

T. Nakano¹, O. Tamura¹, H. Sakurai¹1 National Metrology Institute of Japan, AIST Central 3, Tsukuba 305-8563, Ibaraki, Japan
tnt@ni.aist.go.jp

The triple points of argon (Ar), oxygen (O₂), neon (Ne) and equilibrium hydrogen (e-H₂) are realized using sealed cells fabricated at the NMIJ / AIST. Melting curves at the triple points of Ar, Ne and e-H₂ show very flat plateaux over a wide range of the melted fraction, F , and linear-dependences on $1/F$ in the wide range from $1/F = 1$ to over $1/F = 20$, when samples are treated thermally as follows before the realization; the sample is completely solidified, and then a portion of the solid is melted and the melted sample is kept for a while in an adiabatic environment, and finally the sample is completely solidified again. But the melting curves obtained without the thermal treatment apparently deviate downward from the linear-dependences obtained after the thermal treatment at $1/F > 2.5$. These indicate that the thermal treatment of the samples of Ar, Ne, and e-H₂ will be effective in realizing the low temperature fixed points for the ITS-90 at the highest level of accuracy. On the other hand, there is only a small deviation of the melting curve obtained without the thermal treatment from that after the thermal treatment at $1/F > 2.5$ for O₂.

This article is the summary of the next two papers concerning the effect of a thermal treatment on the melting curves of the cryogenic fixed points of the ITS-90.

1) Realization of the triple points of Ar and e-H₂ at NMIJ/AIST, *Proceedings of 2nd International Seminar and Workshop on Low Temperature Thermometry*, edited by Szymrka-Grzebyk A. and Kowal A., Wroclaw (2003) 45

by T. Nakano, O. Tamura and H. Sakurai.

2) Melting curves of low temperature fixed points of the ITS-90 using sealed cells, submitted to *Proceedings of Tempmeko 2004*

by T. Nakano, O. Tamura and H. Sakurai.

1. Introduction

Sakurai pointed out by using sealed cells for the triple point of Ar that a thermal treatment of samples before the realization of the triple point is effective in obtaining single and flat plateaux for Ar, although double plateaux are observed in the case without the thermal treatment before the realization of the triple point [1]. The thermal treatment is as follows; (1) the sample is completely solidified, and (2) about a half of the solid is melted and the half melted sample is kept for a while in an adiabatic environment, and then (3) the sample is completely re-solidified [1]. Fellmuth et al. also confirmed the effect of refreezing on the width of argon melting by using another type of sealed cells [2]. Since the triple points of e-H₂, Ne and O₂ are realized in a similar way to the triple point of Ar, it is interesting whether the thermal treatment is effective for realization of the triple points of e-H₂, Ne and O₂ at the highest level of accuracy. In the present article, we report the effect of a similar thermal treatment on the melting curves of cryogenic fixed points of the ITS-90.

2. Experimental

The triple points of Ar, O₂, Ne and e-H₂ are realized using sealed cells fabricated by NMIJ, which have the same design as previously reported [3, 4]. The sealing system and the detailed procedure to fill the cells with the gas substances were

described in Ref. 3. The nominal purities of Ar, O₂, Ne and e-H₂ are better than 99.999 9 %, 99.999 95 %, 99.999 % and 99.999 99 %, respectively. The sealed cells for the triple points of Ar (NMIJ A-2), O₂ (NMIJ O-1), Ne (NMIJ Ne-1) and e-H₂ (NMIJ H-5) contain about 85 mmol of Ar, about 70 mmol of O₂, about 80 mmol of Ne and about 90 mmol of H₂, respectively.

To realize these triple points by the sealed cells, we use a calorimeter using a two stage GM refrigerator [3, 4]. A platinum resistance thermometer was used for the measurements of the triple points of Ar and O₂, and a rhodium-iron resistance thermometer was used for the measurements of the triple points of Ne and e-H₂. Details of the experimental procedure and the method of analysis of the observed melting curves were similar to those described previously [3, 4].

