Int J Thermophys (2008) 29:861–870
DOI 10.1007/s10765-008-0408-y

Development of Fixed-Point Cells at the SMU

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Published online: 18 March 2008

Abstract One of the research programs realized at the thermometry laboratory of the Slovak Institute of Metrology (SMU) in recent years has focused on the development of fixed-point cells. In the frame of this research, several primary cells for realization of the International Temperature Scale of 1990 (ITS-90) and several secondary cells for industrial thermometer calibrations were built and studied. This article discusses primary cells for the gallium and mercury fixed points and miniature cells for the zinc point that were developed at the SMU. Information about the cell designs is provided, the materials that were used are specified, and the procedures for their manufacture are described. Briefly, the realization of the fixed points of mercury, gallium, and zinc by using these cells is also described. Many experiments were carried out to study the characteristics of these cells. One of the gallium cells was compared with the circulating transfer cell during the key comparison CCT-K3, and it and the mercury cell were used for the EUROMET Project No. 552. The results of the experiments together with the results of the comparisons show the high quality of these cells. Secondary zinc-point cells were compared against SMU primary zinc-point cells. The comparison shows agreement within 0.12 mK.

Keywords Calibration · Fixed points · SPRT

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1 Introduction

Although a wide range of primary fixed-point cells for realization of the International Temperature Scale of 1990 (ITS-90) and also secondary fixed-point cells for the calibration of industrial thermometers are commercially available, many thermometry laboratories develop, build, and use their own cells. In addition to the economic benefit to these laboratories, this approach is worthwhile for thermal metrology in general. Diversity of the cells involved in intercomparisons minimizes possible systematic errors related to specific designs, materials, manufacturers, etc.

All these reasons were taken into account when the manufacture of fixed-point cells was launched at Slovak Institute of Metrology (SMU). As this article is meant to be rather brief, it is not possible to discuss all the fixed-point cells built at SMU in recent years. We have chosen to focus on the gallium and mercury cells, because they were involved in key comparisons, and miniature zinc-point cells, because they are the newest cells built at the SMU.

2 Primary Fixed-Point Cells Built at SMU

2.1 Gallium Fixed-Point Cells

Gallium fixed-point cells built at SMU are designed for the calibration of long-stem SPRTs. The thermally controlled enclosure for realization of the phase transition is a stirred liquid bath. A drawing of the cell is presented in Fig. 1. The total length of the cell is 360 mm. Its outside diameter is 50 mm (upper part) and 40 mm (bottom part of the cell). The inner diameter of the thermometer well is 8 mm. High-purity gallium (99.999 99%) is contained within the crucible which is accommodated in the outer case. The lid to which the thermometer well is attached is screwed into the crucible. The head of the cell with the gas inlet is fixed to the top of the outer case. The crucible was designed with several ribs to permit the thermal expansion of gallium on freezing. High-purity argon, which is periodically pumped out and replaced, fills the space within the outer case that is not occupied by the crucible. When the cell is not in use, the head of the cell is covered by a cap. All components of the cell (i.e., crucible, outer case, lid with thermometer well, and the head of the cell with cap) are made from virgin Teflon supplied by Mikro-Technik GmbH & Co. (Germany). High-purity gallium was supplied by the Slovak producer CMK Ltd.—The Gallium Arsenide Company. The impurity concentrations determined by glow-discharge mass spectrometry (provided by the supplier) are presented in Table 1.

All Teflon parts that are in direct contact with gallium undergo a cleaning procedure consisting of washing with detergent, rinsing and ultrasonic washing with distilled water, washing with dilute aqua regia, rinsing with vapor from doubly-distilled water, followed by heating in an argon atmosphere. The filling of the crucible with gallium and the assembly of the cells were performed under an argon atmosphere inside a glove box.

