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# A NEW METHOD OF DETERMINING THE TRANSITION PRESSURE OF MERCURY AT 0°C AS A FIXED POINT OF HIGH PRESSURES

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The solid-liquid phase transition pressure of mercury at 0°C as a fixed point of high pressures is determined by a new method, the principle of which is to observe the transition from the change of temperature due to latent heat using thermoelements of semiconductors and to measure the pressure by the direct use of a lever type controlled-clearance piston gage with a large piston lately developed which operates in a state of no leak and no friction.

The value obtained is 7,571.0±1.2 bar (7,720.3±1.2 kgw/cm$^2$). The paper concludes with a brief comparison with the results of other investigations and some words desiring to find an opportunity of the international discussions on these results for establishing an International Practical Scale of High Pressures.

## Introduction

In recent years, it has become very important to measure high pressures up to 10 kb with the best available accuracy in the fields of science and industry. Then it is strongly demanded to realize the practical scale of high pressures identified by the physical phenomena reproducible everywhere like the temperature measurement using fixed points in defining the International Practical Scale.

Experimental observations of the liquid-solid phase transition pressure of pure mercury at 0°C based on this concept have been carried out of late at Harwood Engineering Co., Inc.,[1] the National Bureau of Standard in U.S.A.[2] and the National Physical Laboratory in U.K.[3] Of course, it is a well-known fact that P.W. Bridgman was a pioneer of those observations.

But, as to the results, it is regrettable to be unable to find out a good coincidence between their values. The object of this work is, therefore, to determine a value of the same phenomenon by a new method quite different from those tried hitherto. The following are two principal points of the new method :

To observe the phase transition phenomenon by measuring temperature changes due to latent heat with thermoelements of semiconductors.

To measure the equilibrium pressures directly in terms of a lever type controlled-clearance piston gage with a large piston newly devised which operates in a state of no leak and no friction.

The experiments reported in this paper were all carried out at the Laboratory of High Pressures

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1) D. H. Newhall, L. H. Abbot and R. A. Dunn, "High-pressure Measurement," pp. 339 (1963)
2) Technical Highlights of the N. B. S., pp. 33 (1962), pp. 38 (1963)
3) R. S. Dadson and R. G. P. Greig, *British J. Appl. Phys.*, 16, 1711 (1965)

in Kobe Steel, Ltd.

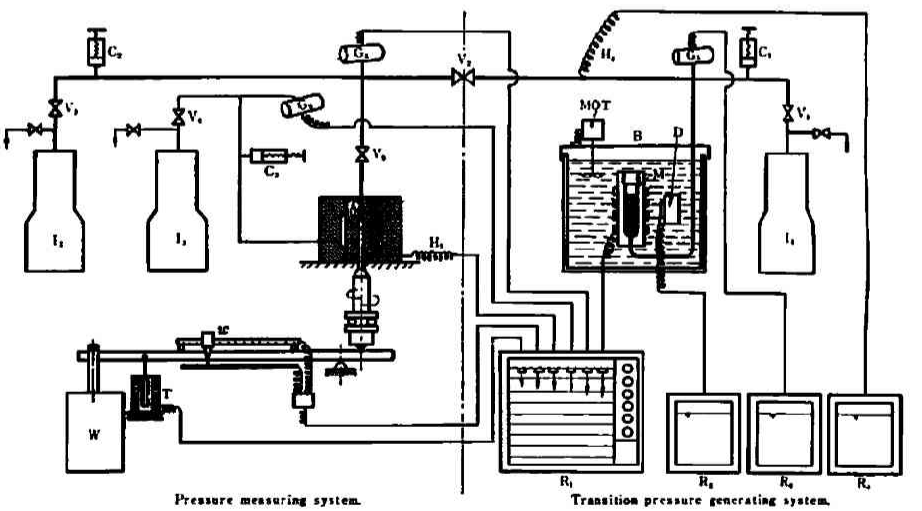
## Apparatus

### General

The general arrangement of the apparatus designed and manufactured in Kobe Steel, Ltd. is shown in Fig. 1. It was composed of the transition pressure generating system and the pressure measuring system which were separated by a stop valve ($V_2$) in order to put them in perfect good condition independently at the same time. The pressure in each system was generated by an intensifier capable of producing steady pressures up to 10,000 bar which was automatically driven by a low oil pressure unit of 140 bar and 400 watt. The pressure transmitting fluid used was glycerine water of 50 : 50%. All the stop valves were constructed so as to act instantaneously at the required moment by the application of low oil pressures. The pressure gages used were of the wire or semiconductor strain transducer type developed in Kobe Steel, Ltd[7]. The laboratory room was equipped for keeping constant ambient temperature at any degree over the range 0~30±1.5°C. All the values of measurements were automatically recorded by means of the electronic recorders of the input, 10 mV, to avoid errors on the part of the observers.

