

# Thermodynamic Temperatures and IPTS-68

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As referee of a paper for this journal, I called in question an author's statement that temperatures measured with a platinum resistance thermometer were thermodynamic temperatures. This article is my response to the editor's invitation to explain my remark.

The dimensions of length, mass, and time are a matter of common experience, and electrical quantities, while not so obvious, are easily appreciated from the mechanical analogue of fluid flow. Temperature, apart from the physiological distinction we make between hot and cold, is not at all obvious since there is no common-sense scale. Historically, understanding of temperature and the imposition on sense data of a scale was a necessary preliminary to the development of thermodynamics. That this is an imposition and not a self-evident truth is borne out by the fact that generations of students have found thermodynamics a difficult study, largely because of its conceptual difficulties rather than because of any inherent complexity.

The significance of a thermodynamic scale of temperature was recognized at the end of the nineteenth century largely through the work of Lord Kelvin. Measurement on the thermodynamic scale depends on the gas thermometer as the primary instrument. Neither in 1890 nor now has this unwieldy apparatus been suitable for use outside standards or other well-equipped, specialized laboratories. Only in recent years have other instruments begun to supplement measurements made with the gas thermometer, which remains with minor exceptions the basis of the thermodynamic scale. Practical thermometry depends on secondary thermometers, the readings of which are related, possibly through several steps, to temperatures measured with a gas thermometer. At first, the secondary thermometers were mercury-in-glass but these soon gave way, for the highest class of measurement, to the resistance thermometer, and this is now the defining instrument for the practical scale between 13.81 and 903.89 K. The discussion following will be confined to this range since the same general considerations affect the ranges above and below. They differ only in the greater difficulties involved in establishing both the thermodynamic scale and practical scales dependent on other secondary thermometers.

It might have been expected that with a sound definition of the thermodynamic temperature scale and the availability of an instrument like the platinum resistance thermometer and the associated measuring equipment, Mueller and Smith's bridges, the measurement of temperature would soon have been established on a satisfactory basis. Standing in the way of this, however, was the fact that measurements with the platinum resistance thermometer could be made and reproduced more precisely than they could be standardized against the gas thermometer. The result was that a very precise but arbitrary scale could be developed, but its relation to the thermodynamic scale was uncertain since measurements on the latter scale could only be made relatively inaccurately. None of the scales for the other base units or the simpler derived units of SI has this peculiarity except perhaps pressure above 250 MPa, for which there is not even a scale that is satisfactory in principle. International discussion led to agree-

ment at the Conférence Général des Poids et Mesures (CGPM) in 1927 on an International Temperature Scale (ITS-27). Decisions relating to temperature scales are made by the CGPM or its committee, the Comité International des Poids et Mesures (CIPM) advised by the Consultative Committee for Thermometry.

This scale, as have been all its modifications agreed upon subsequently, was based on a number of reproducible equilibrium states (defining fixed points), to which numerical values of the temperature were assigned, and on formulas relating temperature to the indications of instruments calibrated by means of the values assigned to the defining fixed points. Two of these points were the freezing and normal boiling points of water, and the temperature interval between them was defined as 100 °C. This definition of the degree and the scale gave continuity with previously used scales but left the "absolute zero" as a quantity to be experimentally determined. As a result, during the following 20 years, in some laboratories (mainly in Europe) the ice point was allocated the value 273.15 degrees absolute, while in others (mainly in USA) it was allocated the value 273.16.

The International Practical Temperature Scale of 1948 (IPTS-48) was a revision of ITS-27 following developments in thermometry. In the range from the boiling point of oxygen (−182.970 °C) to the freezing temperature of antimony (630.5 °C) the new scale was identical with the old, but the name for °C became degree Celsius instead of degree Centigrade, a change usually forgotten. In 1954 it was agreed that the temperature of the triple point of water was 0.01 °C and that its thermodynamic temperature was 273.16 K. This decision recognized a practical change, that the temperature of the triple point of water had been demonstrated as reproducible within closer limits than the freezing temperature, and implied the change in the definition of the degree incorporated in IPTS-68.

