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CERTAIN PROBLEMS RELATED TO THE VISCOSITY OF FUSED METALS

By Ye. G. Shvidkovskiy

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CERTAIN PROBLEMS RELATED TO THE VISCOSITY OF FUSED METALS

/Following is a full translation of a Russian-language monograph entitled Nekotoryye voprosy vyazkosti rasplavlennykh metallov (Certain Problems Related to the Viscosity of Fused Metals), by Ye. G. Shvidkovskiy, Moscow, 1955, 206 pages, published by the State Publishing House for Technical and Theoretical Literature./

Annotation

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This monograph examines the theory of the torsional oscillation method for measuring the viscosity of liquids, and experimental technical problems associated with the use of this method, presents the results obtained during the measurement of the viscosity of fused metals and alloys, and gives a theoretical interpretation of certain problems concerned with the nature of the liquid state (structure of the liquid, mechanism of the viscous flow, kinetics of crystallization, the effect of insoluble impurities on the viscosity, etc.).

The monograph includes original studies conducted by the author and his associates.

This book is of interest to scientific workers, such as physicists and engineers, engaged in a study of the problem of the liquid state, and also to aspirants (post-graduate students) and senior students, specializing in the field of molecular physics and physics of metals.

Table of Contents

Page

Certain basic designations 1

Preface 2

Introduction 3

Chapter I
Experimental Methods for Measuring the Viscosity of Liquids

1. Capillary outflow method 7
2. Rotating cylinder method 13
3. Falling ball method 14
4. Non-stationary methods of viscosity measurement 16

Page

5. Formulation of the problem related to the theory of a non-stationary method of viscosity measurement 19

Chapter II
Theory of the Torsional-Oscillation Method for Measuring the Viscosity of Liquids

1. Basic theoretical concepts of the method 22

2. Velocity distribution 23

3. Moment of frictional forces on the internal surfaces of the small bucket 26

4. Equation describing the oscillations of the bucket 27

5. First approximation for the friction function L 31

6. Physical meaning of the first approximation for the friction function 32

7. Second approximation for the friction function L. Low-viscosity liquids 34

8. Equation for calculating the viscosity 36

9. Second approximation for the friction function L. High-viscosity liquids 41

10. Liquids with an intermediate viscosity value 48

11. Evaluation of the role performed by non-linear terms in the equation describing the motion of the liquid 49

12. Thickness of the liquid flow (stream) adjacent to the wall of the bucket 53

13. Conclusion on the general theory of the method 54

Chapter III
Theory of the Method (Continuation)

1. Plotting of $\bar{\delta}(\xi)$ and $\bar{f}(\xi)$ curves 55

Page

2. Range of variations in the viscosity which can be investigated 59

3. Height to which the bucket can be filled with liquid 62

4. Sensitivity of the instrument to viscosity changes 63

5. Condition specifying the absence of turbulence 66

6. Value of the initial amplitude 67

7. Conditions causing the appearance of convection inside the bucket 68

8. Influence of an off-centering of the suspension device 70

9. Measurement of the moment of inertia of the suspension system 71

10. Determination of $\delta_0(t)$ and $\tau_0(t)$ 72

11. Calculation of the attenuation (damping) decrement 73

12. Accounting for the condensation of liquid on the lid of the bucket 75

13. Correction for a protruding column 79

14. Calculation of the suspension system 82

15. Experimental check of the calculation system used in the theory of the method 85

F
8
8

Chapter IV
Experimental Realization of the Method and the Results Obtained

1. Viscosity of steels 90

2. Viscosity of cast iron and ferrochromes 93

3. Viscosity of lead, tin and bismuth 95

4. Viscosity of aluminum 98

Page

5. Viscosity of tin-lead alloys 99

6. Viscosity of tin-bismuth alloys 100

7. Viscosity of tin during supercooling 102

8. Viscosity of lead-bismuth alloys. Viscosity in a heterogenous region 103

9. Viscosity of zinc and cadmium 104

10. Certain remarks concerning the design of the viscosimeter 105

Chapter V
Relation Between the Hydrodynamics of a Viscous Liquid and the Theory of Hereditary Media and Rheology

1. Tangential and bulk viscosity 107

2. Theory of hereditary media and rheology 109

3. Thermodynamic derivation of a linear rheological equation 114

4. Energy of absorption in a relaxing medium 116

5. Viscosity of a liquid from the standpoint of the theory of hereditary media 118

6. Certain experimental results 120

Chapter VI
Structure and Viscous Properties of Metallic Liquids

1. A. I. Bachinskiy's viscosity equation 125

2. Structure of a liquid 127

3. The phenomenon of crystallization of liquids 138

4. Viscosity of metals and A. I. Bachinskiy's formula 140

5. Mechanism of the viscous flow of liquids 147

Page

6. Viscosity-composition isotherms of binary alloys 153

7. Viscosity of heterogenous systems and sound absorption in such systems 156

8. The viscosity and critical temperature of liquids 160

Appendix -- List of books published by the State Publishing House of Technical and Theoretical Literature (GITTL) 165

Figure Appendix 166

Certain Basic Designations

q -- Cyclic frequency of macroprocesses (torsional oscillations of the suspension system, acoustic waves, external effects).

τ -- Period of these processes.

v, v_r, v_z -- Velocity components in cylindrical coordinates.

K -- Axial moment of inertia of the suspension system.

δ -- Logarithmic damping decrement of oscillations of the suspension system.

ϑ -- Relaxation time.

ρ -- Density.

ν, ν' -- Kinematic shear viscosity and bulk (second) viscosity, respectively.

η, η' -- Dynamic shear viscosity and bulk (second) viscosity, respectively.

R -- Internal radius of the small bucket.

H -- Half of the height to which the small bucket is filled with liquid.

σ -- Factor (multiplier) in the formulas used for calculating the viscosity, which takes into account the effect exerted by the bottom and lid of the small bucket; in Chapter V -- the stress.

ϵ -- Relative deformation.

G_0, G_∞ -- Moduli of rigidity during prolonged and instantaneous load.

$y = R^2 \frac{q}{\nu}$ -- Basic parameter in the theory of the method for measuring the viscosity.

$\xi = \sqrt{y}$ -- In Chapter V, the relaxation parameter.

T -- Absolute temperature.

t° -- Temperature according to the Celsius (centigrade) scale.

Preface

The study of the viscous properties of metallic liquids occupies a prominent place in the elaboration of a theory of the liquid state.

Metallic liquids are characterized by a relatively simple structure, and therefore represent a favorable object of research from the standpoint of the establishment of connections between the structure and macroscopic properties. In addition, a knowledge of the viscous properties of fused metals is also very important from an applied (practical) standpoint. In the Soviet Union, the problem involving a study of the viscosity of metallic liquids was made necessary as a result of the technical progress achieved during the first five-year plans. As later years have shown, this problem became one of the most important problems dealing with the liquid state. However, the experimental study of the viscosity of fused metals is associated with considerable difficulties, resulting from the actual lack of a method for measuring the viscosity, which would be sufficiently convenient during the course of work with metallic liquids.

In addition, the absence of a monograph, describing the basic laws and rules applicable to the viscous properties of metallic liquids and their physical interpretation, represents a notable gap in the theory of the liquid state. This book has been written precisely in order to partially fill this gap, and also in order to make available to experimenting physicists the theory and practice of the torsional oscillation method for measuring the viscosity of fused metals. This book does not pretend to give an exhaustive coverage of all the experimental data in this field, since it is based primarily on work done by the author and his associates. During the course of this work, a number of new problems have appeared, related to viscous properties of fused metals, and some of these problems are included in this book for purposes of presentation and discussion.

The first half of this book (Chapters I-III) is devoted to the theory of the torsional oscillation method for measuring the viscosity. The second half (Chapters IV-VI) presents the results of the experimental study of the viscosity of a number of metallic systems and also an attempt to clarify the relationship between the viscous properties and the structure of the liquid.

The author of this book wishes to express his deep gratitude to A. S. Predvoditelev for his constant attention and valuable discussion during the course of work on the development of this problem.

My students took part in the work dealing with individual problems, and their work represents a valuable contribution to the research carried out in connection with the writing of this book. I extend my deep gratitude to all of my students, and especially to G. I. Goryaga and L. S. Priss, who have solved a number of independent problems related to the viscous properties of metallic liquids.

The author also extends his sincere thanks to the late V. I. Danilov, and to B. V. Deryagin and B. N. Finkel'shteyn, who have critically reviewed the manuscript and have made a number of valuable remarks.

Moscow, October 1954 Ye. Shvidkovskiy

Introduction

The viscous properties of a liquid, which constitute the expression of a process involving the irreversible conversion of the energy of macroscopic movements, are characterized by two factors: the shear or standard viscosity (η) and the bulk or second viscosity (η').

It is assumed that the connection between the components of the tensor of viscous stresses σ_{ik} and the components of the deformation velocities is expressed by the following equation:

$$\sigma_{ik} = \eta\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial v_l}{\partial x_l}\right) + \eta'\delta_{ik}\frac{\partial v_l}{\partial x_l},$$

where $v_{i,k,l}$ are the components of the flow rate of the liquid, and δ_{ik} is the unit tensor, having components equal to unity when i = k, and equal to zero when i $\neq$ k.

This expression represents a generalization for arbitrary deformations of Newton's well-known law of internal friction, which states that the viscous stress under shearing conditions is proportional to the deformation rate, i.e., in our recording system:

$$\sigma_{ik} = \eta\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right) \qquad (i \neq k).$$

Since in case of an incompressible liquid, $\frac{\partial v_l}{\partial x_l} = 0$ (div v = 0), the viscous properties of flows, in which the compressibility can be disregarded, can be described to a sufficient extent by means of the single factor η. However, we should not forget that the same liquid can exhibit a different behavior in regard to compressibility depending upon the process which takes place in the liquid. For example, water behaves as an incompressible liquid when it flows through a pipe, and as a compressible liquid during the propagation of acoustic waves through this water.

Further in this text, with the exception of Chapter V, we shall be concerned only with the shear viscosity factor η, which will be often designated, for the sake of brevity, simply as viscosity.

Along with η and η', the kinematic viscosity factors ν and ν' also play a role in hydrodynamics, and these factors are determined by the following relations:

$$\nu = \frac{\eta}{\rho}, \quad \nu' = \frac{\eta'}{\rho},$$

where ρ is the density of the liquid. In the literature, η and η' are frequently designated as the dynamic viscosity factors, thus pointing out their difference from kinematic viscosity factors.

Based on the above relations, the dimensions of the viscosity factors can be easily established:

$$[\eta] = [\eta'] = \mathrm{g} \cdot \mathrm{cm}^{-1} \cdot \mathrm{sec}^{-1},$$
$$[\nu] = [\nu'] = \mathrm{cm}^2 \cdot \mathrm{sec}^{-1}.$$

Liquids are designated as normal in regard to their viscous properties if η and η', and consequently also ν and ν', are independent of the flow rate.

The experimental material available on the viscosity of metallic liquids (pure metals and alloys) is rather limited, which is due to the great difficulties associated with the conduct of corresponding research studies. However, in view of the fact that the molecular mechanism of a viscous flow constitutes one of the major aspects of the theory of the liquid state of matter, the study of the relationship between viscosity and the parameters expressing the condition of the liquid is of great scientific importance.

Already D. I. Mendeleyev, in his "Foundations of Chemistry," wrote: "The connection which (already noted in part) exists between the viscosity and other physical and chemical properties compels us to assert that the magnitude (or value) of internal friction will play an important role in molecular mechanics."

N. S. Kurnakov and A. I. Bachinskiy must be credited with the important idea of a connection between viscous properties and the structure of a liquid. Since metallic liquids have the most simple structure and have been more fully investigated from a structural standpoint than other substances, these liquids constitute a suitable object for research purposes.

On the other hand, the viscous properties of metals and alloys play an important role in the casting technology of nonferrous and ferrous metals (metal teeming, ingot crystallization in casting molds, production of continuous billets, etc.), and also in connection with new problems in the field of metallurgy related to the production of heat-resistant alloys. The importance of an experimental study of the properties of fused metals, including the study of viscosity, was pointed out by the prominent Soviet metallurgist A. A. Baykov.

The study of the nature and type of connection between the structure of a liquid and its viscous (and other) properties constitutes one of the important problems forming a part of the general problem of the liquid state. Apparently the physical properties of a liquid are determined to the same extent by its structure as the properties of a crystal are determined by the structure of the latter.

Any theory of the viscous flow is based (in an explicit or non-explicit form) on the assumption made in connection with the character of the structure of the liquid. For this reason, a study of the connection between the structure and the viscosity can be conducted by analyzing the extent to which a given viscosity theory can be experimentally corroborated for liquids of different structures.

Certain attempts in this direction are presented in this book; however, in view of the extremely rudimentary nature of all viscosity theories and the still unclarified reasons for the wide discrepancies in the experimental results on the viscosity of metallic liquids, these attempts can be considered merely as a first step in this direction.

A medium, in which the product of the relaxation time and the variation rate of the stress is much smaller than the stress itself, when the "prolonged" modulus of rigidity is equal to zero, can be considered as a viscous liquid in the usual (Newtonian) conception. In this case, η and η' represent the product of the relaxation time of the stress and the instantaneous modulus of elasticity (in case of shear deformations and a uniform manifold compression, respectively).

On this basis, it is possible to use the concept of viscosity in the case of heterogeneous systems, which is essential for the understanding of viscous properties of alloys in the field of solidification (or setting).

The viscosity of a binary alloy, during the transition from the state of a homogeneous liquid into the heterogeneous region of the fusion diagram, increases several hundreds of times over a small range of a temperature drop as a result of the formation and growth of solid phase crystals of one of the components. It should also be noted that (during the propagation of a wave process in a heterogeneous liquid system), a maximum absorption is observed at a definite value of the viscosity of the uniform liquid making up a part of the heterogeneous system.

Thus there is a definite connection between the crystallization kinetics of a binary alloy and changes in its viscous properties, which makes it possible to study the process involving the crystallization of an alloy according to the temperature vs. viscosity curve. Moreover, the existence of a relationship between viscosity and crystallization not only in alloys, but also in pure liquids, is indicated by the fact that, during the supercooling of tin, a characteristic branching in the temperature vs. viscosity curve is observed, as well as a sharp increase in the temperature coefficient of the viscosity below the crystallization point. A study of this relationship also constitutes one of the important tasks in connection with the problem of the liquid state.

In connection with the already previously mentioned discrepancies in the experimental results obtained during the determination of the viscosity of fused metals, it should be noted that the addition of insoluble impurities to the liquid results in a change in the viscosity of the system: liquid + particles, considered as a single whole system.

In view of the fact that metallic liquids, unless they were subjected to a special purification treatment, contain insoluble impurities, the viscosity of these liquids is determined to a considerable extent by these impurities. For this reason, the presence of insoluble impurities, mainly lower oxides, in a fused metal usually exerts a greater effect on the viscosity than the contamination of this fused metal with small amounts of another metal. As a rule, this particular fact was previously disregarded during the measurement of the viscosity of liquid metals. It is possible that this is the cause for the discrepancies in the results obtained by different authors. However, the possibility is not excluded that the main reason for these discrepancies is to be found in factors of an experimental and methodical nature. F88

For this reason, this book presents only data obtained with the aid of the torsional oscillation viscosimeter, the theory of which is examined in the first portion of the book, and the data obtained in this manner are not compared with other data reported in the literature.

All the results dealing with viscosity listed below refer to metallic systems, which were not subjected to a process involving the removal of insoluble impurities, unless such a process is specifically mentioned. Certain other problems outlined above are examined in this book as part of an extensive formulation of the problem and may be characterized as "working" hypotheses, which make it possible to clarify to a certain extent the nature of a metallic liquid.

Chapter I

Experimental Methods for Measuring the Viscosity of Liquids

Experimental methods for measuring the viscosity of liquids are described in a monograph by Marr (1) (Note: See bibliography at the end of this chapter). Viscosimetric studies conducted up to 1939 are systematically classified according to the measurement methods used by M. P. Volarovich (2). Therefore, we shall refer to the available methods for measuring the viscosity only to the extent necessary for our direct purposes.

All the principal methods used for measuring the tangential (shear) viscosity can be divided into stationary and non-stationary methods. The first category includes the capillary outflow method, the rotating cylinder method and the falling ball method. The second category includes various methods, which are based on the observation of the torsional oscillations of a system connected with the liquid being studied.

1. Capillary Outflow Method

This method is based on the well-known Poiseuille law. The theory of this method contains the problem (not yet fully clarified) concerned with the method for calculating the boundary (or marginal) effect near the ends of the capillary tube. The boundary effect includes two phenomena: the change in the kinetic energy during the transition of the liquid from zero velocity in the upper reservoir to a velocity different from zero in the capillary tube (correction for kinetic energy), and the effect exerted by the initial sector of the capillary tube (correction for length). Various researchers estimate the magnitude of these effects in a different manner and differ in their opinion concerning the necessity of introducing appropriate corrections. For this reason, contrary to a widely held opinion, the capillary method lacks a strict theoretical foundation. We shall examine below the influence of the boundary effect on the results of viscosity measurements, after considering first the characteristic features of a moving liquid at the boundary of its contact with a hard wall.

The type of boundary conditions in the hydrodynamics of a viscous liquid formed the subject of investigations of many scientists. Without mentioning the history and content of these investigations (3), let us note only their final result. It can be considered as an established fact that, regardless of the degree of wetting of the hard wall by the liquid, there is no slip at the boundary: liquid-wall. Therefore, the boundary condition adopted in problems of hydrodynamics is based on the assumption that the relative velocity of the liquid at the surface where it comes into contact with a hard wall is equal to zero. The basic significance of this condition for the theory of all viscosimetric methods is obvious. If we did not adopt this condition, it would be necessary to introduce into the computing formulas, used for calculating the viscosity from experimental observations, a slip parameter, the physical meaning of which could be established only with the aid of special assumptions in regard to the slip mechanism. If the presence of a slip of the liquid in relation to the wall were established in any kind of test, this would require a revision and new interpretation of all the experimental results on viscosity obtained so far. All conclusions derived from hydrodynamics, reached in the assumption that the relative velocity of the liquid at the boundary is equal to zero, were always confirmed experimentally, and the capillary method for measuring the viscosity gave a direct proof of this fact. For this reason, the absence of a slip at the liquid-wall boundary line will be adopted by us as a firmly established experimental fact (<u>Note</u>: For further information on this problem, see also # 12 in Chapter II).

As is well known, by solving equations for the hydrodynamics of a viscous liquid, in case of a stationary flow through a capillary tube and a laminar flow, without taking into account boundary effects and the consumption of pressure energy required to impart a velocity to the liquid, we arrive at Poiseuille's law, which can be expressed by the following equation:

$$Q=\frac{\pi R^4}{8\eta}\left(\frac{p_1-p_2}{l}\right). \tag{1.1}$$

Here Q is the volume of liquid flowing through the capillary tube per unit of time, R is the radius of the capillary tube, η is the dynamic viscosity, $(p_1 - p_2)$ is the pressure difference at the capillary ends, measured from the same constant level, and l is the length of the capillary tube. By introducing the designation:

$$P=p_1-p_2, \tag{1.2}$$

the latter expression can be written in the generally known form:

$$\eta=\frac{\pi R^4 P}{8Ql}. \tag{1.3}$$

It is obvious, however, that equation (1.3) does not quite correspond to the actual conditions which are found during the measurement of the viscosity. Indeed, during all measurements performed by means of this method, the capillary tube connects two or more wide reservoirs, whereby the volume of the liquid which has traveled through the capillary (Q) is determined on the basis of the change in the level of these reservoirs. The velocity of a liquid in a wide bend is always several score of times smaller than in the capillary itself, and therefore part of the pressure difference P can impart to the liquid a certain amount of kinetic energy.

At the same time, formula (1.3) was derived without taking into consideration the nonlinear terms in the motion equation. The validity of this consideration was acknowledged by all researchers, although there was no general agreement among them as to the magnitude of the necessary correction which had to be made to account for this fact (4).

Taking this correction into account, we arrive at an equation, which, after elementary transformations, can be written as follows:

$$\eta=\frac{\pi R^4 P}{8lQ}\left(1-\frac{mQ^2\rho}{\pi^2 P R^4}\right). \tag{1.4}$$

In this equation, m is a numerical factor close to unity. By adopting the expression given in formula (1.3) as a first approximation for Q, forming a part of the correction member, the relation (1.4) can be expressed in the following form:

$$\eta=\frac{\pi R^4 P}{8lQ}\left(1-\frac{mPR^4}{64l^2\nu^2\rho}\right), \qquad (1.5)$$

where $\nu=\frac{\eta}{\rho}$ is the kinematic viscosity.

The pressure difference P is usually created by the excess column of the same liquid which is being studied. Under these conditions, formula (1.5) can be written as follows:

$$\eta=\frac{\pi R^4 P}{8lQ}\left(1-\frac{mR^4 Hg}{64l^2\nu^2}\right), \qquad (1.6)$$

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where H is the excess height of the liquid in the inlet bend above the outlet, and g is the gravity acceleration.

Let us make a numerical estimate of the correction term in the viscosity expression (1.6), by selecting for this purpose one of the recent studies dealing with the application of the capillary method to the measurement of the viscosity of a metallic alloy (5). In this particular case, the measurements were performed under non-stationary outflow conditions (H variable), although, in its other features, the theory of the method does not differ from a stationary case. In order to calculate the correction term, let us use the data presented in thi article. Let us adopt, as the average pressure of a column of metallic liquid, a value equal to about 5 mm of a mercury column, which probabl was the case during the tests. In this case, the value of the correction term was equal to 10-15%. If the viscosity of water had been measured with the same viscosimeter, the value of the correction would hav amounted approximately to 0.15%.

The correction for the kinetic energy of a liquid flowing throug the capillary tube, entering into equation (1.4), depends to a significant extent on the character of the inflow of the liquid into the capillary tube and its outflow from this tube.

Let us assume that the current line in the capillary is a straig line, i.e., the movement of the liquid does not have a helical nature. The equation of the energy of a unit volume of the moving liquid can then be written in the following form:

$$\frac{D}{Dt}[U+T]+k\eta v^2=0, \qquad (1.7)$$

where U is the density of the potential energy, equal to the pressure T is the kinetic energy of a unit volume, equal to $\frac{\rho v^2}{2}$; $k\eta v^2$ is a dissipation function, in which k has the dimension $[k]=\frac{1}{cm^2}$, i.e., does not contain ρ and η; $\frac{D}{Dt}$ is the operator of the substantial derivative.

The representation of the dissipation function in the form of $k\eta v^2$ is based on the assumption that the process involving the transition (conversion) of the energy of visible movements into heat along the entire cross section of the capillary takes place according to Newton's law of internal friction. By the same token, the initial sector of the process involving the formation of a parabolic velocity distribution is excluded from our examination.

By carrying out a differentiation (with one geometrical coordinate), we obtain:

$$\frac{\partial U}{\partial t}+v\frac{\partial U}{\partial x}+\frac{\partial T}{\partial t}+v\frac{\partial T}{\partial x}+k\eta v^2=0. \tag{1.8}$$

If the movement is stationary, then $\frac{\partial U}{\partial t}=\frac{\partial T}{\partial t}=0$, and, by substituting p for U and $\frac{1}{2}\rho v^2$ for T, assuming that ρ = const, we obtain: F 8 8

$$\frac{\partial p}{\partial x}+\frac{1}{2}\rho\frac{\partial v^2}{\partial x}+k\eta v=0. \tag{1.9}$$

By integrating this equation along the current line from x = 0 to x = 1, we find:

$$p_l-p_0+\frac{1}{2}\rho(v_l^2-v_0^2)+k\eta\int_0^l v\,dx=0. \tag{1.10}$$

Let us designate:

$$p_0-p_l=P,\quad v_l^2-v_0^2=\Delta v^2,\quad \frac{1}{l}\int_0^l v\,dx=\bar{v}, \tag{1.11}$$

where $\bar{v}$ apparently stands for the average velocity on a sector of the current line extending from 0 to 1. Now, equation (1.10) is transformed into the following equation:

$$-P+\frac{1}{2}\rho\Delta v^2+k\eta\bar{v}l=0. \tag{1.12}$$

Let us select a point in which the true value of the velocity is equal to $\bar{v}$. Let us assume that the cross section of the current tube at this point is equal to ds. Let us multiply the last equation by ds and let us integrate this equation by the area of the surface normal to the current lines and running through points in which $v = \bar{v}$; we shall then obtain:

$$lk\eta \int_s \bar{v}\, ds = \int_s P\, ds - \frac{1}{2}\rho \int_s \Delta v^2\, ds. \tag{1.13}$$

Since the distributions of $\bar{v}$, Δv^2 and P on the surface s are unknown, as a result of the integration, we can write the following expression:

$$k_1 k\eta l\bar{v}s = k_2 Ps - \frac{1}{2}\rho k_3 \Delta v^2 s, \tag{1.14}$$

where k_1, k_2, k_3 are dimensionless factors, determined by the geometry of the velocity and pressure field. Equation (1.14) can be written differently in the following form:

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$$lk_1 k\eta Q = k_2 Ps - \frac{1}{2}\rho k_3 \Delta v^2 s, \tag{1.15}$$

where Q is the volume rate of discharge of the liquid per second through any cross section of the capillary tube. By comparing this expression, when $\Delta v^2 = 0$, with Poiseuille's law (1.3), we find:

$$k_1 k = \frac{8k_2 s}{\pi R^4}. \tag{1.16}$$

Now, equation (1.15) can be written as follows:

$$\eta = \frac{\pi R^4}{8Ql} P\left(1 - \frac{1}{2}\frac{k_3}{k_2}\frac{\rho\Delta v^2}{P}\right). \tag{1.17}$$

The difference of the square velocities on the free surfaces of the liquid in the inlet and outlet reservoirs of the viscosimeter $v_1^2 - v_0^2$ can be considered as equal to:

$$\Delta v^2 = v_1^2 - v_0^2 = k_4 Q^2 \pi^2 R^4, \tag{1.18}$$

where k_4 is a dimensionless factor, determined by the type of connection of the capillary with the inlet and outlet reservoirs of the viscosimeter. The latter (last) equation will then be written as follows:

$$\eta = \frac{\pi R^4 P}{8Ql}\left(1 - \frac{1}{2}\frac{k_3 k_4}{k_2}\frac{\rho Q^2}{\pi^2 R^4 P}\right), \tag{1.19}$$

coinciding with equation (1.4) when:

$$\frac{1}{2}\frac{k_3 k_4}{k_2} = m. \tag{1.20}$$

From this formula, one can see that the correction for the kinetic energy is equal to zero when $k_4 = 0$, equivalent to $v_1 = v_0$.

The fulfillment of this condition depends upon the structural design of the connections between the capillary section of the viscosimeter and its wide reservoirs. However, during the construction of capillary viscosimeters, this problem usually does not get the proper attention, as a result of which the value of the correction for the kinetic energy remains indefinite (undefined). The appearance of the correction term in equations (1.5) and (1.19) indicates that the value of this term depends upon the conditions under which the experiment is conducted and upon the kinematic viscosity of the studied liquid. For this reason, this member may play a substantially different role in different tests.

Since in case of an identical rate of discharge of a given liquid, the pressure difference P is approximately proportional to l, then according to (1.5), the value of the correction member is approximately inversely proportional to l. Consequently, the correction for the kinetic energy can be practically reduced to zero, if a sufficiently long capillary tube is used. However, such a solution of the problem is unsatisfactory from an experimental standpoint.

The above calculations point to definite theoretical complications, arising during the application of the capillary method to the study of the viscosity of fused metals characterized by small v values (see formula 1.5).

At the same time, it can be noted that A. Ya. Milovich (6), who has developed the theory of the helical motion of a liquid, believes that all motions of a viscous liquid are helical or vortex motions. According to Milovich, only motions of a liquid near points where a strong dissipation or absorption of energy takes place constitute an exception to this rule.

Such a point of view, taken as a general concept, appears to us as not sufficiently substantiated (unfounded). However, if a helical motion will still take place during the flow of a liquid from a wide opening into a capillary, then, according to Milovich, the following relationship must take place, instead of Poiseuille's equation (1.3):

$$\eta = \frac{\pi R^4 P}{9{,}58 Q l}. \qquad (1.21)$$

In this case, a capillary viscosimeter must yield a viscosity value which is 20% greater (higher) than the true viscosity value for any liquid. Of course, the effect of a change in kinetic energy, examined above and expressed by formulas (1.5) and (1.19), is not taken into consideration in this case.

The reason for the appearance of a helical motion in a viscosimeter of the capillary type may lie in the type of connection between the capillary and the wide bend of the instrument during the course of glass blowing work.

The second correction for the effect exerted by the initial sector of the capillary actually plays a significantly smaller role. In order to account for this correction, a value of the order of several diameters, determined experimentally, should be added to the length of the capillary tube. In case of long capillaries used in viscosimetric measurements, this correction is very small.

In spite of a certain amount of incompleteness of the theory, the capillary method has found a wide field of application, which is quite understandable if we consider its simplicity and convenience when used at room and elevated temperatures. In addition to this fact, we can also state that, in case of liquids possessing a value of kinematic viscosity of about 1 centistoke and above (such as water, and many organic liquids) under normal experimental conditions, the correction for kinetic energy is expressed in fractions of a percent. It is only necessary to note that the accuracy of measurements, equal to four significant digits in the expression of the dynamic viscosity, which is frequently proposed by authors of experimental studies, must be generally considered as too high.

Much worse is the situation in regard to the use of the capillary method for studying the viscosity of fused metals. As was already mentioned, in view of the small value of the kinematic viscosity of these metals (of the order of decimal fractions of a centistoke), the value of the correction member for the kinetic energy is sharply increased, which in itself represents a sufficient reason for raising serious objections against the use of the capillary method in this field. The main difficulties during the application of the capillary method for studying the viscosity of fused metals, however, are of a purely experimental nature. These difficulties are connected primarily with the selection of an adequate material for the capillary, with its manufacturing technique, requiring a high degree of accuracy, with methods for recording changes in the level of the liquid in case of opaque walls of the instrument, and with other similar complications.

During the solution of many problems related to modern technology, a knowledge of the viscosity of slags and other systems with a high viscosity and high crystallization points is required. Here, the capillary method was also found to be unsuitable, not only for the reasons mentioned above, but also in view of the fact that a substantial increase in the diameter of the capillary is necessary in this case, which is associated with a corresponding increase in its length, thus making the instrument very unwieldy.

2. Rotating Cylinder Method

A widely used method for measuring the viscosity is the method based on the use of rotating coaxial cylinders. The solution of the corresponding hydrodynamic problem for an infinitely long cylinder, on which the theory of this method is based, is of elementary simplicity. Boundary effects are usually excluded by means of experimental techniques (7). The method of coaxial cylinders is particularly convenient in the case of liquids with a high viscosity and is widely used during the study of fused slags (see Note). It should be noted, however, that when this method is used in the high temperature region, it becomes necessary to install unwieldy units (<u>Note</u>: The development and improvement of this method, as well as its practical application on a wide scale, are based to a considerable extent on work done by M. P. Volarovich).

The method of rotating cylinders has practically not been used at all in studying the viscosity of fused metals, and only a few (not very satisfactory) studies have been published in this field (8). The reason for this is the fact that, in view of the relatively small viscosity values of metals, the torque transmitted from one cylinder to another is also extremely small. In order to increase the torque value, the clearance between the cylinders must be sharply reduced, which causes great experimental difficulties. In addition, the necessity of excluding boundary effects makes the experiments exceedingly unwieldy and laborious. A further disadvantage of this method lies in the large dimensions of the instrument.

3. <u>Falling Ball Method</u>

The most perfect, from the theoretical standpoint, of all stationary methods is the falling ball method, which is based on Stokes' problem. For a cylindrical vessel, the calculation of boundary effects has been achieved theoretically, and since their influence can be made quite insignificant, the theoretical aspect of this method must be considered as being in a highly perfected state.

The well-known formula of Stokes, derived for the stationary motion of a small ball in an unlimited viscous medium, when nonlinear members in the hydrodynamic equations are disregarded, has the following appearance

$$\eta = \frac{2r^2(\rho' - \rho)g}{9v}, \qquad (1.22)$$

where v is the velocity of the uniform motion of a ball with the radius r; ρ' and ρ are the densities of the ball and liquid, respectively. The condition at which it is possible to disregard nonlinear terms is expressed by the inequation:

$$r \ll \frac{\eta}{\rho v}. \qquad (1.23)$$

Experimental studies have shown, however, that the observance of a less rigid (strict) condition is possible:

$$r \leqslant 0{,}6\,\frac{\eta}{\rho v}. \qquad (1.24)$$

If the condition (1.24) is fulfilled, then, after taking into account the corrections for the finite dimensions of the vessel, in which the falling or floating of the ball takes place, we arrive at the following expression for the viscosity (Note: see reference (4) in the bibliography):

$$\eta = \frac{2r^2(\rho' - \rho)g}{9v\left(1 + 2{,}4\,\frac{r}{R}\right)\left(1 + 3{,}1\,\frac{r}{L}\right)}, \qquad (1.25)$$

where R is the radius of a cylindrical vessel, along the axis of which a ball is moving in the viscous liquid, and L is the length of the vessel. The correction terms do not contain the viscosity and depend only on the ratios $\frac{r}{R}$ and $\frac{r}{L}$, thus making it possible to use the falling ball method as a relative method.

Strictly speaking, a relative method for measuring any kind of physical value must be based on a theory having the same degree of accuracy as an absolute method, i.e., the analytic dependence of the value which must be measured on the values which are directly observed during the experiment must be known. Only under these conditions is it possible to determine the relation between the values directly observed during the experiment, which refer to a substance with an unknown characteristic, and the same values referring to a substance with a known characteristic. This factor is frequently overlooked, as a result of which an excessively high accuracy is attributed to experimental data. For example, if boundary effects are taken into account, the ratio of the viscosities of two liquids will not be simply inversely proportional to the outflow times (rates) of identical volumes, as is usually assumed when using the capillary method for relative measurements.

In spite of the theoretical strictness of the falling ball method, the application of this method is associated with considerable experimental difficulties. The large dimensions of the instrument, requiring large amounts of liquid for research purposes, the need for an accurate manufacture of balls with a very small diameter, and the necessity of observing the motion of these balls -- all these factors greatly limit the possible application of this particular method, especially at nigh temperatures and even more so in case of metallic liquids.

4. Non-Stationary Methods of Viscosity Measurement

By means of non-stationary methods, it is possible to determine directly the kinematic viscosity of a liquid, and not its dynamic viscosity.

From a mathematical standpoint, the theory of non-stationary methods is much more complex than that of stationary methods; precisely for this reason, these methods are not as widely used as stationary methods.

As a result of the study of the viscosity of liquids, especially metals, at high temperature, which has become an extremely urgent problem during the past 10-15 years, and also in view of the great interest in the study of the viscosity of liquefied gases, efforts have been made to overcome these serious mathematical difficulties in order to achieve a maximum simplification of experimental techniques.

Vershaffelt (9) has developed a theory for a method of viscosity measurement based on observations of the torsional oscillations of a sphere submerged in the studied liquid (external hydrodynamic problem). This method was used by E. B. Polyak and S. V. Sergeyev (10) for studying the viscosity of fused metals. However, the use of the oscillating ball method in metal research is associated with two serious difficulties. First, the ball must be attached on a rod (stem), running through the free surface of a metal having a high surface tension; in this case, it is impossible to evaluate the effect exerted by the surface film on the stem during the course of oscillations, especially in view of the fact that the surface film may be oxidized. Second, the ball must sink in the metal being studied, and this cannot always be achieved without using an additional load in the upper portion of the stem. In case of such a method of loading the suspension system, the center of gravity of this system is raised and the system is subjected to precessional movements and to a dynamic instability, which in turn results in distorted values of the damping decrement.

The oscillating ball method was subjected to a thorough experimental investigation by V. A. Konstantinov (11). The results of this study point to a number of significant factors which complicate somewhat the use of this method for measuring the viscosity of fused metals.

Methods based on an internal hydrodynamic problem (liquid located inside the oscillation system) are free of the above-mentioned defects, but the mathematical theory of these methods is even more complicated. However, precisely those viscosimeters which are based on an internal problem can be most conveniently used within a wide range of temperature and pressure variations.

The study performed by Helmholtz and Piotrowsky (12) contains a theory of a viscosimeter consisting of a hollow spherical casing (sheath), filled with the liquid being studied, and an elastic thread performing free torsional oscillations. The theory elaborated by these authors makes it possible to establish a connection between the damping decrement and the oscillation period, on the one hand, and the viscosity of the liquid enclosed in the casing, on the other hand. However, the experiments conducted by these authors were aimed rather at checking the correct nature of the solution of the hydrodynamic problem, than at the actual measurement of the viscosity. By the way, these experiments allowed the authors to reach the conclusion about the presence of a slip at the liquid-hard wall boundary, a conclusion which later could not be confirmed.

Since the calculation performed by Helmholtz did not meet the requirements imposed on the theory of the experimental method, this calculation was later performed again in a sufficiently complete form. The instrument built on the basis of this theory was used for measuring the viscosity of water and hexane (13). However, this method did not find a wide field of application, apparently in view of technical difficulties involved in the manufacture of the instrument and the setting up of experiments, which are not balanced by the results obtained. Great difficulties are encountered during the manufacture of the hollow spherical casing, which requires a high degree of accuracy, especially in case the viscosity of metals in the fused state must be measured. Ceramic products are the best material for this purpose, although the use of ceramic products in the manufacture of a spherical casing is extremely difficult. Similar difficulties are experienced in connection with the filling of the casing with the metal to be studied, the possibility of ensuring a free expansion of this metal, the consideration of this effect during the calculation of the viscosity, and other factors.

In view of the technical difficulties associated with the use of a hollow spherical casing as a vessel for holding the liquid to be tested, consideration has been given a long time ago to the possibility of using a small cylindrical bucket for this purpose. A corresponding calculation, relating the oscillation period and the damping decrement of such a system with the viscosity of the liquid enclosed in the bucket, was performed for the first time by Meyer (14). In order to simplify the problem, Meyer used a number of limiting hypotheses, and specifically he assumed that the cylinder had a large radius and that its height was small in comparison to this radius. With the aid of an instrument built according to these specifications, measurements of the viscosity of salt solutions were performed (15), which showed that this instrument could be conveniently used in the room temperature range. Nevertheless, as in the preceding case, this method did not find a wide field of application. The reason for this is the fact that the theory of the method exhibited a number of defects, the calculating system was not adequately developed, convenient formulas for processing actual experimental data could not be obtained, and the large dimensions of the instrument made it unsuitable for work in the high temperature range.

However, the idea of measuring the viscosity by observing the torsional oscillations of a small cylindrical bucket, filled with the liquid to be tested, no doubt deserves the most serious consideration from the standpoint of simplicity of the experimental technique used during such measurements. It was natural, therefore, that this problem again attracted the attention of research workers.

A study published in 1936 (16) described the solution of the hydrodynamic problem concerned with the motion of a liquid in a small cylindrical bucket performing free torsional oscillations. This problem was solved without the limitations mentioned above. The article also describes certain experiments which confirmed the correct nature of the calculations. A second study (17) was concerned with the problem of obtaining calculating formulas for determining the viscosity on the basis of actual experimental data. By means of rather complex calculations, eight formulas were derived, with the aid of which the viscosity can be determined. Final formulas can be used within a definite range of variation of a certain parameter, containing the viscosity. The theory does not take into account the damping (attenuation) of the system when the liquid is not present.

On the basis of the factors mentioned above, we are forced to conclude that the above studies cannot be considered as representing a theory of an experimental method for measuring the viscosity, but rather as a solution of a certain theoretical problem followed by an experimental checkup.

In view of the necessity of measuring the viscosity of fused metals at high temperatures, there was an urgent need for a method which would be satisfactory from an experimental standpoint and which would be based on a well-developed theory, yielding convenient formulas for processing the results obtained during observations.

The method based on oscillations of a cylinder filled with the liquid to be tested satisfies the requirement involving simplicity and convenient use, but the various modifications of the theory cannot by any means be considered satisfactory.

For this reason, it was necessary to devise a completely new approach to the problem concerned with the oscillations of a hollow cylinder, filled with the liquid to be tested, involving the use of a method for solving this problem which was different from the ones previously used, and thus to obtain formulas, tables and graphs for processing the results of direct observations, which would be acceptable from a practical standpoint, moreover in such a form that this method could be considered as an absolute method.

5. Formulation of the Problem Related to the Theory of a Non-Stationary Method of Viscosity Measurement

The solution of two different problems must be considered in setting up the theory for a viscosity measurement method. The first problem consists in finding a connection between the kinematic viscosity, entering into hydrodynamic equations, and the parameters expressing the motion of the system connected with the liquid, which are observed during the course of measurements. The second problem involves the development of a calculating system, which will allow us to find in the most efficient way the viscosity value of the liquid according to the observed parameters describing the motion of the system. The following chapters will be devoted to the solution of both of these problems; at this point, however, we have to make some preliminary remarks related to this particular problem.

Let us assume that a certain physical process is described by a single differential equation consisting of partial derivatives in relation to an unknown function φ, which is determined by the time and the coordinates. Let us further assume that a single constant (a) enters this equation as a parameter.

Let us write this equation as follows:

$$L[a, \varphi(x, y, z, t)] = 0 \qquad (1.26)$$

A typical problem of mathematical physics consists in finding the field of function φ, when the initial and boundary conditions are given. Let us assume that this problem has been solved. Then, if it is possible to determine φ experimentally as a function of time in any given point, which does not coincide with the boundary of the solution field, by the same token it then becomes possible to determine the parameter (a) in a differential equation. However in those cases when it is not possible to effect an experimental determination of φ within the solution field, parameter (a) cannot be determined without introducing supplementary conditions.

This is quite understandable from a physical standpoint. Indeed, the field of φ values is formed at a given (a) in accordance with the type of differential equation and the initial and boundary conditions. By keeping the boundary conditions constant, it is possible to change (a) in any way desired, and accordingly the field of φ values will be deformed only within the solution range. Consequently to determine (a), one more condition is needed. A supplementary equation for the boundary value of the function may be used as such a condition, but this equation should contain only known constants as parameters.

Let us assume that the solution of the differential equation (1.26), satisfying the initial and boundary conditions is expressed by the formula:

$$\varphi = f(a,\ x,\ y,\ z,\ t) \tag{1.27}$$

and let the boundary value of this function be equal to φ_0. It is possible to determine (a) if the following supplementary equation is given:

$$M[\varphi_0(a,\ t)] = 0, \tag{1.28}$$

where M is a certain operator.

All these considerations are also applicable when the problem is set up (postulated) without an initial condition. Let us explain this based on an example. Let us assume that it is necessary to determine the thermal diffusivity of a rod insulated on the sides by the temperature wave method. This means that we are faced with the following problem:

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$$\frac{1}{a}\frac{\partial\varphi}{\partial t} = \frac{\partial^2\varphi}{\partial x^2}\,(0 < x < \infty,\quad 0 < t < \infty), \tag{1.29}$$

$$\varphi(0,\ t) = A\cos qt, \tag{1.30}$$

where $\varphi(x,\ t)$ is the temperature, a is the unknown (sought) parameter of the differential equation, i.e., the thermal diffusivity, q is the given (prescribed) cyclic frequency of the temperature fluctuations at the boundary, and A is the known amplitude of these fluctuations.

The solution is expressed in the following form:

$$\varphi(x,\ t) = Ae^{-\sqrt{\frac{q}{2a}}x}\cdot\cos\left(qt - \sqrt{\frac{q}{2a}}\,x\right). \tag{1.31}$$

Let us assume that it is possible to measure the temperature at point x_1 of the rod within the solution range. Obviously, the measurement results will be expressed in the form of a known harmonic time function:

$$B\cos(qt - \varepsilon_1) = Ae^{-\sqrt{\frac{q}{2a}}x_1}\cdot\cos\left(qt - \sqrt{\frac{q}{2a}}\,x_1\right), \tag{1.32}$$

and from here:

$$\ln B = \ln A - \sqrt{\frac{q}{2a}}\,x_1. \tag{1.33}$$

In order to find (a) with the aid of this equation, it is necessary to use the value of the amplitude A of the temperature fluctuations at the boundary.

In addition, we have:

$$\varepsilon_1 = \sqrt{\frac{q}{2a}}\, x_1. \tag{1.34}$$

Consequently, after subjecting the temperature curve at point x_1 to a harmonic analysis and thereby determining phase ε_1 from the last equation, it is possible to determine (a), even without using the value of the amplitude at the boundary. However, the situation is substantially different in case the temperature can be measured only at the boundary of the solution range (when x = 0). In this case, formula (1.32) is satisfied at any value of (a), and consequently, the system of equations (1.29), (1.30) and (1.31) is not sufficient to allow the determination of (a). In this case, a supplementary equation is necessary for the temperature at the boundary of the solution range x = 0. The following expression of a heat flow can be used as such an equation:

$$-\lambda \left.\frac{\partial \varphi}{\partial x}\right|_{x=0} = Q(t). \tag{1.35}$$

Here it is assumed that λ is a known parameter of equation (1.35). By finding:

$$\left.\frac{\partial \varphi}{\partial x}\right|_{x=0} = A \sqrt{\frac{q}{2a}} \{\sin qt - \cos qt\} \tag{1.36}$$

and inserting this expression into (1.35), we obtain an equation for calculating (a), which is based on experimental data and which refers only to the boundary of the solution range, i.e., to the boundary condition.

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Chapter II

Theory of the Torsional-Oscillation Method for Measuring the Viscosity of Liquids

1. Basic Theoretical Concepts of the Method

In a number of studies conducted by us (1), a mathematical theory of a method for measuring the viscosity of liquids is given, which is based on the observation of torsional oscillations of a small bucket filled with the liquid to be tested and suspended on an elastic thread coinciding with the axis of the bucket.

The theory of this method is based on the following concepts:

1. There is no slip between the liquid and the internal surface of the bucket.

2. The oscillations of the bucket are examined after a sufficiently long interval of time following the start of such oscillations, when the initial velocity distribution does not exert any effect on the movement (motion) of the liquid (regular regime).

3. The oscillations of the bucket have a small amplitude.

4. The motion of the liquid in the bucket is described with a sufficient degree of accuracy, without taking into consideration nonlinear terms in Navier-Stokes equations for an incompressible liquid.

In the following paragraph and further in the text (see # 11 of
this chapter), this particular problem forms the subject of a special
F discussion, in order to find out to what extent the formulated concept
8 can be substantiated experimentally and theoretically and to what extent
8 it should be considered as an independent hypothesis.

The first concept (which has already been mentioned in Chapter I) is generally recognized in viscosimetry and forms the basis of all methods for measuring the viscosity.

The second concept means, from an experimental standpoint, that regular oscillations must be taken into consideration, which satisfy the condition of a linear dependence between the logarithm of the amplitude and the oscillation number. A linear dependence sets in after several oscillations following the beginning of the process.

When the condition of a linear dependence is fulfilled, the third condition must also be fulfilled, since the latter determines the constancy of factors in the differential equation describing the motion of the bucket.

2. Velocity Distribution

First we shall examine the hydrodynamic problem concerned with the distribution of velocities in the liquid filling up the viscosimeter.

The working space of the viscosimeter and the arrangement of the coordinate axes are illustrated in Figure 1.

We shall use the Navier-Stokes equations for an incompressible liquid as a starting point. If an elementary ring $2\pi r\,dr\,dz$ is selected in the liquid, then this ring will perform a rotary motion with a tangential velocity v. At the same time, the velocity components v_r and v_z must be equal to zero; in this case, the following two conditions result from the continuity equation and the axial symmetry of the motion:

$$\frac{\partial v}{\partial \varphi} = 0, \quad \frac{\partial p}{\partial \varphi} = 0, \tag{2.1}$$

where p is the pressure, φ is the angular polar coordinate in a plane perpendicular to the axis Oz. From here, one can conclude that the only velocity component (tangential) is the function $v(z, r, t)$.

Thus, during an annular motion of the liquid, as one can easily see, the nonlinear terms in the hydrodynamic equations are identically converted to zero. The validity of this concept, in case of small amplitudes of the torsional-oscillation motion (equal to fractions of a radian) was checked experimentally by Verschaffelt (see references 1 and 9 in the bibliography of Chapter I, pages 21 and 22).

The concept of the small size of the amplitude in this particular problem requires a special examination. At present, we shall base our study on the fact that, in case of low oscillation frequencies, when the motion proceeds at a slow rate, the liquid really moves in concentric layers and nonlinear terms are identically converted to zero.

Thus, when used in connection with this particular problem, the Navier-Stokes equations assume the following appearance (2):

$$\frac{1}{\rho}\frac{\partial p}{\partial r} = \frac{v^2}{r}, \tag{2.2}$$

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$$-\frac{1}{\rho}\frac{\partial p}{\partial z} = g, \tag{2.3}$$

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2} - \frac{v}{r^2} = \frac{1}{\nu}\frac{\partial v}{\partial t}, \tag{2.4}$$

where ρ is the density, $\nu = \frac{\eta}{\rho}$ is the kinematic viscosity, η is the dynamic viscosity, and g is the gravity acceleration.

During the course of measurements, the bucket performs a damped torsional-oscillation motion, and therefore the boundary conditions for the liquid, in accordance with the first concept (see # 1 of this chapter), can be written in complex form as follows:

$$v(R, z, t) = i\Omega R e^{-kt}, \tag{2.5}$$

$$v(r, \pm H, t) = i\Omega r e^{-kt}. \tag{2.6}$$

Here, Ω is the real initial amplitude of the angular velocity of the torsional-oscillation motion of the bucket.

$$k = \gamma + iq, \tag{2.7}$$

where γ is the attenuation (damping factor) of the oscillations, and q is the cyclic frequency.

