Temperature Scales and Temperature Fixed Points

In low-temperature physics and technology the measurement of a temperature is very often as difficult and, of course, as important as actually reaching that temperature. Therefore, low-temperature physicists have to spend a substantial part of their time considering thermometry. Before we can talk about thermometry we have to talk about temperature; we have to define a temperature scale. Actually, temperature is one of the most important parameters in physics and technology. It is one of the basic units in all systems of units. In spite of this fact – as we will see in the following – the absolute temperature is not very accurately known; our knowledge of temperature is much less precise than our knowledge of time, length, mass, voltage, etc. But let me start with a recollection of the definition of the temperature scale and some temperature fixed points.

11.1 Thermodynamic Temperature

The definition of the temperature scale is obtained from the Carnot cycle, which is based on the second law of thermodynamics. This reversible cycle gives

$$
\oint T^{-1} \mathrm{d}Q = 0,\tag{11.1}
$$

which is equivalent to

$$
T/Q = \text{const.}\tag{11.2}
$$

Hence, this or any other process gives the temperature only in terms of ratios or to within a multiplicative constant; the absolute values in a temperature scale have to be fixed by definition.

The most important proposal for the definition of a temperature scale, in general everyday practical use, was made in 1742 by A. Celsius, who proposed that the range of temperature between that at which water boils and that at which ice melts should be divided into 100◦:

$$
1742 \text{ Celsius}: T(\text{H}_2\text{O boiling}) - T(\text{H}_2\text{O melting}) = 100^{\circ}. \tag{11.3}
$$

In 1887 the name "centigrade" and in 1948 the name "degree Celsius" were internationally accepted for the unit of this scale. Of course, we know that we have to decide at which pressure this definition should be valid; the accepted value is 1 bar.

Physicists know that the definition of a temperature scale in which the temperature of melting ice is set at 0◦C is not very appropriate for physics and for many processes in nature, because we have an absolute zero in temperature. That an absolute zero exists had actually already been realized 40 years before Celsius' proposal, in 1702, by the French scientist Amontons. He found from his experiments with gases that there must be a lower limit for the temperature, and he estimated this lower limit to be at $\approx-240^{\circ}$ C. This was an outstanding achievement for that time.

Almost 150 years passed before Lord Kelvin made the proposal in 1848 to take absolute zero, T_0 , as the starting point of a thermodynamic temperature scale. It was not until 100 years later, in 1954, that this and the proposal that one should count from T_0 in steps of

$$
1^{\circ} = 1 \,\mathrm{K} = T_{\text{triple}}(H_2O)/273.16 \tag{11.4}
$$

was internationally adopted. Thus the unit of the thermodynamic temperature is defined as 1/273.16 of the temperature of the triple point of water which is taken as the second fixed point of the Kelvin scale. A degree in this scale is the same size as in the Celsius scale. The following values relate the Celsius to the Kelvin scale

1848 Kelvin :
$$
T(H_2O \text{ melting}) = 0^{\circ}C = 273.15 \text{ K},
$$

\n $T_0 = 0 \text{ K} = -273.15^{\circ} \text{ C}.$ (11.5)

So, we have a point for the zero of our temperature scale, and in principle we can use an experiment which is related to a Carnot cycle to establish the temperature scale, but this is rarely done by experimentalists. A handier procedure is to establish a number of fixed temperature points and to use them to calibrate the chosen thermometric method, which makes use of some temperature dependent property of a suitable material in the desired temperature range.

Presently, the Kelvin is defined by the temperature of the triple point of water which is a material property with a present standard uncertainty 3×10^{-7} . It would be a great advantage if this unit could be related to fundamental constants, as it has been possible for most of the other units. For the Kelvin, the corresponding fundamental constant is the Boltzmann constant $k_{\rm B}$, because temperature always appears as thermal energy $k_{\rm B}T$ in fundamental laws of physics. Unfortunately, the present standard uncertainty for k_B is 2×10^{-6} , which is even worse than the uncertainty for the water triple point. This value is based on one measurement applying one method; this is unsatisfactory for such an important fundamental constant. Therefore, substantial efforts at several national standards laboratories are under way to determine k_B by a variety of methods. The aim is an adoption of a reliable value for k_B with an uncertainty of 1 to 2×10^{-6} in 2011 by the Comite' International des Poids et Messures; this "modest" target value already indicates the involved difficulties.

11.2 The International Temperature Scale ITS-90

In 1968 international agreement was reached on the definition of an offical temperature scale, at least for temperature above about 14 K. This temperature scale, the IPTS-68 (amended in 1975) [11.1] is given by fixed temperature points which are defined by equilibrium phase transitions of pure substances. It superseded the earlier scales IPTS-48, ITS-48 and ITS-27. There was no internationally adopted and binding temperature scale for temperatures lower than 14 K, only recommendations for temperatures between 0.5 and 30 K. One was the "provisional $0.5-30 \text{ K}$ temperature scale (EPT-76)" [11.2, 11.3] (see Sect. 11.4.1), which again is given by fixed points which are defined by equilibrium phase transition temperatures of pure substances, in particular the transition temperatures into the superconducting states of five metals at $0.5 K \leq T < 10 K$ (Table 11.7). In addition, it was recommended to use the vapour pressures of ⁴He and ³He at $0.5 K \leq T \leq T_{\text{crit}}$ whose temperature dependences are given with a very high accuracy in Tables 11.3 and 11.4.

