NIST Technical Note
NIST TN 2278

Binary Metal-Carbon Phase-Transition Temperatures

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https://doi.org/10.6028/NIST.TN.2278

NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
U.S. DEPARTMENT OF COMMERCE

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February 2024

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NIST TN 2278
February 2024

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Publication History
Approved by the NIST Editorial Review Board on 2023-11-27

How to Cite this NIST Technical Series Publication
Burgess DR (2024) Binary Metal-Carbon Phase-Transition Temperatures. (National Institute of Standards and Technology, Gaithersburg, MD), NIST Technical Note (TN) NIST TN 2278. https://doi.org/10.6028/NIST.TN.2278

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Abstract

In this work, we compiled and evaluated eutectic and peritectic phase-transition temperatures for metal-carbon (e.g., Co-C, Re-C) and metal carbide-carbon compounds (e.g., Fe3C-C, HfC2-C) and selected recommended values for possible future use on the International Temperature Scale as primary or secondary fixed points. Most of these phase-transition temperatures are at high temperatures (1400 K to 3000 K) above the highest fixed point, the freezing point of copper (1357.77 K), on the ITS-90 temperature scale, The selected systems include 18 phase-transition temperatures: eight of these have very low uncertainties (0.12 K to 0.27 K) that likely will become primary fixed points on the International Temperature Scale, while ten of these have slightly higher uncertainties (0.4 K to 2.5 K) that may become secondary fixed points. Phase transitions for all other measured metal-carbon systems with higher uncertainties are also provided for completeness.

Keywords

Metal-carbon, metal carbide-carbon, phase-transition temperatures, eutectic points, peritectic points, International Temperature Scale, ITS-90, critical evaluation.

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1. Introduction

1.1. Overview

In this work, we compiled and evaluated eutectic and peritectic phase-transition temperatures for metal-carbon and metal carbide-carbon compounds and selected 18 recommended values for likely use as primary or secondary fixed points on a revised International Temperature Scale. All these phase-transition temperatures are at high temperatures (1400 K to 3000 K) above the highest fixed point, the freezing point of copper (1357.77 K), on the ITS-90 temperature scale. Eight of the phase-transition temperatures have very low uncertainties (0.12 K to 0.27 K) that likely will become primary fixed points on the temperature scale, and ten of the phase-transition temperatures have somewhat higher uncertainties (0.4 K to 1.5 K) that may become secondary fixed points. For completeness, we have also made recommendations for all other metal-carbon and metal carbide-carbon systems with phase-transition temperatures having high uncertainties (3 K to 40 K) and, thus, not suitable for fixed points on the temperature scale.

Note that currently, at very high temperatures, ITS-90 is defined by the Planck radiation law using the freezing points of silver, gold, or copper as reference points. The 2019 report "*Mise-en-Pratique* for the definition of the kelvin in the SI" by the Consultative Committee for Thermometry (CCT) of the Bureau International des Poids et Mesures (BIPM) indicated that at very high temperatures relative radiometric primary thermometry employing high-temperature fixed points (*e.g.*, metal-carbon phase transition temperatures) would be used for realizing the new definition of the kelvin and replace the ITS-90 as the basis of temperature measurement.[1] [2] [3]

A number of the many systems have both graphitic (M-C or MC_n-C) and (non-graphitic) mixed-carbide (MC_m-MC_n) phase transitions, the latter being transitions from one metal-carbon phase to another. For the most part, we present here only the graphitic phase transitions. In total, we compiled about 600 to 700 values for about 40 metal-carbon systems and about 70 phase transitions taken from about 300 to 400 references in the literature. In this report, we provide only a selection of "best values" for the phase-transition temperatures reported in the literature. For a more detailed compilation and evaluation of the many systems, see another work, currently in press.[4]

The phase transitions for the graphitic systems are two-phase solids, either metals (M) or metal carbides (MC_n) with "dissolved" carbon that transition to liquids (containing a metal and carbon), *e.g.*, (Ni) + (C) → Liquid(Ni, C), or (TiC_2) + (C) → Liquid(Ti, C). The non-graphitic transitions are transitions from one metal-carbide phase to another, *e.g.*, (Cr_7C_3) → Liquid + (Cr_3C_2). The M-C (metal-carbon) and MC-C (metal carbide-carbon) eutectics are generally two solid phases – (metal or metal carbide) and carbon, that melt to form a single liquid phase, while the peritectics are generally single solid-phase metal carbides, that melt to form a two-phase mixture consisting of a liquid metal plus carbon.

