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A REPORT ON THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968

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LONDON BUTTERWORTHS

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ABSTRACT

This report summarizes the essential parts of the International Practical Temperature Scale of 1968, indicates the differences from the International Practical Temperature Scale of 1948, as amended in 1960, and discusses the problem of conversion of temperatures and certain calorimetric data obtained under the previous scale.

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1. INTRODUCTION

The purpose of this paper is to present in a simple way, for the benefit of practising thermodynamicists and thermochemists, the essential features

of the new International Practical Temperature Scale of 1968, how the changes may affect their work and measurements, and the manner of correcting to the new scale temperatures and data produced under the International Practical Temperature Scale of 1948. This paper has been prepared at the request, made in July 1969, of the Commission on Thermodynamics and Thermochemistry of the International Union of Pure and Applied Chemistry. For additional details, readers are referred to references 1 to 5 inclusive. References 1, 4 and 5 include manuscripts made available to the present author prior to their publication, by Dr T. B. Douglas, Dr R. P. Hudson and Dr C. W. Beckett, of the National Bureau of Standards, Washington, D.C., U.S.A., and by Dr S. Angus, of the Imperial College of Science and Technology, London, U.K.

At its meeting in October 1968, the International Committee on Weights and Measures, on the recommendation of its International Committee on Thermometry, set up the International Practical Temperature Scale of 1968 (IPTS-1968). Effective 1 January 1969, IPTS-1968 replaces the International Practical Temperature Scale of 1948, as amended in 1960 (IPTS-1948).

The basic temperature is the thermodynamic temperature, to which is given the symbol T, and the unit for which is the kelvin, to which is given the symbol K. The kelvin is the fraction, $1/273\cdot16$, of the thermodynamic temperature of the triple point of water.

Temperatures on the Celsius scale are denoted by the symbol t, the unit for which is the degree Celsius, to which is given the symbol $^{\circ}$ C. The unit on the Celsius scale is exactly equal to the unit on the thermodynamic scale. That is, one kelvin is exactly equal to one degree Celsius. Any difference in temperatures may be expressed either in kelvins or in degrees Celsius.

Temperatures on the Celsius scale are related to those on the Kelvin scale by the relation:

$$t = T - 273.15 \text{ (exactly)} \tag{1}$$

2. BASIS OF THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968

IPTS-1968 differs from IPTS-1948 in a number of ways: several new fixed points have replaced some old ones; some new fixed points have been included; significant changes have been made in the values assigned to a number of the fixed points; the lower end of the scale has been extended down from the boiling point of oxygen ($\sim 90~\rm K$) to the triple point of hydrogen ($\sim 14~\rm K$); a new value for the constant c_2 in the Planck radiation formula results in significant changes (about $0.1~\rm to~0.2$ per cent) in the values calculated with the radiation formula for temperatures above the gold point; new equations are provided for calculating temperatures with the platinum resistance thermometer; the range of use of the platinum resistance thermometer is extended down from the boiling point of oxygen ($\sim 90~\rm K$) to the triple point of hydrogen ($\sim 14~\rm K$). In addition, new specifications for materials of construction of thermometers and new procedures for calibrating thermometers are given.

IPTS-1968 distinguishes temperatures on the International Practical Kelvin

Scale with the symbol T_{68} and temperatures on the International Practical Celsius Scale with the symbol t_{68} . The relation between T_{68} and t_{68} is

$$t_{68} = T_{68} - 273.15$$
 (exactly) (2)

IPTS-1968 has been set up in such a way that the temperatures measured on it are very close to thermodynamic temperatures, the difference between the two being within the limits of accuracy of present day measurements. IPTS-1968 is constructed by assigning an exact value of temperature to the defining point and selected best experimentally determined values of temperature to a number of reproducible primary fixed points. These points involve thermodynamic equilibrium between two phases (solid–liquid or liquid–gas) or three phases (solid–liquid–gas) of a pure substance, with standard instruments calibrated at these temperatures. Interpolation between adjacent primary fixed points is done by means of formulas relating readings with the standard instruments and thermometers to values of temperature on IPTS-1968.

3. DEFINING POINT: TRIPLE POINT OF WATER

The defining point for IPTS-1968 is the triple point of water (equilibrium of water in three phases, solid, liquid and gas, in the absence of air or other substance). The value of temperature assigned to this point is 273·16 K (exactly). This definition determines the size of the degree kelvin, as previously stated, and hence also the size of the degree Celsius.

The triple point of water replaced the freezing point of water (equilibrium between the solid and liquid phases of water, in the presence of air at a pressure of one atmosphere) because the former is much more reproducible and stable than the latter.

