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COMMISSION OF THE EUROPEAN COMMUNITIES — EURATOM

**SURFACE TENSIONS OF MOLTEN SALTS  
AND  
CONTACT ANGLE MEASUREMENTS OF MOLTEN  
SALTS ON SOLIDS**

by

**C. F. MOREL**

**1970**



**Joint Nuclear Research Centre  
Petten Establishment — Netherlands**

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## **ABSTRACT**

In chapter 1 the different methods to measure surface tensions and contact angles are discussed.

In chapter 2 an apparatus is described with which it is possible to measure the surface tension of molten salts and their mixtures as well the contact angle between these molten salts or their mixtures and a solid (graphite). These measurements can be performed under different gas atmospheres and in a temperature range from 800-1100°C. The sessile drop method on a flat solid is used. The system is heated indirectly and mounted in a bell which can either be evacuated or filled with a gas. Photographs of the sessile drop can be recorded through windows in the belljar. Interesting is that the salt during the measurements can be purified by means of a kind of zone refining, while being already under the experimental conditions.

In chapter 3 experimental results are given. The contact angle is measured as function of different parameters such as temperature, time, purity. The surface tension is calculated out of the dimensions of the drop using different methods.

In chapter 4 the surface tension is compared with the contact angle.

## **KEYWORDS**

MOLTEN SALTS  
SURFACE TENSION  
ANGULAR DISTRIBUTION  
GRAPHITE  
TEMPERATURE  
REFINING

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SURFACE TENSIONS OF MOLTEN SALTS AND CONTACT ANGLE MEASUREMENTS  
OF MOLTEN SALTS ON SOLIDS

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## LIST OF SYMBOLS

- $\theta$  = contact angle
- $\gamma_{GS}$  = interfacial energies between gas-solid phase
- $\gamma_{SL}$  = interfacial energies between solid-liquid phase
- $\gamma_{LG}$  = interfacial energies between liquid-gas phase
- $\Delta p$  = excess pressure
- $R_1$  = curvature at a given point of the surface
- $R_2$  = curvature at the same point in different direction
- $D_1$  = diameter of the drop
- $D_2$  = diameter of the graphite sample
- $D_3$  = diameter of the contact surface liquid-solid
- $h_1$  = height between equatorial plane and apex of the drop
- $h_2$  = total height of the drop
- $v$  = volume of the drop
- $\Delta \rho$  = difference in density between the liquid and the gas phase
- $g$  = the acceleration due to gravity

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## INTRODUCTION

During the last fifteen years research on molten salts has increased considerably.

The object of most investigations has been the determination of the physical and chemical properties of pure molten salts and molten salt mixtures while the study of interaction between molten salts and solids was given less attention (1).

A more profound knowledge of the interfacial behaviour between molten salts and solids, i.e. the wettability serves for a better understanding of phenomena such as :

- 1) The anode effect (2), (3)
- 2) The corrosion of materials by molten salts
- 3) The transfer properties between molten salts and solids, such as mass and heat transfer between molten salts and solids.

An increase of the heat transfer coefficient between liquid and solid has been observed (4) when the solid surfaces are wetted by the liquid. In nuclear molten salt reactors the permeation of the porous graphite is governed by the interfacial behaviour. Wettability is determined directly through the contact angle at the three phase boundary, liquid-solid-gas. By definition the contact angle is the angle between the liquid-solid and liquid-gas interface. The larger the contact angle, the smaller the wettability.

The contact angle is related to the interfacial energies between liquid and gas phases (LG), gas and solid phases (GS) and solid and liquid phases (SL) through the Young equation (5) - (6).

$$\cos \theta = \frac{\gamma_{GS} - \gamma_{SL}}{\gamma_{LG}} \quad (1)$$

At every point on a liquid surface, the Laplace relation (6, 7) equates the surface tension and the hydrostatic pressure due to the curvature.

Therefore

$$P = \gamma_{LG} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

where  $\Delta p$  = excess pressure,  $\gamma_{LG}$  = liquid-gas surface tension and  $R_1$  and  $R_2$  are the two principle radii of curvature at the given point of the surface. A number of approximate solutions of this drop

equation have been proposed by Bashforth and Adams (8), Dorsey (9), Porter (10), Wheeler et al (11), Staicopolus (12), Butler and Bloom (13).

In order to contribute to a better understanding of the wettability an apparatus with which it is possible to determine contact angles between molten salts and different materials and surface tensions of molten salts under a variety of conditions, has been developed. This apparatus is described in the present thesis whereas results obtained with it are presented and described.

## 1. REVIEW OF THE CONTACT ANGLE AND SURFACE TENSION MEASUREMENTS.

### 1.1. Introduction

Adamson (6) and others (14) give excellent reviews of the various methods available for measuring contact angles and surface tensions. The different methods to measure contact angles are :

#### 1) Tilting plate method

A slab several centimetres wide is dipped into the liquid and turned into such a position that the liquid surface appears flat right up to the solid.

#### 2) Sessile drop method

A drop of a liquid is placed on a solid and the contact angle is measured at the point of the three-phase boundary liquid-gas-solid.

The following methods for measuring the surface-tension can be distinguished:

#### 1) Capillary rise method

The height of the rise from a liquid in a capillary is measured, by which it is possible to calculate the surface tension.

#### 2) Maximum bubble pressure method

By this method bubbles of an inert gas are blown slowly into the liquid below the surface of the liquid in question, by means of a tube. The pressure needed to do it is a measure for the surface tension.

#### 3) The drop weight method

This method consists of forming drops of a liquid at the end of a tube. By collecting them the weight per drop can be determined and so, also, the surface tension.

#### 4) Detachment methods

These methods are based on determining the surface tension by detaching an object from the surface of a liquid. We can distinguish two methods:

a plate method

b pulling ring method

#### 4a) Plate method

The plate method or Wilhelmy slide method is a method which

consists of detaching a thin plate vertically from the surface of a liquid. The plate is suspended from one arm of a balance. The surface tension can be calculated from the difference in weight between the plate just in contact with the liquid and free from the liquid.

#### 4b) Pulling ring method

A ring or a loop of wire is detached from the surface of a liquid. Just as with the plate method the surface tension can be measured from the difference in weight between the object just in contact with the liquid and free from it.

#### 5) The sessile or pendant drop or bubble methods

##### 5a) The sessile drop method

A drop of a liquid is formed on a flat solid surface and from the form of the contour it is possible to calculate the surface tension.

5b) The bubble method is similar to the sessile drop method

5c) The pendant drop is almost similar to the sessile drop method.

It is possible to calculate the surface tension from the dimensions of the drop.

5d) The pendant bubble is similar to 5c)

Nearly all the methods to determine the surface tension depend in a critical way on the contact angle - a difficulty which does not exist with the sessile drop or bubble and pendant drop method. The sessile drop method even allows contact angle measurements to be made simultaneously with the surface tension measurements.

## 1.2. Contact angle measurements

### 1.2.1. Tilting plate method

The tilting plate method developed by Adam and Jessop (15) is probably more accurate than the sessile drop method. Fowkes and Harkins (16) used this last method in combination with the tilting plate method to determine the surface tension at the same time. They used an entirely closed apparatus and worked under an inert gas atmosphere so as to avoid contamination. Ablett (17) changed the slab for a cylinder of the solid. By raising and lowering the cylinder in a horizontal position the moment is recorded when the surface of liquid appears undisturbed up to the solid. By a simple formula the contact angle can be calculated.

This method suffers from the disadvantage that a large quantity of the liquid is needed. At high temperatures this method is never used because of the difficulty of maintaining uniform temperature and other constructional difficulties.

### 1.2.2. Sessile drop or bubble method

The first method is used even at temperatures of up to 2000°C.

The need of material is small, specially for the sessile drop method. Measurements in time are easy and it is possible to record measurements at different time intervals by taking a photograph of the drop or bubble. The angle can be measured directly or calculated by measuring the dimensions of the drop.

The sessile drop method was used by Ellefson and Taylor (18) to measure the contact angle of fused salts and glasses in contact with gold and platinum at high temperatures in various atmospheres. Later this method was used by Comeforo and Hursh (19) to measure the wetting of  $\text{Al}_2\text{O}_3\text{-SiO}_2$  refractories by molten glass. Wartenberg (20) used this method to measure the influence of oxygen on the contact angles of molten salts on solids.

## 1.3. Surface-tension measurements

### 1.3.1. Capillary rise method

The capillary rise method is on a firm theoretical base (21) (22) (23). It is important that the contact angle should be zero. Also the capillary must be accurately vertical, of well-known and uniform diameter and circular in diameter. At high temperatures this gives considerable experimental difficulties for it is by no means easy to obtain truly uniform tubes and the capillaries will be badly corroded by the salts. It is also difficult to maintain uniform temperature over the length of the tube and to measure the height accurately. This method has never been used at high temperature.

### 1.3.2. The maximum bubble pressure method

This method is mostly applied at high temperatures. It was

first suggested by Simon (24) but it was Jaeger (25) who used it on a large scale at high temperatures. He measured the surface tension of about fifty salts, with temperatures up to as high as 1600°C.

The maximum bubble pressure method can be employed either by using single capillary tubes, or two capillary tubes of different bore as Sugden did (26).

Cantor (27), Fenstel (28) and Schroedinger (29) derived an equation with which it is possible to calculate the surface tension by measuring the different variables.

Peake and Bothwell (30) used this method to measure the surface tension of mixtures of potassium chloride with barium chloride.

Boardman et al (31) measured the surface tensions from several molten salts such as AgCl, KCl, PbCl<sub>2</sub> and CdCl<sub>2</sub> and their mixtures.

Desyatinkov (32) studied the system KCl - NaCl - MgCl<sub>2</sub> at 700°C.

Bloom et al (33) measured surface tensions of pure molten salts and the systems NaNO<sub>3</sub> + NaNO<sub>2</sub>, KNO<sub>3</sub>+KNO<sub>2</sub>, NaNO<sub>3</sub>+AgNO<sub>3</sub>, PbCl<sub>2</sub> + NaCl and KCl + NaI.

Reding (34) did surface tension measurements in the systems MgCl<sub>2</sub>, KCl, BaCl<sub>2</sub> and compared his results with those obtained by other investigators. The difference is sometimes as great as 7%.

Dahl and Duke (35) measured the surface tension of some systems and more specially the systems AgNO<sub>3</sub> with alkali metal nitrates and PbCl<sub>2</sub> with alkali metal chlorides.

### 1.3.3. Drop weight method

This is a rapid and simple method. It consists of forming drops of a liquid at the end of a tube and of collecting them. Because the drop never has an ideal form when falling off the tube, corrections have to be made. Lohnstein (36), Dunken (37), Harkins and Brown (23) calculated these corrections.

Hauser et al (38) show with a high speed motion picture camera the growth of a drop. When the drop breaks off it is nearly spherical. A narrow stem, attached to the remainder of the droplet, then breaks off forming one or more droplets.

#### 1.3.4. Detachment method

##### 1.3.4.1. Plate method

The first person to publish this method was Wilhelmy (39), and so it is also called the Wilhelmy slide method. Bertozzi and coworkers used this method to measure the surface tensions of nitrate systems (40), of alkali halide binary systems (41), some binary systems of alkali halides, alkaline earth halides (42), and alkali sulfate and chloride-sulfate binary systems (43).

##### 1.3.4.2. Pulling ring method

This method also called Du Nouy method requires corrections on the simple theory. In the papers of Harkins and Jordan (44), and Fox and Chrisman (45) corrective factors can be found.

There are very few investigations at high temperature. Washburn and Libman (46) used a dipping cylinder method to determine the surface tensions of several glasses at 1206 and 1454°C.

#### 1.3.5. Sessile or pendant drop or bubble method

##### 1.3.5.1. Sessile drop method

This method with the aid of photography, is particularly well-adapted to the investigation of any secular change that may occur in the surface.