Fig. 1 Gallium fixed-point cell

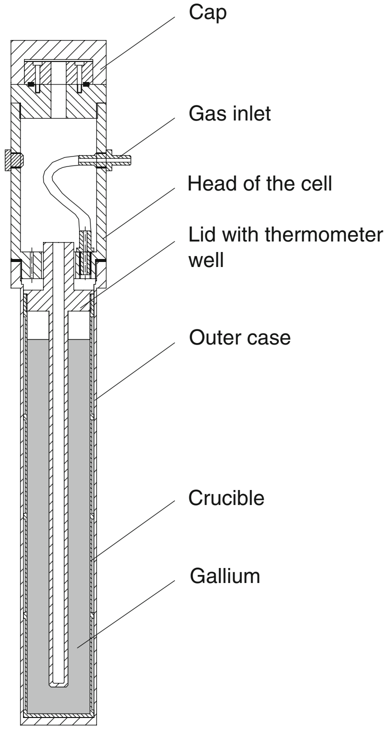

Table 1 Impurity content of the gallium (ppb mass)

Li	<0.1	K	<3	Si	0.7	Ni	<0.2	In	<0.3	Ce	<20	Bi	<0.15
Be	<0.1	Ca	<0.4	P	<0.3	Cu	<0.5	Sn	<2	Hf	<0.15	Th	<0.04
B	1	Sc	<0.03	S	<0.3	Zn	<0.6	Sb	<0.6	W	<0.3	U	<0.06
O	850	Ti	<0.1	Cl	1	Zr	<0.6	Te	<0.8	Pt	0.5		
F	<4	V	<0.04	Ge	<10	Nb	<0.07	I	<0.05	Au	<4		
Na	0.6	Cr	<0.3	As	<0.5	Mo	<0.5	Cs	<0.06	Hg	<2		
Mg	<0.2	Mn	<0.1	Se	<3	Ag	<30	Ba	<1	Tl	<0.1		
Al	0.8	Fe	1	Co	<0.05	Cd	<2	La	<0.1	Pb	<0.2		

2.1.1 Realization of Gallium Melting Point

To prepare the cell for realization of the melting point, it is necessary to assure the freezing of all gallium in the cell. The influence of the freezing technique on the gallium phase transition temperature was studied [1], and no significant temperature difference was found when applying various freezing techniques for gallium of purity ≥99.999 995%. Because some of our gallium fixed-point cells are frequently used and they may become contaminated over time, we prefer to freeze them from the inside outward by using an immersion cooler.

When the gallium is completely solidified, the cell is kept in a refrigerator overnight, and we usually start the gallium-point realization the next morning. To start the

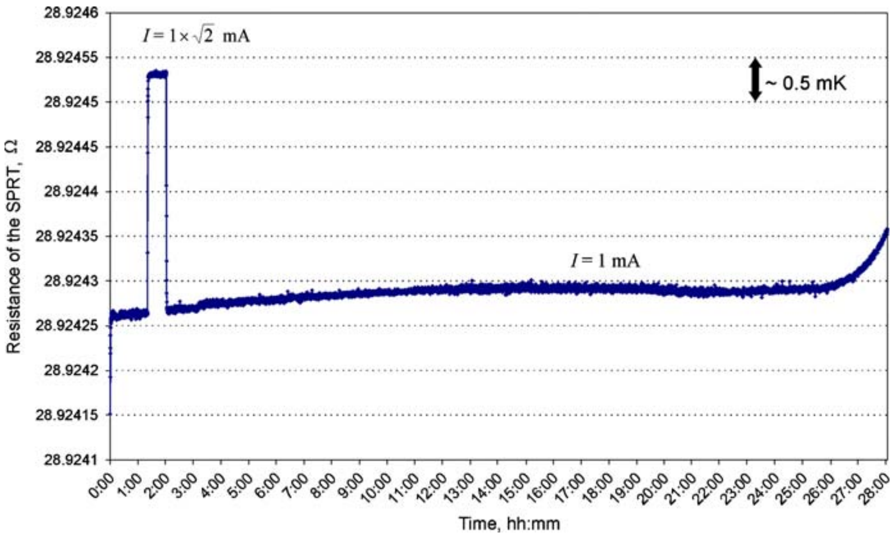

Fig. 2 Typical melting plateau realized with cell Ga-B

formation of the outer liquid–solid interface, the cell is placed in a water bath at a temperature of about 40°C for 30 min. Then, it is moved to a temperature-controlled liquid bath at 31°C. To start the development of the inner solid–liquid interface (along the thermometer well), an immersion heater is inserted into the thermometer well. The thermometer well is then filled by water from the thermostatted bath to improve the thermal contact between the cell and the SPRT, and the SPRT is inserted into the thermometer well. The temperature of the bath is then set to 30.2°C (about 0.5°C above the gallium melting-point temperature).