The initial condition in the problem is absent, according to concept No. 2 (see # 1 of this chapter). Therefore, a solution can be sought in the form:

$$v(r,\ z,\ t)=\psi(r,\ z)e^{-kt}. \tag{2.8}$$

The function $\psi(r,\ z)$ satisfies the condition:

$$\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{\partial r}+\frac{\partial^2\psi}{\partial z^2}+\left(\frac{k}{\nu}-\frac{1}{r^2}\right)\psi=0 \tag{2.9}$$

and the conditions:

$$\psi(R,\ z)=i\Omega R, \tag{2.10}$$

$$\psi(r,\ \pm H)=i\Omega r. \tag{2.11}$$

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Let us assume that:

$$\psi(r,\ z)=\psi_1(r)+\psi_2(r,\ z). \tag{2.12}$$

$\psi_1(r)$ satisfies equation (2.9) without the term $\frac{\partial^2\psi}{\partial z^2}$ and the condition:

$$\psi_1(R)=i\Omega R. \tag{2.13}$$

$\psi_2(r,\ z)$ satisfies the equation (2.9) and the conditions:

$$\psi_2(R,\ z)=0, \tag{2.14}$$

$$\psi_2(r,\ \pm H)=i\Omega r-\psi_1(r). \tag{2.15}$$

One can easily see that:

$$\psi_1(r)=\frac{i\Omega R}{J_1(\beta)}\cdot J_1\left(\beta\frac{r}{R}\right), \tag{2.16}$$

$$\beta=R\sqrt{\frac{k}{\nu}}; \tag{2.17}$$

here, J_1 is a Bessel function of the first type and of the first order, and

$$\psi_2(r,\ z)=\sum_{n=1}^{n=\infty}\frac{a_n}{\mathrm{ch}\,(\vartheta_n H)}\cdot J_1(\mu_n r)\cdot \mathrm{ch}\,(\vartheta_n z). \tag{2.18}$$

The characteristic numbers μ_n are determined from the equation:

$$J_1(\mu_n R)=0, \tag{2.19}$$

where a_n, the expansion factors of the function $\psi_2(r, \pm H)$, according to $J_1(\mu_n r)$, are determined from the known formula:

$$a_n = \frac{2}{R^2 [J_1'(\mu_n R)]^2} \int_0^R r\psi_2(r, \pm H) \cdot J_1(\mu_n r)\, dr = \\ = \frac{i2\Omega}{\mu_n J_0(\mu_n R)} \left[\frac{\mu_n^2}{\vartheta_n^2} - 1 \right] \tag{2.20}$$

$$\vartheta_n^2 = \mu_n^2 - \frac{k}{\nu}. \tag{2.21}$$

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Thus, by designating the complex angular velocity of the liquid as $\omega = \frac{v}{r}$, we obtain the solution which we were looking for:

$$\omega(t, r, z) = \\ = \frac{e^{-kt}}{r} \left[\frac{i\Omega R}{J_1(\beta)} \cdot J_1\left(\beta \frac{r}{R}\right) + \sum_{n=1}^{\infty} \frac{a_n}{\operatorname{ch}(\vartheta_n H)} \cdot J_1(\mu_n r) \cdot \operatorname{ch}(\vartheta_n z) \right]. \tag{2.22}$$

3. Moment of Frictional Forces on the Internal Surfaces of the Bucket

The internal friction force per surface unit is equal to:

$$f = \eta r \frac{\partial \omega}{\partial r}. \tag{2.23}$$

The moment of frictional forces, acting upon the internal surfaces of the bucket, can be expressed as follows:

$$P = 2\pi\eta R^3 \int_{-H}^{+H} \left(\frac{\partial \omega}{\partial r} \right)_{r=R} dz + \\ + 2\pi\eta \int_0^R \left(\frac{\partial \omega}{\partial z} \right)_{z=H} r^3\, dr - 2\pi\eta \int_0^R \left(\frac{\partial \omega}{\partial z} \right)_{z=-H} r^3\, dr. \tag{2.24}$$

Let us introduce the complex angular displacement of the bucket, α. Then, in accordance with the boundary condition (2.5), we get:

$$i\Omega R e^{-kt} = R\frac{d\alpha}{dt}. \tag{2.25}$$

By means of appropriate calculations, we arrive at the following expression for the moment of frictional forces on the internal surfaces of the bucket, caused by the action of a viscous liquid:

$$P = L\frac{d\alpha}{dt}, \tag{2.26}$$

where:

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$$L = -4\pi\eta R^2 H\beta\frac{J_2(\beta)}{J_1(\beta)} + 8\pi\eta R^3\frac{k^2}{\nu^2}\sum_{n=1}^{n=\infty}\frac{\operatorname{th}(\vartheta_n H)}{\mu_n^2\vartheta_n^3}. \tag{2.27}$$

The first addend in the right side of the equation describes the friction which takes place on the side surface of an infinitely long cylinder with a height of 2H. The second addend takes into account the friction occurring on the bottom and on the lid of the bucket, and also the change in the side friction introduced by these end surfaces. The latter expression for the moment of friction forces is generally applicable and can be used for any values of R and H.

4. Equation Describing the Oscillations of the Bucket

Three types of moments of force act upon the suspension system, consisting of the bucket filled with liquid and the attachments of the bucket to the suspension thread.

First, an elastic (restoring) moment of torsion of the suspension, proportional to the torsion angle.

Second, a moment of internal friction forces, caused by the presence of the liquid in the bucket. These forces not only cause the appearance of an attenuation (damping) of the torsional oscillations of the suspension system, but also increase the oscillation period in comparison to the period observed when the bucket is empty. An increase in the period takes place as a result of the fact that a certain amount of liquid (combined mass) also takes part in the process of oscillations of the bucket, which results in a greater effective moment of inertia of the suspension system. In view of this fact, this particular moment of forces consists of two terms: a term proportional to the velocity, and a term proportional to the acceleration.

Third, it is necessary to take into account the effect of friction forces caused by the presence of the gaseous medium surrounding the bucket and by defects of the suspension thread. It is obvious that, in this case, the combined mass is vanishingly small, so that the corresponding moment is simply proportional to the velocity.

Let us introduce the designation:

$$\alpha = \alpha' + i\alpha''. \tag{2.28}$$

Then, the total moment of friction, caused by the gaseous environment and defects of the suspension thread, can be assumed as being equal to:

$$-L_0 \frac{d\alpha'}{dt}. \tag{2.29}$$

The equation describing the motion of the bucket can be written in the following form:

$$K\frac{d^2\alpha'}{dt^2} + N\alpha' = -L\frac{d\alpha}{dt} - L_0\frac{d\alpha'}{dt}, \tag{2.30}$$

where K is the moment of inertia of the entire suspension system without the liquid, and N is the elasticity factor of the suspension thread.

The first member in the right side of the equation represents a complex expression, and therefore yields addends which are proportional to the velocity and acceleration. Let us designate:

$$L = L' + iL''. \tag{2.31}$$

The actual (real) portion of $-L\frac{d\alpha}{dt}$, apparently, can be expressed by the relation:

$$\mathrm{Re}\left(-L\frac{d\alpha}{dt}\right) = -L'\frac{d\alpha'}{dt} + L''\frac{d\alpha''}{dt}{}^{1)}. \tag{2.32}$$

(<u>Note</u>: The symbols Re(X) and Im(X) are used to designate the real and imaginary parts of the complex expression X.)

In this expression, it is necessary to exclude $\frac{d\alpha''}{dt}$, which can be easily accomplished. By differentiating (2.25), we get:

$$\frac{d^2\alpha'}{dt^2} + i\frac{d^2\alpha''}{dt^2} = -(p + iq)\left(\frac{d\alpha'}{dt} + i\frac{d\alpha''}{dt}\right), \tag{2.33}$$

from which, after dividing the real and imaginary parts, we get:

$$\frac{d\alpha''}{dt}=\frac{1}{q}\frac{d^2\alpha'}{dt^2}+\frac{\mathfrak{p}}{q}\frac{d\alpha'}{dt}. \tag{2.34}$$

Thus, the perturbing force caused by the action of the liquid can be expressed as follows:

$$\mathrm{Re}\left(-L\frac{d\alpha}{dt}\right)=-\left(L'-\frac{\mathfrak{p}}{q}L''\right)\frac{d\alpha'}{dt}+\frac{1}{q}L''\frac{d^2\alpha'}{dt^2} \tag{2.35}$$

F88 and the equation describing the motion of the bucket will assume the form:

$$\left(K-\frac{1}{q}L''\right)\frac{d^2\alpha'}{dt^2}+\left(L'-\frac{\mathfrak{p}}{q}L'+L_0\right)\frac{d\alpha'}{dt}+N\alpha'=0. \tag{2.36}$$

As will be shown below (see 2.45), L" is a negative value. For this reason, the presence of an internal friction of the liquid affects the increase in the moment of inertia of the system caused by the entrained layers of the liquid, and also affects the appearance of an additional attenuation (damping) $L'-\frac{\mathfrak{p}}{q}L''$, which plays a predominant role in comparison to L_0. By substituting in equation (2.36) α', $\frac{d\alpha'}{dt}$, $\frac{d^2\alpha'}{dt^2}$, according to the expression:

$$\alpha'=\alpha_0'e^{-\mathfrak{p}t}\cos(qt+\varphi) \tag{2.37}$$

and by equating to zero the factors at sine and cosine, we shall obtain the following two equations:

$$\frac{L'+L_0}{K}=\mathfrak{p}\left(1+\frac{N}{K}\frac{1}{\mathfrak{p}^2+q^2}\right), \tag{2.38}$$

$$\frac{L''}{K}=q\left(1-\frac{N}{K}\frac{1}{\mathfrak{p}^2+q^2}\right). \tag{2.39}$$

Let us exclude from these equations the member $\frac{N}{K}\frac{1}{\mathfrak{p}^2+q^2}$. Considering that the equation describing the motion of the bucket, in the absence of a liquid, has the following appearance:

$$K\frac{d^2\alpha'}{dt^2}+L_0\frac{d\alpha'}{dt}+N\alpha'=0 \tag{2.40}$$

and consequently:

$$L_0 = 2K\mathfrak{p}_0, \tag{2.41}$$

where $\mathfrak{p}_0$ is the attenuation (damping factor) of the oscillations of an empty system, we get:

$$L' + \frac{\mathfrak{p}}{q} L'' = 2K(\mathfrak{p} - \mathfrak{p}_0). \tag{2.42}$$

If the frequency of oscillations of an empty system is designated by q_0, then:

$$\mathfrak{p}_0^2 + q_0^2 = \frac{N}{K} \tag{2.43}$$

and, instead of (2.38) and (2.39), we shall obtain:

$$\frac{L'}{K} = \mathfrak{p}\left(1 + \frac{\mathfrak{p}_0^2 + q_0^2}{\mathfrak{p}^2 + q^2}\right) - 2\mathfrak{p}_0, \tag{2.44}$$

$$\frac{L''}{K} = q\left(1 - \frac{\mathfrak{p}_0^2 + q^2}{\mathfrak{p}^2 + q^2}\right). \tag{2.45}$$

All three equations (2.42), (2.44) and (2.45), in their left sides, contain the viscosity of the liquid, expressed by means of L' and L", and in the right sides only the experimentally observed values, and are suitable for the derivation of calculating formulas expressing the viscosity by means of the attenuation (damping) and oscillation period of the bucket.

However, from the standpoint of the requirements imposed on the theory of the method, there is a substantial difference between the first of these equations and the last two equations. The first equation, i.e., (2.42) is obtained by excluding N, and therefore this equation does not contain the condition specifying the independence of N from the load and the temperature. This equation will later play a major role. The last two equations, i.e., (2.44) and (2.45), are obtained by replacement of N with the oscillation frequency of the empty system q_0, and the latter is determined by the load applied on the thread and by the temperature of this thread (insofar as N exhibits such a dependence). Therefore, q_0 must be measured over the entire temperature range, in which the viscosity is measured, and precisely at the load on the thread, at which the measurement of the viscosity is performed. In view of this fact, equation (2.44) will not be used at all in our further study, and equation (2.45) will be used to a limited extent precisely in the viscosity range in which the logarithmic damping decrement does not depend to a great extent on the viscosity of the liquid.

5. First Approximation for the Friction Function L

Equation (2.27) is too complex to be used directly in viscosimetry. Therefore, this equation must be reduced to a more simple form, by using reasonable approximations. Let us assume that:

$$\vartheta_n = \vartheta_n' + i\vartheta_n''. \qquad (2.46)$$

With the aid of (2.7) and (2.21), it is possible to arrive at the following expressions:

F
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$$\vartheta_n' = \frac{1}{\sqrt{2}}\sqrt{\left(\mu_n^2 - \frac{p}{\nu}\right) + \sqrt{\left(\mu_n^2 - \frac{p}{\nu}\right)^2 + \frac{q^2}{\nu^2}}}, \qquad (2.47)$$

$$\vartheta_n'' = -\frac{1}{\sqrt{2}}\sqrt{-\left(\mu_n^2 - \frac{p}{\nu}\right) + \sqrt{\left(\mu_n^2 - \frac{p}{\nu}\right)^2 + \frac{q^2}{\nu^2}}}. \qquad (2.48)$$

Let us examine th$(\vartheta_n H)$. According to the well-known formula, coupling a hyperbolic and simple (prime) tangent:

$$\mathrm{th}\,(\vartheta_n H) = -i\,\mathrm{tg}\,(i\vartheta_n H). \qquad (2.49)$$

With the aid of this relation and the expression for tg$(i\vartheta_n H)$, in case of a high value of the imaginary part of the complex variable, i.e., when $\vartheta_n' H \gg 1$, one can obtain the following expression:

$$\mathrm{th}\,(\vartheta_n H) = 1 + i2e^{-2\vartheta_n' H}\sin\,(2\vartheta_n'' H). \qquad (2.50)$$

It can be easily seen, that, when $\vartheta_n' H > 5$, the imaginary part has a value smaller than $1 \cdot 10^{-4}i$. Therefore, setting up the requirement that:

$$\vartheta_n' H \geqslant s \quad (s = 5) \qquad (2.51)$$

at any value of s, one can write accurately up to an addend not greater than $i2e^{-2s}$:

$$\mathrm{th}\,(\vartheta_n H) = 1. \qquad (2.52)$$

It should be noted that it is not always permissible to leave out (discard) the purely imaginary part of the expression, as compared to the real part. In the case being studied here, this can be done because unity is the main addend in the expressions for the real and imaginary parts of L (equations (2.72) and (2.73)).

Thus, when the condition (2.51) is fulfilled, the following expression for L is obtained:

$$L = -4\pi\eta R^3 H\beta \frac{J_2(\beta)}{J_1(\beta)} + 8\pi\eta R^3 \frac{k^2}{\nu^2} \sum_{n=1}^{\infty} \frac{1}{\mu_n^2 \vartheta''_n}. \tag{2.53}$$

6. Physical Meaning of the First Approximation for the Friction Function

The second addends in formulas (2.22) and (2.27) for ω and L are based on the effect exerted by the end surfaces of the bucket. The corresponding member in (2.22) can be written in the following form, with the aid of the relations (2.7) and (2.46):

$$\omega_b(t, r, z) = \sum_{n=1}^{\infty} A_n(r) \left[e^{-pt+\vartheta'_n z - i(qt-\vartheta''_n z)} + \right.$$
$$\left. + e^{-pt-\vartheta'_n z - i(qt+\vartheta''_n z)} \right]. \tag{2.54}$$

Apparently, this portion of the total (over-all) solution represents an infinite sum of waves, propagated in both directions of the z axis with an amplitude determined by r and subject to an exponential attenuation in space and in time.

The amplitude along the z axis in (2.54) can be transformed as follows:

$$e^{-\vartheta'_n z} = e^{-2\pi \frac{\vartheta'_n}{|\vartheta_n|} \cdot \frac{z}{L_n}}, \tag{2.55}$$

where L_n is the wavelength corresponding to the wave number $|\vartheta''_n|$. Then:

$$\Delta_n = 2\pi \frac{\vartheta'_n}{|\vartheta''_n|} \tag{2.56}$$

is the logarithmic decrement of the spatial attenuation of the amplitude. From a comparison of ϑ'_n and $|\vartheta''_n|$, it follows that $\Delta_n > 2\pi$. This means that the waves examined here are totally attenuated (damped) at a distance equal to the wavelength and belong to the type of temperature waves (3). At a distance z = H, the amplitude along the z axis is equal to:

$$A = A_0 e^{-\Delta_n \frac{H}{L_n}}; \tag{2.57}$$

if:

$$\frac{H}{L_n} = \frac{s}{\Delta_n}, \tag{2.58}$$

where s is a whole number or a fraction, then the amplitude at a distance H will be reduced e^s times.

On the other hand, from (2.56) it is easy to obtain:

$$\frac{H}{L_n} = \frac{\vartheta'_n H}{\Delta_n}, \tag{2.59}$$

and, according to the requirement of (2.51) must be equal to:

$$\frac{H}{L_n} \geqslant \frac{s}{\Delta_n}. \tag{2.60}$$

From here it is obvious that condition (2.51), at the fulfillment of which $\mathrm{th}(\vartheta_n H) = 1$, physically means that all viscous waves, arising from the bottom and lid of the bucket, are damped e^s times at a distance H. When s = 5, this results in a ratio of the amplitude in a medium plane of the bucket to the amplitude at the bottom or on the lid, $\frac{A(0)}{A(H)} = 0.006$.

Consequently, in case the inequation (2.51) is fulfilled, viscous waves propagated from the bottom and the lid of the bucket are unable to reach the opposite surfaces, and are totally damped along their propagation course, i.e., the effect of friction from the bottom and the lid of the bucket is an additive effect. In case of a free surface, L will be determined by the expression:

$$L = -4\pi\eta R^2 H\beta \frac{J_2(\beta)}{J_1(\beta)} + 4\pi\eta R^3 \frac{k^2}{\nu^2} \sum_{n=1}^{\infty} \frac{1}{\mu_n^2 \vartheta_n^3}. \tag{2.61}$$

At the same time, the waves arising from the bottom of the bucket are damped without reaching a free surface and are incapable of being reflected from this surface.

7. Second Approximation for the Friction Function L. Low Viscosity Liquids

The expressions for L, given by formulas (2.53) and (2.61), contain the viscosity in complex arguments of Bessel functions, and are therefore unsuitable for processing experimental results. In order to simplify these expressions, it is possible to use either an asymptotic representation for Bessel functions, or an expansion in a series, or to draw up tables.

Let us make use at first of the first possibility. From the theory of Bessel functions, it is known that an asymptotic representation with the aid of two members gives good results for values of an argument higher than 8-10. According to (2.17), with an accuracy of $\nu_0 \ll 1$, the modulus of the argument of Bessel functions is equal to:

$$|\beta| = R\sqrt{\frac{q}{\nu}}. \tag{2.62}$$

Let us set up the requirement that:

$$R\sqrt{\frac{q}{\nu}} \geqslant 10. \tag{2.63}$$

Liquids which comply with this condition will be designated by us as low-viscosity liquids (Note: Obviously, this concept does not characterize merely the physical properties of the liquid, but rather the combination of physical properties and experimental conditions).

On the basis of recurring formulas, we have:

$$\frac{J_2(\beta)}{J_1(\beta)} = \frac{2}{\beta} - \frac{J_0(\beta)}{J_1(\beta)}. \tag{2.64}$$

By using an asymptotic representation:

$$\frac{J_0(\beta)}{J_1(\beta)} = \frac{\cos\left(\beta - \frac{\pi}{4}\right) + \frac{1}{8\beta}\sin\left(\beta - \frac{\pi}{4}\right)}{\sin\left(\beta - \frac{\pi}{4}\right) + \frac{3}{8\beta}\cos\left(\beta - \frac{\pi}{4}\right)}, \tag{2.65}$$

we obtain:

$$\frac{J_0(\beta)}{J_1(\beta)} = -i + \frac{1}{2\beta}; \tag{2.66}$$

By substituting into (2.64), we get:

$$\frac{J_2(\beta)}{J_1(\beta)} = i + \frac{3}{2\beta}. \tag{2.67}$$

Thus, when condition (2.63) is fulfilled, the expression for L assumes the following appearance:

$$L = -4\pi\eta R^3 H\left(i\beta + \frac{3}{2}\right) + 8\pi\eta R^3 \frac{k^2}{\nu^2} \sum_{n=1}^{\infty} \frac{1}{\mu_n^2 \vartheta_n^3}. \tag{2.68}$$

According to (2.17):

F88

$$\beta = R\sqrt{\frac{k}{\nu}} = R\sqrt{\frac{q}{2\nu}}\left[\sqrt{x+\sqrt{x^2+1}} + \right. \\ \left. + i\sqrt{-x+\sqrt{x^2+1}}\right], \tag{2.69}$$

where:

$$x = \frac{p}{q}. \tag{2.70}$$

Since x is a small value, by expanding β in series according to the power of x and discarding members of an order higher than x², we find:

$$i\beta = R\sqrt{\frac{q}{2\nu}}\left[-\left(1 - \frac{1}{2}x + \frac{1}{8}x^2\right) + \right. \\ \left. + i\left(1 + \frac{1}{2}x + \frac{1}{8}x^2\right)\right]. \tag{2.71}$$

From here, the following expressions are obtained for the real and imaginary parts of L:

$$L' = 2V\rho\nu R\sqrt{\frac{q}{2\nu}}\left[1 - \frac{1}{2}x + \frac{1}{8}x^2 - \frac{3}{2R\sqrt{\frac{q}{2\nu}}} + \right. \\ \left. + \frac{2}{HR\sqrt{\frac{q}{2\nu}}} \sum_{n=1}^{\infty} \operatorname{Re}\left(\frac{k^2}{\nu^2 \mu_n^2 \vartheta_n^2}\right)\right], \tag{2.72}$$

$$L'' = 2V\rho\nu R\sqrt{\frac{q}{2\nu}}\times \tag{2.73}$$

$$\times\left[-1-\frac{1}{2}x-\frac{1}{8}x^3+\frac{2}{HR\sqrt{\frac{q}{2\nu}}}\sum_{n=1}^{\infty}\operatorname{Im}\left(\frac{k^2}{\nu^2\mu_n^2\vartheta_n^3}\right)\right],$$

where V represents a volume of liquid in the bucket equal to $2\pi HR^2$.

8. Equation for Calculating the Viscosity

Let us calculate the expression L' + L". By introducing, instead of ϑ_n, the value θ_n according to the equation:

$$\theta_n^2 = \vartheta_n^2 R^2 = \mu_n^2 R^2 - \frac{k}{\nu} R^2, \tag{2.74}$$

one can easily see that:

$$L' + xL'' = 2V\rho\nu R\sqrt{\frac{q}{2\nu}}\,\sigma, \tag{2.75}$$

where:

$$\sigma = 1-\frac{3}{2}x-\frac{3}{8}x^3-\frac{3}{2R\sqrt{\frac{q}{2\nu}}}+ \tag{2.76}$$

$$+\frac{4R}{2H}\sum_{n=1}^{\infty}\frac{1}{R\sqrt{\frac{q}{2\nu}}}\left[\operatorname{Re}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right)+x\operatorname{Im}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right)\right].$$

By substituting the value of L' + xL" which we have found into (2.42), we get:

$$V\rho R\sqrt{\nu}\sqrt{\frac{q}{2}}\,\sigma = K(\mathfrak{p}-\mathfrak{p}_0). \tag{2.77}$$

By replacing in this equation $q, \mathfrak{p}, \mathfrak{p}_0$ with the aid of the obvious relations:

$$q = \frac{2\pi}{\tau}, \tag{2.78}$$

$$\vartheta = \frac{\delta}{\tau}, \qquad (2.79)$$

$$\vartheta_0 = \frac{\delta_0}{\tau_0}, \qquad (2.80)$$

where τ and τ_0 represent, respectively, the oscillation period of the bucket with and without the liquid, δ and δ_0 -- the logarithmic decrement of attenuation of these oscillations, we arrive at the following formula for calculating the kinematic viscosity of the liquid filling up the bucket:

F 8 8

$$\nu = \frac{1}{\pi}\left(\frac{K}{V\rho R}\right)^2 \frac{\left(\delta - \frac{\tau}{\tau_0}\delta_0\right)^2}{\tau\sigma^2}. \qquad (2.81)$$

Since in the last equation, $V\rho = M$ represents the mass of the liquid in the bucket, this equation can be written in the following form:

$$\nu = \frac{1}{\pi}\left(\frac{K}{MR}\right)^2 \frac{\left(\delta - \frac{\tau}{\tau_0}\delta_0\right)^2}{\tau\sigma^2}, \qquad (2.82)$$

where σ is expressed by the relation:

$$\sigma = 1 - \frac{3}{2}x - \frac{3}{8}x^2 - \frac{3}{R\sqrt{\frac{4\pi}{\tau\nu}}} + \frac{4R}{2H}\sum_{n=1}^{\infty}\frac{1}{R\sqrt{\frac{\pi}{\tau\nu}}}\left\{\mathrm{Re}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right) + x\,\mathrm{Im}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right)\right\}. \qquad (2.83)$$

Let us introduce the following designations:

$$Q = \sum_{n=1}^{\infty}Q_n = \sum_{n=1}^{\infty}\frac{1}{R\sqrt{\frac{\pi}{\tau\nu}}}\left\{\mathrm{Re}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right) + x\,\mathrm{Im}\left(\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^3}\right)\right\} \qquad (2.84)$$

and

$$y = R^2 \frac{q}{\nu} = R^2 \frac{2\pi}{\tau\nu}. \tag{2.85}$$

Let us examine the series $\sum\limits_{n=1}^{\infty} Q_n$. We get:

$$\frac{k^2R^4}{\nu^2\mu_n^2R^2\theta_n^2} = \frac{k^2R^4\theta_n}{\nu^2\mu_n^2R^2\theta_n^4} =$$

$$= \frac{\left(1 - x\frac{\mu_n^2R^2}{y^2} + x^2\right)^2 - \frac{\mu_n^2R^4}{y^2} - 2i\frac{\mu_n^2R^2}{y}\left(1 - \frac{\mu_n^2R^2}{y}x + x^2\right)}{\left(1 + \frac{\mu_n^4R^4}{y^2} - 2\frac{\mu_n^2R^2}{y}x + x^2\right)^2} \times \tag{2.86}$$

$$\times \sqrt{\frac{y}{2}}\left(\sqrt{\frac{\mu_n^2R^2}{y} - x + \sqrt{1 + \frac{\mu_n^4R^4}{y^2} - 2\frac{\mu_n^2R^2}{y}x + x^2}} - \right.$$

$$\left. - i\sqrt{-\frac{\mu_n^2R^2}{y} + x + \sqrt{1 + \frac{\mu_n^4R^4}{y^2} - 2\frac{\mu_n^2R^2}{y^2}x + x^2}}\right).$$

The terms of the series (2.84) decrease in proportion to $\frac{1}{\mu_n^2R^2}$, and therefore, without the risk of a great error, one can limit oneself to the first m terms of the series, which comply with the condition $\mu_n^2R^2 \leqslant$ 70-80% of y.

By expanding the radicals in series in (2.86), and by disregarding during all transformations, terms of an order higher than x and $\frac{\mu_n^6R^6}{y^3}$ in comparison to unity, we obtain the following approximate formula for the sum of the first m terms of the series (2.84):

$$\sum_{n=1}^{m} Q_n \approx -\frac{3}{4}\frac{m}{y}(2 + x) + \sum_{n=1}^{m}\left\{\left(1 - \frac{3}{2}x\right)\frac{1}{\mu_n^2R^2} - \right.$$

$$\left. - \frac{5}{8}\frac{\mu_n^2R^2}{y^2}(3 - 11x) - \frac{7}{4}\frac{\mu_n^4R^4}{y^3}(1 + x)\right\}. \tag{2.87}$$

However, the use of formula (2.87) is associated not only with unwieldy calculations, but also introduces a certain inaccuracy into the calculation.

It is more expedient to draw up a table and charts (grapl), which make the calculation of σ considerably more simple and accurate. For this purpose, let us expand $Q_n(x, y)$ in series according to the powers of x. Since x and the coefficient of x in Q_n are small values in comparison to unity, one can limit oneself to the first power of x:

$$\sum_{n=1}^{\infty} Q_n(x, y) = \sum_{n=1}^{\infty} Q_n(0, y) + \sum_{n=1}^{\infty} \frac{\partial Q_n(x, y)}{\partial x}\bigg|_{x=0} \cdot x = b - cx. \tag{2.88}$$

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Now, σ can be written in the form:

$$\sigma = 1 - \frac{3}{2}x - \frac{3}{8}x^2 - a + \frac{4R}{2H}(b - cx). \tag{2.89}$$

Here:

$$a = \frac{3}{\sqrt{2y}}. \tag{2.90}$$

The coefficients a, b, c are listed in Table 1 and are represented in Figure 2 as functions of y. The range of variations of y between 100 and 3,500 is quite sufficient for working purposes. Since in case of high values of y, all three coefficients vary very slowly, the values of these coefficients can be selected directly from the table in the region where $y > 2{,}500$, rounding off y to two significant digits.

Factor b, which plays a major role in σ, is calculated by direct summation of series (2.84). Factor c is calculated in an approximate way according to formula (2.87). The values of b, calculated accurately and by means of the approximate formula (2.87), exhibit a divergence of up to 15% when $y = 150$, of up to 5% when $y = 1{,}000$, and of up to 1% when $y = 2{,}000$. The figures mentioned above characterize the accuracy of formula (2.87).

The calculation of ν is conducted in the following order: first, ν^* is calculated by means of formula (2.82) when $\sigma = 1$, then factors a, b, c are determined with the aid of the curves illustrated in Figure 2, when $y = \frac{2\pi}{t\nu^*} R^2$, after which σ is calculated by means of formula (2.89), and finally, the final result is determined:

$$\nu = \frac{\nu^*}{\sigma^2}. \tag{2.91}$$

In case σ differs considerably from unity, the second approximation for ν is determined in the same manner.

Table 1

y	*a*	*b*	*c*	*y*	*a*	*b*	*c*
100	0,2121*	0,0466	0,1150	1700	0,0514	0,1032	0,1683
150	1732	587	1243	1800	500	1037	1688
200	1500	669	1312	1900	487	1042	1693
250	1342	725	1366	2000	474	1047	1697
300	1224	765	1409	2100	463	1052	1701
350	1130	798	1444	2200	452	1056	1704
400	1061	826	1472	2300	442	1060	1707
450	1000	850	1496	2400	433	1064	1710
500	947	870	1517	2500	424	1067	1713
600	865	901	1552	2600	416	1070	1716
700	801	926	1579	2700	408	1073	1718
800	750	946	1601	2800	401	1076	1720
900	708	962	1618	2900	394	1078	1722
1000	671	975	1631	3000	387	1080	1724
1100	639	986	1642	3100	381	1082	1725
1200	612	995	1651	3200	375	1084	1726
1300	588	1004	1659	3300	369	1086	1727
1400	567	1012	1666	3400	364	1088	1728
1500	547	1019	1672	3500	358	1090	1729
1600	530	1026	1678				

*In this and all other tables containing "commas", these represent decimal points

It should be noted that, during the derivation of (2.29), the constancy N was not used anywhere, which makes it possible to avoid any limitations during the selection of a material for the suspension thread.

During calculations according to formula (2.82), an exact knowledge of τ_0 and δ_0 is not required, since the member containing these values is usually quite small in comparison to δ.

Finally, we wish to emphasize that the expression for σ, given by formula (2.89), is obtained in the assumption that there are two end surfaces of contact (tangency) between the liquid and the bucket: namely, at the bottom and on the lid. In case a single contact surface (bottom) and a free surface of the meniscus are present, the coefficient $\frac{4R}{2H}$, adjacent to the last addend in the right side of formula (2.89), must be reduced two times (i.e., made 2 times smaller).

9. Second Approximation for the Friction Function L. High-Viscosity Liquids

The previously obtained equations (2.27) and (2.42) are quite general and do not contain any limitations, except for physical premises of the theory, which were formulated in # 1. Computing formulas for calculating the viscosity of low-viscosity liquids were obtained as shown in # 5-8. The limitations introduced for this purpose are expressed by the inequations (2.51) and (2.63).

L. S. Priss has presented a modification of the theory, adapted to the problem of measuring the viscosity of high-viscosity liquids. The material presented in # 9-10 is based on the work of L. S. Priss (4).

F 8 8

Let us retain the first approximation for the friction function L, expressed by inequation (2.51) and the resulting condition (2.52). Consequently, L can be still expressed as before by means of the equation (2.53), or in a different form, considering that $\pi R^2 \cdot 2H\rho = M$ and (2.64):

$$L = 2M\nu\left[\beta\frac{J_0(\beta)}{J_1(\beta)} - 2\right] + \frac{4M\nu}{H}\sum_{n=1}^{\infty}\frac{k^2}{\nu^2\mu_n^2\theta_n^3}. \qquad (2.92)$$

Let us discard for the time being the last term in this equation, which corresponds to an examination of an infinitely long column of liquid, and let us insert the corresponding expression for L into equation (2.42). By discarding $\frac{\nu}{q}$ and $\frac{\nu_0}{\nu}$ in comparison with unity, and taking (2.17) into account), we shall obtain the following expression for the attenuation decrement (damping ratio):

$$\delta = \mathrm{Re}\left\{\frac{2\pi M R^4}{K}\left(\frac{\sqrt{i}}{\xi}\frac{J_0(\xi\sqrt{i})}{J_1(\xi\sqrt{i})} - \frac{2}{\xi^2}\right)\right\}, \qquad (2.93)$$

where:

$$\xi = R\sqrt{\frac{2\pi}{\tau\nu}} = \sqrt{y} \approx |\beta|. \qquad (2.94)$$

The dependence of δ on ξ is illustrated in Figure 3 in relative units.

Since ν is inversely proportional to y, it can be seen from the figure that the attenuation decrement approaches zero at small and high values of ν, reaching a maximum value when $\xi = 4.3$. This result is quite understandable from a physical standpoint, since in the first case the properties of the liquid are such that it approaches the state of an ideal liquid, and in the second case, that of a solid body.

By introducing the limitation $\xi \geqslant 10$, we examined the falling part of the curve $\delta(\xi)$ and obtained formulas for low-viscosity liquids. It is obvious that the use of this sector of the curve for measuring high-viscosity liquids with a high value of ν yields values of R or q which are too high, i.e., results in practically unacceptable experimental conditions.

The ascending part of the $\delta(\xi)$ curve is quite suitable for calculating the viscosity of high-viscosity liquids. The statements made above in regard to the shape of the $\delta(\xi)$ curve help to clarify the concepts of a low- and high-viscosity liquid: the former corresponds to the falling part of the curve, and the latter -- to the rising part of the curve.

At values of $|\beta| \leqslant 1.2$, the function $\frac{J_0(\beta)}{J_1(\beta)}$ can be expanded in series according to the powers of β:

$$\beta\frac{J_0(\beta)}{J_1(\beta)} = 2\left(1 - \frac{\beta^2}{8} - \frac{\beta^4}{192} - \frac{\beta^6}{3072} - \frac{\beta^8}{46\,080} - \ldots\right). \tag{2.95}$$

Then, (2.92) assumes the following appearance:

$$L = -2M\nu\left(\frac{\beta^2}{4} + \frac{\beta^4}{96} + \frac{\beta^6}{1536} + \frac{\beta^8}{23\,040} - 2U\right), \tag{2.96}$$

where:

$$U = \frac{1}{H}\sum_{n=1}^{\infty}\frac{k^8}{\nu^2\mu_n^2\theta_n^8}. \tag{2.97}$$

After separating in (2.96) the real and imaginary parts L' and L", forming the expression $L' + \frac{\mathfrak{p}}{q}L''$ and substituting this expression into (2.42), by means of rather cumbersome calculations, it is possible to obtain the following formula:

$$\left(K + \frac{MR^2}{2}\right)\mathfrak{p} - K\mathfrak{p}_0 = \frac{MR^4}{96\nu}q^2\left[1 - 3\frac{\mathfrak{p}^3}{q^3} + \frac{\mathfrak{p}}{4\nu}R^2 - \right.$$
$$\left. - \frac{q^2}{240\nu^2}R^4 - 192\frac{R}{H}\sum_{n=1}^{\infty}\frac{1}{\mu_n^6 R^6}\right], \tag{2.98}$$

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in which all members smaller than 10^{-3} are dropped in the bracket. By designating this bracket as σ and replacing ν, ν_0 and q by periods and decrements, we obtain the following equation for calculating the viscosity:

$$\nu = \frac{0{,}8225\,\frac{MR^2}{2}\cdot R^2\sigma}{\tau\left[\left(K+\frac{MR^2}{2}\right)\delta - K\frac{\tau}{\tau_0}\delta_0\right]}, \qquad (2.99)$$

where:

$$\sigma = 1 + 0{,}250z\delta - 0{,}076\delta^2 - 0{,}1645z^2 - 0{,}4924\,\frac{R}{2H} \qquad (2.100)$$

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and:

$$z = \frac{R^2}{\tau\nu}. \qquad (2.101)$$

When only one contact surface (liquid with a free surface) is present, the last member in σ must be reduced (made smaller) two times.

As previously, the calculation of ν is performed by the method of successive approximations: first, the rough value $\nu = \nu^*$ at $\sigma = 1$ is determined, which is then substituted into σ, and the final result is obtained by means of the formula:

$$\nu = \nu^*\sigma. \qquad (2.102)$$

The criterion for the applicability of formula (2.99) is:

$$\xi = R\sqrt{\frac{2\pi}{\tau\nu}} \leqslant 1{,}0 \sim 1{,}2,$$

or, otherwise:

$$\frac{MR^2}{\left(K+\frac{MR^2}{2}\right)\delta - K\frac{\tau}{\tau_0}\delta_0} > 2{,}2. \qquad (2.103)$$

Equation (2.99) differs substantially in its structure from equation (2.82). According to the former equation (2.99), at small δ values, the viscosity is inversely proportional to the attenuation decrement; according to the latter (2.82), the viscosity is directly proportional to the square of the decrement. This difference is based on sufficiently obvious physical reasons.

As was already mentioned, formula (2.99) covers the range of variation $0 < \xi \leqslant 1.2$, while formula (2.82) covers the range $10 \leqslant \xi < \infty$, and thus, there remains a range of variation in the viscosity (on the given instrument), which corresponds to values of ξ, lying within the range $1.2 < \xi < 10$. This range, naturally, can be spanned not by one, but by two instruments, having appropriately selected τ_0, K, R and M characteristics.

In order to narrow down this range, L. S. Priss performed a calculation of L, by representing this value in the following form:

$$L = \frac{2MR^2q}{2\pi}\left[P_1(x, \xi) + \frac{4R}{2H}Q_1(x, \xi)\right], \tag{2.104}$$

where $P_1(x, \xi)$ corresponds to the first addend in the right part of (2.92) and $Q_1(x, \xi)$ -- to the second addend. Then, the formula used for calculating ν with the aid of tables, in case of friction surfaces at the bottom and on the lid, assumes the appearance: F 88

$$\frac{10K}{MR^2}\left(\delta - \frac{\tau}{\tau_0}\delta_0\right) + 5\delta = a + b\delta - \frac{4R}{2H}(d + e\delta) - c\delta^2. \tag{2.105}$$

The values of factors a, b, c, d, e, corresponding to the range $1.0 \leqslant \xi \leqslant 4.2$, represented not as functions of ξ, but as functions of the parameter $\frac{\nu\tau}{R^2}$ in order to make the calculations more convenient, are listed in Table 2. Calculation with the aid of this table is performed in the following manner: at first, the numerical value of the following quantity is determined:

$$\frac{10K}{MR^2}\left(\delta - \frac{\tau}{\tau_0}\delta_0\right) + 5\delta = A, \tag{2.106}$$

and then the two closest values of A_1 and A_2 ($A_1 < A < A_2$) are found in the table, after which $\frac{\nu\tau}{R^2}$, corresponding to the found value of A, is determined by linear interpolation. In this connection, one should be guided by the fact that the value of A is mainly determined by factor a. For this reason, prior to performing an accurate calculation, it is necessary to mentally appraise which line in the table corresponds approximately to the calculated value of A; usually, this line is located slightly above the line with a value of A = a. With a little practice, a rapid finding of A_1 and A_2 does not present any difficulty.

Let us give an example of such a calculation. We shall assume that $A = 4.230$, $\delta = 0.2405$, $\tau = 9.433$ sec, $2H = 5.0$ cm, $R = 1.296$ cm, $R^2 = 1.680$.

Table 2

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8

$\sqrt{\frac{b}{R^2}}$	*a*	*b*	*c*	*d*	*e*
0,35	5,363	2,495	0, 99	0,233	0,264
0,36	5,357	2,455	0,101	0,244	0,264
0,37	5,349	2,415	0,103	0,255	0,264
0,38	5,339	2,375	0,105	0,266	0,263
0,39	5,327	2,336	0,107	0,277	0,263
0,40	5,313	2,297	0,110	0,287	0,263
0,41	5,297	2,259	0,113	0,296	0,262
0,42	5,279	2,220	0,116	0,305	0,262
0,43	5,259	2,182	0,119	0,314	0,261
0,44	5,238	2,144	0,122	0,322	0,261
0,45	5,216	2,107	0,125	0,329	0,260
0,46	5,192	2,071	0,128	0,336	0,260
0,47	5,167	2,034	0,131	0,343	0,259
0,48	5,140	1,998	0,133	0,349	0,258
0,49	5,113	1,963	0,136	0,354	0,257
0,50	5,085	1,928	0,139	0,359	0,255
0,52	5,027	1,859	0,144	0,369	0,252
0,54	4,966	1,793	0,149	0,377	0,248
0,56	4,902	1,729	0,154	0,384	0,243
0,58	4,837	1,667	0,159	0,390	0,238
0,60	4,771	1,607	0,163	0,394	0,233
0,62	4,704	1,549	0,167	0,398	0,228
0,64	4,636	1,493	0,171	0,400	0,223
0,66	4,569	1,439	0,175	0,402	0,218
0,68	4,502	1,388	0,178	0,403	0,213
0,70	4,435	1,339	0,181	0,404	0,207
0,72	4,369	1,292	0,183	0,403	0,202
0,74	4,304	1,247	0,185	0,402	0,197
0,76	4,239	1,204	0,186	0,401	0,192
0,78	4,175	1,163	0,188	0,400	0,187
0,80	4,112	1,123	0,189	0,399	0,182
0,82	4,049	1,085	0,190	0,397	0,177
0,84	3,988	1,049	0,190	0,395	0,172
0,86	3,928	1,014	0,191	0,393	0,168
0,88	3,869	0,980	0,191	0,391	0,163
0,90	3,811	0,948	0,191	0,388	0,159
0,92	3,755	0,917	0,191	0,386	0,155
0,94	3,699	0,888	0,191	0,383	0,151
0,96	3,644	0,860	0,190	0,380	0,147
0,98	3,591	0,833	0,190	0,376	0,143
1,00	3,539	0,808	0,190	0,373	0,140
1,04	3,438	0,759	0,189	0,366	0,132
1,08	3,342	0,715	0,188	0,360	0,125
1,12	3,250	0,674	0,187	0,353	0,118

(Table 2 continued)

$\frac{\tau}{R^2}$	*a*	*b*	*c*	*d*	*e*
1,16	3,162	0,636	0,186	0,346	0,112
1,20	3,078	0,601	0,184	0,340	0,106
1,24	2,998	0,569	0,182	0,333	0,101
1,28	2,922	0,532	0,180	0,327	0,096
1,32	2,849	0,511	0,178	0,320	0,092
1,36	2,779	0,485	0,176	0,314	0,088
1,40	2,712	0,461	0,173	0,308	0,084
1,44	2,648	0,439	0,171	0,302	0,080
1,48	2,586	0,418	0,168	0,297	0,076
1,52	2,527	0,399	0,166	0,291	0,073
1,56	2,470	0,381	0,163	0,285	0,070
1,60	2,416	0,363	0,161	0,280	0,067
1,64	2,364	0,347	0,158	0,275	0,065
1,68	2,314	0,332	0,156	0,270	0,062
1.72	2,266	0,319	0,153	0,265	0,060
1,76	2,220	0,306	0,151	0,260	0,057
1,80	2,175	0,293	0,148	0,255	0,055
1,84	2,132	0,281	0,146	0,251	0,053
1,88	2,091	0,270	0,143	0,246	0,051
1,92	2,051	0,260	0,141	0,242	0,049
1,96	2,012	0,250	0,139	0,238	0,047
2,00	1,975	0,241	0,137	0,234	0,046
2,05	1,930	0,230	0,135	0,229	0,044
2.10	1,887	0,220	0,132	0,224	0,042
2,15	1,847	0,210	0,130	0,220	0,041
2,20	1,808	0,201	0,127	0,215	0,039
2,25	1,770	0,193	0,125	0,211	0,037
2,30	1,734	0,185	0,123	0,207	0,036
2,35	1,700	0,177	0,121	0,203	0,034
2,40	1,666	0,170	0,119	0,199	0,033
2,45	1,634	0,164	0,117	0,196	0,032
2,50	1,603	0,158	0,115	0,192	0,030
2,60	1,545	0,146	0,112	0,186	0,028
2,70	1,490	0,136	0,109	0,179	0,026
2,80	1,439	0,127	0,105	0,173	0,024
2,90	1,391	0,119	0,102	0,168	0,023
3,00	1,347	0,111	0,099	0,163	0,021
3,10	1,305	0,104	0,096	0,158	0,020
3,20	1,265	0,098	0,093	0,153	0,019
3,30	1,228	0,092	0,090	0,149	0,018
3,40	1,193	0,087	0,088	0,145	0,017
3,50	1,160	0,082	0,086	0,141	0,016
3,60	1,129	0,078	0,083	0,138	0,015
3,70	1,099	0,074	0,081	0,134	0,014

(Table 2 continued)

$\nu\frac{\tau}{R^2}$	a	b	c	d	e
3,80	1,071	0,070	0,079	0,131	0,013
3,90	1,044	0,067	0,077	0,127	0,013
4,00	1,019	0,063	0,075	0,124	0,012
4,20	0,971	0,057	0,072	0,119	0,011
4,40	0,927	0,052	0,069	0,114	0,010
4,60	0,887	0,048	0,066	0,109	0,009
4,80	0,851	0,044	0,063	0,104	0,008
5,00	0,818	0,041	0,060	0,100	0,008
5,20	0,787	0,038	0,058	0,096	0,007
5,40	0,758	0,035	0,056	0,092	0,006
5,60	0,731	0,033	0,054	0,089	0,006
5,80	0,706	0,030	0,053	0,087	0,006
6,00	0,683	0,028	0,051	0,084	0,006
6,20	0,661	0,026	0,050	0,081	0,005

F88

In Table 2, we find the line in which $a = 4.239 \approx A$, which corresponds to a value of $\nu\frac{\tau}{R^2} = 0.76$. We note the factors b and d on this line: $b\delta \approx 0.300$, $\frac{4R}{2H} d \approx 0.400$. Consequently, in order to obtain the value of A which we are looking for, we must pick a line in which the value of a is greater than 4.239 by approximately 0.100 (since $b\delta$ is included in formula (2.105) with a plus sign, and $\frac{4R}{2H}d$ - with a minus sign). We select a line in which a = 4.369, and we calculate $A_1 = 4.369 + 1.292\delta - \frac{4R}{2H}(0.403 + 0.202\delta) = 4.201$.

We have obtained $A_1 < A$. Now, we have to find $A_2 > A$. For this purpose, we select the next line above and we get: $A_2 = 4.435 = 1.339\delta + 0.181\delta^2 - \frac{4R}{2H}(0.404 + 0.207\delta) = 4.275$. Values of $\nu\frac{\tau}{R^2}$, equal to 0.72 and 0.70, correspond to the values of A_1 and A_2. From here, we find the value of $\nu\frac{\tau}{R^2}$ which we are looking for:

$$\nu\frac{\tau}{R^2} = 0{,}70 + 0{,}02\frac{A_1 - A}{A_1 - A_2} = 0{,}712 \quad \text{and} \quad \nu = 0{,}712\frac{R^2}{\tau} = 0{,}127.$$

10. Liquids With an Intermediate Viscosity Value

As can be seen from the curve shown in Figure 3, the sector of the $\delta(\xi)$ curve in the interval of $4.2 \leqslant \xi \leqslant 10$ cannot be used for calculating ν, first, in view of the weak dependence of δ on ν near the maximum (peak), and second, in view of the insufficient accuracy of the asymptotic representation of Bessel functions when $\xi < 10$.

Thus, the calculations described above cannot be linked (tied) together. The above-mentioned discrepancy in the calculations, upon which the calculation of the kinematic viscosity is based, apparently is of no practical significance in view of the considerations listed below. The intervals within which the viscosity varies, corresponding to the regions $0.4 \leqslant \xi \leqslant 4.2$ and $\xi \geqslant 10$, are quite sufficient for studying the vast majority of homogenous liquids, which are characterised in general by a weak temperature dependence of the kinematic viscosity. In case of a strong temperature dependence of the kinematic viscosity, on the other hand (as for example, in the case of glycerine), the region where a discrepancy occurs is sufficiently narrow and the transition from values of $\xi > 10$ to values of $\xi < 4.2$ in the continuous process of viscosity measurements makes it possible to solve in a reliable manner the problem concerned with the temperature dependence of the kinematic viscosity.

However, in case of necessity, it is possible to set up calculation tables also for the region of discrepancy of $4.2 < \xi < 10$. We shall briefly point the method used for solving this problem. Let us take formula (2.45) and let us plot for this formula the graph $\frac{\tau^2}{\tau_0^2} - 1 = \bar{f}(\xi)$, using the same assumptions as those used during the plotting of the graph for $\bar{\delta}(\xi)$. We have:

$$\frac{\nu_0^2 + q_0^2}{\nu^2 + q^2} - 1 = -\frac{1}{q}\frac{L''}{K} \approx \frac{\tau^2}{\tau_0^2} - 1 = \bar{f}(\xi). \qquad (2.107)$$

This value is presented as a function of ξ in Figure 3.

A comparison of the $\bar{f}(\xi)$ curve with the $\bar{\delta}(\xi)$ curve shows that, precisely in the region where δ is not greatly dependent upon the viscosity, $\frac{\tau^2}{\tau_0^2} - 1$ exhibits a sharply expressed dependence upon ν.

As was pointed out above, the use of formula (2.45) is connected with the assurance that N is independent of the load (constancy of τ_0 at a given K and various loads on the suspension thread) and with the measurement of τ_0 over the entire temperature range in which the viscosity is measured. When these conditions are fulfilled, the utilization of formula (2.45) is quite analogous to the utilization of formula (2.42).