Further developments in thermometry led to the International Practical Temperature Scale of 1968 (IPTS-68) (1), which is in form thermodynamically based in accordance with the suggestion made by Giauque nearly 30 years previously. The defining interval is now 0–273.16 K, and the new unit is "the fraction 1/273.16 of the thermodynamic temperature of the triple point of water." The name kelvin with the unadorned K as its symbol was adopted for this unit. There were numerical changes throughout the scale (except at 273.16 K) as the thermodynamic temperatures of all the fixed points had been determined more exactly. It is, however, important to recognize that though IPTS-68 may have the form of the thermodynamic scale, temperatures  $T_{68}$  expressed on it are not, except at 273.16 K by definition and elsewhere by accident, thermodynamic temperatures, even though in practice and for the accuracy of many experiments, they may be indistinguishable from them. Temperatures  $T_{68}$  depend on the defining fixed points of the scale, and the temperatures of these are subject to amendment. In particular, the 100 K interval between the ice and steam points is no longer fixed by definition, and it is already probable that we shall have to reconcile ourselves in due course to accepting that the boiling point of water is not 100 °C. However, it is to be hoped that

the temptation to amend the scale will be resisted for a long time, in view of the vast amount of work involved in converting published data from one scale to another.

As Guildner and Edsinger (2) well say, "New realizations of the thermodynamic scale need not, and should not, be regarded as justifying modification of the international scale. Next to its exactness and versatility, the invariance of the international scale is its most important quality. As improved realizations of the thermodynamic scale appear, they can then be recognized by adopting values of differences from the IPTS."

It may be thought by some that the distinction just made between thermodynamic temperatures and those on the practical scale is an unnecessary pedantry, since for most people it has no practical effect. Nevertheless, confusion here may lead to misunderstanding, and, in my opinion, the text of IPTS-68 would have been more useful if it had laid emphasis on the difference in principle between the thermodynamic and practical scales. As it is, the reader is led to assume that IPTS-68 and the thermodynamic scale are one by the statement, "The International Practical Temperature Scale of 1968 (IPTS-68) has been chosen in such a way that the temperature on it closely approximates the thermodynamic temperature; the difference is within the limits of the present accuracy of measurement" (7). At least one author

has claimed that the first clause is untrue to the extent that in the range 0–100 °C, IPTS-48 is a closer approximation to the thermodynamic scale than is IPTS-68 (5). The second clause was so nearly untrue at the time of its writing that it could with confidence have been omitted or modified accordingly. The kind of trap this produces, into which even the expert may fall, is illustrated by the sentence, "The thermodynamic scale can only be realized by thermodynamic thermometry and thus, is constantly changing as measurement techniques improve." It is not the thermodynamic scale that is changing but the numbers by which the practical scale is related to it.

The contributors to this journal and its readers, including the writer of this article, are not primarily concerned with the standardization of the temperature scale but with its use in an unambiguous way. How then should we make sure that we are not ambiguous and that collators and correlators have the least difficulty in arriving at the true significance of the numbers published? First, I suggest, by declaring that temperatures are expressed on IPTS-68, preferably as International Practical Kelvin Temperatures  $T_{68}$ , unless it is obvious that the thermometry is so crude that the scale is unimportant. Evidently, some authors are not aware of the magnitude of the differences between IPTS-48 and IPTS-68. For example, papers have been published which do not identify the temperature scale, but which report temperatures measured with

Table I. Approximate Differences,  $(t_{68} - t_{48})/K = (T_{68} - T_{48})/K$ , Between Values of Temperature Given by IPTS-68 and IPTS-48 on Celsius and Kelvin Scales

