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The Triple Point of Krypton

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Abstract. Phase transitions of pure substances provide the key reference temperatures, otherwise known as "defining fixed points", of the International Temperature Scale. At temperatures below the triple point of mercury (234.3156 K), the substances involved are gases at room temperature and include the triple points of hydrogen (13.8033 K), neon (24.5561 K), oxygen (54.3584 K) and argon (83.8058 K). The Consultative Committee for Thermometry also provides a list of "secondary reference points" whose quality approaches (or is equivalent to) that of the defining fixed points of the ITS Here, we report direct measurements of the triple point of krypton on the ITS-90, review the historical measurements that CCT WG2 relied upon for its 1996 assessment, and demonstrate that the triple point of krypton is a "first quality" secondary reference point. Based on our measurements, the temperature of the triple point of krypton is 115.7755 K.

Keywords: krypton, triple point, fixed point, cryogenic, melting curve, impurities, phase diagram
PACS: 07.20.Dt, 07.20.Mc, 64.70.dj

INTRODUCTION

Phase transitions of pure substances provide the key reference temperatures, otherwise known as "defining fixed points", of the International Temperature Scale of 1990 (ITS-90) [1]. At temperatures below the triple point of mercury (234.3156 K), the substances involved are gases at room temperature and include the triple points of hydrogen (13.8033 K), neon (24.5561 K), oxygen (54.3584 K) and argon (83.8058 K). The Consultative Committee for Thermometry (CCT) also provides a list of "secondary reference points" whose quality approaches (or is equivalent to) that of the defining fixed points of the ITS. Although the list of secondary reference points includes vapor-pressure/temperature relations for selected gases, triple points can be realized more precisely than boiling points and other vapor-pressure-dependent temperatures.

The 1996 CCT Working Group 2 (WG2) list of secondary reference points [2] describes the triple points of deuterium (18.724 K), neon-20 (24.541 K), nitrogen (63.151 K), methane (90.694 K), xenon (160.405 K) and carbon dioxide (216.592 K) as "first-quality points" while the triple point of krypton (115.775 K) is considered a "second-quality" point. The recommended temperatures in the CCT WG2 publication were obtained by taking original measurements reported as IPTS-68 temperatures and converting them to the ITS-90. This process introduced additional uncertainty due to the non-uniqueness of IPTS-68.

Here, we review the historical measurements that CCT WG2 relied upon for its 1996 assessment and report direct measurements of the triple point of krypton on the ITS-90 that demonstrate it is worthy of inclusion in the list of "first quality" secondary reference points.

HISTORICAL DETERMINATIONS

Ramsey and Travers were the first to identify krypton as a separate component of air [3] and reported measurements of its vapor pressure, melting point and boiling point [4] shortly following their initial discovery. Table 1 summarizes the published triple point determinations reported since 1901. The values are just as reported by the authors, except that where noted the original values expressed in units degrees centigrade have been converted to kelvin by adding 273.15 in order to have a more uniform basis for comparison. No attempt has been made to convert the values to a common scale, such as IPTS-68, so the reader is advised to consult the original publications for the details of how the employed thermometers were calibrated – it should not be assumed from the various dates that the measurements are on the version of the International Temperature Scale (e.g. ITS-27, ITS-48, IPTS-68) prevailing at the time the measurements were reported.

In 1977, CCT WG2 published [22] a list of secondary reference points that included krypton and listed a subset of the Table 1 values [14-17], converted to IPTS-68 temperatures. With the exception of [15], the difference from the original values (on ITS-48) is 8 mK. For [15], the original calibration methodology was not consistent with ITS-48 so a more complex conversion is necessary [23].