4. DIFFERENCE BETWEEN THE TRIPLE AND FREEZING POINTS OF WATER

In 1960, when the original International Practical Temperature Scale of 1948 was amended to produce what we now label as IPTS-1948, and the triple point of water became the defining point, it was necessary to know rather well the difference between the triple point of water and the freezing point of water. Fortunately, this difference had been determined experimentally with considerable accuracy and precision⁶:

$$T_{\text{triple pt}} - T_{\text{ice pt}} = 0.0100 \pm 0.0001 \,\text{K}$$
 (3)

or

$$t_{\text{triple pt}} - t_{\text{ice pt}} = 0.0100 \pm 0.0001^{\circ} \text{C}$$
 (4)

With the foregoing relations, we can write

$$T_{\text{triple pt}} = 273.16 \text{ (exactly) K, by definition}$$
 (5)

$$T_{\text{ice pt}} = 273.1500 \pm 0.0001 \,\text{K}$$
 (6)

$$t_{\text{triple pt}} = 0.01 \text{ (exactly)} \,^{\circ}\text{C}$$
 (7)

$$t_{\text{ice pt}} = 0.0000 \pm 0.0001 \,^{\circ}\text{C}$$
 (8)

5. PRIMARY FIXED POINTS

The primary fixed points on IPTS-1968, and the values assigned to them, are given in *Table 1*. The values actually selected are underlined—on the Kelvin scale below the freezing point of water and on the Celsius scale above the triple point of water. The defining point, the triple point of water, is set in bold type. The value for the freezing point of water (now a secondary fixed point) is included in this table simply for convenience. The values for the same temperature on the Kelvin and the Celsius scales differ by 273-15 (exactly).

Table 1. Values of the temperatures of the primary fixed points on the International Practical Temperature Scale of 1968, and their estimated uncertainties in terms of thermodynamic temperatures^a

Substance	Equilibrium	Т ⁸ К	t ^g °C	Estimated uncertainty K
Hydrogen ^b	solid-liquid-gas	13.810	-259.340	±0.010
Hydrogen ^b	liquid-gas, at $\frac{25}{76}$ atm	<u>17·042</u>	-256.108	± 0.010
Hydrogen ^b	liquid-gas, at 1 atm	20.280	-252.870	+0.010
Neon°	liquid-gas, at 1 atm	27.102	-246.048	+0.010
Oxygen	solid-liquid-gas	54:361	-218.789	-0.010
Oxygen	liquid-gas, at 1 atm	90.188	-182.962	± 0.010
(Water)d	(solid-liquid, in air at 1 atm)	$(273 \cdot 1500)$	(0.0000)	(± 0.0001)
Water	solid-liquid-gas	273 16	0.01	exact
Water	liquid-gas, at 1 atm	373-150	100.000	± 0.005
(Tin)f	solid-liquid, at 1 atm	505-118	<u>231·968</u>	± 0.015
Zinc	solid-liquid, at 1 atm	692.73	<u>419·58</u>	± 0.03
Silver	solid-liquid, at 1 atm	1235.08	<u>961·93</u>	± 0.20
Gold	solid-liquid, at 1 atm	1337-58	1064.43	± 0.20

^a In interpreting the facts given in this table the following points are to be noted. The abbreviation 'atm' means the standard atmosphere defined as $1013250 \text{ dynes cm}^{-2}$ or $101325 \text{ Newtons m}^{-2}$. The numbers 25/76 and 1 before atm are atmosphere defined as $1013250 \text{ dynes cm}^{-2}$ or $101325 \text{ Newtons m}^{-2}$. The numbers 25/76 and 1 before atm are taken as exact. Near 1 atm. the freezing point of various metals changes in amounts ranging only 000001 to 00001 degree per 001 atm change in pressure. The depth of immersion of the thermometer in the liquid phase of various metals affects the temperature only by amounts ranging from 000001 to 00001 degree per 1 cm change in depth of immersion.

^b The hydrogen referred to in this table means 'equilibrium' hydrogen, which, at any given temperature, is in equilibrium with respect to the ortho and para forms of hydrogen. At the normal boiling point, 1 atm, the composition of 'equilibrium' hydrogen is 0.21 per cent ortho and 99.79 per cent para. While at room temperature it is near 75 per cent ortho and 25 per cent para. The latter mixture, retained unchanged in composition, has a normal boiling point, at 1 atm, which is 0.12 degree above that of 'equilibrium' hydrogen. Equilibrium between the ortho and para forms of hydrogen is achieved by use of ferric hydroxide as a catalyst.

^e Neon, which is largely ²⁰Ne, normally contains 0.0026 mole fraction of ²¹Ne and 0.088 mole fraction of ²²Ne.

^d The value for the temperature of the ice-point is a secondary reference point, but is included here for the convenience of the reader. (See *Table 2*, following).

^e The water should have the isotopic composition of ocean water. The extreme differences in temperature of the triple point of water from natural sources, ocean water and continental surface water, has been found to be about 0.00025 degree.

f The freezing point of tin may be used in place of the normal boiling point of water as one of the primary fixed points.

