BUREAU INTERNATIONAL DES POIDS ET MESURES

TECHNIQUES FOR APPROXIMATING THE INTERNATIONAL TEMPERATURE SCALE OF 1990

This document, although it is by now quite out of date, remain available for the time being. It is presently successively being updated and some chapters have already been published, cf. ***Guide to Secondary Thermometry*** *https://www.bipm.org/en/committees/cc/cct/guides-to-thermometry.*

BIPM, Sèvres, 23 August 2021

1997

Pavillon de Breteuil, F-92312 Sèvres

Organisation intergouvernementale de la Convention du Mètre

TECHNIQUES FOR APPROXIMATING
THE INTERNATIONAL TEMPERATURE SCALE OF 1990

1997 reprinting of the 1990 first edition

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When this monograph, prepared by Working Group 2 of the Comité Consultatif de Thermométrie (CCT), was published in 1990, it was expected that a revised and updated edition would follow in five to seven years. This intended revision is still a few years away. Consequently, for this reprinting of the first edition, the CCT felt that it was necessary to include a list of amendments to various items in the text that have been made obsolete (or obsolescent) by events in thermometry since 1990. At the same time we list all of the errata in the first edition that have been brought to our attention. Of these latter, happily, there have been very few.

This group of inserted pages contain these errata and amendments keyed to the pages in the text to which they pertain.

R. E. Bedford
Chairman, Working Group 2

T.J. Quinn
Director, BIPM
President, CCT

July 1997

Errata

1. Page (iii), item 3.3.1: change to read “Copper 28.1 % Silver 71.9 % Eutectic Alloy”.
2. Page 2, penultimate line of text: “Appendix A” should read “Appendix B”.
3. Page 20, line 7 of text: delete “the calibration approximates that state” and insert “that state is approximated during the calibration”.
4. Page 35, Sec. 3.3.1 title: should read “Copper 28.1 % Silver 71.9 % Eutectic Alloy”.
5. Page 35, Sec. 3.3.1, line 4: should read “Cu 28.1 % Ag 71.9 %”.

Amendments

1. Page 4, line 12: The reference Bedford et al (1984) should be updated to Bedford et al (1996).
2. Page 4, line 14: The sentence beginning “The value of ...” should be deleted.
3. Page 5, lines 15-16: Note that there are now revised values for (t_{90} – t_{68}) in the temperature range 630 °C to 1064 °C [Rusby et al (1994), and item 14 below].
4. Page 5, lines 29-31: These specifications and tables have now been published (see items 10 and 12 below).
5. Pages 20-24, Sections 3.1.1 and 3.1.2: The superconductive devices SRM767 and SRM768 are no longer available from the NIST.
6. Page 24, Section 3.1.3: Vapour pressure thermometers are discussed in detail by Pavese and Molinar (1992).
7. Page 27, Table 3.4: Revised values for some of the table entries appear in Table 2.1 (page 46) of Pavese and Molinar (1992).
8. Page 60, Section 6: Vapour pressure thermometry is discussed in detail by Pavese and Molinar (1992).
9. Page 96, lines 21-22: New thermocouple reference tables for types R, S and B based upon the ITS-90 have been published [Burns et al (1992a); Burns et al (1992b); Guthrie et al (1992); Burns et al (1993); IEC(1995a)]. See item 17 below.
10. Page 139, Section 16.3: New international specifications for industrial platinum resistance thermometers that relate the thermometer resistance R to t_{90} have been published by the IEC (1995b). The equations relating R to t_{90} are identical in form to equations (16.5) and (16.6) (on page 139) with t_{90} replacing t_{68}. For IPRTs with

W(100 °C) = 1.385 (exact value for calculational purposes 1.385 055) the values for the coefficients A, B, Care:

$A = 3.9083 \times 10^{-3}\ °C^{-1}$

$B = -5.775 \times 10^{-7}\ °C^{-2}$

$C = -4.183 \times 10^{-12}\ °C^{-4}$.

The range of Eq. (16.5) is 0 °C to 850 °C and of Eq. (16.6) is –200 °C to 0 °C.

No mention is made in IEC (1995b) of IPRTs with W(100 °C) = 1.391.

11. Page 142, Table 16.3: This table should be replaced by an equivalent one with entries generated from the (new) equations (16.5) and (16.6) of item 10 above [see IEC(1995b)].
12. Page 147, Section 18.1: New international thermocouple reference tables for Type R, S, B, J, T, E, K, N based upon the ITS-90 have been published [Burns et al (1994); IEC (1995a)]. See item 17 below.
13. Page 169, Section 20: The following additional references should be included in Section 20:

Bedford, R.E., Bonnier, G., Maas, H. and Pavese, F. (1996): Recommended Values of Temperature on the International Temperature Scale of 1990 for a Selected Set of Secondary Reference Points; Metrologia 33, 133-154.

Burns, G.W., Strouse, G.F., Mangum, B.W., Croarkin, M.C., Guthrie, W.F., Marcarino, P., Battuello, M., Lee, H.K.; Kim, J.C., Gam, K.S., Rhee, C., Chattle, M., Arai, M., Sakurai, H., Pokhodun, A.I., Moiseeva, N.P., Perevalova, S.A., de Groot, M.J., Zhang, J., Fan, K., Wu, S. (1992a): New Reference Function for Platinum - 10 % Rhodium versus Platinum (Type S) Thermocouples based on the ITS-90, Part I and Part II; Temperature, Its Measurement and Control in Science and Industry (American Institute of Physics, New York) 6, 537-546.

Burns, G.W.; Strouse, G.F.; Mangum, B.W.; Croarkin, M.C.; Guthrie, W.F.; Chattle, M. (1992b): New Reference Functions for Platinum - 13 % Rhodium versus Platinum (Type R) and Platinum - 30 % Rhodium versus Platinum - 6 % Rhodium (Type B) Thermocouples based on the ITS-90; Temperature, Its Measurement and Control in Science and Industry (American Institute of Physics, New York), 6, 559-564.

Burns, G.W.; Scroger, M.G.; Strouse, G.F.; Croarkin, M.C.; Guthrie, W.F. (1993): Temperature-Electromotive Force Reference Functions and Tables for the Letter Designated Thermocouple Types Based on the ITS-90; National Institute of Standards and Technology (U.S.) Monograph 175.

Guthrie, W.F.; Croarkin, M.C.; Burns, G.W.; Strouse, G.F.; Marcarino, P.; Battuello, M.; Lee, H.K., Kim, J.C.; Gam, K.S.; Rhee, C.; Chattle, M.; Arai, M.; Sakurai, H.; Pokhodun, A.I.; Moiseeva, N.P.; Perevalova, S.A.; de Groot, M.J.; Zhang, J.; Fan, K.; Wu, S. (1992): Statistical Analysis of Type S Thermocouple Measurements on the International Temperature Scale of 1990; Temperature, Its Measurement and Control in Science and Industry (American Institute of Physics, New York) 6, 547-552.

IEC (1995a): Thermocouples, Part 1: Reference Tables; International Electrotechnical Commission, IEC International Standard, Publication 584-1, 2nd edition 1995-09. (Central Bureau of the International Electrotechnical Commission, Geneva.)

IEC (1995b): Industrial Platinum Resistance Thermometer Sensors, IEC Standard, Publication 751, 1st edition 1983, Amendment 2, 1995-07. (Central Bureau of the International Electrotechnical Commission, Geneva.)

Pavese, F. and Molinar, G. (1992): Modern Gas-Based Temperature and Pressure Measurements; (Plenum Press, New York and London).

Rusby, R.L.,Hudson, R.P. and Durieux, M. (1994): Revised Values for ($t_{90} – t_{68}$) from 630 °C to 1064 °C; Metrologia 31, 149-153.

14. Page, 189, Appendix A: The values of ($t_{90} – t_{68}$) in the range 630 °C to 1064 °C have been revised [Rusby et al (1994)]. These revised values may be obtained from the following equation:

$$(t_{90} - t_{68}) / °C = \sum_{i=o}^{5} b_i (t_{90} / °C)^i$$

where $b_0 = 7.868\ 720\ 9 \times 10^{1}$

$b_1 = -4.713\ 599\ 1 \times 10^{-1}$

$b_2 = 1.095\ 471\ 5 \times 10^{-3}$

$b_3 = -1.235\ 788\ 4 \times 10^{-6}$

$b_4 = 6.773\ 658\ 3 \times 10^{-10}$

$b_5 = -1.445\ 808\ 1 \times 10^{-13}$

15. Page 191, Appendix B: Two entries should be deleted: Amt für Standardisierung Messwesen und Warenprüfung and Kamerlingh Onnes Laboratorium. Four other entries should be changed, as follows:

National Institute of Standards and Technology
Process Measurements Division
Chemical Science and Technology Laboratory
Gaithersburg, Maryland 20899
U.S.A.

Centre for Quantum Metrology
National Physical Laboratory
Teddington, TW11 OLW U.K.
Fax: +44 181 943 6755

Institute for National Measurement Standards
National Research Council of Canada
Ottawa, Canada, K1A OR6

Nederlands Meetinstituut
P.O. Box 654
2600 AR Delft (NL)
Schoemakerstraat 97
2628 VK Delft (NL)
Fax: +31 15 261 2971

16. Page 194, Appendix C: There are four (known) changes of address:

Scientific Instruments
4400 W. Tiffany Drive
Mangonia Park
West Palm Beach, Florida 33407
U.S.A.
Fax: 1 (516) 881-8556

Cryogenic Ltd.
Unit 30, Acton Park Estate
London W3 7QE
U.K.
Fax: +44 181 749 5315

H. Tinsley and Co. Ltd.
275 King Henry's Drive
Croydon CRO OAE
U.K.
Fax: +44 1689 800 405

Oxford Instruments Inc.
Scientific Research Division
Old Station Way
Eynsham Witney
Oxford OX8 1TL
U.K.
Fax: +44 1865 881 567

Additionally, the Fax numbers for the first two firms listed are:

Cryo Cal
Fax: 1 (612) 646-8718

Lake Shore
Fax: 1 (614) 891-1392

17. Page 200, Appendix F: The original Appendix F should be deleted and replaced by the following new Appendix F.

Appendix F

Interpolation Polynomials for Standard Thermocouple Reference Tables

i) All tables are for a reference temperature of 0 °C.
ii) Throughout, E is in mV and t_{90} is in °C.
iii) All of the polynomials (except one for Type K as noted below) are of the form $E = \sum_{i=0}^{n} d_i (t_{90})^i$. The values of n and of the coefficients d_i are listed for each thermocouple type and each range.

1. Type T

a) temperature range from –270 °C to 0 °C: n = 14

d_0 = 0.0
d_1 = 3.874 810 636 4 x 10^{-2}
d_2 = 4.419 443 434 7 x 10^{-5}
d_3 = 1.184 432 310 5 x 10^{-7}
d_4 = 2.003 297 355 4 x 10^{-8}
d_5 = 9.013 801 955 9 x 10^{-10}
d_6 = 2.265 115 659 3 x 10^{-11}
d_7 = 3.607 115 420 5 x 10^{-13}
d_8 = 3.849 393 988 3 x 10^{-15}
d_9 = 2.821 352 192 5 x 10^{-17}
d_{10} = 1.425 159 477 9 x 10^{-19}
d_{11} = 4.876 866 228 6 x 10^{-22}
d_{12} = 1.079 553 927 0 x 10^{-24}
d_{13} = 1.394 502 706 2 x 10^{-27}
d_{14} = 7.979 515 392 7 x 10^{-31}

b) temperature range from 0 °C to 400 °C: n = 8

d_0 = 0.0
d_1 = 3.874 810 636 4 x 10^{-2}
d_2 = 3.329 222 788 0 x 10^{-5}
d_3 = 2.061 824 340 4 x 10^{-7}
d_4 = -2.188 225 684 6 x 10^{-9}
d_5 = 1.099 688 092 8 x 10^{-11}
d_6 = -3.081 575 877 2 x 10^{-14}
d_7 = 4.547 913 529 0 x 10^{-17}
d_8 = -2.751 290 167 3 x 10^{-20}

2. Type J

a) temperature range from -210 °C to 760 °C: $n = 8$

$d_0 = 0.0$

$d_1 = 5.038\ 118\ 781\ 5 \times 10^{-2}$

$d_2 = 3.047\ 583\ 693\ 0 \times 10^{-5}$

$d_3 = -8.568\ 106\ 572\ 0 \times 10^{-8}$

$d_4 = 1.322\ 819\ 529\ 5 \times 10^{-10}$

$d_5 = -1.705\ 295\ 833\ 7 \times 10^{-13}$

$d_6 = 2.094\ 809\ 069\ 7 \times 10^{-16}$

$d_7 = -1.253\ 839\ 533\ 6 \times 10^{-19}$

$d_8 = 1.563\ 172\ 569\ 7 \times 10^{-23}$

b) temperature range from 760 °C to 1200 °C: $n = 5$

$d_0 = 2.964\ 562\ 568\ 1 \times 10^{2}$

$d_1 = -1.497\ 612\ 778\ 6...$

$d_2 = 3.178\ 710\ 392\ 4 \times 10^{-3}$

$d_3 = -3.184\ 768\ 670\ 10 \times 10^{-6}$

$d_4 = 1.572\ 081\ 900\ 4 \times 10^{-9}$

$d_5 = -3.069\ 136\ 905\ 6 \times 10^{-13}$

3. Type E

a) temperature range from -270 °C to 0 °C: $n = 13$

$d_0 = 0.0$

$d_1 = 5.866\ 550\ 870\ 8 \times 10^{-2}$

$d_2 = 4.541\ 097\ 712\ 4 \times 10^{-5}$

$d_3 = -7.799\ 804\ 868\ 6 \times 10^{-7}$

$d_4 = -2.580\ 016\ 084\ 3 \times 10^{-8}$

$d_5 = -5.945\ 258\ 305\ 7 \times 10^{-10}$

$d_6 = -9.321\ 405\ 866\ 7 \times 10^{-12}$

$d_7 = -1.028\ 760\ 553\ 4 \times 10^{-13}$

$d_8 = -8.037\ 012\ 362\ 1 \times 10^{-16}$

$d_9 = -4.397\ 949\ 739\ 1 \times 10^{-18}$

$d_{10} = -1.641\ 477\ 635\ 5 \times 10^{-20}$

$d_{11} = -3.967\ 361\ 951\ 6 \times 10^{-23}$

$d_{12} = -5.582\ 732\ 872\ 1 \times 10^{-26}$

$d_{13} = -3.465\ 784\ 201\ 3 \times 10^{-29}$

b) temperature range from 0 °C to 1000 °C: $n = 10$

$d_0 = 0.0$

$d_1 = 5.866\ 550\ 871\ 0 \times 10^{-2}$

$d_2 = 4.503\ 227\ 558\ 2 \times 10^{-5}$

$d_3 = 2.890\ 840\ 721\ 2 \times 10^{-8}$

$d_4 = -3.305\ 689\ 665\ 2 \times 10^{-10}$

$d_5 = 6.502\ 440\ 327\ 0 \times 10^{-13}$

$d_6 = -1.919\ 749\ 550\ 4 \times 10^{-16}$

$d_7 = -1.253\ 660\ 049\ 7 \times 10^{-18}$

$d_8 = 2.148\ 921\ 756\ 9 \times 10^{-21}$

$d_9 = -1.438\ 804\ 178\ 2 \times 10^{-24}$

$d_{10} = 3.596\ 089\ 948\ 1 \times 10^{-28}$

4. Type K

a) temperature range from -270 °C to 0 °C: n = 10

d_0 = 0.0
d_1 = 3.945 012 802 5 x 10^{-2}
d_2 = 2.362 237 359 8 x 10^{-5}
d_3 = -3.285 890 678 4 x 10^{-7}
d_4 = -4.990 482 877 7 x 10^{-9}
d_5 = -6.750 905 917 3 x 10^{-11}
d_6 = -5.741 032 742 8 x 10^{-13}
d_7 = -3.108 887 289 4 x 10^{-15}
d_8 = -1.045 160 936 5 x 10^{-17}
d_9 = -1.988 926 687 8 x 10^{-20}
d_{10} = -1.632 269 748 6 x 10^{-23}

b) temperature range from 0 °C to 1372 °C:

The polynominal has the form

$$E = \sum_{i=0}^{9} d_i (t_{90})^i + b_0 \exp\left[b_1 \left(t_{90} - 126.9686\right)^2\right]$$

d_0 = -1.760 041 368 6 x 10^{-2}
d_1 = 3.892 120 497 5 x 10^{-2}
d_2 = 1.855 877 003 2 x 10^{-5}
d_3 = -9.945 759 287 4 x 10^{-8}
d_4 = 3.184 094 571 9 x 10^{-10}
b_0 = 1.185 976 x 10^{-1}
b_1 = -1.183 432 x 10^{-4}
d_5 = -5.607 284 488 9 x 10^{-13}
d_6 = 5.607 505 905 9 x 10^{-16}
d_7 = -3.202 072 000 3 x 10^{-19}
d_8 = 9.715 114 715 2 x 10^{-23}
d_9 = -1.210 472 127 5 x 10^{-26}

5. Type S

a) temperature range from -50 °C to 1064.18 °C: n = 8

d_0 = 0.0
d_1 = 5.403 133 086 31 x 10^{-3}
d_2 = 1.259 342 897 40 x 10^{-5}
d_3 = -2.324 779 686 89 x 10^{-8}
d_4 = 3.220 288 230 36 x 10^{-11}
d_5 = -3.314 651 963 89 x 10^{-14}
d_6 = 2.557 442 517 86 x 10^{-17}
d_7 = -1.250 688 713 93 x 10^{-20}
d_8 = 2.714 431 761 45 x 10^{-24}

b) temperature range from 1064.18 °C to 1664.5 °C: n = 4

d_0 = 1.329 004 440 85...
d_1 = 3.345 093 113 44 x 10^{-3}
d_2 = 6.548 051 928 18 x 10^{-6}
d_3 = -1.648 562 592 09 x 10^{-9}
d_4 = 1.299 896 051 74 x 10^{-14}

c) temperature range from 1664.5 °c to 1768.1 °C: n = 4

d_0 = 1.466 282 326 36 x 10^{2}
d_1 = -2.584 305 167 52 x 10^{-1}
d_2 = 1.636 935 746 41 x 10^{-4}
d_3 = -3.304 390 469 87 x 10^{-8}
d_4 = -9.432 236 906 12 x 10^{-15}

6. Type B

a) temperature range from 0° C to 630.615 °C: n=6

d_0 = 0.0
d_1 = -2.465 081 834 6 x 10^{-4}
d_2 = 5.904 042 117 1 x 10^{-6}
d_3 = -1.325 793 163 6 x 10^{-9}
d_4 = 1.566 829 190 1 x 10^{-12}
d_5 = -1.694 452 924 0 x 10^{-15}
d_6 = 6.299 0347 09 4 x 10^{-19}

b) temperature range from 630.615 °C to 1820 °C: n = 8

d_0 = -3.893 816 862 1 ...
d_1 = 2.857 174 747 0 x 10^{-2}
d_2 = -8.488 510 478 5 x 10^{-5}
d_3 = 1.578 528 016 4 x 10^{-7}
d_4 = -1.683 534 486 4 x 10^{-10}
d_5 = 1.110 979 401 3 x 10^{-13}
d_6 = -4.451 543 103 3 x 10^{-17}
d_7 = 9.897 564 082 1 x 10^{-21}
d_8 = -9.379 133 028 9 x 10^{-25}

7. Type N

a) temperature range from -270°C to 0 °C: n = 8

d_0 = 0.0
d_1 = 2.615 910 596 2 x 10^{-2}
d_2 = 1.095 748 422 8 x 10^{-5}
d_3 = -9.384 111 155 4 x 10^{-8}
d_4 = -4.641 203 975 9 x 10^{-11}
d_5 = -2.630 335 771 6 x 10^{-12}
d_6 = -2.265 343 800 3 x 10^{-14}
d_7 = -7.608 930 079 1 x 10^{-17}
d_8 = -9.341 966 783 5 x 10^{-20}

b) temperature range from 0 °C to 1300 °C: n = 10

d0 = 0.0
d1 = 2.592 939 460 1 x 10^{-2}
d2 = 1.571 014 188 0 x 10^{-5}
d3 = 4.382 562 723 7 x 10^{-8}
d4 = -2.526 116 979 4 x 10^{-10}
d5 = 6.431 181 933 9 x 10^{-13}
d6 = -1.006 347 151 9 x 10^{-15}
d7 = 9.974 533 899 2 x 10^{-19}
d8 = -6.086 324 560 7 x 10^{-22}
d9 = 2.084 922 933 9 x 10^{-25}
d10 = -3.068 219 615 1 x 10^{-29}

8. Type R

a) temperature range from -50 °C to 1064.18 °C: n = 9

$d_0 = 0.0$

$d_1 = 5.289\,617\,297\,65 \times 10^{-3}$

$d_2 = 1.391\,665\,897\,82 \times 10^{-5}$

$d_3 = -2.388\,556\,930\,17 \times 10^{-8}$

$d_4 = 3.569\,160\,010\,63 \times 10^{-11}$

$d_5 = -4.623\,476\,662\,98 \times 10^{-14}$

$d_6 = 5.007\,774\,410\,34 \times 10^{-17}$

$d_7 = -3.731\,058\,861\,91 \times 10^{-20}$

$d_8 = 1.577\,164\,823\,67 \times 10^{-23}$

$d_9 = -2.810\,386\,252\,51 \times 10^{-27}$

b) temperature range from 1064.18 °C to 1664.5 °C: n = 5

$d_0 = 2.951\,579\,253\,16...$

$d_1 = -2.520\,612\,513\,32 \times 10^{-3}$

$d_2 = 1.595\,645\,018\,65 \times 10^{-5}$

$d_3 = -7.640\,859\,475\,76 \times 10^{-9}$

$d_4 = 2.053\,052\,910\,24 \times 10^{-12}$

$d_5 = -2.933\,596\,681\,73 \times 10^{-16}$

c) temperature range from 1664.5 °C to 1768.1 °C: n = 4

$d_0 = 1.522\,321\,182\,09 \times 10^{2}$

$d_1 = -2.688\,198\,885\,45 \times 10^{-1}$

$d_2 = 1.712\,802\,804\,71 \times 10^{-4}$

$d_3 = -3.458\,957\,064\,53 \times 10^{-8}$

$d_4 = -9.346\,339\,710\,46 \times 10^{-15}$

Foreword

This monograph, published by the Bureau International des Poids et Mesures (BIPM), has been compiled by the Comité Consultatif de Thermométrie, one of the eight consultative committees established by the Comité International des Poids et Mesures.

The approximations to the International Temperature Scale of 1990 described here provide levels of accuracy that are adequate for the great majority of thermometric requirements, and in general do so with greater convenience or at lower cost than would be the case in realizing the ITS-90 itself. Thermometrists who do require the accuracy only available from, or the imprimatur of, the ITS-90 are referred to the text of that scale and, more particularly, to the companion monograph to this one: "Supplementary Information for the ITS-90", also published by the BIPM in 1990. The Comité Consultatif de Thermométrie expects to update both monographs periodically, probably at intervals of the order of five to eight years.

H. PRESTON- THOMAS	T.J. QUINN
President, CCT	Director, BIPM

July 1990

Acknowledgments

This monograph has been prepared by the Working Group of the Comité Consultatif de Thermométrie (CCT) identified hereunder. Although a large part of the material originated with members of this Working Group, much also was originally contributed by colleagues, either in our laboratories, or in other National Standards Laboratories. In addition, (parts of) various drafts underwent critical review by some members of the CCT and thermometry groups. We thank all of these people for their assistance, and express special appreciation to H. Ronsin (Institut National de Métrologie, France), B. Fellmuth (Amt für Standardisierung Messwesen und Warenprüfung, German Democratic Republic), L. Crovini (Istituto di Metrologia "G. Colonnetti", Italy), R.P. Hudson (then of Bureau International des Poids et Mesures, Paris), R. Rusby (National Physical Laboratory, United Kingdom), and members of the Temperature and Pressure Section (National Bureau of Standards, United States of America). We also thank Mrs. P. Vineham (National Research Council of Canada) for having typed so excellently and so patiently the several successive drafts of this monograph.

Working Group 2: R.E. Bedford, National Research Council of Canada
Chairman
G. Bonnier, Institut National de Métrologie, France
H. Maas, Amt für Standardisierung Messwessen und
Warenprüfung, German Democratic Republic
F. Pavese, Istituto di Metrologia “G. Colonnetti”, Italy.

TECHNIQUES FOR APPROXIMATING
THE INTERNATIONAL TEMPERATURE SCALE OF 1990

Contents

Appendices

1. Introduction

The Comité Consultatif de Thermométrie (CCT) has always had as its chief concern the perfecting of the International Temperature Scale (ITS) and, consequently, has been occupied with thermometric measurements of the very highest accuracy. There are many laboratories in the world, including even some of the national standardizing laboratories in countries adhering to the Convention du Metre, that, while requiring temperature measurements to be related to the ITS, do not require this ultimate accuracy. In an attempt to address this need, the CCT assigned to a Working Group the task of preparing a monograph describing methods for approximating the ITS that are simpler and more practicable than the fundamental definition, giving estimated accuracies of the various approximations. That the need for this information is high can be inferred from the result of a study in the U.S.A. [Frost and Sullivan (1984)] which reveals that temperature is the most commonly measured physical variable today. The study forecast annual expenditures in the U.S.A. of $0.9 x 10^9 on temperature measurement and control devices and instrumentation by 1988 for a real annual growth rate of 10% in the industrial temperature instrumentation market over a 5-year span. This monograph is meant to be a companion to "Supplementary Information for the ITS-90" [CCT (1990)], a forthcoming revision of "Supplementary Information for the IPTS-68 and the EPT- 76" [CCT (1983)]. The latter is directed to those who wish to realize the ITS-90 with accuracies ranging from moderately high to the very highest level; the present monograph is to give guidance to those who wish to approximate the ITS-90 using simpler techniques and for whom those levels of accuracy are unnecessarily high. It is clear that in such a monograph care must be taken to emphasize that the approximations described do not constitute official recipes for realizing the ITS-90, different from but less accurate than the fundamental definition. Such a proliferation of "official" scales would be highly undesirable.

This monograph therefore provides information on how one can approximate the ITS-90 to a modest but specified level of accuracy with a variety of techniques. It necessarily includes considerable discussion of the sensors themselves - their properties, reliability and limitations, and guidelines for proper handling and use - but this discussion is in no way exhaustive. A large literature already exists on these sensors to which the reader is referred for extensive treatments.

For a formal realization of the ITS-90, the response of (one of) the defining instruments* is measured at the appropriate defining fixed points and the thermometer is then used to interpolate temperatures between the fixed points according to the relationships specified in the definition of the scale. Methods for doing this have been outlined [CCT (1990)]. For the approximations described herein the thermometer has to be calibrated in a way that can be related to such a formal realization of the ITS-90. This can be done either by a comparison calibration or by using fixed points, approaches which differ slightly but subtly. Formerly, comparison calibrations were the most-used mechanism for dissemination of the ITS, but more and more the fixed-point method is being used. In France and in the German Democratic Republic, for example, the ITS-90 is already disseminated largely in terms of calibrated fixed point devices.

A comparison calibration (or simply a calibration) of a thermometer usually implies a direct comparison of the thermometer response with that of a calibrated defining instrument at many temperatures in some sort of isothermal environment (such as a liquid bath or a metal block in an electric furnace). Either the calibration itself, or, more usually, the calibration of the defining instrument, is carried out in a national standards laboratory or in an accredited secondary laboratory, thereby ensuring a direct link to the ITS-90. For a great many users this can be the simplest and most straightforward way to obtain direct access to the ITS-90. It can be, but is not necessarily, inexpensive. Temperatures are measured directly on the ITS-90 if the calibrated thermometer is one of the defining instruments. Under the best conditions the uncertainties in measured temperatures can be as small as those of the calibration, which in turn may be within a factor of two or three of the standards laboratory's primary realization. More generally, of course, the accuracy will be determined by the quality of the thermometer and by the measurement procedures. One disadvantage of direct calibration by a standards laboratory is that it does not constitute an independent realization of the ITS-90, if such is required. Another is that any calibration by comparison involves the transport of thermometers between laboratories, a procedure that can affect their reliability.

There are many national standards laboratories world-wide that offer a calibration service over the complete range of the ITS-90 (see Appendix A, which is not necessarily complete). Some standards laboratories are not prepared to calibrate large numbers of

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* The term "defining instrument" is used to mean any one of the standard thermometers specified in the text of the ITS-90 for interpolating between defining fixed points.

thermometers except in special extenuating circumstances; these laboratories are prepared, however, to calibrate thermometers intended to be supplied to national secondary calibration services.

Commonly, a user of large numbers of thermometers (university, factory, etc.) will not rely upon a national standards laboratory for all of its calibrations, but instead will acquire a selected number of calibrated thermometers as its secondary standards against which it will calibrate its working thermometers (or, if the user is itself another standards laboratory or an accredited calibration laboratory, its customers' thermometers). In such circumstances it is highly desirable to maintain a minimum of three secondary standards of each type that have undergone reasonably recent primary calibrations. One or, usually, two of these will become general working standards; at least one, and preferably two or more, will see very little service except for periodic checks of the calibrations of the working standards and of each other. In this way, any apparent changes in calibration can easily be traced to the offending instrument. The more secondary standards that are available, the more reliable this procedure becomes. The thermometers used as secondary standards will almost always be standard platinum resistance thermometers (SPRTs) ; germanium or rhodium-iron resistance thermometers; platinum 10% rhodium/platinum, platinum 13% rhodium/platinum, gold/platinum, or palladium/platinum thermocouples; tungsten strip-filament lamps; or infrared radiation thermometers, depending upon the temperature range required and the instrument to be calibrated. These standards should be maintained according to the procedures outlined in the "Supplementary Information for the ITS-90" [CCT (1990)]. It is recommended that fixed points (for example, triple points of water, gallium, or cryogenic substances) also be obtained so as to monitor the stability of resistance thermometers. For SPRTs this serves two important additional purposes: (a) changes in the resistance (R(t)) of an SPRT due to cold work, oxidation, strain, etc. are, to a first approximation, proportional to R(t) so that the resistance ratio $W(t) = R(t)/R(0.01\ °C)$ remains relatively unchanged. The ability to monitor a particular value of R(t), such as R(t) at a fixed point, then leads to higher temperature measurement accuracy. (b) W(t) is independent of the unit used to measure R(t) so long as all resistance values are measured with the same instrument (for example, bridge and standard resistor). Thus, laboratory measurement of resistance at a fixed point as opposed to reliance on a calibration-supplied value of resistance at that fixed point obviates the need for measurement in ohms.

The tungsten strip-filament lamp mentioned in the preceding paragraph is not itself a thermometer, but acts as a transfer device. The lamp is calibrated with a standard optical pyrometer in terms of spectral radiance temperature at a particular wavelength versus current, and this calibration is subsequently transferred to another pyrometer.

For a calibration using fixed points (which has been called a secondary realization, but this term is not recommended), the thermometer is calibrated at a number of such points (that may include both defining and secondary fixed points) and temperatures are interpolated between fixed points according to a functional (usually an empirical) relationship that experience has shown will generate values of temperature on the ITS-90 to within some specified degree of accuracy. Secondary fixed points are fixed points that are not used in the definition of the ITS-90, but which have been well-characterized, and the temperatures of which have been carefully determined on the ITS-90. Bedford et al. (1984) give recommended values of temperatures, together with an assessment of their uncertainties, for a large number of secondary fixed points. The values of temperature, which are on the IPTS-68, can be converted to the ITS-90 using the tables included here in Appendix A.

A thermometric reference material might, in some circumstances, also be used in the sense of a secondary fixed point. Caution should be exercised, however, in the use of thermometric reference materials, which differ in principle from fixed points. A fixed point (whether primary or secondary) is a phase transition temperature of a substance of extremely high purity; any two samples of the substance will exhibit precisely the same transition temperature, so long as the experimental apparatus (furnace, cryostat) is properly designed and the thermometer is in temperature equilibrium with the sample. A thermometric reference material, on the other hand, is simply a batch of certified material from which samples can be drawn; a sample of this material, when used according to a specific recipe, undergoes a phase transition at a temperature that has been previously measured and certified with a calibrated thermometer. The material need not be especially pure, and the assigned transition temperature applies only to the particular lot from which the sample is drawn. Another lot of nominally the same substance may have a different transition temperature. In this monograph the many references to secondary fixed points should not be construed as being applicable to reference materials. A thermometric sealed cell, depending upon its construction, can be used either in the sense of a fixed point or of a reference material [Pavese (1980), (1986)]. If a reference material is used as a fixed point, the value of temperature associated with it should be that given by the supplier.

The accuracies with which temperatures may be referred to the ITS-90 as a result of a comparison calibration or a calibration with fixed points are comparable; if anything, the former is the more accurate except near the fixed point temperatures unless many fixed points are used. It is difficult to make any single statement regarding the limits of accuracy that may apply. As a rough guide, the largest uncertainty for any technique described herein will be ± 0.05 K below 100 K, ± 0.2 K near and above room temperature, ± 0.5 K up to 1000 °C, and ± 1 to 2 K above. Many of the techniques, of course, may give substantially better results than this. In Table 1.1 are listed all of the thermometers discussed in this monograph, their temperature ranges under various conditions, and typical associated uncertainties.

The ITS-90 became the officially-recognized International Temperature Scale on January 1, 1990. In this monograph there are a few unavoidable references to its predecessor, the IPTS-68. Furthermore, there are undoubtedly users of this monograph who are measuring temperatures with thermometers calibrated on the IPTS-68. We emphasize that any temperature T_{68} (or t_{68}) can be converted to its equivalent value of T_{90} (or t_{90}) by use of the tables given here in Appendix A. Similarly, any previous edition of the ITS can be used to approximate the ITS-90 to within the combined accuracies of the associated conversion tables.

This monograph is divided into two parts. Part 1 includes those methods and thermometers that are considered to be best suited for directly approximating the ITS-90, and the associated calibration techniques. Part 2 deals with a number of thermometers that are important because they are widely used or are used for special purposes, but that are in general less accurate than those of Part 1, and for which temperatures measured with them must still be traced to the ITS-90. Thus, for example, approximations based upon SPRTs are described in Part 1 but treatment of industrial platinum resistance thermometers (IPRTs) is relegated to Part 2 because, although IPRTs are in wide use, they are as a class not accurate enough for approximating the ITS-90 directly in the sense defined here. International specifications for IPRTs and standard thermocouple reference tables as developed for use with the IPTS-68 are included herein. At the time of writing, corresponding specifications and tables with respect to the ITS-90 had not yet been published. Approximate equivalents can be obtained using the tables in Appendix A.

There is, naturally, a degree of overlap between the material contained herein and that in "Supplementary Information for the ITS-90" [CCT (1990)]. Methods for highly accurate fixed point realizations, for example, are described in some detail there, so will not be repeated here, but several special ways to use fixed points for approximating the ITS-90 are described in Chapter 3. On the other hand, there is some duplication in descriptions of the various sensors since all of the defining instruments are also used for secondary measurements. Except for the standard platinum resistance thermometer, there is a rather fuller description of the sensors in the present monograph. For the platinum 10% rhodium/platinum thermocouple*, in particular, which is one of the most important thermometers for approximating the ITS-90 even though it is no longer a defining instrument of the ITS, the information contained in Chapter 5 of the "Supplementary Information for the IPTS-68 and the EPT-76" [CCT-1983] has been included and substantially augmented here, and has been deleted from the revised "Supplementary Information for the ITS-90" [CCT (1990)].

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* In this monograph, specific thermocouple designations are written with the positive element first, separated from the negative element by the oblique symbol. Frequently, also, they will be written in an abbreviated form: platinum 10% rhodium/platinum will also be written as Pt10Rh/Pt, for example. Standard international letter designations, such as Type S for Pt10Rh/Pt, are also used of course.

Table 1.1: Summary of Some Properties of Most-Commonly-Used Thermometers

Thermometer	Usual Temperature Range	Thermometric Quantity	Typical Uncertainty
Germanium	1 K to 100 K	elec. resist.*	ΔT / T < 2x10-4
Rhodium-Iron	0.5 K to 30 K	elec. resist.*	0.3 mK
Platinum-Cobalt (industrial type)	2 K to 20 K	elec. resist.*	10 mK
Carbon	0.5 K to 30 K	elec. resist.*	ΔT / T < 5x10-3
Carbon-glass	0.5 K to 100 K	elec. resist.*	ΔT / T < 1 x1 0-3
Diode	4 K to 300 K	junction voltage	-50 mK
Vapour-pressure	various subranges between 0.5 K and 100 K	pressure	-1 mK
Mercury-in-glass	-50 °C to 250 °C	thermal expansion of mercury	0.1 K
Thermocouples	4 K to 2500 °C	thermoelectromotive force	
Type S	-50 °C to 1600 °C		0.3 K < 1000 °C 1 K > 1000 °C
Type R	-50 °C to 1600 °C		0.3 K < 1000°C 1 K > 1000 °C
Type B	300 °C to 1800 °C		0.5 K to 2 K
Type T	-200 °C to 350 °C		0.1 K
Type E	-200 °C to 870 °C		0.1 K < 300 K 1 K > 300 K
Type J	0 °C to 760 °C		0.5 K < 300 °C 2 K > 300 °C
Type K	-200 °C to 1260 °C		0.1 K < 200 °C 1 K 200-1000 °C 3 K > 1000 °C
Type N	0 °C to 1300 °C		0.1 K < 200 °C 0.5 K 200-1000 °C 3 K > 1000 °C
W/Re	1000 °C to 2400 °C		3-10 K

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* elec. resist. is the electrical resistance

Table 1.1: (Continued)

Thermometer	Usual Temperature Range	Thermometric Quantity	Typical Uncertainty
Thermistor	-80 °C to 250 °C	elec. resist.*	0.1 K (much better if use confined to very small temperature range)
Platinum: SPRT	14 K to 630 °C	elec. resist.*	0.5 mK
IPRT	20 K to 600 °C		50 mK
Radiation	100 °C to 3000 °C	spectral radiance of source	1 K < 1000 °C 5 K > 1000 °C

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* elec. resist. is the electrical resistance

PART 1: TECHNIQUES AND THERMOMETERS FOR APPROXIMATING THE INTERNATIONAL TEMPERATURE SCALE OF 1990

The most common and best-characterized thermometers for very low temperature use are those that relate temperature to electrical resistance. In Part 1 there is a discussion of germanium, rhodium-iron, and platinum resistance thermometers together with their associated calibrations and interpolation formulae for approximating the ITS-90. The use of germanium is normally restricted to below 30 K. The same has been true for rhodium-iron although the chief reason for not using it to near 300 K has been competition from platinum. With platinum, calibration at a few fixed points coupled with simple interpolation will reproduce the ITS-90 moderately accurately. Germanium and rhodium-iron thermometers, on the other hand, must be individually calibrated because no two thermometers of the same type have exactly similar resistance/temperature characteristics, and there must be calibration at many points because interpolation of the resistance/temperature relationship is difficult. They are used as transfer standards for maintaining the ITS-90 below about 25 K, defined in terms of thermodynamic thermometry.

Germanium resistance thermometers are small, relatively inexpensive, and very sensitive at the lower end of their range. Standard-type rhodium-iron resistance thermometers are much larger, much more expensive and less sensitive than germanium, but are more stable and have a wider range of use. Platinum costs the same as, or more than, rhodium-iron, and is the clear choice above about 25 K. Both platinum and rhodium-iron are extremely stable; with proper handling, which means treating the thermometers as fragile and not subjecting them to mechanical shocks or vibrations, variations as large as a millikelvin are unusual. Germanium thermometers are about an order of magnitude less stable.

Vapour pressure thermometry and magnetic thermometry are also discussed in Part 1 because of their fundamental use. No comparable treatment of the former appears to exist. Platinum thermocouples and infrared radiation thermometers are also included in Part 1 because they are widely used to approximate the ITS-90.

The discussion of these various thermometers is preceded by a description of the methods, and hence of cryostats, baths, and furnaces, for attainment of uniform temperature environments (Chapter 2) and by some discussion of fixed points (Chapter 3), the latter intended to complement, rather than duplicate, that in "Supplementary Information for the ITS-90" [CCT (1990)].

2. Uniform-Temperature Enclosures

Calibration of thermometers requires uniform-temperature enclosures. All of the apparatuses described here to produce such enclosures may be constructed in the laboratory, or, alternatively, may be obtained commercially. The latter tend to be more costly and to provide poorer, although adequate, uniformity. For comparison calibrations, the uncalibrated thermometer and the laboratory standard are mounted in such a way as to be in good mutual thermal contact, as in a solid metal block or a stirred liquid. Significant errors can be avoided by proper attention to immersion depths, heat transfer along thermometer leads, thermal time lags, thermometer self-heating, temperature differences within the enclosure, radiation exchange with the environment, and so on. The type of enclosure used depends upon the temperature range involved.

2.1 1 K TO 300 K

Several apparatuses that serve for the calibration of thermometers have been described. The temperature stability and uniformity of the apparatuses depend upon both their thermal design and the quality of the associated temperature controller. One that is simple, that has worked extremely well for calibrating capsule PRTs, and that can be used with germanium (Ge) or rhodium-iron (RhFe) resistance thermometers is shown in Fig. 2.1. A small copper block with holes for four thermometers is surrounded by two concentric copper radiation shields in an insulated container which is open at the bottom. The container hangs by a thin-walled metal tube in a liquid helium dewar. To prevent heat transfer along the thermometer leads, the latter pass through insulated holes in the copper block and one of the shields. Heaters are wound on both the block and the shields, and the temperature difference between them is measured with differential thermocouples. The block is cooled to liquid helium temperatures and the liquid is then blown out of the insulated container, leaving helium gas at atmospheric pressure therein. The liquid helium remaining in the dewar provides the necessary cooling. The block is heated to, and then maintained at, each desired temperature in turn, the shield temperatures being adjusted to be that of the block by a servo-control. The apparatus requires no vacuum feed-throughs for the leads and the thermometers rapidly reach equilibrium as a result of the good thermal contact between the block and the thermometer provided by the helium gas. With this system a PRT can be calibrated to within 1 mK.

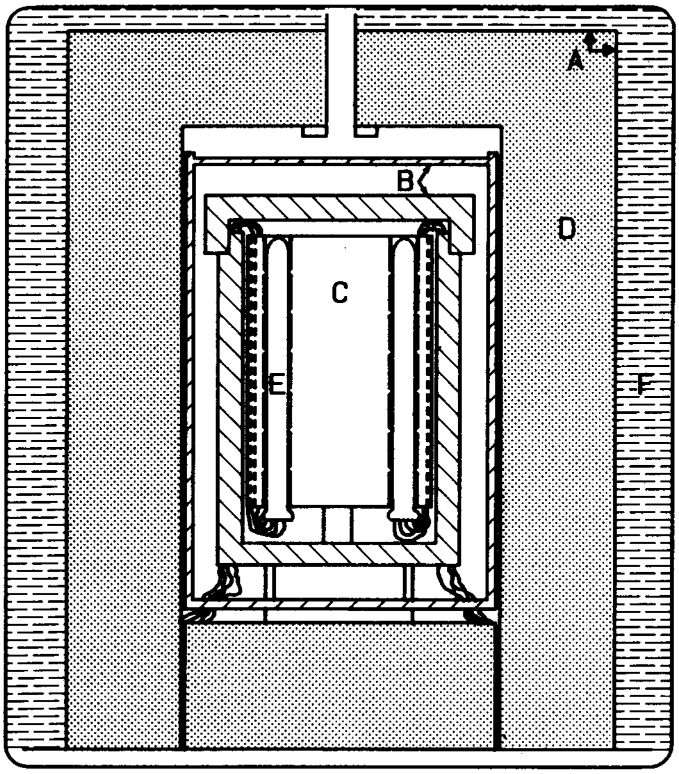

Fig. 2.1: One form of apparatus used at NRC for calibration of resistance thermometers from 4.2 K to 273.15 K: A, metal cover; B, copper shields; C, copper block; D, expanded polystyrene; E, capsule PRT; F, liquid helium.

An alternative procedure that is also widely used is to place the thermometers in a copper block that is enclosed within suitable radiation shields in an evacuated cryostat as shown in Fig. 2.2 (see, for example, Rusby et al. (1972), Compton and Ward (1975), or Besley and Kemp (1977)). Details of operation are given in the suggested references. It is sometimes useful to design the cryostat in a modular way to allow for the use of a single apparatus for different experiments. This may be facilitated by the incorporation of a cylindrical re-entrant well in the tube connecting the cryostat chamber to the part of the apparatus that is at room temperature. In this way, different modules, designed for different experiments, can be interchanged from the top flange, without one's having to disassemble the cryostat itself [see Pavese (1981)].

For temperatures above 4 K, it is also possible to use closed-cycle refrigerators, so avoiding conventional liquid refrigerants and allowing convenient and faster operation. The thermal design of measuring modules for such a system is similar to that of a flow cryostat (Fig. 2.3) [Blanke and Thomas (1979)], but care must be taken to prevent mechanical - vibrations from adversely affecting the thermometer.

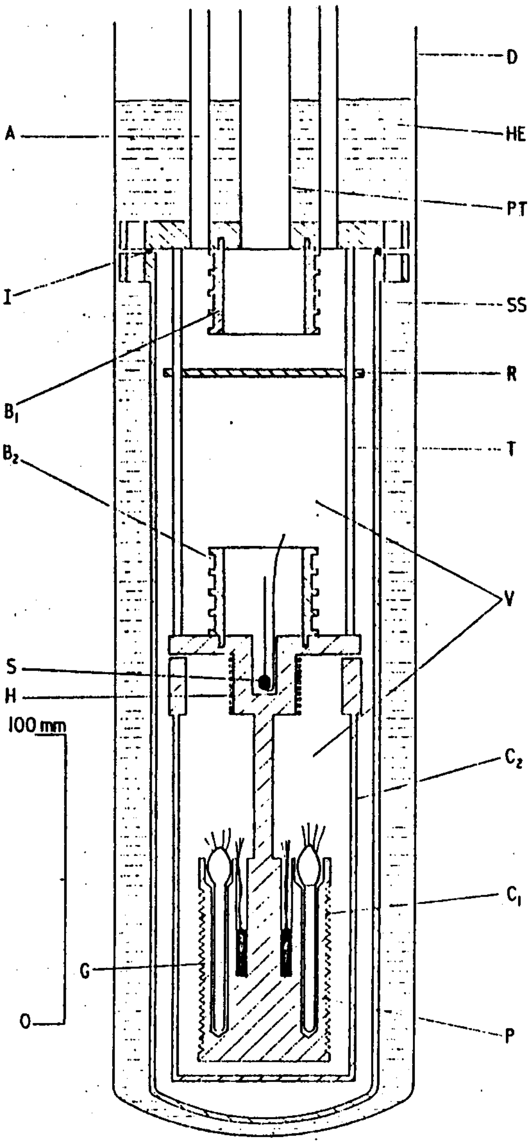

Fig. 2.2: Cryostat for calibration of resistance thermometers: D, outline of helium dewar; HE, liquid helium reservoir; PT, pumping tube; SS, stainless-steel vacuum can; I, indium seal; R, radiation shield; A, one of four access tubes for wires; B, binding post for wires; T, one of four support tubes; V, vacuum; S, temperature control sensor; H, heater; C 1, copper thermometer block; C2, copper isothermal shield; P, platinum thermometer; G, germanium thermometer [after Rusby et al. (1972)].

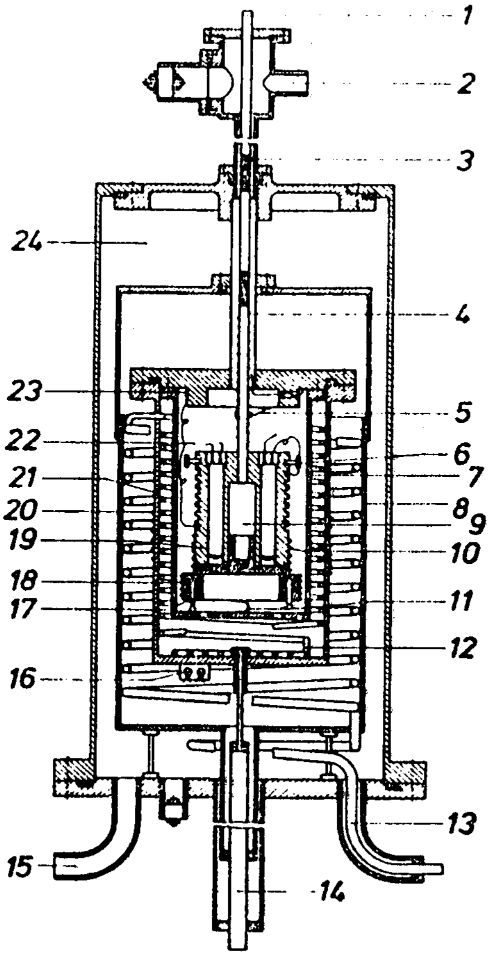

Fig. 2.3: Flow cryostat, shown with a vapour pressure bulb fitted: 1, pressure tube with radiation traps; 9, bulb with thermometers; 15, 24, vacuum space pumped through; 8, outer shield, nitrogen cooled through inlet 13 and coil 7; 20, inner shield, helium cooled through syphon 14 and coils 12 and 21; 23, isothermal shield, with internal independent vacuum 22; 16, thermometers : for temperature regulation of the shield. [Blanke and Thomas (1979)].

The sealed-cell cryostat of Ancsin and Phillips (1984) can also be used as a comparator over the temperature range 84 K to 400 °C (see Sec. 3.1.4).

In any of these systems, it is important that the thermometers be in good thermal contact with the block, as through the use of a vacuum grease. It is also important to prevent heat exchange between the thermometer and room temperature via the connecting leads; for this reason the thermometer leads, *and* an appropriate length [Hust (1970); Fellmuth and Seifert (1988)] of the connecting wires must be put in good thermal contact with the measuring block or with a body maintained at block temperature. However, this procedure must not prejudice the maintaining of a sufficiently high electrical insulation resistance. The necessary resistance depends upon the accuracy required and the thermometer resistance. In measuring the insulation resistance, care must be taken not to damage the thermometer by too-high currents from the high-resistance-measuring device. In general, the minimum allowable insulation resistance is tens of megohms. The wires coming into the experimental chamber of the cryostat should also be thermally anchored at the refrigerant temperature. A suitable thermal-anchoring material is made of copper evaporated over a thin plastic foil such as Kapton.

2.2 150 K to 350 °C

In this range the most convenient enclosures for mounted thermometers are stirred-liquid baths. The approximate temperature ranges that may be covered by various liquids are: 150 K to 225 K, isopentane; 225 K to 20 °C, methyl alcohol; 2 °C to 90 °C, water, with the range extendable to -5 °C by the addition of a small quantity of glycol; 50 °C to 350 °C, mineral or synthetic oils. The essential features of a bath used at NRC are shown in Fig. 2.4. The liquid is contained between 50 cm long concentric cylinders of diameters about 10 cm and 6 cm respectively. A propeller driven through a seal at the bottom of the bath and with appropriate anti-spin vanes forces the liquid up the inner cylinder and down between the two. An immersion heater between the cylinders controls the temperature and a second heater on the outer cylinder maintains the external temperature a few degrees below the required calibration temperature. For the water bath, cooling is obtained by circulating Freon through the refrigerant coils shown on the outer shell. With the oil bath, which operates only above ambient temperature, the refrigerant is unnecessary. For the alcohol or isopentane baths, liquid nitrogen or solid carbon dioxide are the usual refrigerants. The thermometers to be calibrated are mounted at suitable depths within the inner cylinder. Uniformity of temperature to better than 10 mK, and with care to within 1 to 3 mK, within this inner cylinder is readily achieved. Other variations of this general design are described by Quinn (1983) and Pavese and Coggiola (1972).

With the oil baths, light mineral oils are used up to about 200 °C, and heavy oils up to about 350 °C or even 375 °C on occasion. The upper limit is set by the flash point of the oil or by the tendency of the oils to carbonize. The lower limit is that at which the viscosity has become too high for efficient heat transfer to be maintained. In using an oil bath, it is essential to provide a proper venting system to remove the noxious fumes from the laboratory. It is also advisable to keep a suitable fire extinguisher at hand if the bath

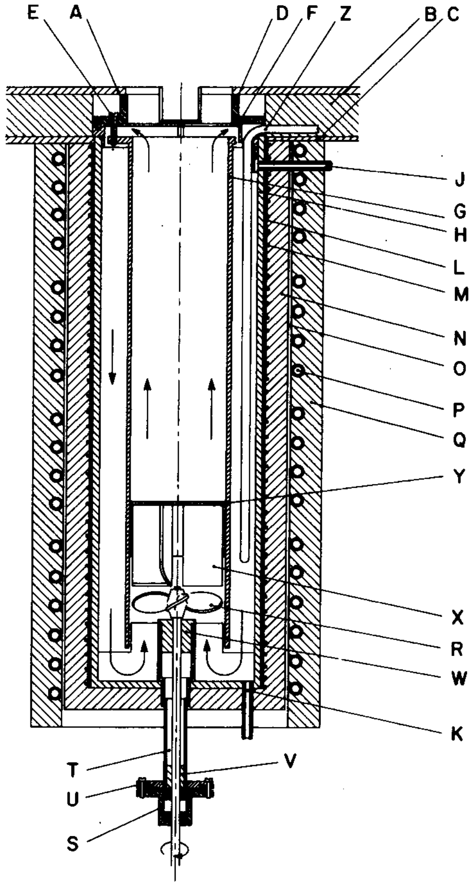

Fig. 2.4: Stirred liquid bath for use from -5 °C to 350 °C: A, top cover, bakelite; B, insulation, expanded polystyrene; C, bakelite; D, top ring, bakelite; E, weir height adjustment screw; F, splash shield; G, weir, brass; H, water container, brass; J, overflow tube, german silver; K, drain, german silver; L, insulation, mica; M, outer heater; N, insulation, fiberglass; O, copper sheet; P, refrigeration coil; Q, insulation, fiberglass; R, propeller, 4 blades brass; S, closure housing including seals and lubricants; T, tube, german silver; U, o-ring seat; V, lower bearing, teflon; W, upper bearing, teflon; X, anti-spin vane; Y, screen, copper.

temperature is to be raised to near the flash point because ignition may occasionally occur below the expected flash point.