The 1996 CCT WG2 list of secondary reference points [2] provided a single recommended value for the temperature of the krypton triple point based on the most recent measurements available [19-21] and one somewhat older value [16]. The conversion from IPTS-68 to ITS-90 can be made by adding 12 mK to the IPTS-68 temperatures. In the case of the Lovejoy value [16], an additional 8 mK must be added to account for the difference between ITS-48 and IPTS-68. The value in Table 1 from Inaba and Mitsui [20] was obtained (by the authors) by extrapolating their melting curve data to $1/F = 0$ (F is the melted fraction). WG2 chose to use $T_{68} = 115.7635$ K, the estimated temperature for $1/F = 1$, as the best estimate from the Inaba and Mitsui experiment. Averaging the four values yields $T_{90} = 115.7749$ K, which was rounded to 115.775 K.

TABLE 1. Historical Triple Point Determinations.

Authors and Year of Publication	Temperature (K)
Ramsay and Travers (1901) [4]	104*
Peters and Weil (1930) [5]	116.2*
Allen and Moore (1931) [6]	116.6*
Justi (1935) [7]	116.11
Keesom, Mazur and Meihuizen (1935) [8]	115.94
Clusius (1936) [9]	116.0
Meihuizen and Crommelin (1937) [10]	115.97
Clusius, Kruis and Konnertz (1938) [11]	115.95
Clusius and Weigand (1940) [12]	115.95
Freeman and Halsey (1956) [13]	115.6
Beaumont, Chihara and Morrison (1961) [14]	115.776
Michels and Prins (1962) [15]	115.743**
Lovejoy (1963) [16]	115.7701*
Fender and Halsey (1965) [17]	115.794
Lee, Eshelman and Bigeleisen (1972) [8]	115.78
Kemp and Kemp (1978) 19]	115.7639
Inaba and Mitsui (1978) [20]	115.7661
Hermier and Bonnier (1986) [21]	115.7623

* converted from the published value (having units °C) by adding 273.15, then rounding to maintain the same number of significant digits as the original

** the value 115.743 K appears in the body of the paper while the value 115.745 K is in Table III of [15]. It is unclear which should be taken as correct.

EXPERIMENTAL DETAILS AND RESULTS

Six capsule-style standard platinum resistance thermometers (CSPRTs) calibrated over the full low-temperature range of the ITS-90 (from 13.8033 K to 273.16 K) were selected to determine the triple-point temperature of our krypton sample. As for our cryogenic comparison experiments [24], a variety of new and old thermometers from different manufacturers were used in this work: Hart Scientific (HS113, HS114), Leeds and Northrup (1158066, 1872182, 1876687), and Tinsley (213865). Sealed triple-point cells having six thermowells and filled with hydrogen, neon, oxygen, argon, krypton, mercury, and water were used for the calibration of the six CSPRTs using the closed-cycle cryostat described in [25]. The 17 K and 20.3 K points were determined in the same apparatus by comparison against a Tinsley rhodium-iron resistance thermometer traceable to the NRC interpolating gas thermometer realization of the ITS-90 [26]. The resistance ratios $W=R(T_{90})/R(273.16)$ were determined using an Automatic Systems Laboratories F18 resistance bridge in conjunction with a 25 Ω Tinsley 5685A reference resistor thermostatted in a Guildline 9732VT oil bath at 25 °C ± 2 m°C.

The pulsed-heating melting experiments were carried out in an analogous fashion to our determinations of the triple points of xenon [27] and the ^{20}Ne and ^{22}Ne isotopes [28]. Figure 1 presents the results of nine such melting experiments.

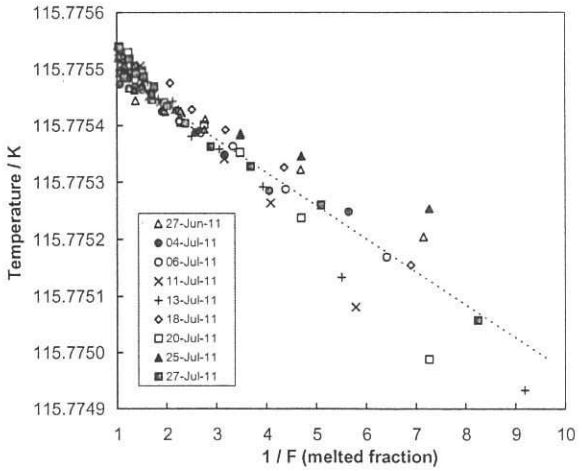

FIGURE 1. Temperature versus inverse melted fraction for the nine melts of our krypton sample.