Measurements at high temperature using this method were done by Ellefson and Taylor (47). They measured the surface tension of several viscous liquids up to 1100°C. They estimate that this method can be used for much higher viscosities than the maximum bubble pressure method, however, Bradley (48) measured the surface tension of liquids with a viscosity up to 2500 poises using the maximum bubble pressure method.

We have chosen this method for our measurements on the surface tension and contact angle, which we will treat more carefully in next section.

### 1.3.5.2. Pendant drop method

This method is almost similar to the sessile drop method. Andreas et al (49) did calculations on the shape of the pendant drop. Winkel (50) did some calculations on pendant drop by means of an computer. Stauffer (51), however, extended the table of Fordham (52) of a correction factor  $I/H$ , which is a function of the ratio  $d_s/d_e$ ,  $d_e$  being the maximum diameter of the drop,  $d_s$  being the diameter on a distance  $d_e$  from the top of the drop.

Kingery (53) measured the surface tension of several oxides by this method.

### 1.3.5.3. Sessile bubble method

This method has nearly never been used.

## 2. SESSILE DROP METHOD

### 2.1. Introduction

The scope of the present work was to determine surface tensions as well as contact angles of a number of molten salts and mixtures under carefully controlled environment. Of the above described methods, the sessile drop technique seemed most suitable for these investigations and this for the following reasons.

- 1) surface tension measurements are independent of the contact angle
- 2) surface tension measurements and contact angle measurements can be made simultaneously.
- 3) the contact angle can be measured directly or calculated from the dimensions of the drop
- 4) only a small quantity of salt is needed
- 5) measurements can be made up to relatively high temperatures
- 6) measurements can be made under vacuum and under different atmospheres
- 7) the method is static and therefore not influenced by viscous effects

- 8) the photographs on which the measurements are made serve as permanent records
- 9) time dependant effects can be studied since the surface is not disturbed by the measurements
- 10) measurements of the profile of the surface can be made upon a suitable photograph. Photographs can be taken at such intervals as may be desired and the time at which each is taken can be accurately determined. While doing this, the surface is not distrubed in any way. By none of the methods commonly used such a series of measurements upon an undisturbed surface can be obtained. Furthermore the measurements of the photographs can be made at one's leisure, and can be repeated as often as may desired.

Among the disadvantage we can mention :

- 1) need of correction terms in surface tension calculations
- 2) need of density data from the liquid in surface tension calculations
- 3) the fact that photographs can be distorted

## 2.2. The principle of the method

Under an inert gas atmosphere a drop of salt is formed on a flat piece of solid (Fig. 3). Then a photograph is taken from the drop. From this photograph the contact angle is directly measured. By measuring the dimensions of the drop it is possible to calculate the contact angle and the surface tension.

## 2.3. Apparatus

The apparatus consists of a metallic bell connected to an oil diffusion and a rotating pump with which it is possible to obtain a vacuum of  $5 \cdot 10^{-5}$  torr (measured with an ionivac gauge). A gas inlet permits the introduction of different gas atmospheres.

The bell (Fig. 1) consists of a stainless steel cylinder (diameter 20 cm.) closed on both ends by removable lids (1). The bell is water-cooled. The solid sample (2), a cylindrical disc on which the contact angle is to be measured, is placed on an iron tripod (3) which allows horizontal adjustment. The tripod is electrically insulated from the bell by teflon discs fixed in the bottom.

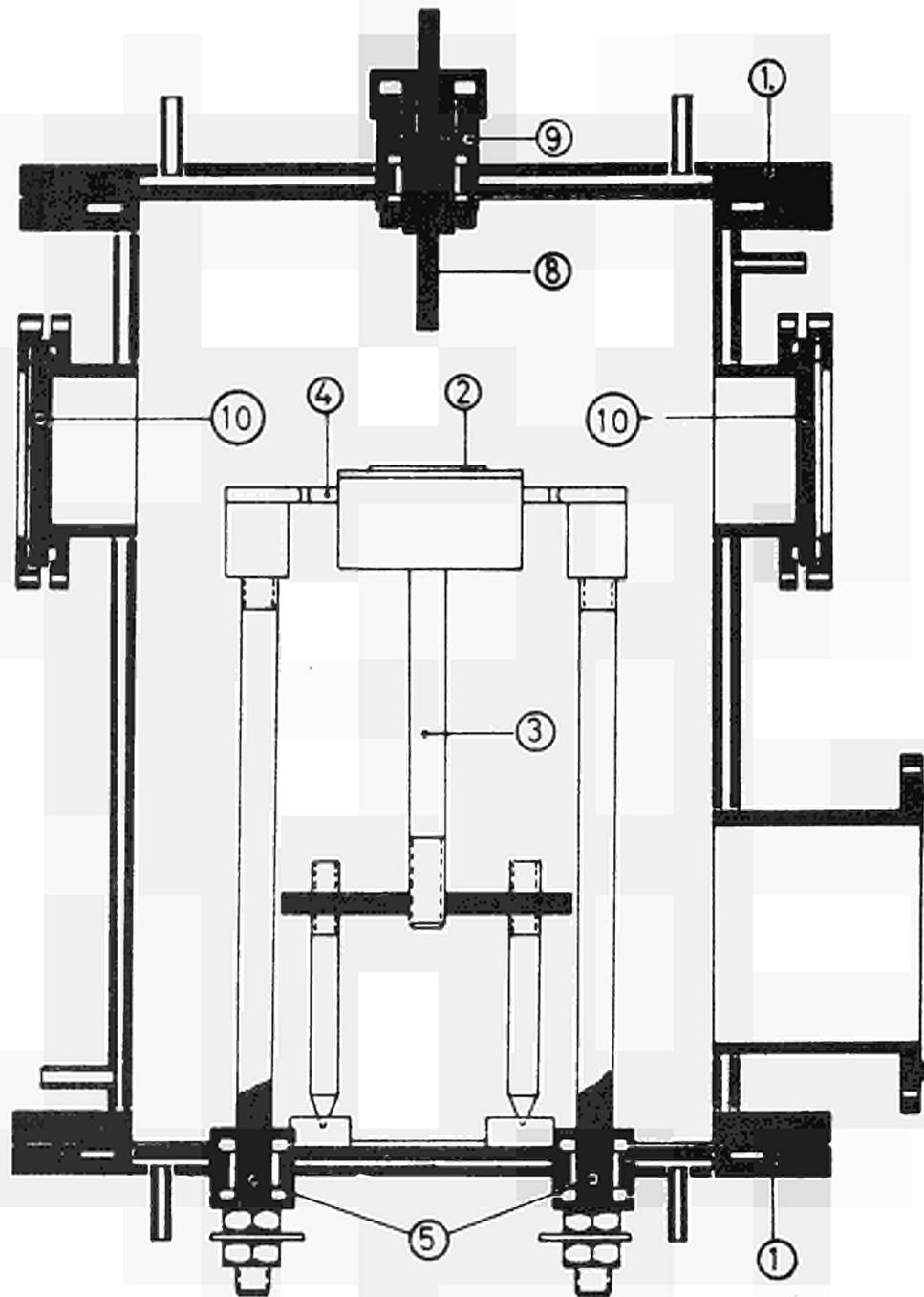


Fig:1

Cross Section of the Bell.

- |                       |                          |
|-----------------------|--------------------------|
| 1. Lids.              | 5. Electric passage.     |
| 2. Solid Sample.      | 8. Movable rod.          |
| 3. Tripod.            | 9. Vacuum-tight passage. |
| 4. Graphite resistor. | 10. Windows.             |

The sample is heated indirectly by a graphite resistor (4) having the form indicated in Fig. 2, clenched between two copper rods with iron upper ends, so that the resistor can be placed as close as desired under the solid sample. The two copper rods are connected through two electric passages (5) (Fig. 1) in the bottom of the bell to a transformer supplying an alternating current of 12V - 150 A. Indentations (6) (Fig. 2) are made in the resistor to adapt it to the maximum output of the transformer. Molybdenum shields (7) are also placed around the resistor to minimize thermal losses. To form a drop of molten salt a piece of salt is fixed on a movable rod (8) with a platinum wire. This rod enters the upper lid through a vacuum tight passage (9).

A drop is formed by bringing the piece of salt in contact with the hot solid sample.

The experiment consisting of a drop of molten salt in equilibrium on the horizontal polished surface of a solid can be observed through windows (10) located in the wall of the bell. The centers of the windows are at the same level as the solid surface.

Photographs of the drop are taken with a reflex camera. One of the windows is used to introduce a Pt-PtRh thermocouple via a vacuumtight passage. The temperature is measured by introducing the thermocouple into the drop.

A system of electrodes is mounted to allow contact angle measurements while an electric current passes through the interface liquid-solid. An insulated wire connected to the solid samples forms one of the electrodes. A platinum wire fixed on the movable rod serves as the second electrode. The movable rod is electrically insulated from the bell.

#### 2.4. Preliminary treatment of the salt

All salts used were analytical grade Prolobo salts in powder form. The experimental arrangement required that the salt be presented in a lump form. The following technique was used for the preparation of the salt, it served simultaneously to dehydrate it.

A platinum crucible (diameter 2 cm, height 3 cm) was half filled with salt powder and a platinum wire inserted. The crucible was placed in a graphite container which was suspended from a movable

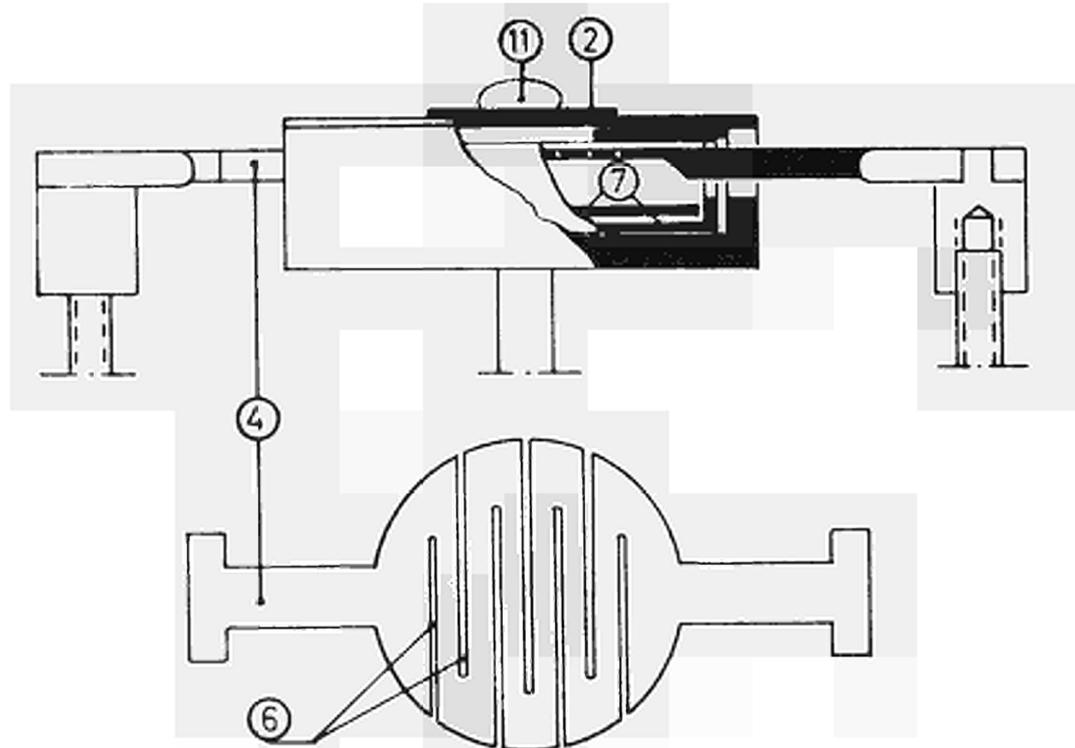


Fig: 2

The Heating Resistor.