### Transition pressure generating system

This system was composed of a mercury container, a latent heat detecting device, a constant temperature bath and a volume change regulator ($C_1$). As shown in Fig. 2, the mercury container made of




| | | | | | |
|---|---|---|---|---|---|
| A | Piston cylinder assemblies of lever type controlled-clearance piston gage. | $G_1$,$G_2$ | Wire strain transducer type pressure gages. | T | Differential transformer. |
| B | Ice bath. | $I_1$,$I_2$,$I_3$ | Pressure intensifiers. | $H_1$,$H_2$ | Thermocouples for measuring piston & tube temperature. |
| $C_1$,$C_2$,$C_3$ | Volume control regulators. | M | Pressure vessel & mercury container. | $V_1$~$V_6$ | Stop valves. |
| D | Measuring device of temperature. | $R_1$ | 6 pen electronic recorder. | W | Dead weights. |
| $G_3$ | Semiconductor strain transducer type pressure gage. | $R_2$,$R_3$,$R_4$ | Single pen electronic recorders. | m | Small adjustable weight. |

Fig. 1 General arrangement

7) K. Yasunami, Japanese Patent 294153 (1961)

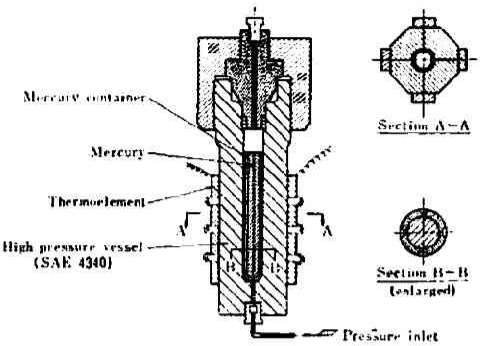



Fig. 2 Details of pressure vessel and mercury container

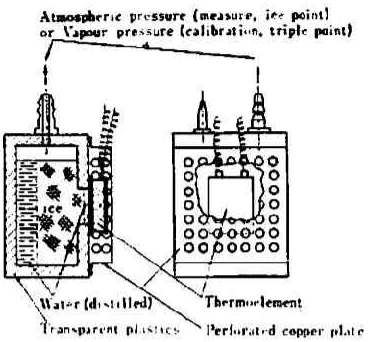



Fig. 3 Details of a measuring device of ice bath tempreature

18–8 stainless steel with grooves at the outer surface forming a path of glycerine water was inserted in a pressure vessel, the outer surface of which was machined in octagonal form. The container, 12.5 mm in inner dia. and 125 mm in depth, was filled with about 11 cc of mercury purified at the National Research Laboratory of Metrology.

The thermoelements of semiconductors ($Bi_2Te_3$) made in Hayakawa Electric Co., Ltd. for detecting latent heat were stuck on the outer surface of the pressure vessel. As seen in Figs. 1 and 2, 16 pieces of thermoelements were used in series connection and their total output due to the temperature changes were measured by a microvoltmeter of $1\mu V \sim 1{,}000\,mV$ with 20 stages and 6 pen electronic recorder. One piece of the thermoelements was composed of 8 pairs of *p*- and *n*- semiconductors having the power of about $400\,\mu V/deg/pair$. Therefore, the ratio of an increase of observation capacity has attained to 1,000 times and more in comparison with the ordinary method using thermocouples. This was a key to lead the experiment to a success under the favorable conditions of easy observation and good accuracy. As to the constant temperature bath, an adopted construction was nearly the same with that reported by D. H. Newhall *et al*[1]. The temperature of the bath filled with natural ice and water was always measured during the observation in terms of a new D. T. A. method using the same thermoelements as the values of difference from the ice point. The device having a piece of thermoelements of 16 pairs shown in Fig. 3, was filled with pure ice and water. A volume control regulator ($C_1$) had the capacity to change the volume up to 0.45 cc with 7.25 revolutions in maximum of a handle balanced by the low oil pressure for the purpose of light handling.