⁸ The selected values are singly underlined, on the Kelvin scale below the freezing point of water, and on the Celsius scale above the triple point of water. The defining point, the triple-point of water, is in heavy type. The values for the same temperature on the two scales differ by 273-15 (exactly). The number of significant figures given here varies in a few cases from the official report¹.

In the last column of *Table 1* are given the estimated uncertainties of the assigned values of temperature for the primary fixed points, referred to the thermodynamic scale of temperature.

As previosuly noted, all of the fixed points, as well as the defining point, involve thermodynamic equilibrium between two or three phases of a pure substance. In general, the triple point (equilibrium between solid, liquid and gas phases) is the most reproducible and reliable, the freezing point (equilibrium between solid and liquid phases) is next, and the boiling point (equilibrium between liquid and gas phases) is next.

6. SECONDARY REFERENCE POINTS

In addition to the primary fixed points discussed above, the International Committee approved a large number of secondary reference points. The identification of these points, and the values of temperature assigned to them, are given in *Table 2*.

Table 2. Values of the temperatures of the secondary reference points on the International Practical Temperature Scale of 1968^a

Substance	Equilibrium	T K	°C
Hydrogen, 'normal'b	solid-liquid-gas	13.956	- 259·194
Hydrogen, 'normal'b	liquid-gas, 1 atm	20.397	-252.753
Neon	solid-liquid-gas	24.555	-248.595
Nitrogen	solid-liquid-gas	63.148	-210.002
Nitrogen	liquid–gas, 1 atm	77-348	-195.802
Carbon dioxide	solid-gas, 1 atm	194.674	78·476
Mercury	solid–liquid, 1 atm	234.288	- 38.862
Water	solid-liquid, in air, 1 atm	273.1500	0.0000
Phenoxybenzene (Diphenylether)	solid-liquid-gas	300.02	26.87
Benzoic acid	solid-liquid-gas	395.52	122.37
Indium	solid-liquid, 1 atm	429.784	156-634
Bismuth	solid–liquid, 1 atm	544.592	271.442
Cadmium	solid-liquid, 1 atm	594.258	321.108
Lead	solid-liquid, 1 atm	600-652	327-502
Mercury	liquid-gas, 1 atm	629.81	356.66
Sulphur	liquid-gas, 1 atm	717.824	444.674
Cu-Al, Eutectic	solid-liquid, 1 atm	821.38	548.23
Antimony	solid-liquid, 1 atm	903.89	630.74
Aluminium	solid-liquid, 1 atm	933.52	660.37
Copper	solid–liquid, 1 atm	1357.6	1084.5
Nickel	solid-liquid, 1 atm	1728	1 455
Cobalt	solid–liquid, 1 atm	1 767	1494
Palladium	solid–liquid, 1 atm	1827	1554
Platinum	solid-liquid, 1 atm	2045	1772
Rhodium	solid-liquid, 1 atm	2236	1963
Iridium	solid-liquid, 1 atm	2720	2447
Tungsten	solid-liquid, 1 atm	3 660	3387

a See the footnotes to Table 1.

b 'Normal' hydrogen is hydrogen having a composition of ortho and para hydrogen corresponding to that of 'equilibrium' hydrogen at room temperature. See Footnote b of Table 1.

7. THERMOMETRIC SYSTEMS

Having established the necessary array of fixed points, the next step is to specify the thermometric systems, that is, the thermometric substances to be used, and the properties to be measured, along with the standard measuring instruments, for the several ranges into which the total scale is subdivided.

IPTS-1968 is based on the use of only three thermometric systems:

- (i) From 14 to 904 K, the platinum resistance thermometer, with measurement of the electrical resistance of a coil of pure, strain-free, annealed platinum;
- (ii) From 904 to 1338 K, the thermocouple, of platinum and an alloy of 90 per cent platinum and 10 per cent rhodium, with measurement of the electromotive force.
- (iii) Above 1338 K, the optical pyrometer, using the Planck radiation formula, with measurement of the intensity of radiation.

Table 3. Specifications for the several ranges of the International Practical Temperature Scale of 1968

Range of	temperature		Measuring
K	°C	Calibrating points	instrument
13.810	-259.340	triple pt, H ₂	platinum
to	to	boiling pt, H_2 , 25/76 atm	resistance
20.280	−252·870	boiling pt, H_2 , 1 atm triple pt, H_2O	thermometer
20.280	-252.870	boiling pt, H ₂ , 1 atm	platinum
to	to	boiling pt, Ne, 1 atm	resistance
54.361	-218.789	triple pt, O ₂	thermometer
		triple pt, H ₂ O	
54-361	-218.789	triple pt, O ₂	platinum
to	to	boiling pt, O_2 , 1 atm	resistance
90.188	-182.962	triple pt, H ₂ O	thermometer
90.188	-182.962	boiling pt, O ₂ , 1 atm	platinum
to ·	to	triple pt, H ₂ O	resistance
273.15	0.00	boiling pt, H ₂ O, 1 atm	thermometer
273·15	0.00	triple pt, H ₂ O	platinum
to	to	boiling pt, H_2O , 1 atm	resistance
903.89	630.74	(or freezing pt, Sn)	thermometer
		freezing pt, Zn	
903-89	630·74	(freezing pt, Sb) ^a	thermocouple:
to	to	freezing pt, Ag	platinum and
1337.58	1064-43	freezing pt, Au	10% Rh-90% P
1337.58	1064-43	freezing pt, Au,	optical pyrometer
and	and	with the Planck	
above	above	radiation equation	

^a See text following equation 22.