$t_{68}/^{\circ}\text{C}$	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100
-100	0.022	0.013	0.003	-0.006	-0.013	-0.013	-0.005	0.007	0.012		
-0	0.000	0.006	0.012	0.018	0.024	0.029	0.032	0.034	0.033	0.029	0.022
$t_{68}/^{\circ}\text{C}$	0	10	20	30	40	50	60	70	80	90	100
0	0.000	-0.004	-0.007	-0.009	-0.010	-0.010	-0.010	-0.008	-0.006	-0.003	0.000
100	0.000	0.004	0.007	0.012	0.016	0.020	0.025	0.029	0.034	0.038	0.043
200	0.043	0.047	0.051	0.054	0.058	0.061	0.064	0.067	0.069	0.071	0.073
300	0.073	0.074	0.075	0.076	0.077	0.077	0.077	0.077	0.077	0.076	0.076
400	0.076	0.075	0.075	0.075	0.074	0.074	0.074	0.075	0.076	0.077	0.079
500	0.079	0.082	0.085	0.089	0.094	0.100	0.108	0.116	0.126	0.137	0.150
600	0.150	0.165	0.182	0.200	0.23	0.25	0.28	0.31	0.34	0.36	0.39
700	0.39	0.42	0.45	0.47	0.50	0.53	0.56	0.58	0.61	0.64	0.67
800	0.67	0.70	0.72	0.75	0.78	0.81	0.84	0.87	0.89	0.92	0.95
900	0.95	0.98	1.01	1.04	1.07	1.10	1.12	1.15	1.18	1.21	1.24
1000	1.24	1.27	1.30	1.33	1.36	1.39	1.42	1.44			
$t_{68}/^{\circ}\text{C}$	0	100	200	300	400	500	600	700	800	900	1000
1000		1.5	1.7	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2
2000	3.2	3.5	3.7	4.0	4.2	4.5	4.8	5.0	5.3	5.6	5.9
3000	5.9	6.2	6.5	6.9	7.2	7.5	7.9	8.2	8.6	9.0	9.3
$T_{68}/\text{K}$	0	10	20	30	40	50	60	70	80	90	100
100	0.009	-0.002	-0.011	-0.014	-0.008	0.000	0.010	0.019	0.027	0.032	0.034
200	0.034	0.032	0.030	0.025	0.020	0.014	0.008	0.002	-0.003	-0.006	-0.008
300	-0.008	-0.010	-0.010	-0.010	-0.009	-0.007	-0.004	-0.001	0.003	0.006	0.011
400	0.011	0.015	0.019	0.024	0.028	0.033	0.037	0.042	0.046	0.050	0.053
500	0.053	0.057	0.060	0.063	0.066	0.068	0.070	0.072	0.074	0.075	0.076
600	0.076	0.077	0.077	0.077	0.077	0.077	0.076	0.076	0.075	0.075	0.075
700	0.075	0.074	0.074	0.074	0.075	0.076	0.077	0.078	0.081	0.084	0.088
800	0.088	0.093	0.098	0.106	0.114	0.123	0.124	0.146	0.161	0.177	0.195
900	0.185	0.22	0.24	0.27	0.30	0.33	0.35	0.38	0.40	0.44	0.46
1000	0.46	0.49	0.52	0.55	0.57	0.60	0.63	0.66	0.69	0.71	0.74
1100	0.74	0.77	0.80	0.83	0.86	0.88	0.91	0.94	0.97	1.00	1.03
1200	1.03	1.06	1.09	1.11	1.14	1.17	1.20	1.23	1.26	1.29	1.32
1300	1.32	1.35	1.38	1.41	1.43	1.46	1.48	1.5			
$T_{68}/\text{K}$	0	100	200	300	400	500	600	700	800	900	1000
1000				1.6	1.7	1.8	2.0	2.2	2.4	2.6	2.8
2000	2.6	2.8	3.0	3.3	3.6	3.8	4.1	4.3	4.6	4.9	5.1
3000	5.1	5.4	5.7	6.0	6.3	6.6	7.0	7.3	7.6	8.0	8.3
4000	8.3	8.7	9.1	9.4							

a platinum resistance thermometer to 0.001 K. At 550 K the failure to specify the scale introduces an uncertainty of 0.07 K. Platinum resistance thermometers have long lives if they are not broken, and many in use were calibrated by the manufacturer or at a standards laboratory on IPTS-48. There can be no objection to use of this scale provided it is declared, but on the other hand, there is little difficulty in applying the corrections detailed in Table I and changing the values to those on the current scale.