**Pressure Measuring System**

The construction of the lever type controlled-clearance piston gage used in this experiment was simply shown in Fig. 1, as a diagrammatic pattern in which the main design data were as follows:

Piston: (5% Co–WC) dia. 11.29 mm area 1 $cm^2$

Inner cylinder: (SAE 4340 HB 400) outer dia. 35 mm

Lever arm: total length 2,500 mm, arm ratio 20, period of free oscillation 17 sec

Loading mechanism: adjustable minimum weight equivalent to 0.1 $kg/cm^2$

Rotation of piston: 0~60 r. p. m. in both direction

Temperature at effective area position: always measurable

Measurable pressure range: 0~10,000 $kg/cm^2$

The determining method of effective area, the external pressure realizing a condition of no leak and no friction, the calibration method of temperature at effective area position, and other theoretical or experimental results of the gage were fully reported in Kobe Steel Engineering Reports Vol. 16, No. 2, April 1966. Accordingly, the main points being developed after the report and having a significant relation to this experiment will be described below.

New piston-cylinder assemblies were prepared for the present observation. The material of the inner cylinder was changed to 18% Ni maraging steel under consideration of strength and durability. The diameter of the piston measured at Osaka Branch of the National Research Laboratory of Metrology was $11.3080 \pm 5 \times 10^{-4}$ mm and a tolal uncertainty in the pressure value measured by this gage was determined within the limits $\pm 1$ kg/cm$^2$, in the region of 7,500 bar after careful considerations to the several corrections obtained theoretically or experimentally.

## Preliminary Test

Before the experiment, a series of preliminary tests was carried out in order to verify the function of the whole apparatus, to obtain some fundamental data necessary for the observations, and to pick out a better procedure. The following were the important results and conclusions: described item by item.

- The pressures to get an initial freezing were about 8,000~8,500 bar on a pressure gage of wire strain transducer type.
- The temperature changes due to heat of compression or expansion and latent heat were easily differentiated in an inspection to the curves recorded on the 6 pen recorder by the thermoelements.
- Total revolutions of the handle of V. C. R. ($C_1$) required to finish freezing or melting of the whole mercury were 5.8, and one revolution of it at the ordinary speed of man handling caused a voltage change of the thermoelements, about 270 $\mu$V at the reading of the 6 pen recorder when glycerine water was shut up between ($V_1$) and ($V_2$) in Fig. 1.
- From the above results, an example of which was seen in Fig. 4, the procedure to set up the experimental condition at any ratio of liquid-solid mercury was easily determined. Fig. 4′ was drawn with the pressure and volume relation to help a better understanding of the pressure and time record in Fig. 4.
- No leak is the most important condition in these experiments. When the apparatus was left with the transition pressure for one night, it was found out that the thermoelements could detect such a small amount of leak as impossible to be caught by an ordinary method. The locus of a pen moved by the thermoelements was shifted from the equilibrium zero line at a constant distance depending on the amount of leak.
- The temperature changes of the room in such range as $\pm 1.5$ deg had also some influences on the movement of the pen. It was proved in checking up the temperature record at the pipe ($H_2$) in Fig. 1 with the record of the thermoelements, that this influence was caused by the