2.3 300 °C to 1100 °C

For temperatures above the range of stirred oil, no completely satisfactory bath is available. A salt bath (containing a mixture of equal parts of potassium nitrate and sodium nitrite) will provide an extremely uniform temperature from about 250 °C to 550 °C, but has substantial drawbacks. These include: a highly corrosive action on the bath container and on any devices inserted into the salt (a quartz-sheathed thermometer must be protected from the salt by an auxiliary Pyrex protection tube); a salt residue left on a device after calibration which is often difficult to remove; a potentially dangerous condition during heat-up if expansion of liquid is prevented by entrapment in solid salt; an extremely long heat-up time for the solid phase; possible violent splatter when foreign (organic) materials come in contact with the salt; requirement for venting fumes; and a generally messy housekeeping problem. Industrial safety codes for the operation of salt baths should be consulted [for example, HMSO (1964)].

An alternative to the salt bath is a fluidized bed, or fluidized powder bath. This can be capable of operation over an extremely wide range (from below ambient to 1100 °C) but it is difficult to obtain within the working volume a temperature that is uniform enough. The fluidizing medium is usually very finely powdered aluminium oxide through which dry air, nitrogen, or argon is allowed to flow slowly upward from an underlying porous diffuser of metal or ceramic. When fluidization begins, the individual Al_2O_3 particles circulate freely, and the powder takes on many of the properties of a liquid. The appearance is much like that of swirling cream with gentle surface bubbling. The powder tends to rise and migrate slowly from the centre to the walls. Heat is supplied in much the same way as in a liquid bath. Frequently, in the higher temperature units, a layer of zirconium oxide that does not fluidize but assists in the diffusion and inhibits the burning of the porous plate lies between the Al_2O_3 and the solid diffuser plates. Typical temperature differences in the fluidized bath range from tenths of kelvins to as high as a few kelvins. If a metal block is used within the fluidizing medium, better uniformity is possible. In addition to a frequently inadequate temperature uniformity, another disadvantage is the deposition of Al_2O_3 dust on everything near the bath. Care must be taken to avoid mechanical vibrations arising from the circulation of the fluid powders.

Wire-wound resistively-heated electric furnaces are the most common uniform-temperature enclosure above the range of liquid baths. These are essentially the same as those described in "Supplementary Information for the ITS-90" [CCT (1990)] for the realization of metal freezing points. A metal block (aluminium, copper, Inconel) is contained within a cylindrical ceramic muffle on which the heaters are wound. The main heater runs the whole length of the muffle, while smaller ones are placed either over it or within the muffle near each end, compensating for heat losses and thereby lengthening the uniform-temperature zone. The whole is suitably insulated. With care, for a 60 to 90 cm furnace, it is possible to adjust the heater powers so as to obtain a central 20 to 30 cm zone that is uniform in temperature to some tenths of a kelvin. The convenient upper temperature limit for such furnaces is 1100 °C, up to which Nichrome or Kanthal heater windings have long lifetimes. For higher temperatures one must resort either to expensive platinum-alloy heaters or to refractory-metal heaters that require protection from air or oxygen.

A simpler arrangement with even better temperature uniformity uses a cylindrical heat-pipe liner within the furnace muffle. In this case a single heater will suffice. A heat pipe is essentially a closed tube or chamber whose inner surfaces are lined with a porous-capillary wick. The wick is saturated with the liquid phase of a working fluid and the remaining volume of the tube contains the vapour phase. Applied heat vaporizes the working fluid in some sections, resulting in a pressure difference that drives vapour to cooler regions where it will condense, releasing the heat of vaporization in that section of the pipe. Depletion of liquid by evaporation causes the liquid-vapour interface to enter into the wick surface. The capillary pressure developed there pumps the condensed liquid back for re-evaporation. That is, the heat pipe can continuously transport the heat of vaporization from the evaporator to the condenser section.

The amount of heat that can be transported in this way is several orders of magnitude larger than that which can be transported in a conventional system; the heat pipe acts as a tube of extremely high thermal conductivity. Hence, when it is placed within an already-heated furnace it increases the uniformity immensely. Quinn (1983) gives a useful, more detailed discussion. The working fluid is usually sodium or potassium for heat pipes of interest here. A metal block may be placed within the heat pipe, but in many cases may be unnecessary. Care must be taken in the use of metal-enclosed sodium or potassium in heat pipes; the usual precautions for use of these metals should be taken.

A more sophisticated use of the heat pipe is in the pressure-controlled or gas-controlled heat pipe [see, for example, Bassani et al. (1980)]. The cylindrical heat pipe is installed in a conventional electric furnace as above, but in this case most of the applied heat is concentrated near one end (the concentrator); a vertical (or tilted, for vertical furnace operation) water-cooled chimney (the condenser) is attached at the other end; and an inert buffer gas (helium) is maintained over the working fluid (sodium) vapour, the buffer-gas pressure being externally controlled by conventional techniques. The furnace temperature can be changed from one level to another by changing the buffer-gas pressure; re-equilibration at the new level is rapid, typically within a few tenths of a kelvin in 20 minutes for a 50 K change. A standard pressure and temperature feedback control system allows the temperature to be controlled at a given level to within a few mK. The response to small pressure changes is very rapid, the speed being determined more by the temperature-sensor response than the heat-pipe response. Temperature uniformity within the furnace to within a few mK is possible. With sodium as the working fluid, the heat-pipe furnace is operable from about 550 °C to 1100 °C; with potassium, from about 400 °C to 950 °C.

Another type of furnace used for the calibration of thermocouples is the electric tube furnace, shown schematically in Fig. 2.5 [Dauphinee (1955)]. The cylindrical Nichrome furnace tube about 3 cm in diameter and 50 cm long forms part of a one-turn secondary of a high-power transformer, and is resistively heated by the high ac secondary current. A silica tube is placed inside the furnace tube, and the thermocouples to be calibrated are inserted inside this with their tips welded or otherwise physically joined together. The furnace is uninsulated so its temperature can be changed very rapidly. A typical calibration run with Pt10Rh/Pt thermocouples takes 2 hours from ambient to 1100 °C and down again. This high speed is possible because the absolute emfs of the unknown and the standard need not be simultaneously known, but only the slowly-changing difference between them. Typically, with Pt10Rh/Pt calibrations for example, this difference when the furnace is heating will have slightly different values from when it is cooling, but it can be shown that the mean of the two is the same as the steady-state difference. With (even slightly) dissimilar base-metal thermocouples, the furnace temperature must be stabilized at the desired calibration points before the emfs are measured. In this furnace there is really no constant temperature zone, but this does not matter so long as the small volume around the welded tips is isothermal.

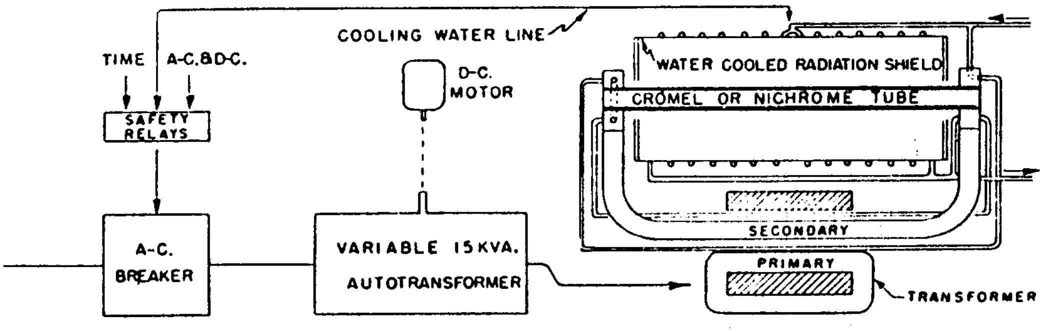

Fig. 2.5: Schematic drawing of a fast-response electric tube furnace for thermocouple calibrations [Dauphinee (1955)].

3. Specialized Fixed Points

A temperature fixed point is a calibration point for thermometers that differs from a comparison calibration point in that its temperature value is not measured, during the calibration process, by another already calibrated thermometer, but has been previously established either by definition (if it is a defining point of the ITS-90) or by previous experiments (if it is a secondary reference point) [Bedford et at. (1984)]. Whether measured or assigned, the temperature value is associated with a thermodynamic state of a substance; how closely that state is approximated during the calibration depends upon the stringency of the specifications on it (e.g. requirements on purity, isotopic compositions, annealing, ...) and upon the experimental uncertainty of the measurements.

The ITS-90 can be approximated not only by simplified interpolation with primary or non-primary thermometers (as will be discussed in the next sections of this monograph), but also by relaxing the fixed point specifications or by using the fixed points in different ways. In this chapter we describe a number of specialized fixed points and unconventional ways of realizing conventional fixed points, with indications of the accuracies that may be attained. Methods for highly accurate fixed point realizations are described in detail in "Supplementary Information for the ITS-90" [CCT (1990)] and will not be repeated here.

3.1 Fixed Points Below 0 °C

3.1.1 Superconductive Fixed Points

3.1.1.1 General Remarks

Superconductive transitions are solid state phase changes of second order in contrast to most fixed points used in thermometry which are first-order phase changes. Second order phase changes are distinguished by the absence of an associated latent heat. Essential peculiarities of the superconductive transitions are the larger influence on them of impurities, crystal defects, and physical strain which affect both the transition widths and temperatures (T^C). This does not prevent their application as thermometric fixed points, however, if special sample preparation techniques and special methods for the detection of the superconductive transitions are used.

With the promulgation of the EPT-76 [CCT (1979)], superconductive transition temperatures (ST -temperatures) were officially used as fixed points for the realization of an international temperature scale. However, connected with the peculiarities mentioned above, the definition of the EPT -76 was based only upon the superconductive fixed-point device SRM 767 [Schooley et al. (1980) and Schooley and Soulen (1982)], so that the ST - temperatures were only used officially in the sense of a reference material (see Sec. 3.1.2). Furthermore, ST-temperatures are not used as fixed points in the definition of the ITS-90. Metrological investigations of SRM 767 fixed-point samples [El Samahy et al. (1982)] verified that T^C values are reproducible within about 1 mK. Efforts towards improvement have shown that a reduction of the non-uniformity of the TC values well below 1 mK is possible by carefully annealing all samples and by selecting them on the basis of maximum allowed transition widths [Schooley (1984)].

3.1.1.2 Requirements for Superconductive Fixed Points

Problems in, and possibilities for, the realization of superconductive transitions as true thermometric reference points are reviewed for the metals Cd, In, Al, In, Pb, and Nb by Fellmuth and Maas (1987). This review shows that modern sample preparation and handling techniques, in conjunction with convenient material characterization methods, are sufficient to guarantee an accuracy and stability of the ST-temperatures of these elements within about 1 mK if definite specifications concerning sample parameters are fulfilled.

The main difficulty in realizing a superconductive fixed point is the influence of impurities and crystal defects on the ST-temperature. The influence of impurities is of the same order of magnitude as for metal freezing points: typically ($|dT^C/dc| \approx 1$ mK per ppma*, where c is the impurity content). The residual resistance is an excellent indicator of this influence except in the few cases where localized magnetic moments exist; in this latter case dTC/dc can be much larger so the concentration of the magnetic impurities must be determined separately. The effect of crystal defects can be reduced to a few tenths of a millikelvin by using suitable preparation techniques, which may differ for different elements. For checking the magnitude of this effect it is important that the transition width be always smaller than the change in the ST-temperature due to the defects. Hence, for the realization of superconductive reference points, detailed information concerning both the physical properties of the materials and the preparation and characterization methods is necessary. Such information is given for the six metals listed above in the review of Fellmuth and Maas (1987) and, for niobium, by Fellmuth et al. (1985), (1987).

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* The abbreviation ppma is used to mean an impurity content of one solute atom per 10^6 solvent atoms.

3.1.1.3 Realization of Superconductive Fixed Points

In Table 3.1 the ST-temperatures on the ITS-90 of the six metals Cd, In, Al, In, Pb, and Nb are listed*. The uncertainties given include the temperature measurement uncertainties assigned for the available experimental data, the non-uniqueness of the EPT-76, the differences of the T^{C}_{76} values published for high-quality samples of different origin and different parameters, and the effect on the ST-temperatures of the various factors that can be expected to influence the parameters of the investigated samples. In the application of superconductive fixed points the dependence of the ST-temperature on detection techniques has to be taken into consideration [Nara (1984)]. The mutual inductive technique is most effective because of its relative ease of application, the minimum stress transmitted to the sample, and the negligible sample contamination [Soulen and Colwell (1971)]. Thermal anchoring of the samples and of the electrical leads is critical for the observation of non-hysteretic and reproducible transitions [Schooley et al. (1980) and Schooley and Soulen (1982)]. Because of the absence of latent heat, a high-quality adiabatic cryostat is necessary for accurate T^{C} measurements. To check that the thermal conditions are adequate, the difference between the ST-temperature values obtained with increasing and decreasing the temperature of the sample through the transition range should always be measured. The temperature should then be stabilized at the mid-point of the transition before thermometer calibrations are carried out. Furthermore, external magnetic fields (earth's magnetic field and measuring field) can have an influence of a few mK on the ST-temperatures; the effect can be corrected for, or, more comfortably, compensated for.

3.1.2 Standard Reference Materials

In contrast to the foregoing fixed point definition, the temperature value assigned to a standard reference material (SRM) is a *device*-temperature, i.e. the device reproduces precisely a temperature value which has been determined by calibration but which, within stated limits, is characteristic only of the individual device. The boundary between a SRM and a fixed point may be ill-defined as the specifications of a SRM can be so strict that the value assigned is the same as that of the physical state, within a comparable uncertainty. For example, below 10 K, several superconductive transitions may be used as fixed points.

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* Note that the temperatures in Table 3.1 are slightly different from those used with the reference material NBS-SRM 767; the latter are given in Table 3.2.

Table 3.1 : Current Best Estimates of Superconductive Transition Temperatures and of the Total Uncertainties of the Estimate [Fellmuth and Maas (1987)] ,

Element	TC90/ K
Cd	0.5200 ± 0.0030
Zn	0.8500 ± 0.0030
Al	1.1810 ± 0.0025
In	3.4145 ± 0.0025
Pb	7.1997 ± 0.0025
Nb	9.2880 ± 0.0025

Table 3.2: Temperatures Assigned to Superconductive Fixed Points in the NBS (now NIST) Fixed-Point Devices

$*T^C$ (K)	Substance	Width (mK)	Reproducibility (1 standard deviation) (mK)
0.0160	°W	0.7	± 0.2
0.0230	°Be	0.2	0.1
0.0990	°Ir	0.8	0.1
0.1605	°AuAl2	0.3	0.1
0.2065	°AuIn2	0.4	0.15
0.5190	+Cd	0.5-8.0	0.3
0.8510	+Zn	2.5-10	0.4
1.1796	+Al	1.5-4.0	0.4
3.4145	+In	0.5-2.5	0.2
7.1996	+Pb	0.6-2.0	0.2

°SRM 768 [Schooley and Soulen (1982)]

+SRM 767 [Schooley et al. (1980)] * T_{90} above 0.5 K.

For these, there exist two SRMs issued by the National Institute of Standards and Technology: SRM 767 [Schooley and Soulen (1972), El Samahy et al. (1982)] and SRM 768* [Schooley and Soulen (1982)], each of which includes five metals with specified superconductive transition temperatures (Table 3.2). Within 1 mK, the devices can be considered to reproduce the temperature values of the physical states, though they are supplied calibrated. For the niobium transition near 9.3 K, another calibrated device is now available [Fellmuth et al. (1985)].

Above 14 K, the fixed points are triple and boiling points obtained from condensing gases; the reliability of bottled gases as SRMs is questionable as their use involves manipulation and consequent risk of contamination. However, the technique of sealing gaseous samples in metal cells makes it possible to obtain both reference fixed points [CCT (1983), Pavese et al. (1984)] and reference materials [Pavese (1980)]. Examples of sealed cells as SRMs as opposed to fixed points are the deuterium triple point when using gas obtained by hydrolysis of heavy water because of the high HD content, and the oxygen triple point when using gas distilled from air because of the unknown remaining contamination by argon. Most of the fixed points listed as second- or third-quality by Bedford et al. (1984) could still be used as SRMs in sealed cells.

3.1.3 Vapour Pressure Thermometers

Vapour pressure scales may be considered as giving a continuous set of fixed points, some of which are used also as defining points of the ITS-90 (the hydrogen boiling points and the helium vapour pressure scales). A realization of the ITS-90 that involves vapour pressure points, however, is complex and must include purity-effect analysis. Even without such analysis, any point of the vapour pressure curve can be used to obtain in a simple way and with an accuracy that depends upon the gas purity (see Chapter 6), a temperature value from the relationship to pressure and so to calibrate thermometers fitted into the same bulb. The use of vapour pressure thermometers is fully described in Chapter 6.

The requirements for the cryostat are essentially the same as for thermometer calibration in a comparison copper block, except that a bulb and sensing tube must be provided. Often the regulation is by control of the pressure rather than of the temperature. At the higher temperatures (for example, in a hypsometer for the steam point or for a sulphur boiling point) the boiler and comparison chamber are connected to a large ballast volume to ensure good stability.

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* SRM 768 provides fixed points below the lower limit of the ITS-90.

The widely-used, but not very reliable, method of taking advantage of an open bath of a boiling cryogen (oxygen, nitrogen, helium, rarely hydrogen or argon) is a very simplified way to do vapour pressure thermometry at a single point at atmospheric pressure. The bath should be stirred or other precautions taken to reduce temperature gradients, for example by lagging the comparison block.

The sensitivities of some fluids commonly used in vapour pressure thermometers are given in Table 3.3.

3.1.4 Sealed Cells

Though possible [Pavese (1981), Bonhoure and Pello (1983)], pressure measurement is generally not convenient with sealed samples, so the sealed-cell method is best used only for triple points. A general discussion is given elsewhere [CCT (1990), Pavese et al. (1984)]. Some thermal parameters of thermometric substances that are relevant to the design of sealed cells are given in Table 3.4; a detailed tabulation of all parameters is available in, for example, L'Air Liquide (1976). To approximate the ITS-90, solid-solid transitions can also be measured although, in general, they are of lower precision. Compared with triple or boiling points, they are at a disadvantage in that there is less self-stabilization of the cell because of the lower heat of transition and the less effective thermal coupling with the condensed sample. Such a self-stabilization is largely due to the presence of the liquid phase, especially when it is kept in thin layers. In solid-solid transitions, on the contrary, the solid has poor thermal contact with the cell and also a much lower vapour pressure. Additionally, the diffusion of the transition is generally a slow process.

The self-stabilization effect can be better understood from Table 3.4 where the enthalpy change in melting of the sample is compared with the heat capacity of the cell. Any small perturbation of the temperature due to stray heat exchanges with the cryostat can be compensated by melting or freezing of a small fraction of the sample. For this reason, any of the cryostats shown in Chapter 2 are satisfactory, and their performances are much less critical than in comparison, or vapour pressure, measurements. Values for temperature error versus heat leak are as low as 10 μK/mW above 20 K, increasing to 500 μK/mW at 14 K. Examples of thermal analyses are given by Seifert and Fellmuth (1989), Seifert (1982), and Bonnier and Hermier (1982). This self-stabilization is also beneficial for simplifying the use of sealed cells. Firstly, the cell can become the reference for an inexpensive differential temperature regulation of the isothermal shield of the cryostat, thus eliminating costly and critical absolute-temperature controllers. Secondly, a cell acts as an almost ideal temperature-generator, able to drive a large thermal load. It may be

Table 3.3: Sensitivities of some Fluids Commonly Used in Vapour Pressure Thermometers

Fluid	Practical Range of Use (K)	Pressure					
		13.3 kPa		100 kPa		133 kPa	
		T/K	$\frac{dP}{dT}$ (kPa/K)	T/K	$\frac{dP}{dT}$ (kPa/K)	T/K	$\frac{dP}{dT}$ (kPa/K)
^4He	1 to 5.22	2.63	24	4.2	96	4.52	115.6
N_2	63.2 to 84	63.5	2.3	77.35	11.7	79.9	14.7
O_2	70 to 98	74.5	2.1	90.18	10.7	92.9	12.7
						1 300 kPa	
CH_4	90 to 170	92	1	141	9.5	180	14
		0.25 kPa				4 000 kPa	
C_2H_6O	160 to 400	255	0.04	250	4.3	380	80
						3 500 kPa	
CCl_2F_2 (Fréon 12)	220 to 380			240	6	373	120
						13 300 kPa	
H_2O	280 to 640	324	0.6	373	3.6	600	1 700
		550 kPa				6 600 kPa	
CO_2	220 to 300	218	9			300	148

Table 3.4: Relevant Parameters for Some Cryogenic Thermometric Substances at their Triple Points.

Gas	T_{tp} (K)	P_{tp} (kPa)	H_f (J/mol)	d_{tp}/d_{NTP}	λ (mW/cm K)	$X=H_f/c_p$* (kg K/mol)
e-Hydrogen	13.8033	7.034	117	1040	1.03	90
e-Deuterium	18.689	17.079	197	1040	1.23	110
Neon	24.5561	43.379	335	1728	1.17	33
Oxygen	54.3584	0.1464	444	980	1.96	4.4
Nitrogen	63.1504	12.526	720	814	1.61	4.8
Argon	83.8058	68.892	1189	980	1.25	6
Krypton	115.776	73.0	1500	812		6
Xenon	1 61 .404	81 .681	3100	647		10
Carbon Dioxide	21 6.589	518	8400	825	1.58	28

T_{tp} = triple point temperature (T_{90}); P_{tp} = triple point pressure; H_f = melting enthalpy; d_{tp}/d_{NTP} = density ratio between the liquid at T_{tp} and the gas at 20 °C; λ = thermal conductivity of the liquid at the triple point; X = "driving" capability (see text, page 25; c_p = copper specific heat).

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* The table uses the example of a copper cell.

designed not only for thermometers fitted internally (Fig. 3.1a), but also so as to thermostat an experiment fitted to the cell [Pavese (1987)] or to a large external comparison block. On the block, more than one cell can be fitted, performing a multiple reference-point arrangement (Fig. 3.1 b). As an alternative, the cell itself may be designed with many compartments for different substances, giving a compact multi-reference device (Fig. 3.1c) [Bonnier and Hermier (1982)]. Another, and a novel, design (from the Physical Technical and Radio Technical Measurements Institute, Moscow) for a multi-reference cell is shown in Fig. 3.1 d. A "sealed" cell with a removable sealing screw to allow for refilling [Ancsin (1982)] is shown in Fig. 3.1 e.

A high accuracy with melting plateaux in sealed cells is still available when using such simplified methods of operation. The slope of the plateau (on a plot of temperature versus fraction of sample melted) can give information regarding impurities in the melting substance (see Section 6.3.6). In addition, the lifetimes of these fixed points is at least of the order of decades; no changes of the reproduced temperatures have yet been observed in about a dozen years.

Sealed cells offer many advantages for disseminating and approximating the ITS-90. They provide the possibility of a whole set of defining and secondary fixed points spanning a wide temperature range, instead of just the triple point of water, for checking the stability of thermometers. For small changes in thermometer calibration, they allow retrieval of a calibration. Furthermore, calibration procedures can be simplified and still maintain good accuracy. The cells also allow dissemination of fixed points (rather than calibrated thermometers) for ITS-90 maintenance.

The sealed cell is well adapted to the cryogenic range and hence, in particular, to the calibration of capsule-type thermometers in adiabatic cryostats. However, the technique has also been applied to the calibration of long-stem SPRTs in the range from the triple point of argon to the triple point of indium [Bonnier (1975), Bonnier and Moser (1983), Ancsin and Phillips (1984)] under heat-flow conditions. Apparatuses that have been used successfully are illustrated in Figs. 3.2a, b.

Sealed cells are also commonly used for calibrations of resistance thermometers or thermocouples at metal freezing points to temperatures as high as the freezing point of copper (1085 °C). The crucibles used are essentially the same as those for non-sealed operation [CCT (1990)]. A national standardizing laboratory usually constructs its own sealed cells, but the procedure is moderately difficult; they are also available commercially. The sealed cell usually consists of enclosing the crucible in a purged, sealed, silica envelope having a re-entrant well close-fitted within the crucible well. Care should be taken to ensure that the pressure of the inert gas filling is such as to give closely one atmosphere pressure during the melting or freezing transition. A typical sealed cell (for the copper freezing point [Crovini et al. (1987)]) is shown in Fig. 3.3. (See also Sections 3.2 and 3.3; see, for example, [Bonnier and Moser (1983)] for discussion of general techniques and especially for filling of the crucible.)

3.2 Fixed Points -50 °C to 630 °C

3.2.1 Ice Point (0 °C)

For many measurements with platinum resistance thermometers and for all measurements with thermocouples (or with liquid-in-glass thermometers) an ice point, rather than a water triple point, is sufficiently accurate [Thomas (1934)].

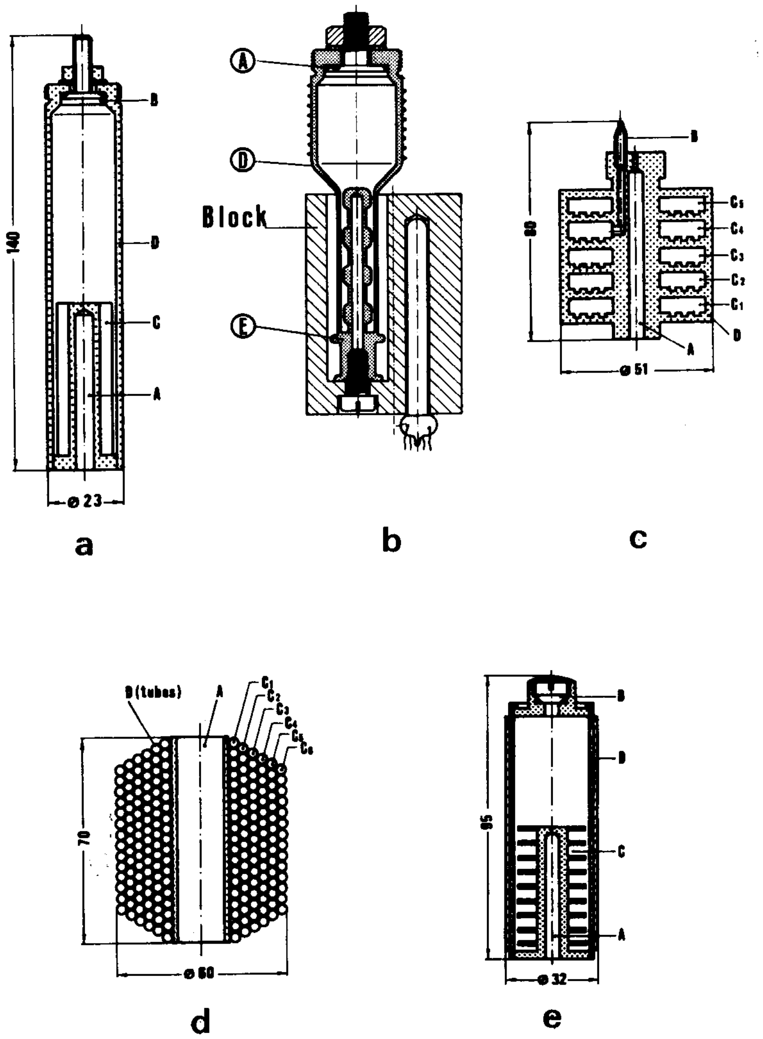

Fig. 3.1: Different approaches with sealed cells: a) thermometers inserted in a well A of the block C protruding inside the cell D [IMGC design, see Pavese et al. (1984)]; b) thermometers inserted in a block C, where one or more cells D (each containing a different substance) can be screwed on at E [Pavese (1987)]; c) thermometers inserted as in a), but the cell itself has many compartments, each containing a different substance (B is the sealing system of the cell: indium gasket or pinch-weld tube) [Bonnier and Hermier (1982)]; d) another multicompartment cell with sample chambers (C_1 - C_6) of copper coils surrounding the thermometer well [PAMI design, see Pavese et al. (1984)]; e) as in a) but with a screw seal to allow for refilling and with thin horizontal copper baffles in the sample chamber to improve thermal contact between thermometer and sample [Ancsin (1982)].

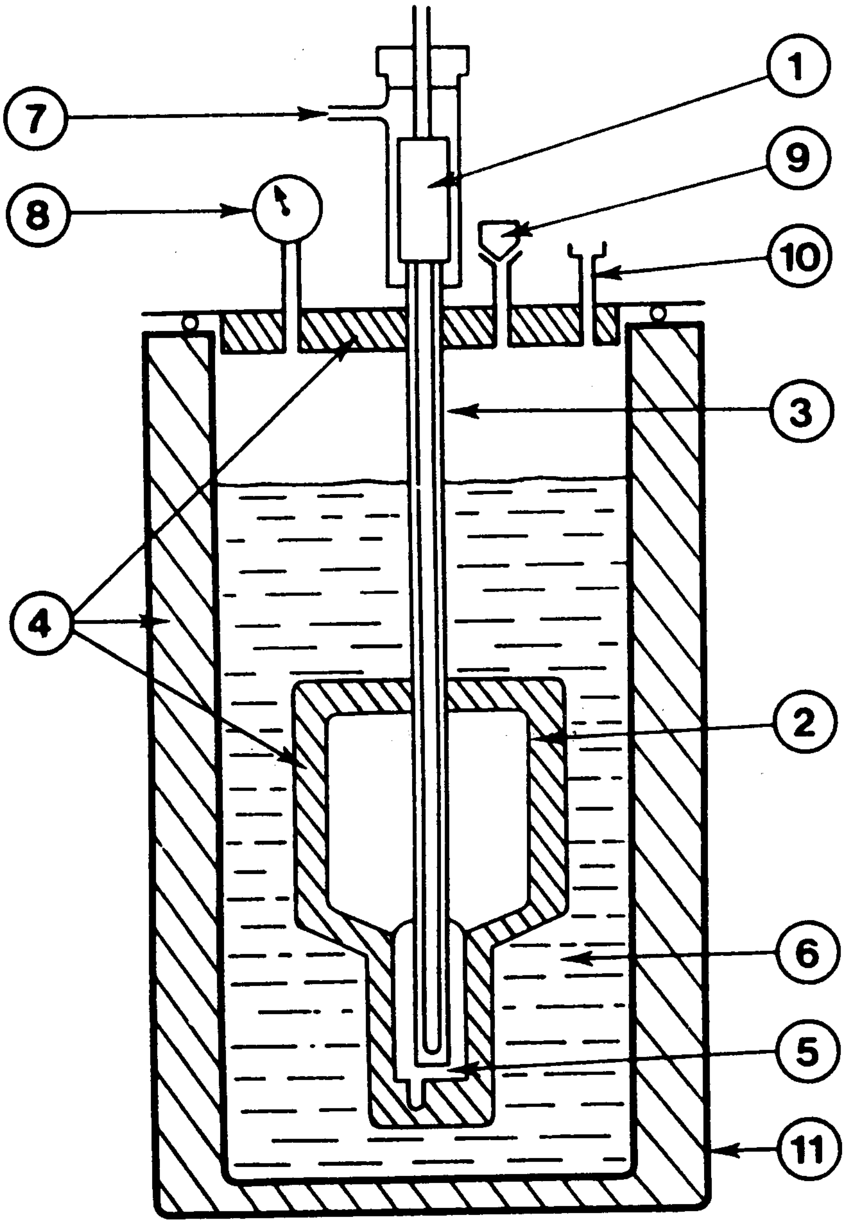

Fig. 3.2a: Apparatus for the calibration of long-stem platinum resistance thermometers at the argon triple point using a sealed cell: 1, long-stem platinum resistance thermometer; 2, stainless-steel body of cell; 3, thermometer tube; 4, polyurethane foam; 5, solid-liquid argon; 6, bath of liquid nitrogen; 7, helium gas inlet; 8, manometer; 9, valve; 10, filling tube for liquid nitrogen; 11, cryostat [Bonnier and Moser (1983)];

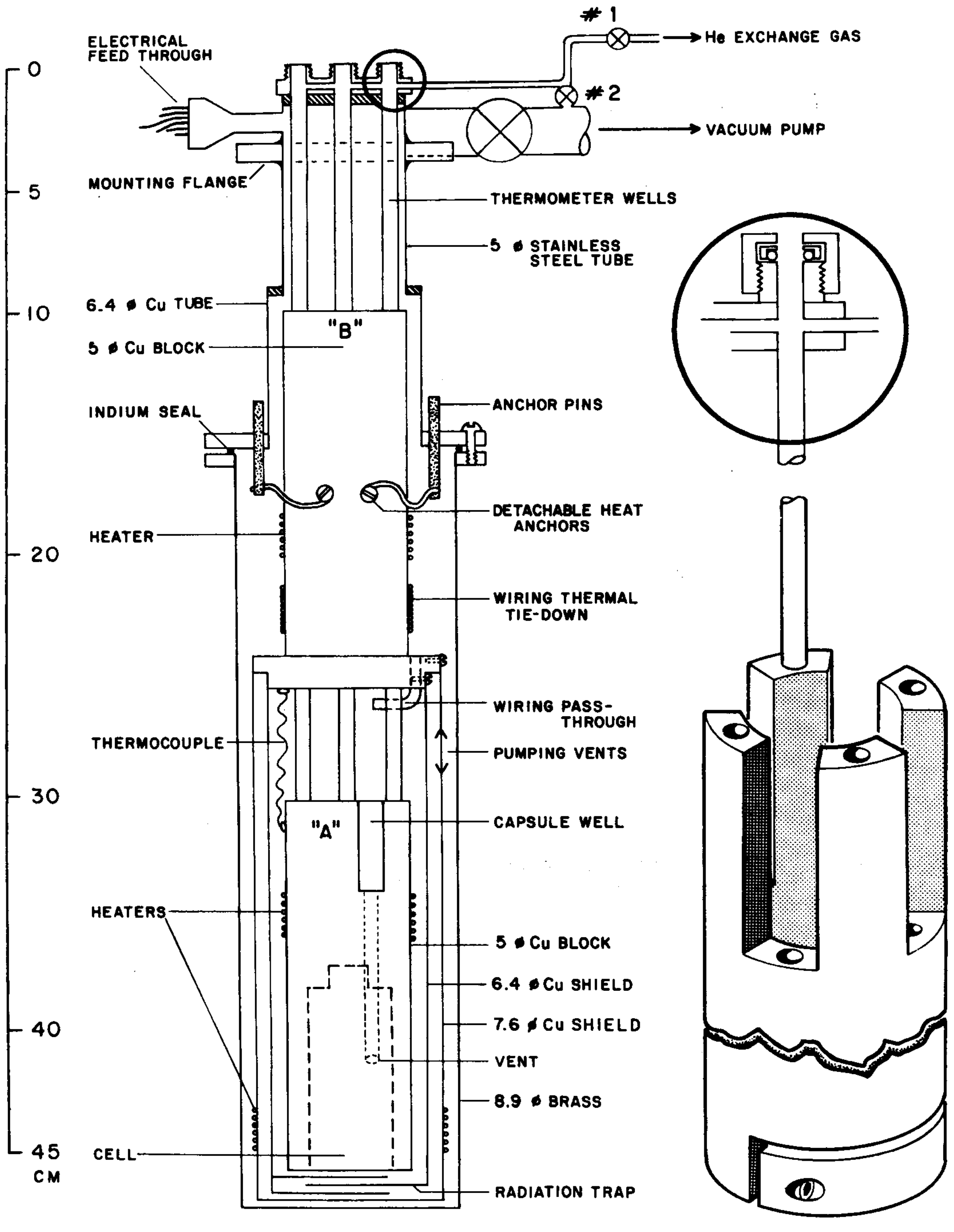

Fig. 3.2b: Apparatus for the calibration and comparison of long-stem and capsule platinum resistance thermometers from the triple point of argon to the triple point of indium [Ancsin and Phillips (1984)].

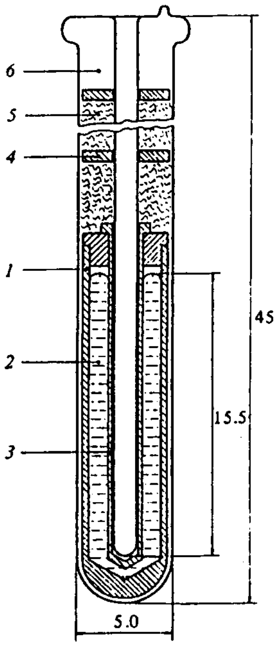

Fig. 3.3: Sealed cell for realization of the copper freezing or melting point (dimensions are in centimetres): 1, graphite crucible; 2, copper; 3, graphite; 4, graphite disk shields; 5, pure silica wool; 6, shielding argon atmosphere [Crovini et al. (1987)].

The equilibrium between ice and water does not require that there be a large amount of water present; the flushing action arising from the melting of surface ice is sufficient when measurements are required only to about 1 mK. However, in such cases an ice point bath must contain enough water to provide good thermal coupling between the ice-water interface and the thermometer. If the ice is melted away from a cooling thermometer it must be carefully repacked when the temperature is nearly stable. A relatively water-free ice bath should routinely provide an uncertainty in the temperature approaching 1 mK if the thermometer immersion is not less than 300 mm; the uncertainty may well be some tens of millikelvins for immersions of the order of 100 mm.

Thermoelectrically-operated ice-point devices are available for use in less accurate thermometry (e.g., with thermocouples).

3.2.1.1 Preparation of the Ice Point

The equipment required for preparing an ice point of high accuracy consists of a wide-mouth dewar flask about 70 or 80 mm inner diameter and long enough to hold the thermometer; a large dewar of about 150 mm inner diameter; a source of clean and pure lshaved ice; a clean container to hold the ice; some pure water either distilled or, at least, de-ionized; and an aluminium or stainless-steel stirrer.

The ice is best made in an ice machine that does not freeze all of the water since the freezing process helps in the purification by concentrating the impurities in the unfrozen liquid. If an uncertainty smaller than 1 mK is required the machine should be supplied with distilled water. With commercial ice that is frozen in large blocks, the center of the block, which freezes last, should not be used; rather one should use only the clear outer layers, after the surface has been carefully washed to remove contamination. The ice should always be transferred with a clean scoop and never touched by the hands.

The procedure for the preparation of an ice point of the highest quality is as follows:

All the utensils, the stirrer and the thermometer are carefully cleaned with mild detergent solution then rinsed two or three times with ordinary water at room temperature. A final wash should be given with distilled water. The large dewar is 2/3 filled with distilled water, and shaved ice is added (by picking it up on the stirrer or with the clean scoop) with strong stirring until there is a water-ice slush thin enough for the stirrer to pass through easily, yet sufficiently thick to allow some of it to be picked up on the stirrer if it is lifted out slowly. The slush is then transferred to fill the smaller dewar and aerated distilled water, precooled by ice, is added to fill it almost to the top, but preferably not enough actually to float the ice.

As an alternative procedure to the above, the ice point may be made up in a dewar or a vessel deep enough to accommodate the longest expected thermometer immersion with the 0 °C mark near the top of the stem. This dewar should be fitted with a syphon or drain cock to permit removal of free water from below the ice water mix. The ice water mix can be flushed with aerated distilled water at 0 °C and the excess water removed by the syphon or drain.

3.2.1.2 Operating Conditions

The precooled thermometer is gently pushed into the centre of the ice mixture. Liquid-in-glass thermometers are immersed so that the ice point marking is just above the lip of the dewar; for thermocouples and resistance thermometers the depth of immersion should be about 300 mm. If there is any doubt as to whether the immersion is sufficient, the thermometer should be read a second time at about 50 mm less immersion to ensure that the reading is truly independent of immersion depth. However, the sensing element must not go beyond the bottom of the ice since very pronounced temperature layering exists in water below the ice level.

Final readings of the thermometer should not be taken until temperature equilibrium has been achieved as indicated by a constant reading over several minutes. A useful check against possible contamination introduced with the thermometer is to withdraw the thermometer and reinsert it immediately in a different location - then go through the reading procedure a second time. In very precise work, or when immersion is limited, a clean aluminium foil over the top of the ice should be used to prevent transmitted radiation from affecting the temperature of the sensing element.

If all of the precautions described above are taken, an ice bath should be capable of providing the conditions for the realization of the ice point to an accuracy within about 0.3 mK. However, at this level of accuracy the triple point of water is preferable: the triple-point cell is simpler to use, less prone to errors, and may be maintained for a longer time without attention.

3.3 Fixed Points above 630 °C

Except for the very highest temperatures, all of the fixed points in this region are metal freezing or melting points. For calibrations to very high accuracy, the metal is contained in a (usually) graphite crucible in such a way that a continuous liquid/solid interface encloses (as nearly as is practical) the sensing element of the thermometer. For resistance-thermometer calibrations, two such interfaces are generally induced. The outer one forms a solid shell that surrounds the liquid phase and the inner one, whose temperature is measured by the thermometer, surrounds the thermometer well. The techniques required in the generation of these interfaces, the crucible assemblies, suitable furnaces, and methods for checking the quality of the results are described in detail in "Supplementary Information for the ITS-90" [CCT (1990)]. Variations of the techniques suitable for resistance thermometer, thermocouple, or optical pyrometer calibrations are included there. Above 630 °C the metals to which the methods apply are Sb (630.633 °C), Al, Ag, Au, and Cu. The methods can also be used for the melting point of the eutectic alloy Cu 71.9% Ag 28.1% (779.91 °C), but because of the nature of eutectic phase transitions the accuracy is limited to about ± 0.03 °C, even with resistance thermometers. Remarks on the eutectic point are given in Sec. 3.3.1. Sealed cells (Sec. 3.1.4) can often be used for the realization of these metal freezing or melting points.

At higher temperatures the most-used fixed points are the melting or freezing points of Pd and Pt, to which the above methods are applicable only with considerable difficulty because the extreme temperatures require different and more complicated furnace construction, different crucible materials, and so on. In any case, above 1100 °C a much lower accuracy is tolerable with fixed-point calibrations and so specialized techniques have been developed. Also, below 1100 °C, much simpler and less costly but less accurate techniques are possible. These various special procedures are discussed in Secs. 3.3.2 - 3.3.3.

3.3.1 Copper 28.1% Silver 71.9% Eutectic Alloy

It is unfortunate that no pure metal has a freezing temperature in the approximately 300 kelvin interval between the freezing points of aluminium and silver - a strategic interval for both thermocouple and resistance thermometry. The melting point of the eutectic alloy Cu 28.1% Ag 79.1 % (Cu/Ag) at 779.91 °C is ideally placed but, even when realized according to the same stringent procedures as for the pure metals, it is reliable to at best ± 30 mK in contrast to ± 1 mK for the pure metals. Nevertheless, the point can be useful in connection with thermocouple calibrations. Studies of it with resistance thermometers are described by Bongiovanni et al. (1972) and McAllan (1982), with thermocouples by Itoh (1983), and with optical pyrometers and thermocouples by Bedford and Ma (1982), all with techniques comparable to the foregoing.

The eutectic freezing point is not a good reference point because its temperature value is freezing-rate dependent. This is so because, during freezing, the components in the liquid have to separate by diffusion to form the two different solid eutectic phases, and because the temperature also depends upon the details of nucleation. Consequently, the eutectic melting point is recommended as the reference. It is much more reproducible, and is not strongly dependent on the overall composition. Itoh (1983) found that changing the relative compositions by ± 2% from the exact eutectic composition had no significant effect on the observed melting temperature.

The eutectic freezing temperature is always lower than the melting temperature and can vary over several tenths of a kelvin depending largely upon the rate of freezing. Because the rate of freezing also affects the slope of the subsequent melting curve, it is recommended that each melting point determination be preceded by a very slow (several hours) freeze. Also, since even under optimum conditions the melting curve has a more pronounced slope than for a pure metal, some consistent criterion for choosing the melting temperature is required. McAllan (1982) suggests that the most reliable estimate for the equilibrium eutectic temperature is given by the intersection of the extrapolation of the region of the melting curve just before the commencement of the rapid rise with the 100%-melted axis. Alternatively, the maximum in a histogram that shows percentage of time spent in consecutive temperature intervals can be taken as the melting temperature. An extension of this latter method when the histogram has several peaks indicating segregation of impurities is to use the centroid rather than the maximum. These three temperatures differ (usually) systematically from each other, the extrapolated value being the highest and the centroid the lowest. The largest difference is seldom more than 20 mK.

3.3.2 Melting Points of Gold (1064 °C), Palladium (1555 °C), and Platinum (1768 °C) by the Wire-Bridge Method

For noble-metal thermocouple calibrations not requiring the highest accuracy, the wire method or wire-bridge method is sufficient. With this technique the temperature of melting of a small piece of metal (wire, disk, or rod) that is fastened (welded, or mechanically clamped) to the thermocouple tip or between the thermocouple legs is measured. The method is simple, rapid, inexpensive, and adequately accurate.

This calibration technique is most commonly used at the gold, palladium, and platinum points. It is also sometimes used at the silver point, but this is not recommended because of the danger of the melting temperature being affected by solution of silver oxide. It is necessary to protect the internal chamber of the furnace from contamination by the fixed-point material by using a protective recrystallized alumina tube. This alumina furnace tube should be kept extremely clean and used only in the calibration of noble-metal thermocouples. To apply the method, a small piece (typical weight < 0.1 g) of metal or short length (5 to 10 mm) of 0.5 mm diameter wire of high purity (at least 99.99%) is used to form the junction between the two elements of the thermocouple by mechanically fastening, wrapping, or welding. Various ways of completing the junction are described by Bedford (1964) and by Bongiovanni and Perissi (1984). For welding, a microtorch with an oxygen-hydrogen gas mixture is convenient. With welding, however, there is risk of contaminating the metal with Pt or Rh. Pre-cleaning of the metal link in cool, dilute nitric acid has been recommended. The thermocouple is then slowly inserted into a furnace maintained several degrees below the melting point of the fixed-point material. When equilibrium is reached, the furnace power is increased by a predetermined amount (a heating rate of 0.3 K/min will yield long and flat melting plateaux) and the thermocouple output recorded as the temperature passes through the melting point. Sometimes, but not usually, the metal bridge breaks on melting, interrupting the thermocouple output. During the melt an increase in emf of 2 to 10 μV is typical (smallest with Au, largest with Pt), with the melting lasting 2 to 8 minutes and with a momentary stabilization (0.5 to 2 min) just before completion of melting. Which emf to assign to the fixed point is somewhat ambiguous; the sudden rise from the melting plateau indicating the completion of melting was considered by Bedford (1964) as the most reproducible index, whereas Crovini et al. (1987) recommend using the median of the plateau. It is advisable to test the reliability with a repeat calibration after clipping about 1 cm of wire from the hot junction to avoid effects of contamination.

Reliable freezing points cannot be obtained with this method because some material from the thermoelements dissolves in the molten bridge, changing its freezing temperature by an indeterminate amount and producing a freezing transition with a rapidly changing temperature.

The melting temperature of palladium is influenced by dissolved oxygen; in an oxygen-free atmosphere the melting temperature is 1554.8 °C and in air is about 1553.5 °C [Jones and Hall (1979), Coates et al. (1983), Bedford (1972a), Jones (1988)]. With a platinum bridge on a thermocouple with a pure platinum thermoelement, either the bridge frequently breaks or the platinum thermoelement melts near, and before, the bridge itself, depending upon the degree of temperature uniformity. The platinum point is best used with double alloy noble metal thermocouples or with refractory metal thermocouples.

The accuracy of the procedure is mainly limited by the contamination of the metal bridge by the thermocouple wire, and by the furnace's tendency to raise the temperature of the thermocouple legs, weakly opposed by the latent heat absorbed by the melting bridge, above the melting point. With Pt10Rh/Pt thermocouples it is possible to obtain a reproducibility (1 standard deviation) of about ± 2 μV between two test runs at the gold point, about ± 4 μV at the palladium point, and about ± 8 μV at the platinum point. A detailed description of the use of the wire-bridge method in an interlaboratory intercomparison is given by Crovini et al. (1987).

3.3.3 Miniature Fixed Points for Thermocouple Calibrations

Tischler and Koremblit (1982) have devised a modification of metal-fixed-point-calibrations for thermocouples using miniature ingots that has some of the advantages of both regular fixed points and the wire-bridge method. It can provide calibrations that in many cases are as accurate as the thermocouples themselves and can also provide the possibility of in-situ calibration. The technique has been applied successfully with In, Sn, Cd, Pb, In, Sb, Al, Ag, Au, Cu. A small crucible (volume - 0.1 cm3, mass - 0.3 g) machined from 6 mm diameter graphite rod to the shape shown in Fig. 3.4 is filled with a pure metal ingot (mass of metal from 0.5 to 2 g). A hole is drilled through the graphite below the ingot chamber and another through the graphite lid. One leg of the thermocouple can be inserted into each hole without touching the metal ingot. This completes the electric circuit, prevents contamination of the metal ingot, and permits repeated use of the crucible with the same thermocouple or the exchange of thermocouples.

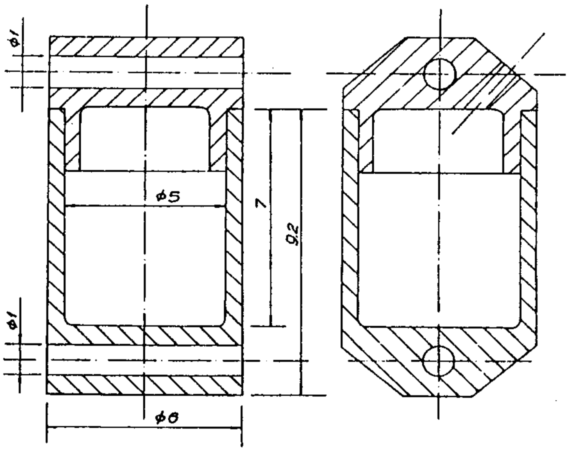

Fig. 3.4: Cross sectional drawing of a miniature graphite crucible for thermocouple calibrations (dimensions are in millimetres) [Tischler and Koremblit (1982)].

The tightly-fitting crucible lid has a small perforation to vent occluded gases that are released as the temperature is raised.

For calibration, the thermocouple with the crucible attached is placed in a small-diameter, fused-silica tube through which a slow flow of nitrogen is maintained to protect against oxidation of the graphite. The silica tube in turn is inserted into a conventional furnace at the appropriate temperature with the silica tube extending to room temperature. The furnace power is then increased so that the furnace equilibrium temperature will be slightly (typically 1 K to 5 K) higher than the melting temperature of the ingot and the melting transition is recorded. Following this, the furnace power is reduced so that the temperature will equilibrate at an equal amount *below* the transition temperature and the freezing transition is recorded. A typical transition plateau lasts about 20 min. Depending upon the rate of change of furnace temperature, and upon the difference between furnace temperature and transition temperature, the temperature of the freezing plateau will be significantly lower than that of the melting plateau because of the relatively small latent heats, large heat transfer, and effect of pressure on the ingot due to surface tension. Let V_P be the thermocouple emf at the temperature of the plateau, V_F the emf when the thermocouple has equilibrated at the furnace temperature following the transition, and V_T the emf at the true transition temperature. On a plot of V_F vs V_P, the intersection of a line joining the points corresponding to melting (V_{Pm}) and freezing (V_{Pf}) with the line $V_F = V_P$ gives the desired emf V_T, which is usually reproducible to about $\pm 1\ \mu V$ and accurate to ± 0.3 K. It is likely almost as accurate to take for V_T the mean of the melt and freeze emfs.

With some deterioration in accuracy (± 0.5 K), a simpler method is not to stabilize the furnace temperature close to the transition temperature, but to let it pass through at a relatively high rate. For Cu, Sb, Pb, Sn, In take $V_T = V_{Pm}$ from the melt; the large amount of undercooling makes V_P from the freeze unreliable. For Au, Ag, In, and Cd take $V_T = (V_{Pm} + V_{Pf})/2$, or $V_T = V_{Pm}$, which will be almost the same. For Al it is necessary to take $V_T = (V_{Pm} + V_{Pf})/2$.

Variations of this technique are described by Tischler and Anteneodo (1986) where the freezing point is a permanent part of the thermocouple. Other workers are applying miniature fixed points for the calibration of standard-welded and metal-sheathed thermocouples.

3.4 Fixed Points for Pyrometry

3.4.1 Blackbody Furnaces

Infrared pyrometers (monochromatic or broad-band) must be calibrated against blackbodies. If modest accuracy is sufficient, it is possible to use semi-miniature furnaces as opposed to those recommended for highest accuracy [CCT (1990)]. Sakuma and Hattori (1982a) have designed furnaces of this sort that are in moderately wide use. A graphite blackbody crucible 4 cm diameter, 6.5 cm long, with a 1 cm aperture (Fig. 3.5) is encapsulated in a stainless-steel cylinder which carries the furnace heater, either embedded in grooves parallel to the axis or wound around the circumference. The steel cylinder extends beyond the blackbody aperture for better temperature uniformity, and includes a stainless-steel disk with a 6 mm aperture covering the front of the blackbody. Argon flows through the steel capsule to prevent oxidation of the graphite. This steel cylinder containing the crucible and furnace heater is mounted in an alumina tube that is surrounded by suitable radiation shields and thermal insulation (Fig. 3.6). The whole furnace is 10 cm diameter by 25 cm long, and is attached to a temperature-control unit consisting of a SCR power regulator, an on-off temperature controller, and indicators. A monitoring thermocouple is attached to the steel capsule. With the main power switch on and the regulator switch off, the furnace is maintained about 10°C above the freezing point of the metal in the blackbody. Then, with the regulator switch on, the crucible cools at a pre-determined rate through the freezing transition. The freezing plateau lasts about 10 min and is accurate to within about -0.1 ± 0.1 K. Such a furnace is available for each of the metals Cu, Ag, Al, Sb, and Zn.