Let us represent (2.107) in the following form:

$$\frac{\tau^2}{\left[1+\left(\frac{\delta}{2\pi}\right)^2\right]\tau_0^2}-1=-\frac{2MR^2}{2\pi K}\left[P'(x,\ \xi)+\frac{4R}{2H}Q'(x,\ \xi)\right] \qquad (2.108)$$

and let us perform calculations similar to those which were performed in connection with formula (2.105). As a result, we will obtain the following relation:

$$\frac{\tau^2}{\left[1+\left(\frac{\delta}{2\pi}\right)^2\right]\tau_0^2}-1=f+g\delta+h\delta^2+\frac{4R}{2H}(j+l\delta). \qquad (2.109)$$

F 88 The factors f, g, h, j, l must be incorporated into a table similar to Table 2; the drawing of such a table represents a solution of the problem concerning the setting up of a calculating system for liquids with an intermediate viscosity of $4.2 < \xi < 10$.

11. Evaluation of the Role Performed by Nonlinear Terms in the Equation Describing the Motion of the Liquid

It was pointed out in # 2 that the assumption of an annular motion of the liquid in the bucket, as a result of which nonlinear terms are identically converted to zero, is valid in case of small angles of the torsional oscillation motion of the suspension system.

Let us attempt to present a theoretical evaluation of the role played by nonlinear terms in equation (2.4), upon which the theory of the method is based. Let us write an equation for the tangential velocity v, retaining the nonlinear terms, but considering at the same time the axial symmetry of the motion, as a result of which the φ derivatives of the pressure and velocity components must be converted to zero:

$$\frac{\partial v}{\partial t}+v_r\frac{\partial v}{\partial r}+v_z\frac{\partial v}{\partial z}+\frac{v_r v}{r}=\nu\left\{\frac{\partial^2 v}{\partial r^2}+\frac{\partial^2 v}{\partial z^2}+\frac{1}{r}\frac{\partial v}{\partial r}-\frac{v}{r^2}\right\}. \qquad (2.110)$$

This equation differs from (2.4) in that it contains, in its left side, a sum of nonlinear terms:

$$\theta=v_r\frac{\partial v}{\partial r}+v_z\frac{\partial v}{\partial z}+v_r\frac{v}{r}. \qquad (2.111)$$

In order to evaluate the partial derivatives entering into the composition of θ and the ratio $\frac{v}{r}$, let us utilize the fact that the flow takes place in a layer adjacent to the wall, having a thickness of the order of the length L of a viscous displacement wave, whereby L is equal to:

$$L = 2\pi\sqrt{\frac{2\nu}{q}}, \tag{2.112}$$

which is propagated at a logarithmic decrement of spatial attenuation, equal to 2π. (<u>Note</u>: See # 6 of this chapter and reference 3 in the bibliography of this chapter.)

The expression for the tangential velocity on the walls of the bucket is given by the boundary conditions (2.5) and (2.6), and during the calculation of the partial derivatives, it can be assumed that the change in the velocity from zero to its value on the wall of the bucket takes place over a distance equal to the length of a viscous wave. On this basis, by making use of (2.5) and (2.6), we find:

$$\theta \approx v_r \frac{l\Omega\,\mathrm{Re}^{-kt}}{L} + v_z \frac{l\Omega r e^{-kt}}{L} + v_r \frac{l\Omega r e^{-kt}}{r}. \tag{2.113}$$

By substituting R for r in the right side (which will only increase the value of θ), and after introducing the designation:

$$v' = l\Omega\,\mathrm{Re}^{-kt}, \tag{2.114}$$

we arrive at the expression:

$$\theta \approx \frac{v'}{L}\left[v_r\left(1 + \frac{L}{R}\right) + v_z\right]. \tag{2.115}$$

However, we should not be interested in the value θ itself, but rather in its relation to $\frac{\partial v}{\partial t}$, which will be designated as θ'. We get:

$$\frac{\partial v}{\partial t} \approx \frac{\partial v'}{\partial t} = -kv', \tag{2.116}$$

and consequently:

$$\theta' \equiv \frac{\theta}{\left(\frac{\partial v}{\partial t}\right)} \approx \mathrm{Re}\left\{\frac{\left|v_r\left(1 + \frac{L}{R}\right) + v_z\right|}{Lk}\right\}. \tag{2.117}$$

By calculating the product Lk with the aid of (2.112) and by introducing the parameter y according to (2.85), the latter expression can be rewritten as follows:

$$\theta' \approx \frac{v_r\left(1 + \frac{L}{R}\right) + v_z}{l4\sqrt{2}\pi^3 R}\tau\sqrt{y}. \tag{2.118}$$

It is natural to assume that components v_r and v_z have the same type of time dependence as the main component v. Therefore, we can write:

$$v_r \approx v_z \approx \gamma v' \qquad (2.119)$$

where γ is a numerical factor (multiplier), indicating how many times the initial amplitude of the radial (and axial) oscillations is smaller than the initial amplitude of torsional oscillations. By designating the former as l_0, and noting that the latter, according to (2.37), is equal to $\alpha_0' R$, we get:

$$\gamma = \frac{l_0}{\alpha_0' R}. \qquad (2.120)$$

After inserting into (2.118), instead of v_r and v_z, their amplitude values according to (2.119) and (2.114), and assuming that $L \approx R$, we arrive at the expression:

$$\theta' \approx \frac{3\Omega e^{-pt} \gamma\tau \sqrt{y}}{4\sqrt{2}\,\pi^2}, \qquad (2.121)$$

in which, in turn, we shall replace the initial amplitude of the angular velocity Ω by the initial amplitude of the angular displacement α_0', by making use of the obvious relation:

$$\Omega = q\alpha_0', \qquad (2.122)$$

after which we shall get:

$$\theta' \approx \frac{3\alpha_0' \gamma e^{-\delta\frac{t}{\tau}} \sqrt{y}}{2\sqrt{2\pi}}. \qquad (2.123)$$

Since measurements are always initiated after a certain number of initial oscillations (regular regime), we can assume that:

$$\frac{3}{2\sqrt{2\pi}} e^{-\delta\frac{t}{\tau}} \approx 0{,}1 \qquad (2.124)$$

and thus we obtain the following estimated expression:

$$\theta' \approx \alpha_0' \gamma \sqrt{\frac{y}{100}}, \qquad (2.125)$$

or, in a different form:

$$\theta' \approx \frac{l_0}{R}\sqrt{\frac{y}{100}}. \tag{2.126}$$

The values of y, listed in Table 1, lie within the range $100 \leqslant y \leqslant 3{,}500$, which yields the following range for θ' within the limits of this table:

$$\alpha'_0\gamma \leqslant \theta' \leqslant 6\alpha'_0\gamma. \tag{2.127}$$

Thus, when y varies within the limits given in Table 1, the variation in the value of θ' does not exceed the limits of one order. For this reason, one can be certain that if, at a certain value of y within the limits of Table 1, the value of θ' will be very small, this value will not increase under any other value of y used in viscosity measurement tests.

As was stated above, the concept of an annular motion of the liquid in the bucket proves to be valid in case of small angles of torsional oscillations $\alpha'_0 < 1$. It can be seen from formula (2.125) that such a case takes place naturally on the basis of the above examination of nonlinear terms. We can note that, assuming $\alpha'_0 \approx 0.1$ (measured in degrees $\approx 6^\circ$), we get $\theta' = 0.1\gamma\sqrt{\frac{y}{100}}$, i.e., it would be possible to assume that even when $\gamma' \approx 1$, θ' remains sufficiently small in case of a maximum value of y.

Finally, it is useful to recall the tests performed by Townend and Fudge (5), in which it was established that, in case of a stationary flow of the liquid, ultramicroscopic particles in the boundary layer move along a trajectory (path) similar to a sine curve (the amplitude of displacements in the direction of a normal to the wall was of the order of 10^{-4} cm). If it is assumed that in our case, l_0 is of the same order of magnitude, then we find that the maximum value of $\theta' \approx 10^{-3}$ (assuming that $R \approx 1$).

In summing up the results of our analysis of nonlinear terms, we can note that, first, when the components v_r and v_z are strictly equal to zero, the ratio θ' is also strictly equal to zero. Second, the variation of θ' within the limits of Table 1, in case v_r and v_z are different from zero, barely exceeds the limits of one order. Third, in spite of the absence of direct data on v_r and v_z, indirect considerations based on experimental observations confirm the small size of the value θ' under actual viscosity measurement conditions. An estimate of the Reynolds number, described in # 5 of Chapter III, also speaks in favor of this conclusion.

12. Thickness of the Liquid Flow (Stream) Adjacent to the Wall of the Bucket

As was already mentioned above, the development of the process involving a viscous flow of the liquid in the bucket takes place in the layer adjacent to the wall near internal surfaces. The thickness of this layer, according to the order of its magnitude, is equal to the length of the viscous wave, which can be determined by means of formula (2.112). One can easily see that the following relationship takes place:

$$L = \frac{\sqrt{8\pi} R}{\sqrt{y}}. \qquad (2.128)$$

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When R = 1 and $0.4 \leqslant \sqrt{y} \leqslant 60$ (possible range of variation of y within the limits of the methods developed for calculating the viscosity), L may vary within the range $0.15 \leqslant L \leqslant 22$, where L is given in cm. When the radius is reduced two times, the lower limit of L will be equal to 0.07 cm.

Thus the experimental possibilities of the method easily allow the realization of various types of motion, starting with flows (currents) typical for wide pipes and ending with flows corresponding to extremely fine (thin) capillary tubes.

On the other hand, by varying the initial amplitude of torsional oscillations, it is possible to vary within wide limits the gradient of the tangential velocity in the vicinity of the wall, the maximum value of which is expressed by the formula:

$$\frac{\partial v}{\partial r} \approx \frac{\alpha'_0 q R}{L} = \frac{q \alpha'_0}{\sqrt{8\pi}} \sqrt{y} = \frac{\alpha'_0}{\sqrt{2\tau}} \sqrt{y}. \qquad (2.129)$$

Obviously, new possibilities are opened up here for studying the behavior of a moving (mobile) liquid near the boundary of a solid wall. In case of large gradients of the tangential velocity, when an extremely thin layer of liquid takes part in the flow process, the thickness of which can be reduced to several microns (by exceeding the limits of $y > 3,500$, as a result of the application of forced oscillations), the possibility that a boundary slide (slip) may arise is not excluded. The correct nature of the consideration of such a problem in regard to colloids is generally beyond doubt, following the work done by D. M. Tolstoy, who has demonstrated the existence of a boundary slide (slip) during the flow of a colloid liquid through capillaries, and who has given a number of interesting theoretical calculations related to this problem (6).

In the absence of wetting, such a slip under appropriate conditions appears to be quite probable also in case of uniform (homophase) liquids. If we attempt to explain this idea by using model terminology, we can make the following statements. In the absence of wetting, the liquid moves together with the wall as a result of the existence of an interaction similar to dry friction. If the molecular friction forces in the liquid, proportional to the velocity gradient, are small, then the boundary layer of the liquid is restrained (held back) by the wall. In case of large velocity gradients, the molecular friction forces can exceed the forces of "dry" friction on the wall, as a result of which a discontinuity of the motion characteristics at the liquid-wall boundary will take place at the given motion velocity. Probably, in the presence of wetting, a slip (slide) of the moving liquid in relation to the wall is impossible in view of the high molecular adhesive power between the wall and the liquid.

An increase in the oscillation frequency also opens up new possibilities for studying the viscous properties of a thin boundary layer of the liquid, including those of a surface film on the liquid.

A study of the problems mentioned above is of great interest both from the standpoint of molecular physics and hydrodynamics. However, a more detailed examination of these problems lies beyond the scope of the various problems which are directly connected with the clarification of viscous properties of metallic liquids.

13. Conclusion on the General Theory of the Method

The experimental method for measuring the viscosity of liquids, based on the observation of the torsional oscillations of a cylindrical bucket filled with the liquid being tested, the theory of which has been presented above, allows us (aided by several formulas and tables) to cover a thousandfold change in the viscosity by means of one series of measurements performed on a single instrument. The basic parameter of this method is the value:

$$\xi = \sqrt{y} = R\sqrt{\frac{2\pi}{\tau\nu}} \approx |\beta|. \qquad (2.130)$$

If $\xi \geqslant 10$, then the viscosity is calculated by means of formulas (2.82) and (2.89) with the aid of Table 1 or Figure 2, whereby the approximate value of the viscosity is determined by means of formula (2.82) when $\sigma = 1$. For the region where $\xi \leqslant 4.2$, in which a change in the attenuation decrement with a change in viscosity has a reverse character to a change in the period, the viscosity is calculated by means of formula (2.105) with the aid of Table 2 (when $1.2 \leqslant \xi \leqslant 4.2$) and equations (2.99) and (2.100) (when $\xi < 1.2$), when the approximate value of the viscosity ν^* is determined by means of the same equation (2.99), in case $\sigma = 1$.

In the region where $4.2 < \xi < 10$, no calculating system for processing direct experimental results has been developed, since no practical need for such a system has arisen so far.

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Chapter III

Theory of the Method (Continued)

1. Plotting of $\bar{\delta}(\xi)$ and $\bar{f}(\xi)$ Curves

Let us consider in greater detail the problem of plotting the $\bar{\delta}(\xi)$ and $\bar{f}(\xi)$ curves shown in Figure 3. We shall start with expression (2.93) for $\delta(\xi)$, which we shall rewrite in the following form:

$$\delta(\xi)=\frac{2\pi MR^2}{K}\,\mathrm{Re}\left(F-\frac{2}{\xi^2}\right). \qquad (3.1)$$

where:

$$F=\frac{\sqrt{i}J_0(\xi\sqrt{i})}{\xi J_1(\xi\sqrt{i})}. \tag{3.2}$$

Expression (2.107) for the function:

$$\frac{\tau^2}{\tau_0^2}-1=f(\xi) \tag{3.3}$$

will be written by us as follows:

$$f(\xi)=-\frac{\tau}{2\pi K}\operatorname{Im}(L). \tag{3.3'}$$

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By making use of (2.92) and adopting the same conditions under which (2.93) or (3.1) were obtained, equation (3.3) can be represented in the following form:

$$f(\xi)=-\frac{2MR^2}{K}\operatorname{Im}(F). \tag{3.4}$$

The argument of Bessel functions will be written by us in a trigonometric form:

$$\xi\sqrt{i}=\frac{\xi}{\sqrt{2}}(1+i)=\xi e^{i\frac{\pi}{4}}, \tag{3.5}$$

and then F will assume the following appearance:

$$F=\frac{\sqrt{i}J_0(\xi e^{i\frac{\pi}{4}})}{\xi J_1(\xi e^{i\frac{\pi}{4}})}. \tag{3.6}$$

Let us assume that:

$$J_0\left(\xi e^{i\frac{\pi}{4}}\right)=A+iB, \tag{3.7}$$

$$J_1\left(\xi e^{i\frac{\pi}{4}}\right)=C+iD, \tag{3.8}$$

With the aid of these expressions, F can be written as follows:

$$F=\frac{\sqrt{i}}{\xi}\,\frac{[AC+BD+i(BC-AD)]}{C^2+D^2} \tag{3.9}$$

and by replacing:

$$\sqrt{i}=\frac{1+i}{\sqrt{2}}, \tag{3.10}$$

we shall finally find the following formula:

F 8 8

$$F=\frac{1+i}{\sqrt{2}}\,\frac{[(AC+BD)+i(BC-AD)]}{\xi(C^2+D^2)}. \tag{3.11}$$

From here:

$$\operatorname{Re}(F)=\frac{1}{\sqrt{2}}\,\frac{AC+BD-BC+AD}{\xi(C^2+D^2)}, \tag{3.12}$$

$$\operatorname{Im}(F)=\frac{1}{\sqrt{2}}\,\frac{AC+BD+BC-AD}{\xi(C^2+D^2)}. \tag{3.13}$$

By substituting the expressions for Re(F) and Im(F) found in this manner into (3.1) and (3.4), we shall obtain $\delta(\xi)$ and $f(\xi)$. A, B, C and D are listed in tables as functions of ξ (1).

The graphs shown in Figure 3 represent an image of the functions found in this manner on a relative scale, designated as $\bar{\delta}(\xi)$ and $\bar{f}(\xi)$, when the maximum values of $\delta(4.3)$ and $f(0)$ are adopted as unity.

We will also be interested in an asymptotic representation for $f(\xi)$, which can be used in case of high ξ values. In this case, according to (2.66) and (3.2), we will obtain the following formula:

$$F=\frac{\sqrt{i}}{\xi}\left(\frac{1}{2\xi\sqrt{i}}-i\right), \tag{3.14}$$

from where:

$$\operatorname{Im}(F)=-\frac{1}{\sqrt{2}\,\xi}, \tag{3.15}$$

and consequently:

$$f(\xi)=\frac{2MR^2}{K}\cdot\frac{1}{\xi\sqrt{2}}. \tag{3.16}$$

In order to coordinate the numerical values of $f(\xi)$ with Figure 3, we shall write:

$$f(\xi) = E \cdot \bar{f}(\xi), \tag{3.17}$$

where the constant E depends upon the scale of the drawing and is determined as a result of the combination of $f(\xi)$ and $\bar{f}(\xi)$ at the point where $\xi = 10$:

$$\frac{2MR^2}{K} \cdot \frac{1}{10\sqrt{2}} = E \cdot 0{,}277. \tag{3.18}$$

Consequently:

$$E = \frac{2MR^2}{K} \cdot 0{,}256. \tag{3.19}$$

F88

Thus, we have:

$$f(\xi) = \frac{2MR^2}{K} \cdot 0{,}256\,\bar{f}(\xi). \tag{3.20}$$

Let us examine the asymptotic expression for $\delta(\xi)$. From (3.14), we will find:

$$\mathrm{Re}(F) = \frac{1}{\xi}\left[\frac{1}{2\xi} + \frac{1}{\sqrt{2}}\right] \tag{3.21}$$

and by substitution into (3.1), we will get:

$$\delta(\xi) = \frac{2\pi MR^2}{K}\,\frac{1}{\xi}\left[\frac{1}{\sqrt{2}} - \frac{3}{2\xi}\right]. \tag{3.22}$$

By comparing it with (3.16), we can see that the last expression can be written in the following form:

$$\delta(\xi) = \pi f(\xi)\left[1 - \frac{3}{\sqrt{2}\,\xi}\right]. \tag{3.23}$$

In order to coordinate the numerical values of $\delta(\xi)$ with the ordinates of the graph (Figure 3), we shall write:

$$\delta(\xi) = G \cdot \bar{\delta}(\xi), \tag{3.24}$$

where the constant G depends upon the scale of the drawing and is determined from the combination of $\delta(\xi)$ and $\bar{\delta}(\xi)$ at the point where $\xi = 10$. Consequently:

$$\frac{2\pi MR^2}{K}\cdot\frac{1}{10}\left[\frac{1}{\sqrt{2}}-\frac{3}{20}\right]=\frac{2\pi MR^2}{K}\cdot 0{,}056=G\cdot 0{,}65. \qquad (3.25)$$

From here:

$$G=0{,}086\cdot\frac{2\pi MR^2}{K} \qquad (3.26)$$

and finally:

$$\delta(\xi)=\frac{2\pi MR^2}{K}\cdot 0{,}086\bar{\delta}(\xi). \qquad (3.27)$$

Formulas (3.20) and (3.27) may be used in making a rough estimate of the oscillation period and attenuation decrement of the suspension system.

2. Range of Variations in the Viscosity Which Can Be Investigated

Let us determine the maximum range of variations in the kinematic viscosity which may be investigated with one instrument in a continuous experiment by using the calculating system of the theory developed above (Tables 1 and 2 with the corresponding formulas, and formula (2.99)).

The maximum value of y, listed in Table 1, is equal to $y_a = 3{,}500$ ($\xi_a = 59$). As a minimum value of y, up to which it is possible to conduct measurements, we shall adopt a value corresponding to $\xi_b = 0.4$, i.e., $y_b = 0.16$. Consequently, the values of y will lie within the range:

$$y_b \leqslant y \leqslant y_a. \qquad (3.28)$$

According to formula (2.85), corresponding to the inequation (3.28), the range of variations in the kinematic viscosity will be determined by the inequation:

$$R^2\frac{2\pi}{\tau_a y_a}\leqslant \nu \leqslant R^2\frac{2\pi}{\tau_b y_b}, \qquad (3.29)$$

or, by adopting the minimum value of the kinematic viscosity as unity, this inequation can be written in relative units as follows:

$$1 \leqslant \nu \leqslant \frac{\tau_a y_a}{\tau_b y_b}. \tag{3.30}$$

From formula (3.3), we get:

$$\tau = \sqrt{1+f(\xi)}\,\tau_0. \tag{3.31}$$

Consequently, (3.30) can be rewritten as follows:

$$1 \leqslant \nu \leqslant \frac{\sqrt{1+f(\xi_a)}\cdot y_a}{\sqrt{1+f(\xi_b)}\cdot y_b}. \tag{3.32}$$

Assuming, as was stated_above, that $y_a = 3{,}500$ and $y_b = 0.16$, and selecting from the graph $f(\xi_b) \approx 1$ and from expression (3.16):

$$f(\xi_a) = 0{,}012\,\frac{2MR^2}{K}, \tag{3.33}$$

we find:

$$1 \leqslant \nu \leqslant \frac{\sqrt{1+0{,}012\,\frac{2MR^2}{K}}}{\sqrt{1+0{,}256\,\frac{2MR^2}{K}}}\cdot\frac{3500}{0{,}16}. \tag{3.34}$$

The two extreme cases occurring here:

$$0{,}256\,\frac{2MR^2}{K} \ll 1 \tag{3.35}$$

and:

$$0{,}012\,\frac{2MR^2}{K} \gg 1 \tag{3.36}$$

lead to the inequations:

$$1 \leqslant \nu \leqslant 22000 \tag{3.37}$$

and

$$1 \leqslant \nu \leqslant 4750. \tag{3.38}$$

Thus, the range of variations in the viscosity, which can be measured on one instrument, is determined in a continuous experiment by the value of the expression $\frac{2MR^2}{K}$.

The following range of variations in the kinematic viscosity corresponds to the intermediate region where $4.2 \leqslant \xi \leqslant 10$:

$$R^2 \frac{2\pi}{\sqrt{1+f(10)}\,\tau_0 \cdot 100} < \nu < R^2 \frac{2\pi}{\sqrt{1+f(4,2)}\,\tau_0 \cdot 18} \tag{3.39}$$

or, when expressed in the previous relative units:

$$\frac{\sqrt{1+f(59)} \cdot 3500}{\sqrt{1+f(10)} \cdot 100} < \nu < \frac{\sqrt{1+f(59)} \cdot 3500}{\sqrt{1+f(4,2)} \cdot 18}. \tag{3.40}$$

By substituting numerical values of f, we get:

$$\frac{\sqrt{1+0{,}012\,\frac{2MR^2}{K}}}{\sqrt{1+0{,}071\,\frac{2MR^2}{K}}} \cdot 35 < \nu < \frac{\sqrt{1+0{,}012\,\frac{2MR^2}{K}}}{\sqrt{1+0{,}166\,\frac{2MR^2}{K}}} \cdot 194. \tag{3.41}$$

In the approximation of (3.35), for the intermediate region not being calculated, we have:

$$35 < \nu < 194 \tag{3.42}$$

and in the approximation of (3.36):

$$14 < \nu < 52. \tag{3.43}$$

Naturally, all this calculation has an approximate character, since it does not take into account the friction on the bottom and lid of the bucket.

In view of the fact that the above calculation was performed in relative units (the viscosity, corresponding to a value of $y = 3{,}500$, was adopted as unity), this calculation obviously refers merely to this particular instrument. For this reason, the kinematic viscosity values corresponding to each of the three regions may vary within a wide range, if the parameters of the suspension system, R, τ_0, and K, are varied accordingly.

During the study of liquids, the viscosity of which varies with the temperature several score of thousands of times, the intermediate region cannot play a significant role in view of the fact that it is relatively narrow. If, however, the kinematic viscosity changes slowly with the temperature, as is the case for the majority of metals, it is not difficult to select the parameters of the unit in such a way as to avoid this region.

By using the torsional-oscillation method, one can observe how, during the process of a uniform change in the viscosity, the attenuation decrement of the suspension system travels (passes) through a maximum. The theory of the method makes it possible to calculate the viscosity both on the ascending and descending (rising and falling) branches of the decrement curve, but of course with the aid of different mathematical relations which were mentioned above.

3. Height to Which the Bucket Can Be Filled With Liquid

According to the first approximation for the friction function, inequation (2.51) must take place, which, after multiplication by R of the right and left side with the aid of (2.47) and introduction of according to equation (2.94), can be rewritten in the following form:

$$\frac{H}{R} \geqslant \frac{s\sqrt{2}}{\sqrt{\left(\varkappa_n^2 - \frac{\delta}{2\pi}\xi^2\right) + \sqrt{\left(\varkappa_n^2 - \frac{\delta}{2\pi}\xi^2\right)^2 + \xi^4}}}, \tag{3.44}$$

where:

$$\varkappa_n = \mu_n R \tag{3.45}$$

represent the roots of the characteristic equation (2.19). Obviously, the right side of (3.44) exhibits a maximum value at a minimum of the following function:

$$\gamma(\xi) = \sqrt{\left(\varkappa_n^2 - \frac{\delta}{2\pi}\xi^2\right) + \sqrt{\left(\varkappa_n^2 - \frac{\delta}{2\pi}\xi^2\right)^2 + \xi^4}}. \tag{3.46}$$

The solution of the corresponding extreme problem, involving a discarding of members of the order of $\left(\frac{\delta}{\pi}\right)^2$ in comparison with unity, leads to the result:

$$\xi^2\Big|_{\gamma=\gamma_{min}} = \frac{\delta}{\pi}\varkappa_n^2. \tag{3.47}$$

After substituting (3.47) into (3.46), we get:

$$\gamma_{min} = \varkappa_n\sqrt{2}. \tag{3.48}$$

Consequently, the maximum value of the right side of inequation (3.44) is equal to $\frac{s}{x_n}$. Thus, (3.44) will be fulfilled if:

$$\frac{H}{R} \geqslant \frac{s}{\varkappa_n}. \tag{3.49}$$

The values of x_n increase as n increases, and the first of these values is equal to 3.83 (see in the table the values of roots of Bessel functions). Therefore, if inequation (3.49) is fulfilled in case of x_1, it is also fulfilled in case of any values of $n > 1$. Consequently, the condition of a first approximation for the friction function (2.50) will be fulfilled, if:

$$\frac{H}{R} \geqslant \frac{s}{3{,}83}. \qquad (3.50)$$

By adopting the extremely strict (rigid) requirement s = 5, we will get the following condition for the total height 2H of the liquid column in the bucket:

$$2H \geqslant 2{,}6R, \qquad (3.51)$$

the fulfillment of which will guarantee a total attenuation (damping) of viscous waves during their propagation from the bottom to the lid of the bucket (and in the opposite direction). Let us recall that, according to # 5 in Chapter II, the equality $\text{th}\,\theta_n H = 1$ in this case proves to be true (correct) with an accuracy of up to 10^{-4}, and the presence of a free surface, or the contact of this surface with the lid of the bucket, is taken into account by doubling the corresponding factor in the expressions used during the calculation of the viscosity (see formulas (2.89), (2.100), (2.105) and (2.109) in # 6 of Chapter II).

By adopting s = 3.5, we will get:

$$2H \geqslant 1{,}85R, \qquad (3.52)$$

and the equality $\text{th}\,\theta_n H = 1$ will then be fulfilled with an accuracy of up to 10^{-3}, while the amplitudes of viscous waves in the medium plane of the bucket (half-way of the total height) will be equal to 0.02 of these values at the bottom and on the lid of the bucket. In case of such an assumption, the structure of the formulas just mentioned will, naturally, not be disturbed (violated), since it is obvious that viscous waves, propagated from the bottom and from the lid, will not be able to affect the distribution of velocities near the opposite surfaces. Therefore, inequation (3.52) can be considered sufficient (satisfactory?) from an experimental standpoint.

4. Sensitivity of the Instrument to Viscosity Changes

By disregarding the term containing δ_0 in equations (2.82) and (2.99), and taking the logarithmic derivative, it is easy to obtain the following relations:

$$\Delta\delta \doteq \frac{\delta}{2}\,\frac{\Delta\nu}{\nu} \qquad (3.53)$$

for low-viscosity liquids, and:

$$\Delta\delta = \delta\,\frac{\Delta\nu}{\nu} \qquad (3.54)$$

for small values of ξ in the field of high-viscosity liquids.

Since in the first and third regions (see Note) of Figure 3, the character of the dependence between the decrement and the viscosity is identical, it is possible to state that the dependence of the attenuation decrement upon the viscosity is the greater, the higher the value of this decrement at the given viscosity (<u>Note</u>: Further in the text, for the sake of brevity, we shall use the terms "first, second and third regions," respectively, to designate the regions of low-viscosity, high-viscosity and intermediate viscosity liquids according to Figure 3).

Let us designate as sensitivity of the unit the factor adjacent to $\frac{\Delta\nu}{\nu}$ in formulas (3.53) and (3.54); this factor is equal to $\frac{1}{2}\delta$ in the first region and δ in the second region (in case of small ξ values). This means that a change in viscosity of 1% causes a change in the decrement of 1/200 δ in the first case, and a change of 1/100 δ in the second case. Since δ usually does not exceed several decimal fractions, it is apparent that special attention should be given to a careful measurement of decrements during the course of an experimental determination of the viscosity.

A different and more general approach can be used in analyzing the sensitivity of the unit. By assuming that δ is a complex function $\delta[\xi(\nu)]$, the following formula can be easily obtained with the aid of expression (2.94):

$$\Delta\delta = -\frac{1}{2}\,\xi\,\frac{d\delta}{d\xi}\cdot\frac{\Delta\nu}{\nu}, \qquad (3.55)$$

and, consequently, the sensitivity $\varepsilon(\xi)$ of the unit, i.e., the magnitude of the change in the decrement in case of a change in the viscosity of 1%, will be determined by the relation:

$$\varepsilon(\xi) = -\frac{1}{2}\,\xi\,\frac{d\delta}{d\xi}. \qquad (3.56)$$

According to formula (3.27):

$$\frac{d\delta}{d\xi} = \frac{2\pi MR^2}{K}\cdot 0{,}086\,\frac{d\bar{\delta}(\xi)}{d\xi}. \qquad (3.57)$$

Since:

$$\delta(4{,}2) = \frac{2\pi MR^2}{K}\cdot 0{,}086 = \delta_m \qquad (3.58)$$

represents the maximum value of the decrement, corresponding to the vertex of the $\bar{\delta}(\xi)$ curve, where $\bar{\delta} = 1$, the expression for the sensitivity can be written as follows:

$$\varepsilon(\xi) = -\frac{1}{2}\xi\delta_m\frac{d\bar{\delta}}{d\xi}. \qquad (3.59)$$

F88 The derivative $\frac{d\bar{\delta}(\xi)}{d\xi}$ is selected directly from the curve shown in Figure 3.

Let us assume, for example, that $\delta_m = 0.400$. Let us find the sensitivity at the point where $\xi = 10$. From the graph, we get $\frac{d\bar{\delta}(10)}{d\xi} \approx - 0.06$, and from here $\varepsilon(10) \approx 0.1$. Consequently:

$$\Delta\delta \approx 0{,}1\,\frac{\Delta\nu}{\nu}, \qquad (3.60)$$

i.e., a change in viscosity of 1% results in a change in the decrement of 0.001.

For the medium portion of the second region in Figure 3, we find that $\frac{d\bar{\delta}}{d\xi} \approx 0.4$, and therefore in the point where $\xi = 2$, the sensitivity $\varepsilon(2) \approx - 0.16$; consequently, when the viscosity changes by 1%, the decrement will vary by the value $\Delta\delta \approx - 0.0016$.

The above calculations show that decrements should be determined with an accuracy of up to the third or fourth significant digit.

From the appearance of the curve shown in Figure 3, it follows that $\frac{d\bar{\delta}}{d}$ undergoes a change opposite to that of ξ, so that their product can be considered as a value which does not vary to a great extent. For this reason, the sensitivity is determined mainly by the value of δ_m.

Nevertheless, this does not mean that one should strive to secure the highest possible values for the attenuation decrement. A twofold reduction of δ_m will also result in a decrease of the sensitivity by approximately two times. Therefore, in order to detect a change in viscosity of 1%, it will be necessary to secure an accuracy in the determination of the decrement, equal, for example, to 0.001, instead of the previously required accuracy of 0.002. In regard to experimental difficulties, these two cases are equivalent. However, in the second case, when the decrement is two times smaller, the system will be present in a state of oscillation for a considerably longer period of time, will perform a greater number of oscillations, and will undoubtedly assume the state of a regular regime. Under these conditions, one can be certain that the decrement is really measured in a regular oscillation regime, and that this decrement is not distorted under the action of the initial state. In the first case, however, when the attenuation decrement is twice as high, the oscillations of the system will be damped much more rapidly, and the system will be able to perform such a small number of oscillations until it comes to a complete rest, that it will be necessary to introduce the first or second deviation of the system from an equilibrium state into the calculation of the decrement. It is clear that the decrement values measured in this case can be distorted under the influence of the initial state.

In practice, it should be possible to skip four or five oscillations of the system, and then to have a sufficient number of oscillations available for a reliable determination of the decrement.

5. Condition Specifying the Absence of Turbulence

During the course of measurements, no turbulent movements should arise in the liquid, which are caused by torsional oscillations of the bucket. In order to estimate the appropriate condition, let us calculate the initial (maximum) amplitude of the angular velocity of the liquid in the bucket in relation to a fixed coordinate system.

By designating, as was done previously, the angular displacement of the bucket as α', we get:

$$\alpha' = \alpha_0' e^{-\nu t} \cos qt \tag{3.61}$$

from which the initial amplitude v_0 of the linear velocity of liquid particles, adhering to the surface of the bucket, can be expressed as follows:

$$v_0 = \alpha_0' R \frac{\nu^2 + q^2}{q} = \alpha_0' R q (x^2 + 1), \tag{3.62}$$

or, with an accuracy of up to x^2:

$$v_0 = \frac{2\pi\alpha_0' R}{\tau}. \tag{3.63}$$

By adopting in the Reynolds parameter, as a characteristic dimension, the length of a viscous displacement wave $L \approx 2\sqrt{\pi\nu\tau}$ (see Note), and by designating the critical value of the Reynolds parameter at which a turbulence arises as Re_{cr}, we get the following inequation:

$$\frac{v_0 L}{\nu} = 2\pi\sqrt{2}\alpha_0' R\sqrt{\frac{2\pi}{\tau\nu}} \leqslant \mathrm{Re}_{cr}. \tag{3.64}$$

(**Note**: In the same way as in the case of a plane temperature wave. See reference 3 in the bibliography of Chapter II.)
By introducing again the parameter $y = R^2 \frac{2\pi}{\tau\nu}$, we get:

$$\alpha_0' \leqslant \frac{\mathrm{Re}_{cr}}{2\pi\sqrt{2y}}. \tag{3.65}$$

An evaluation of the critical value of the Reynolds number is
F difficult in our case; however, we can adopt as Re_{cr} a number correspond-
8 ing to the axial flow along a pipe. In this case, the latter inequation
8 will assume the following appearance:

$$\alpha_0' \leqslant \frac{1000}{2\pi\sqrt{2y}}. \tag{3.66}$$

This condition makes it possible to estimate the initial angular displacement of the bucket, at which the absence of any turbulence will be guaranteed. It was found that, even in case of very high y values ($\sim$4,000), the initial amplitude may amount to several radians and that a turbulence does not arise in this case.

6. Value of the Initial Amplitude

The amplitudes of the oscillations of the bucket must be small. From the motion equation (2.30), we can see that this condition is connected, specifically, with the maintenance of a proportionality of the restoring elastic moment and the deformation of the wire. In other words, the deformation of the suspension wire during torsion must lie in the region of Hooke's law. This fact determines the condition which the wire material must fulfill. If we designate the length of the wire as l, and its diameter as d, then the maximum value of the relative deformation φ during the course of oscillations:

$$\varphi = \frac{\alpha_0' d}{2l} \tag{3.67}$$

should not lie outside the scope of Hooke's law.

Naturally, it is not difficult to examine the problem of oscillations of the bucket in case of a quadratic dependence between the force and the deformation, especially if we take into account the obvious small value of the corresponding correction, although this is not indispensable.

It is more correct to simply check, on the assembled instrument filled with the liquid, the independence of the attenuation decrement from the amplitude. By means of such a check, it is also possible to establish other possible sources of deviation from the theory of the method, according to which there must be an independence of the decrement from the amplitude, provided the viscosity factor itself remains constant during the oscillation process.

7. Conditions Causing the Appearance of Convection Inside the Bucket

During the measurement of the temperature dependence of the viscosity, convective drifts may arise in the liquid, which are caused by a nonuniformity of the temperature field. F88

If the convection has a laminar character, then only additional components of the velocities v_r and v_z may show up in the hydrodynamic equations. It can be easily seen that the moments of friction caused by these velocities cannot affect the torsional-oscillation motion of the bucket, since the attenuation decrement is determined only by the component of velocity v, which remains constant during the appearance of a laminar convective drift.

Two different types of experiments were set up in order to confirm this fact. In the first group of tests, the liquid was heated at a noticeable speed. In comparing the decrement values obtained in this manner with the values found during a stationary thermal state, it was found that the former are characterized by a greater random error, but, in regard to the general temperature dependence, can be fitted well on the curve obtained during measurements in a stationary thermal state. The second group of experiments consisted in placing a small bucket filled with fused metal in different zones of a long tubular furnace, characterized by a different value of the axial temperature gradient. In all cases, measurements were performed during a stationary thermal state. It was found in this case that the value and temperature dependence of the decrement remained constant.

Thus, the absence of an effect of a laminar convective drift on the value of the attenuation decrement of oscillations can be considered as an experimentally established fact.

However, it is possible to assume that a turbulent convective drift is capable of causing a change in the value of the decrement. For this reason, one should strive to achieve a maximum uniformity of the temperature field through the entire mass of the liquid being tested.

Conditions for the appearance of convection in a metallic liquid are extremely favorable. In the theory dealing with heat exchange, free convection is usually characterized as the product of Prandtl's parameter:

$$\Pr = \frac{\nu}{k}, \tag{3.68}$$

where k is the thermal diffusivity of the liquid, and Grashoff's parameter

$$\mathrm{Gr} = \frac{g l^3 \beta \, \Delta T}{\nu^2}, \tag{3.69}$$

where g is the gravity acceleration, l is the characteristic size, ΔT is the characteristic temperature difference, and β is the volume coefficient of thermal expansion, i.e., the free convection is described by the following parameter: F 88

$$\Pr \cdot \mathrm{Gr} = \frac{g l^3 \beta \, \Delta T}{k \nu} = S. \tag{3.70}$$

Here, only the following value is determined by the properties of the liquid:

$$\frac{\beta}{\nu k} = S'. \tag{3.71}$$

In case of fused metals, $\beta \approx 10^{-4}$. The product νk decreases with the temperature. No experimental data on the thermal diffusivity of metallic liquids are available. Therefore, we shall use values of k in the solid phase in the vicinity of the melting point (2). We can adopt $k \approx 10^{-1}$. As the kinematic viscosity of fused metals, we can use the value $\nu \approx 10^{-3}$. From here, we get:

$$S' \approx 1. \tag{3.72}$$

It should be noted that Prandtl's parameter for metallic liquids is approximately 100 times smaller than for air, and is of the order of 10^{-2}.

Thus, the expression for S in case of metallic liquids can be written in the form:

$$S \approx 10^3 l^3 \Delta T. \tag{3.73}$$

If l is assumed to represent the height of a liquid cylinder in the bucket (l = 2H), and ΔT the temperature difference corresponding to this height, then the latter expression can be written as follows:

$$S \approx 10^4 H^3 \Delta T, \tag{3.74}$$

or finally, by assuming, as is done in most tests, that $H \approx 1$, we get as a final result:

$$S \approx 10^4 \cdot \Delta T. \tag{3.75}$$

This result indicates the extremely favorable conditions for the appearance of convection in a metallic liquid filling up the bucket, and consequently, the necessity of securing to a maximum possible extent a uniform temperature field in the working portion of the furnace.

An overheating of the upper lid of the bucket in relation to the temperature at the bottom of the bucket constitutes a natural obstacle for the appearance of convection. Such an overheating should always be provided during viscosity measurements of metals, especially in view of the fact that this measure is required in order to avoid the condensation of metal on the lid of the crucible when working in a high vacuum (see # 12 of this chapter).

F 88

8. Influence of an Off-Centering of the Suspension Device

The calculations upon which the theory of the method is based have been made in the assumption that the thread of the suspension device coincides strictly with the axis of the bucket. However, when the suspension system is assembled, it is possible that the point where the thread of the suspension device is attached to the bucket is shifted in relation to the bucket axis. Such a position will be designated by us briefly as off-centering, and the value of the shift ΔR will be adopted as its quantitative characteristic.

The theoretical calculation of the effect exerted by an off-centering on the value of the logarithmic attenuation decrement and the oscillation period appears to be very difficult. For this reason, special tests were set up for a quantitative determination of this effect.

The study was conducted with a bucket having an internal diameter $R \approx 1$ cm, containing mercury filled to a height of $2H = 4$ cm (test No. 1) and $2H = 2$ cm (test No. 2); in addition, a light metal disk was attached to the bucket in test No. 1 in order to increase the oscillation period of the suspension system.

The values of the attenuation decrement δ and of the oscillation period τ were expressed approximately by the following figures: in test No. 1, $\delta \approx 0.2$ and $\tau \approx 2.5$ sec, in test No. 2, $\delta \approx 0.4$ and $\tau \approx 1$ sec.

The results obtained during these tests are shown in Figure 4.

The logarithmic attenuation decrement and the oscillation period, in case of a relative off-centering $\frac{\Delta R}{R}$, are designated as $\delta\left(\frac{\Delta R}{R}\right)$ and

$\tau(\frac{\Delta R}{R})$ respectively. Along the ordinate axis, the values $\frac{\delta(\frac{\Delta R}{R})}{\delta(0)} = \varphi$ and $\frac{\tau(\frac{\Delta R}{R})}{\tau(0)} = \psi$ are plotted in percent, and refer to the first and second tests (marked by corresponding symbols):

The value of the off-centering ΔR in an accurately designed instrument must not exceed several decimal fractions of a millimeter, i.e., $\frac{\Delta R}{R}$ should hardly exceed 5%.

F 8 8

From Figure 4, it can be seen that, in case of an off-centering of such a magnitude, the relative variation of δ and τ lies within the limits of usual measurement errors. Moreover, it was found that, even when the relative off-centering amounts to 25%, the variation of δ and τ apparently does not exceed 1%. It is obvious, however, that an off-centering of such magnitude is not permissible and should not take place in viscosity measurement tests.

If we consider that both tests refer to very different conditions, we must conclude that, in case the design of the suspension system is sufficiently accurate, the off-centering which actually takes place is incapable of introducing a noticeable error into the experimental results. The physical reason for this important fact lies in the dynamic stability of the oscillating motion of the suspension system.

9. Measurement of the Moment of Inertia of the Suspension System

An important element in the measurement process is the correct determination of the moment of inertia of the suspension system K. As is known, an accurate determination of this value is far from being an elementary experimental problem. A determination of K can be conveniently performed by means of the following two observations of the oscillation period of the suspension system: in case of an empty bucket without any kind of additional load -- τ_0 and oscillation period τ' of the suspension system, loaded with a standard load having a known moment of inertia K'.

The standard must be light in comparison to the empty system, in order that both measurements of the oscillation periods should be performed under identical thread load conditions; at the same time, it should possess a sufficiently large moment of inertia, in order that the oscillation periods τ_0 and τ' should greatly differ from each other. For this reason, it is convenient to design the standard in the form of a thin and light disk with a large radius.

The following obvious formula is applicable to K:

$$K=\frac{K'\tau_0^2}{\tau'^2-\tau_0^2}, \tag{3.76}$$

which is obtained in the assumption that the rigidity factor of the suspension thread N remains constant.

10. Determination of $\delta_0(t)$ and $\tau_0(t)$

The calculating formulas include the attenuation decrement and the oscillation period of an empty system δ_0 and τ_0. Both of these values depend upon the temperature. This is so, because the suspension thread may become heated, and its elastic properties may vary during the course of the test, and also, in view of the fact that the viscosity of the gaseous medium surrounding the bucket increases with the temperature. Consequently, the above-mentioned values must be measured over the entire temperature range in which the viscosity is measured.

It is necessary to recall that, when using the calculation methods applicable to low- and high-viscosity liquids, an accurate (exact) knowledge of τ_0 and δ_0 is not necessary, since these values only form a part of the small correction term. On the contrary, in case of liquids with an intermediate viscosity, τ_0 enters into the dominant term of the viscosity expression and therefore must be measured accurately over the entire temperature range in which the viscosity is investigated.

Let us consider the problem of determining δ_0 and τ_0, on the basis of the requirement for obtaining the exact value of these magnitudes.

From equations (2.41) and (2.43), we get:

$$\delta_0=\frac{L_0\tau_0}{2K}, \tag{3.77}$$

$$\tau_0=2\pi\sqrt{\frac{K}{N}}. \tag{3.78}$$

Here, L_0 and N are functions of the temperature t.

In order to increase the measurement accuracy of δ_0 and τ_0, it is advisable to perform an auxiliary test, which consists in the following: after placing into the bucket a solid sample with an axial moment of inertia K" and creating in the unit a gas pressure similar to the one present during the measurement of viscosity, the temperature dependence of the attenuation decrement and of the oscillation period is measured. Let us designate the values obtained in this manner as $\delta_0'(t)$ and $\tau_0'(t)$. Then from formulas (3.77) and (3.78), by means of an obvious transformation, we will obtain the necessary values of $\delta_0(t)$ and $\tau_0(t)$, corresponding to the moment of inertia K, namely:

$$\delta_0(t) = \delta_0(t)\sqrt{\frac{K+K''}{K}}, \tag{3.79}$$

$$\tau_0(t) = \tau_0'(t)\sqrt{\frac{K}{K+K''}}. \tag{3.80}$$

These values must be incorporated into the calculating formulas used for calculating the viscosity. A typical temperature dependence of $\frac{\delta_0}{\tau_0}$ is illustrated in Figure 5.

11. Calculation of the Attenuation (Damping) Decrement

The constancy of δ in a given series of oscillations was frequently confirmed during tests. F88

The calculation of decrements can be performed by means of the obvious formula:

$$\delta = \frac{1}{f}\ln\frac{A_0}{A_f}, \tag{3.81}$$

where f is the number of oscillations in a given series, and A_0 and A_f are the initial and final amplitudes. The relative error in the determination of δ according to this formula is equal to:

$$\frac{\Delta\delta}{\delta} = \frac{\frac{\Delta A_0}{A_0} + \frac{\Delta A_f}{A_f}}{\ln\frac{A_0}{A_f}}, \tag{3.82}$$

i.e., this error is mainly determined by the error in the final amplitude A_f and by the ratio $\frac{A_0}{A_f}$, but does not depend upon the value of δ and the oscillation number f.

The calculation of δ by means of formula (3.81) coincides with an accuracy of up to 0.5% with the value of the decrement, calculated by the method of least squares. The general theory of the method of least squares gives the following formula for the calculation of the logarithmic decrement (see Note):

$$\delta = \frac{6}{(f+1)[(f+1)^2-1]}\left\{f\sum_{i=0}^{i=f}\ln A_i - 2\sum_{i=0}^{i=f} i\ln A_i\right\} \tag{3.83}$$

(Note: This formula can be derived as follows. Let us assume that the theoretical dependence between the logarithm of the amplitude and the oscillation number has the following appearance:

$$\ln A_i = \ln A_0 - \delta i,$$

where $i = 0, 1, 2, 3 \ldots, f$. If the measurements were absolutely exact (accurate), then this equality would be strictly fulfilled. However, the experimental values of the logarithms of amplitudes contain a certain error, and therefore we will have the following, instead of the equality written above:

$$\ln A_i - \ln A_0 + \delta i = v_i.$$

We shall require that the sum of the squares of deviations:

$$\sum_{i=0}^{i=f} v_i^2 = \sum_{i=0}^{i=f} \{\ln A_i - \ln A_0 + \delta i\}^2 = f(\ln A_0, \delta)$$

F
88

will be a minimum. We shall then have: $\frac{\partial f}{\partial \ln A_0} = 0$ and $\frac{\partial f}{\partial \delta} = 0$. These equations are designated as normal equations of the method of least squares. The number of such equations is always equal to the number of unknowns (in this case, there are two such equations, corresponding to $\ln A_0$ and δ). Since:

$$\sum_{i=0}^{i=f} \ln A_0 = (f+1)\ln A_0,$$

from the normal equations, after excluding $\ln A_0$, it is easy to obtain:

$$\sum i \ln A_i - \frac{\sum i}{f+1}\sum \ln A_i + \delta\left[\sum i^2 - \frac{\sum i \cdot \sum i}{f+1}\right] = 0,$$

where summation extends from $i = 0$ to $i = f$.

It is known that:

$$\sum_{i=0}^{i=f} i = \frac{f(f+1)}{2} \quad \text{и} \quad \sum_{i=0}^{f} i^2 = \frac{(f+1)f(2f+1)}{6},$$

and from here we obtain formula (3.83).)

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During calculations, the following diagram of arrangement of operations may be conveniently used. The following table is drawn up:

i	$\ln A_i$	$i \ln A_i$
0	$\ln A_0$	0
1	$\ln A_1$	$1 \cdot \ln A_1$
2	$\ln A_2$	$2 \cdot \ln A_2$
3	$\ln A_3$	$3 \cdot \ln A_3$
. . . . . .	. . . .	. . . .
f	$\ln A_f$	$f \ln A_f$

F 8 8 We find the sums $P = \sum_{i=0}^{i=f} \ln A_i$ and $Q = \sum_{i=0}^{i=f} i \ln A_i$ and we draw up the expression fP - 2Q = D. Then:

$$\delta = \frac{6D}{(f+1)[(f+1)^2 - 1]}. \qquad (3.84)$$

12. Accounting for the Condensation of Liquid on the Lid of the Bucket

In tests, conducted with a free surface of the metal under a pressure of 10^{-2} to 10^{-3} mm mercury column, individual liquid droplets may sometimes be formed on the lid of the bucket. Apparently, this is accompanied by a reduction in the mass of the liquid M with a simultaneous increase in the moment of inertia K. Naturally, this fact, if it takes place, requires the introduction of an appropriate correction into the viscosity values, calculated from the initial value $\frac{K}{M}$.

