THE DEVELOPMENT OF β-MAGNESIA WINDOWS AND AN APPARATUS FOR USING THEM

A Thesis
by
Richard Theobold Brice

In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

The California Institute of Technology
Pasadena, California

1 9 3 6

TABLE OF CONTENTS

	Page
Preface	1
Abstract	2
Introduction	4
Physical Properties of β-Magnesia	9
Chemical Properties of β-Magnesia	12
Photo-Micrographs of an Etched β-Magnesia Window (Plate 1)	15
Optical Properties of β-Magnesia	17
Infra-red Transmission of β-Magnesia Crystals (Table)	18
Index of Refraction for β-Magnesia Crystals (Table)	19
Change of the Optical Constants of β-Magnesia with Temperature (Table)	19
Comparison of Quartz-Fluorite and Quartz-Magnesia Combinations (Table)	21
Seals	22
Needle Valve	33
Vacuum System	39
Furnace	41
Mounted Furnace (Plate 2)	42
Appendix	44
A - Seals (Attempts)	44
B - Test Runs	49

PREFACE

The use of β-magnesia for windows to resist caustic metal vapors is in no way original with the author. Dr. R. W. Wood suggested and tried MgO windows in the early nineteen hundreds. Since then various attempts have been made to use them. Most of these attempts were failures because of the scarcity of suitable crystals. Not until recent years when large optical crystals became available as by-products of the commercial manufacture of periclase, did the use of these windows become easily practicable.

The development of the technique for using the windows, and the apparatus connected therewith, is largely due to the suggestions and help of the staff and graduate students of the California Institute. Particular credit is due to Dr. I. S. Bowen for directing the research, and for his many helpful suggestions. Also, the help of Dr. W. R. Smythe in the mechanical design of parts of the apparatus, and the constructive criticism of Mr. Julius Pearson on the details of the needle valve and windows, is gratefully acknowledged.

Richard T. Brice
March, 1937

Abstract

The properties of optically clear β-magnesia crystals have been investigated with an eye toward using them as windows in a vacuum furnace. β-magnesia was found inert to most metallic vapors below 1000° C, and well adapted for use as windows in spectroscopic problems. Windows have been made and tested satisfactorily, and a technique for cutting and polishing the windows was developed by Mr. Pearson in his optical shop. The optical constants of a large clear crystal of β-magnesia were measured and a preliminary investigation made to see whether or not it is suitable for use in lenses transparent out to 2150 Angstroms. It was concluded that the hygroscopic properties of the substance render it unsuitable for such lenses, even though it has advantageous optical constants. Many experiments were made in an attempt to find some technique for sealing the windows into steel tubes so that an absorption furnace could be built where metal vapors could be investigated under conditions of thermodynamic equilibrium. One successful method was found and is described in detail in this thesis. Seals were made by this method and found satisfactory up to at least 587° C. Some of the more important unsuccessful trials are described in the appendix.

In order to utilize the windows and their properties, a furnace was constructed with a specially designed needle valve that permitted control of evacuation through a port in the side of the absorption chamber wall, but which did not introduce any cold spots in the furnace. The

design of the needle valve is discussed at length.

The specific accomplishments reported in this thesis are: (1) The determination of the optical constants of β-magnesia. (2) The development of a technique for sealing β-magnesia windows into a furnace. (3) The design of a needle valve which, together with the windows, permits the realization of thermodynamic equilibrium in an absorption chamber containing caustic metal vapors.

I

INTRODUCTION

The absence of suitable windows for absorption furnaces has long been a detriment to investigations of the absorption spectra of caustic metals. Much progress has been made utilizing the common technique of placing the windows as far as possible from the hot portion of the furnace, and streaming some inert gas through the furnace to prevent diffusion. This technique has decided disadvantages, the most important of which is the absence of thermodynamic equilibrium along the absorbing path. The temperature gradient from the cold windows to the hottest part of the furnace is never accurately known, and since the molten metal and its gas is never in equilibrium, the amount of material in the light path can only be guessed at in subsequent calculations.

If a window could be found which would withstand the effects of the metal vapors, and which could be heated to the same temperature as the furnace itself, a number of important problems would be opened to investigation. A sealed absorption chamber could be built in which the temperature could be accurately controlled, and in which the vapor pressure could be known, so that the number of molecules in the absorbing path might be directly computed. Also, the ability to control conditions inside the furnace would permit the use of very small samples of the caustic element, since none of it need escape to any cold spots or react with the windows. This might make possible the use of the minute samples of pure isotopes collected in mass spectrometers.

With these problems in mind, Dr. D. S. Hughes, working on a National Research Fellowship, started investigations at this Institute to develop suitable windows. His experiments were not completed at the expiration of his appointment, and the work was taken over by the author when Dr. Hughes left in the summer of 1933. Although he did not succeed in finding any suitable material, he tested and eliminated a number of likely optical substances, and thereby cleared the path of several trials which the author would otherwise have had to make.

The development of any apparatus or technique is usually centered around some definite experiment. The investigation of the β-magnesia windows, the measurement of their optical properties, and the design of a furnace in which to use them, were all a part of the problem of obtaining an absorption spectrum from a small sample of an alkali metal which could be collected in a mass spectrometer. The ultimate object of the apparatus has certainly affected the solution of technique problems, and has made the details of the design of the furnace of more importance than is the case in normal spectroscopic problems. However, the uses to which the technique and apparatus may be put are not limited to the specific problem at hand. The allied problems, which the success of the windows makes possible, warrant a description of the results accomplished without waiting for the completion of the larger problem.

The quantity of metal which can be collected under even the most favorable conditions in a mass spectrometer is so small that it would soon congregate in any cold spot - particularly cold windows - and seriously diminish the amount of vapor available for absorption. Furthermore, any chemical reaction between the vapor and the windows would further tend to diminish the available metal, and the alkali-metals are extremely active in the presence of hot glass, pyrex or quartz. Dr. Hughes began the search by trying sapphire windows, using metalic lithium to charge the furnace. The windows were eaten out and rendered opaque, so as to make them completely useless, and a new substance had to be found. Of several materials which had been suggested for trial, the only one on hand at the time was a small sample of MgO, which was loaned by Dr. John Strong for the tests.

The first samples of β-magnesia available were satisfactory from the standpoint of resistance to metalic vapors, but were disappointing because of their small size and poor optical quality. Accordingly, a search was started for good optical crystals. After many inquiries, a supply of large water clear crystals was furnished through the courtesy of the Norton Company, Chippawa Falls, Ontario. After more trials on their resistant properties, it was decided to include the optical constants of the substance in the investigation. In conjunction with Dr. John Strong of this Institute, the transmission, index of refraction and dispersion were measured and reported in a paper before the American Physical Society.[1] The resistant properties

1. John Strong & R. T. Brice, Optical Properties of Magnesium Oxide; J. O. S. A. - 25; 207; 1935.

of the material created such a demand for the crystals, that their price rose from $1.00 per pound in 1935 to $10.00 per pound in 1936, and in a recent letter (September 1936) from the Norton Company, they report that they are considering the manufacture of the optical crystals on a commercial basis with a price somewhere between that of optical glass and quartz. Apparently no use has yet been made of the crystals in optical systems - probably because of the hygroscopic tendencies of the β-magnesia.

The next difficulty encountered was the lack of any method for sealing the windows into a tube. The first design for obtaining a seal consisted of a small aluminum gasket against which the windows were pressed by a suitable collar. The absorption tube was placed inside a vacuum furnace and both furnace and absorption tube evacuated together. The absorption tube was arranged with a valve operated by a tungsten spring and Woods-metal catch, so that it would seal itself as the temperature of the furnace rose. This arrangement was satisfactory for large quantities of the metal, but the windows loosened during the course of the run and permitted some of the metal to escape, rendering this method useless for small quantities.

It became apparent that satisfactory results could be obtained only if a furnace were constructed which would permit the absorption tube to be opened and closed to the pumps at will, and which would permit accurate tests on the condition of the window seals. A new furnace was designed and constructed involving a needle valve which could be operated by hand at any temperature of the furnace, and a design for holding the windows firmly against their gaskets.

The original design provided for double windows with a means of evacuation of the space between the two windows. The use of double windows is probably unnecessary, and the original design for the window seals has proven unsatisfactory and been supplanted by the improved design to be described in part V. The needle valve has proven satisfactory.

The furnace, as designed and built, and as it now stands, has been a great improvement over the previous attempts. However, in the course of the experiments, some points of weakness have developed, and some improvements which could be made have become apparent. The improved method of sealing the windows has considerably reduced the amount of machine work necessary in building the furnace. As it is now, the furnace could undoubtedly be used to obtain some results on the absorption spectra of the alkali metals. However, the incorporation of some tested improvements, and the elimination of some of the weak spots and sources of difficulty, will probably warrant the rebuilding of the furnace itself before any extensive program is attempted. Later in this thesis a design is given for a furnace which is essentially like the present furnace, but in which the improvements suggested have been included. Since a knowledge of what has been tried and why such attempts have failed may be of value to anyone attempting to repeat this or a similar problem, a discussion of the most important trials and failures is included in the appendix.

II

PHYSICAL PROPERTIES OF β-MAGNESIA

Magnesium Oxide does not occur free in nature since it reacts slowly with carbon dioxide in the air, and is changed into magnesium carbonate (magnesite). To obtain magnesium oxide the magnesite is calcined in a furnace to produce light porous chunks of magnesium oxide. These chunks are then fused in large electric-arc furnaces and allowed to cool. The result is an ingot usually weighing a ton or more which is composed for the most part of milky white or slightly yellowish crystals fused into an extremely hard honeycomb mass. This product, called periclase, is ground to a fine powder and used for insulation in electrical appliances where the insulating material must also be a good heat conductor. When special care is taken to make the run of extreme purity, the resulting powdered periclase is sometimes used as a refractory substance for crucibles. It has long been known to make excellent crucibles for the processing of chemically pure metals because it is one of the few refractories which does not react with the metal at high temperatures.

About three inches in from the outside of the ingot, the temperature and cooling conditions are such as to permit the formation of large clear single crystals of magnesium oxide. These large single crystals are referred to in this thesis as β-magnesia. Up until about 1934, these crystals were only curiosities, and were usually ground up with the rest of the mass. Since that time, investigations have shown them to have useful properties, and a market has developed for them. The demand now exceeds the supply. It is probable that the crystals may be marketed commercially in the future, but at the present time the only satisfactory method of obtaining them, is to have someone capable of selecting good crystals make a personal choice as the ingots are broken open. The research laboratories of the Norton Company have kindly done this on request, and the Vitrefrax Corporation in Los Angeles has permitted the author to make personal selections at their factory in Vernon. A pound of the selected crystals will make from eight to ten windows measuring from 1/2 to 3/4 inches in diameter, and about 1/4 inch thick. In view of the fact that they appear accidentally in large scale production, and since the crystals are always of greater purity than the remainder of the ingot, it is reasonable to believe that a melt whose temperature and purity were carefully controlled might furnish much larger crystals than those heretofore found.

The crystals, as obtained from the factory, are first cleaved with a knife to the appropriate size, and then ground and polished to form round disc-shaped windows. The crystals are cubic and cleave readily. They grind well with carborundum, and polish with tin oxide. Rouge does not polish them well, and emery tends to make them flake and scratch. They seem to be somewhat harder than quartz. (6 ± 1). Thin plates are stronger than similar plates of window glass and seem to resist a larger bending moment without breaking. However, the presence of a flaw along a cleavage plane will greatly reduce their strength, and it has been found impractical to attempt to use windows which exhibit the beginning of any cleavage. Such imperfect windows either break from the pressure of the gasket, or they cleave and separate under thermal stresses. In general, it is difficult to obtain windows greater than 3/4 inch in diameter, although larger crystals are occasionally found. The largest single crystal so far seen by the author measured $1\frac{1}{2}$ inches on the edge of a square face of 3/8 inch thickness.

β-magnesia crystals melt at a temperature of 2800° C. They are extremely resistant to heat below 2100° C where they begin to sublime. This sublimation is very rapid in a vacuum, and limits their use to temperatures below 2000° C. A small piece of β-magnesia heated to incandescence to the limit of an oxyacetylene flame and allowed to cool in air, gave evidence of sublimation, but was otherwise unaffected. Cooling the crystals too rapidly will cause fracture along the cleavage planes. A piece heated to 100° C and dropped in cold water shattered into many small cubes. The coefficient of thermal expansion of β-magnesia is 10.9×10^{-6} from 0° to 100° C, and 15.0×10^{-6} from 700° to 800° C.[2] This is of significance because of its approximation to the expansion of wrought iron, which is 11.4×10^{-6} from -18° to 100° C, and annealed steel which is 10.95×10^{-6} evaluated at 40° C.[3]

2 - Milo A. Durand, Coefficient of Thermal Expansion of Magnesium Oxide, Physics, Vol. 7; 297; Aug. 1936.

3 - Handbook of Chemistry and Physics, 15th edition, 1930, page 846.

III

CHEMICAL PROPERTIES OF β-MAGNESIA

Since the purpose of this investigation of β-magnesia is to determine its suitability for windows or optical systems, it is only necessary to consider here those chemical properties which have affected its use for this purpose. Of first importance is its reaction with the metalic vapors and secondly its stability in air and ordinary cleaning reagents.

The tests on the resistance of β-magnesia were carried out by exposing the windows to the hot vapors in a vacuum furnace. Six windows, 12.5 mm diameter by 2.5 mm thickness, were cut from single crystals of β-magnesia. These windows were placed, two at a time, inside a vacuum furnace containing about a gram of an alkali metal. The temperature was slowly raised until the vapor pressure of the alkali metal was approximately 1 cm and after exposure to the metal vapor over night, the furnace was cooled and the windows removed for examination.

With lithium[4] it was possible to compare the effect of the vapor on β-magnesia with its effect on a sapphire. A sapphire window was placed in one end of the furnace, and a β-magnesia window in the other end. The sapphire was rendered opaque and eaten out to a depth of about 1 mm, while the β-magnesia window was quite unaffected. Sodium and potassium showed practically no effect on β-magnesia.

4 - The orignal paper which claimed this comparison was made with calcium instead of lithium, was in error.

On another test lithium vapor showed a slight reaction with the window. The etching was sufficient to cause a slight blurring when viewing printed matter on which the window was lying. No color effects of any kind were observed.

The windows were not protected from the condensation of molten metal upon their surface, and so, in each case, drops of the metal collected on the windows during the tests. The outer layer of the metal used to charge the furnace was somewhat oxidized. It is therefore probable that the conditions which obtained in these tests represent the least favorable conditions under which the windows would be used as far as impurities are concerned. Table I lists the data for these tests with corrosive metals.

