THE DENSITY OF SELENIUM

by

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CONTENTS

In 1840 Berzelius[1] introduced the term allotropy
to denote the existence of several forms of an element, as
distinguished from isomerism, which indicates the existence
of different modes of combination of equal numbers of atoms
of the same elements. He also stated that the different
modifications of an element cannot be explained by the
differences in the arrangements of the atoms, but that the
differences lie in the atoms themselves. This would indicate
that the allotropes would adhere to their forms, even in
chemical combination.

In accordance with Avogadro's doctrine the
existence of molecules of elements composed of several atoms
was accepted, and therefore Berzelius' distinction between
isomers and allotropes has lost its meaning. The term
allotropy is retained to denote the existence of different
modifications both of an element and of a compound.

Ostwald and Nernst based their definition of
allotropy on energy change, while Benedick, Honda and Le
Chatelier used the discontinuity of forms, phases, and
physical properties as their criterion.

Allotropy is then taken as a term covering the
different states of matter and also isomerism, polymerism,
and polymorphism.

The fundamental weakness of all these definitions is that they interpret the phenomena in terms of effects and do not concern themselves with the causes underlying them.

Apparently there has been a tendency to exclude polymorphism from the category of allotropy and Lowry[2] warns against such exclusion, because of the danger of excluding what appear to be polymorphic changes but which, in reality, are isomeric changes.

The first observations of allotropy were made by Smithson Tennant in 1796, in the case of Carbon (diamond and graphite). Mitscherlich[3] discovered dimorphism in sodium phosphate, sulphur, and mercuric iodide. Since then allotropy has been noted in numerous compounds and elements, of which selenium is one.

The early work on allotropy was discriptive in nature and no attempt was made to explain the phenomena. One of the early attempts to present a theoretical basis for allotropy was made by Frankenheim[4], who prepared a set of rules governing the general behavior of allotropy, based on the differences of physical properties, relative structures, and heat relationships associated with transition points.

Lehmann[5], from his observations of many cases of allotropy, classified allotropic substances in the following manner:

(1) Substances whose allotropes are reversible or interconvertible with temperature.

(2) Those whose allotropes are irreversible, i.e. conversion of one allotrope into another takes place in one direction only, the resulting allotrope being stable with respect to the other.   He recognized the existence of the transition point in the latter case as   lying above the melting point, and thus recognized that the two cases were essentially the same.   He referred to the first type as enantiotropy, and to the second type as monotropy.

Tammann[6] did not accept Lehmann's classification and based his objections mainly on his researches on ice.[7] He found that transformation of Ice I into Ice III between -22° and -40° at a pressure of 2220 kilograms was reversible; the latter formed on increase of pressure, and thus represented an example of enantiotropy.   He found however that if Ice III was cooled to -180° and the pressure decreased even as far as atomospheric pressure, it did not transform into Ice I.   He thus showed that monotropy and enantiotropy were functions of pressure, and consequently, Lehmann's classification was not justifiable.   On this basis he considered the relationship between graphite and diamond to be possibly both monotropic and enantiotropic since the complete stability curves were not known.

Tammann accordingly offered a new classification based purely on thermodynamics.   As his criteria he used indications of total instability, to which he referred as monotropy, and indications of stability as enantiotropy.

As a measure of stability he chose the ζ - temperature-pressure surface, where ζ was the thermodynamic potential, a function of pressure, temperature and composition. This surface gave the order of stability of the different phases, the unstable phase possessing a greater ζ value than the stable phase.

Applying the ζ - surface as the criterion he classified allotropic phenomena into two classes:

(1) The ζ - surfaces of the two forms do not intersect under realizable pressure-temperature conditions and therefore one form is always unstable with reference to the other.

(2) The ζ - surfaces intersect in space resulting in a curve which, when projected on the pressure-temperature diagram, represents the transition curve.

Tammann offers some experimental criteria for the classification.[8] They are chiefly, the complete knowledge of the equilibrium curves, the importance of which he illustrated in the case of ice, and if this is not experimentally available, the relative magnitudes of volumes and heat contents of the forms. By means of thermodynamic considerations he laid down the following specifications. If the heat of fusion of the unstable form is greater than that of the stable form, at the melting point of the former, then the former form will remain unstable at all temperatures below its melting point; if the reverse is true then the unstable form will be stable
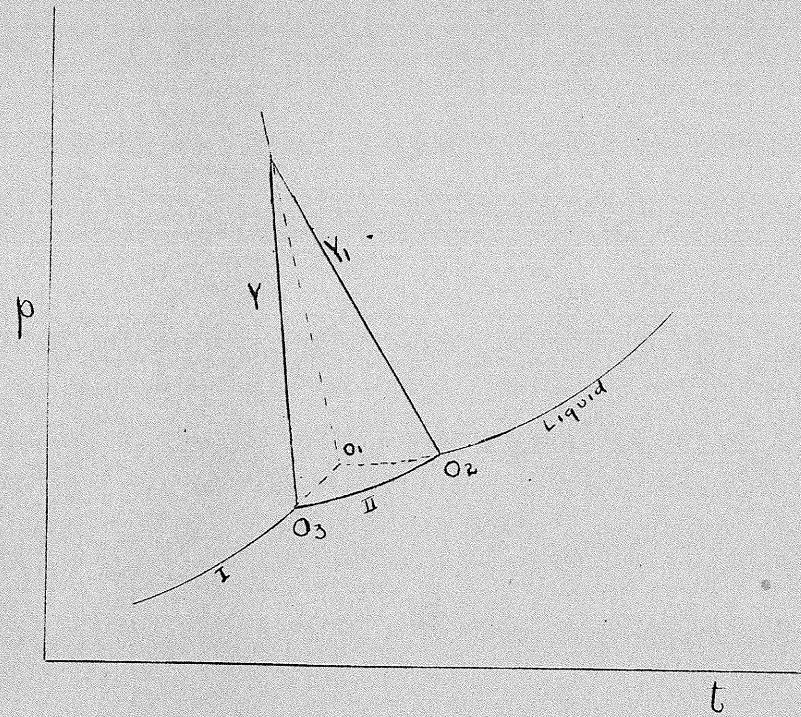
Fig 1
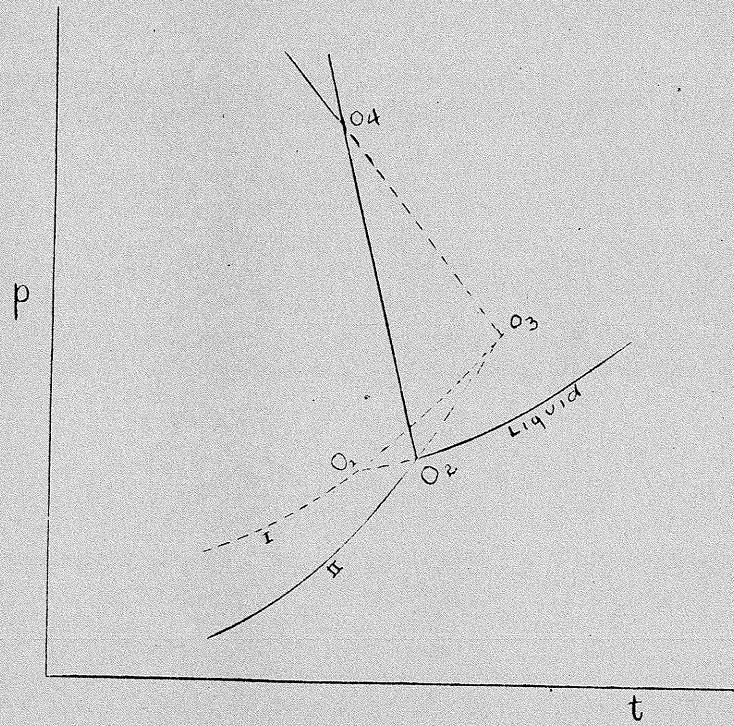
Fig 2

at some temperature below the melting point. If the volume of the unstable form is greater at low pressures than that of the stable form, then it is probable that the unstable form will remain so at all pressures; if the reverse is true then at some pressure the stability will be reversed. He also indicates that if the volume of the unstable form is greater but the heat of fusion smaller, or if the reverse is true, a change in instability is not to be expected.

Enantiotropy and monotropy as defined by Lehmann, and the effect of pressure on them are diagramatically represented in Figures 1 and 2. In these figures O_3 represents the transition point of solid I $\rightleftharpoons$ solid II, and O_1 and O_2 the respective melting points of the metastable and stable form. From figure 2 it may be seen that solid I is, at temperatures up to its melting point, metastable with respect to solid II.