Many experiments were performed to study these cells. The shapes and durations of melting plateaux obtained with these cells are very similar. The temperature remains within 0.33 mK for about 25 h. A typical melting plateau obtained from one of these cells (cell Ga-B) is presented in Fig. 2. Cell Ga-B was involved in the key comparisons CCT-K3 and EUROMET Project No. 552. The difference $T_{\mathrm{GaSMU}} - T_{\mathrm{ref552}} = -0.13$ mK and its associated expanded uncertainty is $U_{(T_{\mathrm{GaSMU}}-T_{\mathrm{ref552}})}(k = 2) = 0.51$ mK. The typical uncertainty budget when calibrating an SPRT using the gallium cell Ga-B is presented in Table 2. Cell Ga-B is included in the national temperature standard.

2.2 Mercury-Point Cells

Up to now, three mercury-point cells (Hg10, Hg11, and Hg12) of the same design have been built at the SMU. The cells are also designed for the calibration of long-stem SPRTs and, as in case of the gallium cells, they are designed to be placed in a thermally controlled liquid bath. A schematic of the mercury cells is shown in Fig. 3. Each cell contains 1.3 kg of mercury. The total length of the cell is 335 mm, and its outside

Table 2 Uncertainty budget for the calibration of an SPRT using the gallium fixed-point cell Ga-B

Components	Uncertainty contribution (mK)
Purity	0.010
Hydrostatic head correction	0.006
Perturbing heat exchanges	0.025
Self-heating correction	0.020
Bridge linearity	0.050
Gas pressure	0.002
R_{SPRT} scatter	0.036
Combined uncertainty	0.070
Expanded uncertainty ($k = 2$)	0.140

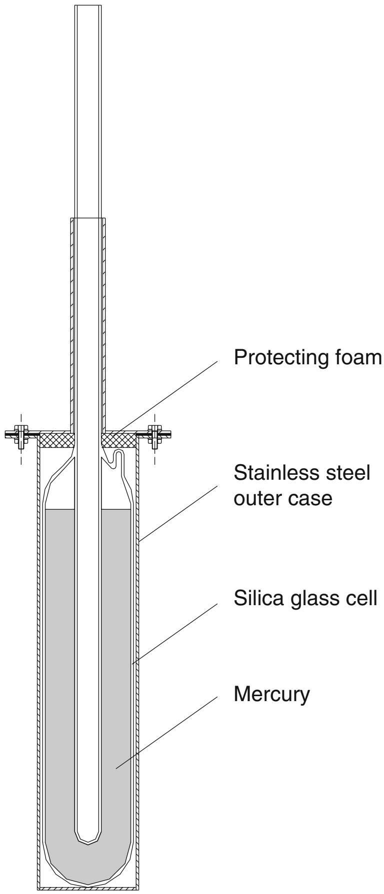

Fig. 3 Mercury fixed-point cell

diameter is 38 mm. The inner diameter of the thermometer well is 8 mm. High-purity mercury (99.999 99%) is sealed into a pre-cleaned silica glass cell. For safety reasons, the glass cell is placed into a stainless-steel case to avoid the spilling of mercury if the glass cell is broken. The stainless-steel case also helps to homogenize the temperature field around the cell. Uncertainty budget when calibrating an SPRT using the mercury fixed-point cell Hg10 is presented in Table 3.

Table 3 Uncertainty budget for the calibration of an SPRT using the mercury fixed-point cell Hg10

Components	Uncertainty contribution (mK)
Purity	0.025
Hydrostatic head correction	0.040
Perturbing heat exchanges	0.100
Self-heating correction	0.030
Bridge linearity	0.050
Gas pressure	0.040
R_{SPRT} scatter	0.081
Combined uncertainty	0.015
Expanded uncertainty ($k = 2$)	0.300

2.2.1 Realization of the Triple Point of Mercury

The first step when realizing the triple point of mercury is to freeze the sample. After the sealing of the cell, we performed several experiments to see the effect of the freezing technique on the temperature of the mercury triple point. No influence was found, but for the same reasons as with the gallium, we freeze the cells by means of an immersion cooler from the inside outward. The frozen cell is kept overnight in a liquid bath at a temperature of −42°C. The next morning, the temperature of the bath is set to −38°C. To create the inner liquid–solid interface, we insert two ceramic rods (each for 2 min) at ambient temperature into the thermometer well. The SPRT is withdrawn from the cell and kept for 4 min at ambient temperature. When it is inserted back into the thermometer well, it works as a third rod. After inserting the SPRT, the thermometer well is filled with alcohol from the bath.