- 2. Solid sample.
- 4. Graphite resistor
- 6. Indentations.
- 7. Molybdenum shields.
- 11. Sessile drop.

metal rod. The whole was contained in a quartz vessel with the metal rod passing through the metal watercooled cover by means of a vacuum-tight seal. A thermocouple entered through the rod into the graphite container. The whole was placed in an oven and connected to a primary vacuum system.

The system was left at a pressure of  $10^{-2}$  torr overnight in order to remove traces of water. Then the salt was heated to about  $50^{\circ}$  above its melting point in a helium (35 cm Hg) atmosphere. This temperature was reached in about four hours. Then it was cooled down slowly. The lithium, sodium and calcium salts were easy to remove from the platinum crucible. Potassium, rubidium and cesium salts gave more difficulties and therefore the platinum crucible was quickly heated in air so that the outside part of the salt melted and the center could be removed by the platinum wire which it contained.

So a lump of salt was formed with a platinum wire protruding from it.

## 2.5. Preparation of solid sample

The solid samples have the form of discs of a given diameter  $D_2$  (Fig. 3) so as to have a standard diameter on the photographs taken from the drop.

Before being placed in the oven the solid sample is polished on glass paper  $n^{\circ} 6$  and cleaned by ultrasonic sound in a convenient liquid. Then it was rubbed on kleenex paper.

After being placed into the oven the solid samples were put horizontal by means of a water-level.

## 2.6. Preparation of the sessile drop

### 2.6.1. Pure salt

A piece of salt is attached to the movable rod which is fixed in the upper lid of the bell, and the solid sample is placed horizontal on the tripod.

Then the bell is closed and evacuated. At the same time the solid sample is heated for several hours to a temperature far above the melting point of the salt used, in order to degas the

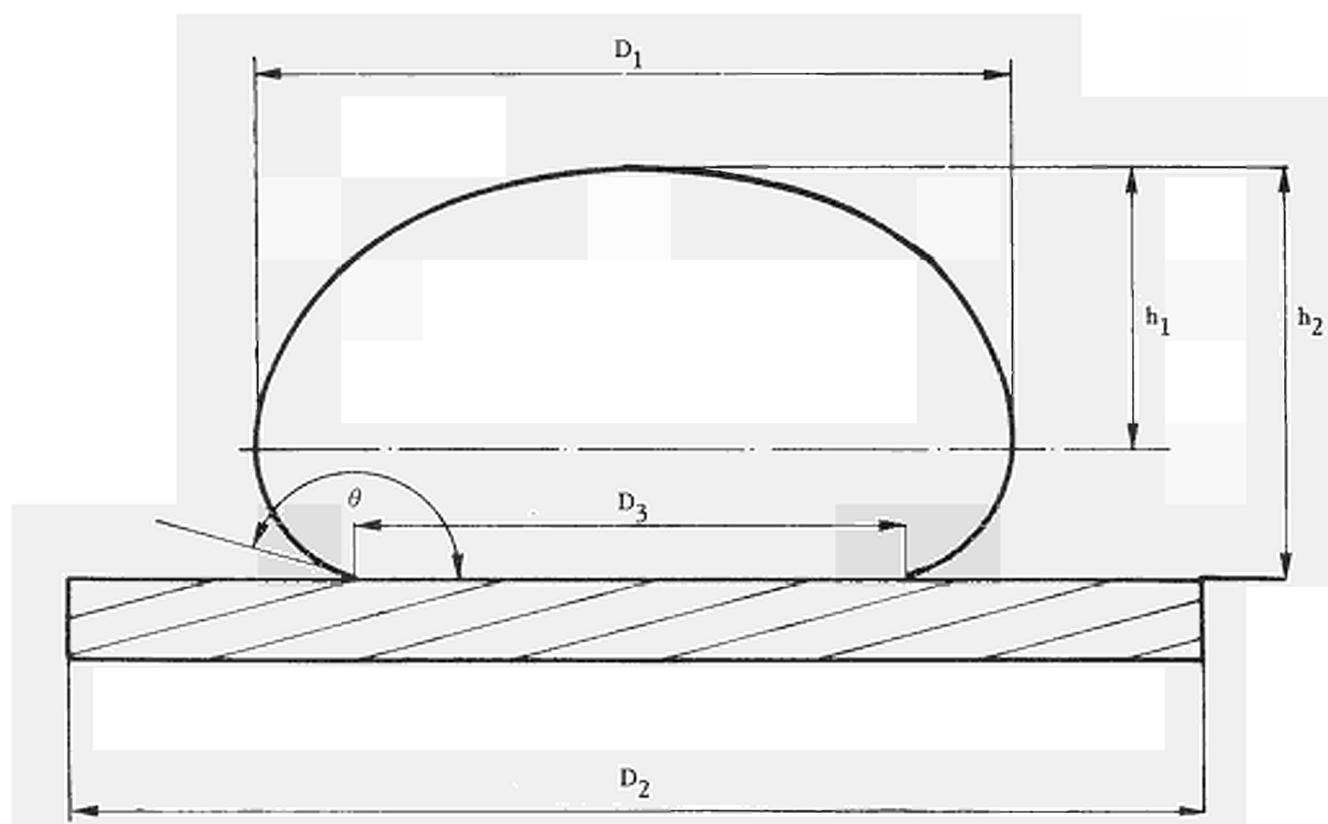


Fig. 3 Molten salt drop on solid.

- $\theta$  - contact angle
- $D_1$  = diameter of the drop
- $D_2$  = diameter of the solid sample
- $D_3$  = diameter of the contact surface liquid-solid
- $h_1$  = height between equatorial plane and apex of the drop
- $h_2$  = total height of the drop

solid as much as possible. Before the drop is formed a dry gas atmosphere is introduced into the bell. Then the solid sample is heated up to the desired temperature. By lowering the movable rod (8) in the lid it is possible to bring the piece of salt in contact with the solid sample and thus to form the drop (photograph 1). When the drop is large enough the rest of the salt is taken away by raising the rod. It is possible to make drops of different size by adding more salt in the same way (photograph 2-3). It is also possible to remove the drop. The platinum wire from the rod (8) is dipped into the molten drop which is then cooled below the melting point ; after solidification it is heated slightly above the melting point and the rod is pulled up. The salt left on the surface of the solid sample can then be evaporated by heating the solid sample sufficiently above the melting point of the salt.

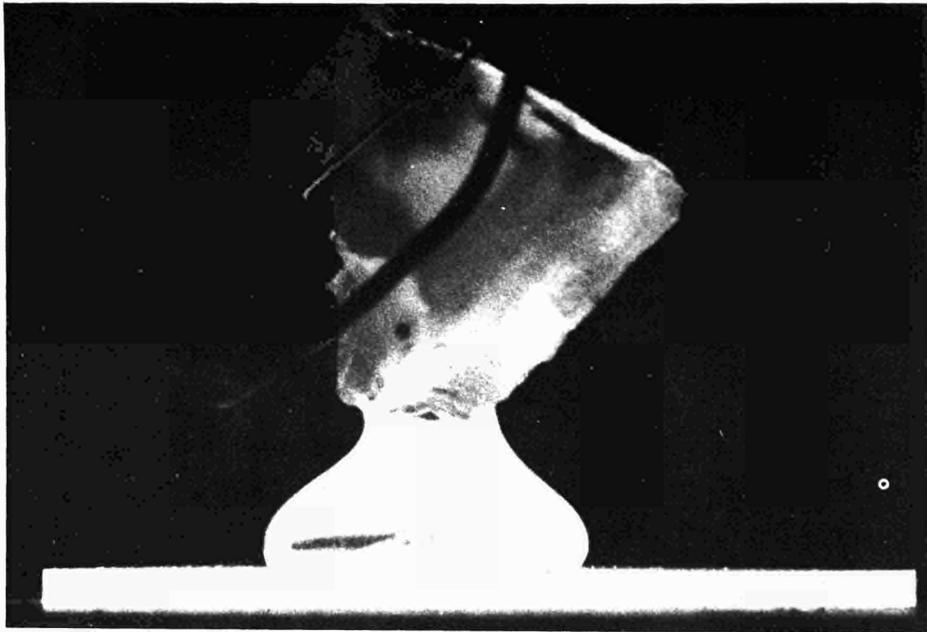
By this technique it is possible to perform several experiments under the same circumstances or by changing the gas atmosphere, the moisture contents of the gas atmosphere, etc..., without changing one of the other parameters.

#### 2.6.2. Mixtures of salts

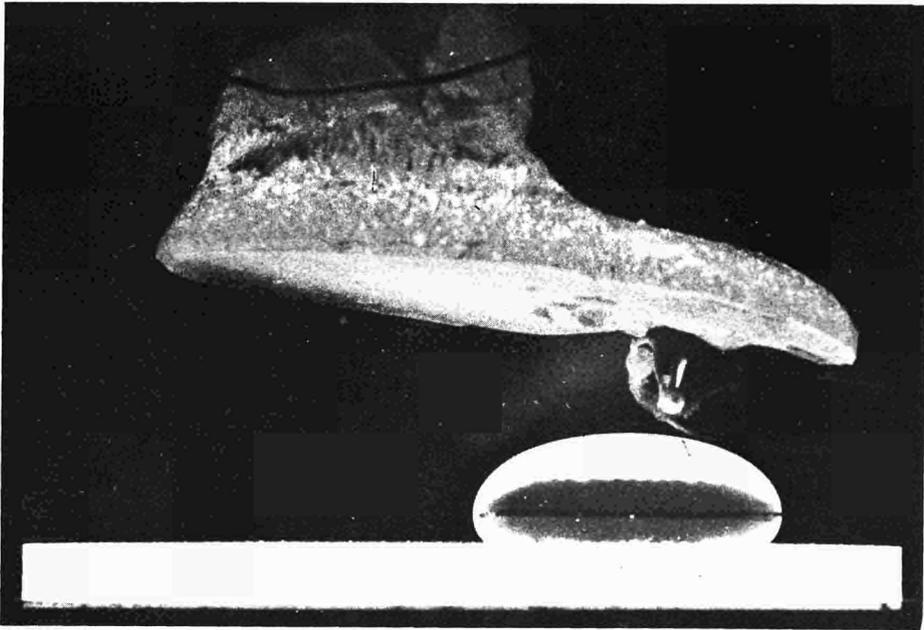
To obtain mixtures of molten salts the following technique was used. From one of the salts a small drop was formed on the solid sample by using the technique described above.