Let us consider first the field of low-viscosity liquids. The approximate expression for the viscosity according to (2.82) can be written in the form:

$$\nu = \frac{K^2}{M^2} \Phi_1, \qquad (3.85)$$

where Φ_1 is independent of K and M. By making use of the identity:

$$\frac{d\nu}{dM} = \frac{\partial\nu}{\partial M} + \frac{\partial\nu}{\partial K} \cdot \frac{dK}{dM}, \qquad (3.86)$$

we get:

$$\frac{d\nu}{dM} = -\frac{2K^2}{M^3}\Phi_1 + \frac{2K}{M^2}\Phi_1\frac{dK}{dM}. \tag{3.87}$$

However:

$$dK = -\frac{R^2}{2}\cdot dM \tag{3.88}$$

(the increase in the moment of inertia takes place at the expense of a reduction in the mass of the liquid). Consequently:

$$\frac{d\nu}{dM} = -\frac{2}{M}\nu_0 - \frac{R^2}{K}\cdot\nu_0, \tag{3.89}$$

where ν_0 is the viscosity value calculated from the initial value $\frac{K}{M}$.

Thus, the true value of the viscosity $\nu_0 + d\nu$ is expressed by the following relation:

$$\nu = \nu_0 + d\nu = \nu_0\left[1 - \left(\frac{2}{M} + \frac{R^2}{K}\right)dM\right]. \tag{3.90}$$

During the course of transition of the liquid from the bulk mass M to the lid of the bucket, $dM < 0$. Consequently, the true value of the viscosity will exceed the value calculated from the initial $\frac{K}{M}$ by the following quantity:

$$\left(\frac{2}{M} + \frac{R^2}{K}\right)\nu_0\,|dM|, \tag{3.91}$$

where $|dM|$ is the absolute value of the mass of the liquid, which has collected in the form of droplets on the lid of the bucket.

For liquids with an intermediate viscosity, we have approximately, according to (2.45) and (2.73):

$$\frac{p_0^2 + q_0^2}{p^2 + q^2} - 1 = \frac{MR}{K}\sqrt{\frac{\nu\tau}{\pi}}, \tag{3.92}$$

or, in a different form:

$$\frac{\tau^2}{\tau_0^2\left[1 + \frac{\delta^2}{4\pi^2}\right]} - 1 = \frac{MR}{K}\sqrt{\frac{\tau\nu}{\pi}}. \tag{3.93}$$

This formula can be written in the following form:

$$\nu = \frac{K^2}{M^2}\Phi_3, \qquad (3.94)$$

where Φ_3 is independent of K and M. The equation obtained in this manner is similar to (3.85) in that respect that the viscosity is also proportional in this case to $\frac{K^2}{M^2}$. Consequently, equation (3.90) can also be used in the third region.

For high-viscosity liquids, in case of small ξ values, one can write according to (2.99):

$$\nu \approx \frac{M}{K + \frac{MR^2}{2}} \cdot \Phi_2, \qquad (3.95)$$

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where Φ_2 is independent of K and M. By making use of the identity (3.87), we get:

$$\frac{d\nu}{dM} = \frac{\Phi_2}{K + \frac{MR^2}{2}} = \frac{\nu_0}{M} \qquad (3.96)$$

or:

$$d\nu = \frac{\nu_0}{M}\,dM \qquad (3.97)$$

and finally:

$$\nu = \nu_0\left(1 + \frac{dM}{M}\right). \qquad (3.98)$$

Consequently, in contrast to the first two cases, the true value of the viscosity in this case is smaller than the value calculated from the initial value $\frac{K}{M}$ $(dM < 0)$.

Such a difference in the effect of condensation is due to the shape of the curve shown in Figure 3 and can be readily explained from a qualitative standpoint.

The condensation of metal vapors on the internal surface of the lid of the bucket will be the more intensive, the higher the vacuum and the greater the overheating of the free surface of the fused metal in relation to the lid of the crucible (bucket). However, it is possible that, in spite of the absence of a condensation on the lid of the bucket (as a result of a certain overheating of the lid in relation to the fused metal), the experiment will have to be interrupted in view of the condensation of metal vapors on the mirror and on other parts of the optical system in the unit. A hermetic sealing of the bucket or the conduct of the test under an inert gas pressure represents a logical way of overcoming this particular difficulty.

Thus, metal evaporation exerts a negative effect in the following two directions. First, the mass of the tested metal and the moment of inertia of the bucket both undergo a change. Second, a reading of oscillation amplitudes may be impossible as a result of the condensation of metal on parts of the optical system of the unit.

In order to get a clear idea of the measures used for combatting the above negative aspects of evaporation, let us examine in greater detail the processes of metal evaporation and condensation.

The evaporation rate of a metal is expressed by Langmuir's well-known formula:

$$m = P\sqrt{\frac{M}{2\pi RT}}, \tag{3.99}$$

where m is the evaporation rate in g/sq cm·sec, P is the vapor pressure of the evaporating metal in dynes/sq cm, M is the atomic weight (in case of a monoatomic vapor), $R = 8.315 \cdot 10^{-7}$ erg/degree · mole is the gas constant, and T is the absolute temperature.

The pressure of metal vapors P in mm Hg can be represented by the following empirical equation:

$$\lg P = -\frac{A}{T} - B\lg T + C. \tag{3.99'}$$

A table listing the values of factors A, B, C for different metals is given in a monograph published by S. A. Vekshinskiy (3).

A curve showing the evaporation rate of bismuth from a surface of $\pi R^2 = 3.14$ sq cm is given in Figure 6.

If we start from the assumption that there is no reflection of metal atoms from the lid, then the curve shown in Figure 6 allows us to make certain statements on the rate of metal condensation on the lid (of course, only in case of a stationary distribution of the vapor density in the clearance between the free surface of the metal and the lid).

Figure 7 illustrates the possible condensation rate on a surface $\pi R^2 = 3.14$ sq cm at different temperatures and temperature differences $\Delta T = T - T'$ between the metal T and the lid T'. From Figure 7, it can be seen that, in case of the assumptions made above, the condensation rate is quite high. It is obvious that the presence of a foreign (extraneous) gas between the metal and the lid will form a serious obstacle to the establishment of an equilibrium condensation of metal vapors in the clearance, and consequently, under these conditions, the actual condensation rate will be much lower.

However, radical struggle with condensation must consist in securing a higher rate of condensation from the lid than from the free surface of the metal, and this is possible only in case $T' > T$, i.e., there must be an overheating of the lid in relation to the metal.

It is precisely this condition which must be achieved during the conduct of an experiment, especially in view of the fact that an overheating of the lid will also prevent the appearance of convection.

13. Correction for a Protruding Column

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If, at the time it is fused, the liquid completely fills up the crucible (bucket) and is in contact with the lid, upon heating, it expands and spills over into the free space over the edge of the crucible.

An appropriate design of the crucible is illustrated in Figure 8. The excess of the expanded liquid, having a mass M', will protrude into the cylindrical opening A.

Let us examine the correction for the protruding column of liquid which must be introduced into formulas (2.82) and (2.89). We shall designate the height of the liquid column in A as h, and its radius as r_0. In view of the small size of r_0, which amounts to several millimeters, the liquid meniscus in A can be considered as a friction surface, provided, of course, the oxide film formed on this surface is sufficiently stable. Consequently, an addend, which determines the friction on the side surface of the column, should be added to the right side of expression (2.68):

$$-2\pi\eta r_0^2 h\left(i\beta_1+\frac{3}{2}\right), \qquad (3.100)$$

where:

$$\beta_1=r_0\sqrt{\frac{k}{\nu}}. \qquad (3.101)$$

In view of the obvious small size of this additional term, it can be written in this form, although it is obvious that, in case of small r_0 values, an asymptotic representation of Bessel functions will express the side friction in a very rough manner.

The expression (2.68) for L, containing a correction for the protruding column of liquid, will assume the following appearance:

$$L = -4\pi\eta R^2 H\left[i\beta\left(1+\frac{hr_0^2}{2HR^2}\right)+\frac{3}{2}\left(1+\frac{hr_0^2}{2HR^2}\right)\right]+ \\ +8\pi\eta R^2\frac{k^2}{\nu^2}\sum_{n=1}^{\infty}\frac{1}{\mu_n^2\theta_n^2}. \tag{3.102}$$

From here, obviously, the following expression is obtained:

$$\sqrt{\nu} = \frac{K}{V\rho R\sqrt{\pi}}\,\frac{\delta-\frac{\tau}{\tau_0}\delta_0}{\sigma_1\sqrt{\tau}} \tag{3.103}$$

when:

$$\sigma_1 = 1+\frac{hr_0^2}{2HR^2}-\frac{3\delta}{4\pi}\left(1+\frac{hr_0^2}{2HR^2}\right)-\frac{3\delta^2}{32\pi^2}\left(1+\frac{hr_0^2}{2HR^2}\right)- \\ -\frac{3}{R\sqrt{\frac{4\pi}{\tau\nu}}}\left(1+\frac{hr_0^2}{2HR^2}\right)+\frac{4R}{2H}\sum_{n=1}^{\infty}Q_n, \tag{3.104}$$

or, in a different form:

$$\sigma_1 = \sigma+\frac{hr_0^2}{2HR^2}a; \tag{3.105}$$

Here:

$$a = \frac{r_0}{R}-\frac{3\delta}{4\pi}\frac{r_0}{R}-\frac{3\delta^2}{32\pi^2}\frac{r_0}{R}-\frac{3}{R\sqrt{\frac{4\pi}{\tau\nu}}}. \tag{3.106}$$

However:

$$M' = \pi r_0^2 h\rho = M - V\rho = M - 2\pi R^2 H\rho, \tag{3.107}$$

Therefore:

$$V\rho R\sigma_1 = V\rho R\left(\sigma + \frac{hr_0^2}{2HR^2}\,a\right) = \\ = R(M-M')\left(\sigma + \frac{M'}{M-M'}\,a\right) \qquad (3.108)$$

or:

$$V\rho R\sigma_1 = MR\sigma\left[1-\left(1-\frac{2\pi HR^2\rho}{M}\right)\left(1-\frac{a}{\sigma}\right)\right]. \qquad (3.109)$$

By designating:

F88

$$1-\left(1-\frac{2\pi HR^2\rho}{M}\right)\left(1-\frac{a}{\sigma}\right) = 1-\frac{\pi h r_0^2\rho}{M}\left(1-\frac{a}{\sigma}\right) = \zeta, \qquad (3.110)$$

we shall write:

$$V\rho R\sigma_1 = MR\sigma\zeta, \qquad (3.111)$$

and from here, we finally get:

$$\nu = \frac{1}{\pi}\left(\frac{K}{MR}\right)^2 \frac{\left(\delta - \frac{\tau}{\tau_0}\delta_0\right)^2}{\tau\sigma^2\zeta^2}. \qquad (3.112)$$

It should be emphasized that the problem as to the adequacy of introducing this correction must be carefully studied for each experiment (naturally, if the latter is conducted with two end friction surfaces). Indeed, let us assume that measurements are performed in such a manner that the formation of an oxide film on the surface of the liquid, which could act as a friction surface, is completely excluded. In this case, the lack of an end friction, resulting from the absence of friction on the free surface of the protruding column, is partially compensated by a side friction, whereby the degree of compensation will be different according to the height of the protruding column. If, on the other hand, a strong oxide film is formed, and it is precisely under such conditions that it is advisable to perform measurements with two end surfaces of contact, then one can be sure that the oxidized meniscus of the protruding column forms a friction surface, and the introduction of the above correction becomes indispensable. This is usually the case during the study of the viscosity of fused metals under low vacuum conditions, or when the inert gas atmosphere in which the measurements are conducted contains a noticeable amount of oxygen.

14. Calculation of the Suspension System

Let us assume that a unit must be built for studying the temperature dependence of a kinematic viscosity smaller than ν_1, using a calculating system applicable to low-viscosity liquids. It is required that the value of the kinematic viscosity ν_1 should correspond to a point $\xi = \xi_1 = 10$, i.e., $y = y_1 = 100$.

The radius of the bucket can be assigned, by using the convenience of the experiment as a guide, and primarily according to the dimensions of the furnace.

In accordance with inequation (3.52), we can assume that:

$$2H = 2R, \tag{3.113}$$

and from here, the volume of the tested liquid will be equal to: F 88

$$V = 2\pi R^3 \tag{3.114}$$

and the mass of the liquid:

$$M = 2\pi R^3 \rho, \tag{3.115}$$

where ρ is the density. Let us assign to ourselves a maximum decrement value, corresponding to the vertex of curve $\bar{\delta}(\xi)$, which will be designated as δ_m. Then, according to Figure 3, the value of the decrement at the point where $\xi = \xi_1 = 10$ will be equal to:

$$\delta_1 = 0{,}65\delta_m, \tag{3.116}$$

and, consequently, we will have to deal in the test with a decrement $\delta < 0.65\delta_m$.

By substituting into the formula:

$$y_1 = \frac{2\pi R^2}{\tau\nu_1} \tag{3.117}$$

the expression for τ, given by equation (3.31), after first excluding $f(\xi)$ from the latter with the aid of (3.23) and using (3.116), we will get:

$$\tau_0 = \frac{2\pi R^2}{y_1\nu_1\sqrt{1 + \dfrac{0{,}65\delta_m}{\pi\left(1 - \dfrac{3}{\xi\sqrt{2}}\right)}}}. \tag{3.118}$$

On the other hand, since $\bar{\delta} = 1$, we will find from (3.27):

$$K = \frac{0{,}086 \cdot 2\pi M R^2}{\delta_m}. \tag{3.119}$$

Equations (3.118) and (3.119) determine the oscillation period and the moment of inertia of an empty suspension system. Since these two values are connected by the relation:

$$\tau_0 = 2\pi \sqrt{\frac{K}{N}}, \tag{3.120}$$

the necessary value of τ_0 for the given K is secured by selecting the suspension thread with the aid of the well-known expression:

$$N = \frac{\pi G d^4}{32 l}, \tag{3.121}$$

where G is the modulus of rigidity, l is the length of the thread, and d is its diameter. Substitution of N into (3.120) leads to the equation:

$$\frac{\pi l}{G d^4} = \frac{\tau_0^2}{128 K}. \tag{3.122}$$

After selecting the material for the suspension thread (modulus of rigidity G), it is possible to determine the required length of the thread at a given diameter. When the suspension thread is twisted to a maximum angle of twist, no residual deformations should be formed in the thread. However, a final selection of the thread, which will secure the necessary oscillation period at the given moment of inertia and with no residual deformations present, is best performed experimentally.

Let us examine a numerical example. In studying most metals we can adopt a value of $\nu_1 = 0.010$ stokes. After assigning a value for the radius R = 0.700 cm and a value of $\delta_m = 0.400$, we will find, by means of (3.118) $\tau_0 = 3$ sec.

According to (3.119) and (3.115), the moment of inertia will be expressed by the formula $K = 1.44\rho$, and, by adopting a value for the density $\rho = 8$ g/cu cm, we will get K = 11.5 g · sq cm. The volume of the crucible cavity (inside area) will be equal to V = 2.13 cu cm, and the mass of the metal M = 17 g.

A simple calculation by means of formula (3.16) shows that, for the given suspension system at $\rho = 8$ g/cu cm:

$$f(\xi) \leqslant 0{,}105. \tag{3.123}$$

Therefore, instead of (3.31), it is possible to adopt $\tau \approx \tau_0$, and from the expression:

$$y \approx \frac{2\pi R^2}{\nu\tau_0} \qquad (3.124)$$

to determine the minimum value of the kinematic viscosity ν_2, which can still be calculated with the aid of Table 1. We will get:

$$\nu_2 = \nu_1 \frac{y_1}{y_2}. \qquad (3.125)$$

Since $y_1 = 100$ and $y_2 = 3{,}500$, then $\nu_2 = 3 \cdot 10^{-4}$ stokes.

After having determined the parameters of the suspension system for the purpose which we had in mind, we can examine the reverse problem, namely to establish the values of the kinematic viscosity and δ_m which can be obtained if liquids of different densities are studied with a given instrument. F 88

In this case, let us designate the values obtained in the calculation described above as ρ^0, δ_m^0, ν^0, and let us use the same letters, but without the indices on top, to designate the values corresponding to the measurement of the viscosity on the instrument examined above, but using a liquid with a different density, differing from ρ^0. By using formulas (3.119) and (3.118) on two liquids in the same instrument, we will get:

$$\delta_m = \frac{\rho}{\rho^0}\delta_m^0 \qquad (3.126)$$

and:

$$\nu_1^0 \sqrt{1 + \frac{0{,}65\delta_m^0}{2{,}47}} = \nu_1 \sqrt{1 + \frac{0{,}65\delta_m}{2{,}47}}. \qquad (3.127)$$

Substitution into the last two formulas of the numerical values $\delta_m^0 = 0.400$, $\nu_1^0 = 0.01$ stokes, $\rho^0 = 8$ g/cu cm will give the following expressions:

$$\delta_m = 0{,}05\rho \qquad (3.128)$$

and:

$$\nu_1 = 0{,}01 \sqrt{\frac{2{,}73}{2{,}47 + 0{,}0325\rho}}. \qquad (3.129)$$

With the aid of these formulas, we can find δ_m and ν_1 in case of liquids of different density, if we use the suspension system calculated above.

Figure 9 presents curves, plotted on the basis of the last two equations, and alsc on the basis of the equations presented in # 1 and 2 of this chapter, for the suspension system examined here.

Since the sensitivity of the suspension system to a change in viscosity at a given ξ is proportional to δ_m (formula (3.59)), the δ_m curve simultaneously describes (characterizes) the change in sensitivity in case of a change in density (this curve is calculated according to (3.59)).

Thus, Figure 9 represents an exhaustive (complete) characteristic of the properties of the given suspension system and the possible limits of its utilization.

15. Experimental Check of the Calculation System Used in the Theory of the Method

F88 If the inequation $y \geqslant 100$ is fulfilled, or, which is the same thing, $\xi \geqslant 100$, then, according to the theory of the method, the results of the calculation of the kinematic viscosity according to equation (2.82) must be independent of y. In order to confirm this concept, measurements of the kinematic viscosity of water, isopropyl alcohol and methyl alcohol were performed. All tests were conducted with the same bucket, but with different suspension threads, which made it possible to vary the oscillation period of the empty system within the range of $2.574 \leqslant \tau_0 \leqslant 9.270$ sec. The temperature during the tests fluctuated between 17 and 19.5°. The results of the processing of the experiments by means of the calculating system, referring to low-viscosity liquids and reduced to a single temperature, are illustrated in Figure 10.

Along the ordinate axis of this figure the value $\frac{(y)}{v}$ is plotted, in which $v(y)$ is the calculated viscosity at the given y, and $\bar{v}$ is a mean value, calculated from data of observations corresponding to a region where $y \geqslant 100$. In the case of isopropyl alcohol, the region where $y \geqslant 100$ was not reached, and the value of the kinematic viscosity at a maximum $y = 82$ was adopted as $\bar{v}$. Values of y were plotted along the abscissa axis.

Absolute values of $\bar{v}$ are listed in Table 3, which also gives the kinematic viscosity, calculated on the basis of average tabulated data of the dynamic viscosity and density.

In this case, from the standpoint of a check of the theory of the method, the appearance (shape) of the curve shown in Figure 10 is of greater interest than the absolute values of the kinematic viscosity, since the degree of purity of the liquids tested was not clarified. Figure 10 shows that the results of the processing of observations by means of the calculating system, referring to low-viscosity liquids, are actually independent of y in the region where the values of $y \geqslant 75$, i.e., $\xi \geqslant 8.5$.

Table 3

Liquid	t° C	$\bar{v}$ Centistokes	v' Centistokes (tabulated data)	$\frac{\bar{v} - v}{v}$, %
Water	18.0	1.07	1.06	1.0
Isopropyl alcohol	19.5	3.09	3.07	0.6
Methyl alcohol	18.1	0.784	0.773	1.4
Mixture of liquids	18.1	0.764	--	--

Thus, the fulfillment of the condition $y \geqslant 100$ ensures the necessary accuracy of calculation for low-viscosity liquids.

In the tests described above, which were conducted with relatively small values of y, it was necessary to make use of several successive approximations during the calculation of v.

An example showing how the calculations coincide (converge) for one of the points of the curve corresponding to isopropyl alcohol is presented in Table 4.

Table 4

Approximation	σ	v Centistokes	y
Zero	1	1.84 (see Note)	134
First	0.819	2.74	91
Second	0.775	2.98	82
Third	0.762	3.09	79

(<u>Note</u>: According to the designations given in # 8-9 of Chapter II in case of a zero approximation ($\sigma = 1$) $v = v^*$.)

This table illustrates a calculation which exhibits the lowest convergence. Its slow convergence is due to the fact that the values of y correspond to the initial part of Table 1 and even extend beyond its limits (small y values), where the dependence of factors a, b, c on y is most strongly expressed.

Table 5 gives an example showing the convergence of calculations when computing the viscosity of water, which also corresponds to one point of the curve.

The convergence in this case is more rapid than in the preceding case, which is due to the higher values of y, where the variation of factors a, b and c follows a slower course.

Table 5

Approximation	σ	ν Centistokes	y
Zero	1	0.817 (see Note)	303
First	0.887	1.04	239
Second	0.876	1.06	233
Third	0.873	1.07	231

(Note: See Note at bottom of Table 4.)

In general, the character of the curves given in Figure 2 shows that the convergence of calculating operations should be the better, the higher the values of y at which the experiment is conducted.

It is possible to estimate the degree of rigidity (strictness) of the condition $2H \geqslant 1.85\ R$ on the basis of the results obtained during the measurement of the viscosity of mercury at temperatures of 16 and 26° C. In this case, the bucket is filled to a height of $2H = 1$ cm with a free surface of the meniscus. Measurements were performed in a ceramic crucible (bucket), which was not wetted by mercury, having a radius of 1 cm. The experiment was conducted in the region corresponding to low-viscosity liquids.

The results of these measurements are listed in Table 6.

Table 6

t° C	ν Centistokes	Method	Name of Experimenter
16	0.115	Described above	Author
26	0.110	"	"
15.7	0.116	Capillary	Bernard

(Table 6 continued)

t° C	ν Centistokes	Method	Name of Experimenter
16.5	0.116	Capillary	Plus
17	0.118	"	Warburg
17	0.114	"	Schmidt
26	0.111	"	Plus

For purposes of comparison, the above table lists data obtained by other researchers, using the capillary method (Note: These data were extracted from Landolt-Börnstein, Physikalisch-Chemische Tabellen, Berlin, 1923).

The above table, of course, is not aimed at providing a further evidence of the correctness of the theory of the torsional-oscillation method, as should be perfectly clear on the basis of the contents of # 1 in Chapter I. These results are of interest precisely from the standpoint that these tests disclosed a coincidence of the data obtained by the capillary and torsional-oscillation method for a metallic liquid, namely mercury. It would not be at all surprising if the results obtained were lower than those obtained by the capillary method.

L. S. Priss (see reference 4 in the bibliography of Chapter II) has measured the viscosity of aqueous glycerin solutions, in order to check the formulas and tables drawn up by him for high-viscosity liquids (approximation of $\xi \leq 4.2$).

The measurements were performed without subjecting the unit to constant temperature conditions, which, of course, affected the accuracy of these measurements. The viscosity of aqueous glycerin solutions not only is greatly dependent upon the concentration, but is also extremely sensitive to temperature changes. For example, when the temperature changes by 1° C, the change in the viscosity of a 95% glycerin solution at room temperature is equal to 0.4 poises. In this particular test series, the possible error in the determination of the temperature amounted to 0.2-0.3° C. The concentration of the solutions was determined according to their density; the resulting accidental errors also affected the viscosity.

The results obtained during the measurement of the viscosity of aqueous glycerin solutions are listed in Table 7, which also contains Shelley's data (1932), extracted from Landolt-Börnstein's tables, obtained by the capillary method. The values of δ and ξ give an indication of the magnitudes (quantities) with which one has to deal in such tests. It is obvious that the results obtained by L. S. Priss are in good agreement with Shelley's data.

Table 7

R = 1.296 cm, 2H = 5.00 cm

Concentration, C %	t° C	ν_{meas}, in stokes	η_{meas}, in poises	η_{tab}, in poises	$\frac{\eta_{meas} - \eta_{tab}}{\eta_{tab}}$, %	δ	ξ
93.38	18.2	3.84*	4.78	4.67	+ 1.9	0.0232	0.516
90.29	20.0	1.98*	2.45	2.47	- 0.8	0.0343	0.714
79.76	19.2	0.496	0.602	0.610	- 1.3	0.0785	1.46
73.87	18.4	0.290	0.346	0.353	- 2.0	0.1231	1.92
68.98	18.2	0.195	0.230	0.228	+ 0.9	0.1827	2.38
62.51	17.0	0.127	0.147	0.146	+ 0.7	0.2405	2.97
57.36	18.5	0.0860	0.0987	0.0976	+ 1.1	0.2949	3.50
51.65	18.4	0.0616	0.0698	0.0699	- 0.1	0.3252	4.14
R = 1.008 cm, 2H = 4.00 cm							
94.85	19.8	4.71*	5.87	5.47	+ 7.3	0.0206	0.456
93.38	19.6	3.32*	4.13	4.24	- 2.6	0.0226	0.554
90.29	19.8	1.95*	2.41	2.49	- 3.2	0.0272	0.716
83.30	18.6	0.806	0.982	1.007	- 2.5	0.0418	1.11
79.76	19.5	0.522	0.640	0.619	+ 3.4	0.0558	1.37
73.87	19.2	0.294	0.350	0.340	+ 2.9	0.0855	1.85
64.04	18.6	0.134	0.156	0.153	+ 2.0	0.1568	2.76
57.36	18.5	0.0899	0.103	0.101	+ 2.0	0.1927	3.34
51.65	18.3	0.0597	0.0678	0.0702	- 3.4	0.2129	4.14

* These results are calculated with the aid of formula (2.99), and the remaining results with the aid of Table 2.

From all that has been said above, it is possible to conclude that the calculating formulas and tables referring to the fields of low- and high-viscosity liquids are correct. In addition, it becomes obvious that inequations (2.63) and (3.52) are not absolutely rigid (strict) and that slight violations of these inequations are possible, although this does not affect the accuracy of calculations.

Bibliography (Chapter III)

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Chapter IV

Experimental Realization of the Method and the Results Obtained

1. Viscosity of Steels

During the measurement of the viscosity of steels in the high temperature region (of the order of 1,500° C), the design of the viscosimeter is determined mainly by the selection of the heating furnace. Since the study of the viscosity of steels is necessary primarily for technical purposes, and in view of the fact that a particularly high accuracy is hardly required in this field at the present time, the viscosimeter can be built on the basis of any kind of open high-temperature furnace. As an example of such a type of unit, we shall give a brief description of a viscosimeter built by us, which involves the use of a Tamman furnace, as well as the results obtained with this unit on the viscosity of steels (1). With the aid of this unit, it was possible to conduct measurements approximately up to 1,800° C with a degree of accuracy sufficiently high for technical purposes.

A diagram of the unit is shown in Figure 11. The suspension system (crucible and rod) must be made out of a material which is not subject to deformation at the above-mentioned temperatures and which does not react chemically with the fused metal. Various types of aluminum oxide, such as alumina (kaolin), alundum and corundum, may be used for this purpose. It should be emphasized that the most serious attention should be given to the problem concerned with a selection of a material for the suspension system and its manufacturing technique.

In view of the presence of carbon monoxide in the combustion space of the Tamman furnace, the metal in the crucible is practically not subject to oxidation. In addition, a small amount of deoxidizing flux can be added to the crucible, which, after becoming fused, coats the metal with a thin liquid film. This measure allows the use of an open crucible without a lid, i.e., the test can be conducted in the presence of a single end (face) friction surface.

The structure of the suspension system used in our tests is illustrated in Figure 12. The suspension system is attached to a metal wire, whose dimensions and elastic properties must be coordinated with the moment of inertia of the suspension system, in order to secure the necessary oscillation period. The length of the wire should preferably be equal to about 25-30 cm.

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A ceramic cement, prepared from a fine kaolin or alumina powder, diluted with water and containing a small amount of liquid glass, can be used to connect (attach) metal to the upper section of the rod in the suspension system.

A metal disk 4 (see Figure 12) acts as a radiator, which promotes the cooling of the upper section of the rod and of the wire connected to this rod. The end of the wire is clamped into a miniature three-jawed chuck, which is firmly mounted on the rod with the aid of the ceramic cement.

The temperature of the metal can be measured by means of an optical pyrometer. A vertical beam (ray), coming out of the inside cavity of the crucible, is transferred into a horizontal plane by means of a total internal reflection prism or with the aid of a mirror, and is directed to the optical system of the pyrometer. The crucible is placed in the region of a uniform temperature field of the furnace. A practically equilibrium radiation is therefore present inside the cavity of the crucible, and a free surface acts as the bottom of this cavity. In this case, the temperature of this cavity, determined by means of the pyrometer, can be considered (adopted) as the temperature of the metal tested. The passage of a light ray through the prisms or mirrors may introduce an error into the pyrometer readings. This error must be taken into account, either by comparing the pyrometer readings during the passage of the light ray through the prism and when this ray goes around the prism (the pyrometer is installed along the vertical axis), or by calculation (2).

In this particular series of tests, the viscosity can be measured not only in case of a stationary thermal state at the given temperatures, but also in case of a slow heating or cooling at a rate of temperature variation of $\sim 1.0^{\circ}$ C per minute.

Free torsional oscillations are imparted to the suspension system by rotation of the knob 12 (see Figure 11) at a small angle fixed by means of a plug (locking device). The oscillation amplitudes are recorded visually on a semi-transparent scale according to the position of the beam (ray), reflected by the small mirror 8.

The first count (reading) of the amplitude should be performed after skipping 3-4 initial oscillations. Simultaneously with the first reading, a stopwatch is set into operation. After reading several full oscillations, simultaneously with a fixation (recording) of the f-th amplitude, the stopwatch is stopped. The equilibrium position can be determined from the remaining oscillations in the same way as during weighing on an analytical balance. On the basis of these data, both the oscillation period and the logarithmic attenuation (damping) decrement can be easily determined with the aid of formula (3.81). For each temperature, several such measurements should be performed, and average values of the period and of the decrement should be determined on the basis of these measurements.

A fusion of the metal can be easily observed when the decrement increases sharply and the period is reduced; the reverse phenomena take place during solidification of the metal.

In the temperature range above 1,500° C, a noticeable spontaneous movement of the system was observed upon heating in certain tests, which made observations extremely difficult. It can be assumed that the reason for this movement consisted in the fact that an intensive evolution of absorbed gases from the metal was taking place, which was even accompanied by an upward splashing (sputtering) of the metal, so that metal droplets above the free surface of the metal could be observed in some cases.

A measurement of the zero decrement (in the absence of a fused metal in the crucible) must be performed over the entire temperature range in which the viscosity is studied. As a result of the increase in the viscosity of gases with the temperature and the slight heating of the suspension wire, the zero decrement increases several times in comparison to its value at room temperature. Steels having the composition given in Table 8 were investigated.

Table 8

Steel Grade	C %	Si %	Mn %	S %	P %	Ni %	Cr %	Mo %
EU10	1.00	0.35	0.30	0.030	0.040	--	--	--
1010	0.09	0.01	0.47	0.025	0.039	0.05	0.04	--
EKhTM	0.30	0.19	0.65	0.004	0.015	0.12	0.18	0.18
EYaZS	0.40	2.52	0.67	0.012	0.031	23.47	17.30	--
EKh12	2.10	0.24	0.19	0.015	0.024	0.30	11.75	--

(Table 8 continued)

Steel Grade	C %	Si %	Mn %	S %	P %	Ni %	Cr %	Mo %
ShKh12	1.05	0.23	0.32	0.014	0.022	0.03	1.63	--
1045	0.49	0.31	0.66	0.026	0.042	0.07	0.18	--

Figure 13 shows the results of the measurement of the kinematic viscosity of these steels, recalculated again on the basis of observations, starting from the assumption that a single friction surface is present on the end plane of the crucible, and assuming that $\tau = \tau_0$ during the calculation of the correction term, which is due to an attenuation of the empty system, i.e., by substituting δ_0 for $\frac{\tau}{\tau_0}\delta_0$.

In these tests, the data of the unit had the following values: $R = 1.0\text{-}1.4$ cm; $M = 50\text{-}200$ g, $2H = 2\text{-}6$ cm, $K = 110\text{-}550$ g · sq cm, $\delta_0 = 0.005\text{-}0.012$, $\tau_0 = 2.5\text{-}5.5$ sec.

The accidental (random) error in the determination of individual values of the kinematic viscosity, according to the test conditions, may be as high as 10%.

In addition, the viscosity of EU10 and 1045 steels was measured in another unit, similar to the one described in # 3, under a vacuum of the order of 10^{-2} mm Hg in a crucible of smaller size. These results are also illustrated in Figure 13. The general character of the curves indicates that the kinematic viscosity of steels does not depend to a great extent upon their composition, varying approximately from 1 centistoke in the vicinity of the liquidus point to 0.6 centistokes at a temperature of 1,600° C.

2. Viscosity of Cast Iron and Ferrochromes

Measurements of the viscosity of cast iron and ferrochromes were performed in a similar unit. In this case, part of the tests were conducted in alumina crucibles, and part of the tests in graphite crucibles. In the latter tests, there obviously occurred a saturation of the alloy with carbon up to a concentration which reached the hypereutectic line in the phase diagrams of iron-carbon and chromium-carbon alloys.

The following characteristic picture was observed during all measurements in graphite crucibles. During the measurement of the viscosity, no peculiar features were observed in the heating process. However, when the metal was cooled 20-30° below the maximum temperature achieved in the test, as soon as this temperature started to drop, it was noticed that the value of the decrement started to drop sharply and the oscillation period increased.

This fact indicates a great increase in the viscosity of the liquid (see Figure 3). The reason for this observed phenomenon lies in the fact that the alloy becomes saturated with carbon during the process of heating, and when it is cooled by 20-30° C, free graphite is separated in the form of extremely thin plates, known to metallurgists under the name of "refining foam," which were clearly visible in the samples after the latter had cooled down. Apparently, in this particular case, we are confronted, during the process of measurement, with a heterogenous system consisting of a liquid melt and "refining foam" suspended in this melt.

In view of the great spread of individual decrement values, the results listed below have an approximate and qualitative character, and refer only to the heating process.

The viscosity was calculated not according to individual decrement values, as was done in other cases, but rather in the following manner. Values of decrements and periods were plotted in a graph opposite to the corresponding temperatures, on the basis of which smooth curves were plotted; then, values of the kinematic viscosity, which are graphically illustrated in Figure 14, were calculated on the basis of points on these curves, located at a distance of 40° C from each other. The error in the location of extreme points on straight lines may be as high as 20%.

The composition of the studied alloys is given in Table 9.

Table 9

			Composition of Alloy Prior to Viscosity Measurement					
Alloys			**% Cr**	**% C**	**% Mn**	**% Si**	**% S**	**% P**
Alloy	No. 1	Measurements in	--	3.7	2.17	0.97	0.019	0.018
	No. 2	alumina crucibles	40.29	6.0	1.90	2.64		
	No. 3		47.90	7.0	0.35	2.50		0.14
	No. 4		47.06	7.0	8.20	2.50		0.14
Alloy	No. 5	Measurements in	29.70	5.04	0.78	1.25		
	No. 6	graphite crucibles	36.07	7.50	0.70	1.35		
	No. 7		47.50	7.00	2.58	2.86		
	No. 8		52.56	7.88	0.32	1.03	0.06	0.076

The crucibles used had an internal radius ranging from 0.75 to 1.3 cm, and the weight of the metal varied from 23 to 50 g.

In spite of their low accuracy, these results, together with data on the viscosity of steels, point out a factor of great technical importance, namely that the kinematic viscosity of the tested ferrous metals does not depend to a great extent upon their composition and is approximately equal to the kinematic viscosity of water. From here we can draw the conclusion that the fluidity of ferrochrome alloys is not so much determined directly by the viscosity of these alloys, as by the liquidus point (Note: The concept of "fluidity" (fluid flow, flowability), used in the technical field, does not have at all the same meaning as the concept of "viscosity" (fluidity, consistency), which is expressed quantitatively by the reciprocal dynamic viscosity. The term "fluidity" (fluid flow) does not have a strictly established physical meaning, in view of the fact that the experimental methods for determining this value include the effect exerted by the surface tension and the process of heat exchange between the sample of the liquid metal and the surrounding medium. There is even no reason to assert that viscous properties in general play a dominant role in the determination (definition) of the term "fluidity" (fluid flow)).

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3. Viscosity of Lead, Tin and Bismuth (3)

With the aid of the unit schematically illustrated in Figure 15, it is possible to perform viscosity measurements at temperatures of up to 850-900° C. Heat insulation is effected by means of a system of polished nickel screens. The instrument is placed under a vacuum hood, and measurements are performed at an air pressure under the hood equal to $10^{-3} - 10^{-1}$ mm Hg. The resistance furnace, containing a Nichrome winding, is heated by an alternating current through an autotransformer with a smooth control (variac); the current was as high as 2.5 amp at a 40 v voltage. The design of the suspension system used in this unit is illustrated in Figure 16. The crucibles were made of graphite. Crucibles made of electrode carbon must first be calcined (fired) in a vacuum, otherwise the hood and the small mirror become coated with a film during the course of operations, and the experiment must then be stopped. The initial elastic pulse, which imparts a torsional-oscillation movement to the system, is created with the aid of an electromagnet by turning at a small angle the upper point of attachment of the suspension wire. A diagram of this section of the unit is shown in Figure 17. Efforts should be made to secure a minimum rigidity of the spring 6 and the current in electromagnet 2, by pulling in its core. Otherwise, a sharp blow of the lever 7 against the arresters (holding devices) may result in a thrust which will set the suspension system into a swinging motion.

Figure 18 illustrates a second possible modification of a twisting mechanism, which transmits a manual rotation through a vacuum cock, and by means of which a smooth but rapid rotation can be achieved.

A small mirror is mounted on a porcelain stick (rod), coinciding with the axis of the crucible. The amplitude of oscillations and the period are measured according to the light beam reflected by this mirror. A semi-transparent scale is mounted directly on the vacuum hood, which is installed in such a way that its axis coincides with the suspension wire.

The temperature of the metal is measured with a thermocouple installed between the furnace and the crucible. This method of measuring the temperature of the metal requires a preliminary comparison of the readings of this thermocouple with the readings of the thermocouple installed inside the crucible. Such a calibration was found to be sufficiently stable, if the measurements are performed at a thermal state of the furnace close to the stationary state.

A compensating (balancing) circuit, equipped with a PPTV potentiometer is used for measuring the thermoelectromotive force of the thermocouple.

The oscillation period of the system at a given temperature is determined with a stopwatch as the mean value of 6-10 series of oscillations whereby each series consists of 5-6 periods.

The suspension wire must coincide with the axis of the crucible, otherwise plane oscillations will be observed. Since in case of plane oscillations, the liquid moves together with the crucible as a whole, plane oscillations are almost undamped and distort the true values of the attenuation (damping) decrements. In the instrument described here, the suspension wire was fastened in miniature three-jawed chucks, rigidly connected with the suspension system and the rotating mechanism.

The metal samples which must be tested can be calculated and prepared in such a way that, during the smelting of the sample, a contact of the metal with the lid of the crucible is secured. Upon further heating, the metal expands and the excess metal flows out into the free space of the crucible 6 (Figure 16), thus always ensuring a full contact of the metal and the crucible on all surfaces of the latter during the test.

The reading of the initial amplitude is effected with a simultaneous start of the stopwatch after several oscillations. Following 4-6 oscillations (depending upon the value of the decrement), a reading of the final amplitude is made and the stopwatch is stopped at the same time. At least 8-10 such measurements should be performed at each temperature.

Naturally, oscillations can be recorded on a photographic film by means of an appropriate scanning mechanism, connected to the viscosimeter. The time recording process can also be automated in the same manner.

Numerous control tests have shown that, when the unit is carefully assembled, the logarithms of successive amplitudes, depending upon the number of the oscillation, can be easily arranged (stacked) in a straight line, and therefore the decrements can be calculated in relation to the initial and final amplitude.

As was already mentioned above, the design of the suspension system described above makes it possible to perform measurements in case of a slight oxidation of the metal surface and to work with an initial vacuum (rough exhaust) pump, without using a diffusion pump. However, oxidation can be avoided and measurements can be performed with a free surface of the fused metal meniscus if a diffusion pump of the TsVL-100 or MM-40 type is introduced into the vacuum system, or if the vacuum hood is filled with pure argon gas.

It is possible to operate in the presence of a high vacuum only with a limited number of metals, possessing a sufficiently low vapor pressure at the temperature of the test. It is impossible to use under a high vacuum metals which have a noticeable rate of evaporation, since the conduct of the experiment is made difficult by metal vapors condensing on cold parts of the system. The presence of a gaseous atmosphere at pressures which ensure the absence of a convection (in the presence of convection, the shielding insulation does not fulfill its purpose and the entire unit is subject to strong heating), i.e., at pressures of the order of 10^{-2} to 10^{-1} mm Hg, greatly reduces the harmful effect of evaporation.

F88

The following order in which the experiment should be conducted in the presence of a free surface of the fused metal meniscus can be recommended. While the diffusion pump is being continuously operated, the metal is heated for a long time below its melting point, in order to effect a degassing of the entire unit and of the sample. After the metal has been fused, the pumping unit is switched off, and the required amount of pure argon is introduced under the hood, until the pressure under the hood reaches a value of about 10^{-1} to 1 mm Hg. It is necessary to keep in mind that technical argon contains a small amount of oxygen. After a stationary state has been established, the viscosity measurement is performed. The gaseous atmosphere under the hood should be periodically renewed by pumping out the gas while the source of argon supply is connected to the unit, in order that during this operation the pressure should not drop below the limit established during the course of measurement. Otherwise, a metal film, which will prevent the further conduct of measurements, will form rapidly on the mirror and on the walls of the hood.

Both basic as well as auxiliary measurements, concerned with the determination of the temperature dependence of the decrement and period in case of an empty crucible, should be performed at a constant pressure of the gaseous medium under the hood. In this manner, it is possible to achieve a good reproducibility of the attenuation decrement of the empty system. The mean accidental (random) error in the viscosity values, measured in such an instrument, amounts to ± 1%.

In the case of tin and lead, the viscosity was calculated by taking into account the correction for the protruding column 6 (Figure 16). The magnitude of this correction at 800° C amounted to 6% for tin, and 5% for lead.

In case of bismuth, the above-mentioned correction was not taken into account, and this could have resulted in a reduction of the viscosity values obtained at 800° C of not more than 1.5%, as compared to the true values. Experimental results on the viscosity of lead, tin and bismuth are presented in Figure 19.

4. Viscosity of Aluminum

The viscosity of aluminum was measured in graphite crucibles by means of the unit described in the preceding paragraph.

The very first tests showed that, if an air pressure of 10^{-1} to 1 mm Hg is maintained under the hood, there is no recurrence of the results and there is a general tendency of a growth in the viscosity with an increase in the time during which aluminum remains in the fused state. This phenomenon is due to the fact that, in view of the high oxidability of aluminum and the relatively low mechanical strength of the oxide film formed on the fused metal, lower oxides are able to penetrate inside the metal during the time the crucible is in motion, thereby forming a heterogeneous system.

F 8 8

A number of special tests were set up in order to clarify this problem. A sample consisting of 99.7% pure aluminum was cut out of a solid block (ingot) and was subjected to an investigation at an air pressure under the hood of 10^{-3} mm Hg.

At the same time, the crucible was filled with metal in such a way that excess metal protruded into the free space 6 (see Figure 16). The correction for the protruding column amounted to 3%. On the basis of the results thus obtained, curve 1, shown in Figure 20, was plotted.

A sample from the same piece of aluminum was then smelted in an open furnace and the liquid metal was poured into a graphite crucible. The height of the cast sample was selected in such a manner as to avoid a contact of the free meniscus with the lid of the crucible. The pressure of the air environment during the course of measurements was maintained between 10^{-1} and 1 mm Hg. Curve 2 represents the result of the calculation performed in the assumption that a rigid oxide film, which constitutes the friction surface, is formed on top of the metal. On the other hand, if we start from the assumption that no oxide film is present, i.e., that there is no friction on the surface of the metal meniscus, then we get a curve 2' (see Figure 20).

Later, the same sample was kept for several hours in a fused state at a temperature of 800° C, and new measurements yielded the results illustrated by curve 3. When the sample was further maintained at the same temperature for 1 hour, a certain increase in the viscosity was observed (curve 4 in Figure 20).

From here we can draw the conclusion that the viscosity of aluminum, exposed to an oxidizing atmosphere, increases under the action of the oxidation process. The presence of insignificant amounts of lower oxides, present in the metal and forming a heterogenous system, is sufficient to effect such an increase in viscosity. This conclusion is important from a technical standpoint, since it was found that the viscosity of technical aluminum during the casting process is higher than the viscosity of pure aluminum, present under conditions which guarantee the absence of any oxidation. In this connection, it should be noted that, according to measurements performed by E. V. Polyak and S. V. Sergeyev (4), the kinematic viscosity of aluminum, measured by the method involving oscillations of a small ball in an open crucible, varies from 2.6 to 0.57 centistokes when the temperature varies from 670 to 800° C. These figures are sharply contradicted by the results of our measurements and this contradiction can be explained in the following manner.

F88 In the unit used by the above authors, the rod attached to the small ball immersed into the metal ran through the surface of fused aluminum, and dissipation effects resulting from the interaction of the surface layer with the rod were noticeable during rotary oscillations of the system. The authors point out that the viscosity data, obtained by them in the presence of a flux (carnollite), were somewhat lower than the data obtained without using a flux. This fact clearly indicates the influence of an oxide film (see reference 11 in Chapter I). In addition, however, the surface tension of the metal, causing additional dissipation effects during the rotation of the rod, must exert an influence in these tests. It is natural, therefore, that at a temperature of 800° C, when the surface tension is small, the authors obtained data close to the viscosity of oxidized aluminum and which coincide approximately with the ends of curves 3 and 4. At a temperature close to the crystallization point, the viscosity of 2.6 centistokes, obtained by E. V. Polyak and S. V. Sergeyev, does not correspond to the actual value, and the figure obtained is caused by surface sources responsible for the dissipation of the oscillation energy.

5. Viscosity of Tin-Lead Alloys (5)

The viscosity of tin-lead alloys was studied in the unit described in # 3. The air pressure under the hood was maintained at 10^{-2} mm Hg. Alloys, having the composition listed in Table 10, were studied.

Table 10

Alloy Number	1	2	3	4	5	6
% Sn	99.92	80.12	65.30	40.39	19.62	0.057
% Pb	--	19.90	34.66	59.59	80.44	99.87

The probable error of individual measurements was equal to 2-3%.

Figure 21 shows a comparison of data for tin and lead with the results given in # 3 of this chapter. From this figure it can be seen that there is a discrepancy between these data in the temperature region covering a range of about 100° C near the melting point. The same figure also gives the results obtained by I. F. Golubev and V. A. Petrov (6), Sauerwald and Topler (7) and Schott (extracted from Landolt-Börnstein tables), obtained by the capillary method and recalculated for the kinematic viscosity. All these results are in good agreement with the data presented in # 3, and discrepancies are observed only in the temperature region near the crystallization point. Results of the measurement of the viscosity of Sn-Pb alloys are presented in Figure 22, and viscosity-composition isotherms for the alloy being tested are presented in Figure 23. As can be seen from this figure, a weakly expressed special point, represented in the figure by a dotted line, is observed near the eutectic concentration of the alloy.

6. Viscosity of Tin-Bismuth Alloys (8)

The study of these alloys was conducted with the viscosimeter described in # 3, the design of which was slightly modified. In the upper section of the furnace muffle, instead of shields, a lid was installed, which was provided with an additional electric heating system, in order to ensure a uniform temperature field along the height of the muffle. This arrangement was dictated by the desire to reduce the condensation of metal vapors on the lid of the crucible. According to the curve represented in Figure 7, a noticeable influence of condensation phenomena can be expected, starting approximately at 500° C. However, since measurements were performed under a pressure of $5\text{-}9 \cdot 10^{-3}$ mm Hg, and the presence of air molecules prevents the establishment of a stationary distribution of the pressure of metal vapors in the space between the free surface of the metal and the lid of the crucible, this temperature must be considered as somewhat lower than the actual temperature.

All measurements were conducted with a free surface of the fused metal. At the air pressure indicated above, no oxidation of the samples took place, and there was certainly no friction surface on the upper base of the liquid cylinder (after the tests, the samples retained their metallic gloss).

The second structural change in the unit was concerned with the method for measuring the temperature (Figure 24). Although the insertion of a thermocouple inside the crucible makes the handling of the viscosimeter more difficult, it offers a definite advantage in regard to the accuracy with which the temperature of the metal is measured. The study covered alloys having the composition listed in Table 11.

Table 11

Alloy Number	1	2	3	4	5	6	7	8	9	10
% Bi	100	89.43	78.97	72.31	56.72	46.44	28.46	19.72	9.96	--
% Sn	--	10.36	20.98	27.53	43.39	53.65	71.39	80.39	90.10	100

The vapor pressure of fused bismuth is slightly higher than that of lead, and much higher than that of tin (at the same temperatures). For this reason, in spite of the precautionary measures adopted, a condensation of metal on the lid of the crucible was observed to take place to a limited extent. After the end of the tests, in the case of alloys with a high bismuth content (Nos. 1-6), individual droplets of condensed metal were observed on the inside surface of the crucible lid, which were uniformly distributed over the entire surface. These droplets form a combined mass for the crucible and a spent mass for the sample. Equation (3.90) gives an expression for the correction which must be made on the viscosity values calculated in the usual manner, and it is indispensable to introduce this correction in this case. The magnitude of this correction, for individual viscosity values of pure bismuth, amounted to as much as 3.5%, and did not exceed 1.5-2% in the case of alloys.