No further direct tests were made on the resistance of these windows. However, in subsequent uses of the material, it has been exposed to tin at 500° C for periods of 12 hours or more, and to Woods-metal for similar periods. In the case of the Woods-metal, the temperature was sufficient to vaporize the cadmium. It is therefore possible to add tin, cadmium and bismuth to the list of metals which can be used. It is, of course, inert to magnesium, iron and nickel, as might be expected.

The results of these tests were announced at the American Physical Society meeting in Los Angeles, December 1934. Professor R. W. Ditchburn immediately wrote from Dublin to obtain samples, and has since extended the investigation. He reports[5], "We have made

5 - R. W. Ditchburn, Nature, 36; 70, July 1935.

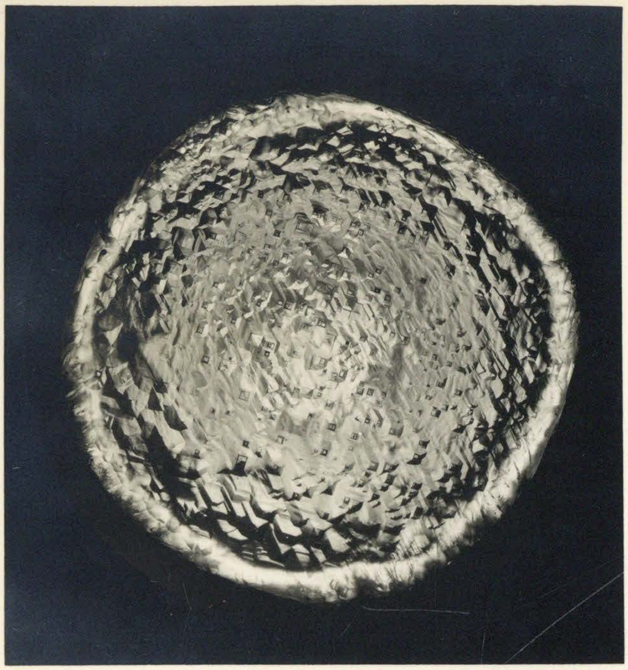
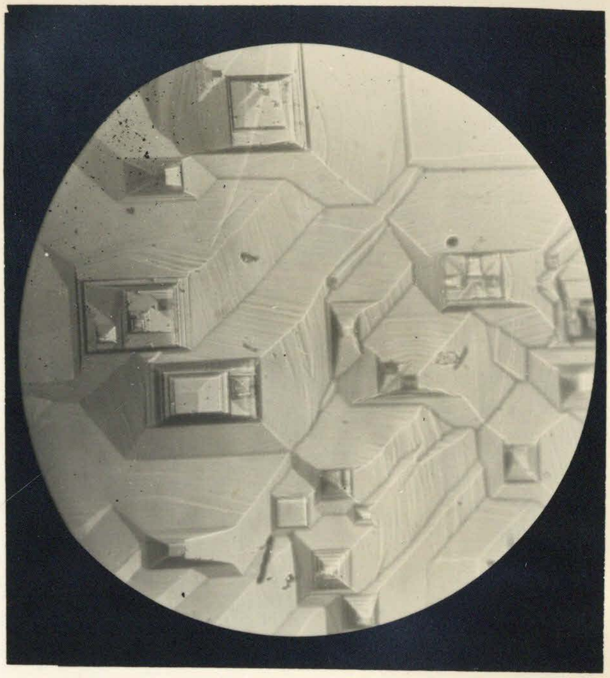
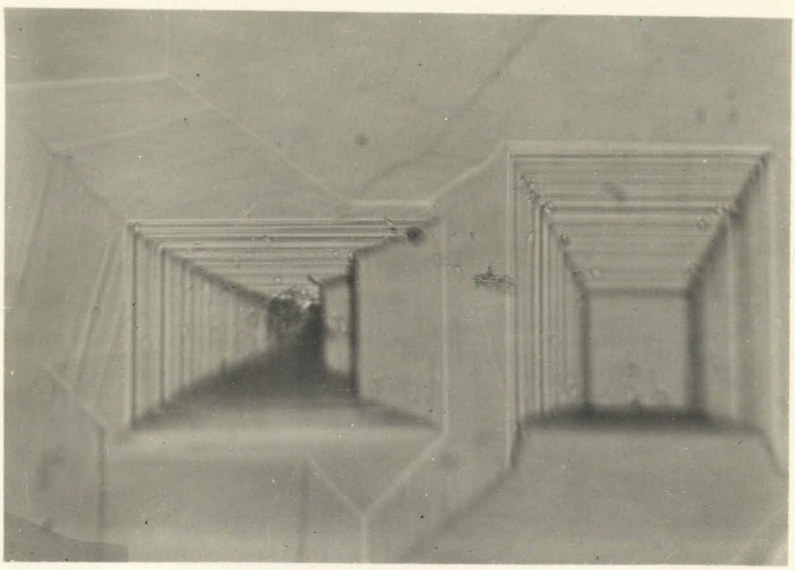
TABLE I

RESULTS OF EXPOSURE OF β-MAGNESIA WINDOWS TO HOT ALKALI-METAL VAPORS.

Metal	Maximum Temperature	Duration of Exposure	Results
Ca	810	36 Hours	No attack
Na	610	1 Hour	No attack
	200	24 Hours	Slight attack ?
K	450	24 Hours	No attack
Li	500	3 Hours	No attack
	688	22 Hours	Surface etched Window not opaque

quantitaive tests by heating the crystal with various metals in small evacuated tubes; the tubes were kept at the specified temperature for one hour. Potassium (400° C), sodium (500° C), lead (1,050° C), magnesium (1,100° C) and aluminum (1,100° C) had no effect; calcium (1,050° C) and copper (1,100° C) etched the surface slightly. X-ray analysis shows that the crystal has a close-packed structure, which probably accounts for this property."

The formation of the crystals is apparently directly dependent upon the purity of the furnace charge. Mr. C. H. Hannon of the Pittsfield Works of the General Electric Company reports in a letter to the author: "We have observed during the normal course of events, that the impurities in the magnesia affect the crystal size. For instance, with a magnesite containing very low silica (below .1%) we have obtained very much larger crystals than with magnesite containing 1½ or 2% silica." The Norton Company furnished a chemical analysis with their crystals as follows: SiO_2 0.04%, Fe_2O_3 0.04%, CaO 0.04%. These figures probably indicate the limit of impurity rather than a rigorous analysis. In commenting on this purity, however, Mr. Raymond R. Ridgway of the Norton Company's Research Laboratories, says, "They are formed by differential crystallization, so that they do not contain as much impurity as the original melt." The presence of too much iron as an impurity sometimes colors the crystal a delicate green. The crystals are occasionally yellow, but what impurity causes this has not been determined. The presence of these impurities does not appear to affect the use of the β-magnesia for windows except as they may limit the transmission of light or exhibit objectionable absorption bands.

The most serious chemical property of the windows is their affinity for carbon dioxide. In the presence of the moisture of the air the windows gradually lose their polish and acquire a coating of magnesium carbonate which renders them milky. Fortunately this reaction is very slow, and the windows may be used in air without harm, provided they are stored in a dessicator when not in use. Crystals have been kept as long as four years in a calcium chloride dessicator without showing any trace of attack. Lying open in the room they lose their polish in from one to three months depending upon the humidity.

Dr. A. S. King of the Mt. Wilson Observatory has made some tests of these windows in his carbon high-temperature furnace. He found that the windows withstood the effects of the air (a few mm) in the furnace as well as any CO_2 vapor which might be present, and they retained their shape and transparency up to about 2100° C. In particular, they were quite satisfactory at temperatures up to 1800° C, but he did not have any caustic substance in the furnace during these tests. He did not investigate the effects of metals at these high temperatures. At about 2100° C, the windows developed an unevenness on their surface and appear to have sublimed and etched so as to bring out a mosaic structure in the crystal. Photomicrographs of the etched surface were taken by Dr. A. Goetz of this laboratory, and are shown in Plate I. I-a shows a 5.2 times linear magnification of the entire window. The lighting used was such as to emphasize the irregularities. The window was still semi-transparent and did not have a ground-glass or milky appearance as might have been expected. I-b is a 72 times enlargement of the surface to show the regular rectangular appearance of the sublimed pits and to show the vicinal planes. I-c is a 325 times enlargement of two individual pits, and shows the terraced structure of the pits themselves.

The Handbook of Chemistry and Physics, 15th Edition, gives the solubility of β-magnesia as .00062 in 100 parts of cold water. It also states that it is soluble in acids and NH_4 salts. However, water may be used in the grinding and polishing process, and they may be washed in it without harm. A series of tests were made with various acids to determine the extent to which they could be used for washing and cleaning the windows. Samples washed in H_2SO_4, HNO_3, HCl, chromic-sulphuric acid cleaning solution, NH_4OH and NaOh all came out unaffected. A window placed in hot HCl for cleaning was immediately attacked.

In summarizing these chemical properties it can be said that the crystals offer great resistance to the caustic effects of most metalic vapors at temperatures ranging from 500° for the lighter metals, to 1100° C for the heavier metals. They can be used satisfactorily up to 1800° with those metals to which β-magnesia is completely inert. The reaction of magnesia to CO_2 in moist air may be minimized by storing it in a dessicator. The traces of hot CO_2 which may exist in iron and carbon vacuum furnaces do not harm the windows. The ordinary cleaning reagents may be used to wash the windows, provided they are rinsed in water and dried thoroughly. Heating the acid cleaning agents is injurious to the windows.

IV

OPTICAL PROPERTIES OF β-MAGNESIA

The only optical property which is of great importance in the use of β-magnesia for windows is its transmission. Dr. John Strong, however, suggested that since β-magnesia transmits to 2150A it might be valuable to know its other optical constants in case it should be suitable for use in lenses or optical instruments, or in case it should be necessary to use the windows in an interterometer beam. An investigation of these optical constants was accordingly made by Dr. Strong and the author, jointly, but the results did not disclose any properties sufficiently valuable to overcome the disadvantage of its instability in air. The results of the investigation are briefly given here, to indicate the work done and the results obtained.

The ultraviolet transmission limit of β-magnesia was obtained with the aid of a Hilger E-3 quartz spectrograph and an iron arc. One of the standard 2.5-mm windows was tested. By visual comparison between the spectra taken directly, and those taken through the window, it was observed that the absorption of β-magnesia is negligible to 2200A. Between 2200 and 2150A the transmission decreases very rapidly. Greatly increased exposures did not extend the spectrum beyond 2150A. Two factors which might have an effect on this limit, and which were not considered, were: First, the windows may have been coated with a thin layer of magnesium carbonate due to reaction with CO_2 in moist air. Second, the windows were all made from the same shipment of β-magnesia, having approximately the same impurities, so that crystals having less impurity may give slightly different results.

The infrared transmission of β-magnesia was estimated from comparison with several crystals of known transmission to be continuous out to about 5 or 6 mu. The total energy emitted by a black-body radiator at 400° C was employed for these tests. The transmissions were measured with the aid of a vacuum radiation thermopile equipped with a KBr window. The various observed transmissions are given in Table II.

Six of the large crystals obtained from the Norton Company were ground and polished on both sides and examined for internal strain in polarized light. Of the six crystals tested, only one showed serious strain when observed with the nicol prisms. Professor Ditchburn[5] reports that his specimens showed some double refraction owing to residual strains. Optical quality was tested by observing the image of the entrance slit of a spectrometer in the telescope eyepiece after passing the light through the β-magnesia plate. All were of optical quality. From the remaining five (one having been discarded because of strain), one was chosen from which two prisms were finished having faces 27 x 24 mm and 25 x 24 mm, and prism angles of 32° 32' 48" and 29° 30' 16" respectively. It is well to keep in mind that both prisms were cut from the same crystal, so that the following determinations are not necessarily true for crystals of different purity. It is hardly to be expected, however, that the effect of the slight impurity present would give rise to a sensible effect on the indices.

TABLE II

INFRARED TRANSMISSION OF β-MAGNESIA CRYSTALS

Material	Thickness	Transmission	Limit of Transmission
KCl	8.36 mm	92%	23 mu
NaCl	4.64	89%	17 mu
Fluorite	2.80	80%	9 mu
β-magnesia	8.37	55%	Estimated 5 or 6 mu
Quartz	2.8	31%	4 mu

The two prisms were aluminized on the back and alternately mounted on the table of a precision Zeiss spectrometer kindly loaned by the Mount Wilson Observatory. Indices of refraction were calculated from the angular deviation of various spectral lines. The prisms were arranged after the Littrow method. In the visible the prism was set at minimum deviation for each line by the aid of a Gauss eyepiece. In the ultraviolet a quartz-fluorite lens was mounted in a box which was equipped with a slit and plate holder and the prism was set at minimum deviation photographically. The prism angles were determined by two of the three commonly used methods. The values of the indices of refraction for the spectral range $\lambda = 2563A$ to $\lambda = 7065A$ for the two prisms are given in Table III. As an additional check, the photographic settings were repeated at a few lines measured by visual settings.

In order to determine the temperature coefficient of the index of refraction, the apparatus was moved to a refrigerated room in Kerchoff Biology Laboratory, kindly placed at our disposal by Dr. T. H. Morgan, and the indices for lines C and F were measured at 2° C. The results are given in Table IV. As a control, the angle of the prism used was remeasured at 2°C, and found to check with the previous value at 23° C to less than 1" of arc.

β-magnesia possesses optical properties which suggest its use in various achromatic combinations. Because of the action of CO_2 on its surface, it would be necessary to cement the β-magnesia between two other components. In the case of a quartz-magnesia doublet, these

TABLE III

INDEX OF REFRACTION FOR β-MAGNESIA CRYSTALS.