Cells Hg10, Hg11, and Hg12 provide very similar plateaux (Fig. 4). Their duration is about 5 h within 0.3 mK. Results of an immersion test are shown in Fig. 5. Cell Hg10 was used for the key comparison EUROMET Project No. 552. The difference from the reference value was found to be $T_{\mathrm{HgSMU}} - T_{\mathrm{ref552}} = 0.16\,\mathrm{mK}$ with an associated expanded uncertainty of $U_{(T_{\mathrm{THgSMU}} - T_{\mathrm{ref552}})}(k = 2) = 0.84\,\mathrm{mK}$. This cell is included in the national temperature standard.

3 Secondary Fixed-Point Cells

Conventional defining fixed-point cells used for the calibration of long-stem SPRTs according to the ITS-90 are not, for practical and economic reasons, considered suitable for the calibration of industrial thermometers [2].

To improve the effectiveness of calibrations when the required uncertainty is lower than the uncertainty obtainable by comparison calibration, SMU began the development of miniature fixed-point cells. Two permanently sealed miniature cells for the zinc point (Zn04/01 and Zn04/02) were built as the first examples. A schematic view of the SMU zinc miniature cell is shown in Fig. 6. The total length of the cell is 200 mm, and its outside diameter is 41.2 mm. The crucible and crucible cap with the thermometer well are made of a higher-density graphite of spectroscopic-grade purity by the company Elektrokarbon a.s. (Slovak Republic). The crucible cap with