In Figure I curves O_3Y and O_2Y_1 represent respectively the changes with rise in pressure of the transition point and of the melting point of solid II. It is interesting to note that if these curves intersect at some point, solid II will cease to exist at pressures above the point of intersection. Tammann observed this phenomenon in sulphur.[9] In Figure 2 curve $O_2 O_4$ represents the change of the melting point with rise in pressure, while the hypothetical curve $O_3 O_4$ indicates the change in the transition temperature of Solid I $\rightleftharpoons$ Solid II with rise in pressure. Assuming that these

curves are continuous and that they intersect at O_4, the point
of intersection will represent the equilibrium mixture Solid I
- Solid II - liquid. At pressures higher than that represented
by O_4, the transition curve will become real. It can there-
fore be seen that a monotropic system may change to an enan-
tiotropic system on applying great pressures. This phenomenon
is observed in the case of phosphorus[10]. Metastable black
phosphorus is obtained from stable violet phosphorus at high
pressures.

Caplsarow[11] defines allotropy in terms of molecular
structure and behavior and thus derives a valence theory of
allotropy. According to this theory there are two possible
causes of allotropy:

(1) intermolecular variation in the association of
elements, accounting for polymorphism

(2) intramolecular variation in structure of
elements and compounds accounting for all other types of
allotropy.

According to the electronic theory of valence, the
above definitions can be understood to apply to the structures
of the molecules only. This theory of valence implies that
the bonds of an atom have a definite direction, depending
on how such an atom is formed. Variation of the direction
will affect the distribution of the charges about the con-
stituent atoms, and molecules of different structures will
arise. These structurally different molecules are the allo-

tropes, and the configuration possessing the most symmetrical distribution of the charges is the stable one. The consideration of the possible modes of freedom of the atoms should render it possible to indicate the constitutional formulae of allotropes, and to calculate the maximum number of allotropes possible.

These possible modes of freedom in accordance with the number of charges are now listed:

(1) Inert gases should not exhibit allotropy since their valences are zero.

(2) Monovalent elements may exist in two possible configurations:

    (a) a form with a fixed valence

    (b) a form with a free valence
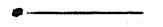
(3) A divalent element may exhibit two forms:

    (a) a fixed valence form
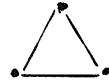
    (b) a free valence form

(4) A trivalent element may possess two configurations:
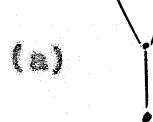
    (a)   and (b)

(5) Tetra, penta and other polyvalent elements may exhibit three forms:

    (a) a saturated and rigidly fixed form

    (b) an unsaturated form, possessing three or more fixed valences, and still rigidly fixed

    (c) an unsaturated atom possessing two or less fixed valences, and possessing the power of rotation.
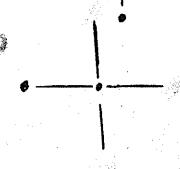
PHASE RULE

In the discussion to follow mention will be made
of unary and pseudo-binary systems and it is therefore advis-
able that definitions of these two terms, and terms connected
with them, be made.

A one component or unary system is one in which
only one independently variable constituent is present, and
in the same way, a two component or binary system has two
independently variable constituents.

A phase may be defined as a body in itself homo-
geneous, but marked off in space and separated from other
phases by bounding surfaces.

The state of a system is defined solely by the
number of components and by the number of phases present; and
therefore a one component system may consist of several
different kinds of molecules in equilibrium. If, however, the
equilibrium is slow in its attainment and measurements are
made before molecular equilibrium is attained, then the system
represented by these measurements is a pseudo-binary,
pseudo-ternary, etc. system, depending on the number of
species of molecules that have not reached molecular equili-
brium in the system.[12]

Bancroft and Roozeboom's Application of Duhem's Theory of Permanent Changes.

In 1897 Duhem[13] developed a theory of "permanent changes" and successfully applied this theory to supercooled sulphur. Bancroft[14] and Roozeboom[15] made graphical representations of this theory as applied to an internal equilibrium in the liquid state. Their adaptation has proved to be of great importance and will be briefly discussed in what follows.

If two components α and β in the liquid state are considered, and if the equilibrium condition $\alpha \rightleftharpoons \beta$ is introduced, then normally the system will behave as a one component system. If, however, a time factor is introduced, then there are three possibilities to be considered.

(1) Equilibrium is attained instantaneously.

(2) Equilibrium is attained in a measurable length of time.

(3) The speed of attainment of equilibrium is practically nil at temperatures just above the freezing points.

In the first case the system will behave in all respects as a one component system.

In the second case the system may act as a two component system and may be diagrammatically represented by a temperature-composition diagram (Figure 3). If any
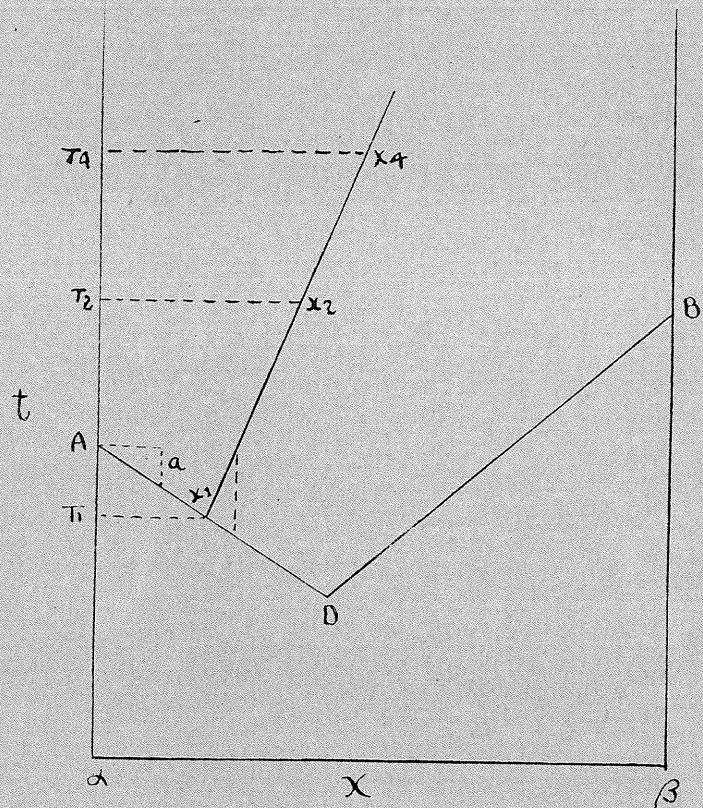
Fig 3
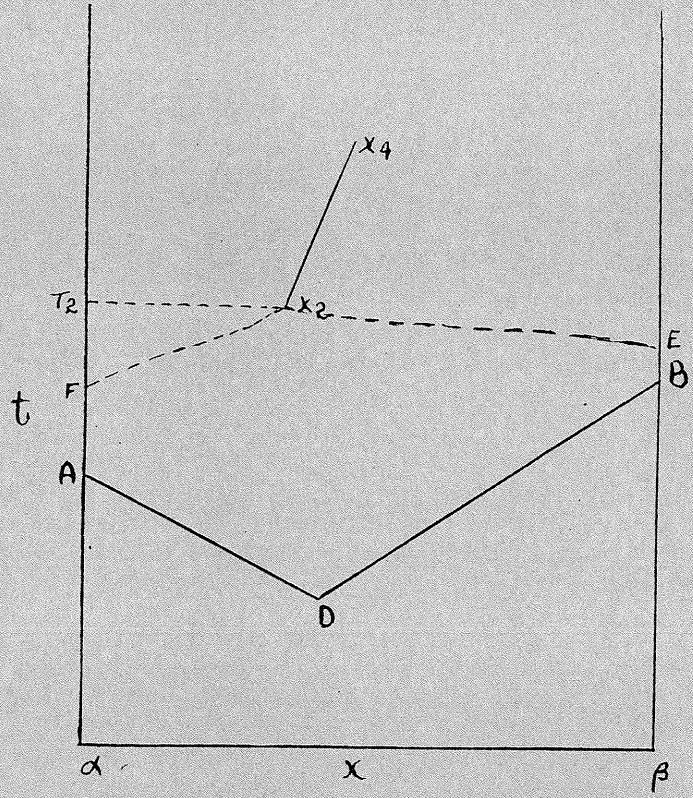
Fig 4

two solid phases be possible and two liquid phases impossible, the diagram will consist wholly of curves AD and BD, where AD represents the composition of the liquid in equilibrium with pure solid α modification at various temperatures, BD the composition of the liquid in equilibrium with pure solid β modification, and D represents the eutectic at which conditions both α and β solids may exist in equilibrium with liquid. If however the liquid consists of two modifications in equilibrium and they are interconvertible, there will be a curve representing this state of molecular equilibrium, which may be obtained in the following manner: If pure solid α is raised to a temperature T_2 and kept at that temperature until equilibrium is attained, some α modification will be converted into β modification, and the composition of the liquid will be X_2. If the temperature of the melt is raised to T_4 and kept at that temperature until equilibrium is reached, then the composition of the melt will be represented by X_4, and similarly, at molecular equilibrium the composition of the liquid at various temperatures above T_1 will be represented by the curve $X_4 X_2 X_1$. The direction of slope of this curve will depend on whether the conversion of α modification into β modification is accompanied by absorption or evolution of heat. If the former is true the curve will slope to the right, and in the latter case, to the left. If there is no heat effect, the equilibrium proportions will be independent of the temperature and therefore the curve will be vertical. This curve, $X_1 X_4$, is referred to as representing

for the liquid, the "natural state."