For comparison, we have plotted in Figure 2 the most recent melting curves from the literature [19-21] together with our measurements. While caution is

clearer required, narrower melting ranges are generally associated with purer substances. Our krypton sample has the narrowest melting range amongst those in Figure 2. Despite its comparatively broad melting range, the liquidus point (F=1) of Inaba and Mitsui [20] compares surprising well with our value and that of Kemp and Kemp [19]. The data of Hermier and Bonnier [21] seem slightly offset from the others – perhaps as a consequence of the combined non-uniqueness of both the IPTS-68 and the ITS-90.

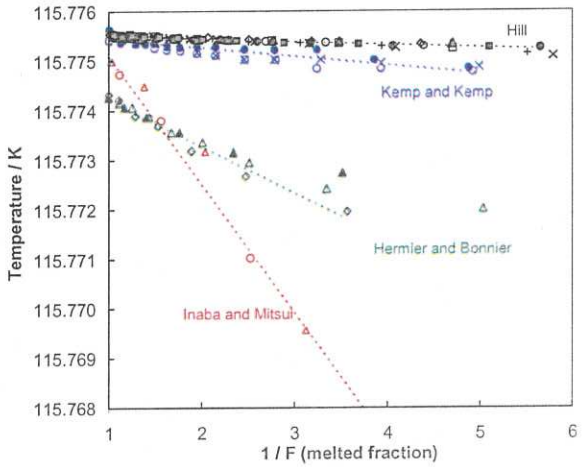

FIGURE 2. Comparison of temperature versus inverse melted fraction of our krypton sample with the most recent data from the literature [19-21] (converted to ITS-90).

When acquiring the melting curves in Figure 1, the heating pulses are stopped at approximately 80% melted fraction so that the resistances of the six CSPRTs can be measured. Each CSPRT is measured at 1 mA, √2 mA and 1 mA (again) to account for the self-heating. Between each change of CSPRTs, a measurement at 1 mA is made using a designated CSPRT to ensure that the temperature remains constant during the round-robin phase of the measurement cycle. This process was repeated for eight of the nine melting curves of Figure 1. The results appear in Table 1, where the temperature measured by each thermometer is listed. The average standard deviation among the six CSPRTs for a single melt is 67 μK. The average standard deviation for a particular CSPRT over the eight melts is 34 μK. The pooled average of the forty-eight individual readings is 115.775 517 K with a standard deviation of 68 μK. Based on the slope of the melting curve in Figure 1, the temperature measured during the round robin at 80% melted fraction is 15 μK less than the value at the liquidus point, F=1. The best estimate of the krypton triple point, based on the data obtained with our Air Products gas sample, is 115.775 532 K.

The total heat of fusion of our sample is approximately 27 J, corresponding to about 16 mmol of krypton.

TABLE 1. Temperature measurements during the round-robin near 80% melted fraction

Date	213865	1872182	HS114	1876687	HS113	1158066	Std. dev.
2011/07/05	115.775 467	115.775 467	115.775 462	115.775 470	115.775 428	115.775 604	0.000 061
2011/07/07	115.775 474	115.775 458	115.775 469	115.775 521	115.775 411	115.775 587	0.000 060
2011/11/12	115.775 462	115.775 486	115.775 482	115.775 519	115.775 433	115.775 613	0.000 063
2011/07/14	115.775 471	115.775 477	115.775 461	115.775 519	115.775 460	115.775 630	0.000 066
2011/07/19	115.775 544	115.775 543	115.775 501	115.775 622	115.775 476	115.775 670	0.000 074
2011/07/21	115.775 510	115.775 514	115.775 554	115.775 541	115.775 480	115.775 655	0.000 061
2011/07/26	115.775 508	115.775 452	115.775 513	115.775 552	115.775 445	115.775 622	0.000 066
2011/07/28	115.775 522	115.775 491	115.775 542	115.775 580	115.775 439	115.775 693	0.000 087
Average	115.775 495	115.775 486	115.775 498	115.775 540	115.775 447	115.775 634	
Std. dev.	0.000 030	0.000 030	0.000 036	0.000 046	0.000 024	0.000 036	