3. Results and discussion

Figures 1 shows melting curves at the triple points of Ar (NMIJ A-2 cell) [4], e-H₂ (NMIJ H-5 cell) [4], Ne (NMIJ Ne-1 cell) [5] and O₂ (NMIJ O-1 cell) [5]. As shown in Fig. 1, the melting curves of Ar, Ne and e-H₂ obtained after the thermal treatment show very flat plateaux in a wide melted fraction, F , at $F > 0.2$. The thermal treatment is the same as described above. On the other hand, the melting curves obtained without the thermal treatment deviate downward from those after the thermal treatment with decreasing F at $F < 0.4$. The melting curves plotted against $1/F$ make the deviation more clear (Figs. 1 (b), (d) and (f)). The melting curves of Ar, Ne and e-H₂ obtained without the thermal treatment apparently deviate downward at $1/F > 2.5$ from those obtained after the thermal treatment, which show nearly linear-dependences on $1/F$ in the wide region from $1/F = 1$ to over $1/F = 20$.

On the other hand, the effect of the thermal treatment for O₂ is much weaker than that for the other substances. The thermal treatment for O₂ are as follows; (1) the sample is completely solidified, (2) about 90% of the solid is melted and it is kept for a while in an adiabatic environment and the sample is completely solidified again, and then (3) about a half of the solid is melted and it is kept for a while in an adiabatic environment, and finally (4) the sample is completely solidified again. The procedure (2) is an additional thermal treatment for O₂. Although the melting curve obtained without the thermal treatment deviates downward from those with the

thermal treatment, the deviation is much smaller for O₂ than those for Ar, Ne, and e-H₂.