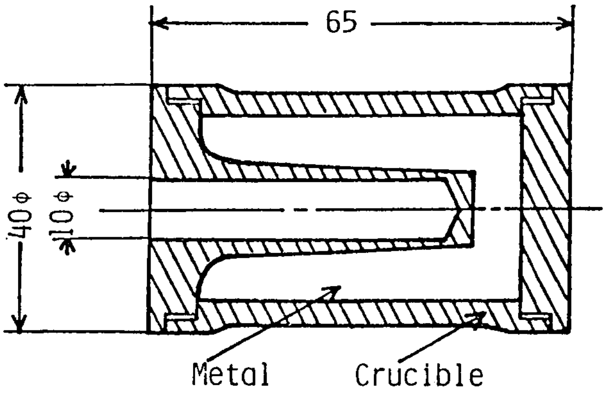

Fig. 3.5: Miniature graphite blackbody crucible for pyrometer calibrations (dimensions are in millimetres) [Sakuma and Hattori (1982a)].

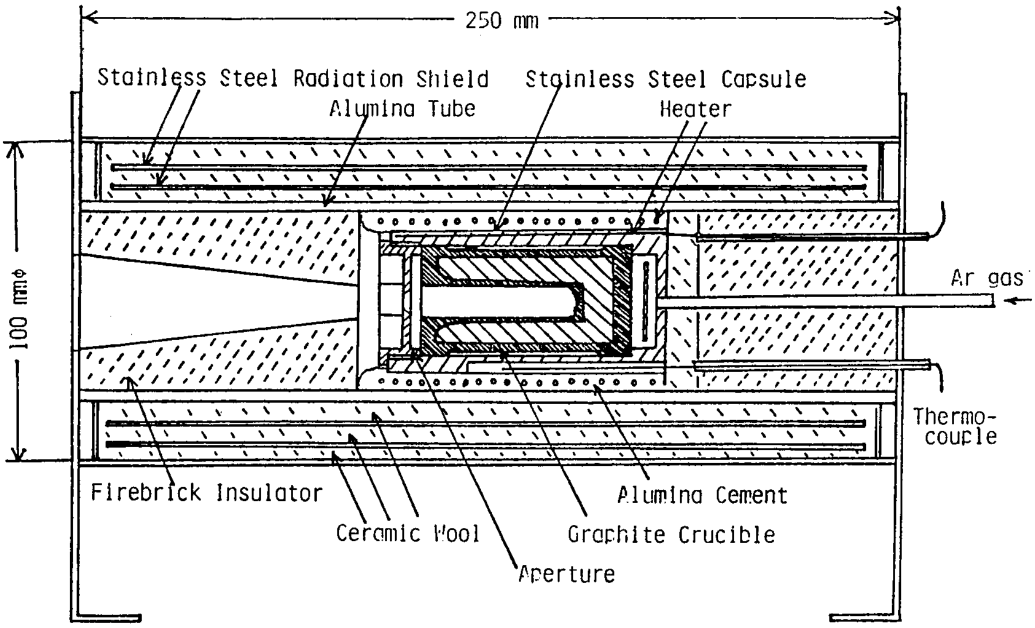

Fig. 3.6: Portable blackbody furnace for pyrometer calibrations [Sakuma and Hattori (1982a)].

3.4.2 Radiance Temperatures on Melting

For optical-pyrometer calibrations, especially at very high temperatures where conventional methods are difficult, the technique of measuring the radiance temperature at the melting point of selected pure metals offers a practical and moderately accurate alternative. In general, the method involves heating (in vacuum or inert atmosphere) a small specimen in the form of a strip or a tube through its melting point by passage of electric current. As used in conjunction with high-speed pyrometers, the specimen is heated from room temperature to the melting point in less than one second and the pyrometer focused on the specimen indicates a melting plateau lasting some tens of milliseconds. For use with conventional pyrometers, a technique would have to be devised to maintain a stable metallic surface for tens of seconds during the melting transition. Various experiments [for example, Cezairliyan et at. (1982)] have indicated that the radiance temperatures are reproducible to about ± 1 K and accurate to within a few kelvins. Bedford et al. (1984) list many such temperatures with their estimated accuracies. The radiance temperature is essentially independent of the initial surface condition of the solid specimen. The technique has the advantage that no emissivity correction is involved (it is, in essence, built into the radiance temperature), but it is important to note that the value of the radiance temperature applies only for the particular wavelength value listed. For widespread use a more comprehensive catalogue of radiance temperatures for more metals and at more wavelengths is required.

4. Germanium Resistance Thermometers

Although germanium resistance thermometers are no longer the only, or necessarily the best, choice for high quality temperature measurements below 30 K, they are still widely used and there exists a large literature on their performance which is summarized here. The principal current commercial manufacturers of germanium thermometers are listed in Appendix C.

4.1 Principles and Range of Use

The thermometric quantity is the electrical resistance of a small single-crystal element of doped germanium. The element is mounted so as to permit a four-wire measurement of resistance through very small diameter gold leads bonded to the crystal. The resistivity (p) of an intrinsic semi-conductor follows an exponential law but in practice a semi-conductor is rarely intrinsic. It contains donor and acceptor atoms, the relative proportions of which determine the mode of conduction. This leads to a general resistance/temperature relationship with four distinct zones as shown schematically in Fig. 4.1. The useful range of germanium thermometers comprises the two zones below roughly 100 K. The conduction is controlled by the thermal excitation of free carriers. From 1 to 10 K (zone 1) the excitation is from one impurity state to another; from 10 to 100 K (zone 2) it is from impurity states into the conduction band. For details of the basics of germanium thermometers see Kunzler et al. (1962), Lindenfeld (1962), and Blakemore (1962), (1972).

4.2 Fabrication

The relatively low melting point (~ 937 °C) of germanium assures the easy growing of crystals of very high purity. The addition of controlled amounts of impurities (usually arsenic, antimony, or gallium) permits the manufacture of thermometers having approximately the desired resistance for the temperature range of use. In general, type-n thermometers have a more regular resistance/temperature (R/T) characteristic than type-p, as shown in Fig. 4.2. Unfortunately, the germanium resistivity is so sensitive to the impurity concentration that close resistance tolerances in manufacture are not yet achieved; interchangeability, therefore, is not usual with germanium thermometers.

A typical germanium element in a thermometer of current manufacture is shown in Fig. 4.3. Other, and smaller, thermometers with different configuration are also

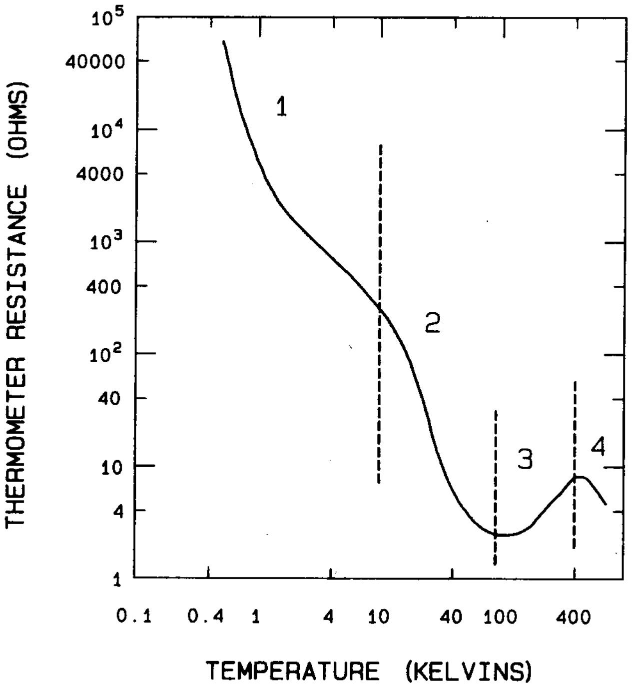

Fig. 4.1: Typical resistance versus temperature response for a germanium resistance thermometer [after Halverson and Johns (1972)].

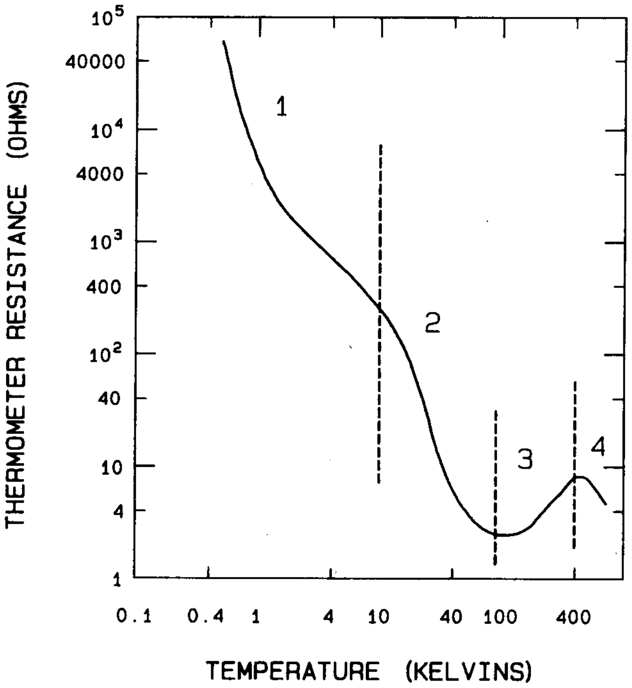

Fig. 4.2: Typical resistance versus temperature response for: (a) n-type germanium (arsenic-doped); (b) p-type germanium [after Blakemore (1972)].

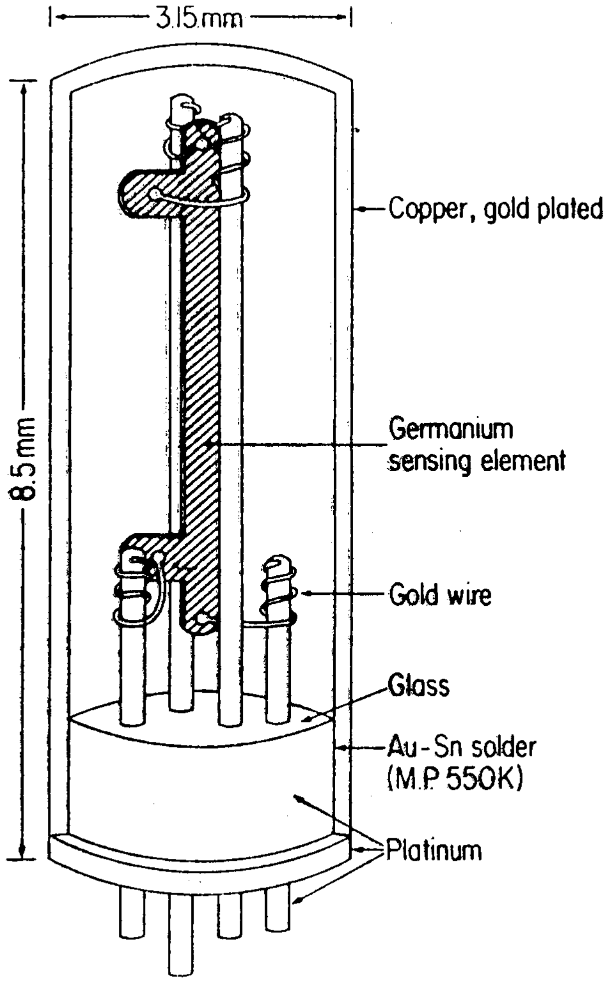

Fig. 4.3: Example of the Π-type construction of a germanium thermometer. The germanium is in the form of a bridge, with current contacts on the ends and potential contacts on side arms [Blakemore (1972)].

commercially available. The dimensions are always smaller than 1 cm and the mass less than 1 g, giving the thermometer a small thermal capacity and short response time. Germanium being strongly piezoelectric, it is essential that the element be mounted without mechanical constraints, and this requirement becomes more stringent with higher impurity concentrations. The four electrical leads to the crystal are small diameter gold wires which, because of the fragility of the contacts, are bonded directly to the element. The germanium element is mounted strain-free in a metal capsule that is filled with ^{4}He or ^{3}He to improve thermal contact between the element and the surrounds of the capsule. In spite of this, more than two-thirds of the heat exchange is by the leads, so that the indicated temperature is largely a function of their thermal anchoring [Hust (1970)].

4.3 Electrical Characteristics

4.3.1 Method of Measurement

The thermometer resistance is measured either by a potentiometric method or with a resistance bridge. The lead resistances, inherent to the construction of the thermometer, are of the order of 20% to 40% of that of the thermometer itself at a given temperature, and vary with T in the same manner. These can cause systematic temperature-dependent errors associated with the shunting effect of the large-but-finite input impedances of ac bridges. Such errors do not occur with a potentiometer [Swenson and Wolfendale (1973)].

With germanium thermometers, differences occur between the results of ac and dc measurements [Swenson and Wolfendale (1973), Kirby and Laubitz (1973), Anderson and Swenson (1978), and Anderson et al. (1976)]. Resistances measured with alternating current are always smaller than with direct current at a given temperature. This effect, intrinsic to the thermometer and dependent upon its geometry, is due to the Peltier heating and cooling at the current lead contacts to the germanium element. With continuous current it produces temperature gradients between the two ends of the sensor resulting in the development of a thermal emf between the potential contacts. For most applications where millikelvin uncertainty is tolerable, either ac or dc calibrations can be used below 40 K, the effect being of the same order as that due to typical self-heating (see Sec. 4.4.1).

Kirby and Laubitz (1973) on the basis of both a theoretical model and measurements in the range 15 to 1500 Hz, show that the Peltier heating component is damped exponentially with the exponent being proportional to $\sqrt{f}$. Since the error term is dependent upon the positions of the potential contacts, there is also a difference in the magnitude of the error between 2-lead and 4-lead thermometers. The magnitudes of the errors measured by Swenson and Wolfendale (1973) agree roughly with those of Kirby and Laubitz (1973). The differences between ac (30 Hz) and dc measurements with typical thermometers below 80 K are shown in Fig. 4.4 [Anderson and Swenson (1978)]. The relative differences between ac and dc measurement of resistance are roughly 0.7% at 300 K, 0.2% at 80 K, 0.02% at 50 K, and 0.0001 % below 10 K, with any Peltier error being greater for the dc measurement. If not compensated for, this corresponds to temperature errors of about 0.2 K at 100 K down to 0.1 mK at 20 K. If very precise measurements are needed, the model proposed by Kirby and Laubitz (1973) allows prediction of the systematic errors providing one knows the thermal conductivity and electrical resistivity of the germanium element and the Seebeck coefficient of germanium relative to the material of the leads.

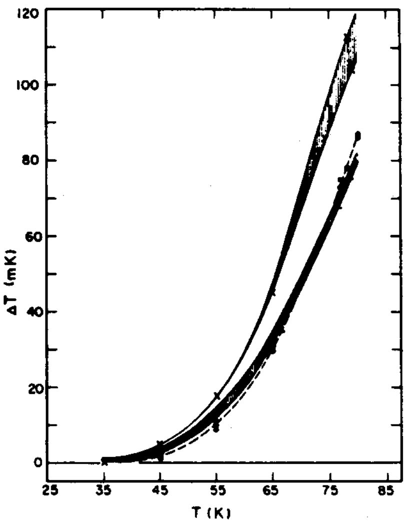

Fig. 4.4: Differences between dc and ac (30 Hz) calibrations for typical germanium thermometers from Minneapolis Honeywell (upper hatched group, 250 to 1250 Ω at 4.2 K), Lake Shore Cryotronics (lower hatched group, 500 Ω at 4.2 K), and CryoCal (dashed curve, 500 Ω at 4.2 K) [after Anderson and Swenson (1978)].

4.3.2 Resistance/Temperature Characteristics and Sensitivity

Typical examples of the variation of resistance (R) with T for commercial germanium thermometers are shown in Fig. 4.5. The resistance at 1 K can be as high as 10^6 Ω and at 100 K as low as 1 Ω, but these are extreme values. For a typical thermometer suited to the temperature range 1 K to 30 K, R ranges from 1000 Ω at 4.2 K to less than 10 Ω at 77 K. The sensitivity (dR/dT) at 4.2 K is about -500 Ω K^{-1}.

In practice the power dissipated in the sensor must be much less than 1 μW, corresponding to a maximum current of 30 μA with a 1000 Ω thermometer, or a voltage across the sensor of 30 mV (see Section 4.4.1 and Fig. 4.8). In order to measure temperatures near 4 K to within 0.01 % (0.5 mK), that would require instrumentation having microvolt resolution. Even lower sensor voltages are desirable, 2 to 4 mV being usual. Commonly, a potentiometric method is used to measure the resistance because of the high resistances involved. At every temperature the current is adjusted to maintain the voltage across the potential terminals as high as compatible with self-heating. This allows one to take advantage of the maximum sensitivity provided by the equipment. Where this procedure is inconvenient, a constant measuring voltage can be used over a wide range and correction made for self-heating (see Sec. 4.4.1).

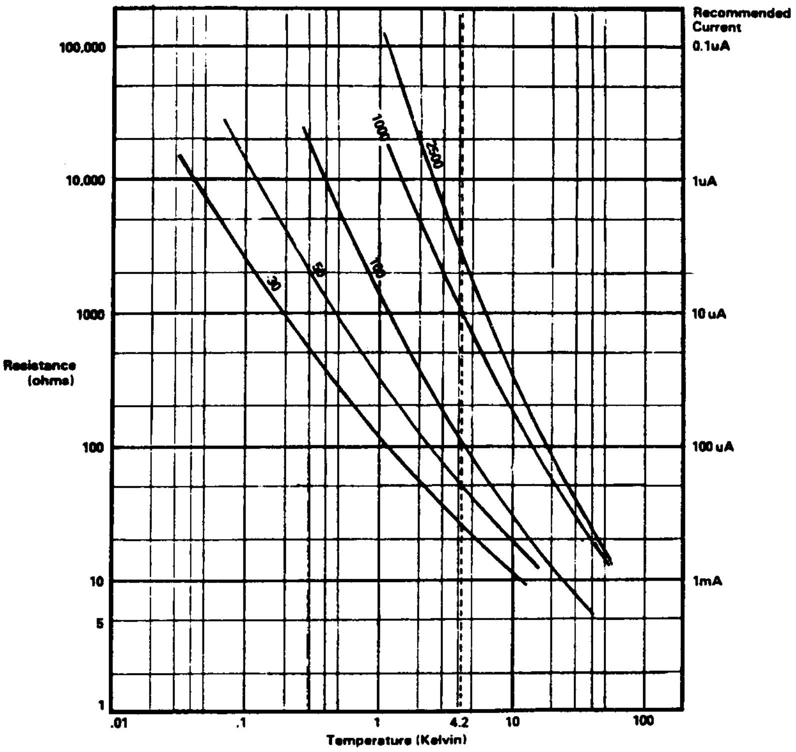

Fig. 4.5: Some typical resistance versus temperature response curves for germanium thermometers.

At very low temperatures the resistance can easily surpass 10^5 Ω so that the measuring current will be of the order of tens of nanoamperes if the power dissipated is to remain tolerable; the tolerable leakage current due to lack of insulation or from the measuring instrument itself must be much smaller. That necessitates a measuring system with excellent signal-to-noise ratio. The very large sensitivity and its rapid change with temperature has both advantages (high precision of measurement) and disadvantages (rather small practical temperature range for any one thermometer).

The complicated behaviour of R and $\frac{1}{R}\frac{dR}{dT}$ as functions of temperature, resulting from changes in the conduction mechanism in germanium, prevents their being expressed by simple functions. On the other hand, since both the resistivity and its temperature coefficient are strongly influenced by doping, one can obtain thermometers especially adapted to particular uses. For example:

- n-doped thermometers have a relatively smoothly-changing sensitivity, and so a fairly wide temperature range.

- conversely, p-doped thermometers are preferred for use in narrow temperature ranges within which the resistance can be represented precisely by a relation of the form In R = f(In T) (see Sec. 4.5). The limits of the temperature range can be chosen by suitable control of the doping which, in turn, controls the temperature at which the conduction mode changes (the hump in curve b in Fig. 4.2).

The value of R becomes inconveniently large at very low temperatures. It can be reduced by changing the doping, so it is possible in principle to have a thermometer with 100 Ω resistance at 0.1 K, but manufacture becomes more difficult [Halverson and Johns (1972)]. Also, the high magnetoresistance of germanium is often restrictive (see Chapter 17).

4.3.3 Stability

Individual germanium thermometers can exhibit good stability, but many do not. Instabilities are generally not large enough to be significant in applications where an accuracy within 10 mK at 20 K is sufficient. For experiments where ± 0.05% uncertainty in temperature is tolerable one can have confidence in the stability of the initial calibration.

Some detailed measurements of instability by Plumb et al. (1977), Besley and Plumb (1978), and Besley (1978), (1980) on about 80 thermometers from 3 manufacturers have shown that a considerable variation in instability occurs during thermal cycling between 20 K and room temperature. Thermometers maintained at a constant temperature can be remarkably stable (much better than 1 mK) but, of course, this type of situation would represent an extremely rare application. After thermal cycling, a variety of types of instability occur, ranging in magnitude from less than a millikelvin to tens of millikelvins. Some thermometer resistances drift slowly but regularly; some can be relatively stable, then jump abruptly by large amounts; some remain stable after a jump but others jump back; some are generally erratic.

It is not possible, a priori, to select stable thermometers. Thermal cycling 10 to 30 times consistent with the eventual use of the thermometer (i.e. rapid cycling if the thermometer will undergo rapid temperature changes; slow cycling otherwise) should routinely be used to detect many unstable ones, but it is not guaranteed that all will be detected. It is obviously useful (and not especially costly) to conserve several of them for periodic intercomparisons with working thermometers so as to identify unstable thermometers. Clearly, also, several thermometers should be used together.

The causes of instability have not been definitively elucidated. There is some suggestion that n-type germanium may be more stable than p-type. However, much of the instability, especially the abrupt jumps, is associated with mechanical shocks; the attachment of the leads to the germanium crystal is particularly vulnerable to damage. Thus it is highly likely that instabilities are geometrical in nature (due especially to change in the geometry of the lead arrangement) and are not caused by fundamental changes in the resistivity of the element. A one-temperature recalibration will not recover the original calibration of an unstable thermometer.

4.3.4 External Influences

a) Hydrostatic pressure: No change larger than 0.1% in resistance for pressures up to 2×10^5 Pa has been observed [Low (1961)].

b) Radio frequency fields: Electromagnetic fields in the frequency range 30 to 300 MHz can have a considerable effect on semiconductor thermometers. In the temperature range 70 K to 300 K this can cause a relative error in $\Delta T/T$ of up to 30% [Zawadzki and Sujak (1983)] that varies with frequency and temperature (see Fig. 4.6). Unfortunately, the electromagnetic field strengths for which these data were taken were not reported. At lower temperatures the effect is equally important, but detailed measurements of the magnitude of the error are unavailable. However, at 4 K for example, the thermometer resistance can increase 0.3% in the field of a nearby television transmitter. Obviously, radio frequency shielding is necessary, and the thermometer should be placed perpendicular to the electrical field. For work down to 1 K and germanium thermometer resistances up to 10^5 Ω, special precautions are normally unnecessary. Occasionally, however, a thermometer will have a rectifying lead, leading to an extremely noisy off-balance signal. In such a case the thermometer must be discarded.

c) Magnetic fields: see Chapter 19.

4.4 Thermal Properties

4.4.1 Self-heating and Thermal Anchoring

The passage of current can, by Joule heating, raise the temperature of the sensor above that of the medium in which it is immersed. The increase in temperature is proportional to the Joule heating and inversely proportional to the thermal resistance between the thermometer and the medium. Figure 4.7 shows typical values of the magnitudes of the

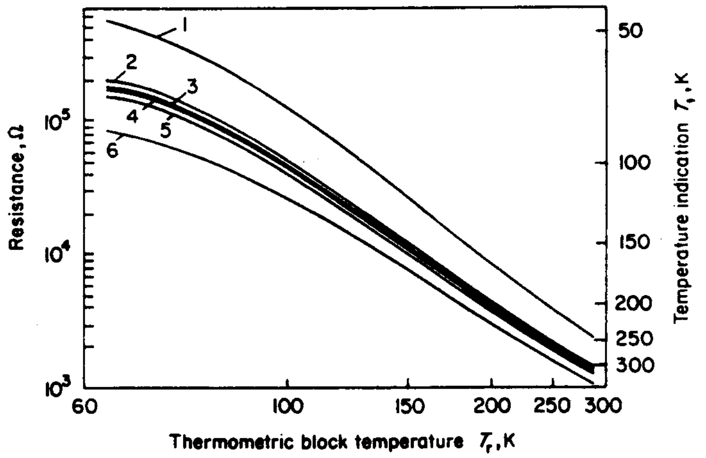

Fig. 4.6: Effect of a radio-frequency electromagnetic field on the response of a germanium thermometer. Curves 1-6 are for external fields of frequency 149 MHz, 170 MHz, no field, 100-200 MHz, 300 MHz, 63 MHz respectively [after Zawadzki and Sujak (1983)].

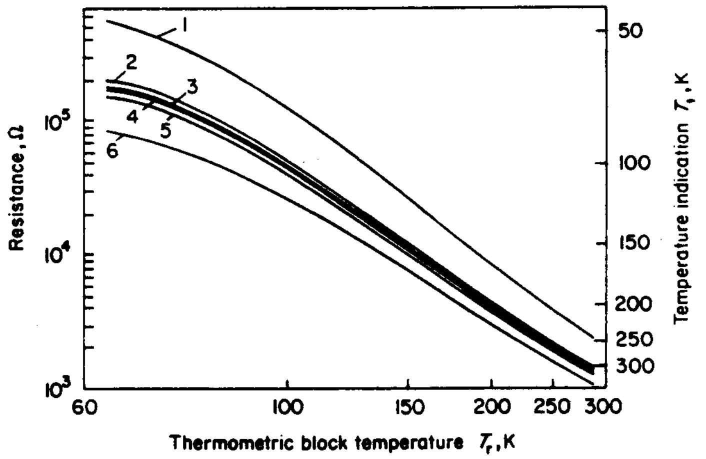

Fig. 4.7: Calibration errors due to self-heating for a germanium resistance thermometer for both constant current and constant voltage operation [Anderson and Swenson (1978)].

effect on temperature measurements under various conditions, indicating that operation at constant voltage rather than at constant current is preferable. As long as the Kapitza resistance can be neglected, the effect varies linearly with the power dissipated and depends upon the effectiveness of the thermal exchange with the environment. When the voltage drop across the potential leads is kept constant, the temperature change due to self-heating varies roughly linearly with temperature below 30 K (Fig. 4.7), independent of thermometer resistance. Rather than calculate powers when the current is changed, it is simpler to maintain a constant voltage and use Fig. 4.7. This is a useful technique when, for example, determining how much self-heating can be tolerated in calorimetric measurements. Another (related) rule-of-thumb can be deduced from Figs. 4.5 and 4.7: for many germanium thermometers, the electrical characteristics are such that $\delta T/T \sim -1/2\ \delta V/V$, and so the sensitivity is roughly 1 μV/mK.

Figure 4.8 shows the self-heating observed in a large group of thermometers [Besley and Kemp (1977)]. It can be used for any particular thermometer to estimate the self-heating after the values at two or more points have been found. To limit the effect to 1 mK at 4 K, the power dissipated must be less than 0.2 μW for a thermometer immersed in liquid helium and less than 0.02 μW if it is immersed in helium vapour. The quality of the thermal anchoring can be estimated through the experimental determination of the self-heating effect.

In order to ensure good thermal contact between the thermometer and the body whose temperature is to be measured, several general rules should be followed that depend essentially upon the geometric configuration of the interior of the cryostat. One of the simplest is to provide a well or hole just large enough to accommodate the thermometer so

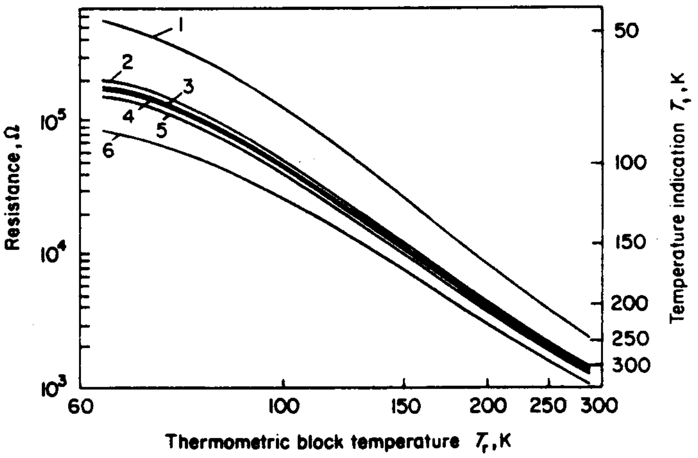

Fig. 4.8: Range of values of self-heating observed with a variety of germanium thermometers [Besley and Kemp (1977)].

that it will not be subject to mechanical constraints, and to fill the remaining gap with a suitable material that allows good heat transfer, such as one of a variety of greases, motor oil, Wood's metal, etc. Anything containing a solvent that can damage the sheath or its seals (which may be an epoxy) should be avoided and, as well, the material should be oxide-free. It is also essential to thermally anchor the leads to the body, or to a shield maintained at the temperature of the body. The leads should be of small diameter ≤ 0.1 mm), electrically insulated, and a considerable length should be attached to the body with, for example, varnish or nail polish [Hust (1970)]. Generally, the largest thermal leak is via the leads.

4.4.2 Time Constant

The value of the time constant depends upon the temperature, the environment, the thermal contact with the environment, and the thermal conductivity of the sheath, lead wires, and other components of the thermometer. It can only be measured in situ. Some typical time constants for germanium thermometers of various types under different conditions are given in Table 4.1 [Blakemore (1972), Halverson and Johns (1972)]. Note that the dimensions and masses of the thermometers do not account for all of the time constant variations. On abruptly cooling a thermometer from 300 K to 4.2 K, about 20 s is required for the thermometer to reach equilibrium.

The time constant increases with temperature because of the rapid increase of the thermal capacity of the thermometer with respect to the thermal conductivity. To minimize the time constant of a germanium thermometer one must ensure that the lead wires are properly thermally anchored as near as possible to the thermometer itself.

4.5 Calibration and Interpolation Formulae

A description of the resistance/temperature characteristics of germanium resistance thermometers is not possible by simple formulae based on theoretical considerations. As the characteristics can be very different from thermometer to thermometer, individual calibrations at a large number of points are necessary. To approximate the characteristic with the minimum possible uncertainty from the experimental data, a suitable fitting method has to be used. Furthermore, the calibration itself should already take into account any peculiarities of the fitting method [Powell et al. (1972)]. The results and conclusions in the literature concerning the efficiency of various fitting methods are obscure and, in some cases, contradictory because

Table 4.1: Typical Time Constants in Helium Liquid and Vapour for Various Germanium Thermometers.

Manufacturer	Thermometer Characteristics	Time Constant (s) in liquid helium	Time Constant (s) in helium vapour at 1.27 cm above the liquid level
Scientific Instruments type p- 1000 Ω at 4.2 K	Mass 0.081 g Length 4.75 mm Diameter 2.36 mm	0.010	0.180
CryoCal type CR1000 type n- 857 Ω at 4.2 K	Mass 0.290 g Length 11 mm Diameter 3.1 mm	0.03	0.200
Honeywell type II (circa 1963)	Mass 0.5 g Length 11 mm Diameter 3.5 mm	0.05	(at 3 cm) 0.38

- only in a few cases are different methods compared directly;
- the results obtained are valid only for the individual thermometer types investigated;
- the uncertainties of the input data are very different in the various papers;
- some questions (for example weighting and smoothing with spline functions) are not sufficiently investigated;
- the mathematical bases are often incompletely described.

Hence it is not possible to give here a recipe which can be applied in all cases. A classification of the various least squares fitting methods with general remarks on their efficiency was made by Fellmuth (1986), (1987). Only one method is recommended here; it allows the characteristics of all germanium resistance thermometers mentioned in Appendix C to be approximated in the temperature range from about 1 K to 30 K with high precision (uncertainty less than 1 mK). The features of this method are:

(i) interpolation equations:

$$\ln T = \sum_{i=0}^{n} A_i \left(\frac{\ln R - M}{N} \right)^i \qquad (4.1)$$

$$\ln R = \sum_{i=0}^{n} B_i \left(\frac{\ln T - P}{S} \right) i \qquad (4.2)$$

where R is the thermometer resistance, T is the temperature, M and P are origin-shifting constants, N and S are scaling constants, and A_i and B_j are coefficients resulting from the curve fitting.

(ii) approximation of the characteristic in two subranges which overlap several kelvins (range of overlap about 5 K to 10 K)

(iii) value of n is about 12 for a range 1 to 30 K, but may be about 5 for the range 1 to 5 K for the same accuracy

(iv) number of calibration points greater than about 3 n, or 2 n if the distribution of points is carefully controlled

(v) calibration points at nearly equal intervals in ln T except near the ends of any calibration range (and perhaps in the range of overlap), where there should be a distinctly higher density of points. An ideal spacing is such that the m points are distributed according to the formula

$$\frac{x_m + x_1}{2} + \frac{x_m - x_1}{2} \cos\left(\frac{i-1}{m-1} p \right) \quad , (i = 1 \text{ to } m)$$

where x_1 and x_m are the lower and upper limits respectively of the independent variable (ln R or ln T in equations 4.1 and 4.2 respectively).

Using this method, the errors introduced by spurious oscillations are comparable with the uncertainty of the input data. For the selection of the optimum degree several criteria must be applied (Fellmuth (1986), (1987)], which is easy if orthogonal functions are used.

It is possible that the number of calibrations points can be greatly reduced if the general behaviour of the characteristic of the individual thermometer is known or if a larger uncertainty is tolerable. Unfortunately, in the literature, only isolated data on this matter are available. It must be emphasized that a direct application of literature techniques is only possible if the same type of thermometer is used; and that special interpolation equations can approximate the characteristics of particular types of thermometers sufficiently closely with a lower degree than would result from application of Eq. (4.1) or (4.2), but their use can cause considerable difficulty if these equations are not matched to the characteristic of the individual thermometer to be calibrated.

5. Rhodium-Iron Resistance Thermometers

Rhodium-iron resistance thermometers were developed by Rusby (1972) for use below the normal range of the platinum resistance thermometer. It was found that, of various small concentrations of iron in rhodium, the one that would give the most sensitive and yet moderately linear thermometer was 0.5 atomic percent iron [Rusby (1975)]. Rusby (1982), who uses a group of them at the National Physical Laboratory to carry the primary temperature scale below 30 K, has given a review of ten years of performance. Present suppliers of rhodium-iron thermometers are listed in Appendix C.

5.1 Range of Use and Sensitivity

The range of use is normally from about 0.5 K to 30 K, although the sensitivity is good up to room temperature and at lower temperatures. For a capsule-type thermometer containing helium gas, the lower limit of about 0.5 K is set by the rapidly-increasing self-heating. The normal upper limit (~ 30 K) is in the region where the superior platinum resistance thermometer has adequate sensitivity.

In contrast to pure metals, for which the sensitivity dR/dT decreases steadily with decreasing T at small values of T, the sensitivity of rhodium with about 0.5% iron impurity is relatively constant at about 0.4 Ω/K down to 100 K, decreases to ≤ 0.2 Ω/K near 25 K, then increases rapidly by about a factor of 10 as T decreases to 0.5 K as illustrated in Fig. 5.1 for a thermometer with an ice-point resistance of 100 ohm. The industrial type has a sensitivity about 6% lower than the standard type. It is in this low temperature region of increasing sensitivity that rhodium-iron has its chief application. The rapid change in sensitivity in the low temperature region means that, to obtain a precision of 1 mK at 30 K, the rhodium-iron resistance must be measured to 1 part in 10^5, compared to 10 in 10^5 for platinum. Because the rhodium-iron resistance is much higher, however, the voltage sensitivity at 30 K is higher than for platinum. The sensitivity of rhodium-iron is much lower than that of germanium.

5.2 Fabrication

The standard-type thermometer of H. Tinsley and Co., Ltd. (U.K.) is constructed as follows: the 0.05 mm diameter wire is wound in the form of coils inside four glass tubes which in turn are encapsulated in a 5 mm diameter platinum sheath as shown in Fig. 5.2. The sheath contains helium at about 1/3 atmosphere pressure. The leads are 0.3 mm

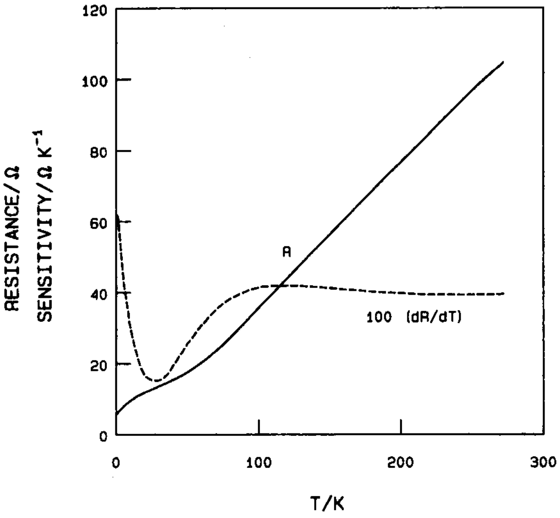

Fig. 5.1: Resistance (Ω) and sensitivity, dR/dT(Ω/K) , of a type 5187W rhodium-iron resistance thermometer [after Rusby (1982)].

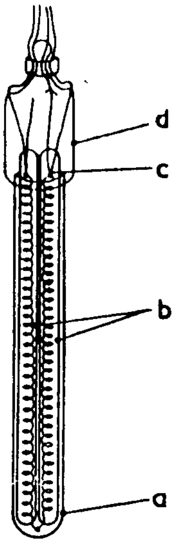

Fig. 5.2: Construction of a rhodium-iron thermometer of the high precision type. The coil of wire is mounted inside four glass tubes, two of which are shown, b; the assembly is inserted into a platinum sheath, a; 4 platinum leads are flame-welded to the rhodium-iron wire, c; the sheath and the leads are sealed in an atmosphere of helium by a glass bulb, d; [after Rusby (1975)].

platinum wire and the element is so mounted as to be strain free. Two versions are available: one (type U) has about 50 Ω resistance at 273 K, is 27 mm long, with overall length including a glass seal around the leads of 45 mm; the second (type W) has about twice the resistance and is about 15 mm longer. The 50 Ω thermometer has a resistance of about 3.5 Ω at 4.2 K.

Oxford Instruments Ltd. supplies two industrial types: Type R3 (R(0 °C) = 20 ohm) is mounted in a vented stainless steel body, 25 mm long and 3.2 mm in diameter. In type R4 (R(0 °C) = 27 ohm) the coil is mounted in four cylindrical chambers of an alumina body 22 mm long and 3.2 mm in diameter. Inside each of these chambers is a layer of a very high temperature glass that bonds a part of each loop of the alloy coil to the alumina body. The latter model is intended for use from cryogenic temperatures up to 700 °C.

More recently Cryogenic Consultants Ltd. have achieved success in producing thin-film rhodium-iron thermometers [Barber et al. (1987)]. The thermometric material is sputtered on to a sapphire substrate. For films between 0.5 μm and 1.0 μm thick the sensitivity is similar to or slightly higher than that of wire-wound thermometers, and variation of resistance with temperature is very similar to that for wire-wound thermometers. Thinner films have lower sensitivities. Ice-point resistances are in the same range as those of wire-wound units. Thin-film thermometers are now available commercially.

5.3 Reproducibility and Stability

More than ten years of study have shown that rhodium-iron thermometers have excellent long term stability. For the standard-type, Rusby (1982) reports that for five thermometers, after at least 50 cycles between 273 K and 20 K, the average shift was 0.2 mK and the largest 0.35 mK (in 8.5 years). The latter corresponds to a resistance change of 60 μΩ or 5 parts in 10^6 of the resistance. At 4.2 K no shifts larger than ± 0.05 mK were observed. This is at the level of uncertainty of the measurements themselves. Also for the standard-type, Besley (1982) describes similar excellent performance: 9 thermometers were cycled 30 times from 293 K to 6 K and 8 were completely stable; the ninth showed only a small change < 0.1 mK at 6 K and 1 mK at 90 K).

Only a limited amount of information is available on the stability of the industrial type. Besley (1984) examined three of the ceramic-type units. After 20 cycles between 20 K and room temperature, stability was almost within the precision of the measurements, i.e. 1 ± 0.3 mK. However, handling (such as by repeated soldering of the thermometer wires) caused a more remarkable change of resistance, equivalent to as much as 3 mK at 2.1 K and 16 mK at 30 K. This apparently was due to relief of strain in the wire and seems to limit the stability of this model.

A limited number of thermal cycling tests on thin-film thermometers indicate that stability to within ± 2 mK is achieved after about 15 cycles between room temperature and 4.2 K, about twice the number of cycles as required for the wire-wound industrial type [Barber et al. (1987)].

5.4 Self-heating

Self-heating has been found to be closely the same for both U and W standard-type thermometers; its magnitude is shown in Fig. 5.3 for currents of 0.1 and 0.3 mA. Near 1.5 K the self-heating falls dramatically as the ^{4}He filling of the capsule condenses to superfluid liquid and thermal contact is vastly improved. As the temperature further decreases, self-heating rises rapidly again. Self-heating in thin-film thermometers is generally smaller than in wire-wound ones.

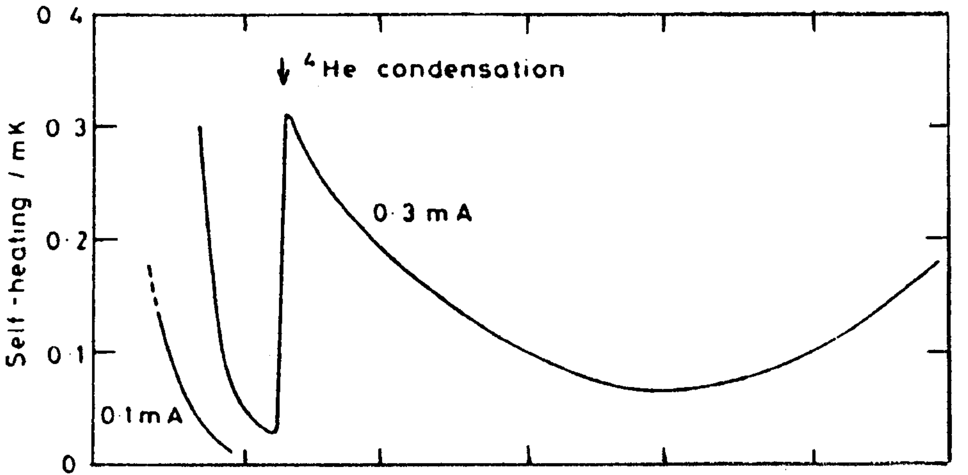

Fig. 5.3: Typical self-heating effect for a ^{4}He-filled rhodium-iron thermometer with measuring currents of 0.1 mA and 0.3 mA [Rusby (1982)].

5.5 Calibration and Interpolation

A rhodium-iron thermometer is normally calibrated at many points in the range of interest and the data fitted by least squares as described for germanium. The equation chosen is usually of the form

$$T = \sum_{i=0}^{n} a_i x^i \tag{5.1}$$

where x = AR + B, and B and A are origin-shifting and scaling constants respectively that change the range of the independent variable to $-1 \le x \le 1$. For a wide range such as 0.5 K to 27 K, n ~ 10 is necessary if fitting errors are to be ~ 0.2 mK. For lesser precision or narrower ranges, lower degree can be used - typically n = 4, 8, 9 for ranges 0.5 K to 4.2 K, 20 K, 24 K respectively. For temperatures above 27 K, R is usually replaced by In R or In Z (where Z is defined by Eq. (8.5)) in Eq. (5.1). If a change in calibration occurs, it is possible to account for it by expressing the calibration data in terms of Z with the two calibration points (for Z) near the extremities of the range.

Another equation, requiring fewer calibration points, has been found to fit calibrations of 25 thermometers satisfactorily [Rusby (1982)]:

$$R = \sum_{i=0}^{n} b_i [\ln(T + \tau)]^i \tag{5.2}$$

For τ of the order of 8 to 10 K, the standard deviation of the residuals is less than 0.3 mK for n = 6 and where the points are weighted by dT/dR. Equation (5.2) is of special interest because it allows interpolation in the range from 0.5 K to 25 K using calibrations at a restricted set of easily realizable temperatures - helium vapour pressures, superconductive transitions, and triple and boiling points.

The characteristics of rhodium-iron are such that the constants of the interpolation equation do not vary greatly from thermometer to thermometer from the same batch of wire, in contrast to germanium for which they vary widely from one to another.

From the limited information available on the industrial-type thermometer [Besley (1985)], it appears that the ceramic type may approximate the ITS-90 in the range 77 K to 273 K to within about 10 or 25 mK using a reference function together with a deviation function that requires 2 or 3 calibration points respectively.

6. Vapour Pressure Thermometry*

Vapour pressure thermometers are based on the saturated vapour pressure in a two-phase system in an enclosure. A boiling point is an example of a point on a vapour pressure curve; i.e. the techniques of vapour pressure thermometry described herein apply also to the special case of a boiling or a triple point determination. The behavior of a liquid-vapour system in equilibrium, for example, is describable by an equation $P = f(T)$ (curve tC of Fig. 6.1). Along the curve for a pure substance, the pressure depends on the temperature and not on the quantity of substance enclosed or vaporized. The temperature range associated with vaporization is limited to temperatures between the critical point and the triple point of the substance. The range is even further reduced if the extreme pressures to be measured are outside the usable range of the pressure sensor.

For a given substance, the sensitivity of the thermometer increases approximately inversely with the temperature since u_v varies roughly as $1/P$ (curve tC in Fig. 6.1). According to the Clausius-Clapeyron equation, we have

$$\frac{dP}{dT} = \frac{L}{T(u_v - u_L)}$$

where L is the molar heat of vaporization which is temperature dependent, and u_v and u_L are the molar volumes of the saturated vapour and liquid respectively. Experimental tables giving $P = f(T)$ have existed for a long time for commonly-used fluids and interpolation formulae have been internationally agreed upon for many of them [Bedford et al. (1984)]. It is therefore easy to obtain temperature from measurement of pressure.

The sublimation curve can be similarly used, but the range of measurable temperatures is then much smaller, limited on the high side by the triple point temperature and on the low side by the pressure becoming too low to be measured accurately enough. Here, the discussion emphasizes thermometers based on liquid-to-vapour

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* This chapter is written in more detail and contains rather more of the fundamentals of the theory than other chapters because no self-contained account of vapour pressure thermometry appears elsewhere, vapour pressure thermometry is one of the best means of approximating the ITS-90, and the techniques are moderately commonly used industrially.

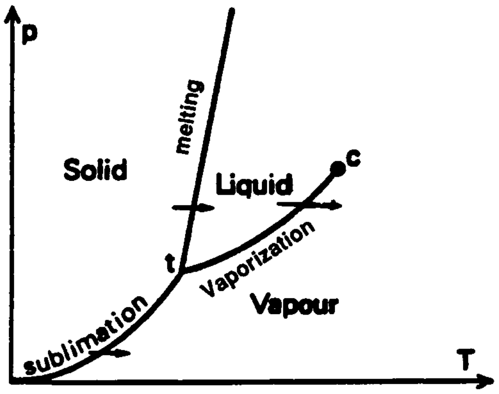


Fig. 6.1: Schematic phase diagram for a pure substance (t is the triple point and C the critical point.

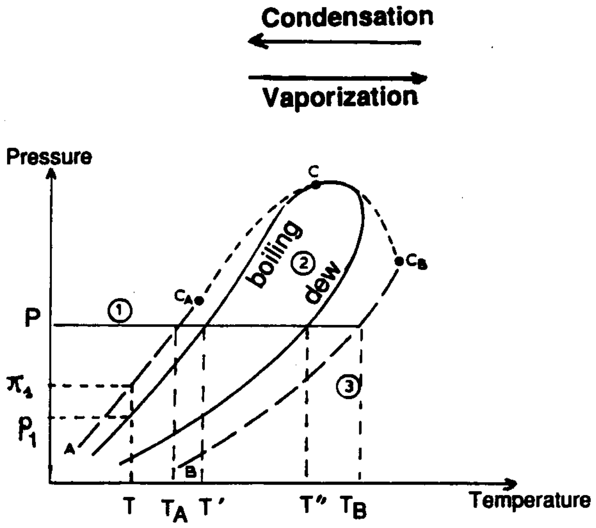


Fig. 6.2: Vaporization curve for a mixture of two pure substances: AC_A, saturated vapour pressure curve of pure substance A; BC_B, saturated vapour pressure curve of pure substance B; GC, critical point of the mixture; C_AC_B, locus of the critical points of the mixture as a function of overall composition.

transitions, but it could be applied also to those based on solid-to-vapour transitions (sublimation) with suitable changes.

6.1 Two-Phase Equilibrium

The number of parameters that can be arbitrarily imposed on a system is given by Gibb's phase rule:

$$v = c + 2 - \Phi$$

where c is the number of constituents of the system, Φ is the number of phases, and v is the number of degrees of freedom (or variance). For a pure substance with two phases ($c = 1$, $\Phi = 2$), $v = 1$. The data for the pressure therefore fix the value of the temperature at the intersection in Fig. 6.1 of a line T = constant with the curve tC; this is the measurement principle of the thermometers described here. In fact, the points of this curve are a series of equilibrium states that are distinguished by the distribution between the two phases of the total number of moles of the substance enclosed.

The equilibrium is regulated by the Gibbs-Duhem relationship, which holds in the simple case described here, by the simultaneous realization of three conditions:

$$P_L = P_v \qquad T_L = T_v \text{ and } \qquad \mu_L(T_L,P_L) = \mu_v(T_v,P_v) \quad ,$$

where the indices L and v refer to the liquid and vapour phases respectively; P and T are the pressure and temperature at the separation surface; and μ, the chemical potential, is identical for a pure substance to the free molar enthalpy. Any variation of one of the three quantities causes displacement of the equilibrium.

If the substance is not pure but contains soluble impurities, the variance of the system, becomes equal to the number of constituents present. Suppose that: each constituent is present at the same time in both liquid and vapour phases; the vapour phase is a mixture of perfect vapours; the surface-tension is negligible; the liquid phase is an ideal solution, that is to say, the substances mix without change of volume or enthalpy. This last assumption is realistic so long as the molar fractions x_i ($i = 2$ to n) of the ($n - 1$) impurities present (solutes) are very small with respect to that ($x_1 \sim 1$) of the pure substance (solvent) filling the thermometer. (Note that the respective concentrations denoted x_i^L and x_i^v ($i = 1$ to n) are generally not equal, as will be seen later.) Under these conditions, the deviation from an ideal solution is less than 1 % so long as the molar fractions of solutes are less than 10^{-3}.

The equilibrium of such a system must always satisfy the Gibbs-Duhem relation; that is, each constituent must have the same chemical potential in the two phases: $\mu_i v = \mu_i^L$ for i = 1 to n. The chemical potential is a function of pressure, temperature, and molar fractions of constituents.

The influence of the impurities present is as follows:

a) At temperature T, the pressure P above the liquid is different from the saturated vapour pressure Π_1 of the pure substance since it is equal to the sum of the partial pressures p_i of the various constituents (Dalton's Law): i.e.

$$P = \sum_{i=1}^{n} p_i = \sum_{i=1}^{n} x_i^v \cdot P$$

This can be used to determine the calibration errors of the apparatus.

b) At temperature T, the saturated vapour pressure Π_i of a pure substance is higher than the partial pressure p_i of this substance in the mixture:

$$p_i = x_i^L \, \Pi_i \qquad \text{(Raoult's Law)} .$$

For the solvent, for which $x_i^L \sim 1$, we can write:

$$p_1 = x_1{}^L \Pi_1 = \left(1 - \sum_{i=2}^{n} x_i{}^L\right) \Pi_1$$

For a weak concentration of solute ($x_i^L \rightarrow 0$) it is necessary to replace the above expression by

$$p_i = x_i^L \, k_i \qquad \text{(Henry's Law)} \quad ,$$

where k_i ($\neq \Pi_i$) is a constant that depends on the temperature and the nature of the constituents present.

As a result of the above, the quantity of every dissolved impurity is proportional to its own partial pressure. We can write

$$P = \Pi_1 - \sum_{i=2}^{n} x_i^L \left[\Pi_1 - k_i\right] \qquad ,$$

where the total pressure is a linear function of the concentrations of impurities in the liquid. The second term will be greater than or less than zero according as the impurities are more or less volatile than the solvent. The boiling temperature of a solution with a given concentration is not that of the pure substance at the same pressure.