Unfortunately, already at the time of the international agreement on IPTS-68 it was realized that there are substantial errors (up to the order of several 10^{-4}) in this temperature scale, deviations from the thermodynamic temperature which are too large for an international standard. It was also obvious that the deviations of the helium vapour pressure scale from IPTS-68 and EPT-76 were a few millikelvins. Even though EPT-76 was established substantially later than IPTS-68 and had a much higher accuracy, the need for a new international scale was obvious. After substantial efforts in various laboratories, the *International Temperature Scale of 1990*, ITS-90, came into effect on January 1, 1990 $[11.4-11.7]$. It was adopted by the Comité International des Poids et Messures at its meeting in September 1989 and has been the official international temperature scale since 1 January 1990. There are significant differences between the new ITS-90 and the earlier scales; for example, 0.6 mK at 10 K between ITS-90 and EPT-76, and 9 mK at 20 K between ITS-90 and IPTS-68.

The ITS-90 extends from 0.65 K to the highest temperatures practicably measurable in terms of the Planck radiation law using monochromatic radiation. The defining fixed points of the ITS-90 are mostly phase transition

material ^a	equilibrium state ^b	temperature(K)	uncertainty $[mK]$
He	VР	$3 - 5$	
$e-H2$	TP	13.8033	$0.5\,$
	$e-H_2$ (or He) VP (or CVGT)	\approx 17	
$e-H_2$ (or He)	VP (or CVGT)	≈ 20.3	
Ne	TP	24.5561	$0.5\,$
O ₂	TP	54.3584	1.0
Ar	TP	83.8058	1.5
Hg	TP	234.3156	$1.5\,$
H_2O	TP	273.16	θ
Ga	MP	302.9146	1
In	FP	429.7485	3
Sn	FP	505.078	
Zn	FP	692.677	
Al	FP	933.473	
Ag	FP	1,234.93	
Au	FP	1,337.33	
Cu	FP	1,357.77	

Table 11.1. Defining fixed points of the temperature scale ITS-90 [11.4–11.7]

^aAll substances (except ³He) are of natural isotopic composition. e–H₂ is hydrogen at the equilibrium concentration of the ortho- and paramolecular forms.

 \rm^b The symbols have the following meanings: VP, vapour pressure point; TP, triple point; CVGT, gas thermometer point; MP, FP, melting point, freezing point (at a pressure of 1.01325 bar).

temperatures of pure substances, given in Table 11.1. In its overlapping ranges the ITS-90 is defined in the following ways [11.4–11.7]:

(a) $0.65-5.0 \text{ K}$: Three vapour pressure/temperature relations of ³He $(0.65-$ 3.2 K) and of 4 He (1.25–5.0 K) given by

$$
T = \sum_{i=0}^{9} A_i \left(\frac{\ln P - B}{C}\right)^i, \tag{11.6}
$$

with the constants A_i , B and C given in Table 11.2 (T in Kelvin, P in Pascal, $1 \text{ Pa} = 10^{-5} \text{ bar}$. The equation is, in fact, valid to 0.5 K .

Tables 11.3 and 11.4 give the new vapour pressure temperature values for 3 He and 4 He in the range from 0.6 to 5.2 K calculated from (11.6). These tables supersede the former $T_{58}(T_{62})$ scale for the ⁴He (³He) vapour pressure.

- (b) 3.0–24.5561 K (triple point of Ne): Constant-volume helium gas thermometer (Sect. 12.1) calibrated at points number 1, 2 and 5 of Table 11.1, and with the P/T relation given in [11.4–11.7].
- (c) 13.8033 (triple point of H_2)–1,234.93 K (freezing point of Ag): Electrical resistance of platinum (Sect. 12.5.1), calibrated at defining fixed points

coeff. or	$\rm{^{3}He}$	4 He	4 He
constant	$(0.65 - 3.2 \text{ K})$	$(1.25 - 2.1768 \text{ K})$	$(2.1768 - 5.0 \,\mathrm{K})$
A_0	1.053 477	1.392 408	3.146 631
A_1	0.980 106	0.527 153	1.357 655
A ₂	0.676 380	0.166 756	0.413 923
A_3	0.372 692	0.050 988	0.091 159
A_4	0.151 656	0.026 514	0.016 349
A_5	-0.002263	0.001 975	0.001 826
A_6	0.006 596	-0.017976	-0.004325
A_7	0.088 966	0.005 409	-0.004 973
A_8	-0.004 770	0.013 259	Ω
A_9	-0.054 943	0	$\overline{0}$
В	7.3	5.6	10.3
$\mathcal C$	4.3	2.9	1.9

Table 11.2. Values of the coefficients A_i , and of the constants B and C for the ³He and 4 He vapour pressure equations (11.6) and the temperature range for which each equation is valid [11.4–11.7]

and with various Pt resistance thermometers designed for the particular T ranges. For the determination of temperatures, various relations of temperature to resistance ratio $W(T_{90}) = R(T_{90})/R(273.16 \text{ K})$ are given. (d) Above 1,234.93 K (freezing point of Ag): Planck's radiation law.

The ITS-90 contains detailed instructions about how to calibrate a thermometer relative to it in the various temperature ranges, as well as differences to earlier scales [11.4–11.7]. It can be used down to 0.5 K with a thermodynamic inaccuracy of about 1 mK, and of about 0.5 mK between 1 and 5 K. Uncertainties at higher temperatures are 1 mK (at 13.8 K), 5 mK (at 933 K), and 10 mK (at 1,235 K).