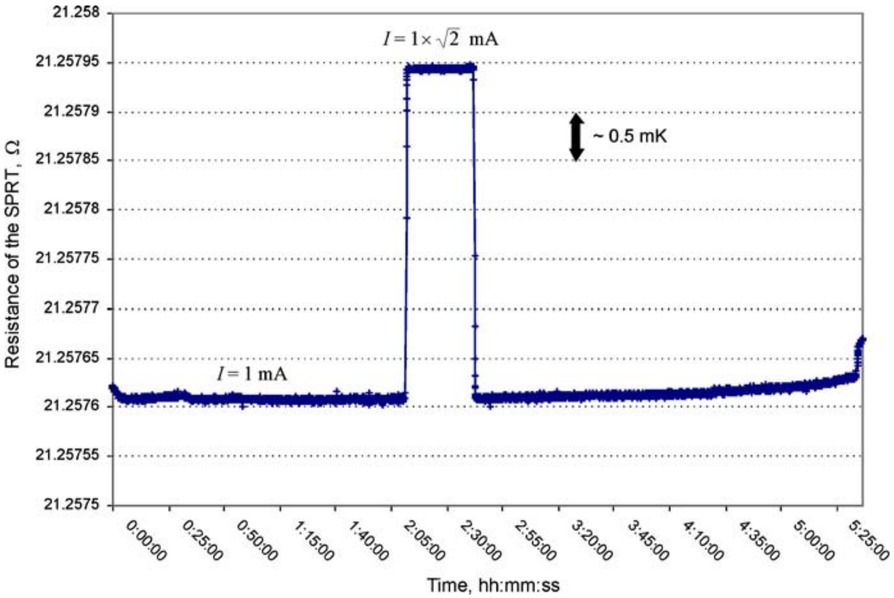

Fig. 4 Typical melting plateau realized with cell Hg12

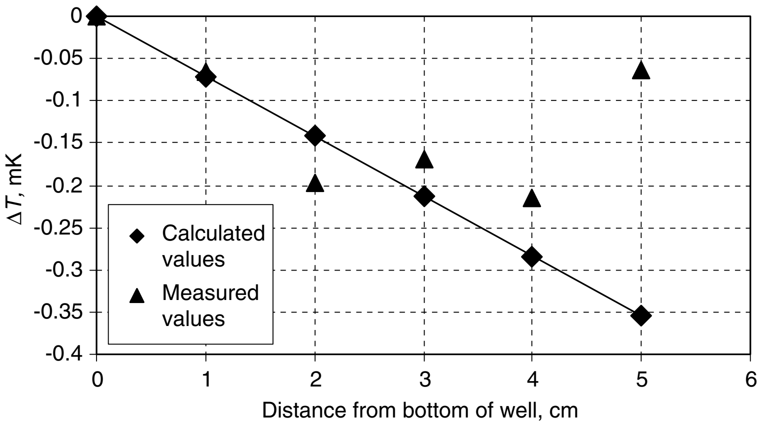

Fig. 5 Immersion profile in the Hg-point cell

the thermometer well is screwed into the crucible. Zinc of 6N purity was supplied by VUK—Ciste kovy a.s. (Czech Republic). It was obtained in granular form. The graphite crucible is surrounded by a silica glass envelope filled with a protecting atmosphere of pure argon. Uncertainty budget for thhe calibration of an SPRT using the miniature zinc-point cell Zn04/02 is presented in Table 4.

Preparation of the cells consists of several steps. First, all graphite components were baked-out for several hours inside the silica glass auxiliary vessel at a temperature 20°C above the zinc-point temperature. During the baking, the auxiliary vessel

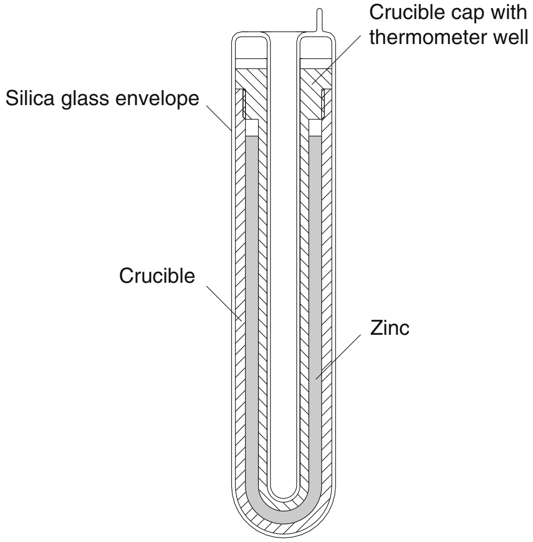

Fig. 6 Miniature zinc-point cell

Table 4 Uncertainty budget for the calibration of an SPRT using the miniature zinc-point cell Zn04/02

Components	Uncertainty contribution (mK)
Purity	0.521
Hydrostatic head correction	0.030
Perturbing heat exchanges	0.250
Self-heating correction	0.030
Bridge linearity	0.060
Gas pressure	0.055
R_{SPRT} scatter	0.392
Combined uncertainty	0.815
Expanded uncertainty ($k = 2$)	1.630

was pumped out by a turbomolecular vacuum pump. Then, the vessel was filled with pure argon and the heating was discontinued. After nearly reaching ambient temperature, the graphite crucible was withdrawn from the vessel, filled with zinc granules, and again put back into the vessel. The crucible cap with the thermometer well was fixed on a stainless-steel rod inserted through the cap of the auxiliary vessel. After assembling the auxiliary vessel, it was inserted into the furnace and connected to the vacuum and gas-handling system. Air was removed and the auxiliary vessel was filled with high-purity argon. As the zinc melted, the crucible cap with the thermometer well was pushed down into the melted metal and screwed to the crucible. When the cap was screwed into position, the cell was slowly cooled at room temperature.

The silica glass components, the sheath, and cap with the thermometer well were chemically cleaned. Then, the filled graphite crucible was inserted into the silica glass sheath and the cap was fused to the sheath. The vacuum and gas-handling system was