As a result of the measurement of the vertical temperature distribution in the muffle, in the presence of a suspension system, it was assumed that the temperature difference between the free surface of the metal and the lid of the crucible did not exceed 3-5° C. Since bismuth is primarily the evaporating component in the tested alloy, no noticeable condensation can take place up to 500° C, as was mentioned above. Therefore, if the alloy had not yet been heated above this temperature, no correction to account for condensation was introduced. If, on the other hand, the alloy had been heated to a temperature above 500° C, and droplets of solidified metal were observed on the lid after completion of the test, then a correction in accordance with equation (3.90) was introduced in all viscosity values obtained after the maximum test temperature was achieved.

For example, in the case of pure bismuth, the amount of metal condensed on the lid was equal to 0.764 g, as compared to the total mass of the sample of 50 g. This case represents the most striking example of condensation. Following the introduction of an appropriate correction, amounting to 3.5%, the resulting viscosity values of bismuth coincided well over the entire temperature range with the results of previous measurements, listed in # 3.

Figure 25 shows the temperature dependence of the kinematic viscosity of Sn-Bi alloys. The accuracy of the results can be estimated at 2%. Viscosity isotherms for all alloys are shown in Figure 26.

In regard to all of the data on the viscosity of tin and Sn-Bi alloys listed above, it should be noted that these data were obtained either during the process of temperature increase of the sample, starting in each test with the solid state, or during the process of cooling of the sample, in case its maximum temperature did not exceed 600° C. Thus the graphs shown in Figure 25 do not contain any points which would correspond to a measurement of the viscosity in the direction of a temperature decrease, in case this temperature was higher than 600° C in a given continuous test. It should also be emphasized that reference to a heating or cooling does not mean a digression from a stationary thermal state of the system during the course of each individual measurement at a given temperature.

7. Viscosity of Tin During Supercooling (9)

Tin can easily be supercooled and therefore affords extensive possibilities for studying the temperature dependence of physical properties of liquid metals, and specifically of the viscosity, during the process of supercooling of a metal. The result obtained is illustrated in Figure 27.

It was found that, during the cooling of supercooled tin, the curve showing the temperature dependence of the viscosity branches off into a region of lower values, in comparison to the "normal" curve (i.e., the curve obtained during the process of heating). This branching takes place in an interval of several score of degrees prior to the equilibrium crystallization point. When the temperature drops further, the viscosity increases, retaining, in the region where supercooling takes place, a value of the same order as the one observed during the fusion process.

A branching of the viscosity curve was observed only in those cases when the metal was later subjected to supercooling. In those cases when supercooling was not observed, there was also no branching of the viscosity curve.

It should be noted that each value of the viscosity during the cooling process and in the region of supercooling was determined at a stationary temperature.

As the measurements performed by G. I. Goryaga have shown, bismuth behaves in the same manner as tin, since this metal is also easily subject to supercooling.

Thus, the process involving a branching of the temperature vs. viscosity curve precedes a supercooling. If no branching is observed, there is no supercooling.

The branching of the viscosity curve and supercooling represent two sides (aspects) of the same phenomenon.

8. Viscosity of Lead-Bismuth Alloys. Viscosity in a Heterogenous Region (10)

The viscosity of this type of alloy was studied with the aid of a viscosimeter, designed on the basis of an open tubular furnace of 1 kw power with a maximum temperature in the combustion space of 800° C. The furnace was 500 mm long and the diameter of the tube was 40 mm.

The diagram of temperature measurement is illustrated in Figure 24. The crucibles are made of graphite and are coated on the outside with a ceramic paste (cement), which protects the graphite from burning up. The structure of the crucible, containing 90 g of alloy, is illustrated in Figure 28. The floating lid can be moved freely up and down, but has no rotational degree of freedom in relation to the crucible. This lid always ensures the presence of an upper end surface of the crucible. As a result of such a crucible design, measurements can F88 be performed at atmospheric pressure, and there is practically no evaporation and condensation of metal on the lid of the crucible.

By using the floating lid, the mass of the sample always remains constant, and thus it is not necessary to introduce a correction for the protruding column (see # 11 in Chapter III).

The instrument was equipped with a photographic recording of the oscillations, with a simultaneous image of the scale for reading the amplitudes and the time markings of the pendulum.

The measurements are performed at a constant growth of the temperature with a speed of 1° per minute. The results of measurements are shown in Figure 29.

During passage through the liquidus line, the viscosity of the heterogeneous alloy increases approximately 500 times in a temperature interval of about 20° C. It can be easily seen (Figure 3) that, in this case, a transition takes place from the first into the second region (i.e., from the region of low-viscosity to high-viscosity liquids), and a mathematical system corresponding to these regions was used in calculating the viscosity. In view of the fact that, in the region corresponding to a heterogeneous state of the alloy, the viscosity changes with the temperature in an extremely sharp manner, the temperature must be determined with a high degree of accuracy. For this reason, the readings of the thermocouple, mounted inside the crucible, were specially compared with the readings of a thermocouple inserted directly into the metal. The corresponding correction did not exceed 1.5° C (at the lowest temperature), and was rapidly reduced to zero when the temperature was increased.

The obtained results on the viscosity of a lead-bismuth alloy in the heterogeneous region of the fusion diagram confirm the observations made during the measurement of the viscosity of cast iron (see # 2 of this chapter) and indicate that, even in case of a very insignificant shift in the temperature of the alloy below the liquidus line, the viscosity of the system exhibits an extremely sharp increase. The reason for this phenomenon lies in the deposition (precipitation) of crystals of the solid phase of one of the components. The heterogeneous medium formed in this manner possesses a low fluidity, in spite of the insignificant number of solid small crystals present in this medium.

9. Viscosity of Zinc and Cadmium

Measurements of the viscosity of zinc and cadmium were performed by I. S. Kuznetsova during the course of her graduation work at the Physics Faculty of Moscow State University in 1953.

Both of these metals are highly volatile, and it was therefore necessary to use a hermetically sealed crucible. I. S. Kuznetsova used a suspension system having the following design. The graphite crucible, containing the metal to be tested, was placed into a cylindrical quartz jacket (casing), which was drawn out at the top into a thin tube and sealed during the course of evacuation with a vacuum pump. The upper part of the quartz jacket (unsoldering) was inserted into the bushing of the suspension system and fastened by means of a ceramic paste (cement). During this operation, special attention should be given to an accurate alignment of the component parts of the suspension system. The soldered joint of the thermocouple was located on the unsoldering of the quartz jacket of the crucible, and the thermocouple wires ran inside the rod of the suspension system, whereby this rod consisted of a two-channel porcelain tube. The wires of the thermocouple extended into the upper section of the porcelain tube and were twisted down in the form of short terminals (ends), running parallel to the tube. Outside of the suspension system, a special mechanism was installed, containing mobile mercury contacts which were placed under the free terminals of the thermocouple at the time the temperature was measured, thereby closing a circuit used for measuring the thermo-emf. During the course of oscillations of the suspension system, the terminals of the thermocouple remained free. This method of measuring the temperature was found to be very convenient. Heating was effected by means of an open tubular furnace.

In the tests performed by I. S. Kuznetsova, the metals to be tested were first purified by removing insoluble impurities by repeated recrystallization in vacuum. For this purpose, a unit for growing single crystals was used, by means of which it was possible to achieve a slow cooling, starting from the lower portion of the vacuum tube. The prepared sample, together with the graphite crucible, was placed into a wide vacuum tube and was remelted into the crucible. The crucible containing the sample to be tested was placed in an almost uniform temperature zone of the furnace, although there was a slight overheating of 2-3° at the top of the quartz jacket. In this manner, it was possible to avoid a condensation of metal vapors on internal surfaces of the quartz jacket during the stationary thermal state and during the heating process.

The results of the measurement of the viscosity of zinc and cadmium, obtained by I. S. Kuznetsova, are shown in Figure 30. These data refer to the heating process. As soon as the furnace started to cool off, the temperature in the upper portion of the zone containing the crucible dropped below the temperature of the metal, and an intensive condensation of vapors took place in the upper section of the quartz jacket, which resulted in a noticeable distortion of the results.

In the case of zinc, two types of measurements were performed. The first type of measurements involved a sealing under vacuum of the quartz jacket containing the graphite crucible, and in the second type of measurement the jacket was sealed under atmospheric pressure. The results of both measurements, calculated by taking the free surface of the metal meniscus into account, agreed well with each other. Consequently, if air is not allowed to enter the crucible, it does not matter whether the jacket containing the crucible was evacuated or not.

Both metals belong to the second group of the periodic system and possess, in the solid state, a loosely packed hexagonal structure with a ratio of axes c/a close to 1.9. In spite of this fact, a great difference in the viscosity values of zinc and cadmium can be observed upon comparing the curves showing the temperature dependence of the kinematic viscosity of these metals.

10. Certain Remarks Concerning the Design of the Viscosimeter

The viscosimeter is highly sensitive to vibrations. The plane oscillations of the suspension system, arising as a result of external influences, have an extremely slow damping rate, since the absorption of energy in these oscillations is very small. Plane oscillations may act as a source of great errors during the determination of the damping ratio. Serious attention must be given to this fact during the design and assembly of the instrument. In order to reduce these influences, it is desirable to use special anti-vibration supports, known in the laboratory technique (11).

The suspension system is the most important part of the instrument. The selection of its structure (design), of the crucible material and of the method for measuring the temperature is determined primarily by the nature of the problems which have to be solved during the study of the viscosity of metals. The entire system will be simple if one can be satisfied with a low accuracy of the results obtained (equal to several percent), and will be accordingly more complex in regard to manufacture and assembly as well as in regard to the quality of the materials used, if high requirements on the accuracy of the results are established.

Unannealed copper can be recommended as a readily available and conveniently used material for the suspension wire. Unannealed copper wires have a low natural damping ratio and a weak dependence of this ratio upon the amplitude. In the case of most metal wires, the natural damping ratio under a load decreases with the course of time; after the load has been thrown off, this ratio assumes its original value more or less rapidly. In the case of unannealed copper wire, these variations of the decrement (ratio) with time are practically independent of the value of the amplitude. The stationary value of the damping ratio of a loaded wire amounts to about 50% of the original ratio, and this value is reached after approximately 2 days. In view of the above-mentioned time dependence of the damping ratio, efforts should be made to secure a minimum value of the damping ratio in an empty system.

Regardless of the conditions under which measurements of the viscosity of metals are performed, it is necessary to achieve a certain overheating of the lid of the crucible in relation to its bottom. This measure will, first, prevent the formation of convection in the crucible, and, second, will prevent the condensation of metal vapors on the walls and lid of the crucible. The phenomenon of condensation requires the introduction of a special correction (see # 12 in Chapter 3) into the formulas used in calculating the viscosity; the practical consideration of this correction at different temperatures is greatly complicated by the complex nature of the condensation kinetics.

When studying the viscosity of highly volatile metals, for example, cadmium, antimony or zinc, special measures should be adopted to combat metal evaporation. Two different kinds of methods can be used for this purpose: either a hermetic sealing of the crucible, following a preliminary degassing of its internal volume, containing the metal sample (for example, by using methods commonly used in the vacuum technique), or else (which, of course, is a less radical measure), by conducting the experiments under a normal and elevated pressure of the gaseous atmosphere surrounding the sample. If this atmosphere had an oxidizing nature (air), then it is indispensable to secure a contact of the upper surface of the metal with the lid of the crucible, in order to create at this point a reliable friction surface. If the atmosphere around the sample is a neutral one, and the sample was not at first noticeably oxidized, then its upper surface (meniscus) can remain free.

In order to record the damped oscillations of the suspension system, it is sometimes convenient to use a device for the photographic scanning of these oscillations. However, one should keep in mind that the processing of photograms consumes additional time. If the unit is carefully assembled and a linear dependence between the logarithm of the amplitude and the oscillation number is ensured, it is usually not necessary to use a photorecording system.

The processing of the results of observations, in spite of the complex nature of the formulas used for calculating the viscosity, usually does not present any particular difficulties when using a correct calculating system.

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Chapter V

Connection Between the Hydrodynamics of a Viscous Liquid and the Theory of Hereditary Media and Rheology

1. Tangential and Bulk Viscosity

The viscous properties of a liquid are characterized by the following two viscosity factors: the tangential viscosity η, corresponding to the velocity of shear deformation, and the bulk viscosity η', corresponding to the rate of deformation of a uniform volume compression (or expansion).

Already Stokes, in the course of his derivation of equations describing the motion of a viscous liquid, realized the necessity of taking into consideration viscous properties with the aid of two viscosity factors, noting at the same time that, in those cases when the density can be considered, without a noticeable error, as constant or varying slowly in time, it can be assumed that $\eta' = 0$. In addition, Stokes pointed out that $\eta' = 0$, if we assume that, in case of a uniform expansion, the pressure in each moment of time depends only on the density and the temperature, and not on the rate of expansion. Thus, Stokes did not assume by any means that η' is generally equal to zero and may be disregarded in case of compressible liquids (1). However, later on, almost all authors excluded from hydrodynamic equations terms containing η', referring usually in this connection to "Stokes' hypothesis," whereby they implied that the last portion of the above-mentioned considerations proposed by Stokes constitutes such a hypothesis.

Both viscosity factors are introduced into hydrodynamics, starting from the assumption made by Newton, which, in its present formulation, states that the components of the tensor of viscous stresses are linearly connected with the components of the tensor of the deformation rates.

There is a formal analogy between Newton's law of internal friction and Hooke's law of elasticity, which consists in the fact that viscous stresses are related in the same manner to deformation rates as elastic stresses to the actual deformations. This analogy is manifested, on the other hand, in the same relation between the energy of elastic deformation and Rayleigh's dissipation function and elastic and viscous stresses, respectively (2).

During the derivation of equations describing the motion of a viscous liquid, it is assumed that only hydrostatic pressure forces are present in the liquid, which manifest themselves during volume deformations, as well as internal friction forces, which exert their effect both during shear and volume deformations, and which are proportional to the corresponding deformation rates. Both of these forces are independent of each other and are governed by the law of superposition. The Navier-Stokes motion equation, obtained under these conditions, when expressed in vector form, has the following appearance:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\nabla)\mathbf{v} = -\frac{1}{\rho}\nabla p + \frac{1}{\rho}P + \nu\Delta\mathbf{v} + \left(\nu' + \frac{1}{3}\nu\right)\nabla(\nabla\mathbf{v}), \tag{5.1}$$

where υ is the velocity vector of an elementary volume of liquid, p is the pressure, P is the volume force, $\nu' = \frac{\eta'}{\rho}$ is the bulk kinematic viscosity, ν is the previously mentioned shear kinematic viscosity.

As can be seen from equation (5.1), η' drops out of the motion equation in the approximation of an incompressible liquid. However, the usefulness of this approximation depends essentially upon the nature of the processes taking place in the liquid. If the liquid can be considered as incompressible, in case of the torsional oscillations of the bucket examined above or during its flow through a capillary, the compressibility of the liquid plays a basic role during the course of propagation of acoustic waves.

L. I. Mandel'shtam and M. A. Leonotovich (3) have shown that the observed abnormally high, in comparison to the classical Stokes-Kirchhoff theory, absorption of ultra-acoustic waves in liquids can be explained in a natural way if the second (bulk) viscosity is taken into account. The investigation of the damping (attenuation) of ultrasonic waves in liquids has become the basic method for measuring the bulk viscosity (4). Therefore, during our theoretical study of the connection existing between a viscous liquid and a hereditary medium, we shall also take into account the bulk viscosity, although this property does not manifest itself in the experimental studies examined in this book.

2. Theory of Hereditary Media and Rheology (5)

F88 From the standpoint of continuum mechanics, the laws of elasticity and internal friction constitute maximum approximations of the properties of physical bodies. In a certain sense, actual properties lie between these extreme cases.

Elastic and viscous properties, which are manifested to a certain extent in all physical bodies, are unified by the theory of hereditary media and rheology, whereby the latter represents a specific case of the former theory. Therefore, both the theory of hereditary media, as well as rheology, which takes into account in a clear form the time aspect of processes involving variations in stresses and deformations, may be considered as the mechanics of the actual properties of continuums.

Boltzmann (6) and Volterra (7) must be credited with the most general approach to the solution of the problem concerned with the actual properties of bodies in relation to the deforming (straining) process. The basic idea proposed by the above authors consists in the following. The state of stress in a given moment of time t is determined not only by the deformation existing at this particular moment, but also by the entire previous deformation (straining) history of the body.

In order to account for this history, it is possible to examine at first two consecutive deforming processes. Let us assume that a deformation $\varepsilon(t')$ is present at the time moment t', the preceding duration of which is equal to $\Delta t'$. Then, during the subsequent deforming, the stress, present at the moment t and equal to $\sigma(t)$, is smaller than the stress specified by the elasticity law by a value which depends upon the previous deformation $\varepsilon(t')$ in such a way that:

$$\sigma(t) = x\varepsilon(t) - \varphi(t - t')\varepsilon(t')\Delta t', \qquad (5.2)$$

where x is a constant, while σ and ε stand for the stress and the deformation either of a uniform manifold compression, or of a shear (according to the possibility of breaking down an arbitrary small deformation into a uniform manifold compression and shear). $\varphi(t - t')$ is called the heredity function. Naturally, in the case of compression and shear, both $\varphi(t - t')$ and x are different.

In view of the fact that the influence of the preceding deformation decreases in the course of time, $\varphi(t - t')$ must be a monotonic decreasing function. This function is a characteristic of the medium undergoing deformation in relation to the type of deformation being studied, and constitutes a generalization of the representation of physical properties by means of material constants, which are encountered when describing processes by means of differential equations.

According to Boltzmann's concept, there occurs a superposition of deformations to which the medium is subjected during different time moments. Consequently, during a continuous deforming, the following relation will take place:

$$\sigma(t) = \varkappa\varepsilon(t) - \int\limits_{-\infty}^{t} \varphi(t - t')\varepsilon(t')\,dt'. \qquad (5.3)$$

This equation accounts for the entire deforming history of the medium at the given moment of time t.

If the resolvent of the kernel of the integral equation (5.3) is designated as $\psi(t - t')$, then the expression for the deformation can be written as follows:

$$\varepsilon(t) = \frac{1}{\varkappa}\sigma(t) + \int\limits_{-\infty}^{t} \psi(t - t')\sigma(t')\,dt'. \qquad (5.4)$$

The determination of the mode of functions $\varphi(t - t')$ and $\psi(t - t')$ constitutes an independent problem, and this problem can be solved by approaching it from two different standpoints.

First, one can attempt to clarify the mode of the heredity function by starting from atomic-molecular concepts about the structure of the medium and the micromechanism of deformations. However, in view of the complex nature of this mechanism and the absence of reliable information on the mechanism of small deformations having a nonelastic character, no progress at all has been achieved so far in this direction.

Second, by conducting experimental observations of the properties of deformed media and systematically classifying the data obtained, it is possible to establish the mode of the heredity function for various bodies. Naturally, it is highly probable that individual properties of the materials studied will exert a strong influence not only on the constants entering into this function, but also on the actual mode of the heredity function. Apparently those failures which accompany attempts at setting up a single rheological equation for a large group of physical bodies are connected with this factor.

Nevertheless, in order to clarify certain general properties of condensed media, one can attempt to introduce a universal heredity function, containing the proper number of material constants, keeping in mind the fact that individual properties of the medium will be reflected in these constants. Naturally, such an assumption constitutes a sufficiently rough approximation, although there are serious reasons for assuming that it is closer to reality than the law of elasticity or of internal friction, taken separately.

Since φ must be a monotonic decreasing function, we can adopt the following for this function:

$$\varphi(t-t')=Ae^{-\alpha(t-t')}, \tag{5.5}$$

where A and α are characteristic constants of the material. Such a representation of the heredity function is not the best one in all cases.

Boltzmann himself demonstrated the unsuitability of an exponential heredity function for calculating the energy dissipation during oscillatory processes in solid bodies. Boltzmann also proposed the use of a heredity function inversely proportional to time. This function was used by B. V. Deryagin in calculating the damping (attenuation) of elastic waves in solid bodies on the basis of his general theory dealing with the propagation of small disturbances in a hereditary medium (8).

On the basis of an analysis of extensive experimental data, dealing with solid bodies, other expressions for φ have also been proposed, which describe the properties of these bodies in a more satisfactory manner (9).

However, we wish to select expression (5.5), since our problem consists in establishing the connection between the solid and liquid state, and therefore all condensed systems must be examined from a single viewpoint.

By substituting (5.5) into (5.3) and replacing the lower limit of the integral by zero, i.e., by counting the time from the moment of the first deformation, we get:

$$\sigma(t)=\varkappa\varepsilon(t)-\int_0^t Ae^{-\alpha(t-t')}\varepsilon(t')\,dt'. \tag{5.6}$$

After differentiating this relation according to t, which is considered as a parameter, we arrive at the following linear rheological differential equation:

$$\dot{\sigma}(t)=\varkappa\dot{\varepsilon}(t)-\alpha\sigma(t)+\alpha\left(\varkappa-\frac{A}{\alpha}\right)\varepsilon(t), \tag{5.7}$$

in which the time derivatives are designated by dots.

By introducing the symbols:

$$\varkappa = \varkappa_{\infty}, \quad \alpha = \frac{1}{\vartheta}, \quad \varkappa - \frac{A}{\alpha} = \varkappa_0, \tag{5.8}$$

the last equation can be rewritten in the following form:

$$\dot{\sigma}(t) = \varkappa_{\infty}\dot{\varepsilon}(t) - \frac{1}{\vartheta}[\sigma(t) - \varkappa_0\varepsilon(t)]. \tag{5.9}$$

An investigation of this equation was conducted by A. Yu. Ishlinskiy (10) and others (11). If the deformation is fixed, i.e., $\dot{\varepsilon} = 0$, the solution of equation (5.9) will appear as follows:

$$\sigma(t) = \varkappa_0\varepsilon + [\sigma(0) - \varkappa_0\varepsilon]\, e^{-\frac{t}{\vartheta}}. \tag{5.10}$$

Consequently, the stress relaxes toward the equilibrium value:

$$\sigma(\infty) = \varkappa_0\varepsilon, \tag{5.11}$$

which is achieved after an infinitely long interval of time.

The constant ϑ has a time dimension and represents the relaxation time of the stress. Equation (5.11) indicates that $\varkappa_0$ has the same meaning as the modulus of elasticity, corresponding to the given type of deformation during a slow deforming. The meaning of constants $\varkappa_0$ and $\varkappa_{\infty}$ can be clarified more fully, if we start from equation (5.6). Assuming:

$$\varepsilon(t) = ae^{iqt} \tag{5.12}$$

and substituting this expression into (5.6), we get:

$$\sigma(t) = \frac{\varkappa\alpha - A + i\varkappa q}{\alpha + iq}\, ae^{iqt}. \tag{5.13}$$

By transforming the latter with the aid of (5.8), we get:

$$\sigma(t) = \mathscr{H} ae^{i(qt+m)}, \tag{5.14}$$

where:

$$\mathscr{H} = \sqrt{\frac{\varkappa_0^2 + \varkappa_{\infty}^2 q^2\vartheta^2}{1 + q^2\vartheta^2}} \tag{5.15}$$

and:

$$\mathrm{tg}\, m = \frac{(\varkappa_\infty - \varkappa_0)\, q\vartheta}{\varkappa_0 + \varkappa_\infty q^2\vartheta^2}. \qquad (5.16)$$

From (5.15) and (5.16), it can be seen that if $\varkappa_0$ and $\varkappa_\infty$ are of the same order of magnitude, then, when:

$$q^2\vartheta^2 \ll 1 \qquad (5.17)$$

the stress is connected with the deformation by the relation:

$$\sigma(t) = \varkappa_0 \varepsilon(t), \qquad (5.18)$$

F88 i.e., the usual law of elasticity is applicable at a modulus equal to $\varkappa_0$. Thus, if the period of variation of the external influence is great in comparison to the relaxation time of the stress, then, during the time the external influence undergoes a change, the stresses are able to undergo a complete relaxation, and the elastic properties of the medium are characterized by the modulus of elasticity $\varkappa_0$.

When:

$$q^2\vartheta^2 \gg 1 \qquad (5.19)$$

the stress is connected with the deformation by the relation:

$$\sigma(t) = \varkappa_\infty \varepsilon(t). \qquad (5.20)$$

Consequently, if the period of the external influence is small in comparison to the relaxation time of the stresses, the latter have no time at all to relax, and the medium again behaves as an elastic medium, but is characterized by a different modulus $\varkappa_\infty$.

As can be seen from (5.16), the phase shift is practically reduced to zero in both cases. These expressions disclose the physical meaning of constants $\varkappa_0$ and $\varkappa_\infty$.

Thus, when the heredity function is represented in the form (5.5), the arbitrary state of stress of the medium can be described by means of the rheological equation (5.9), which includes six material constants $\varkappa_0$, $\varkappa_\infty$ and ϑ -- of which three correspond to a deformation caused by a uniform manifold compression, and three correspond to shear deformations (if the medium is an isotropic one). This conception is applicable to a certain extent both to solid bodies and liquids.

3. Thermodynamic Derivation of a Linear Rheological Equation

A thermodynamic substantiation (base) can be given, in case of an exponential heredity function φ, to the linear rheological equation (5.9) derived from the theory of hereditary media, which shows that the relaxation of stresses may represent a secondary effect and may be the result of relaxation processes of a finer nature.

If changes in the state of stress of the medium take place with a finite velocity, then a deviation from the state of statistical equilibrium is present in the medium in each moment of time. These deviations are the cause of the irreversible nature of the deforming process, which expresses itself in the conversion of the energy of elastic deformation into heat, i.e., in the presence of viscosity effects. Such concepts were evolved by M. A. Leontovich and L. A. Mandel'shtam (3) in their theory of sound absorption in liquids. Starting from the same concepts, B. N. Finkel'shteyn and N. S. Fastov (12) obtained an equation for the theory of hereditary media in case of an exponential heredity function, and consequently, also the linear rheological equation (5.9).

In order to characterize the deviation of the system from the state of equilibrium, B. N. Finkel'shteyn and N. S. Fastov have introduced a relaxation tensor ξ_{ik}, without clarifying the meaning of this tensor in greater detail. In this case, in the presence of small deformations and slight deviations from the equilibrium state, the free energy of the medium can be represented in the form of a linear combination of quadratic invariants of the tensors ε_{ik} and ξ_{ik}. By separating the deformations caused by shear and manifold compression, we can write:

$$F(\varepsilon, \xi) = F_0 + a\varepsilon^2 + b\xi^2 + c\varepsilon\xi, \tag{5.21}$$

where F is the free energy of a unit volume, ξ is the scalar parameter of relaxation. ε and ξ refer either to a deformation caused by compression, or one caused by shear.

If the equilibrium value of ξ is equal to ξ_0, then:

$$\frac{\partial F}{\partial \xi} = 0 \qquad \xi = \xi_0, \tag{5.21'}$$

and from (5.21) we obtain:

$$\xi_0 = -\frac{c}{2b}\varepsilon. \tag{5.22}$$

Equation (5.21), by means of the substitution:

$$\xi - \xi_0 = \zeta(t) \tag{5.23}$$

and replacement of ξ_0 according to (5.22), can be represented in the following form:

$$F = F_0 + \left(a - \frac{c^2}{4b}\right)\varepsilon^2 + b\zeta^2. \tag{5.24}$$

From here, the stress can be represented as follows:

$$\sigma = \frac{\partial F}{\partial \varepsilon} = 2\left(a - \frac{c^2}{4b}\right)\varepsilon + 2b\zeta\frac{\partial \zeta}{\partial \varepsilon}. \tag{5.25}$$

Since, according to (5.23) and (5.22):

$$\frac{\partial \zeta}{\partial \varepsilon} = -\frac{\partial \xi_0}{\partial \varepsilon} = \frac{c}{2b}, \tag{5.26}$$

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the expression for the stress assumes the following appearance:

$$\sigma = 2\left(a - \frac{c^2}{4b}\right)\varepsilon + c\zeta. \tag{5.27}$$

The following relaxation law is adopted as an equation describing the reaction of the medium toward an external influence:

$$\dot{\xi} = -\frac{1}{\theta}(\xi - \xi_0) = -\frac{1}{\theta}\zeta, \tag{5.28}$$

with the aid of which, after replacement of ξ_0 according to (5.22), we get:

$$\zeta(t) = \frac{c}{2b}\int_{-\infty}^{t} e^{-\frac{t-t'}{\theta}}\dot{\varepsilon}(t')\,dt' \tag{5.29}$$

and after integration by parts:

$$\zeta(t) = \frac{c}{2b}\left\{\varepsilon(t) - \frac{1}{\theta}\int_{-\infty}^{t} e^{-\frac{t-t'}{\theta}}\varepsilon(t')\,dt'\right\}. \tag{5.30}$$

By substituting the found expression for $\zeta(t)$ into (5.27), we finally get:

$$\sigma(t) = 2a\varepsilon(t) - \frac{c^2}{2b\theta}\int_{-\infty}^{t} e^{-\frac{t-t'}{\theta}}\varepsilon(t')\,dt', \tag{5.31}$$

i.e., an equation for the theory of hereditary media in case of an exponential kernel. By comparing this expression with (5.6), and taking (5.8) into account, we get:

$$\left.\begin{aligned} \varkappa_\infty &= 2a = \left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_0, \\ \varkappa_0 &= 2a - \frac{c^2}{2b} = \left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_0 - \frac{\left(\frac{\partial^2 F}{\partial \varepsilon\,\partial \xi}\right)_0^2}{\left(\frac{\partial^2 F}{\partial \xi^2}\right)_0}. \end{aligned}\right\} \tag{5.32}$$

Thus all consequences resulting from the linear rheological equation (5.9) which in turn results from the theory of hereditary media in case of an exponential kernel, can be deduced (derived) by using as a base a relaxation mechanism for the establishment of a statistical equilibrium in the system, resulting in a relaxation of stresses.

The primary process consists in a disruption (violation) of the statistical equilibrium, which may arise in the formation of temperature nonuniformities, in the disruption of the equilibrium structure of the medium, in a disruption of the equilibrium energy distribution between internal and external degrees of freedom (as happens in the theory of sound absorption in gases, developed by Knezer), and in other similar processes.

4. Absorption of Energy in a Relaxing Medium

The process of energy absorption in a relaxing medium is marked by certain characteristic features, which differentiate it from analogous processes occurring in purely viscous media.

After rewriting the rheological equation (5.9) in the following form:

$$\sigma(t) = \varkappa_0\varepsilon(t) + \theta\varkappa_\infty\dot{\varepsilon}(t) - \theta\dot{\sigma}(t) \tag{5.33}$$

and multiplying it by $d\varepsilon(t) = \dot{\varepsilon}dt$, we will get the following, after integration:

$$\int_0^t \sigma(t)\,d\varepsilon(t) = \frac{1}{2}\varkappa_0\varepsilon^2 + \theta\varkappa_\infty\int_0^t \dot{\varepsilon}^2\,dt - \theta\int_0^t \dot{\sigma}(t)\,\dot{\varepsilon}(t)\,dt. \qquad (5.34)$$

The left side of this equation represents the work performed by external forces over the system. The first term of the right side expresses the energy increase of the elastic portion of the deformation, and the second term is the usual Rayleigh dissipation function, associated with pure viscous effects; the role of the viscosity factor (in case the latter is always considered to be the factor preceding the dissipation function) is performed by the following product:

$$\theta\varkappa_\infty = \eta_l. \qquad (5.35)$$

In regard to the third term, $\int_0^t \delta\dot{\varepsilon}dt$, it can be noted that its sign depends on the beginning of the time reading and the value of the interval t, since the stress does not follow immediately the deformation, and in case of a periodic change of ε in one portion of the period, the signs of $\dot{\varepsilon}$ and $\dot{\sigma}$ are identical, while in the other portion — they are different. This particular fact is clearly visible if $\varepsilon = a \cos qt$ is inserted into equation (5.34) (then, according to (5.14), $c = \mathcal{K} a \cos (qt + m)$), and a calculation of the integrals is performed. The energy dissipated during the period $\frac{2\pi}{q}$ is equal in this case to:

$$\theta\varkappa_\infty q a^2\pi - \pi\theta q a^2\mathcal{H}\cos m, \qquad (5.36)$$

and, since cos m > 0, this quantity is always smaller than the energy dissipated as a result of purely viscous effects (i.e., $\vartheta\varkappa_\infty q a^2\pi$). This phenomenon can be explained as being due to the fact that relaxation effects reduce the stresses arising in the medium, and can be considered as an illustration of the Le Chatelier-Braun principle. It is also obvious that it is precisely the phase shift between the stress and the deformation which is the cause for an elastic hysteresis, which manifests itself to a smaller or greater extent in all solid bodies.

By retaining:

$$\theta\varkappa_\infty\int_0^t \dot{\varepsilon}^2\,dt = D_t \qquad (5.37)$$

as the designation of a dissipation function, the expression:

$$-\theta\int_0^t \dot{\sigma}\dot{\varepsilon}\,dt = D_3 \tag{5.38}$$

can be called the relaxation function of absorption. It is obvious that, during the deforming of relaxation media, the work of external forces is equal to the sum of the elastic energy, the dissipation function and the relaxation function of absorption (it is assumed that the kinetic energy of the elements undergoing deformation can be disregarded).

5. Viscosity of a Liquid From the Standpoint of the Theory of Hereditary Media

By introducing into the rheological equation the viscosity, according to the relation (5.35), we will get:

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$$\sigma+\theta\dot{\sigma}=\eta\dot{\varepsilon}+\varkappa_0\varepsilon. \tag{5.39}$$

By limiting ourselves only to such deforming processes, for which:

$$|\theta\dot{\sigma}|\ll|\sigma|, \tag{5.40}$$

the latter relation can be written in the form:

$$\sigma=\eta\dot{\varepsilon}+\varkappa_0\varepsilon. \tag{5.41}$$

If, from the total stress, corresponding to a deformation of a given type, it is possible to separate the addend having the nature of a hydrostatic pressure, in such a way that:

$$\sigma=\sigma'+p, \tag{5.42}$$

where p is the hydrostatic pressure and σ' is the remaining part of the stress, then equation (5.41) can be represented in the form:

$$\sigma'+p=\eta\dot{\varepsilon}+\varkappa_0\varepsilon. \tag{5.43}$$

In case of an isothermic uniform manifold compression of the medium, the change in the pressure is entirely determined by the change in volume:

$$dp=\frac{\partial p}{\partial V}\,dV=-\frac{\partial p}{\partial V}\,V\left(-\frac{dV}{V}\right)=\varkappa_0\,d\varepsilon, \tag{5.44}$$

and if the modulus is independent of the deformation, then:

$$p = \varkappa_0 \varepsilon. \tag{5.45}$$

Consequently, in case of a uniform manifold compression, the rheological equation breaks down into two parts: an equation, connecting the viscous stress σ' with the deformation rate:

$$\sigma' = \eta \dot{\varepsilon}, \tag{5.46}$$

and an equation, connecting the hydrostatic pressure with the deformation (5.45).

Consequently, a viscous liquid is a medium which, in regard to deforming processes, fulfills the condition (5.40), and, in regard to properties, allows the isolation of an additive stress, corresponding to the hydrostatic pressure during bulk (volume) deformations, and which has a modulus of rigidity equal to zero during a slow deforming.

By separating manifold compression and shear deformations, dropping the accent in the viscous stress and adopting tensor designations, we will now get the following expressions instead of the former equations:

For the manifold compression deformation:

$$\sigma_{ee} = \eta' \dot{\varepsilon}_{ee}, \tag{5.47}$$

where η' is the bulk viscosity:

$$\eta' = k_\infty \vartheta', \tag{5.48}$$

in which ϑ' is the relaxation time during manifold compression, k_∞ is the modulus of manifold compression during instantaneous deformation.

For the shear deformation:

$$\sigma_{ik} = \eta \left(\dot{\varepsilon}_{ik} - \frac{1}{3} \dot{\varepsilon}_{ee} \delta_{ik} \right), \tag{5.49}$$

where η is the shear viscosity, δ_{ik} is the unit tensor.

$$\eta = G_\infty \vartheta, \tag{5.50}$$

where ϑ is the relaxation time during the shear, G_∞ is the modulus of rigidity during an instantaneous deformation.

For all known liquids, as long as there are no restoring forces in these liquids during slow shear deformations, there is no reason to consider that G_0 is different from zero. The modulus of elasticity of volume during an instantaneous deformation k_∞ always differs from zero, and in an extreme case has a minimum value equal to k_0. For this reason, the bulk viscosity factor becomes equal to zero in those cases when the relaxation time ϑ' is equal to zero and when the elastic state of the liquid during manifold compression is wholly determined by the modulus k_0, corresponding to a slow deformation.

This particular conclusion agrees with the opinion held by Stokes that the bulk viscosity is equal to zero in those cases when the pressure during a uniform manifold compression depends only on the value of the deformation and the temperature, but not on the rate of deformation.

On this basis, one can also understand the fact that the bulk viscosity of monoatomic gases is equal to zero, since in this case not one of the above-mentioned mechanisms of a relaxation process can take place. The disruption of the statistical equilibrium caused by the formation of temperature nonuniformities should not be taken into consideration, since in this case, as was shown by Kirchhoff, the absorption of energy is accounted for, not by means of the viscosity, but by the heat conduction of the medium. On the other hand, it is obvious that, for liquids having a structure of a short-range order (even monoatomic metallic liquids), η' must be different from zero. We believe that the measurement of the bulk viscosity of metallic liquids, for example, by the acoustic wind method (13), is one of the most important experimental problems in the field of the theory concerned with the liquid metallic state.

6. Certain Experimental Results

A study of the modulus of rigidity of liquids during rapid deformations is of great interest both for rheology and for the theory of the liquid state.

We shall now examine certain studies conducted in this field, without attempting to give a full description of this work and limiting ourselves only to an illustration of a number of concepts, dealing with the relationship between the hydrodynamics of a viscous liquid and the theory of hereditary media.

First of all, we shall examine in somewhat greater detail the properties of a continuous medium, in which $G_0 = 0$, and which, therefore, starting at certain rates of deformation, behaves like a viscous liquid. Let us assume that this medium is subjected to a periodic external influence with a frequency q. If the period of this influence, $\frac{2\pi}{q} = \tau$, is much smaller than the relaxation time of shear stresses, then, according to (5.19), the medium will behave as an elastic medium with a modulus G_∞. The condition (5.40), which, in case of a periodic external influence according to the law $\sigma = \sigma_0 e^{iqt}$ can be represented in the form:

$$q\vartheta \ll 1, \qquad (5.51)$$

of course, cannot be fulfilled in this case, since it directly contradicts (5.19). After determining G_∞, and having at our disposal the values of viscosity η, obtained for our medium during a slow flow, it is possible to determine the relaxation time of shear stresses ϑ by means of equation (5.50).

The values G_∞, η and ϑ, from the standpoint of the conception on which a linear rheological equation is based, are material constants.

During a reduction of q, after inequation (5.19) has been disturbed, the medium will retain its elasticity properties, but when:

$$G \approx G_\infty q \vartheta, \tag{5.52}$$

as follows from formula (5.15), when the action has a zero frequency, the medium will completely lose its shear elasticity. Somewhere during the course of this transition the condition (5.51) will begin to be fulfilled, and the medium will start behaving like a viscous liquid.

If the flow is stationary, then in any point of this flow, $\dot{\sigma} = 0$, and in this case the inequation (5.40) is satisfied identically, i.e., the stationary flow can be described by equations of a viscous liquid independently (regardless) of the value of the viscosity (of course, when $G_0 = 0$).

Let us examine now certain experimental results from the standpoint of the concepts described above. It has been established experimentally (14) that a number of thick liquids (such as paraffin, salol, hyposulfite, rosin, etc.) have a modulus of rigidity of $\approx 10^8$ in case of external action periods of ≈ 0.5 sec ($q \approx 10$). By using data applicable to rosin ($G_\infty = 1.45 \cdot 10^8$ and $\eta = 1.5 \cdot 10^{14}$ at a temperature of 30° C), the authors of the work mentioned above have found that the relaxation time of shear stresses in rosin is equal to $\approx 10^6$ sec. Thus, the product $\vartheta q \approx 10 \gg 1$, i.e., the modulus G_∞ was actually measured in this case. Apparently, the flow of the medium examined here can comply with Navier-Stokes equations only in case of very small deformation frequencies $q \approx 10^{-7}$ to 10^{-8}.

Of considerable interest is the work done by M. Kornfel'd (15) on the study of the temperature dependence of the modulus of rigidity of rosin at different frequencies ($\frac{1}{\tau} = 2.8 \cdot 10^3$, $1.3 \cdot 10^5$ and $2.9 \cdot 10^5$ cycles per second). These studies have shown that the modulus of rigidity in the above range is independent of the frequency and is approximately equal to $1.2 \cdot 10^{10}$ dynes/sq cm at 0° C, dropping with an increase in temperature to $0.2 \cdot 10^{10}$ dynes/sq cm at 60° C.

By using the data on the temperature dependence of the viscosity of rosin listed in M. Kornfel'd's monograph, we can calculate the relaxation time of shear stresses according to formula (5.50), assuming that in all cases the measured values of the modulus of rigidity are really equal to G_∞. The corresponding data are listed in Table 12, which should be considered as a characteristic of the order of the relaxation time of shear stresses of rosin in the temperature variation range of 56-68° C.

Table 12

Temperature °C	Viscosity, in poises	G dynes/sq cm	ϑ sec
56.5	$1.30 \cdot 10^6$	$0.6 \cdot 10^{10}$	$220 \cdot 10^{-6}$
58.5	$1.06 \cdot 10^6$	$0.4 \cdot 10^{10}$	$270 \cdot 10^{-6}$
61.0	$3.00 \cdot 10^5$	$0.3 \cdot 10^{10}$	$100 \cdot 10^{-6}$
64.0	$1.55 \cdot 10^5$	$0.2 \cdot 10^{10}$	$78 \cdot 10^{-6}$
68.5	$4.75 \cdot 10^4$	$0.1 \cdot 10^{10}$	$48 \cdot 10^{-6}$

The high value of the modulus of rigidity, which is close to the values characteristic for crystalline bodies, is worthy of attention. In regard to the discrepancy in the values of ϑ obtained (10^6 seconds at 30° C and 10^{-5} seconds at 68° C), the reason for this discrepancy is mainly due to the extremely great temperature dependence of the viscosity of rosin (16). By selecting the maximum frequency $\frac{1}{\tau} = 2.9 \cdot 10^5$ cycles per second ($q = 18 \cdot 10^5$) and the maximum relaxation time $\vartheta = 220 \cdot 10^{-6}$ seconds, we get $\vartheta q = 400$, i.e., G_∞ was measured in this case.

The situation is different in case the frequency of the external influence (action) $\frac{1}{\tau} = 2.8 \cdot 10^3$ cycles per second ($q = 18 \cdot 10^3$) at a temperature of about 70° C, when $\vartheta \approx 48 \cdot 10^{-6}$ sec. In this case, $\vartheta q \approx 0.13$, and the elastic properties of rosin are no longer characterized by the modulus G_∞, but, according to (5.52), by the modulus $G \approx G_\infty q \vartheta$, which, with the aid of (5.50), can be written in the following form:

$$G \approx \eta q \qquad \vartheta^2 q^2 \ll 1. \tag{5.53}$$

By substituting into (5.53), $\eta = 4.75 \cdot 10^4$ and $q = 18 \cdot 10^3$, we get $G \approx 0.85 \cdot 10^9$, as against the observed value $1 \cdot 10^9$ (see Table 12).

If we take into account that, for the two other frequencies used, the measured modulus is G_∞, the above examination of experimental data does not contradict the assumption that $G_0 = 0$ for rosin in the temperature interval studied. Consequently, we can assert that, at these temperatures, the stationary flow of rosin must be governed by Navier-Stokes equations. Moreover, it can be stated that the same equations will describe the flow of rosin at frequencies of $q < 10^4$.

In regard to metallic liquids, no measurement of the modulus of rigidity G_∞ was performed on these liquids. However, it is still possible to make a certain rough estimate in this case.

Condition (5.51), with the aid of (5.50), can be written in the form:

$$\eta \ll \frac{G_\infty}{q}, \tag{5.54}$$

and, by taking into consideration that $\eta \approx 10^{-2}$ poises represents a typical value for the viscosity of metallic liquids, we can note that the concept of viscosity will retain its meaning up to frequencies determined by the following inequation:

$$q \ll 10^2 G_\infty. \tag{5.55}$$

If the value $10^{10} - 10^{11}$ dynes/sq cm is adopted for the modulus of rigidity (obtained at low frequencies for metals in the crystalline state), then the concept of viscosity and the equations of hydrodynamics for metallic liquids must retain their meaning up to frequencies of the order of $10^{12} - 10^{13}$ cycles per second. The relaxation time of shear stresses will then have a value of the order of 10^{-13} sec.

Condition (5.40) can be considered to a certain extent as the limit of the applicability of hydrodynamic equations on the part of media having a high viscosity, regardless of the nature of this viscosity, which may depend on the heterophasic character of the medium. This factor is significant for our further study, which will be concerned with an examination of the results obtained during the measurement of the viscosity of alloys in the heterogeneous region of the fusion diagram.

The experimental study of the problems discussed here must greatly increase our knowledge and understanding of the nature of the liquid state.

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Chapter VI

Structure and Viscous Properties of Metallic Liquids

1. A. I. Bachinskiy's Viscosity Equation

In 1913, A. I. Bachinskiy (1) proposed his formula for the viscosity of simple (non-associated) liquids:

$$\eta = \frac{C}{v - b}; \tag{6.1}$$

where C and b are constant values, v is the specific volume.

F 88 Organic liquids, with the exception of alcohols and organic acids, are well described by means of formula (6.1). As M. P. Volarovich (2) has shown, the viscosity of certain salts also satisfies this equation.

We shall write Bachinskiy's formula as follows:

$$\nu = \frac{C}{1 - b\rho} \tag{6.2}$$

or, in a different form:

$$\frac{1}{\nu} = \frac{1}{C} - \frac{b}{C}\rho, \tag{6.3}$$

where ρ is the density.

Bachinskiy's formula is based on the assumption that the viscosity of a liquid is determined by the interaction of molecules. As the intermolecular distance increases, and consequently, as the forces of intermolecular interaction are reduced, the viscosity decreases. On the basis of an analysis of a large volume of experimental data, A. I. Bachinskiy assumed that the fluidity $\frac{1}{\eta}$ of a liquid is proportional to the difference v - b. The constant b, in the opinion of Bachinskiy, must be close to the natural (eigen) volume of the molecules, i.e., to the correction for the specific volume in the Van der Waals equation of state. A. I. Bachinskiy himself believed that $b = 0.307\ v_{cr}$, where v_{cr} is the critical volume, whereas the constant b, entering into the Van der Waals equation of state, is connected with the critical volume by the relation $b = 0.333\ v_{cr}$. Thus, the difference v - b is close to the free volume of the liquid.

The concepts held by A. I. Bachinskiy represented a new step in the development of the theory of the liquid state. They attracted the attention of researchers to the determining role played by the free volume in processes causing a viscous flow, and exerted a considerable influence on the development of theoretical concepts related to the viscosity mechanism. According to the concepts held by Bachinskiy, the temperature does not affect the viscosity directly, but rather through the effect of thermal expansion. Consequently, the formula of this effect must be considered as an approximate formula, since an increase in the temperature of the liquid increases the mean kinetic energy of the molecules and therefore must increase the mobility of these molecules.

A. I. Bachinskiy associates the value b with the critical volume, which constitutes an absolutely natural approach, if we start from the idea of the continuity of the liquid and gaseous state, inherent in Van der Waals equation. However, a different approach is possible, namely from the side of the solid state. In that case, it is possible to consider as a basic (starting) concept the fact that the fluidity of a crystal is vanishingly small, even in the vicinity of the melting point, in comparison to the fluidity of the liquid. By assuming that the fluidity is equal to zero when $v = v_s$, where v_s is the specific volume of the solid phase near the melting point, we get:

$$b \approx v_s, \qquad (6.4)$$

and, therefore, the constant b in Bachinskiy's formula can be interpreted as the specific volume of the solid phase at the melting point.

The fact that the viscosity of organic liquids does not comply with formula (6.1) is usually ascribed to their association. Indeed, almost all organic liquids exhibiting an abnormal behavior in regard to Bachinskiy's formula have a tendency to form a hydrogen linkage, discovered in 1877 by N. N. Beketov, and exhibit anomalies also in connection with a number of other properties.

These deviations from Bachinskiy's formula are of two different types: either the function $\frac{1}{v}(\rho)$ is expressed by a curve, whose convexity is directed toward the density axis, or by a curve whose concavity is directed toward the density axis. A deviation of the first type is exhibited by alcohols and organic acids, while a deviation of the second type is exhibited by water and fused metals. The first type will be designated as deviations of the alcohol type, and the second as deviations of the water type.

The action of the hydrogen linkage (bond) in the first group of liquids manifests itself in an actual aggregation of molecules. In regard to water, it can be stated that, according to x-ray diffraction analysis data and the structural theory of Bernal and Fowler (3), a hydrogen linkage (bond) in this case results in the formation of different structures of water. In the vicinity of the crystallization point, approximately up to 4° C, "water I" has the structure of ice-tridymite (a hexagonal silica). When the temperature is increased, "water II" is formed, having a quartz structure, which is retained almost up to the critical temperature. Further, in the vicinity of the critical region, the structure of water becomes tightly packed. With a change in the temperature, the structures are constantly (continuously) converted into each other, so that only on an average does the mutual arrangement of molecules come close to a smaller or greater extent to the structures mentioned above. On the basis of a comparison of x-ray diffraction analysis data with the degree to which experimental results on the viscosity of organic liquids and water comply with Bachinskiy's formula, we are led to the conclusion that deviations from this formula are associated to a certain extent with structural transformations in the liquid phase.

A. I. Bachinskiy and N. S. Kurnakov have stressed that the viscosity constitutes a structurally sensitive characteristic of a liquid. N. S. Kurnakov has selected the viscosity as one of the basic indices of physical-chemical analysis. For this reason, it can be expected that a study of the viscosity, as well as of other macroscopic properties, for example, heat conduction and electrical resistance, can yield valuable information on structural changes occurring in a liquid. It is known that the study of precisely macroscopic properties of solid alloys constitutes the principal method of studying the phase conversions taking place in these alloys.