If X_1 X_4 represents the state of homogenous equilibrium in the liquid phase then X_1, must be the "natural" freezing point of the melt, that is, it must represent the composition of the melt which will be in a state of internal equilibrium and also, in equilibrium with pure solid α .   The stable solid form at a temperature in the neighborhood of the melting point, is the form which will be in equilibrium with the melt, at its "natural" freezing point.

From the above discussion predictions as to the behavior of the system under various conditions may be made. IF pure solid α is heated rapidly so that it melts before any conversion of α modification into β modification takes place, it will melt at A.   If the melt is kept at this temperature for some time and then cooled, the melt will begin to freeze at a lower temperature, represented by some point along curve AX_1.   The cause of this lowering is the conversion of some of the α modification into β modification.   This case is graphically represented by curve 'a'. Similarly if the melt is kept at temperature A until equilibrium is attained, the freezing point of this quickly cooled melt should lie somewhere along X_1D.   Suppose now, the melt is kept at temperature T_2 for a great length of time and equilibrium is attained, and then cooled very slowly, the melt will begin to freeze at T_1.   If the rate of freezing is slow, the melt will freeze completely at

temperature T_1. If the rate of freezing is comparatively rapid, the freezing temperature will drop along curve XD until D is reached; and at this point the temperature will remain constant until the melt freezes completely. This continuous lowering of the freezing point is due to the fact that the α modification solidifies faster than it is formed from β and therefore the melt becomes richer and richer in β modification until the eutectic is reached at which both forms solidify simultaneously; and therefore, at a constant temperature.

Similarly if pure solid β is heated rapidly it will melt at B but the freezing point will fall gradually due to the formation of the α modification and the composition of the melt will pass along the curve BD. If the cooling is slow and if the equilibrium is capable of establishing itself with sufficient speed, the freezing point will begin to rise again. After reaching D the composition of the melt will pass along the curve DX. The freezing point will rise until the "natural" freezing point is reached, and there solidification will take place at constant temperature.

In this manner melting point determinations of synthetic mixtures of α and β modifications will permit the determination of the diagram, and from the diagram the composition of any equilibrium melt can be determined by simply finding the temperatures at which solidification

begins on quick cooling.

The ease with which the phenomenon may be studied is obviously proportional, to a limited extent, to the slowness of conversion of one modification into the other.

The third case to be considered is one in which transformation of one modification into the other, does not occur in measurable length of time, in the neighborhood of the melting point. Figure 4 represents this case. In this case the curves AD and BD may be experimentally realized with great ease since α and β modifications will remain in their original quantities after fusion.

If T_2 is the lowest temperature at which reversible conversion may take place with measurable speed, the curve of the "natural state" below this temperature will be hypothetical and its composition at various temperatures above T_2 will be represented by $X_4 X_2$. At temperatures below T_2 pure liquid α is thought to undergo changes so that finally a point on the curve FX_2 is reached and similarly pure liquid β will undergo some conversion to liquid α so that the equilibrium melts will have compositions represented by points along X_2E. At temperatures below F, both α and β modifications will remain in their respective pure states. The equilibriums represented by lines FX_2 and EX_2 are analagous to the equilibrium $2H_2O \leftrightharpoons 2H_2 + O_2$, at low temperatures, and is referred to as "false equilibrium."

In the case of a pseudo-ternary system,

this theory would also be applicable.   Under dynamic
equilibrium conditions the system will behave as a one
component system, and if measurements are taken before inner
equilibrium is established the system will act as a ternary
system.

The verification of this theory has been carried
out by many workers and consequently the theory has been
used to explain many phenomena which seemed out of the
ordinary.   Zincke[16] and Lehmann[17] studied stilbene dichloride
and found that the α modification melted at 192° - 193°;
and upon heating at a temperature above the melting point,
the freezing point first fell and then rose to 160° - 165°
after which it did not change no matter how long it was
heated.

This theory was also found applicable to studies
made by Dunstan and Dymond[18], and Carveth[19] on acetaldoxime,
which consisted of two isomers α and β in dynamic
equilibrium.   The α form was found to melt at 34° - 35° C
and the β form at 136° C.   The eutectic D was found to
lie at 25°-26° and X_1, the "natural freezing point" was found
to be at 27.7°.   They also found the "natural state" curve
to be a vertical line.

Reference should also be made to applications of
this theory made by Cohen[20] to metals.   By means of density
and electro-chemical measurements, he was able to detect
the presence of allotropes in metals such as potassium,

cadmium, zinc, lead, sodium and tin, and thus disproved the
belief, general up to that time, that metals had no allo-
tropic forms. This conception, in Cohen's opinion, was due
to the fact that transformation of allotropes into one
another is so extremely slow and hard to detect, that only
by employing certain devices can the velocity of transforma-
tion be made appreciable. He consequently concludes that
the metals dealt with up to that time were really complicated
metastable systems, in which the amounts of the various
modifications were undefined; and therefore the physical
constants obtained for these metals, and which did not refer
to defined conditions of the metals, were fundamentally
useless.

SMITS' THEORY OF ALLOTROPY

The hypothesis, upon which the Smits theory of
allotropy[21] is based, consists of two parts:

(1) Every phase, and therefore every crystalline
phase, of an allotropic substance represents a state, which
under certain circumstances can behave as a polycomponent
phase.

(2) The cause of this behavior must be assumed to be
complexity, that is, the existence of different molecular
species which are in inner equilibrium when the system
behaves like a one component system.

For the purpose of illustrating the behaviour of
a one component system as interpreted by the theory of
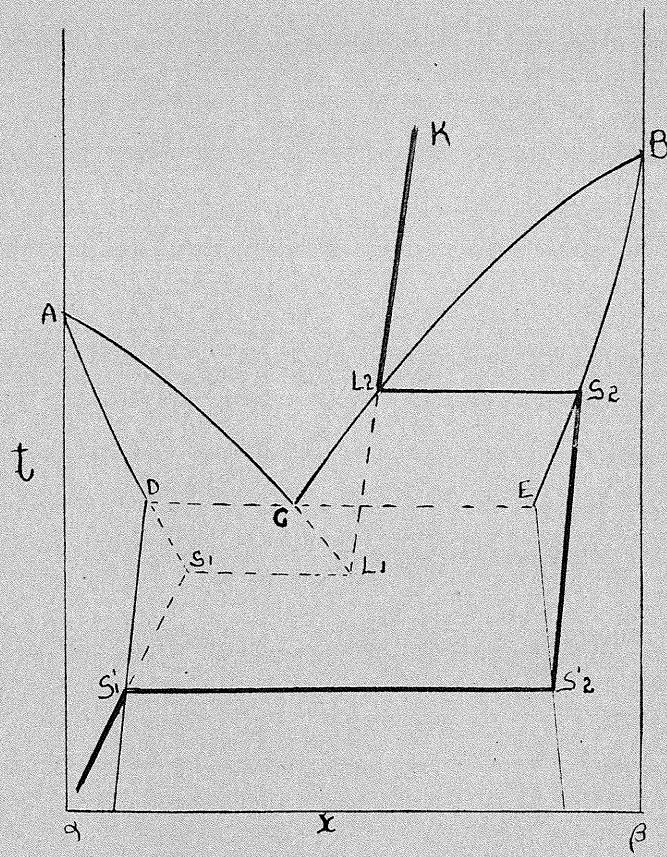
Fig 5
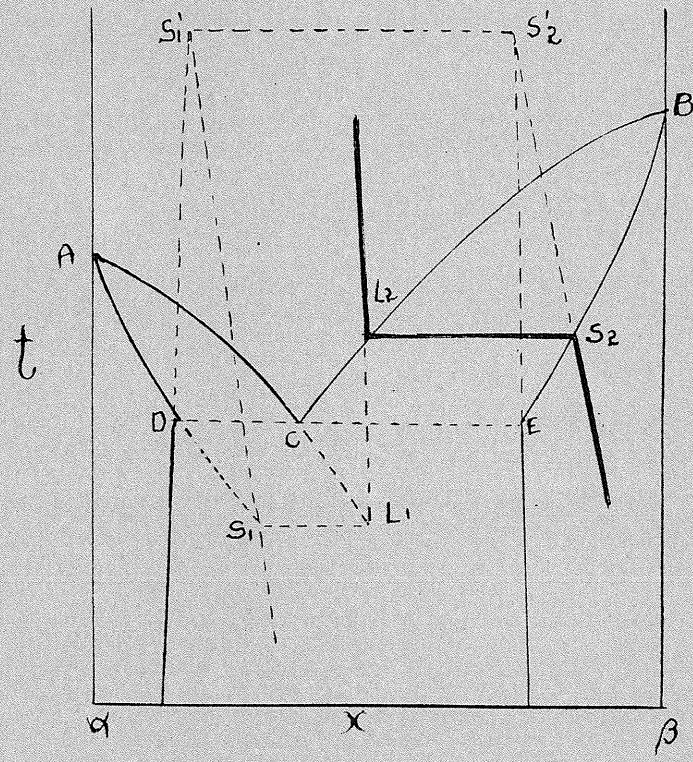
Fig 6