After removing the piece of the first salt from the rod, a piece of the second salt was fixed to the rod. The small drop of the first salt was left on the solid sample. The bell was closed and well degassed up to a temperature just below the melting point of the salt on the solid sample. Thereafter a gas was introduced which was dried by passing through a liquid nitrogen trap. It was possible to remove the salt left on the solid sample by heating it above the melting point putting in the movable thermocouple wires and cooling it down. By slowly reheating the drop could be removed by means of the thermocouple wires just after melting of the salt at the salt-solid interface. Subsequently a drop from the second salt was formed on the solid sample, and the salt frozen on the thermocouple wires was added. By means of the thermocouple it was possible to remove the salt mixture and to make a fresh drop of the mixture. Furthermore it

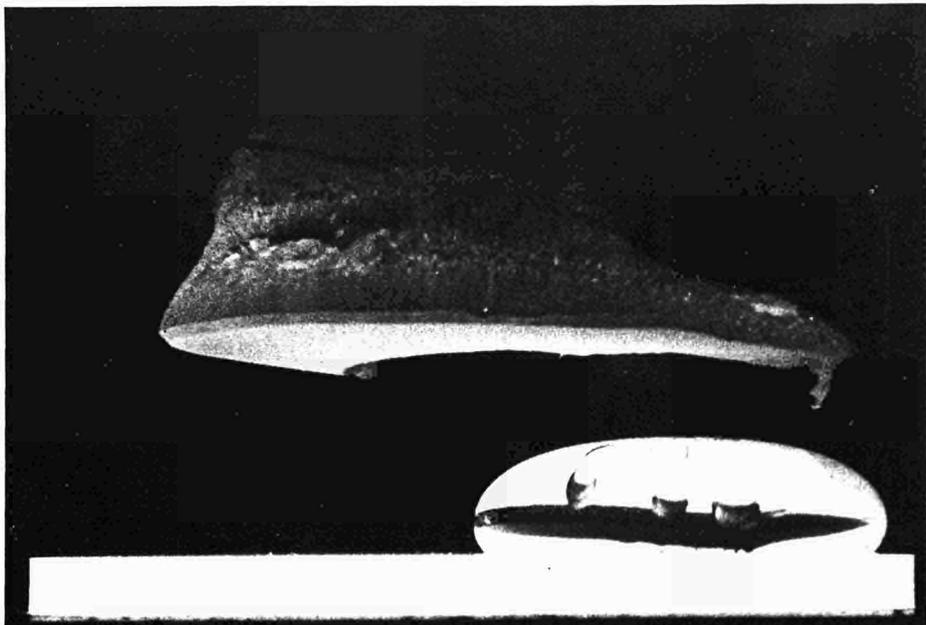




Photograph 1: Formation of sessile drop.



Photograph 2: Sessile drop.



Photograph 3: Sessile drop.



was possible to make other compositions of the two salts by the same technique. By knowing approximately the two quantities of the salt used it was possible to determine the composition of the mixture. To obtain the more exact composition, the salt was slowly cooled down and the temperature was measured at the moment the first crystals were observed in the salt. Also by warming up the crystallized salt the temperature was determined when the salt had just melted entirely. By means of the phase-diagram the composition could be determined using the average of the two temperatures, which had never a difference of more than 4° C. By this technique it is possible to perform several experiments under the same circumstances or by changing only one of the parameters.

## 2.7. Purification of the drop of molten salt

It is possible to purify the drop of salt. If a drop of molten salt is cooled down below its melting point, the impurities will be collected in the layer in contact with the graphite, which solidified last of all. If the salt drop is heated above its melting point again, this layer will melt the first, and if the as yet unmelted salt is then removed, the molten salt containing impurities is left behind on the graphite. The impurities can be removed by evaporation, and the lump of salt will be purer than before.

## 2.8. Photographic technique

A reflex camera (Edixa) was used with a tele-photo lens. The camera was fixed on one of the windows by a metal tube of variable length. Distance camera-molten salt drop  $\pm$  30 cm. Diaphragma normally used 32. Time of exposure was varied between 1/50 - 5 sec.

In the temperature range between 800°C and a maximum of 1150°C it was possible to obtain photographs of the sessile drop by using rapid films (400 ASA) and the light emitted from the drop. At temperature below 800°C, a spotlight was used in front of one of the windows, while taking the photographs through another window. Better results were obtained by placing a lamp in the bottom, which gave diffused illumination of the background of the drop.

## 2.9. Determination of the contact angle

The contact angle can be measured directly from the picture of the sessile drop and also be calculated from the dimensions of a sessile drop. The angle so obtained may be regarded as the integral of the sum of all various contact angles existing along the circumference of the drop. Bartell and Zuidema (58) proposed, when drops of relatively small size were used so that the shape of the drop would not be largely influenced by gravity, the following relation

$$\tan \frac{\theta}{2} = 2 \frac{h_2}{D_3} \quad (3)$$

$\theta$  being the contact angle (Fig. 3),  $h_2$  the total height of the drop and  $D_3$  the diameter of the contact surface of the drop with the solid. Mack and Lee (59) using the tables of Bashfort and Adams (8) tabulated the contact angle  $\theta$  for  $\theta > 90^\circ$  as a function of two parameters.

Staicopolus (12) gives in his study the contact angle as a function of the volume  $V$  of the drop and the maximum diameter  $D_1$  and  $h_1$ , the distance between equatorial plane and the apex of the drop. Bikerman (60) developed a method to calculate the contact angle by measuring the mean diameter of a drop  $d_1$  of known volume  $V$ . He

$$\text{tabulated } (\theta) = f\left(\frac{d_1^3}{V}\right)$$

## 2.10. Influence of drop size

If contact angles are to be calculated from the dimensions of a drop using formula (3) small drops have to be used. However, as the drop size decreases, the errors introduced in the measurements of  $h_1$  and  $d_1$  increase. Mack (55) gives the opinion that the use of small drops is advantageous if contact angles are measured.

His arguments are :

- 1) Small drops may be applied successfully to small plane areas in an irregular surface.
- 2) Small drops show a much greater variation in height for small variations in magnitude of contact angle than do large drops.
- 3) Small drops assume the advancing angle of contact while

larger drops exhibit a fluctuating angle of contact varying roughly between the advancing and receding angles.

Also Wartenberg (20) supposed that small drops were advantageous: his only argument was that during contraction of the drops this could happen with irregular edges.

Baes and Kellogg (56) and later Dismukes (57) demonstrate clearly that for surface measurements, the use of large drops is preferable.

Baes and Kellogg (56) have treated quantitatively the relation between size and the error in surface tension calculated by the Bashforth and Adams (8) method. These authors constructed a graph to show that increasing the size of the drop, appreciably lowers the "errors factor" defined as the ratio of the percentage error in the calculated surface tension value to the percentage error in the experimentally measured value of  $h_1$  being the distance from the equatorial plane to the apex of the drop.

Dismukes (57) discussed also another question concerning accuracy. The accuracy in  $h_1$  depends primarily on locating the equatorial plane. This plane is located by designating the two points where the tangents to the drop are vertical, namely, the two points at the ends of the maximum diameter. Clearly, these points can be designated more accurately the greater the curvature of the drop at these point is, or the greater the drop. Large drops are also to be recommended, because of the inability to place a lens close to the drop at high temperatures and because of the evaporation of the liquid when the surrounding vapour is not in equilibrium with the liquid, a condition which is difficult to accomplish, and even more difficult to maintain.

## 2.11. Calculation of surface tension

Equation 2 can further be developed. The following expressions can be found from analytical geometry for  $R_1$  and  $R_2$

$$\frac{1}{R_1} = \frac{y''}{(1 + y'^2)^{3/2}} \quad (4)$$

and

$$\frac{1}{R_2} = \frac{y'}{x (1 + y'^2)^{1/2}} \quad (5)$$

where  $x$  and  $y$  are the planar coordinates and where  $y'$  and  $y''$  are the first and second derivatives of  $y$  with respect to  $x$ .

For the excess pressure we can write  $\Delta p = \Delta \rho g h_1$  where  $\Delta \rho$  denotes the difference in density between the liquid and the gas phase and  $g$  is the acceleration due to gravity and  $h_1$  is the height from the equator plane up to the apex at the drop (Fig. 3).

Equation 2 becomes then

$$\Delta \rho g h_1 = \gamma LG \left( \frac{y''}{1 + y'^2)^{3/2}} + \frac{y'}{x (1 + y'^2)^{1/2}} \right) \quad (6)$$

Many are the investigators (8, 9, 10, 11, 12, 13) who proposed approximate solutions of the equation (6). Bashforth and Adams (8) were amongst the first to publish calculations on drop contours. In order to calculate the surface tension, most investigators measured in general the maximum diameter  $D_1$  of the drop and the vertical distance  $h_1$  between the equatorial plane and the apex of the drop in the plane of maximum vertical section.

Dorsey (9) proposed a formula with which it was possible to calculate the surface tension of drops with contact angles of  $45^\circ$  and larger than  $45^\circ$  while all formulae given by other investigators are for contact angles larger than  $90^\circ$ .

Wheeler et al (10) determined equations with which it was possible to calculate the surface tension with a pretended precision of 0,2%.

Staicopolus (12) obtained a solution of the differential equation (6) on a digital computer by using a numerical approximation.

Smolders and Duyvis (61) used a graphical interpolation method to calculate interfacial tensions. The method consisted in drawing an accurately scaled enlargement of the drop contour, comparing it with a number of theoretical curves, and interpolate it to get the correct values for the drop shape parameters, which make it possible to calculate the surface tension. Their method, however, is time consuming.

Recently Butler and Bloom (13) described a method of calculating the surface tension using a computer. They fitted experimental measurements of the shape of a sessile drop to the theoretical curve for the drop shape.

### 3. EXPERIMENTAL RESULTS WITH COMMENTS

#### 3.1. Contact angle measurements

The contact angles were measured directly on photographs taken from the drop. The accuracy was within  $2^\circ$ . In the literature methods are given to calculate the contact angle using the dimensions of the drop (see 2.9.). We used rather big drops (see 2.10) so that the method given by Bartell and Zuidema (58) is not applicable. Other methods use the volume of the drop as one of the parameter which is difficult to measure. Mack and Lee (59) tabulated the contact angle as a function of two parameters. In one of the parameters the quantity  $b$  (the curvature of the drop at the apex) is used. This is a quantity which is very difficult to determine accurately. We extended a computer program given by Butler and Bloom (13) so that it was possible to calculate the contact angle using the height  $h_1$  of the drop.

##### 3.1.1. Contact angle as function of temperature

In general the results obtained indicate that the contact angle varies little with the temperature. A similar insensitivity has been reported by other investigators (62, 63). However in one case a remarkable change was obtained, when LiF was brought in contact with Pt. Fig. 4 shows the results of this experiment.

##### 3.1.2. Contact angle as function of the time

The Figs. 5 and 6 show the contact angle for different salts as a function of the time. In Fig. 7 some results are compared with results given by Zhemchuzhina (64). The difference is remarkable and probably due to a great amount of impurities in the gas or liquid phase or impurities on the solid in the experiments of Zhemchuzhina.