Table 3 summarizes the specifications for the several ranges of IPTS-1968, showing the temperature covered in each range, the calibrating points for the given range, and the measuring instrument for that range.

8. REALIZATION OF THE SCALE OVER THE RANGE 13.810 TO 903.89 K

For this range, where the platinum resistance thermometer applies, the basic measurement is the resistance ratio W. For the unknown temperature T_{r} , the resistance ratio is

$$W_{T_{\rm x}} = R_{T_{\rm x}} / R_{273 \cdot 15} \tag{9}$$

Here, R_{T_x} is the resistance at T_x and $R_{273\cdot15}$ is the resistance at 273·15 (exactly) K or 0·00 (exactly) °C, which is 0·01 (exactly) kelvin below the triple point of water. This is also the freezing point of water (within 0·0001°C). One condition applies to W, namely, that its value at 373·15 K (100·00 °C) must not be less than 1·39250.

Below 273·15 K, the relation between temperature and resistance of the thermometer is obtained from a reference function and certain specified deviation equations. For the range 13·81 to 273·15 K, a reference function, W-CCT, has been tabulated as a function of temperature to provide interpolation with a precision of 0·0001 kelvin². With W-CCT thus defined, T_x is evaluated from the relation,

$$W_{T_x} = R_{T_x}/R_{273\cdot 15} = (W-CCT)_{T_x} + \Delta W_{T_x}$$
 (10)

Here, ΔW_{T_x} is determined separately for each of four subranges, as follows:

From 13.810 to 20.280 K.

$$\Delta W_{T_x} = A_1 + B_1 T_x + C_1 T_x^2 + D_1 T_x^3 \tag{11}$$

where the constants, A_1 , B_1 , C_1 and D_1 , are evaluated from observations at the four calibrating points specified for this subrange (see *Table 3*): by the measured deviations at the triple point of 'equilibrium' hydrogen (13·810 K), the temperature of 17·042 K (the boiling point of 'equilibrium' hydrogen at 25/76 atmosphere), and the normal boiling point of 'equilibrium' hydrogen* (20·280 K), and by the temperature derivative of ΔW_{T_x} at the normal boiling point of 'equilibrium' hydrogen (20·280 K) as derived from the following equation 12.

From 20.280 to 54.361 K,

$$\Delta W_{T_x} = A_2 + B_2 T_x + C_2 T_x^2 + D_2 T_x^3 \tag{12}$$

where the constants, A_2 , B_2 , C_2 and D_2 , are evaluated from observations at the four calibrating points specified for this subrange (see *Table 3*): by the measured deviations at the normal boiling point of 'equilibrium' hydrogen (20·280 K), the normal boiling point of neon (27·102 K), and the triple point of oxygen (54·361 K), and by the temperature derivative of ΔW_{T_x} at the triple point of oxygen (54·361 K) as derived from the following equation 13.

^{*} As used here, the terminology 'normal boiling point' means the boiling point (thermodynamic equilibrium between the liquid and gas phases) at a pressure of exactly one atmosphere.

From 54·361 to 90·188 K.

$$\Delta W_{T_x} = A_3 + B_3 T_x + C_3 T_x^2 \tag{13}$$

where the constants, A_3 , B_3 and C_3 , are evaluated from observations at the three calibrating points specified for this range (see *Table 3*): by the measured deviations at the triple point of oxygen (54·361 K) and the normal boiling point of oxygen (90·188 K), and by the temperature derivative of ΔW_{T_x} at the normal boiling point of oxygen (90·188 K) as derived from the following equation 14.

From 90.188 to 273.15 K.

$$\Delta W_{T_x} = A_4 T_x + C_4 T_x^3 (T_x - 100) \tag{14}$$

where the constants, A_4 and C_4 , are evaluated from observations at the two calibrating points specified for this range (see *Table 3*): by the measured deviations at the normal boiling point of oxygen (90·188 K) and the normal boiling point of water (373·150 K or $100\cdot000^{\circ}$ C).

