z r O 2 #16.06



$ZrO_2$ # 16.07


10
9
8
7
6
5
3'5",4
0.000 ST/m
3'5",7
663 sX
10:50
11:00
10
20
30
40
50
12:00
10
20

$ZnO_2$ # 16,08

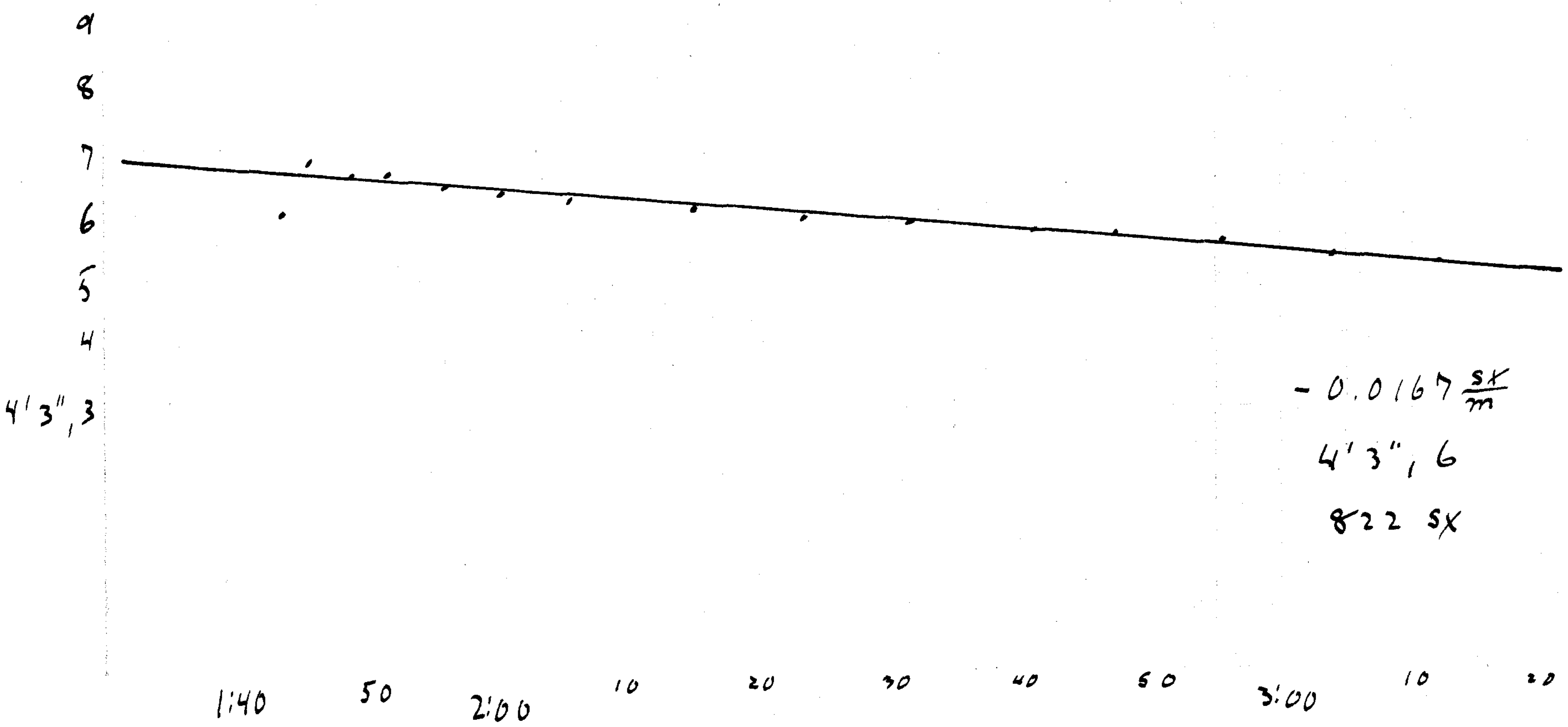


$-0.0092 \frac{sx}{m}$

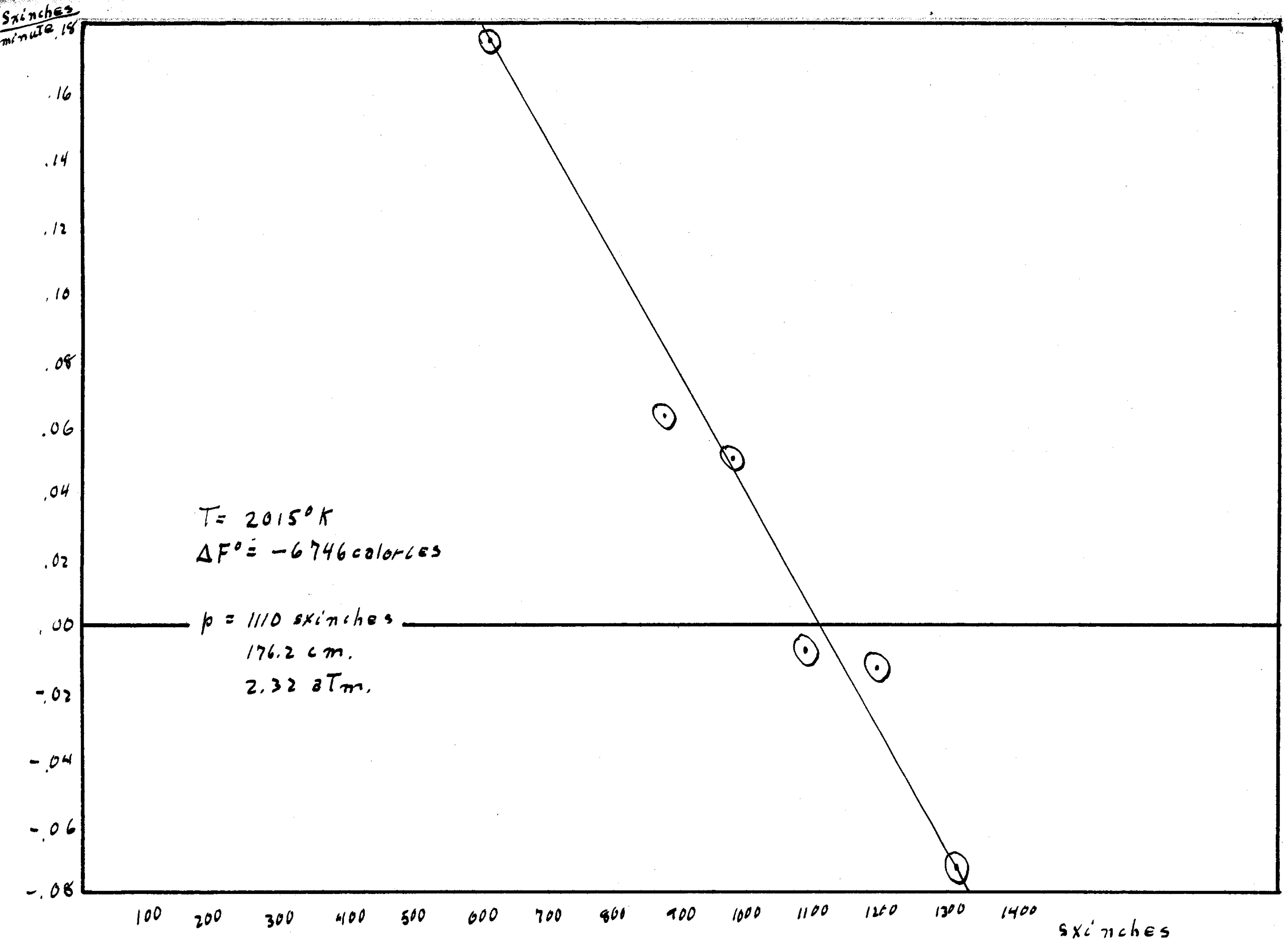
3' 10", 2.5

238.5 sx

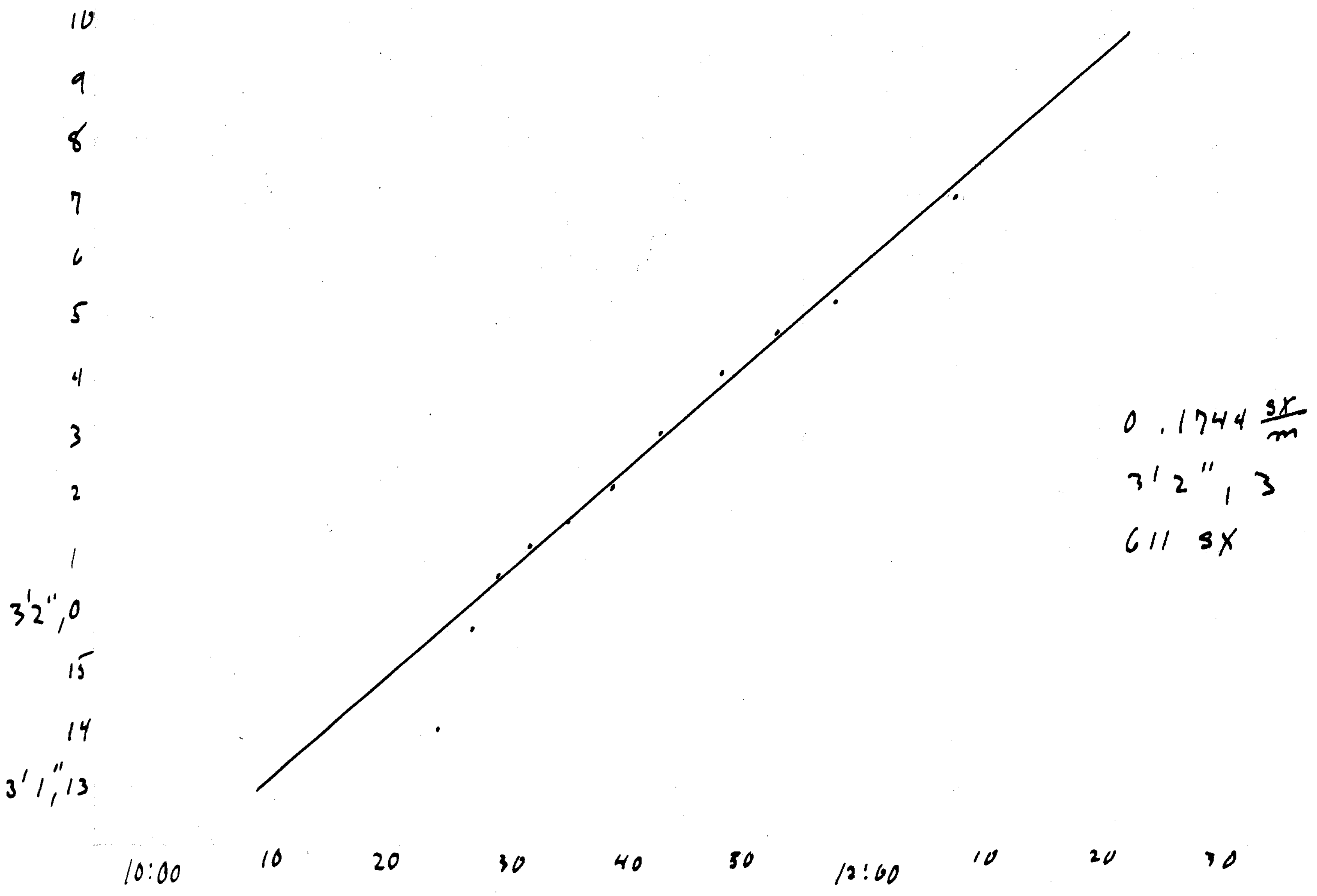
$ZrO_2$ # 16.09

9
8
7
6
5
4
4'3",3
-0.0167 sx/m
4'3",6
822 sx
1:40
50
2:00
10
20
30
40
50
3:00
10
20