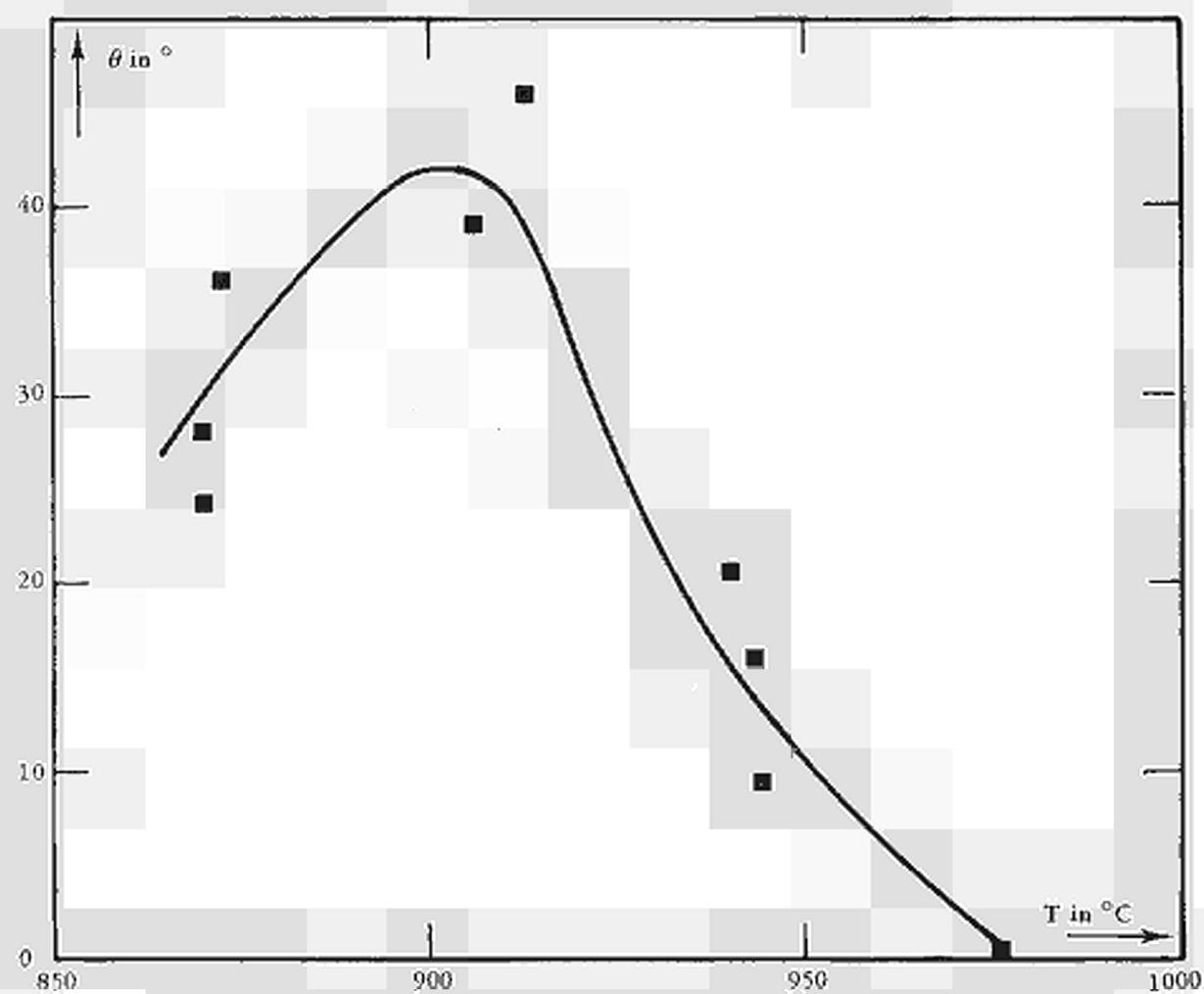


Fig. 4 Contact angle of LiF on platinum as a function of temperature.

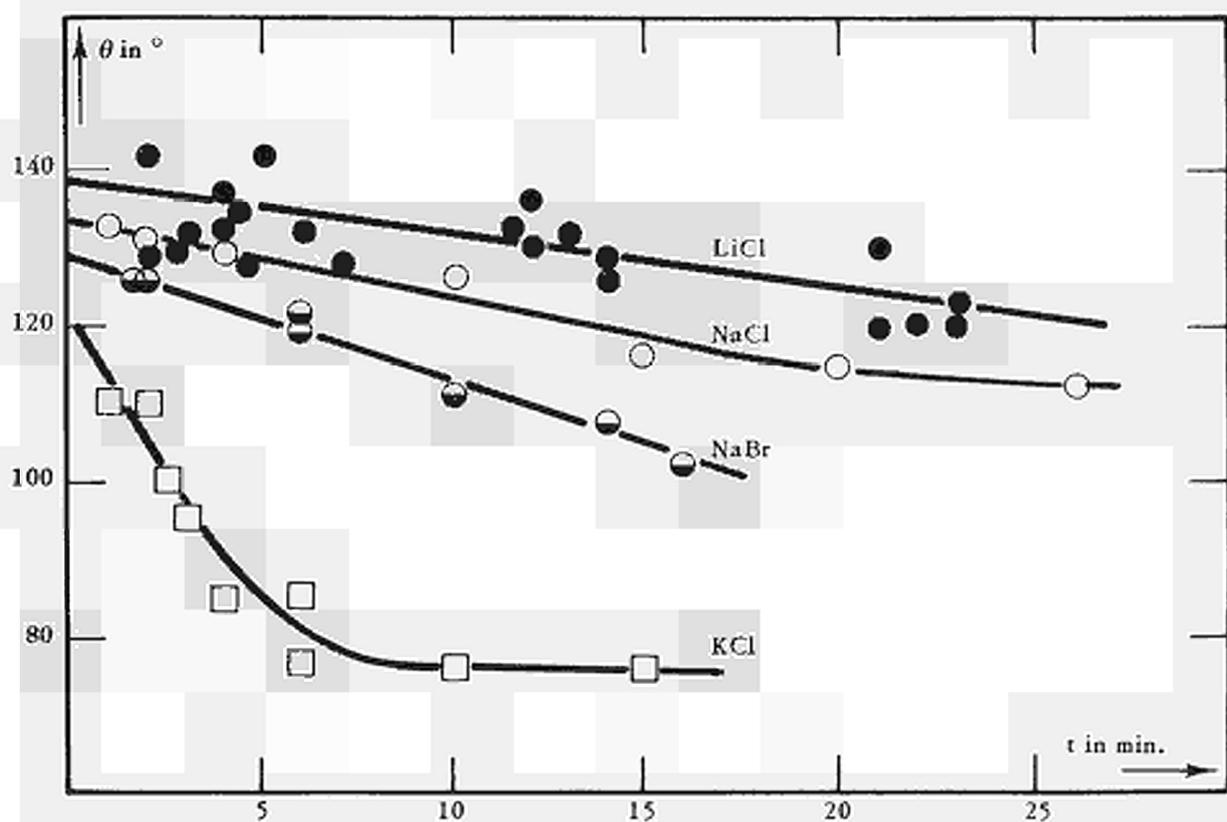


Fig. 5 Contact angle as function of the time.

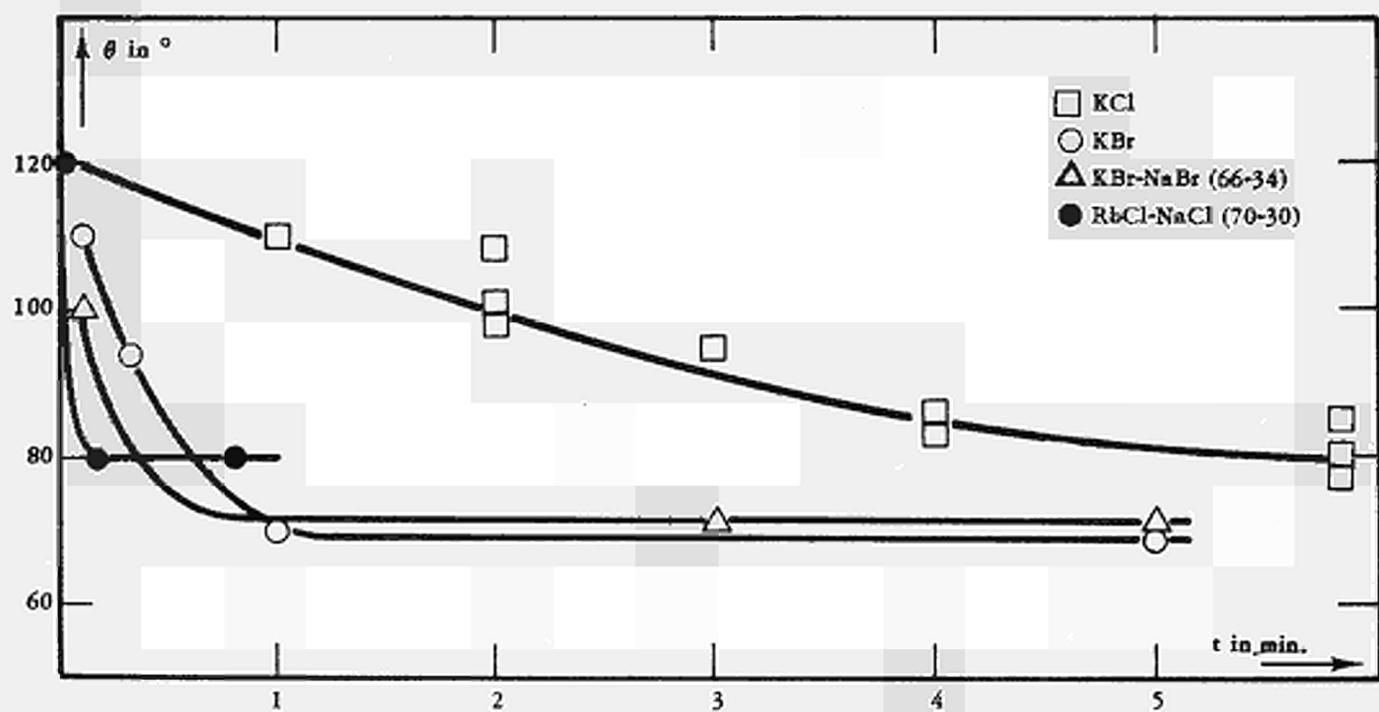


Fig. 6 Contact angle as function of time.

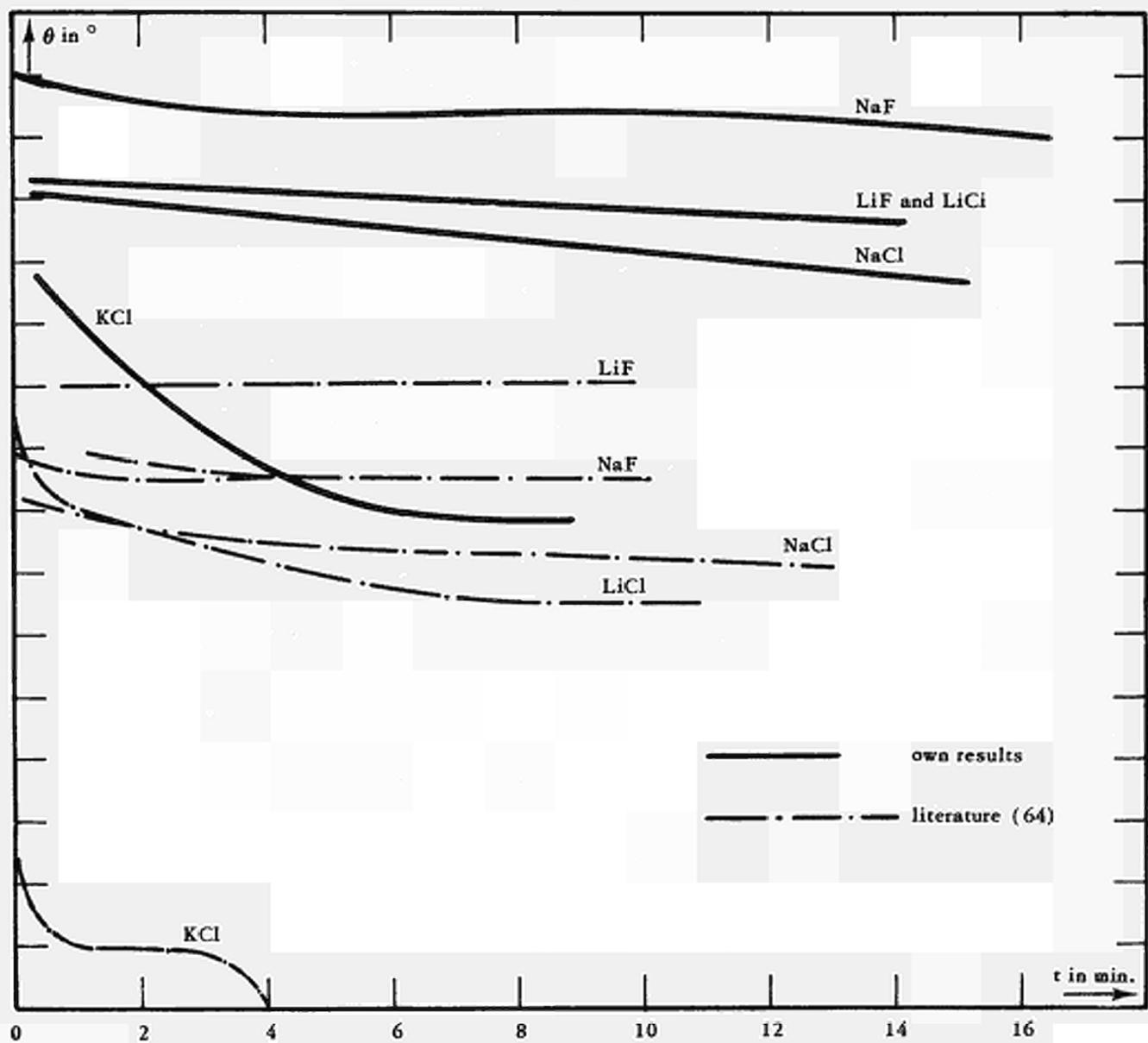


Fig. 7 Contact angle of different molten salts on graphite as a function of the time.