There is still substantial work going on to improve the ITS-90 and to check its thermodynamic consistency. For example in [11.8], reports can be found on the recent work on new sealed fixed point devices aiming to improve the accuracy of the cryogenic triple points of ITS-90 to 0.1 mK or of the influence of the deuterium content on the triple point of hydrogen. Because it is known that ITS-90 deviates by about 1 mK from the thermodynamic temperatures at $T < 1$ K [11.6–11.18], very careful new ³He vapor-pressure measurements have been performed at PTB from 0.65 to 1.2 K [11.9]. In these investigations, different vapor-pressure cells and different pressure-sensing tubes between the sample and the manometers at room temperature have been used. This allowed reducing the errors from heat input to the samples, and in particular from thermo-molecular pressure differences as well as from aerostatic head corrections (see Sect. 12.2). Pressures were measured at room temperature with calibrated commercial differential capacitive diaphragm gauges and temperatures were measured with calibrated rhodium-iron resistance thermometers

T(K)	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.6	0.071	0.079	0.087	0.096	0.105	0.116	0.127	0.139	0.152	0.166
0.7	0.180	0.195	0.211	0.229	0.247	0.267	0.287	0.308	0.330	0.353
0.8	0.378	0.404	0.431	0.459	0.489	0.520	0.552	0.586	0.621	0.657
0.9	0.695	0.734	0.775	0.817	0.861	0.907	0.954	1.003	1.054	1.106
1.0	1.160	1.216	1.274	1.333	1.395	1.459	1.523	1.590	1.660	1.731
1.1	1.804	1.880	1.957	2.037	2.118	2.202	2.288	2.376	2.466	2.559
1.2	2.654	2.752	2.851	2.954	3.059	3.165	3.275	3.387	3.501	3.618
1.3	3.738	3.860	3.985	4.112	4.242	4.375	4.511	4.649	4.790	4.934
1.4	5.081	5.231	5.383	5.538	5.697	5.858	$6.022\,$	6.189	6.360	6.533
1.5	6.709	6.889	7.071	7.257	7.446	7.638	7.834	8.033	8.235	8.440
1.6	8.649	8.861	9.076	9.295	9.517	9.742	9.972	10.20	10.44	10.68
1.7	10.92	11.17	11.42	11.68	11.93	12.19	12.46	12.73	13.00	13.28
1.8	13.56	13.84	14.13	14.42	14.72	15.02	15.32	15.63	15.94	16.26
1.9	16.58	16.99	17.23	17.56	17.90	18.24	18.58	18.93	19.28	19.64
2.0	20.00	20.37	20.74	21.11	21.49	21.87	22.26	22.65	23.05	23.45
2.1	23.85	24.26	24.68	25.10	25.52	25.95	26.38	26.82	27.26	27.71
2.2	28.16	28.61	29.08	29.54	30.01	30.49	30.97	31.45	31.94	32.44
2.3	32.94	33.44	33.95	34.47	34.99	35.51	36.04	36.58	37.12	37.67
2.4	38.22	38.77	39.33	39.90	40.47	41.05	41.63	42.22	42.82	43.41
2.5	44.02	44.63	45.24	45.87	46.49	47.12	47.76	48.40	49.05	49.71
2.6	50.37	51.04	51.71	52.38	53.07	53.76	54.45	55.15	55.86	56.58
2.7	57.29	58.02	58.75	59.49	60.23	60.98	61.74	62.50	63.27	64.04
2.8	64.82	65.61	66.41	67.21	68.01	68.83	69.65	70.47	71.30	72.14
2.9	72.99	73.84	74.70	75.57	76.44	77.32	78.21	79.10	80.00	80.91
3.0	81.83	82.75	83.68	84.61	85.96	86.51	87.46	88.43	89.40	90.38
3.1	91.37	92.36	93.37	94.38	95.39	96.42	97.45	98.49	99.54	100.60
3.2	101.66	102.73	103.82	104.90	106.00	107.10	108.22	109.34	110.47	111.61

Table 11.3. Helium-3 vapour pressure (kPa) according to ITS-90 [11.4, 11.5]

(see Sect. 12.5.1). The data with a standard uncertainty of about 0.1 mK confirm the above-mentioned deviation and the requirement to amend ITS-90 to bring it in agreement with the new low-temperature scale PLTS-2000 (see below).

11.3 The New Provisional Low-Temperature Scale PLTS-2000

The International Temperature Scale ITS-90 has its lower end at 0.65 K. However, important research is being performed at substantially lower temperatures, requiring an internationally accepted, thermodynamically consistent temperature scale down to at least 1 mK. For this purpose, a new low-temperature scale, the PLTS-2000 [11.10] has been introduced in January 2000 and was formally accepted by the Comite' International des Points et