2. Structure of a Liquid

The theory of the scattering of x-rays by a system consisting of atoms of one type leads to the equivalent expressions (4), (6.5) and (6.6), by means of which it is possible to get an idea of the structure of a monoatomic liquid on the basis of a study of the angular distribution of the intensity I(s) of scattered x-rays:

$$I(s)=N\psi^2\left\{1+4\pi\int_0^\infty r^2\,[m(r)-m_0]\,\frac{\sin sr}{sr}\,dr\right\}. \qquad (6.5)$$

From (6.5), by means of a Fourier transformation, the following relation can be obtained:

$$4\pi r^2 m(r)=4\pi r^2 m_0+\frac{2r}{\pi}\int_0^\infty s\left[\frac{I(s)}{N\psi^2}-1\right]\sin sr\cdot ds; \qquad (6.6)$$

where $s=\frac{4\pi}{\lambda}\sin\frac{\vartheta}{2}$, ϑ is the scattering angle, λ is the wavelength, N is the number of atoms in the scattering volume, ψ is an atomic factor, m(r) is the density of atomic distribution, selected in such a way that in a spherical layer r, r + Δr there are $\int_{r}^{r+\Delta r} 4\pi r^2 m(r)dr$ atoms present, $m(\infty) = m_0$. Formula (6.5) makes it possible to select such a function of the density m(r), which will yield a distribution of the intensity that agrees with the one obtained during a test. By using the second equation, one can obtain the intensities I(s) directly according to the distribution which has been found. Thus, both of these relations allow the determination of the density of atomic distribution m(r) for a monoatomic liquid.

In order to describe the arrangement of atoms, a function of atomic arrangement n(r) is introduced, which is selected in such a way that the expression $\int_{r}^{r+\Delta r} n(r)dr$ represents the number of atoms located in a spherical layer r, r + dr. From here, it is obvious that:

$$n(r) = 4\pi r^2 m(r). \tag{6.7}$$

In case of an ideal crystal lattice, the expression $\lim_{\Delta \to 0} \int_{r_i-\Delta}^{r_i+\Delta} n(r)dr = N_i$ gives the number of atoms lying on a sphere with a radius r_i, constructed near any arbitrary atom adopted as the center. From this standpoint, the crystal lattice can be characterized by means of a system of numbers N_i and r_i (i = 1, 2, 3, ...). The function of the atomic arrangement for the entire crystal lattice will be a discontinuous function, different from zero for a series of discrete values $r_1 < r_2 < r_3$ ..., and accordingly equal to N_1, N_2, N_3, ... If this is the case for any kind of values, then the arrangement of atoms represents an ideal crystal lattice. By designating the minimum distance between two atoms as r_1, the dependence between the coordination number N_i and the ratio $\frac{r_i}{r_i}$ can be calculated geometrically for each type of crystal lattice. For example, in case of a face-centered cubic lattice, we shall have: $\frac{r_i}{r_i} = 1; 1.41; 1.73,$ and accordingly $N_i = 12, 6, 24$ when $i = 1, 2, 3$.

The same results can be interpreted from the standpoint of the probability law. The probability that atom 1 is located in a fixed volume dv_1, while atom 2 is located in a volume dv_2, can be represented in the form: $W(r)dv_1dv_2$, where r is the mutual distance of volumes dv_1 and dv_2, and W(r) is the probability factor. Since the probability of the fact that atom 2 is located at a distance r from atom 1 is proportional to the average number of atoms in a unit volume, located at a distance r from atom 1, then, obviously, $m(r) = m_0W(r)$, where m_0 is the uniform density of a chaotic (random) distribution (in case of a completely random orientation of atoms $W = 1$). In reality, the atoms of a crystal are not stationary (motionless), but vibrate near equilibrium positions. For this reason, W(r), and consequently, also m(r) must be continuous functions of r with sharply expressed maxima (peaks) at values $r = r_i$ ($i = 1, 2, 3$, etc.). Values of r_i, at which $n(r_i)$ has a clearly marked maximum (peak), are apparently not limited by anything, except by the natural boundaries of a crystal.

Such a distribution (orientation), which can be naturally derived from an ideal crystal lattice when the thermal agitation of atoms is taken into account, will be designated by us as a structure of a long-range order. This definition of a long-range order structure reflects the presence of a correlation in the arrangement of atoms to infinity (5). However, it expresses a more rigid (strict) requirement from the standpoint of the order of the atomic arrangement. From a physical viewpoint, this definition of a long-range order structure makes it possible to effect a direct comparison of the spatial arrangement of liquid particles with the arrangement exhibited by these particles in the solid state and with an ideal crystal lattice.

The probability of the displacement of an atom from the equilibrium position, as a result of thermal motion, by a magnitude $\xi_i = r - r_i$, can be expressed by the formula:

$$dP_i = \left(\sqrt{2\pi\overline{\xi_i^2}}\right)^{-1} e^{-\frac{(r-r_i)^2}{2\overline{\xi_i^2}}} dr; \qquad (6.8)$$

in case of any value of i:

$$\overline{\xi_i^2} = \frac{kT}{f}, \qquad (6.9)$$

where f is the quasi-elastic linkage factor in the equation describing the oscillatory motion of the atom, and T is the absolute temperature.

The idea underlying considerations leading to the concept of a short-range order consists in applying the expression (6.8) to the case of a statistical **scattering** of atoms. In other words, it is necessary to find for ξ^2 an expression which depends on r.

By means of the method used in the theory of the Brownian motion, it is possible to establish a connection between ξ^2 and r for a statistical **scattering** having the following form:

$$\overline{\xi_i^2} = 2D'r_i. \qquad (6.10)$$

where D' is a constant known as the structural diffusion factor (see Note).

<u>Note</u>: Formula (6.10) can be derived in the following manner. Let us examine an atomic chain, in which the coordinates of the i-th atom in a state of ideal order (equal interatomic distances) are equal to r_i, while the actual coordinates are equal to r^i. By designating the atomic displacements as u_i, we will get, obviously:

$$r^i = r_i + u_i, \quad r^j = r_j + u_j, \quad r^{i-j} = r_{i-j} + u_{i-j}.$$

In case of an equal probability of positive and negative displacements, $\bar{u}_i = \bar{u}_j = 0$ (mean values are designated by a straight line on top of the symbols). In case of a statistical independence of displacements:

$$\overline{u_j u_i} = \bar{u}_j \bar{u}_i = 0 \qquad i \neq j.$$

By combining the first three equations, we find:

$$r^j + r^{i-j} - r^i = (r_j + r_{i-j}) - r_i + u_j + u_{i-j} - u_i.$$

However, since $r_i = r_j + r_{i-j}$, then $u_i = u_j + u_{i-j}$, and consequently, by squaring and taking the mean, we get:

$$\overline{u_i^2} = \overline{u_j^2} + \overline{u_{i-j}^2}. \qquad (*)$$

This is a functional equation of the form:

$$f(u_i) = f(u_j) + f(u_{i-j}),$$

the solution of which is a linear function of r:

$$f(u_i) = \overline{u_i^2} = 2D' r_i. \qquad (**)$$

By checking, one can easily see the identical nature of the relation:

$$2D'r_i = 2D'r_j + 2D'r_{i-j}.$$

Consequently, (**) represents the solution of equation (*) which was sought.

Therefore, in case of a maladjustment (disarrangement) of an ideal crystal lattice, due to a statistical **scattering** of atoms, r_i formally plays the same role as the temperature T during a derangement of the lattice caused by thermal motion, or as the time t in the phenomenon of the Brownian motion.

Expression (6.8), when (6.10) is substituted into this expression, has the meaning of the probability of the fact that an atom, which in an ideally ordered lattice must possess a coordinate r_i, possesses a coordinate r as a result of a statistical scattering. By multiplying (6.8) by N_i and summing up all i values, obviously, we shall find the function of the atomic arrangement of particles, in the presence of a statistical scattering having the following form:

$$n(r)dr = \sum_i N_i \left(\sqrt{4\pi D' r_i}\right)^{-1} e^{-\frac{(r-r_i)^2}{4D' r_i}} dr. \qquad (6.11)$$

Here, n(r) is a continuous function of r, but its essential feature consists in the fact that the n(r) maxima, corresponding to values $r = r_i$, become rapidly blurred (washed out) when i increases. Since any atom may act as the origin of the radius-vector r, then consequently, in the vicinity of any atom, the first coordination sphere will be clearly expressed (marked), the second one will be weaker, the third one will be still weaker, the fourth and following spheres may yield an equally probable arrangement of particles, i.e., a completely disorderly (random) arrangement. Such an arrangement of atoms is called a structure of a short-range order.

It should be noted that if only the first two n(r) maxima are clearly expressed, giving, for example, $\frac{N_1}{N_2} = 2$, this type of coordination is met both by a face-centered cubic structure as well as by a closely packed hexagonal structure. Already from here we can see that a knowledge of the short-range order is not always sufficient for determining the type of crystal structure, which is understandable, since the type of crystal structure is associated with the concept of long-range order.

The discussions presented above, which substantiate the concept of a short-range order and which belong to Prins (6), can still not be considered as a theory of the structure of a liquid, in view of the fact that the problem concerned with the applicability of a relation of the (6.10) type to a three-dimensional arrangement of particles still remains unclear. Ya. I. Frenkel' (7) criticizes Prins' conception and agrees with the fact that $\overline{\xi_i^2}$ is independent of r in a three-dimensional system. However, this problem requires additional research. Therefore the derivation of relationship (6.10) given here should be considered only as a model illustration of a certain type of arrangement of particles.

Figure 31 presents a typical experimental picture of the scattering of x-rays by a monoatomic liquid, obtained with fused aluminum at a temperature of 700° C. As is known from the theory, the zero intensity at small scattering angles and the oscillating dependence of the intensity on the parameter s indicate the presence of a certain order in the arrangement of particles. For purposes of comparison, the same figure shows a curve corresponding to a scattering from aluminum in the gaseous state (uniformly dropping line). It should be noted that, in case of large scattering angles, the intensity curve for liquid aluminum can be fully superimposed on the intensity curve for chaotically distributed atoms, and thus the arrangement of atoms in liquid aluminum exhibits both orderly and chaotic features.

Figure 32 shows the result of processing of the I(s) curve given in Figure 31 according to formula (6.6). In this figure, the discontinuous function of the atomic arrangement for the face-centered lattice of crystalline aluminum is represented by means of vertical lines. The factor (multiplier) $4\pi r^2 m_0$, where m_0 is the uniform density of the random distribution of particles, is represented by a curve of the parabolic type.

Thus, a comparison of the atomic arrangement functions for the same substance in the crystalline and liquid state shows the presence in the liquid of a coordination in the arrangement of atoms, similar to the one observed in a crystal. However, in a liquid, the orderly nature of the atomic arrangement is observed only in the vicinity of an arbitrarily selected atom and disappears upon moving away from this atom. The arrangement of atoms becomes disorderly (random) over a range of several interatomic distances.

From a local standpoint, the structure of a liquid is close to the structure of a crystal; however, at great distances, there is no correlation of individual quasi-crystalline regions in regard to their orientation. Regions, in regard to which one may speak about an orderly atomic arrangement in the liquid, cover an area equal to a score of angstroms. Consequently, experiments lead us to conclude about the presence in the liquid of a short-range order structure in the arrangement of particles.

From the standpoint of the probability law, the results of the study of the distribution of the intensity and position of diffraction maxima (peaks), and of x-rays scattered by the liquid, indicate the presence of a set of preferential distances between atom pairs. Whereas certain atomic distances are encountered most frequently, others may not be observed at all or may be equally probable, if they exceed a certain value.

For purposes of illustration, Figure 33 shows the curve of the probability factor:

$$W(r) = \frac{n(r)}{4\pi m_0 r^2}, \qquad (6.12)$$

obtained for the amorphous modification of arsenic As_1. The most probable interatomic distances are approximately equal to 2.5; 2.8; 5.5 Å. Distances of less than 2 and 3 Å are not encountered at all. $W(r) = 1$ corresponds to a uniform distribution of particles in a volume.

The studies conducted by G. V. Stuart and his associates, V. I. Danilov and his school, P. Debye, Tsernik and Prins, and Ya. I. Frenkel' represent a particularly valuable contribution to development work on the problem concerned with the structure of a liquid. In the work done by these authors, as well as in the studies performed by other researchers, one can find the necessary details on the experimental results dealing with the study of the structure of liquids and the physical interpretation of these results (8).

The experimental studies illustrated in Figures 31-33 may be due to a different mode of arrangement of particles in a macroscopic volume of the liquid. The question as to which type of arrangement is actually encountered in reality represents a basic problem of the theory of the structure of a liquid, which is still unsolved at the present time.

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We shall not present here again a description and critique of the various concepts dealing with the structure of a liquid, which have been expressed at different times, since it can be stated that the inadequacy of these concepts has already been established. For this reason, we believe that it is more expedient to attempt to present a new description of the structure of a liquid, based on experimental data, and to retain those elements of the concepts which have been previously evolved, which, in our opinion, appear to be correct. Such an attempt represents a statement of the problem.

Using the picture of the diffraction of x-rays as a basis, we can assume that a liquid contains ordered groups of scattering centers (atoms, molecules, ions), covering an area of several score of angstroms. However, such quasi-crystals cannot be considered as a continuous filling of crystalline lattice points. During the process of fusion (smelting), the volume of the vast majority of liquids increases by approximately 10%, and this increase corresponds to 100 unsubstituted (vacant) points in the crystal lattice of a cube with an edge length equal to 10 average interatomic distances. The presence of unsubstituted points must necessarily result in a statistical disarrangement of the atomic distribution (in relation to an ideal order of the crystal lattice), and consequently, will result in local decreases in the height of the potential barrier of interactions between particles. (Note: The above discussions on the structure of a liquid are also applicable to abnormal substances such as bismuth, which undergo a contraction during fusion. Although these substances are subject to a denser packing of atoms during the fusion process, as a result of a change in the structure type, the presence of unsubstituted points in this new lattice is just as necessary in abnormal substances as in normal liquids.) This factor in turn causes an increase in the probability of particles breaking away from equilibrium positions as a result of thermal fluctuations, as compared to the probability of a break-away, which is characteristic for the solid state. A particularly favorable environment for the formation of particles, which are not connected with any equilibrium position, is found at former boundaries of mosaic units (blocs) and on microfissures, and especially at the boundaries between individual crystalline grains present in the solid phase.

Thus, in accordance with the concepts being developed here, at any moment of time, all particles of a liquid can be divided into two groups. The first group includes particles performing oscillating movements in the vicinity of oscillation centers, coinciding with a statistically disturbed (deranged) structure of the crystal lattice (an arrangement which can be characterized by one distribution function, i.e., the structure of a quasi-crystal); the second group includes particles moving according to laws of random walks and which are not connected with any equilibrium positions (structure of a random arrangement).

For this reason, the picture of the thermal motion in a liquid includes simultaneously features of the thermal motion of a solid body (oscillations near equilibrium positions) and of a gas (random wanderings). Any particle may transfer from the first group into the second, and vice versa, so that the entire picture of the structure of a liquid represents the result of a dynamic equilibrium between particles of the first and second group. However, whereas in a crystal the duration of the coupling of a particle with a given center of oscillation is practically infinitely great, in a liquid, this duration has a value of the order of the oscillation period.

Let us now examine the problem concerned with the nature of the spatial arrangement (distribution) of particles of the first and second group. Let us assume that ε is the height of the potential barrier, which the particle must overcome in order to switch over from an oscillating state into a state of random wandering. The probability of such a transition is proportional to $e^{-\frac{\varepsilon}{kT}} d\varepsilon$, and therefore, the number of particles present in a state of random wandering will be proportional to $\int_{\varepsilon}^{\infty} e^{-\frac{\varepsilon}{kT}} d\varepsilon$, i.e., to the value of $e^{-\frac{\varepsilon}{kT}}$, while the number of particles remaining in a state of oscillations will obviously be proportional to the value of $(1 - e^{-\frac{\varepsilon}{kT}})$.

It is natural to assume that, immediately after fusion, areas of the liquid which are located far away from any interfaces present prior to fusion (boundaries of mosaic blocks, crystalline grains, microfissures) contain a relatively larger number of high potential barriers ε than areas corresponding to former interfaces. Therefore, we can introduce a value $\varepsilon = \varepsilon_0$, which is a mean value for a local microvolume of the liquid, and in that case, the number of particles which have broken away from the equilibrium position in this volume will obviously be proportional to $v_0 e^{-\frac{\varepsilon_0}{kT}}$, where ε_0 is a certain nonmonotonous function of the radius-vector r, which determines the position of the given microvolume v_0 in relation to an arbitrarily selected point in space.

The concentration of wandering particles, the maximum number of which are formed near former interface boundaries and in general near structural defects, shows a tendency to level off over the entire microvolume of the liquid by means of a self-diffusion mechanism. However, such a leveling off cannot take place until the effect exerted by former defects in the structure of the crystal will no longer be felt in the liquid, and until ε_0 will become a constant value no longer dependent on r.

Thus, during the initial post-smelting stage of existence of the liquid, the latter apparently consists of ordered quasi-crystals and
F individual particles present in a state of random wandering.

8 Quasi-crystals, as a possible form of structure in the region of
8 pre-crystallization temperatures, have no clearly expressed interfaces and therefore cannot be considered as a phase from a thermodynamic standpoint. The central region of a quasi-crystal exhibits a maximum order of atomic arrangement, which decreases toward the periphery. From the standpoint of a quantitative formulation of the concept of a short-range order (formula (6.10)), this means that, in the region of a quasi-crystal, the structural diffusion factor D'(r) must be an increasing function. The structure of a quasi-crystal is illustrated in Figure 34.

It is natural to assume that, in the course of time and with an increase in temperature, defects in the structure of the solid phase must be deprived of their determining role in the structure of a liquid. In this state, the liquid probably represents a continuous structure of a short-range order of the dense (compact) packing type, in which wandering (stray) particles are distributed, having an energy greater than ε_0.

Unfortunately, it is at present impossible to state which role the time and the temperature play in the process of transformation of ε_0 into a value independent of r. There is no doubt, however, that two processes can take place simultaneously when the temperature is increased: an increase in the number of particles present in a state of random wandering, and a change in the type of short-range order structure of quasi-crystals in the liquid.

In connection with the above statements, it appears reasonable to mention the recent tests conducted by Honig (9) on the mass-spectrometric analysis of vapors of metals belonging to the fourth group in the periodic system (germanium, tin, lead). It was found that vapors of these metals contain polyatomic ions. Thus, at a temperature of 1,300-1,700° C, molecular ions of germanium contain from 1 to 7 atoms per ion. At the same time, the results of the mass analysis are independent of the pressure within the limits of the variation of the latter, which takes place during tests (from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-4}$ mm Hg). This fact speaks in favor of the assumption that molecular ions are formed not in the vaporous phase, but rather during the course of evaporation, i.e., these ions are probably present in the liquid. It is possible that these ions are fragments of quasi-crystals.

Both individual atoms and complex molecules may act as the structural units of a liquid. Various researchers have observed the presence of polyatomic molecules in simple nonmetallic liquids (see the review article published by Gingrich, cited under reference 8 in the bibliography to this chapter), for example N_2, O_2, O_3, P_4, S_8 (open chains and rings). The existence of such molecules can be detected on the basis of the presence of isolated maxima (peaks) in the atomic arrangement function in case of minimum values of the interatomic distance r. It is known, for example, that the coordination number of phosphorus is equal to 6-8 at an average interatomic distance of about 3.9 Å, although the structural unit in this case is the P_4 molecule with an internal interatomic distance of 2.25 Å.

When the temperature is increased, not only can a change occur in the degree of the short-range order, which involves a decrease of this order, but also a change in the type of this order. The general tendencies observed in this field consist in the fact that a substance, having a close-packed structure in the solid state, retains a corresponding type of coordination also in the liquid state. A substance having a loosely packed structure, during fusion and in the course of further heating, undergoes a structural change and assumes a close-packed structure. A further increase in the temperature results in all cases, in view of an increase in the mean interatomic distance, in a loss of structural traces and in a transition of the liquid into a state of random distribution of particles and into a vapor state (10). This process takes place in the critical region. It is necessary to point out that the above-mentioned character of temperature changes in the structure of a condensed system during fusion and in the liquid state represents merely an expression of the most typical tendency prevailing in this case, and so far cannot be considered as a universal rule for temperature transformations of the structure in view of the insufficient amount of experimental data available in connection with this problem.

The concept stated above, namely that the closer the temperature of the liquid to the crystallization point, the greater the similarity between the structure of a liquid and the structure of a crystal, should not be understood in an excessively simplified manner. For example, the study of the structure of salol in the liquid state (11) has shown that, although there is an ordered arrangement of atoms in this liquid, this arrangement has an entirely different character from the one which is observed in the solid state. Such a difference in the type of structural order found in the liquid and solid phase is also observed (although to a lesser extent) in certain metals such as bismuth.

On the other hand, it has been established that in metals the character of the structure observed in the vicinity of the solidification point of the liquid phase may be retained when the liquid is overheated by 100-300° C above the melting point. When the temperature of the liquid is reduced, the effect of intermolecular forces becomes more and more apparent, and these forces are striving to aggregate the entire complex of molecules into a crystalline structure, characteristic for these particular forces at the given temperature. For this reason, there is a natural similarity between the structures of a liquid and a crystal near the solidification point.

These facts are important from the standpoint that they indicate the presence of a preparatory stage of crystallization and its influence on the mechanism of structure formation. In other words, the properties of a crystal are already present to a definite extent in the liquid phase. Therefore, the kinetics of crystallization must be studied in close relationship with phenomena taking place in the liquid, and in connection with the structure of the liquid in the pre-crystallization temperature range.

At elevated temperatures, when the energy of the thermal motion is high, the mean interatomic distance is large, the effect of intermolecular interaction forces is extremely small (minimal), and thermal motion predominates over intermolecular forces. For this reason, it becomes clear why the structure of a liquid strives toward a random distribution of particles.

The study of combination scattering in alcohols and water (12) in the critical region has shown the existence of a spectral band, typical for the liquid state, in scattered light at a temperature notably higher than the critical temperature, and vice versa, the presence of scattering lines typical for gases at a temperature lower than the critical temperature. When the temperature is increased near the critical region, the scattering bands become narrower, which indicates a continuous transformation of liquid into vapor. It is also known that, with an increase in temperature, a gradual destruction of the short-range order structure takes place in the critical region, which is retained to a certain extent in the vaporous state region. These facts, as well as others, definitely indicate the continuous nature of changes in the properties of the liquid in the critical region. As can be easily seen, this continuity also agrees well with the picture of the structure of a liquid outlined above. From the standpoint of this picture, a system of noninteracting molecules up to the critical temperature (scattering lines), and a system of interacting molecules above the critical temperature, represents a natural result of temperature changes in the structure of a liquid.

It should be noted that the critical "point" does not differ in any way from neighboring states, either in regard to the structure, or in regard to the combination scattering or the density. All three of these properties, with a change in the state of the system, pass through the critical "point" without any distinctive features.

In conclusion, it should be emphasized that insofar as the results of an x-ray study of liquids make it possible to establish unambiguously only the existence of a short-range order structure in a liquid, to the same extent, the picture of the structure of a liquid outlined above is a hypothetical one.

The question concerning the expediency of introducing this picture in the capacity of a working hypothesis can be answered in the affirmative in view of the fact that this picture makes it possible to clarify physically a number of facts which will be discussed below.

3. The Phenomenon of Crystallization of Liquids

As a result of the work done by V. I. Danilov and his associates (13), it has been shown that insoluble admixtures (impurities) exert a decisive influence on the kinetics of crystallization of liquids.

Certain liquids, for example, salol, would not crystallize at all in the absence of impurities. In contrast, ortho-chloronitrobenzene and metals crystallize after a most thorough purification and removal of impurities. According to this symptom, liquids can be subdivided into those which crystallize only as a result of the presence of impurities, and those which crystallize spontaneously.

As is known from thermodynamics, a solid phase nucleus with a mean radius a is in equilibrium with the surrounding liquid at an absolute temperature T, which is determined by the equality:

$$T = T_0 - \frac{2\sigma v T_0}{aQ}, \qquad (6.13)$$

where σ is the mean surface tension of the nucleus, v is the volume of the solid phase, calculated for one molecule, T_0 is the temperature of the phase equilibrium in case of a negligibly small value of the surface energy in comparison to the internal energy, Q is the latent melting heat, calculated per molecule.

The difference

$$T_0 - T = \theta \qquad (6.14)$$

represents the supercooling depth of the liquid. According to formula (6.13), it is obvious that, if at a given supercooling depth, a nucleus with a mean radius $a_1 < a$ is formed in a fluctuating manner, this nucleus can be present in a state of equilibrium only when the liquid is subjected to a deeper supercooling; consequently, in relation to the given temperature, the nucleus will be overheated and must again pass into the liquid state. If, at the same supercooling depth, the nucleus formed will have a mean radius of $a_2 > a$, then, in relation to the given temperature, this nucleus will be additionally supercooled and will grow.

It was noted above that a spontaneous crystallization was not observed in certain liquids. However, it is possible that the time intervals, during which observations were conducted, were too short to allow the spontaneous formation of nuclei of the required size, which would be capable of growing. We should recall that common glass is a supercooled liquid, present in a metastable state, but which is capable, after a long period of time, to switch over into a stable state, i.e., to crystallize.

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It is possible to assume that the reason for such a behavior of a liquid lies in the small size of individual quasi-crystals, the dimensions of which are not sufficiently large to allow the formation on their basis of a nucleus at a given supercooling rate. Then, after a sufficiently long, and possibly very long, time lag, as a result of fluctuations, a reorientation of adjacent quasi-crystals may take place, which will result in the formation of a large quasi-crystal, capable of acting as the initial onset of a crystallization center.

Such an approach eliminates the difference between crystallizing and non-crystallizing liquids, since the only difference between these two types of liquids consists in the average period of time required for the formation of a nucleus.

If the crystallization sets in and proceeds at a temperature T_0, then in this case all atoms must be combined in the form of quasi-crystals, which are converted, during the course of solidification, into solid phase crystals. Thus, from the standpoint of the picture of the structure of a liquid outlined above, the crystallization process consists in the conversion of a short-range order into a long-range order in each quasi-crystal.

In the narrow range of temperatures near the solidification point, the mode of arrangement of scattering centers in quasi-crystals is very similar to the one present in the solid phase of the given substance near the melting point, while the number of particles present in a state of random wandering is small in comparison to the number of particles combined in the form of quasi-crystals.

Regardless of the fact as to whether the onset of crystallization centers takes place on impurities or these centers arise spontaneously, there is a definite connection between the depth of supercooling and the rate of onset of crystallization centers w. The nature of this relationship is illustrated in Figure 35. This type of curve characterizes both the process of spontaneous crystallization as well as the crystallization on insoluble impurities.

In the case of salol, this complete curve can be obtained experimentally (14).

As was noted above, the crystallization of salol is based primarily on the presence of impurities, and in this case, the curve shown in Figure 35 also reflects the rules governing crystallization on impurities. In case of metals, the peak and the falling branch of the curve shown in Figure 35 cannot be obtained experimentally. In this case, a spontaneous crystallization certainly takes place, and the initial sector of the curve (in case of a slight supercooling) at least reflects the rules governing spontaneous crystallization.

From the standpoint of the concepts being developed here, the process of spontaneous crystallization takes place in such a way that, as the depth of supercooling is increased, an ever greater number of quasi-crystals per second are converted into crystallization nuclei. This process grows in intensity like an avalanche and is interrupted when the entire mass of the liquid solidifies. The linear velocity of crystal growth is expressed to a minimum degree, and as a result a finely dispersed metal structure is obtained. When the crystallization process proceeds in this manner, it is indispensable that the dimensions of the quasi-crystals should be so small that their number is very large; on the other hand, the dimensions of these crystals should be large enough so that each quasi-crystal may cause the onset of an independent crystallization center. If, on the other hand, a single crystal is obtained as a result of cooling, this indicates that the liquid contained crystals of an excessively large size near the crystallization point, so that the latter could not act as centers for the onset of nuclei, and only as a result of accidental reasons did one of these crystals act as a foundation for the formation of a nucleus of a new phase. During the further process of crystallization, the linear velocity of the growth of the nucleus plays a major role. This fact plays such a dominant role that the bulk of the metal crystallizes before the appearance of any other new nucleus.

4. Viscosity of Metals and A. I. Bachinskiy's Formula

A study of the viscosity of metallic liquids in connection with Bachinskiy's formula is of interest in view of the fact that metallic liquids have a simple structure in comparison with polyatomic organic liquids.

The extent to which metals comply with Bachinskiy's formula is illustrated in Figures 36 and 37. Figure 36 is derived from Figures 19 and 30 on the basis of our data, and Figure 37 is based on data obtained by other researchers, with the exception of the bismuth and lead curves, which were obtained during the study of the viscosity of a lead-bismuth alloy. The presence of water-type deviations from Bachinskiy's formula must be considered as a typical property of metals.

In case of many metals, deviations in the viscosity from Bachinskiy's formula are not expressed in a particularly striking degree. Among the metals listed in Figures 36 and 37, the greatest deviations are exhibited by gallium and mercury; however, in this case, one should keep in mind that the study of the viscosity of these metals covers a maximum wide range of temperature variations in view of the extremely low melting points of these metals (Hg: - 38.9° C, Ga: + 29.8° C).

According to their type of structure in the solid phase, the metals listed in Figures 36 and 37 can be classified as follows. Pb and Al have a highly close-packed face-centered cubic lattice with a coordination number of 12. K and Na have a body-centered cubic lattice with a coordination number of 8. Cd and Zn are characterized by a hexagonal loosely packed lattice with a coordination number of 6 + 6. A lattice, which, in the first approximation, represents a simple cube with a coordination number of 6 is characteristic for Bi and Sb. The tetragonal cell of Sn has a coordination number of 4 + 2 (two atoms are located at a somewhat greater distance than the other four atoms). Ga has a rhombic structure and its coordination number is expressed by the sum 1 + 1 + 1 + 1 + 1 + 1 + 1. Finally, the structure of Hg is related (similar) to a face-centered cube and has a coordination number of 6 + 6.

By examining Figures 36 and 37, it is possible to draw the conclusion that these metals can be arranged in approximately the same sequence if one attempts to arrange them in an order of growing deviations from Bachinskiy's formula. And the same sequence must be adopted if, after excluding mercury, the metals are arranged in order of decreasing compactness of atoms (packing density).

In case of all metals, the greatest deviations from Bachinskiy's formula are observed primarily in the narrow temperature range near the solidification point. These deviations are clearly observed in those cases when, during the course of the viscosity measurement, it was possible to come very close to the solidification point.

In addition, a slight bend (inflection) of the curves $\frac{1}{v}\left(\frac{\rho}{\rho_0}\right)$ is apparently typical for all metals. It should be noted that in most cases the character of this bend is such that points can be lined up rather easily even on straight lines. Straight lines are plotted in Figure 36, and this curvature is especially emphasized in Figure 37. It follows from the statements made above that Bachinskiy's formula for metals is an approximate formula, but at the same time this formula describes rather well the behavior of the viscosity, particularly if the temperature range in which the viscosity is studied is not too wide.

If we disregard the narrow pre-crystallization temperature region, we can see that the extent to which the viscosity complies with Bachinskiy's formula is determined mainly by the behavior of the curve $\frac{1}{v}(\rho)$ in the region of high temperatures (700° C and above). For example, in case of bismuth (Figure 19), the shape of the viscosity curve was found to be somewhat different in two tests with different samples. The bifurcation of the upper part of the bismuth curve shown in Figure 36 corresponds to this bifurcation of the viscosity curve, which is observed at 700° C. Whereas a linear dependence of $\frac{1}{v}$ on the density was obtained in one test, the second test can be described only by means of a clearly expressed curvilinear dependence of $\frac{1}{v}(\rho)$. The bismuth curve shown in Figure 37 also exhibits a concavity toward the abscissa axis as a result of a bend in the high-temperature region.

A comparison between the structure of liquids and the degree to which the viscosity of these liquids complies with Bachinskiy's formula is certainly of great interest. Unfortunately, in view of the insufficient experimental data available, we are forced to limit ourselves here to certain considerations which are qualitatively supported by experiments.

The close-packed structure of lead and aluminum is preserved in the liquid state. The structure of these metals, while undergoing a gradual destruction, probably remains unchanged over the entire temperature range in which their viscosity is studied.

Zinc, cadmium, potassium and sodium possess an almost close-packed structure (although of a different type), and even if changes in this structure do take place during the heating process, these changes are insignificant.

In regard to bismuth and tin, although their structure in the liquid state is far from being close-packed, nevertheless, according to the study conducted by V. I. Danilov and V. Ye. Neymark (15), it can be stated that this type of structure is retained during strong overheatings of about 100-300° C above the melting point, i.e., the structure of bismuth and tin remains unchanged in a rather wide range of temperature changes. Probably the same thing happens in the case of antimony since the structure of the latter in the solid state is identical with the structure of bismuth.

Mercury and gallium retain their type of structure over the entire temperature range in which their viscosity is studied. In any case, it is known in regard to mercury that the latter has a close-packed structure in the liquid state, except for an interval of several degrees near its solidification point, where its structure undergoes a change and assumes a structure corresponding to the solid phase (16). A similar phenomenon, apparently, is observed in the case of gallium.

Thus, if we limit ourselves to regions where metallic liquids are not subject to an excessive overheating, the viscosity of these liquids, provided there is no structural change in the liquid phase, complies sufficiently well with Bachinskiy's formula. The deviations which are observed occur in the pre-crystallization temperature range.

In this connection, it is interesting to note that deviations from Bachinskiy's formula are much more strongly expressed in water (Figure 36) than in metals. These deviations occur in a more narrow temperature range, in which a change corresponding to the type of structure of liquid water takes place, as was mentioned in # 1 in this chapter.

Consequently, it is possible to assume that deviations in the viscosity from Bachinskiy's formula are smaller when the structure of the liquid remains unchanged (constant), and greater when this structure undergoes a change. Specific deviations from Bachinskiy's formula near the solidification point, in this case, are not taken into account.

In addition to points taken from Figure 19, 3 points from Figure 21, obtained during the cooling of the metal, are also plotted on Figure 36 (tin). These 3 points fit well on the straight line drawn. A comparison of the results shown in Figure 21 with those shown in Figure 27 indicates that in this particular case we are dealing with the phenomenon of supercooling.

Thus, during the supercooling of tin, the rectilinear dependence of $\frac{1}{v}$ on ρ continues all the way up to the equilibrium crystallization point. This fact can be interpreted as a delay in the process involving the formation in the liquid phase of a short-range order structure according to a type corresponding to the crystalline state. In other words, the supercooling is determined by a delay in the preparation of the crystalline structure in the liquid phase, leading to the formation of a metastable state of the liquid.

The phenomenon of supercooling takes place with great difficulty in the case of lead, which in the solid phase has a close-packed structure. Possibly the reason for this lies in the fact that a short-range order structure, corresponding to the structure of a crystal, in this case is present in the liquid phase practically at any temperature. Consequently, the liquid always possesses structural elements capable of paving the way for the structure formation of a crystal, provided the temperature conditions are suitable for this purpose.

As was already pointed out above, Bachinskiy's formula accounts for the temperature dependence of the viscosity only by means of thermal expansion, and does not account for this dependence in an explicit form. If, on the other hand, this factor is taken into consideration in the form of an additional addend in the right side of equation (6.3), then, on the basis of physical considerations, it becomes clear that $\frac{1}{v}$ must necessarily increase in relation to the fluidity, which is due only to a thermal expansion. At the same time, the fluidity curves of metallic liquids in the high temperature region are actually deflected not upwards, but rather downwards, from a straight line corresponding to Bachinskiy's formula.

Further, it is obvious that the temperature dependence of the viscosity cannot also be accounted for by means of the factor b in Bachinskiy's formula. Indeed, if we assume that b depends on the temperature, then, since b is a quantity proportional to the intrinsic (eigen) volume of molecules, it can only decrease when the temperature increases (according to the decrease in the effective molecular diameter during heating), and this in turn results in higher values of the fluidity in relation to the straight line $\frac{1}{v}(\rho)$ in the high temperature region, which contradicts experimental data.

Thus, the temperature dependence of the viscosity cannot be explained in explicit form either in the form of an additional term in the fluidity expression (6.3), or by means of the temperature dependence of factor b. Consequently, only the modulus of viscosity C remains, which must increase with the temperature, in order that a change in viscosity may be properly expressed by means of a Bachinskiy-type equation.

Values of the constants found in Bachinskiy's formulas, according to Figure 36, are presented in Table 13.

Table 13

Metal	$C \cdot 10^6$, sq cm/sec	b, cu cm/g	$\frac{b}{C} \cdot 10^{-6}$	v'	v_s
Bismuth	95	0.095	1.04	0.100	0.102
Lead	99	0.091	0.92	0.094	0.091
Tin	125	0.136	1.09	0.143	0.137
Aluminum	545	0.364	0.67	0.407	0.392
Zinc	148	0.140	0.95	0.144	0.134
Cadmium	124	0.120	0.97	0.125	0.119

Here, C and b are constants in Bachinskiy's formula (6.1), v' and v_s are the specific volumes of the liquid and solid phase at the melting point, respectively. If we disregard bismuth, which exhibits an abnormal volume change during fusion, we find that, for the remaining metals, the value of b is close to that of v_s.

It can be stated that, to the extent to which Bachinskiy's formula is in general suitable for describing the viscosity of liquids, b is a constant quantity and coincides with the value of the specific volume of the solid phase at the melting point.

The rectilinear dependences of $\frac{1}{V}(\rho)$, shown in Figure 36, are preserved when using data on the density of metals obtained by various authors (naturally, in case of slightly different C and b values). This fact served as a basis for the expression of definite statements concerned with the possible use of Bachinskiy's formula for metallic systems, without measuring the density of these systems. It is difficult to check Bachinskiy's formula for metal alloys in view of the lack of density data, corresponding to the required concentrations of the tested alloys. However methods are known by means of which it is possible to overcome the difficulty arising at this point.

For alloys, the densities of which are known, it is possible to obtain values of $\rho(t)$, corresponding to the necessary interpolation concentrations. This method has been used on bismuth-tin systems. In case the viscosity-composition isotherms do not clearly point out the existence of a chemical compound, the additivity rule may be used to determine the density of alloys. This method has been used in connection with the tin-lead system. Finally, it is known that the density of metals and metal alloys linearly depends, with a high degree of accuracy, on the temperature, within a wide range of temperature variations. For this reason, $\frac{1}{V}$ for metal alloys, according to Bachinskiy's formula, must be a linear function of the temperature. This method has been used for lead-bismuth alloys.

The results of a corresponding processing of the data shown in Figures 25, 22 and 29 are presented in Figures 38, 39 and 40. An examination of these figures allows us to conclude that the alloys studied yield deviations from Bachinskiy's formula of the water type. For different alloys, these deviations are expressed in a different degree.

According to V. I. Danilov and I. V. Radchenko (17), who performed an x-ray diffraction study of the structure of Pb-Bi, Sn-Bi, Sn-Pb and Sn-Zn alloys in eutectic concentration, these alloys in a liquid state consist of individual regions, the structure of which is closely related to the structure of pure components. A complete molecular mixing was not observed in the above studied alloys, and individual regions exhibit a predominant concentration of one or another component, i.e., the alloy constitutes a system similar to a solid eutectic. This conclusion on the structure of liquid alloys was confirmed on the basis of the eutectic alloy lead-bismuth in a study conducted by A. I. Danilova and V. I. Danilov (18).

The absence of a molecular uniformity in the structure of liquid mixtures is observed not only in metallic systems. For example, the systems acetone-water and nicotine-water also exhibit a nonuniform molecular structure (19). The above statements concerning the structure of binary systems refer to such systems, in which, according to other data, chemical compounds in the liquid phase are absent.

An entirely different structure is observed in binary systems which are capable of forming an intermetallic compound, for example Tl_2Hg_5. In this case, the diffraction picture obtained from liquid Tl_2Hg_5 differs sharply from the diffraction pictures formed by thallium and mercury in the liquid state.

As in the case of pure metals, deviations of the water type from Bachinskiy's formula, established for metallic alloys, are associated by us with the phenomenon involving an alignment of the atomic arrangement with the crystalline structure of the solid phase.

From the standpoint of the concepts developed here, deviations from Bachinskiy's formula must be greater in alloys, which do not contain a component having a close-packed structure, than in an alloy, one or both components of which have a close-packed structure. In structures which are close-packed in the solid state, the process involving an alignment of atomic arrangement extends over a narrower temperature range than in the case of loosely packed structures. In temperature regions with a constant type of short-range order in the liquid, the viscosity complies with Bachinskiy's formula. Therefore, the following arrangement of the studied alloys according to the degree of increasing deviations from Bachinskiy's formula can be expected: lead-tin, lead-bismuth, bismuth-tin. An examination of Figures 38, 39 and 40 shows that experiments do not contradict such a sequence.

V. A. Konstantinov (20), while measuring the viscosity of eutectic alloys Sn-Zn and Sn-Bi near the crystallization point by the oscillating ball method, noted that when the alloy is held at a temperature several degrees higher than the liquidus, crystallization may take place on the steel surface of the ball.

The reason for the phenomenon noted above may consist in the fact that a heat removal (cooling) from the liquid metal was taking place through the ball and the rod connected with this ball, and therefore the surface of the ball assumed the crystallization temperature before this temperature was established in the entire volume of the liquid. In addition, it can be assumed that the author was confronted with the phenomenon of settling of quasi-crystals on inhomogeneities at temperatures somewhat higher than the crystallization temperature. Under these conditions, the quasi-crystals, being close to crystals in regard to the strength of their interatomic linkages, exert a noticeable effect on the torsional oscillations of the ball, and, naturally, are immediately converted into solid crystals as soon as the ball is taken out of the liquid.

As a rule, a discrepancy is noted in viscosity measurements of the same metals near the solidification point (see Figure 21). If, in the tests performed by V. A. Konstantinov, a settling of quasi-crystals actually takes place on inhomogeneities (wall of the ball), then discrepancies of the type shown in Figure 21 can naturally be explained as being due to a different influence of quasi-crystals during different tests.

5. Mechanism of the Viscous Flow of Liquids

The presently known theories of the viscous properties of liquids lead to a number of interesting results. The monographs published by Ya. N. Frenkel', Green, Eyring, and co-authors, G. M. Panchenkov, and the studies of Andrade may serve as a good illustration of the progress achieved in this field (21).

We are not concerned with a critical discussion and examination of the existing concepts on the viscosity of liquids (Note: A review of the theories of the viscosity of liquids is presented in Panchenkov's monograph, cited under reference 21 in the bibliography of this chapter). Such a task would lead us too far away from our main topic and in general hardly appears to be advisable. Indeed, the principal defects of the existing theories on the viscosity of liquids are sufficiently clear, and none of these theories contain any kind of fine elements which are hard to detect. Therefore, we shall limit ourselves to a very brief description of the physical picture of the mechanism of viscous flow, which lies at the base of certain viscosity theories of interest to us in connection with the picture of the structure of a liquid outlined above.

Let us start our examination by considering the concepts which lead to an exponential formula showing the dependence of the viscosity on $\frac{1}{T}$, where T is the absolute temperature. A model of a liquid is based on the concept of a quasi-crystalline structure, exhibiting a derangement in the order of its atomic arrangement. This derangement of the atomic arrangement (in relation to an ideal crystal lattice) results in the fact that, for certain atoms, the potential barrier of the energy of interaction with the closest neighboring atoms is reduced. As a result, by applying a small tangential force, it is possible to effect a transition of an atom from one equilibrium position into a neighboring position, and, as a resulting effect, to effect the movement of one layer of the liquid in relation to another, i.e., to create a viscous flow. Therefore, the assumption concerning the appearance of vacant spots in a disrupted crystal lattice of the liquid plays a basic role in this particular scheme of a viscous flow. This assumption is based on data obtained during the x-ray analysis of the structure of liquids, and also on the determining role of a free volume in phenomena involving the presence of a viscous flow.

Such is the mechanism of a viscous flow, sketched in the most general and schematic features, which leads to an exponential dependence of the viscosity on $\frac{1}{T}$.

The most strict application of this conception is found in the works of Eyring and his associates, although it was first formulated by Ya. I. Frenkel'. According to these concepts, the viscous properties of a liquid are intimately associated with the statistical theory of absolute velocities of chemical reactions. According to Eyring (21), the free energy of activation of a viscous flow, calculated per mole of liquid, F_{vis}, can be expressed by means of the following relation:

$$F_{vis} = RT \ln \frac{\mu\nu}{hN} = RT \ln \frac{V\eta}{hN}. \tag{6.15}$$

where μ is the molecular weight of the liquid, ν is the kinematic viscosity of this liquid, N is the Avogadro number, h is Planck's constant, V is the molecular volume, η is the dynamic viscosity, and R is the gas constant.

Expression (6.15) obviously is a somewhat different form of recording the well-known exponential expression for the viscosity

Note: From (6.15), with the aid of (6.17), the following formula can be obtained:

$$\eta = \left(\frac{h\nu}{V} e^{-\frac{S}{R}}\right) e^{\frac{E_{vis}}{RT}}$$

The temperature dependence of F_{vis} for metallic liquids (assumed to be monoatomic liquids) is illustrated in Figures 41, 42 and 43. From these figures it can be seen that F_{vis} is an increasing linear function of the temperature (steel 1010 represents an exception), with a certain disturbance in the linearity near the crystallization point in the case of bismuth, lead and tin, approximately in the same region where a deviation from Bachinskiy's formula is observed.

The consequence resulting from experiments:

$$F_{vis} = A + BT, \tag{6.16}$$

where A and B are positive constants, when compared with the thermodynamic formula:

$$F_{vis} = E_{vis} - TS_{vis} \tag{6.17}$$

leads to the following relations:

$$\left.\begin{aligned} E_{vis} &= A = \text{const}, \\ S_{vis} &= -B = \text{const}. \end{aligned}\right\} \tag{6.18}$$

Consequently, the change in the entropy, when an atom participates in the viscous flow process, does not depend on the temperature and is a negative change. In other words, the entropy of an activated atom is smaller than the entropy of an atom present in the original state of stable equilibrium.

Over 100 nonmetallic liquids have approximately the same ratio between the evaporation energy E_{ev} and the free energy of viscous flow F_{vis}:

$$\frac{E_{ev}}{F_{vis}} \approx 2{,}45. \tag{6.19}$$

F 88 In addition, the following inequation applies to these liquids:

$$3 < \frac{E_{ev}}{E_{vis}} < 4. \tag{6.20}$$

In the case of metallic liquids, the last ratio lies predominantly in the range of 10-30. If, in the case of metals, we take the following function:

$$\frac{E_{ev}}{E_{vis}} \left(\frac{r_{ion}}{r_{atom}}\right)^{3},$$

where r_{ion} and r_{atom} stand for the ionic and atomic radius of the given element, respectively, then the value of this function will be close to 3 or 4.

From here, Eyring concludes that an ion, freed of its valence electrons, acts as the individual structural particle which takes part in the viscous flow process in metals. A neutral atom acts as a similar particle in the evaporation process.

As far as it is possible to judge on the basis of the available experimental data, there is no correlation whatsoever between F_{vis} and other physical characteristics (atomic and ionic radii, valence, atomic numbers, etc.).

Table 14 gives the values of the energy E_{vis} and of the entropy S_{vis}, calculated from the rectilinear dependencies shown in Figures 41-43.

As Ya. I. Frenkel' has shown even earlier, the exponential formula of the (6.15) type can be derived with the aid of the rheological concepts presented in Chapter V.

According to these concepts, the viscosity is expressed by the formula: $\eta = G_{\infty}\vartheta$. The condition $|\vartheta\sigma| \ll |c|$ indicates that the medium under study is a liquid which complies with Newton's internal friction law. Thus, in order to obtain a formula which will express the viscosity, it is necessary to find the expression for the relaxation time.

Table 14

Metal	E_{ev} cal/mole	E_{vis} cal/mole	$\frac{E_{ev}}{E_{vis}}$	S_{vis} cal/mole • degree
Tin	86,000	1,280	65	- 6.2
Bismuth	39,000	1,800	22	- 6.0
Lead	45,000	2,240	20	- 6.4
Aluminum	59,000	2,010	29	- 5.0
Zinc	30,000	2,550	12	- 4.6
Cadmium	26,000	2,550	10	- 4.6
Iron	72,000	--	--	--
Steel, grade 1045	--	9,700	--	- 4.0
" " EKh12	--	6,300	--	- 5.1
" " ShKh12	--	7,600	--	- 4.8
" " EYa2S	--	13,800	--	- 1.1
" " 1010	--	--	--	--
" " EKhTM	--	10,800	--	- 3.3
" " EU10	--	14,000	--	- 1.3

Ya. I. Frenkel' assumes that the relaxation time can be identified with the time during which an atom in the liquid is connected with a given constant equilibrium position. In that case, the probability that an arbitrary atom will overcome the potential barrier during a definite time interval will, obviously, be proportional to the value of $e^{-\frac{E_{vis}}{RT}}$. It is obvious, further, that the time during which the atom will remain in the vicinity of the given equilibrium position is inversely proportional to the probability of the transition of this atom into a new equilibrium position; consequently, by taking into account the assumption made by Ya. I. Frenkel', we can write:

$$\eta = \theta_0 O_\infty e^{\frac{E_{vis}}{RT}}. \tag{6.21}$$

By rewriting (6.15) with the aid of (6.17) and comparing it with (6.21), we get:

$$\frac{hN}{V} e^{-\frac{S_{vis}}{R}} = \theta_0 O_\infty. \tag{6.22}$$

By making use of somewhat different viscous flow mechanisms, Andrade and G. M. Panchenkov have obtained results on the temperature dependence of the viscosity of liquids, which are of a similar nature (content).

Andrade (21) bases his analysis of the process of viscous flow of a liquid on the concept of a structural affinity between a liquid and a solid body, which manifests itself in that the molecules of a liquid at rest, on an average, oscillate for quite a long time near their equilibrium positions. The extremely small value of the self-diffusion factor in a liquid confirms this assumption.