λ	Index of Refraction A = 29° 30' 16" Visual	A = 29° 30' 16" Photo	A = 32° 32' 48" Visual	A = 32° 32' 48" Photo
2536		1.8450		
2654		1.8315		1.8316
2804		1.8171		1.8171
2967		1.8046		1.8045
3128		1.7945		1.7945
3658		1.7720		1.7720
4046	1.76132	1.7614	1.76142	1.7614
4340 (G')	1.75531		1.75532	
4358	1.75506	1.7549	1.75514	
4471	1.75325		1.75307	
4713	1.74955		1.74940	
4861 (F)	1.74742		1.74745	
4921	1.74676		1.74672	
5016	1.74560		1.74562	
5460	1.74119		1.74126	
5790	1.73853	1.7385	1.73853	
5876	1.73787		1.73795	
5893 (D)	1.73790		1.73788	
6563 (C)	1.73364		1.73365	
6678	1.73310		1.73308	
6708	1.73304		1.73307	
7065	1.73127		1.73125	

TABLE IV

CHANGE OF THE OPTICAL CONSTANTS OF β-MAGNESIA WITH TEMPERATURE

λ	$n(23^o)$	$n(2^o)$	dn	$dn/dt \times 10^5$
6563	1.73364	1.73340	0.00024	1.14
4861	1.74742	1.74711	0.00031	1.47
			Rocksalt	3.749
			Quartz	0.649
			Fluorite	1.22
			Calcite	0.071

Dispersion 53.55(23^o); 53.80(2^o);

$dv = 0.25$; $(dv/v) \times 100$ 0.022

outer components could both be quartz. Since β-magnesia transmits into the ultraviolet, we shall make a preliminary survey of the possibilities for its use in the particular case of a quartz-magnesia doublet lens.

The focal length of a lens with two thin components in contact is given by the relation,

$$C_a(n_a-1)+C_b(n_b-1)=1/f,$$

which can, in general, be rigorously satisfied for only two wavelengths, v and r, simultaneously. Setting up the two equations and solving for the constants gives

$$C_a = 1/f(V_a - V_b)$$

$$\text{or } C_a/C_b = \Delta n_b/\Delta n_a$$

$$C_b = 1/f(V_b - V_a)$$

in which the dispersion $V=(n_d-1)/(n_c-n_f)$,

and

$$\Delta n = (n_v - n_r).$$

In order to have the focal length constant for all wavelengths, it is necessary that $\frac{\Delta n_b}{\Delta n_a}$ be a constant independent of the wavelength chosen for $\lambda=v$ and $\lambda=r$. This condition is never precisely fulfilled, the degree to which it is fulfilled being a measure of the suitability of the two materials for combination. The values of this ratio for various increments are shown in Table V, along with values for the usual quartz-fluorite combination. The table indicates that the secondary spectrum may deviate more for the magnesia-quartz combination than for the quartz-fluorite combination. A final appraisal of the value of β-magnesia for combination with quartz, as well as its value in various combinations with quartz, fluorite, sylvine, rocksalt or glass for doublets or triplets, is left to the opticians. It may be remarked, however, that fluorite is yearly becoming more scarce, so that there may appear a need for a cheap ultraviolet achromat where expense or availability is a greater factor than excellent color correction.

TABLE V

COMPARISON OF THE RELATIVE INDEX CHANGES FOR A QUARTZ-FLUORITE AND A QUARTZ-MAGNESIA LENS COMBINATION

$\lambda_v + \lambda_r$	β-magnesia MgO	Quartz SiO_2	Fluorite CaF_2	$\frac{\Delta n_{MgO}}{\Delta n_{SiO_2}}$	$\frac{\Delta n_{SiO_2}}{\Delta n_{CaF_2}}$
	$\eta_v - \eta_r = \Delta n$				
2536 4046	0.0836	0.04152	0.02465	2.02	1.69
4046 4340	.00607	.00317	.00190	1.92	1.67
4340 4861	.00787	.00428	.00256	1.84	1.67
4861 5460	.00621	.00353	.00208	1.76	1.70
5460 5893	.00334	.00191	.00114	1.75	1.67
5893 6563	.00425	.00233	.00133	1.82	1.75
6563 7065	.00238	.00143	.00081	1.67	1.77

V

SEALS

If any material is to be wholly satisfactory for windows in a vacuum absorption furnace, it must be possible to make a vacuum tight seal between the window material and the tube itself. This seal may be one of three different types: (1) A fused seal, as between glass and glass; (2) a chemical seal involving some form of binding material, such as the silver chloride seals commonly used with quartz and pyrex; or (3) a mechanical seal involving mechanical pressure between the window, a suitable gasket, and the material of the absorption tube. Seals involving waxes or greases as vacuum tight lubricants have been omitted because all such substances now known break down at the higher temperatures.

All three types of seals have been used with β-magnesia windows. Professor R. W. Ditchburn[5] reports having successfully sealed the windows to soda glass. The edge of a thin window was first polished smooth, and then pressed against or into a soda glass tube which had been heated until soft. The molten soda glass appeared to wet the polished β-magnesia and form the seal. Attempts to seal a window between two tubes failed although the windows remained sealed if they were on the end of a single soda glass tube. So far the author has seen no reports of successful seals of Pyrex to β-magnesia. Unfortunately the coefficients of expansion of Pyrex and β-magnesia are not of the same order of magnitude.

This type of seal is probably useful for some problems. In the particular problem under consideration (alkali vapors), it is useless because alkali vapors attack the glass. Also, the soda glass has a sufficiently low melting point to limit the useable temperature to low values.

The author has succeeded in obtaining a seal between β-magnesia windows and pyrex tubes, using the usual silver chloride technique. The edge of the window was first coated with platinum by means of the commercial product known as "Liquid Platinum." Liquid Platinum is a brown liquid, probably composed of a platinum salt and lavender oil. It is used commercially to decorate china, and may be obtained from china decorators. (Woods & Bailey, Los Angeles). A very thin coat of the liquid is painted around the outside edge of the window, which is then heated slowly with a torch to a dull red heat. The oil evaporates and the platinum salt decomposes to leave a thin coating of metalic platinum on the window. The pyrex is similarly treated and the two platinum surfaces are coated with silver chloride when they are both at a temperature of about 450° C. The two surfaces are then pressed together while the silver chloride is still molten, and allowed to cool. A similar seal was made with a β-magnesia window and a steel tube on the end of which a thin sheet of platinum foil had been silver soldered. Considerable difficulty was encountered in obtaining good seals, but this was probably due to the inexperience of the author in this technique. Two of the seals thus made appeared to be strong, held the vacuum, and remained tight over the period of testing which was a week or more.

Unfortunately, silver chloride is itself an active reagent. In the presence of light it gives off chlorine, which attacks most of the metals. The alkali vapors will reduce the silver chloride, giving free silver and an alkali halide. For this reason the silver chloride seals were discarded and not tried in the vacuum furnace. In the case of glass and pyrex, this type of seal is known to be satisfactory and to hold up to temperatures of about 400° C.

Two mechanical seals of β-magnesia to steel have been made and tested. The general design is shown in Fig. 1. Since the configuration of the steel outside of the hole into which the window fits is of no importance, it will simplify matters to assume that the window is to be mounted in a plain round steel tube. In actual application of the seals, it will be necessary to have the outside of the steel tube in some convenient shape such as a bolt, a tapered plug, a thick steel plate, or other convenient shape for assembling into the apparatus. The window tested was mounted inside a 3/4 inch cold-rolled steel bolt, having a 1 inch head and 28 threads per inch. It is of importance to have the wall of the bolt or tube sufficiently thick to absorb any strain from the threads. It is sometimes necessary to tighten the steel-aluminum bolt seals with great force, and it is important that this force should not be transmitted to the window. The window used was 1/2 inch in diameter (before tapering), and 1/4 inch thick.

The window mounting is performed in an accurate lathe. The procedure is as follows: First, set the swivel of the lathe to cut a 1° taper. This setting should not be disturbed during the rest of the

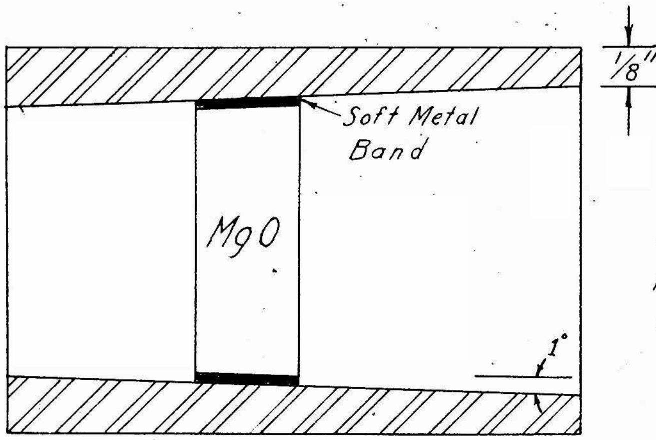


Fig. 1
Mounted Window

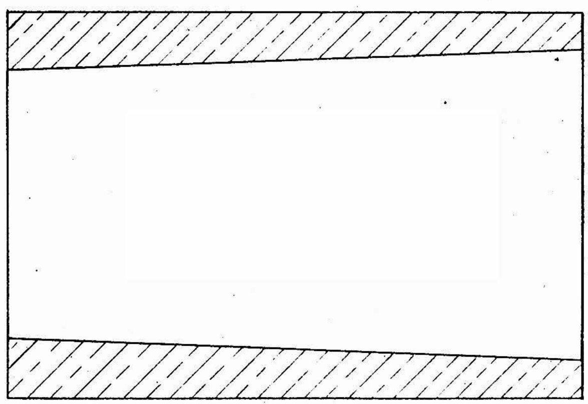


Fig. 2
Brass Tool For Grinding Window From 3/4" Blank

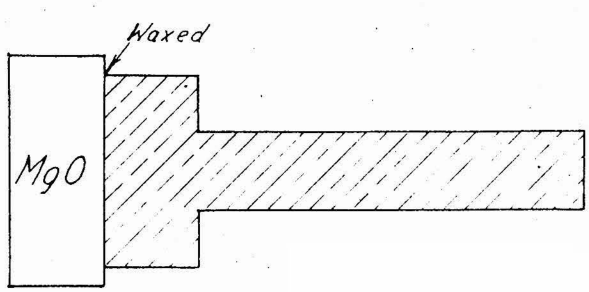


Fig. 3
Window Mounted Ready For Grinding

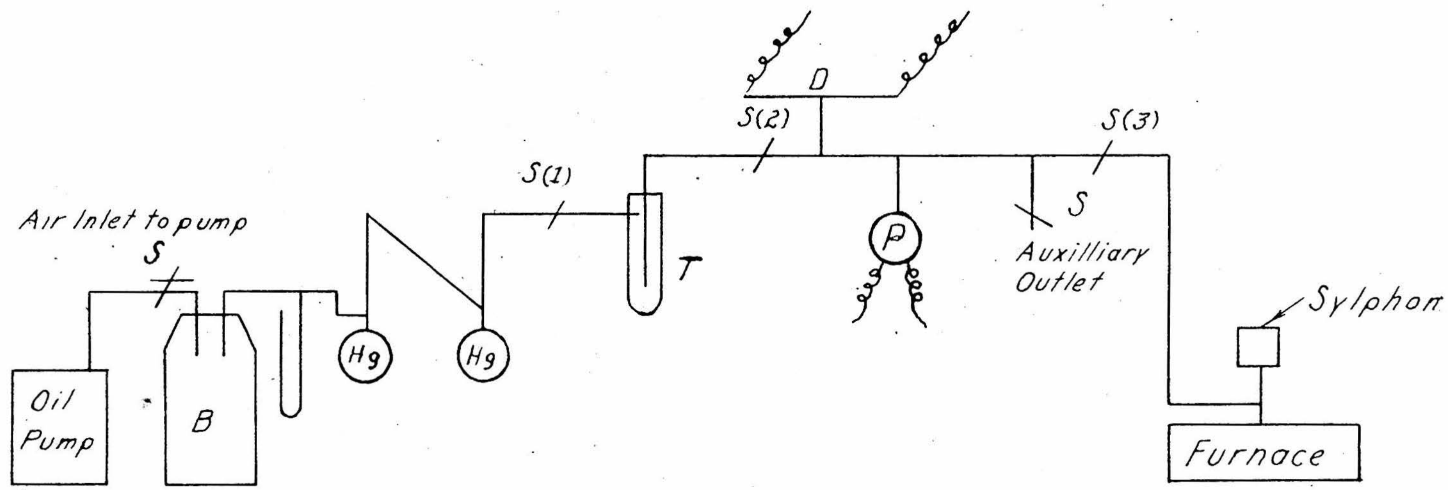


Fig 4-a
Improved Pumping System

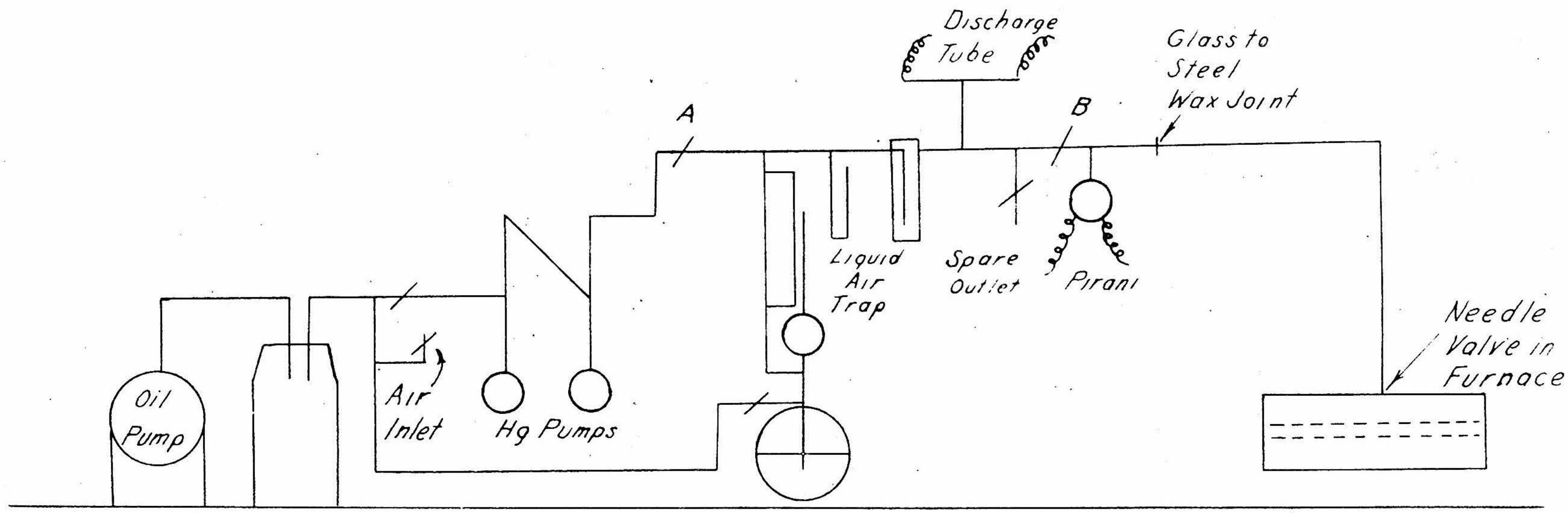


Fig. 4
Vacuum System

construction, as it is important that all the tapers be identical. Second, make a brass grinding tool similar to that shown in the diagram (Fig. 2), and leave the tool in the lathe chuck. Third, mount the window on a brass rod with sealing wax (Fig. 3). Place the brass rod in a three jawed chuck in the tail stock of the lathe, leaving the rod loose in the chuck so that it requires only a little torque to make it turn. The reason for this is that the tail stock may not be accurately in line with the rotating chuck. With the window mounted thus loosely, it will center itself as it grinds. Further, as the window edges assume the taper of the brass grinding tool, there will be a tendency to grab and "freeze" the window into the brass tool. The window will then break loose from its wax unless the rod can rotate easily. A window so frozen into the grinding tool is usually ruined. If the brass rod can rotate easily, the grabbing will only rotate the rod. The lathe can then be stopped and the window worked loose without breaking it. By careful manipulation the tail stock chuck can be tightened until the brass rod and window will not rotate when grinding properly, but will turn in the chuck if the window shows any tendency to stick and grab.