T(K)	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
1.2	0.082	0.087	0.093	0.100	0.107	0.115	0.123	0.131	0.139	0.148
1.3	0.158	0.168	0.178	0.189	0.201	0.213	0.226	0.239	0.252	0.267
1.4	0.282	0.298	0.314	0.331	0.348	0.367	0.387	0.407	0.428	0.449
1.5	0.472	0.495	0.519	0.544	0.570	0.597	0.625	0.654	0.684	0.715
1.6	0.747	0.780	0.814	0.849	0.885	0.922	0.961	1.001	1.042	1.084
1.7	1.128	1.173	1.219	1.266	1.315	1.365	1.417	1.470	1.525	1.581
1.8	1.638	$1.697\,$	1.758	1.820	1.883	1.948	2.015	2.084	2.154	2.226
1.9	2.299	2.374	2.451	2.530	2.610	2.692	2.776	2.862	2.949	3.039
$2.0\,$	3.130	3.223	3.317	3.414	3.512	3.613	3.715	3.818	3.925	4.032
$2.1\,$	4.141	$4.253\,$	4.366	4.481	4.597	4.716	4.836	4.958	5.082	5.207
2.2	5.335	5.465	5.597	5.731	5.867	6.005	6.146	6.288	6.433	6.580
$2.3\,$	6.730	6.882	7.036	7.192	7.351	7.512	7.675	7.841	8.009	8.180
$2.4\,$	8.354	8.529	8.708	8.889	9.072	$\boldsymbol{9.258}$	9.447	9.638	9.832	$10.03\,$
$2.5\,$	10.23	10.43	10.64	10.84	11.05	11.27	11.48	11.70	11.92	12.15
$2.6\,$	12.37	12.60	12.84	13.07	13.31	13.55	$13.80\,$	14.05	14.30	14.55
$2.7\,$	14.81	15.07	15.33	15.60	15.87	16.14	16.42	16.70	16.98	17.26
2.8	$17.55\,$	17.84	18.14	18.44	18.74	19.05	19.36	19.67	19.98	20.30
2.9	20.63	20.95	21.28	21.61	21.95	22.29	22.64	22.98	23.33	23.69
3.0	24.05	24.41	24.77	25.14	25.52	25.89	$26.27\,$	26.66	$27.05\,$	27.44
$3.1\,$	27.84	28.24	28.64	29.05	29.46	29.87	30.29	30.72	31.14	31.58
3.2	32.01	32.45	32.89	33.34	33.79	34.25	34.71	35.17	35.64	36.11
$3.3\,$	36.59	37.07	37.56	38.05	38.54	39.04	39.54	40.05	40.56	41.08
3.4	41.60	42.12	42.65	43.18	43.72	44.26	44.81	45.36	45.92	46.48
$3.5\,$	47.05	47.62	48.19	$48.77\,$	49.35	49.94	50.54	$51.13\,$	51.74	52.35
3.6	52.96	53.57	54.20	54.82	55.46	56.09	56.73	57.38	58.03	58.69
3.7	59.35	60.02	60.69	61.37	62.05	62.73	63.43	64.12	64.83	65.53
3.8	66.25	66.96	67.69	68.41	69.15	69.89	70.63	71.38	72.14	72.90
3.9	73.66	74.43	75.21	75.99	76.78	77.57	78.37	79.17	79.98	80.80
4.0	81.62	$82.44\,$	83.27	84.11	84.95	85.80	86.66	87.52	88.38	89.26
4.1	90.13	91.02	91.91	92.80	93.70	94.61	95.52	96.44	97.37	98.30
$4.2\,$	99.23	100.18	101.13	102.08	103.04	104.01	104.98	105.96	106.95	107.94
$4.3\,$	108.94	109.94	110.95	111.97	113.00	114.03	115.06	116.11	117.15	118.21
4.4	119.27	120.34	121.42	122.50	123.51	124.68	125.79	126.89	128.01	129.13
4.5	130.26	131.40	132.54	133.69	134.84	136.01	137.18	138.36	139.54	140.73
4.6	141.93	143.13	144.35	145.57	146.79	148.03	149.27	150.52	151.77	153.04
4.7	154.31	155.58	156.87	$158.16\,$	159.46	160.77	162.09	163.41	164.74	166.08
4.8	167.42	168.78	170.14	171.51	172.89	174.27	175.66	177.07	178.47	179.89
4.9	181.32	182.75	184.19	185.64	187.10	188.56	190.04	191.52	193.01	194.51
5.0	196.08	197.53	199.06	200.59	202.13	203.68	205.24	206.81	208.39	209.97

Table 11.4. Helium-4 vapour pressure (kPa) according to ITS-90 [11.4, 11.5]

Mesures in October 2000. It is based on thermodynamic properties of liquid and solid ³He, in particular its melting curve.

In the 1990s, several low-temperature laboratories had advanced the precision and reliability by which the P–T relation of a mixture of solid and liquid ³He could be measured over more than three decades in temperature, from about 1 mK to about 1 K (Sect. 12.3). The melting pressure of 3 He was chosen because it is a thermodynamic property usable over a very wide temperature range, complications from impurities and imperfections in the substance are essentially absent, thermodynamic consistency checks are possible (see below), and because of the relative ease and reliability by which it can be unequivocally realized in laboratories around the world. In addition, liquid and solid ³He due to its outstanding superfluid and nuclear magnetic properties provide four unique fixed points along the melting curve (see Fig. 2.4): the minimum of the melting pressure at $P_{\text{min}} = 2.93113 \text{ MPa}$, allowing a calibration of the used pressure transducer; the two unique transitions to the superfluid A-phase and from the A- to the superfluid B-phase of liquid 3 He as well as the nuclear antiferromagnetic transition of solid ³He offer temperature calibration points. The values for these temperature-pressure fixed-points are given in Table 11.5.

Because of the melting pressure minimum, a plug of solid 3 He will form in the sensing line between a pressure transducer at room temperature and the sample at low temperatures at a point where $T(P_{\min})$ is reached first, isolating the pressure cell. Therefore, the pressure has to be measured in situ at low temperatures, usually by a low-temperature capacitive transducer as described in Sect. 13.1. The transducer has to be calibrated at a temperature above the one of the melting curve minimum (or at another fixed point of liquid and solid ³He mentioned above). The plug, of course, leads to a very good stability of the low-temperature setup. More information on helium melting pressure thermometry can be found in Sect. 12.3.