The metal-carbon (graphitic) phase transitions (*e.g.*, Co-C) are "carbon-poor" with atomic carbon fractions of about (10 to 20) %, although there are several that are very dilute at about (0.1, 1, and 4) %. The metal carbide-carbon (graphitic) phase transitions are most generally "carbon-rich" either

nominally metal “monocarbides” (*e.g.*, $VC_{1\pm x}$-C) or nominally metal “dicarbides” (*e.g.*, $HfC_{2\pm x}$-C). The monocarbide phase transitions have atomic carbon fractions of close to one-half (x = 0.43 to 0.60) and the transition temperatures on the order of (100 to 200) K below the melting point of the stable monocarbide. The dicarbide phase transitions have atomic carbon fractions of close to two-thirds (x = 0.61 to 0.71), but are generally shifted to higher carbon content (about $MC_{2.2}$ to $MC_{2.5}$), and the phase transition temperatures are well below, by (400 to 800) K, the melting points of the stable dicarbides.

In addition, there are two non-graphitic phase transitions that we provide recommendations for the phase-transition temperature from one metal-carbon system to another (Si-SiC, Cr_7C_3-Cr_3C_2) that have relatively low uncertainties and could be used as likely secondary fixed points on the International Temperature Scale. The Si-SiC phase-transition is very carbon-poor (x = 0.8 %) and the phase-transition temperature is very slightly (3 K) below the melting point of silicon. On the other hand, the Cr_7C_3-Cr_3C_2 phase-transition is only slightly carbon-poor (x = 33 %) and the phase-transition is slightly (13 K) below the melting point of Cr_7C_3.

As indicated above, these systems include 18 transitions with low expanded uncertainties for the transition temperatures that could be used as primary (about eight with $U(T_{trs})$ = 0.12 K to 0.27 K) or secondary (about ten with $U(T_{trs})$ = 0.4 K to 1.5 K) temperature reference points. In addition, there are another about 55 transitions with high uncertainties $U(T_{trs})$ = (2.5 to 40) K that are not suitable to be used as temperature reference points. We only include here the graphitic metal-carbon (M-C) or metal carbide-carbon (MC_n-C) phase transitions, except as stated above, we do include phase transition temperatures for the Si-SiC and Cr_7C_3-Cr_3C_2 transitions. For a more detailed compilation and evaluation of both graphitic and non-graphitic phase transitions, see another work, currently in press.[4]

All the uncertainties in this work are reported as expanded uncertainties U (k=2, or 95 % coverage).

1.2. International Temperature Scale

This work compiles and evaluates metal (carbide)-carbon phase-transition temperatures for possible use on the International Temperature Scale. Most of these are at high temperatures above the ITS-90 temperature scale, where the highest fixed point is the freezing point of copper (1357.77 K). They range from the eutectic points for Fe_3C-C at about 1427 K to HfC_2-C at about 3459 K. Those fixed points at very high temperatures with very low uncertainties are likely to be used for realizing the new definition of the kelvin and replace the ITS-90 scale as the basis of temperature measurement employing relative radiometric primary thermometry.[1] [2] [3]

The International Temperature Scale of 1990 (ITS-90)[5] is defined by the temperatures of phase equilibrium temperatures of pure substances – 15 fixed points plus vapor-pressure/temperature relations. These include highly accurate melting or freezing points and triple points of mostly atoms (and three molecules). The lowest temperatures on the scale (about 0.65 K to 24.6 K) are defined by vapor-pressure/temperature relations and triple points of ^{3}He, ^{4}He, and H_2. At higher, but still low temperatures (about 24.6 K to 234.3 K), the temperature scale is defined by the triple points of Ne, O_2, Ar, and Hg. The triple point of water which is defined exactly at 273.16 K and is the most important fixed point on ITS-90. At moderate temperatures (about 302.9 K to 692.7 K), the fixed

points include the melting point of gallium and the freezing points of In, Sn, and Zn. At the high end of ITS-90, it is defined by the freezing points of Al, Ag, Au, and Cu at about 933.5 K, 1234.9 K, 1337.3 K, and 1357.8 K, respectively. Above the temperatures of these fixed points, ITS-90 is defined by the Planck radiation law using the freezing points of silver, gold, or copper as reference points.

ITS-90 is a "practical" temperature scale, an equipment calibration standard, for realization and dissemination of temperatures that approximates thermodynamic temperatures through "best fit" splined interpolation functions to the fixed points. Prior practical scales include the International Practical Temperature Scales of 1948 and 1968 (IPTS-48, IPTS-68). Temperature measurements before 1990 need to be corrected to the ITS-90 scale.[5] [6] [7] Note that the work by Rusby *et al*. (1994)[7] revises temperature corrections in the range (903.765 to 1337.33) K for the IPTS-48 and IPTS-68 scales provided in the 1992 report by Goldberg and Weir.[6]