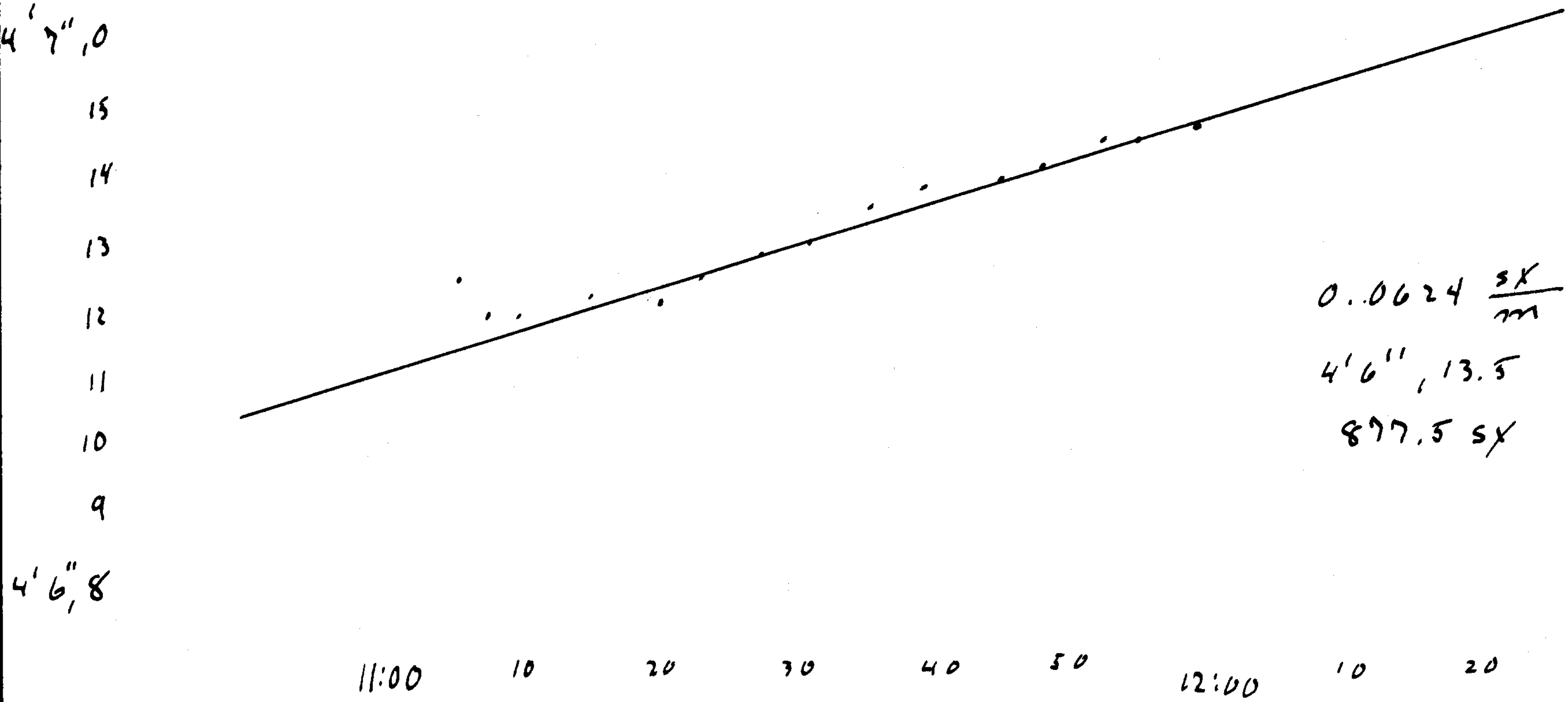
$ZrO_2$ #16.10


Sxinches / minute
.18
.16
.14
.12
.10
.08
.06
.04
.02
.00
-.02
-.04
-.06
-.08
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
sxinches
T= 2015°K
ΔF°= -6746 calories
p = 1110 sxinches
176.2 cm.
2.32 aTm.

$ZrO_2$ #16.1


10
9
8
7
6
5
4
3
2
1
3'2",0
15
14
3'1",13
10:00
10
20
30
40
50
12:00
10
20
30
0.1744 sx/m
3'2",3
611 sx

