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SOME RESULTS OF WORK IN THE FIELD OF HIGH-PRESSURE MEASUREMENTS

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A short review of the present state in the field of high-pressure measurements is provided in [1] and an opinion is expressed about the possible ways of further extending the measurement range on the basis of plotting a thermodynamic pressure scale. Since then a considerable amount of work has been carried out in various directions, and it has contributed appreciably to the development of this field of measurements. It is interesting to sum up this work and discover the extent to which the predictions in [1] have been justified.

Piston-gauge measurements, which form the basis for all other methods of measuring high pressure, have been developed in various respects. The top measuring limit of piston gauges with hydraulic boosters has been raised first to 20000 kg-wt/cm^2 ($\sim 19600 \cdot 10^5$ N/m^2) [2], and then to 25000 kg-wt/cm^2 ($\sim 24500 \cdot 10^5$ N/m^2) [3]. The same limit has been attained by a piston gauge using direct loading without a boosting device, and made at the VNIIM. An apparatus with a gauge measuring up to 20000 kg-wt/cm^2 ($\sim 19600 \cdot 10^5$ N/m^2) has also been produced for comparing two instruments with different piston systems, thus providing experimental investigations of deformation errors in piston gauges up to the above pressure limit.

The problem of deformation errors in piston gauges, which becomes of primary importance at high pressures, has been investigated in two ways.

Numerous experiments were carried out [4-6] for determining these errors up to 10000 kg-wt/cm^2 ($\sim 9800 \cdot 10^5$ N/m^2) and comparing them with theoretical computations [7]. The piston systems used in these experiments were of various types (cylindrical systems with and without counterpressure) and sizes, and were made of different materials.

At first, experiments were carried out at pressures up to 5000-7000 kg-wt/cm^2 (~ 4900-$6900 \cdot 10^5$ N/m^2) [4], and then the pressure was raised to 10000 kg-wt/cm^2 ($\sim 9800 \cdot 10^5$ N/m^2) and the number of piston systems was increased [5]. In [6] deformation errors were evaluated up to pressures of 2500 kg-wt/cm^2 ($\sim 2450 \cdot 10^5$ N/m^2) with a group of piston systems made of materials with widely different elastic constants. In almost all the above experiments the validity of correction formulas was confirmed. Discrepancies were only observed when the initial value of the clearance between the piston and the cylinder (for cylinders with counterpressure) was smaller than the tolerated value, thus making the clearance at high pressures so small that the normal hydrodynamic conditions of flow were disrupted. An increase in the initial clearance in such manometers inevitably led to a reduction of the deformation errors to the computed values.

The second approach to the solution of this problem involved the elimination, or at least the reduction to insignificant values, of the deformation errors in piston manometers. The idea was expressed and substantiated theoretically [8] concerning the production of a piston manometer in which the deformation of the cylinder is of the same value and in the same direction as that of the piston. Under such conditions the size of the clearance between the piston and the cylinder remains constant irrespective of the pressure. This automatically excludes the largest component of the deformation correction due to the deformation of the cylinder. There remains the component due to the deformation of the piston, but it is only a small quantity and the problem is thus solved.

A piston system which meets the above requirements was also suggested in [8]. Such an instrument, which was called a gauge whose effective piston area does not change with pressure, was produced and investigated [9]. The fundamental propositions on which the constancy of the piston's effective area was based were fully confirmed, although a considerable leakage of the liquid through the auxiliary clearance of the piston was discovered. This deficiency has no fundamental significance and can be eliminated by changing the instrument's design.

Thus, the research carried out with piston gauges has led to an extension of their range, experimental confirmation of their computed correction formulas for a substantially larger range of pressures, and to new prospects for a considerable reduction of deformation errors.