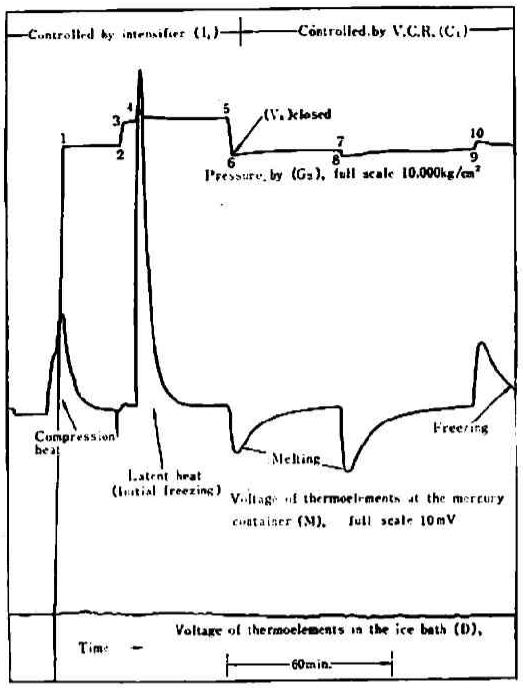



Fig. 4 A preliminary test example

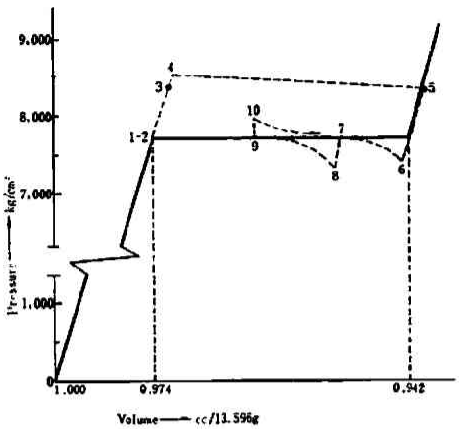



Fig. 4′ An imagined diagram of $P$–$V$ relation corresponding to Fig. 4

expansion or contraction of glocerine water in the pipe line excluding a part in the ice box. Of course, the amount of the influence depended rather on the temperature change rate. For example, 0.17deg/min corresponded to 4 $\mu$V of the thermoelements.

- On the other tests it was also proved that an amount of difference from the transition pressure. 1kg/cm² was equivalent to the voltage change of about 7 $\mu$V of the thermoelements.
- In view of this fact, the final observation should be carried out at a minimum rate of room temperature change, so that the use of the room temperature regulator was given up. Weather and time to make observations was rather chosen.
- Before and after the test, the device measuring temperature of the ice bath was calibrated in another bath with the ice point and the triple point of water defined internationally. The result was 5 $\mu$V for 0.001 deg.

## Final Experimental and Results

The following was a typical procedure adopted for the final observations.

- Prepared the ice bath. the bath temperature measuring devices, and instruments. Left them for several hours until temperature reached a stable state.
- Set the range of the microvoltmeter for the thermoelements at 10mV and with stop valves ($V_3$) and ($V_5$) closed, glycerine water was pumped into the mercury vessel and pipe lines building up pressure about 7,500 bar, the pressure of which was kept for 20 minutes and more until the compression heat vanished away.

- Increased again the pressure as slowly as possible until the pen of the thermoelements moved suddenly indicating the initiation of mercury freezing.
- About 30 minutes later, decreased the pressure to about 7.600 bar and closed the stop valve ($V_1$), then awaited the disappearance of latent heat watching the return of the pen to zero line.
- Changed the microvoltmeter range of the thermoelements to 1mV. Found out a handle position of V. C. R. corresponding to the end point of the transition by means of observations of the relation between the revolution of V. C. R. and the resultant voltage of the thermoelements.
- From this position, withdrew the V. C. R. handle at 2.9 revolutions. Thus the equilibrium state of one-half solid mercury was realized.
- Changed the microvoltmeter range of the thermoelements to 250 $\mu$V. Left them as they were for one night recording the voltage of the thermoelements and the temperature at the surface of the pipe ($H_2$) in Fig. 1.
- After the confirmation of no leak at the valves, connections, packings, and others, inspecting the above record, closed the valve ($V_2$), then opened ($V_3$) and ($V_5$).
- After bringing the thermocouple circuit ($H_1$) in the piston gage apparatus in operation, loaded the piston gage as equally as possible to the transition pressure obtained roughly by the preliminary test and brought it in operation.
- Opened the valve ($V_2$) and observed the balance of pressure and weights in a condition of no leak and no friction when the lever arm stood still to a level.
- Adjusted the small weight (w) to get a final balance in which two pens of the thermoelements and the lever arm wrote respectively locus lines in keeping with each zero line, as seen in Fig. 5, thus the final observations were accomplished.
- Temperature of the ice bath during the observations was kept within the range +0.001 ± 0.001°C.