$ZrO_2$ # 16.11

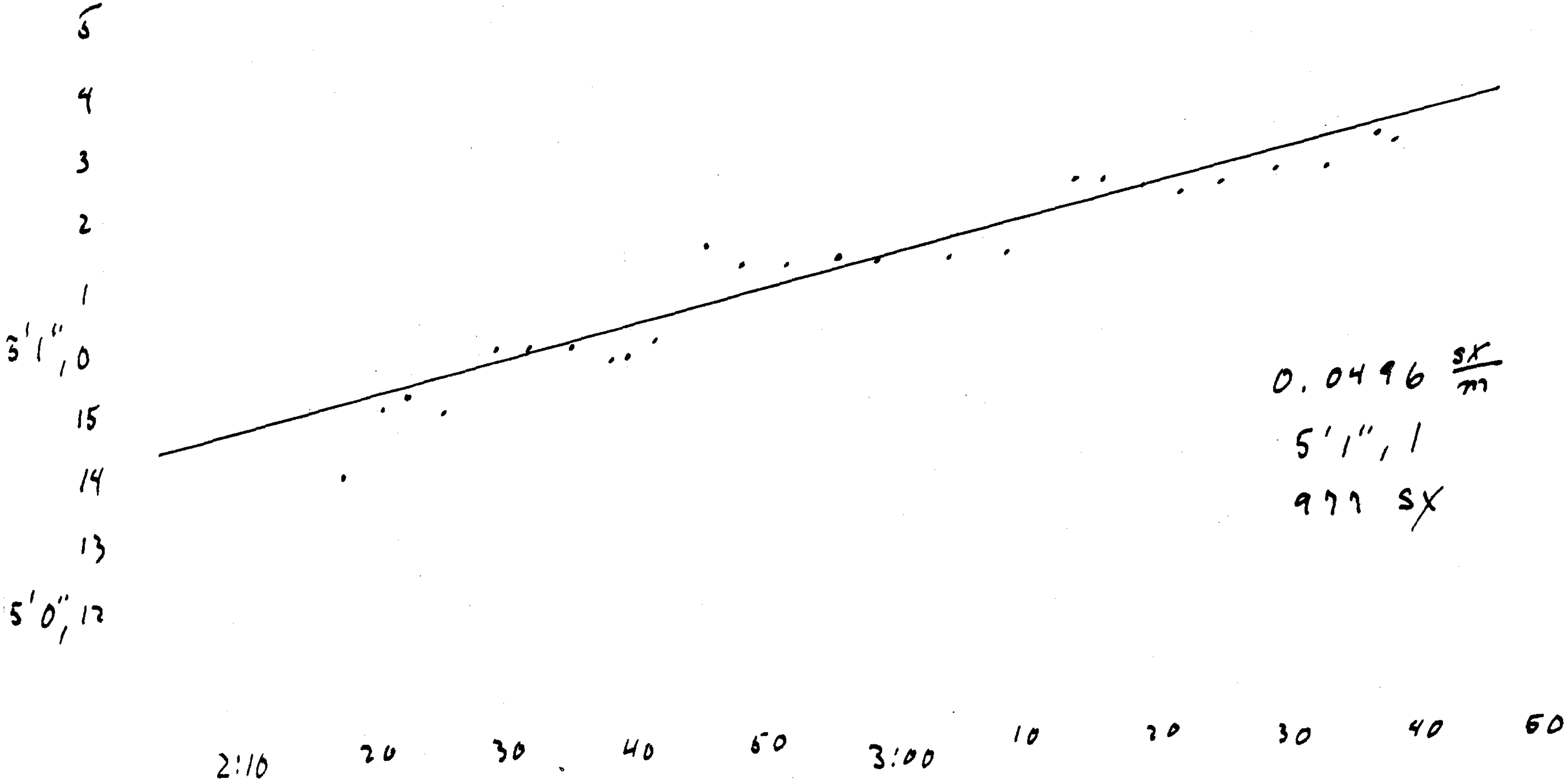


$0..0624 \frac{sx}{m}$

4'6", 13.5

877.5 sx

$ZrO_2$ #16.12

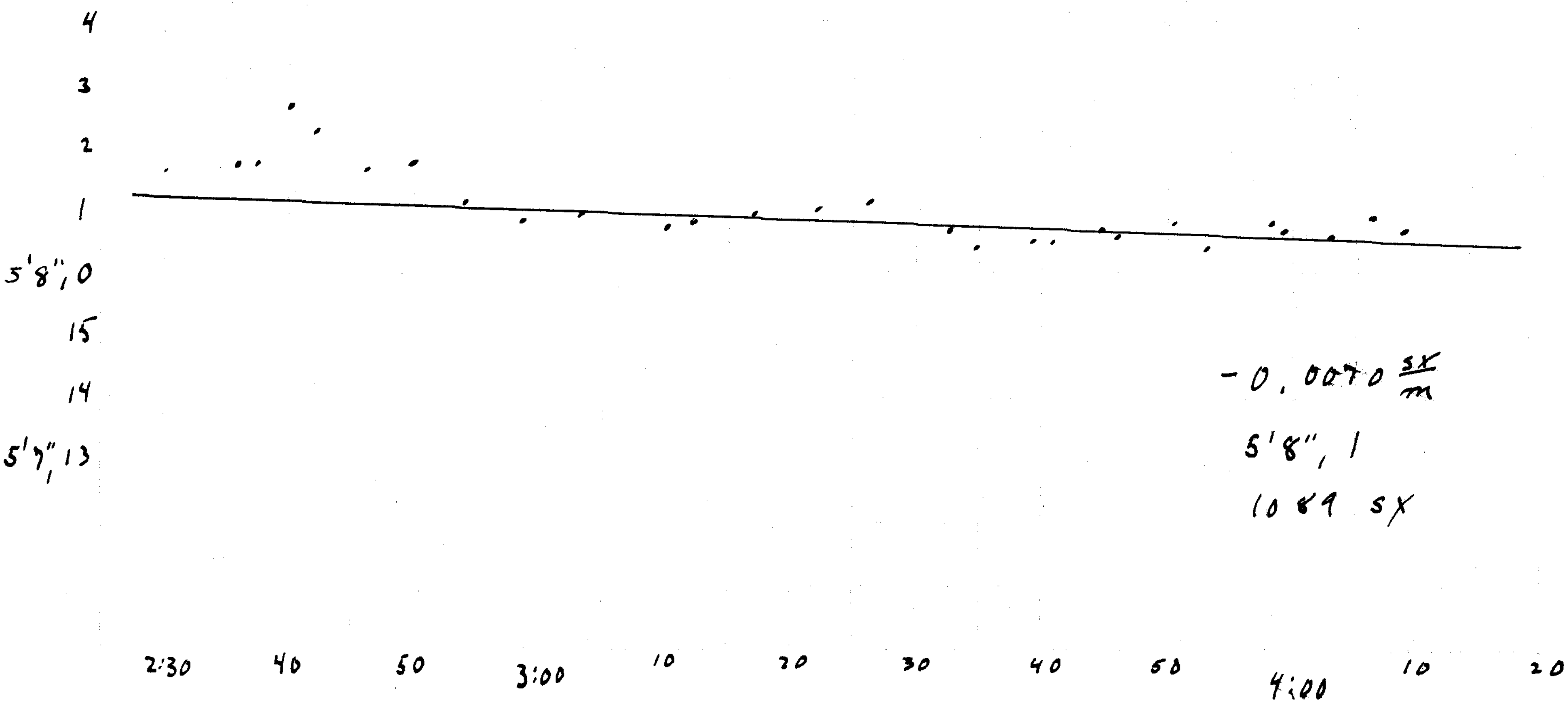


$0.0496 \frac{sx}{m}$

5'1",1

977 sx

$ZrO_2$ # 16.13

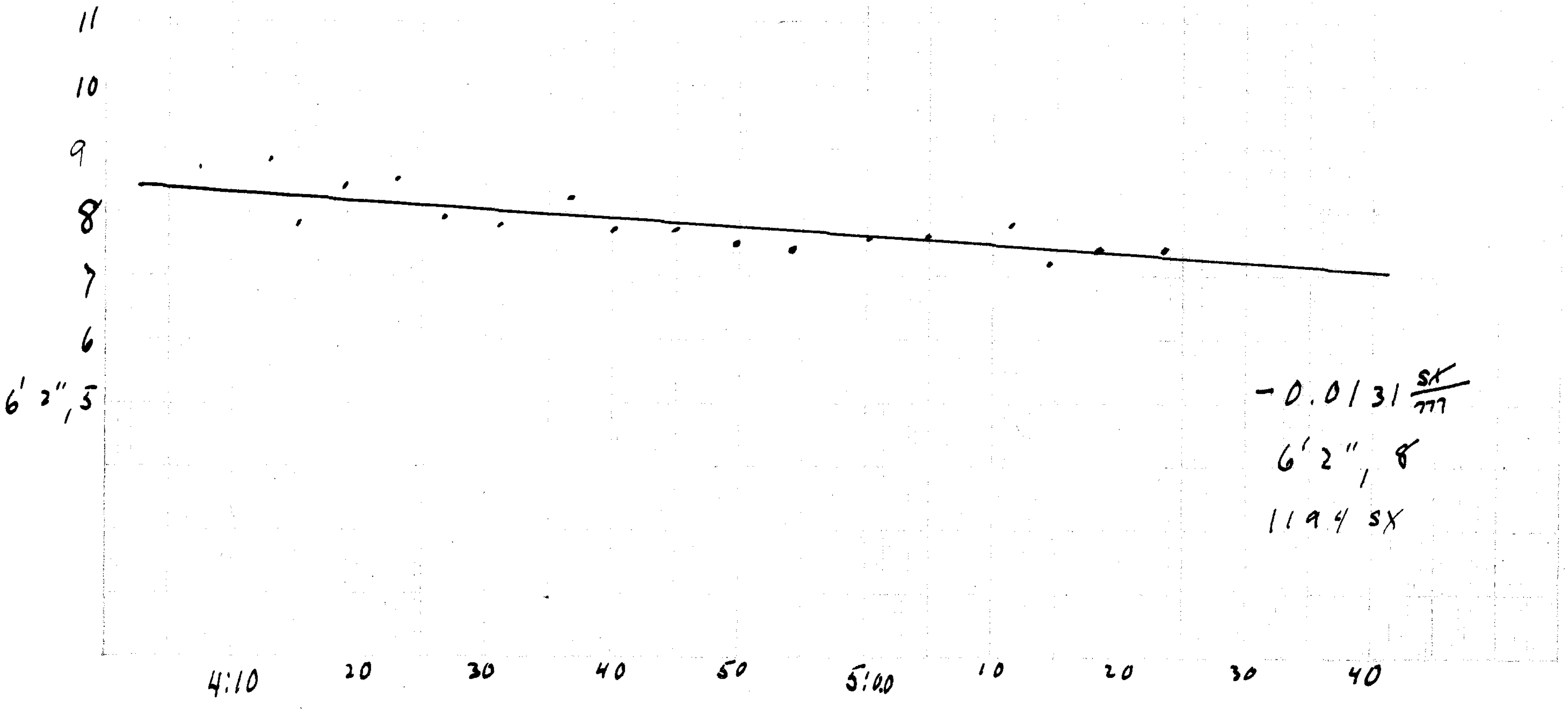


$-0.0070\ \frac{sx}{m}$

5'8",1

1089 sx

ZrO$_2$ #16.14

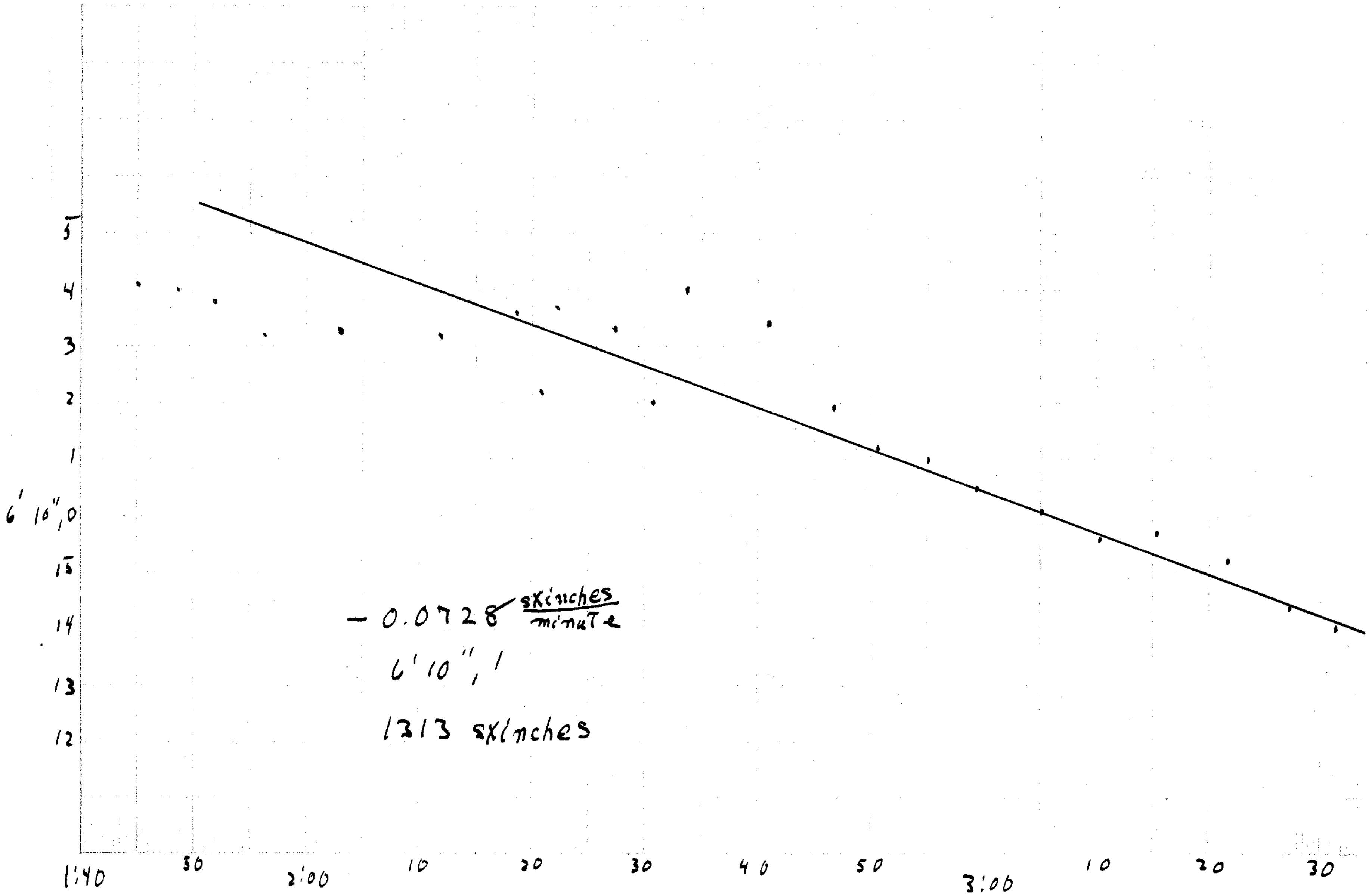


$-0.0131 \frac{sx}{m}$

6'2",8

1194 sx

$ZrO_2$ # 16.15