The use of the ³He melting pressure as a temperature standard was already proposed by Scribner and Adams in 1970 [11.11]. It was in full use at Cornell University in the late 1970s [11.12], and later substantially refined by Greywall $[11.13]$. The work leading eventually to the 3 He melting pressure scale PLTS-2000 [11.10] was mostly performed in the nineties by the following three laboratories:

Physikalisch-Technische Bundesanstalt (PTB), Berlin; scale PTB-96 [11.6, 11.14–11.16]:

The scale of this laboratory is based in particular on noise thermometry using a SQUID as detector (Sect. 12.7). The data have been obtained on a 20-μΩ resistor in five measurements over 11 h with a gate time $τ=20 \text{ ms}$ from 0.88 mK to 1 K. The obtained noise temperatures were substantiated by measurements of the susceptibility of a single crystal of the paramagnetic salt

Table 11.5. Fixed points of liquid and solid ³He according to the PLTS-2000 scale [11.10]

$315.24 \,\mathrm{mK}$
$2.444 \,\mathrm{mK}$
$1.896\,\mathrm{mK}$
$0.902 \,\mathrm{mK}$

Fig. 11.1. Melting pressure of ³He as a function of temperature. The insets demonstrate the high resolution of the pressure measurements performed by a capacitive strain gauge similar to the one shown in Fig. 13.2. In the inset for the pressure minimum, the pressure is plotted vs. time. T_N is the temperature of the nuclear antiferromagnetic transition of solid 3 He, whereas W and Mo indicate the superconducting transitions of these metals taken as reference values. Reprinted from [11.6], publ. by IOP Publishing. See also [11.16]

CMN (Sect. 12.9) from 23 mK to 1.2 K , as well as by pulsed nuclear magnetic resonance on ¹⁹⁵Pt at 250 kHz/28.5 mT in a pure platinum sample with the rather long spin-lattice relaxation time of 0.9 ms (see Sect. 12.10.3) from 0.9–50 mK. For the nuclear magnetic moments of platinum it is know that they follow a Curie law into the low microkelvin range (see Fig. 10.18). The ³He pressure was measured by a capacitive transducer (Sect. 13.1) at low temperatures with a resolution of 0.1 Pa at 3 MPa (Fig. 11.1). It was calibrated by a room temperature quartz oscillator pressure transducer and a pressure balance carrying a calibration against the national pressure standard of PTB. The standard uncertainties are 40 Pa for the pressure at the melting curve minimum, and $1(0.04)$ % in temperature at $1 \text{ mK}(1 \text{ K})$. A detailed description of the design, construction, installation, filling to the correct gas pressure, the room temperature part, calibration, and use of the PTB pressure transducers can be found in [11.16].

National Institute of Standards and Technology (NIST), Boulder, Colorado; scales NIST-92/-98 [11.17, 11.18]:

The temperature scale of this laboratory, too, is based on resistive SQUID noise thermometry used as a primary method from 6–738 mK. It was checked from 1.25–3.0 K against the Curie-Weiss law of the susceptibility of CMN, which was calibrated against the ITS-90, as well as against a 60 Co nuclear orientation thermometer from 7–22 mK. The reproducibility and accuracy of the data was 0.1%. The PTB and NIST temperature scales agreed within experimental error after the original NIST temperatures were reduced by 0.15% when an error in the calculation of the noise temperature was discovered. The dominant uncertainty in the NIST scale is the uncertainty of 15 ppm in the effective area of the piston pressure gauge used for establishing the 3 He pressure scale.

University of Florida, Gainesville, Florida; scale UF-95 [11.19]:

This group used the anisotropic emission of the γ -rays from ⁶⁰Co (Sect. 12.11) as a primary thermometer with counting times of 8 h at each of 63 T–P points along the 3 He melting curve between 0.5 and 25 mK. This thermometer did serve to calibrate a 195 Pt wire NMR thermometer (Sect. 12.10.3) operated at 3.427 MHz with a precision of 0.2% achieved by signal averaging over the above-mentioned counting time; this latter temperature sensor was used only below 7 mK. The stated accuracy of their scale at $T > 0.93$ mK is 1%. A quartz pressure transducer with an accuracy of 0.04% was used to calibrate the capacitive pressure transducer at low temperatures. A small correction of the minimum pressure value toward that of the NIST value improved the pressure scale.

The remaining differences between the scales of the three laboratories and their likely origins were examined in a collaboration between the involved laboratories. The consistency checks relied in particular on the application of thermodynamics to the melting pressure-temperature relation. This analysis followed essentially the reasoning of Greywall [11.20] who had calculated the melting pressure by using the Clausius-Clapeyron equation and his data for the heat capacities of liquid and solid 3 He (see below). Eventually, agreement on slight adjustments of the various scales as well as on a compromise equation for the melting pressure of 3 He was reached, and the PLTS-2000 scale was subsequently formulated. This equation is (for P in MPa)

$$
P = \sum_{i=-3}^{+9} a_i T^i \tag{11.7}
$$

at $0.9 \text{ mK} < T < 1 \text{ K}$, and with the coefficients a_i given in Table 11.6 [11.10]. In addition, the mentioned fixed points of liquid and solid ³He at low millikelvin temperatures (Table 11.5) are incorporated in the PLTS-2000. The standard uncertainty of the PLTS-2000 in thermodynamic terms is $0.5 \text{ mK at } T > 0.5 \text{ K}$, decreasing linearly to 0.2 mK at 100 mK. Eventually, it is about 0.3% at 25 mK and 2% at 0.9 mK. The standard uncertainty in pressure is about 60 Pa. The consistency with the ITS-90 temperatures is 0.3 mK at 1 K.