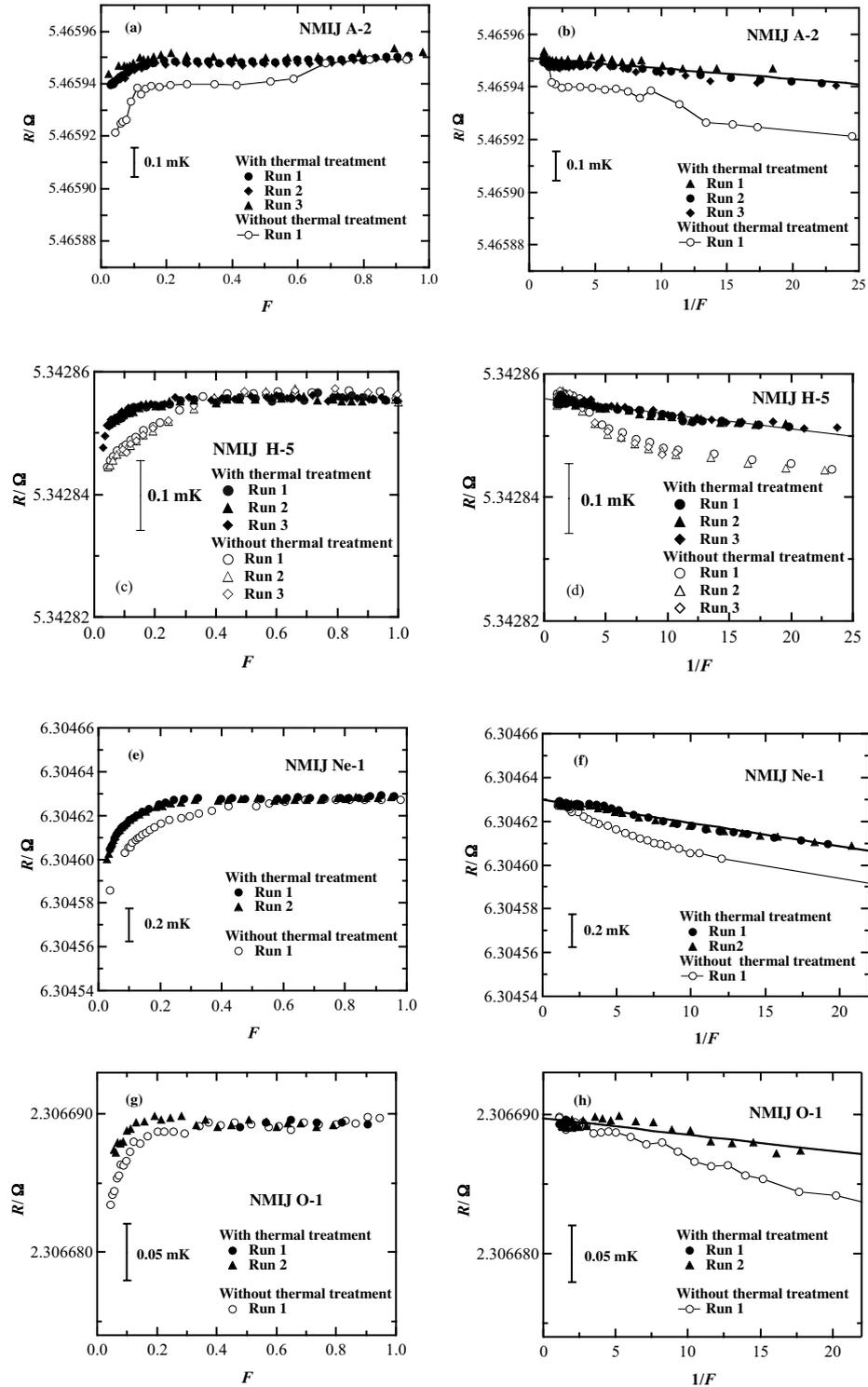


Figure 1: Melting curves obtained with and without the thermal treatment of the Ar cell, NMIJ A-2 [4], (a) plotted against the melted fraction, F , and (b) plotted against $1/F$, those of the e-H₂ cell, NMIJ H-5 [4], (c) plotted against F and (d) plotted against $1/F$, those of the Ne cell, NMIJ Ne-1 [5], (e) plotted against the melted fraction, F , and (f) plotted against $1/F$, and those of the O₂ cell, NMIJ O-1 [5], (g) plotted against F and (h) plotted against $1/F$. A platinum resistance thermometer were used for the measurements of melting curves for Ar and O₂, and a rhodium-iron resistance thermometer were used for Ne and e-H₂.

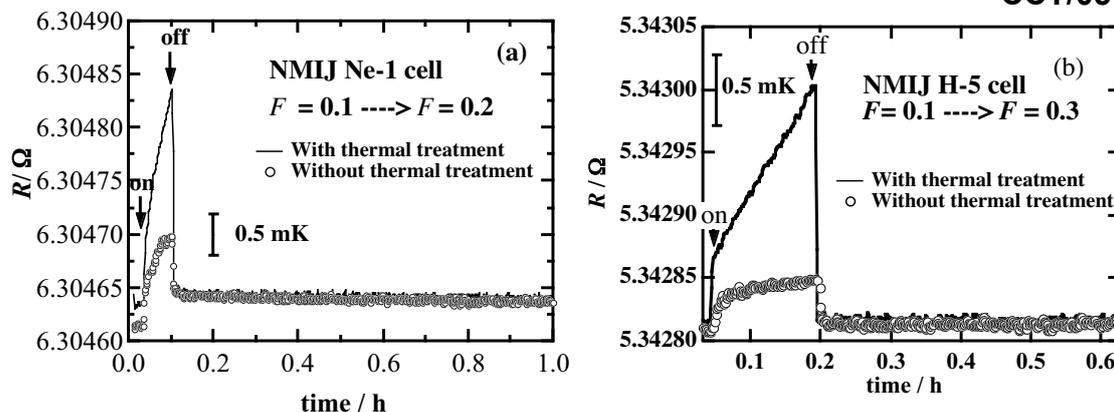


Figure2: Response curves of temperature of (a) NMIJ Ne-1 [5] cell and (b) NMIJ H-5 cell [4] for the cases with and without the thermal treatment of the sample. The arrows, on and off, indicate the starting and ending points of the heat pulses, respectively.