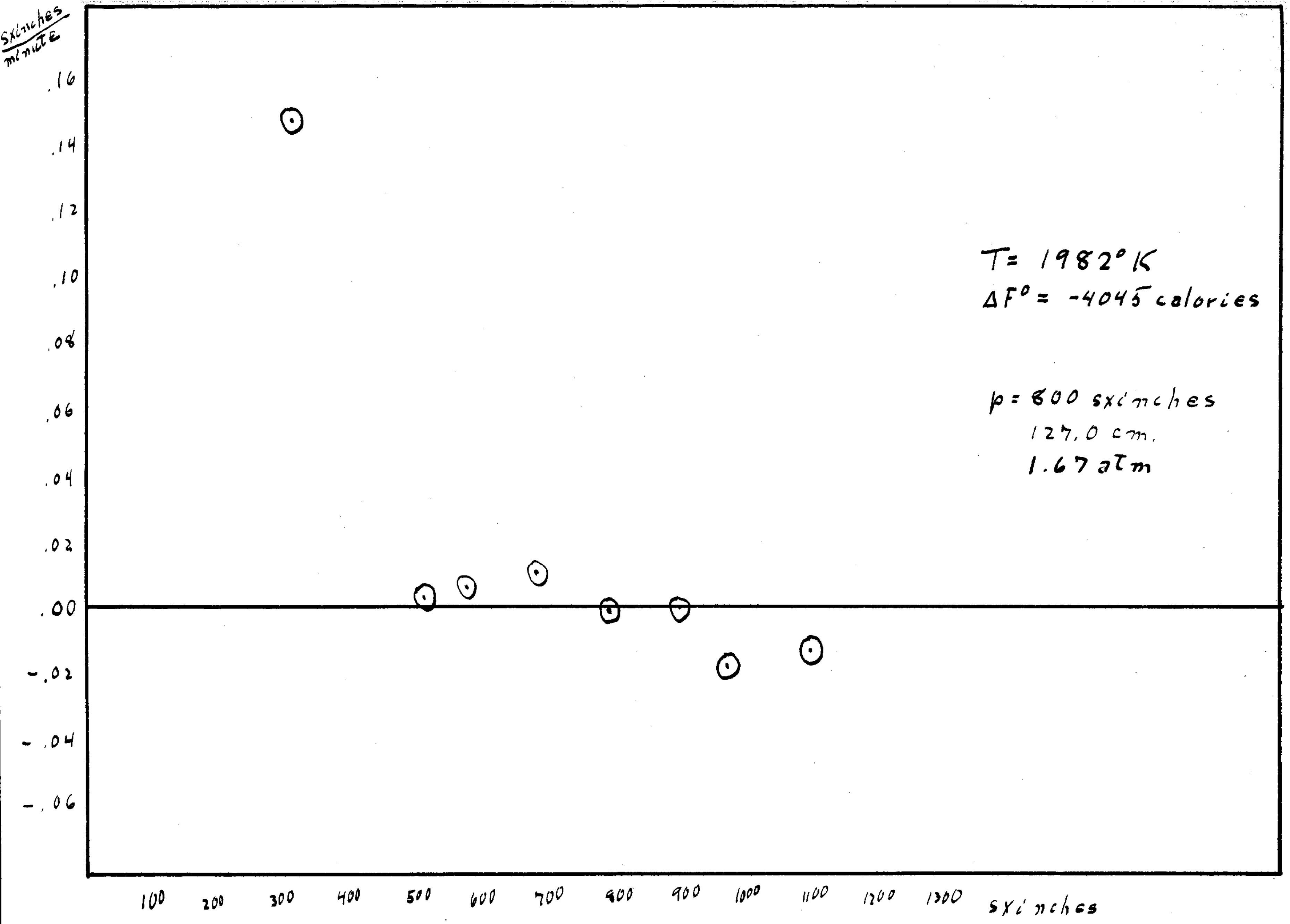


$-0.0728 \frac{\text{sxinches}}{\text{minute}}$

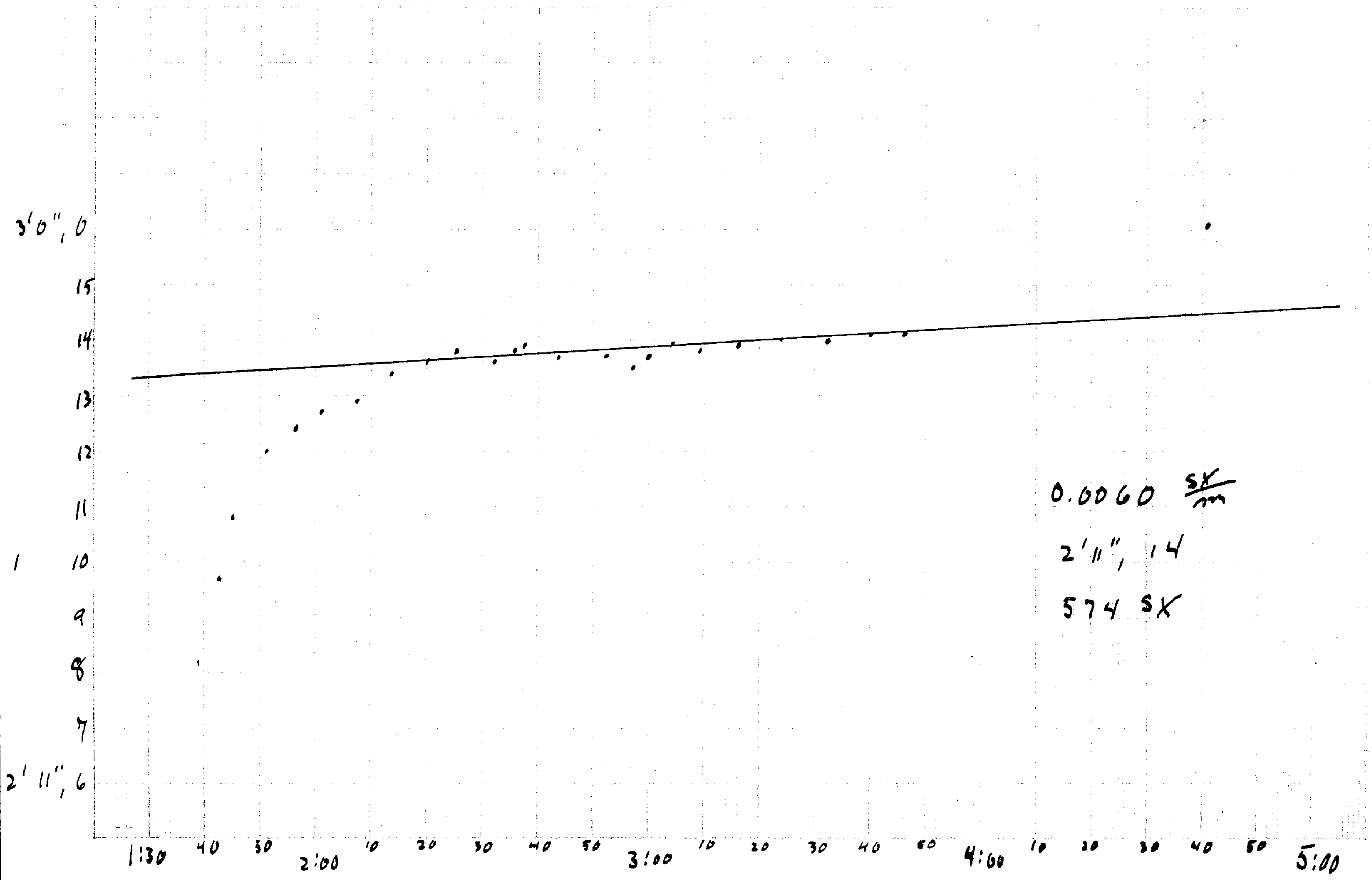
6' 10",1

1313 sxinches

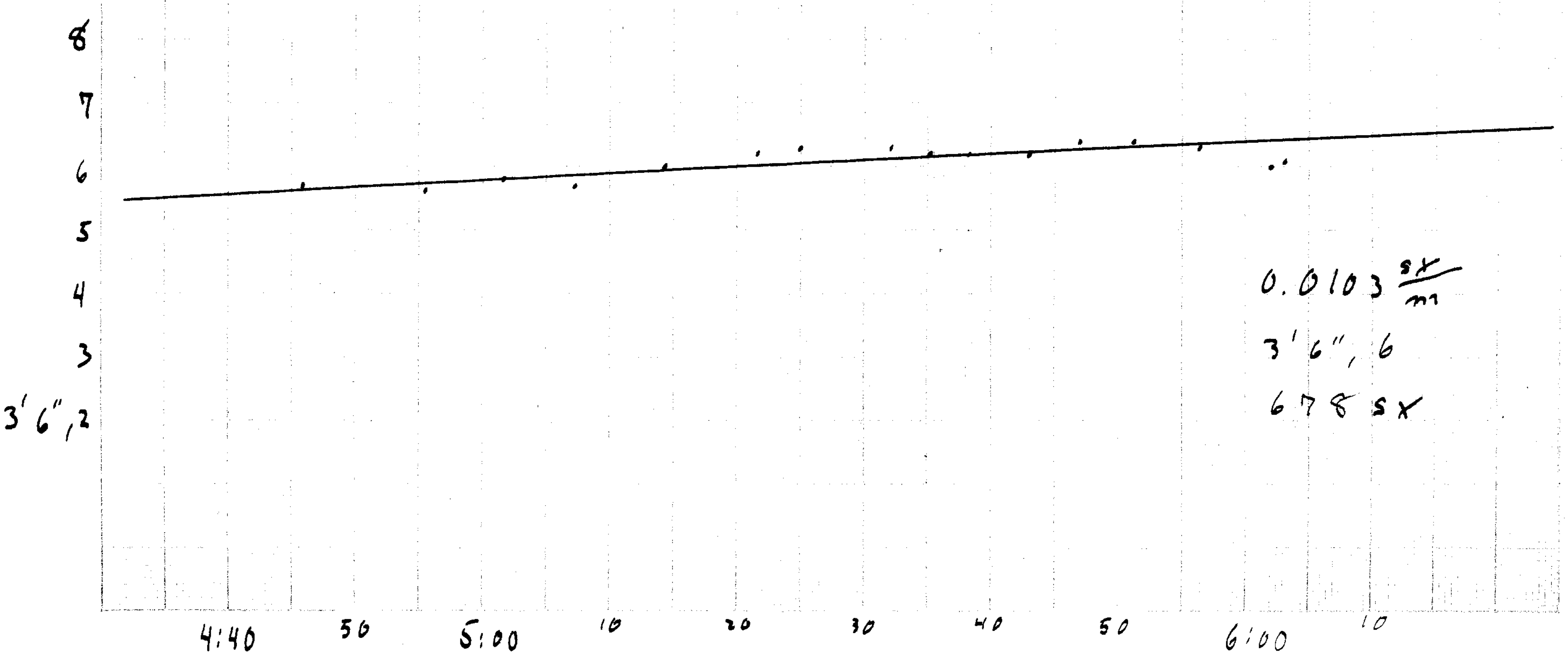
$ZrO_2$ # 16.16


sxinches/minute
.16
.14
.12
.10
.08
.06
.04
.02
.00
-.02
-.04
-.06
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
sxinches
T= 1982°K
ΔF° = -4045 calories
p = 800 sxinches
127.0 cm.
1.67 atm