allotropy put forward by Smits, a brief discussion of the
behaviour of characteristic graphs of the liquid-solid
equilibrium under constant pressure for cases of enantiotropy
(Fig. 5) and monotropy (Fig. 6) in pseudo-binary systems, may
be given. The molecular species existing in equilibrium are
represented as α and β. A and B are the melting points
of pure α and pure β. AC represents the liquid solutions
in equilibrium with solid solutions AD, and BC represents
the liquid solutions in equilibrium with solid solutions
BE. DS_1^s and ES_2^s indicate the limits of stable mutual solid
solubilities of mixtures of α and β. L_2 represents
the inner equilibrium of the liquid phase and $L_2 L_1$ is the
metastable prolongation of the liquid equilibrium. S_2 defines
the solid phase in equilibrium with liquid phase L_2, and S_1
represents the metastable equilibrium solid phase in equili-
brium with the metastable equilibrium liquid phase L_1.
Horizontal $S_1^s S_2^s$ represents the change in composition accompany-
ing transformation of one stable solid form into the other.
In the case of monotropy this horizontal is not real, since
this conversion exists above the melting point.

If attainment of internal equilibrium is not too
rapid, the melting point of stable solid in inner equilibrium,
and on sudden heating, will depend on the temperature at
which the inner equilibrium is attained. By examining Fig. 6
it may be seen that the stable solid form in equilibrium at
a lower temperature will, on sudden heating, begin to melt
at a higher temperature than the same form in equilibrium at

a higher temperature, conversely, if such a phenomenon occurs, it may, on the basis of the theory put forward by Smits, be explained by a diagram similar to fig. 6.

Smits' theory is therefore fundamentally somewhat similar to that of Bancroft and Roozeboom. It extends the existence of an inner equilibrium in the liquid state to the solid state, assuming also, that if the velocity of establishment of equilibrium is slow enough, measurements should indicate the presence of a pseudo-binary, pseudo-ternary etc. system.

THE ALLOTROPY OF SELENIUM

Selenium was first discovered in 1817 by Berzelius[22] at the sulphuric acid works at Gripsholm. He noticed that if pyrites from a certain source was used, a peculiar residue was left; and this fact caused him to investigate this residue. He found it to contain an element similar to tellurium and sulphur and named it Selenium.

Selenium like sulphur exhibits the property of allotropy. Berzelius[23] recognized a non-crystalline form, which on heating softens before melting, a red amorphous variety, a steel grey crystalline form, and a black crystalline form.

Von Schaffgotsch[24] and Hittorf[25] showed that the steel grey and black crystalline forms were really one allotrope.

Peterson[26] believed that selenium really exists in three forms:

    (1) the amorphous form

    (2) the red crystalline form

    (3) the grey crystalline form

Muthmann[27], however, indicated that there are three crystalline forms of selenium. They are two red monoclinic forms and/a grey trigonal form.

Korinth[28] investigated red crystalline selenium

and found that it does possess two forms. One form is isomorphous with η sulphur, while the other is not.

Schultz[29] established the existence of colloidal selenium.

Saunders[30] and Muthmann[31] attribute to selenium the following forms:

    (1) Liquid selenium
        (a) vitreous selenium
        (b) colloidal variety
        (c) amorphous form

    (2) Crystalline red monoclinic selenium
        (a) isomorphous with η sulphur
        (b) not isomorphous with η sulphur

    (3) Grey metallic trigonal selenium

The first two groups are soluble in carbon bisulphide, while the grey metallic is not. The various forms of selenium will now be considered.

Liquid selenium is fundamentally like any other liquid. Not much work has been done on it and except for the peculiarity in its electrical conductivity, it possesses the properties typical of simple liquids.

The vitreous form is the supercooled liquid selenium. If selenium is rapidly cooled to room temperature, the resulting vitreous selenium may remain in that state for an indefinite length of time. It is in a state of metastability and its ability to remain in such a state is due to the extremely small velocity of conversion, which, in turn, may be due both to low temperature and great viscosity. If the

temperature of the vitreous selenium is raised to 90°, the velocity of conversion becomes appreciable and according to Regnault[32] it approaches a maximum at 125° C. It is of interest to note that 90° was at one time considered a transition point, in other words, vitreous selenium was considered a solid allotrope.

The red amorphous form is essentially the same as the vitreous form. Briegleb[33], however, by means of solubility measurements, attributes to vitreous selenium the state of a solid solution of two components, Se" and Se'. Se' is thought to be Se_1 and Se", Se_2. He believes red amorphous selenium to be pure Se".

The red crystalline form is most easily obtained by crystallization from a carbon bisulphide solution. It separates out in red monoclinic crystals. It is a metastable form which may exist indefinitely at room temperature but passes into the metallic form at about 125° C. Its melting point lies between 170°-180°.

Both Muthmann[27] and Mitscherlich[34] attribute to the monoclinic form two crystalline habits, which they refer to as α and β monoclinic selenium. Their difference lies in their axial ratios. The α form possesses the following indices:

a: b: c = 1.63 : 1 : 1.609 angle = 104°1'

The β form has these indices:

a: b: c = 1.59 : 1 : 1.135 angle = 93°4'

X-ray analysis has failed to confirm the existence of these forms.[33]

Metallic selenium may be obtained by keeping any other form at a temperature between 180° and 200°. It is the only stable solid form of selenium and melts at 217°.

The discovery of the light sensitivity of metallic selenium, led to a number of theories to explain this phenomenon. The first was advanced by Siemens[35] and was subsequently developed by Marc[36]. This theory attributes the increase of conductivity, with increase of intensity of light and heat, to an existence of two modifications SeA and SeB in dynamic equilibrium. Marc[37] found that at room temperature the selenium was brittle and hard, and on heating at 180°, the lustre became duller and the selenium became more malleable. He also found[38] that at room temperature the resistance of selenium to a current of electricity was higher than at higher temperatures, a behavior contrary to the general behavior of metals. The continuity of the increase of conductivity with rise of temperature and with increase of intensity of light led him to believe that metallic selenium consists of a non-conductor SeA and a conductor SeB in dynamic equilibrium and that both light and heat tend to increase the amount of SeB.

The possibility of a volume change with shifting equilibrium was studied by Ries[39]. He found a slight volume change but suggested that this change was due to the heating effect of the light.

Briegleb[40] by means of x-ray photographs, showed that the crystal structure of metallic selenium is the same under all conditions and concluded that the existence of two modifications as defined by Marc, is improbable. He attributes the change of conductivity to mechanical factors such as grain size. The duplication of the character of the conductivity curve with rising and falling temperature tends to invalidate such an explanation, since increase in size of crystals is not a reversible phenomenon.

The very significant fact that selenium is sensitive to light at temperatures as low as -180° C, at which chemical processes are usually retarded or stopped, tends to lessen the probability of the explanation of light sensitivity as due to the existence of an inner equilibrium.[41]

Another explanation of the light sensitivity of selenium was put forward by Bidwell[42]. He attributed this phenomenon to the formation of selenides. His basis for this explanation was the deterioration of the sensitivity of the cell with age.

Ries,[43] working on the effect of moisture on the conductivity of selenium, concluded that the variation of electrical conductivity with intensity of light was due to chemical action arising from the presence of moisture. Here it may be noted that the catalytic power of water has been noted by many workers, and that this may be a case of moisture catalyzing shifts in a possible equilibrium.