IMPURITY EFFECTS

Krypton comprises approximately 1 part per million of air (Table 2) and is commercially obtained from the liquefaction of air, so it is natural to expect the components of air to be the most likely contaminants.

The krypton utilized for the measurements reported here was supplied by Air Products in 1984. The research-grade gas (minimum guaranteed purity 99.995%) was supplied with analysis no. SG-16011-84, as detailed in Table 3.

To determine the sensitivity of the krypton triple point to specific contaminants, a survey of the literature showed binary phase diagrams for krypton with oxygen [30], nitrogen [31-32], argon [32-33], methane [33] and xenon [32, 35]. The sensitivity coefficients, $\partial T/\partial x$, can be obtained by estimating the slope of the liquidus line near the pure krypton part of the phase diagram (rather crudely estimated by eye, O_2: -70 μK/ppm, N_2: -40 μK/ppm, Ar: -20 μK/ppm,

CH_4: -15 μK/ppm, Xe: -10 μK/ppm). The corresponding ideal solution values are:
O_2: -28 μK/ppm, N_2: -32 μK/ppm, Ar: -26 μK/ppm, CH_4: -16 μK/ppm, Xe: +65 μK/ppm. These values can be compared with the sensitivity derived from the cryoscopic constant for krypton,

$A = \Delta H_f/(RT^2)$
$= 1.64$ kJ/mol / ((8.3144621 J/mol·K)(115.775 K)^2)
$= 0.0147$ K^{-1}
$\partial T/\partial x = -A^{-1} = -68$ μK/ppm is the resulting sensitivity coefficient.

Pavese and Molinar [36] provide the following sensitivity estimates: O_2: -60 μK/ppm (eutectic point at 53.94 K at $x(O_2)$=0.92), Ar: -20 μK/ppm, CH_4: -20 μK/ppm.

Having established a context (by means of the phase diagrams) to consider the effect of specific impurities on the krypton triple point temperature, we can return to the data of Table 3. Nitrogen and methane were not detected and there is no indication that argon was included in the analysis, so quantitative consideration is limited to oxygen (0.8 ppm) and xenon (< 10 ppm). Using the sensitivities estimated from the phase diagrams, the oxygen is expected to reduce the temperature by 56 μK and the reduction by xenon is < 100 μK, for a total of ~156 μK. We consider this the lower limit for the influence of impurities on our sample temperature.

TABLE 2. Composition of Dry Air [29].

Component	Percent by Volume
Nitrogen	78.084
Oxygen	20.946
Argon	0.934
Carbon Dioxide	0.033
Neon	0.0018
Helium	0.000524
Methane	0.00016
Krypton	0.000114
Hydrogen	0.00005
Nitrous Oxide	0.00003
Xenon	0.0000087

TABLE 3. Chemical analysis of the NRC krypton sample as supplied by Air Products in 1984. (N.D. = not detected)

Component	ppm by Volume
Nitrogen	< 5 N.D.
Oxygen	0.8
Carbon Dioxide	< 0.5 N.D.
Carbon Monoxide	< 1.0 N.D.
Helium and Hydrogen	< 5 N.D.
Methane	< 0.5 N.D.
Nitrous Oxide	< 0.1 N.D.
Xenon	< 10
Hydrocarbons	< 0.2
Water	0.15