Although the fixed points are defined exactly, they are just approximations of the true thermodynamic temperatures, albeit highly accurate relative to the thermodynamic temperatures. At low temperatures (below about 500 K), they have expanded uncertainties of about (0.2 to 3) mK. At temperatures relevant to this work, they have expanded uncertainties of (12 to 15) mK between 600.612 K (Pb MP) to 933.473 K (Al FP), and (28 to 52) mK between 1052.78 K (Cu/71.9 % Ag eutectic MP) and 1357.77 K (Cu FP). (Note the Pb MP and Cu/Ag eutectic are not primary fixed points on ITS-90, but are important secondary fixed points). The differences between thermodynamic temperatures and ITS-90 temperatures (T–T_{90}) range from about +10 mK at the boiling point of water (373.124 K) to +29 mK at the freezing point of Al (933.473 K) and above that are about +(40 to 50) mK in the range (1000 to 1357.77) K, see Fischer *et al.* (2011).[8] We note that the differences between thermodynamic temperatures and those on ITS-90 below 335 K have recently been updated by Gaiser *et al.* (2022).[9]

Companion to the ITS-90 temperature scale are recommended secondary fixed points – these are not part of the official ITS-90 scale, but are nevertheless important for realization and dissemination of temperatures, see Bedford *et al.* (1996).[10] The secondary fixed points include: the boiling points of water and Na at (373.124 and 1156.09) K with very low uncertainties of (2 and 10) mK, respectively; at high temperatures above the melting point of copper, the freezing points of Pd and Pt at (1828.0 and 2041.3) K with modest uncertainties of (0.2 and 0.8) K, respectively; the freezing points of Ni, Co, Fe, and Rh, and the melting points of Ti and Al_2O_3 in the range (1828 to 2326) K have yet larger uncertainties of (1 to 3) K; and at very high temperatures the melting points of Ir, Mo, and W in the range (2719 to 3687) K have very large uncertainties of (4 to 7) K.

1.3. Phase Transitions

A phase transition is where a substance changes from one thermodynamic state to another. There are various types of phase transitions. Here we report values for eutectic and peritectic phase transitions for the metal (carbide)-carbon systems. A eutectic point is a temperature where a liquid phase is in equilibrium with two solid phases (Liquid $\rightarrow \alpha + \beta$). A peritectic point is a temperature where a solid phase and liquid phase are in equilibrium with a second solid phase (Liquid + $\alpha \rightarrow \beta$).

Figure 1 shows an example of eutectic and peritectic phase transitions for metal (carbide)-carbon systems, in this case for the hafnium-carbon system. The carbon-rich (HfC_2-C) eutectic point occurs

near 3453 K at ≈68 % atomic carbon – at this point the two phase solid hafnium monocarbide plus carbon (HfC+C) decomposes to a liquid (containing hafnium and carbon). As shown, solid hafnium carbide (HfC) itself melts near 4201 K. There is also a carbon-poor Hf-C eutectic transition for hafnium with dissolved carbon at much lower temperatures near 2491 K at ≈2 % atomic carbon. This phase-transition temperature is just 9 K below the melting point of hafnium metal itself near 2500 K (melting point depression). At intermediate temperatures (and intermediate carbon loadings), there is a peritectic phase transition between two phases of solid Hf/HfC mixtures occurring near 2633 K at ≈14 % atomic carbon. As shown, there are about ten different phase regions for this system. Hafnium monocarbide exists at exactly $HfC_{1.0}$ and just below that at about ($HfC_{0.5}$ to $HfC_{1.0}$) (x=0.33–0.50), there is an HfC_{1-x} phase consisting of HfC with carbon vacancies.