The ionic theory due to Fournier de'Albe[44] states that the changes in donductance of selenium during and after exposure to light aredue to a kind of progressive ionization of selenium under the action of incident radiation, the number of ions produced in unit time being proportional to the intensity of illumination. No explanation of the meahanism of ionization is offered/the theory therefore suffers in this respect.

Vonwiller[45] assumed that the selenium is made up of molecules, some of which have temporarily lost an electron. Absorption of energy is then supposed to increase the probability of liberation of electrons, and decrease of absorption of energy to increase the rate of recombination. The conductance, being proportional to the number of electrons, increases and decreases with rise and fall of energy falling on the surface of the selenium. In support of this theory de Kronig's[46] experiements show that the conductivity of selenium is increased by electronic bombardment of its surface.

In accordance with this theory of free electrons, a solid conductor should have a higher specific heat value than a dielectric. In the case of selenium, the selenium in the dark should have a lower specific heat than the selenium exposed to light. Employing calorimeters which could detect .2 per cent variation in specific heats[47], no change in specific heat was detected. These experiments tend to show either, that the theory is not applicable to selenium or, that less than .2 per cent of the molecules lose an electron.
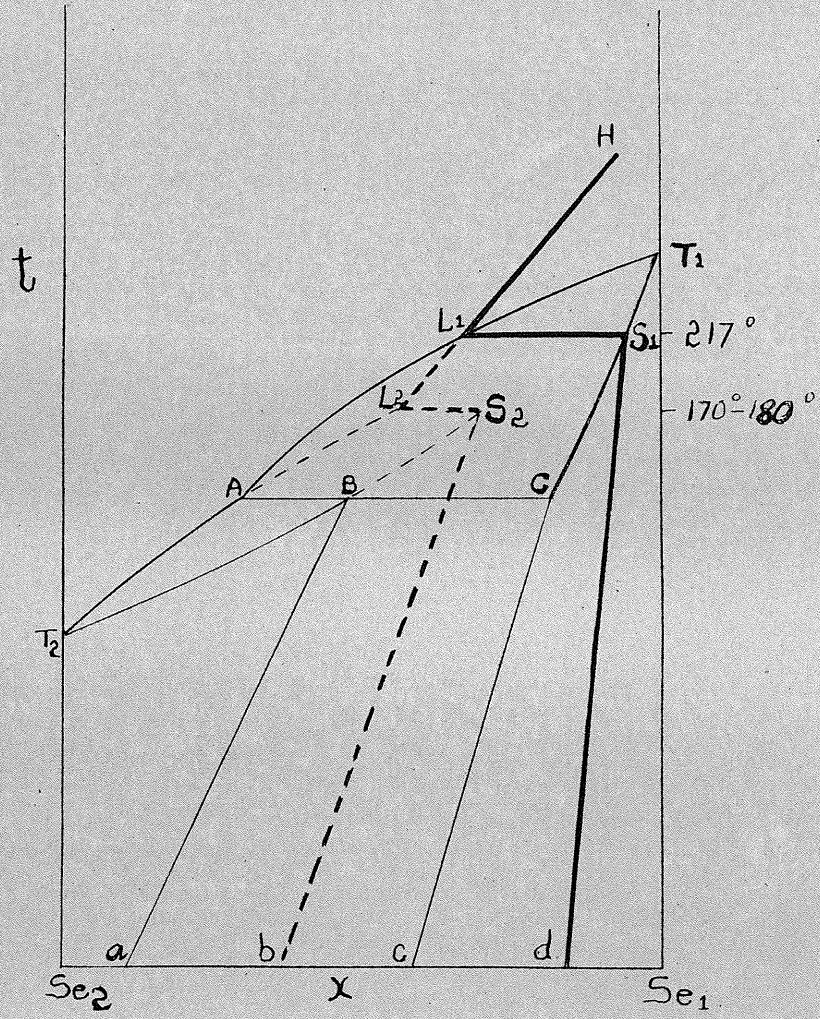
Fig. 7.

Subsequent work points towards the former alternative.

Finally reference is made to the study of selenium in the light of Smits'theory of allotropy[47]. In this case simplification of allotropy of selenium is afforded by this theory, which is diagramatically represented in fig. 7. This diagram represents a pseudo-binary system in which one component is a dissociation product of the other. The two forms concerned are Se_2 and Se_1.

Curve T_2 B represents the composition of solid solutions in equilibrium with liquid solutions T_2 A and curve T_1 C represents the composition of solid solutions in equilibrium with liquid solutions T_1 A. B and C indicate the compositions of solid solutions existing simultaneously in equilibrium with liquid of composition defined by A. Ba and Ca represent the limits of stable solid solubility of Se_1 in Se_2 and Se_2 in Se_1. HL_1 is the composition of the liquid selenium in molecular equilibrium. $L_1 L_2$ is the metastable prolongation of the liquid state. $L_1 S_1$ represents the change in composition accompanying the conversion of liquid selenium at molecular equilibrium into the stable metallic form at molecular equilibrium. S_2 shows the composition of the metastable monoclinic form in equilibrium with the supercooled liquid L_2. Curves S_2 b and S_1d represent the composition of the red monoclinic form and the metallic form at molecular equilibrium and at various temperatures.

Experimental support for this diagram lies in the

variation of the solubilities of quenched selenium, which
had been kept at various temperatures above its melting point.
Briegleb conceives selenium to exist in two complexes, Se_1
and Se_2. Se_2 is soluble in carbon bisulphide while Se_1 is
not.   This agrees with the fact that red amorphous selenium
is very soluble in carbon bisulphide, while metallic selenium
is not.

EXPERIMENTAL

INTRODUCTION

The analogous properties of solid sulphur and solid selenium suggest that liquid selenium may display properties similar to those of liquid sulphur. It is a well established fact that liquid sulphur consists of two modifications, sulphur λ and sulphur μ in dynamic equilibrium, and that the properties of liquid sulphur display irregularities because of this equilibrium.

With this in mind Pelabon[49] determined the conductivity of liquid selenium at temperatures ranging from 220° C (the melting point of selenium) to 688° C (the boiling point of selenium). He found that the conductivity varied irregularly up to 300° C and that from that temperature, it increased regularly with rise in temperature.

Dobinski and Wesolowski[50] determined the densities of liquid selenium at temperatures up to 350° and reported a perfectly regular relationship. They made their determination by noting the loss of weight of a calibrated plummet when immersed in liquid selenium.

The same workers[51] determined the viscosity of liquid selenium with rise in temperature and even in this highly sensitive property no irregularities in the temperature-viscosity relationship were found.

There was a possibility that Dobinski and Wesolowski did not make determinations at high enough temperatures and that Pelabon's irregularities were not due to an internal

equilibrium. If this were true it might still be possible that singularities might exist at temperatures above 350° C. Determination of viscosity at these higher temperatures was the original problem contemplated, but in order to make these determinations, it was necessary to know the densities at these higher temperatures. These density determinations presented a complete problem and work proceeded in that direction only. The problem was extended to include measurements of density from room temperature up to 350° C and to attempt to duplicate the values obtained by Dobinski and Wesolowski.

The change in density with temperature is usually a straight line relationship and the change in equilibrium with temperature is not, therefore, if the density of two modifications in an inner equilibrium is not the same, a density curve, displaying a sudden change in some region of temperature, should be obtained.

PURIFICATION OF SELENIUM

The selenium available was a crude sample, melting to a sintered mass, and probably containing silica and other natural impurities. The method of purification adopted was a modification of the method used by Hugot[25].

The crude selenium was digested with concentrated nitric acid by adding it slowly to the acid and heating on a sand bath, enough acid being used to insure complete solution. The solution together with the residue was boiled to dryness. The resulting solid was placed in small charges in one end of a combustion tube and kept in place by plugs of glass wool. The charge was then heated strongly and the sublimed selenium dioxide was drawn into the upper and cooler part of the tube by passing a current of air through the tube. The resulting selenium dioxide was scraped into a beaker and dissolved. This procedure was repeated until all the impure selenium dioxide was sublimed. The residue consisted of a brown clay. The solution was acidified with hydrochloric acid and a stream of sulphur dioxide gas passed into it. The resulting precipitate was red amorphous selenium.

The precipitated selenium was washed with alcohol and dried. The precipitate was then placed in a tube, which was sealed off at one end. The pressure in the tube was reduced by suction; at the same time the charge was heated strongly. This heating drove off any volatile matter still present, and completed the purification of selenium. The

resulting selenium was an impressive sample of a high degree of purity.