The window having been mounted in the lathe, the next (fourth) step is to grind the window to the proper taper. A thin paste of Number 320 carborundum in water is used for the abrasive, and the window is ground until it is apparent that it is making contact with the grinding tool at all points on its edge. If the grinding is insufficient, or if the window tends to wobble, a slightly elliptical window will result which will not seal. The grinding must be done slowly, using plenty of grinding material. The actual grinding is very similar to valve grinding on an automobile. The tail stock of the lathe is screwed in and out gently with about 1/8 inch amplitude. During the very short interval of the stroke when the window is grinding, the pressure must be very light to prevent grabbing. It was found difficult to judge the proper pressure by the feel of the tail stock screw, but by listening to the sound made by the window as it begins to grind, the correct pressure can be determined. A little practice will enable one to grind the windows "by ear" with few accidents, but a few preliminary trials on glass discs is recommended since the β-magnesia windows are expensive and difficult to obtain. After the window is ground to the proper taper, the edge is polished by successive grinding with 400 and 600 carborundum and tin oxide. This can be done very quickly by mounting the window (still waxed to the brass rod) in the rotating chuck of the lathe, and using three hardwood sticks. One stick is charged with 400 carborundum and machine oil, the next with 600 carborundum and machine oil, and the last stick is charged with tin oxide, dry, by rubbing the oxide into the wood. Pressing the wood against the edge of the rapidly rotating window will produce sufficient polish.

The window having been ground to the shape of a perfect truncated circular cone, the sixth step is to prepare a thin soft-metal casing to protect the window and to serve as a gasket. On two β-magnesia windows aluminum was used for one seal and copper for the other.

The preparation of the collar is best accomplished by boring a tapered hole in a soft metal rod, using the same 1° taper as for the window. The window is pressed tightly into this hole, using the tail stock of a lathe to produce a sufficient pressure along the axis of the window. The β-magnesia will withstand great pressure when being forced into the collar, but it is possible to break them so that some care and judgment must be used to obtain sufficient force without exceeding the safe limit. Since the thin walls of the soft metal will not withstand the expansive force of the window, it is best to start with a rod about 3/4 inch larger in diameter than the window. After the window has been pressed in, and while the soft metal is still mounted in the lathe chuck, the outside of the rod is turned down with the same 1° taper. The result is a tapered window tightly fitted into a tapered protective collar about .010 to .020 inches thick.

The final step is to bore a smooth tapered hole in the steel rod and press the cased window into the hole. With care, the size of the hole can be made such that the window seats several mm in from the end of the rod, and is thus protected from accidental breakage as well as being surrounded by heat conducting metal.

The tests on these seals have not progressed far enough to be able to say with certainty whether or not the seal stands up for an indefinite number of runs. The window using an aluminum casing was the first one made and tried, and was not as accurately made as the one using copper. The window was tested by making a series of runs. The results of these runs are as follows:

Run 1 - Raise temperature to 389° and cool back to room temperature. Small leak in window at end of run.

Run 2 - Press window in with greater force. Raise temperature to 358° and return. Window tight at end of run.

Run 3 - Raise temperature to 114° C and return rapidly. Window tight.

Run 4 - Raise temperature to 362° and return. Window tight.

Run 5 - Raise temperature to 442° and leave standing at that temperature for 24 hours. Window sprang a bad leak when temperature back to 144° C.

It appears from this data that tight windows may be made with aluminum casings, and that they will function for a few runs. Whether this leak was an indication that the temperature limit had been reached, or whether some physical accident or imperfection existed which would not be present in other such mountings, is not known. Since aluminum melts at 660° C, the useful limit of such mountings must lie below this point.

The second window was mounted in an identical manner with the first, except that improved workmanship and familiarity with the method permitted somewhat better contact. Copper was used, since it has a higher melting point and is apparently inert to some of the alkali metals. The final choice between aluminum and copper or some other metal will doubtless depend upon the resistance of the soft metal used to the vapor in the absorption tube. For vapors which do not attack it, copper should be superior because it does not tend to flow outwards and relieve the pressure on the window, and because it has a higher melting point. In tests with both copper and aluminum, failures of the seals always occur on the falling temperature curve.

This is because the coefficient of expansion of both metals is greater than that of β-magnesia or steel so that the window tightens with increasing temperature and loosens with falling temperature. The log of the runs made with the copper-sealed window are as follows:

Run 1 - Temperature raised to 424° C and returned. No leaks during or after the run.

Run 2 - Raised temperature to 522°. No leaks.

Run 3 - Raised temperature to 585°. Leak, if any, below limit of detection.

The method of testing these windows consisted of mounting them in one end of a furnace, the other end of which was permanently sealed. The vacuum system diagram is shown in Fig. 4. The temperature of the furnace was raised to the desired point over a period of about 12 hours and then lowered back to room temperature in a similar period. During the course of the run the rate of drift of the Pirani gauge was read at frequent intervals, and the rate of leak through the windows was assumed to be proportional to the rate of drift of the Pirani. Since the resistance of the Pirani depends upon the conduction through the filament supports, and since this heat conduction changes by jarring or vibration, it was necessary to mount an electric buzzer in contact with the Pirani bulb, in order to stabilize the readings to within .1 ohm in a total change of about 63 ohms. In order to further standardize the conditions under which this drift was measured, the same procedure was always followed: With all stopcocks open the Pirani was read and recorded. Then stopcock "A" was closed for 30 minutes and the Pirani read again. It was determined empirically

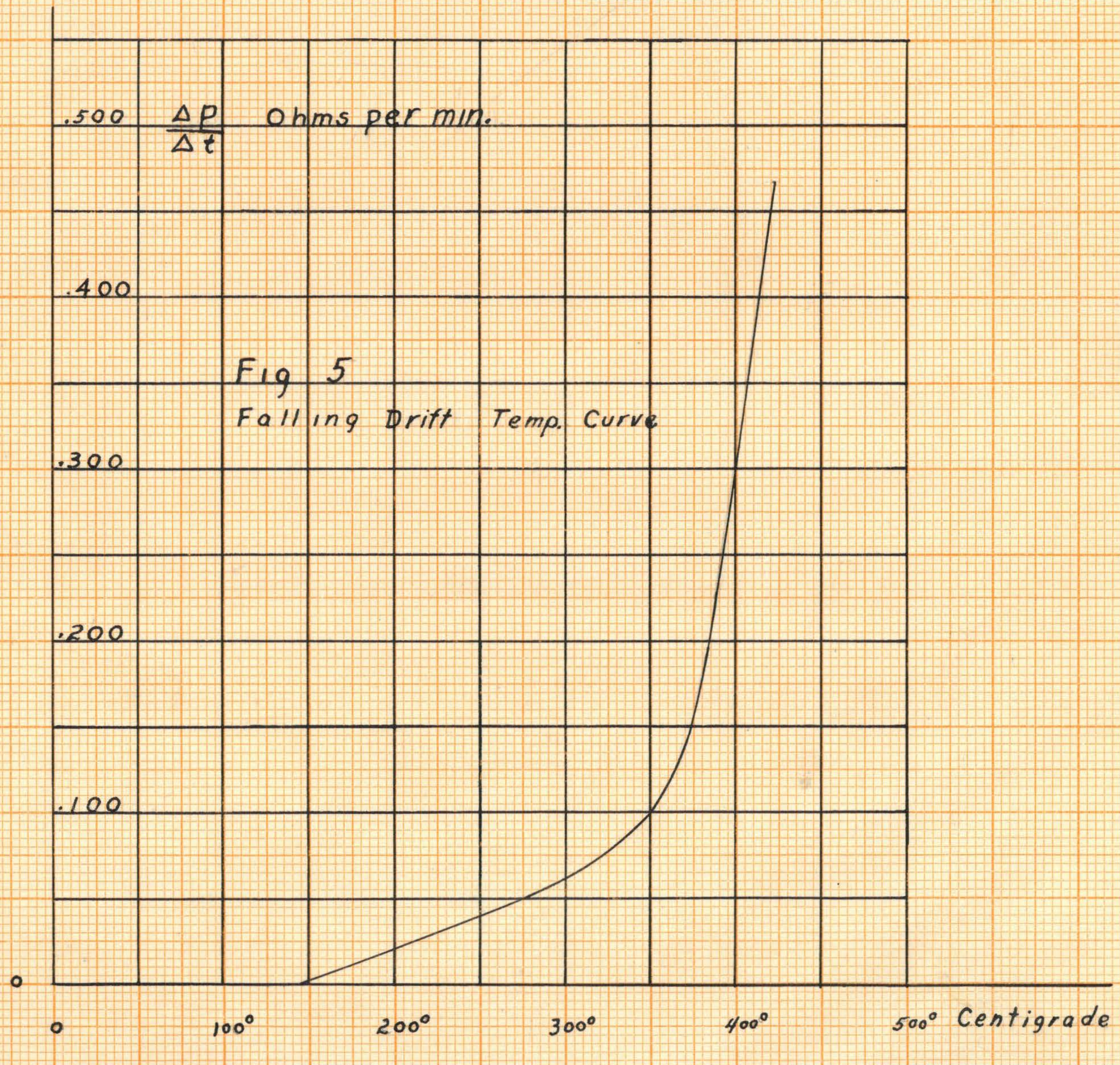


Fig 5
Falling Drift Temp. Curve

that if the Pirani drift was less than .03 ohms per minute during the first 30 minutes after closing "A", the influx of gas into the system would not produce a discharge in less than 12 hours. This was arbitrarily chosen as the boundary between satisfactory and unsatisfactory performance. The windows frequently held sufficiently tight so that the drift of the Pirani gauge would be less than three ohms in 12 hours (.004 ohms/min.).

A great deal of gas was given off by the furnace walls while the temperature was rising, and continued to come off as long as the temperature was maintained at a maximum. Since this gas was sufficient to mask leaks of considerable magnitude, importance is only attached to a falling drift-temperature curve. Such a typical curve is shown in Fig. 5 taken from Run 1, with the copper sealed window.

The rapid fall of the curve as the temperature is lowered indicates that the leaks, if any, are very small. No leak,as evidenced by a discontinuity in the drift-temperature curve (either rising or falling), was ever observed to disappear on either rising or falling of temperature, so that the tightness of the window at the end of the run may be taken to indicate that the window remained tight during the entire run.

Having successfully sealed the window into a convenient steel housing, the problem of sealing this housing into the furnace is not a difficult one, providing the furnace has been built for the purpose. Two methods of sealing a metal bolt into the furnace have been devised. The first and simplest method is shown in Fig. 6. The

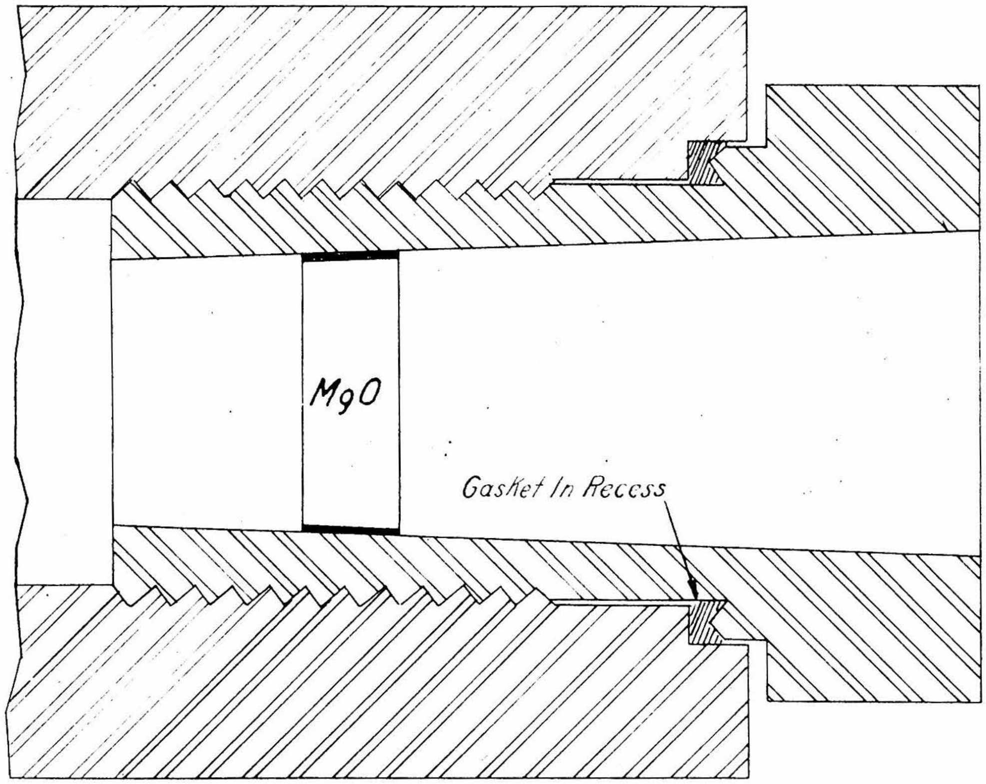


Fig. 6
Window Mounted In Bolt
Bolt Sealed by Soft Gaskets

bolt is carefully made on a lathe and the hole into which it fits is recessed so that a soft metal gasket fits snugly into the recess. The purpose of this recess is to furnish an unyielding wall into which the gasket is forced, so that it is prevented from flowing or spreading out laterally. Attempts to form pressure seals without a recess were all unsuccessful, and even if the gasket seals properly cold, it will anneal and release the pressure as the temperature rises. Both copper and aluminum have been used for such seals.