For the range 273·15 to 903·89 K, the following equations are used:

$$T_x = t_x + 273.15 \text{ (exactly) K}$$
 (15)

$$t_x = t' + 0.045 \left(\frac{t'}{100}\right) \left(\frac{t'}{100} - 1\right) \left(\frac{t'}{419.58} - 1\right) \left(\frac{t'}{630.74} - 1\right) ^{\circ} C$$
 (16)

$$t' = \frac{1}{\alpha}(W_{t'} - 1) + \delta\left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right)$$
 (17)

In equation 17, the constants, α and δ are evaluated from measurements of the resistance ratio, $W_{t'}$, at the normal boiling point of water (100·000°C or 373·150 K) or the freezing point of tin (231·968°C or 505·118 K) and the freezing point of zinc (419·58°C or 692·73 K). Here, we have, for the normal boiling point of water,

$$W_{373\cdot15} = R_{373\cdot15}/R_{273\cdot15} \tag{18}$$

for the freezing point of tin,

$$W_{505\cdot118} = R_{505\cdot118}/R_{273\cdot15} \tag{19}$$

and for the freezing point of zinc,

$$W_{692\cdot73} = R_{692\cdot73}/R_{273\cdot15} \tag{20}$$

9. REALIZATION OF THE SCALE OVER THE RANGE 903-89 TO 1377-58 K

For the range 903-89 to 1337-58 K, the following equations are used:

$$T_x = t_x + 273.15 \text{ (exactly)} \tag{21}$$

$$E_{t_x} = a + bt_x + ct_x^2 \tag{22}$$

Here, E_{t_x} is the electromotive force of the standard thermocouple, of platinum and an alloy of 90 per cent platinum–10 per cent rhodium, with one junction at 273·15 K, or zero degrees C, and the other at the unknown temperature t_x . The constants, a, b and c, are evaluated from the measured values of the

electromotive force at the freezing point of gold (1337.58 K or 1064.43° C), the freezing point of silver (1235.08 K or 961.93° C), and at $630.74 \pm 0.20^{\circ}$ C (903.89 K) as determined by the platinum resistance thermometer as specified in the foregoing. (The temperature, 903.89 K or 630.74° C, is a secondary reference point, corresponding to the freezing point of antimony.)

The specifications require that the standard thermocouple shall be annealed and that the purity of the platinum wire shall be such that the resistance ratio $W_{373\cdot15}$, equal to $R_{373\cdot15}/R_{273\cdot15}$, shall be not less than $1\cdot3920$. The companion wire shall be an alloy containing 90 per cent platinum and 10 per cent rhodium, by weight.

Further, the thermocouple shall satisfy the following relations:

At the gold point (1337.58 K or 1064.43°C),

$$E_{\rm Au} = 10300 \pm 50 \text{ microvolts} \tag{23}$$

For the difference in electromotive force between the gold point and the silver point (1235.08 K or 961.933°C),

$$E_{\text{Au}} - E_{\text{Ag}} = 1183 + 0.158 (E_{\text{Au}} - 10300) \pm 4 \text{ microvolts}$$
 (24)

For the difference in electromotive force between the gold point and 630·74°C (or 903·89 K),

$$E_{Au} - E_{903.89} = 4766 + 0.631 (E_{Au} - 10300) \pm 8 \text{ microvolts}$$
 (25)

10. REALIZATION OF THE SCALE ABOVE 1337:58 K

Above the gold point (1337-58 K), the unknown temperature, T_x , is defined by the Planck radiation formula:

$$J_{T_x}/J_{T_{Au}} = [\exp(c_2/\lambda T_{Au}) - 1]/[\exp(c_2/\lambda T_x) - 1]$$
 (26)

In this equation: T_x and $T_{\rm Au}$ refer to the unknown temperature and the temperature of the gold point on the Kelvin scale, respectively; J is the spectral concentration, $\partial L/\partial \lambda$, of the radiant energy, L, per unit wavelength interval at the given wavelength, λ , emitted per unit time by unit area of a black body at the given temperature; c_2 is the second radiation constant with the following value:

$$c_2 = 0.014388 \text{ metre kelvin} \tag{27}$$

The measurements involve determination, with an optical pyrometer, of the ratio of the intensity of monochromatic visible radiation of a given wavelength emitted by a black body at the unknown temperature to the intensity of the same radiation of the same wavelength emitted by a black body at the gold point.

11. RECOMMENDATIONS REGARDING APPARATUS, METHODS AND PROCEDURES

The official publication on the International Practical Temperature Scale of 1968 gives some detailed recommendations on apparatus, methods and procedures, covering the following items:

Standard resistance thermometer

Standard thermocouple
Triple point and the normal boiling point of 'equilibrium' hydrogen
Normal boiling point of neon
Triple point and normal boiling point of oxygen
Normal boiling point of water
Freezing point of tin
Freezing point of zinc
Freezing point of silver
Freezing point of gold

12. NUMERICAL DIFFERENCES BETWEEN THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968 AND THAT OF 1948

Values of the numerical differences between IPTS-1968 and IPTS-1948, $T_{68} - T_{48}$, for the range 90 to 10000 K, are given in *Tables 4* and 5*. These values are taken from the paper of Douglas⁴, which values are equivalent, to the same number of significant figures, with the values of $T_{68} - T_{48}$ given