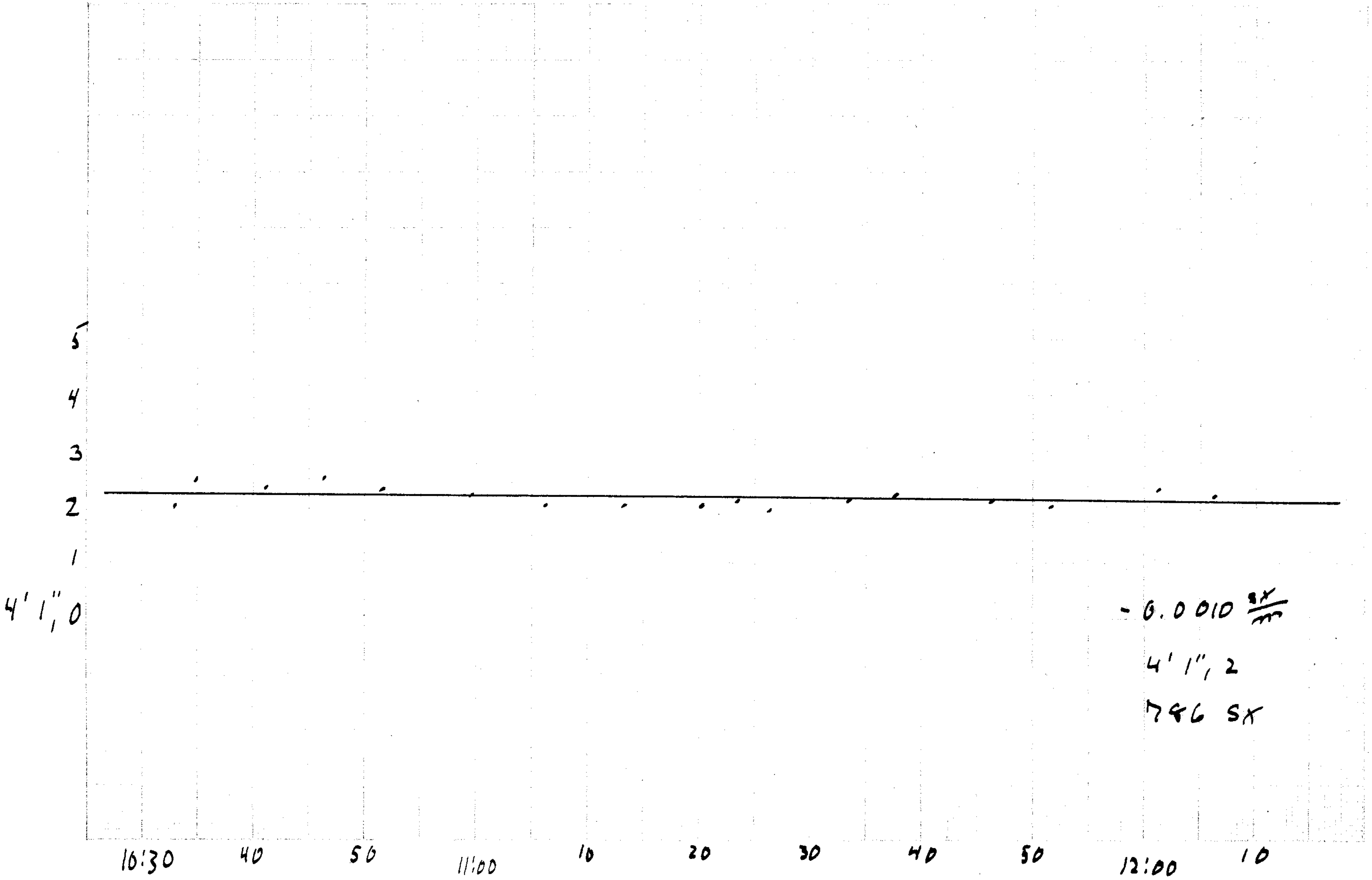
$ZrO_2$ # 16.2

3'0",0
15
14
13
12
11
1
10
9
8
7
2'11",6
1:30
40
50
2:00
10
20
30
40
50
3:00
10
20
30
40
50
4:00
10
20
30
40
50
5:00
0.0060 $\frac{sx}{m}$
2'11", 14
574 sx

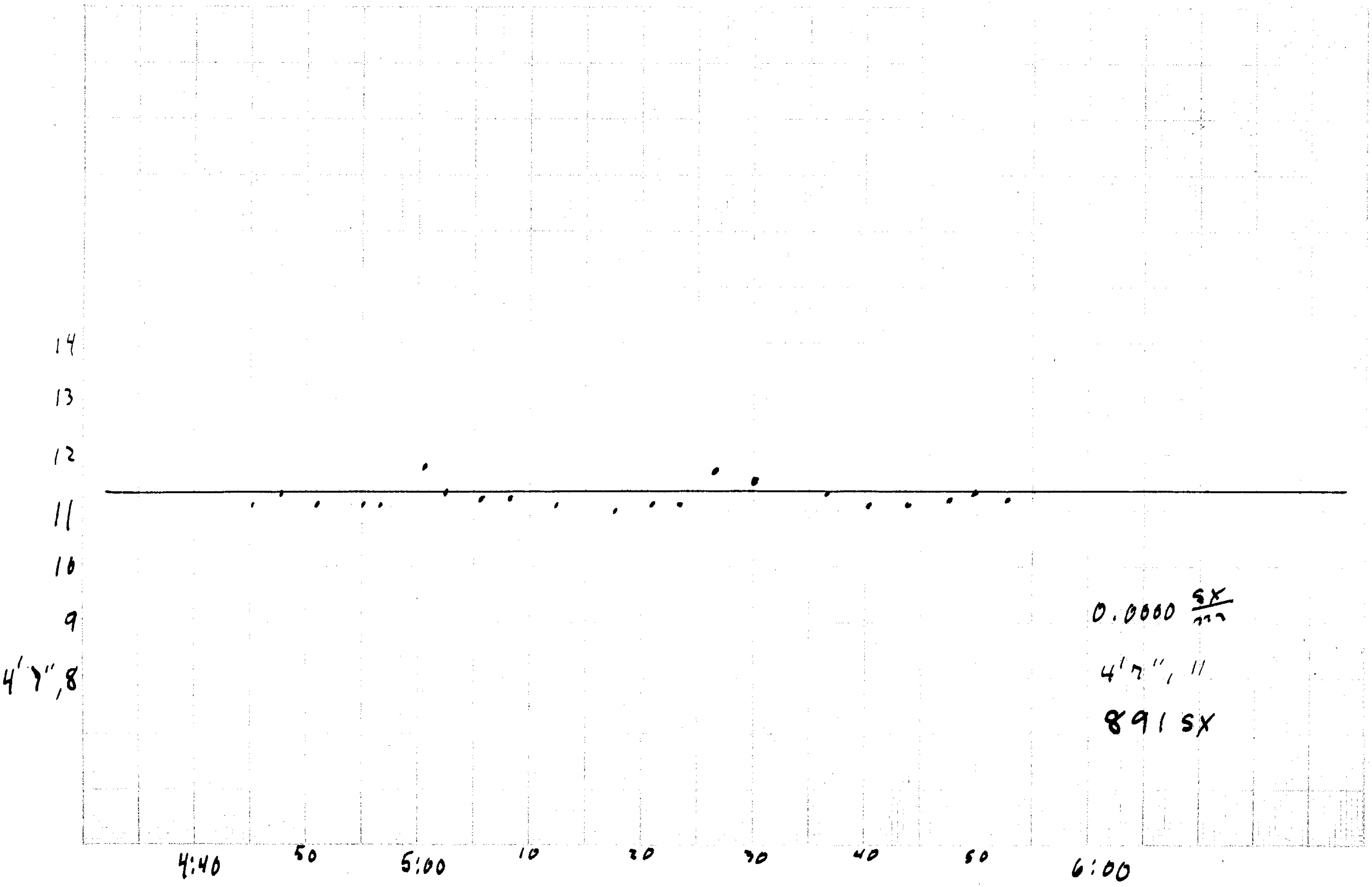
$ZrO_2$ # 16.21


8
7
6
5
4
3
3'6",2
4:40
50
5:00
10
20
30
40
50
6:00
10
0.0103 $\frac{sx}{m}$
3'6", 6
678 sx

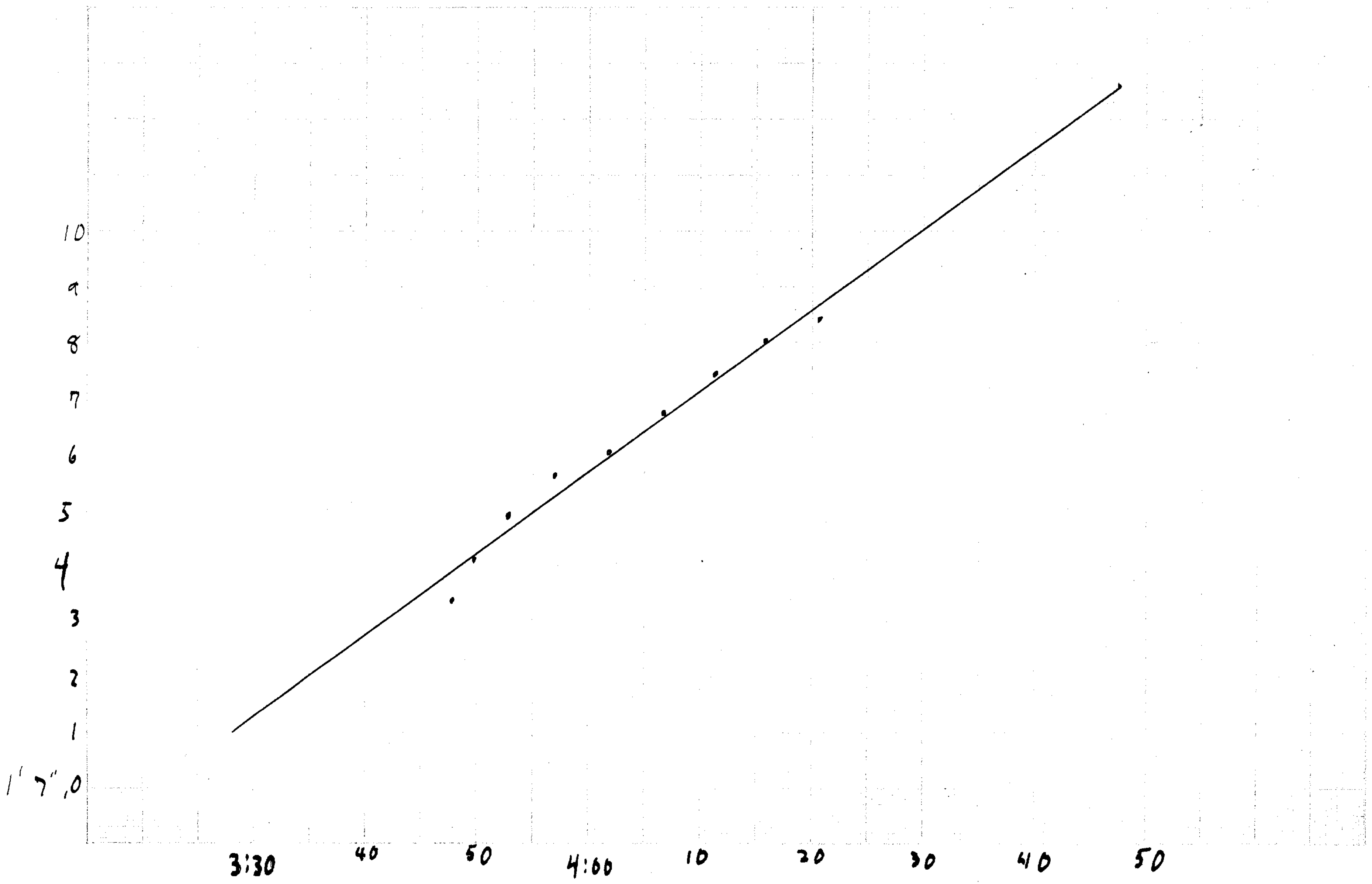
$ZrO_2$ # 16.22


5
4
3
2
1
4' 1", 0
10:30
40
50
11:00
10
20
30
40
50
12:00
10
-0.0010 sx/m
4' 1", 2
786 sx