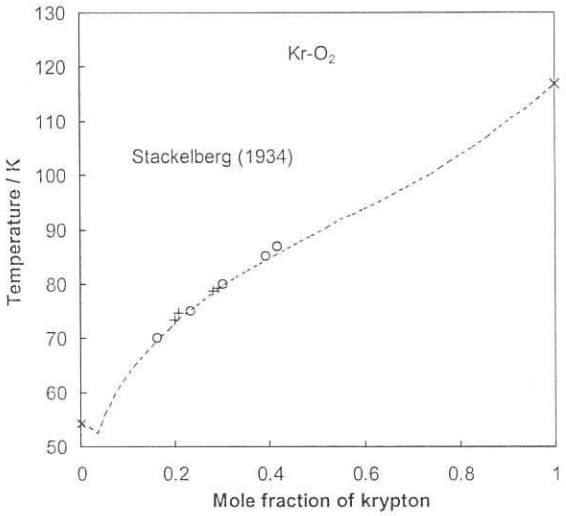

FIGURE 3. Phase diagram for the binary system Kr-O_2 [30].

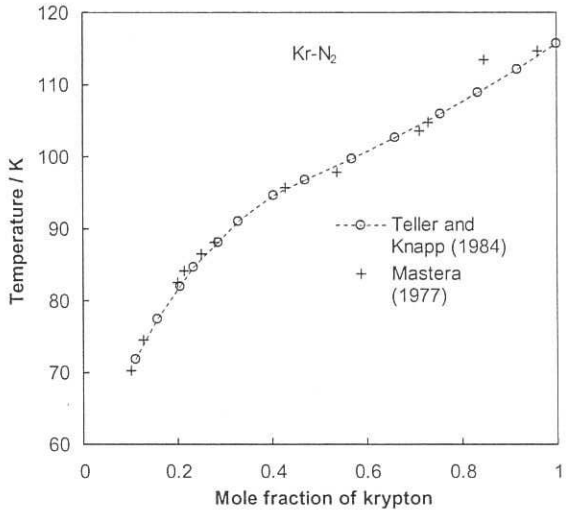

FIGURE 4. Phase diagram for the binary system Kr-N_2 [31-32].

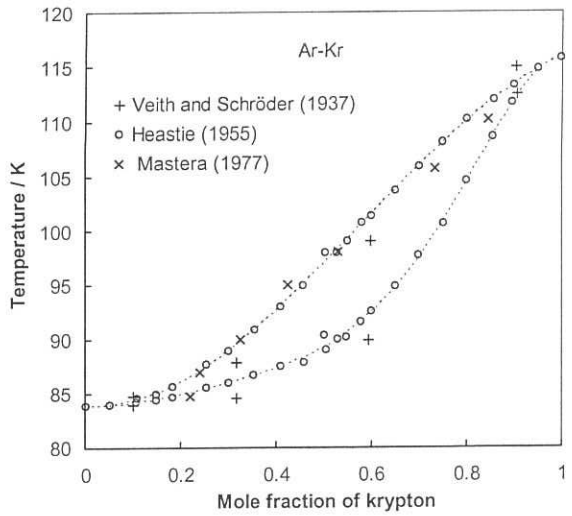

FIGURE 5. Phase diagram for the binary system Ar-Kr [32-34].

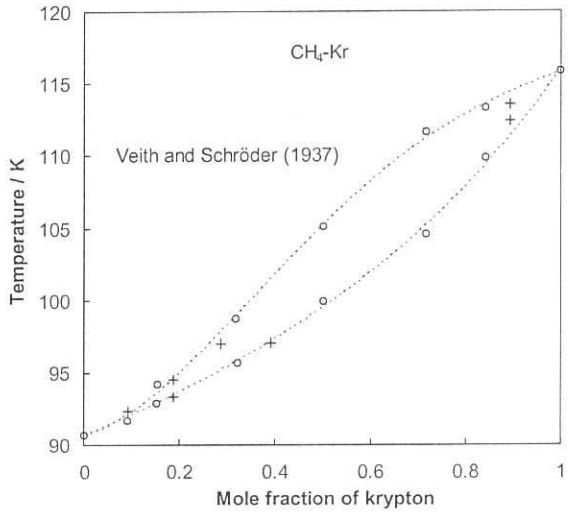

FIGURE 6. Phase diagram for the binary system CH_4-Kr [33].