In fact, since the publication of [1] the top measuring limit of a gauge with a packless piston has been raised from 15000 kg-wt/cm^2 ($\sim 14700 \cdot 10^5$ N/m^2) to 20000-25000 kg-wt/cm^2 ($\sim 19600\text{-}24500 \cdot 10^5$ N/m^2), the theoretical correction formulas have been confirmed experimentally up to 10000 kg-wt/cm^2 ($\sim 9800 \cdot 10^5$ N/m^2), whereas in preceding works the pressures dealt with did not exceed 2500 kg-wt/cm^2 ($\sim 2450 \cdot 10^5$ N/m^2), and the production of a manometer with an effective piston area "invariable" with pressure provides the possibility of decreasing substantially the deformation errors. It should also be noted that in the theoretical respect the same final result (an expression for the deformation error) was obtained by D. P. Johnson et al. [10] in the National Bureau of Standards for a piston manometer with an adjustable clearance, but it is interesting to note that the fundamental methods for solving the problem were completely different from those used by us.

The successful solution of the enumerated problems was facilitated substantially, as in the previous investigations, by the theory of a packless piston [8] and the experimental data which provided the required relationship between the viscosity of various liquids and pressure up to 15000 kg-wt/cm^2 ($\sim 14700 \cdot 10^5$ N/m^2). Thus, it became possible to apply formulas for computing all the basic parameters in piston systems of gauges over almost the entire required pressure range.

Secondary instruments in the form of resistance pressure-gauges are another means for solving the general problem of measurements at high pressures. Work for perfecting these instruments has been concentrated on improving the design of various transducer components, on developing methods for artificial ageing of resistors and for investigating temperature errors. As the result of this it has become possible to extend the linear relationship range between resistance and pressure and obtain greater stability with time for the readings of these instruments.

The above improvements of the resistance gauge properties provide more favorable conditions for their use as secondary instruments and commercial carriers of the thermodynamic pressure scale. Let us also note that the production of a differential-resistance pressure-gauge [11] suitable for measuring small differences of high pressures has become extremely useful for the experimental investigation of deformation errors in piston gauges.

Work on the problem for establishing a thermodynamic scale at high pressures has been conducted in two independent ways. Let us recall that this scale is based on the method of reproducing pressures by fusing substances under pressure [1]. For implementing the thermodynamic scale in practice [1] a piston gauge should be used for establishing experimentally the relationship between equilibrium values of temperature and pressure in the course of the substance's transition from the solid to the liquid phase. Extrapolation of the thus obtained empirical equation for the fusing curve of a given substance beyond the range of a piston gauge should be based on special investigations. In [1] two methods for substantiating the validity of such an extrapolation are suggested, namely, the method of a manganin pressure-gauge, and that of intersecting curves. Further improvements entailed experimental and theoretical investigation of the fusing process, whose study could be useful for solving the problem of the thermodynamic scale. These two methods, consisting of practical plotting of the scale and a study of the fusing process, were developed in subsequent work.

The operating substance for implementing the thermodynamic scale consisted of mercury, whose fusing curve had been previously [12] studied up to 10000 kg-wt/cm^2 ($\sim 9800 \cdot 10^5$ N/m^2), and the extrapolation technique was substantiated by the manganin pressure-gauge method. At first a thermodynamic pressure scale was plotted in the first approximation up to 20000 kg-wt/cm^2 ($\sim 19600 \cdot 10^5$ N/m^2) [13], and then it was confirmed up to 25000 kg-wt/cm^2 ($\sim 24500 \cdot 10^5$ N/m^2) [14]. The readings of the manganin gauge used in this work were carefully studied by means of a piston gauge first up to 10000 kg-wt/cm^2 ($\sim 9800 \cdot 10^5$ N/m^2) and later up to 15000 kg-wt/cm^2 ($\sim 14700 \cdot 10^5$ N/m^2) [14].