To consider an origin of the difference of the melting curves between two cases with and without the thermal treatment, the response of the temperature to heat pulses gives us a clue. Figure 2 shows response curves of temperature for NMIJ Ne-1 cell and NMIJ H-5 cell to heat pulses [4, 5]. The heat pulses fuse the solid sample of Ne and H₂ from $F=0.1$ to $F=0.2$ and from $F=0.1$ to $F=0.3$, respectively. Although the energy of the heat pulses is the same for the cases with and without the thermal treatment, the transient increase of the temperature in the case with the thermal treatment is much larger than that without it.

The mechanism for the effect of the thermal treatment may be not clear from this study alone, but we infer the main origin of the effect as follows. Figure 3 shows schematic images of a solid sample inside a cell. When a heat pulse is introduced to the cell at the triple point, a liquid sample is created on the inside surface of the sample space around the thermometer well and the temperature of the liquid sample increases during the heat pulse. However, if solid samples are distributed on the inside surface of the ballast volume apart from the sample space, the increase of temperature of the cell will become slower during the heat pulse because a portion of the heat is consumed on fusing the solids on the surface of the ballast volume. Around the solids of the ballast volume, the melted fraction F will be completely different from that in the sample space even when the triple point is realized. Possibly, there are some coexisting phases between solid and vapor on the surface of the ballast volume especially at low F in the sample space, because some liquid created by the heat pulses run down from the surface of the ballast volume to the sample space. So, the existence of the solid of the ballast volume will disturb the thermal equilibration in the cell. Probably, such a disturbance will occur in our sealed cells during the realization of the triple points without the thermal treatment and prevent one from obtaining reliable melting curves. On the other hand, the thermal treatment will make such solids almost vanish from the surface of the ballast volume and allow one to obtain very flat melting curves in the wide region of F .

As mentioned above, the effect of the thermal treatment for O₂ is much weaker than those for Ar, Ne and e-H₂. If the effect of the thermal treatment is related to the existence of some solids on the surface of the ballast volume, it is expected that the amount of the solids for Ar, Ne and e-H₂ is much larger than that for O₂. Actually, vapor pressures at the triple point of Ar (68.892 kPa), Ne (43.379 kPa) and e-H₂ (7.034 kPa) are much

larger than that of O₂ (0.1464 kPa). This apparently indicates that amounts of Ar, Ne and e-H₂ in the ballast volume are much larger than that of O₂. So, creation of solids of Ar, Ne and e-H₂ on the inside surface of the ballast volume is much more easier than that of O₂. The effect of the thermal treatment for e-H₂ is also smaller than those for Ar and Ne. This is also consistent to the difference of vapor pressures of them at their triple points.

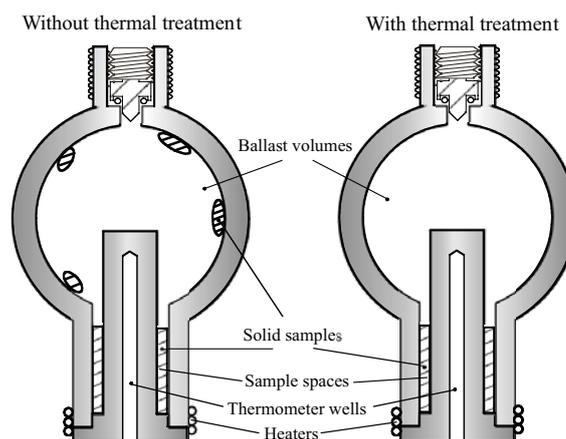


Figure3: Schematic image of solid sample inside cells created with and without the thermal treatment of the sample [5].

As shown in Fig. 4, there is a peak due to a small enhancement of temperature before the freezing plateau for NMIJ Ne-1 cell. Similar peaks are often observed for NMIJ A-2 and NMIJ H-5 cells. MacConville and Pavese reported such a peak behavior caused by condensation of a portion of sample on the wall of the cell outside the bulk sample due to cold spots of some sealed cells [6]. Probably, the peak behaviors for our sealed cells are also corresponding to solidification of a portion of sample on the inside surface of the ballast volume. It is consistent with our inference described above for the main origin of the effect of the thermal treatment. On the other hand, since supercooling of O₂ using NMIJ O-1 cell is much larger (>1 K) than those of Ar, Ne and e-H₂, we have observed just a jump of temperature due to solidification without any freezing plateaux. The difference of freezing behavior between O₂ and others may also be related to the difference of the effect of the thermal treatment.