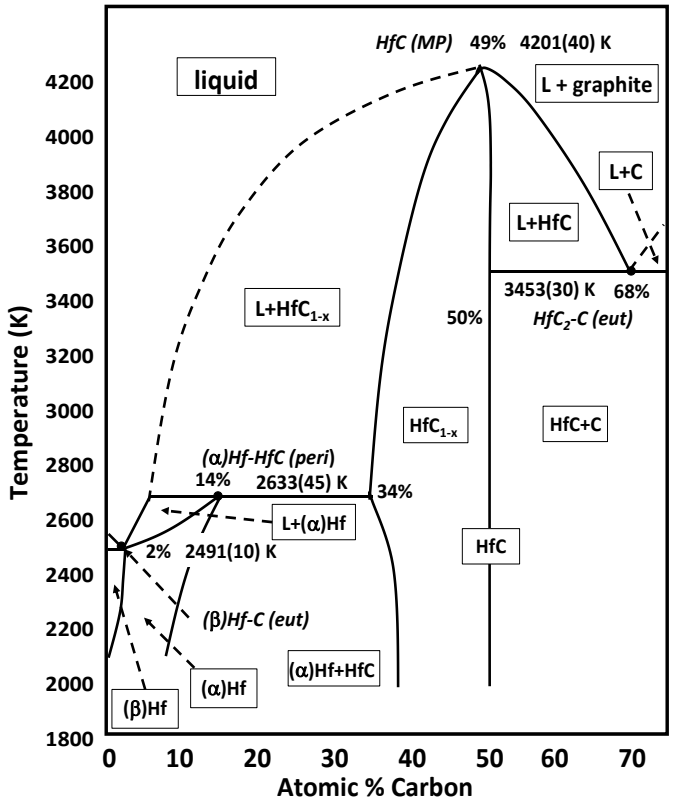

Figure 1. Hafnium-Carbon Phase Diagram

Other systems have similar features. Many of the metal-carbon systems (e.g., Co-C, Ni-C, Pd-C) have single carbon-poor eutectic points at low carbon atomic fractions (≈20 %), others that are carbon-rich, such as the metal monocarbide and metal dicarbide systems may have graphitic carbon-rich phase transitions, graphitic carbon-poor phase transitions, and non-graphitic phase transitions (sometimes multiple) between different metal carbide phases. The different types of transitions for each metal (carbide)-carbon system are provided in tables below.

A phase-transition temperature is generally determined from the melting plateau, which is the point-of-inflection (POI) in the melting curve. The melting point is much more reproducible and is used to determine the transition temperature. The freezing temperature is slightly lower and is

dependent upon the rate of cooling and inhomogeneous precipitation of the components during freezing – this leads to a hysteresis in the melting/freezing curves.

1.4. Notation Used

In the tables, we utilized standard literature notation to identify the systems (e.g., Fe_3C), which is the composition of the phase, not the composition at the transition which is provided both as "Compos" (*e.g.*, $FeC_{0.21}$) and in weight percent carbon (%C wt**)**. We provide recommended phase-transition temperatures (T_{trs}). Where we have estimated uncertainties, we provide these in parentheses (*e.g.*, "(5)").

Eutectic and peritectic transitions ("trans") are designated with "eut" and "peri", respectively. All transition temperatures were "point-of-inflection" (POI) determinations, except those labeled "eut(liq)" where the true thermodynamic liquidus temperature was determined (a POI temperature is a mathematical approximation). Those labeled with "eut-mc" indicate non-graphitic transitions from one metal-carbon phase to another metal-carbon phase (*e.g.*, Cr_7C_3-Cr_3C_2). The notation for methods used in the determinations is provided in Table 1. When a number in parentheses is given for a method, for example "pyr(5)", this indicates the number of different determinations (*i.e.*, different laboratories, cells, methods) were used to provide an averaged value (usually weighted). In the transition-temperature tables below for the various systems, we have tagged transition temperatures having very low uncertainties (U = 0.12 K to 0.27 K) with "*" and those having still relatively low uncertainties (U = 0.4 K to 1.5 K) with "#" to denote the suitability for primary and secondary high-temperature reference points, respectively. Other transition temperatures have much higher uncertainties (U = 1.5 K to 40 K) and are not suitable for temperature reference points.

A number of different methods were used to determine the transition temperatures: radiometric methods such as absolute and relative pyrometry, and filter radiometry; thermocouple measurements using Type N, Type S, Type R, and Pt/Pd thermocouples; thermal measurements using differential thermal analysis and differential scanning calorimetry; imaging methods such as microscopy or XRD; other techniques such as equilibrium, vapor pressure, and magnetic susceptibility measurements; and, of course, thermodynamic modeling of phase diagrams.

Table 1. Notation Used

Notation	Description
DSC	differential scanning calorimetry
DTA	differential thermal analysis
equil	equilibrium method
mag susc	magnetic susceptibility
microsc	microscopy method
model	phase diagram thermodynamic modeling
na	not available
no MC	no metal-carbon compound exists
nr	not recorded or not available
pyr	one of different pyrometric methods

Pt/Pd	Pt/Pd thermocouple
Type A	Type A thermocouple
Type B	Type B thermocouple
Type N	Type N thermocouple
Type R	Type R thermocouple
Type S	Type S thermocouple
resist	electrical resistance
VP	vapor pressure method
XRD	x-ray diffraction
unk	unknown

1.5. Uncertainties

There are a number of uncertainties in measurements of high-temperature reference points using radiometric and thermocouple thermometry. They will be only briefly outlined here. A detailed discussion is beyond the scope of this work and we refer readers to work by Todd *et al*. (2021),[11], Saunders (2020),[12], Saunders *et al*. (2018),[13] Saunders (2011),[14] and Fischer *et al*. (2003).[15]

There are several primary measurement techniques for the determination of high-temperature references points: 1) Relative primary radiometric thermometry using reference cells (Ag, Au, or Cu) from either the literature or integrated into the measurement to extrapolate from the temperatures of one or more of the reference cells; 2) Absolute primary radiometric thermometry by determining the optical power emitted (including emissivity) which is a function of wavelength and solid angle; and 3) Thermocouple measurements which depend on the uncertainties in calibrations of thermocouples above the ITS-90 temperature scale (International Temperature Scale of 1990), where the fixed points end at the freezing point of copper at 1377.77 K.[5]