The above type of seal is probably the easiest to construct and the most positive in action of the various steel-to-steel seals that were tried. However, the furnace as it was originally built was not provided with proper recesses for use with the gaskets, and it was necessary to devise some type of seal which would press against a flat shoulder, not recessed, and which would not release with the thermal changes. This second type of seal is shown in Fig. 7. It consists of a pure nickel gasket machined with pointed surfaces of contact. The end of the tube or bolt is pressed tightly against the gasket, which in turn presses against a ledge provided in the furnace as shown. Immunity to thermal changes is provided by the similarity in expansion between nickel and steel.

Both types of seals have been used in the construction of the furnace, and have given good service. One nickel seal was used to close permanently one end of the furnace tube, and has been in constant use over a period of months without leaking. The "stoke-hole"

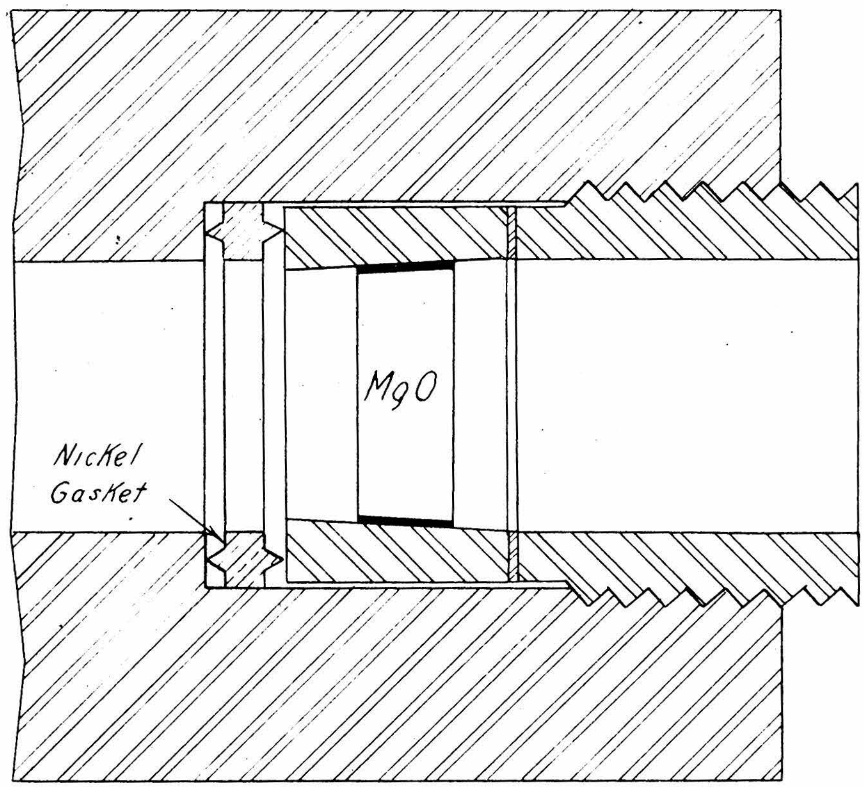


Fig. 7

Window Mounted in Heavy Tube
Tube Sealed by Nickel Gaskets

and needle valve seats are both provided with recessed soft-metal seals, and these have also given good service. Either type of seal requires tightening with a wrench, and the furnace should be anchored in such a manner as to prevent the tightening force from being transmitted to the pumping system.

VI

NEEDLE VALVE

The preceding sections have dealt with the development of a window which can be used to seal the ends of a spectroscopic absorption furnace. These windows have the unique property of being able to withstand both the heat and the caustic effects of certain metalic vapors. On first thought it would seem that the problem of obtaining a sealed chamber in which a vapor can be raised to a given temperature and maintained in thermodynamic equilibrium is practically solved. There remains, however, the problems of introduction of the sample of metal and of evacuation control. The first of these is very simple: The wall of the chamber is made thick. Through the wall a hole is bored which is counter bored and threaded so as to permit sealing with a steel bolt and soft metal gasket as already described. This opening or "stoke hole" has been in use many months and has never given any trouble. It always seats firmly and has never leaked. Occasionally, if the gasket is scarred on opening, it is necessary to replace the aluminum gasket.

The problem of suitable evacuation control is a more difficult one. No outlets can be introduced into the tube through which gas could escape to the pumps, or into which metal could distil, and thus escape from the furnace. Such conditions would immediately destroy the equilibrium, as well as allow small samples of metal to disappear from the absorption chamber. It is desirable to be able to evacuate at any temperature, and then shut the furnace off from the pumps for the remainder of the run. These requirements necessitate the design and construction of a valve which will satisfy the following conditions: (1) It must operate at the same temperature as the furnace, and preferably within the furnace itself. (2) It must resist the caustic effects of hot metalic vapors, and of oxygen in the air. (3) It must remain tight over temperature changes of several hundred degrees. (4) It must be rugged and capable of being operated many times with a certainty that it will seat and seal the chamber properly each time. (5) It should be easy to operate and simple in construction.

Experiments have been made on various types of steel needle valves, in order to determine what design, if any, would best fit these requirements. As a result, a satisfactory design has been evolved, and has now been in constant use for more than nine months. The essential features of this valve are shown in Figs. 8 and 9. Fig. 8 shows the lower half of the needle valve assembly, including the needle and seat; while Fig. 9 shows the upper half and operating mechanism. Details of threads and joints are omitted for simplicity. The important details are the design for the valve seat and needle, which are shown in Fig. 10. By making both seat and valve from stainless steel, a great deal of the corrosion from oxygen at the higher temperatures may be avoided. In valves made from less resistant steel, the layer of oxide coating became thick enough to crack, causing the valve to leak. In building the valve it was anticipated that some experimenting might be necessary as well as occasional replacements. The seat was accordingly designed inside a bolt, as shown, and the bolt sealed into the furnace wall with an aluminum gasket as already described. It has not been found necessary to replace the original seat, but it has been removed and cleaned several times, and has never failed to seal properly when returned to place.

The operation of the valve from outside the furnace is accomplished by means of the "Sylphon" bellows and heavy steel spring shown in Fig. 9. All the motion (about 1/8") takes place in a vertical direction through the bellows, so that the entire assembly is sealed and does not require any ground joints or stopcock grease with their attendant difficulties. The thrust is transmitted through the stainless steel tube, C, so that the force on the valve may be many times greater than the sylphon itself could deliver. The steel block, D, is free to move vertically, but is restrained from lateral displacement or rotation by the supporting posts, E. This further protects the bellows from undue stress and helps to keep the needle in line with the seat.

All of the limiting conditions have been satisfied in this valve. The wall of the furnace was made purposely thick (1 1/4"), so that the valve is imbedded well below the surface, insuring that the temperature of the valve closely approximate that of the furnace. The valve actually operates and seals within a very short distance from the inside wall of the absorption chamber. Adequate tests have not been made on the caustic effects of the metalic vapors. However, since iron and most of its alloys are inert and extremely resistant to the alkali metals and their vapors, it is assumed that little difficulty will be encountered from that source. Any bad effects from oxidation have had ample opportunity to show themselves, and so far have not appeared.

The problem of obtaining constant pressure and tight seals over a large range of temperature was solved by the use of the spring, S. The thermal expansion and contraction of the various parts of the valve will produce only very small changes in the length of the compression column from top to bottom. Small as these changes are, however, they are sufficient to greatly alter the stress in a solid, unyielding column. The use of the spring allows these thermal changes to take place without changing the pressure on the needle point by more than a few percent. In operation, the spring is also used to obtain the same pressure each time the needle is seated. Upon first assembling the valve, the nut, B, is tightened until the required pressure is exerted on the needle - usually between two and five hundred pounds. All further operations are performed by loosening or tightening nut "A". A study of the diagram will show that when A is tightened, the spring is further compressed but the needle is raised. Loosening A results in the needle being pressed into its seat, but all the pressure is furnished by the spring. This prevents over ambitious tightening from injuring the needle or seat.

The valve is rugged and practically fool proof. With any reasonable care, it should last as long as the apparatus to which it is attached. There are no wearing parts, and the strains in the metal and

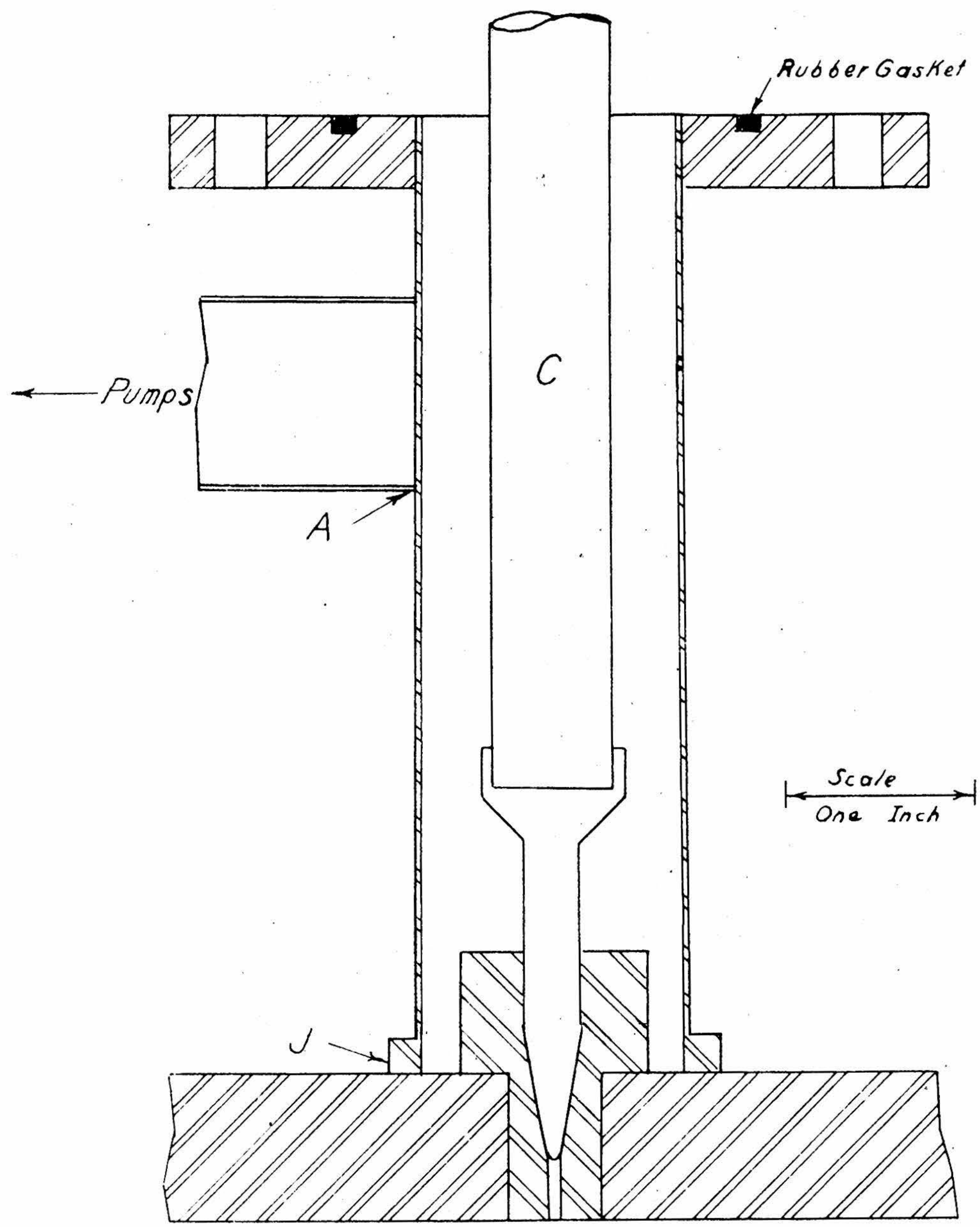


Fig. 8
Simplified diagram of lower half of needle valve assembly

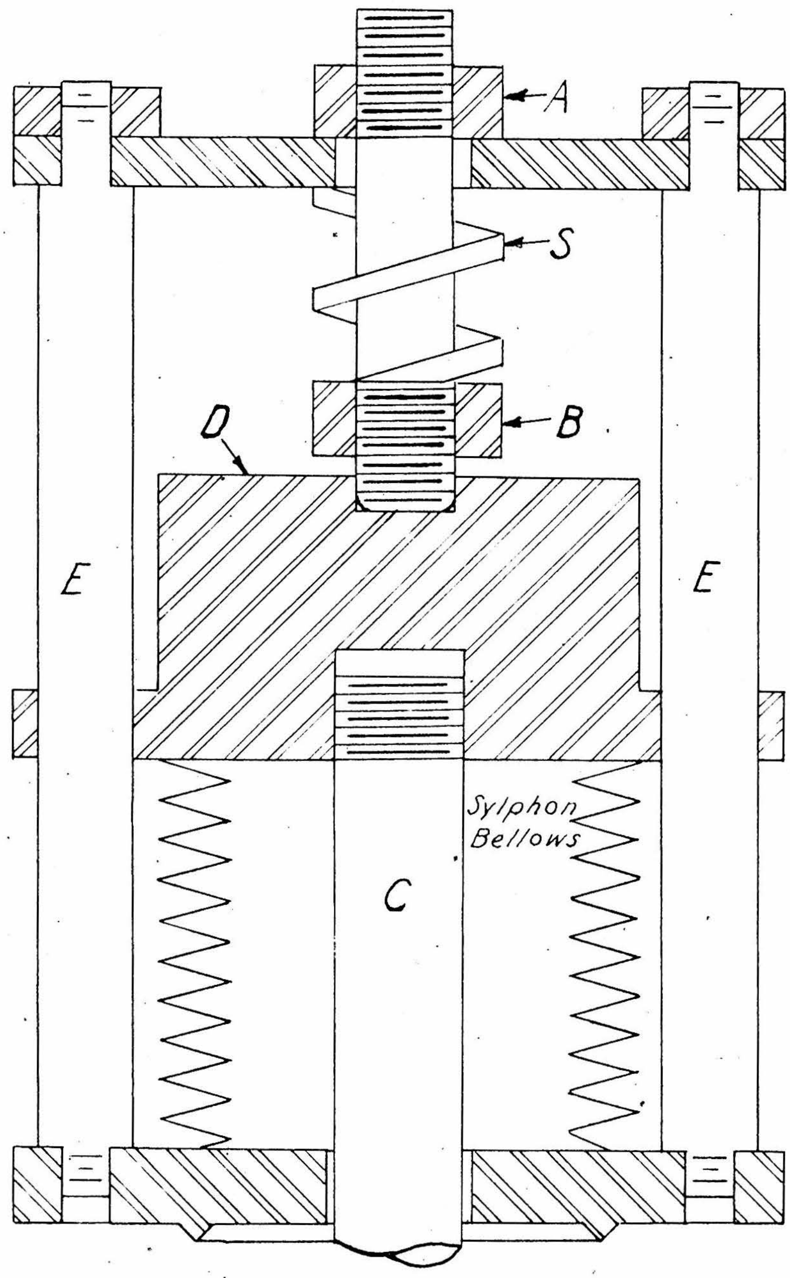
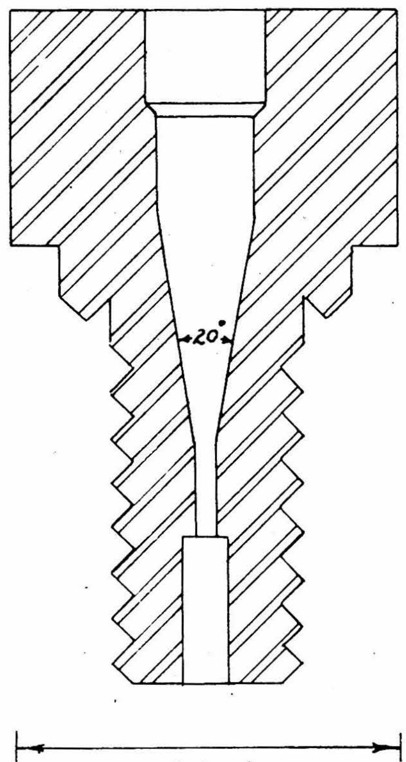
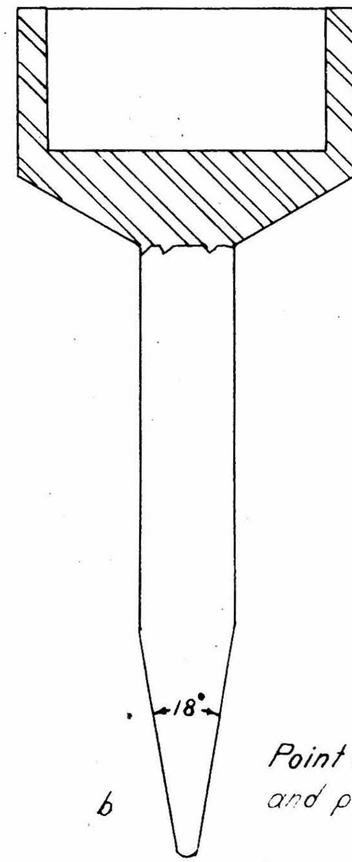