The purification of selenium may be represented by the following equation:

$$3Se + 4HNO_3 \longrightarrow 3SeO_2 + 4NO + 2H_2O$$

$$SeO_2 + 2SO_2 \longrightarrow Se + 2SO_3$$
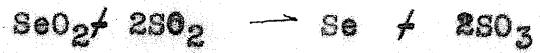
THE PYKNOMETER METHOD

The first method employed for density determinations
involved a pyknometer. This vessel consists of a small
bottle with a stopper made from capillary tubing. The
pyknometer was in all cases filled to the brim. The general
procedure of this method may be outlined in the following
steps:

(1) The volume of the pyknometer was determined by
using mercury and distilled water. The water was previously
boiled to expel all the dissolved air, then permitted to
cool in a tightly stoppered bottle

(2) The pyknometer was then filled to a convenient
level with powdered selenium and the weight of the selenium
accurately noted.

(3) The selenium was then covered with a liquid of
known density and the air present in the powder expelled by
tapping and by suction

(4) The pyknometer after filling was placed in a
thermostat. After staying in the bath for a required length
of time, and after excess liquid resting on top of the stopper
was removed, the pyknometer was taken out, its surface wiped
clean, and weighed. From the weight of the oil and selenium,
the density of the selenium was calculated in the usual
manner.

LIQUID SELENIUM

This method was first applied to determine the
density of liquid selenium at the different temperatures.
The oil used in this case was paraffin oil (Russian Mineral Oil).

Its density was determined for temperatures ranging from 20°
to 300° C. Some of the values obtained are given in Table I.

Table I

Temperature ° C	Density
20.5	0.8523
80	0.8484
151	0.8004
230.5	0.7574
300	0.6971

On plotting the values of the densities against temperature,
a straight line relationship was obtained, which may be re-
presented by the formula

$$D = 0.8523 - .000628 (t - 20.5)$$

The pyknometer was filled with selenium; enough
selenium being added so that in its liquid state it filled
three quarters of the vessel. The paraffin oil was now
added and the mixture kept in a 250° C bath until all the
selenium melted. While the selenium was liquid, air bubbles
were expelled by gentle tapping and by applying the vacuum
pump.

At first, commercial soft glass pyknometers were
used, but when they were placed in the hot bath, they
cracked. This cracking was thought to be due to the sudden
heating of the glass, but even if the necessary precautions
were taken, the cracking persisted. A pyknometer of hard glass
was then constructed, but even this vessel cracked. These
repeated failures indicated that it was the unequal expansion
of the selenium that caused the cracking of the pyknometers.

Consequently, a pyknometer of thick combustion tubing was constructed and this vessel was found satisfactory.

Before using the paraffin oil, a series of experiments were carried out to determine the suitability of this oil for the purpose. Its boiling point was found to be in the neighborhood of 310° C. The solubility of selenium in boiling oil was found to be .0013 grams per cubic centimeter of oil. The selenium did not react chemically with the oil, for on cooling the hot saturated oil, red selenium precipitated out. These experiments indicated that paraffin oil was suitable to use in the determination of density of liquid selenium.

A series of density determinations were made at temperatures ranging from 227°- 277°C. Determinations of density at higher temperatures by this method were unsatisfactory because the temperatures were getting too close to the boiling point of the oil and in many cases little bubbles of oil vapor were observed. In all determinations the selenium was kept at one temperature for approximately two hours, to insure attainment of a possible equilibrium. Determinations were made with rising and with falling temperatures.

The volume of the pyknometer was 25.043 c.cs.
The weight of selenium used was 80.2240 grams.
The results obtained are listed in Table II
in their chronological order.

TABLE II

Temperature	Density
227	3.9486 ⧸
241	3.9540
257.5	3.9276
257	3.9278
277	3.8904
296	3.8329 ⧸
276	3.8877
257	3.9236
244.5	3.9394
225	3.9705

⧸ These results were discarded due to the presence of air bubbles in the selenium.

DENSITY OF METALLIC SELENIUM

For determining densities of solid metallic selenium, a new liquid had to be used. The paraffin oil proved to be too viscous at the low temperatures and the powdered selenium tended to remain suspended in the liquid. The new liquid had to have a high boiling point but a low viscosity. Nitrobenzene was tried, but proved unsatisfactory. Benzyl benzoate, however, produced satisfactory results. The density of benzyl benzoate at various temperatures was determined. Results are given in Table III.

TABLE III

Temperature	Density
21.8	1.1200
175.0	.99359
193.0	.97723
203.0	.96834

The formula representing the variation of the density with temperature is:

$$D = 1.12001 - .000834 (t-22)$$

The metallic selenium was finely powdered, introduced into the pyknometer, weighed and covered with benzyl benzoate. The mixture of powder and oil was thoroughly stirred with a glass rod and heated for a few hours at 150° C, to insure that the whole sample of selenium was in the metallic form. A density determination at room temperature was then made. The selenium and oil were then stirred and heated again and density at room temperature was again determined. This was repeated until constant values for the densities were obtained. Density determinations were made at temperatures up to 205° C. At various intervals, density at room temperature was determined. This was done to note any change in the contents during the process of making determinations at higher temperatures. The results are given in Table IV in the sequence of their determination.

The weight of selenium used = 40.1373 grams

The volume of the pyknometer = 25.066 c.cc.

TABLE IV

Temperature	Density
21.9	4.7272
159.5	4.6541
188.5	4.6224
20.4	4.7277
197.5	4.6187
205.5	4.6199
21.8	4.7274
90	4.6916

VITREOUS SELENIUM

Determinations of density of the vitreous form were also carried out. Liquid selenium was quenched in a Hershenann mould and ground to a fine powder. The procedure outlined for the metallic form was repeated in this case with exception of the heat treatment. At 90° C the vitreous form began to transform into the metallic form. This was visually detected by the falling of the oil thread in the capillary of the stopper of the pycnometer. The reading obtained at room temperature was:

$$d\frac{21.3}{4^o} = 4.2824$$

Selenium contaminated with oil was purified by extracting the oil with ether by means of a Soxhlet extractor.

DILATOMETER METHOD

To determine the density of selenium at temperatures above 277° C, a method involving a dilatometer was chosen. The dilatometer consisted of a long glass tube of a small diameter with a bulb sealed on to one end. It was calibrated so that the height of the column of liquid in it would indicate the volume it occupied. By means of a cathetometer, the height of the column was read to one hundredth of a centimeter. The average volume of the dilatometer was 10 c.cs. and .01 cms. in height represented .001 c.cs. in volume. The error in determination should therefore have not exceeded .01 per cent. Theoretically

this was a highly desirable method; practically it did not prove to be so.

Difficulty was encountered in charging the dilatometer. On melting, the selenium was forced up the narrow glass tube by rising air bubbles. This formed a broken column that made readings impossible. The high viscosity of the liquid selenium prevented the liquid from running down.