The discrepancies between the extrapolated values of the mercury fusing curve and those of the manganin gauges in the first work attained a maximum of 0.8%, and in the second they were reduced to 0.5%. The latter value was taken for evaluating the reliability of the thermodynamic scale in the first approximation up to 25000 kg-wt/cm^2 ($\sim 24500 \cdot 10^5$ N/m^2). Although these results do not attain the desired limit, they have confirmed the theoretical possibility of implementing the thermodynamic scale. It was shown in [1] that the manganin method is not the best, but it was used because it is the simplest method. Therefore, the results thus obtained should be considered encouraging. The method of interesecting curves can also be used, and new possibilities have become available for implementing the scale from the investigation results of the fusing process.

These results have been found to be very interesting. From fusing curves of various substances based on Bridgeman's extensive experimental data the general pattern of the fusing process was found [15, 16]. By introducing a generalized parameter for this process, the specific fusion energy $\lambda/\Delta V$ (λ is the fusion heat and ΔV is the sudden change in the volume), we find that the relationships of ln $(\lambda/\Delta V)$ to the logarithm of temperature lnT and of $\lambda/\Delta V$ to pressure p are linear functions along the fusing curve. The slope angle of these relationships is numerically equal to constant c of Simon's empirical equation, which is normally used for approximating experimental data by means of fusion curves. Thus, this constant has now been provided with a direct physical meaning.

On the basis of the patterns thus discovered it has become possible to present Simon's equation in a new form, in which the second empirical constant a is replaced by parameter $\lambda_0/\Delta V_0$, i. e. by the specific fusion energy of the given substance at the triple point. The equation of the fusion curve now assumes the form

$$p=\frac{1}{c}\frac{\lambda_0}{\Delta V_0}\left[\left(\frac{T}{T_0}\right)^c-1\right]. \tag{1}$$

One of the coefficient c values which is basically important for plotting the thermodynamic scale is represented as:

$$c=\frac{\ln\left(\frac{\lambda}{\Delta V}\cdot\frac{\Delta V_0}{\lambda_0}\right)}{\ln\frac{T}{T_0}}. \tag{2}$$

It follows from the above relationship that a constant value for c can be determined from experimental data without direct measurements of pressure. It is sufficient to measure the heat of fusion λ, the jump in volume ΔV and temperature T along the fusion curve over a given range. In these experiments it is only necessary to register reliably the pressure balance, which is easily attainable by means of a sensitive indicator. It is then unnecessary to determine the actual values of pressure, which is very important, since we have no reliable means for measuring them.

Thus, it is sufficient to find a constant value for c from (2) in order to use (1) as an analytical expression for the thermodynamic pressure scale over a given range. Direct experimentation will show the extent to which this method is suitable in practice.

Yet another regular feature in the melting process is indicated in [17]. It was found for a large number of substances investigated experimentally by Bridgeman that the ratio of the derivative of the jump in volume with temperature to the jump in volume remains constant along the fusion curve. From the above the following expression for the jump in volume is derived

$$\Delta V=\Delta V_0 e^{-\varkappa(T-T_0)}, \tag{3}$$

where ΔV_0 and T_0 are the jump in volume and temperature at the triple point, T is the existing temperature along the fusion curve, $\varkappa$ is a constant coefficient.

The pattern thus discovered was not only observed in a small number of substances, but even in some of these instances errors in the experimental data were discovered at a later stage.

The combined use of all the above patterns of behavior led to an analytical expression for the basic thermodynamic relationships in the melting process [18]. Expressions were provided for variations in enthalpy, internal energy, entropy and free energy along the fusion curve, as well as relationships for the difference between the compression coefficients of the liquid and solid phases and for the jump in thermal capacity.

Thus, the possibility of establishing a thermodynamic pressure scale and the possible means [1] of attaining this have been confirmed in practice. A first approximation scale has already been established up to 25000 kg-wt/cm^2 ($\sim 24500 \cdot 10^5$ N/m^2), and the investigations of the melting process have provided a more reliable foundation for it and the possibility of its further extension.

We continue to consider that the great practical value and advantage of the thermodynamic method for reproducing pressure and of the scale based on this method consist of the fact that this method possesses great potentialities in solving the problems of measuring not only high hydrostatic pressures, but also ultrahigh pressures in the solid phase.

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