Fig. 9
Simplified diagram of upper half of needle valve assembly



a

Removeable Valve Seat



b

Needle

Fig 10

spring are not large enough to cause failure or cracking. The valve never failed to seat properly or to remain seated during the temperature changes. It has been tested up to 587° C, and has held perfectly with one atmosphere difference of pressure between inside and out. It may be operated at any temperature and may be opened or closed as rapidly as a glass stopcock.

After making 19 consecutive temperature runs, the valve was dismantled to investigate the condition of the needle and seat. All the stainless steel parts have remained unaffected by the heat and vapors except for a slight discoloration. The metal was clean and shiny and did not show any scratches or deformation from dust or gritty particles. No hardened or oxide coating was observed. There was a grey dust deposited on the valve stem, beginning about two centimeters up from the point of the needle, which was probably caused by re-condensation of gas given off by the furnace walls. The fact that this deposit did not appear within two centimeters of the needle-point, probably indicates that the temperature of the needle was sufficiently close to the temperature of the furnace for all practical purposes.

Before leaving the discussion of the valve, two indirect sources of annoyance should be reported. The conduction of heat up the supporting tube is sufficient to raise the temperature of the rubber gasket to about 100° C. Since this was considered dangerous, it was necessary to blow cold air on the sylphon to reduce this temperature to around 60°. The dismantled valve showed that the rubber had been dried and charred on the exposed edges, though the rubber which was actually under pressure and making contact with the steel was in good condition and remained resilient.

The other source of trouble was the junction between the supporting tube and the furnace wall, shown at J, Fig. 8. In the present furnace, the junction was arc-welded. This weld has been a continuous source of trouble. It contracted unevenly when first made, so as to throw the tube out of line, thereby displacing the whole valve stem and making further machining necessary. Secondly, this weld has developed several leaks, and since it is next to the furnace and hot, it cannot be painted with shellac or glyptal. The leaks, when they are definitely located, are closed by tapping around them with a blunt punch and hammer. This apparently deforms the steel so as to close the opening in much the same manner as steel plate joints are calked. In designing this junction it must be remembered that it will be in tension up to about 500 pounds, so that whatever joint is used must not crack or bend under the force. It may be that an oxy-acetylene weld would be more satisfactory if suitable precautions are taken to keep the tube in line. The thickness of the tube at the base must be at least 1/4 inch, in order to prevent the weld from puncturing it.

VII

VACUUM SYSTEM

The preceding sections have described all those improvements which have been made in ordinary vacuum furnace technique as a result of this research. In order to use these improvements, they must be assembled into a suitable furnace with an evacuating system and means of temperature control. The description of these remaining items is given, not because there is any new contribution to be made, but merely to show how the advances have been incorporated in one piece of apparatus to produce a furnace having the desired characteristics.

Fig. 4 is a diagram of the vacuum pumping system. As is the case with most such systems, it was built up by adding one part at a time as the need for various stopcocks and gauges arose. If it should become necessary to rebuild the glass system, or to design another one, a few improvements and changes should be made, although the present system has given very satisfactory service. A re-designed system is shown in Fig. 4-a. The McLeod gauge has been eliminated because the Pirani is much more useful for measuring leaks, and for indicating the state of the vacuum. It should be placed as close to the furnace as convenient. The entire pumping line from the oil pump to the furnace should be made as short as possible. The stopcocks, S(1) and S(2), are particularly convenient when hunting for leaks, or when it is desired to let the apparatus stand idle without the pumps running. In hunting for leaks by means of a hydro-carbon vapor, the liquid-air trap will frequently remove the vapor from the system as fast as it can enter, and if the leak is very small, it will not affect the discharge. Closing stopcock S(2) will facilitate the hunt. In differentiating between occluded gasses and air leaks, the greatest difference to be noted is that liquid-air removes most of the occluded gas but not the gas from an air leak. Opening S(2) and leaving S(1) closed will serve to introduce the liquid air trap into the system being tested. When the system is allowed to stand idle, it is often convenient to leave a vacuum inside to prevent absorption of gasses. If S(2) is closed, the vacuum may be held in the furnace and metal system without the necessity of keeping liquid-air on the traps, and without danger from mercury vapor. The use of the Pirani gauge in conjunction with stopcocks S(1) and S(2) has been invaluable in testing for leaks and in testing the windows for tightness. The provision of an auxiliary outlet permits the use of the vacuum system on numerous small experiments, without interfering with its major purpose.

VIII

FURNACE

Figure 11 is a diagram illustrating the design of a furnace which makes use of the windows and the needle-valve as previously described. It consists, essentially, of a solid steel rod 3 inches in diameter, having a 1/2 inch hole drilled down the center, and counter-bored and threaded on the ends to take a 3/4 inch bolt with aluminum gasket, thereby permitting the insertion of the windows. On top of this furnace the needle valve is fastened, and on one side a hole is bored to receive a charge of metal. This hole forms a well, so that the light path is not obstructed by the solid metal forming the charge, or by any boats which might be inserted.

Since it might be desirable to use double windows, Fig. 12 shows a method for utilizing interior windows of β-magnesia, and exterior windows of pyrex or quartz. A pyrex-aluminum seal, similar to the β-magnesia seals, using a 3/4 inch diameter window, has been made and tested cold, but has not been tested hot.

The furnace is heated by means of an exterior winding of chromel wire. With temperatures below 600° C, it was found satisfactory to wrap the furnace with one layer of asbestos insulating paper on top of which the chromel wire was wound, followed by one layer of heavy asbestos tape. A further coating of alundum cement may be used if desired. The remainder of the insulation was furnished by "Celite" bricks