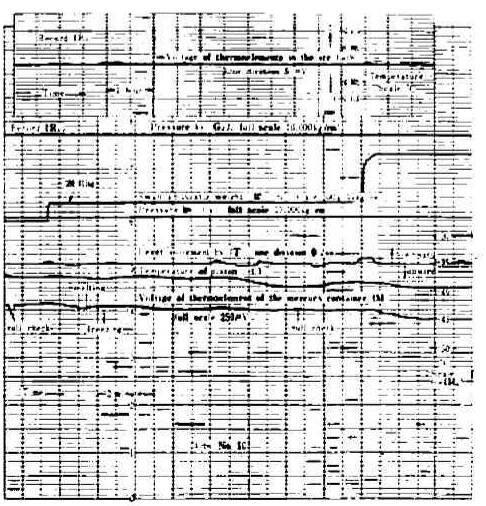


Fig. 5 An example of the records at the final balance

Table 1 Final values of observations

| Obs. No. | Weights finally bal. kg | Temperature of piston °C | Pressure after corrections kg/cm² | Details of corrections |
|---|---|---|---|---|
| 1 | 388.005 | 36.5 | 7727.1 | Distortion of piston, Air buoyancy on the weights, Arm ratio, Height of glycerine water, Cork-screw effect, Thermal expansion of effective piston area, Temp. of ice bath. |
| 2 | 387.997 | 38.5 | 7726.8 | |
| 3 | 387.990 | 40.0 | 7726.5 | |
| 4 | 388.005 | 42.5 | 7726.7 | |
| 5 | 387.990 | 36.0 | 7726.8 | |
| 6 | 388.000 | 39.0 | 7726.8 | |
| 7 | 387.975 | 36.0 | 7726.5 | |
| 8 | 387.985 | 39.0 | 7726.5 | |
| 9 | 387.995 | 40.5 | 7726.5 | |
| 10 | 388.015 | 39.0 | 7727.1 | |
| 11 | 388.015 | 42.5 | 7726.9 | |
| 12 | 388.020 | 42.5 | 7727.0 | |
| 13 | 388.020 | 42.5 | 7727.0 | |
| 14 | 388.020 | 42.5 | 7727.0 | |
| 15 | 388.025 | 43.0 | 7727.0 | |
| 16 | 388.000 | 40.0 | 7726.7 | |
| Mean | 338.004 | | 7726.8 | |
| standard deviation | ±0.014 | | ±0.2 | |

The results indicated as the values of gage pressure at Kobe are given in Table 1 in unit kg/cm² where kg is local weight. These values were obtained from the final balanced weights after all corrections due to the whole apparatus, excluding a correction for gravity and adjustment to the absolute pressure. An observation value of acceleration of gravity at Kobe by Kyoto University was 979.710 cm/sec² and the atmospheric pressure measured during the observations was within the range 1020 ±5 mbar.

A standard deviation of the observed values was about 0.2 kg/cm² which corresponds to an uncertainty of them of ±0.6 kg/cm² or to an uncertainty of the mean observed value of 0.15 kg/cm² on the basis of 99.7% confidence limits. The former may be taken to estimate a total uncertainty. In addition to it, an uncertainty on the same basis of ±1.0 kg/cm² due to the piston gage and of ±0.2 kg/cm² due to the ice bath must be taken in to account. With the integration of corrections and considerations stated above, the final value of the mercury transition pressure at 0°C and its uncertainty were determined as follows.

$$7{,}720.3 \pm 1.2\ \mathrm{kgw/cm^2}$$

$$7{,}571.0 \pm 1.2\ \mathrm{bar}$$

To discuss these results, comparison with the important results published in recent years for the same purpose was made in Table 2 and Fig. 6. Three values of pressure seen in this table are in agreement with each other with accuracy of $10^{-3}$. But there are small differences between them with accuracy

Table 2 Comparison with former experiments

| Year | (1) 1962 | (3) 1965 | (this paper) 1967 | Other results bar |
|---|---|---|---|---|
| Author | Newhall, Abbot and Dunn | Dadson and Greig | Yasunami | |
| Place | Harwood Engineering Co., Inc. | National Physical Laboratory | Kobe Steel Ltd. | |
| Observation of transition | Volume changes | Electrical resistance changes | Temp. changes due to latent heat | 1909 Bridgman 7,581 [4] |
| Method of temperature measurement | | Pt resistance | Differential thermal method by thermoelements | 1912 Bridgman 7,492 [4]<br>1953 Johnson & Newhall 7,568 ±52 [5] |
| Piston size of piston gage | 2.87mm 0.0645cm² | 2.87mm 0.0645cm² | 11.29mm 1.00cm² | 1959 Zhokhovskii 7,568 $^{+6}_{-30}$ [6] |
| Determination of effective area | Theoretical and experimental based on dimensions of piston and cylinder | Experimental based on similarity method | Theoretical based on dimension of piston only | 1962 Dadson & Greig (Provisional) 7,573.7 [1] |
| Pressure measuring state | Dynamic | Dynamic | Static | 1963 N.B.S. 7,565.1±2 [2] |
| Temperature of piston | Estimation | | always measured | |
| Result bar | 7,565.4±3.7 | 7,569.2±1.2 (95% confidence limits) | 7,571.0±1.2 (99.7% confidence limits) | |