The uncertainties vary depending on the system (mostly a function of temperature). The largest overall are systematic uncertainties, which depend on the apparatus in each laboratory. Specific uncertainties include furnace effects, stability, identification of the melting plateau, the difference between the true thermodynamic liquidus temperature versus the (mathematical) point-of-inflection (POI) in the melting plateau, difference between the thermodynamic temperatures versus the ITS-90 scale, impurities, temperature distribution and temperature gradients/drop in the furnace, emissivity, and size-of-source effect (SSE)/aperture size. Other factors include non-linearity effects, the filling process employed, and drift in the measurements over time. We note that we corrected reported temperatures from the IPTS-48 and IPTS-68 scales to the ITS-90 scale employing tabular data from Goldberg (1992)[6] and the update by Rusby *et al*. (1994),[7] which revised Goldberg's corrections in the range (903.765 to 1337.33) K.

1.6. Phase Transitions Suitable for Fixed Temperature References

There are about 18 metal-carbon systems with phase-transition temperatures having low expanded uncertainties $U(T_{trs})$ = (0.12 to 1.5) K and, consequently, are suitable for possible primary or secondary fixed temperature reference points on a revised International Temperature Scale: the carbon-poor metal-carbon systems: Co-C, Ni-C, Pd-C, Rh-C, Pt-C, Ru-C, Ir-C, and Re-C; the metal monocarbides: WC-C and MoC-C; the metal dicarbides: TiC_2-C, ZrC_2-C, HfC_2-C; non-stoichiometric carbides: Fe_3C-C, Cr_3C_2-C, Mn_7C_3-C; and the non-graphitic metal-carbide phase transitions Si-SiC and Cr_7C_3-Cr_3C_2.

The metal-dicarbide transitions TiC_2-C, ZrC_2-C and HfC_2-C have carbon atomic fractions of about (63 to 68) % and the metal-monocarbide transitions MoC-C and WC-C have carbon atomic fractions of about (45 to 50) %. Note that when we refer to metal-dicarbides and metal-monocarbides transitions, these are nominal compositions for the transitions and are associated with the metal-dicarbide (MC) and metal-monodicarbide (MC_2) phases, but the transitions may be slightly non-stoichiometric and have carbon atomic fractions slightly lower or higher than stoichiometric 66.67 % or 50 %, respectively, because the transition may be slightly carbon-poor or carbon-rich. For example, the molybdenum-monocarbide transition (MoC-C) has a composition that is slightly carbon poor ($MoC_{0.75}$ or MoC_{1-x}-C).

The modestly carbon-poor metal-carbon transitions (not carbides) Fe-C, Rh-C, Pt-C, Ru-C, Ir-C, and Re-C have carbon atomic fractions of about (16 to 24) %, that is, carbon-poor M_4-C. The very carbon-poor

metal-carbon transitions Ni-C and Co-C have carbon atomic fractions of about (0.09 to 0.12) %, while the extremely dilute Si-SiC metal-carbide transition has a carbon atomic fraction of just 0.016 % or 160 ppm.

As indicated above, in the transition-temperature tables below, we have tagged transition temperatures having very low uncertainties (“*”) and those having relatively low uncertainties (”#”) to denote possible primary and secondary high-temperature reference points on the International Temperature Scale, respectively. Other transition temperatures (not tagged) have much higher uncertainties and are not suitable for high-temperature reference points.

2. Main Group and *p*-Group Metal-Carbon Phase Transitions

The graphitic metal-carbon phase-transition temperatures for the main group metal-carbon systems (lithium and beryllium) and p-group metal-carbon systems (boron and aluminum) are provided in table 2. The uncertainties are generally high – on the order of (15 to 20) K. We have estimated uncertainties for the eutectics of Li-C, Be_2C-C and B_4C-C. The Li-C is very dilute (≈0.8 % carbon atomic fraction) and is at very low temperatures (about 15 K below the melting point of lithium). We have also provided the Si-SiC phase transition, which is a non-graphitic metal-carbon phase transition (denoted as "eut-mc") from one metal-carbon phase (denoted "SiC") to another metal-carbon phase (denoted "Si" indicating a very carbon-poor phase). This transition is important as a possible high-temperature fixed point for future extension of the temperature scale (currently ITS-90) beyond the freezing point of Cu at 1357.77 K, because it has a low uncertainty (0.2 K) and the transition temperature is tagged with the symbol "#" to indicate this.