In Fig. 6.2 showing a mixture of two components, the vaporization curve of pure substance A is AC_A and that of pure substance B is BC_B. The critical point of the mixture is somewhere on the dashed curve C_AC_B, depending upon the concentrations of the two components. If it is at C, the vaporization of the mixture takes place on the solid curve. Referring to Fig. 6.2, at the temperature T the pure substance boils at pressure Π_1. The solution boils at the partial pressure p_1, less than Π_1, since

$$\frac{\Pi_1 - p_1}{\Pi_1} = \sum_{i=2}^{2} x_i^L$$

Suppose the total pressure above the solution is P. At this pressure A would boil at T_A and B at T_B. If the solvent A is more volatile than the solute B, the solution begins to boil at $T' > T_A$. In the opposite case (solvent B less volatile than solute A), the closest the boiling temperature of the solution comes to T_B is T'', obtained at the end of vaporization or the beginning of condensation (dew point).

c) The concentration of impurities is different in the two phases and changes during the course of vaporization. We can write:

$$x_i^v = \frac{p_i}{P} = \frac{x_i^L \Pi_i}{P}$$

(Π_i being replaced by k_i if $x_i \rightarrow 0$) ,

so that $$\frac{x_i^v}{x_1^v} = \frac{x_i^L}{x_1^L} \cdot \frac{\Pi_i}{\Pi_1} \qquad \text{for all } i = 2 \text{ to } n . \qquad (6.1)$$

Suppose again there are two constituents. If 1 is more volatile than 2, i.e. if

$$\Pi_1 > \Pi_2 \text{ , then } \frac{x_2^{\,v}}{x_1^{\,v}} < \frac{x_2^{\,L}}{x_2^{\,L}} \text{ , so that } x_1^{\,v} > x_1^{\,L} \text{ , and } x_2^{\,v} < x_2^{\,L} \text{ .}$$

Thus the vapour is always richer than the liquid in the more volatile constituent. A useful method to detect impurities is to compare the boiling temperatures for two different fillings of the bulb. If the total quantity of impurities is constant, the pressure for a given temperature will depend upon the level of liquid. The result deduced immediately following Eq. (6.1) may also be used for purifying a substance by withdrawing vapour during boiling. Conversely, if the impurity (constituent 1) is less volatile than the solvent (constituent 2), this procedure will increase the concentration of impurities in the solution.

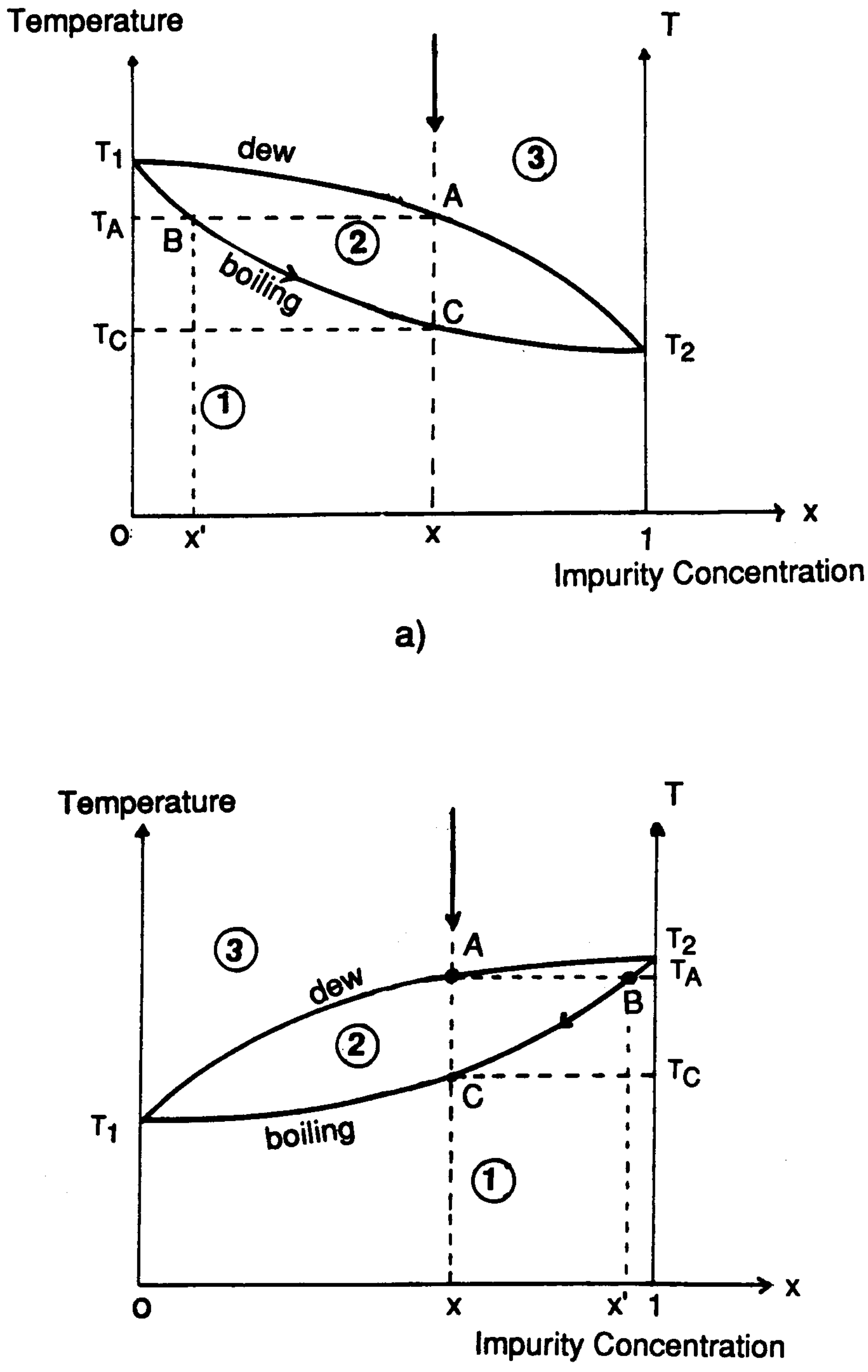
For a given pressure P, we can trace figuratively the evolution of the system in Fig. 6.3a. For simplicity, suppose once more there is only one type of impurity ($x_2 = 1 - x_1$) . Two cases occur depending upon whether constituent 2 is more or less volatile than constituent 1. Let T_1 and T_2 be the boiling temperatures of pure substances 1 and 2 at pressure P. Suppose first $T_1 > T_2$ (i.e. impurity more volatile than solvent). If we cool a sample of vapour with concentration $x_2^v = x$, a drop of liquid will appear at temperature $T_A < T_1$ when the dew point is reached. The impurity concentration in this drop of liquid is $x_2^L = x' < x$, corresponding to point B. The temperature T_A obtained is the closest to T_1 that can be reached starting from the vapour concentration x_2^v. As the temperature continues to decrease, the condensation continues along the curve B → C until all the gas is liquified at point C with temperature $T_C < T_A$, and with a concentration $x_2^L = x$.

Conversely, with increasing temperature, the point C is attained first; the temperature the closest to T_1 is obtained at the end of the vaporization.

An analogous reasoning in the case of an impurity less volatile than the solvent shows that the temperature closest to T 1 will be obtained at the beginning of the vaporization (Fig. 6.3b).

If there are many types of impurities, some more volatile and others less volatile than the solvent, the reasoning becomes more complicated, and an experimental study is more profitable.

The above examples concern ideal solutions that can exist only if the constituents present have very similar properties. This approximation is made for a mixture of isotopes or for sufficiently dilute impurities. It becomes complicated for insoluble impurities that are present only in the vapour phase or for substances that have several stoichiometric forms with change of abundance ratios during vaporization. Moreover,



a)

b)

Fig. 6.3: Diagram at constant pressure of a two-phase mixture (1, liquid; 2, liquid-vapour; 3, vapour): (a) $T_1 > T_2$, impurity more volatile than solvent; (b) $T_2 > T_1$, impurity less volatile than solvent.

impurities with densities different from that of the pure substance can create concentration gradients in the liquid phase; the preceding reasoning is then valid only near the surface of separation.

This shows the necessity of selecting an easily purifiable substance for use as a vapour pressure thermometer.

6.2 Technical Details of Construction

A vapour pressure thermometer essentially consists of: a bulb containing the pure measuring substance in thermal equilibrium with the sample whose temperature is to be measured; a pressure sensor; a connecting tube long enough to connect the bulb to the pressure sensor; and a valve for filling (Fig. 6.4).

6.2.1 Bulb

The bulb can be very small depending upon the quantity of substance necessary to cover the required temperature range. It is necessary to ensure that at no time during temperature cycling the substance reassembles into a single phase. The maximum pressure that will occur determines the thickness of the walls of the bulb. The bulb is formed from a material that is a good heat conductor, is chemically neutral, and neither absorbs nor desorbs gases. It is thermally anchored into a copper block which also contains the sample whose temperature is to be measured. If the thermometer is intended to measure the temperature of a large body, the bulb is most often an elongated cylinder (for an industrial thermometer, typically 120 mm long by 15 mm diameter, giving a volume ~ 20 cm^3), but its shape can vary as required. For example, if it is intended to calibrate resistance thermometers, those sensors are located within the walls of the bulb.

The quantity of filling substance is determined by the necessity to ensure that the surface between the two phases be in the bulb and not in the connecting tube. Moreover, as we have seen, the temperature changes during boiling according to the nature of the impurities. Referring to Figs. 6.3a and 6.3b, we note that the bulb should contain relatively little substance if the impurities are more volatile than the solvent, and should be almost completely filled with liquid if the impurities are less volatile than the solvent.

The bulb's form is dictated by the necessity to take account of eventual concentration gradients caused by impurities in the liquid phase. If the enclosed substance is a poor conductor of heat in the condensed phase, e.g. non-superfluid helium, the interior of the bulb is so structured that no large thickness of the substance can become the centre of a temperature gradient. An example of a device used for calibration of germanium resistance thermometers is shown in Fig. 6.5 [after Moser and Bonnier (1972)].

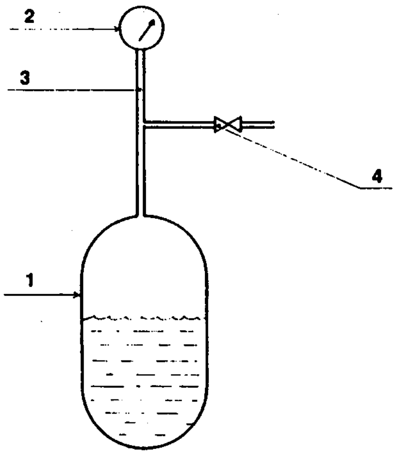


Fig. 6.4: Schematic construction of a saturated vapour pressure thermometer: 1, bulb containing two phases of a substance; 2, pressure sensor; 3, connecting tube; 4, filling system.

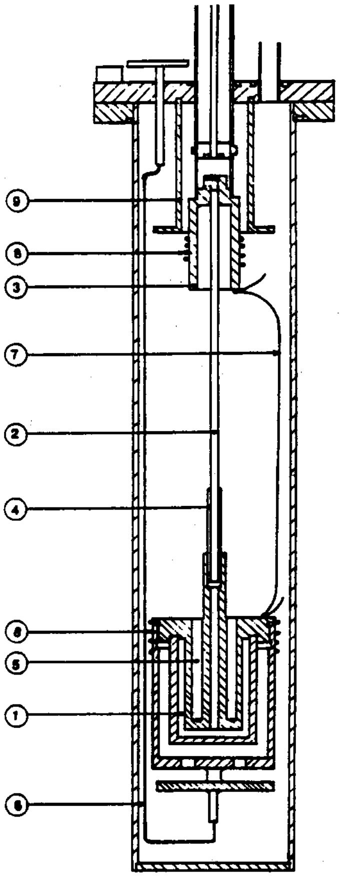


Fig. 6.5: Bulb of a helium vapour pressure thermometer [Moser and Bonnier (1972)]: 1, ^{4}He; 2, connecting tube; 3, radiation trap; 4, jacket; 5, thermometer well; 6, thermal leak; 7, differential thermocouple; 8, resistance heating; 9, conduction cooling.

6.2.2 Connecting Tube

Because the pressure sensor is usually at room temperature, the connecting tube must bea poor heat conductor; long enough to limit the contribution of heat due to the temperature gradient; equipped with a radiation trap to avoid direct radiation heating of the separation surface between the two phases; small enough that its volume is small compared to the volume of vapour in the bulb to prevent a large change in the liquid/vapour ratio; of cross section sufficient to limit thermomolecular effects and to avoid blocking. It is necessary to avoid creating a cold spot in the connecting tube where the enclosed substance can condense to form a drop of liquid that blocks the tube (although with helium such a cold spot does not form (it is self-quenching) [Ambler and Hudson (1956)] (see also Sec. 6.3.7)). Then the pressure measured would correspond to the temperature of the cold spot. This latter difficulty can be avoided by placing the connecting tube inside an evacuated tube (Fig. 6.6) and/or imposing a small heat flow along the connecting tube. The temperature gradient so created must be controlled (Fig. 6.5) and accounted for as a correction to the measurement results. For example, for a stainless steel connecting tube of 1 m length, internal diameter 2 mm, and external diameter 2.5 mm between 300 K and the helium temperature, the heat flux is about 6 mW (0.8 mW with glass), a heat leak which could produce a temperature difference of 3 mK between the bulb and the liquid helium.

The inner diameters used are generally 0.5 to 3 mm unless thermomolecular effects are likely to arise.

6.2.3 Pressure Sensor

The sensor is chosen according to the temperature range and the precision required. For an industrial thermometer it is most often a Bourdon gauge, or a mercury or oil (or any substance having small vapour pressure) manometer, used with a cathetometer. For high precision measurements, one can also use a Bourdon quartz spiral gauge periodically calibrated against a pressure balance. A diaphragm pressure transducer is also used, giving a signal that can be amplified and handled by a computer. It can be placed very close to the evaporation surface, which reduces many problems related to the connecting tube (Fig. 6.7), but then there are problems in calibrating it.

Whatever pressure sensor is chosen, its internal volume must be small (see Appendix D) and the metrological characteristics of the thermometer will be determined by the manometer. If the substance used in the thermometer is corrosive, the pressure can be transmitted across a membrane or incompressible liquid.

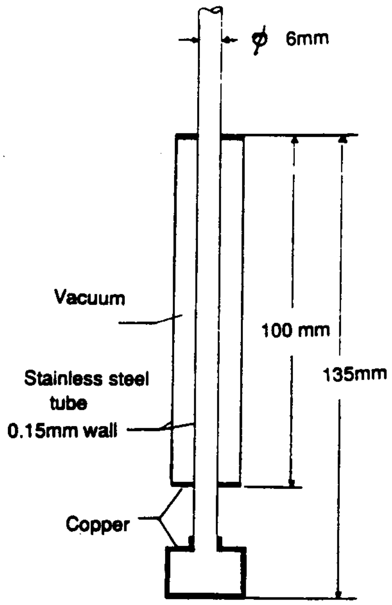


Fig. 6.6: Use of an evacuated jacket to avoid a cold spot in a helium vapour pressure thermometer [Cataland et al (1962)].

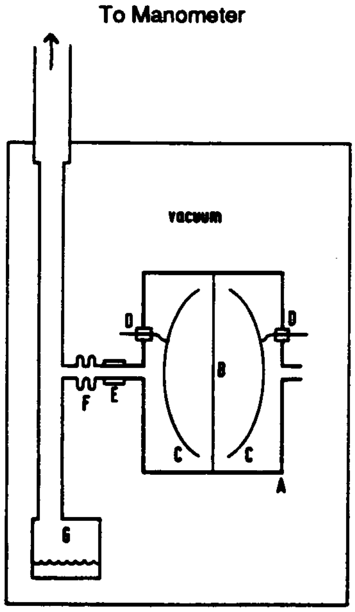


Fig. 6.7: Illustration of the use of a capacitive sensor with a vapour pressure thermometer [Gonano and Adams (1970)]: A, sensor sheet; B, diaphragm; C, capacitor plates; D, insulating feedthrough; E, insulating ceramic tube; F, bellows; G, bulb.

6.2.4 Filling the Thermometer

Before filling the bulb it is important to analyze the filling substance for the nature and quantity of impurities, to clean the enclosure with suitable chemicals or solvents, to bake it above 100 °C if possible, and to flush the enclosure several times with the filling substance to avoid contamination. When filling the thermometer, one must be certain that the volumes of the bulb, connecting tube, and manometer are compatible with the temperatures to be measured. To obtain the required quantity, it is necessary to include an extra reservoir (see Fig. 6.8); for example, one litre of liquid helium at normal pressure occupies 746 litres when it is transformed into the vapour phase at room temperature under normal pressure. The necessary details to determine the quantity of the substance at the pressure and temperature of filling are given in Appendix D.

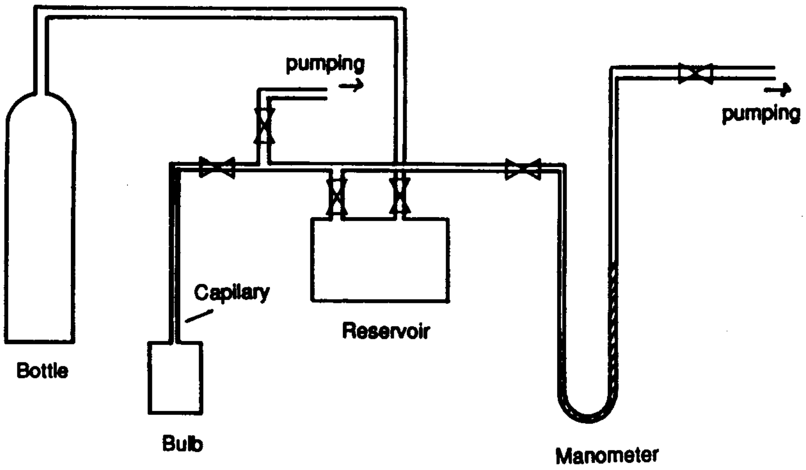


Fig. 6.8: Schematic drawing of an installation for filling a vapour pressure thermometer.

The filling proceeds as follows: after flushing and evacuating of the installation, the ensemble is filled under pressure P; on closing the inlet valve for the filling gas, the desired quantity is condensed into the bulb at temperature T_f and the pressure evolution followed until it reaches P_f. This can take a very long time because of the low thermal conductivities of the gas in the connecting tube and of the connecting tube itself [Van Mal (1969)]. The time is proportional to the length and diameter of the tube (30 min for a diameter of 5 mm and length of 50 cm for helium between 300 K and 4 K).

Following this, the connecting tube, bulb, and manometer are isolated from the remainder of the installation (see Fig. 6.8).

6.3 Metrological Characteristics and Measurement Corrections

6.3.1. Extent of Sensitivity and Measurement

Many substances could be used as a vapour pressure thermometer. The only constraint is to obtain a sufficient purity. The response curves P = f(T) of some substances are shown in Fig. 6.9. For each substance the temperature range is restricted. In the cryogenic domain, there are three temperature zones that are not covered: below 0.5 K (all pure substances have too low a vapour pressure), between 5.22 K and 13.81 K, and between 44.4 K and 63.15 K. These zones could be partially covered by sublimation vapour pressure thermometers. (Sublimation for nitrogen is possible between 56 K and 63.146 K [Bedford et al. (1984)] and for hydrogen between 10 K and 13.81 K). The response curve is usually an empirical relation of the form

$$\ln\frac{p}{p_0} = A - \frac{B}{T} + CT + \ldots \qquad \text{(with } p_0 = 101325 \text{ Pa)}$$

For ^{3}He and ^{4}He, vapour pressure equations were derived for the EPT -76 by Durieux et al. (1982) and Durieux and Rusby (1983). Inverted forms (T = f(P)) were subsequently produced by Rusby and Durieux (1984), and these are now included in the ITS -90. For other substances (H_2, Ne, N_2, Ar, O_2, S) the coefficients are given by Bedford et al. (1984).

The sensitivity of vapour pressure thermometers can be high, especially the higher the pressure, and this is one of their advantages.

6.3.2 Reproducibility and Accuracy

The reproducibility of a vapour pressure thermometer is essentially determined by the pressure sensor. The actual magnitude of the imprecision is dependent upon the particular manometer; as typical examples, for a mercury manometer between 233 000 Pa and 6 600 Pa, the imprecision can be $\leq$ 1.3 Pa; for an oil manometer with $p < 6\,600$ Pa, the imprecision is 0.09 to 0.18 Pa.

The excellent intrinsic reproducibility (10^{-3} to 10^{-4} K for helium, 10^{-2} to 10^{-3} K for other cryogenic fluids) has led to vapour pressure thermometers being used to define some thermometric scales. In particular, ^{3}He and ^{4}He gave birth to T_{62} and T_{58} respectively [Sydoriak and Sherman (1964) and Brickwedde et al. (1960)]. Later, with

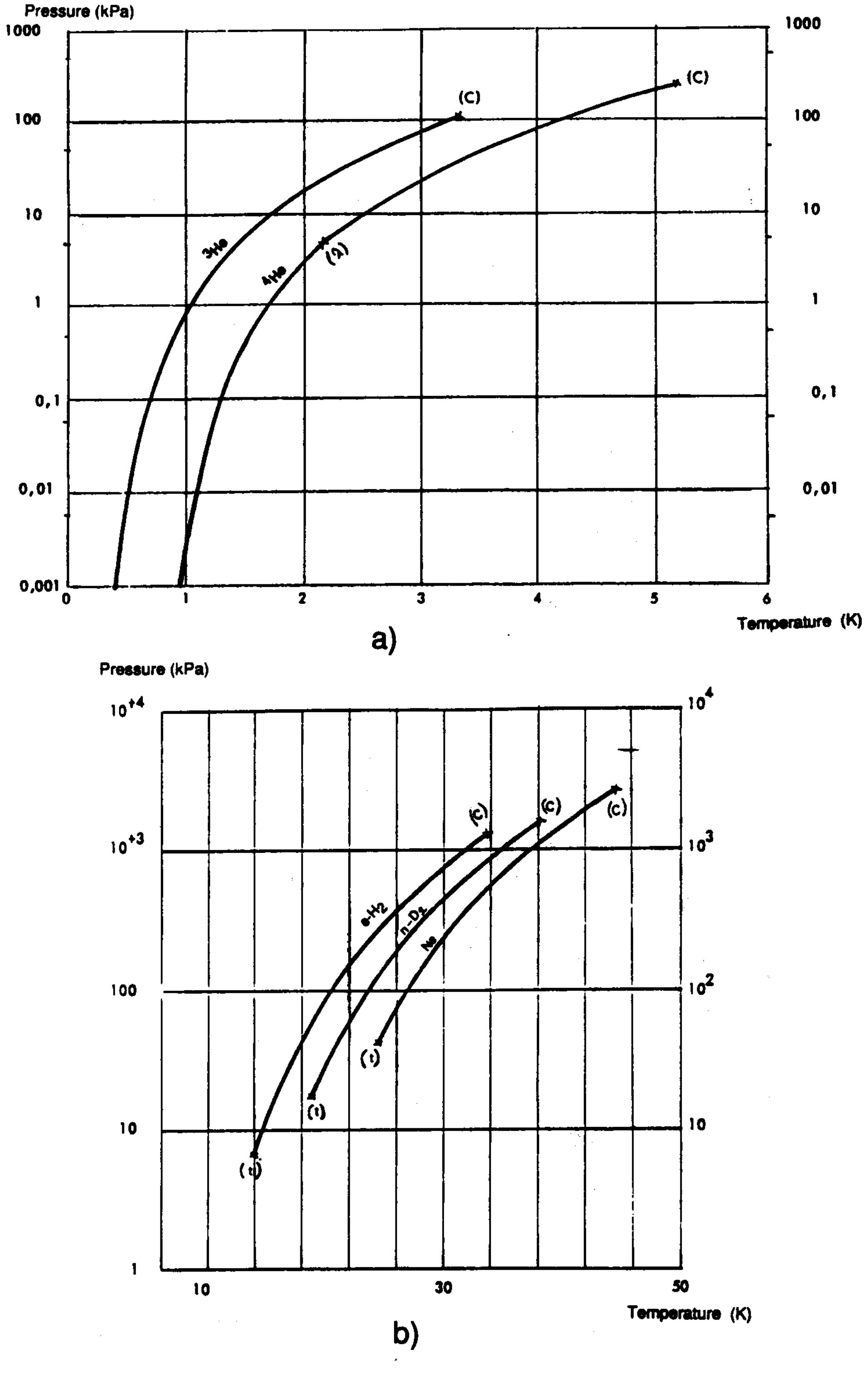


Fig. 6.9: Equilibrium vapour pressure curves for some substances used in saturated vapour pressure thermometers. The crosses on each curve are the triple point (lower) and the critical point (higher). (a) ^{3}He, ^{4}He; (b) normal H_2 and D_2 and Ne;

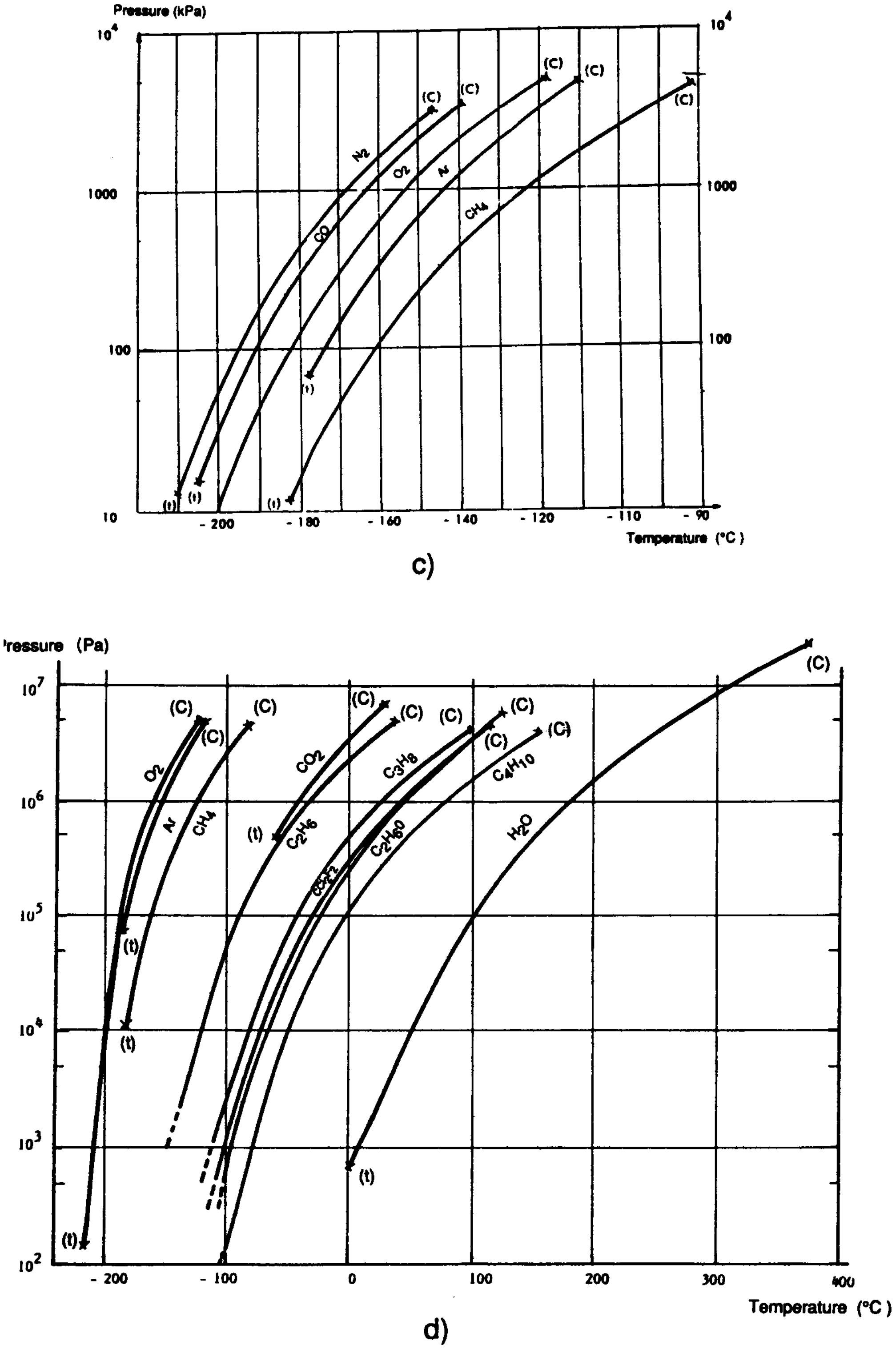


Fig. 6.9: (c) N_2, CO, Ar, O_2, CH_4; (d) Ar, O_2, CH_4, CO_2, C_2H_6, C_3H_8, CCl_2F_2, C_2H_6O, C4H10, H_2O.

some corrections, these scales served to extend the IPTS-68 to lower temperatures and to form part of the EPT-76 [Durieux et al. (1982)], and are now incorporated as part of the definition of the ITS-90.

Although the vapour pressure thermometer is an excellent secondary thermometer, it can only measure thermodynamic temperatures with many corrections and uncertainties and by using empirical values for the parameters.

6.3.3 Response Time

The time constant of a vapour pressure thermometer is essentially a function of that of the pressure sensor, of the thermal contact between the bulb and the object whose temperature is to be measured, and of the thermal diffusivity of the liquid. Certain particular configurations can make the time response very long.

6.3.4 Correction for Aerostatic Pressure

When the connecting tube is long, it is necessary to correct for the weight of the enclosed vertical vapour column. The correction requires a knowledge of the distribution of the temperatures because of the density variation in the connecting tube; it therefore depends upon the design and can be rather inaccurate (see Appendix E). The correction depends essentially on the part of the connecting tube which is close to the bulb.

For oxygen at the boiling point (~ 90 K) the pressure correction in a vacuum-jacketed sensing tube about 50 cm long is about 1 Pa, equivalent to a temperature correction of 1.3 mK. The uncertainty of the correction due to the inability to measure or predict the true temperature of the gas is at least 0.2 mK [Compton and Ward (1976), Kemp et al. (1976), Ancsin (1973a)]. For a 1 metre connecting tube containing helium joining room temperature to bulb temperature, Moser and Bonnier (1972) calculated corrections of 0.1 mK and 0.03 mK for bulb temperatures of 4.2 K and 2 K, respectively. The aerostatic correction may be determined with a 1 % uncertainty using an auxiliary tube [Klein et al. (1979)], but the procedure is difficult.

If possible, it is preferable to use a horizontal tube, or to pass the connecting tube through an isothermal enclosure, thus reducing the effects of a temperature gradient.

6.3.5 Thermomolecular Effect

There exists in the connecting tube a thermomolecular pressure gradient between the hot (higher pressure) and cold (lower pressure) extremities that is sizeable when the mean free path of the molecules is not much smaller than the tube diameter, e.g. for ^{4}He around 1 K. When the effect is not measured, one usually corrects for this gradient using the Weber-Schmidt equation [Weber et al. (1936)], although also the experimental tables of Roberts and Sydoriak (1956), or the calculation of Bennett and Tompkins (1957) can be used for the two helium isotopes. The Weber-Schmidt equation is

$$\ln\frac{P_1}{P_2}=\frac{1}{2}\ln\frac{T_1}{T_2}+0.18131\ln\frac{y_1+0.1878}{y_2+0.1878}+0.41284\ln\frac{y_1+1.8311}{y_2+1.8311}-0.15823\ln\frac{y_1+4.9930}{y_2+4.9930}$$

where $y=\frac{RP}{X(T/273.1)^{1+n}}$

X = 1.8087, n = 0.147 for helium,

X = 1.1470, n = 0.195 for hydrogen.

Index 1 indicates the hot end of the tube, index 2 the cold end; R designates the tube radius in cm, P the pressure in Pa, and T the temperature in K.

The trend of the effect is shown in Fig. 6.10 [Roberts and Sydoriak (1956), Durieux et al. (1982)].

Some temperature values for a vapour pressure thermometer using He or H_2 are shown in Table 6.1

With oxygen, the correction reaches 20 mK near 54 K (when P = 100 Pa), but it is already less than 0.05 mK at 64 K for an Inconel tube 1.6 mm in diameter [Tiggelman (1973)]. For neon near 20 K it is less than 1 mK [Tiggelman (1973)].

In general, these calculations can be 10% to 25% in error [McConville et al. (1966) and McConville (1972)], since the correction depends upon the material used for the tube and the physico-chemical conditions of its inner surface, which may also vary with time. They can be calculated [McConville et al. (1966)] as a function of the reflection coefficient of the tube but, unfortunately, the latter is never well known and may change after long exposure to the gas.

The thermomolecular effect can be measured with an additional tube [Berry (1979)]. Another solution, which eliminates the correction, is to use a diaphragm transducer located in the lower temperature region [Gonano and Adams (1970)] (see Fig. 6.7).

Current practice consists of using pressure tubes of the largest section possible compatible with keeping heat transfer losses reasonably small (and to include some means of blocking radiation (gains, not losses) and damping oscillations). If the calculated correction is to be realistic, it is indispensable to have a constant diameter in the parts of the tube where the temperature is ill-defined.

The two corrections from Secs. 6.3.4 and 6.3.5 are usually small and in many cases the only significant uncertainty is that due to the reading of the pressure.

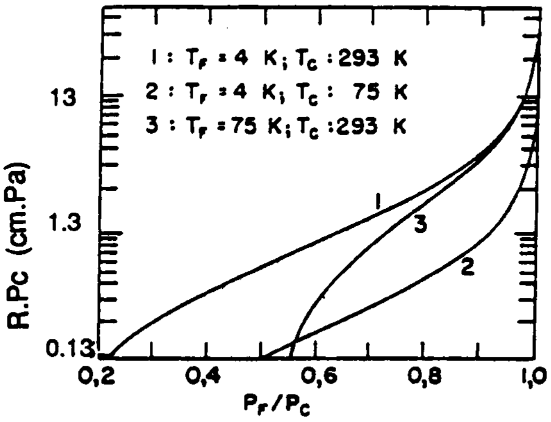


Fig. 6.10: Ratios of thermo molecular pressures for ^{3}He and ^{4}He (R, radius of tube in centimetres; p_F and p_C, pressure in Pa at the cold (T_F) and hot (T_C) extremities of the tube) [Roberts and Sydoriak (1956)].

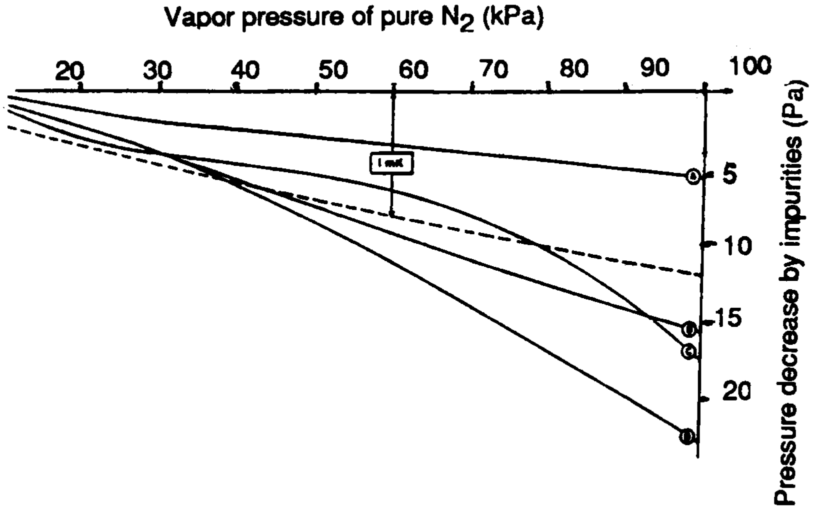


Fig. 6.11: The observed lowering of the vapour pressure of N_2 by nonvolatile impurities, as a function of the vapour pressure of pure N_2. Curve A, N_2:100 ppmv. CO; curve B, N_2:100 ppmv. Ar; curve C, N_2:100 ppmv. Kr; curve D, N_2:100 ppmv. O_2 [Ancsin (1974a)].

Table 6.1: Temperature values (K) at the cold extremity of the connecting tube of a vapour pressure thermometer using helium or hydrogen for various tube diameters, a hot extremity at room temperature, and thermomolecular effects of 10 mK and 1 mK.

Filling gas	Thermomolecular Effect	Tube Diameter (mm) 0.5	1	5	10
^{3}He:	dT = 10 mK	0.76	0.65	0.48	0.42 K
	dT= 1 mK	1.08	0.90	0.64	0.56 K
^{4}He:	dT = 10 mK	1.45	1.30	1.05	0.96 K
	dT= 1 mK	1.83	1.62	1.27	1.16 K
H_2:	dT = 10 mK	below 10 K			
	dT = 1 mK	below 10 K			

Table 6.2: Amounts by which small Concentrations of ^{3}He in liquid ^{4}He affect Vapour Pressure.

Concentration of ^{3}He (%)	Temperature (K)	Pressure Change (kPa)	Equivalent Temperature Change (K)
0.12	1.5	1.6	0.5
0.02	1.5	0.3	0.2
0.12	2.6	5.2	0.2
0.02	2.6	0.6	0.04

6.3.6 Corrections Due to Impurities

a. Helium (^{3}He, ^{4}He)

The only impurity problem with helium is isotopic since all other substances are solid at these temperatures and the solids are not soluble in liquid helium.

The presence of ^{4}He in liquid ^{3}He lowers the vapour pressure below that of pure ^{3}He. The concentration of ^{4}He in the vapour phase is much less important than in the liquid phase. For concentrations of ^{4}He in the liquid phase of < 10%, we can use [Sydoriak and Sherman (1964)] the approximate formula (derived from Raoult's Law)

$$\Pi - P_x = (1 - x)\frac{d(\ln P_x)}{dx}$$

In this expression x is the concentration of ^{3}He (> 90%); Π is the saturated vapour pressure of pure ^{3}He and P_x is the pressure of the mixture at temperature T; the derivative is taken for x = 1 at temperature T. One can obtain correction curves at the calculated temperatures according to this formula [Sydoriak and Sherman (1964)]. For 0.1 % of ^{4}He in the liquid phase, this gives a temperature correction of 0.02 mK at 0.4 K and of 0.71 mK at 3.2 K.

In ^{4}He, the only awkward impurity would be ^{3}He. Commercially supplied ^{4}He contains no ^{3}He, so the only risk of error would be from its accidental introduction from, e.g., poor manipulation of a dilution refrigerator. Not many measurements have been made, but they are confirmed by theoretical calculation. Even a small concentration of ^{3}He in ^{4}He causes a considerable increase in the vapour pressure, as shown in Table 6.2. The numerical values in the table concern the concentration of ^{3}He in the liquid phase of ^{4}He. The concentrations of ^{3}He in the vapour phase are even more important than in the liquid phase.

b. Hydrogen [Ancsin (1977)]

The only volatile impurity, He, seems not to be soluble in liquid hydrogen and is therefore not in contact with the separation surface. Other impurities are condensed and cause no problem except for Ne which can cause errors up to $\Delta P = 210$ Pa ($\Delta T = 1$ mK) at 19 K for a concentration of 410 ppm in volume.

Other errors can occur because the ortho-para conversion of hydrogen is not instantaneous and the proportion of these two states is a function of the temperature. At room temperature, normal hydrogen is 75% ortho and 25% para, while at 20 K equilibrium hydrogen is 0.21 % ortho and 99.79% para with a boiling point 0.12 K lower than that of normal hydrogen. To obtain reproducible results, one must introduce a catalyst into the bulb (hydrous ferric oxide). It should be enclosed in a metallic mesh to avoid its dispersing to the walls during boiling. The quantity of catalyst is not important (e.g. 0.15 g) but it is inefficient if it is not in good contact with the liquid phase.

There are similar problems with deuterium, which is more easily contaminated, and always contains some hydrogen deuteride (HD) even after the most careful preparation. HD will also be formed in measurable quantities (over 1%) from hydrogen atoms that diffuse from the bulk of the container or, more commonly, from exchange with H_2O if a hydrated catalyst is used. Errors of several hundredths of a kelvin may arise near 18.7 K [Pavese and McConville (1987)].

c. Neon [Ancsin (1978), Furukawa (1972), Tiggelman et al. (1972), Tiggelman (1973)]

The volatile impurities, H2 and He, are not soluble in the liquid phase and do not influence the vaporization curve. Their presence in the vapour phase causes a decrease in the boiling temperature of Ne. Their effect can be minimized by increasing the volume of the vapour phase [Ancsin (1978)].

Most of the possible nonvolatile impurities have small partial pressures below 27 K and are trapped somewhere in the tube. Only nitrogen has a notable influence. The limit of solubility of N_2 in Ne is 150 ppmv*. The triple point temperature of saturated Ne is 2.25 mK lower than for pure Ne. For a mixture with 1000 ppmv* of N_2, the vapour pressure is lowered by 100 to 300 Pa, giving a boiling temperature 6 to 10 mK higher than pure Ne between 24.562 K and 27.102 K.

It appears that the isotopic constitution of natural neon varies so little from one supplier to another that there is no need to be concerned with variations in it. Natural neon as described in "Supplementary Information for the ITS-90" [CCT (1990)] is composed of 90.5% of ^{20}Ne, 0.27% of ^{21}Ne, and 9.2% of ^{22}Ne. The ^{21}Ne is in too small a quantity to influence the results, but this is not the case for ^{22}Ne and ^{20}Ne which have different boiling and triple points: the latter are 24.546 K and 24.687 K respectively (corresponding to a pressure difference of 326 Pa). An increase of the concentration of ^{20}Ne by 0.1% increases the normal boiling point by 0.13 mK.

There also exists an isotopic composition difference between the liquid and vapour phases. The molar concentration of ^{22}Ne is higher in the liquid phase than in the vapour phase by 0.3% at the boiling point and 0.4% at the triple point [Furukawa (1972)]. This

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* The abbreviation ppmv is used to mean an impurity content of one part by volume of solute per 10^6 parts by volume of solvent.

creates an uncertainty of 0.4 mK in the value of the normal boiling point depending upon whether the ITS composition applies to the liquid or the vapour phase. In the absence of a precise analysis, the error can be minimized if the volume of the liquid phase is much larger than that of the vapour phase.

d. Nitrogen [Ancsin (1974a)]

For nitrogen in the liquid phase, volatile impurities such as He, H_2, and Ne, if present, stay entirely in the vapour phase and have no detectable effect on the temperature of the boiling liquid. Non-volatile impurities such as O_2 and Ar lower the triple point value, while CO and (especially) Kr raise it.

Impurities have a complex effect on the *whole* vapour pressure relationship, which cannot simply be represented as a shift proportional to the temperature changes at the triple and normal boiling points (Fig. 6.11). There is a consequent change of all the constants in the vapour pressure equation.

e. Argon [Ancsin (1973b)]

As impurities, He, Ne, and H_2 have no influence; N_2 (volatile) decreases the temperature of the dew point by more than 2 mK for 100 ppmv. Oxygen (nonvolatile) has no influence if the concentration is less than 200 ppmv, whereas CH_4 and Kr (nonvolatiles) increase the dew point temperature by approximately 2 mK for 100 ppmv.

f. Oxygen [Ancsin (1973a, 1974b), Tiggelman (1973), Compton and Ward (1976), Kemp et al. (1976)]

Since the principal impurities are volatile it is necessary to use a well-filled bulb. Helium and neon are not soluble in liquid oxygen. For a concentration of 1 ppmv, nitrogen decreases the boiling (condensation) point temperature by 19 µK; krypton increases it by 5.6 µK; argon decreases it by approximately 5 µK. The influence of H_2O and CO_2 is imperceptible up to a concentration of 100 ppmv.

As observed with nitrogen, the effect of the impurities on the *whole* vapour pressure curve is highly non-linear, and therefore distorts the whole vapour pressure equation (Fig. 6.12) [Ancsin (1974b)]. Some of the discrepancies observed in the literature between different vapour pressure scales can be attributed to this effect.

The isotopic effects in oxygen are perceptible only when the volume of residual liquid is small. The vapour pressure of pure ^{18}O is about 1.5% less than that of the "normal" mixture; the associated correction is about 11 µK at the boiling point for an isotopic composition of 0.210% instead of 0.204% [Tiggelman and Durieux (1972b)].

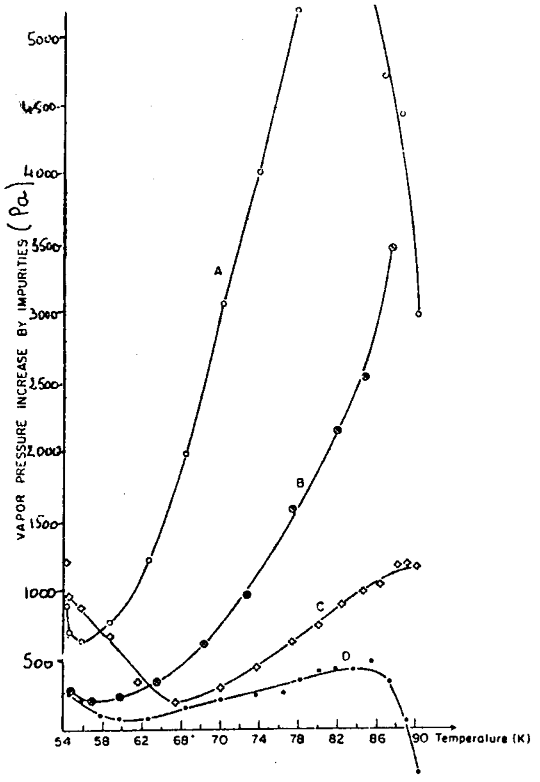

Fig. 6.12: Effect on the vapour pressure of oxygen due to the indicated volatile impurities as a function of temperature. Curve A, O_2:1000 ppmv. N_2 V (vapour phase) = 1.61; curve 8, O_2:1000 ppmv. Ar V (vapour phase) = 1.61; curve C, O_2:100 ppmv. N_2 V (vapour phase) = 0.41; curve D, O_2:100 ppmv. N_2 V (vapour phase) = 1.61 [Ancsin (1974b)].

6.3.7 Particular Problems with Helium [Cataland et al. (1962), Kerrik (1970), Montgomery and Pells (1963), Rusby and Swenson (1980)]

Information on the realization of helium vapour pressure scales is available in "Supplementary Information for the ITS-90" [CCT (1990)]. As for other substances, it is necessary to avoid the formation of cold spots which can cause an error in reading. In ^{4}He, such a cold spot can be at the same level as the liquid surface. In fact, He I above the λ-point (2.1768 K) has a very low thermal conductivity so temperature gradients can occur, especially near the surface if evaporation is taking place. Below the first 4 millimeters, the temperature variation under static (non-convective) conditions would be equal to that of the hydrostatic pressure (0.14 mK/cm at 4.2 K; 0.27 mK/cm at 3.34 K; 1 mK/cm at 2.2 K). Nearer the surface, the effect depends upon the cryostat design; at 4.2 K a temperature increase of up to 5 mK above the surface temperature in the first 4 mm has been observed [Durieux (1960)]. The vapour temperature above the surface is therefore lower by several mK than that of a body immersed just below the surface. The vertical gradient can cause an error of up to 20% of the measured temperature if the temperature of an immersed body is deduced from the pressure in the vapour phase and accounted for only with the hydrostatic correction. This temperature gradient, detectable by the appearance of bubbles in the center of the liquid, depends also on the rate of evaporation. It is necessary to use a well-insulated dewar and to fractionate the liquid mass with fins or massive braids to improve the thermal contact with the surface of the bulb (Fig. 6.5). Rather than measure the pressure just above the liquid in which the body whose temperature is required is immersed, one can also use a small auxiliary bulb in good thermal contact with it. The pressure tube must then cross the liquid-vapour surface in the dewar and it is there that there is a risk of a cold spot forming, although according to Ambler and Hudson (1956) this is unlikely (see also Sec. 6.2.2). A vacuum jacket around the capillary tube will suffice to avoid this cold spot but it must not reach to room temperature which would make thermal isolation difficult (Fig. 6.6). A heat flux along the wall of the internal tube must also be avoided; if it cannot be otherwise controlled, some copper foil in the bath and surrounding the capillary would prevent the formation of temperature gradients. In summary, large and unquantifiable temperature gradients can arise in bulk He I and therefore a bulb should be used.

Below 2.1768 K He II is an excellent thermal conductor so the temperature gradient does not exist. On the other hand, being a superfluid, He II climbs along the bulb walls, vaporizes, and returns to the liquid surface. This produces a heat input to the bulb by refluxing because the superfluid film does not carry away entropy, so the entropy density of the remaining liquid increases. The large Kapitza resistance is also troublesome. The temperature of the liquid can be many millikelvins higher than that of the walls (15 mK to 1.5 K). This phenomenon can be corrected for (but not reliably) by calculation, and can be reduced by increasing the surface of the bulb/liquid contact up to several hundreds of cm^2 (metal mesh or spirals of copper in the bulb). Furthermore, the viscosity of the return gas induces a pressure gradient in the capillary which can become important below 1 K.

Note that if these problems are not under control, the measured temperatures will be discontinuous at the λ-point. For precise measurements, the error due to the Kapitza effect (which can be about 4 mK at 1.5 K) is too important to ignore [Lounasmaa (1974) for temperatures below 1 K; Wilks (1967) for higher temperatures]. It can be calculated, or it can be avoided by using ^{3}He, which does not become superfluid, instead of ^{4}He in the temperature range where the two scales overlap; for ^{4}He one should always use a bulb above the λ -point, and always measure the bath pressure directly below the λ -point. Below the λ -point the refluxing and Kapitza effects can be avoided by measuring the vapour pressure a short distance up the pumping tube [Rusby and Swenson (1980)].

6.3.8 Other Corrections

Other corrections to be considered in pressure measurements include: expansion of the mercury of the manometer and variation of its density with the temperature; the shape of the meniscus; hydrostatic pressure correction (if we measure the temperature of a body immersed in the liquid). The latter can be uncertain but can usually be kept small because the depth of liquid is seldom large.

6.4 Conclusion

The vapour pressure thermometer can be used as a thermodynamic thermometer only within the limits of application of the Clausius-Clapeyron equation which result from lack of knowledge of several of the parameters. Otherwise it is an excellent practical thermometer based upon a physical property of a pure substance. Simple and practical, it allows a high measurement precision once the pressure-temperature relationship has been established. The bulb is simple to construct and can be very small. There are not many corrections to apply (a few for impurities possibly, but no dead space corrections as in the gas thermometer). The major inconveniences are its small working range (no pure substance covers a large temperature range) and its nonlinearity of response. The development of new pressure sensors may give renewed interest in vapour pressure thermometers.

7. Magnetic Thermometry

7.1 Magnetic Thermometer

Magnetic thermometry is based upon measurement of paramagnetic susceptibility. Useful papers concerned with the EPT-76 temperature range are Rusby and Swenson (1980); Cetas and Swenson (1972); van Rijn and Durieux (1972); Cetas (1976); Mangum and Bowers (1978). For an ideal paramagnet the zero-field susceptibility is related to temperature through the Curie law $\chi = C/T$ where C is the Curie constant. Although in magnetic thermometry one approximates to this by using dilute paramagnetic salts, it is generally necessary to take account of interactions and other effects and write $\chi = C/(T + \Delta + \gamma/T)$, where Δ includes first-order dipole-dipole and exchange couplings and also a shape factor, while γ is due primarily to crystal field splitting of the ground state and second-order interaction effects [Hudson (1972)]. The existence of interactions implies a lower limit for the use of any given salt, while the upper limit is set by diminishing sensitivity ($d\chi/dT$ is approximately equal to $-C/T^2$). The susceptibility measurement is usually made by the ac mutual inductance method in which the salt sample is situated in a set of coils whose mutual inductance M is balanced against a reference in a Hartshorn bridge or a variant thereof [Hudson (1972)] (SQUID techniques do not appear to have been applied much above 1 K). The bridge balance X is linearly related to M and hence to χ. The working equation for a magnetic thermometer becomes

$$X = A + B/(T + \Delta + \gamma/T) \qquad (7.1)$$

Unless Δ or γ is obtainable from theory, a minimum of four fixed points is needed to calibrate the thermometer.

Salt crystals must be grown carefully from ingredients of high purity. Most of the suitable salts are hydrates and almost all of these are efflorescent, tending to lose water-of-crystallization if kept at room temperature. This tendency is considerably diminished if the enclosing volume is small and is filled with an inert gas; but it is catastrophically increased if the enclosure is evacuated. Simple refrigeration, however, avoids most such problems. The properties of the most important salts have been widely discussed and tabulated [e.g. Hudson (1972)]. Cerous magnesium nitrate (CMN) is the closest approximation to an ideal paramagnet in common use: $\gamma = 0$ and for a sphere Δ is about 0.3 mK. It is, however, highly anisotropic and its usefulness is limited to temperatures below 3 K because of its low

Curie constant ($C_\perp$ is about 0.011 K in SI units referred to unit volume) and the existence of an excited state which becomes significantly populated at higher temperatures [Rusby and Swenson (1980)]. Another rare-earth salt, neodymium ethylsulphate (NES), is less anisotropic and about four times stronger than CMN. It has been used successfully between 2 K and 16 K [Mangum and Bowers (1978)] and there appears to be no bar to using it down to 0.5 K or lower [Hudson (1972)].

Chromic methylammonium alum (CMA) is a salt of intermediate strength (C being about 0.077 K) which has been used for the range 1 to 20 K [Cetas and Swenson (1972); Durieux et al. (1962)]. Manganous ammonium sulphate (MAS) [Cetas and Swenson (1972); Cetas (1976); Durieux et al. (1962)], and gadolinium sulphate (GS) [Cetas (1976); Durieux et al. (1962)] are classed as strong, with C about 0.26 K and 0.79 K respectively, and they are therefore more suitable if the range is to extend to 30 K. Another possibility is gadolinium metaphosphate (GP) [Mangum and Bowers (1978)], which has the practical advantage of being anhydrous, but for all of these strong salts Δ and γ would have to be determined in the experiment using at least four fixed points, and the lower limit for accurate use might not be below 2 K.