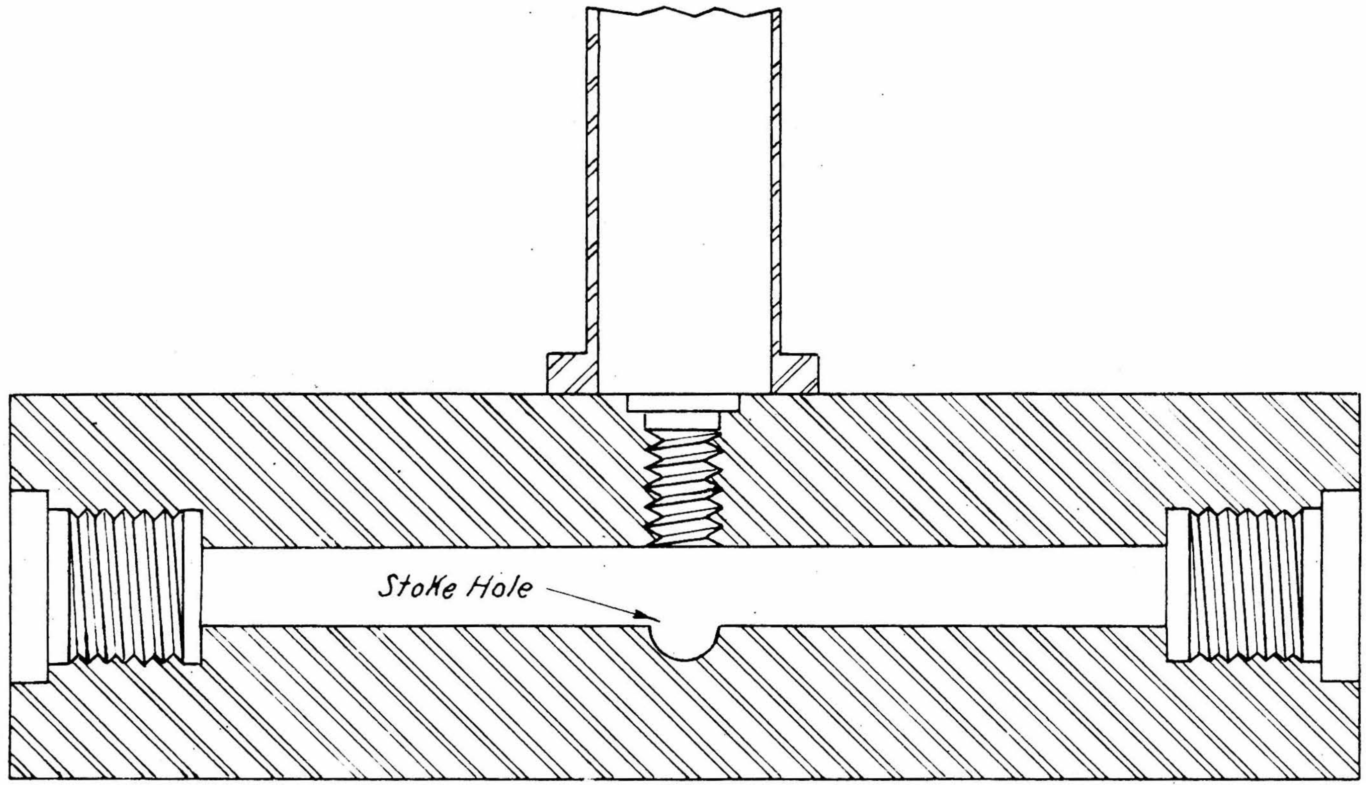


Fig. 11
Vacuum Furnace For Use With
B-Magnesia Windows

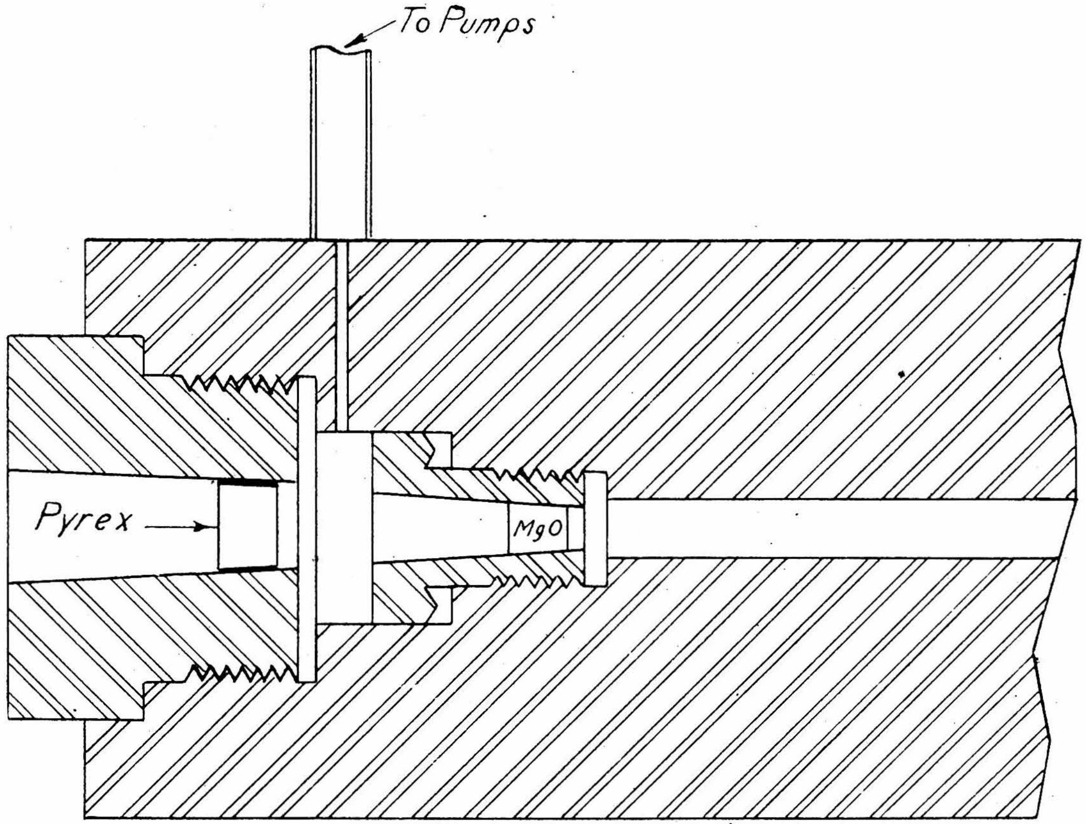
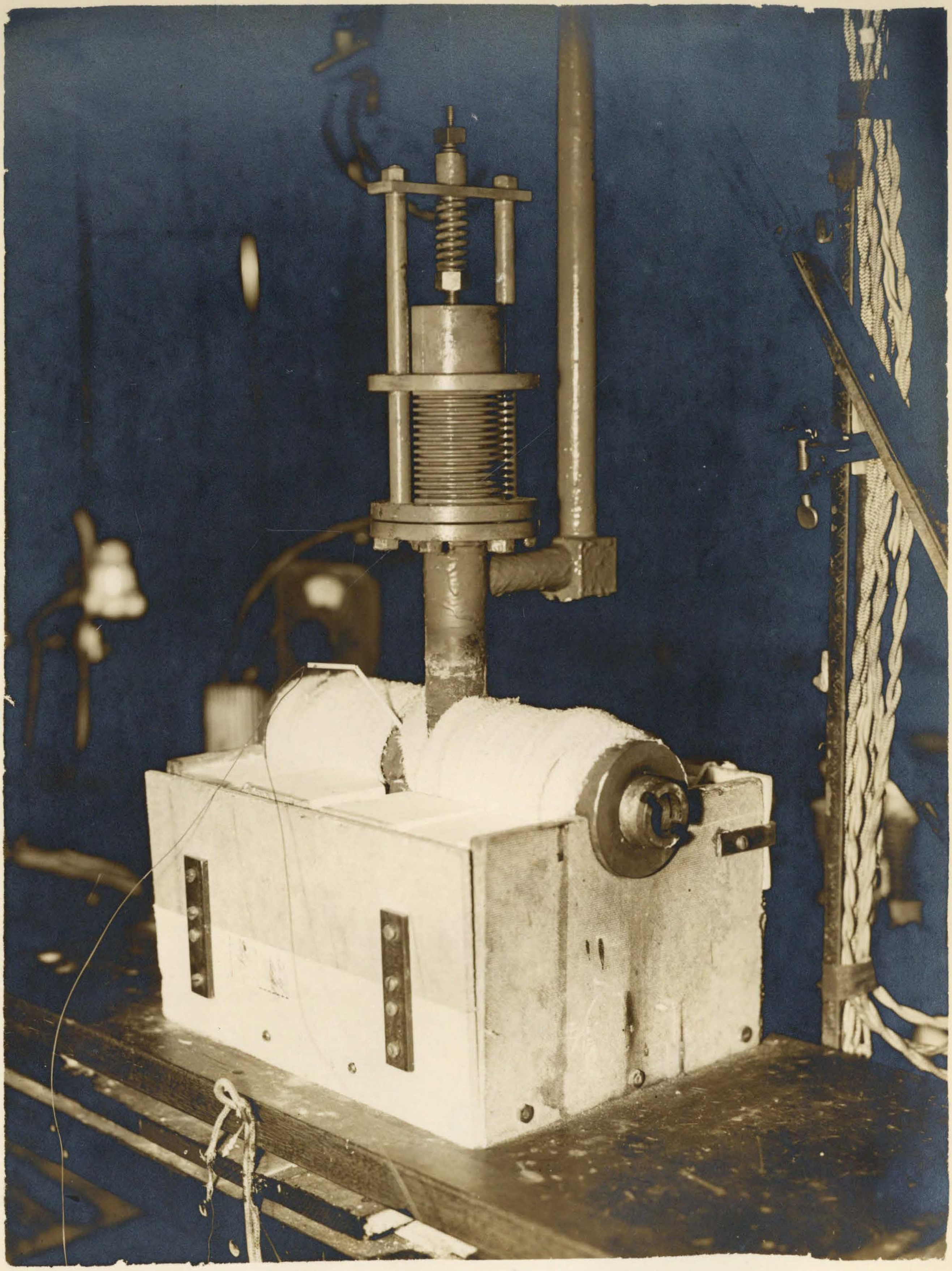


Fig. 12
Design For Using Double Windows



(diatomatious earth) appropriately carved so as to fit snugly around the furnace leaving only the ends exposed. At 400° C the furnace and controlling rheostat consumed 480 watts. At 587° they consumed 605 watts. 800 to 1000 degrees can probably be obtained with this winding and insulation.

Tightening the window bolts into place is usually done by means of a six inch wrench. This places considerable torque on the furnace itself, which is transmitted to the pumping tube, shown at A, Fig. 8. For that reason, it is necessary either to design this junction to withstand the torque, or to anchor the furnace in some other manner so as to release this joint from strain. The latter is probably more satisfactory, since mechanical strains in a vacuum joint are apt to cause leaks even though the joint is mechanically strong.

Plate 2 shows the furnace as it appeared when mounted and ready for use. The upper half of the heat-insulation has been removed to show the furnace, wound with asbestos tape, and the needle-valve mounting and sylphon projecting upward from the center. A thermocouple is inserted, through a hole in the side of the furnace, to within a few millimeters of the inside wall, and the leads brought out through porcelain tubing, as may be seen in the picture. The "Stoke Hole" for the insertion of the alkali metal may be seen just below the needle-valve mounting and flush with the top of the insulating bricks.

A furnace of this type may be easily adapted to many types of problems. An auxiliary tube, brought out through the stoke-hole and separately heated, will serve as a means of holding the vapor pressure of the metal constant, while heating the furnace above the temperature of the charge to study Doppler-broadening, line width, or higher energy-levels in absorption. By using double windows, and adjusting the position of the interior windows, any desired length of absorbing path may be obtained. Uniform temperature may be obtained in this type of furnace by making the furnace longer than the absorbing light path, using two windows, and winding the outside of the furnace (including the needle-valve mounting) with separately controlled heating elements. Any number of thermo-couples may be used, since it is not necessary to have the thermo-couple actually enter the absorption chamber.

APPENDIX

A

SEALS (Attempts)

A number of designs for sealing the β-magnesia windows into steel tubes were tried before a successful one was found. A brief description of these attempts may be useful in indicating what did not work and why they were unsuccessful.

All of the unsuccessful designs were modifications of the method illustrated in Fig. 13. A β-magnesia window was pressed against a metal gasket which in turn pressed against a flat shoulder in the steel furnace. The modifications of this method were of two types: (1) - Variations in the shape and materials of the gasket; and (2) - variations in the method of obtaining suitable pressure.

The alterations in the shape of the gaskets and the results obtained were:

1 - A gasket was formed by pressing a soft metal ring in a machined die until it assumed the shape shown in Fig. 14-a. The tests were made on both aluminum and copper. These gaskets sealed satisfactorily cold and remained tight at 380° C, but released the pressure and leaked on reduction of temperature. The leak usually occurred at about 250° C. The gaskets were annealed during the pressing proces and also immediately before use. Increasing the pressure to values approximating the breaking point of the windows did not improve the operation, and a number of windows were broken in the

attempts.

2 - Gaskets were machined in a lathe to approximately the shape shown in Fig. 14-b. Aluminum, copper and nickel were tried. The angle of the point on the gaskets was varied from 15° included angle to 30°, and the gaskets were annealed by heating to a red heat and quenching in water. A properly machined aluminum or copper gasket sealed cold but did not remain tight when the temperature was raised and lowered. The nickel gaskets were too hard, even when annealed, and consistently broke the windows when sufficient pressure was applied to seal them. This type of nickel gasket, with 30° included angle on the points, is the type of gasket used successfully with a pressure seal between steel and steel. A steel "window" of the same size and shape as the β-magnesia windows sealed satisfactorily with these nickel gaskets, and remained sealed over many runs. It was used as a plug in one end of the furnace.

3 - One attempt was made with an annular gold ring made of 1 mm gold wire in place of the machined gaskets, but it was difficult to obtain uniform diameter and hardness. The point of junction of the ends of the wire was always irregular and usually harder than the rest of the wire, because of the solder used.

4 - It was suggested by Dr. I. S. Bowen that nickel gaskets might work satisfactorily if a very thin layer of pure tin could be melted onto the sharp edges of the gasket so as to form a soft cushion. If this layer were very thin, it might act as a lubricant and allow sealing without such high pressures and still retain the vacuum at

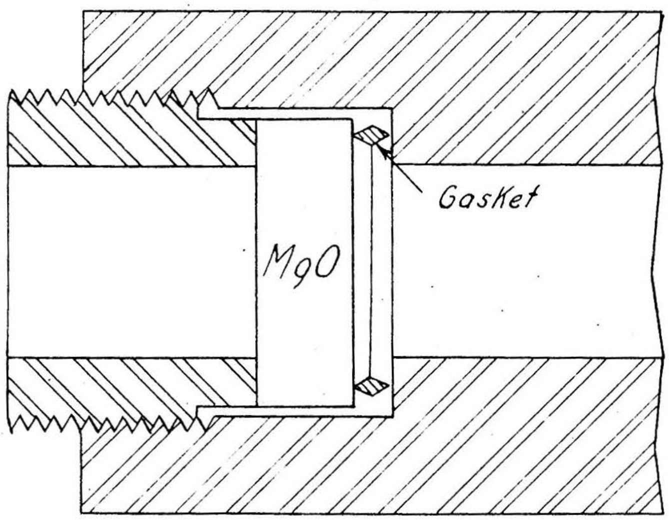


Fig. 13
General Scheme of First Attempts to Seal MgO Windows

Fig. 14
Trial Gaskets

temperatures where the tin would be a liquid. Some attempts were made to make such gaskets, but a suitable coating of tin was not obtained, and the gaskets were not given a thorough trial. Potassium forms a compound with tin, and unless the amount of tim present were very small, it might fix the potassium vapor and remove it from the absorption tube.

Inasmuch as these attempts all seemed to fail because of the release of pressure on the windows as the gaskets annealed further and "flowed" out in a lateral direction, it was thought that some method of allowing thermal contraction and expansion while keeping the pressure constant would rectify the trouble. Accordingly, designs were made for a spring to be used in maintaining pressure.

1 - The first attempt to use a spring consisted of a crimped piano-wire washer inserted between the pressure sleeve and the window, shown in Fig. 15. This was not satisfactory because the wire lost its spring too easily, and because it did not furnish uniform pressure around the circumference of the window.

2 - The next attempt was with a helical spring would of square wire with the ends ground flat. The spring was made of S. A. E. 1095 steel and heat treated. Unfortunately the maximum pressure available was only 148 pounds which was insufficient. Also, the pressure was not uniformly distributed.

3 - Figure 16 shows the design for an "equaliser" unit to be used with various springs to insure even pressure around the window. It will be observed that the equaliser is itself a spring, since the points of contact on one side are displaced

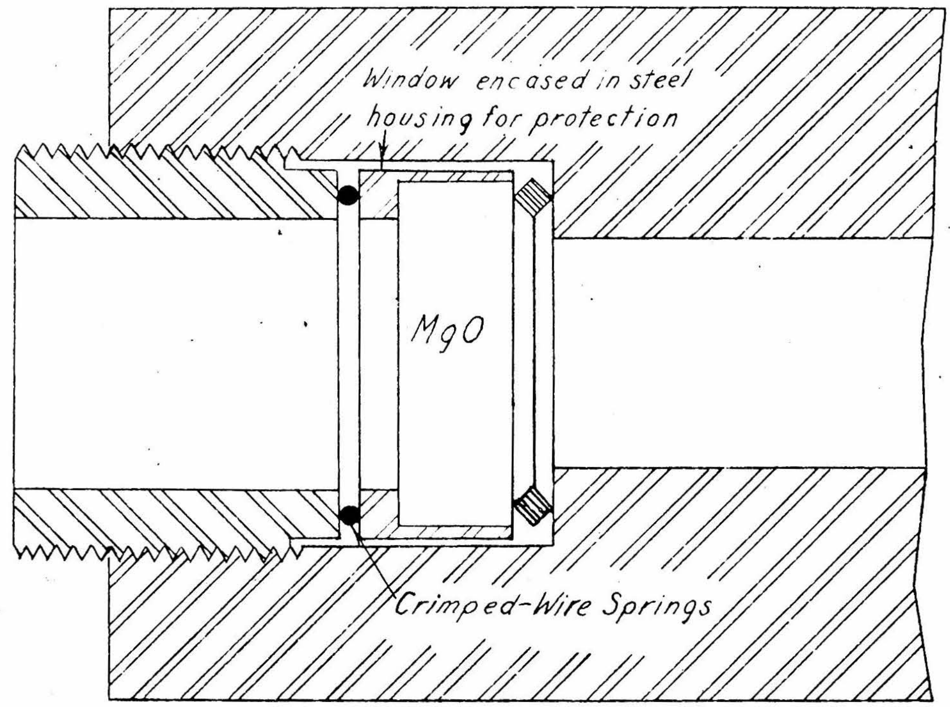


Fig. 15
Method of Inserting Springs

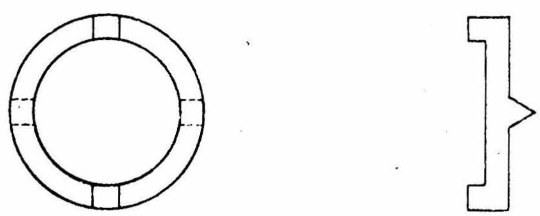


Fig. 16
Equaliser

90° from those on the other. They were made of tungsten "high speed" tool steel, hardened at 2500° F and drawn at 1250° F. A unit .125" thick gave a displacement of .005" when tested under 500 pounds compression. One whose thickness was .075" broke under a force of 336 pounds.

In order to determine what force would be necessary, two glass windows were tested in a compression machine. It had been observed that the pressure necessary to seal the β-magnesia windows was close to their breaking point, and it was assumed that glass windows of like dimensions, mounted in a similar manner, would have a breaking point of the same order of magnitude. The experience seems to indicate that the β-magnesia window is somewhat stronger than the glass, if it has no flaws or cleavages started. A plate glass window 3/4 inch in diameter by 1/4 inch thick broke with a total force of 533 pounds, and a pyrex window of similar dimensions broke under a total force of 479 pounds. It was accordingly decided to design springs which would stand 500 pounds working load

4 - Figure 17 shows the design of a two unit spring with an equaliser unit making three live turns. The tests for deflection and force on these springs gave the following results:

(a) - One spring .105" thick - deflection .022" at 500 pounds loaded six consecutive times and broke on seventh loading.

(b) - One spring .110" thick - deflection .020" at 500 pounds loaded ten consecutive times without breaking.

Temperature runs made with these springs all gave better results than runs without springs, but they were never satisfactory because the windows continued to leak with falling temperature, and the life of the springs was very short. Aluminum, copper and nickel gaskets were tried with them. The springs were finally abandoned in favor of beveled windows.