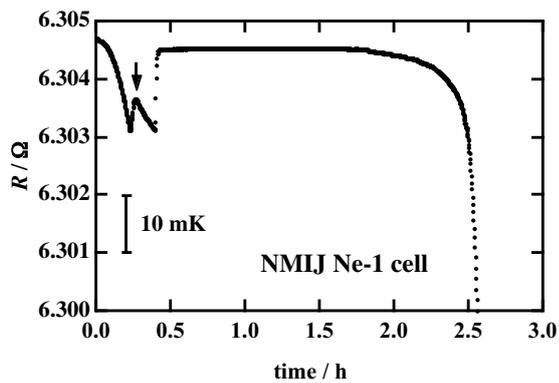


Figure 4: Freezing curve of Ne using NMIJ Ne-1 cell [5].

Conclusion

The melting curves of Ar, O₂, Ne and e-H₂ at the triple points have been observed using sealed cells fabricated at the National Metrology Institute of Japan / AIST. The melting curves at the triple points of Ar, Ne and e-H₂ obtained after the thermal treatment of the samples inside the cells show very flat plateaux over a wide range of the melted fraction, F , and linear-dependences on $1/F$ in the wide range from $1/F = 1$ to over $1/F = 20$. However, those without the thermal treatment deviate downward from the linear-dependences at $1/F > 2.5$. Although the effect of the thermal treatment for O₂ is much smaller than those for Ar, Ne and e-H₂, the melting curves of O₂ plotted against $1/F$ also show a small deviation of the melting curve obtained without the thermal treatment from a linear-dependence on $1/F$ obtained the thermal treatment at $1/F > 2.5$. These indicate that melting curves plotted against $1/F$ are good tools to check quality of the melting curves and the thermal treatment allows one to obtain more reliable melting curves of the low temperature fixed points of the ITS-90. An optimum procedure of the thermal treatment of samples will depend on conditions of their solidification, kinds of material of cells, circumstances of the cells for the outflow of heat and so on. To obtain more reliable melting curves, the optimum procedure should be sought for each realization of the low temperature fixed points of the ITS-90.

Acknowledgements

The authors thank Dr. Shimazaki and Dr. Nakagawa for their valuable discussions and useful suggestions.

References

- [1] Sakurai H., "Precise Realization of the Triple points of Equilibrium Hydrogen and Argon Using a Closed Cycle Refrigerator", *Proceedings of TEMPMEKO '99*, edited by Dubbeldam J. F. and de Groot M. J., Van Swinden Laboratorium, Delft, 1999, pp. 124-128.
- [2] Fellmuth B., et al, "An International Star Intercomparison of Low-Temperature Fixed Points Using Sealed Triple-Point Cells", *Temperature: Its Measurement and Control in Science and Industry*, edited by Ripple D., Am. Inst. Phys, Chicago, 2003, **Vol. 7**, pp.885-890.

- [3] Nakano T., Tamura O. and Sakurai H., "New Sealed Cells for Realization of Cryogenic Fixed Points at NMIJ/AIST", *Temperature: Its Measurement and Control in Science and Industry*, edited by Ripple D., Am. Inst. Phys, Chicago, 2003, **Vol. 7**, pp. 185-190, and their references.
- [4] Nakano T., Tamura O. and Sakurai H., "Realization of the Triple points of Ar and e-H₂ at NMIJ/AIST", *Proceedings of 2nd International Seminar and Workshop on Low Temperature Thermometry*, edited by Szymrka-Grzebyk A. and Kowal A., Wroclaw, 2003, pp. 45-50.
- [5] Nakano T., Tamura O. and Sakurai H., "Melting curves of low temperature fixed points of the ITS-90 using sealed cells", submitted to *Proceedings of Tempmeko 2004*.
- [6] McConville G. T. and Pavese F., "Physicochemical problems involved in measuring thermodynamic properties of normal and equilibrium deuterium at the triple point", *J. Chem. Thermodynamics*, **20**, 1988 pp. 337-358.