Table 2. Main Group and *p*-Group Metal-Carbon Phase Transitions

System	trans	Compos	%C wt	T_{trs}/K	$U(T_{trs})$/K	Method	Author[ref]	Year
Main Group								
Li-C	eut	$LiC_{0.008}$	1.4	438	(5)	DTA	Fedorov[16]	1957
Be_2C-C	eut	$BeC_{1.29}$	63	2012	(2)	DTA	Liu[17]	2019
B_4C-C	eut	$BC_{0.41}$	31.2	2653	(5)	DTA	Schwetz[18]	1991
				2659	na	evaluation	Edler[19]	2017
p-Group								
Al_4C_3-C	peri	$AlC_{0.75}$	25.0	2425	15	pyrometry	Deffrennes[18]	2019
Si-SiC	eut-mc	$SiC_{0.0076}$	0.32	1679.9 #	0.2	DSC/Type S	Kwon[20]	2010

Note: see Section "Notation Used" and Table 1 "Notation Used" for symbols and notation used in this table

3. Transition Metal-Carbon Phase Transitions

3.1. First-Row Transition Metals

We provide here (Table 3) recommended transition temperatures for the graphitic metal-carbon phase transitions of the first-row transition-metal systems. Many of these transitions are suitable for high-temperature fixed reference points on the International Temperature Scale having low uncertainties. The expanded uncertainties are very low U = (0.12 to 0.28) K for iron, cobalt, and nickel, but are higher U = (0.8 to 1.5) K for chromium and titanium.

We have also provided the Cr_7C_3-Cr_3C_2 phase transition, which is a non-graphitic metal-carbon phase transition (denoted as "eut-mc") from one metal-carbon phase (denoted "Cr_7C_3") to another metal-carbon phase (denoted "Cr_3C_2"). This transition is important as a possible high temperature fixed point, because it has a relatively low uncertainty (0.88 K). The transition temperature for Cu-C which is extremely carbon-poor (4 % carbon) at 1373 K is just about 5 K below the freezing point of copper at 1377.77 K.

The phase-transition temperatures for these different first-row transition-metal carbon phase transitions generally decrease on the order of about 250 K with increasing atomic number Z (TiC_2-C: Z=22, T_{trs}= 3032 to Ni-C: Z=28, T_{trs}=1602 K), although there is significant variability because of varying compositions, valence states, and crystal structures.

Table 3. First-Row Transition Metal-Carbon Phase Transitions

At #	System	trans	Compos	%C wt	T_{trs}/K	$U(T_{trs})$/K	Method	Author[ref]	Year
21	**Sc_3C_4-C**	eut	$ScC_{1.63}$	30.3	1995	4	DTA, pyr	Gordiichuk[21]	1987
22	**TiC_2-C**	eut	$TiC_{1.20}$	30	3031.6 #	1.5	pyr(2)	Hartmann[22]	2005
23	**VC-C**	eut	$VC_{0.98}$	18.8	2898	6	DTA	Rudy[23]	1969
24	**Cr_3C_2-C**	peri	$CrC_{1.41}$	32.6	2099.3 #	0.8	pyrometry	Yamada[24]	2006
	Cr_7C_3-Cr_3C_2	eut-mc	$CrC_{1.60}$	37	2015.26 #	0.88	pyrometry	Pearce[25]	2014
25	**Mn_7C_3-C**	peri	$MnC_{1.70}$	27	1603.87 #	0.4	pyrometry	Yamada[24]	2006
26	**Fe_3C-C**	eut(liq)	$FeC_{0.20}$	4.26	1427.02 *	0.15	pyr(9)	Sadli[3]	2023
		eut(poi)			1426.92	0.15	pyr(9)	Sadli[3]	2023
27	**Co-C**	eut(liq)	$CoC_{0.13}$	2.6	1597.48 *	0.12	pyr(9)	Lowe[26]	2017
		eut(poi)			1597.39	0.13	pyr(9)	Woolliams[27]	2016
28	**Ni-C**	eut	$NiC_{0.15}$	3	1602.17 *	0.28	pyr, Pt/Pd	Karmalawi[28]	2018
29	**Cu-C**	peri	$CuC_{0.04}$	0.008	1373	(1)	pyrometry	Bever[29]	1946
30	**Zn-C**	no MC			na				

Note: see Section "Notation Used" and Table 1 "Notation Used" for symbols and notation used in this table.
Note: transition temperatures with very low and low uncertainties are tagged with "*" and "#" to denote possible primary and secondary high-temperature reference points on the International Temperature Scale, respectively.

3.2. Second-Row Transition Metals

We provide here (Table 4) recommended transition temperatures for the graphitic metal-carbon phase transitions of the second-row transition-metals. Some of these transitions are suitable for high-temperature fixed reference points on the International Temperature Scale where the expanded uncertainties are very low U = (0.26 to 0.4) K for the palladium and ruthenium metal-carbon phase transitions, and for the rhenium, molybdenum, and zirconium metal-carbon phase transitions, which are still relatively low U = (0.6 to 1.5) K. The uncertainties for YC_2-C and NbC-C are very high (25 K and 12 K, respectively).

The phase-transition temperatures for these different first-row transition-metal carbon phase transitions first increase by about 330 K with increasing atomic number Z from YC_2-C to NbC-C and then decrease by about 360 K with increasing atomic number.