5 - The Wallace Barnes Company, Bristol, Connecticut, were kind enough to have their Planning Department consider the requirements of these springs. They suggested some arrangement of dish-faced units as shown in Fig. 18. They have not been tried, however.

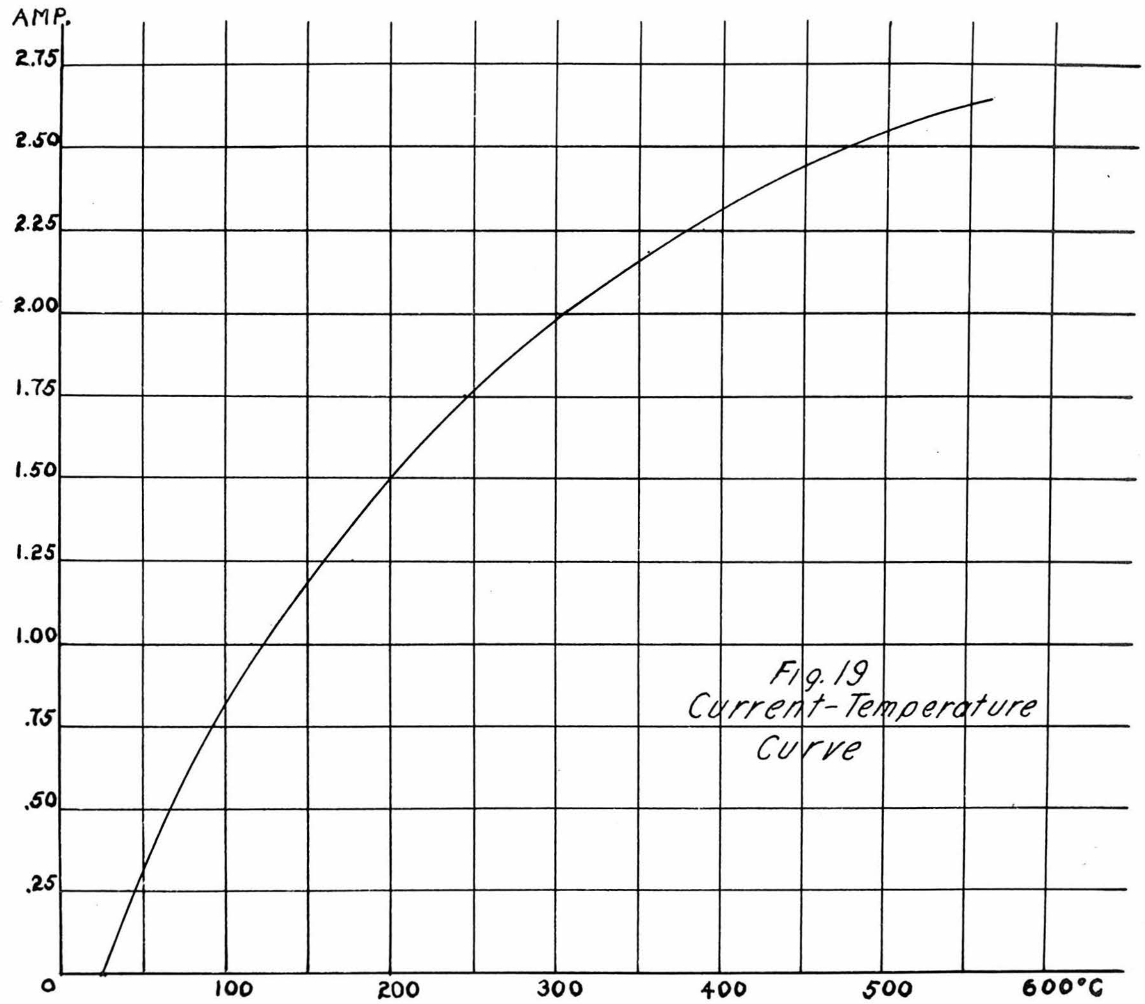


Fig. 19
Current-Temperature
Curve

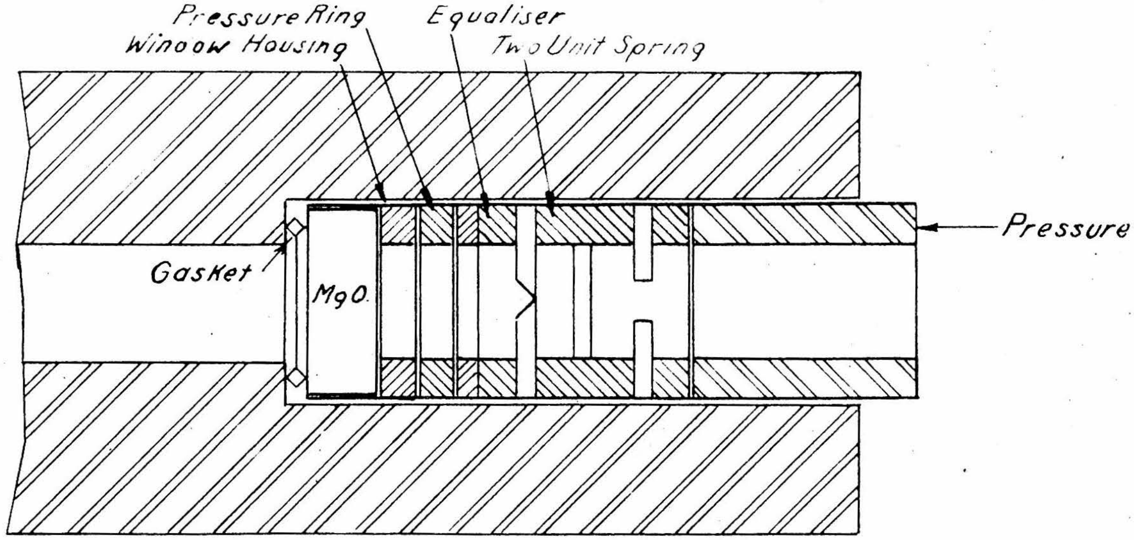


Fig. 17
Window Mounted With Spring And Equaliser

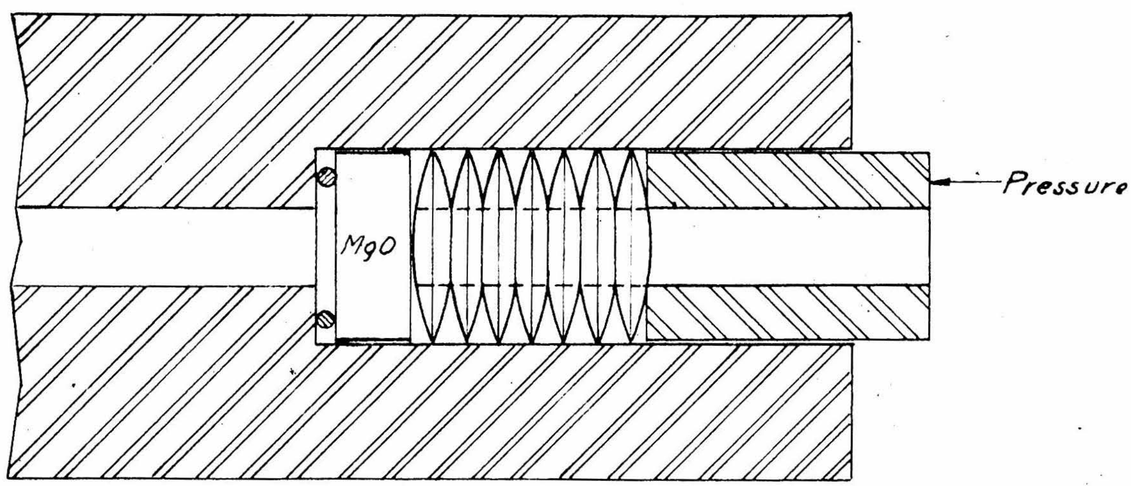


Fig. 18.
Spring Made From Concave-Convex Discs

APPENDIX

B

TEST RUNS

The apparatus being assembled and tight, the next step is to make a test run to out-gas the furnace at a high temperature and to see that all the parts function properly and remain tight with the thermal expansions. The procedure is perfectly straight-forward, consisting of raising the temperature to the desired point, and lowering it again while watching the pressure changes in the system. A discussion of some previous test runs may be of benefit:

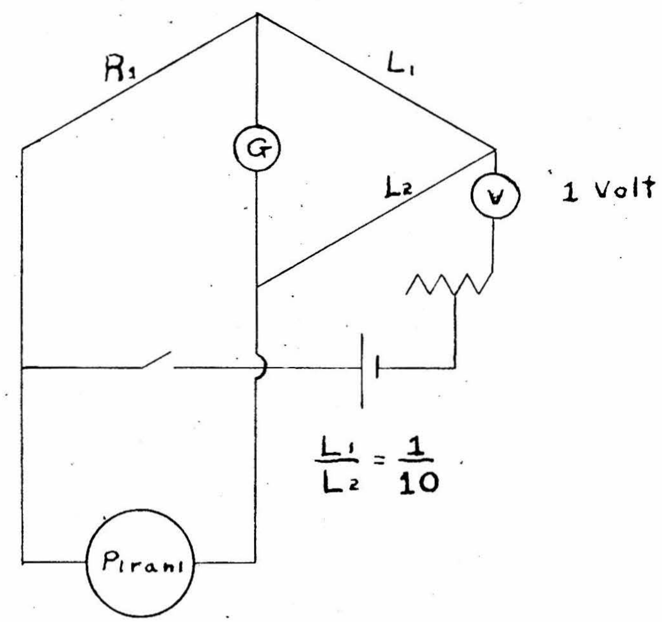
1 - CURRENT-TEMPERATURE. The large heat capacity of the furnace prevents rapid heating. The furnace is usually started with a current of about 1.5 amperes, which is gradually increased to some final value, depending on what temperature was desired. Fig. 19 shows the equilibrium temperature of the furnace with various values of current. It is usually convenient to start a run in the morning and allow the current and temperature to approach the maximum value by evening. Then, after standing all night, the furnace will be at its equilibrium temperature. A motor-driven rheostat has been used to gradually raise the current to a pre-determined value where it shut itself off. While this is a convenience, it is not necessary. Past experience indicates that it may be possible to start the current at its final value with no ill effects, but the experiment has not been tried. The

apparatus must be cooled as slowly as it is heated.

2 - DRIFT-TEMPERATURE. It is always instructive to take hourly readings on current, temperature, and Pirani-drift while the temperature is rising or falling. The rising drift curve is not of great significance because it depends upon the past history of the apparatus, presence of oil in the system, etc., and is not in general reproducable. It should, however, be a continuous curve. The presence of any sharp discontinuities usually indicates a leak. After the maximum temperature has been reached, the Pirani drift will fall slowly with time. Over a period of 12 hours the drift changed from 1.2 to 1.05 ohms per minute at a temperature of 430° C. Out-gassing is better accomplished by exceeding the working temperature for a short time, rather than leaving the furnace at the working temperature for a longer time.

When the temperature begins to fall, the drift curve should fall rapidly to about .2 ohms per minute, and then tail off to less than .03. Leaks are most likely to occur on this falling curve and are evidenced by a discontinuity, or by the slope of the curve indicating that it will not fall to zero.

3 - LEAKS. Once a leak has occurred, it will not close itself. A leak of any appreciable size will draw hot oxygen back into the system and quickly rust the metal parts as well as boil out the liquid air. So it is best, when a large leak is detected, to close the needle valve and allow the furnace to cool before



Pirani Gauge
WIRING DIAGRAM

Fig. 20

attempting to locate or stop the leak. In measuring the drift it is important not to disturb the state of the system while taking the measurement. In particular, putting on more liquid air while waiting for the Pirani to drift will often cause anomalous readings. The presence of too much oil or foreign liquids in the liquid air trap may cause vapors which look like leaks when the liquid air is low. It is occasionally necessary to close stopcock "B" and allow the trap to out-gas by warming it and replacing the liquid air with boiling water. With this treatment the trap will pump out and the discharge go black in a few hours.

4 - THE PIRANI GAUGE. Fig. 20 shows the wiring diagram for the Pirani. A multiplication ratio of .1 was used on the bridge. It is obvious that the absolute resistance of the bridge and the bridge ratio will both alter the Pirani readings with such a wiring diagram. A more accurate arrangement would be to maintain the one volt across the lamp terminals, but this involves readjusting the voltage for every reading. With the arrangement as used, the Pirani is a continuous reading device, and with any given bridge and voltage supply will reproduce itself to about one part in six hundred, which is closer than the voltage can be set. Since absolute pressures are not required, the error introduced by maintaining the voltage across the bridge instead of the lamp is not important. It was observed that the Pirani altered

its readings over about five ohms, depending upon the vibration of the table and any sudden jars. To stabilize this effect, which is caused by altered thermal contacts, a buzzer was mounted on the Pirani and allowed to vibrate during all readings.

5 - The following extract from the log of one run may be useful in comparing with the first few runs after assembling the apparatus, and shows the behavior of the apparatus when there are no leaks. For comparing the Pirani-drift values with other gauges, it was observed that when the furnace was cold, a Pirani-drift of .032 ohms per minute from an air leak would produce a visible discharge in about 12 hours.

Oct. 15 - 5:00 P. M. Made new window mounting and fit new window into it using copper instead of Al. Pumps now pumping and system black. Rubber stopper in furnace.

Oct. 16 - Furnace tight. Insert new window with rubber gasket to test window.

2:08 P. M. Pirani drift - .02. Conclude window is tight. Remove rubber gasket and put in new nickel gasket.

3:10 P. M. System tight, start run.

Time	Temp.	Current	Pirani-Drift	
2:45 P	26 °C	1 amp.		Automatic rheostat running
11:07	290	2.26	.406 ohms per min.	

Time	Temp.	Current	Pirani-Drift	Notes
October 17				
9:10 A	424° C	2.25	.468 ohms per min.	Set I at 2 amps and start rheostat back.
10:15	377	1.75	.173	
11:15	345	1.45	.083	
12:00 N	307	1.30	.066	
2:50 P	202	.80	.021	
4:23	160	.60	.012	
5:32	140	.55	.000	Current off.
7:35 P	86			Close system from pumps.
7:55 P	78		.000	Pirani reading - 179.5 ohms
October 18				
10:08 A	26			Pirani reading - system closed all night - 180.3 ohms. This apparent negative drift is probably due to the cooling metal reabsorbing some of the gasses in the system, thus improving the vacuum.