### 3.1.3. Reversibility of the contact angle

Remarkable was an experiment with NaCl. Having a contact angle of about  $120^{\circ}$  the salt and graphite were brought in contact with air at room temperature. Then after 5 minutes the sample was degassed at room temperature for about one hour. The contact angle of NaCl had been decreased and found to be  $50^{\circ}$ . After degassing the sample for 5 minutes at  $1000^{\circ}\text{C}$  the contact angle was increased again to about  $100^{\circ}$ .

### 3.1.4. Influence on the contact angle of the way of degassing graphite

The contact angle was highly influenced by the procedure of graphite degassing. In general irreproducible contact angles were obtained when graphite was degassed at  $20^{\circ}\text{C}$  and a vacuum of  $10^{-5}$  torr. Even after an overnight period when the graphite was degassed at room temperature and a vacuum of  $10^{-5}$  torr, the ionization tube gave a light blue colour when the graphite was heated and a lot of gas was emanated from the sample. The light blue colour indicates that water was present.

In general stable contact angles were obtained when the sample was degassed at  $1000^{\circ}$  -  $1100^{\circ}\text{C}$  even when the vacuum was only  $10^{-3}$  torr. Overholser and Blakely (65) did measurements on a type of graphite in which up till  $700^{\circ}\text{C}$  water presence was measured.

### 3.1.5. Contact angle as a function of the salt purity.

Using the technique described in 2.7. to purify the salt a serie of measurements was made with CaCl and graphite. Table 2 gives the average contact angle for the measurements between the formation of entirely new drops.

|        |     |     |
|--------|-----|-----|
| 1 drop | 132 | ± 2 |
| 2 drop | 155 | ± 3 |
| 3 drop | 156 | ± 1 |

Table 2 contact angle as a function of purity

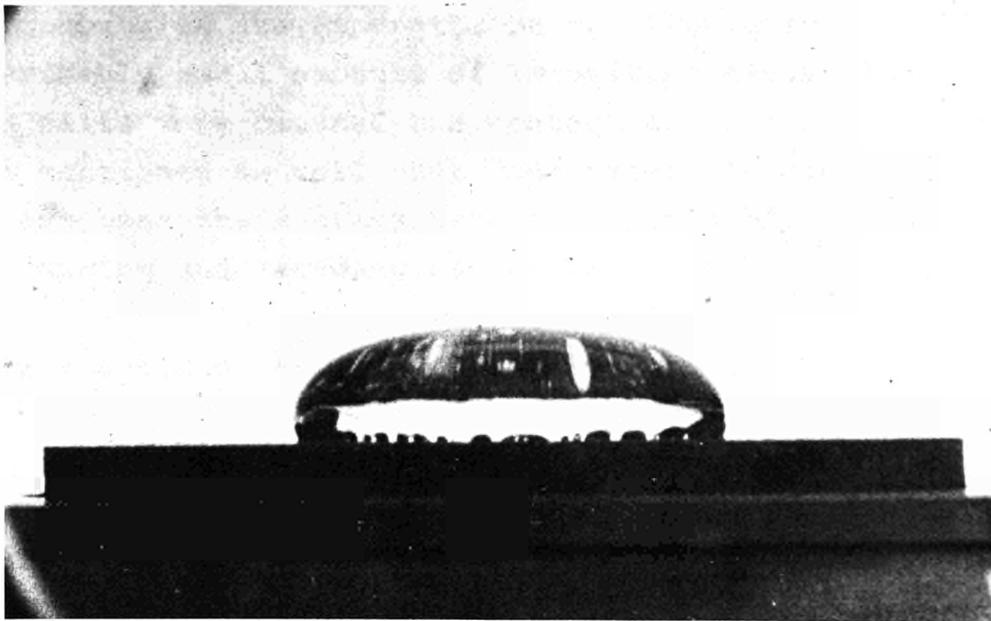


Fig. 8 Irregular contact angle.

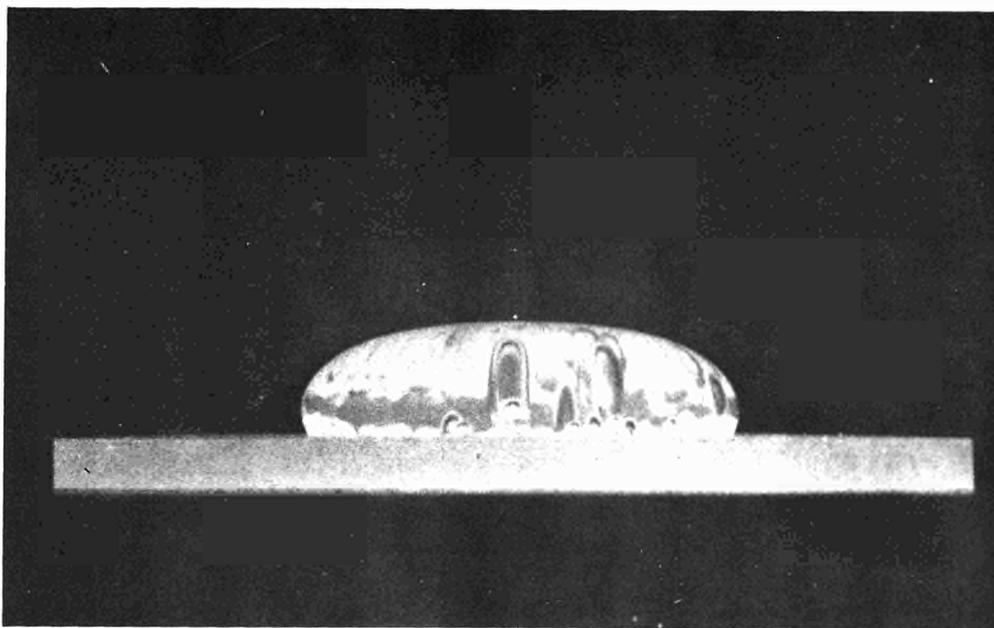


Fig. 9 Gasbubbles in the drop on the liquid-solid interface.



Also in the case that the salt contains impurities the drop wets the solid irregularly (Fig. 8). When such drops of molten salt are heated gasbubbles are generated on the liquid-solid interface (Fig. 9). Probably small amounts of impurities are surface active. When molten salts were cleaned the contact angle behaved reproducibly. Zisman (67) mentioned as well that when carefully cleaned liquids and solids are used the systems behaved reproducibly and furthermore, that the advancing and receding angle are the same.

### 3.1.6. Contact angle as a function of the composition of the melt

The dependence of the contact angle on the composition shows an identical positive deviation from a straight line for the systems KCl-NaCl and KF-NaF (Fig. 11 and 12). On the contrary, the system RbCl-NaCl (Fig. 10) shows a negative deviation. A remarkable characteristic of the last system is that a fast change in time is observed (Fig. 6) of the contact angle for several compositions. For the measurements the contact angles were supposed to be stable when the change was less than  $3^\circ$  per minute.

### 3.2. Surface tension measurements

Nearly all methods given in the literature use the two dimensions  $h_1$  and  $d_1$  of the drop to calculate the surface tension of the liquid. It is very difficult to measure accurately  $h_1$  because it is difficult to determine the apex of the drop and specially the equatorial plane (see 2.13). Butler and Bloom (13) use the dimensions of the whole contour of the drop in the surface tension calculations. They used the diameter of the drop at a different distance of the apex of the drop. Then they compared this points with a theoretical curve by means of a computer program. (In Fig. 13 the surface tension of LiF is plotted against the temperature). In the calculations the density data given by Klemm (67) are used. From the methods using  $h_1$  and  $d_1$ , in their calculations, the methods of Wheeler et al (11) and Porter (10) are chosen. Also the method of Butler and Bloom (13) based on a computer program was used. The calculations using the method of Butler and Bloom gave much better agreement with the measurements done by Jaeger (25) who used the maximum bubble pressure,

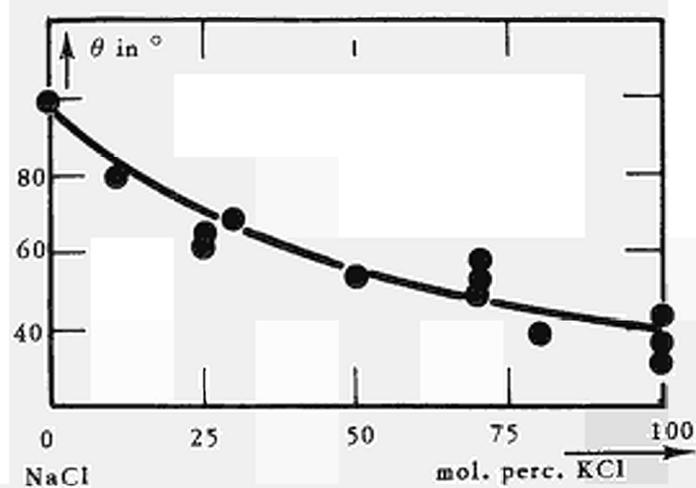


Fig. 10 Contact angle on graphite as a function of composition.

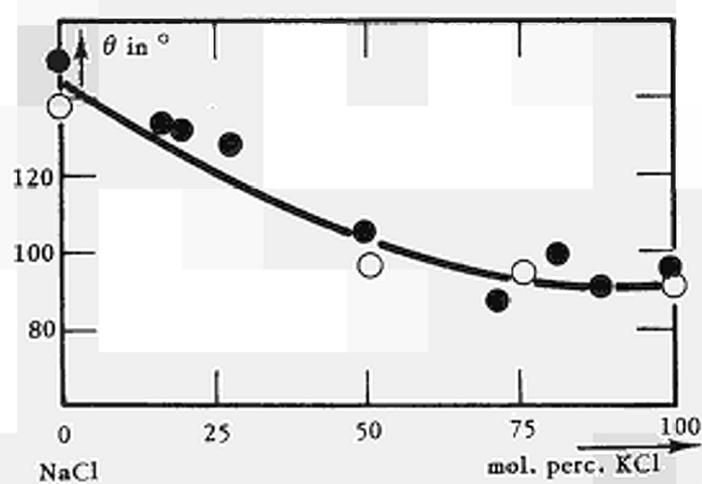


Fig. 11 Contact angle on graphite as a function of composition.

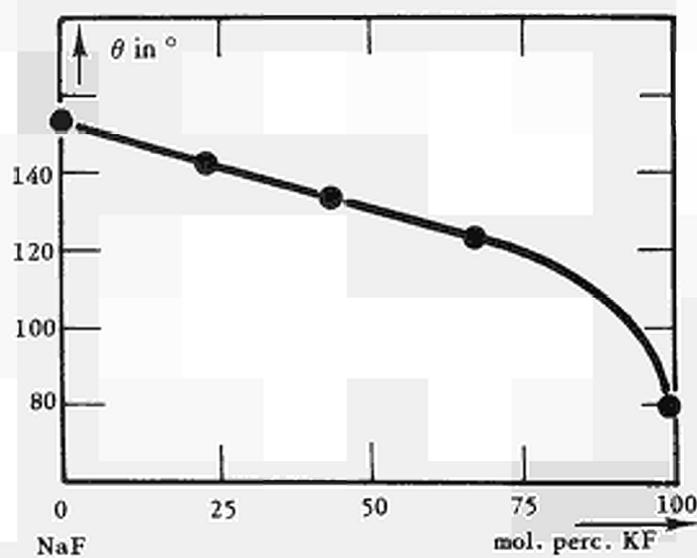


Fig. 12 Contact angle on graphite as a function of composition.