7. 2 Technical Aspects of Magnetic Thermometry

For the simple case of a primary solenoid of m turns per metre and a secondary of turns-area product nA wound on it, the mutual inductance M is $\mu\mu_0 mnA$. If the coils contain a salt with a geometrical filling factor f, then $\Delta = (1 + f\chi)$ and if $\chi = C/T$ the sensitivity $d\ln M/dT$ is approximately $- fC/T^2$. For f = 0.5 and C = 0.26 K as for MAS, one therefore requires a precision $\Delta M/M$ of 2 parts in 10^7 if 1 mK is to be resolved at 25 K.

With a primary current i_p of angular frequency ω the solenoidal field H is Mi_p and the voltage across the secondary is $i_p\omega M$ or $\mu\mu_0 HnA\omega$. The design of the thermometer and bridge must be such that this is large enough to achieve the desired sensitivity. Typically $\mu_0 H$ might be 0.1 to 0.3 mT without departing seriously from the zero field limit, and the frequency is usually between 30 and 300 Hz. Taking 0.2 mT and 100 Hz and a secondary of 500 turns on a radius of 1 cm, the voltage would be 0.02 volt, 2 parts in 10^7 of which is 4 nV. This is not unreasonable, but there is need for caution and the design should aim to provide greater sensitivity than is indicated by such calculations. While the product nA can be gauged in advance, the frequency and field may be limited by the effect of eddy currents (roughly proportional to $\omega^2 H$) induced in nearby metallic components. To combat them, glass and plastic materials should be used where possible, and the coil system should be as well separated from the thermometer block as is practicable. Good heat transfer may be achieved through varnished copper wires, but tests of their effectiveness should be undertaken. Various other precautions could include [Cetas and Swenson (1972)] using a quadrupolar configuration of secondary coils, and shielding the coil system with superconductive Pb sheeting. The latter reduces external interference and ensures that eddy currents are independent of metallic resistivities and hence are independent of temperature.

As regards the measurement technique, it is standard practice to include in the cryostat a set of empty coils identical to those surrounding the salt, with the secondaries connected in opposition. Then the net mutual inductance is small and relatively insensitive to extraneous magnetic and electrical interference. Suitable mutual inductance bridges with adequate sensitivity can be assembled using commercially-available measuring equipment.

An essential preliminary to magnetic thermometry is a check of the performance of the bridge and coil system in the absence of the salt. After the system is cooled from room temperature, the bridge balance should first be checked for stability at a constant temperature for a period of hours during which time any dependence on primary current, coolant liquid level, exchange gas pressure, room temperature, or disturbance to the cryostat should be tested. Then the bridge balance should be monitored as a function of block temperature in order to establish the background effects at all currents to be used. If these effects are not small, steps should be taken to reduce them or at least to ensure their reproducibility from one assembling of the coils to another.

Only when the background has been satisfactorily characterized should a salt be mounted and magnetic thermometry begin. Again, the stability of the measuring system should be monitored after initial cooling. Bridge balance and thermometer resistance may then be measured at many temperatures in the range, with enough time allowed at each temperature to reach equilibrium. It is advisable to make measurements at more than one value of the primary current and to check for drifts in the bridge balance by returning to the starting temperature at the end of a measurement session. It may help the analysis if there is some overlap between data taken in different sessions, particularly after an overnight interval or a transfer of liquid helium or nitrogen. After correction for bridge drifts and background effects, the unknown constants are evaluated from the measurements taken at the chosen reference temperatures, and values of T_{90} at intermediate temperatures are calculated.

8. Platinum Resistance Thermometers

8.1 General Remarks

The platinum resistance thermometer (PRT) is very widely used below 500 °C as a thermometric sensor. There is a wide range of quality of PRT available, from the standard instrument (SPRT) of the ITS-90 to some industrial types (IPRT) that are accurate only to within a few tenths of a kelvin or, perhaps, even a kelvin or more. The major difference of the industrial type of fabrication from the standard type is not just the purity of platinum, but also the less strain-free mounting of the film or wire which is embedded (partially or totally) in a cement (glass or refractory). Furthermore, in most cases, the thermometer body is not hermetically sealed.

The ITS restricts the quality of the thermometer that may be used as a standard instrument. For the ITS-90 an acceptable PRT must be made from pure, strain-free platinum, and it must satisfy at least one of the following two relations:

$$W(29.7646\ °\mathrm{C}) \geq 1.118\,07$$

$$W(-38.8344\ °\mathrm{C}) \leq 0.844\,235\ ,$$

where $W(t_{90}) = R(t_{90})/R(0.01\ °\mathrm{C})$*. If the PRT is to be used to the freezing point of silver, it must also satisfy the relation

$$W(961.78\ °\mathrm{C}) \geq 4.2844\ .$$

These relations are closely equivalent to the restriction that

$$(dW(t_{90})/dt_{90})_{0.01\ °\mathrm{C}} \geq 3.986 \times 10^{-3}\ \mathrm{K}^{-1} \qquad .$$

These relations, in essence, assure that the platinum in an SPRT is highly pure. They are equivalent to the requirement that $W(H_20\ \mathrm{b.p.}) > 1.392\,44$, whereas it is estimated that

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* Note that this definition of $W(t_{90})$ is different from the equivalent one for $W_{68}(t_{68})$. The latter uses R(0 °C) as the reference in the ratio. It follows that $W_{68}(t_{68}) = 1.000\,040\ W(t_{90})$ to better than 1 part in 10^6 for any SPRT.

for ideally pure platinum W(H_20 b.p.) ~ 1.392 74. No such restrictions apply, in principle, to a PRT used to approximate the ITS-90. Various national and international bodies place restrictions on the quality of PRT that is suitable to meet their requirements for accuracy, the restriction taking the form of a specification on W(H_20 b.p.). In addition, in conjunction with the use of standard tables of resistance, the value of R(0 °C) is specified. Also, the resistance ratio W(4.2 K) is sometimes used as a quality indicator. The most accurate thermometers (corresponding to W(H_20 b.p.) > 1.3925 have W(4.2 K) < 4×10^{-4}, whereas industrial thermometers (corresponding to W(H20 b.p.) ~1.385) have W(4.2 K) nearer 2×10^{-2}. It must also be remembered that for industrial purposes the platinum sensing element is usually mounted within a protective sheath which can modify some of the characteristics of the sensor itself. It is the latter that has been most often studied in the references to follow.

In Section 8.2 we outline a few simple methods for approximating the ITS-90* based upon fixed-point calibrations and simple interpolation formulae to be used with SPRTs, with indications of the accuracies that may be achieved. Discussion of IPRTs is given in Chapter 16 in Part 2.

8.2 Interpolation Equations for Standard Platinum Resistance Thermometers*

The approximations described here are concerned with SPRTs calibrated with simplified methods for medium to high accuracy. Several such simplified procedures have been suggested but only some of the more promising of them are described here. Some of the others appear either to be too complicated or to have been insufficiently tested (e.g. too few thermometers) to be suitable for recommendation.

(a) Perhaps the simplest secondary realization is an extrapolation below 273 K of the following defining equations of the IPTS-68 from above 273 K:

$$t_{68} = t' + 0.045\left(\frac{t'}{100\ °\mathrm{C}}\right)\left(\frac{t'}{100\ °\mathrm{C}} - 1\right)\left(\frac{t'}{419.58\ °\mathrm{C}} - 1\right)\left(\frac{t'}{630.74\ °\mathrm{C}} - 1\right) \qquad (8.1)$$

$$W_{68}(t') = 1 + At' + Bt'^2 \qquad (8.2)$$

---

* All of these methods were devised as approximations to the IPTS-68 but they are also applicable to the ITS-90.

For a group of 45 thermometers having $W_{68}(H_20\ b.p.) > 1.3925$, Bedford (1972b) showed that if the thermometers were calibrated only at the triple and boiling points of water and if a common value of B were assumed for every thermometer, then the extrapolated temperatures (T_e) diverge smoothly from T_{68} (or T_{90}) by up to 1 K at 100 K, 1.7 K at 70 K, and -12 K near 20 K, and variations in these temperatures are small (Fig. 6.1). Using a tabulated or functional correction, one can measure T_{68} (and, consequently, T_{90} using the tables of Appendix A) to within ± 3 mK down to 150 K, ± 15 mK at 77 K, and ± 30 mK at 30 K. We note that:

(i) The method is simple. The thermometers are calibrated *only* at the triple and boiling points of water. If B were measured by a tin-point or zinc-point calibration, the extrapolated scale uncertainty might be marginally smaller. This would be feasible for a long-stem thermometer but not for many capsule thermometers.

(ii) The procedure is equally valid for capsule or long-stem PRTs.

(iii) There is no definitive test of the extrapolation; there is a high probability, but no certainty, that any particular PRT will fall within the uncertainties quoted.

(b) Another simple secondary realization for the range 90 K to 273 K uses only two fixed points and obtains a third from an experimentally-observed linear correlation between $W(O_2\ b.p.)$ and $W(H_20\ b.p.)$. This correlation was first pointed out by Brodskii (1968), who found the following relation for thermometers with $W_{68}(H_20\ b.p.) > 1.3920$:

$$W(O_2\ b.p.) = a_1 + b_1\ (W(H_20\ b.p.) - 1)\ . \qquad (8.3)$$

Berry [(1963), (1972)] examined similar correlations in detail. For platinum of the highest available purity, he determined [Berry (1972)] a linear relation of the form of Eq. (8.3) corresponding to various equilibrium concentrations of quenched-in vacancies. This is shown as curve V in Fig. 8.2, which Berry suggested would be an upper bound for all real PRTs. Similarly, his curve L [Berry (1963)] approximates the mean behaviour for his large group of thermometers. From Fig. 9 of Berry (1963) one can deduce a lower bound (curve M) below which no SPRT is likely to lie.

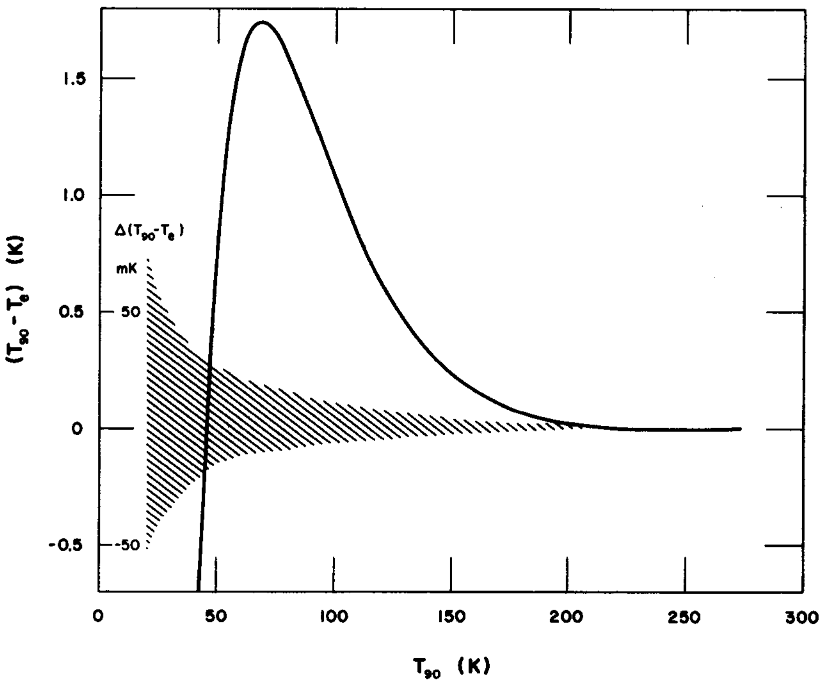

Fig. 8.1: Differences from T_{90} of temperatures T_e extrapolated below 0 °C using the IPTS-68 defining equations for above 0 °C. The hatched area shows the maximum observed deviations $\Delta(T_{90} - T_e)$ in $(T_{90} - T_e)$ for a group of 45 thermometers [Bedford (1986)].

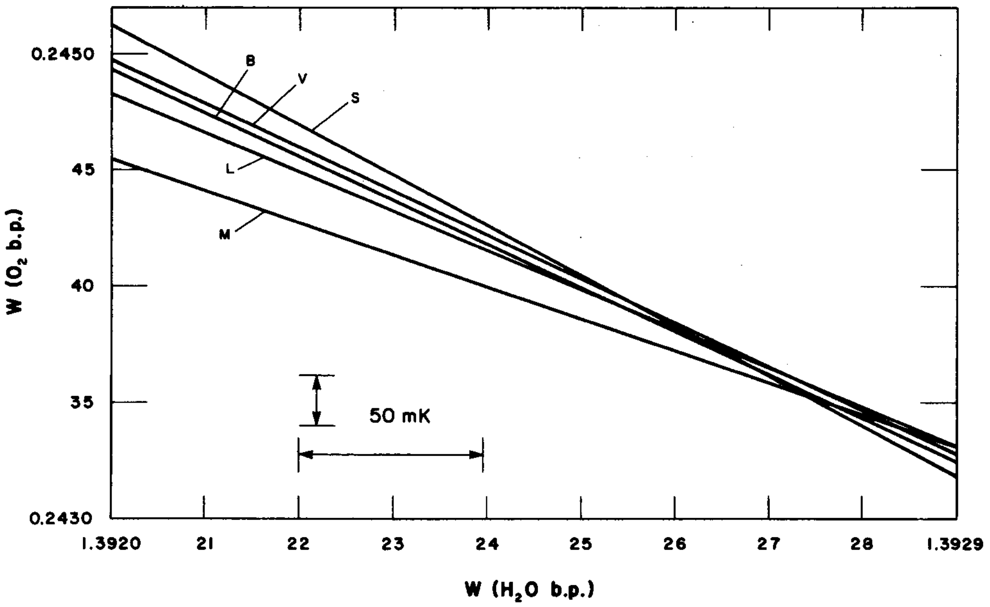

Fig. 8.2: Linear relationships between W(O_2 b.p.) and W(H_20 b.p.) for platinum: B, after Brodskii (1968); V, ideally pure platinum [Berry (1972)]; L, mean of many thermometers [Berry (1963)]; M, lower bound for SPRT [Berry (1963)]; S, result when argon replaces oxygen, converted to oxygen [Seifert (1980), (1984)]; [Bedford (1986)].

More recently, Seifert [(1980), (1984)] considered a relation similar to Eq. (8.3) relating W_{68}(Ar t.p.) to W_{68}(H_20 b.p.):

$$W_{68}(H_20 \text{ b.p.}) = -0.525\,29\, W_{68}(\text{Ar t.p.}) + 1.506\,108 \qquad (8.4)$$

Using the $W_{CCT-68}(T_{68})$ ratio of 1.128 402 for W_{68}(O_2 b.p.)/W_{68}(Ar t.p.), Seifert's equation can be converted to the form of Eq. (8.3); the result is shown as curve S in Fig. 8.2. Curve S has a more negative slope than the others and rises above V at lower values of W(H_20 b.p.). The coefficients a_1 and b_1 of Eq. (8.3) are given in Table 8.1 for all of the curves in Fig. (8.2).

Table 8.1: Coefficients a_1, b_1 of Eq. (8.3) for the Curves in Fig. (8.1).

Curve	a_1	b_1	reference
B	0.977 86	-1.870 0	Brodskii (1963)
V	0.982 826	-1.882 572	Berry (1972)
L	0.903 485	-1.680 508	Berry (1963)
M	0.779 641	-1.365 254	Berry (1963)
S	1.087 070	-2.148 156	Seifert (1980), (1984)

Equation (8.3) allows a secondary realization from 90 K to 273 K with calibration at only the triple point of water and the boiling point of either oxygen or water, the other being estimated from Eq. (8.3). The coefficients a_1, b_1 for curve L are probably the most representative. Used with the IPTS-68 defining equation for the range 90.188 K to 273.15 K, this secondary realization is probably accurate to within ± 30 mK when W(H_20 b.p.) ~ 1.3920 and ± 10 mK when W(H_20 b.p.) > 1.3925. In Eq. (8.3), W(O_2 b.p.) could be replaced with W(Ar t.p.) and W(H_20 b.p.) by W(In f.p.) (with suitable adjustment of the coefficients a_1 and b_1), and an equivalent accuracy would result. According to the finding of Bedford (1972b), extrapolation to about 70 K will produce little further degradation in accuracy. Although temperatures between 125 K and 273 K are less sensitive to an error in W(O_2 b.p.) than in W(H_20 b.p.), it is probably better and usually more convenient to calibrate at the oxygen or argon point and deduce the resistance ratio at the steam point. Moreover, few laboratories now maintain a steam point, and most capsule thermometers cannot safely be heated as high as the tin freezing point, another reason to prefer calibration at the oxygen point and deduction of W(H_20 b.p.). As indicated by Seifert, a relation similar to Eq. (8.3) based upon the argon triple point is even better. It obviates the need for any boiling-point measurement, requiring only two simple triple-point determinations. Seifert (1984) has extended this method by using one- or two-point comparisons with a standard PRT (at, e.g., 160 K and 78 K) to replace the argon-triple-point measurement. The accuracy is little degraded thereby.

(c) Several possibilities for secondary realization based upon Cragoe Z-functions rather than simple resistance ratios have been proposed. Among early investigations were those of Cragoe (1948), Corruccini (1960), (1962), and Barber (1962). The Z-function is defined by

$$Z(T) = \frac{R(T) - R(T_1)}{R(T_2) - R(T_1)} \quad , \tag{8.5}$$

where T_1 and T_2 are fixed-point calibration temperatures at or near the extremities of the range. The Z-function for a particular choice of calibration temperatures is tabulated and temperatures are calculated by interpolating deviations from the table in some specified way. The Z-function tabulation acts as a reference function equivalent to $Wr(T_{90})$. Besley and Kemp (1978) incorporate the Z-function into a reference function using T_1 = 4.2 K (boiling helium) and T_2 = 273.15 K (melting ice) in Eq. (8.5). They define a reference function of the form

$$T^* = \sum_{n=0}^{16} A_n \left[\frac{\ln(Z) + 3.54}{3.54}\right]^n \tag{8.6}$$

using the mean value of Z of a group of 19 thermometers each with W(4.2 K) < 4 x 10^{-4}. Temperature ($T = T^* - \Delta T^*$) is determined for any particular thermometer in terms of a deviation from Eq. (8.6) of the form

$$\Delta T^* = a\left[1 - \left(\frac{T^*}{40\,K}\right)^{1/2}\right]\Delta T \,, \tag{8.7}$$

where $\Delta T = b + c\,W(4.2\ K) + d\,W(4.2\ K)^2$, $T^* \leq 40$ K (8.8)

and $\Delta T = 0$. $T^* > 40$ K (8.9)

For thermometers with W(4.2 K) < 4 x 10^{-4} this scheme allows calibration of thermometers to within ± 0.02 K from 14 K to 273 K.

Using the same method for a group of 31 thermometers having 4 x 10^{-4} < W(4.2 K) < 7 x 10^{-4}, but using a different reference function (in place of Eq. (8.6)) and correction polynomial (in place of Eq. (8.8)), Besley and Kemp (1978) obtained an accuracy within ± 0.02 K above 40 K for 31 thermometers, and within ± 0.04 K below 40 K for 29 thermometers.

In summary, the thermometer is calibrated only at 4.2 K and 273.15 K. A temperature T is obtained by measuring R(T), calculating Z(T) from Eq. (8.5), calculating T* from Eq. (8.6), and calculating ΔT* from Eqs. (8.7) - (8.9). When 4 x 10^{-4} < W(4.2 K) < 7 X 10^{-4}, the procedure is similar, but uses different reference and correction polynomials. With this proposal:

(i) only a relatively simple 2-point calibration is required,

(ii) only SPRTs are likely to have W(4.2 K) < 4 X 10^{-4},

(iii) it is not applicable to long-stem thermometers; to measure any temperature below 273 K, a calibration at 4.2 K is necessary,

(iv) there is no test for the accuracy of interpolation for any particular thermometer.

(d) Several other useful approximations to the ITS have been described (see the original papers for details). Kirby et al. (1975) proposed a single deviation function from 14 K to 273 K determined by calibration against a previously-calibrated SPRT at four points using three boiling liquids (He, H_2, N_2) and the ice point; the resulting inaccuracy is about ± 10 x 10^{-6} in W. Pavese et al. (1978) suggested using the same equations as in the IPTS-68 but a different set of fixed points that included only triple points. Tiggelman and Durieux (1972a) showed that a polynomial in the form

$$W(T) = \sum_{n=0}^{6} A_n T^n \qquad (8.10)$$

can fit 14 calibration points between 2 K and 15 K with a standard deviation of ± 2 mK at 4.2 K decreasing to ± 0.3 mK above 11 K for 10 high quality SPRTs (W($H_2$0 b.p.) > 1.3926). In the range 4 - 15 K a mere five points allow an accuracy of ± 3 mK.

9. Platinum Thermocouples

9. 1 General Remarks

Thermocouples employing platinum in combination with platinum-rhodium alloys, gold, or palladium have been found to be the most reproducible of all the various types. They are resistant to oxidation in air and, because of their high melting points, can be used up to very high temperatures. The best-known member of this group is Pt10Rh/Pt* (or type S, or 10/0). It was long considered more accurate and has probably been studied more than any other thermocouple; moreover, and presumably for these reasons, it served as a defining instrument in the ITS-27, the IPTS-48 and the IPTS-68. It is not one of the defining instruments of the ITS-90, its role having been taken over by the SPRT. Any Pt10Rh/Pt thermocouple, in order to qualify as a defining instrument for interpolation in the range from 630.74 °C to the gold point (1064.43 °C), had to meet strict requirements for purity and thermocouple emf [CCT (1976)].

The Pt13Rh/Pt (or type R, or 13/0) thermocouple is very similar in its properties to the type S; containing 13% Rh by weight, it has a little higher sensitivity and probably also a little higher reproducibility.

In many situations the precision of types Sand R thermocouples, especially above 500 °C, is limited to about ± 0.2 °C. For more precise measurements Mclaren and Murdock (1987) have shown that the gold/platinum thermocouple is clearly superior in stability, homogeneity, and sensitivity (about twice that of type S). It even challenges the SPRT on the basis of simplicity and economic practicality. With care, temperatures can be measured to within ± 10 mK in the range 0 °C to 1000 °C. For higher temperatures the palladium/platinum thermocouple has likewise shown considerable promise as being more accurate than type S or R. Precision within ± 20 mK at 1100 °C and ± 50 mK at 1300 °C has been achieved. Studies of both of these types are in progress.

The upper temperature limit of use for types R and S thermocouples in an oxidizing atmosphere is quoted as high as 1600 °C (for 0.5 mm diameter wires). Better platinum-rhodium alloy combinations for thermometry under oxidizing conditions above 1100 °C, however, are Pt30Rh/Pt6Rh (or type B, or 30/6) or the non-standardized combinations Pt20Rh/Pt5Rh (20/5) and Pt40Rh/Pt20Rh (40/20). These have proven to be exceptionally stable and may be used continuously in air to 1700 °C. In one test, for example, after 200 h heating at 1700 °C in air, the emf of the 20/5 thermocouples had decreased the equivalent of about 5 K at the palladium point (1555 °C) [Bedford (1964)];

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* See footnote on page 6.

after 500 h at 1700 °C in air, the 40/20 thermocouples exhibited changes equivalent to 4 K at the palladium point [Bedford (1965)]. Compared with 20/5, type B (30/6) has some superior thermoelectric properties, better tensile properties at higher temperatures, and the additional characteristic that its emf varies only between -2.5 and 2.5 μV in the range from 0 to 50 °C, meaning that the temperature of the reference junction can often be neglected or simply corrected for [Burns and Gallagher (1966)].

As the melting point of platinum-rhodium thermoelements increases with increasing rhodium content, thermocouples comprising platinum-rhodium elements of higher rhodium content are relatively more stable to higher limits of temperature. The 40/20 thermocouple is useful for accurate measurements up to 1850 °C and is superior to type B in stability at 1700 °C, although its thermoelectric power in the range 1700 to 1850 °C is only about 4.5 μV/K or less than half of that of type B. Which one is chosen for measurements from 1500 to 1700 °C would have to be based on the total temperature range, the duration of the measurements, the availability of the thermoelements, and the importance of the magnitude of the thermoelectric power for the user's measuring equipment.

For all of the above thermocouple types (except Pd/Pt and Au/Pt) the emf-versus-temperature characteristics based upon the IPTS-68 were determined by national metrological institutions, resulting in the establishing of reference tables [Bedford (1964), Bedford (1965), Burns and Gallagher (1966), Bedford (1970), Bedford et al. (1972), Powell et al. (1974)]. Those for types R, S, and B have been internationally accepted [IEC (1977)]. The equations with which to generate these tables are given in Appendix F. These reference tables ensure, for users throughout the world, that manufacturers supply wires with a guaranteed accuracy of the emf-versus-temperature characteristics within known tolerances. The requirements of the user dictate whether calibration is required or not. If the desired accuracy is higher than the allowed tolerances of the standard reference tables, or when it is expected that the emf has drifted outside of these tolerances, the thermocouple should be calibrated (see Sec. 9.4).

9.2 Construction

The pure platinum and the alloy wires used for constructing a 10/0 thermocouple to be used as a standard interpolating instrument should be at least 0.35 mm in diameter (preferably 0.5 mm) and at least 1 m long. Smaller-diameter wires are prone to damage during unsheathed annealing at high temperatures (see Sec. 9.3) and homogeneity during fabrication is more difficult to achieve; larger-diameter wires are more expensive and can be the cause of significantly altering the junction temperature by heat conducted to or from the junction. The wires of a standard thermocouple should run in continuous lengths from the hot junction to the reference junction. In most calibration equipment 1 m is about the minimum length that will allow this.

After the wires have been electrically annealed (see Sec. 9.3), they are mounted in an appropriate insulator. For accurate thermocouple thermometry it is better to assemble the thermocouple than to purchase it as a complete sheathed unit. This allows for the best choice for each part of the system.

The insulators which separate and protect the thermocouple wires are an extremely important part of the installation. The choice of refractory will depend upon the particular operating conditions so it is difficult to lay down rules that cover every installation. Insulators should be of highest quality. For an oxidizing atmosphere the choice of refractory is very wide. Fused silica will withstand thermal shock and can be used satisfactorily to 1000 °C. Pure alumina can be used to 1900 °C. The alumina-silica refractories such as sillimanite and mullite can be used up to 1700 °C but are not recommended for highly accurate work. These alumina-based refractories are less resistant to thermal shock than is fused silica; if they must be immersed suddenly they should be preheated to avoid fracture. Under reducing conditions, or in vacuum, silicious refractories must be avoided because, in contact with platinum, they are reduced, releasing elemental silicon which embrittles the wire. In the worst case a platinum/platinum-silicide eutectic will be formed and since this has a melting point of 820 °C, failure of the thermocouple will result. In this context pure magnesia is one of the more stable refractories and will usually provide satisfactory service. Pure alumina can be used under inert conditions, but under reducing conditions it has been found occasionally to be reduced and alloyed with platinum. Beryllia and thoria are particularly good refractories to use in conjunction with platinum but they are far more expensive than those mentioned before. Also, beryllia is slightly toxic and thoria slightly radioactive, so extreme caution should be exercised [Zysk (1964)].

These ceramic insulators are fired with organic binders so that some carbon impurities remain. In order to reduce the carbon concentration and to remove surface contamination, all insulators should be fired for an hour at 1200 °C in air before assembly. It has been demonstrated that impurities in the insulator produce substantial changes in the thermoelectric power of type S thermocouples. The largest effect is caused by iron and can be minimized by the use of ultra-high-purity alumina or beryllia. The effect is smaller in an oxidizing atmosphere than in vacuum or inert atmospheres.

Each wire can be mounted into a separate single-bore insulator or, more commonly, both are mounted in a single twin-bore insulator of outside diameter 3 to 4 mm which normally extends about 50 cm back from the junction. This length should be sufficient to reach from the centre to the outside of the furnace. The wires at the hot junction are joined by welding. The weld should be mechanically sound and as small as possible. The wires from the reference junction to the ceramic are insulated with a flexible material such as plastic or fibreglass. Care should be taken to avoid kinking when threading the wires into the insulators. For insertion into a fixed-point or other furnace, the hot junction and ceramic insulator are enclosed in a close-fitting, closed-end, fused-silica or alumina tube to minimize thermocouple contamination.

For the reference junction, good practice is to solder or mechanically connect a small-gauge (≈ 0.25 mm diameter) copper wire to each thermocouple wire.

Types S and R thermocouples of the mineral-insulated metal-sheathed construction are also in wide use. In general, they are not as stable as those of the standard construction but they have many compensating advantages (see the discussion of base metal thermocouples of this construction in Section 18.3.4).

9. 3 Annealing of the Thermoelements

All thermocouples should be in a condition which is metallurgically stable over the envisaged temperature range. Generally this involves annealing the wires along their entire length. A thermocouple wire which is not uniformly annealed, particularly over that portion which is subjected to a temperature gradient, will not give a repeatable output. The purpose of annealing the wires of a standard thermocouple is to remove strain due to cold work, remove contaminants, and equilibrate point defects, without at the same time allowing excessive grain growth or significant evaporation of platinum or rhodium from the alloy wire.

The annealing is usually done by passing an electric current through each wire as it hangs between two electrodes in air. If the wire diameter is smaller than 0.35 mm the annealed wires may not support their own weight, as a result of grain growth or intermittent local superheating, and may stretch substantially or even break.

It is recommended [CCT (1976)] that the bare platinum thermoelement be annealed at 1100 °C and that the bare platinum-rhodium thermoelement be annealed at 1450 °C for up to 1 h to remove strain due to cold work, to oxidize residual impurities, and to dissociate rhodium oxide. The wires should be cooled slowly (10 to 30 minutes) in order to avoid quenching-in of non-equilibrium concentrations of point defects. After the wires are mounted in insulators, the portion of the thermocouple that will be above ambient temperature in use should be briefly reheated to 1100 °C and slowly cooled to remove cold work introduced during assembly. Following this, a measurement uncertainty of a single determination is about ± 0.2 K at the 99% confidence level in the IPTS-68 defining range (630.74 °C to 1064.53 °C) for a constant immersion depth and constant temperature gradient of the furnace used [Jones (1968)]. It has been shown, however, that such thermocouples as ordinarily prepared are inhomogeneous, and variations of the immersion depth or the temperature gradient of the furnace can result in emf variations approaching 1 K at the copper point (1084.88 °C) [McLaren and Murdock (1972)].

Another annealing procedure that appears to give a stable thermoelectric power at higher temperatures (≥ 1100 °C) is to heat the thermocouple wires electrically to about 1450 °C for 45 min and then to cool them quickly in air to 750 °C. They are held at that temperature for 30 min, then cooled to room temperature in a few minutes in air. After assembly into insulators, all of the thermocouple that will be at high temperature or in a temperature gradient is annealed at 1100 °C in a furnace and then cooled slowly, taking about 2 h to fall to 300 °C [Guildner and Burns (1979)].

A more sophisticated annealing procedure which leads to better reproducibility involves the following steps [McLaren and Murdock (1972), Murdock and McLaren (1972)]: New platinum and platinum-rhodium thermoelements are first given full-length, electric, bare-wire anneals at 1300 °C for from 1 to 10 h and are then quenched (abrupt switch-off of current) to room temperature to minimize permanent oxidation of the alloy elements. This is followed by a separate 1 h bare-wire anneal of each element at 450 °C. After assembly into a sheath, the sheathed portion of the thermocouple receives a further anneal at 450 °C (16 to 24 h). This preparatory anneal places the thermoelements in a reference state. That is, they are homogeneous in thermoelectric power, are as oxide-free as possible along their full length, and are equilibrated for vacancy concentrations at 450 °C. The subsequent sequence of restoring and maintenance anneals differs from the preparatory anneal only by shortening the 1300 °C wire anneal to 10 min, a time normally sufficient to remove the surface and internally-diffused oxide from the alloy elements that have been immersed for short times in air in the oxidizing region 500 to 900 °C. Longer, oxide-cleaning anneals at 1300 °C are required to restore the thermoelectric power and homogeneity in alloy elements that have been more heavily oxidized during long periods.

9.4 Guidelines for Proper Handling and Use - Installation and Sources of Errors

Because the thermocouple emf is generated in the region of temperature gradient along the wires and not at the isothermal junctions, the principal errors arise from inhomogeneities in the portions of the wires that lie in the temperature gradient. These inhomogeneities result from the unavoidable production of rhodium oxide on the alloy wires and from changes in vacancy concentrations in both wires in those portions that experience temperatures between 500 °C and 850 °C. Other mechanisms probably contribute also, such as order-disorder transitions in the structural lattices and differential thermal expansion between wires and the ceramics in which they are imbedded.

McLaren and Murdock (1979a, 1979b, 1983) have shown in detail that the emf of a Type S thermocouple annealed according to the procedures given in Sec. 9.3 is not constant for different depths of immersion of the hot junction in a freezing metal ingot. In freezing copper, for example, the emfs vary somewhat irregularly but generally increase with a 10 cm increase in immersion, followed by a significantly higher decrease on withdrawal. The maximum variations in emf are typically a few microvolts. These variations are caused by inhomogeneities along the wires resulting from the processes mentioned above. A different type of anneal will produce homogeneous wires, but unfortunately they cannot be maintained in the homogeneous state in service. As a result, an initial insertion of a thermocouple with this type of anneal into a fixed-point ingot produces a constant emf if the temperature is not higher than 1000 °C, but subsequent withdrawals and insertions produce emfs that increase almost linearly (but moderately reproducibly) with immersion depth. A reanneal returns the wires to their original homogeneous state. Errors from the other sources can be reduced, with a little care, below ± 0.2 K.

Apart from this, contamination is by far the most common cause of thermocouple error and often results in ultimate mechanical failure of the wires. Elements such as Si, Al, P, In, and Sn combine with platinum to form low-melting-point eutectics and cause rapid embrittlement, leading to failure of the thermocouple wires. Elements such as Ni, Fe, Co, Cr, and Mn all affect the emf output of the thermocouple to a greater or smaller degree, but contamination by these elements may not result in wire breakage and can only be detected by regular checking of the accuracy of the thermocouple.

Contamination can be minimized by careful handling of the thermocouple materials during assembly and by using appropriate refractory sheathing. Care should be taken to prevent dirt, grease, oil, or soft solder from coming into contact with the thermocouple wires. If the atmosphere surrounding the thermocouple sheath contains any metal vapor, the sheath must be impervious to such vapors. Contamination of the pure-platinum arm by transfer of rhodium (probably through the oxide phase) from the alloy arm can be suppressed by using a continuous twin-bore alumina insulator to support and protect the wire over its whole length in the temperature gradient. For the higher temperatures where this is likely to occur, it is preferable to use Pt30Rh/Pt6Rh or other double-alloy thermocouples because these are much less affected by contamination or rhodium transfer.

Contamination by reduction of the alumina can be avoided by ensuring that the furnace within which the thermocouple is used allows free access of air to the thermocouple. If the furnace itself operates under an inert or reducing atmosphere the thermocouple must be protected by a closed-end alumina or silica sheath, one end of which is open to the air.

Errors can also result from loss of homogeneity due to strain in one or both wires. The effect of strain is to reduce the emf and so give a temperature reading that is too low. The strain can be removed by reannealing the whole thermocouple. Thermocouple installations should be designed in such a way that there is no strain on the wire while in service; for example, use in a horizontal position is preferable to use in a vertical position.

Thermocouples must be installed in such a way that they have adequate immersion and the reference junction is at a uniform and known temperature (preferably 0 °C, see below). Immersion is adequate when the heat transfer to the thermocouple is such that the difference between the measuring-junction temperature and the temperature to be measured is smaller than a given tolerance. On the other hand, the means of ensuring adequate immersion must not invalidate the measurement sought. It is common that the design of the experiment is substantially affected by balancing these requirements.

Thus the installing of the thermocouple requires considerations regarding annealing, calibration, tempering, insulation of the thermoelements from each other and from the surroundings, and protection from chemical or physical deterioration. The installation should also provide for means of occasional recalibration.

Very important to the correct use of a thermocouple is the realizing of a stable reference junction. It is easy to make a reference junction at 0 °C reliable to ± 0.01 °C by using a vacuum flask into which is placed a mixture of shaved ice and distilled water. This will enable the user to refer this thermocouple cold junction directly to 0 °C, which is advantageous because most reference tables are so referred. The thermocouple wires are connected to pure copper wires, by suitably twisting them together or by soldering without flux, and inserted into separate closed-end glass tubes that are in turn inserted into the ice mixture. The thermocouple-to-copper junction is placed at a sufficient depth (> 20 cm) in the reference unit that a stable and accurate reference temperature is ensured [Sutton (1975)]. Oil should not be placed in the glass tubes (in an attempt to improve thermal contact) as this can do more harm than good; the oil tends to migrate up the insulation towards the hot zone and, in any case, thermal contact is adequate without it.

Automatically-operating ice-point devices with sufficient reproducibility are also available.

It is not recommended to use extension wires for accurate temperature measurements as they cause additional errors.

9.5 Approximations to the ITS-90

Platinum rhodium thermocouples can be calibrated by comparison with a laboratory standard thermocouple in an electric furnace by the techniques described in Chapter 2. Typical accuracies achievable in this way are listed in Table 18.7.

A thermocouple can also be calibrated at fixed points according to the methods described in "Supplementary Information for the ITS-90" [CCT (1990)]. However, for most thermocouple measurements, the requirements described there are unnecessarily extreme. Because of the much lower accuracy expected in secondary measurements, the quality of the furnace can be lower, melts as well as freezes are adequate, the metal need not be as pure, the mass of metal may be smaller, etc. Especially at high temperatures, where it becomes difficult to provide proper furnaces and crucibles for freezing-point determinations, fixed-point calibrations can be made by the wire, or wire-bridge, method as described in Sec. 3.3.2. Similarly, the thermocouple can be calibrated using miniature fixed points as described in Sec. 3.3.3 [Tischler and Koremblit (1982)].

Whatever method is used, to complete the calibration the differences of the thermocouple emfs from the standard-reference-table emfs at the appropriate assigned temperatures on the ITS-90 for the particular fixed points are plotted and a smooth curve is drawn through all points including the origin. These differences are generally small and the curve is only slightly non-linear. It is recommended that a second- to fourth-degree polynomial be fitted to these differences [Jones and Hall (1978); Bedford and Ma (1980)]. This deviation curve in conjunction with the reference table [Powell et al. (1974); IEC (1977)] gives the emf-versus-temperature characteristics of the individual thermocouple. The accuracy of the calibration depends upon the methods used, the temperature range of the calibrations, and the thermocouple materials. The calibration accuracy, however, is seldom the limiting factor in thermocouple measurements, being outweighed by errors associated with the type of installation and with instability and drift of the thermocouple emf. As a rough guide, overall accuracies may be better than ± 0.5 K to the gold point (1064 °C), ± 1.0 K to the palladium point (1555 °C) and ± 2.0 K to the platinum point (1769 °C). The precision attainable with thermocouples under well-defined and constant conditions (immersion depth and temperature gradient) is somewhat better than these accuracies. If only the wire-bridge method of calibration is used, accuracies can be worse. For example, in a comparison of wire-bridge Au and Pd calibrations with optical pyrometer calibrations, agreement was within 0.7 K at Au and 1.5 K at Pd amongst three laboratories [Crovini et al. (1987)]. Comparison of quadratic interpolation of these differences of Au and Pd emfs from the standard table with the pyrometer calibrations showed disagreement of from ± 0.2 K to ± 0.9 K for different thermocouples between the two fixed points. Use of this quadratic interpolation below 1064 °C or above 1554 °C was not recommended.

10. Infrared Radiation Thermometers

Monochromatic optical pyrometers working at wavelengths in or near the visible spectrum are generally calibrated using tungsten strip-filament lamps as transfer standards. For temperatures below 1100 K (or 700 °C) such a procedure is not possible, even when the instrument is monochromatic, because there is insufficient short-wavelength radiation at these lower temperatures. Much radiation thermometry, moreover, relies upon infrared wavelengths over broad bands. These infrared pyrometers must be calibrated against blackbodies. A calibration on the ITS-90 would demand that the radiation thermometer be sighted on a blackbody the temperature of which was simultaneously measured with a standard platinum resistance thermometer. An alternative secondary realization that is just as accurate as a primary calibration below 1064 °C has been devised by Sakuma and Hattori (1982b). They use a set of metal freezing point (Cu, Ag, Al, Zn, and optionally Sb) blackbody furnaces, each of rather small dimensions and housing a graphite blackbody crucible containing 26 cm^3 of 99.999% pure metal (see Sec. 3.4). Freezing plateaux of about 10 minute duration are shown to be accurate to -0.1 ± 0.1 K. A monochromatic infrared radiation thermometer with a silicon-photodiode detector operating at 900 nm with a passband halfwidth of 14 nm is used as a transfer with these furnaces. It is known that in general the mean effective wavelength (λ_e) of a monochromatic radiation thermometer varies with temperature as

$$\lambda_e = A + (B / T) \tag{10.1}$$

So long as the detector current is sufficiently small (say, < 1 μA), the signal voltage (V(T)) is proportional to the blackbody spectral radiance, i.e.

$$V(T) = C \exp(-c_2/\lambda T) \ , \tag{10.2}$$

where Wien's equation is taken as a close enough approximation to Planck's equation. Substituting for λ in Eq. (10.2) from Eq. (10.1) gives

$$V(T) = C \exp\left(- \frac{c_2}{AT + B} \right) \qquad . \tag{10.3}$$

In principle the parameter C, which depends on geometrical and spectral factors and on the detector responsivity, contains a quantity λ_e^{-5}; it is assumed that λ_e is constant insofar as the parameter C is concerned. The three parameters A, B, C are calculated from a least-squares fit of V(T) to the voltages measured at the four (or five) fixed points and Eq. (10.3) is used to interpolate from 400 °C to 2000 °C. A typical calibration is shown in Fig. 10.1. In this way a secondary realization is obtained that is accurate to within ± 0.3 °C at the fixed points, ±t 0.5 °C from 600 °C to 1100 °C. and ± 2 °C at 1500 °C. The scale can be disseminated by calibrating sets of fixed-point furnaces against which other pyrometers are calibrated as above (the preferred way), or by using a variable-temperature blackbody radiator to compare an uncalibrated thermometer with the standard radiation thermometer at a number of temperatures.

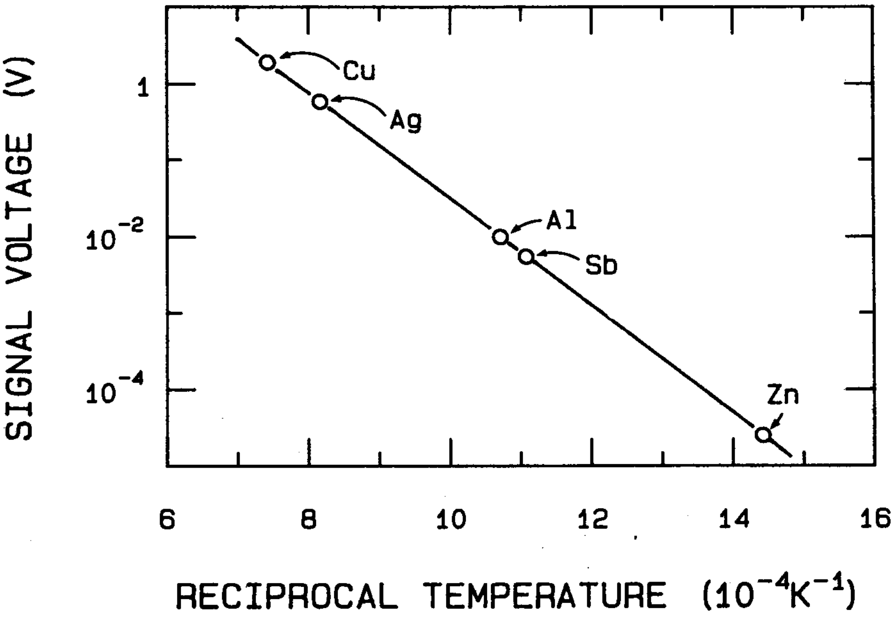


Fig. 10.1: Relationship between signal voltage of an infrared radiation thermometer and reciprocal temperature after calibration at five metal freezing points [after Sakuma and Hattori (1982b)].

Continuous advances in photodetector technology in recent years have also led to new precision pyrometers working in the visible and near infrared. Typical examples are the instrument developed by Woerner (1982) that works at the conventional 650 nm, and those of Rosso and Righini (1984) and Ruffino (1984) that use silicon detectors and are thus capable of operation either in the visible or in the near infrared near 900 nm. Each of these newer instruments is based on a single optical channel and the temperature scale realized with the original calibration is then maintained for long periods of time on the detector itself and its related optical and electronic components. This is made possible by the good stability and linearity of the photodetectors so that corrections for linearity are almost negligible. The final accuracy achievable with these instruments depends on the overall stability of the various optical components over long periods of time and on the possibility of recalibration at one point using an external lamp or freezing-point blackbody. The long-term stability of these instruments and the preferred calibration techniques for them have still to be assessed.

PART 2: TECHNIQUES AND THERMOMETERS TRACEABLE TO THE INTERNATIONAL TEMPERATURE SCALE OF 1990

In all temperature ranges there are thermometers that are widely used because of certain advantages such as low cost and ease of use (e.g. base metal thermocouples), yet they are insufficiently reproducible to be included with those of Part 1. Temperatures measured with them are of course traceable to the ITS-90 through proper calibration procedures. There are also thermometers of only modest quality that are nevertheless extremely useful for certain special measurements (e.g. measurements in the presence of high magnetic fields). In Part 2 there are discussed the more commonly used thermometers in these categories. For the cryogenic range there are included the carbon, carbon-glass, and platinum-0.5% cobalt resistance thermometers, and silicon and gallium arsenide diodes. For higher temperatures, thermistors, liquid-in-glass thermometers, IPRTs, and base-metal thermocouples are so widely used, largely because they can provide in appropriate circumstances adequate reproducibility or accuracy at very low cost, that discussion of them is mandatory. Additionally, Chapter 19 treats the behaviour in magnetic fields of several of the thermometers of both Parts 1 and 2.

11. Carbon Resistance Thermometers

Carbon resistors are widely used as secondary thermometers at low and very low temperatures. They are very sensitive, their readings depend little on magnetic field, and they are compact and easy to handle. They are stable enough for a 10 mK precision or even better with special care. In every case, one must be cautious of any overheating because the thermal conductance of the sensor is very low.

11.1 Fabrication and Use

Commercial carbon-composition resistors manufactured by Allen-Bradley were introduced as temperature sensors by Clement and Quinnell (1952). Since that time carbon resistance thermometers (CRTs) have been widely used for low temperature applications from about 100 K to below 1 K. Although they are less reproducible than the resistance thermometers described in Part 1, they are exceedingly inexpensive and their small size is advantageous. Since they are selected from mass-produced components for use in electronic circuits, it is not surprising that differences from batch to batch can occur. The carbon composition resistor is a small cylinder consisting of graphite with a binder encased in an outer phenolic shell. Embedded in the phenolic are two opposing copper leads which make ohmic contact with the graphite. The types used as thermometers are generally characterized by their room temperature resistance and their wattage [Rubin (1980)], and have come largely from the following manufacturers: Allen-Bradley, Airco Speer (usually referred to simply as Speer), Ohmite (prior to 1970, Ohmite supplied Allen-Bradley resistors under their own label. Both had the same characteristics. Thereafter the company distributed Speer resistors.), Matsushita, CryoCal, Physicotechnical and Radiotechnical Measurement Institute (PRMI).

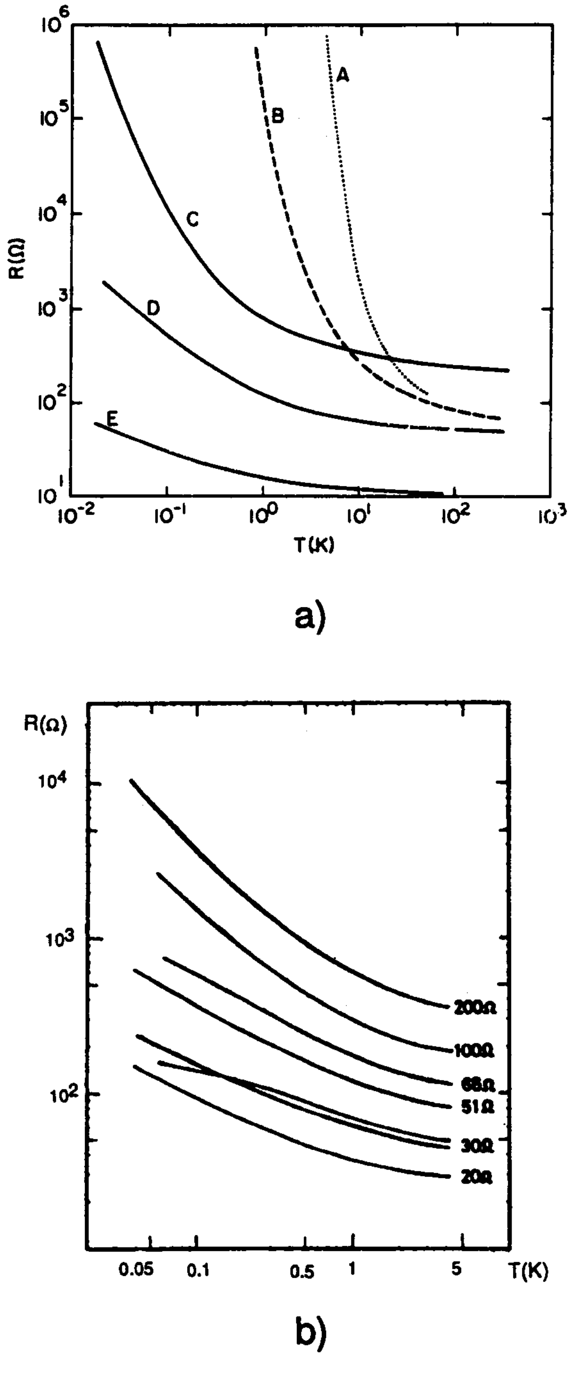
CRTs can be mounted directly as received, but generally the outer epoxy coating is removed and lead contacts are resoldered. The resistor is then inserted inside a tube (a copper tube for example) with grease as a convenient bonding agent. Great care must be taken with these operations because they can have a great influence on the stability of the sensor (see below). Some general recommendations for the use of a CRT are: do not modify the electrical contacts once they are soldered; do not heat the resistor excessively during the connection of the leads; protect the resistor from high humidity and solvents; cool it slowly; if the resistor is to be used in vacuum, it should be calibrated in vacuum.

11.2 Resistance-Temperature Characteristics and Sensitivity

The resistance of a CRT increases roughly exponentially (Fig. 11.1) and the sensitivity increases smoothly (Fig. 11.2) with decreasing temperature. The resistance of a typical unit will be roughly 1 kΩ at 1 K. The nominal resistance value R(300 K) determines the temperature range of use; the region where the slope of the R-T curve becomes very steep shifts towards higher temperatures for higher values of R(300 K), and at any given temperature, the smaller the value of R(300 K), the smaller the sensitivity (dR/R)/(dT/T). This characteristic is independent of the size (wattage) of the unit provided that R(300 K) is the same, although significant differences are often found between units that are nominally the same but come from different batches, even from the same manufacturer. Thus interchangeability of units is not possible, or otherwise, because the cost is small, it is recommended to purchase all resistors that will be needed for a given application at the same time [Anderson (1972), Ricketson (1975), Kopp and Ashworth (1972), Kobayasi et al. (1976)].

Baking a resistor for a short time (~ 1 h) at a relatively high temperature (~ 400 °C) modifies its R- T characteristic. For example, baking a 100 Ω Matsushita unit at 375 °C in argon for one hour reduces R by a factor of three [Steinback et al. (1978)]. The sensitivity and (mainly) R(300 K) are reduced while the general behaviour remains unchanged. Thus, one can adjust the sensitivity of a thermometer by annealing. This can be advantageous since a lower slope at low temperatures means a wider useful range of temperature for a given sensor, without the resistance becoming prohibitively high [Anderson (1972), Johnson and Anderson (1971)]. On the other hand, any local heating of the thermometer, even for short periods, such as when soldering new electric contacts, will irreversibly alter its characteristic and necessitate recalibration.

Heating of the resistor can arise from [Oda et al. (1974), Hudson et al. (1975)] the measuring current (Joule effect), vibrations, spurious emfs, thermal conduction along the leads, residual gas in the cryostat, thermal radiation, and radio frequency pickup. In the latter case, heating of 10^{-10} W is easily introduced below 1 K by switching circuits, digital equipment, noise from power supplies enhanced by ground loops, etc. The problem becomes much more serious as the temperature is reduced. Shields and filters are effective in reducing the heat leak to 10^{-15} W but caution is needed to avoid interference with the resistance measurement if an ac technique is used.



a)

b)

Fig. 11.1: Resistance-temperature characteristic for several commercial resistors: (a) A, thermistor; B, 68 Ω Allen-Bradley; C, 220 Ω Speer (grade 1002); D, 51 Ω Speer (grade 1002); E, 10 Ω Speer (grade 1002) [Anderson (1972)]; (b) various nominal Matsushita carbon resistors of grade ERC-18SGJ [Saito and Sato (1975)].