Table 4. Second-Row Transition Metal-Carbon Phase Transitions

At #	System	trans	Compos	%C wt	T_{trs}/K	$U(T_{trs})$/K	Method	Author[ref]	Year
39	**YC_2-C**	eut	$YC_{2.33}$	31.5	2578	25	evaluation	Gschneidner[30]	1986
40	**ZrC_2-C**	eut	$ZrC_{1.50}$	20	3153.83 #	1.14	pyr(2)	Hartmann[22]	2005
41	**NbC-C**	eut	$NbC_{1.5}$	19.4	3578	12	DTA	Rudy[23]	1969
42	**MoC-C**	eut	$MoC_{0.75}$	9.3	2856.54 #	1.46	pyrometry	Karmalawi[28]	2018
43	**Tc-C**	no MC			na				
44	**Ru-C**	eut(liq)	$RuC_{0.21}$	2.5	2227.08 *	0.24	pyr(9)	Sadli[3]	2023
		eut(poi)			2226.99	0.22	pyr(9)	Sadli[3]	2023
45	**Rh-C**	eut	$RhC_{0.19}$	2.2	1929.91 #	0.62	pyr(2)	Yamada[31]	2001
46	**Pd-C**	eut(liq)	$PdC_{0.24}$	2.7	1765.18 *	0.16	pyr(9)	Sadli[3]	2023
		eut(poi)			1765.05	0.16	pyr(9)	Sadli[3]	2023
47	**Ag-C**	no MC			na				
48	**Cd-C**	no MC			na				

Note: see Section "Notation Used" and Table 1 "Notation Used" for symbols and notation used in this table.
Note: transition temperatures with very low and low uncertainties are tagged with "*" and "#" to denote possible primary and secondary high-temperature reference points on the International Temperature Scale, respectively.

3.3. Third-Row Transition Metals

We provide here (Table 5) recommended transition temperatures for the graphitic metal-carbon phase transitions of the third-row transition-metals. A number of these phase-transition temperatures are suitable for high-temperature fixed reference points on the International Temperature Scale, where the expanded uncertainties are very low U = (0.22 to 0.44) K for the platinum, iridium, rhenium, and tungsten systems. In this table, these transition temperatures have been designated "*" or "#" to denote those with very low uncertainties or low uncertainties, respectively. For the other systems, the uncertainties are either modest or high: 1.3 K, 5 K, and 12 K for HfC_2-C, TaC_2-C and Os-C, respectively.

The phase-transition temperatures for these different third-row transition-metal carbon phase transitions decrease overall about 250 K from low to high atomic number Z, although the decrease is not monotonic because of varying compositions, valence states, and crystal structures.

Table 5. Third-Row Transition Metal-Carbon Phase Transitions

At #	System	trans	Compos	%C wt	T_{trs}/K	$U(T_{trs})$/K	Method	Author[ref]	Year
72	**HfC_2-C**	eut	$HfC_{2.13}$	12.5	3458.5 #	2.5	review	Sadli[32]	2005
73	**TaC_2-C**	eut	$TaC_{1.56}$	10.4	3718	5	DTA	Rudy[23]	1969
74	**WC-C**	peri(liq)	$WC_{1.00}$	6.1	3020.92 *	0.27	pyr(9)	Sadli[3]	2023
		peri(poi)			3020.85	0.25	pyr(9)	Sadli[3]	2023
75	**Re-C**	eut(liq)	$ReC_{0.31}$	2	2747.91 *	0.44	pyr(9)	Lowe[26]	2017
		eut(poi)			2747.84	0.35	pyr(9)	Woolliams[27]	2016
76	**Os-C**	eut	$OsC_{0.21}$	1.3	3578	12	DTA, VP	Harmon[33]	1966
77	**Ir-C**	eut	$IrC_{0.26}$	1.6	2564.4 #	0.4	pyrometry	Khlevnoy[34]	2005
78	**Pt-C**	eut(liq)	$PtC_{0.20}$	1.2	2011.50 *	0.22	pyr(9)	Lowe[26]	2017
		eut(poi)			2011.43	0.18	pyr(9)	Woolliams[27]	2016
79	**Au-C**	no MC			na				
80	**Hg-C**	no MC			na				

Note: see Section "Notation Used" and Table 1 "Notation Used" for symbols and notation used in this table.
Note: transition temperatures with very low and low uncertainties are tagged with "*" and "#" to denote possible primary and secondary high-temperature reference points, respectively.

4. Lanthanide and Actinide Metal-Carbon Phase Transitions

We provide here (Table 6) recommended phase-transition temperatures for the graphitic lanthanide and actinide dicarbide-carbon (MC_2-C) eutectic transitions. We also provide recommended phase-transition temperatures for the carbon-poor (x = 0.18 to 0.26) La-C, Ce-C, Pr-C, and Pm-C phase transitions. We note that Babizhetskyy *et al*. (2017)[35] provides a good overview and evaluation of the phase diagrams for all of the lanthanide-carbon systems. The expanded uncertainties for these phase transitions are generally large with U = (15 to 40) K, although the uncertainties for the cerium and praseodymium dicarbide-carbon phase-transition temperatures are only modestly high U = (4 to 6) K.