Table 4. Differences in the values of temperature, over the range 90 K to the gold point, 1337-58 K, given by IPTS-1968 and IPTS-1948, reported as $T_{68} - T_{48} = \Delta$. (The values in this table are rounded from the tabulation of Douglas⁴)

Unit	s: T ₆₈ in	degrees	on the K	Kelvin so	cale of IF	TS-196	58;⊿i	n millikel	vins
T ₆₈	Δ	T ₆₈	Δ	T ₆₈	Δ	T ₆₈	Δ	T ₆₈	Δ
90	+ 8	140	_ 9	280	- 3	480	45	860	134
92	11	145	- 5	290	- 7	490	49	880	160
94	13	150	0	300	- 9	500	53	900	194
96	13	155	+ 5	310	 10	520	60	920	245
98	12	160	10	320	-10	540	66	940	300
100	11	165	15	330	-10	560	70	960	354
102	9	170	20	340	- 9	580	74	980	409
104	6	175	24	350	- 7	600	76	1000	464
106	4	180	27	360	- 4	620	77	1020	519
108	1	185	30	370	- 1	640	77	1040	575
110	- 1	190	32	380	+ 2	660	76	1060	63.1
112	- 4	195	33	390	ϵ	680	76	1080	687
114	- 6	200	34	400	10	700	75	1100	743
116	- 8	210	33	410	15	720	74	1150	886
118	-10	220	30	420	19	740	75	1200	1029
120	-11	230	25	430	24	760	77	1250	1173
124	-13	240	20	440	28	780	81	1300	1319
128	-14	250	14	450	32	800	88	1337.58	1430
132	-13	260	7	460	37	820	98		
136	-11	270	2	470	41	840	113		

in the official report¹ of the International Committee, for the range (up to 4000°C) covered in the latter report.

^{*} For detailed information on the several scales of temperature in the range 14 to 90 K in use before 1968, and their relation to IPTS-1968, see ref. 3.

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Table 5. Differences in the values of temperature, from the gold point, 1337.58 K, to 10000 K, given by IPTS-1968 and IPTS-1948, reported as $T_{68} - T_{48} = \Delta$. (The values in this table are from the tabulation of Douglas⁴)

T_{68}	Δ	T_{68}	Δ	T_{68}	Δ	T_{68}	Δ	T_{68}	Δ
1 337-58	1.43	1850	2.34	2800	4.6	3900	8.0	5000	12.3
1350	1.45	1900	2.44	2900	4.8	4000	8.3	5 500	14
1400	1.53	1950	2.54	3000	5.1	4100	8.7	6000	17
1450	1.61	2000	2.65	3 100	5.4	4200	9.1	6 500	19
1 500	1.70	2 100	2.86	3 200	5.7	4300	9.4	7000	22
1550	1.78	2200	3.08	3 300	6.0	4400	9.8	7 500	25
1600	1.87	2300	3.31	3400	6.3	4500	10.2	8 000	27
1650	1.96	2400	3.55	3 500	6.6	4600	10.6	8 500	30
1 700	2.05	2500	3.79	3 600	7.0	4700	11.0	9000	33
1750	2.15	2600	4.0	3 700	7.3	4800	11.4	9 500	37
1800	2.24	2 700	4.3	3 800	7.6	4900	11.8	10000	40

Douglas⁴ also provides values of $d(T_{68}-T_{48})/dT$, the change of $T_{68}-T_{48}$ with temperature, up to 10000 K. His values are given in *Tables 6* and 7.

Table 6. Differences in the values of the temperature derivatives, over the range 90 K to the gold point, 1337-58 K, given by IPTS-1968 and IPTS-1948, reported as $d(T_{68}-T_{48})/dT=d\Delta/dT$. (The values in this table are from the tabulation of Douglas⁴)