Zr O$_2$ # 16.2 3

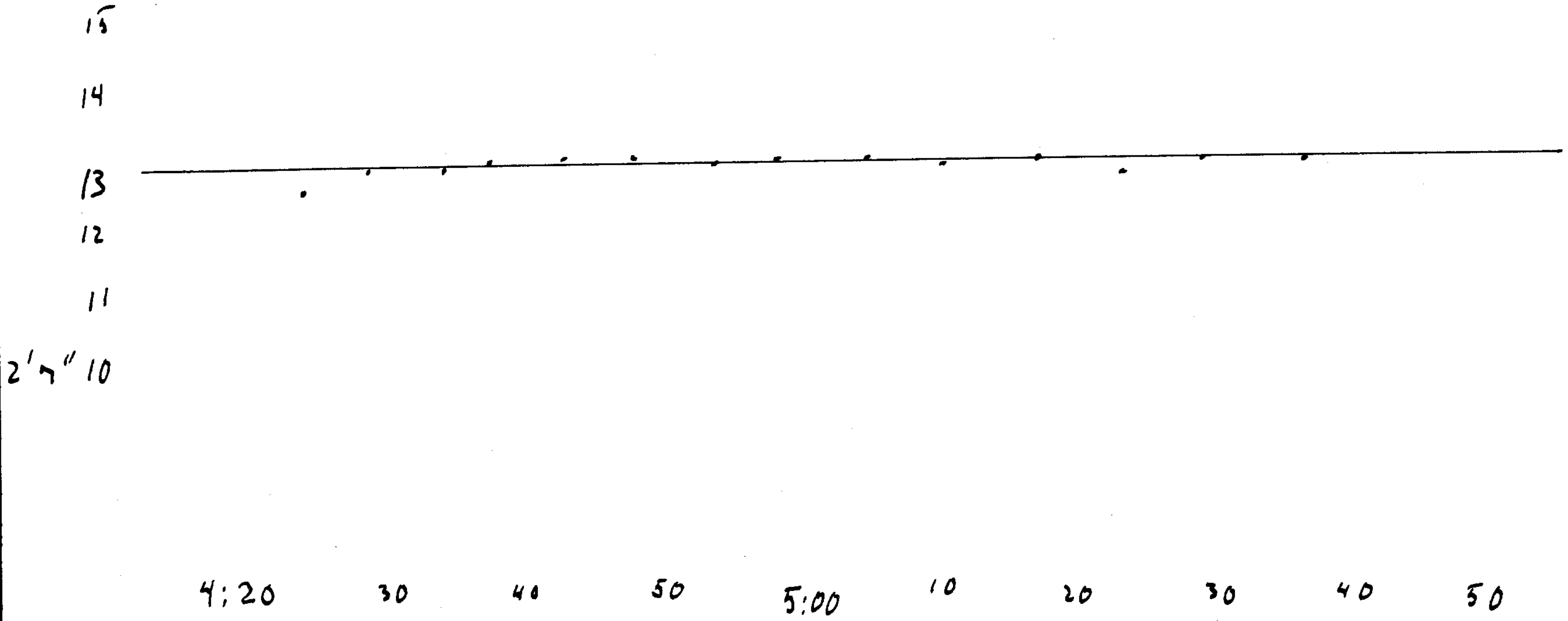

14
13
12
11
10
9
4'7",8
0.0000 sx/mm
4'7",11
891 sx
4:40
50
5:00
10
20
30
40
50
6:00