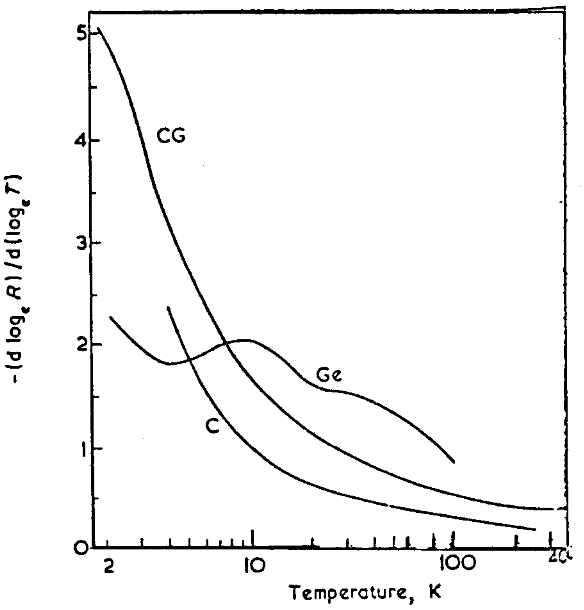


Fig. 11.2: Relative sensitivity versus temperature for carbon (C), carbon-glass (CG), and germanium (Ge) thermometers [Swartz and Swartz (1974)].

11.3 Thermal Contact

Providing good thermal contact is one of the main problems that limits the usefulness of carbon resistors. The heat dissipated in the sensor must flow to the surroundings without causing a relative temperature rise greater than $\Delta T/T \approx 10^{-3}$. At 1 K, for a 220 Ω Speer resistor for example, the maximum power dissipated in the CRT must remain smaller than 10^{-7} W for a 1% accuracy in the measurement.

The thermal boundary resistance between the unit and the environment depends upon the mounting, but is roughly 10^{-2} K/W for an area of 10^{-4} m^2.

Different thermal grounding techniques have been proposed [Polturak et al. (1978), Johnson and Anderson (1971)]. Thermally grounding the resistor via its leads only is not recommended. It is important to bind the unit with a copper housing that is thermally anchored to the device to be studied, with grease, stycast, varnish or other equally good agent. The paint used for color coding the resistor should be removed because it may loosen after several thermal cycles.

11.4 Response Time

The thermal response time of a CRT is short; some typical values are given in Table 11.1. Longer time constants (up to tens of minutes) can be observed if the copper

Table 11.1: Typical Time Constants, τ, for a Carbon Resistance Thermometer [Linenberger et al. (1982)].

Temperature	4.2 K		77 K	
	τ(ms)		τ(ms)	
Environment	Liquid	Vapour	Liquid	Vapour
Type of Sensor				
AB 1/8 W 220 Ω	6	7	113	7276
AB 1/2 W 220 Ω	30	31	426	3290

leads are not thermally grounded. Grinding the resistor clearly shortens the thermal time constant. Also, to improve time response, attempts have been made to use carbon thin films deposited on different substrates. Time constants approaching 0.42 ms at 4.2 K have been achieved [Bloem (1984)]. :

11.5 Influence of External Factors

a. Pressure

CRTs are only slightly dependent upon pressure [Dean and Richards (1968) and Dean et al. (1969)]; a typical value for the pressure dependence is $\Delta R/R \sim -2 \times 10^{-9}\ \mathrm{Pa}^{-1}$.

b. Radiation

CRTs are relatively insensitive to nuclear irradiations. After long exposure to gamma rays and fast neutrons, changes observed in resistance were less than 1 % at 20 K [NASA (1965)].

c. Humidity

CRTs are very sensitive to humidity. The nominal resistance value R(300 K) increases by 5 to 10% after the resistor has been soaked for 240 h at 95% humidity [Ricketson (1975)]. Since $\Delta R/R$ is about the same at 77 K and at 300 K, the indication is that the absorbed water introduces, a temperature dependent resistance, i.e. changes in calibration come from changes in the exponential coefficient. The process is not reversible, but the resistance can be reduced by heating the unit.

d. Magnetic Field

The effects of magnetic fields on CRTs is discussed in Chapter 19.

11.6 Stability and Reproducibility

It is difficult to determine the extent of the repeatability of CRTs. Reports on repeatability vary widely, from ± 1 mK up to 2% change in resistance at 4.2 K. By cycling resistors between room temperature and the temperature of use, it is possible to select units that are stable to within 10 mK. Nevertheless, one must be alert for changes in the R-T characteristic. Provided that they are not mistreated between runs, both Allen-Bradley and Speer units will retain their calibration within about 1 % over a two year span and 30 or 40 thermal cyclings.

When the resistance is monitored at a fixed temperature, a drift with time is observed which is mostly towards higher resistance, giving an apparent reduced temperature. It occurs in all units tested [Ricketson (1975), Johnson and Anderson (1971), Forgan and Nedjat (1981)]. For example, at 77 K, drift rates have been as high as 50 mK/h just after immersion, decreasing to 25 mK/day after a two-day soak. The higher the temperature sensitivity of the unit, the greater the drift in terms of $\Delta T/T$. This means that the problem becomes more serious for a given thermometer as the temperature is reduced. Resistors of the same nominal value and brand exhibited the same drift rates to within about 15%. Therefore, the drift is intrinsic to the resistance material itself and is probably associated with a decrease in carrier concentration.

An increase in the resistance at liquid helium temperature is always observed after the first few thermal cycles (2% for a 1000 Ω Allen-Bradley unit). The phenomenon is associated with carbon granule rearrangement due to thermal shocks. Typically, maximum changes observed for an Allen-Bradley unit of 220 Ω are 13 mK at 4.2 K, 337 mK at 20 K and 2 K at 60 K [Ricketson (1975)]. After nearly twenty thermal cyclings between low temperature and 300 K during two years, the change in resistance of Matsushita units have remained within 1.5% [Kobayasi et al. (1976)]. The observed instabilities can be roughly explained by the thermal history of the unit, remembering the extreme sensitiveness to annealing and thermal heating of a CRT.

Broadly speaking, CRTs are less stable by more than an order of magnitude than germanium thermometers. Considerable improvement might be achieved if the low-cost CRTs were treated with as much care as encapsulated germanium sensors. Nevertheless, it is always wise to check that the resistance has not drifted nor undergone a step change during measurements. Whether a carbon resistance thermometer requires a new calibration after each cool-down depends upon the accuracy desired. In practice the calibration may be no better than several parts in 10^3, in terms of $\Delta T/T$, so to obtain a thermometer capable of better reproducibility and stability than this after an arbitrary history, one should choose a unit having lower temperature sensitivity and sacrifice resolution. When recalibration is needed, it may be sufficient to check only a few points and to derive the new calibration curve from the original one.

11.7 Calibration and Interpolation Formulae

The lack of a simple R-T characteristic has limited large scale use of CRTs. Their initial low price is partially offset by the need for individual calibration. One of the advantages of the CRT is its smooth R-T dependence, close to exponential, without any higher-derivative irregularities. Nevertheless, none of the existing interpolation equations are sufficiently exact to allow precise measurement to better that 10^{-3} T over a wide range that includes temperatures above 20 K. Many of the various equations that have been used (summarized by Anderson (1972)) relate ln R to 1/T in some non-linear fashion, with the number of coefficients to be determined by calibration ranging from two to five depending upon the temperature range, the accuracy required, and the type of CRT. For their original empirical equation, which is still widely used

$$\ln R + \frac{C}{\ln R} = A + B/T \qquad (11.1)$$

Clement and Quinnell (1952) found an accuracy of ± 0.5% in the range 2 K to 20 K when applied to a group of Allen-Bradley resistors. Schulte (1966) found Eq. (11.1) accurate to within several percent for 270 Ω Allen-Bradley resistors over the much wider range from 4 K to about 200 K when the three coefficients were obtained from least-squares fits to four calibrations at the boiling points of helium, hydrogen, and nitrogen, and at room temperature. On the other hand, when applied to some specially constructed resistors, Eq. (11.1) failed by up to 0.25 T, although replacement of the term in $(\ln R)^{-1}$ by one in $(\ln R)^2$ provided an interpolation accuracy of 0.3% from 4 K to 20 K.

Oda et al. (1974) found that Eq. (11.1) also fitted Speer Grade 1002,1/2 W, 220 and 100 Ω CRTs from 1 K to 0.1 K but below 0.1 K the deviations became large. The equation

$$\ln R = a(\ln T)^2 + b \ln T + c \qquad (11.2)$$

fitted the experimental data from 1 K to 30 mK. Similarly, Kobayasi et al. (1976) found that Eq. (11.1) fitted Matsushita ERC 18 SG 1/8 W CRTs from 0.4 K to 4 K, but that Eq. (11.2) provided a better fit over the range 15 mK to 1 K.

It may be more economical in time to proceed to a least-square analysis with a polynomial relationship of the type

$$1/T = \sum_{i=0}^{n} a_i (\ln R)^i \qquad (11.3)$$

It is sufficient for most practical applications to limit the regression to third degree. With 15 to 30 experimental points, Kopylov and Mezhov-Deglin (1974) were able to describe the R-T characteristic of an Allen-Bradley 1/8 W, 40 Ω CRT in the range 1.2 K to 8 K with an error less than the random error of the measurement. For calibrations to higher temperatures, Groger and Strangler (1974) used Eq. (11.3) with index i running from -1 to 3 and calibration at five temperatures and found a maximum error in computed temperatures of ± 1.5 mK at 4.2 K, ± 20 mK at 20 K, ± 80 mK at 77 K, and ± 400 mK at 190 K.

12. Carbon-Glass Resistance Thermometers

Lawless (1972) suggested that carbon-glass thermometers be used instead of the classical carbon thermometer because of the latter's instability. Some thermometers also exist that use plastic instead of glass [Besley (1983)], but they are not commonly available and so are not discussed here.

12.1 Fabrication

A porous glass is prepared by removing the boron-rich phase from a borosilicate alkaline glass to leave a material having the appearance of silicate spheres of about 30 nm diameter, randomly distributed and separated by 3 to 4 nm pores. The spaces are then partially filled with high-purity carbon to form amorphous fibres. The resulting material is cut in pieces of about 5 x 2 x 1 mm on which are deposited electrodes of Nichrome-gold to which copper leads are attached. The pieces are heated at 100 °C for 24 h to desorb gases and water vapour and are then sealed in platinum capsules under an atmosphere of helium.

The amorphous nature of the carbon gives the advantage that the specimens have no piezoresistance, so there is no problem of mounting without constraint as there is for a germanium resistor; this shortens the response time.

The thermal capacity of these elements [Lawless (1981)] varies with temperature much like that of the silica substrate but it is more important at very low temperatures. Between 2 and 30 K, the quantity CT^{-3} (where C is the heat capacity) passes through a maximum near 10 K of 50×10^{-4} J kg^{-1} K^{-4}, for example, for a specimen having a resistivity of 9 Ωcm at 4.2 K.

The carbon also plays a small role in the thermal conductivity. For the same specimen as above, the order of magnitude is 5×10^{-2} Wm^{-1}K^{-1}.

12.2 Resistance- Temperature Characteristics; Sensitivity; Calibration

The resistivity of these thermometers is small; those available commercially have a resistivity of 10 to 25 Ωcm at 4.2 K, decreasing to 0.7 Ωcm at 300 K.

The resistance of carbon-glass thermometers decreases exponentially and slowly with increasing temperature so that the useful range of a given specimen is easily 1.5 K to 350 K (Fig. 12.1). Typical values of resistance are 2100 Ω at 4.2 K, 34 Ω at 77 K, and 17 Ω at 300 K.

Few measurements have been made using alternating current but the thermometers seem to be perfectly ohmic.

The carbon-glass thermometer sensitivity is compared with that of germanium and carbon thermometers in Fig, 11.2.

The sensitivity is a monotonic function of temperature, which permits calibration of thermometers using a semi-empirical equation of the form .£... , and so avoiding interpolation with polynomials of high degree. On the one hand this reduces the number of calibration points necessary, and on the other the same formula is valid over a large temperature range within the measurement precision. For example, between 4.2 K and 30 K, a calibration has been obtained [Swartz et al. (1976)] with a standard deviation of 0.43 mK with the following formula:

$$R = k_1\, T^{-3/2} e^{-k2/T} + k_3 T^{-k4} e^{-k5/T} \qquad (12.1)$$

$$k_1 = 7231.956; \quad k_2 = 10.76346; \quad k_3 = 727.7906$$

$$k_4 = 0.4644607; \quad k_5 = 6672207$$

The carbon-glass elements are not interchangeable but for specimens i and j coming from the same batch it is possible to relate the calibration of one to the other by using the relation: $R_i = aR_j^b$, where a and b are temperature-independent constants and b is near unity. The accuracy of this procedure is not yet truly established; its use has led to a standard deviation with respect to a classical calibration of 4×10^{-3} in ln R.

12.3 Stability

Carbon-glass is not as stable as germanium. The behaviour of carbon-glass thermometers when thermally cycled is not identical from one specimen to another. Between room temperature and 4.2 K, instabilities have ranged from tenths of millikelvins to many dozens of millikelvins [Besley (1979)]. This suggests that the instabilities have a variety of causes, such as structural defects and diffusion of impurities due to the passage of electrical current. There appears to be no improvement of stability through aging the specimens. The thermometer resistance does not suffer from drift or abrupt jumps. The reproducibility suffices for most applications; for the most part it is of the order of 0.5 mK at 4.2 K, 10 mK at 20 K, and 60 mK at 77 K.

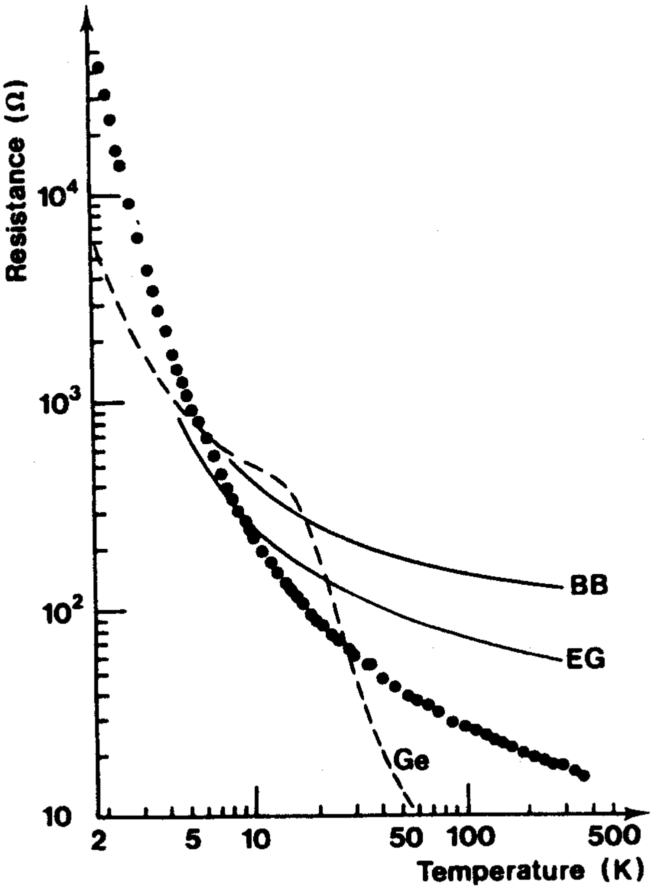


Fig. 12.1: Resistance-temperature characteristic of typical carbon-glass thermometer (solid circles) compared with that of germanium (broken curve) and two Allen-Bradley carbon thermometers (BB: 1/8 W; EG: 1/2 W) [Lawless (1972)].

Although less stable than germanium, carbon-glass thermometers are also less sensitive to a magnetic field, although in magnetic fields higher than 5 to 8 teslas capacitive thermometers are preferable (see Chapter 19).

13. Platinum-Cobalt Resistance Thermometers

The platinum-cobalt thermometer having a cobalt content of 0.5tomic percent has been developed since 1978 (Shiratori and Mitsui (1978), Shiratori et al. (1982)]. This type of thermometer is available in a standard capsule and in an IPRT-like package (stainless-steel hermetic case). Results of testing and an assessment of stability are available at present only for the industrial type: Shiratori et al. (1982) reported changes of less than 10 mK after several hundreds of cycles between room temperature and 4 K, and Pavese and Cresto (1984) confirmed this behaviour. When the thermometers are cycled between 77 K and 500 K (total heating time ~ 200 h), changes of R(0 °C) are smaller than the equivalent of 100 mK and changes of R(77 K) smaller than the equivalent of 30 mK. Most of the change occurs after the first 50 h of heating. Specific testing for reproducibility between 2 and 20 K [Sakurai and Besley (1985)] has confirmed reproducibility within ± 10 mK when the thermometer is cycled to room temperature, and has shown that it may improve to a few millikelvins if the thermometer need never return above 100 K.

Shiratori and Mitsui (1978) studied the resistance/temperature characteristic of the standard type and proposed as a reference function the following equation that fits the experimental points between 3 K and 27 K to within 10 mK:

$$\frac{R(T')}{R(0\,^{\circ}C)} = A_0 + A_1T' + A_2T'^3\left(1 + B_1T' + B_2T'^2\right) \tag{13.1}$$

where $T' = T - 11.732$ K; $A_o = 7.7510 \times 10^{-2}$; $A_1 = 8.6680 \times 10^{-4}$; $A_2 = 2.8377 \times 10^{-6}$; $B_1 = 2.3167 \times 10^{-2}$; $B_2 = 1.4370 \times 10^{-5}$.

For the industrial type, the manufacturer supplies a reference table of resistance versus temperature which matches any particular thermometer within ± 0.5 K (4-30 K) or ± 0.4 K (above 30 K). With three calibration points at 0 °C, 77.3 K and 4.2 K, the accuracy is claimed to improve to ± 0.1 K above 16 K and to ± 0.2 K between 4.2 K and 16 K (Shiratori et al. (1982)]. Between 2 K and 29 K a simple sixth-degree polynomial was found to fit the experimental data with a maximum deviation of ± 1 mΩ (equivalent to ± 10 mK) at the sensitivity minimum near 13 K. The estimated accuracy of the experimental data was ± 5 mK (Pavese and Cresto (1984)].

The commercially-available, standard-type platinum-cobalt thermometer is probably less reproducible than the corresponding rhodium-iron thermometer; its stability on thermal cycling is likely to be in the range of a few millikelvins.

14. Diode Thermometers

Diodes can be used above room temperature (e.g. in clinical thermometry) but not with sufficiently-high accuracy to be considered in this monograph. There is an extensive literature on semiconducting diodes with possible application as cryogenic thermometers [e.g. Swartz and Swartz (1974), Lengerer (1974), and Rubin and Brandt (1982)] but only two types intended for use as thermometers are commercially available: GaAs and Si. The temperature-indicating parameter is the forward-biased junction voltage, which decreases approximately linearly with increasing temperature when the current is kept constant.

Because of their almost trivial cost, silicon diodes mass-produced for the electronics industry have been widely tested as thermometers. They would have particular appeal in large engineering projects requiring hundreds of sensors. It turns out, however, to be very costly to select the very small percentage that are adequate for thermometric use. The following discussion does not apply to these devices, but to diodes that are manufactured for specific use as thermometers. There are some specific drawbacks to diode thermometers:

a) The typical I-V characteristic is such as to make the internal impedance of the device very high (easily greater than 100 kΩ) at small currents; or else - using a larger current - one encounters unacceptably high power dissipation at low temperatures.

b) There is a transition region in the conduction mechanism around 20 K that makes fitting a V-T characteristic over the whole temperature range difficult for GaAs and impossible for Si (Figs. 14.1 and 14.2).

For GaAs the least-squares fitted equation [Pavese (1974)]

$$V = \sum_{i=0}^{7} A_i (\ln T')^i \qquad (14.1)$$

(where $T' = (T/T_1) + 1$) fits to within about ± 0.1 K (~ ± 100 parts per million in voltage) from 4 K to 300 K. For higher accuracy, the range is subdivided into two sections with the junction near 90 K. An effective equation for the two-range fitting is [Swartz and Gaines (1972)]:

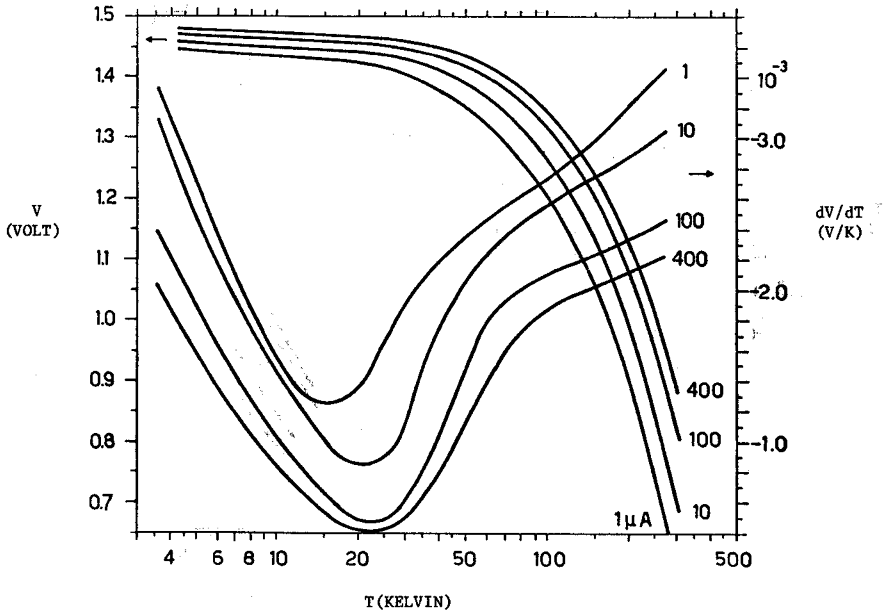


Fig. 14.1: Voltage and sensitivity of a gallium arsenide diode as a function of temperature and current (labels on curves) [after Pavese and Limbarinu (1972)].

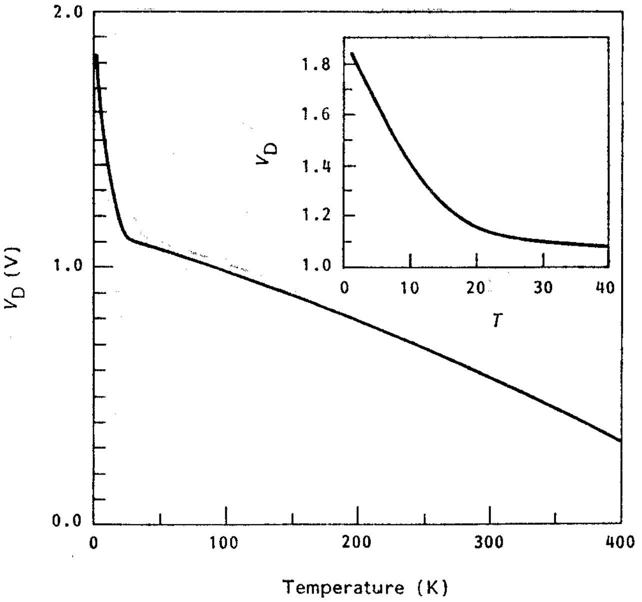


Fig. 14.2: Forward biased voltage of a silicon diode as a function of temperature. The lower temperature region is shown to larger scale in the inset [Lanchester 1989)].

$$V = E_0 - \frac{BT^2}{T + T_0} - CT\ln(DT) \quad . \tag{14.2}$$

Equation (14.2) fits experimental data to better than ± 15 mK below 54 K and ± 25 mK above 90 K.

With silicon diode thermometers, the complete range must be fitted in two sections, omitting a small range around 20 K where the thermometer cannot be used because of the afore-mentioned sharp change in slope. On either side of this critical region the V versus T characteristic is smooth, allowing non-critical fitting with simple polynomials. The fitting equations require a dozen or more calibration points, suitably spaced in temperature, in each range. An accuracy within ± 0.05 K cannot be obtained from calibration at a smaller number of fixed points.

No general statement can be made regarding the stability of diode thermometers. Selected ones can be as stable as ± 0.01 K on thermal cycling but much larger instabilities can occur unpredictably.

In zero magnetic field and below 20 K, diodes show high sensitivity associated with a readily-measurable voltage (millivolts in 1-2 V).

15. Liquid-in-Glass Thermometry

Even though the liquid-in-glass thermometer is used much less frequently today than formerly, it is still a very commonly used device. Although it is normally an instrument of only moderate accuracy, the very best of them, when used with sufficient attention to detail, have millikelvin capability over a narrow temperature range. Amongst its advantages are easy portability, independence of auxiliary equipment, low cost, compatibility with most environments, moderate ruggedness, and wide range (it has been used to measure temperatures as low as 70 K and as high as 1000 °C, but its most frequent use is within the range -40 °C to 250 °C). Disadvantages include a large sensing element, impossibility for continuous or automatic readout, long time constant, awkward dimensions, secular changes, and hysteresis (except for special types).

The components of a ypical liquid-in-glass thermometer are shown in Fig. 15.1. These include:

Bulb: The reservoir for containing most of the thermometric liquid.

Stem: The glass tube having a capillary bore along which the liquid moves with changes in temperature.

Auxiliary Scale: A narrow-temperature-range scale for reading a reference temperature (usually the ice point). It should be marked as for the main scale (below). If the main scale range includes the reference temperature no auxiliary scale is supplied.

Contraction Chamber: An enlargement of the capillary bore between the auxiliary and main scales, or between the reservoir and the main scale, to limit the length of the capillary (and hence the thermometer).

Immersion Line: A line marking the depth to which a partial-immersion thermometer should be immersed.

Main Scale: An engraved, etched, or otherwise permanently attached scale with well-defined, narrow graduation lines against which the height of the liquid in the capillary is measured. There may be a colored backing material for better visibility of the lines. The main scale is graduated in fractions or multiples of degrees Celsius. If its range incorporates the reference temperature, it is the only scale.

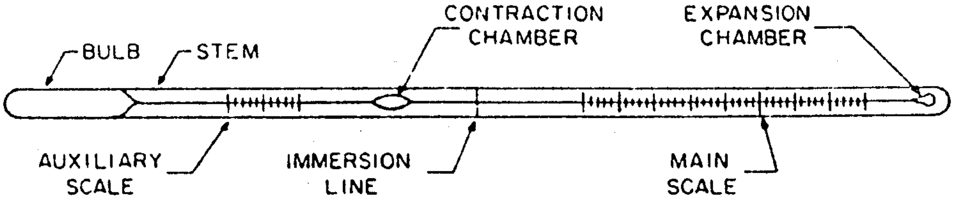


Fig. 15.1: Principal features of a solid-stem liquid-in-glass thermometer [after Wise (1976)].

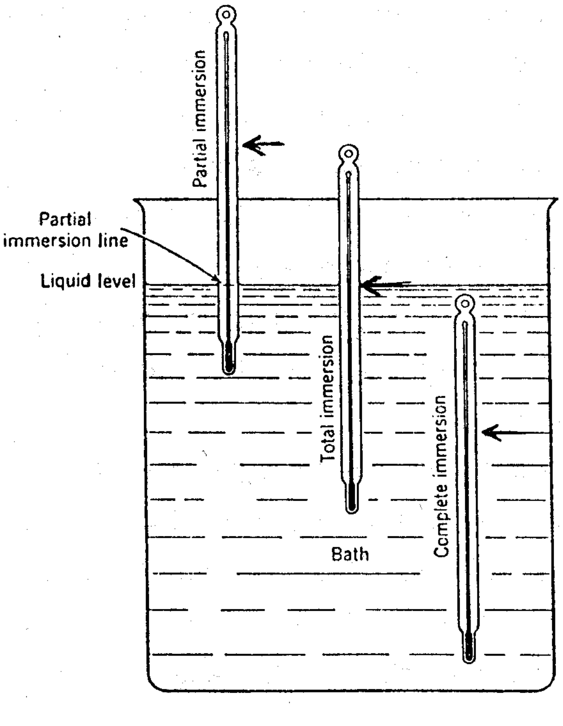


Fig. 15.2: Illustrating the proper immersion techniques for the three types of liquid-in-glass thermometers. The arrow shows the location of the meniscus in each case.

Expansion Chamber:	An enlargement at the top of the capillary into which the liquid can flow if the thermometer temperature exceeds the scale limit. It is undesirable for liquid to enter the expansion chamber, however, so it is much better to ensure that there is no overheating of the thermometer. The expansion chamber also prevents excessive gas pressure when the thermometer is used near the top of its range, especially in high-temperature pressurized thermometers.

The range of a liquid-in-glass thermometer is limited by the liquid, by the glass, and by the construction. The commonest and best liquid is mercury. The recommended range of use is from near the mercury freezing point (-38 °C) to about 350 °C with soda-lime glasses; higher temperatures require borosilicate or other special glasses. The capillary above the mercury is filled with a dry gas (frequently nitrogen) to prevent separation of the column and to inhibit distillation of the mercury; in the higher-temperature models, substantial gas pressures are required to raise the mercury boiling point above the range of the thermometer. Air is not a good filling gas because it may lead to oxidation of the mercury and consequent sticking of the latter in the capillary. A eutectic alloy of mercury containing 8.5 weight percent of thallium is used to extend the lower temperature limit to -56 °C; commonly the upper limit is at or a little above 0 °C to allow for ice-point reference checks. Organic liquids are used in thermometers for lower temperatures (alcohol, toluene, pentane, butane), in some cases down to -200 °C. These lower-temperature thermometers suffer from drainage problems associated with the low surface tension of the liquids and from vaporization; they are less reliable than mercury thermometers where the latter can be used.

Thermometers are designed and calibrated for vertical immersion of the bulb and stem to the top of the liquid column (*total immersion*), of the bulb and stem to the immersion line (*partial immersion*), or of the whole thermometer (*complete immersion*). These three types are illustrated in Fig. 15.2. The total-immersion type is the most accurate and is recommended wherever possible; the complete-immersion type is the least common.

For calibration, the ice (or other reference) point is always taken first, but not before the thermometer has been at least 72 h at room temperature. Suitable preparation of an ice bath is described in Supplementary Information. The thermometer must be allowed to attain thermal equilibrium with the ice and should be *gently* tapped with the fingernail or a pencil to ensure a non-sticking meniscus before reading.

For a thermometer graduated above 300 °C, a requisite quality check is to raise its temperature to the highest point on the scale immediately after taking the ice point, then to allow a rest period of three days at room temperature and to take a second ice point. If the agreement between the first and second ice points is not within the stated accuracy limit of the thermometer, the thermometer should be discarded. Following the ice-point checks, the thermometer is calibrated from the lowest to the highest temperature against a laboratory standard in a suitable bath. Readings may be taken with the bath temperature slowly increasing to ensure that the meniscus is fully convex (less than one scale division per five minutes is recommended to ensure that the exposed stem remains in thermal equilibrium) or with the bath stabilized at the calibration temperature. In the latter case, bath-temperature excursions should be smaller than the precision of reading and the thermometer should be tapped before reading. After calibration at the highest temperature, the ice point should be retaken after the thermometer has had time (in hours, approximately $t_{max}/100$) to relax back to its static condition.

Calibration temperatures should be approximately equally spaced, their number depending upon the thermometer range, the accuracy required and the scale graduation interval. Calibration every 50 to 100 scale divisions should give an accuracy within one-half of one division. For linear interpolation between calibration points on a plot of scale correction versus temperature, the uncertainty is about one-half the largest discrepancy found by extrapolating each linear segment to the next calibration point.

A thermometer calibration applies as long as the ice-point reading remains the same as during calibration. Subsequent changes in the ice-point reading will result from small changes in the glass of the thermometer bulb which affect its volume. Volume changes in the capillary are minimal by comparison and, as a result, changes in the ice-point reading of the thermometer (taken after not less than 3 days at room temperature) will be accompanied by similar changes in readings at each point along the scale. The ice point should be taken periodically, and scale corrections adjusted as necessary. If the ice point change is too large, the thermometer must be recalibrated. How large a change is "too large" depends upon the application and the type of thermometer .

Parallax errors of many tenths of a division may easily occur in reading a liquid-in-glass thermometer. To avoid them one must view the thermometer from exactly the same angle as was used for calibration, virtually always perpendicular to the liquid column. One of the better ways of avoiding parallax and at the same time obtaining a precise reading is to view the thermometer through a telescope which is aligned at the proper angle, or through a magnifying lens attached to the thermometer. In the latter case, lack of parallax is indicated by a straight (as opposed to curved) image of the graduation mark. In the former case, a cross-hair can be centered by eye very accurately at the midpoint between the scale lines; if this is done, a good scale can be read to better than 1/20 division. For this reason it is recommended not to use too sensitive a thermometer; any attendant gain in sensitivity is outweighed by lack of stability, lack of linearity, increased fragility, and smaller temperature range of use. Similarly, it is recommended not to use a thermometer with graduations smaller than 1/10 °C, even if it is desired to measure temperatures to within a few hundredths oC.

With a partial-immersion thermometer, the average temperature (t_c) of the emergent stem (that part of the stem between the point of immersion and the top of the liquid column) during calibration should be stated. In subsequent use the average emergent-stem temperature (t_s) should be measured [Wise (1976)] and an additional correction (Δt) added to the reading, where Δt is given by

$$\Delta t = k\,n(t_c - t_s) \quad . \tag{15.1}$$

In Eq. (15.1) n is the equivalent number of degrees of the emergent stem and k is the differential coefficient of thermal expansion of the thermometer liquid relative to the thermometer glass. For mercury in pyrex for example, $k = 1.6 \times 10^{-4}/°C$; for organic liquids $k \approx 10^{-3}/°C$. Variations of coefficient of expansion among glasses are negligible in this connection.

A similar correction applies if a total-immersion thermometer is used at partial immersion, where now for t_c in Eq. (15.1) the temperature of the thermometer bulb is used.

The readings of a liquid-in-glass thermometer change with changes in both internal and external pressure: the former include change in bulb pressure resulting from the head of mercury in the capillary and from change of temperature of the gas above the mercury; the latter are usually due to variations in atmospheric pressure and in depths of immersion. Since there are approximately "6000 °C of mercury" contained in the bulb, obviously a small change in bulb volume can cause a large change in reading. The external pressure coefficient of a mercury-in-glass thermometer depends upon the internal and external bulb radii, and is usually about 1×10^{-6} °C/Pa. The internal pressure coefficient is about 10% larger.

Changes in bulb volume also occur because of both irreversible (secular) and reversible (temporary depression) structural changes in the glass that are influenced by time and heat treatment respectively. The secular change is almost always a slow contraction of the bulb, producing an increased thermometer reading. The rate of secular rise decreases with time but increases with exposure of the thermometer to high temperatures. The maximum secular rise is unlikely to exceed 0.1 °C over several years in well-constructed thermometers provided the glass is not heated beyond its exposure limit. The reversible changes appear as a hysteresis on thermal cycling. The bulb expands on exposure to high temperatures and does not return to its original volume immediately on cooling, resulting in a depression of the ice-point reading (and all other readings). Recovery may not be complete for 24 to 72 hours or, if the thermometer is cooled very slowly, no depression may occur. It is to monitor and correct for these changes in bulb volume that ice points are taken before and after calibration, as described earlier. In a good thermometer the temporary depression is small.

For a variety of reasons the mercury in the capillary tube may become separated, leading to spurious readings until the separation is removed. Methods for doing this are described by Ween (1968); among these are centrifuging, shaking, rejoining in the contraction chamber or in the bulb, and (a very slow process) distillation. Ice-point checks are an easy way of detecting abnormal thermometer behaviour: a substantial increase in ice-point reading frequently indicates a separated column; a substantial decrease may mean that mercury is trapped in the expansion chamber or that the thermometer has been overheated. A small amount of mercury trapped in the expansion chamber can be detected by careful visual observation.

More detailed discussion of the calibration and use of liquid-in-glass thermometers is given by Wise (1976), ASTM (1985a), Ween (1968), Thompson (1968), and BS (1985).

16. Industrial Platinum Resistance Thermometers

Industrial platinum resistance thermometers (IPRTs) are constructed from platinum of a lower quality than is used for SPRTs; typically, values of $W(H_2O \text{ b.p.})$ range from 1.385 to 1.3925 and values of residual resistance from 10^{-3} to 2×10^{-2}. Since IPRT design must provide sufficient reproducibility in the presence of shocks, vibration, high pressure and other hostile environments such as are found in industrial applications, it does not comply with some requirements of the ITS-90, such as strain-free mounting of the wire. Therefore IPRTs are less reproducible than SPRTs. Nevertheless, it is possible to select IPRTs that are only an order of magnitude less reproducible than SPRTs and in a restricted temperature range this difference might be even smaller. In particular environments an IPRT can be even more reproducible than an SPRT where, of course, an SPRT would not be considered for use anyway. Although this chapter delineates many of the drawbacks of IPRTs, we must emphasize that they are among the most-commonly-used thermometers. It is possible to purchase IPRT elements of a selected design or configuration at relatively low cost, to assemble them into sheaths with a minimum of laboratory practice, to anneal them at 450 °C, and finally to calibrate them according to one of the proposed schemes and so obtain an approximation to the ITS-90 to within about ± 50 mK between -180 to 0 °C, and within about ± 10 mK between 0 and 420 °C [Actis and Crovini (1982), Bass and Connolly (1980), and Connolly (1982)].

16.1 Quality of Industrial Platinum Resistance Thermometers

IPRTs are manufactured in a great variety of models and the actual fabrication has a definite influence on their metrological quality. The accuracies discussed in Section 16.2 for IPRTs can be achieved only with thermometers that are suitably stable. This variability led to the specifications codes discussed in Section 16.3 which allow a minimum level of uniformity in the thermometer characteristics. The tolerances allowed are wide (~ 0.2 °C to 2 °C), however, so they are satisfactory only for the more common industrial uses.

A wide variety of techniques have been devised for winding the platinum wire (Fig. 16.1 a). Many thermometers are formed by winding a fine wire or coil on a glass support and imbedding the winding in glass. This can introduce strain into the wires and cause contamination of the wires at higher operating temperatures. The configuration so far introduced that offers the best stability [Actis and Crovini (1982)] and the lowest hysteresis [Curtis (1982)] is that in which a platinum coil is supported inside the

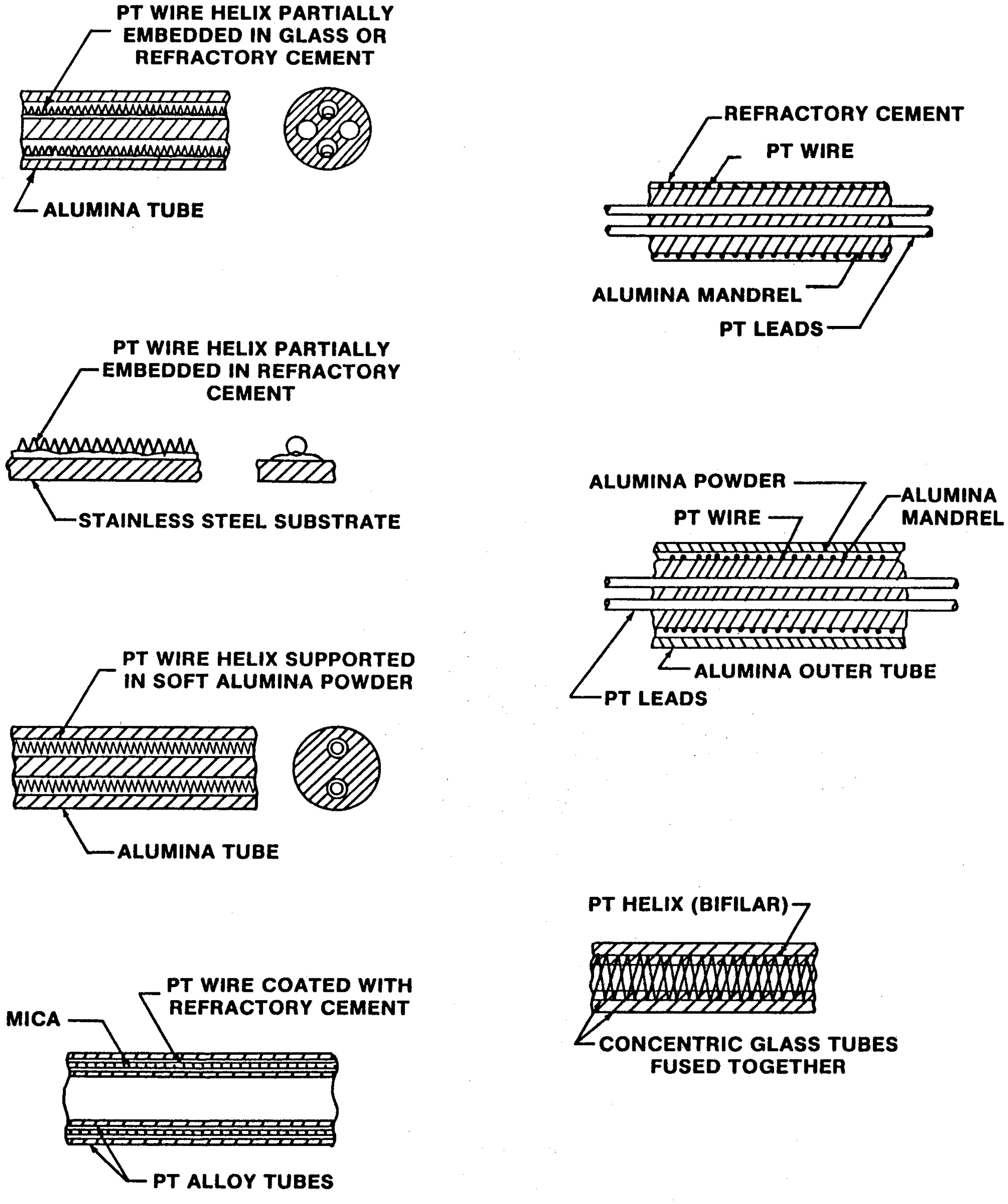


Fig. 16.1: (a) Fabrication of IPRTs: wire-wound;

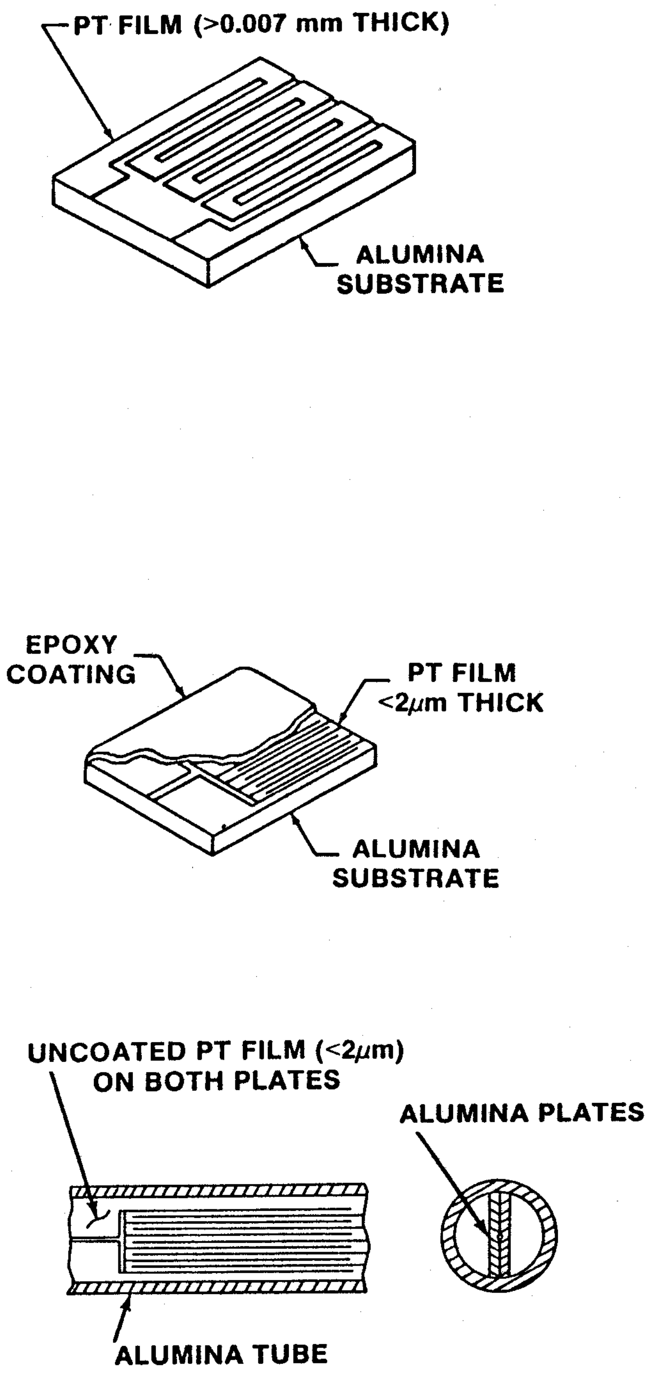


Fig. 16.1: (b) Fabrication of IPRTs: thick film [Curtis (1982)].

capillaries of a twin- (or four-) bore, high-purity-alumina insulator. Either the use of a cement to clamp one side of the coil to the capillary wall or, preferably, the insertion of soft alumina powder prevents the platinum coil from vibrating freely and helps in achieving good reproducibility in industrial applications. IPRTs having the platinum wire fully embedded in cement or hard glass (as above) and thick-film IPRTs (as below) do not afford a comparable reproducibility. Advances in thick film technology led to the development of resistance thermometers having a deposited platinum ink as the detecting element, rather than a platinum wire. These films are deposited on ceramic wafers in a variety of forms (Fig. 16.1 b), including the standard detector size of 3 mm diameter by 25 mm long. They also match the specifications of the national and international codes. One advantage of film sensors appears to be that they are less susceptible to mechanical shock and so are more rugged than conventional wire-wound detectors. However, they can suffer from strain due to differential thermal expansion.

16.1.1 Stability

A wire-wound thermometer is a delicate instrument since strain in the platinum wire causes a change in electrical resistance and so a shift of the W(T) versus T relationship. Also, change in impurity concentration (such as oxidation) affects the thermometric properties [Berry (1982a), (1982b)]. Therefore PRTs should be tested for stability with time on thermal cycling between extreme temperatures in the expected range of operation. For example, Mangum and Evans (1982) investigated the stability upon thermal cycling and handling of 60 IPRTs from 5 manufacturers. Most of them exhibited calibration drifts, instability caused by moisture, and hysteresis. After cycling to 235 °C, one-half of the thermometers showed changes in R(0 °C) larger than the equivalent of 15 mK and one-quarter larger than 50 mK. Comparable results were obtained in other experiments [Sinclair et al. (1972), Curtis (1982)]. Actis and Crovini (1982), Connolly (1982) and Bass and Connolly (1980), on the other hand, found rather better behaviour. Most of the national codes give tolerances for the permitted variation in resistance after a given number of thermal cycles.

IPRTs exhibit *hysteresis* on thermal cycling; this means that the IPRT may have different but reproducible R vs T relationships depending upon the thermal history of the thermometer and on whether a given temperature is being approached from lower or higher temperatures [Curtis (1982)]. A typical example is shown in Fig. 16.2. The span or width of the hysteresis loop can be correlated with W(H_2O b.p.) as shown in Fig. 16.3. For different thermometer constructions the hysteresis effect can be different. The user is

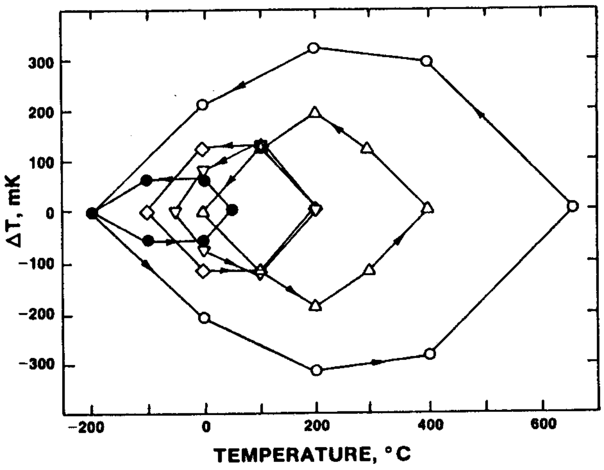


Fig. 16.2: A typical example of hysteresis in an IPRT [Curtis (1982)].

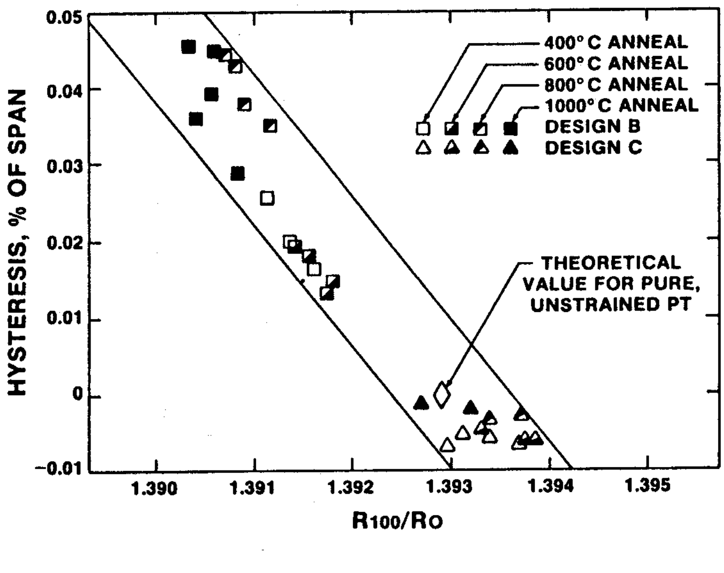


Fig. 16.3: Correlation between width of hysteresis loop and R(H_20 b.p.)/R(0 °C) for industrial platinum resistance thermometers cycled between -200 °C and : 200 °C [after Curtis (1982)].

advised to choose the thermometer type that exhibits the smallest hysteresis span. Similar effects have been observed by Besley and Kemp (1983) and Chattle (1977) on cycling between 100 °C and -200 °C.

It follows then that a procedure should be developed to bring the IPRTs into a stable state that is needed for accurate measurements. Since the hysteresis behaviour is caused by reversible changes in resistance from annealed to strained conditions in the platinum (at least below the temperature range where hysteresis due to reversible oxidation of the platinum can also occur), this means that the IPRT must be strained for work below room temperature and annealed for work above room temperature and, subsequently, all thermal cycling must never exceed the limits of this stabilization thermal cycle. Consequently, since the thermometer is almost always stored at room temperature, this temperature must not be substantially crossed after stabilization at any temperature below 100 K (strained) or at 200 °C to 450 °C (annealed).

Another reason for hysteresis is connected with moisture inside the encapsulation (most of the IPRTs are not hermetically sealed) [Mangum (1984)] which acts as a shunting resistance on the platinum wire. Moisture was observed to produce changes as large as 35 mK on sensor cycling between 0 °C and 40 °C. Moisture (69% of the cases) rather than strain (19% of the cases) was believed to account for most of the drift in IPRTs as a result of tests on 94 IPRTs in the range 0°-100 °C (and with annealing up to 235 °C).

IPRTs are generally produced to match the (inter-) national codes but the production is not 100% reliable [Chattle (1975)]. Tests are therefore necessary to select thermometers that match within closer tolerances.

Many experiments have been done, especially below 650 °C, to evaluate the *stability* of IPRTs (the distinction between instability and hysteresis is slight, but the latter is considered to be reversible). These have involved, in total, about 250 thermometers in about 80 batches and models from most of the manufacturers. Most of the thermometers had R(0 °C) = 100 Ω, and most of the tests were in the range -50 °C to 250 °C. There was not much uniformity in the results. Some thermometers were stable to within 5 mK, many to within 10 mK, and most to within 50 mK. Increasing the test range to 420 °C did not affect the results much. Instability increases rapidly at higher temperatures; drifts in R(0 °C) equivalent to from 0.2 K to several kelvins can be expected. Figures 16.4-16.7 show examples of instability in tests of various batches of thermometers.

16.1.2 Self-heating

In measuring the electrical resistance of the thermometer it is impossible not to dissipate thermal energy by Joule heating. Consequently there exists a difference between

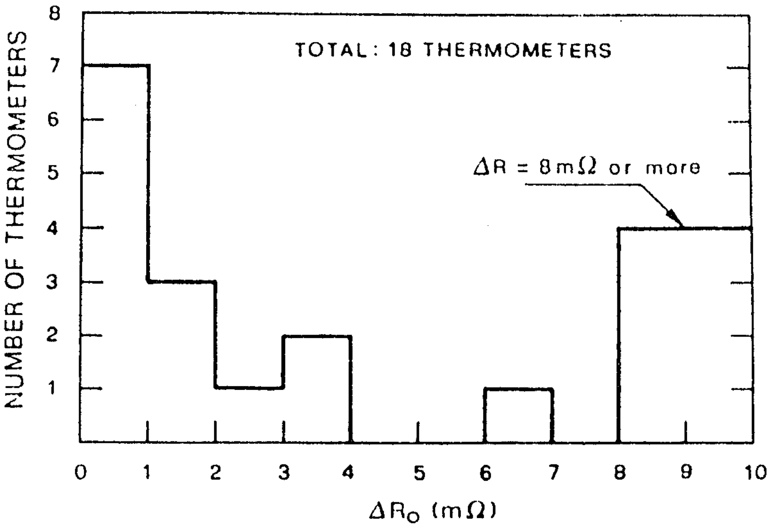


Fig. 16.4: Histogram showing the amount of the shift in R(0 °C) after a single exposure to liquid oxygen following stabilization at 450 °C for a group of 18 industrial platinum resistance thermometers having R(0 °C) = 100 Ω [Actis and Crovini (1982)].