Work related to improvements of the PLTS-2000 scale has still been going on since its acceptance. At PTB, the thermodynamic consistency of the scale

$a_{-3} = -1.385\,544\,2\times10^{-12}$ $4.555\ 702\ 6\times 10^{-9}$ $a_{-2} =$ -6.443 086 9×10^{-6} $a_{-1} =$ 3.4467434×10^{0} $a_0 =$ -4.4176438×10^{0} $a_1 =$ 1.5417437×10^{1} $a_2 =$ -3.5789853×10^{1} $a_3 =$ 7.1499125×10^{1} $a_4 =$ -1.041 437 9×10^2 $a_5 =$ 1.0518538×10^{2} $a_6 =$ $-6.944\,376\,7\times 10^{1}$ $a_7 =$ 2.6833087×10^{1} $a_8 =$ -4.587 570 9×10^{0} $a_9 =$	

Table 11.6. Coefficients a_i of (11.7) for the ³He melting curve according to the Provisional Temperature Scale PLTS-2000 (in the units MPa; K) [11.10]

has been checked with new measurements using noise and platinum NMR thermometry [11.21], supported again by calculations using Greywall's specific heat data [11.20]. These investigations indicated that the deviation of PLTS-2000 from thermodynamic consistency with the specific heat data is of order 1%.

Substantial efforts have been undertaken within an EU project to disseminate PLTS-2000 in Europe [11.22]. This has led to instrumentation and several thermometers for this purpose: a current sensing noise thermometer (Sect. 12.7), a CMN susceptibility thermometer (Sect. 12.9), new 195 Pt and 3 He NMR thermometry devices (Sect. 12.10), a Coulomb blockade thermometer (Sect. 12.6), a ${}^{3}He^{-4}He$ second-sound acoustic thermometer (T obtained from the strong temperature dependence of the velocity of second sound in a 1% mixture) [11.23], the superconducting fixed-point device SRD 1000 (Sect. 11.4.3), as well as ruthenium oxide resistance thermometers (Sect. 12.5.3). They are being checked as secondary devices and fixed points against the noise and the melting curve thermometers.

I shall now reproduce the arguments given by Greywall [11.20] to demonstrate the thermodynamic consistency of his temperature scale and of the input data. Because in the beginning of the 1980's there were differences of up to 40% in the specific heat of liquid 3 He measured at various laboratories, he performed accurate measurements of this specific heat in the temperature range 7 mK–2.5 K. From these data he was able to calculate the entropy of liquid ³He along the melting curve

$$
S_{\text{liq,m}} = \int_0^{T_{\text{m}}} \left(\frac{C_{\text{v},\text{liq}}}{T'}\right)_{\text{m}} dT'.
$$
 (11.8)

With the Clausius-Clapeyron equation

$$
S_{\rm sol,m} = S_{\rm liq,m} - (V_{\rm liq,m} - V_{\rm sol,m}) \left(\frac{\rm dP}{\rm dT}\right)_{\rm m},\qquad (11.9)
$$

and the known values of the slope of the melting curve [11.13] and the difference of the molar volumes of ³He in the liquid and solid phases along the melting curve $(1.31 \text{ m}^3 \text{ mol}^{-1})$ [11.12, 11.24], he was able to calculate the entropy of solid ³He along the melting curve. This calculation gave the values (Fig. 11.2) $S_{\text{sol,m}}/R = 0.688(0.693) \text{ at } T = 0.02(0.32) \text{ K}.$ (11.10)

$$
S_{\text{sol,m}}/R = 0.688(0.693) \text{ at } T = 0.02(0.32) \text{ K.}
$$
 (11.10)

These values are in excellent agreement with the value which is expected between about 10 mK (which is substantially above the nuclear magnetic ordering temperature of 0.93 mK) and 0.32 K (which is below a temperature where other excitations, e.g., phonons, start to contribute), which would be

$$
S_{\text{sol,m}}/R = \ln(2) = 0.693\tag{11.11}
$$

for the fully disordered ³He nuclear spins.

These are the same arguments used by the above-mentioned three groups to check the thermodynamic consistency of their new scale. Greywall's temperature scale [11.13] was the most accurate and most widely used temperature scale for the millikelvin temperature range until the PLTS-2000 scale was established. It is in good agreement (to within about 2%) with the PLTS-2000 scale at $T<40$ mK. For his measurements, he used a calibrated superconducting fixed-point device SRM 768 (Sect. 11.4.2) to calibrate an LCMN susceptibility thermometer (Sect. 12.9), ensuring that on this temperature scale the

Fig. 11.2. Entropies of liquid and solid ³He along the melting curve calculated from measured specific heat data of liquid 3 He [11.20]

specific heat of liquid ³He, which he measured, would follow at low temperatures the linear law predicted by the Landau theory for a Fermi liquid at $T \ll T_{\text{Fermi}}$ (see Fig. 2.15).

11.4 Practical but not Officially Accepted Low-Temperature Fixed Points

There are various very useful temperature fixed points – besides the unique fixed points of liquid and solid 3 He at low millikelvin temperatures on the 3 He melting curve (Table 11.5) - for low-temperature thermometry which are in wide use but which are not officially accepted or officially recommended.

11.4.1 Fixed Points of EPT-76

Even though the low-temperature scale EPT-76 [11.2, 11.3] is not an official scale anymore, it contains a number of fixed points which are very useful for low-temperature thermometry. These fixed points are given in Table 11.7. They differ from ITS-90 by less than 1 mK at $T < 13 \text{ K}$, which is close to the uncertainty of EPT-76 at these temperatures. In detailed comparisons between the Curie–Weiss behavior of the susceptibility of powdered CMN (Sect. 12.9) and EPT-76 as well as ITS-90 (which have the same thermodynamic basis below $4 K$), consistency was found between 3 and $1.2 K$; below 1.2 K the differences increase monotonically with decreasing temperature and reach 1.3 mK at 0.5 K.