Thermodynamic arguments ought to depend on thermodynamic temperatures, but in most instances, experimental errors will cause greater uncertainty in any derived quantities than will arise from scale uncertainty. If, then, a sentence such as "Temperatures in this paper are expressed as International Practical Kelvin Temperatures  $T_{68}$ , which for most purposes are indistinguishable from the thermodynamic temperatures  $T$ ," or "which it is convenient to treat as interchangeable with thermodynamic temperatures  $T$  where no confusion arises and theoretical considerations do not demand differentiation of the two," is included in the text, it is quite clear what is being done and allows the author to write equations in terms of  $T$ , which is thermodynamically correct, rather than the cumbersome  $T_{68}$ . Sometimes, however, this approximation is inadequate and the author may need to maintain the distinction between  $T$ ,  $T_{68}$ , and  $T_{48}$ . Here no problem arises as long as the author knows what he is doing and gets his subscripts in the correct places.

If the careful specification suggested is not given, a reader at some point will encounter difficulty. Corrections to the scale in future may be smaller than they were in the past, but

they will still be necessary and unless the numbers printed now are adequately specified, it may not be possible to apply them. There are papers of 30 years ago in which the authors have declared their temperatures are thermodynamic but do not say whether they added 273.15 or 273.16 to their Celsius temperatures, and it may not be obvious whether they have then adjusted their measured values by what were believed to be the true corrections. To unravel this difficulty, it is necessary to know the custom of the particular laboratory, and this may require extensive search through other papers which are not necessarily by the same authors. At the time, what was done no doubt seemed so obvious to the authors as not to need stating, but it is no longer obvious, and the same situation will arise in respect of papers written today if some things that seem self-evident are not recorded.

The objective of this article is action by authors in the future, not an account of the past—a history of temperature scales. The latter is complex, and simplification to make the presentation as brief as that just given, cannot fail to lead to minor errors in detail. For comprehensive and expert coverage of the subject, the reader is referred elsewhere (3–5).

#### Literature Cited

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## Determination of Saturated Vapor Pressure in Range $10^{-1}$ – $10^{-4}$ Torr by Effusion Method

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An effusion method was used to determine the vapor pressure of six organic compounds, 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, and *S*-ethylpropylpropynylcarbamoate, one of its isomers, and three of its homologs at 25 and 40 °C. The vapor pressure of one novel organic compound, 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, was determined at seven temperatures between 25 and 55 °C. The following equation was obtained from a computerized least-squares curve fit for its solid phase:  $\log_{10} P = 15.34 \pm 0.98^* - 4882 \pm 305^*/T$ , where  $P$  = vapor pressure, torr;  $T$  = absolute temperature; and  $^*$  = confidence limits at 95% level. This equation can be used for calculating the vapor pressure at any desired temperature in the range of 25–55 °C.

The basic theory of the effusion method was reviewed in the literature (2, 3, 5, 12). The apparatus used consisted of the following basic parts: a large tube for the effusion cells placed in a constant temperature bath, a cold trap (dry ice and acetone), a pressure gauge, and an oil diffusion pump backed by a mechanical pump. Temperature was controlled

to  $\pm 0.05$  °C by a mercury-glass thermoregulator in conjunction with an electronic relay. The temperature of the bath was read from ASTM certified thermometers provided with correction charts and considered to be equal to the temperature of the samples. After the organic compounds were prepared, they were purified by recrystallization from chloroform–hexane or vacuum distillation at about 0.004 torr and 60–65 °C. Structure and chemical names of the compounds used in this investigation are listed in Table I.

Effusion cells were made of stainless steel, with threaded lid, a stainless steel foil with the effusion hole, and a Teflon washer. Since the cells were calibrated with pure mercury whose vapor pressure was taken as a standard, there was no need to know the effusion hole area, thickness, and correction factors. In each determination, two calibrated effusion cells were placed in the large tube for the cells. Under these conditions, the operation was greatly simplified and accelerated.

**Safety.** All compounds cited in Table I should be handled wearing gloves and a respirator.

The cells were calibrated by placing pure mercury in each cell, tightening the lids with a wrench, weighing to  $\pm 0.1$  mg, and introducing the cells into the apparatus and evacuating quickly to a pressure about 0.1 or less of the vapor pressure to be determined. After a suitable time, the vacuum was bro-