During the course of the relative movement of liquid layers, the exchange in quantity of motion (momentum), which causes the appearance of viscosity forces, takes place during the collision of molecules in different layers with a duration of the collision event differing from zero. By taking into account the effect of thermal expansion, and adopting Van derWaals' expression for the energy of intermolecular attraction forces, Andrade arrives at the formula:

$$\eta = A \cdot \rho^{1/3} e^{-\frac{B\rho}{T}}, \tag{6.23}$$

where A and B are constants. This formula describes well the change in viscosity with the temperature for many liquids, including fused metals.

G. M. Panchenkov (21) starts from the concept, according to which the process of internal friction of liquids is caused by the temporary combination of two moving molecules, as a result of the formation of a short-lived bond (linkage) between these molecules. According to the author of this theory, the nature of this phenomenon lies in the fact that, in the presence of a short-range order, there exists a certain average distance between molecules in the liquid, similar to the equilibrium distance between atoms in a crystal. Then, in case of a relative motion of these molecules, if the distance between these molecules is smaller than the equilibrium distance, the molecules repel each other and the formation of a bond (linkage) is impossible, and consequently, an exchange in quantity of motion (momentum) is also impossible. If, on the other hand, the distance becomes greater than the critical distance, an attractive force arises and a bond (linkage) is formed, and consequently, an exchange in quantity of motion takes place. As a final result, G. M. Panchenkov obtains a formula for the viscosity, which is close (related) to the exponential type and which contains, as constants, the value of the entropy change during the formation of the bond and the binding energy. In case of an appropriate selection of these values, the formula agrees well with experimental results for a considerable number of liquids.

A trend which differs considerably from the one outlined above, is developed in a theory of condensed media by A. S. Predvoditelev (22), who combines molecular and phenomenological concepts in his research on the kinetic properties of liquids.

According to A. S. Predvoditelev, thermal motion in a liquid assumes a dual form. First, it involves accidental (random) wanderings of atoms (molecules). The state of each atom is characterized by a set of three geometrical coordinates and the conjunction of these states forms a Markov chain. Second, thermal motion in a liquid includes oscillations of atoms (molecules) near the changing positions of temporary equilibrium. Such oscillations can be considered as a superposition of elastic waves of the Debye type.

Random wanderings are described by Fokker-Planck equations, and oscillations are described by equations of elastic oscillations in an isotropic medium.

Differential equations, describing macroscopic processes, such as, for example, the flow of a viscous liquid or heat conductance, are extrapolated "up to such space-time variations, which can be considered as elements determining the macroscopic properties of a substance" (23). By making use of certain additional assumptions, A. S. Predvoditelev obtains the following formula:

$$\nu = \frac{\gamma k}{\varepsilon (1 - \rho b)}, \qquad (6.24)$$

where γ is the specific heat ratio $\frac{c_p}{c_v}$, k is the thermal diffusivity of the liquid, ε is a certain factor, determined by the nature of interatomic forces, b is a constant value, and ρ is the density.

It can be easily seen that the above expression is similar to Bachinskiy's formula, and that it differs from this formula in that the modulus of viscosity:

$$C = \frac{\gamma k}{\varepsilon} \qquad (6.25)$$

depends in this case on the temperature, since k depends on the temperature. Formula (6.24) is justified for a large number of liquids with complex molecules. This formula will correctly describe experimental results, provided that:

$$\frac{\partial}{\partial p}\left(\frac{1}{v}\right) = -\frac{bp}{kT} \qquad (6.26)$$

drops with the temperature. However, the volume of data available so far is insufficient to allow a further analysis of this problem. A. S. Predvoditelev considers that equation (6.24) can be used all the way up to the critical state of the liquid, as a result of which it seems possible to find the values of indeterminate constants ε and b by switching over to a "degenerated" state of matter, whereby the gaseous or critical state can be adopted as such a "degenerated" state.

While considering the thermal motion in a liquid as a superposition of Debye waves, M. F. Shirokov (24) assumed that the absorption of these waves by a moving plane layer of the liquid causes the appearance of a dissipation force, directed against the movement. The viscosity expression obtained by this author depends upon the maximum Debye frequency. In order to exclude this frequency from the final result, M. F. Shirokov derives a formula for the heat conductance factor λ of the liquid and obtains the following expression:

$$\frac{\eta}{\lambda} = \frac{T}{a^2}, \qquad (6.27)$$

where a is the sound velocity in the liquid at the temperature T. A comparison of this formula with certain experimental data shows that it yields a result which, on the average, is higher by one order. However, the work of M. F. Shirokov is of definite interest, since he is able to obtain an equation which does not contain any empirical constants.

In a previously published work (25), M. F. Shirokov has attempted to derive Bachinskiy's formula on the basis of a concept involving the same mechanism of internal friction as the one which occurs in gases, but using Van der Waals' corrections during the derivation of corresponding formulas.

In summing up to a certain extent the theoretical structures examined above, we are forced to conclude that none of them can be considered as a theory of viscosity, which draws its conclusions from a clearly formulated mechanism of viscous flow with the aid of a small number of physically clear hypotheses.

6. Viscosity -- Composition Isotherms of Binary Alloys

The information available on the structure of tin-lead and bismuth-tin alloys indicates the absence in these alloys of intermetallic compounds in the solid phase (26). However, an examination of the viscosity-composition isotherms illustrated in Figures 23 and 26 forces us to consider this statement with a certain amount of caution.

As N. S. Kurnakov has established, and as A. I. Bachinskiy has also frequently pointed out, the viscosity is a structurally sensitive characteristic of a liquid. According to opinions forming a part of the basic ideas of physical-chemical analysis, developed by N. S. Kurnakov, if special points are observed on composition-property isotherms, this fact indicates the presence of structural transformations in the system.

Consequently, the presence of special points on viscosity-composition isotherms must indicate the presence in the system of intermolecular interactions having a chemical nature.

When an intermetallic compound is present in the liquid phase, x-ray photographs indicate the presence of an individual structure of such a compound. If no intermetallic compound is present in a binary system, then the x-ray photograph is a simple superposition of the x-ray pictures of the components (taking into account the percentage composition of the alloy).

As was noted above (17, 18), a complete molecular displacement is not observed, according to data obtained in an x-ray diffraction study, in lead-tin and bismuth-tin alloys, and the system represents a mixture of regions with a predominant concentration of one of the two components. Thus, data on the structure of lead-tin and bismuth-tin alloys indicate the absence in these alloys of intermetallic compounds, both in the solid and liquid state. Nevertheless, we have to admit the presence of certain peculiar features in the viscosity-composition diagrams.

The lead-tin and bismuth-tin binary systems belong to the group of alloys of the eutectic type with a limited solubility of their components. In Figure 23, which refers to a lead-tin alloy, the eutectic concentration of which is equal to 64% (by weight) of tin, at a concentration of 60% tin, a weakly expressed special point of such a type is observed, which must arise during the formation of a chemical compound. A reduction to an atomic concentration shows that this may be a compound of an intermetallic type Pb_2Sn_5.

Similarly, an examination of Figure 26 makes it possible to assume the presence in the liquid phase of compounds of an intermetallic type Si_3Sn_{10}, and possibly, Bi_5Sn at low temperatures, and in addition, of $BiSn_3$ and BiSn, which are preserved even at high temperatures. The eutectic concentration of this alloy is equal to 42% (by weight) of tin.

The peculiar features of the viscosity isotherms, observed on Figures 23 and 26, are expressed rather weakly, and it would seem that the most simple way of explaining these features would be to consider them as the result of experimental inaccuracies. Indeed, the study of a lead-tin system was conducted in different types of crucibles, and therefore the constants of the oscillating system with alloys of various concentrations were different. It can be assumed that the somewhat higher viscosity values of the alloy near the eutectic concentration were obtained as a result of an error introduced during the determination of the constant of the oscillating system for this alloy. However, such considerations are quite unsuitable as an explanation of the curves shown in Figure 26, in view of the fact that the tin-bismuth alloy was studied with the aid of a constant oscillating system in such a way that an error in the determination of the constant of the instrument could not affect the nature of the isotherms.

Similar isotherms were observed by Sauerwald and Bienias (27) in copper-antimony and copper-tin alloys, for which, as a result of x-ray diffraction studies, the intermetallic compounds Cu_3Sb, Cu_2Sb, Cu_6Sn, Cu_3Sn, Cu_6Sn_5 and $Cu_{31}Sn_8$ were established in the solid state, and the character of viscosity-composition isotherms confirms the presence of some of these compounds in the liquid phase. Alloys of copper-antimony and copper-tin systems possess complex equilibrium diagrams in the presence of intermediate phases in the solid state. For this reason, the peculiar features observed on viscosity-composition isotherms appear to be natural, and the existence of certain intermetallic compounds in the liquid phase also appears probable.

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Gekhbardt and Bekker (29) have recently studied the viscosity of alloys of the gold-silver system by the torsional oscillation method, using relative measurements. The instrument built by these authors duplicates to a considerable extent the unit based on the use of a Tamman furnace described above. The suspension system was first calibrated with the aid of three liquids (mercury, tin and zinc) (Note: It should be noted that the method involving torsional oscillations of a small bucket has recently found an extensive application for the purpose of measuring the viscosity of fused metals. See, for example, M. R. Hopkins and T. S. Toy, Proc. Phys. Soc., B 63, No. 370, 1950 (viscosity of zinc); A. I. Blum and A. R. Regel', Zhurnal tekhnicheskoy fiziki (Journal of Technical Physics), Vol. 23, No. 6, 1953 (viscosity and electric conductivity of a selenium-tellurium alloy).).

Alloys of the gold-silver system exhibit an unlimited solubility of their components in the solid state without any kind of intermediate phases. No peculiar features of any kind are observed on viscosity isotherms, which would indicate the presence of intermetallic compounds in the liquid state. Results of research work agree well with Andrade's formula, expressing the viscosity at the melting point:

$$\eta_s = 5{,}1 \cdot 10^{-4} A^{1/2} T_s^{1/2} V_A^{-2/3}, \qquad (6.28)$$

where A is the atomic weight, T_s is the absolute melting point, V is the atomic volume. Pure gold and silver and their alloys comply with the formula expressing the exponential dependence of the viscosity on the temperature.

After comparing all the data presented above, we must come to the conclusion that products of the Pb_2Sn_5 type and similar products, possessing a bond (linkage) strength characteristic for true intermetallic compounds, are not present in tin-lead and tin-bismuth alloys. At the same time, however, the possible existence of atomic complexes is not excluded, resulting from collective interactions and having an atomic concentration expressed by the formula Pb_2Sn_5, whereby these compounds are much less stable than intermetallic compounds. Such complexes, the dissociation heat of which is small in comparison to the heat required for the dissociation of molecules into the component atoms, will still be sufficiently stable in order to act as independent units in viscous flow phenomena, during the course of which tangential forces are immeasurably smaller than the forces necessary for the destruction of a chemical compound. Quasi-crystals with a predominant concentration of one or another component may represent such compounds or complexes.

The second possible explanation of the character of the viscosity isotherms which is observed consists in the assumption of the existence of certain processes in alloys, which result in a change of the viscous properties depending upon the previous history of the sample. Such phenomena of a rheological nature may take place as a result of the presence (in the metallic liquid) of insoluble impurities, and also as a result of structural characteristics of the liquid (Note: This problem deserves the most serious attention and study).

7. Viscosity of Heterogenous Systems and Sound Absorption in Such Systems

As was already pointed out in Chapter V, the concept of shear viscosity is introduced into rheology as the product of the instantaneous modulus of rigidity and the relaxation time (formulas 5.35 and 5.50). Such a definition of the viscosity coincides with Newton's definition, if processes involving a deformation of the medium satisfy condition (5.40). These two statements are equivalent to the fact that the absorption of energy in the medium is determined only by Releigh's dissipation function, and the factor (multiplier) preceding the squares of the deformation rates represents the viscosity factor (formula 5.37).

The rheological conception makes it possible to expand the concept of viscosity and to apply it to systems which are not subordinate to Newton's internal friction law. However, it is apparent that, in order to allow an experimental determination of the viscosity factor in case of such a broad definition, it is also necessary that the theory of the measurement method should be elaborated on the basis of a corresponding rheological equation. This constitutes an independent problem, which will not be examined here.

We shall start from the concept that the viscous properties of a heterogenous medium are formally determined by Newton's internal friction law. The analysis of experimental results, presented at the end of the preceding chapter, gives us a reason to assume that condition (5.40) is fulfilled in case of the observed viscosity values obtained with the heterogeneous systems which have been investigated. Consequently, the viscous properties of a heterogeneous system may be characterized by means of a viscosity factor, determined with the aid of Newton's internal friction law.

The damping (attenuation) of the oscillations of a heterogeneous medium exhibits certain specific characteristics, which may be sufficiently fully clarified with the aid of Figure 3. The curves showing the logarithmic decrement of attenuation (or damping) and the period, given in this figure, constitute a reflection of the fact that a relative movement (motion) of the liquid and of the solid wall is taking place in the instrument, i.e., a reflection of the fact that the bucket-liquid system is a heterogeneous system. Figure 3 shows that, if, during the relative motion of the liquid and solid wall, the viscosity of the liquid is very high (y is small), then the absorption of the oscillation energy, characterized by δ, remains small and the oscillation period τ remains high. The reason for this lies in the fact that, in this case, the angular velocity gradient is small precisely in view of the high velocity of the liquid, as result of which the entire liquid as a whole moves together with the bucket. Such a type of motion is responsible for the low energy absorption and the high oscillation period, corresponding to the moment of inertia of the suspension system, which is approximately equal to the sum of the moments of inertia of the bucket and of the solidified liquid inside the bucket.

If the viscosity of the liquid, which fills up the bucket, starts to decrease, for example, as a result of heating, this will result in an increase of the angular velocity gradient in the vicinity of the bucket wall, which will result in a higher absorption. At the same time, the oscillation period will decrease, since a steadily smaller amount of liquid will take part in the movement (motion) of the bucket.

After a certain time, the effect of a decrease in viscosity will predominate over the increase in the angular velocity gradient, and the absorption will start to decrease parallel to the change in the viscosity factor of the liquid. The oscillation period will remain practically constant in view of the small mass of the liquid carried along (entrained) during the motion.

These basic features of the oscillating motion of the bucket filled with liquid can be briefly formulated in the form of a statement, according to which the absorption of energy during the oscillating motion of a heterogeneous medium exhibits a maximum at a certain value of the viscosity of the pure liquid.

From what has been said above, it follows specifically that during the propagation of acoustic waves in a medium consisting of liquid and solid particles of macroscopic size (see Note) distributed in this liquid, the damping of waves will be small in case of a very high viscosity of the liquid; then, when the viscosity drops, the damping will increase up to a certain maximum value, after which it will start to drop parallel to the drop in the viscosity of the pure liquid (<u>Note</u>: In this case, the macroscopic size of the particles must be interpreted in the sense that their streamline flow can be described hydrodynamically with a sufficient degree of accuracy).

Indeed, the relative motion of the liquid and of solid particles can be described by means of the same hydrodynamic equations as in the preceding case. In regard to changes in the character of flows in the vicinity of each particle, which take place during changes in the viscosity of the liquid, the same considerations which have been described above can be repeated. Therefore, the $\delta(\xi)$ curve shown in Figure 3 simultaneously represents a direct characteristic of the damping intensity of acoustic waves in a heterogeneous medium depending upon the viscosity of the pure liquid. These conclusions can be used as a basis for a hydrodynanic theory of sound propagation in heterogeneous media at any concentrations of solid macroparticles (<u>Note</u>: An abnormal absorption of the type described above was observed by I. G. Mikhaylov and A. A. Shagalova, <u>Doklady AN SSSR</u> (Reports of the Academy of Sciences USSR), Vol. 89, No. 5, 1953. A theory of sound absorption, based on considerations similar to those presented here, is given by M. V. Vol'kenshteyn and Yu. Ya. Gotlib, <u>Doklady AN SSSR</u> (Reports of the Academy of Sciences USSR), Vol. 89, No. 5, 1953).

In a number of practically interesting cases, during the course of appropriate calculations, it is possible to start from the assumption of an ordered distribution of particles having approximately the same size and shape.

A macroscopically heterogeneous medium can be easily achieved during the course of fusion of a binary alloy in those states of the alloy which lie between solidus and liquidus lines. It can be assumed that, in this case, the viscous properties of the medium in the oscillation process will be mainly determined by the concentration and dimensions of the suspended particles. Here, the possibility is afforded to associate the kinetics of the solidification process of the alloy with its viscous properties.

Figure 44 illustrates the temperature dependence of viscous losses, obtained on a torsional oscillating viscosimeter, for an alloy having the composition 15% Pb + 85% Bi, from the beginning of its fusion (smelting) through the region of heterogeneous equilibrium and the liquidus point, and further into the region of a homogeneousliquid (<u>Note</u>: Experimental observations were performed by N. K. Rakova during the course of her graduation work at the Physics Faculty of Moscow State University in 1953).

It can be easily seen that the general character of the temperature dependence of the logarithmic decrement of damping (damping ratio) is similar to the dependence of the damping decrement on the parameter $\xi = \sqrt{y}$ (Figure 3), which is quite natural, in view of the fact that a change in ξ follows the same course (i.e., proceeds in the same direction) as the change in temperature.

Figure 29 shows the result of the processing of a curve similar to the one shown in Figure 44 (namely, of its ascending branch), represented in the form of values of the kinematic viscosity as a function of the temperature for the alloy: 75% Pb + 25% Bi. Attention is directed to the very high values of the viscosity in the heterogeneous region, caused by the presence of solid phase crystals.

The results of these and previously cited studies constitute a proof of the great influence exerted by insoluble impurities on the viscous properties of liquids. Strictly speaking, all metallic liquids, unless they have been subjected to a very thorough purification, are heterogeneous systems. The concentrations of insoluble impurities in different samples of the same metal may vary within a wide range.

Specifically, the system of curves shown in Figure 20, characterizing the viscosity of aluminum in different tests, can be explained as being due to a different, but significant, concentration of insoluble impurities. The absence of any kind of regularity (rule) in the relative arrangement of viscosity curves of steels and ferrochrome alloys can also be explained as being due to the influence exerted by insoluble impurities.

When the amount of insoluble impurities in the studied metal remains constant, these impurities will rise to the surface (since in most cases they consist of light lower oxides) as the metal is held in the fused state, and a purification of the metal will take place. As a result of this process, the viscosity will change with the course of time, striving to reach a certain limit, corresponding to an ideal pure metal. Specifically, such a phenomenon may take place during the actual process of viscosity measurement, if the conditions for the rising of impurities are favorable (such as the absence of stirring).

For this reason, the degree of purification of metals from insoluble impurities during viscosimetric studies plays the same important role as during the study of crystallization processes. In experimental viscosimetry, it is advisable to introduce the concept of the viscosity of a metallic liquid, which in its original state corresponds to the presence of insoluble impurities, as well as the concept of a viscosity, which in its final state corresponds to a complete removal of insoluble impurities from the fused metal. There are serious reasons to assume that, practically in many cases, the effect of insoluble impurities present in the fused metal on the viscosity is greater than the contamination of the metal with other chemical elements present in the fused state. All of the experimental results on the viscosity listed above refer to fused metals in the original state. Observations have shown that, in the case of lead, tin, bismuth and certain other metals with similar melting points, the original state is preserved when these metals are heated to approximately 600° C. Above this temperature, the process involving a separation of impurities and of the liquid phase takes place with a noticeable speed (rate).

The theory of the viscosity of suspensions, elaborated by Einstein (30), is not applicable in many cases to metallic liquids contaminated with insoluble impurities, since this theory covers a region of low concentrations of solid particles, in which an increase in viscosity amounts to several percent. Even more so, this theory is inapplicable to an analysis of the viscosity of binary alloys at temperatures lying below the liquidus line, since in this region, in case of a slight cooling, an increase in the viscosity amounting to entire orders is observed (see Figure 29).

Consequently, in order to establish a connection between the behavior of the viscosity in the heterogenous region of the fusion diagram of alloy and the kinetics of the growth and formation of particles, it is necessary to create a new theory of the viscosity of heterogeneous systems, free of limitations in regard to the concentration of solid particles.

8. The Viscosity and Critical Temperature of Liquids

On the basis of an analysis of experimental data and an examination of theoretical connections between critical parameters, the structure of the molecular field and the macroscopic properties of liquids, A. Z. Golik (31) has established the presence of a certain rule in the arrangement of $\eta(T)$ curves in the case of liquids possessing a similar structure and type of interactions between particles. The higher the critical temperature of a given liquid, the higher lies the curve showing the temperature dependence of the viscosity (i.e., the higher is this curve located in the region of high values). This statement applies to normal alcohols, paraffins, a number of metallic liquids (sodium, potassium, zinc, cadmium, mercury), and also to certain solutions. In case of metals, the critical temperature is estimated by means of Guldberg-Hewey(?)'s rule (Note: According to this rule, the absolute critical temperature is proportional to the absolute boiling point. The factor of proportionality is equal to 1.55, if the boiling point is selected at a normal pressure, and is equal to 2, if the boiling point is selected at a pressure of 20 mm Hg). According to this rule, the critical temperature of aluminum and lead is equal to 2,470 and 2,028° K, respectively. In case of zinc and cadmium, this temperature is equal to 1,820 and 1,610° K respectively, and in case of tin and bismuth, 2,540 and 1,830° K respectively. The first two metals have a close-packed structure with a coordination number of 12, the next two metals have a loose-packed hexagonal structure with a coordination number of 6 + 6, and the last two metals have lattices with a coordination number of 6. By taking the equality $\eta = \rho\nu$ into account, one can see that the arrangement (disposition) of the viscosity curves for zinc and cadmium, tin and bismuth is indeed in agreement with Golik's rule; this does not apply, however, to aluminum and lead. The deviation from the typical order of arrangement of the viscosity curves exhibited by the last two metals is possibly associated with a very high difference in density, or maybe is due to an inaccurate determination of the critical temperature. In this connection, it is interesting to note that the kinematic viscosity curves for all six metals listed above comply with this rule.

F88

The rule established in this manner is of great practical importance. Indeed, let us assume that we have a liquid, having a certain (known) critical temperature, molecular structure and nature of intermolecular forces, the viscosity of which is expressed by the function $\eta(T)$, and that it is necessary to obtain another liquid with the same viscosity function $\eta(T)$. In that case, this second liquid must be selected in such a way that it will have the same type of molecular structure, nature of interaction forces and critical temperature. It was found that this can be achieved in many practically important cases by making use of liquid mixtures.

A. Z. Golik has given a theoretical interpretation of this established rule, starting from very general considerations on the connection between the intermolecular potential, on one hand, and the internal energy of the liquid and its macroscopic properties, on the other hand. An exponential formula showing the dependence of the viscosity on $\frac{1}{T}$ is used as a basis. Briefly stated, the essence of the point consists in the following. The deeper the potential well of intermolecular interactions and the greater the binding energy, the higher the latent heat of evaporation and the critical temperature of the substance. However, in case of an identical molecular structure, the deeper the potential well, the steeper are its edges. During a relative displacement of molecules, tangential forces make their appearance; the value of these forces is the greater, the steeper the slopes of the potential well, i.e., in the final analysis, the higher the value of the critical temperature. An examination of this problem clearly discloses the role of the nature of intermolecular forces, since the shape of the potential energy curves, in case of the same type of molecular structure, is determined by the nature of the bonding forces.

Conclusion

In this chapter, an attempt has been made to describe the connection between the structure, the viscosity and the crystallization kinetics of metallic liquids. A solution of this problem lies, on one hand, in the further accumulation of experimental data on the properties of liquids, and, on the other hand, in the development and application on liquids of general theoretical methods for analyzing a system of interacting particles. A number of encouraging results in this direction, obtained by N. N. Bogolyubov, M. Born, and A. A. Vlasov, are available to us.

So far, however, the theories mentioned above are still far from yielding results which may be quantitatively compared with experimental results. Therefore, the attempts of many scientists, working in the field of physics of condensed media, are understandable; these attempts are directed at the solution of experimental and theoretical problems concerned with the theory of the liquid state.

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USSR, Physics Series), Vol. 7, No. 1, 1941 (Other works by V. I. Danilov are cited during the discussion of corresponding problems); N. S. Gingrich, Uspekhi khimii (Progress of Chemistry), Vol. 15, No. 3, 1946; Ya. I. Frenkel', Kineticheskaya teoriya zhidkostey (Kinetic Theory of Liquids), 1945; P. P. Kobeko, Amorfnyye veshchestva (Amorphous Substances), published by the Academy of Sciences USSR, 1952; G. W. Stewart, Uspekhi khimii (Progress of Chemistry), Vol. 1, No. 5, 1932; P. Debye, Uspekhi fizicheskikh nauk (Progress of Physical Sciences), Vol. 14, No. 7, 1934; Ibid., Vol. 21, 1939, p. 120. The following works might also be mentioned: G. W. Stewart, Journ. Chem. Phys., Vol. 2, 1934, p. 147; Ibid., Vol. 2, 1934, p. 558; K. P. Mamedov, N. A. Aliyev, Trudy Instituta fiziki i matematiki Azerb. AN, Seriya fizicheskaya (Transactions of the Institute of Physics and Mathematics of the Azerbaydzhan Academy of Sciences, Physics Series), 1953 (see also reference 32). On the results of a neutron diffraction study of the structure of liquids, see the review article in Uspekhi fizicheskikh nauk (Progress of Physical Sciences), Vol. 42, No. 1, 1950, and P. C. Sharrah and P. Smith, Journ. Chem. Phys., Vol. 21, No. 2, 1953.

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13. V. I. Danilov, Problemy metallovedeniya i fiziki metallov (Problems in the Field of Metal Science and Physics of Metals), Collection of Works, p. 7, 1949, published by Metallurgizdat; Sbornik nauchnykh rabot Laboratorii metallofiziki (Collection of Scientific Works of the Laboratory for the Physics of Metals), p. 95, 1948, published by the Academy of Sciences Ukrainian SSR.
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16. V. I. Danilov, Rasseyaniye rentgenovskikh luchey v zhidkostyakh (Scattering of X-Rays in Liquids), pp. 106-111 (see reference 8).
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32. See *Stroyeniye i fizicheskiye svoystva veshchestva v zhidkom sostoyanii* (Structure and Physical Properties of Matter in the Liquid State), Proceedings of Conference in Kiev, published by Kiev University imeni T. G. Shevchenko, 1954.

Appendix

List of Books Published by the State Publishing House for Technical and Theoretical Literature (GTTI)

The following books are available for sale:

1. Ambartsumyan, V. A., et al., *Teoreticheskaya astrofizika* (Theoretical Astrophysics), recommended by the Ministry of Higher Education USSR as a textbook for state universities, 636 pages. Price: 15 rubles.
2. Kedrov, B. M., *Razvitiye ponyatiya elementa ot Mendeleyeva do nashikh dney* (Development of the Concept of an Element from the Days of Mendeleyev to the Present Time), Philosophical problems in the field of modern natural sciences, 247 pages. Price: 8.15 rubles.
3. Kuznetsov, V. D., *Kristally i kristallizatsiya* (Crystals and Crystallization), 412 pages. Price: 19 rubles.
4. Lewes, W. B., *Metody elektricheskogo scheta al'fa i beta chastits* (Methods for the Electric Count of Alpha and Beta Particles), 2d edition, Translated from the English, G. D. Latyshev, editor, 164 pages. Price: 3.85 rubles.
5. Meshcherskiy, I. V., *Raboty po mekhanike tel s peremennoy massoy* (Studies on the Mechanics of Bodies With a Variable Mass), 2d

edition, with a preface and introductory article by Prof. A. A. Kosmodemyanskiy, 280 pages. Price: 6 rubles.

6. Morse, F., Kolebaniya i zvuk (Oscillations and Sound), Translation from the English, edited by Prof. S. N. Rzhevkin, 496 pages. Price: 18.60 rubles.
7. Sena, L. A., Stolknoveniya elektronov i ionov s atomami gaza (Collisions of Electrons and Ions With Gas Atoms), Series "Modern Problems of Physics," 216 pages. Price: 6 rubles.

These books are sold in bookstores and are also shipped by mail C.O.D. without a down payment by all republican, kray and oblast sections of "Kniga-Pochtoy" (Books by Mail).

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Figure Appendix

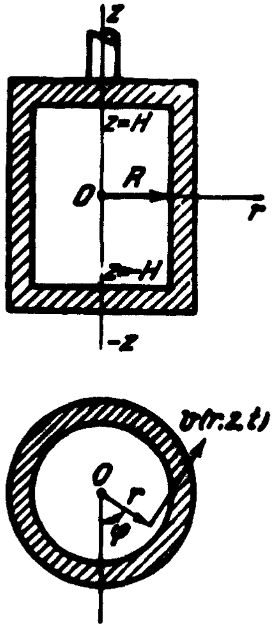

Figure 1. Working space of viscosimeter and arrangement of coordinate axes.

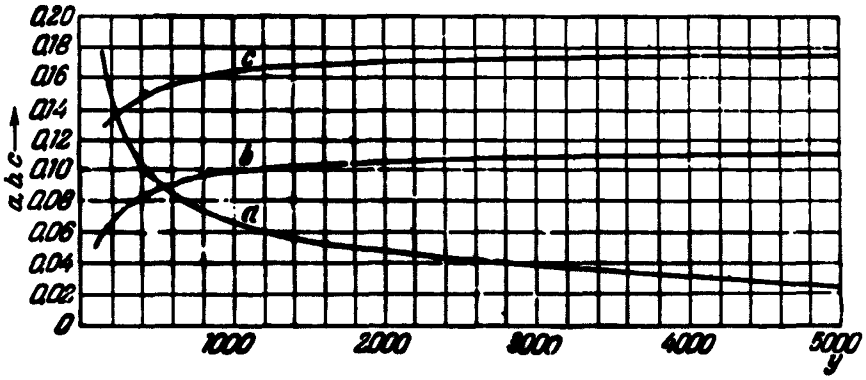

Figure 2. Graphs used in the determination of factors, a, b and c in formula (2.89).

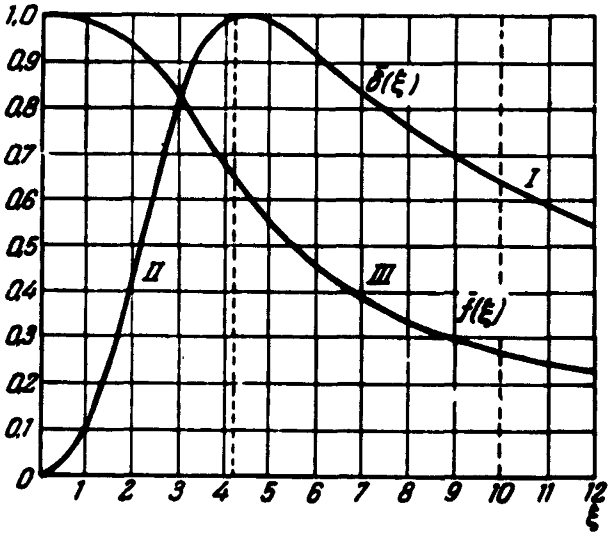

Figure 3. Dependence of the damping decrement $\delta(\xi)$ and function $\frac{\tau^2}{\tau_0^2} - 1 = f(\xi)$ on $= R\sqrt{\frac{2\pi}{\tau V}}$. Arbitrary units are plotted along the ordinate axis, and for this reason $\bar{\delta}(\xi)$ and $\bar{f}(\xi)$ differ from their true values by constant factors (multipliers).

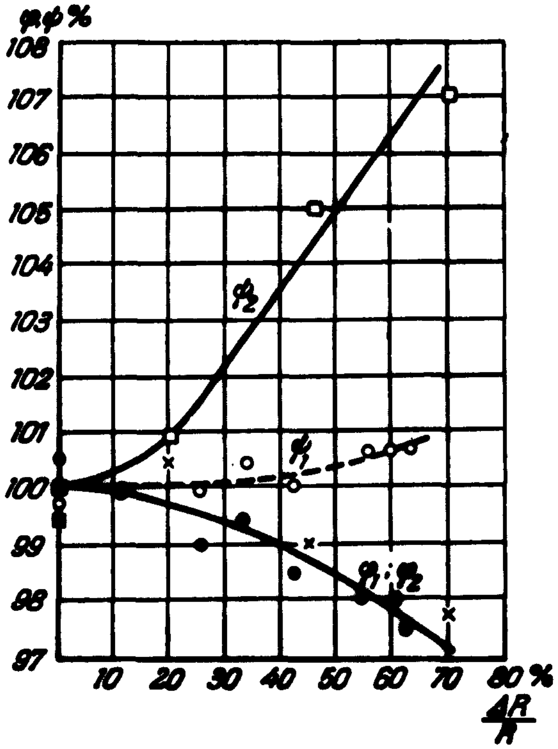

Figure 4. Effect of a relative off-centering of the bucket on the values of the damping decrement δ and the oscillation period τ.

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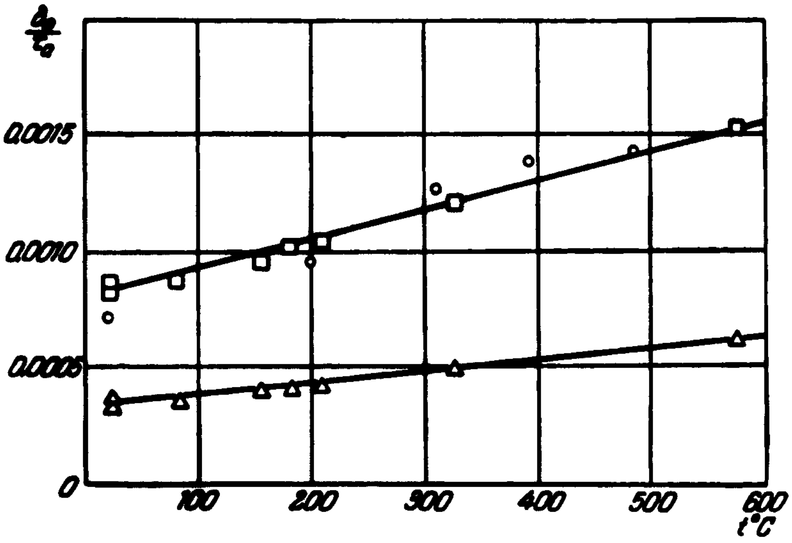

Figure 5. Dependence of $\frac{\delta_0}{\tau_0}$ for various suspension systems. Experimental results.

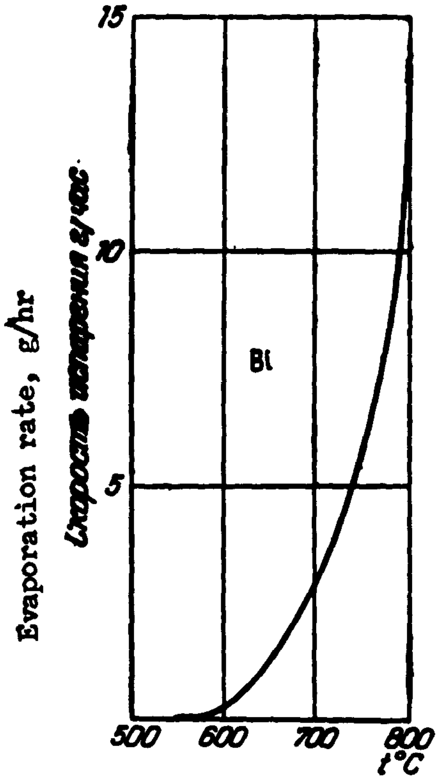

Figure 6. Evaporation rate of bismuth from a free surface depending upon the temperature.

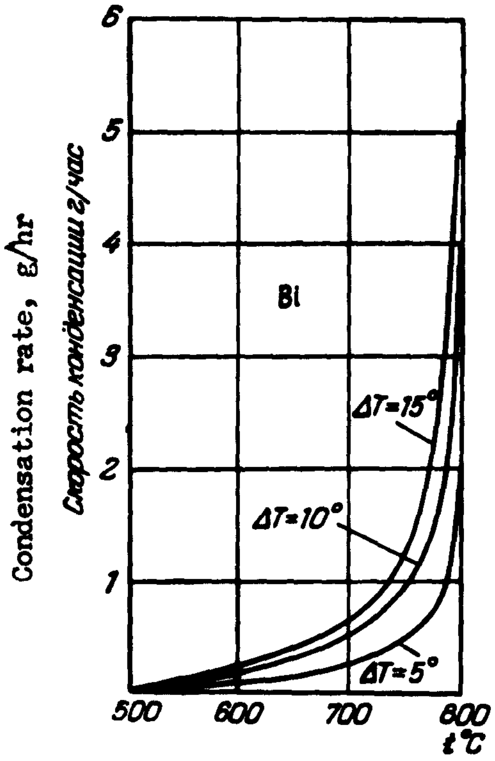

Figure 7. Condensation rate of bismuth vapors on the lid of the bucket depending upon the temperature of the metal and the temperature difference between the metal and the lid, in the absence of a foreign gas in the clearance between the free surface of the metal and the lid.

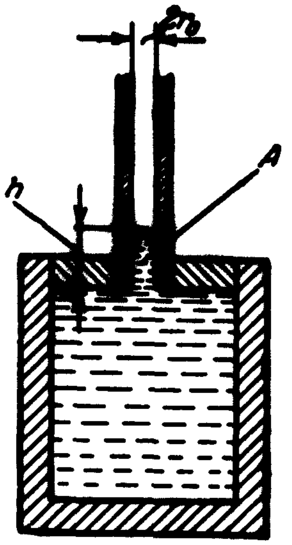

Figure 8. Sketch of the bucket filled with liquid, in case of two end surfaces of contact.

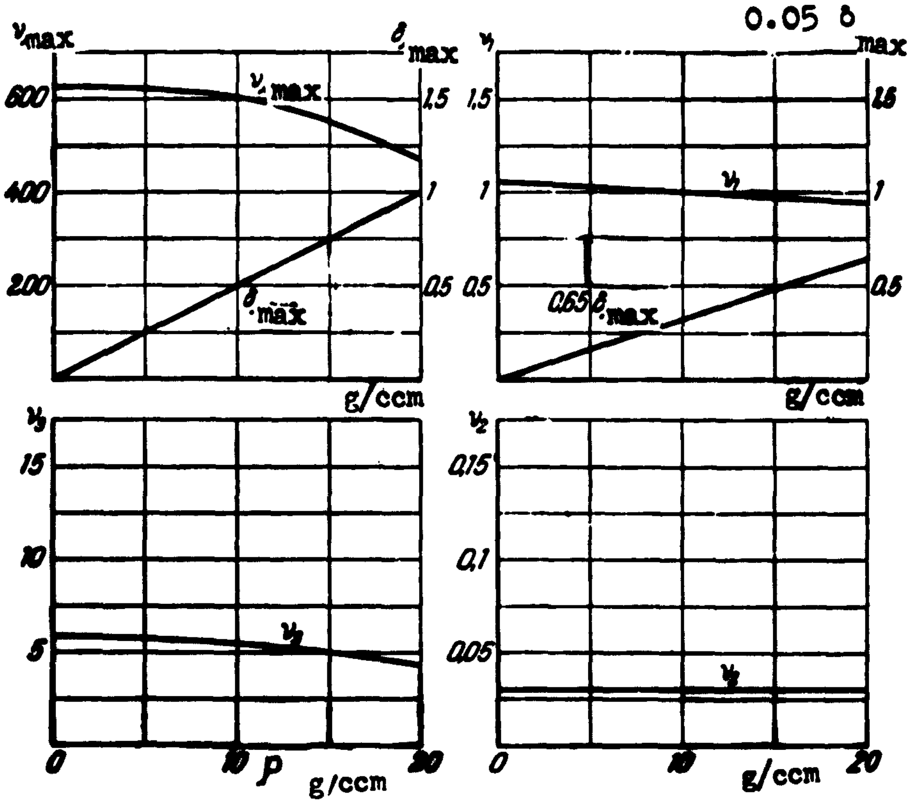

Figure 9. Range of kinematic viscosity values which can be investigated by means of the suspension system, calculated in # 14. v_1 and 0.65 δ_{max} are, respectively, the values of the viscosity and of the damping decrement when y = 100. v_2 corresponds to the viscosity value when y = 3,500, v_3 when y = 16, v_{max} when y = 0.16, δ_{max} is the maximum value of the damping decrement (see Figure 3).

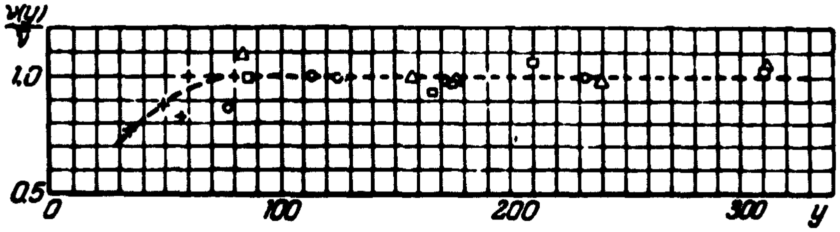

Figure 10. Effect exerted by the value of parameter y on the numerical value of the kinematic viscosity, calculated according to the theory of the method for low-viscosity liquids.

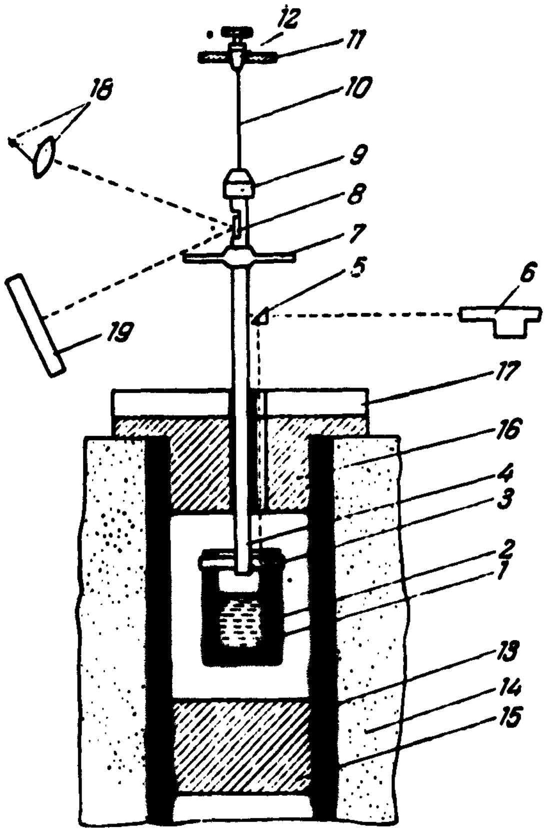

Figure 11. Sketch of the unit used in measuring the viscosity of steels and ferrochrome alloys: 1 -- metal tested, 2 -- crucible, 3 -- ceramic bar, 4 -- rod, 5 -- prism, 6 -- optical pyrometer, 7 -- aluminum disk-radiator, 8 -- small mirror, 9 -- small chuck for fastening the wire suspension, 10 -- suspension wire, 11 -- attachment of the upper point of the suspension device, 12 -- twisting mechanism with limited angle of rotation, 13 -- graphite heating cylinder of Tamman furnace, 14 -- filling of Tamman furnace, 15 -- heat insulating stopper (plug), 16 -- heat insulating plug with an opening for the outlet of the light ray, 17 -- water cooling, 18 -- illuminator, 19 -- scale.

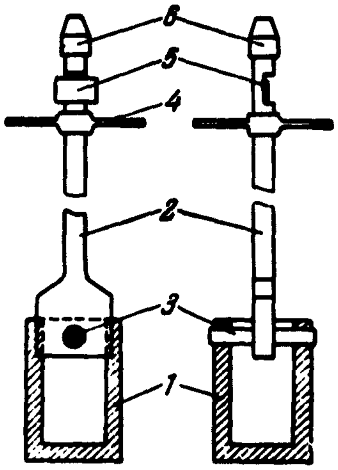

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Figure 12. Structure of the suspension system: 1 -- crucible, 2 -- rod, 3 -- holding bar (all these parts are made of ceramic material), 4 -- aluminum shield (disk-radiator), 5 -- small mirror, 6 -- small chuck for fastening the suspension device.

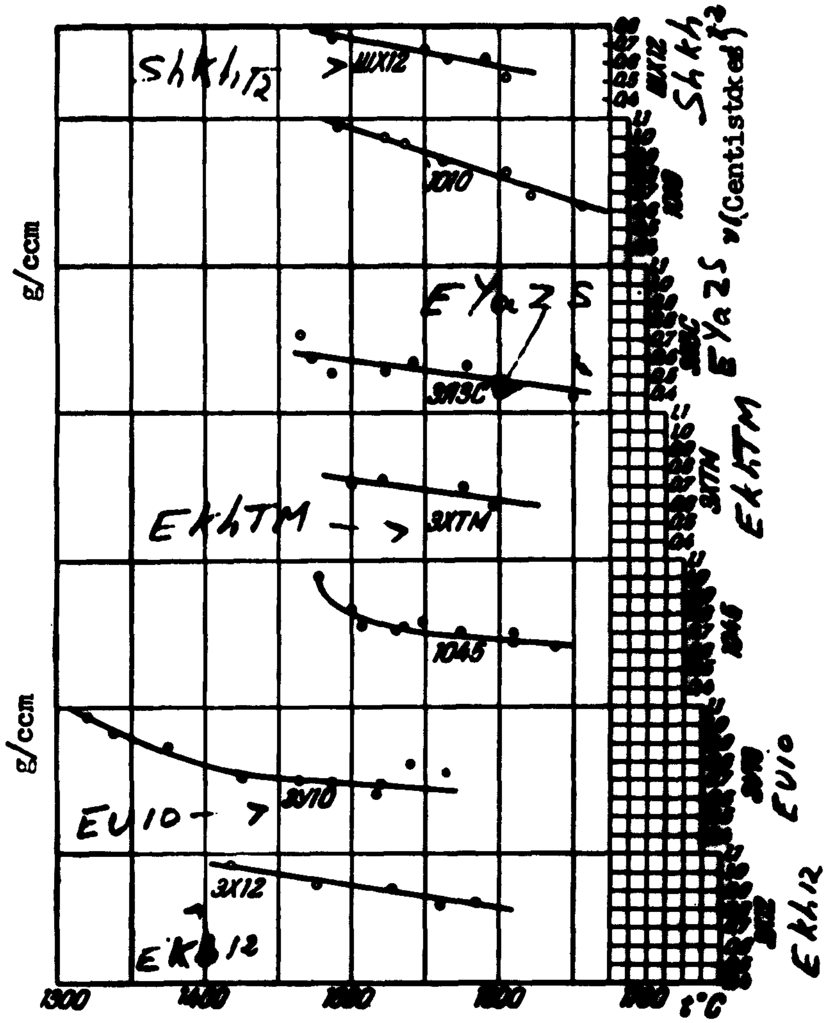

Figure 13. Kinematic viscosity of steels. (Θ) -- measurements in a Tamman furnace with a large crucible, (●) -- repeated measurements in a vacuum viscosimeter ($\sim 10^{-2}$ mm Hg) with a smaller crucible.

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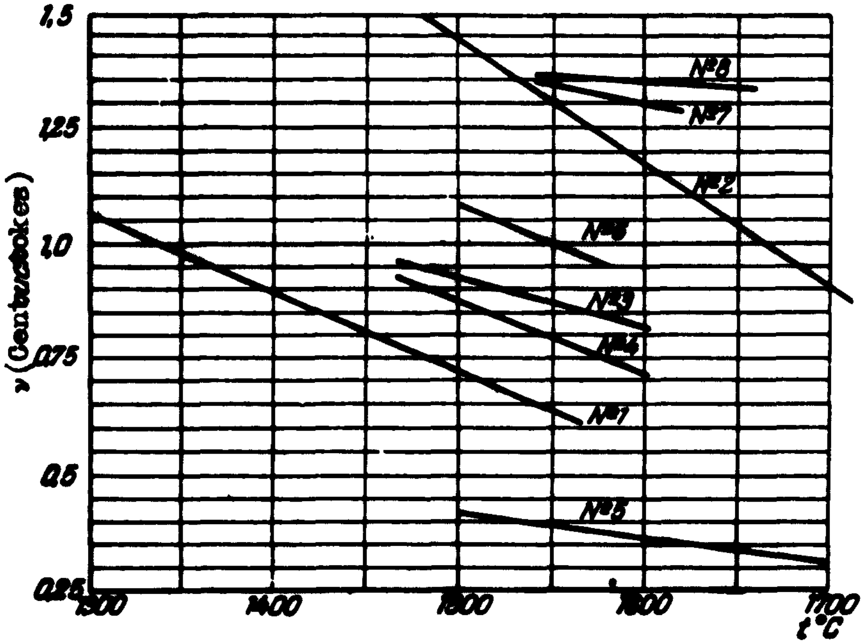

Figure 14. Kinematic viscosity of cast iron and ferrochrome alloys. The length of the straight lines corresponds to the studied viscosity range.