11.4.2 The NBS Superconducting Fixed-Point Device

Superconducting transitions are very suitable fixed points for low-temperature thermometry, owing to their ease of detection, their reproducibility, their accuracy and fast response time, if the precautions discussed below are taken into account.

The American National Bureau of Standard (NBS; now National Institute of Standards and Technology, NIST) did offer a device (NBS-SRM 767 a) containing the five superconductors with transitions between 0.5 and 7.2 K of the EPT-76 temperature scale, as well as Nb with $T_c = 9.3 \text{K}$ [11.25].

Table 11.7. Some fixed points (in K), mostly from the superseded low-temperature scale EPT-76 [11.2, 11.3]

			$T_{\rm b}$ (H ₂) ^a $T_{\rm tr}$ (H ₂) $T_{\rm c}$ (Pb) $T_{\rm b}$ (⁴ He) ^a $T_{\rm c}$ (In) T_{λ} (⁴ He) ^b $T_{\rm c}$ (Al) $T_{\rm c}$ (Zn) $T_{\rm c}$ (Cd)		
20.27 13.80 7.20 4.21 the contract of the contract of the contract of			3.415 2.1768 1.180 0.851 0.520		

 \overline{A} ^aAt a pressure of 1 bar.

^bAt saturated vapour pressure.

However, thermometry in the Kelvin range is not too great a problem and is widely performed with the helium vapour pressure scale.

For a number of years the NBS (NIST) also offered a very useful superconducting fixed-point device for the millikelvin temperature range (NBS-SRM 768) [11.26]. The temperatures for the superconducting transitions of five metals contained in this device together with other relevant information are given in Table 11.8. The temperature scale of this device is based on a scale called "NBS-CTS-1" established at 0.01–0.5 K by the American NBS by ${}^{60}Co$ γ -ray anisotropy (Sect. 12.11), by Josephson noise thermometry (Sect. 12.7), and the paramagnetic susceptibility of CMN (Sect. 12.9) [11.27]. Each device is individually calibrated. The reproducibility and traceability to the NBS temperature scale is about $0.1-0.2 \text{ mK}$. This device is very useful for calibrating other millikelvin thermometers and it is a simple standard, widely used in low-temperature laboratories working in the millikelvin temperature range.

The design of this device, a self-contained assembly of coils and samples, is shown in Fig. 11.3. Thermal contact between the samples and the Cu body is provided by Cu wires welded to the body and connected to the samples by varnish. The device contains two primary coils to generate a magnetic field $(B = 0.016 \cdot I)$ and two secondary coils to measure the AC susceptibility of the samples; they are wound directly on the primary coils. The coils are connected in series opposition, so that only four leads are required. When a sample enters the superconducting state it expels the magnetic field (Meissner effect) generated by the primary coil, which is observed as a change in the mutual inductance of the secondary coils. A typical electronic setup to measure

material	T_c (mK)	B_c (mT)	RRR
W	$15.5 - 15.6$	0.12	10 ³
Be	$22.6 - 22.8$	0.114	79
$Ir_{0.8}Ru_{0.2}$	$99 - 100$	(type II)	2.5
AuAl ₂	$159 - 161$	1.21	50
AuIn2	$203 - 206$	1.45	50

Table 11.8. Properties of the superconductors in the NBS superconducting fixed point device SRM 768 [11.26]

Fig. 11.3. Schematic of the superconducting fixed-point device SRM 768 of the NBS (now NIST) containing five superconducting samples as well as the primary and secondary coils for measuring the transition temperatures of these metals in a Cu holder [11.26]

the superconducting transitions is shown in Fig. 11.4; the generated signals are $0.1-1 \,\mathrm{uV}$.

The NBS (NIST) has put substantial effort into the selection of samples with reproducible, sharp superconducting transitions and into investigations of external influences on these transitions, in particular by a magnetic field. The influence of an external magnetic field on the transition of Be is shown in Fig. 11.5. An external magnetic field shifts the superconducting transition to lower temperatures. Even more important, in an external magnetic field the superconducting transition is a first-order phase transition. Therefore supercooling effects can occur for pure elements, as is shown for pure Be. In the device this effect is reduced by spot-welding small pieces of Al to the W and Be samples so that Al, with $T_c \simeq 1$ K, serves as a nucleation center to induce superconductivity in the samples by the proximity effect. Because the

Fig. 11.4. Mutual inductance bridge for detecting the superconducting transitions of a superconducting fixed-point device like the SRM 768 shown in Fig. 11.3

Fig. 11.5. Superconducting transitions of pure Be indicating the influence of a magnetic field. The data in cooling and warming are taken in fields of $0.5 \mu T$ (1), $9.5 \,\mu T$ (2) and $19 \,\mu T$ (3) [11.26]

earth's magnetic field (about 50μ T) is substantially larger than fields which have a substantial influence on some of the transitions of the metals in this device, one has to shield carefully (to less than 10^{-7} T) against the earth's magnetic field. This shielding is of course even more important in an experimental setup where large fields are applied, as in a magnetic refrigerator. I shall discuss magnetic field shielding in Sect. 13.5.

The experimental conditions recommended by the NBS (NIST) for use of their device are:

- (a) ambient magnetic field: $\leq 1 \mu$ T
- (b) peak-to-peak field in primary coil: $\leq 2.3 \mu$ T for tungsten, $\leq 0.40 \mu$ T for the other superconductors (Joule and eddy current heating: 1.8 and 0.08 nW, respectively).

The reproducibility and the shifts in T_c in a $1 \mu T$ field are about 0.1 mK. The sweep rate used to trace out the superconducting transitions should be less than 0.1 mK min^{-1} (for Be and W) to avoid hysteresis effects; then widths of the transitions of less than 1 mK are achievable. Unfortunately this very useful superconducting fixed point device is no longer produced by the NBS (NIST).