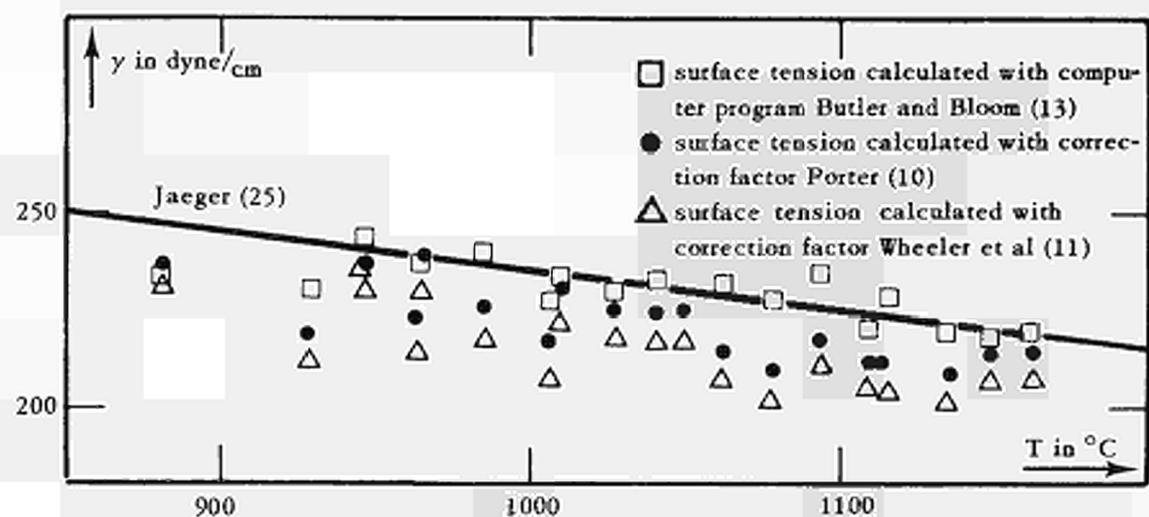


Fig. 13 Surface tension LiF as function of the temperature.

than the calculations using the method of Wheeler. The systematic error of the points calculated with the method of Wheeler is probably due to the systematic error in the determination of the equatorial plane. To show the influence of the drop size on surface tension calculation, a serie of experiments has been done for  $\text{CaCl}_2$  at  $1000^\circ\text{C} \pm 30^\circ$ . The results are reported in Fig. 14 giving the surface tension calculated by the formula (11) as a function of  $4h_1^2/D_1^2$ , being the parameter normally used in surface tension calculations.

#### 4. DISCUSSION

Investigations by von Wartenberg (20) indicated that the wetting of metals by molten salts is slightly influenced by the presence of oxygen. He assumed an exchange of  $\text{O}^{2-}$  ions from the liquid with the  $\text{O}^{2-}$  ions in the surface layer of the solid. The influence of oxygen on the wettability was also demonstrated by Kreyger (63). He was able to obtain a drop with a contact angle greater than  $90^\circ$  for LiF on platinum only in the absence of oxygen and moisture in the atmosphere surrounding the drop. In his studies of the anode effect and wettability Beliaev (69) established the existence of a direct relation between the contact of oxygen compounds of the electrolyte and the wettability of the anode by the electrolyte. The chapters 3.1.2., 3.1.3., 3.1.4. and 3.1.5. show that very small amounts of impurities have a great influence on the contact angle. It is therefore of great importance to determine first of all the contact angles of pure liquids in contact with pure solids in a pure gas atmosphere. Table 1 gives the contact angles of different molten salts under helium or nitrogen atmosphere. The accuracy is estimated from the spread in the results. The different values for one salt are from different series of measurements. For LiF a serie of contact angles is calculated from the photographed contours using a slightly modified computer program given by Butler and Bloom (13) (see anex), contact angle measurements of molten salts in contact with graphite given in literature are also reported in table 1.

The results obtained show that the contact angle for different anions but the same cations are all of the same order of magnitude, while for same anions but different cations it differ much. This may indicate that the interactions at the boundary are due to

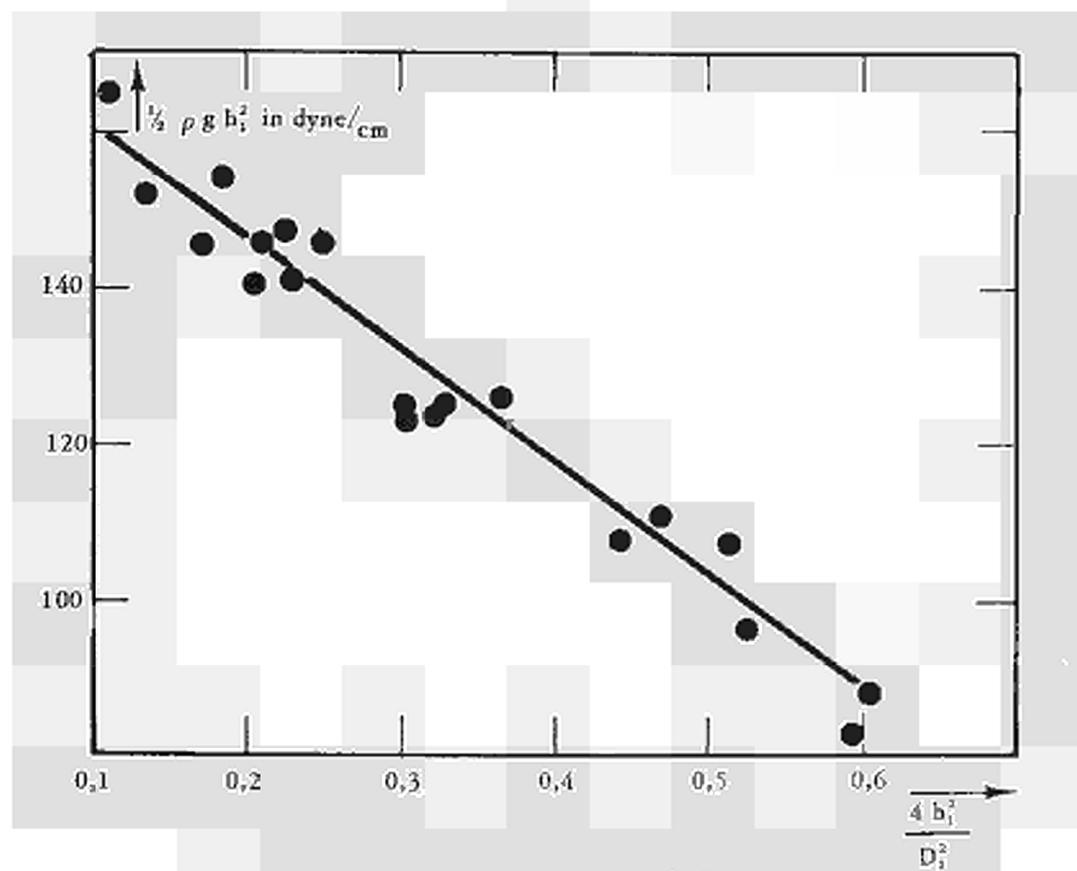


Fig. 14  $\frac{1}{2} \rho g h_i^2$  as function of  $\frac{4 h_i^2}{D_i^2}$  of  $\text{CaCl}_2$  at  $1000^\circ\text{C}$ .

TABLE I

Contact angle of different molten salts graphite  
at temperature range 800° - 1100°C.

|                   |              |             |      |
|-------------------|--------------|-------------|------|
| LiF               | 150 $\pm$ 5  | 130 $\pm$ 5 | (70) |
|                   | 127 $\pm$ 3  |             |      |
|                   | 131 $\pm$ 5  |             |      |
| NaF               | 145 $\pm$ 5  | 135         | (18) |
|                   | 137 $\pm$ 5  |             |      |
|                   | 139 $\pm$ 5  |             |      |
| KF                | 80 $\pm$ 5   | 60 $\pm$ 3  | (70) |
| RbF               |              | 38 $\pm$ 3  | (70) |
| CsF               |              | 41 $\pm$ 2  | (70) |
| LiCl              | 137 $\pm$ 5  |             |      |
|                   | 133 $\pm$ 3  |             |      |
|                   | 130 $\pm$ 3  |             |      |
| NaCl              | 128 $\pm$ 5  |             |      |
|                   | 125 $\pm$ 5  |             |      |
| KCl               | 70 $\pm$ 5   | 68 $\pm$ 2  | (70) |
| RbCl              | 47 $\pm$ 10  |             |      |
| NaBr              | 120 $\pm$ 10 |             |      |
| KBr               | 70 $\pm$ 5   |             |      |
| CaCl <sub>2</sub> | 156 $\pm$ 3  |             |      |
| CaBr <sub>2</sub> | >125         |             |      |

graphite-cations interactions since the influence differs much by different cations. With contact angle measurements it is probably possible to get knowledge about the interaction forces between the different cations.

#### 4.1. Contact angle as a function of the surface tension

In Fig. 15 the cosine of the contact angle between molten salts and graphite is plotted against the surface tensions of this liquids. Zisman (66) has pointed to a linear relationship that exists between the surface tensions of families of organic liquids and the contact angle between these liquids and solids. Similar relationships are found here for fluoride, chloride and bromide salts. Although more data are desired, the available results obtained now indicate that the change from nonwetting to wetting, in the sense of  $\theta > 90^\circ$  to  $\theta < 90^\circ$ , at  $1000^\circ\text{C}$  takes place at a surface tension of about 140 dyne/cm. for fluoride salts, 90 dyne/cm. for the chloride salts and 80 dyne/cm. for the bromide salts.

This conclusion might be important when predicting the permeation of molten salts into graphite.

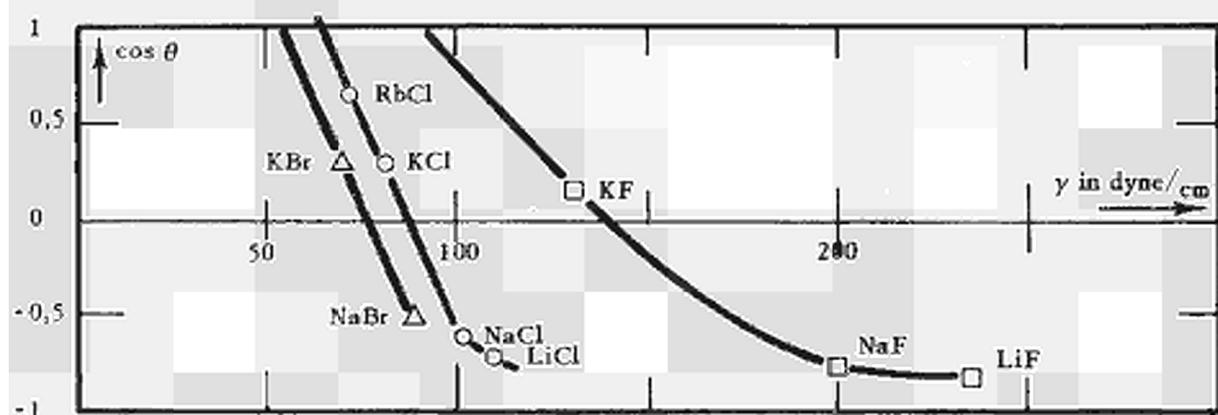


Fig. 15 Contact angle as function of the surface tension at 1000°C.