The only known actinide metal-carbon phase transitions are ThC_2-C, UC_2-C, and PuC_2-C.

Table 6. Lanthanide and Actinide Metal-Carbon Phase Transitions

At #	System	trans	Compos	T_{trs}/K	$U(T_{trs})$/K	Method	Author[ref]	Year
Lanthanide metal-dicarbide graphitic phase transitions								
57	**LaC_2-C**	eut	$LaC_{2.51}$	2544	15	VP	Spedding[36]	1959
58	**CeC_2-C**	eut	$CeC_{2.28}$	2519	4	DTA, pyr	Gordiichuk[21]	1987
59	**PrC_2-C**	eut	$PrC_{2.51}$	2527	6	DTA, pyr	Gordiichuk[21]	1987
60	**NdC_2-C**	eut	$NdC_{2.23}$	2533	30	evaluation	Gschneidner[37]	1986
61	**PmC_2-C**	eut	$PmC_{2.38}$	2554	na	DTA, pyr	Eremenko[38]	1992
62	**SmC_2-C**	eut	$SmC_{2.13}$	2513	30	DTA, pyr	Eremenko[38]	1992
63	**EuC_2-C**	eut	≈$EuC_{2.33}$	2488	na	DTA, pyr	Eremenko[38]	1992
64	**GdC_2-C**	eut	≈$GdC_{2.33}$	2553	30	evaluation	Gschneidner[39]	1986
65	**TbC_2-C**	eut	≈TbC_2	2548	20	DTA	Krikorian[40]	1967
66	**DyC_2-C**	eut	≈DyC_2	2533	25	evaluation	Gschneidner[41]	1986
67	**HoC_2-C**	eut	≈HoC_2	2543	20	DTA	Krikorian[40]	1967
68	**ErC_2-C**	eut	$ErC_{2.33}$	2533	25	Evaluation	Gschneidner[42]	1986
69	**TmC_2-C**	eut	$TmC_{2.33}$	2518	35	DTA	Krikorian[40]	1967
70	**YbC_2-C**	eut	$YbC_{2.33}$	2488	40	DTA	Krikorian[40]	1967
71	**LuC_2-C**	eut	≈LuC_2	2503	20	DTA	Krikorian[40]	1967
Lanthanide carbon-poor graphitic phase transitions								
57	**La-C**	eut	$LaC_{0.26}$	1079	na	DTA	Spedding[36]	1958
58	**Ce-C**	eut	$CeC_{0.24}$	974	na	DTA, pyr	Gordiichuk[21]	1987
59	**Pr-C**	eut	$PrC_{0.18}$	1073	4	DTA, pyr	Gordiichuk[21]	1987
61	**Pm-C**	eut	$PmC_{0.18}$	1169	na	DTA, pyr	Eremenko[38]	1992
Actinide carbon-poor graphitic phase transitions								
90	**ThC_2-C**	eut	$ThC_{2.38}$	2773	35	resist, pyr	Chiotti[43]	1967
92	**UC_2-C**	eut	$UC_{2.02}$	2723	30	pyrometry	Wallace[44]	1964
94	**PuC_2-C**	eut	≈PuC_2	2473	20	VP, pyr	Marcon[45]	1970
89-103	**(Ac)C_2-C**	no MC		na				

Note: see Section "Notation Used" and Table 1 "Notation Used" for symbols and notation used in this table.
Note: where the composition of the dicarbide phase transition is undetermined, it is given as "≈MC_2.
Note: "At # 89-103" and "(Ac)MC_2-C" row means no actinides have metal-carbon eutectics except Th, U, Pu.

5. Summary

In this work, we compiled and evaluated eutectic and peritectic (graphitic) phase-transition temperatures for 18 metal-carbon (*e.g.*, Co-C, Re-C) and metal carbide-carbon compounds (Fe_3C-C, HfC_2-C) with low expanded uncertainties U = (0.15 to 1) K and selected recommended values for use on the International Temperature Scale. In the tables, those transition temperatures with very low uncertainties which may become primary fixed points are tagged with "*" and those with slightly higher, but still relatively low uncertainties that will likely be only secondary fixed points are tagged with "#". We have also compiled and evaluated many other phase transitions with high uncertainties U = (2.5 to 40) K that are not suitable for primary or secondary temperature reference points, but are included in this work for completeness. We have updated most of the values recommended in the BIPM/CCT (Bureau International des Poids et Mesures/Consultative Committee for Thermometry) 2017 report (which was partially updated in 2022).[19]

Declaration of Competing Interest

The authors have no conflicts to disclose.

Data Availability

The data that support the findings of this study are available within the article.

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