11.4.3 The SRD 1000 Superconducting Fixed-Point Device

Since NIST has discontinued the production of the NBS-SRM 768 fixedpoint device, it is very fortunate for the low-temperature community that the Dutch company Hightech Developments Leiden, Leiden, NL in cooperation with Leiden University and PTB Berlin has developed and is offering the new Superconducting Fixed-Point Device SRD 1000 [11.28, 11.29]. Its main purpose is to provide a direct, convenient, reliable, and practical means to transfer the new temperature scale PLTS-2000 (see Sect. 11.3) to the lowtemperature research community. The principle of the device is identical to the SRM 768. However, the SRD 1000 contains ten carefully prepared superconducting samples providing reference temperatures between 15 and 1,200 mK (see Table 11.9 and Fig. 11.6). Each device has been individually calibrated at PTB against the PLTS-2000 because differences in preparation and in inhomogeneities of the samples result in slightly different transition temperatures.

Table 11.9. Properties of the superconductors in the pilot production of the SRD 1000 superconducting fixed-point device [11.28, 11.29]

material		W Be Ir ₈₀ Rh ₂₀ Ir ₉₂ Rh ₀₈ Ir AuAl ₂ AuIn ₂ Cd Zn Al					
nominal $T_c(mK)$ 15 21 30 65				98 145	208 520 850 1,180		
$90/10\%$							
width $(mK) < 0.2 \t0.3 \t0.5 \t0.5$				$0.5 \;\; 0.5$	$\mathbf{1}$	4 3	

Fig. 11.6. Inductively measured superconducting transitions of the ten samples in the superconducting fixed-point device SRD 1000 of [11.28–11.30]

The change in magnetization of each sample is detected by planar microcoils, realized by a thin-film niobium structure on a silicate wafer. The device is provided with the low-temperature sensor (10 mm diam., 50 mm length), a degaussing system for the magnetic shields (see Sect. 13.5), a preamplifier, and a phase-sensitive mutual inductance measurement system giving a DC output signal with a staircase pattern (Fig. 11.6).

Prototypes of the device have been evaluated by several European institutes for metrology [11.30]. The results confirm that (1) the uncertainties in the transition temperatures are about $0.1-0.3\%$, or less than $0.2 \,\mathrm{mK}$ for the samples with the lower transition temperatures and between 1 and 4 mK for Cd, Zn, and Al; (2) the field dependence of the transition temperatures is about $-0.1 \text{ mK}/\mu\text{T}$. Magnetic shielding by a Cryoperm magnetic shield and a superconducting niobium shield degaussed in situ before the measurement (see Sect. 13.5) is very effective (attenuation factor higher than 500), so that depressions of T_c due to residual and measuring fields (AC-field with 0.3 μ T amplitude) can be neglected.

11.4.4 The Superfluid Transition of Liquid ⁴He

The superfluid transition of pure ⁴He at saturated vapour pressure provides a very sharp fixed-point reference for thermometry at 2.1768 K (see Fig. 2.10). Self-contained, sealed fixed-point devices, based on the rapid change of thermal conductivity at the superfluid transition of 4 He, have been described in [11.31–11.33]. They can have nanokelvin resolution, are virtually immune to drift, and almost unaffected by magnetic fields $(dT_\lambda/dB \approx 0.3 \mu K/T)$. However, the transition depends weakly on pressure $(dT_{\lambda}/dP = -8.78 \text{ mK/bar})$, and therefore – via gravity – on sample height $\left(\frac{dT}{\lambda}\right)dt = 1.27 \,\mu\text{K/cm}$, somewhat on ³He impurity concentration $x \frac{d T_\lambda}{dx} = -1.45 \mu K/ppm$, and, above all, on heat flux Q, primarily due to the thermal boundary resistances of the device [11.31]; the fixed-point temperature should be taken by extrapolation to $Q = 0$ at 2.1768 K.

Problems

11.1. The Joule–Kelvin coefficient is given by

$$
\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p} \left[\frac{T}{V} \left(\frac{\partial V}{\partial T}\right)_p - 1\right].
$$
\n(11.12)

Since it involves the absolute temperature T , this relation can be used to determine the absolute temperature T. Consider any readily measurable arbitrary temperature parameter ϑ (e.g., the height of a mercury column). All that is known is that ϑ is some (unkown) function of T, i.e., $\vartheta = \vartheta(T)$.

- (a) Express (11.12) in terms of the various directly measurable quantities involving the temperature parameter ϑ instead of the absolute temperature T, i.e., in terms of $\mu' \equiv (\partial \partial/\partial p)_H$, $C'_p \equiv (\partial Q/\partial \partial)_p$, $\alpha' \equiv v^{-1}(\partial V/\partial \partial)_p$, and the derivative $d\partial/dT$.
- (b) Show that by integrating the resulting expression, one can find T for any given value of ϑ if one knows that $\vartheta = \vartheta_0$ when $T = T_0$ (e.g., if one knows the value of $\vartheta = \vartheta_0$ at the triple point where $T_0 = 273.16 \text{ K}$.

11.2. Perform a qualitative calculation of the deviation of the actual vapour pressure curve of liquid ⁴He, as given by (11.6) and Table 11.4, to the approximate equation deduced in Sect. 2.3.2.

11.3. Calculate the heat of magnetization at the superconducting transitions of the metals mentioned in Table 11.8, if the transitions occur in a field of 1 μT, see also Problem 4.2. How much are the superconducting transitions of these metals shifted by a field of $1\,\mu\text{T}$?