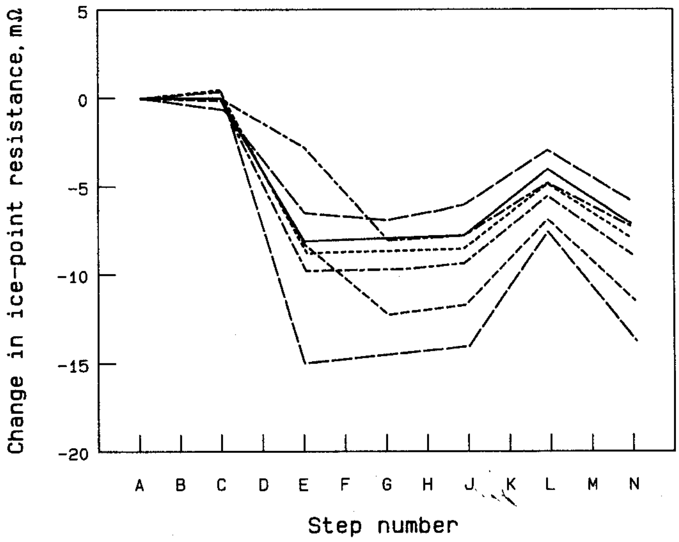


Fig. 16.5: Changes in R(0 °C) for seven industrial platinum resistance thermometers after 10 cycles between 20 °C and -196 °C (with occasional measurement also of R(100 °C): A, measurement of R(0 °C); B, measurement of R(100 °C); C, measurement of R(0 °C); D, ten cycles between 293 K and 77 K; E, measurement of R(0 °C); F, ten cycles between 293 K and 77 K; G, measurement of R(0 °C); H, ten cycles between 293 K and 77 K; J, measurement of R(0 °C); K, measurement of R(100 °C); L, measurement of R(0 °C); M, ten cycles between 293 K and 77 K; N, measurement of R(0 °C); [after Besley and Kemp (1983)].

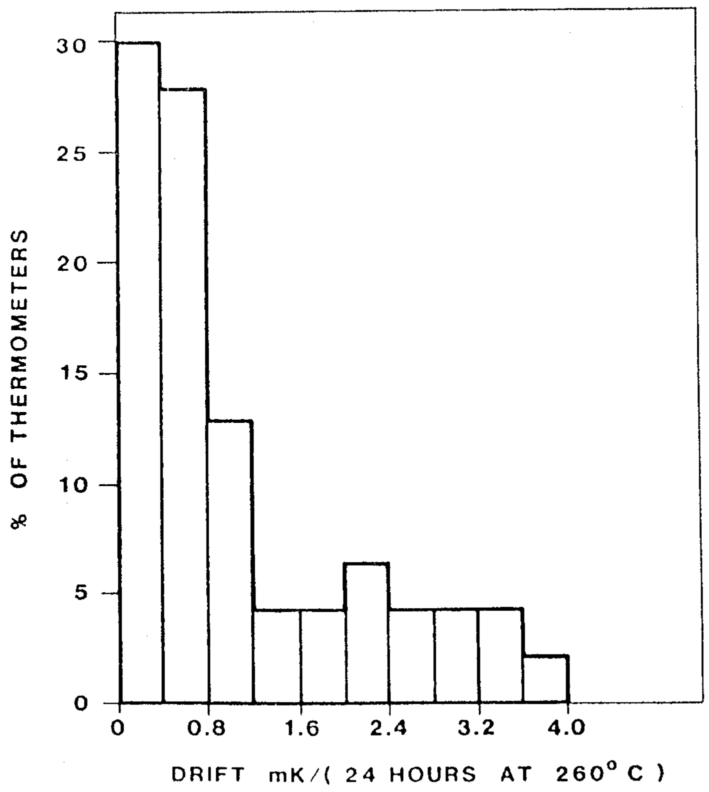


Fig. 16.6: Distribution of the rate of drift of R(0 °C) due to exposure to 260 °C for up to 100 hours for a group of 87 IPRTs [Connolly (1982)].

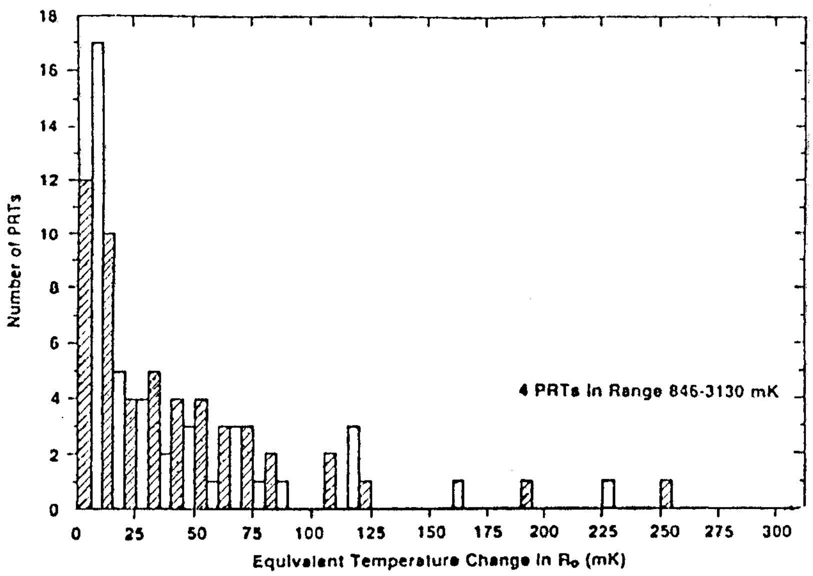


Fig. 16.7: Histogram of the maximum equivalent temperature change in R(0 °C) during ten 24 hour exposures to 235 °C for a group of 98 IPRTs [Mangum (1984)].

the temperature of the thermometer and that of the medium being measured. This difference is a function of the thermal characteristics of the thermometer and its coefficient of thermal exchange with the medium. It is proportional to the square of the thermometer current (i). Commonly, the PRT resistance is measured at 1 mA and $\sqrt{2}$ mA, plotted as a function of i^2, and extrapolated linearly to 0 mA. One can therefore evaluate the influence of the self-heating by measuring the variation of thermometer resistance with measuring current.

16.1.3 Response Time

Just as with self-heating, the response time of a thermometer depends upon both the characteristics of the thermometer and of the medium in which it is immersed. There are two methods to determine the response time. The first consists of immersing the thermometer in a fluid, measuring the response time under these conditions, and then by similarity deducing the response time in the medium to be used. The second method consists of studying, in situ, the response of the thermometer by using the thermometer resistance itself as a heating element. Then, by analyzing this response one can obtain the response time through the use of an algorithm [e.g. Kerlin et al. (1982)].

16.2 Interpolation Equations for Industrial Platinum Resistance Thermometers*

In principle, any of the approximations of Section 8.2 can also be used with IPRTs, although within some (generally unknown) broader limits of accuracy, but in practice few of them have been. Recall also that the techniques described here have been tested for sensors mounted by the experimenters in suitable glass or metal sheaths and not in the manufacturers' rugged sheaths meant for industrial applications. It is not known if the same accuracies apply in the latter case. No simple approximation for use above about 200 °C is yet available. The two most-used techniques are:

(a) Polynomials for $W(t_{68})$ versus t_{68}:

For secondary realizations extending above 0 °C it is possible to interpolate between fixed-point measurements with polynomials relating $W(t_{68})$ to t_{68} similar to the defining equations of the IPTS-68. There are two distinctly different aspects that limit the accuracy of such realizations: one is the inherent irreproducibility of the IPRTs themselves, both repeatedly with one thermometer

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* As in Section 8.2, these approximations were originally devised with reference to the IPTS-68, and so many of the equations in this section still carry an IPTS-68 designation. Generalization to the ITS-90 is straightforward.

and between different thermometers; the other is the indifferent agreement of the interpolating equation with the IPTS-68. There are not many data available on the accuracy that may be obtained. Actis and Crovini (1982) use the equations

$$W(t') = 1 + At' + Bt'^2 \tag{16.1}$$

and $$t = t' + \gamma\left(\frac{t}{100°C}\right)\left(\frac{t}{t_1} - 1\right)\left(\frac{t}{t_2} - 1\right)\left(\frac{t}{630.74°C} - 1\right) \tag{16.2}$$

where t_1 and t_2 are the temperatures of the fixed points used to evaluate A and B, and γ is a constant determined by calibration at a third fixed point. They tested these equations with 20 IPRTs from 6 manufacturers over the temperature ranges 0 °C to 420 °C or 0 °C to 330 °C, depending upon the particular IPRT. They found rather close agreement between the calibration constants of all thermometers but one, although two had to be calibrated in a restricted range. For a sub-group of 15 IPRTs from 5 manufacturers, all having the same configuration (sensing element diameter between 2.5 and 3.5 mm, length between 15 and 30 mm, multi-bore alumina insulator containing a minimally constrained platinum coil, operation up to 500 °C) the agreement provided by Equations 16.1 and 16.2 was better. In the range from 0 °C to 420 °C, with A, B and γ determined from calibrations at the steam, zinc, and tin points respectively, the 15 thermometers showed a mean difference with respect to the IPTS-68 of (3.6 ± 2.7) mK at 327 °C and of (-4.2 ± 1.5) mK at 150 °C (one-standard-deviation estimates). The stability of R(0 °C) for these IPRTs upon repeated cycles between 0 °C and 450 °C and 0 °C and -190 °C was always inside ± 5 mK, and for 13 of them better than ± 2 mK. If Eq. (16.2) was omitted, the differences with respect to the IPTS-68 at 327 °C and 150 °C were (45 ± 5.9) mK and (16 ± 1.8) mK respectively. In this latter case, a maximum difference of about 50 mK was reached between 250 °C and 300 °C. Using both equations with different calibration points, provided they were reasonably spaced, produced equivalent results.

(b) Besley and Kemp (1983) investigated a group of 27 IPRTs having W(H_20 b.p.) in the range 1.3912 to 1.3923. They first stabilized the ice-point resistance of the thermometers by thermal cycling between 77 K and 273 K. They then used the ice point and the oxygen boiling point as the reference temperatures in a Z-function (Eq. 8.5) related to T by

$$Z(T) = \sum_{i=0}^{8} a_i T^i \tag{16.3}$$

and found an inaccuracy of ± 0.035 K from 70 K to 273 K.

(c) A simple polynomial fit of degree 2 to 4 for W(t) against t is frequently a good approximation depending upon the range and the number of calibration points. Calibrations accurate to within ± 20 mK can usually be obtained with a quadratic fit to 5 to 10 points in the range -50 °C to 200 °C. Connolly (1982) and Bass and Connolly (1980) found that a cubic equation

$$W(t) = 1 + at + bt^2 + ct^3 \tag{16.4}$$

fitted 87 wire-wound IPRTs (that came largely from one manufacturer) from 0 °C to 250 °C to within ± 10 mK. Selected thermometers were better than this. However, with thick film sensors the uncertainty was as high as ± 35 mK.

(d) Above 100 K the Callendar and Callendar-Van Dusen equations can be used with IPRTs with the coefficients determined from least-squares fits to calibrations at from 5 to 15 temperatures, depending upon the range. Such fits are typically uncertain to a few tens of millikelvins.

16.3 National and International Specifications for IPRTs*

Various organizations, including the International Electrotechnical Commission (IEC) and the International Organization of Legal Metrology (OIML), have promulgated specifications and manufacturing tolerances for IPRTs*. The relationship between R and t_{68} is generated from the Callendar and Callendar-Van Dusen equations

$$R(t_{68})/R(0\ °C) = 1 + At_{68} + Bt_{68}^2 \qquad t_{68} \geq 0\ °C \tag{16.5}$$

and $$R(t_{68})/R(0\ °C) = 1 + At_{68} + Bt_{68}^2 + Ct_{68}^3\,(t_{68}-100\ °C) \qquad t_{68} < 0\ °C\ . \tag{16.6}$$

Two sets of values of the coefficients A, B, C typical of IPRTs with W(H_2O b.p.) = 1.385 and 1.391 respectively are used (Tables 16.2, 16.3). The equation (or tables derived

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* Since these international specifications and tolerances have not yet been reformulated to refer directly to the ITS-90, they are summarized here with their IPTS-68 designations.

therefrom) can then be used with any IPRT that has the specified R(0 °C) and W(H_20 b.p.) to give temperatures accurate to within specified tolerances. These tolerances (the ones specified by IEC (1983) are shown in Fig. 16.8) vary with the temperature, having minimum values of a few tenths of a °C at 0 °C, rising to about ± 0.5 °C (Class A) and ± 1.3 °C (Class B) at -200 °C and to several °C above 600 °C. These, naturally, are much larger than the uncertainty that results with a *calibrated* thermometer. The thermometer specifications currently and formerly issued by various standards organizations are summarized in Table 16.1. If one IPRT is interchanged for another nominally the same, temperature readings can differ by up to several degrees, depending upon the value of temperature. The tables issued by OIML (1985) for platinum with values of W(H_20 b.p.) = 1.385 and 1.391 are reproduced here as Tables 16.2 (the same numerically as the equivalent table of IEC (1983)) and 16.3 respectively. The tables are in the form of R(t_{68})/R(0 °C) as a function of temperature.

Table 16.1: Summary of Current and Past IPRT Specifications

	International Agreed Specifications		Former National Specifications				
Organization*	IEC Publ. 751 (1983)	OIML 1985	BS 1904:1984	DIN 43760	GOST 6651-84	JEMIMA	SAMA RC-4-1966
R(0°C) (Ω)	100	5 to 1000	100	100	10, 46, 100	100	100
tolerance:**							
Class A	± 0.06		± 0.075	± 0.06	± 0.15	~ 0.03	special standard
Class B	± 0.12		± 0.1	± 0.12	± 0.3	~ 0.5	
α (°C^{-1})	3.85$\times 10^{-3}$	3.85$\times 10^{-3}$ and 3.91$\times 10^{-3}$	3.85$\times 10^{-3}$	3.85$\times 10^{-3}$	3.85$\times 10^{-3}$ and 3.91$\times 10^{-3}$	3.916$\times 10^{-3}$	3.923$\times 10^{-3}$
tolerance:**							
Class A	± 1.3$\times 10^{-5}$	± 0.7$\times 10^{-5}$	± 0.7$\times 10^{-5}$	± 1.3$\times 10^{-5}$	± 0.7$\times 10^{-5}$		
Class B	± 3.0$\times 10^{-5}$	± 1.2$\times 10^{-5}$	± 2 $\times 10^{-5}$	± 3.0$\times 10^{-5}$	± 1.1$\times 10^{-5}$		
ranges (°C)							
Class A	-200 to 650		-183 to 630		-200 to 600	-200 to 600	-200 to 600
Class B	-200 to 850	-200 to 850	(-220 to 1050)	-200 to 850	-200 to 850		
coefficients:		(Type I)			(Type I)		
A (°C^{-1})	3.908 02 $\times 10^{-3}$	3.908 02$\times 10^{-3}$	3.968 35$\times 10^{-3}$	3.908 02$\times 10^{-3}$	3.908 02$\times 10^{-3}$	3.974 78$\times 10^{-3}$	3.981 53$\times 10^{-3}$
B (°C^{-2})	-5.802 $\times 10^{-7}$	-5.802 $\times 10^{-7}$	-5.8349 $\times 10^{-7}$	-5.801 95$\times 10^{-7}$	-5.802 $\times 10^{-7}$	-5.8775 $\times 10^{-7}$	-5.8531 $\times 10^{-7}$
C (°C^{-4})	-4.273 50 $\times 10^{-12}$	-4.274 $\times 10^{-12}$	-4.3557 $\times 10^{-12}$	-4.2735 $\times 10^{-12}$	-4.273 50$\times 10^{-12}$	-3.4813 $\times 10^{-12}$	-4.3545 $\times 10^{-12}$
		(Type II)			(Type II)		
A (°C^{-1})		3.968 68$\times 10^{-3}$			3.968 47$\times 10^{-3}$		
B (°C^{-2})		-5.8677 $\times 10^{-7}$			-5.847 $\times 10^{-7}$		
C (°C^{-3})		-4.141 $\times 10^{-12}$			-4.3558 $\times 10^{-12}$		

* BS = British Standard
DIN = Deutschen Institut für Normung
GOST = (All-Union State Standard, USSR)
JEMIMA = Japanese Standard
SAMA = Scientific Apparatus Makers of America
IEC = International Electrotechnical Commission
OIML = International Organization for Legal Metrology

** Type I refers to thermometers with $\alpha = 3.85 \times 10^{-3}$ °C^{-1} and Type II to thermometers with $\alpha = 3.91 \times 10^{-3}$ °C^{-1}. Class A and Class B refer to accuracy tolerances, A being the higher.

Table 16.2

RESISTANCE RATIOS FOR INDUSTRIAL PLATINUM RESISTANCE THERMOMETERS WITH $R(100\ ^0C)/R(0\ ^0C) = 1.3850$

Interpolation equation for the temperature range from − 200 to 0 ^0C : $R(t_{68})/R(0\ ^0C) = 1 + At_{68} + Bt_{68}^2 + C(t_{68} - 100)t_{68}^3$

from 0 to 850 ^0C : $R(t_{68})/R(0\ ^0C) = 1 + At_{68} + Bt_{68}^2$

where
$A = 3.90802.10^{-3}\ ^0C^{-1}$
$B = -5.8020\ .10^{-7}\ ^0C^{-2}$
$C = -4.274\ .10^{-12}\ ^0C^{-4}$

t_{68} (^0C)	0	-5	-10	-15	-20	-25	-30	-35	-40	-45	-50	-55	-60	-65	-70	-75	-80	-85	-90	-95	-100
-100	0.6025	0.5822	0.5619	0.5415	0.5211	0.5006	0.4800	0.4594	0.4387	0.4179	0.3971	0.3763	0.3553	0.3343	0.3132	0.2920	0.2708	0.2494	0.2280	0.2065	0.1849
0	1.0000	0.9804	0.9609	0.9412	0.9216	0.9019	0.8822	0.8625	0.8427	0.8229	0.8031	0.7832	0.7633	0.7433	0.7233	0.7033	0.6833	0.6631	0.6430	0.6228	0.6025

t_{68} (^0C)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
0	1.0000	1.0195	1.0390	1.0585	1.0779	1.0973	1.1167	1.1361	1.1554	1.1747	1.1940	1.2132	1.2324	1.2516	1.2707	1.2898	1.3089	1.3280	1.3470	1.3660	1.3850
100	1.3850	1.4039	1.4229	1.4417	1.4606	1.4794	1.4982	1.5170	1.5358	1.5545	1.5731	1.5918	1.6104	1.6290	1.6476	1.6661	1.6846	1.7031	1.7216	1.7400	1.7584
200	1.7584	1.7768	1.7951	1.8134	1.8317	1.8499	1.8682	1.8863	1.9045	1.9226	1.9407	1.9588	1.9769	1.9949	2.0129	2.0308	2.0488	2.0667	2.0845	2.1024	2.1202
300	2.1202	2.1380	2.1557	2.1735	2.1912	2.2088	2.2265	2.2441	2.2617	2.2792	2.2967	2.3142	2.3317	2.3491	2.3665	2.3839	2.4013	2.4186	2.4359	2.4531	2.4704
400	2.4704	2.4876	2.5048	2.5219	2.5390	2.5561	2.5732	2.5902	2.6072	2.6242	2.6411	2.6580	2.6749	2.6918	2.7086	2.7254	2.7422	2.7589	2.7756	2.7923	2.8090
500	2.8090	2.8256	2.8422	2.8587	2.8753	2.8918	2.9083	2.9247	2.9411	2.9575	2.9739	2.9902	3.0065	3.0228	3.0391	3.0553	3.0715	3.0876	3.1038	3.1199	3.1359
600	3.1359	3.1520	3.1680	3.1840	3.1999	3.2159	3.2318	3.2476	3.2635	3.2793	3.2951	3.3108	3.3266	3.3423	3.3579	3.3736	3.3892	3.4047	3.4203	3.4358	3.4513
700	3.4513	3.4668	3.4822	3.4976	3.5130	3.5283	3.5437	3.5590	3.5742	3.5894	3.6047	3.6198	3.6350	3.6501	3.6652	3.6802	3.6953	3.7103	3.7252	3.7402	3.7551
800	3.7551	3.7700	3.7848	3.7997	3.8144	3.8292	3.8440	3.8587	3.8733	3.8880	3.9026	-	-	-	-	-	-	-	-	-	-

Tables corresponding to various national specifications can be generated using the coefficients given in Table 16.1

Table 16.3

RESISTANCE RATIOS FOR PLATINUM RESISTANCE THERMOMETERS WITH $R(100\ ^{0}C)/R(0\ ^{0}C) = 1.3910$

Interpolation equation for the temperature range from -200 to $0\ ^{0}C$: $R(t_{68})/R(0\ ^{0}C) = 1 + At_{68} + Bt_{68}^{2} + C(t_{68} - 100)t_{68}^{3}$

from 0 to $850\ ^{0}C$: $R(t_{68})/R(0\ ^{0}C) = 1 + At_{68} + Bt_{68}^{2}$

where

$A = 3.96868.10^{-3}\ ^{0}C^{-1}$

$B = -5.8677\ .10^{-7}\ ^{0}C^{-2}$

$C = -4.141\ .10^{-12}\ ^{0}C^{-4}$

t_{68} (^{0}C)	0	-5	-10	-15	-20	-25	-30	-35	-40	-45	-50	-55	-60	-65	-70	-75	-80	-85	-90	-95	-100
-100	0.5964	0.5758	0.5552	0.5345	0.5137	0.4929	0.4721	0.4511	0.4302	0.4091	0.3880	0.3668	0.3456	0.3243	0.3029	0.2814	0.2599	0.2382	0.2165	0.1947	0.1729
0	1.0000	0.9801	0.9603	0.9403	0.9204	0.9004	0.8804	0.8604	0.8403	0.8202	0.8000	0.7798	0.7596	0.7394	0.7191	0.6987	0.6784	0.6580	0.6375	0.6170	0.5964

t_{68} (^{0}C)	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
0	1.0000	1.0198	1.0396	1.0594	1.0791	1.0989	1.1185	1.1382	1.1578	1.1774	1.1970	1.2165	1.2360	1.2555	1.2749	1.2944	1.3137	1.3331	1.3524	1.3717	1.3910
100	1.3910	1.4102	1.4295	1.4486	1.4678	1.4869	1.5060	1.5251	1.5441	1.5631	1.5821	1.6010	1.6200	1.6389	1.6577	1.6765	1.6954	1.7141	1.7329	1.7516	1.7703
200	1.7703	1.7889	1.8075	1.8261	1.8447	1.8632	1.8818	1.9002	1.9187	1.9371	1.9555	1.9739	1.9922	2.0105	2.0288	2.0470	2.0652	2.0834	2.1016	2.1197	2.1378
300	2.1378	2.1559	2.1739	2.1919	2.2099	2.2278	2.2458	2.2637	2.2815	2.2994	2.3172	2.3349	2.3527	2.3704	2.3881	2.4057	2.4234	2.4410	2.4585	2.4761	2.4936
400	2.4936	2.5111	2.5285	2.5459	2.5633	2.5807	2.5980	2.6153	2.6326	2.6499	2.6671	2.6843	2.7014	2.7186	2.7357	2.7527	2.7698	2.7868	2.8038	2.8207	2.8376
500	2.8376	2.8545	2.8714	2.8882	2.9051	2.9218	2.9386	2.9553	2.9720	2.9886	3.0053	3.0219	3.0384	3.0550	3.0715	3.0880	3.1044	3.1209	3.1373	3.1536	3.1700
600	3.1700	3.1863	3.2026	3.2188	3.2350	3.2512	3.2674	3.2835	3.2996	3.3157	3.3317	3.3477	3.3637	3.3797	3.3956	3.4115	3.4274	3.4432	3.4590	3.4748	3.4906
700	3.4906	3.5063	3.5220	3.5376	3.5533	3.5689	3.5844	3.6000	3.6155	3.6310	3.6465	3.6619	3.6773	3.6926	3.7080	3.7233	3.7386	3.7538	3.7691	3.7842	3.7994
800	3.7994	3.8145	3.8297	3.8447	3.8598	3.8748	3.8898	3.9047	3.9197	3.9346	3.9494	-	-	-	-	-	-	-	-	-	-

Tables corresponding to various national specifications can be generated using the coefficients given in Table 16.1

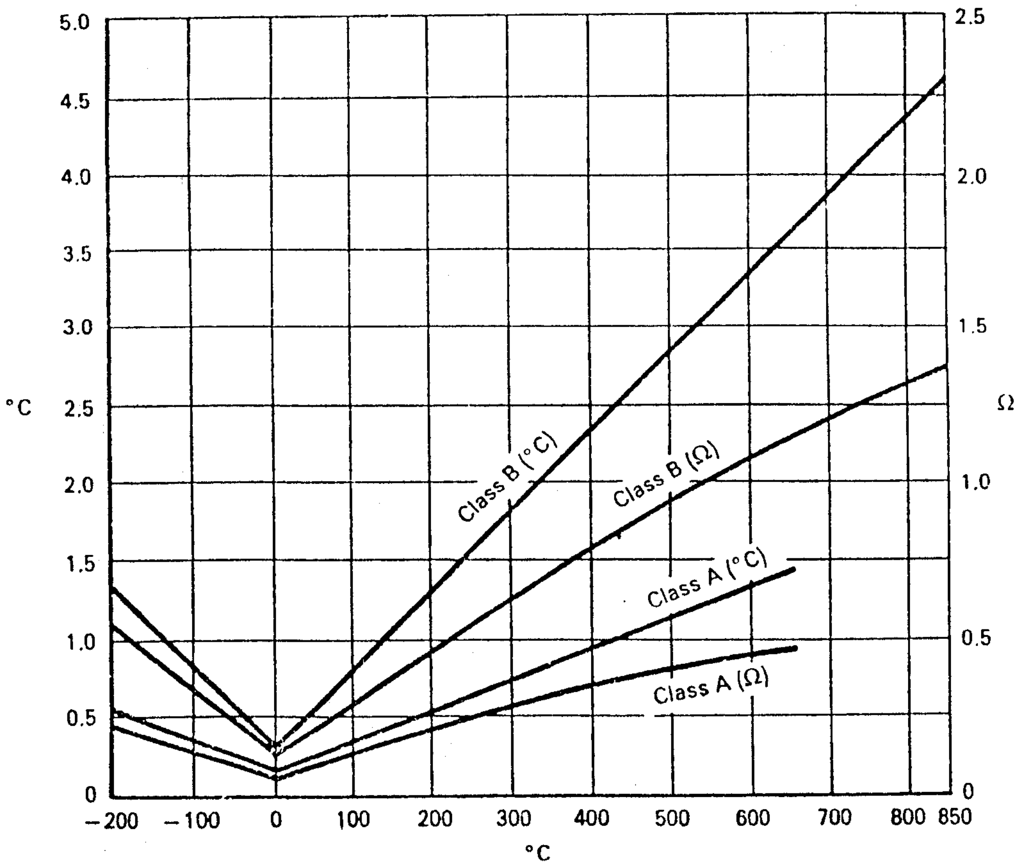

Fig. 16.8: Tolerances for industrial platinum resistance thermometers as specified by IEC (1983).

17. Thermistors

The term thermistor refers to semiconducting ceramic materials, generally oxides, acting as sensing elements of devices for measuring temperature. A very extensive literature is available on this subject: especially valuable is a book by Sachse (1975), and many papers in Temperature, Its Measurement and Control in Science and Industry, Vol. 4 (1972) and Vol. 5 (1982).

It is difficult to discuss thermistors within the framework of this document; their characteristics are much more device-dependent than those of other thermometers, so their properties must be related to specific commercial devices and a general description cannot be given in terms of materials, at least for a moderately high level of accuracy. On the other hand, the thermistor is very widely used and may show a stability comparable with that of an IPRT.

The range of use of each particular thermistor is narrow since the resistance/temperature relationship is exponential of the form

$$R = R_0 \ \exp[-b((1/T) - (1/T_0))] \tag{17.1}$$

where R_0 is the zero-power resistance (typically between 2 and 30 kΩ) of the thermistor at some reference temperature T_0 (kelvins), frequently 298 K (zero power resistance is the resistance when the current is low enough to produce negligibly small self-heating). The constant b is such that R changes about 4 percent per kelvin. Therefore a suitable type of thermistor must be chosen for each specific application.

Although thermistors can be used at very low temperatures (liquid helium [Schlosser and Munnings (1972)]) and at high temperatures (above 500 °C [Sachse (1975)]), the main area of application is between about -80 °C and 250 °C. They may be considered as secondary thermometers (accurate to within 50 mK to 5 mK) only in an even narrower range, between 0 °C and 100 °C. The following discussion is restricted to this latter range.

Both disk and bead types can have this quality when they are glass-coated to limit the deleterious effect of moisture. Apart from the effect of moisture on the thermistor itself, the probe where the thermistor is usually mounted can also be moisture-sensitive; for example, moisture can cause shunting between the connecting leads.

Interchangeability of thermistors can be within 50 mK, especially with disk types because the larger sensing element more easily allows constancy in the unit-to-unit distribution of materials in the mixture of oxides.

Stability on thermal cycling is the main guide to thermometer quality. Several studies [LaMers et al. (1982), Wood et al. (1978), Edwards (1983), Mangum (1986)] reveal a large variety of behaviours. As with germanium thermometers, it is difficult to express a general rule on stability or even on drift trends. In the most extensive of these studies, Wood et al. (1978) present a large number of figures that show the aging of a large variety of thermistors at various temperatures. The reader is referred to these figures for the details. Some types from two manufacturers appear to show a stability better than 10 mK/year .

Mangum (1986) found the bead-in-glass thermistors to be much more stable than the disk type. During about 4000 h aging at 100 °C, 11 of 12 bead-type thermistors were stable to within 5 mK but 10 of 11 disk-type thermistors changed several tenths of a degree. The bead-type sensors became much less stable if subjected to heating at 300 °C. When they were thermally cycled to 150 °C, about 30% of a sample of 20 changed by 50 to 250 mK. Mangum found no significant differences between the products of various manufacturers.

Moderately large calibration changes due to drift are reported [Code (1985)] to be retrievable by a single-point recalibration, since the whole characteristic shifts by the same amount in the whole temperature range.

Since the sensing element is generally mounted in a stem, the self-heating effect, dynamic response, and immersion error are determined essentially by the stem; therefore the magnitudes of these are common to those of other types of thermometers used in the same temperature range, such as IPRTs (see Section 16.3).

Interpolation equations of the exponential type, with two or more exponential terms, or the following inverse equation:

$$T^{-1} = A + B \ln R + C (\ln R)^3 \tag{17.2}$$

can be used for approximation of the thermistor R-T characteristics within a few millikelvins over several tens of kelvins [Sapoff et al. (1982), Steinhart and Hart (1968)].

18. Base-Metal Thermocouples

18.1 General Remarks

By far the largest number of thermocouples used are composed of base metals and their alloys. They are produced in large quantities by many manufacturers to conform, within acceptable tolerances, with standard reference tables [IEC (1977) (1982), CMEA (1978), GOST (1977), ASTM (1987b)].*

Although base-metal thermocouples cannot be recommended for approximating the ITS-90 with accuracies comparable to that of, for example, IPRTs, they are nevertheless so widely used that some description of them is necessary here. These thermocouples are identified by letter designations originally assigned by the Instrument Society of America and now accepted internationally (Table 18.1) [IEC (1977)]. The use of base-metal thermocouples for temperature measurements of moderate precision requires careful consideration regarding design, specifications, and application (atmosphere, temperature range).

Table 18.1: Letter-designation for Thermocouples.

Type T: Copper(+)/Copper-nickel alloy(-)
Type J: Iron(+)/Copper-nickel alloy(-)
Type K: Nickel-chromium alloy(+)/Nickel-aluminium alloy(-)
Type E: Nickel-chromium alloy(+)/Copper-nickel alloy(-)
Type N: Nickel-chromium-silicon alloy(+)/Nickel-silicon alloy(-)
Type R: Platinum13%Rhodium(+)/Platinum(-)
Type S: Platinum10%Rhodium(+)/Platinum(-)
Type B: Platinum30%Rhodium(+)/Platinum6%Rhodium(-)
-- : Tungsten5%Rhenium(+)/Tungsten20%Rhenium(-)

18.2 Types of Base-Metal Thermocouples

Brief descriptions of the most-commonly used thermocouples are given here. The most useful of these, having a wide temperature range coupled with good accuracy, is Type N. Considerably more detail may be found in ASTM (1981).

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* ASTM: American Society for Testing and Materials (USA)
CMEA: Council for Mutual Economic Assistance (USSR)
GOST: Gosudarstvennyj Komitet Standartov (USSR)
IEC: International Electrotechnical Commission

18.2.1 Type T Thermocouple

Within its range (-200 to 350 °C) this thermocouple is the most accurate base-metal thermocouple, due in large part to the ready availability of high-purity, strain-free copper. Above 370 °C it is limited by oxidation of the copper. The accuracy usually attainable is 0.1 K, but with special calibration it may approach 0.01 K from 0 °C up to 200 °C. Because copper is universally used for electrical conductors, one may easily obtain thermal-free connections to the measuring instruments. On the other hand the high thermal conductivity of the copper thermoelement may be disadvantageous in some applications. The type T thermocouple can be used in a vacuum and in oxidizing, reducing, or inert atmospheres.

18.2.2 Type J Thermocouple

This thermocouple is most commonly used for industrial purposes in the temperature range from 0 to 760 °C in both oxidizing and reducing atmospheres. The accuracy attainable is fair to poor (0.1 to 0.5 K below 300 °C, 1 to 3 K above 300 °C); the stability is fair below 500 °C but poor above 500 °C because of the higher oxidation rate of the iron thermoelement.

18.2.3 Type K Thermocouple

This thermocouple has a wide temperature range (-200 to 1260 °C) ; in the range : above 0 °C it is the most widely used thermocouple. It is recommended for continuous use in oxidizing or inert atmospheres. At high temperatures it and Type N are the most oxidation-resistant base-metal thermocouples. In reducing, sulfurous atmospheres or in a vacuum it is necessary to use suitable protection tubes. Atmospheres with reduced oxygen content promote the so-called "green-rot" corrosion of the positive thermoelement because of the preferential oxidation of chromium; this causes large negative errors in calibration. This is most serious in the temperature range from 800 to 1050 °C, for example when the thermocouple is exposed to carbon dioxide in this temperature range. Green-rot corrosion frequently occurs when thermocouples are used in long unventilated protecting tubes of small diameter. It can be minimized by increasing the oxygen supply with large-diameter protecting tubes or ventilated tubes. Both elements of the Type K thermocouple are subject to oxidation in air above about 850 °C, but this normally leads to only a very slow increase with time of the thermocouple emf for a given temperature. Type K can be used above 1200 °C for very short periods in air without serious decalibration. Changes of up to 10 K can occur in the positive thermoelement due to short-range ordering in the nickel-chromium solid solutions, especially if the thermoelements are annealed or used near 400 °C [Fenton (1972)].

The accuracy attainable is 0.1 K below 300 °C and 1 K up to about 1000 °C. Stability is fair. The accuracy and stability of this thermocouple are limited by its susceptibility to inhomogeneities and mechanical strain (cold work) and to previous heat treatment.

18.2.4 Type E Thermocouple

This thermocouple is recommended for use up to 870 °C in oxidizing or inert atmospheres. In reducing atmospheres, marginally oxidizing atmospheres, and in vacuum it is subject to the same limitations as Type K thermocouples.

Type E thermocouples develop the highest emf per kelvin (80 μV/K at 700 °C) of all the commonly-used types and are often used primarily because of this feature. Their accuracy is better than 1 K below 300 °C and 1 to 3 K from 300 to 1000 °C.

18.2.5 Type N Thermocouple

The Type N thermocouple shows enhanced thermoelectric stability, particularly at high temperatures, compared to the other standard base-metal thermocouples (except Type T), obtained as a result of careful choice of composition of the two elements.

By suitable adjustment of composition [Burley (1972), Burley et al. (1978), Burley et al. (1982)], it has been possible to achieve higher oxidation resistance at temperatures above 1000 °C; reduce short-term cyclic variations in thermal emf due to structural phenomena (temperature range from 300 °C to 500 °C); and reduce time-independent perturbation in thermal emf due to magnetic transformations (temperature range from 50 °C to 230 °C). Furthermore, the Type N thermocouple can now be obtained in a mineral-insulated metal-sheathed construction (Section 18.3.4) with a Nicrosil sheath [Burley (1987)]. The result is an overall better long-term stability, higher reproducibility, and higher accuracy than for all other base-metal thermocouples (except Type T). Below about 500 °C, however, these advantages are not dramatic; for example, from 0 °C to 500 °C they may be more reproducible than Type K by a factor of about 2.

18.2.6 Tungsten-Rhenium Thermocouple

There are several tungsten-rhenium alloy thermocouples in use, but the only one standardized is tungsten 5% rhenium/tungsten 20% rhenium [CMEA (1978), GOST (1977)]. All have been used at 2500 °C to 2750 °C but general use is below about 2200 °C. These thermoelements are supplied as matched pairs guaranteed to meet an emf output of producer-developed tables within ± 1 percent or of standard reference tables within ± 0.5 to 0.7 percent. Tungsten as the positive leg can pose problems because heating it to or above its recrystallization temperature (about 1200 °C) causes embrittlement, resulting in a loss of room-temperature ductility, an effect that does not occur with legs containing rhenium (3 5 percent). Use is only possible in a vacuum or in high-purity reducing (hydrogen) or inert atmospheres.

18.3 Construction

A complete thermocouple temperature-sensing assembly consists of: a sensing element assembly including, in its most basic form, two dissimilar wires supported by an electrical insulator and joined at one end to form a measuring junction; a protection tube (ceramic or metal), sometimes referred to as a thermowell, which protects the sensing element assembly from the deleterious effects of corrosive, oxidizing, or reducing atmospheres; and a connector for the wire terminations of the sensing element assembly.

It is, of course, necessary to ensure that the sheath and protection tube do not themselves contaminate the thermocouple. The reader should consult ASTM (1981) for details.

18.3.1 Thermoelements

The positive and negative thermoelements for a given type of thermocouple, as supplied by anyone manufacturer, will conform to the calibration curve for that thermocouple within specified limits of error. However, because materials used for a given thermoelement by various manufacturers may differ slightly in thermal emf, larger errors may occur if positive and negative thermoelements from different sources are combined.

Recommended maximum-temperature limits according to the wire diameter of the thermoelements are given in Table 18.2. These limits apply to protected thermocouples; that is, to thermocouples in conventional closed-end protecting tubes. In actual operation, there may be instances where the temperature limits recommended can be exceeded. Likewise, there may be applications where satisfactory life will not be obtained at the recommended temperature limit.

18.3.2 Sheaths

A wide variety of materials are available for thermocouple sheaths. Up to about 100 °C the commonest include enamels and varnishes, cloth, plastics, and rubber. Most of these organic materials begin to decompose, or at least to conduct, at higher temperatures. Some silicone varnishes may be satisfactory up to about 300 °C, fibreglass up to 400 °C and with silicone as the binder up to 500 °C. The sheath has to ensure a sufficient electrical

Table 18.2: Recommended Upper Temperature Limits for Protected Thermocouples [ASTM (1987b), ASTM (1981)].

Thermocouple	Diameter				
	3.2 mm	1.6 mm	0.8 mm	0.51 mm	0.33 mm
J (JP)	760 °C	590 °C	480 °C	370 °C	370 °C
E (IN, TN, EN)	870 °C	650 °C	540 °C	430 °C	430 °C
T (TP)	--	370 °C	260 °C	200 °C	200 °C
K (KP, EP, KN), N	1260 °C	1090 °C	980 °C	870 °C	870 °C

Table 18.3: Properties of Refractory Oxides [ASTM (1981)].

Material	Composition	Maximum use Temperature	Thermal stress Resistance	Thermocouple Commonly used with
Sapphire crystal	99.9 Al_2O_3	1950 °C	very good	any
Sintered alumina	99.8 Al_2O_3	1900 °C	good	any
Sintered beryllia	99.8 BeO	1900 °C	excellent	high temperature
Sintered magnesia	99.8 MgO	1900 °C	fair-poor	any
Sintered mullite	72 Al_2O_3, 28 SiO_2	1750 °C	good	base-metals
Sintered stabilized zirconia	92 ZrO_2, 4 HfO_2, 4 CaO	2200 °C	fair-good	high temperature
Silica Glass	99.8 SiO_2	1100 °C	excellent	base-metal
Mullite porcelain	70 Al_2O_3, 27 SiO_2	1400 °C	good	base-metal
High alumina porcelain	90-95 Al_2O_3, 4-7 SiO_2	1500 °C	very good	base-metal, noble metal below 1100 °C for a variety of constructions

insulation even though it be affected adversely by moisture, abrasion, flexing, temperature extremes, chemical attack, or nuclear radiation. Hence an insulation should be selected only after considering possible exposure temperatures, the number of temperature cycles, mechanical movement, moisture, routing of the thermocouple wire, and chemical deterioration.

Above about 500 °C the various ceramics are the only materials with high enough resistivity and stability for sheaths. Fused-silica insulators are satisfactory to about 1000 °C and have excellent thermal-shock resistance. Low-purity aluminium oxide, such as porcelain or mullite, is also frequently used in this range, but above 1000 °C there is risk of contamination of the thermoelements and so its use is not recommended. Beyond 1000 °C the sheath is usually a high-purity ceramic oxide, mainly recrystallized alumina that has fair thermal-shock resistance and excellent chemical stability except in reducing atmospheres. Some properties of various refractory oxides used are given in Table 18.3.

18.3.3 Protection Tubes

A thermocouple protection tube is in principle simply a gas-tight closed-end tube containing a suitable atmosphere; it may be in the form of a well into which the thermocouple is inserted, or it may be an integral part of the thermocouple assembly. In choosing a material for the protection tube we must consider its stability, not only with respect to the thermocouple, but also with respect to the medium in which it is immersed. The choice of the proper protection tube is therefore governed by the conditions of use, such as gas tightness, thermal-shock resistance, or chemical compatibility with the medium. Metal protection tubes are adequate for base-metal thermocouples up to 700 °C (steel) or even up to 1150 °C (Ni-Cr alloys). Ceramic protection tubes are usually used at higher temperatures and sometimes also at lower temperatures in atmospheres harmful to metal tubes.

18.3.4 Thermocouple Construction

The classic construction has two wires sheathed in two single-bore or one twin-bore tube, the wire tips joined to form the hot junction, and the whole encased in a protection tube if necessary. Any of a number of methods is available for forming the hot junction (welding, brazing, hard-soldering, soft-soldering, clamping or twisting the wires). The junction must provide good electrical contact and should be as small as possible. Fluxes should be used sparingly or not at all, as the risk of contamination is great.

The compacted ceramic-insulated (also called mineral-insulated metal-sheathed) construction affords thermocouple protection together with flexibility and thermal-shock resistance. In this construction the wires are insulated by immersion in a pure, compacted. refractory-oxide powder which is contained in a thin metal sheath. Recommended sheath diameters for long-term service in air at various temperatures are given in Table 18.4. The advantages of this configuration are:

- isolation of the thermocouple wires from environment that may cause rapid deterioration ;
- reduction of long-term calibration drift;
- the lessening of temperature versus wire-size problems; whereas in the classic construction small-diameter wires have shorter lifetimes at high temperatures than large-diameter wires for a variety of reasons, in this construction the wires are firmly held in the protective sheath so that small-diameter wires can be exposed to high temperatures for long periods of time without serious deterioration.
- excellent high-temperature insulation for the thermocouple wires;
- ease of use, in particular to form bent configurations or to weld the sheath without loss of insulation;
- availability in a wide variety of sizes and materials.

For most practical purposes the sheathed thermocouple material should have a minimum insulation resistance of 100 megohms at room temperature at 500 V dc for outside diameters larger than 1.5 mm. This is readily obtained by dry, uncontaminated, compacted ceramics. The addition of moisture by hygroscopic action and subsequent movement by capillary action through exposed ends will decrease the insulation resistance. Also, the insulation resistance of all ceramics decreases with increasing temperature (approximately a factor of ten for a 200 K temperature rise).

18.3.5 Circuit Construction

The thermal emfs that must be measured are always small, ranging from near zero to a maximum of about 100 mV. Precise absolute measurements may well require a detector sensitivity of better than 0.1 μV and an accuracy of about 1 μV for base-metal thermocouple thermometry, which are possible to realize with modern digital voltmeters or classically with dc potentiometers.

In the construction of such low-level thermocouple circuits the following points must be considered [Bedford et al. (1970)]:

Table 18.4: Recommended Sheath Diameters for Mineral-Insulated Metal-Sheathed Base Metal Thermocouples for Long Term Service in Air [ASTM (1981)].

Sheath diameter (in mm)	1.0	1.5	3.0	4.5	6.0
Nominal wall (in mm)	0.18	0.25	0.5	0.62	0.8
Type K	760 °C	870 °C	870 °C	870 °C	980 °C
Type J	540 °C	650 °C	760 °C	760 °C	870 °C
Type E	650 °C	760 °C	760 °C	870 °C	925 °C

Table 18.5: Thermoelectric Power at Room Temperature of Copper versus Various Metals in Thermocouple Measurement Circuits [Bedford et al. (1970)].

Metal	Thermoelectric power in μV/K	Remarks
group a		preferred materials
copper from a different spool of wire	± 0.02	
low thermal solder	0.1	
lead free-turning copper	0.1	
group b		materials are likely to require some thermal uniformity
silver	0.2	
gold	0.2	
coin silver	-0.4	
group c		materials need very good thermal uniformity
carbon	0.6	
platinum10%rhodium	0.8	
beryllium copper	0.9	
manganin	1.5	
coin copper	1.6	
yellow brass	1.6	
phosphor bronze	3.2	
lead50%tin solder	3.0	
group d		materials likely to be unsuitable
steels	3.2 … -5.6	
Chromel	-20	
constantan	40	

- temperature gradients and variations of temperature with time should be kept as small as possible. Only strain-free copper should be used in the regions of appreciable temperature gradients; all junctions should be in a zero-gradient region.
- all connections should be shielded from thermal radiation; this applies particularly when non-copper components are involved. A further improvement in accuracy is likely to result from the introduction of some heat capacity around the components, since this tends to reduce transient temperature fluctuations.
- conductor materials should be as thermoelectrically similar as possible; in practice this means that they should have thermoelectric powers near that of copper. The relative quality of various metals that can be used in thermocouple circuits is shown in Table 18.5.

Highest system accuracy can be obtained by running the thermocouple conductors directly to the reference junction, so avoiding the use of extension wires. If extension wires must be used, however, as in the case of metal-sheathed mineral-insulated thermocouples, the extension wires become an integral part of the temperature-sensing system. The user must be aware of the need to keep the temperature of the reference junction below 200 °C in the interest of overall accuracy. In any case, the termination should be designed in such a way as to guarantee that the temperature of the terminals is uniform.

18.4 Annealing of the Thermoelements

As with noble-metal thermocouples the base-metal thermoelements should be in a condition of thermodynamic equilibrium to ensure metallurgical stability over the temperature range of application. Accurate temperature measurements are generally impossible when this equilibrium condition does not exist. Annealing removes existing non-equilibrium states; for example, strains introduced by cold working. Inadequate annealing may result in errors varying in magnitude from a few tenths of a kelvin to several kelvins depending upon the temperature being measured and the temperature gradients along the thermoelements.

All base-metal thermocouple wires are usually delivered in an annealed state. The heat treatment given by the producer can be generally considered as sufficient, and seldom is it advisable to further anneal the thermoelements before testing. If an annealing should be necessary, however, the annealing temperature should be higher and the depth of immersion greater than will be encountered in service. A rough test for the adequacy of the annealing procedure is the reproducibility of the thermocouple emf at some fixed temperatures (such as fixed points) after consecutive annealing periods.

In the case of the Types K and E thermocouples and the negative legs of Types T and J thermocouples (all containing nickel or nickel-chromium), the thermodynamic equilibrium is limited by diffusion of constituents (temperature range from 300 °C to 500 °C) and magnetic-transformation processes (temperature range from 50 °C to 200 °C) so that a high accuracy (0.1 K) can be obtained only by special heat treatment, using specified calibration procedures, and in special application conditions [Burley et al. {1982)].

18.5 Guidelines for Proper Handling and Use -Installation and Sources of Errors

For accurate temperature measurements by means of base-metal thermocouples, in particular by metal-sheathed thermocouples, the following guidelines should be considered [ASTM (1981)]:

- be sure that the sheath or protection tube material will survive the environment.
- be sure that the thermocouple assembly is fully annealed for maximum life of sheath or protection tube and stability of the thermocouple calibration.
- remember that the life of the thermocouple will decrease with higher application temperatures and smaller thermoelement and sheath diameters and is limited by grain growth (Tables 18.2 and 18.4).
- in the case of metal-sheathed thermocouples, it must be possible to bend the sheath around a mandrel twice the sheath diameter without damage.
- in metal-sheathed thermocouples, the appearance of moisture in the assembly is indicated by a diminution in insulation resistance; this can cause an error in temperature measurement by electrical shunting. Moisture can be removed by heating and sealing the exposed ends of the thermocouple.
- metal-sheathed thermocouples should not be repeatedly bent at the same location as this work-hardens the sheath and may change the thermocouple calibration.

To evaluate the performance of a thermocouple circuit, the numerous possible sources of error should be considered: thermal shunting; electrical shunting; calibration; decalibration (from instability or drift); extension wires; reference junction.

A thermocouple, just as any other contacting temperature sensor, disturbs the temperature distribution of any object to which it is attached because it has a finite size and Iconducts heat away from (or to*)* the object. The thermocouple itself loses heat to (or gains heat from) its surroundings by conduction, convection, and radiation. This heat transfer can cause the thermocouple hot junction to be at a different temperature from that of the object.

These effects cause a thermal-shunting error, the magnitude of which depends largely on the method of thermocouple installation. This error is avoided when the portion of the thermocouple near the hot junction is isothermal and at the temperature of the object whose temperature is to be measured. This error can be especially large when the heat transfer from the measuring object to the thermocouple is poor and/or the heat transfer from the thermocouple to the surroundings is large (such as in surface temperature measurement).

At higher temperatures, where the electrical resistivity of the insulator will be lower, an electrical shunting will occur and can cause temperature-measurement errors, especially at temperatures above 1500 °C. This effect is greater in metal-sheathed thermocouples than it is in the classic type of construction because of the larger area of electrical contact between the insulator and the thermoelements.

Calibration errors depend upon the accuracy of the calibration standards and the calibration method applied (Sec. 18.6).

Decalibration errors or drift, i.e. a change of the emf-temperature relationship with time, can occur even if the thermocouples are heat-treated, assembled, calibrated, and installed with utmost care. In the literature (e.g. [Kinzie (1973)]) many results are reported that show the same trends of decalibration but the magnitudes differ because of undetected differences in experimental variables that control the drift rates.

Several factors cause a thermocouple to drift, such as: chemical reactions of the thermoelements with the gaseous environment, with the electrical insulator, or with the object whose temperature is to be measured (including impurities in the environment, insulator, or object); metallurgical transformations (such as order-disorder transformations or secondary recrystallization); loss of alloying elements by selective evaporation or oxidation at higher temperatures; transmutation by nuclear radiation.

Drift rates generally increase rapidly with increasing temperature and are larger for smaller-diameter thermoelements.

Extension-wire errors arise from the differences between the thermoelectric properties of the thermoelements and of the corresponding extension wires. In high-precision measurements the use of such wires should be avoided whenever possible. If extension wires must be used due to installation conditions, any error can be reduced by calibration of the complete thermocouple/extension-wire assembly and by ensuring a uniform temperature at the junctions.

In thermocouple thermometry all emf measurements are referred to the temperature of the reference junction. Any error in this temperature, therefore, is directly involved in the error of the measured temperature. Reduction of this error is possible by ensuring that both thermoelement reference junctions have the same temperature and that this temperature is measured with the desired accuracy with another thermometer (mercury-in-glass thermometer or resistance thermometer) or by realization of a fixed-point temperature (ice point or water triple point, see Sec. 9.4).

18.6 Calibration of Base-Metal Thermocouples

The calibration of a thermocouple consists of the determination of its emf at a sufficient number of known temperatures, some of which can be fixed points, so that with some accepted means of interpolation its emf will be known over the entire temperature range in which it is to be used. In comparison to the situation with noble-metal thermocouples (Sec. 9.5), the number of calibration points necessary with base-metal !thermocouples to reach their limit of accuracy will be greater because of the more complex emf-temperature relationships and because more factors can influence the deviation of the real thermocouple characteristics from the reference table or polynomial values. Because of this the methods of interpolating between the calibration points become of prime importance for interpolation accuracies approaching 0.1 K [ASTM (1981)]. For lower accuracies comparatively simple methods of calibration will usually suffice (comparison with a standard thermometer in an isothermal environment).

The errors in calibration are of two sorts: those influencing the observations at the calibration points and those arising from the interpolation between the calibration points. The influence of the first can be reduced by use of well-designed equipment and careful techniques. The recommended method to reduce the second error is to fit the differences between the observed calibration values and the values obtained from standard reference tables, i.e. the deviation of the real characteristics of the thermocouple from the nominal one. In order to determine the mean deviation curve the application of least-squares fitting is useful, but in several cases a graphical interpolation method will be sufficient (Sec. 9.5).

Typical accuracies to be expected with the various thermocouples if calibrated using fixed points are given in Table 18.6, and when calibrated by comparison techniques are given in Table 18.7. The interpolation formulae used to generate the standard reference tables are given in Appendix F. No such formulae have *yet* been internationally agreed upon for the tungsten-rhenium types.

Table 18.6: Accuracies Attainable with Thermocouples using Fixed Point Techniques [ASTM (1981)].

Type	Temperature range (°C)	Calibration points	Calibration uncertainty at observed points (K)	total uncertainty of interpolated values (K)
S or R	0... 1100	Zn,Sb,Ag,Au	0.2	0.3
S or R	0...1100	Sn,Zn,Al,Ag,Cu	0.2	0.3
B	600...1100	Al,Ag,Au	0.2	0.5
E	0... 870	Sn, Zn, Al	0.2	0.5
J	0...760	Sn,Zn,Al	0.2	1.0
K	0...1100	Sn,Zn,Al,Ag,Cu	0.2	1.0
N	0... 1100	Sn, Zn, Al, Ag, Cu	0.2	1.0
W/Re	1000 ...	Au, Ni, Pd, Pt, Rh	0.5 ...	2.7 ...
	...2000		...5.0	...7.0

Table 18.7: Accuracies Attainable with Thermocouples using Comparison Techniques in Laboratory Furnaces [ASTM (1981)].