T_{68}	$d\Delta/dT$	T_{68}	$\mathrm{d}\varDelta/\mathrm{d}T$	T_{68}	$\mathrm{d}\varDelta/\mathrm{d}T$	T_{68}	$\mathrm{d}\varDelta/\mathrm{d}T$	T_{68}	$d\Delta/dT$
90	2.2	140	0.71	280	-0.41	480	0.41	860	1.2
92	1.3	145	0.89	290	-0.29	490	0.39	880	1.5
94	0.5	150	1.00	300	-0.18	500	0.37	900	1.9
96	-0.1	155	1.03	310	-0.08	520	0.3	903.89	$\begin{cases} 2.0^{a} \\ 2.7^{b} \end{cases}$
98	-0.6	160	1.02	320	+0.01	540	0.3	920	2.7
100	-0.89	165	0.96	330	0.09	560	0.2	940	2.7
102	-1.12	170	0.87	340	0.16	580	0-1	960	2.7
104	-1.24	175	0.75	350	0.23	600	0.1	980	2.7
106	-1.30	180	0.61	360	0.28	620	0.0	1000	2.8
108	-1.30	185	0.47	370	0.33	640	0.0	1020	2.8
110	-1.25	190	0.32	380	0.36	660	0.0	1040	2.8
112	-1.16	195	0.17	390	0.39	680	0.0	1060	2.8
114	-1 ·06	200	0.05	400	0.42	700	0.0	1080	2.8
116	-0.92	210	-0.20	410	0.44	720	0.0	1100	2.8
118	-0.78	220	-0.38	420	0.45	740	+0.1	1150	2.9
120	-0.63	230	-0.51	430	0.45	760	0-1	1 200	2.9
124	-0.30	240	-0.59	440	0.45	780	0.3	1250	2.9
128	0.00	250	-0.62	450	0.45	800	0-4	1 300	2.9
132	+0.28	260	-0.61	460	0.44	820	0.6	1337-58	$\begin{cases} 3.0^{\text{b}} \\ 1.6^{\text{c}} \end{cases}$
136	0.52	270	-0.54	470	0.43	840	0.9		(10

^{*} From the range of platinum thermometer.

b From the range of the thermocouple (Pt and 10%Rh-90%Pt.).

[&]quot; From the range of the radiation scale.

Table 7. Differences in the values of the temperature derivatives, from the gold point, 1337.58 K, to 10000 K, reported as $d(T_{68} - T_{48})/dT = d\Delta/dT$. (The values in this table are from the tabulation of Douglas⁴).

T_{68}	$\mathrm{d}\Delta/\mathrm{d}T$	T_{68}	$\mathrm{d}\Delta/\mathrm{d}T$	T_{68}	$\mathrm{d} \Delta/\mathrm{d} T$	T_{68}	$\mathrm{d}\Delta/\mathrm{d}T$	T_{68}	d⊿/d7
1337-58	3·0b	1 700	1.9	2200	2.2	3 500	3	7000	5
	1.6°	1800	1.9	2300	2.3	4000	4	8000	6
1 400	1.6	1900	2.0	2400	2-4	4500	4	9000	6
1 500	1.7	2000	2.1	2500	2.5	5000	4	10000	6
1600	1.8	2100	2.2	3 000	3	6000	5		

b, c See corresponding footnotes to Table 6.

13. THE PROBLEM OF CONVERTING EXISTING CALORIMETRICALLY DETERMINED DATA TO THE BASIS OF THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968

With new calor metric data being determined under the International Practical Temperature Scale of 1968, it becomes necessary to arrange for the conversion of existing calorimetrically determined data, obtained under IPTS-1948, to the basis of IPTS-1968.

Douglas⁴ has prepared a report which gives detailed and exact formulas for making such conversions for calorimetric data on enthalpy, heat capacity and entropy. Douglas⁴ also gives equations for converting extrapolated data, on the basis of the " T^3 ", or the other theoretical or empirical relation, from a lowest temperature of measurement to zero K, for enthalpy, heat capacity and entropy.

The problem is to convert experimentally measured calorimetric data, obtained at a given numerical value of temperature on IPTS-1948, to the same numerical value of temperature on IPTS-1968. Letting the given numerical value of temperature on IPTS-1948 be T_{48}' and the same numerical value of temperature on IPTS-1968 be T_{68}' , one can therefore write

$$T_{68}^{"} = T_{48}^{'} \tag{28}$$

There is one point on IPTS-1948 which has not only the same numerical value but also exactly the same temperature as on IPTS-1968. This point is the triple point of water, at $273\cdot16$ K. For convenience, the enthalpy, H, the heat capacity, C_p , and the entropy, S, at the same numerical value of temperature on IPTS-1968 and IPTS-1948, are designated as H'' and H', C_p'' and C_p' , and C_p'' and C

Also, at a given actual temperature, the value on IPTS-1968 will be T_{68} and that on IPTS-1948 will be T_{48} .

(a) Conversion of calorimetric data on enthalpy

Douglas⁴ gives an exact equation, of an infinite series type, for calculating the conversion of calorimetric data on enthalpy from a given numerical value of temperature, T'_{48} , on IPTS-1948, to the same numerical value of temperature T''_{68} , on IPTS-1968.

However, it is shown that all of the terms of this equation beyond the first are normally negligible in actual practice⁴. Consequently, one obtains for the correction in enthalpy⁴:

$$\delta H = H'' - H' = -C_p(T_{68} - T_{48}) \tag{29}$$

Here C_p is the measured value of the heat capacity at the given temperature, $T_{68} - T_{48}$ is taken from *Tables 4* and 5, and H'' - H' is the correction to be added to the value of enthalpy previously reported under IPTS-1948.