The isotopic abundance of krypton in air [37] is presented in Table 4. Variations in the isotopic composition of specific krypton gas samples will undoubtedly influence the triple point temperature. However, the variation is not expected to be large. According to Lee *et al.* [18], the triple points of ^{80}Kr and ^{84}Kr should differ by 10 mK based on their experiments with natural and enriched Kr samples. Tew [38] uses this and other results from the literature in his analysis of the triple-point isotope effect. Tew argues that $\Delta T_{tp} / T_{tp} \sim \Delta M / M^3$ (T_{tp} denotes the triple point temperature and M the molar mass). For krypton, we can use the available information to generate an expression for the change in the triple-point temperature as a function of the variation in the molar mass of the gas sample: $\Delta T_{tp} \sim 0.21\ (\Delta M / M)$ K. Our experience with xenon indicated a relative mass variation of 172 ppm among the six samples. For neon, Pavese *et al.* [39] found a relative mass variation of 165 ppm among seven samples. If similar variations can be expected with Kr, this implies a range of 36 μK in the triple-point temperatures. Based on the standard deviation of the measured variations for xenon and neon, the standard uncertainty in the triple point temperature of krypton due to isotopic variation is approximately 13 μK.

TABLE 4. Natural isotopic composition of krypton in air [37].

Isotope	percent	Isotope	percent
^{78}Kr	0.355	^{83}Kr	11.500
^{80}Kr	2.286	^{84}Kr	56.987
^{82}Kr	11.593	^{86}Kr	17.279

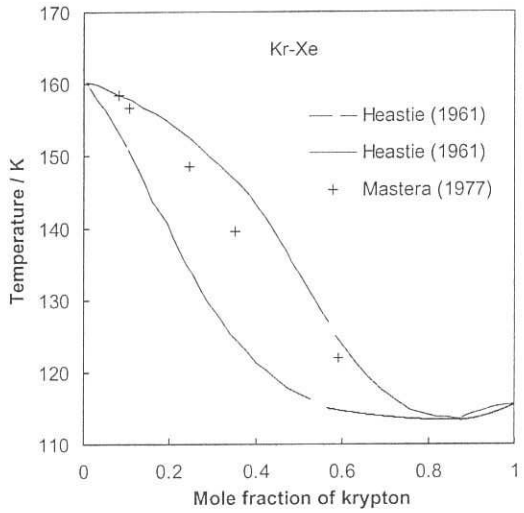

FIGURE 7. Phase diagram for the binary system Kr-Xe [32, 35].

CONCLUSIONS

The triple point of krypton has clear utility as a secondary reference point. The estimated uncertainty of our determination appears in Table 5. Based on the results obtained we propose that the triple point of krypton be assigned the value T_{90} = 115.7755 K with an uncertainty of 0.3 mK (k=1). From Table 5, it is evident that the largest component of the uncertainty is the propagated uncertainty from the calibration using the defining fixed points of the ITS-90. If this

component were zero, the combined uncertainty from the other components would be 0.18 mK (k=1).

TABLE 5. Standard uncertainty of the krypton triple point determination.

Component	μK
Chemical impurities	156
Isotopic composition	13
Hydrostatic pressure	18
Heat flux	10
CSPRT self-heating	7
Accuracy of resistance bridge ratio	13
Standard resistor	2
Uncertainty propagated from the TPW	35
Repeatability (melt-to-melt)	34
CSPRT stability	10
CSPRT non-uniqueness	67
Propagated calibration uncertainty	270
Total	324

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