Type	Temperature range (°C)	Calibration points	Calibration uncertainty at observed points (K)	total uncertainty of interpolated values (K)
S or R	0...1100	every 100 K	0.3	0.5
B	600... 1100	" " "	0.3	0.5
E	0... 870	" " "	0.5	0.5
J	0... 760	" " "	0.5	1.0
K	0...1100	" " "	0.5	1.0
N	0...	" " "	0.5	1.0

19. Thermometry in Magnetic Fields

Most thermometers change their calibration in the presence of a magnetic field. In this chapter we discuss by how much traceability to the original calibration can be affected and how accuracy can be preserved for the different types. The discussion will include types of thermometers from both Parts 1 and 2, as the problem of ensuring a traceable temperature value in the presence of a magnetic field is not restricted to industrial applications. It is very important in cryogenics and in thermophysical-property measurements at the highest possible accuracy. Some types of thermometer specifically developed for use in a magnetic field will also be briefly considered.

The general problem has two possible solutions: a) use of a thermometer insensitive, within the required accuracy, to magnetic fields up to the maximum strength likely to be encountered; b) accurate correction of the thermometer reading for the shift due to the magnetic field. The latter solution is made difficult by possible anisotropy of the magnetic-field sensitivity of the thermometer, or of the magnetic field itself, and, in addition, needs the local magnetic field strength to be known with sufficient accuracy. The first solution is almost mandatory for thermometers used in temperature regulation; otherwise, change of the magnetic field value would result in a change of the regulated temperature. In addition, for thermometers that exhibit a high magnetic-field shift, the sensitivity to temperature changes may be dramatically lower [Pavese and Cresto (1984)], resulting in a much worse regulation. Table 19.1 collects the data available on the magnetically-induced temperature errors of thermometers. It should be cross-checked with Table 1.1 which gives the quality of the thermometers with regard to general reproducibility.

All of the thermometers for use at cryogenic temperatures included in Part 1 exhibit substantial sensitivity to a magnetic field.

Although platinum resistance thermometer calibrations change considerably in magnetic fields [Brandt and Aubin (1988)], the magnetic error can be well corrected for because it is only slightly orientation dependent and varies little from thermometer to thermometer since the thermometers are well characterized by their values of W(H_20 t.p.). Below the liquid-nitrogen temperature range, however, the correction becomes too large to allow the best accuracy in fields larger than a few teslas. If lesser accuracy is acceptable the range of use of the correction may be extended to lower temperatures and higher fields, but the error then becomes dependent on the value of W(H_20 t.p.). The correction is lower for IPRTs with W(H_20 t.p.) = 1.385 and can be used to 30 K at 19 T, or to 20 K at 5 T. A correction must always be applied, even for uncertainties of the order of ± 0.1 K. It should

Table 19.1: Magnetic Field-Dependent Temperature Errors for Low Temperature Thermometers

Magnitude of relative temperature
error $|\Delta T|/T$ (%) for values of B

Type of Sensor	T(K)	Magnetic Flux Density, B					Notes	References
		1 T	2.5 T	8 T	14 T	19 T		
Carbon radio resistors							a	Sample and Rubin (1977)
Allen-Bradley (2.7, 3.9, 5.6, 10 C)	0.5		2-4	5-13	7-20			
	1.0		2-4	6-15	9-25			
	2.5		1-5	6-18	10-30			
	4.2		1-5	5-20	10-35			
Allen-Bradley (47, 100, 220 Ω)	4.2		<1	5	10		a	ibidem
	10		<1	3	5			
	20		<1	1	2			
Speer, Grade 1002 (100, 220, 470 C)	0.5		0-2	0-1	0-6		b	ibidem
	1.0		1-2	2-4	3-9			
	2.5		3-5	1-4	7-14			
	4.2		4-9	2-5	4-13			
Matsushita (68, 200, 510 C)	1.5		1-2	10-15			c	ibidem
	2.1		1	10-15				
	4.2		2-3	4-8				
KVM carbon composite resistors	2.4		3	8 (5T)			d	Astrov et al. (1977)
	4.2		1.5	5 "				
	10		0.4	1.4 "				
	20		0.1	0.4 "				
	80		<0.01	<0.01 "				
Carbon-Glass Resistors	2.2		0.1	1.5	3	4	e	Rubin and Brandt (1986)
	4.2		0.5	2	5	7		
	10		0.2	1.1	3	4		
	20		<0.01	0.02	0.03	0.13		
	45		0.07	0.5	1.3	2		
	88		0.06	0.5	1.3	2		
	190		0.04	0.3	1.0	1.7		
	310		<0.01	0.2	0.6	1.1		
Thermistors	4.2		<0.05	1	3		f	Sample and Rubin (1977)
	10		<0.05	0.3	1			
	20		<0.05	0.1	0.5			
	40		<0.05	0.1	0.5			
	60		<0.05	0.1	0.3			
Germanium Resistors	2.0		8-10	60			g	ibidem
	4.2		5-20	30-55	60-70			
	10		4-15	25-60	60-75			
	20		3-20	15-35	50-80			
	70		3-10	15-30	25-50			
Germanium Resistors TSG-2	4.2		30	120			g	Astrov et al. (1977)
	20		2.5	6				
Specially doped Ge resistors KG	4.2		<0.2.	0.5 (6T)			h	ibidem; Matacotta et al. (1984)
	10		<0.2	<0.5 "				
	20		<0.5	2-3 "				
	30		<0.5	5 "				
	80		0.15	0.5 "				
Platinum Resistors	10		100|	250|	|	|	i	Pavese & Cresto (1984); Neuringer et al. (1971); Rubin & Brandt (1986)
	20		2-8|20	25|100	250|	|		
	40		0.5|<1	3|5	6|10	9|		
	66		0.1|<0.5	0.8| 2	2| 5	4|		
	87		0.04|<0.5	0.4| 1	1| 2	2|		
	110		0.02|	0.2|	0.6|	1|		
	190		<0.01|	0.06|	0.2|	0.3|		
	300		<0.01|	0.02|	0.07|	0.13|		
			(a) (b)	(a) (b)	(a) (b)	(a) (b)		

Type of Sensor	T(K)		Magnetic Flux Density, B				Notes	References
		1 T	2.5 T	8 T	14 T	19 T		
Rhodium-Iron resistors	2.0		22				j	Pavese & Cresto (1984); Rusby (1972); Rubin & Brandt (1986)
	4.2	2	11	40(6T)				
	20	0.8	4	10(5T)				
	40		1.5	12	30	40		
	66		0.3	2.5	6	9		
	87		0.2	1.5	4	6		
	110		0.1	0.9	2.4			
	190		0.03	0.3	0.9			
	300		<0.01	0.1	0.4			
Platinum-Cobalt resistors	2	25	30				k	Shiratori et al. (1982); Pavese & Cresto (1984)
	4.2	8	3	40 (5T)				
	10	1	<0.1	12 "				
	20	0.2	1	3.5 "				
	30	0.2	0.3	1.5 "				
Cryogenic linear resistance sensor	4	20	250				l	McDonald (1973)
	10	17	100					
	20	8	50					
	30	5	30					
KELTIP resistors (Au/Mn)	4.2		4	13	20		m	Rubin & Brandt (1986)
	40		2	30	70	110		
	66		0.4	4	12	20		
	87		0.15	1.5	5	10		
	110		0.03	0.25	1			
	190		0.02	0.2	0.5			
	300		0.02	0.1	0.4			
SrTi03 capacitors	2.2		<0.02	<0.02	0.02		n	ibidem
	4.2		<0.01	<0.01	0.01			
	20		<0.05	<0.05	<0.05			
	50		<0.05	<0.05	<0.05			
	88		<0.01	<0.01	<0.01	<0.01		
	110		<0.01	<0.01	<0.01	<0.01		
	190		<0.01	<0.01	<0.01	<0.01		
Si Diodes	4.2		75				o	Sample & Rubin (1977)
	10		20	30	50			
	20		4	7	10			
	30		3	4	5			
	77		0.2	0.5	0.5			
GaAs Diodes	4.2		2-3	30-50	100-250		p	ibidem
	10		1.5-2	25-40	75-200			
	20		0.5-1	20-30	60-150			
	40		0.2-0.3	4-6	15-30			
	80		0.1-0.2	0.5-1	2-5			
Au + 0.07 % Fe/ Chromel P thermocouple	5		2	10	15		q	Sample et al. (1974)
	10		3	20	30			
	20		2	15	20			
	45		1	5	7			
	100		0.1	0.8				
Chromel P/Constantan thermocouple (Type E)	10		1	3	7		r	ibidem
	20		<1	2	4			
	45		<1	<1	2			
Cu + 0.01 % Fe/Cu thermocouple	5		2	3.5 (5T)			q,r	Astrov et al. (1977)
	10		0.8	2 "				
	20		0.6	1.5 "				
	50		0.3	0.6 "				
Vapour pressure thermometers	no intrinsic error except with 0_2						s	
Helium gas thermometer	no intrinsic error						s	Van Degrift et al. (1980)

Notes to Table 19.1

a) $\Delta R/R_0$ monotonic in B and T, and always positive. Higher nominal resistance units have smaller $|\Delta T|$. Good agreement between similar units.

b) $\Delta R/R_0$ both positive and negative with complicated B and T dependence. Variations between similar units.

c) $\Delta R/R_0$ approximately independent of nominal resistance value. Higher resistance units have smaller $|\Delta T|$.

d) Specifically developed for use as a thermometer.

e) Behavior similar to Allen-Bradley resistors. Negative $\Delta R/R_0$ below -20 K.

f) Very low magnetoresistance, but few types useful or available below 77 K.

g) Not recommended except at very low fields because of large, and strongly orientation dependent, $|\Delta T|$.

h) Orientation dependent only above 20 K. Complicated behaviour below 10 K makes corrections difficult.

i) Some orientation dependence. Useful at all B only for T > 30 K. Magnetoresistance depends on W(H_20 t.p.) value (a) 1.385 (b) 1.3914.

j) Little orientation dependence. Useful only at low fields.

k) Little orientation dependence. ΔR negative below about 12 K and 2.5 T. Useful only below 3T, where it is the best high-stability thermometer.

l) Linear foil-type thermometer; magnetoresistance is negative and extremely high above 1 T.

m) Errors are negative for $T \leq 140$ K.

n) Maximum in capacitance versus temperature near 70 K, so that sensitivity is very low between about 60 K and 80 K.

o) Strongly orientation dependent; values are given for junction parallel to B.

p) Orientation dependent. Smaller values of $|\Delta T|/T$ apply to diode junction parallel to B.

q) Gradients in the magnetic field crossed by the wires can cause higher errors.

r) Different % Fe gives rise to larger errors.

s) With use of non-magnetic bulb and connecting tube.

be noted that these lower temperature limits are approaching the overall low temperature limit for optimum advantage in using PRTs.

For temperatures below about 20 K, rhodium-iron resistance thermometers are in general preferred to PRTs. The sensitivity of their calibrations to magnetic fields is also much less marked than that of SPRTs below 30 K, but is comparable to it above. Anisotropy, correctability, and interchangeability of units are also comparable. The corrections become especially significant below 10 K, even for low fields (1 T). It is next to impossible to trace back to the zero-field calibration with high accuracy, but the correction must be applied even for low accuracy and low fields (1 T). At 4.2 K the change in resistance divided by the zero-field resistance is roughly proportional to the square of the magnetic flux density [Rusby (1972)]. The dependence of the calibration on temperature and magnetic flux density is shown in Fig. 19.1.

The platinum 0.5% cobalt resistance thermometer shows a much better behaviour in magnetic fields than does the rhodium-iron thermometer, while anisotropy, correctability, and interchangeability of units are comparable with those of SPRTs. The sensitivity to magnetic fields is smaller than for rhodium-iron, though it has a more complicated behaviour, as shown in Fig. 19.2; in fact, there is a change of sign of magnetoresistivity below about 14 K and 2.5 T. At 30 K the sensitivity to magnetic fields up to 6 T is less than one-third of that for PRTs. For low levels of accuracy, this thermometer can be used *without* corrections, within an uncertainty of ± 0.2 K, in the region above 8 K and below 3 T. Should the cobalt content of the alloy be reduced to about 0.3 atomic %, the low-temperature limit would become 4 K, with only a small change in the magnetic field limit (2.5 T) [Pavese and Cresto (1984)].

Germanium resistance thermometers have a high sensitivity to magnetic fields, even higher than that of PRTs above 10 K, and comparable with that of rhodium-iron below 10 K. Correctability is good, but the corrections can be made only in situ because they are strongly orientation-dependent (for best accuracy the sensing element of the thermometer should be parallel to the magnetic field). Consequently, the correction also applies only to a specific unit, with no interchangeability, even for low accuracy. Because of this, germanium thermometers are all but useless at all temperatures in the presence of a strong magnetic field. $\Delta R/R$ increases more or less proportionally with B^2 and decreases monotonically as T increases (see Fig. 19.3). Table 19.1 gives values of the error that may be expected in various magnetic fields. Research has been undertaken in the USSR [Astrov et al. (1977), Zinov'eva et al. (1979)] and, more recently, in China [Fu Chiying et al. (1986)] to try to overcome the high magnetosensitivity of germanium thermometers. At present only the USSR type is available; it is a multiply-doped germanium resistor (type

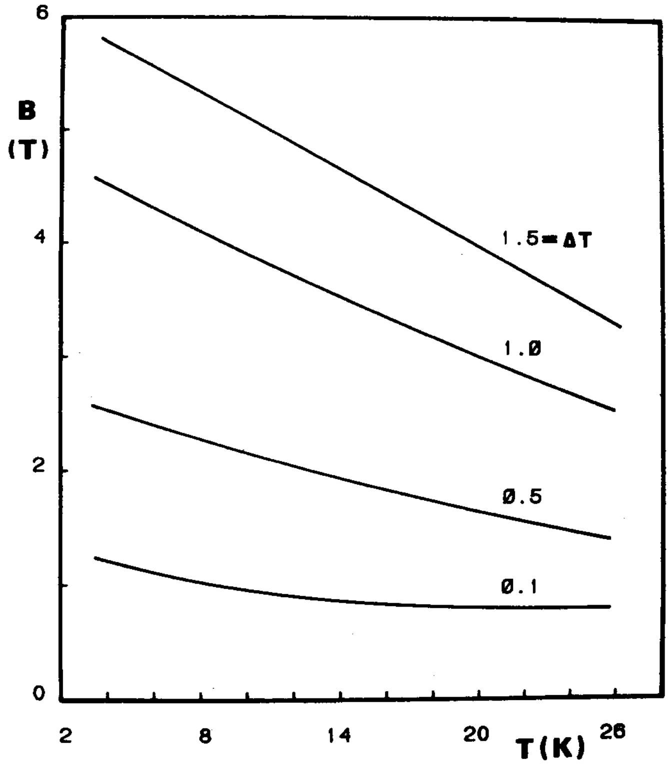

Fig. 19.1: The change in calibration (ΔT(mK)) of rhodium 0.5% iron as a function of temperature and magnetic flux density [Pavese and Cresto (1984)].

KG) which shows a much lower sensitivity to magnetic fields than any other of the above thermometers without its stability to thermal cycling being very much lower than that of regular germanium thermometers [Besley et al. (1986)]. The main problem is correctability, as the behaviour of the correction versus temperature is complicated; on the other hand, the thermometers are much less orientation-dependent than ordinary germanium thermometers below 20 K.

Among other semiconducting resistance thermometers, carbon resistors are known to have relatively small and reproducible magnetic field dependence [Sample and Rubin (1977), Sample and Neuringer (1974), Sample et al. (1974), Sanchez et al. (1977), Saito and Sa to (1975), Neuringer and Rubin (1972), Alms et al. (1979)] (see Table 19.1 for the relative errors in temperature that may be expected). For temperatures below about 50 mK typical errors in temperature incurred by neglect of the magnetoresistance are shown in Fig. 19.4.

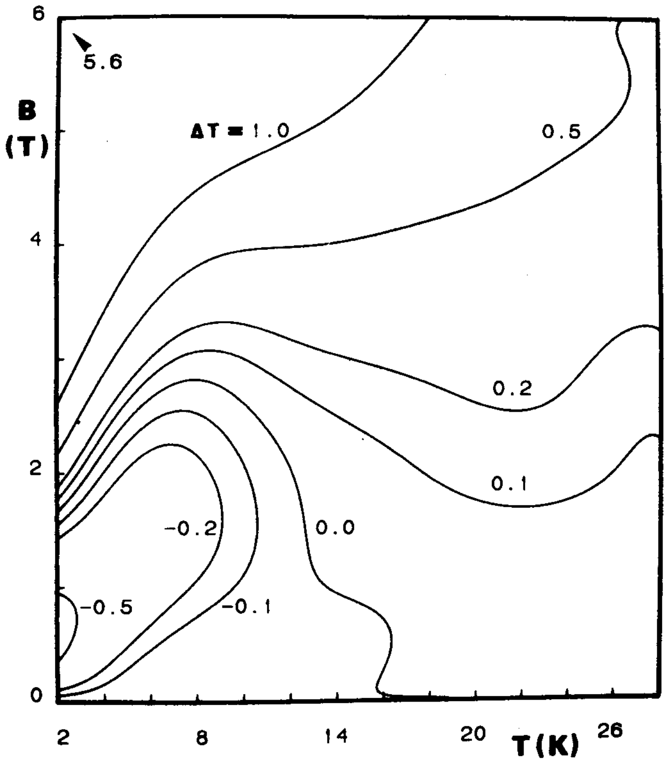

Fig. 19.2: The change in calibration (ΔT(mK)) of platinum 0.5% cobalt as a function of temperature and magentic flux density [after Pavese and Cresto (1984)].

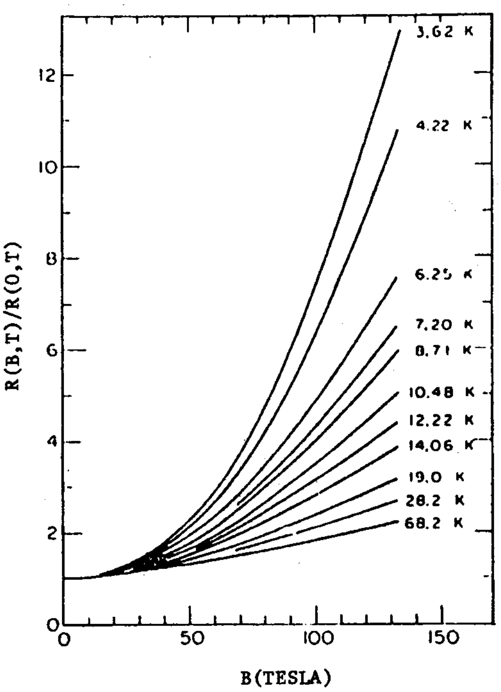

Fig. 19.3: Ratio of a CryoCal germanium thermometer resistance in a magnetic field to its resistance in the absence of a field when the thermometer current is perpendicular to the magnetic field [after Neuringer and Rubin (1972)].

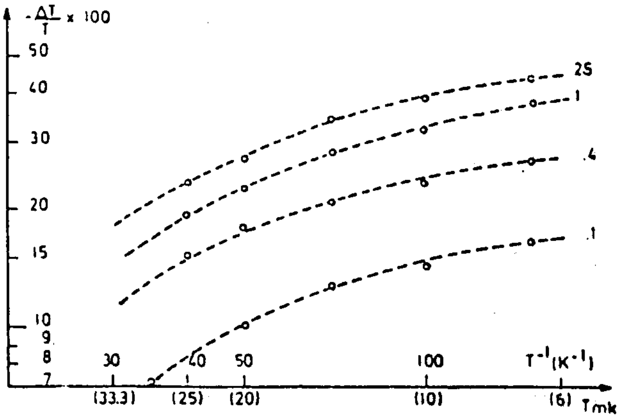

Fig. 19.4: Error in the temperature for carbon thermometers when magnetoresistance effects are neglected at the magnetic flux densities (teslas) indicated [Sanchez et al. (1977)].

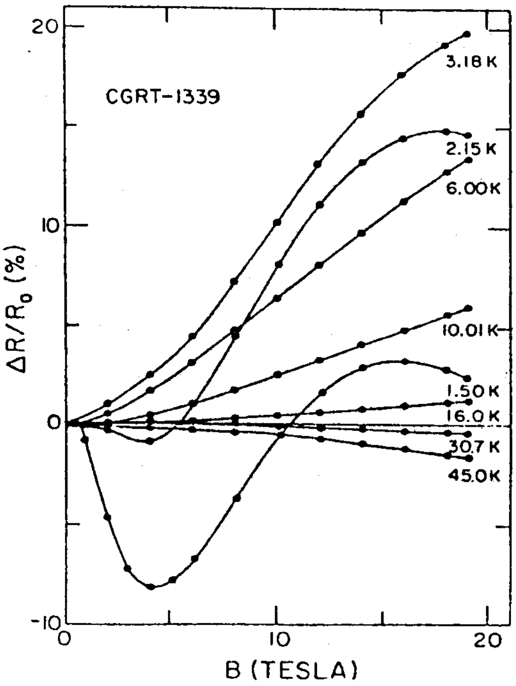

Fig. 19.5: Longitudinal magnetoresistance versus magnetic field for a typical carbon-glass thermometer [Sample et al. (1982)].

Carbon-glass thermometers (Chapter 12) were developed in an attempt to combine the low sensitivity of carbon resistance thermometers to magnetic fields with an improved stability. Carbon-glass shows good correctability (to within 10 mK [Sample et al. (1982)]) and little orientation dependence (equivalent temperature change less than 0.3% at 19 T from parallel to perpendicular position, between 4.2 K and 77 K). On the other hand, interchangeability is bad, as with germanium thermometers. The magnetoresistance of carbon-glass is much smaller (Fig. 19.5) than that of the previous types up to the highest field strengths but the same level of stability is never reached. In particular, carbon-glass thermometers have been reported to drift severely after a few years use in fields up to 12 T [Couach et at. (1982)].

Amongst the non-resistive thermometers used in cryogenics, none shows a reproducibility comparable with those of the resistance types. The magnetoresistance of diode thermometers (Chapter 14) is strongly orientation-dependent in magnetic fields. Correctability and interchangeability are poor. Some types of thermocouple have limited magnetic shift (see Table 19.1) but, apart from the intrinsic low accuracy, correction is almost impossible as the error develops along the *whole* length of the wire immersed in the magnetic field and stray emfs develop especially where field gradients are strong (there is no effect at all if the magnetic field region is isothermal). A capacitive thermometer is impervious to magnetic-field errors but the capacitance of the usual material ($SrTiO_3$) is known to be unstable on thermal cycling and dependent on charge effects and on the applied voltage. In addition, the capacitance versus temperature characteristic is not monotonic below 100 K. Some new ceramic materials may avoid these drawbacks [Chen Pufen and Li Jinwan (1986)].

At present none of these non-resistive thermometers should be considered as reliable storage for a traceable temperature scale, whether a magnetic field is involved or not. It is perhaps worth noting that two non-electric thermometers are best-suited as standards for approximating the temperature scales in the presence of a magnetic field: vapour pressure thermometers (except when using oxygen, which is paramagnetic) and gas thermometers. They are intrinsically immune to magnetic errors. They suffer the drawbacks, of course, of large size and complicated measurement requirements.

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Appendix A

Differences between the ITS-90 and the EPT -76, and between the ITS-90 and the IPTS-68.

$(T_{90} – T_{76})$/mK

T_{90}/K	0	1	2	3	4	5	6	7	8	9
0						-0,1	-0,2	-0,3	-0,4	-0,5
10	-0,6	-0,7	-0.8	-1,0	-1,1	-1,3	-1,4	-1,6	-1,8	-2,0
20	-2,2	-2,5	-2,7	-3,0	-3,2	-3,5	-3,8	-4,1		

$(T_{90} – T_{68})$/K

T_{90}/K	0	1	2	3	4	5	6	7	8	9
10					-0,006	-0,003	-0,004	-0 006	-0,008	-0,009
20	-0,009	-0,008	-0,007	-0,007	-0,006	-0,005	-0,004	-0,004	-0,005	-0,006
30	-0,006	-0,007	-0,008	-0,008	-0,008	-0,007	-0,007	-0,007	-0,006	-0,006
40	-0,006	-0,006	-0,006	-0,006	-0,006	-0,007	-0,007	-0,007	-0,006	-0,006
50	-0,006	-0,005	-0,005	-0,004	-0,003	-0,092	-0,001	0,000	0,001	0,002
60	0,003	0,003	0,004	0,004	0,005	0,005	0,006	0,006	0,007	0,007
70	0,007	0,007	0,007	0,007	0,007	0,008	0,008	0,008	0,008	0,008
80	0,008	0,008	0,008	0,008	0,008	0,008	0,008	0,008	0,008	0,008
90	0,008	0,008	0,008	0,008	0,008	0,008	0,008	0,009	0,009	0,009

T_{90}/K	0	10	20	30	40	50	60	70	80	90
100	0,009	0,011	0,013	0,014	0,014	0,014	0,014	0,013	0,012	0,012
200	0,011	0,010	0,009	0,008	0,007	0,005	0,003	0,001		

$(t_{90} – t_{68})$/°C

t_{90}/°C	0	-10	-20	-30	-40	-50	-60	-70	-80	-90
-100	0,013	0,013	0,014	0,014	0,014	0,013	0,012	0,010	0,008	0,008
0	0,000	0,002	0,004	0,006	0,008	0,009	0,010	0,011	0,012	0,012

t_{90}/°C	0	10	20	30	40	50	60	70	80	90
0	0,000	-0,002	-0,005	-0,007	-0,010	-0,013	-0,016	-0,018	-0,021	-0,024
100	-0,026	-0,028	-0,030	-0,032	-0,034	-0,036	-0,037	-0,038	-0,039	-0,039
200	-0,040	-0,040	-0,040	-0,040	-0,040	-0,040	-0,040	-0,039	-0,039	-0,039
300	-0,039	-0,039	-0,039	-0,040	-0,040	-0,041	-0,042	-0,043	-0,045	-0,046
400	-0,048	-0,051	-0,053	-0,056	-0,059	-0,062	-0,065	-0,068	-0,072	-0,075
500	-0,079	-0,083	-0,087	-0,090	-0,094	-0,098	-0,101	-0,105	-0,108	-0,112
600	-0,115	-0,118	-0,122	-0,125	-0,08	-0,03	0,02	0.06	0,11	0,16
700	0,20	0,24	0,28	0,31	0,33	0,35	0,36	0,36	0,36	0,35
800	0,34	0,32	0,29	0,25	0,22	0,18	0,14	0,10	0,06	0,03
900	-0,01	-0,03	-0,06	-0,08	-0,10	-0,12	-0,14	-0,16	-0,17	-0,18
1000	-0,19	-0,20	-0,21	-0,22	-0,23	-0,24	-0,25	-0,25	-0,26	-0,26

t_{90}/°C	0	100	200	300	400	500	600	700	800	900
1000		-0,26	-0,30	-0,35	-0,39	-0,44	-0,49	-0,54	-0,60	-0,66
2000	-0,72	-0,79	-0,85	-0,93	-1,00	-1,07	-1,15	-1,24	-1,32	-1,41
3000	-1,50	-1,59	-1,69	-1,78	-1,89	-1,99	-2,10	-2,21	-2,32	-2,43

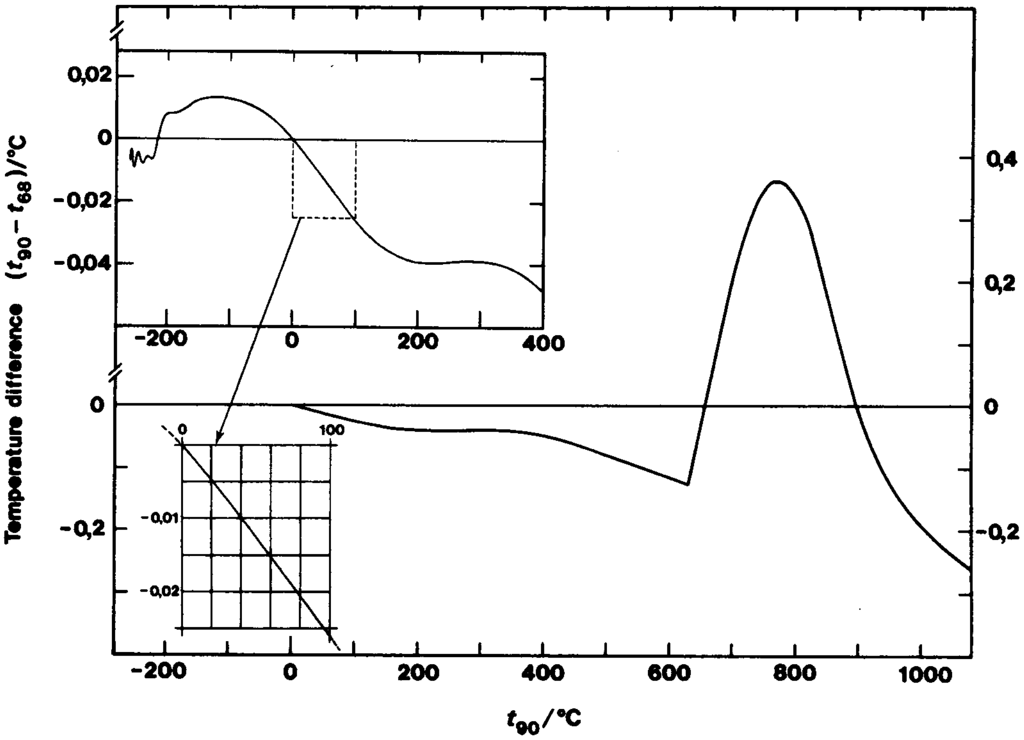

Fig. A.1: Differences between the ITS-90 and the IPTS-68.

The differences (t_{90} - t_{68}) in the temperature range -200 °C to 630 °C in the preceding table can be reproduced to within 1.5 mK below 0 °C and 1 mK above 0 °C by the following polynomial:

$$(t_{90}-t_{68})/°C=\sum_{i=1}^{8} a_i\,(t/630\,°C)^i \qquad (A1)$$

The values of the coefficients a_i are:

a_1 = -0.148 759

a_2 = -0.267 408

a_3 = 1.080 760

a_4 = 1.269 056

a_5 = -4.089 591

a_6 = -1.871 251

a_7 = 7.438 081

a_8 = -3.536 296.

Appendix B

Addresses of National Standards Laboratories

Amt für Standardisierung
Messwesen und Warenprüfung
Fürstenwalder Damm 388
Postfach 1542
Berlin 1162, DDR
Telex: 112630 ASMW DD

Bureau International des Poids et Mesures
Pavilion de Breteuil
92310 Sèvres, France
Telex: 201067 BIPM F
Fax: (33)(1) 45 342021

Institut National de Metrologie
C.N.A.M.
292, rue St. Martin
75141 Paris 03, France
Telex: 240247 CNAM F
Fax: (33) (1) 42 719329

Istituto di Metrologia "G. Colonnetti"
Strada delle Cacce 73
10135 Torino, Italy
Telex: 212209 IMGCTO I
Fax: (39)(11) 346-761

Kamerlingh Onnes Laboratorium
Rijkuniversiteit te Leiden
Nieuwsteeg 18 - Postbus 9506
2300 RA Leiden
The Netherlands
Telex: 39058 Astro NL
Fax: (31) (71) 275819

National Institute of Standards and Technology
Center for Chemical Technology
Chemical Process Metrology Division
Gaithersburg, Maryland 20899, U.S.A.
Telex: 0023-197674 NBS UT
Fax: (301) 948-4087

National Institute of Metrology
P.O. Box 2112 Beijing
People's Republic of China
Telex: 210028 NIM CN
Fax: (86) (1) 421-8703

National Measurement Laboratory
C.S.I.R.O.
Division of Applied Physics
P.O. Box 218
Lindfield NSW 2070, Australia
Telex: 26296 NATMEASURE SYDNEY
Fax: (61) (2) 467-1902

National Physical Laboratory
Quantum Metrology Division
Teddington, Middlesex
TW11 OLW, England
Telex: 262344
Fax: (44)(81) 943-2155

National Research Council of Canada
Laboratory for Basic Standards
Division of Physics
Ottawa, Ontario, K1A OR6, Canada
Telex: 053-4322
Fax: (613) 952-

National Research Laboratory of Metrology
1-4, 1-Chome, Umezono, Tsukuba
Ibaraki 305, Japan
Telex: 0072-3652570 AIST J
Fax: (81) (298) 54 4135

Nederlands Meetinstituut nv
Schoemakerstraat 97
2628 VJ Dekft, Postbus 654
2600 AR Delft
The Netherlands
Telex: 38373 IJKWZ NL
Fax: (31)(15) 612 971

Physikalish- Technische Bundesanstalt
Bundesallee 100
3300 Braunschweig
Germany
Telex: 952822 PTB D
Fax: (49)(531) 592-7614

Physikalish- Technische Bundesanstalt
Abbestrasse 2-12
D-1000 Berlin 10
Federal Republic of Germany
Fax: (49)(30) 34 81 490

VNIIFTRI Mendeleev
Moscow Region 141 570
USSR
Telex: 411 038 KCSVSU

VNIIM
19, Moskovsky Prospekt
198005 Leningrad
USSR

Appendix C

Some Suppliers of Various Cryogenic Thermometers

Germanium:

CryoCal, Inc.
2303-2W Wycliff St.
St. Paul, Minnesota 55114
U.S.A.

Lake Shore Cryotronics, Inc.
64 East Walnut St.
Westerville, Ohio 43081
U.S.A.

Scientific Instruments, Inc.
1101 25th St.
West Palm Beach, Florida 33407
U.S.A.

All-Union Research Institute for Physical,
Technical, and Radio-Technical Measurement
(VNIIFTRI)
USSR State Committee for Standards
9 Leninsky Prospekt
117049 Moscow M-49
USSR

Rhodium-Iron:

All-Union Research institute for Physical,
Technical, and Radio-Technical Measurement
(VNIIFTRI)
USSR State Committee for Standards
(see entry for germanium)

Cryogenic Consultants Ltd.
The Metrostore Building
231 The Vale
London W3 70S
U.K.

H. Tinsley and Co. Ltd.
Standards House
61 Imperial Way
Croydon CRO 4RR
U.K.

Oxford Instruments Ltd.
Eynsham
Oxford OX8 1 TL, U.K.

Carbon-Glass: Lake Shore Cryotronics, Inc.
(see entry for germanium)

Platinum-Cobalt: Chino Works, Ltd.
Sunshine 60, 19 Fl.
3-1-1 Higashi-ikebukuro, Toshina-ku
Tokyo 170
Japan.

Silicon Diodes: Institute of Cryogenics
University of Southampton
Southampton S09 SNH
U.K.

Appendix D

Calculations Relative to the Filling of a Vapour Pressure Thermometer

Notations

T_a - minimum temperature to be attained. At this temperature the bulb is completely filled with liquid.

T_b - maximum temperature to be attained. The bulb is empty of liquid except for a small quantity v which remains for security and which can be neglected.

Π_a, Π_b - the corresponding saturated vapour pressures.

T_f - temperature used for condensation when filling.

Π_f - corresponding saturated vapour pressure.

T_0 - room temperature.

P_0 - filling pressure at T_0.

T_m - average temperature along the capillary, equal to $\frac{T_0 + T_f}{2}, \frac{T_0 + T_a}{2}$, or $\frac{T_0 + T_b}{2}$ as the case may be.

V_b - the bulb volume partially filled with a volume v_c of liquid.

V_c - volume of the capillary.

V_T - volume of the reservoir.

V_0 - totality of volumes of connectors and manometer that remain at room temperature.

M - molar mass of the pure filling substance. N - number of moles to be introduced.

n_1 - number of moles of liquid = $\frac{v_L}{M} \cdot \rho$

n_2 - number of moles of vapour in the bulb = $\frac{P(V_b - v_L)}{RT}$ (p, pressure in the bulb, = p_a, p_b, p_M, or p_0).

ρ_a, ρ_b - density of liquid at temperature T_a, T_b respectively.

n_3 - number of moles in the capillary = $\frac{PV_c}{RT_m}$

n_4 - number of moles in the various volumes at room temperature = $\frac{PV_0}{RT_0}$

n_5 - number of moles in the volume of the reservoir = $\frac{PV_T}{RT_0}$

N - total number of moles.

We assume that the vapour phase obeys the perfect gas law.

V_T being generally much larger than the other volumes, we can make some approximations:

1. *At the lowest temperature,* T_a, we have $v_L \sim V_b$

$$n_1 = \frac{V_b}{M}\rho_a$$

$n_2 = 0$; $\qquad n_3 = \frac{2\Pi_a V_c}{R(T_0 + T_a)}$; $\qquad n_4 = \frac{\Pi_a V_0}{RT_0}$

V_T not connected; $n_5 = 0$

The total number of moles, N, must be ≤ n1 + n3 + n4

$$N \le \frac{\Pi_a}{RT_0}\left[\frac{2V_c T_0}{T_0 + T_a} + V_0\right] + \frac{V_b}{M}\cdot\rho_a \tag{D1}$$

2. *At the highest temperature,* T_b, there is only a small volume v of liquid in the bulb

(v - 0).

$n_1 = \frac{v}{M}\rho_b$ $\qquad n_2 = \frac{Vb - v}{RT_b}\Pi_b$; $\qquad n_3 = \frac{2\Pi_b V_c}{R(T_0 + T_b)}$;

$n_4 = \frac{\Pi b V_0}{RT_0}$; $\qquad n_5 = 0$.

The total number of moles, N, must be

$$N \ge \frac{v\rho_b}{M} + \frac{\Pi_b}{RT_0}\left[\frac{T_0}{T_b}(V_b - v) + V_0 + \frac{2V_c T_0}{T_0 + T_b}\right] \tag{D2}$$

3. *From relations (D1) and (D2),* we obtain

$$\rho_b\frac{v}{M} + \frac{\Pi_b}{RT_0}\left[\frac{T_0}{T_b}(V_b - v) + V_0 + \frac{2V_c T_0}{T_0 + T_b}\right] \le \frac{\Pi_a}{RT_0}\left[\frac{2V_c T_0}{T_0 + T_a} + V_0\right] + \frac{v_b\rho_a}{M} \quad ,$$

or

$$v_b\left[\frac{\rho_a}{M} - \frac{\Pi_b}{RT_b}\right] \ge \frac{V_0}{RT_0}\left[\Pi_b - \Pi_a\right] + v\left[\frac{\rho_b}{M} - \frac{\Pi_b}{RT_b}\right] + \frac{2V_c}{R}\left[\frac{\Pi_b}{T_0 + T_b} - \frac{\Pi_a}{T_0 + T_a}\right] \quad . \tag{D3}$$

This expression determines the volume V_b of the bulb (to a first approximation, we can neglect the last two terms and overestimate the value).

4. The calculation of the number of moles to introduce:

Knowing V_b, we can determine the number N = n1 + n2 + n3 + n4 of moles to introduce (staying within the limits where inequalities (D1) and (D2) are applicable).

At the time of filling, all of the moles are in the vapour and it is necessary to predict the reservoir volume V_T. P_0 must be chosen so that at T_0 the pure substance is all gaseous.

At the condensation pressure, Π_f. and just before isolating the thermometer, there remains in the reservoir n_5 moles, where $n_5 = \frac{\Pi_f V_T}{RT_0}$.

Then N' = N + n_5 moles of pure substance must be introduced. At pressure P_0 and temperature T_0 these N' moles occupy a total volume $V = V_b + V_c + V_0 + V_T = \frac{N'RT_0}{P_0}$, from which the following equation allows the determination of the necessary volume V_T, taking account of the chosen pressure P_0:

$$V_T\left[1-\frac{\Pi_f}{P_0}\right]=\frac{NRT_0}{P_0}-\left(V_b+V_c+V_0\right) \quad . \qquad \text{(D 4)}$$

Appendix E

Calculation of the Aerostatic Pressure Correction
for a Vapour Pressure Thermometer

The problem is to know the distribution of temperatures along the capillary. By neglecting the contribution by radiation and by conduction across the vapour, we can write:

$$\Delta L_i = \frac{1}{\phi}\int_{T_{i-1}}^{T_i} k(T)\,dT \qquad \text{with} \qquad \phi = \frac{1}{L_n}\int_{T_f}^{T_e} k(T)\,dT$$

where

ΔL_i is a vertical section of the capillary at temperature T between T_i and T_{i-1},

k (T) is the conductivity of the material of the capillary (stainless steel),

L_n is the total length of the capillary,

T_e and T_f are the temperatures of the hot and cold extremeties.

Knowing ΔL_i and the corresponding T_i, the pressure correction is

$$\Delta P = g\sum_{i=1}^{n} \rho_i \Delta L_i \quad ,$$

where g is the acceleration of gravity,

and ρ_i is the density of vapour at temperature T_i.

The temperature correction is calculated from the pressure correction and the sensitivity of the thermometer.

Appendix F

Interpolation Polynomials for Standard Thermocouple Reference Tables.*
All tables are for a reference temperature of 0 °C.

1. Interpolation polynomial for type T thermocouples

(E in mV, t_{68} in °C)

- temperature range from -270 °C to 0 °C:

$$E = \sum_{i=0}^{14} d_i \cdot t_{68}^i$$

where:

$d_0 = 0$;
$d_1 = 3.8740773840 \text{ X } 10^{-2}$;
$d_2 = 4.4123932482 \text{ X } 10^{-5}$;
$d_3 = 1.1405238498 \text{ x } 10^{-7}$;
$d_4 = 1.9974406568 \text{ x } 10^{-8}$;
$d_5 = 9.0445401187 \text{ X } 10^{-10}$;
$d_6 = 2.2766018504 \text{ x } 10^{-1\,1}$;
$d_7 = 3.6247409380 \text{ X } 10^{-13}$;
$d_8 = 3.8648924201 \text{ x } 10^{-15}$;
$d_9 = 2.8298678519 \text{ x } 10^{-17}$;
$d_{10} = 1.4281383349 \text{ X } 10^{-19}$;
$d_{11} = 4.8833254364 \text{ x } 10^{-22}$;
$d_{12} = 1.0803474683 \text{ x } 10^{-24}$;
$d_{13} = 1.3949291026 \text{ x } 10^{-27}$;
$d_{14} = 7.9795893156 \text{ x } 10^{-31}$;

- temperature range from 0 °C to 400 °C:

$$E = \sum_{i=0}^{8} d_i \cdot t_{68}^i$$

where:

$d_0 = 0$;
$d_1 = 3.8740773840 \text{ x } 10^{-2}$;
$d_2 = 3.3190198092 \text{ x } 10^{-5}$;
$d_3 = 2.0714183645 \text{ X } 10^{-7}$;
$d_4 = -2.1945834823 \text{ x } 10^{-9}$;
$d_5 = 1.1031900550 \text{ x } 10^{-11}$;
$d_6 = -3.0927581898 \text{ x } 10^{-14}$;
$d_7 = 4.5653337165 \text{ x } 10^{-17}$;
$d_8 = -2.7616878040 \text{ x } 10^{-20}$.

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* These polynomials relate to the IPTS-68. In due course they will be reformulated so as to relate to the ITS-90.

2. Interpolation polynomial for type J thermocouples
(E in mV, t_{68} in °C)

- temperature range from -200 °C to 760 °C:

$$E = \sum_{i=0}^{7} d_i \cdot t_{68}^i$$

where:

$d_0 = 0$;
$d_1 = 5.0372753027 \text{ X } 10^{-2}$;
$d_2 = 3.0425491284 \text{ X } 10^{-5}$;
$d_3 = -8.5669750464 \text{ X } 10^{-8}$;
$d_4 = 1.3348825735 \text{ X } 10^{-10}$;
$d_5 = -1.7022405966 \text{ X } 10^{-13}$;
$d_6 = 1.9416091001 \text{ X } 10^{-16}$;
$d_7 = -9.6391844859 \text{ X } 10^{-20}$;

- temperature range from 760 °C to 900 °C:

$$E = \sum_{i=0}^{5} d_i \cdot t_{68}^i$$

where:

$d_0 = 2.9721751778 \text{ X } 10^{2}$;
$d_1 = -1.5059632873 \text{ x } 10^{0}$;
$d_2 = 3.2051064215 \text{ X } 10^{-3}$;
$d_3 = -3.2210174230 \text{ X } 10^{-6}$;
$d_4 = 1.5949968788 \text{ X } 10^{-9}$;
$d_5 = -3.1239801752 \text{ X } 10^{-13}$.

3. Interpolation polynomial for type E thermocouples (E in mV, t_{68} in °C)

- temperature range from -270 °C to 0 °C:
-

$$E = \sum_{i=0}^{13} d_i \cdot t_{68}^i$$

where:

$d_0 = 0$;
$d_1 = 5.8695857799 \text{ X } 10^{-2}$;
$d_2 = 5.1667517705 \text{ X } 10^{-5}$;
$d_3 = -4.4652683347 \text{ X } 10^{-7}$;
$d_4 = -1.7346270905 \text{ X } 10^{-8}$;
$d_5 = -4.8719368427 \text{ X } 10^{-10}$;
$d_6 = -8.8896550447 \text{ X } 10^{-12}$;
$d_7 = -1.0930767375 \text{ x } 10^{-13}$;
$d_8 = -9.1784535039 \text{ X } 10^{-16}$;
$d_9 = -5.2575158521 \text{ X } 10^{-18}$;
$d_{10} = -2.0169601996 \text{ X } 10^{-20}$;
$d_{11} = -4.9502138782 \text{ X } 10^{-23}$;
$d_{12} = -7.0177980633 \text{ X } 10^{-26}$;
$d_{13} = -4.3671808488 \text{ X } 10^{-29}$;

- temperature range from 0 °C to 1000 °C:

$$E = \sum_{i=0}^{9} d_i \cdot t_{68}^{i}$$

where:

$d_0 = 0$;

$d_1 = 5.8695857799\ \mathrm{X}\ 10^{-2}$;

$d_2 = 4.3110945462\ \mathrm{X}\ 10^{-5}$;

$d_3 = 5.7220358202\ \mathrm{x}\ 10^{-8}$;

$d_4 = -5.4020668025\ \mathrm{x}\ 10^{-10}$;

$d_5 = 1.5425922111\ \mathrm{x}\ 10^{-12}$;

$d_6 = -2.4850089136\ \mathrm{x}\ 10^{-15}$;

$d_7 = 2.3389721459\ \mathrm{x}\ 10^{-18}$;

$d_8 = -1.1946296815\ \mathrm{X}\ 10^{-21}$;

$d_9 = 2.5561127497\ \mathrm{x}\ 10^{-25}$.

4. Interpolation polynomial for type K thermocouples
(E in mV,1Gs in °C)

- temperature range from -270 °C to 0 °C:

$$E = \sum_{i=0}^{10} d_i \cdot t_{68}^{i}$$

where:

$d_0 = 0$;

$d_1 = 3.9475433139\ \mathrm{X}\ 10^{-2}$;

$d_2 = 2.7465251138\ \mathrm{X}\ 10^{-5}$;

$d_3 = -1.6565406716\ \mathrm{x}\ 10^{-7}$;

$d_4 = -1.5190912392\ \mathrm{x}\ 10^{-9}$;

$d_5 = -2.4581670924\ \mathrm{x}\ 10^{-11}$;

$d_6 = -2.4757917816\ \mathrm{x}\ 10^{-13}$;

$d_7 = -1.5585276173\ \mathrm{x}\ 10^{-15}$;

$d_8 = -5.9729921255\ \mathrm{x}\ 10^{-18}$;

$d_9 = -1.2688801216\ \mathrm{x}\ 10^{-20}$;

$d_{10} = -1.1382797374\ \mathrm{x}\ 10^{-23}$;

- temperature range from 0 °C to 1372 °C:

$$E = \sum_{i=0}^{8} d_i \cdot t_{68}^{i} + 0.125 \exp\left[-\frac{1}{2}\left(\frac{t_{68} - 127}{65} \right)^2 \right]$$

where:

$d_0 = -1.8533063273\ \mathrm{X}\ 10^{-2}$;

$d_1 = 3.8918344612\ \mathrm{x}\ 10^{-2}$;

$d_2 = 1.6645154356\ \mathrm{x}\ 10^{-5}$;

$d_3 = -7.8702374448\ \mathrm{x}\ 10^{-8}$;

$d_4 = 2.2835785557\ \mathrm{x}\ 10^{-10}$;

$d_5 = -3.5700231258\ \mathrm{x}\ 10^{-13}$;

$d_6 = 2.9932909136\ \mathrm{x}\ 10^{-16}$;

$d_7 = -1.2849848798\ \mathrm{x}\ 10^{-19}$;

$d_8 = 2.2239974336\ \mathrm{x}\ 10^{-23}$.

5. Interpolation polynomial for type S thermocouples
(E in mV, t_{68} in °C)

- temperature range from -50 °C to 630.74 °C:
-

$$E = \sum_{i=0}^{6} a_i \cdot t_{68}^{i}$$

where: $a_0 = 0$; $a_4 = 2.8452164949 \times 10^{-11}$;
$a_1 = 5.3995782346 \times 10^{-3}$; $a_5 = -2.2440584544 \times 10^{-14}$;
$a_2 = 1.2519770000 \times 10^{-5}$; $a_6 = 8.5054166936 \times 10^{-18}$;
$a_3 = -2.2448217997 \times 10^{-8}$;

- temperature range from 630.74 °C to 1064.43 °C:

$$E = \sum_{i=0}^{2} g_i \cdot t_{68}^{i}$$

where: $g_0 = -2.9824481615 \times 10^{-1}$;
$g_1 = 8.2375528221 \times 10^{-3}$;
$g_2 = 1.6453909942 \text{ X } 10^{-6}$;

- temperature range from 1064.43 °C to 1665 °C:

$$E = \sum_{i=0}^{3} b_i \left(\frac{t_{68} - 1365}{300} \right)^{i}$$

where: $b_0 = 1.3943438677 \times 10^{1}$; $b_2 = -5.0281206140 \times 10^{-3}$;
$b_1 = 3.6398686553$; $b_3 = -4.2450546418 \times 10^{-2}$.

6. Interpolation polynomial for type B thermocouples
(E in mV, t_{68} in °C)

- temperature range from 0 °C to 1820 °C:

$$E = \sum_{i=0}^{8} d_i \cdot t_{68}^{i}$$

where:
d_0 = 0;
d_1 = -2.4674601620 x 10^{-4};
d_2 = 5.9102111169 x 10^{-6};
d_3 = -1.4307123430 x 10^{-9};
d_4 = 2.1509149750 x 10^{-12};
d_5 = -3.1757800720 x 10^{-15};
d_6 = 2.4010367459 x 10^{-18};
d_7 = -9.0928148159 x 10^{-22};
d_8 = 1.3299505137 x 10^{-25};

7. Interpolation polynomial for type N thermocouples
(E in mV, t_{68} in °C, wire diameter 1.6 mm)

- temperature range from 0 °C to 1300 °C: .

$$E = \sum_{i=0}^{9} d_i \cdot t_{68}^{i}$$

where:
d_0 = 0;
d_1 = 2.589 779 8582 x 10^{-2};
d_2 = 1.665 612 7713 x 10^{-5};
d_3 = 3.123 496 2101 x 10^{-8};
d_4 = -1.724 813 0773 x 10^{-10};
d_5 = 3.652 666 5920 x 10^{-13};
d_6 = -4.439 083 3504 x 10^{-16};
d_7 = 3.155 338 2729 x 10^{-19};
d_8 = -1.215 087 9468 x 10^{-22};
d_9 = 1.955 719 7559 x 10^{-26}.

8. Interpolation polynomial for type R thermocouples
(E in mV, t_{68} in °C)

- temperature range from -50 °C to 630.74 °C:

$$E = \sum_{i=0}^{7} a_i \cdot t_{68}^{i}$$

where.
a_0 = 0
a_1 = 5.289 139 5059 x 10^{-3}
a_2 = 1.391 110 9947 x 10^{-5}
a_3 = -2.400 523 8430 x 10^{-8}
a_4 = 3.620 141 0595 x 10-^{11}
a_5 = -4.464 501 9036 x 10^{-14}
a_6 = 3.849 769 1865 x 10^{-17}
a_7 = -1.537 264 1559 x 10^{-20}

- temperature range from 630.74 °C to 1064.43 °C:

$$E = \sum_{i=0}^{3} g_i \cdot t_{68}^{i}$$

where: $g_0 = -2.641\ 800\ 7025 \times 10^{-1}$
$g_1 = 8.046\ 868\ 6747 \times 10^{-3}$
$g_2 = 2.989\ 229\ 3723 \times 10^{-6}$
$g_3 = -2.687\ 605\ 8617 \times 10^{-10}$

- temperature range from 1064.43 °C to 1665 °C:

$$E = \sum_{i=0}^{3} b_i \cdot t_{68}^{i}$$

where: $b_0 = 1.490\ 170\ 2702 \times 10^{0}$
$b_1 = 2.863\ 986\ 7552 \times 10^{-3}$
$b_2 = 8.082\ 363\ 1189 \times 10^{-6}$
$b_3 = -1.933\ 847\ 7638 \times 10^{-9}$

- temperature range from 1665 °C to 1769 °C:

$$E = \sum_{i=0}^{3} d_i \cdot t_{68}^{i}$$

where: $d_0 = 9.544\ 555\ 9010 \times 10^{1}$
$d_1 = -1.664\ 250\ 0359 \times 10^{-1}$
$d_2 = 1.097\ 574\ 3239 \times 10^{-4}$
$d_3 = -2.228\ 921\ 6980 \times 10^{-8}$.