$ZrO_2$ #16.24

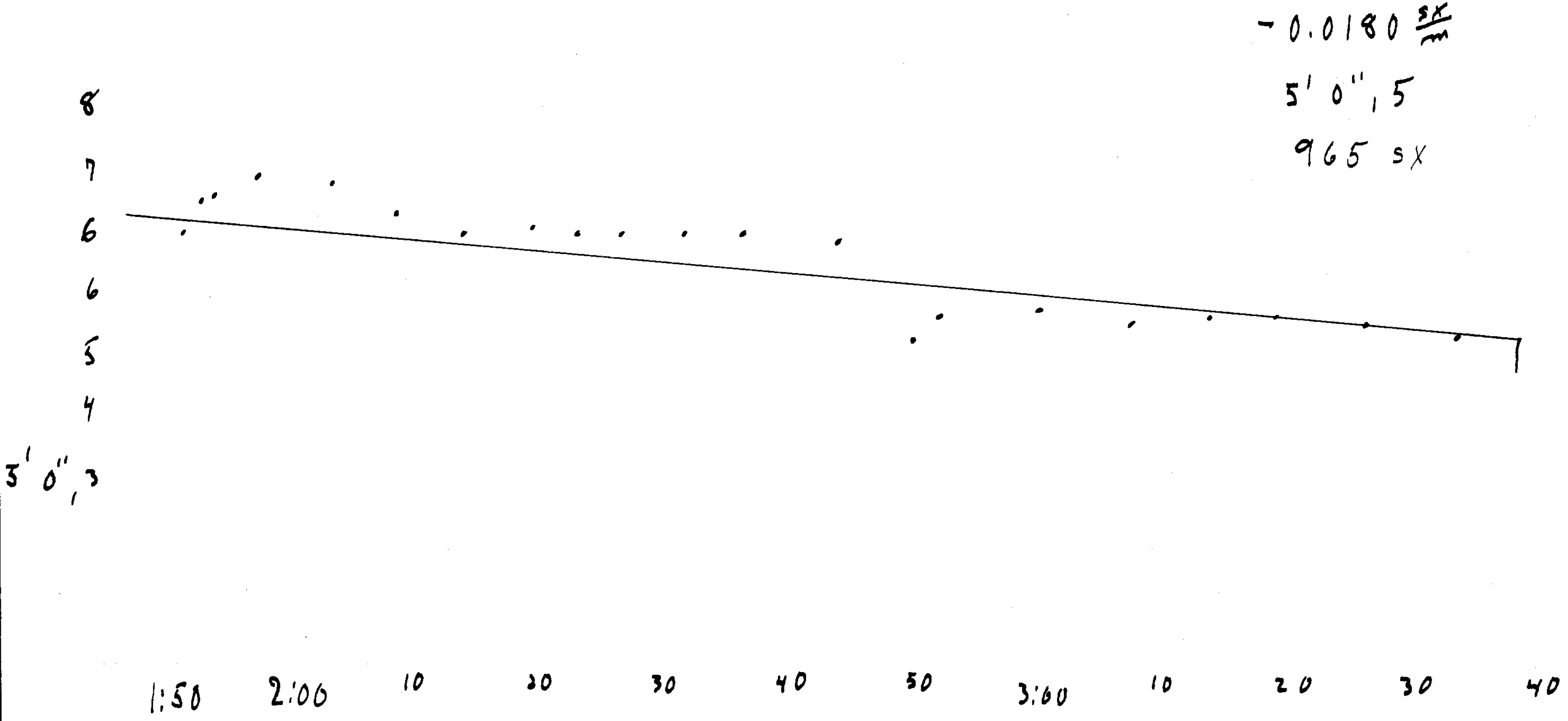


$ZrO_2$ #16.28

0.0026 $\frac{sx}{m}$
2'7", 13
509 sx



$ZrO_2$ # 16.29

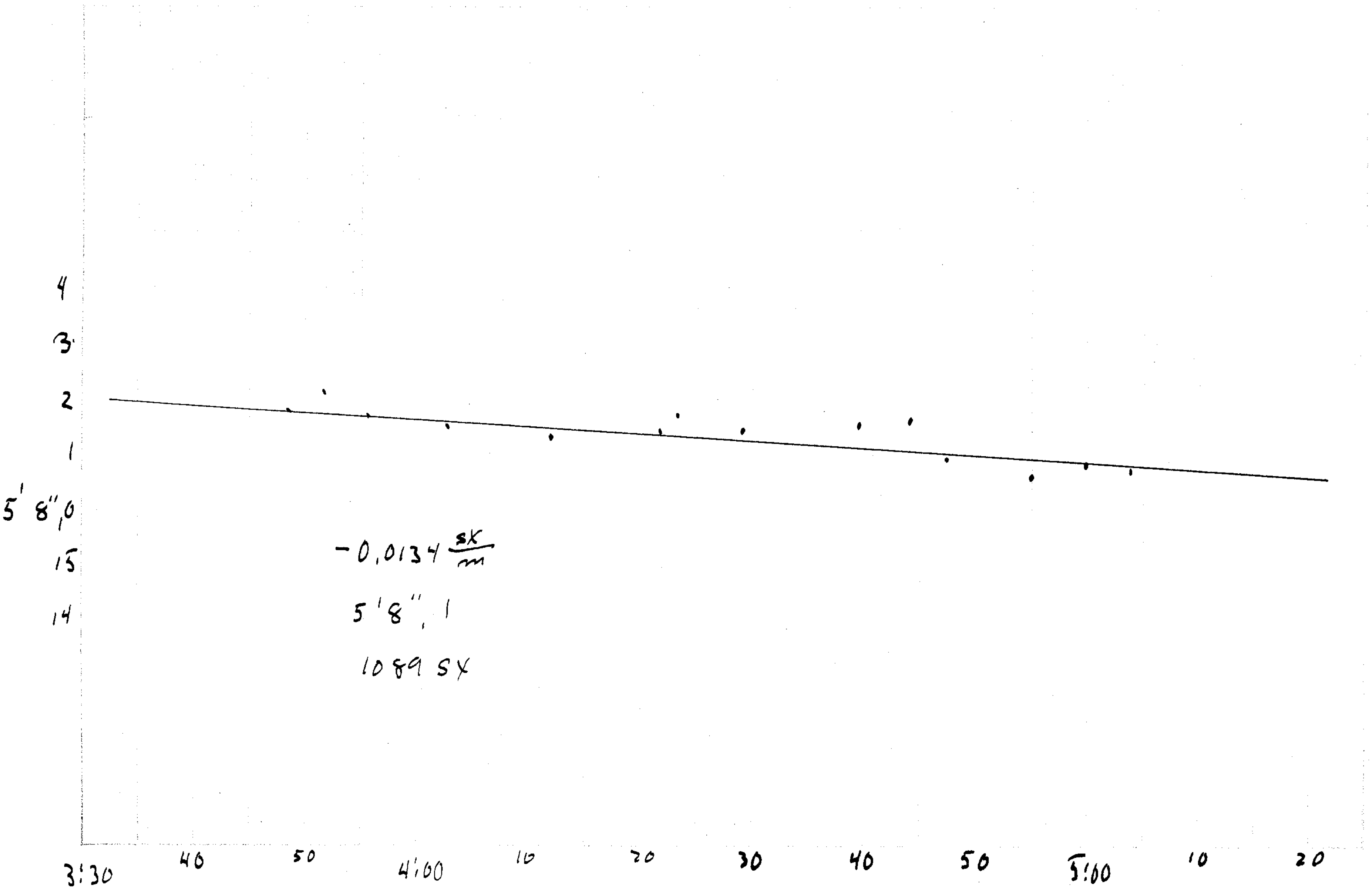


−0.0180 $\frac{sx}{m}$

5' 0",5

965 sx

$ZrO_2$ # 16.32

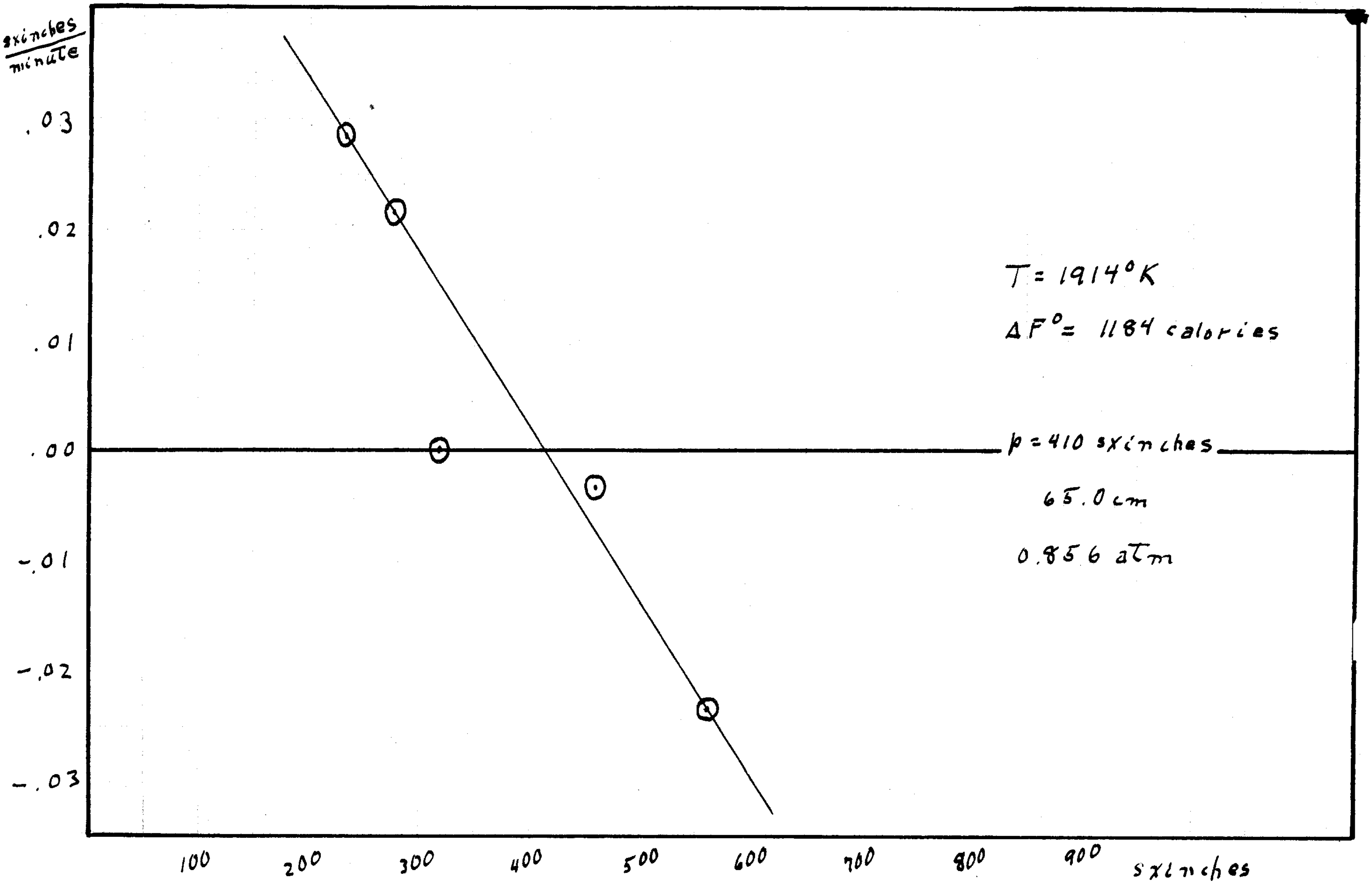


$-0{,}0134 \frac{sk}{m}$

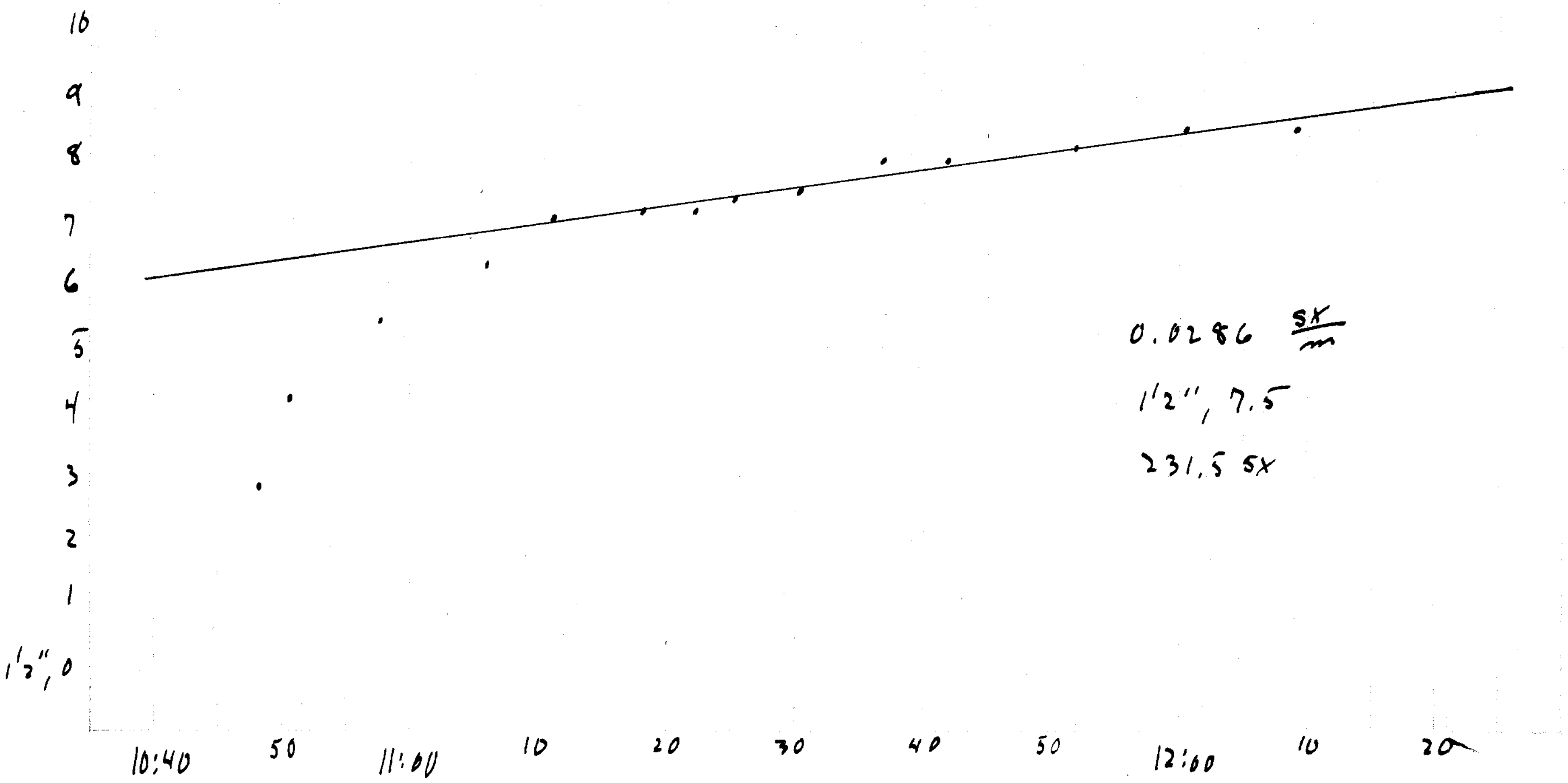
5'8",1

1089 SX

$ZrO_2$ # 16.33


sxinches/minute
.03
.02
.01
.00
-.01
-.02
-.03
100
200
300
400
500
600
700
800
900
sxinches
T = 1914°K
ΔF° = 1184 calories
p = 410 sxinches
65.0 cm
0.856 atm