To add to the conviction, that this method was not applicable, tiny globules of selenium stuck to the wall of the glass and no matter how much heat was applied, they persisted in staying where they were. In accordance with the facts recorded, the method was given up.
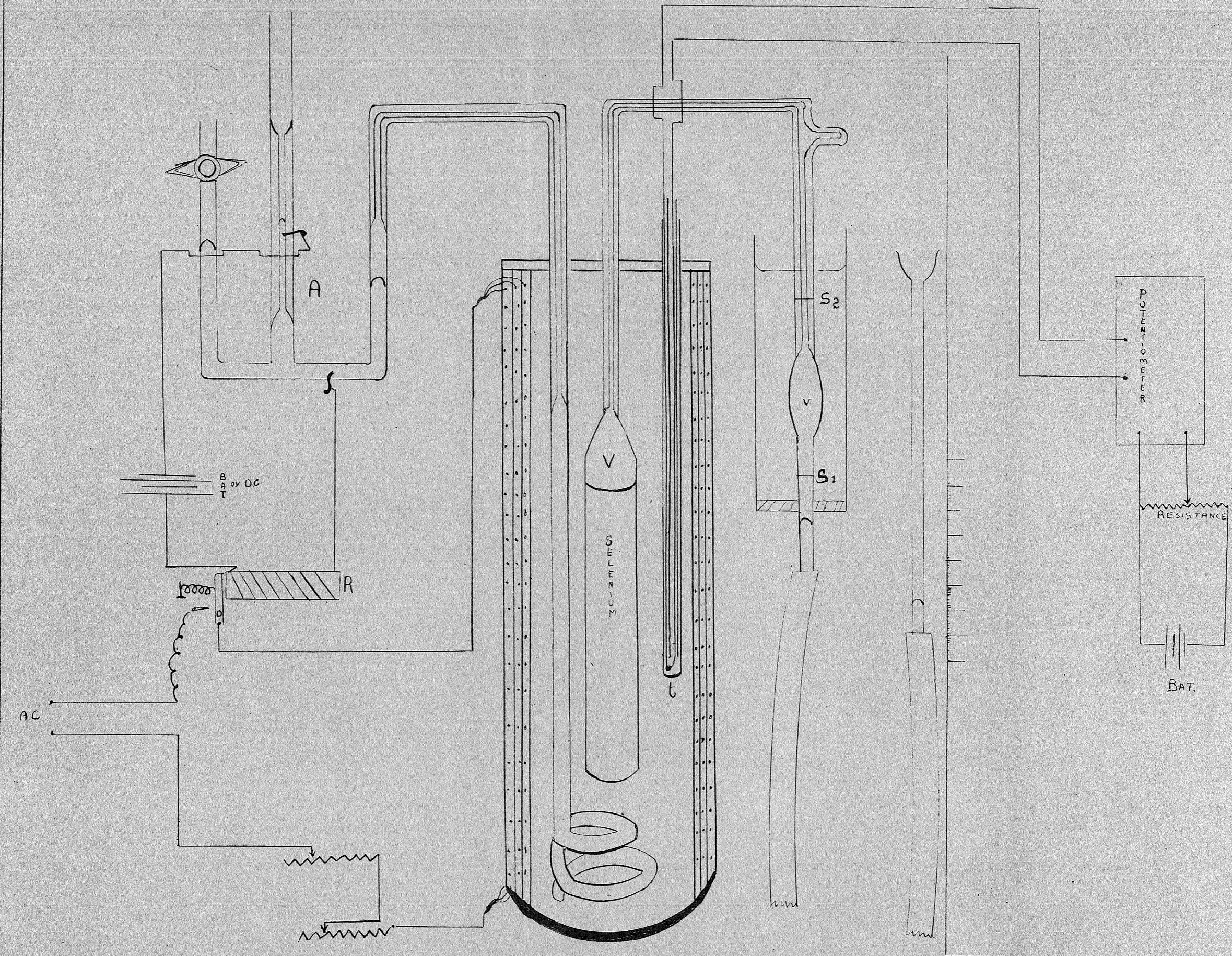
Fig 8

THE VOLUMENOMETER METHOD

The final method applied involves a volumenometer. This method of determining density is based on Boyle's law, where at constant temperature, changes in volume may be expressed in terms of changes in pressure. Thus:

If V = a given volume and p the corresponding pressure and v = a small increase or decrease in volume and p' = the pressure after the change has been made, then $V p = (V \neq v) p'$

Suppose V represents an air space in a vessel filled with a substance whose density is to be determined, an increase or decrease of density will cause a change in V. At one temperature this volume may be determined by decreasing it by a known volume v, and noting the pressure before and after the change. In this manner changes in V, that is, changes in the density of the substance may be determined. If the density of the substance is known at one temperature and if the corresponding V is calculated, densities at various temperatures may be calculated.

The volumenometer constructed is shown in Fig. 8. The apparatus consists essentially of a bulb (V), nearly filled with selenium and attached by means of a capillary tube to another similar bulb (v). This bulb is calibrated for volume between marks S_1 and S_2.

The apparatus was first constructed with inclusion

of a three-way stopcock just above the small bulb. This was
included to permit the release of pressure in case it rose
too high. It was found, however, that the stopcock caused
a leak and was therefore excluded from the apparatus. In-
stead, a side arm was joined on, and if the pressure rose
too high, it could be released by breaking the seal on the
end of the side arm.

Pressure tubing was joined on and a thistle
funnel with a long arm, was attached to the other end of
the tubing. The pressure tubing permitted the raising and
lowering of the column of mercury with rise and fall of
pressure. The height of the mercury level was adjusted
by means of a pulley extending from the ceiling. The scale
consisted of meter sticks.

The other apparatus shown in the diagram consists
of a thermocouple (t) and the electric circuit accompanying
it, and a high temperature regulator (A) with the accompany-
ing relay (B) rheostats and circuit.

In applying this method for determination of
densities of liquid selenium at temperatures above 217° C.,
various factors had to be taken into account.

(1) The two bulbs could not be kept at the
same temperature since the temperatures involved were above
the boiling point of mercury.

(2) The volume change of liquid selenium was
very small and therefore subject to enormous error.

(3) The temperature of the furnace had to be kept constant throughout a reading, since a small temperature fluctuation might cause a large error in the density determination.

To account for the first factor, a formula had to be adapted which would take into account the difference in temperature. It was quite obvious that in terms of pressure a volume at lower temperature would record itself as a larger volume at higher temperatures. With this in mind, the following formula was used:

(1) $V_p = (V \neq v \times \frac{T_2}{T_1})$ p, where T_2 = Temperature of the selenium

and T_1 = Temperature of the calibrated volume.

To read T_1 a water-jacket was placed about the calibrated bulb and its temperature read.

The second factor was accounted for by using a large amount of selenium and by leaving a small air space. A small change in density of selenium therefore recorded itself as an appreciable change of its total volume, while a small change in volume was appreciable with reference to the small air space. The volume change therefore registered itself to an appreciable extent in terms of pressure change.

The third factor shall be discussed in a later chapter under the heading of "Thermostatic Control".

PROCEDURE

The levels of S_1 and S_2 were read on the scale. These readings represented atmospheric pressure at these levels. The barometer was then read. After the required temperature was attained, the mercury level was brought up to S_1 and the pressure reading taken. The difference between this reading and the reading representing level S_1 was calculated, and by means of this difference, the pressure in the air space determined. The level of the mercury was then raised to S_2 and after a short interval of time the reading on the scale taken. The pressure in the air space was determined by correcting the atmospheric pressure by the difference between the reading representing S_2 and this reading. In the meantime the temperatures of the furnace and of the water-jacket were read.

Applying the readings to the formula (1), V was determined for that temperature.

The total volume of the bulb was obtained by determining V at a temperature at which the density of selenium was known. In determining the densities, correction for the expansion of the glass bulb was made.

Determinations were made at temperatures 225° C to 478° C.

The readings obtained varied from day to day. The possible causes for the variation were thought to be:

(1) the presence of air bubbles in the liquid and

their failure to respond to pressure changes.

(2) the formation of a permanent gas due to the decomposition of traces of oil present in the selenium.

(3) the solubility of air in selenium and its increase with increase of pressure.

To eliminate the first two sources of error, the volumenometer was subjected to a lengthy pumping by means of a high vacuum pump, while the pumping was going on the charge was heated up to 300° C. After the pumping, the results obtained were in good agreement. Ten to twenty readings were taken for each temperature and the highest discrepancy between the readings at one temperature was .1 cc., representing a possible error of 0.1 percent. It was thought, however, that in averaging a great number of readings, this error would be reduced.

The results obtained by this method are listed in Table V.

Weight of selenium.............52.094 grams

Volume of the bulb up to upper calibration

mark.....................................16.9143 c.cs.

TABLE V

Temperature	No. of observation	Density (mean)	Maximum variation between readings ±
286	10	3.92	.01
325	10	3.89	.01
378	8	3.77	.01
431	11	3.71	.02
479	17	3.68	

THERMOSTATIC CONTROL

A large beaker of water, which had been kept at room conditions for a day, was found satisfactory for maintaining constancy for room temperature determinations.

For the range $90°-277°$ an oil bath was used. This thermostat consisted of a metal tank filled with paraffin oil, placed in a beaker-shaped electrical resistance furnace. This furnace, in the thermoregulator circuit, provided the regulated heat supply. Temperature control was maintained by a mercury regulator, while uniformity of temperature of the bath was assured by a high speed electric stirrer. The lag in cooling down and heating up of the furnace, caused a uniform fluctuation of a magnitude ranging up to $5°$. The fluctuations were very slow; a single one required about twenty minutes. As indicated by the rise and fall of the oil thread in the capillary of the stopper, the selenium and oil responded quickly to small changes in temperature. It was therefore safe to assume that the temperature of the bath and selenium never differed by more than $.5°$. This difference caused a negligible error in the density determinations.

The cross-section of the furnace used in the volumenometer method is shown in Fig. 8. By adjusting the resistance of the circuit by means of a series of rheostats, rigid temperature control was maintained. An air regulator was included as a safety measure, in case an unexpected rise in temperature occurred.

The temperatures up to 277° C. were read by an ordinary 360° thermometer, while temperatures higher than 277° C by an iron-constantin thermocouple.

CALCULATIONS AND RESULTS

The summary of the results of measurements made by means of a pyknometer are given in Table VI.