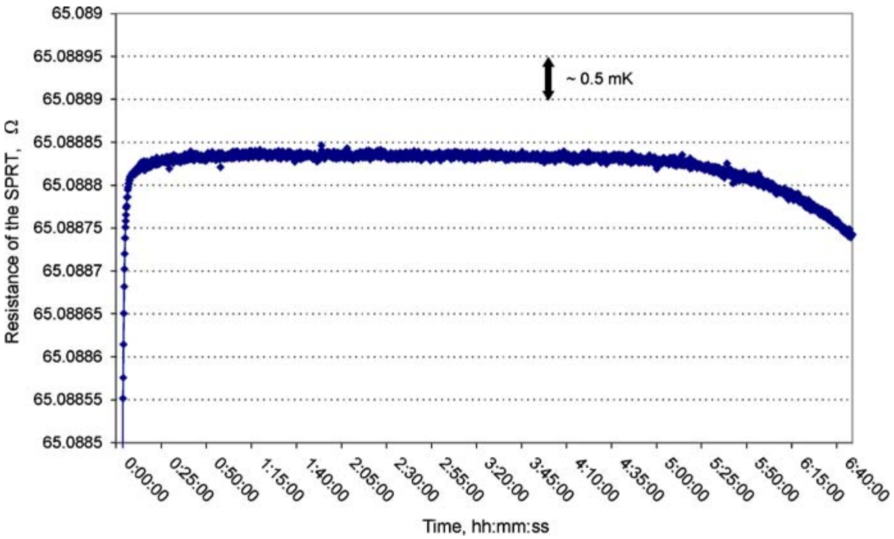

Fig. 7 Typical freezing plateau realized with the miniature zinc-point cell

connected through the capillary on the top of the cap. The cell was evacuated and filled with argon. Then, the pumping connection was sealed.

Several realizations of the zinc point were performed to observe the behavior of these cells. Zinc-point miniature cells were compared with the SMU primary standard zinc-point cell. The zinc point was realized in the conventional way. The temperature of the furnace was set about 5°C above the freezing point and kept overnight at this temperature. The next morning, the temperature of the furnace was set close to (1°C above) the freezing-point temperature. The temperature profile in the cell was checked after stabilization. Then, the temperature was decreased 2°C below the freezing-point temperature and, after recalescence, two ceramic rods were inserted into the thermometer well for 1 min.

The duration of the plateaux obtained from the cells (within 0.3 mK) is about 6 h for cell Zn04/02 and about 7 h for cell Zn04/01. A typical freezing plateau realized by cell Zn04/02 is shown in Fig. 7. A heat-flux test (immersion profile) was performed using a Tinsley Model 5178 SA SPRT (25Ω) in both the cells. Figure 8 presents the results obtained from cell Zn04/01. The immersion profile obtained from cell Zn04/02 is nearly identical. The comparison of miniature Zn cells against the SMU primary standard zinc-point cell showed agreement within 0.12 mK.

4 Summary

The article provides information about the batch of gallium and mercury primary fixed-point cells and miniature zinc-point cells for industrial thermometer calibration built at the SMU. Many experiments have been carried out to study the characteristics of these cells. One of the gallium cells was compared with the transfer standard cell

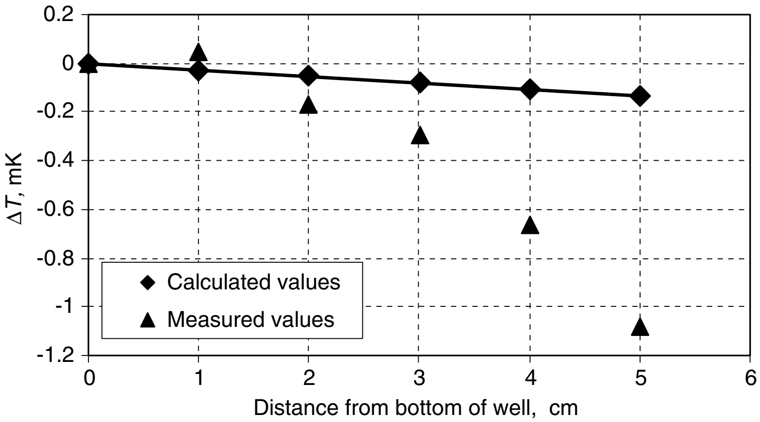

Fig. 8 Immersion profile in the miniature zinc-point cell Zn04/01

during key comparison CCT-K3, and it was used together with a mercury cell for EUROMET Project No. 552. The results of the experiments together with the results of the intercomparisons show the high quality of these cells. The comparison of miniature Zn cells against the SMU primary standard zinc-point cell showed agreement within 0.12 mK.

Acknowledgments The authors thank, for their support, the Slovak Institute of Metrology, Faculty of Mechanical Engineering Slovak University of Technology, and the grant agency VEGA—Grant No. 1/3131/06.

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