$ZrO_2$ # 16.4

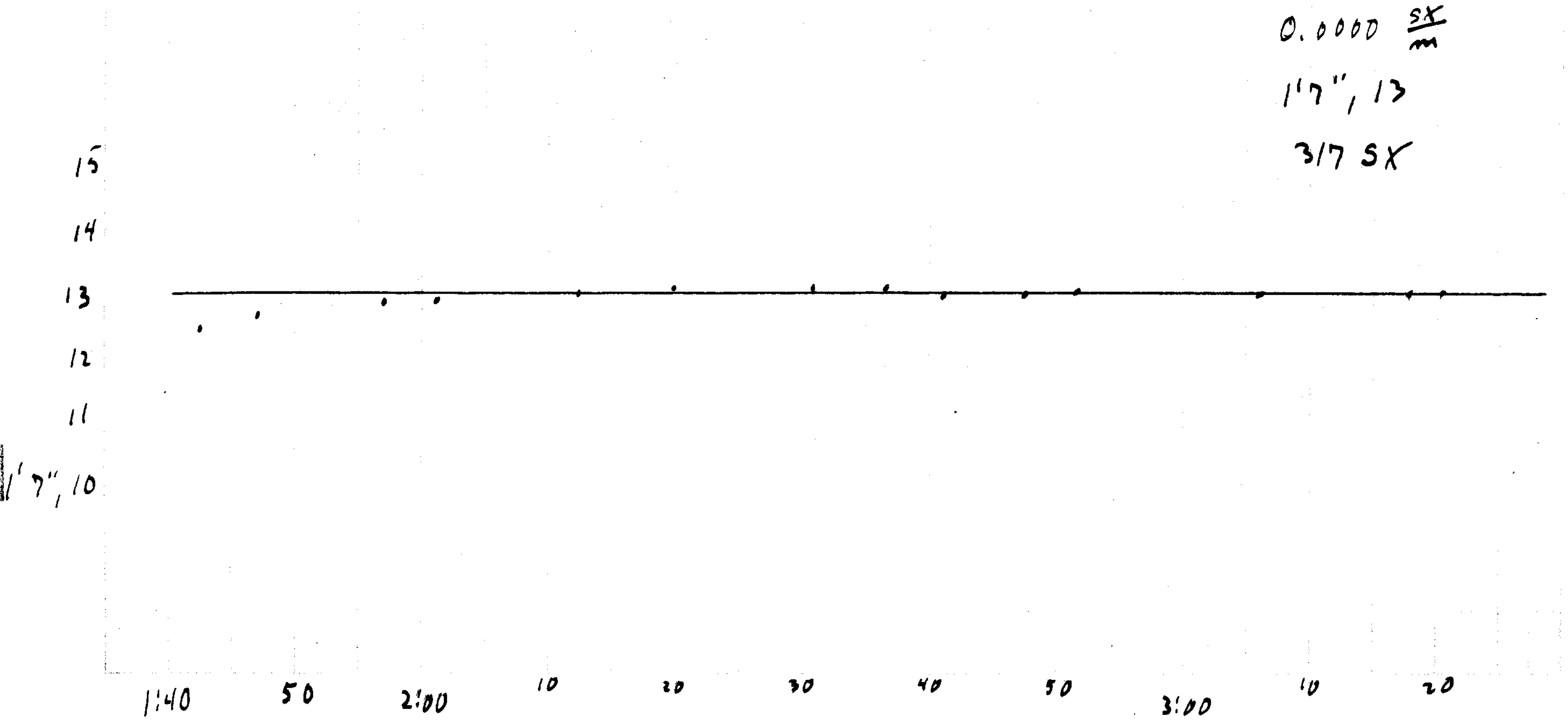


0.0286 $\frac{sx}{m}$

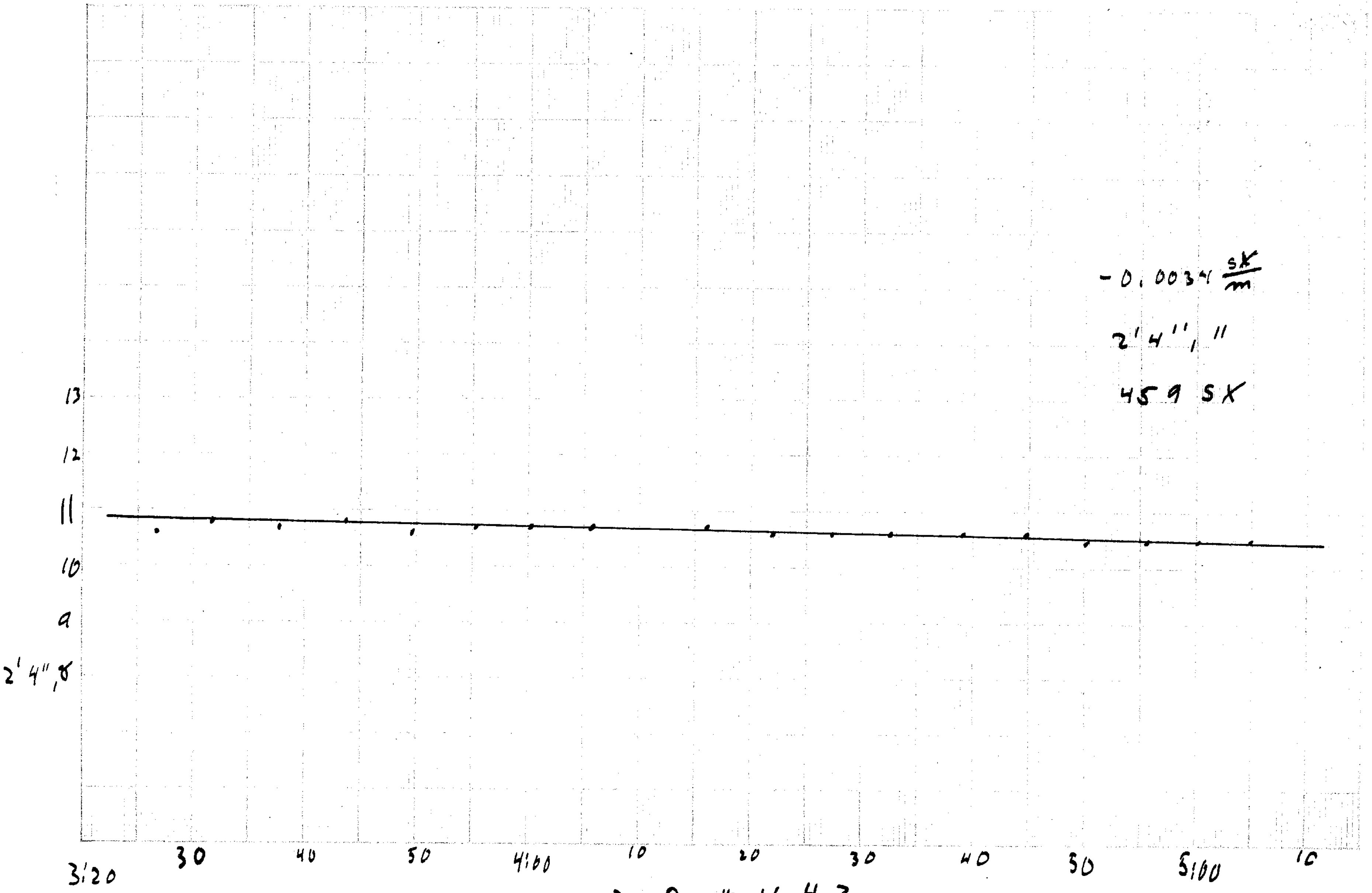
1'2'', 7.5

231.5 sx

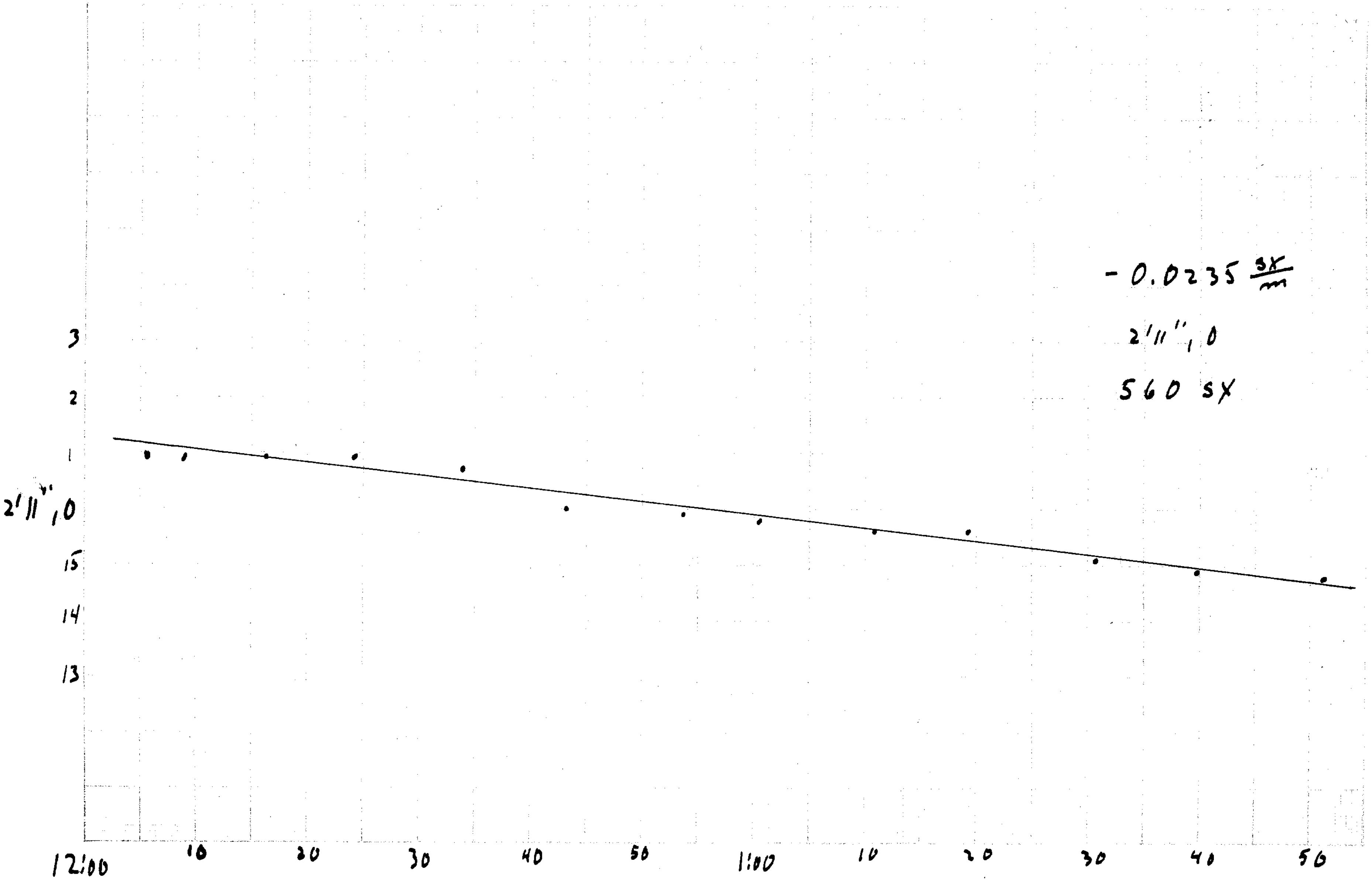
$ZrO_2$ # 16.41


0.0000 sx/m
1'7", 13
3/7 SX
15
14
13
12
11
1'7", 10
1:40
50
2:00
10
20
30
40
50
3:00
10
20

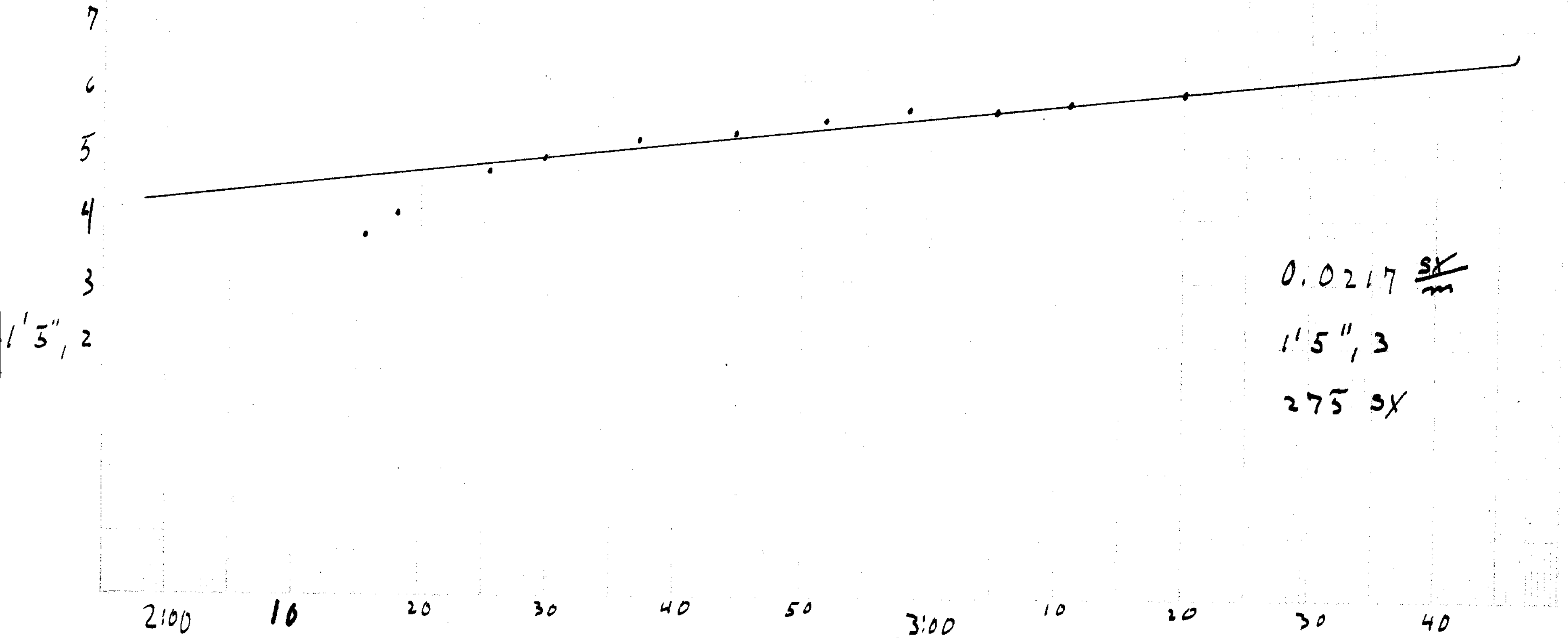
$ZrO_2$ # 16.42


-0.0034 $\frac{sK}{m}$
2'4",1"
459 sK
13
12
11
10
9
2'4",8
3:20
30
40
50
4:00
10
20
30
40
50
5:00
10

$ZrO_2$ # 16.43


- 0.0235 $\frac{sx}{m}$
2'11'',0
560 sx
3
2
1
2'11'',0
15
14
13
12:00
10
20
30
40
50
1:00
10
20
30
40
50

ZrO$_2$ # 16.44



$ZrO_2$ #16.45