TABLE VI

t °C	d exp.	d$_{calc.}$	$\triangle$ d	Lit. Values
		Solid selenium (metallic)		
20.4	4.7924	4.7966	$\neq$ .0040	$4.80_4^{17°}$
90	4.7641	4.7560	- .0081	
159.5	4.7152	4.7165	$\neq$ .0013	
188.5	4.6954	4.6989	$\neq$ .0035	
197.5	4.6940	4.6937	- .0003	
205.5	4.6919	4.6891	- .0028	
		Liquid selenium		Dobinski & Wesolowski[50]
225	3.9705	3.9727	$\neq$ .0022	3.976
241	3.9540	3.9479	- .0061	3.955
244.5	3.9394	3.9424	$\neq$ .0030	3.947
257	3.9276	3.9236	- .0040	3.9286
277	3.8904	3.8926	$\neq$ .0024	3.8914

In the above table "t" represents the temperatures in the °C, "d" exp., the values of density obtained and "d" calc., those calculated from the formulae. The formulae used are:

(2) $d = 4.8073 - .0005753\ t$ (for metallic selenium).

(3) $d = 3.9851 - .001551\ (t-217)$ (for liquid selenium)

These formulae were computed by means of the method of "least squares." $\triangle$ d represents the difference between d$_{calc.}$ and

d.exp.   Literature values are listed in the fifth column.

The values determined were plotted against temperature and the curves obtained are shown as a solid line in Fig. 9.   The comparison between experimental values and those obtained by the linear expressions, as well as the graph show that the formulae give a good approximation of the density-temperature relationship in the range under consideration.

The formula obtained by Dobinski and Wesolowski is:
d = 3.987 - .0016 x (t-220).

The literature values for densities of metallic selenium at 17° C. and of water and mercury were obtained from the 'International Critial Tables'.

From the graph it may be seen that the change in volume on melting may be calculated.   From this and the latent heat of fusion, the change in the melting point with rise of pressure may be calculated by applying these data to the Clausius-Clapeyron equation

$$\frac{dt}{dp} = \frac{T \times dv}{l}$$ where   T = freezing temp. °A

1 = latent heat of fusion

dv = change in volume accompanying melting at atmospheric pressure.

Latent heat of fusion for metallic selenium at 220° C [53].....
= 13.4 calories.

Increase of volume per gram of selenium on melting...........
0.03737 c.c.
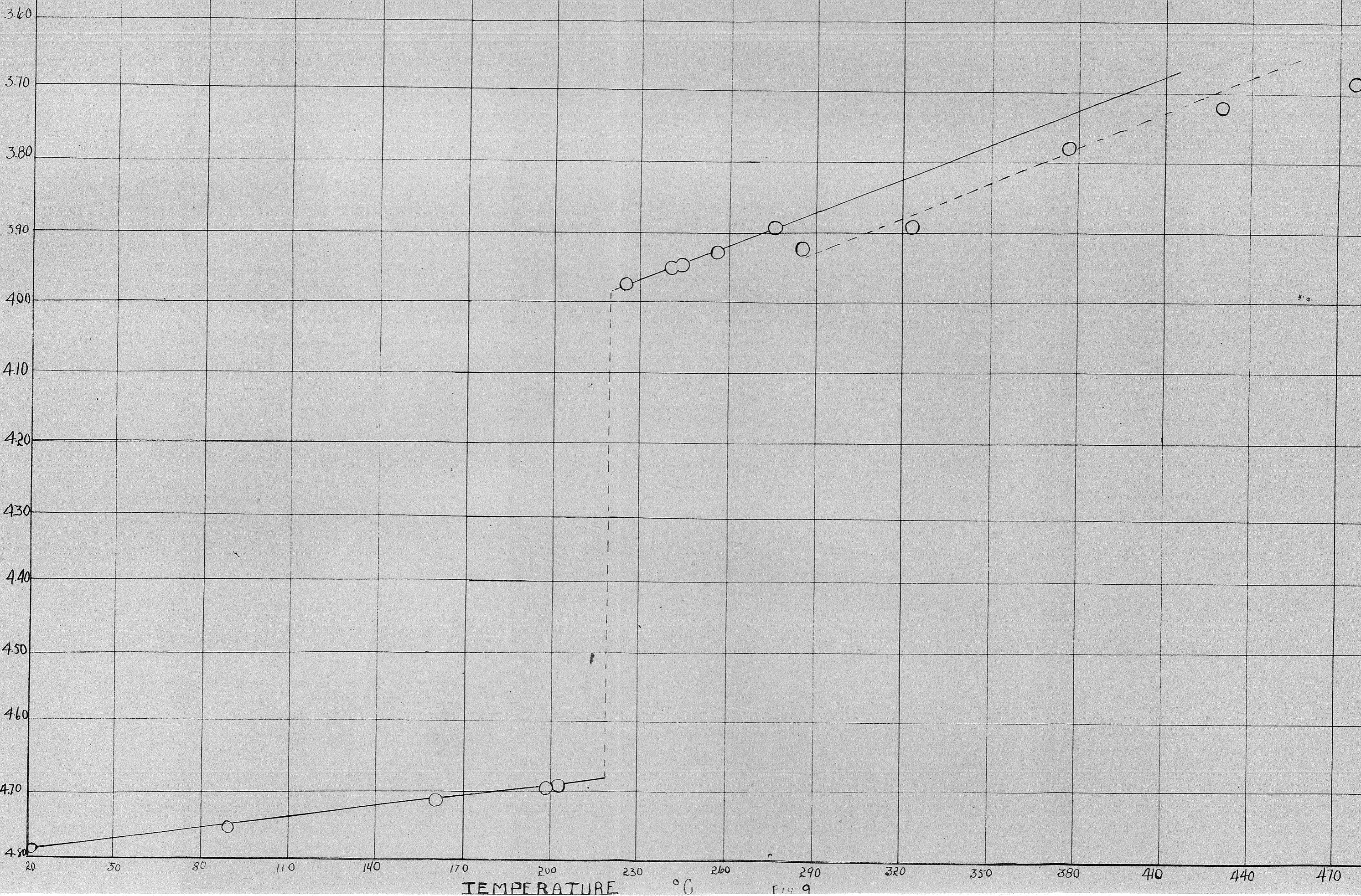
Fig 9

Therefore the rise in melting point $= 0.033124^\circ$/atmosphere.

The results obtained by means of the volumenometer are given in Table VII.

The densities determined at one temperature were averaged, and those varying by more than .02 were discarded. The remaining readings were then re-averaged.

<center>TABLE VII</center>

Temperature	Density$_{exp.}$	Density$_{calc.}$	$\triangle$ d
286	3.917	3.879	- .038
348	3.895	3.818	- .077
378	3.775	3.734	- .041
431	3.713	3.644	- .069
479	3.683	3.572	- .111

The results were plotted on a temperature-density graph and the curve obtained was represented by dotted line, as in Fig. 9.

DISCUSSION OF RESULTS

The close agreement of results obtained for the densities of liquid selenium between 220°- 277° with those of Dobinski and Wesolowski, indicates the accuracy of the methods employed in both cases. From this it may also be assumed that the results obtained by Dobinski and Wesolowski for temperatures, 277°- 345°, are equally reliable.

The linear relationship between density and temperature indicates that as far as density is concerned the behavior of both solid and liquid are quite regular.

Although the results, obtained by means of the volumenometer method may be considered significant to the third figure only, they indicate several things:

(1) The empirical formula obtained for liquid selenium may be applied to temperatures up to 480° C. This is indicated by the fact that the dotted line on the graph is parallel to the one obtained by means of the empirical formula. The constant difference between the two curves mentioned can be ascribed to experimental error, since the density determined at 277° by means of the volumenometer shows the same difference from the more accurate determination obtained at the same temperature by the pyknometer method.

(2) The fact that the error is in the direction of increase of density while dissociation and equilibrium changes

should cause an abnormal decrease in density, indicates that liquid selenium is a simple liquid up to 480°. It must be noted here, that the basis of the latter statement is density data only, and because density is not very sensitive to temperature changes, definite conclusions cannot be drawn from it alone.

The accuracy of the Volumenometer can be made higher if standardization with a substance of known densities for the range to be investigated is made and if other local factors are accounted for, but this alone would constitute a complete problem.

CONCLUSIONS

(1) The densities of selenium were measured over
a range of 20°-480°.   The values for the/350°-480° have
not been previously determined.

(2) In accordance with the conclusions drawn by
Dobinski and Wesolowski[50], these measurements, although
made by a different method, gave no evidence of a
shifting equilibrium.

(3) The rise of the melting point with increase
of pressure was calculated.

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