(b) Conversion of calorimetric data on heat capacity

Douglas⁴ gives an exact equation, also of an infinite series type, for calculating the conversion of calorimetric data on heat capacity from a given numerical value of temperature, T'_{48} , on IPTS-1948, to the same numerical value of temperature, T'_{68} , on IPTS-1968.

However, it is shown that the following approximate equation, adequate for nearly all cases encountered in actual practice, can be derived⁴:

$$\delta C_p = C_p'' - C_p' = -C_p \, d(T_{68} - T_{48}) / dT - (T_{68} - T_{48}) \, dC_p / dT \qquad (31)$$

Here C_p and $T_{68} - T_{48}$ have the same significance as above for enthalpy values of $d(T_{68} - T_{48})/dT$, the rate of change of $T_{68} - T_{48}$ with temperature are given in *Tables 6* and 7, dC_p/dT is the rate of change of C_p with temperature, and $C_p'' - C_p'$ is the correction to be added to the value of heat capacity previously reported under IPTS-1948.

(c) Conversion of calorimetric data on entropy

Douglas⁴ gives an exact equation, also of an infinite series type, for calculating the conversion of calorimetric data on entropy from a given numerical value of temperature, T'_{48} , on IPTS-1948, to the same numerical value of temperature, T''_{68} , on IPTS-1968.

However, it is shown that the following approximate equation, adequate for nearly all cases in actual practice, can be derived⁴:

$$\delta S = S'' - S' = -\int_0^T \left[(T_{68} - T_{48}) C_p / T^2 \right] dT - (T_{68} - T_{48}) C_p / T$$
 (32)

Here C_p and $T_{68} - T_{48}$ have the same significance as above for enthalpy, the integration is taken from 0 to T, and S'' - S' is the correction to be added to the value of entropy previously reported under IPTS-1948.

14. CONVERSION OF P–V–T DATA TO THE BASIS OF THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE OF 1968

Angus⁵ has prepared a report in which he discusses the correction of experimental P-V-T data obtained under IPTS-1948 to the basis of IPTS-1968. In general, the procedure involves the conversion of data labelled for a given numerical value of temperature, T'_{48} , under IPTS-1948, to the same numerical value of temperature, T'_{68} , under IPTS-1968. In setting up the procedure for correcting the existing experimental data on P-V-T

measurements to the new IPTS-1968, one simply traces the effect of shifting the temperature by the amount $T_{68}-T_{48}$ (from Tables 4 and 5) at each temperature of measurement, utilizing values of $d(T_{68}-T_{48})/dT$ (from Tables 6 and 7) as appropriate. Since this report is mainly concerned with calorimetric data, the reader is referred to the report of Angus⁵ for further details.

15. THERMODYNAMIC PROPERTIES CALCULATED STATISTICALLY

In each case of values of thermodynamic properties calculated statistically from spectroscopic and other molecular data, with the proper values of the fundamental physical constants being used, no changes are necessary as a result of the introduction of the new IPTS-1968. Following is the reasoning. (a) The values of thermodynamic properties calculated statistically are specified for temperatures on the thermodynamic scale. (b) The values of temperature on the new IPTS-1968 are as near the corresponding temperatures on the thermodynamic scale as is possible at the present time.

16. CONCLUSION

Utilizing the information given in this report, and the references cited, the bench scientist or engineer should be able to determine readily what effect the shift from IPTS-1948 to IPTS-1968 has on his current experimental measurements involving temperature, what he must do to have his measurements of temperature conform to the new IPTS-1968, and how he should proceed to correct his previous data, obtained under IPTS-1948, to the basis of the new IPTS-1968.

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REFERENCES

- ¹ 'The International Practical Temperature Scale of 1968'. Comptes Rendus de la 13ème Conférence Général des Poids et Mesures, 1967-68, Annex 2; Metrologia, 5, 35-44 (1969).
- ² Bedford, R. E., Preston-Thomas, H., Durieux, M. and Muijlwijk, R. 'Derivation of the CCT-68 Reference Function of the International Practical Temperature Scale of 1968'. *Metrologia*, 5, 45-47 (1969).
- ³ Bedford, R. E., Durieux, M., Muijlwijk, R. and Barber, C. R. 'Relationships between the International Practical Temperature Scale of 1968 and the NBS-55, NPL-61, PRMI-54, and PSU-54 Temperature Scales from 13.81 to 90.188 K'. Metrologia, 5, 47-49 (1969).
- Douglas, T. B. 'Conversion of Existing Calorimetrically Determined Thermodynamic Properties to the Basis of the International Practical Temperature Scale of 1968'. J. Res. Nat. Bur. Stds, 73A, 451–470 (1969).
- ⁵ Angus, S. A. 'Note on the 1968 International Practical Temperature Scale.' Report PC/D26. Available from S. Angus, Imperial College of Science and Technology, London, United Kingdom.
- ⁶ Stimson, H. F., J. Wash. Acad. Sci. 35, 201-217 (1945).