of $10^{-4}$ which are significant for science and industry. They are considered to be mainly ascribed to the apparatus and procedures of observations. Nevertheless, the value of N. P. L. is in good agreement with the result of this work. For the reason that both methods are quite different to each other, it may be difficult to conclude this agreement as a mere chance.

## Conclusion

The observations of the transition pressure of mercury at 0°C have been carried out by a new method and have yielded a value with expected accuracy. The new method of detecting the transition phenomenon by measuring temperature changes due to latent heat using the thermoelements of semiconductors and of determining the transition pressure by the large piston gage in a state of no leak and no friction, proved very successful and showed the advantages of easy measuring with good

4) P. W. Bridgman, "Collected Experimental Papers, 1", pp. 391, 432 (1964)
5) D. P. Johnson and D. H. Newhall, *Trans. A.S.M.E.* 75, 301 (1953)
6) M. K. Zhokhovskii, V. N. Razuminkhin, E. V. Zolotykh and L. L. Burova, *Izmerit. Tekh.*, **11**, 26 (1959)

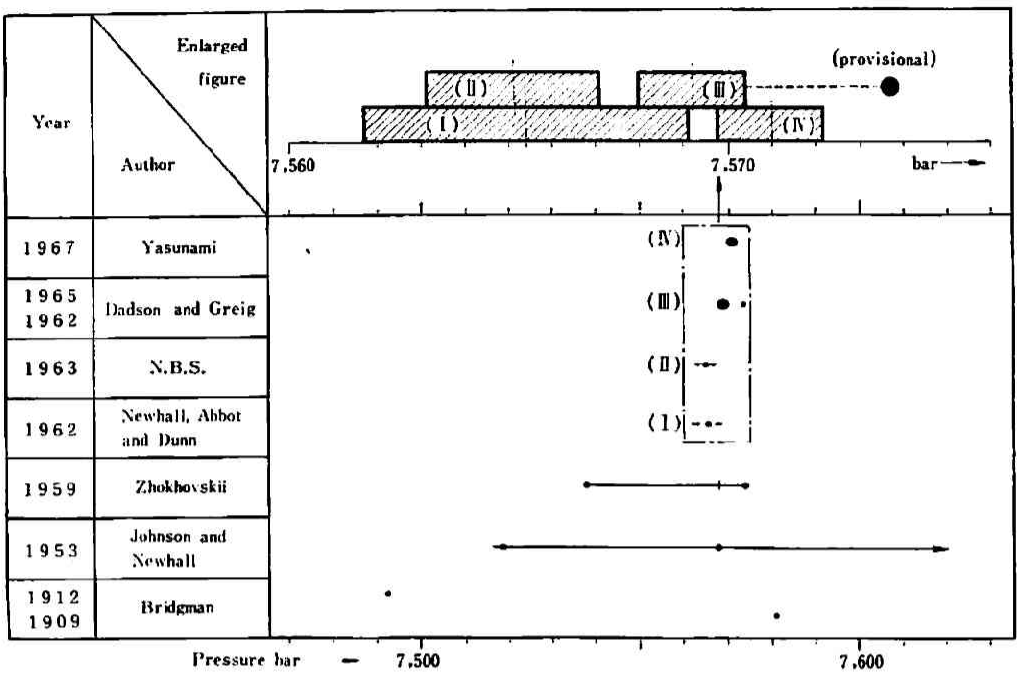



Fig. 6 Historical value of the transition pressure of Hg at 0°C

accuracy and easy controlling to generate an equilibrium state with no procession of the transition. And further, it was discovered that the transition pressure generating apparatus is available as a good detector against very slight leak.

As to the value obtained, it is desirable that an international discussion will be given in the near future together with the former values seen in Table 2 and others for the purpose of making preparations for establishing the International Fixed Points of Pressures like those of temperature.

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