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ANNEX

The computer program given in this annex is a slightly modified computer program given by Butler and Bloom (13). With this new computer program it is also possible to calculate the contact angle. The instructions given by Butler and Bloom (13) have to be followed. The only difference is that in the input data the  $z$  coordinate of the contact plane of the liquid with the solid has to be added. The contact angle is then be given as the last data in the column under  $\phi$ .

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0001 DIMENSION XP(720), ZP(720), PSI(720)
0002 DIMENSION XTAB(101), Xb(50), Zb(50), X1(50), X2(50), Z2(50)
0003 DIMENSION BETAB(101)
0004 DIMENSION XRR(50), ZRR(50)
0005 DIMENSION XINT(50), ZINT(50), PINT(50)
0006 DIMENSION SNI(720), CSI(720)
0007 DIMENSION CODE(14)
0008 FFA(5,907) (BETAB(I), I=1,101)
0009 PEAD(5,906) FRRMAX,G
0010 FRRM2 = FRRMAX/2.
0011 FRRM4 = FRRM2/2.
0012 XP(1) = 0.
0013 ZP(1) = 0.
0014 SNI(1) = 0.
0015 CSI(1) = 1.
0016 PSI(1) = 0.
0017 C = 3.141593/720.
0018 F2 = 3.141593/180.
0019 DD 1 1=2,720
0020 C = I-1
0021 PSI(I) = R*C
0022 ICNT3 = SIN(PSI(I))
0023 1 CSI(I) = COS(PSI(I))
0024 R00 READ(5,903) N,FACT,DENS,(CODE(I), I=1,12)
0025 IF(N)99,999,807
0026 R07 IF(1-5C1801,801,812
0027 R12 WRITE(6,913)
0028 STOP
0029 R01 READ(5,905) (Z2(I), X1(I), X2(I), I=1,N)
0030 WRITE(6,901) (CODE(I), I=1,12)
0031 FACT=4./FACT
0032 FACT2 = FACT/2.
0033 N = N-1
0034 L=N-1
0035 PN=L
0036 DD 810 I=1,N
0037 X(I) = FACT2*ABS(X1(I+1)-X2(I+1))
0038 810 Z(I) = FACT*ABS(Z2(I+1)-Z2(I))
0039 X90=X(I)
0040 Z90 = Z(I)
0041 DD 802 I=2,N
0042 IF(X90-X(I))803,804,804
0043 803 X90=X(I)
0044 802 Z90=Z(I)
0045 R04 TAU=X90/Z90
C***** INITIATE FROM TABLE
0046 DD 2 I=1,101
0047 IF(BETAB(I)-TAU)2,4,5
0048 2 CONTINUE
0049 4 BETA = I-1
0050 GO TO 6
0051 5 D = I-2
0052 PETA = D*(TAU-BETAB(I-1))/(BETAB(I)-BETAB(I-1))
C***** INITIATE ZP BY ELLIPSE EQUATION
0053 6 DD 10 I=2,720
0054 L = SQRT(TAU**2*SNI(I)**2+CSI(I)**2)
0055 XP(I) = SNI(I)/L
0056 ZP(I) = (1. -CSI(I)/L)/TAU**2
0057 10 CONTINUE
0058 ICNT3 = 0
0059 P = X9C/XP(361)
0060 TETAMI = 0.
0061 RETAPL = 0.
C***** CALCULATE XP AND ZP UNTIL THEY CONVERGE TO WITHIN ERRMAX/4, OR
C***** THEY HAVE
C***** BEEN ITERATED 20 TIMES, WHICHEVER OCCURS FIRST
0062 24 ICNT = 0
0063 21 ERROR = 0.
0064 DX1 = P
0065 DZ1 = 0.
0066 DD 20 I=2,720
0067 F = R/(2.+BETA*ZP(I)-SNI(I)/XP(I))
0068 DX2 = F*CSI(I)
0069 DZ2 = F*SNI(I)
0070 TX = XP(I-1)+(DX1+DX2)/2.
0071 TZ = ZP(I-1)+(DZ1+DZ2)/2.
0072 ERROR = AMAX1(ERROR, ABS(TX-XP(I)) + ABS(TZ-ZP(I)))
0073 XP(I) = TX
0074 ZP(I) = TZ
0075 DX1 = DX2
0076 DZ1 = DZ2
0077 20 CONTINUE
0078 ICNT = ICNT + 1
0079 IF(ICNT-20)23,100,100
0080 23 IF(ERROR-ERRM4)100,100,21
C***** FIND CLOSEST XP, ZP TO DATA POINTS AND RECOMPUTE B. ITERATE UNTIL
C***** CONVERGES TO WITHIN FPRMAX/2. IF BETA OLD/BETANEW-1 IS WITHIN
C***** ERRMAX
C***** THEN EXIT, OTHERWISE RECYCLE
0081 100 ICNT2 = 0
0082 BMI = 0.
0083 BPL = 0.
0084 103 DD 101 I=1,N
0085 XB(I) = X(I)/R
0086 ZB(I) = Z(I)/B
0087 101 CONTINUE
0088 M = 1
0089 DD 200 I=1,N
0090 K = M
0091 DD 250 J=K,720
0092 M = J+1
0093 XR(M) = XP(M)
0094 ERR = (XP(M)-XP(J))*(XB(I)-XP(M))+(ZP(M)-ZP(J))*(ZB(I)-ZP(M))
0095 IF(ERR)251,252,250
0096 250 CONTINUE
0097 WRITE(6,900)
0098 GO TO 998
0099 252 XINT(I) = XP(M)
0100 ZINT(I) = ZP(M)
0101 PINT(I) = PSI(M)
0102 GO TO 200
0103 251 A = ((XP(J)-XB(I))*(XP(J)-XP(M))+(ZP(J)-ZB(I))*(ZP(J)-ZP(M)))/
1.((XP(J)-XP(M))**2+(ZP(J)-ZP(M))**2)
0104 XINT(I) = A*XP(M)+(1.-A)*XP(J)
0105 ZINT(I) = A*ZP(M)+(1.-A)*ZP(J)
0106 PINT(I) = A*PSI(M)+(1.-A)*PSI(J)
0107 M = M-1
0108 CONTINUE
0109 BOLD = B
0110 DELXT = 0.
0111 DD 300 I=1,L
0112 DELXT = DELXT+XB(I)-XINT(I)
0113 DELXT = DELXT/PN
0114 IF(DELXT)350,310,352
0115 350 BMI = B
0116 DELBM = DELXT
0117 IF(BPL)353,354,353
0118 RPL = B
0119 DELRP = DELXT
0120 IF(BMI)353,351,353
0121 R = 1.1*B
0122 GO TO 360
0123 354 R = .9*B
0124 GO TO 360
0125 353 B = RPL - DELRP*(BPL-BMI)/(DELBP-DELB)
0126 GO TO 360
0127 360 IF(ABS(BOLD/R-1.)-FRRM2)310,310,311
0128 311 ICNT2 = ICNT2 + 1
0129 IF(ICNT2-20)103,312,312
0130 312 WRITE(6,908)
0131 GO TO 998
0132 310 RETOLD = BETA
0133 DELT = 0.
0134 DD 315 I=1,L

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0135      315 DELZT = DELZT+ZB(I)-ZINT(I)
0136      DELZT = DELZT/PN
0137      IF(DELZT)322,998,323
0138      322 BETAMI=BETA
0139      DELM = DELZT
0140      IF(BETAPL)324,330,324
0141      330 BETA = 1.1*BETA
0142      GO TO 326
0143      323 BETAPL = BETA
0144      DELP = DELZT
0145      IF(BETAMI)324,325,324
0146      325 BETA = .9*BETA
0147      GO TO 326
0148      324 BETA=BETAPL-DLLP*(BETAPL-PETAMI)/(DELP-DLLM)
0149      GO TO 326
0150      326 IF(ABS(RETOLD/BLTA-1.)-ERRMAX)998,998,328
0151      328 ICNT3 = ICNT3+1
0152      IF(ICNT3-20)24,327,327
0153      327 WRITE (6,912)
0154      GO TO 998
0155      998 DXBAR = 0.
0156      DZBAR = 0.
0157      DX2BAR = 0.
0158      DZ2BAR = 0.
0159      T = G*DENS**2/BETA
0160      DO 950 I=1,N
0161      PINT(I) = PINT(I)/R2
0162      XINT(I) = XINT(I)*R
0163      ZINT(I) = ZINT(I)*B
0164      XRR(I) = X(I) - XINT(I)
0165      ZRR(I) = Z(I) - ZINT(I)
0166      X1(I+1) = (X1(I)-.5*(X1(I+1)+X2(I+1)))*FACT
0167      DX2BAR = DX2BAR + XRR(I) * XRR(I)
0168      DZ2BAR = DZ2BAR + ZRR(I) * ZRR(I)
0169      DZBAR = DZBAR+ZRR(I)
0170      950 DXBAR = DXBAR+XRR(I)
0171      PINT(N) = PINT(N)/R2
0172      XINT(N) = XINT(N)*R
0173      ZINT(N) = ZINT(N)*B
0174      XRR(N) = 0.
0175      ZRR(N) = Z(N) - ZINT(N)
0176      X1(N+1) = 0.
0177      DXBAR = DXBAR/PN
0178      DZBAR = DZBAR/PN
0179      SDEV = SQRT ((DX2BAR + DZ2BAR) / (PN-1.))
0180      SDEVX = SQRT (DX2BAR/ (PN-1.))
0181      SDEVZ = SQRT (DZ2BAR/ (PN-1.))
0182      WRITE (6,910)
0183      WRITE (6,909) (X(I),Z(I),PINT(I),XINT(I),ZINT(I),XRR(I)
0184      1,ZRR(I),X1(I+1),I=1,N)
0185      WRITE (6,911) T,BETA,B,DENS,DXBAR,DZBAR,SDEVX,SDEVZ,SDEV
0186      GO TO 800
0187      999 WRITE (6,902)
0188      STOP
0189      900 FORMAT (29H NO INTERPOLATION POINT FOUND)
0190      901 FORMAT (1H,10X,12A4//)
0191      902 FORMAT (20H JOB DONE. GOODBYE.)
0192      903 FORMAT (13,2F10.5,12A4)
0193      904 FORMAT (3F10.5)
0194      905 FORMAT (2F10.5)
0195      906 FORMAT (8F9.5)
0196      907 FORMAT (38H B HASNT CONVERGED AFTER 20 ITERATIONS)
0197      908 FORMAT (2F10.5,F10.3,5F10.5)
0198      909 FORMAT (6X,1MX,9X,1M2,9X,3MHPH,6X,2MX*,8X,2HZ*,8X,2HOX,8X,2HDZ,6X,
0199      14MERRX//)
0200      910 FORMAT (/10H TENS = ,F10.5/10H BETA = ,F10.5/10H B = ,F10
0201      1.5/10H DENSITY = ,F10.5/10H DXBAR = ,F11.6/10H DZBAR = ,F11.6/10H
0202      2 SDEVX = ,F11.6/10H SDEVZ = ,F11.6/10H SDEV = ,F11.6)
0203      911 FORMAT (4H BETA HASNT CONVERGED AFTER 20 ITERATIONS)
0204      912 FORMAT (19H N GREATER THAN 50.)
0205      END

```



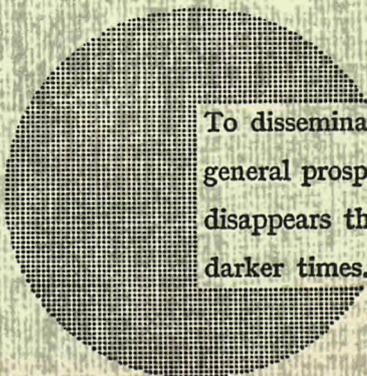
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Alfred Nobel

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