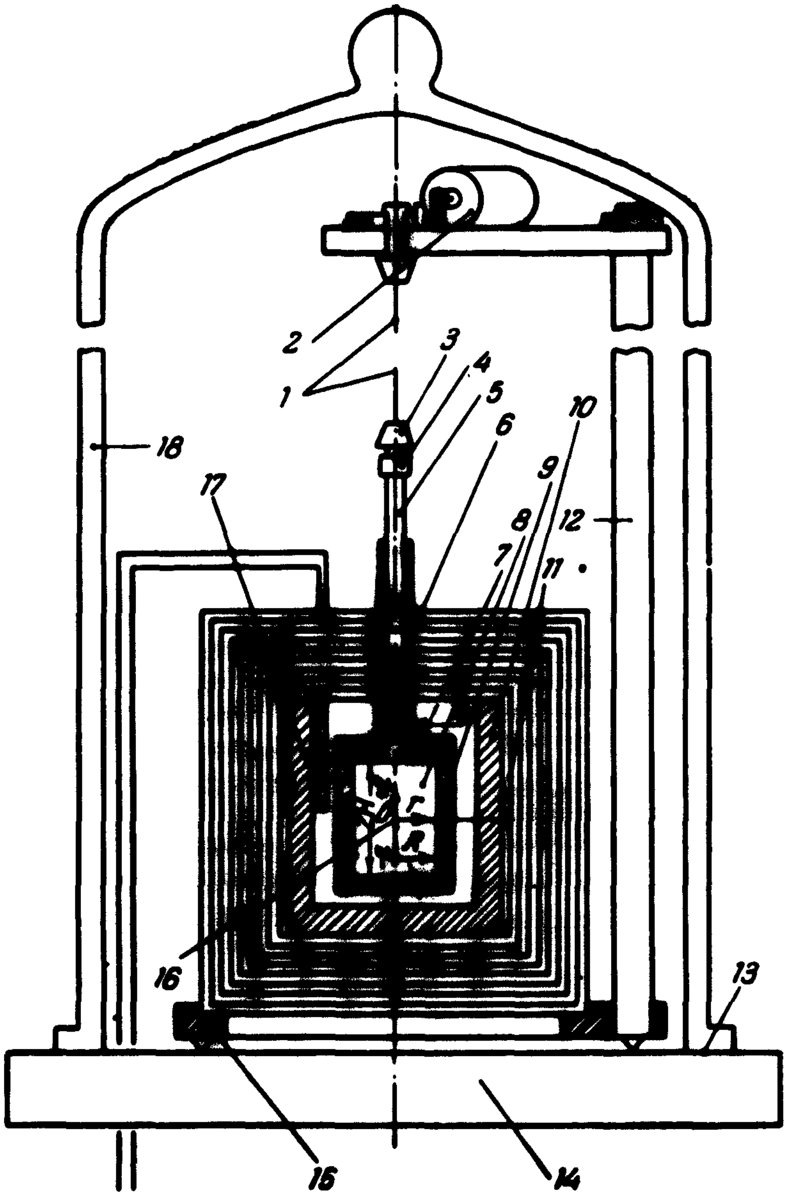

Figure 15. Structure of a vacuum viscosimeter: 1 -- small wire of the suspension device, 2 -- rotating electromagnetic mechanism, 3 -- three-jawed chuck for clamping the suspension wire, 4 -- small mirror, 5 -- porcelain rod, 5 mm in diameter, 6 -- free space for excess metal, 7 -- graphite lid of crucible, 8 -- crucible space filled with the metal to be

tested, R = 1.00 cm, 2H = 2.45 cm, 9 -- graphic crucible, with a wall thickness of 0.4-0.5 cm, 10 -- alumina muffle with a bifilar nichrome heating winding, 11 -- nine reflector shields, made of nickel, 12 -- instrument rack, 13 -- polished section, 14 -- marble plate, 15 -- base of the instrument, 16 -- coordinate system, in relation to which the equations are written, 17 -- Chromel-Alumel thermocouple, 18 -- glass hood.

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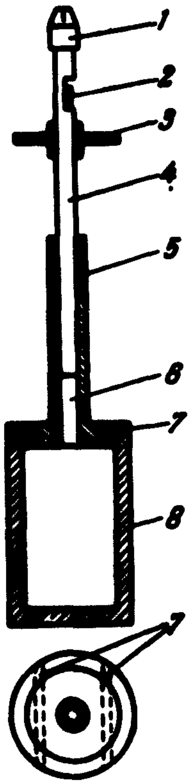

Figure 16. Structure of the suspension system: 1 -- three-jawed chuck for fastening the suspension wire, 2 -- small mirror, 3 -- aluminum disk-radiator, 4 -- porcelain rod (bar), 5 -- graphite lid of crucible, 6 -- free space for excess metal, 7 -- steel bars, for attaching the lid to the crucible, 8 -- graphite crucible.

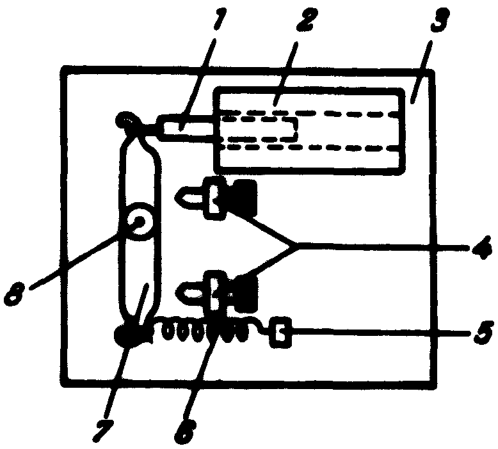

Figure 17. Rotating electromagnetic mechanism (plane view): 1 -- electromagnet core, 2 -- electromagnet, 3 -- base, 4 -- regulated arresters (holding devices), limiting the angle of rotation of the lever 7, 5 -- attachment of the small spring to the base, 6 -- small spring, 7 -- lever, rotating axis 8, 8 -- axis, attached to the upper three-jawed chuck.

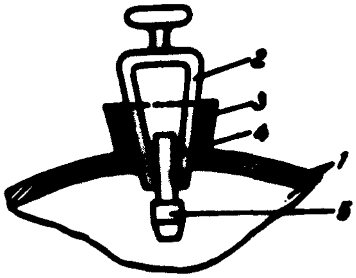

Figure 18. Modification of the rotating mechanism: 1 -- vacuum hood with a ground section in the upper section, 2 -- glass stopcock-plug, 3 -- vacuum ground section, 4 -- picein (?), 5 -- three-jawed chuck. The stopcock-plug must be provided with arresters (holding devices), which limit the angle of rotation.

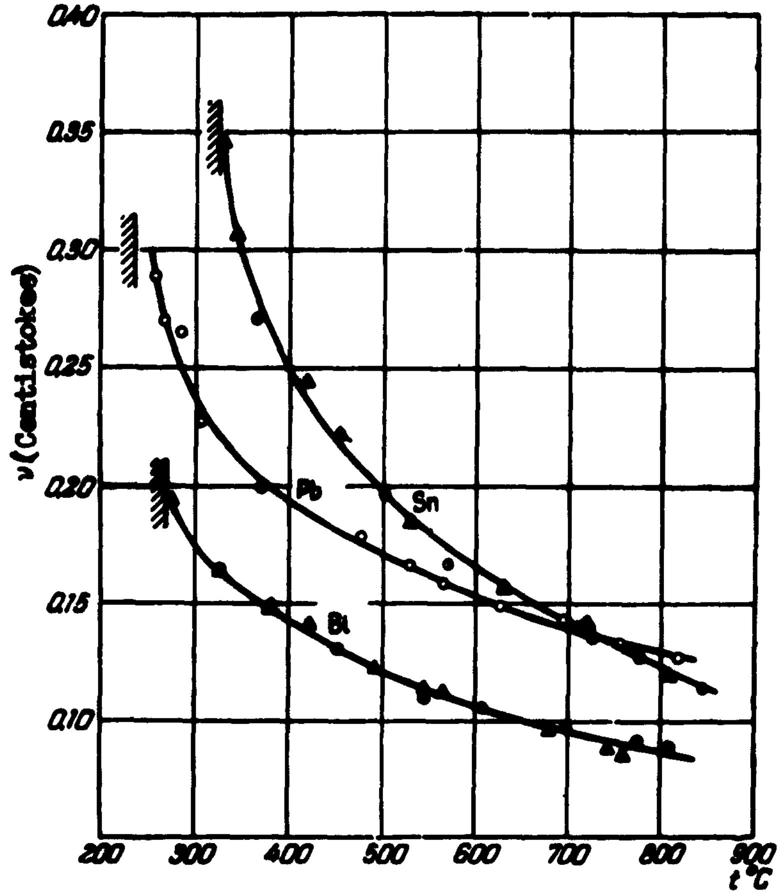

Figure 19. Kinematic viscosity of bismuth, lead and tin. The crystallization point is represented by means of vertical lines. The various signs correspond to different series of experiments.

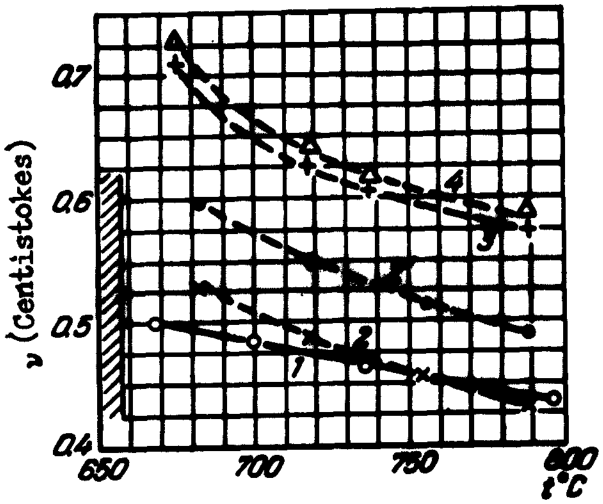

Figure 20. Kinematic viscosity of aluminum. Curve 1 indicates the most probable data on the viscosity of pure unoxidized aluminum. The other curves are explained in the text (see # 4).

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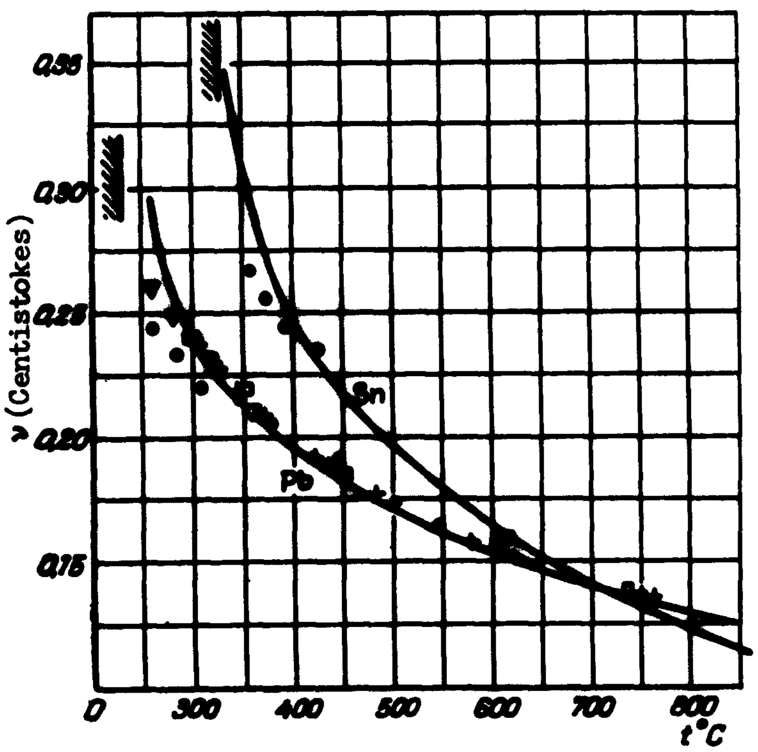

Figure 21. Kinematic viscosity of tin and lead near the crystallization point. The solid lines are transferred from Figure 19; the results from # 5 are represented as (●); measurements performed by Golubev and Petrov as (+); measurements performed by Sauerwald and Taylor as (◘); measurements performed by Schott as (▼).

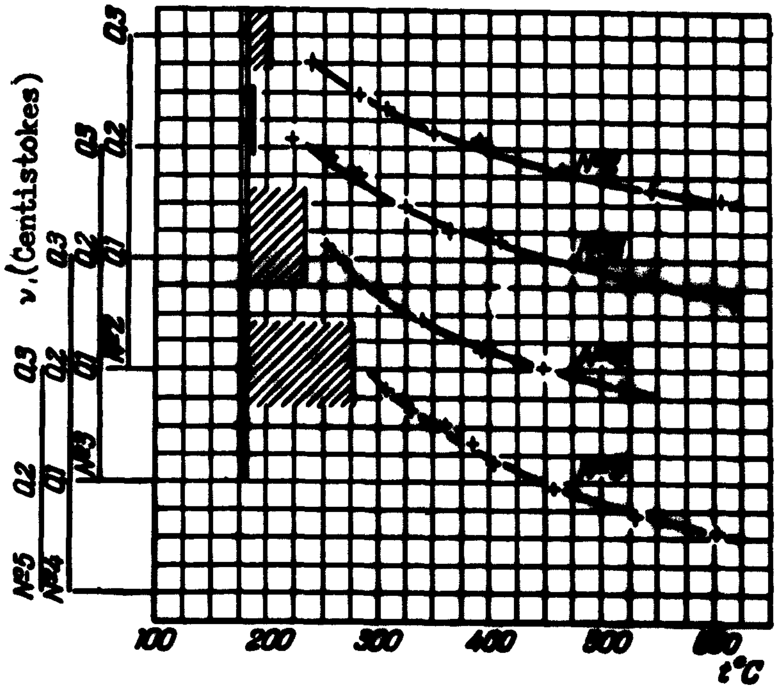

Figure 22. Kinematic viscosity of Sn-Pb alloys. For the composition of the alloys, see Table 10. Shaded areas correspond to regions of a heterogeneousequilibrium of the phase diagram.

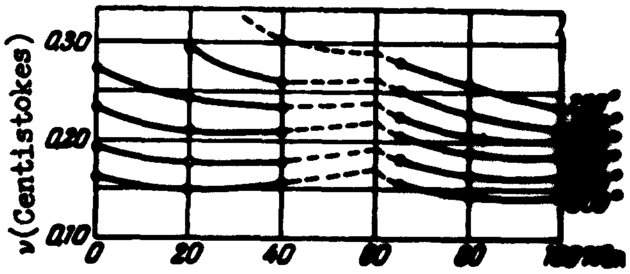

Figure 23. Isotherms of kinematic viscosity-composition of Sn-Pb alloys.

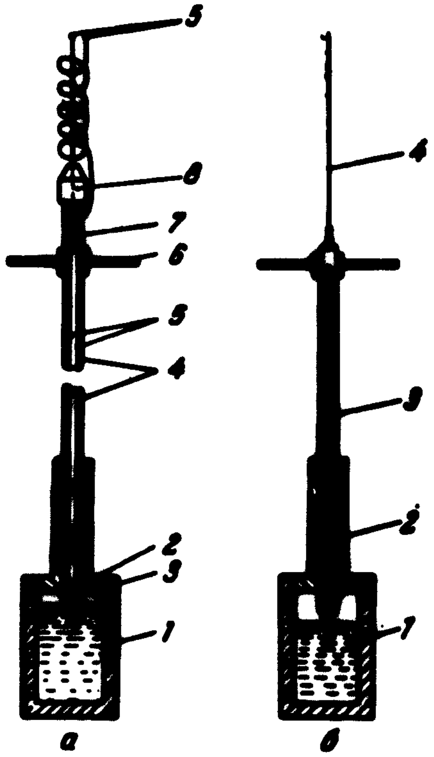

Figure 24. (a) Measurement of the temperature of the metal with a thermocouple: 1 -- crucible, 2 -- lid of the crucible, 3 -- seal (junction) of the thermocouple (must be protected from the action of metal vapors), 4 -- two-channel porcelain tube, 5 -- thermocouple wires. One of these wires serves as the suspension wire, the second wire is led out from the channel near the small mirror 7 and is coiled in the form of a spiral around the first (suspension) wire, as is done in mirror galvanometers. This wire must be very thin, having a diameter of several score of microns. 6 -- shield (radiator), 8 -- three-jawed chuck. (b) Measurement of the temperature of the metal with a thermometer: 1 -- crucible, 2 -- lid of the crucible, 3 -- thermometer, 4 -- suspension wire.

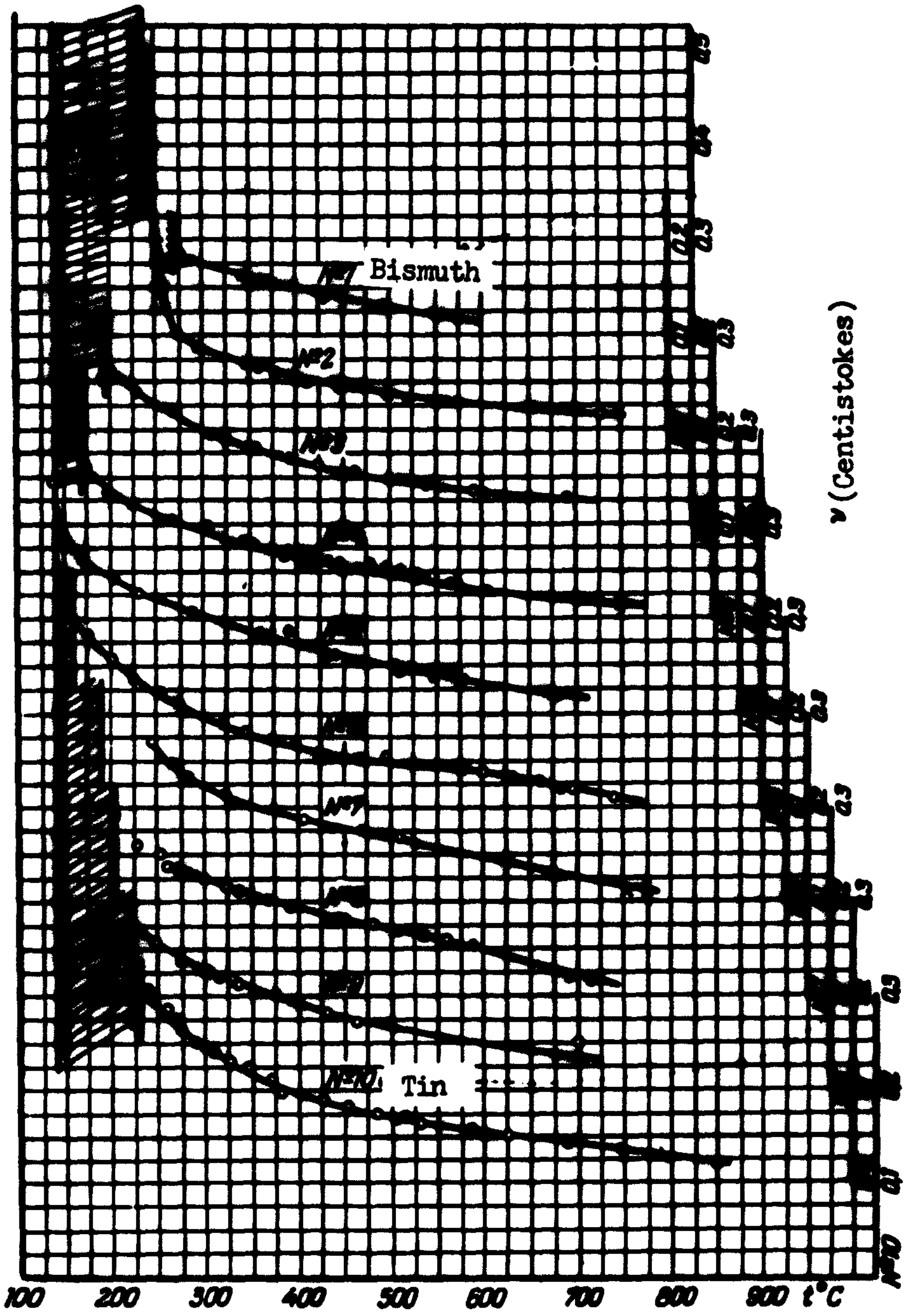

Figure 25. Kinematic viscosity of Sn-Bi alloys. Composition of the alloys, see Table 11. Shaded areas correspond to the regions of heterogeneous equilibrium of the phase diagram.

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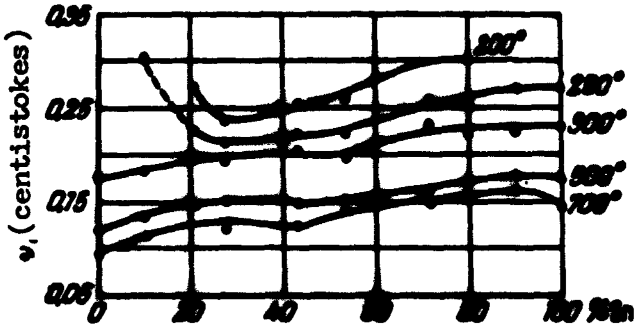

Figure 26. Isotherms of the kinematic viscosity-composition of Sn-Bi alloys.

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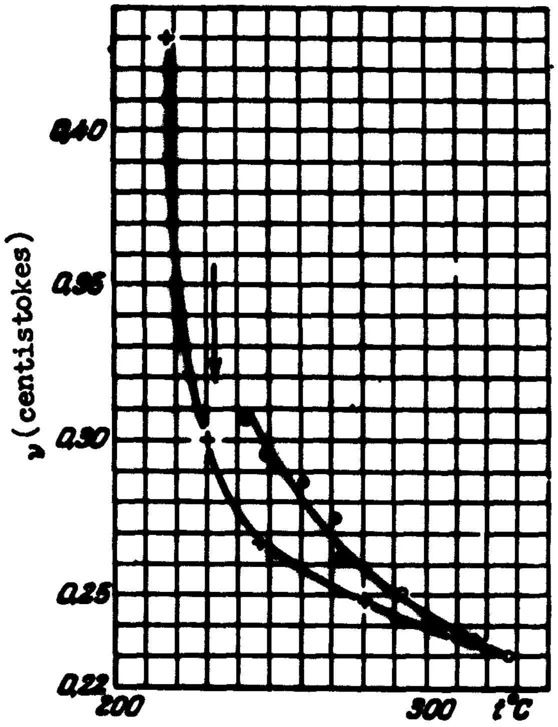

Figure 27. Effect of supercooling of tin on the kinematic viscosity (o) -- change in viscosity during the process of heating from the solid state; (+) -- change in viscosity during the process of cooling from 850° C. The arrow indicates the equilibrium crystallization point.

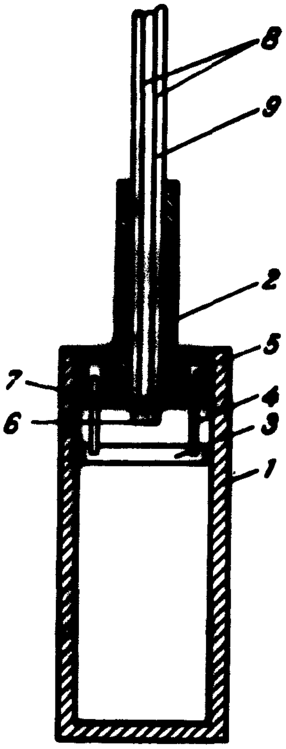

Figure 28. Structure of crucible with floating lid: 1 -- crucible, 2 -- lid of crucible, 3 -- floating graphite lid lies on the surface of the fused metal, due to guide pins 4, entering into grooves 5, 6 -- protective hub of thermocouple (against the action of metal vapors), 7 -- thermocouple seal (junction), 8 -- thermocouple wires, 9 -- two-channel porcelain tube.

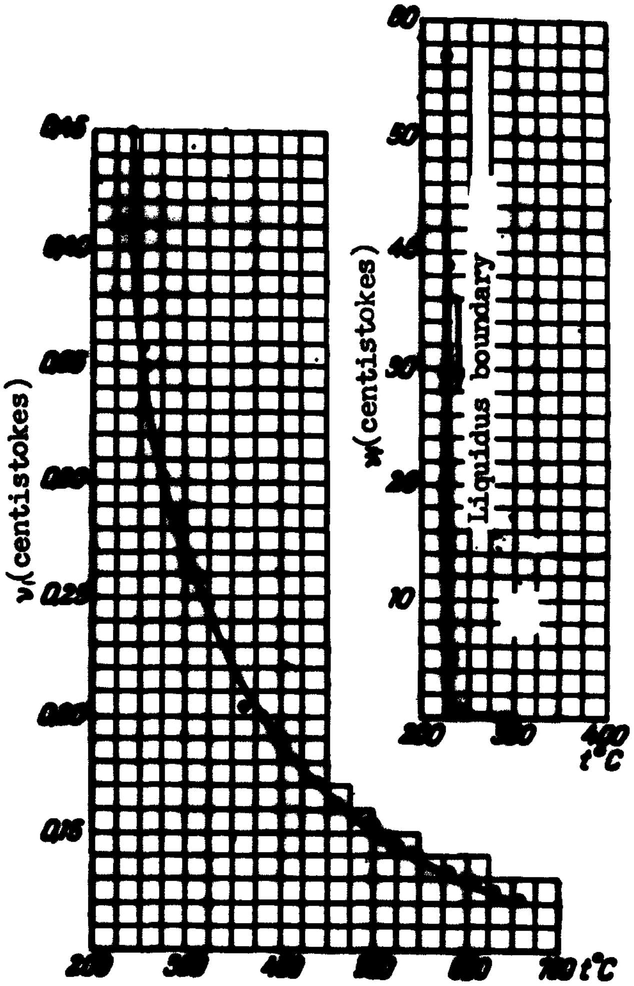

Figure 29. Kinematic viscosity of an alloy containing 75% Pb and 25% Bi. In the right upper corner, the viscosity of this alloy in the heterogeneous region of the fusion diagram is plotted along the ordinate axis on a reduced scale. The liquidus line is indicated by an arrow.

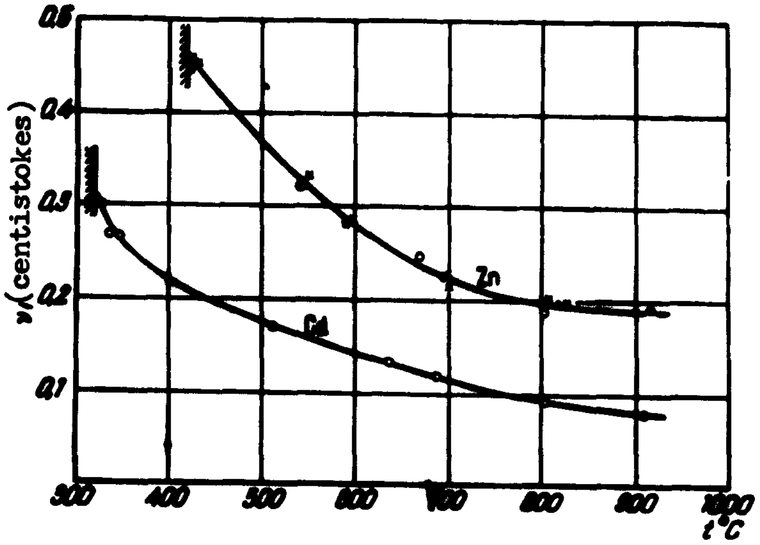

Figure 30. Kinematic viscosity of cadmium and zinc. The crystallization point is indicated by means of vertical shaded lines. The points shown on the zinc curve correspond to a crucible sealed-off under vacuum (x), and in the atmosphere (o).

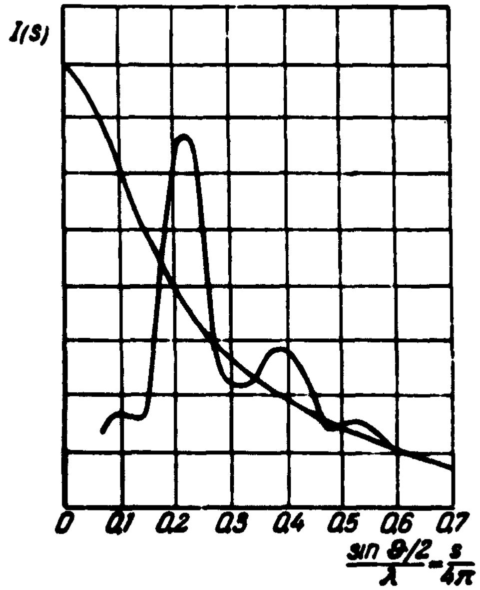

Figure 31. Distribution of the intensity I(s) of x-rays scattered by liquid aluminum.

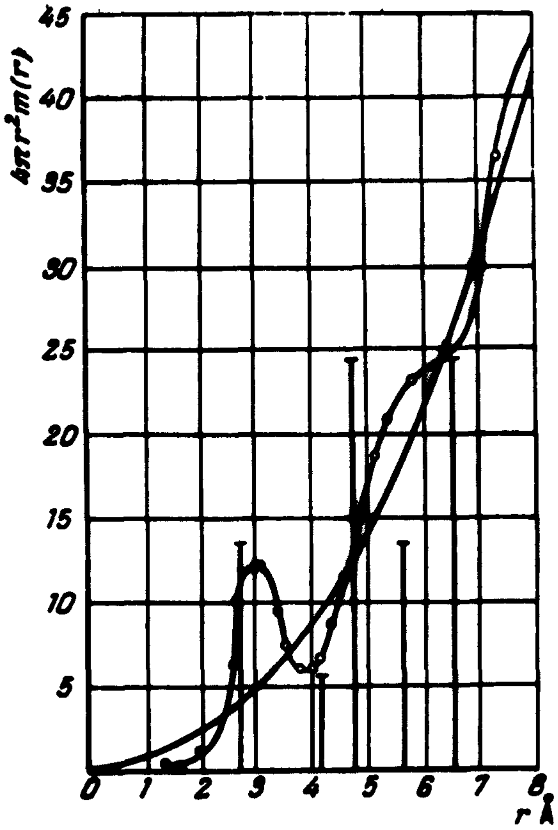

Figure 32. Function of the atomic arrangement n(r) for liquid aluminum, as a result of the processing of the curve shown in Figure 31 by means of the formula (6.6).

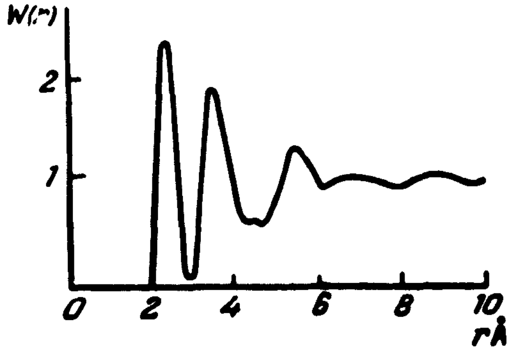

Figure 33. Curve of the probability factor of atomic distribution in amorphous As1.

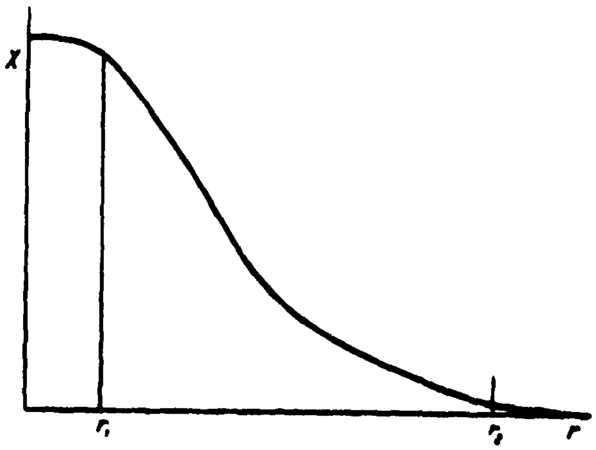

Figure 34. Structure of a quasi-crystal. Degree of short-range order x as a function of the distance from the center of the quasi-crystal r. The falling branch of the curve in the region $r_1 < r < r_2$ corresponds to a clearly expressed increase in the structural diffusion factor with the distance.

Figure 35. Rate of onset of crystallization centers w as a function of the depth of supercooling θ, determined by expression (6.14).

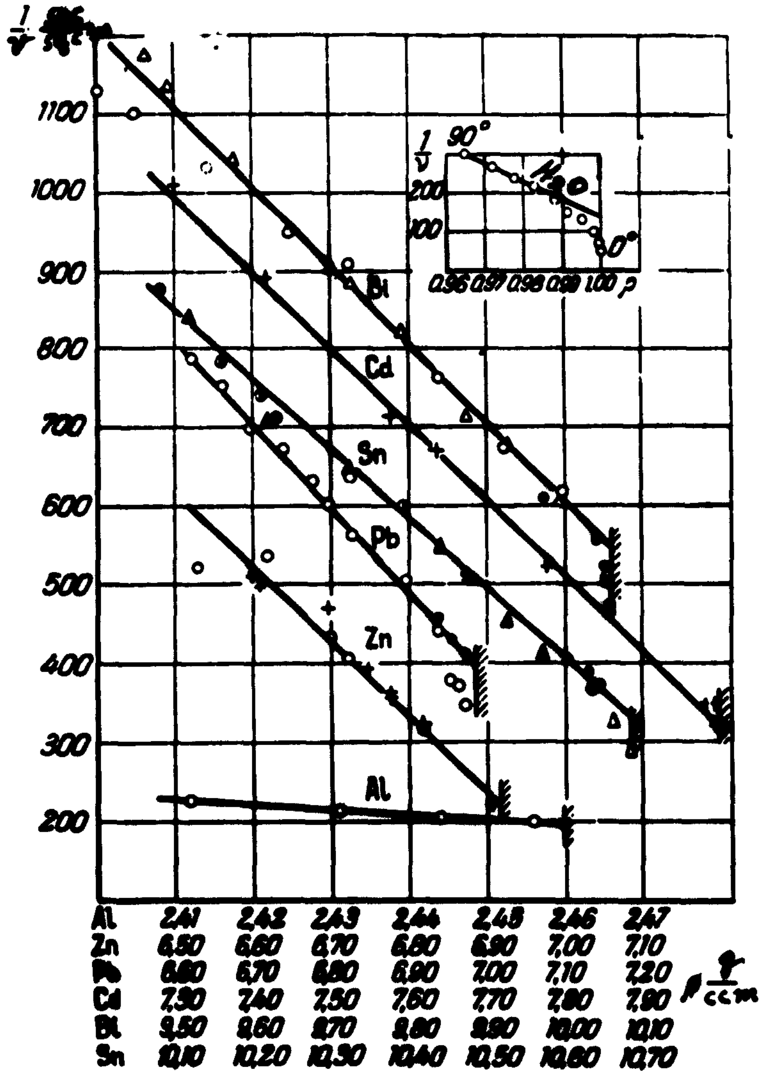

Figure 36. Reciprocal of the kinematic viscosity $\frac{1}{\nu}$ $\frac{\text{sec}}{\text{sq cm}}$ as a function of the density. As an example, a similar dependence for water is plotted in the right upper corner. Vertical lines indicate the boundary of the liquid phase, corresponding to the crystallization point T_0 (see equation 6.13). Points from Figure 19 are indicated by the symbols 0, ●, ▲, Δ, the symbols ● are used for tin and lead -- the 3 lower leftside points in Figure 21, and for bismuth -- additional control measurements. Density values are taken from Landolt-Börnstein's handbook.

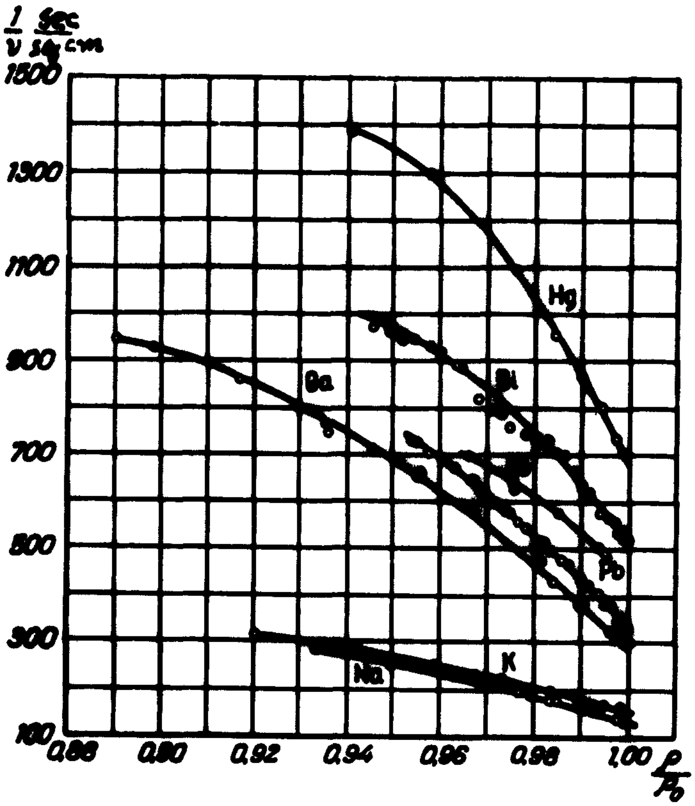

Figure 37. Reciprocal of the kinematic viscosity $\frac{1}{\nu}\,\frac{\text{sec}}{\text{sq cm}}$, as a function of the relative density $\frac{\rho}{\rho_0}$ (ρ_0 is the density of the liquid at the fusion point).

F
8
8

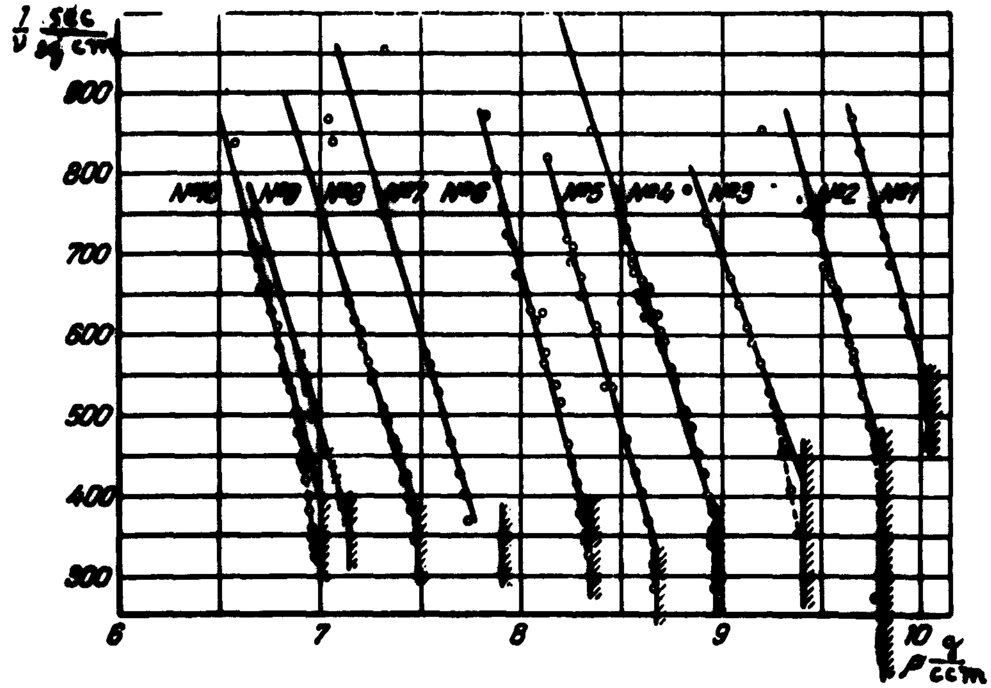

Figure 38. Dependence of $\frac{1}{\gamma}(\rho)$ for tin-bismuth alloys. No. 1 -- bismuth, No. 10 -- tin. The composition of the alloys is listed in Table 11 (the concentration of tin increases with a growing number of the alloy). Liquidus lines are represented by vertical shaded straight lines.

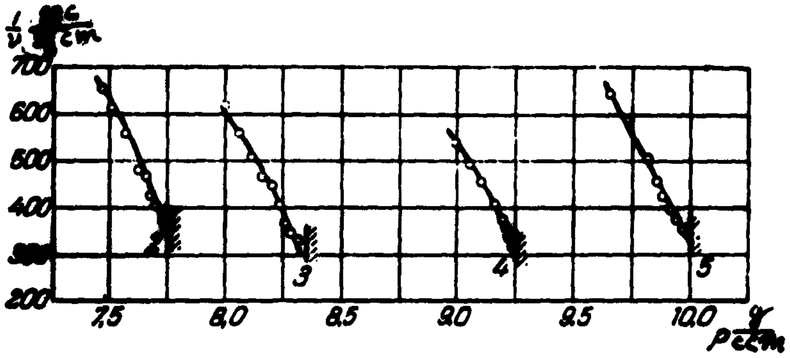

Figure 39. Dependence of $\frac{1}{v}(\rho)$ for tin-lead alloys. The composition of the alloys is listed in Table 10 (the concentration of lead increases with a growing number of alloy). Liquidus lines are represented by vertical shaded straight lines.

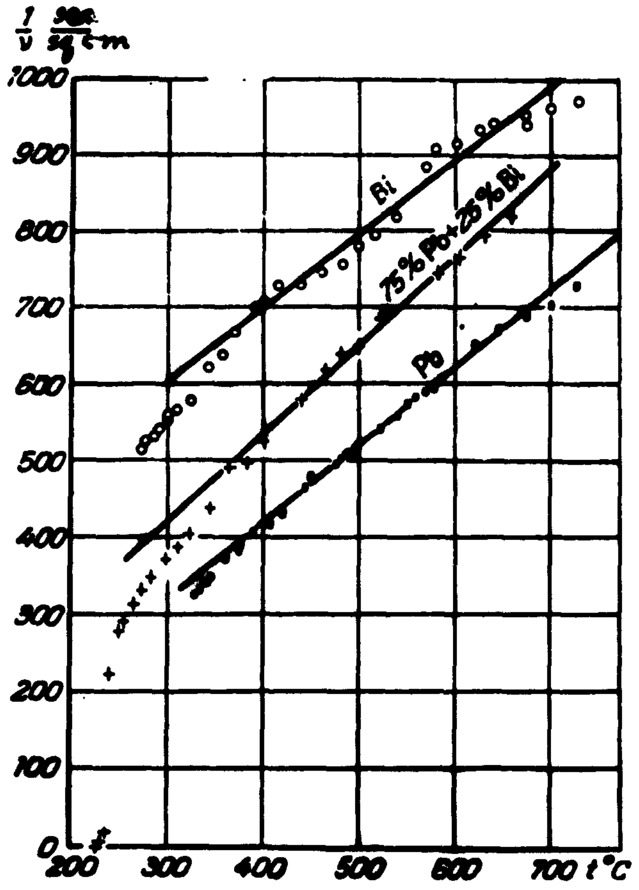

Figure 40. Dependence of $\frac{1}{v}(t)$ for bismuth, lead and a 75% Pb + 25% Bi alloy according to data given in # 8 of Chapter IV.

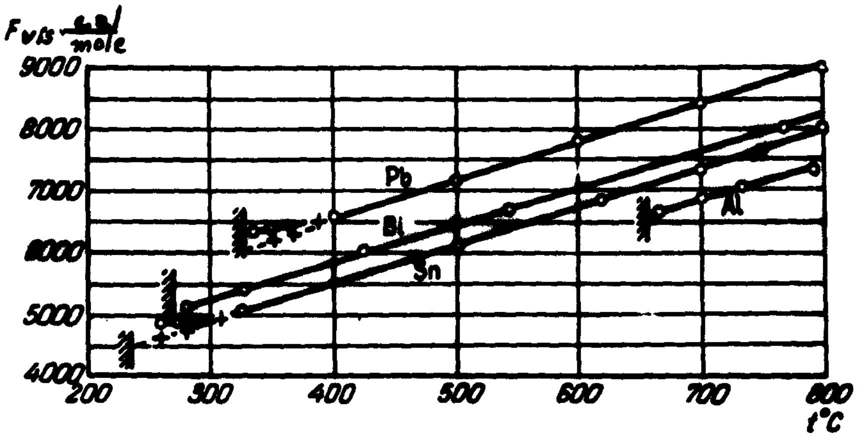

Figure 41. Temperature dependence of the free energy of activation of the viscous flow F_{vis} for lead, bismuth, tin and aluminum. The crystallization point is represented by means of vertical shaded lines.

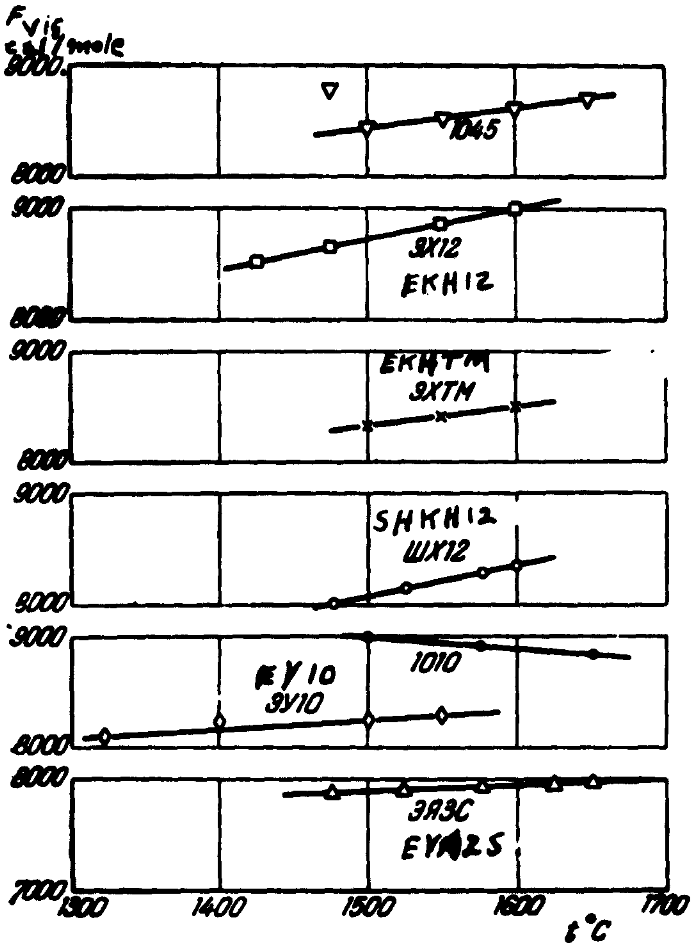

Figure 42. Temperature dependence of the free energy of activation of the viscous flow F_{vis} for steels (the composition is listed in Table 8).

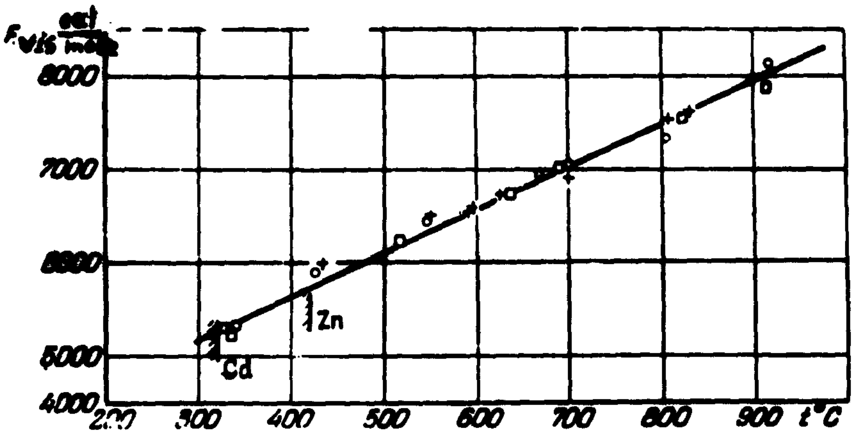

Figure 43. Temperature dependence of the free energy of activation of the viscous flow for cadmium (□) and zinc (+) and (o). The crystallization point is represented by means of vertical shaded lines.

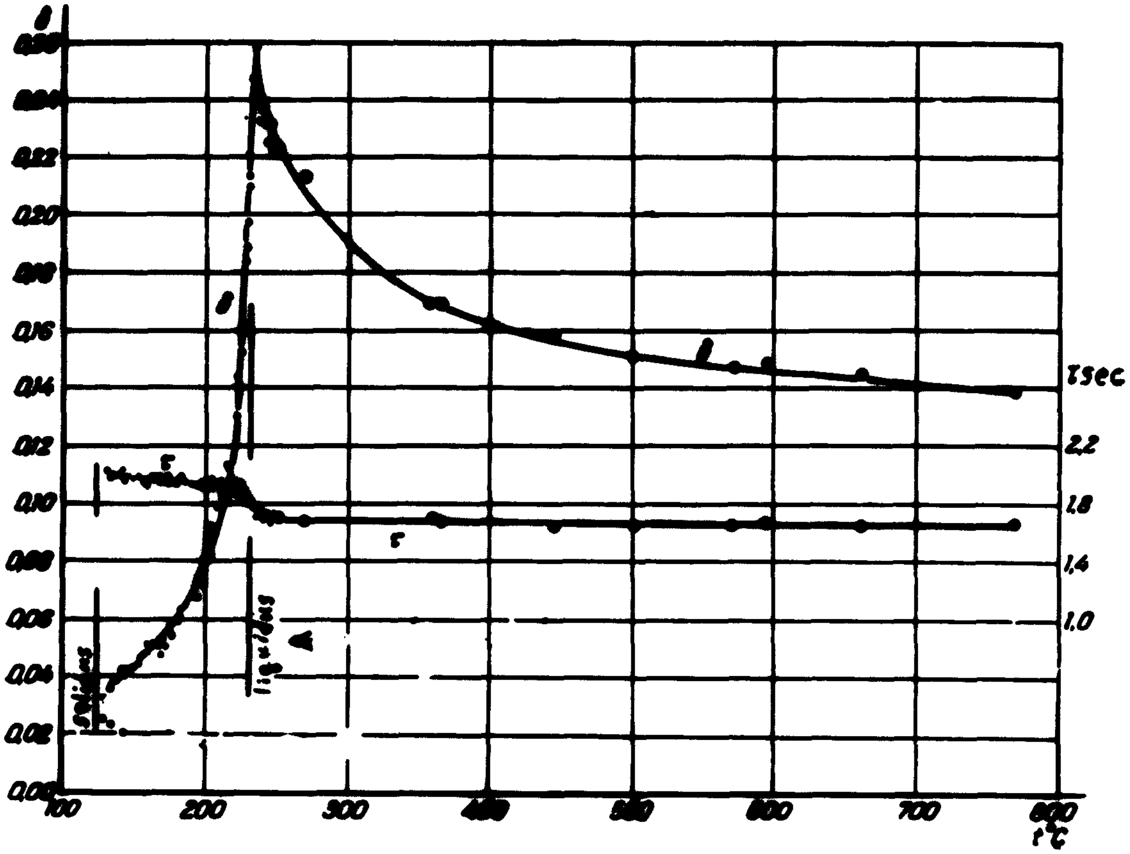

Figure 44. Temperature dependence of the damping decrement and period in a suspension rotary-oscillating viscosimeter, during the study of the viscosity of a 15% Pb + 85% Bi alloy. The solidus and liquidus points (temperatures) are represented by means of vertical lines. The difference in the manner in which points on the curves are represented is due only to their different density of distribution on the line.

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The theory of the torsional oscillation method for measuring the viscosity of liquids and the experimental technical problems associated with the use of the method are examined. Results obtained during the measurement of the viscosity of fused metals and alloys are presented, and a theoretical interpretation is made of certain problems concerned with the nature of the liquid state.

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